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Theoretical Physics 7

Quantum Mechanics - Methods and Applications

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General Preface

The nine volumes of the series *'Basic Course: Theoretical Physics'* are thought to be textbook material for the study of university-level physics. They are aimed to impart, in a compact form, the most important skills of theoretical physics which can be used as basis for handling more sophisticated topics and problems in the advanced study of physics as well as in the subsequent physics research. The conceptual design of the presentation is organized in such a way that

Classical Mechanics (volume 1)
Analytical Mechanics (volume 2)
Electrodynamics (volume 3)
Special Theory of Relativity (volume 4)
Thermodynamics (volume 5)

are considered as the theory part of an *'integrated course'* of experimental and theoretical physics as is being offered at many universities starting from the first semester. Therefore, the presentation is consciously chosen to be very elaborate and self-contained, sometimes surely at the cost of certain elegance, so that the course is suitable even for self-study, at first without any need of secondary literature. At any stage, no material is used which has not been dealt with earlier in the text. This holds in particular for the mathematical tools, which have been comprehensively developed starting from the school level, of course more or less in the form of recipes, such that right from the beginning of the study, one can solve problems in theoretical physics. The mathematical insertions are always then plugged in when they become indispensable to proceed further in the program of theoretical physics. It goes without saying that in such a context, not all the mathematical statements can be proved and derived with absolute rigor. Instead, sometimes a reference must be made to an appropriate course in mathematics or to an advanced textbook in mathematics. Nevertheless, I have tried for a reasonably balanced representation so that the mathematical tools are not only applicable but also appear at least 'plausible'.

The mathematical interludes are of course necessary only in the first volumes of this series, which incorporate more or less the material of a bachelor

program. In the second part of the series which comprises the modern aspects of Theoretical Physics,

Quantum Mechanics: Basics (volume 6)
Quantum Mechanics: Methods and Applications (volume 7)
Statistical Physics (volume 8)
Many-Body Theory (volume 9),

mathematical insertions are no longer necessary. This is partly because, by the time one comes to this stage, the obligatory mathematics courses one has to take in order to study physics would have provided the required tools. The fact that training in theory has already started in the first semester itself permits inclusion of parts of quantum mechanics and statistical physics in the bachelor program itself. It is clear that the content of the last three volumes cannot be part of an *'integrated course'* but rather the subject matter of pure theory lectures. This holds in particular for *'Many-Body Theory'* which is offered, sometimes under different names as, e.g., *'Advanced Quantum Mechanics'*, in the eighth or so semester of study. In this part new methods and concepts beyond basic studies are introduced and discussed which are developed in particular for correlated many particle systems which in the meantime have become indispensable for a student pursuing master's or a higher degree and for being able to read current research literature.

In all the volumes of the series *'Basic Course: Theoretical Physics'* numerous exercises are included to deepen the understanding and to help correctly apply the abstractly acquired knowledge. It is obligatory for a student to attempt on his own to adapt and apply the abstract concepts of theoretical physics to solve realistic problems. Detailed solutions to the exercises are given at the end of each volume. The idea is to help a student to overcome any difficulty at a particular step of the solution or to check one's own effort. Importantly these solutions should not seduce the student to follow the *'easy way out'* as a substitute for his own effort. At the end of each bigger chapter I have added self-examination questions which shall serve as a self-test and may be useful while preparing for examinations.

I should not forget to thank all the people who have contributed in one way or another to the success of the book series. The single volumes arose mainly from lectures which I gave at the universities of Muenster, Wuerzburg, Osnabrueck, and Berlin (Germany), Valladolid (Spain), and Warangal (India). The interest and constructive criticism of the students provided me the decisive motivation for preparing the rather extensive manuscripts. After the publication of the German version I received a lot of suggestions from numerous colleagues for improvement and this helped to further develop and enhance the concept and the performance of the series. In particular I appreciate very much the support by Prof. Dr. A. Ramakanth, a long-standing scientific partner and friend, who helped me in many respects, e.g., what concerns the checking of the translation of the German text into the present English version.

Special thanks are due to the Springer company, in particular to Dr. Th. Schneider and his team. I remember many useful motivations and stimulations. I have the feeling that my books are well taken care of.

Berlin, Germany Wolfgang Nolting
May 2017

Preface to Volume 7

In the prefaces of the preceding volumes, especially in that of volume 6 (*Quantum Mechanics: Basics*), which is the first part of Quantum Mechanics, I have already set out the goal of the basic course in *Theoretical Physics*. This goal remains of course unchanged for the second part *Quantum Mechanics: Methods and Applications* (volume 7) as well. The vast mass of matter to be presented makes it imperative that the material has to be divided into two parts. Needless to say that both parts have to be viewed as a unity. Formal sign for that is the consecutive numbering of the chapters over both volumes.

The first part deals with the basics and some first applications to relatively simple (one-dimensional) potential problems. We now begin the second part with the detailed discussion of the important quantum-mechanical observable *angular momentum*. We will call any vector operator an angular momentum, whose Hermitian components fulfill a certain set of commutation relations (Sect. 5.1). To this class of operators, there belongs, besides the orbital angular momentum known from *Classical Mechanics*, which we can transplant into *Quantum Mechanics* by the use of the *principle of correspondence*, the classically not understandable *spin*, for which such an analogy consideration is not possible. One could be content with postulating the spin, in a certain sense, as an empirical necessity, and analyzing the properties and consequences resulting from this postulate (Sect. 5.2). Since *spin, magnetic moment of the spin, and spin-orbit interaction* turn out to be properties, which are justifiable only relativistically, they therefore need the relativistic *Dirac theory* (Sect. 5.3) for the rigorous derivation. Furthermore, the *spin-orbit interaction* gives us the motivation to think about the rules for the *addition of angular momenta* (Sect. 5.4).

With the discussion of the *angular momentum*, the essential pillars of the abstract theoretical framework of Quantum Mechanics are now introduced so that we can turn in the next chapters toward somewhat more application-oriented problems. This starts in Chap. 6 with the important *central potentials*. For the historical development of *Quantum Mechanics*, in particular, the theory of the hydrogen atom has played a decisive role. The orbital electron moves in the Coulomb field of the positively charged hydrogen nucleus (proton), and underlies therewith the influence of a special central potential, to which, especially because of its historical importance, a rather broad space is devoted in this volume.

Only very few (realistic) problems of *Theoretical Physics* can be mathematically rigorously solved. A *'reasonable' approximation* to a not exactly solvable problem poses, according to experience, a non-trivial difficulty to the learner. We therefore discuss in Chap. 7 a series of well-established, but conceptually rather different methods: the *variational method* (Sect. 7.1), the different versions of *perturbation theory* (Sects. 7.2 and 7.3), and the semi-classical *WKB-method (phase integral method)* (Sect. 7.4). In current scientific research, one is frequently confronted with the task to develop one's own methods of approximation, which are specific just to the problem at hand. Also in such a case, the subtle understanding of the standard methods and the exact knowledge of their regions of validity may guide the way.

The Quantum Theory so far presented and discussed is, strictly speaking, a one-particle theory, whereas the real world is built up of interacting *many-particle systems*. Therefore we have to investigate (Chap. 8) what is additionally to be taken into account when treating many-particle systems. The demarcation between *distinguishable particles* and the so-called *identical particles* will turn out to be decisively important and will lead to the *principle of indistinguishability of identical particles*, which has no analog in Classical Physics. The *Pauli principle (exclusion principle)* is surely its weightiest consequence, by which the total composition of matter is regulated. For the description of *many-particle systems*, the *formalism of second quantization* has proven to be not only very elegant but also very often rather advantageous. The modern research literature is hardly readable without the knowledge of second quantization. In particular, in volume 9 of this basic course in Theoretical Physics, the formalism will be used almost exclusively. It therefore appears to be reasonable to present this method in some detail.

The final chapter deals with the *scattering theory*, which represents an important region of application of Quantum Mechanics. Via microscopic scattering (collision) processes, far-reaching information can be found about elementary interaction potentials, provided the theory succeeds in constructing connections between these potentials and the experimentally accessible cross sections.

This volume on *Quantum Mechanics* arose from lectures I gave at the German Universities in Würzburg, Münster, and Berlin. The animating interest of the students in my lecture notes has induced me to prepare the text with special care. The present one as well as the other volumes are thought to be the textbook material for the study of basic physics, primarily intended for the students rather than for the teachers.

I am thankful to the Springer company, especially to Dr. Th. Schneider, for accepting and supporting the concept of my proposal. The collaboration was always delightful and very professional. A decisive contribution to the book was provided by Prof. Dr. A. Ramakanth from the Kakatiya University of Warangal (India), a long-standing scientific partner and friend, who helped me in many respects. Many thanks for it!

Berlin, Germany Wolfgang Nolting
May 2017

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Chapter 5

Quantum Theory of the Angular Momentum

This chapter is devoted to the important quantum-mechanical observable *angular momentum*. We already know this quantity from Classical Mechanics, and we will therefore introduce the corresponding quantum-mechanical operator, at first (Sect. 5.1), by the use of the **principle of correspondence**. It will turn out, though, to be necessary to refer to the so defined observable in a somewhat more special manner as *orbital angular momentum*, since we will get to know other realizations of the angular momentum.

Starting at the classical Poisson brackets between the components of the classical angular momentum, we are led to a set of commutation relations, which will turn out to be so general that, from this moment on, we will call **every** vector operator, which fulfills these relations, an *angular momentum*. We will derive a basic relation between the *rotation operator* and the angular momentum, which will help us to recognize the deep physical relationships, which manifest themselves in the mentioned commutation relations.

It will then be possible to discuss the actual eigen-value problem of the angular momentum completely detached from the particular definition of the *orbital angular momentum*. The general result will be that the square of an angular momentum operator $\mathbf{J}^2$ will have eigen-values of the form $\hbar^2 j(j+1)$, where the *quantum number* j can assume integral or half-integral values. The z-component J_z of the operator of the angular momentum possesses, together with $\mathbf{J}^2$, common eigen-states with the eigen-values $\hbar m_j$, where the *magnetic quantum number* m_j runs through the values $m_j = -j, -j+1, \cdots, +j$. In the special case of the *orbital angular momentum*, j, and therewith also m_j, is an integer.

We know that not all quantum-mechanical observables possess a classical analog. A prominent example is the spin (Sect. 5.2), which is an *angular momen-*

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tum, which can assume integral as well as half-integral quantum numbers. We are going to introduce, at first *'correspondence-like'*, the observable *magnetic moment*. This is coupled, in the Hamilton operator, linearly to the external magnetic field **B**. The comparison between theory and experiment, for example in the case of the energy levels of an atom, leads to serious discrepancies, which make the incorporation of the **spin as intrinsic angular momentum** into Quantum Mechanics undoubtedly necessary. One can discuss the properties and the consequences of the, in such a way, empirically introduced spin, without referring to a strict justification of this term.

We postpone the convincing justification of the spin to Sect. 5.3 using the relativistic Dirac-theory of the electron. **Spin, spin magnetic moment** and the **spin-orbit interaction** turn out to be the particle properties, which can only be relativistically understandable. The spin-orbit interaction will finally provide us the motivation to think in Sect. 5.4 in detail about the rules which are to be obeyed for the *addition of angular momenta*.

5.1 Orbital Angular Momentum

5.1.1 Angular Momentum and Principle of Correspondence

When we recall Classical Mechanics (Vol. 1), we realize that for one important classical dynamic variable, we so far did not get to know the corresponding quantum-mechanical observable, namely for the angular momentum. For Classical Physics, we defined this quantity in Sect. 2.4.3 in Vol. 1 as follows: When a particle of the mass m with the momentum $\mathbf{p}$ passes a certain point of the space, which has, with respect to an arbitrary but fixed origin of coordinates, the position vector $\mathbf{r}$, then one denotes

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \tag{5.1}$$

as the *angular momentum* of this particle with the components:

$$\begin{aligned} L_x &= y\,p_z - z\,p_y \ , \\ L_y &= z\,p_x - x\,p_z \ , \\ L_z &= x\,p_y - y\,p_x \ . \end{aligned} \tag{5.2}$$

The definition reveals that $\mathbf{L}$ is not a genuine property of the particle since it also depends on the choice of the point of reference. As to the notation of the components of the angular momentum, we will use, according to expedience, one of the index triples (x, y, z) or $(1, 2, 3)$ as we already practiced with other vectorial quantities also ($L_x = L_1$, $L_y = L_2$, $L_z = L_3$). The three equations in (5.2), e.g., can be combined in the $(1, 2, 3)$-notation to:

$$L_i = \sum_{m,n} \varepsilon_{imn}\, x_m\, p_n \ . \tag{5.3}$$

Here ε_{imn} is the fully antisymmetric unit tensor of third rank ((1.193), Vol. 1):

$$\varepsilon_{imn} = \begin{cases} +1\ , & \text{if } (i,m,n) \text{ cyclic permutation of } (1,2,3)\ , \\ -1\ , & \text{if } (i,m,n) \text{ anticyclic permutation of } (1,2,3)\ , \\ 0\ , & \text{if two indexes are equal}\ . \end{cases} \tag{5.4}$$

As Exercise 3.5.1 (Vol. 6) we have shown that each component of the angular momentum can be written as a **Poisson bracket** between the two other components:

$$\{L_i,\, L_j\} = \sum_k \varepsilon_{ijk}\, L_k\ . \tag{5.5}$$

This relation will still turn out to be rather far-reaching. The same holds for the bracket between the square of the angular momentum,

$$\mathbf{L}^2 = L_x^2 + L_y^2 + L_z^2 = \sum_{i=1}^{3} L_i^2\ , \tag{5.6}$$

and the components L_i:

$$\{L_i,\, \mathbf{L}^2\} = 0\ . \tag{5.7}$$

Further Poisson brackets, also derived in Exercise 3.5.1 (Vol. 6), link the angular momentum with the position and the momentum of the particle:

$$\{L_i,\, \mathbf{r}^2\} \;=\; \{L_i,\, \mathbf{p}^2\} = 0 \qquad \forall i\ , \tag{5.8}$$

$$\{L_i,\, x_j\} \;=\; \sum_k \varepsilon_{ijk}\, x_k \qquad \forall i,j\ , \tag{5.9}$$

$$\{L_i,\, p_j\} \;=\; \sum_k \varepsilon_{ijk}\, p_k \qquad \forall i,j\ . \tag{5.10}$$

By using the principle of correspondence, formulated in Sect. 3.5 (Vol. 6), we now introduce the quantum-mechanical

orbital angular momentum

by the prescription to replace position and momentum in the classical definition of $\mathbf{L}$ (5.1), (5.3) by the corresponding Hermitian operators (observables):

$$\widehat{\mathbf{L}} \;=\; \hat{\mathbf{r}} \times \hat{\mathbf{p}}\ , \tag{5.11}$$

$$\widehat{L}_i \;=\; \sum_{m,n} \varepsilon_{imn}\, \hat{x}_m\, \hat{p}_n\ . \tag{5.12}$$

The non-commutability of *position* and *momentum* normally requires, for such a *'correspondence-like'* transition from classical variables to quantum-mechanical operators, a *symmetrization*, such as we discussed in Sect. 2.3.3 (Vol. 6). This

we can disregard here, though, because $\hat{x}_m$ and $\hat{p}_n$ do not commute only for $m = n$. But then ε_{imn} is equal to zero.

We call, intentionally, $\widehat{\mathbf{L}}$ *orbital* angular momentum, although for the classical analog we have always used only the term *angular momentum*. The reason is, in the next chapter we will get to know the *spin*, another angular momentum, which does not have such a classical analog, and can therefore not be represented by (5.11). Most of the properties, which we are now going to derive for the particular case of the orbital angular momentum, are, however, valid for every type of angular momentum. That means, they are also valid for the still to be introduced *spin*, or for the *total angular momentum*, which is an additive combination of the *spin* and the *orbital angular momenta*, or also for the *resulting angular momentum* of a multi-particle system.

To simplify the notation, we will again omit, as of now, the *'hat'*-symbol for marking quantum-mechanical operators, because our brief reminiscence of Classical Mechanics is already over, a mix-up with classical variables is not to be feared any longer.

It can be proved easily (Exercise 5.1.3), but nevertheless it is an important statement that the novel physical quantity, the *'orbital angular momentum'*, introduced in (5.11), is indeed an **observable**, i.e., it is a Hermitian operator:

$$\mathbf{L} = \mathbf{L}^{+} \; . \tag{5.13}$$

According to the principle of correspondence (3.229) (Vol. 6), the Poisson brackets between classical variables correspond, except for the trivial factor $i\,\hbar$, to commutators between corresponding quantum-mechanical observables. So we directly take from (5.5) the important commutation relation:

$$[L_i, L_j]_- = i\,\hbar \sum_k \varepsilon_{ijk}\, L_k \qquad \forall i, j \; . \tag{5.14}$$

The various components of the orbital angular momentum thus do not commute with each other. It is therefore impossible to precisely measure any two components at the same time. Because of the formal similarity of (5.14) and the vector product ((1.195), Vol. 1), one sometimes expresses the full set of commutation relations in the compact form

$$\mathbf{L} \times \mathbf{L} = i\,\hbar\,\mathbf{L} \; . \tag{5.15}$$

One has to read this equation of course as an operator-vector product, since for *normal* vectors the left-hand side would be zero:

$$\mathbf{L} \times \mathbf{L} = \begin{pmatrix} L_y\,L_z - L_z\,L_y \\ L_z\,L_x - L_x\,L_z \\ L_x\,L_y - L_y\,L_x \end{pmatrix} = \begin{pmatrix} [L_y,\, L_z]_- \\ [L_z,\, L_x]_- \\ [L_x,\, L_y]_- \end{pmatrix} = i\,\hbar \begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} \; .$$

The representation (5.15), though, is without big practical benefit, being more or less a *'playing around'*. The statement, which we derive from (5.7), namely that

the square of the orbital angular momentum $\mathbf{L}^2$ commutes with **each** component of $\mathbf{L}$, is much more important:

$$\left[\mathbf{L}^2,\, L_i\right]_- = 0 \qquad \forall i\ . \tag{5.16}$$

$\mathbf{L}^2$ and one component of $\mathbf{L}$ thus build a system of simultaneously precisely measurable observables. For these operators—it is common to take $\mathbf{L}^2$ and $L_z = L_3$—there must therefore exist a common set of eigen-states. We will deal with their explicit derivation in the section after the next.

Non-commutability of observables and uncertainty principle are rather closely coupled quantum-mechanical phenomena. Because of (5.14), the components of the orbital angular momentum are, according to ((3.155), Vol. 6), subject to the following generalized uncertainty relations:

$$\begin{aligned} \Delta L_x\, \Delta L_y &\geq \frac{\hbar}{2} |\langle L_z \rangle|\ , \\ \Delta L_y\, \Delta L_z &\geq \frac{\hbar}{2} |\langle L_x \rangle|\ , \\ \Delta L_z\, \Delta L_x &\geq \frac{\hbar}{2} |\langle L_y \rangle|\ . \end{aligned} \tag{5.17}$$

We have been able to take the commutators (5.14) and (5.16) here directly, by the use of the principle of correspondence ((3.229), Vol. 6), from the previously calculated Poisson brackets. Of course, one could have derived them directly from the definition (5.11) of the orbital angular momentum by means of the fundamental position-momentum commutator

$$[x_i,\, p_j]_- = i\,\hbar\,\delta_{ij}\ .$$

We recommend this direct calculation as Exercise 5.1.4, together with the verification of the following relations, which are related to the Poisson brackets in (5.8), (5.9), (5.10):

$$[L_i,\, \mathbf{r}^2]_- = [L_i,\, \mathbf{p}^2]_- = 0 \quad \forall i\ , \tag{5.18}$$

$$[L_i,\, x_j]_- = i\,\hbar \sum_k \varepsilon_{ijk}\, x_k \quad \forall i, j\ , \tag{5.19}$$

$$[L_i, p_j]_- = i\,\hbar \sum_k \varepsilon_{ijk}\, p_k \quad \forall i, j\ . \tag{5.20}$$

We want to introduce, finally, two further operator combinations which will turn out as rather useful for the following argumentations:

$$L_+ = L_x + i\,L_y\ ; \qquad L_- = L_x - i\,L_y\ . \tag{5.21}$$

Sometimes they are called *ladder operators* or *steps operators*. In Sect. 5.1.4 they will remind us, in their properties and applications, of the *creation operator* and *annihilation operator* used for the harmonic oscillator (Sect. 4.4, Vol. 6). These are adjoint to each other and are non-Hermitian. Later we will frequently use the following commutators, built with $L_\pm$:

$$[L_+,\, L_-]_- = 2\hbar\, L_z\ . \tag{5.22}$$

Proof:

$$\begin{aligned}[L_+, L_-]_- &= [L_x + i\,L_y,\, L_x - i\,L_y]_- = -i[L_x, L_y]_- + i[L_y, L_x]_- \\ &= \hbar\,L_z + \hbar\,L_z = 2\hbar\,L_z \qquad \text{q.e.d.}\,,\end{aligned}$$

$$[L_z, L_\pm]_- = \pm\hbar\,L_\pm\,. \tag{5.23}$$

Proof:

$$\begin{aligned}[L_z, L_\pm]_- &= [L_z, L_x \pm i\,L_y]_- = [L_z, L_x] \pm i[L_z, L_y]_- \\ &= i\,\hbar\,L_y \pm i(-i\,\hbar\,L_x) = \pm\hbar(L_x \pm i\,L_y) = \pm\hbar\,L_\pm \qquad \text{q.e.d.}\,,\end{aligned}$$

$$[\mathbf{L}^2, L_\pm]_- = 0\,. \tag{5.24}$$

This relation follows of course immediately from the fact that $\mathbf{L}^2$ commutes with each component of $\mathbf{L}$.

We close this section with **two remarks**:

1. For the handling of the eigen-value problem (see Sect. 5.1.4) we actually need only the commutation relations (5.14) and (5.16), where the latter is already a consequence of (5.14). We can therefore ignore for the further discussion the concrete definition of the orbital angular momentum. We will consider each vector operator, whose components fulfill (5.14), as *angular momentum*.

2. We had found in Sect. 1.4.3 of Vol. 2, in the framework of Lagrange Mechanics, by means of simple symmetry considerations, that, for a closed system, the constancy of the classical angular momentum is fundamentally related to the **isotropy of the space**. In turn, *isotropy of the space* means that the properties of the system are invariant with respect to arbitrary space rotations. How does, however, this connection between space rotations and operator of angular momentum manifests itself in Quantum Mechanics? We try to answer this question in the next section, before we go to the actual solution of the eigen-value problem in Sect. 5.1.4.

5.1.2 Rotations and Operator of Angular Momentum

There are two equivalent possibilities to represent rotations. One can think of a rotation by the system itself, where the reference system remains fixed (*active rotation*), or one holds the system down and rotates the reference system correspondingly (*passive rotation*). Both versions of course lead to the same results. In Sect. 1.6.3 of Vol. 1 we have for the first time dealt with rotations, and have described them in their *passive* form. Let us choose here the other possibility and reenact once more the line of thought from Vol. 1.

Let Σ be a space-fixed system of coordinates, whose axial directions are given by the orthogonal unit vectors $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$. Within this reference system Σ,

our physical system is to be *rotated*. We define, in a way as *auxiliary quantity*, the system of coordinates $\overline{\Sigma}$, which co-rotates with the physical system. Let its axes be oriented in the directions of the also orthogonal unit vectors $\overline{\mathbf{e}}_1$, $\overline{\mathbf{e}}_2$, $\overline{\mathbf{e}}_3$. Let Σ and $\overline{\Sigma}$ share the same fixed origin of coordinates. We now consider the position vector of a point in the system,

$$\mathbf{r} = (x_1,\, x_2,\, x_3) \;\text{ in }\; \Sigma\,,$$

which performs in the space-fixed system of coordinates the rotation, thereby of course changing its components:

$$\mathbf{r} \to \overline{\mathbf{r}} = (\overline{x}_1,\, \overline{x}_2,\, \overline{x}_3) \;\text{ in }\; \Sigma\,.$$

In the co-rotating system of coordinates $\overline{\Sigma}$ the position vector retains its *old* components:

$$\overline{\mathbf{r}} = (x_1,\, x_2,\, x_3) \;\text{ in }\; \overline{\Sigma}\,.$$

This means:

$$\sum_{i=1}^{3} \overline{x}_i\, \mathbf{e}_i = \sum_{j=1}^{3} x_j\, \overline{\mathbf{e}}_j\,. \tag{5.25}$$

Scalar multiplication by $\mathbf{e}_i$ yields the components after the rotation in Σ:

$$\overline{x}_i = \sum_{j=1}^{3} (\mathbf{e}_i \cdot \overline{\mathbf{e}}_j)\, x_j \equiv \sum_{j=1}^{3} D_{ij}\, x_j\,. \tag{5.26}$$

This relation is valid for arbitrary position vectors. It defines the (3×3)-rotation matrix:

$$D = (D_{ij})_{i,j\,=\,1,2,3}\,; \quad D_{ij} = \cos\varphi_{ij} = (\mathbf{e}_i \cdot \overline{\mathbf{e}}_j)\,. \tag{5.27}$$

φ_{ij} is the angle, enclosed by the i-axis in Σ and the j-axis in $\overline{\Sigma}$. The elements of the rotation matrix are all real. By the use of D, Eq. (5.26) can also be read as matrix equation:

$$\overline{\mathbf{r}} = D\,\mathbf{r}\,. \tag{5.28}$$

Especially for the basis vector $\overline{\mathbf{e}}_i$ of the co-rotated system $\overline{\Sigma}$, we find in Σ:

$$\overline{\mathbf{e}}_i = \sum_{j=1}^{3} x_j^{(i)}\, \mathbf{e}_j\,; \quad x_j^{(i)} = (\mathbf{e}_j \cdot \overline{\mathbf{e}}_i) = D_{ji}\,.$$

It follows immediately from the orthonormality of the basis vectors $\overline{\mathbf{e}}_i$ that the columns of the rotation matrix are pairwise orthonormal:

$$\overline{\mathbf{e}}_i \cdot \overline{\mathbf{e}}_j = \delta_{ij} = \sum_{k,m} D_{ki}\, D_{mj}\, (\mathbf{e}_k \cdot \mathbf{e}_m) = \sum_{k} D_{ki}\, D_{kj}\,. \tag{5.29}$$

That can be shown, similarly simply, also for the rows of the rotation matrix (see Exercise 5.1.7). To guarantee that the rotated system of coordinates $\overline{\Sigma}$ is a right-handed system like Σ, we still have to require

$$\det D = 1 \, .$$

The proof of this fact is provided by Eq. (1.344) in Vol. 1.

Because of $D^{-1} D = \mathbb{1}$, the inverse rotation matrix undoes the rotation (5.28) and is therefore defined by

$$\mathbf{r} = D^{-1} \, \overline{\mathbf{r}} \, . \tag{5.30}$$

When one multiplies (5.25) scalarly by $\overline{\mathbf{e}}_j$, one obtains:

$$x_j = \sum_i (\mathbf{e}_i \cdot \overline{\mathbf{e}}_j) \, \overline{x}_i = \sum_i D_{ij} \, \overline{x}_i \overset{!}{=} \sum_i (D^{-1})_{ji} \, \overline{x}_i \, .$$

Thus D^{-1} arises from D simply by interchanging rows and columns, and is, according to that, just the transposed matrix:

$$D^{-1} = D^T \, . \tag{5.31}$$

We have therewith recalled the most important properties of the rotation matrix, which can easily be demonstrated by the example of the

rotation by the angle φ around the $x_3 = z$-axis:

$$D_z(\varphi) = \begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{5.32}$$

But what is to be understood quantum-mechanically by the *rotation of a physical system*? How can we introduce a rotation operator $\widehat{D}$, which quantum-mechanically does just the same job as is classically done by the rotation matrix? We now want to consider these questions.

As a start, we have to assume that the state of the system $|\psi\rangle$ will be changed by the application of the still unknown rotation operator:

$$|\overline{\psi}\rangle = \widehat{D} |\psi\rangle \, . \tag{5.33}$$

Analogous to the fact that the lengths of vectors do not change with rotations in the three-dimensional space, the norm of the state $|\psi\rangle$ should remain invariant under the action of $\widehat{D}$:

$$\langle\overline{\psi}|\overline{\psi}\rangle = \langle\psi|\psi\rangle \implies \widehat{D}^+ = \widehat{D}^{-1} \, . \tag{5.34}$$

$\widehat{D}$ should thus be a unitary operator! That corresponds, in the case of the classical rotation, to Eq. (5.31) and to the fact that the elements of the rotation matrix are all real.

$\widehat{D}$ should now *quantum-mechanically rotate* not only the states but also the observables. Figuratively, rotation of an observable always means rotation of the corresponding measuring equipment, and that too in such a way that the measurement of the *rotated* observable $\overline{A}$ in the *rotated* state $|\overline{\psi}\rangle$ yields the same results as the measurement of A in the state $|\psi\rangle$:

$$\left\langle \overline{\psi}\middle|\overline{A}\middle|\overline{\psi}\right\rangle \stackrel{!}{=} \langle\psi|A|\psi\rangle \implies \overline{A} = \widehat{D}\,A\,\widehat{D}^{+} \,. \tag{5.35}$$

The rotation operator thus mediates a **unitary transformation** (see (3.90), Vol. 6) of states and observables.

So far, the considerations concerning $\widehat{D}$ are still performed rather generally. We now want to become more concrete and exploit the fact that, in the classical limit, $\widehat{D}$ should have the same action as the rotation matrix. When we apply the rotation operator $\widehat{D}$ to the position operator, we can use that in the position representation the position operator is just the vector $\mathbf{r}$. In the position representation, $\widehat{D}$ has to therefore reproduce the action of the rotation matrix formulated in Eq. (5.28). What does this mean for the wave function $\psi(\mathbf{r})$? For a start, it holds, if we perform in (5.33) the transition into the position representation according to the rule ((3.253), Vol. 6):

$$\overline{\psi}(\overline{\mathbf{r}}) = \left\langle \overline{\mathbf{r}}\middle|\overline{\psi}\right\rangle = \left\langle \overline{\mathbf{r}}|\widehat{D}|\psi\right\rangle = D\,\psi(\overline{\mathbf{r}}) \,. \tag{5.36}$$

Because of the unitarity of $\widehat{D}$ it must also be:

$$\overline{\psi}(\overline{\mathbf{r}}) = \langle\overline{\mathbf{r}}|\overline{\psi}\rangle = \left\langle \mathbf{r}|\widehat{D}^{+}\widehat{D}|\psi\right\rangle = \langle\mathbf{r}|\psi\rangle = \psi(\mathbf{r}) \,.$$

When we combine these two equations, we get:

$$D\,\psi(\overline{\mathbf{r}}) = \psi(\mathbf{r}) = \psi\left(D^{-1}\,\overline{\mathbf{r}}\right) \,. \tag{5.37}$$

Let us explicitly evaluate this formula for the example (5.32), where we restrict ourselves, however, to an **infinitesimal rotation** $d\varphi$, for which we can replace the cosine by 1 and the sine by its argument:

$$D_z(d\varphi) = \begin{pmatrix} 1 & -d\varphi & 0 \\ d\varphi & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \;; \quad D_z^{-1}(d\varphi) = \begin{pmatrix} 1 & d\varphi & 0 \\ -d\varphi & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \,.$$

This means in (5.37):

$$\begin{aligned} D_z(d\varphi)\psi(\overline{x},\overline{y},\overline{z}) &= \psi(\overline{x}+d\varphi\,\overline{y}, -d\varphi\overline{x}+\overline{y},\overline{z}) \\ &= \psi(\overline{x},\overline{y},\overline{z}) + d\varphi\left(\overline{y}\frac{\partial\psi}{\partial\overline{x}} - \overline{x}\frac{\partial\psi}{\partial\overline{y}}\right) + \mathcal{O}(d\varphi^2) \,. \end{aligned}$$

We have added a Taylor expansion. From the fact that ψ is arbitrary, we infer the following operator identity (bars can now be removed):

$$D_z(d\varphi) = \mathbf{1} + d\varphi\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right) \,.$$

On the right-hand side we recognize with (5.2), except for a numerical factor, the z-component of the orbital angular momentum in its position representation $\big(p_x = (\hbar/i)\,(\partial/\partial x),\, p_y = (\hbar/i)\,(\partial/\partial y)\big)$:

$$D_z(d\varphi) = \mathbf{1} - d\varphi\,\frac{i}{\hbar}\,L_z\ . \tag{5.38}$$

This result takes a bit more general form when the rotation is carried out around an arbitrary axis in the direction of the unit vector $\mathbf{n}$:

$$D_{\mathbf{n}}(d\varphi) = \mathbf{1} - d\varphi\,\frac{i}{\hbar}(\mathbf{n}\cdot\mathbf{L})\ . \tag{5.39}$$

We have derived therewith the important statement:

The orbital angular momentum is the generating function of infinitesimal rotations!

The result (5.39) can easily be transferred to finite angles φ. At first we can use of course:

$$D_{\mathbf{n}}(d\varphi + d\psi) = D_{\mathbf{n}}(d\varphi)\,D_{\mathbf{n}}(d\psi)\ .$$

When we now take $\Delta\varphi = \varphi/m \underset{m\to\infty}{\longrightarrow} d\varphi\,(m \in \mathbb{N})$, we can write:

$$D_{\mathbf{n}}(\varphi) = \lim_{m\to\infty}\left[1 - \frac{1}{m}\,\frac{i}{\hbar}\,\varphi(\mathbf{n}\cdot\mathbf{L})\right]^m\ .$$

With the definition of the exponential function

$$e^x = \lim_{m\to\infty}\left(1 + \frac{x}{m}\right)^m$$

we have eventually:

$$D_{\mathbf{n}}(\varphi) = \exp\left[-\frac{i}{\hbar}\,(\mathbf{n}\cdot\mathbf{L})\varphi\right]\ . \tag{5.40}$$

The last element in our chain of conclusions is now, to move away from the special position representation and to interpret (5.40) as the general representation-independent connection between rotation operator $\widehat{D}_{\mathbf{n}}(\varphi)$ and component of the orbital angular momentum $\mathbf{n}\cdot\mathbf{L}$.

When one compares (5.40) with ((3.249), Vol. 6), one recognizes that the orbital angular momentum plays for rotations the same role as the momentum $\mathbf{p}$ for translations.

5.1.3 Commutation Relations

In order to be fully convinced that the orbital angular momentum $\mathbf{L}$, introduced with (5.40), is indeed the same operator as that which we transferred in Sect. 5.1.1 *'correspondence-like'* from Classical Physics into Quantum Mechanics, we still have to verify that its components fulfill the fundamental commutation relations (5.14).

For this purpose we go back once more to the infinitesimal rotation about the axis $\mathbf{n}$. As to this, the vector $\mathbf{e}$ is rotated by the angle $d\varphi$. We read off from

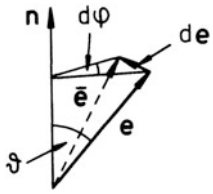

Figure 5.1: Angle relations for the rotation of the unit vector **e** about the axial direction **n**

Fig. 5.1:

$$\begin{aligned} \overline{\mathbf{e}} &= \mathbf{e} + d\mathbf{e}\,; \quad d\mathbf{e} \uparrow\uparrow \mathbf{n} \times \mathbf{e}\,, \\ de &= e \sin\vartheta\, d\varphi = |\mathbf{n} \times \mathbf{e}| d\varphi\,. \end{aligned}$$

This means altogether:

$$\overline{\mathbf{e}} = \mathbf{e} + (\mathbf{n} \times \mathbf{e})\, d\varphi\,. \tag{5.41}$$

Let us now consider an arbitrary vector operator:

$$\mathbf{A} = \sum_{i=1}^{3} A_i\, \mathbf{e}_i \qquad (A_i = \mathbf{A} \cdot \mathbf{e}_i)\,. \tag{5.42}$$

Its components A_i transform, according to (5.35) and (5.39), with an infinitesimal rotation by $d\varphi$, as

$$\overline{A}_i = \widehat{D}_{\mathbf{n}}(d\varphi)\, A_i\, \widehat{D}^{+}_{\mathbf{n}}(d\varphi) = A_i - d\varphi\, \frac{i}{\hbar}\, [\mathbf{n} \cdot \mathbf{L},\, A_i]_-\,.$$

This corresponds to the *infinitesimal unitary transformation*, which was formulated, very generally, in ((3.95), Vol. 6).

It must now be possible, however, to calculate the transformed components also by using the formula (5.41), which is of course valid for unit vectors, too:

$$\overline{A}_i \equiv \mathbf{A} \cdot \overline{\mathbf{e}}_i = \mathbf{A} \cdot [\mathbf{e}_i + (\mathbf{n} \times \mathbf{e}_i)\, d\varphi] = A_i + \mathbf{A} \cdot (\mathbf{n} \times \mathbf{e}_i)\, d\varphi\,.$$

The comparison of these two equivalent expressions for $\overline{A}_i$ leads to the very useful relation:

$$[\mathbf{n} \cdot \mathbf{L},\, \mathbf{e}_i \cdot \mathbf{A}]_- = i\,\hbar (\mathbf{n} \times \mathbf{e}_i) \cdot \mathbf{A}\,. \tag{5.43}$$

Note that this equation is valid for **arbitrary** vector operators. It holds of course also when $\mathbf{A} = \mathbf{L}$. But then we get immediately with

$$[L_x,\, L_y]_- = i\,\hbar\, (\mathbf{e}_x \times \mathbf{e}_y) \cdot \mathbf{L} = i\,\hbar\, L_z\,, \tag{5.44}$$

$$[L_y,\, L_z]_- = i\,\hbar\, (\mathbf{e}_y \times \mathbf{e}_z) \cdot \mathbf{L} = i\,\hbar\, L_x\,, \tag{5.45}$$

$$[L_z,\, L_x]_- = i\,\hbar\, (\mathbf{e}_z \times \mathbf{e}_x) \cdot \mathbf{L} = i\,\hbar\, L_y \tag{5.46}$$

the fundamental commutation relations (5.14) of the components of the orbital angular momentum. When choosing $\mathbf{A} = \mathbf{r} = (x_1, x_2, x_3)$ we find with (5.43):

$$[L_i,\, x_j]_- = i\,\hbar\,(\mathbf{e}_i \times \mathbf{e}_j)\cdot\mathbf{r} = i\,\hbar \sum_k \varepsilon_{ijk}\, x_k \ .$$

This agrees with (5.19). For $\mathbf{A} = \mathbf{p} = (p_1, p_2, p_3)$ (5.43) yields with

$$[L_i,\, p_j]_- = i\,\hbar\,(\mathbf{e}_i \times \mathbf{e}_j)\cdot\mathbf{p} = i\,\hbar \sum_k \varepsilon_{ijk}\, p_k$$

exactly the relation (5.20). Now we are sure that the operator of the orbital angular momentum, *'correspondence-like'* introduced in Sect. 5.1.1 and the operator from (5.40), which generates the rotation, are completely identical. The considerations to (5.40), though, help us to recognize more clearly the deep physical connections.

More important conclusions result for the **scalar rotation-invariant operators** S, as for instance $\mathbf{p}^2$, $\mathbf{r}^2$ and $\mathbf{L}^2$, which, by definition, remain uninfluenced by rotations. For these it must be $\overline{S} = S$ and therewith according to (5.35):

$$S \stackrel{!}{=} \overline{S} = \widehat{D}\, S\, \widehat{D}^{+} \iff S\,\widehat{D} = \widehat{D}\, S \iff [S,\, \widehat{D}]_- = 0 \ .$$

A scalar rotation-invariant operator thus commutes with the rotation operator and therewith, because of (5.40), also with each component of the orbital angular momentum:

$$[S,\, (\mathbf{n}\cdot\mathbf{L})]_- = 0 \ . \tag{5.47}$$

From our symmetry considerations, it follows therewith immediately (5.16),

$$[\mathbf{L}^2,\, L_i]_- = 0 \qquad \forall i \ ,$$

as well as (5.18):

$$[\mathbf{r}^2,\, L_i]_- = [\mathbf{p}^2,\, L_i]_- = 0 \ .$$

In Chap. 6 we will investigate central fields, which are characterized by $V(\mathbf{r}) = V(r)$. The full Hamilton operator is then invariant with respect to rotations, so that we can assume, without explicit investigation, that in such a case H, $\mathbf{L}^2$ and L_z must have a common set of eigen-states, since H commutes with each component of $\mathbf{L}$.

5.1.4 Eigen-Value Problem

For the following purely algebraic considerations we need out of the properties of the orbital angular momentum only its fundamental commutation relations (5.14) and the fact that its components are all Hermitian operators. We had already agreed upon calling **any** vector operator, which fulfills these conditions, an *angular momentum*. We therefore detach ourselves in this chapter from

the concrete view of an orbital angular momentum, formally indicating that by the use of the symbol J for the more general angular momentum, instead of L. The results of this section are then correct in particular for the orbital angular momentum, but not exclusively for it. They are for instance also valid for the important observable *spin*, which will be introduced in a forthcoming section.

We know that $\mathbf{J}^2$ commutes with each component of $\mathbf{J}$, and that, on the other hand, the various components do not commute with one another. It is conventional to pick out $J_3 = J_z$. We can then assume that $\mathbf{J}^2$ and J_z possess a common set of eigen-states. We want to mark these common eigen-states, at first, by the symbol $|\alpha_j m\rangle$, and assume that they are normalized to one. In the eigen-value equations

$$\begin{aligned} \mathbf{J}^2|\alpha_j\, m\rangle &= \hbar^2\alpha_j|\alpha_j\, m\rangle\,, & (5.48)\\ J_z|\alpha_j\, m\rangle &= \hbar\, m|\alpha_j\, m\rangle & (5.49) \end{aligned}$$

α_j and m are dimensionless numbers. Furthermore, we start from a Hilbert space, in which $\mathbf{J}^2$ and J_z represent a complete set of compatible observables.

The further course of action will remind us strongly of the considerations on the harmonic oscillator in Sect. 4.4.2 in Vol. 6. The ladder operators $J_\pm$, defined in (5.21), allow for a similar solution of the eigen-value problem as for the harmonic oscillator by the use of the creation and annihilation operators a^+ and a. J_+ and J_- comply with the commutation relations (5.23) and (5.24), since these have been derived directly by the use of the commutators (5.14). We prove therewith the following assertion:

If $|\alpha_j\, m\rangle$ is an eigen-state of $\mathbf{J}^2$ and J_z, then $J_\pm|\alpha_j\, m\rangle$ is also an eigen-state of $\mathbf{J}^2$ with the same eigen-value $\hbar^2\alpha_j$, and of J_z with the eigen-value $\hbar(m \pm 1)$.

The assertion consists of two parts. Since, according to (5.24), $\mathbf{J}^2$ commutes with $J_\pm$, it follows at first:

$$\mathbf{J}^2(J_\pm|\alpha_j\, m\rangle) = J_\pm\, \mathbf{J}^2|\alpha_j\, m\rangle = \hbar^2\alpha_j(J_\pm|\alpha_j\, m\rangle)\,. \tag{5.50}$$

$J_\pm|\alpha_j\, m\rangle$ is thus indeed an eigen-state of $\mathbf{J}^2$ with the same eigen-value as $|\alpha_j\, m\rangle$. We now use (5.23), in order to prove the second part of the assertion:

$$\begin{aligned} J_z(J_\pm|\alpha_j\, m) &= ([J_z,\, J_\pm]_- + J_\pm\, J_z)|\alpha_j\, m\rangle\\ &= (\pm\hbar\, J_\pm + \hbar\, m\, J_\pm)|\alpha_j\, m\rangle\\ &= \hbar(m \pm 1)\,(J_\pm|\alpha_j\, m\rangle)\,. \end{aligned} \tag{5.51}$$

The application of J_+ and J_- to the eigen-state $|\alpha_j\, m\rangle$ raises and lowers, respectively, the eigen-value of J_z by one $\hbar$.

We want to collect further information about the eigen-values α_j and m: Because of the hermiticity of the components J_x and J_y of the angular momentum the expectation values of the operators $J_{x,y}^2$ in arbitrary states $|\psi\rangle$ are non-negative:

$$\begin{aligned} \langle\psi|J_x^2|\psi\rangle &= \|J_x\,\psi\|^2 \geq 0\,,\\ \langle\psi|J_y^2|\psi\rangle &= \|J_y\,\psi\|^2 \geq 0\,. \end{aligned}$$

On the right-hand side there stands the norm of the state $J_{x,y}|\psi\rangle$, which, according to ((3.18), Vol. 6), cannot be negative. When we choose, in particular, $|\psi\rangle = |\alpha_j\, m\rangle$, then it follows from

$$\langle \alpha_j\, m|(J_x^2 + J_y^2)|\alpha_j\, m\rangle \geq 0\ ,$$

because of $J_x^2 + J_y^2 = \mathbf{J}^2 - J_z^2$:

$$\hbar^2(\alpha_j - m^2) \geq 0\ .$$

This in turn means:

$$-\sqrt{\alpha_j} \leq m \leq +\sqrt{\alpha_j}\ . \tag{5.52}$$

Since we have shown with (5.51) that, by application of J_+ to $|\alpha_j\, m\rangle$, an eigenstate results with a *quantum number* m raised by one and an unchanged α_j, we have to argue from (5.52) that there must exist a maximal $m = j$. A state $|\alpha_j\, m\rangle$ with $m > j$ can not appear. Thus it must be:

$$J_+|\alpha_j\, j\rangle = 0\ . \tag{5.53}$$

We will deliver at a later stage the proof that in the interval (5.52) there is indeed **only one** $m = j$, which fulfills (5.53). The same line of thought leads, with the properties of J_-, to the existence of a minimal $m = \hat{m}$:

$$J_-|\alpha_j\, \hat{m}\rangle = 0\ . \tag{5.54}$$

Also here, we will later be able to show that there exists **exactly one** of such an $m = \hat{m}$ in the interval (5.52).

One easily proves by complete induction, as generalization of (5.23), the commutation relation:

$$[J_z,\, J_\pm^n]_- = \pm n\, \hbar\, J_\pm^n \qquad (n = 0, 1, 2, \ldots)\ . \tag{5.55}$$

The assertion is surely true for $n = 0$ and $n = 1$. In the case that it is true for n, we draw the conclusion for $n + 1$:

$$\begin{aligned} [J_z,\, J_\pm^{n+1}]_- &= J_\pm [J_z,\, J_\pm^n]_- + [J_z,\, J_\pm]_-\, J_\pm^n \\ &= \pm n\, \hbar\, J_\pm\, J_\pm^n \pm \hbar J_\pm\, J_\pm^n = \pm(n+1)\, \hbar\, J_\pm^{n+1}\ . \end{aligned}$$

As in (5.51) one then shows:

$$J_z\, (J_\pm^n|\alpha_j m\rangle) = \hbar(m \pm n)\, (J_\pm^n|\alpha_j m\rangle)\ . \tag{5.56}$$

$J_\pm^n|\alpha_j m\rangle$ is thus as $|\alpha_j m\rangle$ eigen-state of J_z with a *quantum number* m changed by $\pm n$.

But if it is really so that in the interval (5.52) there is **exactly one** $m = j$, for which (5.53) is fulfilled, and **exactly one** $m = \hat{m}$ according to (5.54), then it must be possible to transfer the states $|\alpha_j\, j\rangle$ and $|\alpha_j \hat{m}\rangle$ by application of J_+^n

and J_-^n, respectively, into each other with the proper n, at least except for an unimportant numerical factor. But that means that the difference between the maximal and the minimal m,

$$j - \hat{m} = n = 0, 1, 2, \dots \ , \tag{5.57}$$

must be a non-negative integer.

We now still exploit two further relations which can easily be verified by insertion of the respective definitions (Exercise 5.1.6):

$$J_+ J_- = \mathbf{J}^2 - J_z^2 + \hbar J_z \ , \tag{5.58}$$
$$J_- J_+ = \mathbf{J}^2 - J_z^2 - \hbar J_z \ . \tag{5.59}$$

The second equation enables, with (5.53), the fixing of α_j:

$$\begin{aligned} J_- J_+ |\alpha_j \, j\rangle = 0 &= (\mathbf{J}^2 - J_z^2 - \hbar J_z)|\alpha_j \, j\rangle \\ &= (\hbar^2 \alpha_j - \hbar^2 j^2 - \hbar^2 j)|\alpha_j \, j\rangle \ . \end{aligned}$$

This means:

$$\alpha_j = j(j+1) \ . \tag{5.60}$$

Using (5.58) we now can easily determine the minimal m:

$$\begin{aligned} J_+ J_- |\alpha_j \, \hat{m}\rangle \overset{(5.54)}{=} 0 &= (\mathbf{J}^2 - J_z^2 + \hbar J_z)|\alpha_j \, \hat{m}\rangle \\ &= \hbar^2(\alpha_j - \hat{m}^2 + \hat{m})|\alpha_j \, \hat{m}\rangle \ . \end{aligned}$$

Hence it must be

$$j(j+1) = \hat{m}(\hat{m} - 1) \ .$$

This equation has two solutions, namely $\hat{m} = j + 1$ and $\hat{m} = -j$. The first does not come into question because j is already the maximal value of m. Therefore, we have to take:

$$\hat{m} = -j \ . \tag{5.61}$$

The difference between maximal and minimal m-value therewith amounts to $2j$. According to (5.57) j must therefore be an integral or half-integral number.

Let us summarize once more, which important statements about the eigenvalue spectrum of the angular momentum, we were able to derive so far, only on the basis of the algebraic form of the commutation relation (5.14):

1. $\mathbf{J}^2$ has eigen-values of the form

   $$\hbar^2 j(j+1) \ ,$$

   with the possible quantum numbers

   $$j = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots \tag{5.62}$$

2. J_z has eigen-values of the form

$$\hbar\, m\ ,$$

where m assumes one of the $(2j+1)$ values

$$m = -j,\ -j+1, \ldots, j-1,\ j\ . \tag{5.63}$$

Since, according to (5.60), α_j is uniquely fixed by j, we change, from now onwards, the state symbol:

$$|\alpha_j\, m\rangle \ \longrightarrow\ |j\, m\rangle\ .$$

One says that the system in the eigen-state $|j\, m\rangle$ possesses the *angular momentum* (j, m).

Let us still comment a bit on the results so far at hand. If one performs a measurement on the system only for the observable $\mathbf{J}^2$, then, after the measurement, the state lies in the $(2j+1)$-dimensional subspace, which is spanned by the states $|j\, j\rangle, |j\, j-1\rangle, \ldots, |j\ -j+1\rangle, |j\ -j\rangle$:

$$|\psi\rangle = \sum_{m\,=\,-j}^{+j} \gamma_m |j\, m\rangle\ .$$

One speaks of *directional degeneracy*. Incidentally, the common eigen-states of $(\mathbf{J}^2, J_x)$ and of $(\mathbf{J}^2, J_y)$ are of course also in this subspace. We have pretty arbitrarily taken J_z for our considerations; we could have taken equally well J_x or J_y. The physically relevant results would have been the same. For instance as a matter of course, J_x and J_y have the same eigen-values (5.63) as J_z. The not directly measurable eigen-states, though, will be different.

By an additional measurement of J_z the *directional degeneracy* is removed and replaced by a **directional quantization**, which states that not all orientations of the angular momentum are allowed. The graphical interpretation of the results uses the semi-classical vector model (Fig. 5.2). Since one cannot precisely measure the three components of the angular momentum simultaneously, it makes little sense to represent $\mathbf{J}$ as a space-fixed vector arrow. One helps oneself with the imagination that $\mathbf{J}$ is **precessing** as a vector arrow around the ***z*-axis**, and that on the barrel surface of a cone, whose height is equal to $\hbar\, m$, while its barrel line amounts to $\hbar\sqrt{j(j+1)}$. The precession of the vector arrow conveys the impression of the uncertainty of J_x and J_y for a simultaneously precisively measured z-component. The cone radius comes out as $\hbar\sqrt{j(j+1)-m^2}$, which corresponds to an eigen-value of the operator $\sqrt{\mathbf{J}^2 - J_z^2} = \sqrt{J_x^2 + J_y^2}$. Some details are classically not explainable, being typical quantum-mechanical effects. So, except for the trivial case $j = 0$, $\sqrt{j(j+1)}$ is always greater than j. Obviously, the angular momentum $\mathbf{J}$ is not able to exactly occupy the direction of its maximal component. The maximal component is with $\hbar\, j$ always smaller than the *vector length* $\hbar\sqrt{j(j+1)}$. The exact orientation along the z-axis, though, would fix precisely J_x and J_y, in contradiction to the uncertainty

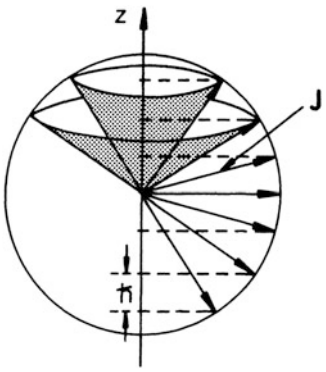

Figure 5.2: Illustration by the semi-classical vector model of the directional quantization of the quantum-mechanical angular momentum

relation. The *classically astonishing* result is of course the directional quantization, which has been postulated already in the older Bohr-Sommerfeld theory, but could not strictly be justified at that time (see Sect. 1.5, Vol. 6).

Let us now come back to our eigen-value problem and try to find out something more about the eigen-states. We had recognized with (5.51) that with $|j\,m\rangle$ also $J_\pm|j\,m\rangle$ is an eigen-state of $(\mathbf{J}^2, J_z)$. Since, because of our initial precondition, $(\mathbf{J}^2, J_z)$ represent a complete set of commutable operators, the eigen-states will not be degenerate. Therefore, from the fact that $J_\pm|j\,m\rangle$ is an eigen-state with the eigen-value $\hbar(m \pm 1)$, we can come to the following ansatz:

$$J_\pm|j\,m\rangle = A_\pm(j,m)|j\,m \pm 1\rangle \; .$$

We determine the coefficients $A_\pm(j,m)$ via the normalization condition. The phase can be put to one, and therefore the $A_\pm$ can considered to be real:

$$\begin{aligned}
\langle j\,m|J_-\,J_+|j\,m\rangle &= A_+^2(j\,m)\langle j\,m+1|j\,m+1\rangle \\
&= A_+^2(j\,m) \overset{(5.59)}{=} \langle j\,m|(\,\mathbf{J}^2 - J_z^2 - \hbar\,J_z)|j\,m\rangle \\
&= \hbar^2[\,j(j+1) - m(m+1)]\;, \\
\langle j\,m|J_+\,J_-|j\,m\rangle &= A_-^2(j\,m) \\
&\overset{(5.58)}{=} \langle j\,m|(\,\mathbf{J}^2 - J_z^2 + \hbar\,J_z)|j\,m\rangle \\
&= \hbar^2[\,j(j+1) - m(m-1)]\;.
\end{aligned}$$

We have therewith found, except for the usual arbitrary phase:

$$\begin{aligned}
J_\pm|j\,m\rangle &= \hbar\sqrt{j(j+1) - m(m\pm1)}|j\,m\pm1\rangle \\
&= \hbar\sqrt{(j\mp m)\,(j\pm m+1)}|j\,m\pm1\rangle\;. \qquad (5.64)
\end{aligned}$$

This expression delivers, in addition, the proof that in the interval (5.52) only $m = j$ fulfills the relation (5.53), and only $m = -j$ the relation (5.54).

For the matrix representations of the various angular momentum operators the matrix elements can be quickly calculated after our preparations, by the use of the complete set of eigen-states $|j\,m\rangle$ of $\mathbf{J}^2$ and J_z ($(\mathbf{J}^2, J_z)$-*representation*):

$$\begin{aligned}
\langle j\,m'|\mathbf{J}^2|j\,m\rangle &= \hbar^2\, j(j+1)\,\delta_{mm'}\ , \\
\langle j\,m'|J_z|j\,m\rangle &= \hbar\, m\,\delta_{mm'}\ , \\
\langle j\,m'|J_+|j\,m\rangle &= \hbar\,\sqrt{(j-m)\,(j+m+1)}\,\delta_{m'm+1}\ , \\
\langle j\,m'|J_-|j\,m\rangle &= \hbar\,\sqrt{(j+m)\,(j-m+1)}\,\delta_{m'm-1}\ .
\end{aligned}$$

Let us look at two examples:

1. $j = 1/2$:
   Because of $2j+1 = 2$, the angular momentum operators are represented by 2×2-matrices:

$$\begin{aligned}
\mathbf{J}^2 &= \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\ ; \quad J_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\ , \qquad (5.65) \\
J_+ &= \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}\ ; \quad J_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}\ , \\
J_x &= \frac{1}{2}(\,J_+ + J_-) = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\ , \qquad (5.66) \\
J_y &= \frac{1}{2i}(\,J_+ - J_-) = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\ . \qquad (5.67)
\end{aligned}$$

   We will meet the matrices of J_x, J_y and J_z again in the next section as Pauli spin matrices when we consider the observable *spin*. In fact we have already used them in some exercises in Chap. 3 of Vol. 6.

2. $j = 1$:
   Because of $2j+1 = 3$ the angular momentum operators are now 3×3-matrices:

$$\begin{aligned}
J^2 &= 2\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\ ; \quad J_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}\ , \\
J_+ &= \hbar \begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix}\ ; \quad J_- = \hbar \begin{pmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix}\ , \\
J_x &= \frac{1}{2}(J_+ + J_-) = \frac{\hbar}{2}\begin{pmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{pmatrix}\ , \\
J_y &= \frac{1}{2i}(J_+ - J_-) = \frac{\hbar}{2i}\begin{pmatrix} 0 & \sqrt{2} & 0 \\ -\sqrt{2} & 0 & \sqrt{2} \\ 0 & -\sqrt{2} & 0 \end{pmatrix}\ .
\end{aligned}$$

After the purely algebraic procedure concerning the treatment of the eigen-value problem of the general angular momentum, we now come back to the particular case of the *orbital angular momentum*, using which we had introduced, at the beginning of this chapter, the quantum-mechanical observable *angular momentum*. By an analytical investigation of its special position representation, we will try to get further information. Thereby we keep the usual notation and replace the *quantum number* j by l (*quantum number of the orbital angular momentum*) for the special case of the orbital angular momentum.

5.1.5 Position Representation of the Orbital Angular Momentum

The formal transition into the position representation takes place, according to ((3.253), Vol. 6), by a scalar multiplication of the eigen-value equations,

$$\begin{aligned} \mathbf{L}^2|l\,m\rangle &= \hbar^2 l(l+1)|l\,m\rangle\,, \\ L_z|l\,m\rangle &= \hbar\,m|l\,m\rangle\,, \end{aligned}$$

by the bra-position eigen-state $\langle\mathbf{r}|$:

$$\langle\mathbf{r}|\mathbf{L}^2|l\,m\rangle = \hbar^2 l(l+1)\langle\mathbf{r}|l\,m\rangle\,, \tag{5.68}$$

$$\langle\mathbf{r}|L_z|l\,m\rangle = \hbar\,m\langle\mathbf{r}|l\,m\rangle\,. \tag{5.69}$$

On the right-hand side there appears, except for numerical factors, the eigen-function belonging to the quantum numbers l and m, which we denote, at first, by

$$\psi_{lm}(\mathbf{r}) \equiv \langle\mathbf{r}|l\,m\rangle\,. \tag{5.70}$$

From (5.68) and (5.69), remembering that in the position representation the position operator $\mathbf{r}$ acts purely multiplicatively, while the momentum operator is essentially replaced by the gradient ∇, it follows that:

$$\mathbf{L}^2\psi_{lm}(\mathbf{r}) = -\hbar^2(\mathbf{r}\times\nabla)^2\psi_{lm}(\mathbf{r}) = \hbar^2 l(l+1)\psi_{lm}(\mathbf{r})\,, \tag{5.71}$$

$$L_z\,\psi_{lm}(\mathbf{r}) = \frac{\hbar}{i}(\mathbf{r}\times\nabla)_z\,\psi_{lm}(\mathbf{r}) = \hbar\,m\,\psi_{lm}(\mathbf{r})\,. \tag{5.72}$$

The position representation of the components of the orbital angular momentum are quickly written down in the Cartesian coordinates, according to (5.2)

$$L_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\,, \tag{5.73}$$

$$L_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\,, \tag{5.74}$$

$$L_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\,. \tag{5.75}$$

For most of the applications, though, the use of Cartesian coordinates turns out to be inexpedient. The close relationship between angular momentum and space rotations (see Sect. 5.1.2) suggests rather the use of spherical coordinates r, ϑ, φ (see Sect. 1.7.4, Vol. 1):

$$\begin{aligned} x &= r\sin\vartheta\cos\varphi\ , \\ y &= r\sin\vartheta\sin\varphi\ , \\ z &= r\cos\vartheta\ . \end{aligned} \tag{5.76}$$

We have exercised, very extensively, the transformation of coordinates in the first volume of this ground course in *Theoretical Physics*. We therefore can revert to what we have learned there.

In particular, it holds for very general unit vectors $\mathbf{e}_{y_i}$ in a curvilinear-orthogonal system of coordinates (y_1, y_2, y_3) ((1.371), Vol. 1):

$$\mathbf{e}_{y_i} = b_{y_i}^{-1}\,\frac{\partial\mathbf{r}}{\partial y_i}\ ; \quad b_{y_i} = \left|\frac{\partial\mathbf{r}}{\partial y_i}\right|\ .$$

This means for the spherical coordinates:

$$\begin{aligned} b_r &= 1,\, b_\vartheta = r,\, b_\varphi = r\sin\vartheta\ , \\ \mathbf{e}_r &= (\sin\vartheta\cos\varphi,\, \sin\vartheta\sin\varphi,\, \cos\vartheta)\ , \\ \mathbf{e}_\vartheta &= (\cos\vartheta\cos\varphi,\, \cos\vartheta\sin\varphi,\, -\sin\vartheta)\ , \\ \mathbf{e}_\varphi &= (-\sin\varphi,\, \cos\varphi,\, 0)\ . \end{aligned} \tag{5.77}$$

As is well-known, it holds for the gradient (nabla operator) in Cartesian coordinates:

$$\nabla \equiv \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)\ .$$

From that one gets the components in any curvilinear-orthogonal system of coordinates by:

$$\mathbf{e}_{y_i}\cdot\nabla = b_{y_i}^{-1}\,\frac{\partial\mathbf{r}}{\partial y_i}\cdot\nabla = b_{y_i}^{-1}\left(\frac{\partial x}{\partial y_i}\,\frac{\partial}{\partial x} + \frac{\partial y}{\partial y_i}\,\frac{\partial}{\partial y} + \frac{\partial z}{\partial y_i}\,\frac{\partial}{\partial z}\right) = b_{y_i}^{-1}\,\frac{\partial}{\partial y_i}\ .$$

In the last step we have used the chain rule. In the special case of spherical coordinates r, ϑ, φ we get:

$$\nabla \equiv \left(\frac{\partial}{\partial r}, \frac{1}{r}\,\frac{\partial}{\partial\vartheta}, \frac{1}{r\sin\vartheta}\,\frac{\partial}{\partial\varphi}\right)\ . \tag{5.78}$$

Therewith we now have all that we need to formulate the orbital angular momentum in spherical coordinates:

$$\mathbf{L} = \frac{\hbar}{i}(\mathbf{r}\times\nabla) = \frac{\hbar}{i}\,r\,(\mathbf{e}_r\times\nabla) = \frac{\hbar}{i}\,r\,\left(\mathbf{e}_\varphi\,\frac{1}{r}\,\frac{\partial}{\partial\vartheta} - \mathbf{e}_\vartheta\,\frac{1}{r\sin\vartheta}\,\frac{\partial}{\partial\varphi}\right)\ .$$

($\mathbf{e}_r$, $\mathbf{e}_\vartheta$, $\mathbf{e}_\varphi$ build, in this sequence, a right-handed system!). We finally insert (5.77):

$$\mathbf{L} = \frac{\hbar}{i} \left\{ \begin{pmatrix} -\sin\varphi \\ \cos\varphi \\ 0 \end{pmatrix} \frac{\partial}{\partial\vartheta} - \begin{pmatrix} \cot\vartheta\cos\varphi \\ \cot\vartheta\sin\varphi \\ -1 \end{pmatrix} \frac{\partial}{\partial\varphi} \right\} . \tag{5.79}$$

One notices the particularly simple form of L_z compared to that of L_x and L_y:

$$L_z = \frac{\hbar}{i} \frac{\partial}{\partial\varphi} . \tag{5.80}$$

That is of course due to the special choice of the system of coordinates, which marks the z-axis out.

The ladder operators (5.21) are also important for us:

$$L_\pm = L_x \pm i\, L_y = \hbar\, e^{\pm i\varphi} \left(\pm\frac{\partial}{\partial\vartheta} + i\cot\vartheta \frac{\partial}{\partial\varphi} \right) . \tag{5.81}$$

For the product formation, the sequence of the terms is of course important because of the differential operators. We calculate as an example:

$$\begin{aligned} L_+ L_- &= \hbar^2 \left[e^{i\varphi} \left(\frac{\partial}{\partial\vartheta} + i\cot\vartheta \frac{\partial}{\partial\varphi} \right) e^{-i\varphi} \left(-\frac{\partial}{\partial\vartheta} + i\cot\vartheta \frac{\partial}{\partial\varphi} \right) \right] \\ &= \hbar^2 \left[-\frac{\partial^2}{\partial\vartheta^2} - \frac{i}{\sin^2\vartheta} \frac{\partial}{\partial\varphi} + i\cot\vartheta \frac{\partial^2}{\partial\vartheta\,\partial\varphi} \right. \\ &\quad \left. + \cot\vartheta \left(-\frac{\partial}{\partial\vartheta} + i\cot\vartheta \frac{\partial}{\partial\varphi} \right) - i\cot\vartheta \frac{\partial^2}{\partial\varphi\,\partial\vartheta} - \cot^2\vartheta \frac{\partial^2}{\partial\varphi^2} \right] \\ &= \hbar^2 \left[-\frac{\partial^2}{\partial\vartheta^2} - i\frac{\partial}{\partial\varphi} - \cot\vartheta \frac{\partial}{\partial\vartheta} - \cot^2\vartheta \frac{\partial^2}{\partial\varphi^2} \right] . \end{aligned}$$

This we can directly exploit, in order to find with (5.58),

$$\mathbf{L}^2 = L_+ L_- - \hbar\, L_z + L_z^2 ,$$

the position representation of the square of the orbital angular momentum in spherical coordinates:

$$\mathbf{L}^2 = -\frac{\hbar^2}{\sin^2\vartheta} \left[\sin\vartheta \frac{\partial}{\partial\vartheta} \left(\sin\vartheta \frac{\partial}{\partial\vartheta} \right) + \frac{\partial^2}{\partial\varphi^2} \right] . \tag{5.82}$$

Needless to say that the operators L_x, L_y, L_z, $L_\pm$, $\mathbf{L}^2$ fulfill the fundamental commutation relations (5.14), (5.16), (5.18)–(5.20), (5.22)–(5.24) in the position representation too. This we check in Exercise 5.1.14 by some examples.

It is certainly not uninteresting for later applications that the representation (5.82) for $\mathbf{L}^2$ exhibits a very close connection with the angular of the **Laplace operator** Δ ((2.145), Vol. 3):

$$\Delta = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{\mathbf{L}^2}{r^2\hbar^2} . \tag{5.83}$$

So it can be shown, for instance, that the kinetic energy T of a particle can be decomposed into a radial part T_r and an angular part $T_{\vartheta,\varphi}$, where the angular

part is determined, according to (5.83), by $\mathbf{L}^2$:

$$T = \frac{\mathbf{p}^2}{2m} = -\frac{\hbar^2}{2m}\,\Delta = T_r + T_{\vartheta,\varphi}\ , \tag{5.84}$$

$$T_r = -\frac{\hbar^2}{2m\,r^2}\,\frac{\partial}{\partial r}\left(r^2\,\frac{\partial}{\partial r}\right)\ , \tag{5.85}$$

$$T_{\vartheta,\varphi} = \frac{\mathbf{L}^2}{2m\,r^2}\ . \tag{5.86}$$

5.1.6 Eigen-Functions in Position Representation

With the operators of the orbital angular momentum, formulated in position representation, (5.80) and (5.82), the to be solved eigen-value equations (5.71) and (5.72) are now to be read as:

$$-\frac{1}{\sin^2\vartheta}\left[\sin\vartheta\,\frac{\partial}{\partial\vartheta}\sin\vartheta\frac{\partial}{\partial\vartheta}+\frac{\partial^2}{\partial\varphi^2}\right]\psi_{lm}(\mathbf{r}) = l(l+1)\psi_{lm}(\mathbf{r})\ , \tag{5.87}$$

$$-i\,\frac{\partial}{\partial\varphi}\,\psi_{lm}(\mathbf{r}) = m\,\psi_{lm}(\mathbf{r})\ . \tag{5.88}$$

One recognizes with these equations that normally $\mathbf{L}^2$ and L_z do not represent a complete set of observables, because the r-dependence of the wave function, the so-called *'radial part'*, remains completely undetermined. $\mathbf{L}^2$ and L_z obviously act only on the *'angular part'* of the wave function. If one chooses for ψ_{lm} the ansatz

$$\psi_{lm}(\mathbf{r}) = R(r)\,Y_{lm}(\vartheta,\varphi)\ , \tag{5.89}$$

then the radial part is canceled out in both equations, (5.87) and (5.88). The special form of the operators $\mathbf{L}^2$ and L_z let us suppose that a separation ansatz will be reasonable also for the angular part:

$$Y_{lm}(\vartheta,\varphi) = \Phi(\varphi)\,\Theta(\vartheta)\ . \tag{5.90}$$

The φ-dependence is easily determined by the use of (5.88):

$$\Phi(\varphi) = e^{im\varphi}\ . \tag{5.91}$$

From this relationship we can already read off a physically important statement. Because of the uniqueness of the wave function, it must be required that $\Phi(\varphi + 2\pi) = \Phi(\varphi)$. But (5.91) allows this only if m is an integer. From this it follows, according to (5.63), that l, too, is an integer. We thus conclude:

quantum numbers of the orbital angular momentum

$$\begin{aligned} l &= 0, 1, 2, 3, \dots\ , \\ m &= -l,\, -l+1, \dots, l-1,\, l\ . \end{aligned} \tag{5.92}$$

If we now insert (5.90) and (5.91) into the $\mathbf{L}^2$-equation (5.87), what remains to be solved is:

$$-\frac{1}{\sin^2\vartheta}\left[\sin\vartheta\frac{d}{d\vartheta}\sin\vartheta\frac{d}{d\vartheta}-m^2\right]\Theta(\vartheta)=l(l+1)\,\Theta(\vartheta)\;. \tag{5.93}$$

We could replace the partial by the total differentiation with respect to ϑ, since Θ depends only on this single variable. We can now bring this differential equation with the substitution,

$$z=\cos\vartheta\;\longrightarrow\;\sin\vartheta\frac{d}{d\vartheta}=(z^2-1)\,\frac{d}{dz}\;,$$

into a form, which we got to know already in Electrodynamics ((2.149), Vol. 3), namely in connection with the multipole moments of electric charge densities:

$$\left[\frac{d}{dz}\,(1-z^2)\,\frac{d}{dz}+\left(l(l+1)-\frac{m^2}{1-z^2}\right)\right]\Theta(z)=0\;. \tag{5.94}$$

It is the

generalized Legendre equation ,

frequently discussed and applied in mathematical physics, from which one knows that it is solved by the so-called

associated Legendre polynomials $P_l^m(z)$.

Hence, we can take over directly from Vol. 3 of this ground course in *Theoretical Physics*:
$\Theta(z)\sim P_l^m(z)$:

$$\begin{aligned}P_l^m(z)&=(-1)^m\,(1-z^2)^{m/2}\,\frac{d^m}{dz^m}\,P_l(z)\;;\quad m\geq 0\;,\\ P_l^{-m}(z)&=(-1)^m\,\frac{(l-m)!}{(l+m)!}\,P_l^m(z)\;.\end{aligned} \tag{5.95}$$

On the right-hand side of this defining equation there appear the

Legendre polynomials

$$P_l(z)=\frac{1}{2^l l!}\,\frac{d^l}{dz^l}\,(z^2-1)^l \tag{5.96}$$

as solutions of the

ordinary Legendre equation

$$\left[\frac{d}{dz}\,(1-z^2)\,\frac{d}{dz}+l(l+1)\right]P_l(z)=0\;. \tag{5.97}$$

One easily realizes that the $P_l(z)$ are polynomials of l-th degree. They build a complete orthogonal system in the interval $[-1,+1]$. They are not normalized to one, in fact it holds:

$$\int_{-1}^{+1} dz\, P_l(z)\, P_k(z) = \frac{2}{2l+1}\,\delta_{lk}\ , \tag{5.98}$$

$$P_l(\pm 1) = (\pm 1)^l\ . \tag{5.99}$$

Their completeness is expressed by

$$\frac{1}{2}\sum_{l=0}^{\infty}(2l+1)\,P_l(z')\,P_l(z) = \delta(z-z')\ . \tag{5.100}$$

These properties of the Legendre polynomials are transferred, because of (5.95), to the associated Legendre polynomials, for instance the orthogonality:

$$\int_{-1}^{+1} dz\, P_l^m(z)\, P_k^m(z) = \frac{2}{2l+1}\,\frac{(l+m)!}{(l-m)!}\,\delta_{lk}\ . \tag{5.101}$$

Let us now come back to the eigen-functions (5.90) of the orbital angular momenta $\mathbf{L}^2$ and L_z. Because of (5.91) and (5.94) their structures are already known to us:

$$Y_{lm}(\vartheta,\varphi) \sim P_l^m(\cos\vartheta)\, e^{im\varphi}\ .$$

We only have to suitably normalize:

$$\int_0^{2\pi} d\varphi \int_{-1}^{+1} d\cos\vartheta\, Y^*_{l'm'}(\vartheta,\varphi)\, Y_{lm}(\vartheta,\varphi) = \delta_{ll'}\,\delta_{mm'}\ . \tag{5.102}$$

With (5.101) and

$$\int_0^{2\pi} d\varphi\, e^{i(m\,-\,m')\varphi} = 2\pi\,\delta_{mm'}$$

that does of course not pose any problem:

$$Y_{lm}(\vartheta,\varphi) = \sqrt{\frac{2l+1}{4\pi}\,\frac{(l-m)!}{(l+m)!}}\,P_l^m(\cos\vartheta)\, e^{im\varphi}\ . \tag{5.103}$$

From (5.95) one easily infers the symmetry relation:

$$Y_{l\,-\,m}(\vartheta,\varphi) = (-1)^m\, Y^*_{lm}(\vartheta,\varphi)\ . \tag{5.104}$$

Eigen-functions of the orbital angular momenta $\mathbf{L}^2$ and L_z are therefore the

spherical harmonics,

well-known from mathematical physics. One knows that these functions represent a complete system on the unit sphere ((2.158), Vol. 3):

$$\sum_{l=0}^{\infty} \sum_{m=-l}^{+l} Y_{lm}^*(\vartheta', \varphi')\, Y_{lm}(\vartheta, \varphi) = \delta(\varphi - \varphi')\, \delta(\cos\vartheta - \cos\vartheta') \,. \tag{5.105}$$

Each arbitrary function $f(\mathbf{r}) = f(r, \vartheta, \varphi)$ can thus be expanded in them:

$$f(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} R_{lm}(r)\, Y_{lm}(\vartheta, \varphi) \,. \tag{5.106}$$

For the *radial components* it holds thereby, because of (5.102):

$$R_{lm}(r) = \int_0^{2\pi} d\varphi \int_{-1}^{+1} d\cos\vartheta \; f(r, \vartheta, \varphi)\, Y_{lm}^*(\vartheta, \varphi) \,. \tag{5.107}$$

The spherical harmonics are present in tabulated form in many textbooks of mathematical physics. We list here only a few examples of lower-indexed functions, which are easily derived from (5.103):

$$l = 0: \qquad Y_{00}(\vartheta, \varphi) \equiv \frac{1}{\sqrt{4\pi}} \,, \tag{5.108}$$

$$l = 1: \qquad Y_{10}(\vartheta, \varphi) = \sqrt{\frac{3}{4\pi}}\, \cos\vartheta \,, \tag{5.109}$$

$$Y_{1\,\pm1}(\vartheta, \varphi) = \mp\sqrt{\frac{3}{8\pi}}\, \sin\vartheta\, e^{\pm i\varphi} \,, \tag{5.110}$$

$$l = 2: \qquad Y_{20}(\vartheta, \varphi) = \sqrt{\frac{5}{16\pi}}\, (3\cos^2\vartheta - 1) \,, \tag{5.111}$$

$$Y_{2\,\pm1}(\vartheta, \varphi) = \mp\sqrt{\frac{15}{8\pi}}\, \sin\vartheta\cos\vartheta\, e^{\pm i\varphi} \,, \tag{5.112}$$

$$Y_{2\,\pm2}(\vartheta, \varphi) = \sqrt{\frac{15}{32\pi}}\, \sin^2\vartheta\, e^{\pm i2\varphi} \,. \tag{5.113}$$

We could make these very detailed statements about the eigen-functions of the orbital angular momentum, because the eigen-value equation of L_z was trivially solvable, and the eigen-value equation of $\mathbf{L}^2$ could be reformulated into a differential equation already known to us. Our task actually consisted only of listing up the already known properties of the solution.

However, we could have derived the eigen-functions of the operators $\mathbf{L}^2$ and L_z also successively by applying the ladder operators L_+ and L_-. Because

of its basic importance we will briefly sketch this method. We start at the intermediate result (5.90), (5.91), which comes out after the solution of the simple eigen-value equation (5.88) for L_z:

$$|l\,m\rangle \;\leftrightarrow\; Y_{lm}(\vartheta,\varphi) = \Theta_{lm}(\vartheta)\,e^{im\varphi}\;.$$

We know that the minimal value of m is equal to $-l$. According to (5.54) it must therefore be

$$L_-|l\,-l\,\rangle = 0\;.$$

This yields, in the position representation with (5.81), the differential equation

$$\hbar\,e^{-i\varphi}\left(-\frac{\partial}{\partial\vartheta} + i\cot\vartheta\frac{\partial}{\partial\varphi}\right)\Theta_{l\,-l}(\vartheta)\,e^{-il\varphi} = 0\;,$$

which, after performing the φ-differentiation, simplifies to:

$$\left(-\frac{d}{d\vartheta} + l\cot\vartheta\right)\Theta_{l\,-l}(\vartheta) = 0\;. \tag{5.114}$$

This equation is obviously solved by

$$\Theta_{l\,-l}(\vartheta) = c_l\,\sin^l\vartheta\;. \tag{5.115}$$

The coefficients c_l can be determined, except for a phase factor which we assume to be one, by the normalization condition for $Y_{l\,-l}(\vartheta,\varphi)$ (Exercise 5.1.15):

$$c_l = \frac{1}{2^l\,l!}\sqrt{\frac{(2l+1)!}{4\pi}}\;.$$

We have therewith completely determined the $(l,\,m=-l\,)$ eigen-function:

$$Y_{l\,-l}(\vartheta,\varphi) = \frac{1}{2^l\,l!}\sqrt{\frac{(2l+1)!}{4\pi}}\,\sin^l\vartheta\,e^{-il\varphi}\;. \tag{5.116}$$

By the application of L_+ we are now able to construct successively all $Y_{lm}(\vartheta,\varphi)$ out of $Y_{l\,-l}(\vartheta,\varphi)$. So we obtain in the first step:

$$\begin{aligned} L_+\,Y_{l\,-l}(\vartheta,\varphi) &= \hbar\,e^{i\varphi}\left(\frac{\partial}{\partial\vartheta} + i\cot\vartheta\frac{\partial}{\partial\varphi}\right)\Theta_{l\,-l}(\vartheta)\,e^{-il\varphi} \\ &= \hbar\,e^{i(-l+1)\varphi}\left(\frac{d}{d\vartheta} + l\cot\vartheta\right)\Theta_{l\,-l}(\vartheta)\;. \end{aligned}$$

For $l\cot\vartheta$ we write $(1/\sin^l\vartheta)\,(d/d\vartheta)\sin^l\vartheta$ and have then:

$$\begin{aligned} L_+\,Y_{l\,-l}(\vartheta,\varphi) &= \hbar\,e^{i(-l+1)\varphi}\,\frac{1}{\sin^l\vartheta}\,\frac{d}{d\vartheta}\,(\sin^l\vartheta\,\Theta_{l\,-l}(\vartheta)) \\ &= -\hbar\,e^{i(-l+1)\varphi}\,\frac{1}{\sin^{l-1}\vartheta}\,\frac{d}{d\cos\vartheta}\,(\sin^l\vartheta\,\Theta_{l\,-l}(\vartheta))\;. \end{aligned}$$

The procedure can be continued step-by-step. By complete induction we prove the following assertion:

$$(L_+)^n\, Y_{l\,-\,l}\,(\vartheta,\varphi) = (-\hbar)^n\, e^{i(-l+n)\varphi}\, \frac{1}{\sin^{l\,-\,n}\vartheta}\, \frac{d^n}{d\cos\vartheta^n}\,(\sin^l\vartheta\,\Theta_{l\,-\,l}(\vartheta))\ . \tag{5.117}$$

For $n = 1$ we have just proved this relation. We then assume that the relation is correct for n, and conclude inductively for $n+1$:

$$\begin{aligned}
& (L_+)^{n\,+1}\, Y_{l\,-\,l}(\vartheta,\varphi) \\
= \;& \hbar\, e^{i\varphi}\, \left(\frac{\partial}{\partial\vartheta} + i\cot\vartheta\frac{\partial}{\partial\varphi}\right)\, (-\hbar)^n\, e^{i(-l\,+\,n)\varphi} \\
& \cdot\frac{1}{\sin^{l\,-\,n}\vartheta}\, \frac{d^n}{d\cos\vartheta^n}\,(\sin^l\vartheta\,\Theta_{l\,-\,l}(\vartheta)) \\
= \;& \hbar(-\hbar)^n\, e^{i(-l\,+\,n\,+1)\varphi}\, \left[\frac{d}{d\vartheta} + (l-n)\cot\vartheta\right]\, \frac{1}{\sin^{l\,-\,n}\vartheta} \\
& \cdot\frac{d^n}{d\cos\vartheta^n}\,(\sin^l\vartheta\,\Theta_{l\,-\,l}(\vartheta)) \\
= \;& -(-\hbar)^{n\,+1}\, e^{i(-l\,+(n\,+1))\varphi} \\
& \cdot\left[-(l-n)\,\frac{\cos\vartheta}{\sin^{l\,-\,n\,+1}\vartheta}\, \frac{d^n}{d\cos\vartheta^n}\,(\sin^l\vartheta\,\Theta_{l\,-\,l}(\vartheta))\right. \\
& +\frac{1}{\sin^{l\,-\,n}\vartheta}\,(-\sin\vartheta)\,\frac{d^{n\,+1}}{d\cos\vartheta^{n\,+1}}\,(\sin^l\vartheta\,\Theta_{l\,-\,l}(\vartheta)) \\
& \left.+\,(l-n)\,\frac{\cos\vartheta}{\sin^{l\,-\,n\,+1}\vartheta}\, \frac{d^n}{d\cos\vartheta^n}\,(\sin^l\vartheta\,\Theta_{l\,-\,l}(\vartheta))\right] \\
= \;& (-\hbar)^{n\,+1}\, e^{i(-l\,+\,(n\,+1))\varphi}\, \frac{1}{\sin^{l\,-\,(n\,+1)}\vartheta}\, \frac{d^{n\,+1}}{d\cos\vartheta^{n\,+1}}\,(\sin^l\vartheta\,\Theta_{l\,-\,l}(\vartheta))\ .
\end{aligned}$$

Therewith the assertion (5.117) is proven. We now insert the result (5.115) and choose especially $n = l + m$:

$$\begin{aligned}
& (L_+)^{l\,+\,m}\, Y_{l\,-\,l}(\vartheta,\varphi) \\
& = \frac{1}{2^l l!}\,\sqrt{\frac{(2l\,+1)!}{4\pi}}\,(-\hbar)^{l\,+\,m}\, e^{im\varphi}\, \sin^m\vartheta\, \frac{d^{l\,+\,m}}{d\cos\vartheta^{l\,+\,m}}\,(1-\cos^2\vartheta)^l \\
& = \sqrt{\frac{(2l\,+1)!}{4\pi}}\,\hbar^{l\,+\,m}\, e^{im\varphi}\, P_l^m(\cos\vartheta)\ .
\end{aligned}$$

In the last step, (5.95) and (5.96) were exploited. In part 2. of Exercise 5.1.8 the following recursion formula is proven

$$|l\,m\rangle = \sqrt{\frac{(l-m)!}{(2l)!(l+m)!}}\, \left(\frac{1}{\hbar}L_+\right)^{l\,+\,m}\, |l\,-\,l\rangle\ . \tag{5.118}$$

After multiplication by the bra-state $\langle\vartheta\varphi|$, this equation yields the corresponding connection between $Y_{lm}(\vartheta,\varphi)$ and $Y_{l\,-\,l}(\vartheta,\varphi)$. The two latter equations can then

be combined to

$$Y_{lm}(\vartheta,\varphi) = \sqrt{\frac{(2l+1)}{4\pi}\,\frac{(l-m)!}{(l+m)!}}\, e^{im\varphi}\, P_l^m(\cos\vartheta)\ .$$

This, however, agrees exactly with (5.103). The spherical harmonics are thus indeed the common eigen-functions of the orbital angular momenta $\mathbf{L}^2$ and L_z.

We want to close this section on the orbital angular momentum with two remarks:

1. As we will discuss in detail in Chap. 6, the orbital angular momentum plays a very essential role in the theory of the atomic structure. From atomic spectroscopy, there stems a special notation of the eigen-states of the operator $\mathbf{L}^2$ characterized by the quantum number l. One speaks for

   $$l = 0 \quad 1 \quad 2 \quad 3$$

   of a

   $$s\text{-} \quad p\text{-} \quad d\text{-} \quad f\text{-state (orbital)}\ .$$

2. The eigen-functions of the orbital angular momenta have a **well-defined parity**. With a space reflection (inversion at the origin),

   $$\mathbf{r} = (r,\vartheta,\varphi) \ \longrightarrow\ -\mathbf{r} = (r,\pi-\vartheta,\varphi+\pi)\ ,$$

   the spherical harmonics change as follows:

   $$Y_{lm}(\pi-\vartheta,\varphi+\pi) = (-1)^l\, Y_{lm}(\vartheta,\varphi)\ . \tag{5.119}$$

   One factor $(-1)^{l+m}$ stems from the associated Legendre polynomials, another factor $(-1)^m$ from the exponential function $e^{im\varphi}$.

   The eigen-functions with even l have even parity, the functions with odd l have odd parity!

5.1.7 Exercises

Exercise 5.1.1
Show that the rows of the rotation matrix, defined in (5.27), are pairwise orthonormal!

Exercise 5.1.2

1. Does the matrix

   $$D = \begin{pmatrix} -\frac{1}{2}\sqrt{2} & 0 & -\frac{1}{2}\sqrt{2} \\ 0 & 1 & 0 \\ \frac{1}{2}\sqrt{2} & 0 & -\frac{1}{2}\sqrt{2} \end{pmatrix}$$

   mediate a rotation? If yes, which one?

2. How do the vectors

$$\mathbf{a} = (0, -2, 1) \;\; ; \;\; \mathbf{b} = (3, 5, -4)$$

change after the rotation? Calculate the scalar product $\mathbf{a} \cdot \mathbf{b}$ before and after the rotation!

3. Show that the *'lengths'* of the vectors do not change by the rotation!

Exercise 5.1.3
Show that the orbital angular momentum $\mathbf{L}$, defined in (5.11), is Hermitian!

Exercise 5.1.4
Calculate with the use of the fundamental commutation relation between position and momentum the following commutators:

1. $[L_x, L_y]_-$, $[L_y, L_z]_-$, $[L_z, L_x]_-$,
2. $[\mathbf{L}^2, L_{x,y,z}]_-$,
3. $[L_x, \mathbf{r}^2]_-$,
4. $[L_y, \mathbf{p}^2]_-$,
5. $[L_z, x]_-$, $[L_z, p_x]_-$.
6. $[L_i, x_j]_-$ (5.19), $[L_i, p_j]_-$ (5.20)

Exercise 5.1.5
Show that an operator, which commutes with two components of the orbital angular momentum, does also commute with the third component.

Exercise 5.1.6
Express the operator products $L_+ L_-$ and $L_- L_+$ by $\mathbf{L}^2$ and L_z.

Exercise 5.1.7
Let $\mathbf{r} = (x, y, z)$ be the position operator. Verify the following commutation relations:

1. $[L_z, z]_- = 0$; $\quad [L_z, x \pm i\, y]_- = \pm\hbar(x \pm i\, y)$,
2. $[\mathbf{L}^2, [\mathbf{L}^2, \mathbf{r}]_-]_- = 2\hbar^2(\mathbf{L}^2\mathbf{r} + \mathbf{r}\,\mathbf{L}^2)$.

Exercise 5.1.8
Verify the following recursion formulas for the eigen-states $|j\, m\rangle$ of the angular momentum:

1.

$$|j\, m\rangle = \sqrt{\frac{(j+m)!}{(2j)!\,(j-m)!}} \left(\frac{1}{\hbar} J_-\right)^{j-m} |jj\rangle \;,$$

2.

$$|j\,m\rangle = \sqrt{\frac{(j-m)!}{(2j)!\,(j+m)!}}\,\left(\frac{1}{\hbar}J_+\right)^{j+m}\,|j-j\rangle\ .$$

Exercise 5.1.9
Let the physical system be in an eigen-state $|j\,m\rangle$ of $\mathbf{J}^2$ and J_z. Calculate the expectation values $\langle J_x\rangle$, $\langle J_y\rangle$ and the mean square deviations ΔJ_x, ΔJ_y.

Exercise 5.1.10
Find for $j = 3/2$ the matrix representations of the operators

$$J_+,\ J_-,\ J_x,\ J_y,\ J_z\ .$$

Use as basis the eigen-states $|j\,m\rangle$ of the operators $\mathbf{J}^2$ and J_z.

Exercise 5.1.11
Let $|jm\rangle$ be the common eigen-states of the angular-momentum operators $\mathbf{J}^2$ and J_z.

1. In which state $|jm\rangle$ with fixed j do the uncertainties ('mean square deviation') of the components J_x, J_y have smallest values and how large are those?

2. Are there states in the considered Hilbert space, for which all components of $\mathbf{J}$ have a precise value?

Exercise 5.1.12
Let the system be in an eigen-state of the observable $\mathbf{J}^2$ with the eigen-value $2\hbar^2$.

1. By an additional measurement of J_z, the pure state $|j\,m_z\rangle$ is prepared. Give, without calculation, the possible measured values $\hbar\,m_x$ due to a subsequent measurement of J_x.

2. Which are the probabilities to observe indeed the values calculated in 1.?

3. After the measurement of J_x, J_z is measured once more. What is the probability to find again the *old* value $\hbar\,m_z$?

Exercise 5.1.13

1. Let a $j = 1$-particle be in the (normalized) state $|\varphi\rangle$, for which it is measured
$$\langle\varphi|J_z|\varphi\rangle = -1\hbar\ .$$
Is $|\varphi\rangle$ an eigen-state of J_z? What comes out for $\langle\varphi|J_x|\varphi\rangle$, $\langle\varphi|J_y|\varphi\rangle$?

2. Let a $j = \frac{7}{2}$-particle be in the (normalized) state $|\psi\rangle$, for which it is measured

$$\langle\psi|J_z|\psi\rangle = \frac{3}{2}\hbar\langle\psi|J_x|\psi\rangle = \langle\psi|J_y|\psi\rangle = 0 \ .$$

Do we have to conclude then that $|\psi\rangle$ is an eigen-state of J_z?

Exercise 5.1.14
Verify for the orbital angular momentum in its position representation the following commutation relations:

1. $[L_x, L_y]_- = i\,\hbar\,L_z$,
2. $[L_y, r^2]_- = 0$,
3. $[L_+, L_-]_- = 2\hbar\,L_z$.

Exercise 5.1.15

1. Calculate the normalization constant c_l of the eigen-functions of the angular momentum

$$Y_{l\,-\,l}(\vartheta,\varphi) = c_l \sin^l\vartheta\, e^{-il\varphi} \ .$$

2. Verify that $Y_{l\,-\,l}(\vartheta,\varphi)$ is indeed eigen-function of $\mathbf{L}^2$ with the eigen-value $\hbar^2 l(l+1)$.

Exercise 5.1.16
Let a two-dimensional rotator (polar angle ϑ, φ) be in a state with the wave function

$$\begin{aligned} \langle\vartheta,\varphi|\psi\rangle \equiv \psi(\vartheta,\varphi) \quad &= \quad \alpha\,(\sin\vartheta\cos\varphi + \sin\vartheta\sin\varphi + \sqrt{3}\cos\vartheta) \\ (\alpha > 0 \quad &: \quad \text{normalization constant}) \end{aligned}$$

1. Find $|\psi\rangle$ as linear combination of eigen-states $|lm\rangle$ of the angular momentum!
2. With which probability is the value $2\hbar^2$ found by a measurement of the square of the angular momentum $\mathbf{L}^2$ of the rotator?
3. With which probability does one find by a simultaneous measurement of $\mathbf{L}^2$ and L_z the pair of values $(2\hbar^2, 0)$?

Exercise 5.1.17
A rigid dumbbell-molecule rotates in the space around the origin of coordinates with two degrees of freedom, corresponding to the polar angles ϑ and φ (*rotator*). It is described by the Hamilton operator

$$H = \frac{1}{2J}\,\mathbf{L}^2 \qquad (J = \text{moment of inertia}) \ .$$

1. Calculate the eigen-values, eigen-functions, and possible degrees of degeneracy!

2. At a certain point of time the rotator is in the state

$$\begin{aligned} \psi(\vartheta,\varphi) &= \alpha(\cos^2\vartheta + \sin^2\vartheta\cos 2\varphi) \\ (\alpha &: \text{ normalization constant}) . \end{aligned}$$

   With which probability does a measurement of $\mathbf{L}^2$ yield the values

$$6\hbar^2,\ 2\hbar^2,\ 0\ ?$$

3. With which probability does the simultaneous measurement of $\mathbf{L}^2$ and L_z yield the pair of values $(6\hbar^2,\ -2\hbar)$?

Exercise 5.1.18

1. How does the distribution of the density of the position probability $|Y_{lm}|^2$ of a particle in the state $Y_{10}(\vartheta,\varphi)$ look like (*polar diagram*)?

2. Which state function would result from an identical distribution but with the x-axis as symmetry axis?

Exercise 5.1.19
The Hamilton operator

$$H = A\,L_z^2 + B\left(L_x^2 + L_y^2\right)$$

is frequently used in solid state physics as so-called *crystal-field operator* for the description of the electric field in a crystal. Determine its eigen-values and its real eigen-functions.

Exercise 5.1.20
Assume there were an eigen-state of the orbital angular momentum with the quantum number $l = \frac{1}{2}$.

1. Consider the 'eigen-state of the angular momentum'

$$|lm\rangle = \left|\frac{1}{2}\ \frac{1}{2}\right\rangle .$$

   Which (ϑ,φ)-dependence would the corresponding wave function

$$\left\langle \vartheta\varphi \left| \frac{1}{2}\ \frac{1}{2} \right\rangle \right.$$

   have?

2. Calculate

$$L_+ \left| \frac{1}{2} \; \frac{1}{2} \right\rangle \; !$$

Is there a contradiction to the assumption $l = \frac{1}{2}$?

3. Calculate

$$L_-^2 \left| \frac{1}{2} \; \frac{1}{2} \right\rangle \; !$$

Is there a contradiction?

5.2 Spin

We have already pointed out that not all quantum-mechanical observables have a classical analog. For a complete characterization of physical systems also, such quantities are needed which can not be traced back, on the basis of the principle of correspondence, to classical dynamical variables. The probably most important quantity of this kind is the *spin*, which we will deal with in this section. We start with the introduction of the so far not yet treated observable *magnetic moment*, which we can find by analogy observations to Classical Electrodynamics. The calculation of the moment leads for an atomic system to discrepancies between theory and experiment, which will necessitate the incorporation of the spin as *intrinsic angular momentum* into Quantum Mechanics. We will discuss properties and consequences of the spin operator, while we postpone the correct justification of the observable spin, by the **relativistic Dirac equation**, to the next chapter (Sect. 5.3).

5.2.1 Operator of the Magnetic Moment

In a certain sense as motivation for the considerations that follow later, we will, at first, deal with the observable *magnetic moment*, which has so far not been a subject of our discussions. We, of course, know the concept of the magnetic moment already from Classical Electrodynamics (Vol. 3), but let us, nevertheless, recall here its definition once more. Consider a physical system (particle), which is thought to occupy a macroscopically tiny volume v and to contain charges in arbitrary form. We will not care about its special structure, but we consider it abstractly as a *local current distribution* $\mathbf{j}$. This creates, according to the rules of Classical Electrodynamics, a **magnetic moment m** ((3.43), Vol. 3):

$$\mathbf{m} = \frac{1}{2} \int_v d^3r \, [\mathbf{r} \times \mathbf{j}(\mathbf{r})] \; . \tag{5.120}$$

Let the *center point* of the *particle* thereby define the origin of coordinates. The current density $\mathbf{j}$ is stationary, and must therefore fulfill:

$$\mathrm{div}\mathbf{j} = 0 \; . \tag{5.121}$$

Then we can make the following ansatz for $\mathbf{j}$:

$$\mathbf{j} = -\mathbf{m} \times \nabla f(\mathbf{r}) = \mathrm{curl}\,(\mathbf{m}\, f(\mathbf{r})) \; . \tag{5.122}$$

The second equality sign holds because $\mathbf{m}$ is a position-independent vector. This ansatz fulfills automatically (5.121), because $\mathrm{div}(\mathrm{curl}\mathbf{a}) = 0$ for arbitrary vectors $\mathbf{a}$. In order to satisfy also (5.120), only two demands have to be made on the function $f(\mathbf{r})$:

1. $f(\mathbf{r}) \equiv 0$ outside of v ,
2. $\int_v d^3r\, f(\mathbf{r}) = 1$.

The validity of (5.120) is verified by insertion of the ansatz (5.122). This we have explicitly performed after Eq. (3.65) in Vol. 3, and therefore it will not be repeated here once more.

If we recall the actual goal of these considerations, then the expression (5.120) appears a bit too unwieldy, in order to *transform* it, according to the concept of correspondence, into Quantum Mechanics. We therefore look for another starting point, and investigate the question, how the energy of the system in the volume v changes when a magnetic field is switched on. An energy change appears as a consequence of the work done by field on the current density $\mathbf{j}$, and that too, indirectly, via the $\mathbf{E}$-field, which is induced by the magnetic induction $\mathbf{B}$:

$$\mathrm{curl}\mathbf{E} = -\dot{\mathbf{B}} \; .$$

We denote the system energy, temporarily, by using the letter W, in order to avoid a mix-up with the electric field. We find for the energy change according to Eq. ((4.44), Vol. 3):

$$\begin{aligned} \frac{dW}{dt} &= \int \mathbf{j} \cdot \mathbf{E}\, d^3r = -\int (\mathbf{m} \times \nabla f) \cdot \mathbf{E}\, d^3r = -\mathbf{m} \cdot \int (\nabla f \times \mathbf{E})\, d^3r \\ &= -\mathbf{m} \cdot \int [\mathrm{curl}(f\,\mathbf{E}) - f\,\mathrm{curl}\mathbf{E}]\; d^3r \; . \end{aligned}$$

The first integral is transformed by the Gauss theorem ((1.58), Vol. 3) into a surface integral over an area lying at infinity, and it therefore vanishes because of f (condition 1.). It thus remains:

$$\frac{dW}{dt} = \mathbf{m} \cdot \int f \mathrm{curl}\mathbf{E}\, d^3r = -\mathbf{m} \cdot \int \dot{\mathbf{B}}\, f(\mathbf{r}) d^3r \overset{1.}{=} -\mathbf{m} \cdot \int\limits_v \dot{\mathbf{B}}\, f(\mathbf{r}) d^3r \; .$$

Since v is macroscopically small, the macroscopic field quantity $\dot{\mathbf{B}}$ will practically not change within v and can therefore be drawn to the front of the integral. It follows then with condition 2. for the function $f(\mathbf{r})$:

$$\frac{dW}{dt} = -\mathbf{m} \cdot \dot{\mathbf{B}} \iff dW = -\mathbf{m} \cdot d\mathbf{B} \; .$$

This yields as alternative to (5.120) a further classical definition of the magnetic moment:

$$\mathbf{m} = -\nabla_{\mathrm{B}} W \; . \tag{5.123}$$

This version is now very much better suited for the *'correspondence-like'* transition to the respective quantum-mechanical observable. We interpret W as the solution of the time-independent Schrödinger equation,

$$H|\psi\rangle = W|\psi\rangle \; ; \quad \langle\psi|\psi\rangle = 1 \; ,$$

and differentiate this equation with respect to the field $\mathbf{B}$:

$$(\nabla_{\mathrm{B}} H - \nabla_{\mathrm{B}} W)\,|\psi\rangle + (H - W)|\nabla_{\mathrm{B}}\psi\rangle = 0 \; .$$

If we now multiply from the left by the bra-state $\langle\psi|$, then the second summand disappears because of the hermiticity of H ($\langle\psi|H = \langle\psi|W$), and what remains is:

$$\langle\psi|\nabla_{\mathrm{B}} H|\psi\rangle = \nabla_{\mathrm{B}} W \; . \tag{5.124}$$

With the usual conclusion by analogy (Sect. 3.2.7), according to which classical quantities correspond to the expectation values of the associated quantum-mechanical observables, we derive by comparison of (5.123) and (5.124):

operator of the magnetic moment:

$$\boldsymbol{\mu} = -\nabla_{\mathrm{B}} H \; . \tag{5.125}$$

This moment operator will be calculated explicitly in the next section for a special concrete situation.

5.2.2 Magnetic Moment and Angular Momentum

As an example, let us apply the theory of the last section to an atom or an ion. This consists of a positively charged nucleus, which we can assume to be *'at rest'* because of its relatively large mass, and p electrons of mass m_e and charge $\hat{q} = -e$. Let the atom (ion) be in a homogeneous field:

$$\mathbf{B} = \mathrm{curl}\mathbf{A} = (0, 0, B) \; .$$

We know from Electrodynamics that the vector potential $\mathbf{A}(\mathbf{r}, t)$ is uniquely determined only except for a gauge function $\chi(\mathbf{r}, t)$. The actual quantities of

measurement, the fields $\mathbf{E}$ and $\mathbf{B}$ do not change when one performs the following substitutions for the vector potential and the scalar potential $\varphi(\mathbf{r},t)$:

$$\begin{aligned}\mathbf{A}(\mathbf{r},t) &\longrightarrow \mathbf{A}(\mathbf{r},t)+\nabla\chi(\mathbf{r},t)\ ,\\ \varphi(\mathbf{r},t) &\longrightarrow \varphi(\mathbf{r},t)-\dot{\chi}(\mathbf{r},t)\ .\end{aligned}$$

Thereby one still has the freedom to choose $\chi(\mathbf{r},t)$ *as convenient as possible*. In the so-called *'Coulomb gauge'* ((4.26), Vol. 3) $\chi(\mathbf{r},t)$ is taken such that

$$\mathrm{div}\mathbf{A}(\mathbf{r},t)=0\ .$$

This relation as well as $\mathrm{curl}\mathbf{A}=\mathbf{B}$ can obviously fulfilled by

$$\mathbf{A}=\frac{1}{2}\mathbf{B}\times\mathbf{r}\ .$$

We know from Analytical Mechanics (Vol. 2), that position and mechanical momentum of a particle in the magnetic field are not canonically conjugate variables. As *canonically conjugate* one denotes variables, which fulfill the fundamental Poisson bracket $\{q,p\}=1$ ((2.110), Vol. 2), and therewith, according to the principle of correspondence, the for Quantum Mechanics equally fundamental commutation relation $[q,p]_-=i\,\hbar$. The **canonical momentum** of a particle with the charge $\hat{q}$ and the mass m in the electromagnetic field reads ((2.38), Vol. 2):

$$\mathbf{p}=m\,\dot{\mathbf{r}}+\hat{q}\,\mathbf{A}(\mathbf{r},t)\ .$$

We formulate therewith now the **Hamilton function** of our p-electron atom (ion):

$$H=\sum_{i=1}^{p}\left[\frac{1}{2m_e}\left(\mathbf{p}_i+e\,\mathbf{A}(\mathbf{r}_i)\right)^2+V(\mathbf{r}_i)\right]\ . \tag{5.126}$$

The potential $V(\mathbf{r}_i)$ contains the interaction of the electron with the positively charged nucleus, as well as, at least in an averaged form, the interaction with the other atomic electrons. The latter can not be easily treated in a rigorous manner. As a rule, however, one is content with the so-called *central-field approximation*, in which these interactions are replaced by a central field $V(\mathbf{r}_i)=V(r_i)$. Therewith the Hamilton function separates according to the individual electron coordinates:

$$H=\sum_{i=1}^{p}H_i\ ;\quad H_i=\frac{1}{2m_e}\left(\mathbf{p}_i+e\,\mathbf{A}(\mathbf{r}_i)\right)^2+V(r_i)\ .$$

We now perform the transition to Quantum Mechanics and use for this purpose the position representation. The Hamilton **operator**, which we already used in ((2.115), Vol. 6), and for which we take the same letter H as for the Hamilton function, then reads:

$$H_i=\frac{1}{2m_e}\left[-\hbar^2\Delta_i+e\frac{\hbar}{i}\left(\mathrm{div}\mathbf{A}(\mathbf{r}_i)+2\mathbf{A}(\mathbf{r}_i)\cdot\nabla_i\right)+e^2\mathbf{A}^2(\mathbf{r}_i)\right]+V(r_i)\ .$$

This expression simplifies when using the Coulomb gauge,

$$H_i = H_{0i} + \frac{e}{m_e}\mathbf{A}(\mathbf{r}_i)\cdot\mathbf{p}_i + \frac{e^2}{2m_e}\,\mathbf{A}^2(\mathbf{r}_i)\;,$$

where we have collected in H_{0i} all terms, which are not directly influenced by the magnetic field. One easily calculates:

$$\begin{aligned}\mathbf{A}^2(\mathbf{r}_i) &= \frac{1}{4}(\mathbf{B}\times\mathbf{r}_i)^2 \\ &= \frac{1}{4}B^2 r_i^2\sin^2\vartheta_i\;; \quad \vartheta_i = \sphericalangle(\mathbf{B},\mathbf{r}_i)\;.\end{aligned}$$

Thereby we could exploit that $\mathbf{B}$ is not an operator, and is therefore arbitrarily commutable with $\mathbf{r}$.

$$\mathbf{A}(\mathbf{r}_i)\cdot\mathbf{p}_i = \frac{1}{2}\,(\mathbf{B}\times\mathbf{r}_i)\cdot\mathbf{p}_i = \frac{1}{2}\,\mathbf{B}\cdot(\mathbf{r}_i\times\mathbf{p}_i) = \frac{1}{2}\,\mathbf{B}\cdot\mathbf{L}_i\;.$$

$\mathbf{L}_i$ is the orbital angular momentum of the ith electron referred to the origin of coordinates. We get therewith as an intermediate result:

$$H_i = H_{0i} + \frac{e}{2m_e}\,\mathbf{L}_i\cdot\mathbf{B} + \frac{e^2\mathbf{B}^2}{8m_e}\,r_i^2\sin^2\vartheta_i\;.$$

Our considerations have been focused so far almost only on a single electron, which possesses the orbital angular momentum $\mathbf{L}_i$. When summing up to the full Hamilton operator it shows up the

$$\textbf{total orbital angular momentum}:\;\; \widehat{\mathbf{L}} = \sum_{i=1}^{p}\mathbf{L}_i\;, \tag{5.127}$$

for which we still have to show, strictly speaking, that it is indeed an angular momentum. This is exactly the case when its Cartesian components fulfill the fundamental commutation relations (5.14). This can easily be shown if one exploits the fact that the angular momenta of different electrons commute with each other:

$$[\widehat{L}_x,\widehat{L}_y]_- = \sum_{i,\,j=1}^{p}\big[L_{x_i},L_{y_j}\big]_- = \sum_{i,\,j=1}^{p}\delta_{ij}\;[L_{x_i},L_{y_i}]_- = \sum_{i=1}^{p} i\,\hbar\,L_{z_i} = i\,\hbar\,\widehat{L}_z\;.$$

In the same way one verifies the two other relations. $\widehat{L}$ is thus *quite a normal* angular momentum.

At the end, the Hamilton operator of the p-electron atom (ion) therewith reads:

$$H = H_0 + \frac{e}{2m_e}\,\widehat{\mathbf{L}}\cdot\mathbf{B} + \frac{e^2B^2}{8m_e}\sum_{i=1}^{p} r_i^2\sin^2\vartheta_i\;. \tag{5.128}$$

According to (5.125) the particle then has the magnetic moment:

$$\boldsymbol{\mu} = -\frac{e}{2m_e}\,\widehat{\mathbf{L}} - \left(\frac{e^2}{4m_e}\sum_{i=1}^{p} r_i^2 \sin^2\vartheta_i\right)\mathbf{B}\,. \tag{5.129}$$

The first term is particularly interesting, because it reveals the close connection between the orbital angular momentum and the magnetic moment. The second term is field-dependent and vanishes therefore as soon as the field is switched off. The first summand in (5.129) represents a **permanent magnetic moment**, and the second term an **induced moment**. The permanent moment results from the electron motion around the nucleus. The field couples linearly to it. The moment persists even after the field is switched off, and is therefore independent of the field. The magnetic field, though, changes the orbit of the electron a bit, inducing therewith an additional magnetic moment, which is again linearly coupled to the field. This induced moment leads to the phenomenon of **diamagnetism** (see Sect. 3.4.2, Vol. 3), which is present in all materials. The existence of permanent magnetic moments leads to **paramagnetism**. That is due to the fact that with the switching on of a magnetic field, the permanent atomic moments try to orient themselves parallel to the field. This ordering tendency is opposed by the thermal motion. The resulting compromise causes the characteristic properties of a paramagnet. If in a solid the permanent atomic moments order themselves spontaneously, i.e., without being forced by an external field, there arises **ferro- (antiferro-)magnetism**. One can show that the induced moment delivers only a very small contribution, so that diamagnetism is observable only if the rival permanent moment vanishes ($l = 0$). For all the other cases it is therefore commonly accepted that the induced moment is suppressed. Note that, because of the negative electronic charge, **angular momentum and permanent magnetic moment** are always oriented **antiparallel**.

Let us draw some further conclusions from our considerations so far. Without field, H_0 is the Hamilton operator of the atom. In the *central field approximation* it is a scalar rotation invariant operator. According to the results in Sect. 5.1.3 (see (5.47)), H_0, $\widehat{\mathbf{L}}^2$ and $\widehat{L}_z$ must therefore have a common set of eigen-states $|\psi_{xlm}\rangle$:

$$H_0|\psi_{xlm}\rangle = E_{xl}^{(0)}|\psi_{xlm}\rangle\,. \tag{5.130}$$

The index x contains all quantum numbers which are, except for l and m, still necessary for the identification of the states. H_0 contains in the kinetic energy the Laplace operator, which is, according to (5.83), closely linked to the square of the orbital angular momentum. We should therefore accept that the energy eigen-values $E_{xl}^{(0)}$ depend on l, while they are certainly degenerate with respect to m.

When we now switch on a homogeneous magnetic field, which may define the z-direction, then not only the eigen-values, but also the eigen-states will change due to the diamagnetic term. When we, however, suppress for our qualitative

considerations here this term, because of its mentioned relative insignificance, then the situation is strongly simplified, since the paramagnetic part in (5.128) ($\sim \widehat{L}_z$) does not change the eigen-states. It removes, though, the m-degeneracy:

$$H|\psi_{xlm}\rangle = E_{xlm}|\psi_{xlm}\rangle \,, \tag{5.131}$$

$$E_{xlm} = E_{xl}^{(0)} + \mu_{\mathrm{B}} B\, m \,. \quad m = -l, -l+1, \ldots, +l \,. \tag{5.132}$$

μ_{B} is the **Bohr magneton**, already used in ((1.59), Vol. 6):

$$\mu_{\mathrm{B}} = \frac{e\,\hbar}{2m_e} = 9.274 \cdot 10^{-24}\,\frac{\mathrm{J}}{\mathrm{T}}\,(= \mathrm{A\,m^2}) = 0.579 \cdot 10^{-4}\,\frac{\mathrm{eV}}{\mathrm{T}} \,. \tag{5.133}$$

In the magnetic field, each atomic energy term $E_{xl}^{(0)}$ should therefore be $(2l+1)$-fold split (*Zeeman effect*), where the single levels are energetically arranged equidistantly. The distance $\mu_{\mathrm{B}}B$ is extremely small. For an already rather strong magnetic field of one Tesla, ΔE would amount to only about $0.6 \cdot 10^{-4}$ eV. The required resolution, however, does not pose any difficulty for the experimental atomic physics. Since the magnetic field removes the *directional degeneracy*, m is called the *magnetic quantum number*.

Let us compare these statements with the experimental findings. The magnetic field-caused splitting of the energy levels is uniquely confirmed, but at the same time, if considered in detail, also with significant deviations from our theoretical predictions. Very generally, one observes, in atoms with an odd number of electrons, splittings, which correspond rather to a **half-integer** magnetic quantum number. In addition, in contradiction to (5.132), it is found that the splitting of different levels can also be different.

We will show in Chap. 6 that the ground state of the simple hydrogen atom belongs to $l = 0$. According to (5.132) it should therefore remain uninfluenced by a magnetic field. This contradicts, however, the experimental findings, according to which the ground state level is twofold split by the field.

Let us recall the **Stern-Gerlach experiment**, discussed in detail in Sect. 1.3.2 (Vol. 6). The properties of the silver atoms, which traverse an inhomogeneous magnetic field in this experiment, are dominated by the so-called *luminous (valence) electron* (5s-electron). The angular momenta of all the other electrons in the Ag-atom are vectorially add up to zero. The *valence electron* possesses in the ground state also $l = 0$. Nevertheless, even in this case a twofold splitting is observed which does not at all agree with our knowledge so far.

All these problems are rather immediately solved when we assume that quantum-mechanical particles possess, besides their orbital angular momentum, further an *intrinsic angular momentum*, which we will call *spin* **S**. It is a vector operator, whose Cartesian components fulfill the commutation relations (5.14). **S** is therewith *quite a normal* angular momentum, for which all statements, derived in Sect. 5.1.4, thus apply. This is true, in particular, for the **eigenvalue equations**:

$$\mathbf{S}^2|S\,m_s\rangle = \hbar^2 S(S+1)|S\,m_s\rangle \,, \tag{5.134}$$

$$S_z|S\,m_s\rangle = \hbar\, m_s|S\,m_s\rangle \,. \tag{5.135}$$

The **spin quantum number** S can thereby be an integral or a half-integral number:

$$S = 0, \frac{1}{2}, 1, \ldots \qquad m_s = -S, -S+1, \ldots, +S \; . \tag{5.136}$$

In Chap. 8 we will get to know a meaningful division of the quantum-mechanical particles into those with half-integral spin and those with integral spin. The particles with half-integral spin are called *fermions* ($S = 1/2$: electron, neutron, proton, ...), and those with integral spin *bosons* ($S = 0$: π-meson; $S = 1$: photon, magnon; ...).

In Classical Mechanics, we could almost always consider *particles* as *mass points*. The only property of the particle was therewith the mass m. In Electrodynamics it came along the charge $\hat{q}$. The classical particle has three (continuous) degrees of freedom. Otherwise, a *quantum-mechanical particle* possesses besides mass m, charge $\hat{q}$ another property *spin* S. As a genuine **particle property**, the spin quantum number S is **unchangeable** for a given particle. Thus S differs, e.g., from the quantum number of the orbital angular momentum l, which can take for a particle, in principle, infinitely many values ($l = 0, 1, 2, \ldots$).

However, with **S** does not come along only a new particle property, but also an additional degree of freedom, namely the orientation of the vector **S** relatively to a given direction. This degree of freedom is independent of the spatial degrees of freedom, and is, in contrast to them, in any case discrete.

5.2.3 Hilbert Space of the Spin

For the complete description of a quantum-mechanical particle, the Hilbert space $\mathcal{H}_\mathrm{O}$ of the orbital motion does no longer suffice. This space is, e.g., spanned by the (improper) eigen-states $|\mathbf{r}\rangle$ of the position operator. We have to extend it by the $(2S+1)$-dimensional **spin space** $\mathcal{H}_\mathrm{S}$. The *full* space is the direct product space of the two partial spaces $\mathcal{H}_\mathrm{O}$ and $\mathcal{H}_\mathrm{S}$:

$$\mathcal{H} = \mathcal{H}_\mathrm{O} \otimes \mathcal{H}_\mathrm{S} \; . \tag{5.137}$$

Up to now we did not yet introduce the concept of the product space. We therefore want to illustrate it here a bit in more detail by our current concrete example. We will meet this concept in other connections also.

For the states $|\psi;\varphi\rangle$ from $\mathcal{H}$ one writes:

$$|\psi;\varphi\rangle = |\psi\rangle_\mathrm{O}|\varphi\rangle_\mathrm{S} = |\varphi\rangle_\mathrm{S}|\psi\rangle_\mathrm{O} \; . \tag{5.138}$$

$|\psi\rangle_\mathrm{O}$ is a state from $\mathcal{H}_\mathrm{O}$, and $|\varphi\rangle_S$ one of the spin space $\mathcal{H}_S$. One denotes the right-hand side as *direct product* of the states $|\psi\rangle_\mathrm{O}$ and $|\varphi\rangle_S$, not to be confused with the scalar product ((3.15), Vol. 6) of states or with the dyadic product ((3.75), Vol. 6). Equation (5.138) expresses the **commutativity** of the direct product. It also possesses **distributivity**. Let

$$|\overline{\psi}\rangle_\mathrm{O} = |\psi_1\rangle_\mathrm{O} + |\psi_2\rangle_\mathrm{O} \; ; \quad |\overline{\varphi}\rangle_\mathrm{S} = |\varphi_1\rangle_\mathrm{S} + |\varphi_2\rangle_\mathrm{S}$$

be states from $\mathcal{H}_{\rm O}$ and $\mathcal{H}_{\rm S}$, respectively. Then:

$$\begin{aligned} |\overline{\psi};\varphi\rangle &= |\psi_1;\varphi\rangle + |\psi_2;\varphi\rangle \ , \\ |\psi;\overline{\varphi}\rangle &= |\psi;\varphi_1\rangle + |\psi;\varphi_2\rangle \ . \end{aligned} \tag{5.139}$$

The scalar product in the Hilbert space $\mathcal{H}$ is traced back to the corresponding products in $\mathcal{H}_{\rm O}$ and $\mathcal{H}_{\rm S}$, where of course only the states of the same subspace can *be scalarly multiplied*:

$$\langle\widehat{\psi};\widehat{\varphi}|\psi;\varphi\rangle = {}_{\rm O}\langle\widehat{\psi}|\psi\rangle_{\rm O}\ {}_{\rm S}\langle\widehat{\psi}|\psi\rangle_{\rm S} \ . \tag{5.140}$$

We can also quickly think over how the basis of the *combined* space $\mathcal{H}$ must look like when the bases of the subspaces are given. Let $\{|\alpha_i\rangle_{\rm O}\}$ be an orthonormalized basis system (continuous or discrete) for $\mathcal{H}_{\rm O}$, and let $\{|\beta_j\rangle_{\rm S}\}$ (discrete) be such a system for $\mathcal{H}_{\rm S}$ with:

$${}_{\rm O}\langle\alpha_j|\alpha_i\rangle_{\rm O} = \delta(i,j) \ ; \quad {}_{\rm S}\langle\beta_m|\beta_n\rangle_{\rm S} = \delta_{mn} \ . \tag{5.141}$$

We have introduced the sign $\delta(i,j)$ in ((3.49), Vol. 6). It is the Kronecker-delta δ_{ij} in the case of a discrete basis, and it is the delta-function $\delta(i-j)$ in the case of a continuous basis. The states $\{|\alpha_i;\beta_m\rangle\}$ then represent in $\mathcal{H}$ an orthonormalized,

$$\langle\alpha_j;\beta_m|\alpha_i;\beta_n\rangle = \delta(i,j)\,\delta_{mn} \ , \tag{5.142}$$

and complete basis system:

$$\sum\!\!\!\!\!\!\int_i \sum_m |\alpha_i;\beta_m\rangle\langle\alpha_i;\beta_m| = \mathbb{1} \ . \tag{5.143}$$

Each arbitrary state $|\psi;\varphi\rangle \in \mathcal{H}$ can be expanded in these basis states:

$$|\psi;\varphi\rangle = \sum\!\!\!\!\!\!\int_i \sum_m |\alpha_i;\beta_m\rangle\langle\alpha_i;\beta_m|\psi;\varphi\rangle \ . \tag{5.144}$$

All rules, theorems and statistical interpretations, which we derived in Chap. 3 (Vol. 6) for states in the Hilbert space, can be directly taken over. That holds in particular for the **spectral representation** ((3.68), Vol. 6) of an operator A acting in $\mathcal{H}$:

$$A = \mathbb{1}\,A\,\mathbb{1} = \sum\!\!\!\!\!\!\int_i \sum_m \sum\!\!\!\!\!\!\int_j \sum_n |\alpha_i;\beta_m\rangle\langle\alpha_i;\beta_m|A|\alpha_j;\beta_n\rangle\langle\alpha_j;\beta_n| \ . \tag{5.145}$$

An exceptional position is taken by such operators which act exclusively in either of the two subspaces. When $A_{\rm O,S}$ acts only in $\mathcal{H}_{\rm O,S}$, then the spectral representation reduces because of

$$\begin{aligned} \langle\alpha_i;\beta_m|A_{\rm O}|\alpha_j;\beta_n\rangle &= {}_{\rm O}\,\langle\alpha_i|A_{\rm O}|\alpha_j\rangle_{\rm O}\ \delta_{mn} \ , \\ \langle\alpha_i;\beta_m|A_{\rm S}|\alpha_j;\beta_n\rangle &= {}_{\rm S}\,\langle\beta_m|A_{\rm S}|\beta_n\rangle_{\rm S}\ \delta(i,j) \end{aligned}$$

in $\mathcal{H}$ to:

$$A_{\mathrm{O}} = \left[\sum_i \sum_j |\alpha_i\rangle_{\mathrm{O}}\, {}_{\mathrm{O}}\langle\alpha_i|A_{\mathrm{O}}|\alpha_j\rangle_{\mathrm{O}}\, {}_{\mathrm{O}}\langle\alpha_j| \right] \mathbb{1}_{\mathrm{S}} \,, \tag{5.146}$$

$$A_{\mathrm{S}} = \left[\sum_m \sum_n |\beta_m\rangle_{\mathrm{S}}\, {}_{\mathrm{S}}\langle\beta_m|A_{\mathrm{S}}|\beta_n\rangle_{\mathrm{S}}\, {}_{\mathrm{S}}\langle\beta_n| \right] \mathbb{1}_{\mathrm{O}} \,. \tag{5.147}$$

$\mathbb{1}_{\mathrm{O,S}}$ is the unit operator in $\mathcal{H}_{\mathrm{O,S}}$. The action of $A_{\mathrm{O,S}}$ on an arbitrary state $|\psi;\varphi\rangle$ of the product space takes place such that the *respective other* part of the state remains uninfluenced:

$$\begin{aligned} A_{\mathrm{O}}|\psi;\varphi\rangle &= |\overline{\psi};\varphi\rangle \longleftrightarrow A_{\mathrm{O}}|\psi\rangle_{\mathrm{O}} = |\overline{\psi}\rangle_{\mathrm{O}} \,, \\ A_S|\psi;\varphi\rangle &= |\psi;\overline{\varphi}\rangle \longleftrightarrow A_{\mathrm{S}}|\varphi\rangle_{\mathrm{S}} = |\overline{\varphi}\rangle_{\mathrm{S}} \,. \end{aligned}$$

In particular, this has the consequence that such operators commute in the product space:

$$[A_{\mathrm{O}}, A_{\mathrm{S}}]_- = 0 \,. \tag{5.148}$$

For our present case, we can immediately affiliate to (5.148) the following important statements:

$$[\mathbf{S}, \mathbf{r}]_- = 0 \,, \tag{5.149}$$

$$[\mathbf{S}, \mathbf{p}]_- = 0 \,, \tag{5.150}$$

$$[\mathbf{S}, \mathbf{L}]_- = 0 \,. \tag{5.151}$$

This result is extremely *becalming*, because it simply states that we do not have to revise any part of the *spinless* Quantum Mechanics, performed so far. All the operators (observables), encountered so far, have, as A_{O} in (5.146), no influence on the spin space $\mathcal{H}_S$.

We had already recognized that the spin operator $\mathbf{S}$ is *quite a normal* angular momentum in the sense that its Cartesian components fulfill the commutation rules (5.14):

$$[S_x, S_y]_- = i\,\hbar\, S_z \;;\; [S_y, S_z]_- = i\,\hbar\, S_x \;;\; [S_z, S_x]_- = i\,\hbar\, S_y \,. \tag{5.152}$$

When we define, as in (5.21), the ladder (step) operators for the spin also,

$$S_\pm = S_x \pm i\, S_y \,, \tag{5.153}$$

then the previously very generally proven relations are of course valid for these operators, too:

$$[S_z, S_\pm]_- = \pm\,\hbar\, S_\pm \;; \quad [S_+, S_-]_- = 2\hbar\, S_z \,. \tag{5.154}$$

Especially, the matrix representations, listed following (5.64), can directly be transferred to the spin operators, if one takes as basis the common eigen-states $|S\,m_s\rangle$ (5.134) and (5.135) of $\mathbf{S}^2$ and S_z.

The $\{|S, m_s\rangle\}$ build in $\mathcal{H}_\mathrm{S}$ a complete orthonormal basis. For a general spin state $|\alpha_\mathrm{S}\rangle$ we therefore have the expansion:

$$|\alpha_\mathrm{S}\rangle = \sum_{m_s=-S}^{+S} \widehat{\alpha}_{m_s} |S\,m_s\rangle \; . \tag{5.155}$$

With respect to the matrix representations of the spin operators, $|\alpha_\mathrm{S}\rangle$ can be represented by a $(2S+1)$-component column vector:

$$|\alpha_\mathrm{S}\rangle = \begin{pmatrix} \langle S\,S|\alpha_\mathrm{S}\rangle \\ \langle S\,S-1|\alpha_\mathrm{S}\rangle \\ \vdots \\ \langle S-S|\alpha_\mathrm{S}\rangle \end{pmatrix} = \begin{pmatrix} \widehat{\alpha}_\mathrm{S} \\ \widehat{\alpha}_{S-1} \\ \vdots \\ \widehat{\alpha}_{-S} \end{pmatrix} \; . \tag{5.156}$$

The eigen-state $|S\,m_s\rangle$ itself is a column vector with a 1 at the m_sth position and otherwise nothing but zeros. One calls (5.156) a *spinor*.

When we still choose as basis of the subspace $\mathcal{H}_\mathrm{O}$ the eigen-states $|\mathbf{r}\rangle$ of the position operator, then it holds, according to (5.144), for an arbitrary state of the product space $\mathcal{H} = \mathcal{H}_\mathrm{O} \otimes \mathcal{H}_\mathrm{S}$:

$$|\psi;\alpha_\mathrm{S}\rangle = \sum_{m_s=-S}^{+S} \int d^3r |\mathbf{r}\rangle |S\,m_s\rangle \langle \mathbf{r}|\psi\rangle \langle S\,m_s|\alpha_\mathrm{S}\rangle \; .$$

$\langle \mathbf{r}|\psi\rangle$ is the wave function $\psi(\mathbf{r})$ associated to the state $|\psi\rangle$:

$$|\psi;\alpha_\mathrm{S}\rangle = \sum_{m_s=-S}^{+S} \int d^3r\, \widehat{\alpha}_{m_s}\, \psi(\mathbf{r}) |\mathbf{r}\rangle |S\,m_s\rangle \; . \tag{5.157}$$

By scalar multiplication of this relation by the bra-position eigen-state $\langle \mathbf{r}|$ one obtains, analogously to ((3.238), Vol. 6) the *position representation* of the state $|\psi;\alpha_s\rangle$, which can be written as a **$(2\mathbf{S}+1)$-component spinor**:

$$|\psi_\mathrm{S}(\mathbf{r})\rangle \equiv \begin{pmatrix} \psi_\mathrm{S}(\mathbf{r}) \\ \psi_{S-1}(\mathbf{r}) \\ \vdots \\ \psi_{-S}(\mathbf{r}) \end{pmatrix} \quad ; \quad \psi_{m_s}(\mathbf{r}) \equiv \langle \mathbf{r}|\psi\rangle \langle S\,m_s|\alpha_\mathrm{S}\rangle \; . \tag{5.158}$$

We can interpret thereby the square of the absolute value of one component,

$$|\psi_{m_s}(\mathbf{r})|^2 = |\widehat{\alpha}_{m_s}|^2\, |\psi(\mathbf{r})|^2 \; , \tag{5.159}$$

as the probability density to find, with a simultaneous measurement of *spin* and *position*, the particle with spin S at the position $\mathbf{r}$ with a spin orientation

characterized by m_s. Note that $\|\psi_{\rm S}(\mathbf{r})\|^2 = |\psi(\mathbf{r})|^2$. Furthermore, it holds in any case:

$$\mathbf{S}^2|\psi_{\rm S}(\mathbf{r})\rangle = \hbar^2 S(S+1)|\psi_{\rm S}(\mathbf{r})\rangle \; . \tag{5.160}$$

If in addition

$$S_z|\psi_{\rm S}(\mathbf{r})\rangle = \hbar\, m_s|\psi_{\rm S}(\mathbf{r})\rangle$$

then one speaks of an *eigen-spinor*. From the components in (5.158) only $\psi_{m_s} \neq 0$.

We will continue the discussion of the spin in the next section for the important special case $S = 1/2$.

5.2.4 Spin $S = 1/2$

Spin $S = 1/2$ is realized, for instance, for electrons, protons and neutrons. It is thus by far the most important special case, which will therefore be investigated in some detail here. The spin space $\mathcal{H}_{S=1/2}$ is two-dimensional for these particles, and the spin operators are represented by 2×2-matrices. We had already calculated these matrices at the end of Sect. 5.1.4:

$$\mathbf{S}^2 = \frac{3}{4}\hbar^2\, \mathbb{1}_2 \; ; \qquad \mathbb{1}_2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \; , \tag{5.161}$$

$$S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \; , \tag{5.162}$$

$$S_+ = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \; ; \qquad S_- = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \; . \tag{5.163}$$

For the spin operator $\mathbf{S}$ sometimes one also writes:

$$\mathbf{S} = \frac{\hbar}{2}\,\boldsymbol{\sigma} \; ; \quad \boldsymbol{\sigma} \equiv (\sigma_x, \sigma_y, \sigma_z) \; . \tag{5.164}$$

The components of the vector operator $\boldsymbol{\sigma}$ are the **Pauli spin matrices**:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \; ; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \; ; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \; . \tag{5.165}$$

For these one easily proves the following properties:

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = \mathbb{1}_2 \; , \tag{5.166}$$

$$[\sigma_x, \sigma_y]_+ = [\sigma_y, \sigma_z]_+ = [\sigma_z, \sigma_x]_+ = 0 \; . \tag{5.167}$$

Note the subscript in the last relation. By $[\ldots,\ldots]_+$ we denote the so-called *anticommutator*,

$$[A, B]_+ = A\,B + B\,A \; , \tag{5.168}$$

which is to be distinguished from the commutator $[A,B]_- = A\,B - B\,A$, with which we are already familiar.

$$\begin{aligned} \mathrm{Tr}\sigma_x = \mathrm{Tr}\sigma_y &= \mathrm{Tr}\sigma_z = 0\,, &(5.169)\\ \sigma_x\,\sigma_y\,\sigma_z &= i\,\mathbb{1}_2\,. &(5.170)\end{aligned}$$

Furthermore, the commutation rules (5.152) are of course also valid, in corresponding form for the Pauli spin matrices:

$$[\sigma_x,\sigma_y]_- = 2i\,\sigma_z\;;\quad [\sigma_y,\sigma_z]_- = 2i\,\sigma_x\;;\quad [\sigma_z,\sigma_x]_- = 2i\,\sigma_y\,. \tag{5.171}$$

For the common eigen-states $|S\,m_s\rangle$ of $\mathbf{S}^2$ and S_z one uses in the case of $S = 1/2$ different *self-explanatory* symbols:

$$\begin{aligned} \left|\frac{1}{2}\,\frac{1}{2}\right\rangle &\equiv |\uparrow\rangle \equiv |+\rangle \equiv \begin{pmatrix}1\\0\end{pmatrix}\,,\\ \left|\frac{1}{2}\,-\frac{1}{2}\right\rangle &\equiv |\downarrow\rangle \equiv |-\rangle \equiv \begin{pmatrix}0\\1\end{pmatrix}\,. &(5.172)\end{aligned}$$

The states are obviously orthonormalized,

$$\langle\pm|\pm\rangle = 1\;;\quad \langle\pm|\mp\rangle = 0\,, \tag{5.173}$$

where, of course, with (5.161) and (5.162), the eigen-value equations

$$\mathbf{S}^2|\pm\rangle = \frac{3}{4}\,\hbar^2|\pm\rangle\;;\quad S_z|\pm\rangle = \pm\frac{\hbar}{2}\,|\pm\rangle \tag{5.174}$$

are fulfilled. Let us still consider the action of the ladder operators, for which we have in accordance with (5.64):

$$\begin{aligned} S_+|-\rangle &= \hbar|+\rangle\;; \quad S_+|+\rangle = 0\,,\\ S_-|-\rangle &= 0\;; \qquad S_-|+\rangle = \hbar|-\rangle\,. &(5.175)\end{aligned}$$

By $S_\pm$ the particle spin is thus *'flipped up'* and *'flipped down'*, respectively. It is clear that a spin $S = 1/2$ can be flipped up (down) at most once, a fact, which in the $\mathcal{H}_{1/2}$ can also be formulated as an operator identity:

$$(S_+)^2 = (S_-)^2 = 0 \tag{5.176}$$

According to our general considerations in the last section, the state of a *spin 1/2-particle* can be written in the postion representation as a two-component spinor:

$$|\psi_{1/2}(\mathbf{r})\rangle = \begin{pmatrix}\psi_+(\mathbf{r})\\ \psi_-(\mathbf{r})\end{pmatrix}\,. \tag{5.177}$$

$|\psi_\pm(\mathbf{r})|^2\,d^3r$ is thereby the probability to find the particle with a simultaneous measurement of *spin* and *position*, which is definitely possible because of (5.149),

in the volume element d^3r at $\mathbf{r}$ with a spin 1/2 *parallel* (+) and *antiparallel* (−), respectively, to the z-axis. $\psi_\pm(\mathbf{r})$ must therefore be square integrable functions. The square of the norm of the spinor,

$$\left\|\psi_{1/2}(\mathbf{r})\right\|^2 = \left\langle\psi_{1/2}(\mathbf{r})\middle|\psi_{1/2}(\mathbf{r})\right\rangle = |\psi_+(\mathbf{r})|^2 + |\psi_-(\mathbf{r})|^2 = |\psi(\mathbf{r})|^2 \ , \qquad (5.178)$$

corresponds to the *normal* density of the position probability for the considered particle.

If for an actual physical problem, only the spin-dependence is of interest, one will of course perform the respective calculations exclusively in the spin space $\mathcal{H}_{1/2}$, in the same manner as we restricted ourselves in the preceding sections to the space $\mathcal{H}_\mathrm{O}$ of the orbital motion, since in those cases investigated, the spin was unimportant. We can expand, according to (5.155), the general normalized spin state $|\alpha_{1/2}\rangle$ in the eigen-states $|\pm\rangle$:

$$\left|\alpha_{1/2}\right\rangle = \alpha_+|+\rangle + \alpha_-|-\rangle \quad = \quad \alpha_+ \begin{pmatrix}1\\0\end{pmatrix} + \alpha_- \begin{pmatrix}0\\1\end{pmatrix} = \begin{pmatrix}\alpha_+\\ \alpha_-\end{pmatrix} \ , \qquad (5.179)$$

$$|\alpha_+|^2 + |\alpha_-|^2 \quad = \quad 1 \ . \qquad (5.180)$$

The spin space $\mathcal{H}_{1/2}$ does not exhibit any peculiarities as Hilbert space. We can directly take over all the statements of our general investigations on operators and states in Hilbert spaces, developed in Chap. 3 (Vol. 6). It is even so that the abstract Hilbert-space theory can be demonstrated especially clearly by the use of the spin space $\mathcal{H}_{1/2}$, because this space is finite-dimensional, and, in particular, does not contain improper states (Sect. 3.2.4, Vol. 6). We have therefore presented already in Chap. 3 (Vol. 6) several exercises on the application of the Hilbert-space theory, which dealt with the observable spin, although at that stage, strictly speaking, we did not know the spin.

To the spin as angular momentum there is an associated magnetic moment. Via this moment the spin couples to an external magnetic field. We recall that the experimentally not confirmed equidistant splitting of the atomic energy levels (5.132), caused by the moment of the orbital angular momentum, was just the motivation for us to postulate the spin with a corresponding magnetic moment. But how does this spin moment really look like? The orbital angular momentum of the electron causes, according to (5.129), a magnetic moment of the form:

$$\boldsymbol{\mu}_L = \frac{-e}{2m_e}\,\mathbf{L} = -\mu_B\,\frac{1}{\hbar}\,\mathbf{L} \ . \qquad (5.181)$$

We could obtain this expression by the use of the principle of correspondence from the corresponding relations of Classical Electrodynamics. The problem with the spin lies now mainly in the fact that we cannot use a classical analog as guideline. So the expectation that the spin moment $\widehat{\boldsymbol{\mu}}_\mathrm{S}$ has exactly the same structure as $\widehat{\boldsymbol{\mu}}_\mathrm{L}$ is actually not supported by any lead. It is therefore, at first, nothing more than a plausible ansatz when we write:

$$\boldsymbol{\mu}_\mathrm{S} = \mu_\mathrm{S} \cdot \mathbf{S} \ . \qquad (5.182)$$

If one permits that the coefficient μ_{S} is different for different spin-1/2-particles, then this ansatz, though, has indeed excellently proven its worth. Especially for **electrons**, the correction of (5.132) by the experimental evaluation of the Zeeman effect yields:

$$\mu_{\mathrm{S}}\,(e^-) = -g\,\frac{\mu_B}{\hbar}\;. \tag{5.183}$$

g is the Landé factor. The experiment requires $g = 2$, what is exactly confirmed by the **relativistic Dirac theory** which we will deal with in the next section. In the course of **Quantum Electrodynamics** this value becomes a bit further corrected:

$$g = 2\,\left(1 + \frac{\alpha}{2\pi} + \ldots\right) = 2.002319\ldots \tag{5.184}$$

$\alpha = 1/137$ is here Sommerfeld's fine-structure constant. μ_B contains the electron mass. The magnetic moments of the proton and the neutron, in spite of the same spin, are thus considerably smaller. For the nucleons one therefore uses as guide value, instead of the Bohr magneton μ_B, the *nuclear magneton*:

$$\mu_{\mathrm{n}} = \frac{e\,\hbar}{2m_{\mathrm{p}}}\;. \tag{5.185}$$

m_{p} is the mass of the proton, which amounts approximately to 1836-times the electron mass m_e ($\mu_{\mathrm{S}}(p) \approx 5,6\,\mu_{\mathrm{n}}/\hbar$; $\mu_{\mathrm{S}}(n) \approx -3,8\,\mu_{\mathrm{n}}/\hbar$).

We have to now use for the total paramagnetic moment of the electron, after we have fixed the spin contribution (5.183):

$$\boldsymbol{\mu}(e^-) = -\mu_B\,\frac{1}{\hbar}\,(\mathbf{L} + 2\mathbf{S})\;. \tag{5.186}$$

It is common to count the diamagnetic component (5.129) separately. The moment $\boldsymbol{\mu}$ then couples linearly to an external magnetic field $\mathbf{B}$ and produces therewith an additional paramagnetic term in the Hamilton operator:

$$H_{pm} = -\boldsymbol{\mu}(e^-)\cdot\mathbf{B} = \mu_B\,\frac{1}{\hbar}\,(\mathbf{L} + 2\mathbf{S})\cdot\mathbf{B}\;. \tag{5.187}$$

The total Hamilton operator of an electron in the homogeneous magnetic field $\mathbf{B}$ and in another potential field $V(\mathbf{r})$ reads therewith, according to our present state of knowledge:

$$H \;=\; \frac{\mathbf{p}^2}{2m_e} + V(\mathbf{r}) + H_{pm} + H_{\mathrm{dia}}\;, \tag{5.188}$$

$$H_{\mathrm{dia}} \;=\; \frac{e^2\mathbf{B}^2}{8m_e}\,r^2\sin^2\vartheta\;; \quad \vartheta = \sphericalangle(\mathbf{r},\mathbf{B})\;. \tag{5.189}$$

Even this expression will turn out to be not fully complete. We have namely tacitly presumed that orbital angular momentum and spin do not influence each

other. This assumption will later turn out as untenable, since a **spin-orbit interaction** (see Sect. 5.3.4) cannot be ignored.

In the position representation, which we used to a large extent in this section, the **time-dependent Schrödinger equation**,

$$i\,\hbar\,\frac{\partial}{\partial t}\left|\psi_{1/2}\left(\mathbf{r},t\right)\right\rangle = H\left|\psi_{1/2}\left(\mathbf{r},t\right)\right\rangle \ ,$$

now reads for the electron in the homogeneous magnetic field $\mathbf{B}$ and the potential $V(\mathbf{r})$, without the not yet introduced spin-orbit interaction which will turn out to be a purely relativistic effect:

$$\begin{aligned} i\,\hbar\,\frac{\partial}{\partial t}\begin{pmatrix}\psi_+(\mathbf{r},t)\\ \psi_-(\mathbf{r},t)\end{pmatrix} \;=\; & \left[\left(-\frac{\hbar^2\Delta}{2m_e}+V(\mathbf{r})+\frac{\mu_B}{\hbar}\,\mathbf{L}\cdot\mathbf{B}+H_{\mathrm{dia}}\right)\mathbb{1}_2\right. \\ & \left.+2\,\frac{\mu_B}{\hbar}\,\mathbf{S}\cdot\mathbf{B}\right]\begin{pmatrix}\psi_+(\mathbf{r},t)\\ \psi_-(\mathbf{r},t)\end{pmatrix} \ . \end{aligned} \tag{5.190}$$

This, without the potential term $V(\mathbf{r})$, is the so-called *'Pauli equation'*, which we will meet again in the next section as the non-relativistic limiting case of the Dirac theory.

For brevity, in the last two sections, we have disregarded the time-dependence of the wave functions, because of being not essential for the considerations there. One can of course easily bring, as done in (5.190), the time-dependence retroactively into play.

Let us finally write down the Schrödinger equation for the important special case of an electron in the time- and position-dependent electromagnetic field (vector potential $\mathbf{A}(\mathbf{r},t)$, scalar potential $\varphi(\mathbf{r},t)$):

$$\begin{aligned} i\,\hbar\,\frac{\partial}{\partial t}\begin{pmatrix}\psi_+(\mathbf{r},t)\\ \psi_-(\mathbf{r},t)\end{pmatrix} \;=\; & \left[\left(\frac{1}{2m_e}\left(\mathbf{p}+e\,\mathbf{A}(\mathbf{r},t)\right)^2-e\,\varphi(\mathbf{r},t)\right)\mathbb{1}_2\right. \\ & \left.+\mu_B\boldsymbol{\sigma}\cdot\mathbf{B}(\mathbf{r},t)\right]\begin{pmatrix}\psi_+(\mathbf{r},t)\\ \psi_-(\mathbf{r},t)\end{pmatrix} \ . \end{aligned} \tag{5.191}$$

In this section we have postulated the existence of the spin, only because of an *'experimental necessity'*, and have discussed its consequences. In the next section, we will rigorously justify, with the use of the relativistic Dirac theory, the electron spin, the spin magnetic moment, and the spin-orbit interaction.

5.2.5 Exercises

Some important exercises concerning the *spin* have already been presented in Chap. 3 (Vol. 6). The repetition of the Exercises 3.3.4–3.3.9, 3.4.1 and 3.4.2 is at this stage very recommendable.

Exercise 5.2.1
Prove, only by the use of the general properties of the angular momentum, i.e., without the explicit matrix representations of the spin operators, the following relations for a spin $S = 1/2$:

1. $[S_x, S_y]_+ = 0$,
2. $S_x^2 = S_y^2 = S_z^2 = \frac{\hbar^2}{4}\,\mathbb{1}_2$,
3. $S_x\,S_y = i\,\frac{\hbar}{2}\,S_z$,
4. $S_x\,S_y\,S_z = i\,\frac{\hbar^3}{8}$.

Exercise 5.2.2

1. Verify the following relation for the Pauli spin matrices,:

$$\sigma_i\sigma_j = \delta_{ij}\,\mathbb{1}_2 + i\sum_k \varepsilon_{ijk}\,\sigma_k\ ; \quad i,j,k \in \{x,y,z\}\ ,$$

   ε_{ijk} is the fully antisymmetric unit tensor of third rank (5.4).

2. Let $\mathbf{a}$ and $\mathbf{b}$ be two vector operators, which commute with all the three Pauli spin matrices. Prove the relation:

$$(\boldsymbol{\sigma}\cdot\mathbf{a})\,(\boldsymbol{\sigma}\cdot\mathbf{b}) = \mathbf{a}\cdot\mathbf{b}\,\mathbb{1}_2 + i\,\boldsymbol{\sigma}\cdot(\mathbf{a}\times\mathbf{b})\ .$$

Exercise 5.2.3
Let $\widehat{A}$ and $\widehat{B}$ be two (2×2)-matrices, which can be expressed as follows by the Pauli spin operator $\boldsymbol{\sigma}$ (5.164):

$$\widehat{A} = a_0\mathbb{1}_2 + \mathbf{a}\cdot\boldsymbol{\sigma}\ ; \quad \widehat{B} = b_0\mathbb{1}_2 + \mathbf{b}\cdot\boldsymbol{\sigma}\ .$$

$\mathbf{a}$ and $\mathbf{b}$ are thereby arbitrary three-dimensional vectors (not operators!), and a_0, b_0 are arbitrary complex numbers.

1. Bring the matrix-product $\widehat{A}\cdot\widehat{B}$ into the form

$$\widehat{A}\cdot\widehat{B} = x\mathbb{1}_2 + \mathbf{y}\cdot\boldsymbol{\sigma}\ .$$

2. Express the inverse matrix $\widehat{A}^{-1}$ by $\mathbb{1}_2$ and $\boldsymbol{\sigma}$ ($\mathbf{a}^2 \neq a_0^2$).

Exercise 5.2.4
Calculate the expectation values $\langle S_x\rangle$, $\langle S_y\rangle$, $\langle S_z\rangle$ in the spin state:

$$|\alpha\rangle = \alpha_+\begin{pmatrix}1\\0\end{pmatrix} + \alpha_-\begin{pmatrix}0\\1\end{pmatrix}\ .$$

Exercise 5.2.5
Let $\{|\frac{1}{2}\ m_S\rangle\}$ be the common eigen-states of $\mathbf{S}^2$ and S_z for a spin-$\frac{1}{2}$ particle.

1. Which are the eigen-values of S_x and S_y?
2. Determine the eigen-states of S_x and S_y in the basis system of the eigen-states of $\mathbf{S}^2$ and S_z.

Exercise 5.2.6

1. Let the unit vector

$$\mathbf{e} = (e_1, e_2, e_3) = (\sin\vartheta\cos\varphi, \sin\vartheta\sin\varphi, \cos\vartheta)$$

define an arbitrary space direction. Calculate

$$(\boldsymbol{\sigma}\cdot\mathbf{e})^2 \; !$$

$\boldsymbol{\sigma}$: Pauli spin operator.

2. Let a particle with the spin $S = 1/2$ be at a certain point of time in the (normalized) state

$$|\psi\rangle = \frac{1}{\sqrt{2}}|+\rangle + \frac{1+i}{2}|-\rangle \; .$$

$|\pm\rangle$ are, as in (5.172), the eigen-states of (S^2, S_z) in the case $S = 1/2$. For which space direction $\mathbf{e}$ does the spin projection $\mathbf{S}\cdot\mathbf{e}$ have the uncertainty zero?

Exercise 5.2.7
Consider an $S = 1/2$-particle with only one spin-degree of freedom. The matrix elements of the Hamilton operator in the basis of the (S^2, S_z)-eigen states $|+\rangle \equiv |10\rangle$ and $|-\rangle \equiv |01\rangle$ are the following:

$$\langle\pm|H|\pm\rangle = 0 \; ; \; \langle+|H|-\rangle = \langle-|H|+\rangle = \eta \;\; (\eta > 0) \; .$$

1. Show that it holds for the time-evolution operator in the Schrödinger picture:

$$U(t,0) = \cos\left(\frac{\eta}{\hbar}t\right) \; \mathbb{1}_2 - i \, \sin\left(\frac{\eta}{\hbar}t\right) \; \sigma_x$$

σ_x: Pauli spin matrix.

2. At the time $t = 0$ the particle is in the state $|+\rangle$. What is the probability that the particle is in this state even for $t > 0$?

3. Calculate the special (time-dependent) space direction $\mathbf{e}(t)$, for which the particle is *definitely* an $\uparrow$-particle, i.e., for which a measurement of the spin projection onto this direction yields *with certainty* the value $+\hbar/2$.

Exercise 5.2.8
Let the spin $S = 3/2$ be in a normalized state $|\varphi\rangle$, for which the following expectation values are found:

$$\langle\varphi|S_z|\varphi\rangle = \frac{\hbar}{2} \; ; \quad \langle\varphi|S_x|\varphi\rangle = \langle\varphi|S_y|\varphi\rangle = 0 \; .$$

Show that the conclusion herefrom that $|\varphi\rangle$ is an eigen-state of S_z, is sufficient but not necessary.

Exercise 5.2.9
Let a spin $S = 3/2$ be in a state $|\psi\rangle$ with

$$\langle\psi|S_z|\psi\rangle = \frac{3}{2}\,\hbar\ .$$

Is $|\psi\rangle$ then eigen-state of S_z?

Exercise 5.2.10
An electron moves in an electromagnetic field $(\mathbf{E}, \mathbf{B})$, fixed by the scalar potential $\varphi(\mathbf{r}, t)$ and the vector potential $\mathbf{A}(\mathbf{r}, t)$. Solution of the time-dependent Schrödinger equation is the two-component spinor (5.177):

$$\left|\psi_{\frac{1}{2}}(\mathbf{r}, t)\right\rangle = \begin{pmatrix} \psi_+(\mathbf{r}, t) \\ \psi_-(\mathbf{r}, t) \end{pmatrix}\ .$$

Show that, in the case of a **homogeneous** magnetic induction $\mathbf{B}(\mathbf{r}, t) \equiv \mathbf{B}(t)$, by the use of a product ansatz,

$$\left|\psi_{\frac{1}{2}}(\mathbf{r}, t)\right\rangle = \eta(\mathbf{r}, t)\ \left|\chi_{\frac{1}{2}}(t)\right\rangle \qquad \left|\chi_{\frac{1}{2}}(t)\right\rangle = \begin{pmatrix} \chi_+(t) \\ \chi_-(t) \end{pmatrix}\ ,$$

spin dynamics and orbit dynamics can be completely separated. Derive the corresponding equations of motion!

Exercise 5.2.11
We describe an electron in the magnetic field $\mathbf{B}$, with only one spin degree of freedom, by the Hamilton operator

$$H = 2\,\frac{\mu_B}{\hbar}\,\mathbf{S}\cdot\mathbf{B}\ .$$

Calculate the time-dependences of the expectation values

$$\langle S_x\rangle_t\ , \quad \langle S_y\rangle_t\ , \quad \langle S_z\rangle_t\ .$$

Choose as the z-direction the direction of the magnetic field $\mathbf{B}$.

Exercise 5.2.12
Calculate for a spin 1/2-particle the eigen-values and the eigen-functions of the operator $A = \alpha(S_x + S_y)$; α: real! What is the probability that a measurement of S_z yields the value $-\hbar/2$, when the particle is in an eigen-state of A?

Exercise 5.2.13
At the time $t = 0$ a spin 1/2-particle is in the eigen-state $|+\rangle$ of S_z. It is subject to the influence of a strong magnetic field B_0 in the z-direction and a weak alternating field

$$\mathbf{B}_1 = B_1\ (\mathbf{e}_x\cos\omega t - \mathbf{e}_y\sin\omega t)\ .$$

What is the probability $w_-(t)$ to find the particle in the state $|-\rangle$ at a later point of time t? Discuss the result (*paramagnetic resonance*)! Take only the

spin-degree of freedom of the particle into consideration, i.e., use as Hamilton operator

$$H = -\mu_S \, \mathbf{S} \cdot \mathbf{B} \; .$$

Exercise 5.2.14
A particle of the mass m and the charge q moves in a homogeneous magnetic field

$$\mathbf{B} = \frac{1}{\sqrt{2}} \, B(\mathbf{e}_y + \mathbf{e}_z)$$

and in a homogeneous electric field $\mathbf{E} = E \, \mathbf{e}_x$.

1. Determine its magnetic moment $\boldsymbol{\mu}$ (operator!)
2. Calculate the commutators

$$[\mu_x, \, p_x]_- \;\; , \;\; [\mu_y, \, p_x]_-$$

and the double-commutator

$$\Big[[\mu_x, \, p_y]_- \, , \, z \Big]_- \; .$$

Exercise 5.2.15
A beam of neutrons is to equal parts spin-polarized in x- and z-direction (perpendicular to the y-direction).

1. Calculate the corresponding statistical operator ρ!
2. Determine the expectation value of the neutron spin for a measurement in the direction $(\vartheta = \frac{\pi}{3}, \varphi = \frac{\pi}{6})$!
3. Find for the measurement in 2.) the uncertainty of the spin measurement (mean square deviation)!

5.3 Relativistic Theory of the Electron

In this section we try to find a rigorous justification of the electron spin, for the existence of which we found up to now only empirical reasons. Starting point for that is the **Dirac equation**, which we will obtain by a linearization of the relativistic generalization of the Scrödinger equation. For this purpose, though, we have to, temporarily, leave the non-relativistic Quantum Mechanics, which we are actually interested in, and avail ourselves of some concepts and theorems of the Special Theory of Relativity, which we have introduced and discussed in Vol. 4 of our ground course in Theoretical Physics. This is indispensable, since **spin**, **spin moment**, and **spin-orbit interaction** turn out to be only purely relativisticly justifiable particle properties. The reader, who is not yet

or no longer familiar with the formalism of the theory of relativity, can skip this section. He must then, however, be content with the introduction of the spin by the use of empirical postulates as done in Sect. 5.2. For the further discussion of the non-relativistic Quantum Mechanics in this volume, though, the full understanding of the Dirac theory of the electron is not an imperative precondition, nevertheless, of course, highly recommendable.

5.3.1 Dirac Equation

The relativistic, classical energy law for a free particle reads according to ((2.63), Vol. 4):

$$E^2 = c^2 \mathbf{p}^2 + m_e^2 \, c^4 \, .$$

c is the velocity of light, m_e is the mass of the electron, and $\mathbf{p}$ is its relativistic mechanical momentum:

$$\mathbf{p} = \gamma \, m_e \, \mathbf{v} \, ; \qquad \gamma = \left(1 - \frac{v^2}{c^2} \right)^{-1/2} \, .$$

$\mathbf{v}$ is the velocity of the electron. In the preceding sections we got from non-relativistic classical relations the corresponding quantum-mechanical concepts, for instance, by the use of the *rule of correspondence* ((2.89), (2.108), Vol. 6)),

$$\begin{aligned} \mathbf{p} \quad &\longrightarrow \quad \frac{\hbar}{i} \nabla \, ; \\ E \quad &\longrightarrow \quad i \, \hbar \, \frac{\partial}{\partial t} \, , \end{aligned}$$

where the so introduced operators have to be applied to time- and position-dependent wave functions $\psi(\mathbf{r}, t)$. In the case of corresponding transformations of **relativistic**, classical laws into Quantum Mechanics, their **covariance** must be preserved. This means that, even after quantization, the laws must be form-invariant under Lorentz transformations because of the fundamental equivalence of all inertial systems. Form-invariance under Lorentz transformations is guaranteed if all additive terms of an equation are **four-(world-)tensors of the same rank**. In this sense, the above classical energy law of the free particle can be written in a compact form as

$$p^\mu p_\mu = m_e^2 \, c^2 \, . \tag{5.192}$$

(Note here the *summation convention*: over Greek indexes of adjacent terms is to be added up!)—p^μ is the **contravariant** four-momentum and therewith as a vector it is a tensor of first rank:

$$\begin{aligned} p^\mu \quad &= \quad \left(\frac{E}{c}, \gamma \, m_e v_x, \gamma \, m_e v_y, \gamma \, m_e v_z \right) \\ &= \quad \left(\frac{E}{c}, \gamma \, m_e \mathbf{v} \right) . \end{aligned}$$

The so-called **covariant** four-momentum p_μ differs from p^μ only by the opposite sign of the space-components. The square of the norm of the four-momentum p^μ is, as the right-hand side of (5.192), a four-scalar. The energy law is thus in the correct covariant form.

But the contravariant *four-gradient* ((2.31), Vol. 4),

$$\partial^\mu \equiv \left(\frac{1}{c} \frac{\partial}{\partial t}, -\nabla \right) ,$$

now allows also to combine the two *rules of correspondence* in a relativistic-covariant form:

$$p^\mu \longrightarrow i\,\hbar\,\partial^\mu . \tag{5.193}$$

With this *relativistic rule of correspondence*, the square of the norm of the four-momentum reads:

$$p^\mu p_\mu \longrightarrow -\hbar^2 \partial^\mu \partial_\mu = \hbar^2 \,\Box . \tag{5.194}$$

$\Box$ is the *d'Alembert operator* ((2.33), Vol. 4),

$$\Box = \Delta - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \qquad (\Delta : \text{ Laplace operator}) ,$$

as a scalar product it is of course a four-scalar. It is clear that with the quantization of (5.192), in this case also, we have to apply the resulting operators to a wave function, which describes the state of the particle. This function will depend on the *four-position*

$$x^\mu \equiv (ct, x, y, z) ,$$

and therewith ultimately again on $\mathbf{r}$ and t. We choose therefore, as before, the notation $|\psi(\mathbf{r}, t)\rangle$. Out of the energy law (5.192), then follows, the relativistic generalization of the Schrödinger equation,

$$\left(\hbar^2 \Box - m_e^2 c^2\right) \left|\psi(\mathbf{r}, t)\right\rangle = 0 ,$$

which in the following form is called **Klein-Gordon equation**:

$$\left(\Delta - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \frac{m_e^2 c^2}{\hbar^2} \right) \left|\psi(\mathbf{r}, t)\right\rangle = 0 . \tag{5.195}$$

This wave equation, however, poses a not insignificant problem. It represents a differential equation of second order with respect to the time. Its solution thus requires initial conditions for $|\psi\rangle$ **and** $|\dot{\psi}\rangle$. The non-relativistic Schrödinger equation, in contrast, is of first order in time. One can surely question whether the inclusion of relativistic effects must indeed lead to such drastic changes in

the required initial information. Dirac's idea was therefore, at first, to linearize the starting equation (5.192), and that by the ansatz:

$$\left(E - c\sum_i \widehat{\alpha}_i\, p_i - \widehat{\beta}\, m_e\, c^2\right)\left(E + c\sum_j \widehat{\alpha}_j\, p_j + \widehat{\beta}\, m_e\, c^2\right) = 0 \qquad (5.196)$$
$$i,j \in \{x,y,z\}$$

The *new quantities* $\widehat{\boldsymbol{\alpha}}$, $\widehat{\beta}$ have to fulfill the following relations:

$$\begin{aligned} [\,\widehat{\alpha}_i, \widehat{\alpha}_j\,]_+ &= 2\delta_{ij}\,\mathbb{1}\,, \\ \left[\,\widehat{\alpha}_i, \widehat{\beta}\,\right]_+ &= 0\,; \quad \widehat{\beta}^{\,2} = \mathbb{1}\,. \end{aligned} \qquad (5.197)$$

This is of course not achievable with *normal numbers* of the $\mathbb{R}$ or $\mathbb{C}$. We will therefore later try to interpret $\widehat{\boldsymbol{\alpha}}$ and $\widehat{\beta}$ as quadratic matrices. These must, after the transition to the quantum-mechanical formulation, imperatively commute with the momentum operator, in order to keep (5.196) valid. In particular, they should not be position-dependent. We will of course come back later to the explicit fixing of $\widehat{\alpha}_i$ and $\widehat{\beta}$.

Each solution of the linearized equations

$$\left(E \mp c\sum_i \widehat{\alpha}_i\, p_i \mp \widehat{\beta}\, m_e\, c^2\right) = 0\,,$$

is of course also solution to (5.196). That leads, with the rule of correspondence (5.193) to the

Dirac equation of the free electron

$$\left(i\,\hbar\,\frac{\partial}{\partial t} + i\,\hbar\, c\,\widehat{\boldsymbol{\alpha}}\cdot\boldsymbol{\nabla} - \widehat{\beta}\, m_e\, c^2\right)|\psi(\mathbf{r},t)\rangle = 0\,. \qquad (5.198)$$

Soon we will recognize that the second linearized equation, for which, compared to the other equation, the second and the third summand both have the opposite sign, leads to the same physical statements. One therefore needs to analyze only one of the two equations. If $\widehat{\boldsymbol{\alpha}}$ and $\widehat{\beta}$ are really $n \times n$-matrices, then the *wave function* $|\psi(\mathbf{r},t)\rangle$ must be correspondingly an n-component vector.

In order that (5.198) gets formally the structure of the time-dependent Schrödinger equation we introduce the

Dirac operator of the free electron

$$H_{\mathrm{D}}^{(0)} = c\,\widehat{\boldsymbol{\alpha}}\cdot\mathbf{p} + \widehat{\beta}\, m_e\, c^2\,. \qquad (5.199)$$

By the use of this operator we formulate the *time-dependent* and the *time-independent Dirac equation*:

$$i\,\hbar\,\frac{\partial}{\partial t}|\psi(\mathbf{r},t)\rangle = H_{\mathrm{D}}^{(0)}|\psi(\mathbf{r},t)\rangle\,, \qquad (5.200)$$

$$H_{\mathrm{D}}^{(0)}|\psi(\mathbf{r},t)\rangle = E|\psi(\mathbf{r},t)\rangle\,. \qquad (5.201)$$

The equal status of position and time components is typical for the theory of relativity, which manifests itself already in the matrix of the Lorentz transformation ((1.16), Vol. 4). A relativistic wave equation should therefore be symmetric with respect to space and time coordinates, i.e., in particular, it should be for the space coordinates, too, a differential equation of first order. That is obviously guaranteed by the Dirac equation (5.198).

We note at this stage that for the description of the electron in the electromagnetic field (vector potential $\mathbf{A}(\mathbf{r},t)$, scalar potential $\varphi(\mathbf{r},t)$) we have only to perform in the so far derived relations the *usual* substitutions

$$\mathbf{p} \;\longrightarrow\; \mathbf{p} + e\,\mathbf{A}\;; \qquad E \;\longrightarrow\; E + e\,\varphi\;.$$

These can be combined with the *four-potential* A^μ ((2.107), Vol. 4) to:

$$p^\mu \;\longrightarrow\; p^\mu + e\,A^\mu\;; \qquad A^\mu = \left(\frac{1}{c}\,\varphi, \mathbf{A}\right)\;. \tag{5.202}$$

Analogously to (5.198) one comes then to the

Dirac equation of the electron in the electromagnetic field

$$\left[i\,\hbar\,\frac{\partial}{\partial t} - c\,\widehat{\boldsymbol{\alpha}}\cdot\left(\frac{\hbar}{i}\,\nabla + e\,\mathbf{A}(\mathbf{r},t)\right) - \widehat{\beta}\,m_e\,c^2 + e\,\varphi(\mathbf{r},t)\right]|\psi(\mathbf{r},t)\rangle = 0\;. \tag{5.203}$$

The corresponding Dirac operator H_D is then of the form:

$$H_\mathrm{D} = c\,\widehat{\boldsymbol{\alpha}}\cdot(\mathbf{p} + e\,\mathbf{A}) + \widehat{\beta}\,m_e\,c^2 - e\,\varphi\;. \tag{5.204}$$

There still remains the task of fixing the **Dirac matrices** $\widehat{\boldsymbol{\alpha}}$ and $\widehat{\beta}$ using the conditions (5.197). As already mentioned, the latter cannot be fulfilled by simple c-numbers. But we remember that the Pauli spin matrices obey with (5.166) and (5.167) the same relations as the three components of $\widehat{\boldsymbol{\alpha}}$. A direct identification is, however, not possible, already because of the existence of $\widehat{\beta}$. One can show that $\widehat{\boldsymbol{\alpha}}$ and $\widehat{\beta}$ must at least be 4×4-matrices, where with the following choice (5.197) can be fulfilled (Exercise 5.3.1):

$$\widehat{\boldsymbol{\alpha}} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}\;; \quad \widehat{\beta} = \begin{pmatrix} \mathbb{1}_2 & 0 \\ 0 & -\mathbb{1}_2 \end{pmatrix}\;. \tag{5.205}$$

The components of the spin operator $\boldsymbol{\sigma}$ (5.164) are the Pauli 2×2-spin matrices. $\mathbb{1}_2$ is the 2×2-unit matrix. The Dirac operator (5.199) becomes therewith a 4×4-matrix:

$$H_\mathrm{D}^{(0)} \equiv \begin{pmatrix} m_e\,c^2 & 0 & c\,p_z & c(p_x - i\,p_y) \\ 0 & m_e\,c^2 & c(p_x + i\,p_y) & -c\,p_z \\ c\,p_z & c(p_x - i\,p_y) & -m_e\,c^2 & 0 \\ c(p_x + i\,p_y) & -c\,p_z & 0 & -m_e\,c^2 \end{pmatrix}\;. \tag{5.206}$$

Correspondingly, the *wave function* $|\psi(\mathbf{r},t)\rangle$ must also be a four-component quantity. One reads off from (5.199) that $H_{\mathrm{D}}^{(0)}$ commutes with the momentum operator. The following ansatz for $|\psi\rangle$ therefore appears rather promising:

$$\begin{aligned} |\psi(\mathbf{r},t)\rangle &= \hat{a}\exp\left(-\frac{i}{\hbar}\,p^{\mu}x_{\mu}\right) \\ &= \hat{a}\exp\left[\frac{i}{\hbar}\,(\mathbf{p}\cdot\mathbf{r}-E\,t)\right]\,. \end{aligned} \tag{5.207}$$

That is nothing else but the relativistic-covariantly written plane wave (eigenfunction of the momentum!), multiplied by a column vector,

$$\hat{a} \equiv \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{pmatrix}\,, \tag{5.208}$$

with four position-independent components. One calls $\hat{a}$ or also $|\psi(\mathbf{r},t)\rangle$ a *Dirac spinor*. If we apply this ansatz in the time-independent Dirac equation (5.201) then we come to the following homogeneous system of equations:

$$\begin{pmatrix} m_e\,c^2-E & 0 & c\,p_z & c(p_x-i\,p_y) \\ 0 & m_e\,c^2-E & c(p_x+i\,p_y) & -c\,p_z \\ c\,p_z & c(p_x-i\,p_y) & -m_e\,c^2-E & 0 \\ c(p_x+i\,p_y) & -c\,p_z & 0 & -m_e\,c^2-E \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}\,. \tag{5.209}$$

In contrast to (5.206) the momenta p_x, p_y, p_z in this matrix are no longer operators, but numbers, which came out as eigen-values after the application of the operators in (5.206) onto the plane wave (5.207). The zeros of the determinant of the matrix of coefficients in (5.209),

$$0 \stackrel{!}{=} \left\{\left(m_e\,c^2\right)^2 - E^2 + c^2\mathbf{p}^2\right\}^2\,,$$

correspond to the energy-eigen values of the Dirac operator:

$$E_\eta = \eta\,E_p\,; \quad \eta = \pm\,; \quad E_p = \sqrt{c^2\mathbf{p}^2 + m_e^2\,c^4}\,. \tag{5.210}$$

Each of the two eigen-values is twofold degenerate. It is, at first, becalming that, as eigen-value, the classical relativistic energy-momentum relation of the free electron comes out. That holds, however, only for E_+. There is a second solution E_-, which, at first glance, seems to describe a *rather unphysical behavior*. The energy E_- **decreases** with increasing momentum! Although highly interesting and important we cannot follow here the detailed interpretation of this aspect. It has the fundamental consequence of the theoretical prediction,

due to P. Dirac, of the **positron**, the *antiparticle* of the electron. The positron has the same mass as the electron and an opposite equal, positive charge. It is in the meantime experimentally uniquely established, so that E_- is indeed a *physical solution*. Since this section, however, is about, exclusively, giving rigorous reasons for the electron spin, we will restrict ourselves in the next sections to the *electronic solution* E_+.

To each of the two eigen-values E_+ and E_- there exist two linearly independent *eigen-spinors* $\hat{a}^{\pm}_{1,2}$, which we will distinguish, at first, by the lower indexes 1 and 2. In order to determine them, we have to take in (5.209) $E = E_\pm$. One recognizes that, for instance, the first two rows of the matrix are orthogonal to each other, while the third and the fourth row can be written as linear combinations of the first two. The other way round, the third and the fourth row are orthogonal, and the first and the second row are linear combinations of them. If we, for the moment, disregard normalizations, then we can quickly fix with the presetting $\left(a^{(+)}_{11} = 1,\ a^{(+)}_{12} = 0\right)$, $\left(a^{(+)}_{21} = 0,\ a^{(+)}_{22} = 1\right)$, $\left(a^{(-)}_{13} = 1,\ a^{(-)}_{14} = 0\right)$, $(a^{(-)}_{23} = 0,\ a^{(-)}_{24} = 1)$ the respective two other spinors $\hat{a}^{(\pm)}_1$, $\hat{a}^{(\pm)}_2$ by the use of (5.209):

$$\hat{a}^{(+)}_1 \equiv d \begin{pmatrix} 1 \\ 0 \\ \dfrac{c\,p_z}{\widehat{E}} \\ \dfrac{c\,p_+}{\widehat{E}} \end{pmatrix} ; \quad \hat{a}^{(+)}_2 \equiv d \begin{pmatrix} 0 \\ 1 \\ \dfrac{c\,p_-}{\widehat{E}} \\ -\dfrac{c\,p_z}{\widehat{E}} \end{pmatrix} , \tag{5.211}$$

$$\hat{a}^{(-)}_1 \equiv d \begin{pmatrix} -\dfrac{c\,p_z}{\widehat{E}} \\ -\dfrac{c\,p_+}{\widehat{E}} \\ 1 \\ 0 \end{pmatrix} ; \quad \hat{a}^{(-)}_2 \equiv d \begin{pmatrix} -\dfrac{c\,p_-}{\widehat{E}} \\ \dfrac{c\,p_z}{\widehat{E}} \\ 0 \\ 1 \end{pmatrix} . \tag{5.212}$$

Here we have written for abbreviation:

$$\widehat{E} = E_p + m_e\,c^2 ; \qquad p_\pm = p_x \pm i\,p_y . \tag{5.213}$$

The normalization constant d can be chosen as real, and then it is the same for all the four spinors:

$$d = \frac{m_e\,c^2 + E_p}{\sqrt{\left(m_e\,c^2 + E_p\right)^2 + c^2\mathbf{p}^2}} = \frac{1}{\sqrt{1 + \dfrac{c^2\mathbf{p}^2}{\widehat{E}^2}}} \underset{v \ll c}{\longrightarrow} 1 . \tag{5.214}$$

The four column vectors are obviously pairwise orthogonal. The vectors $\hat{a}_1^{(+)}$ and $\hat{a}_2^{(+)}$ hence build a basis of the E_+-eigen space; $\hat{a}_1^{(-)}$ and $\hat{a}_2^{(-)}$ span the eigen-space of the eigen-value E_-. Any arbitrary linear combination of $\hat{a}_1^{(\pm)}$ and $\hat{a}_2^{(\pm)}$ is then of course also an eigen-solution to the energy $E_\pm$. The Dirac equation (5.198) is therewith in principle solved. However, let us try to find out something more about the degenerate solutions $\hat{a}_{1,2}^{(+)}$ and $\hat{a}_{1,2}^{(-)}$, respectively. In the sense of our general discussion in Sect. 3.3 (Vol. 6) we did not yet succeed in *preparing* **pure states**. We should search for an observable, whose *measurement* removes the still existing degeneracy. On the other hand, the observable must commute with the Dirac operator $H_{\mathrm{D}}^{(0)}$, in order to build together with it a *complete set of compatible observables* (see Sect. 3.3.3, Vol. 6).

5.3.2 Dirac Spin Operator

We define as relativistic generalization of the Pauli spin operator $\boldsymbol{\sigma}$ in (5.164) the **Dirac spin operator**:

$$\widehat{\mathbf{S}} = \frac{\hbar}{2}\,\widehat{\boldsymbol{\sigma}}\;; \quad \widehat{\sigma} = \begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix}\;. \tag{5.215}$$

This is, at this stage, only a definition, which ascribes to this 4×4-matrix a certain name. We have discussed the physical property *spin* in the preceding section. That the operator $\widehat{\mathbf{S}}$ has something to do with this property, which would justify its name, is still to be shown.

We had agreed upon in Sect. 5.1 that a vector operator can always be interpreted as *angular momentum* when its components fulfill the fundamental commutation relations (5.14). For the components of $\widehat{\mathbf{S}}$,

$$\begin{aligned}
\widehat{S}_x &= \frac{\hbar}{2}\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}\;; \\
\widehat{S}_y &= \frac{\hbar}{2}\begin{pmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{pmatrix}\;; \\
\widehat{S}_z &= \frac{\hbar}{2}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}\;,
\end{aligned} \tag{5.216}$$

the validity of (5.14) can indeed be shown (Exercise 5.3.2), so that $\widehat{\mathbf{S}}$ actually represents an *angular momentum*. A special component of the Dirac spin operator is interesting for our purposes here, namely the component in the direction

of the momentum $\mathbf{p}$:

$$\widehat{S}_p = \frac{1}{p}\left(\widehat{\mathbf{S}}\cdot\mathbf{p}\right) = \frac{\hbar}{2p}\begin{pmatrix} p_z & p_- & 0 & 0 \\ p_+ & -p_z & 0 & 0 \\ 0 & 0 & p_z & p_- \\ 0 & 0 & p_+ & -p_z \end{pmatrix} . \tag{5.217}$$

$\widehat{S}_p$ is a Hermitian operator which commutes with the Dirac operator $H_{\mathrm{D}}^{(0)}$. One easily calculates:

$$H_{\mathrm{D}}^{(0)}\,\widehat{S}_p = \widehat{S}_p\,H_{\mathrm{D}}^{(0)} = \frac{\hbar}{2p}\begin{pmatrix} m_e\,c^2 p_z & m_e\,c^2 p_- & c\,\mathbf{p}^2 & 0 \\ m_e\,c^2 p_+ & -m_e\,c^2 p_z & 0 & c\,\mathbf{p}^2 \\ c\,\mathbf{p}^2 & 0 & -m_e\,c^2 p_z & -m_e\,c^2 p_- \\ 0 & c\,\mathbf{p}^2 & -m_e\,c^2 p_+ & m_e\,c^2 p_z \end{pmatrix} .$$

The other components of $\widehat{\mathbf{S}}$, in contrast, do **not** commute with $H_{\mathrm{D}}^{(0)}$.

But $\widehat{S}_p$ might be now the wanted observable, which together with $H_{\mathrm{D}}^{(0)}$ builds a *complete set of compatible observables*, and whose measurement uniquely classifies the energetically degenerate (*mixed*) states $\hat{a}_{1,2}^{(+)}$ and $\hat{a}_{1,2}^{(-)}$ in (5.211) and (5.212).

The eigen-spaces to the energy-eigen values E_+ and E_- are both two-dimensional. The operator $\widehat{S}_p$ is therefore represented in these spaces by 2×2-matrices, which turn out to be the same in both spaces: With the basis states (5.211) and (5.212) one finds:

$$\widehat{S}_p \equiv \left(\left\langle \hat{a}_i^{(\pm)} \,\middle|\, \widehat{S}_p \,\middle|\, \hat{a}_j^{(\pm)} \right\rangle\right)_{i,\,j\,=\,1,2} = \frac{\hbar}{2p}\begin{pmatrix} p_z & p_- \\ p_+ & -p_z \end{pmatrix} . \tag{5.218}$$

From the secular determinant

$$\det\left(\widehat{S}_p - \hbar\, m_\sigma\, \mathbb{1}_2\right) \stackrel{!}{=} 0$$

we get the eigen-values $\hbar\, m_\sigma$ of the Dirac spin operator $\widehat{S}_p$:

$$m_\uparrow = +\frac{1}{2}\,; \quad m_\downarrow = -\frac{1}{2}\,. \tag{5.219}$$

$\widehat{S}_p$ is thus an *angular momentum*-1/2-*operator*, exactly like the electron spin, which was empirically introduced in Sect. 5.2.4. The physical reason for the twofold degeneracy of the energy E_+ and E_-, respectively, is therefore to be found in the **two possibilities for the orientation of the Dirac spin relative to the momentum direction**. The corresponding eigen-states are of course special linear combinations of the *original* basis states $\hat{a}_{1,2}^{(+)}$ and $\hat{a}_{1,2}^{(-)}$.

One finds:

$$|+,\uparrow\rangle \equiv \hat{a}_{\uparrow}^{(+)} = \sqrt{\frac{p+p_z}{2p}}\,\hat{a}_1^{(+)} + \frac{p_+}{\sqrt{2p(p+p_z)}}\,\hat{a}_2^{(+)}$$
$$= \frac{d}{\sqrt{2p(p+p_z)}} \begin{pmatrix} p+p_z \\ p_+ \\ \frac{cp}{\widehat{E}}\,(p+p_z) \\ \frac{cp}{\widehat{E}}\,p_+ \end{pmatrix}, \qquad (5.220)$$

$$|+,\downarrow\rangle \equiv \hat{a}_{\downarrow}^{(+)} = -\sqrt{\frac{p-p_z}{2p}}\,\hat{a}_1^{(+)} + \frac{p_+}{\sqrt{2p(p-p_z)}}\,\hat{a}_2^{(+)}$$
$$= \frac{-d}{\sqrt{2p(p-p_z)}} \begin{pmatrix} p-p_z \\ -p_+ \\ -\frac{cp}{\widehat{E}}\,(p-p_z) \\ \frac{cp}{\widehat{E}}\,p_+ \end{pmatrix}, \qquad (5.221)$$

$$|-,\uparrow\rangle \equiv \hat{a}_{\uparrow}^{(-)} = \sqrt{\frac{p+p_z}{2p}}\,\hat{a}_1^{(-)} + \frac{p_+}{\sqrt{2p(p+p_z)}}\,\hat{a}_2^{(-)}$$
$$= \frac{d}{\sqrt{2p(p+p_z)}} \begin{pmatrix} -\frac{cp}{\widehat{E}}\,(p+p_z) \\ -\frac{cp}{\widehat{E}}\,p_+ \\ p+p_z \\ p_+ \end{pmatrix}, \qquad (5.222)$$

$$|-,\downarrow\rangle \equiv \hat{a}_{\downarrow}^{(-)} = -\sqrt{\frac{p-p_z}{2p}}\,\hat{a}_1^{(-)} + \frac{p_+}{\sqrt{2p(p-p_z)}}\,\hat{a}_2^{(-)}$$
$$= \frac{-d}{\sqrt{2p(p-p_z)}} \begin{pmatrix} \frac{cp}{\widehat{E}}\,(p-p_z) \\ -\frac{cp}{\widehat{E}}\,p_+ \\ p-p_z \\ -p_+ \end{pmatrix}. \qquad (5.223)$$

The common eigen-spinors of the operators $H_{\rm D}^{(0)}$ and $\widehat{S}_p$ are thus characterized by the four possible combinations of the eigen-values $E = \pm E_p$ and $m_\sigma = \pm 1/2$: $\eta = \pm; \quad \sigma = \uparrow, \downarrow$:

$$H_{\rm D}^{(0)}|\eta,\sigma\rangle = \eta\, E_p|\eta,\sigma\rangle\,,$$
$$\widehat{S}_p|\eta,\sigma\rangle = \hbar\, m_\sigma|\eta,\sigma\rangle\,. \qquad (5.224)$$

With the constant d from (5.214) the four eigen-states $|\eta,\sigma\rangle$ are each normalized to one!

The considerations of this section, with the complete solution of the Dirac equation (5.198) and the subsequent analysis of the degenerate eigen-states of

the Dirac operator $H_{\rm D}^{(0)}$ by the use of the *spin operator* $\widehat{S}$ (5.215), have brought about distinct leads to the physical property *spin*. In any case, the relativistic electron possesses besides the mass m_e and the charge $-e$ another particle property, namely the *angular momentum* 1/2. This property is intrinsic and is for all electrons the same. It holds for the square of the Dirac spin operator $\widehat{\mathbf{S}}^{\,2}$:

$$\begin{aligned}\widehat{\mathbf{S}}^{\,2} &= \frac{\hbar^2}{4}\left[\begin{pmatrix}\sigma_x^2 & 0\\ 0 & \sigma_x^2\end{pmatrix}+\begin{pmatrix}\sigma_y^2 & 0\\ 0 & \sigma_y^2\end{pmatrix}+\begin{pmatrix}\sigma_z^2 & 0\\ 0 & \sigma_z^2\end{pmatrix}\right]\\ &\overset{5.166}{=} \frac{3\hbar^2}{4}\begin{pmatrix}\mathbb{1}_2 & 0\\ 0 & \mathbb{1}_2\end{pmatrix} = \hbar^2\,\frac{1}{2}\left(\frac{1}{2}+1\right)\mathbb{1}_4\,,\end{aligned} \tag{5.225}$$

so that it likewise follows for all basis states (5.220)–(5.223):

$$\widehat{\mathbf{S}}^{\,2}|\eta,\sigma\rangle = \hbar^2 S(S+1)|\eta,\sigma\rangle\;;\quad S=\frac{1}{2}\,. \tag{5.226}$$

Any arbitrary, the Dirac-electron characterizing state in the space of solutions can be written as linear combination of the $|\eta,\sigma\rangle$, therewith also possessing the *property* $S = 1/2$.

We have gained the hints for this particle property, though, so far only by a mathematically abstract evaluation of the Dirac equation. A pictorial interpretation as *intrinsic angular momentum* actually did not suggest itself anywhere. The *physical equivalence* of the spin $\widehat{\mathbf{S}}$ with the orbital angular momentum $\mathbf{L}$, which is *familiar to us* because it has a classical analog, is revealed by the following consideration:

According to the discussion at the end of Sect. 5.1.3 (see (5.47)), we expect *non-relativistically*, that the orbital angular momentum $\mathbf{L}$ is a constant of motion in a central potential, and therefore commutes with the Hamilton operator. That should then be valid especially for the *free* particle. This expectation is not fulfilled, though, by the Dirac-operator $H_{\rm D}^{(0)}$. It rather holds, as we will explicitly check again as Exercise 5.3.3 (part 2.):

$$\left[\mathbf{L}, H_{\rm D}^{(0)}\right]_- = i\,\hbar\,c\,(\widehat{\boldsymbol{\alpha}}\times\mathbf{p})\;. \tag{5.227}$$

This *non-commutability* remains unchanged even in the *non-relativistic limit* $v \ll c$. The orbital angular momentum $\mathbf{L}$ is obviously not at all the complete angular momentum of the electron. Let us therefore consider, in addition, the Dirac spin operator $\widehat{\mathbf{S}}$. For the calculation of the commutator of $\widehat{\mathbf{S}}$ with $H_{\rm D}^{(0)}$, done as Exercise 5.3.3 (part 1.), we exploit that all components of $\widehat{\mathbf{S}}$ commute with those of the momentum operator $\mathbf{p}$:

$$\left[\widehat{\mathbf{S}}, H_{\rm D}^{(0)}\right]_- = -i\,\hbar\,c\;(\widehat{\boldsymbol{\alpha}}\times\mathbf{p})\,. \tag{5.228}$$

We recognize that neither $\widehat{\mathbf{S}}$ nor $\mathbf{L}$ are conserved quantities, while the sum of both of them is conserved:

$$\left[\mathbf{L}+\widehat{\mathbf{S}},\, H_{\rm D}^{(0)}\right]_- = 0\,. \tag{5.229}$$

This suggests the following interpretation:

$$\begin{aligned} \widehat{\mathbf{S}} &\iff \text{spin operator with the character of an angular momentum,} \\ \mathbf{J} = \mathbf{L} + \widehat{\mathbf{S}} &\iff \text{total angular momentum operator of the electron.} \end{aligned}$$

There still remains, however, a problem: The empirically motivated theory of the electron spin in Sect. 5.2, which finally led to the *Pauli equation* (5.190), was a *two-component theory*. The Dirac spin operator $\widehat{\mathbf{S}}$ as well as $H_{\mathrm{D}}^{(0)}$ act, however, on four-component spinors. That does not yet really fit! On the other hand, we have established in this section a *fully relativistic* theory, while all our previous considerations never left the framework of the *non-relativistic* Quantum Mechanics. It thus suggests itself to analyze the statements of the Dirac theory tentatively for the *non-relativistic limit* $v \ll c$.

5.3.3 Electron Spin (Pauli-Theory)

In order to demonstrate that a magnetic moment is also associated with the quantity *spin*, introduced in the last section, we use for the following considerations, directly the Dirac operator (5.204) for the electron in the electromagnetic field. For this purpose, we restrict ourselves from now on to the subspace of solutions with positive energies (electrons!).

We now decompose the general four-component Dirac spinor into two *two-component vectors*:

$$|\psi\rangle = \begin{pmatrix} \psi_1 \\ \vdots \\ \psi_4 \end{pmatrix} = \begin{pmatrix} \widehat{\psi} \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ \chi \end{pmatrix} , \tag{5.230}$$

with

$$|\widehat{\psi}\rangle = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}; \quad |\chi\rangle = \begin{pmatrix} \psi_3 \\ \psi_4 \end{pmatrix} . \tag{5.231}$$

This is, at first, only a slightly changed notation, which, however, will turn out to be convenient under certain conditions. This is for instance the case when the components of $|\widehat{\psi}\rangle$ and $|\chi\rangle$ are of different orders of magnitude. We are, in the last analysis, really interested in the non-relativistic Quantum Mechanics, i.e., we are interested in the corresponding *non-relativistic limiting case* $v \ll c$ of the Dirac theory. In this limit, the energy-eigen value E_p of the free electron (5.210) differs only slightly from its **rest energy** $m_e\, c^2$ ((2.55), Vol. 4). The difference

$$T = E_p - m_e\, c^2 = m_e\, c^2 \left(\sqrt{1 + \frac{\mathbf{p}^2}{m_e^2 c^2}} - 1 \right) = \frac{\mathbf{p}^2}{2m_e} \left[1 + \mathcal{O}\left(\frac{v^2}{c^2} \right) \right] \tag{5.232}$$

is then just the well-known expression of the kinetic energy of the electron. Let us estimate therewith the relative orders of magnitude of the two components

$|\widehat{\psi}\rangle$ and $|\chi\rangle$. Since $|\psi\rangle$ can be written as linear combination of the basis states (5.211) with coefficients of the order one, we can perform the intended estimation also directly with the components in (5.211):

$$\begin{aligned}\left|\frac{\hat{a}_{13}^{(+)}}{\hat{a}_{11}^{(+)}}\right|^2 &= \left|\frac{\hat{a}_{24}^{(+)}}{\hat{a}_{22}^{(+)}}\right|^2 = \frac{c^2 p_z^2}{(E_p + m_e\, c^2)^2} \\ &\leq \frac{c^2 p^2}{(E_p + m_e\, c^2)^2} = \frac{E_p - m_e\, c^2}{E_p + m_e\, c^2} = \frac{T}{T + 2m_e\, c^2} = \mathcal{O}\left[\left(\frac{v}{c}\right)^2\right] .\end{aligned}$$

Analogously, one finds:

$$\left|\frac{\hat{a}_{14}^{(+)}}{\hat{a}_{11}^{(+)}}\right|^2 = \left|\frac{\hat{a}_{23}^{(+)}}{\hat{a}_{22}^{(+)}}\right|^2 = \frac{c^2(p_x^2 + p_y^2)}{(E_p + m_e\, c^2)^2} = \mathcal{O}\left[\left(\frac{v}{c}\right)^2\right] .$$

The components $\hat{a}_{13}^{(+)}$, $\hat{a}_{14}^{(+)}$ and $\hat{a}_{23}^{(+)}$, $\hat{a}_{24}^{(+)}$ thus become in the *non-relativistic limit* negligibly small compared to $\hat{a}_{11}^{(+)}$ and $\hat{a}_{22}^{(+)}$. That transfers immediately to our general spinor (5.230). The magnitudes $|\psi_{3,4}|$ will be very much smaller than $|\psi_{1,2}|$. This fact, which we have estimated here for a *free* electron, will not change substantially even when we switch on a *'normal'* electromagnetic field. Ultimately, this is the motive for the decomposition (5.230), because therewith the Dirac-theory becomes in the *non-relativistic limit* equivalent to a *two-component theory*, the so-called *Pauli-theory*, which we now want to deal with.

We apply the Dirac operator H_D from (5.204) to the four-component spinor (5.230). If the actions of the Dirac matrices $\widehat{\boldsymbol{\alpha}}$ and $\widehat{\beta}$ are, according to (5.205), already made, then it remains as an eigen-value equation:

$$H_\mathrm{D} \begin{pmatrix}\widehat{\psi}\\ \chi\end{pmatrix} = c(\mathbf{p} + e\,\mathbf{A}) \cdot \begin{pmatrix}\boldsymbol{\sigma} & \chi\\ \boldsymbol{\sigma} & \widehat{\psi}\end{pmatrix} + m_e\, c^2 \begin{pmatrix}\widehat{\psi}\\ -\chi\end{pmatrix} - e\,\varphi \begin{pmatrix}\widehat{\psi}\\ \chi\end{pmatrix} \stackrel{!}{=} E \begin{pmatrix}\widehat{\psi}\\ \chi\end{pmatrix} .$$

This leads to the following system of equations:

$$\left(E - m_e\, c^2 + e\,\varphi\right)|\widehat{\psi}\rangle = c(\mathbf{p} + e\,\mathbf{A}) \cdot \boldsymbol{\sigma}|\chi\rangle , \tag{5.233}$$

$$\left(E + m_e\, c^2 + e\,\varphi\right)|\chi\rangle = c(\mathbf{p} + e\,\mathbf{A}) \cdot \boldsymbol{\sigma}|\widehat{\psi}\rangle . \tag{5.234}$$

So far everything is exact. The last equation demonstrates once more the different orders of magnitude:

$$|\chi\rangle = \left(E + m_e\, c^2 + e\,\varphi\right)^{-1} c(\mathbf{p} + e\,\mathbf{A}) \cdot \boldsymbol{\sigma}|\widehat{\psi}\rangle . \tag{5.235}$$

The eigen-value E of the Dirac-electron in a *normal* electromagnetic field is of course, like that of the *free* electron E_p, also of the order of magnitude $m_e\, c^2$. One can therefore estimate:

$$E \approx m_e\, c^2 + e\,\varphi \approx m_e\, c^2 ; \qquad E + m_e\, c^2 \approx 2m_e\, c^2 .$$

The still exact equation (5.235) can be therewith simplified:

$$|\chi\rangle \approx \frac{1}{2m_e\,c}\,(\mathbf{p}+e\,\mathbf{A})\cdot\boldsymbol{\sigma}|\widehat{\psi}\rangle + \mathcal{O}\left(\frac{v^2}{c^2}\right)\,. \tag{5.236}$$

Because of $|\chi\rangle \approx \mathcal{O}\,(v/c)\,|\widehat{\psi}\rangle$ the notations *small component* for $|\chi\rangle$ and *large component* for $|\widehat{\psi}\rangle$ have established themselves in the literature.

For the **Pauli-theory** as the *non-relativistic* limiting case of the Dirac-theory, the estimation (5.236) for the *small component* suffices. Inserting this expression into (5.233) we obtain an eigen-value equation for the *large component* $|\widehat{\psi}\rangle$:

$$\begin{aligned} H_p|\widehat{\psi}\rangle &= (E-m_e\,c^2)|\widehat{\psi}\rangle\,, \\ H_p &= \frac{1}{2m_e}\,[(\mathbf{p}+e\,\mathbf{A})\cdot\boldsymbol{\sigma}]\,[(\mathbf{p}+e\,\mathbf{A})\cdot\boldsymbol{\sigma}] - e\,\varphi\,\mathbb{1}_2\,. \end{aligned} \tag{5.237}$$

We call H_p the *Pauli-Hamilton operator*. Since the Pauli spin matrices commute with $\mathbf{p}$ and $\mathbf{A}$ we can apply for a further reformulation the relation, which we proved in part 2. of Exercise 5.2.2,

$$(\boldsymbol{\sigma}\cdot\mathbf{a})\,(\boldsymbol{\sigma}\cdot\mathbf{b}) = \mathbf{a}\cdot\mathbf{b}\,\mathbb{1}_2 + i\,\boldsymbol{\sigma}\cdot(\mathbf{a}\times\mathbf{b})\,. \tag{5.238}$$

Thereby we still need:

$$\begin{aligned} (\mathbf{p}+e\,\mathbf{A})\times(\mathbf{p}+e\,\mathbf{A}) &= e(\mathbf{p}\times\mathbf{A}+\mathbf{A}\times\mathbf{p}) \\ &= e\left(\frac{\hbar}{i}\,\mathrm{curl}\mathbf{A} - \mathbf{A}\times\mathbf{p} + \mathbf{A}\times\mathbf{p}\right) = e\,\frac{\hbar}{i}\,\mathbf{B}\,. \end{aligned}$$

$\mathbf{B} = \mathrm{curl}\mathbf{A}$ is as usual the magnetic induction. The Pauli-Hamilton operator, which finally represents a 2×2-matrix, has then the form:

$$H_p = \left[\frac{1}{2m_e}\,(\mathbf{p}+e\,\mathbf{A})^2 - e\,\varphi\right]\,\mathbb{1}_2 + \frac{e\,\hbar}{2m_e}\,\boldsymbol{\sigma}\cdot\mathbf{B}\,. \tag{5.239}$$

That is the Hamilton operator of a particle of mass m_e, charge $q=-e$ and the **magnetic moment**

$$\boldsymbol{\mu}_{\mathrm{S}} = -2\,\frac{\mu_B}{\hbar}\,\mathbf{S} = -\frac{e\,\hbar}{2m_e}\,\boldsymbol{\sigma} = -\mu_B\boldsymbol{\sigma}\,. \tag{5.240}$$

We recognize that H_p agrees exactly with the Hamilton operator (5.191) from the Pauli equation, which was *empirically justified* in Sect. 5.2. With the angular momentum *spin*, derived from the Dirac-theory, there is an associated magnetic moment $\boldsymbol{\mu}_{\mathrm{S}}$, which has exactly the structure (5.183) required from experiment. This perfect link of the *non-relativistic limit* of the Dirac-theory with the empirical theory of Sect. 5.2.4, which was *forced by experimental facts*, now proves

without any additional plausibility-assumption the following statements:

1. The **spin** $\mathbf{S} = (\hbar/2)\boldsymbol{\sigma}$ exists as a fundamental **relativistic** property of the electron. It is an angular momentum with the eigen-values $\pm\hbar/2$ for the z-component.
2. A magnetic moment $\boldsymbol{\mu}_{\mathrm{S}} = \mu_{\mathrm{S}}\,\mathbf{S}$ is associated with the spin, which, in the Hamilton operator couples **linearly** to the external magnetic field $\mathbf{B}$ (5.239).
3. The **Landé factor** g of the electron, $\mu_{\mathrm{S}} = -g(\mu_B/\hbar)$, is exactly equal to two.

Two fundamental demands of the experiment are therewith theoretically explained without any additional assumption.

5.3.4 Spin-Orbit Interaction

We had already conjectured in Sect. 5.2 that the Hamilton operator, derived in (5.188), which agrees for $V(\mathbf{r}) = -e\,\varphi(\mathbf{r})$ with the Pauli-Hamilton operator H_p from (5.239), is in this form perhaps not yet complete. If, in the last analysis, orbital angular momentum $\mathbf{L}$ and spin $\mathbf{S}$ are congenial angular momenta, then a mutual impact on each other should not be completely excluded. Such an interference is indeed the case. One speaks of a **spin-orbit interaction**, which is, however, a purely relativistic effect, and therefore needs for its investigation the Dirac-theory of the last sections.

One realizes already the essential with a simple *classical* estimation, which we will present here before the exact solution. The electron moves in the rest system of the positively charged nucleus, which creates an electromagnetic field:

$$\mathbf{E} = -\nabla\,\varphi(\mathbf{r})\;.$$

Since the electron moves **relatively** to the nucleus, it *sees* an electromagnetic field $\mathbf{E}'$, $\mathbf{B}'$, for which the relativistic Electrodynamics ((2.142), (2.143), Vol. 4) provides the expressions:

$$\begin{aligned}
\mathbf{B}' &= \gamma\left[\mathbf{B} - \frac{1}{c}(\beta\times\mathbf{E})\right] - \frac{\gamma^2}{\gamma+1}\,\beta(\beta\cdot\mathbf{B}) \\
&\qquad\qquad\qquad\qquad\qquad\qquad ;\quad \beta = \frac{\mathbf{v}}{c} \\
\mathbf{E}' &= \gamma\,[\mathbf{E} + c(\beta\times\mathbf{B})] - \frac{\gamma^2}{\gamma+1}\,\beta(\beta\cdot\mathbf{E})\;.
\end{aligned}$$

Thereby, $\mathbf{E}$ and $\mathbf{B} = 0$ are the fields in the rest system of the nucleus, $\mathbf{E}'$ and $\mathbf{B}'$ those in the rest system of the electron, in which the positively charged nucleus *circulates* around the electron. In the here interesting *non-relativistic limit* $v \ll c$, $\gamma \approx 1$. The relatively to the electron moving, positively charged nucleus thus generates in the rest system of the electron a magnetic induction,

$$\mathbf{B}' \approx -\frac{1}{c^2}\,(\mathbf{v}\times\mathbf{E})\;,$$

with which the electronic spin moment interacts. As derived in the last section, in connection with (5.239), this interaction appears in the Hamilton operator of the electron as an additional additive term:

$$H_{\mathrm{SO}}^{\mathrm{cl}} = 2\,\frac{\mu_B}{\hbar}\,\mathbf{S}\cdot\mathbf{B}' = \frac{2\mu_B}{\hbar\,c^2}\,(\mathbf{E}\times\mathbf{v})\cdot\mathbf{S}\;.$$

If we still assume that the potential of the nucleus is a central potential ($\varphi(\mathbf{r}) = \varphi(r)$), for which

$$\mathbf{E}(\mathbf{r}) = -\frac{d\varphi}{dr}\,\mathbf{e}_r = -\frac{1}{r}\,\frac{d\varphi}{dr}\,\mathbf{r}\;,$$

then we recognize in the vector product the orbital angular momentum $\mathbf{L}$:

$$H_{\mathrm{SO}}^{\mathrm{cl}} = -\frac{e}{m_e^2\,c^2}\left(\frac{1}{r}\,\frac{d\varphi}{dr}\right)(\mathbf{L}\cdot\mathbf{S})\;. \tag{5.241}$$

This additional term expresses in direct manner the coupling of the electron spin to the orbital motion in the field of the nucleus and therewith to the orbital angular momentum. Except for a factor 2, (5.241) will even turn out to be exact. We note in passing that this discrepancy can be traced back to the fact that the rest system of the electron is not an inertial system. The above transformation formulas $(\mathbf{E},\mathbf{B}) \to (\mathbf{E}',\mathbf{B}')$, however, imply inertial systems.

For the rigorous derivation of the spin-orbit interaction we use again the **non-relativistic limiting case of the Dirac theory**, where we, however, have to develop the approximation one step further than in the preceding section where we established the spin moment. There we had neglected already terms of the order of magnitude $\mathcal{O}\left(v^2/c^2\right)$, in order to eliminate the *small component* $|\chi\rangle$ and to come therewith from the original *four-component theory* to an effective *two-component theory*. When neglecting $|\chi\rangle$, i.e., at the transition from the general four-component state $|\psi\rangle$ to the *large component* $|\widehat{\psi}\rangle$, we did not care about, whether the normalization, important for the probability interpretation, is conserved. We want to investigate this point now a bit more precisely:

$$|\psi\rangle = \begin{pmatrix}\widehat{\psi}\\ \chi\end{pmatrix} \implies \langle\psi|\psi\rangle = \langle\widehat{\psi}|\widehat{\psi}\rangle + \langle\chi|\chi\rangle\;.$$

We will take care of a conserved normalization during the transition to the *two-component theory* by the following ansatz:

$$|\widehat{\psi}\rangle = \alpha|\eta\rangle \tag{5.242}$$

The quantity α will thereby be an operator. But we presume, what later has to be explicitly checked, that it is an Hermitian operator with an existing inverse α^{-1}:

$$\langle\psi|\psi\rangle \stackrel{!}{=} \langle\eta|\eta\rangle = \langle\widehat{\psi}|\widehat{\psi}\rangle + \langle\chi|\chi\rangle\;. \tag{5.243}$$

$|\eta\rangle$ is the *new* state of our *non-relativistic two-component theory*, which replaces $|\widehat{\psi}\rangle$ and possesses the correct normalization.

Let us discuss the same situation as that of the preceding *classical* consideration, which led to (5.241). In this sense, the electron moves in an electrostatic potential $\varphi(\mathbf{r})$, which may be generated by a positively charged nucleus. An external magnetic field $\mathbf{B}$ is irrelevant for the spin-orbit interaction, which we want to derive. It is therefore in this section not taken into consideration. Then we have, at first, according to (5.235) with $\mathbf{A} \equiv 0$, for the *small component* $|\chi\rangle$:

$$|\chi\rangle = \frac{c}{E + m_e\, c^2 + e\,\varphi}\,(\mathbf{p}\cdot\boldsymbol{\sigma})|\widehat{\psi}\rangle\ . \tag{5.244}$$

The energy, which is small in the *non-relativistic region*, is, according to (5.232), not E but

$$T = E - m_e\, c^2\ . \tag{5.245}$$

We substitute correspondingly and then expand (5.244) in powers of v/c. We apply thereby the useful series expansion:

$$\begin{aligned}(1+x)^m \;&=\; 1 + m\,x \,+\, \frac{m(m-1)}{2!}\,x^2 + \ldots \\ &\qquad \ldots + \frac{m(m-1)\cdots(m-n+1)}{n!}\,x^n + \ldots \\ &\qquad (m \text{ integer or rational})\ ,\end{aligned} \tag{5.246}$$

which for $x \ll 1$ can be terminated, according to the required accuracy, already after a few terms.

$$\begin{aligned}|\chi\rangle \;&=\; \frac{1}{2m_e\, c}\left(1 + \frac{T + e\,\varphi}{2m_e\, c^2}\right)^{-1}(\mathbf{p}\cdot\boldsymbol{\sigma})|\widehat{\psi}\rangle \\ &=\; \frac{1}{2m_e\, c}\left[1 - \frac{T + e\,\varphi}{2m_e\, c^2} + \mathcal{O}\left(\frac{v^4}{c^4}\right)\right](\mathbf{p}\cdot\boldsymbol{\sigma})|\widehat{\psi}\rangle\ .\end{aligned} \tag{5.247}$$

The expansion is therefore done one step further than in (5.236). However, the decoupling of *large component* and *small component* is no longer so simple. By insertion of (5.247) into (5.243) we fulfill the normalization condition up to the terms of the order of magnitude $\mathcal{O}\left(v^2/c^2\right)$:

$$\begin{aligned}\langle\psi|\psi\rangle \overset{!}{=} \langle\eta|\eta\rangle \;&=\; \langle\widehat{\psi}|\alpha^{-2}|\widehat{\psi}\rangle = \langle\widehat{\psi}|\widehat{\psi}\rangle + \langle\chi|\chi\rangle \\ &\overset{(5.247)}{=}\; \langle\widehat{\psi}|\left[1 + \frac{1}{4m_e c^2}(\mathbf{p}\cdot\sigma)^2 + \mathcal{O}\left(\frac{v^4}{c^4}\right)\right]|\widehat{\psi}\rangle \\ \curvearrowright\ \alpha \;&\approx\; 1 - \frac{1}{8m_e c^2}(\mathbf{p}\cdot\sigma)^2\ .\end{aligned}$$

According to the vector formula (5.238), $(\mathbf{p}\cdot\boldsymbol{\sigma})^2$ is equal to $p^2\mathbb{1}_2$. The normalization condition is then obviously satisfied, in correspondence to our ansatz (5.242), by

$$|\widehat{\psi}\rangle = \left(1 - \frac{\mathbf{p}^2}{8m_e^2\,c^2}\right)|\eta\rangle\ . \tag{5.248}$$

By insertion into (5.247), the *small component* $|\chi\rangle$, too, can be expressed by the *new* state $|\eta\rangle$:

$$|\chi\rangle = \frac{1}{2m_e\,c}\left[(\mathbf{p}\cdot\boldsymbol{\sigma})\left(1 - \frac{\mathbf{p}^2}{8m_e^2\,c^2}\right) - \frac{T + e\,\varphi}{2m_e\,c^2}\,(\mathbf{p}\cdot\boldsymbol{\sigma}) + \mathcal{O}\left(\frac{v^4}{c^4}\right)\right]|\eta\rangle\ . \tag{5.249}$$

One should regard the non-commutability of $\varphi(\mathbf{r})$ and $\mathbf{p}$ in the third summand. This and also the second summand are new compared to the estimation (5.236) in the last section. They are, compared to the first term in the square bracket, smaller by a factor of the order v^2/c^2 and have therefore been irrelevant for the considerations in Sect. 5.3.3.

We now insert the expressions (5.248) and (5.249) into the exact relation (5.233):

$$\begin{aligned}(T + e\,\varphi)\left(1 - \frac{\mathbf{p}^2}{8m_e^2\,c^2}\right)|\eta\rangle \approx \\ \approx \frac{1}{2m_e}\left[\mathbf{p}^2\left(1 - \frac{\mathbf{p}^2}{8m_e^2\,c^2}\right) - (\mathbf{p}\cdot\boldsymbol{\sigma})\,\frac{T + e\,\varphi}{2m_e\,c^2}\,(\mathbf{p}\cdot\boldsymbol{\sigma})\right]|\eta\rangle\ .\end{aligned} \tag{5.250}$$

Because of the non-commutability of $\varphi(\mathbf{r})$ and $\mathbf{p}$,

$$[\mathbf{p}, \varphi(\mathbf{r})]_- = \frac{\hbar}{i}\,\nabla\,\varphi(\mathbf{r})\ ,$$

the last term on the right-hand side must be handled with special care:

$$\begin{aligned}(\mathbf{p}\cdot\boldsymbol{\sigma})\,(T + e\,\varphi)\,(\mathbf{p}\cdot\boldsymbol{\sigma}) \;=\; & \frac{1}{2}\left[\mathbf{p}^2(T + e\,\varphi) + (T + e\,\varphi)\mathbf{p}^2\right] \\ & + \frac{1}{2}\,\frac{\hbar}{i}\,e\left[(\nabla\varphi\cdot\boldsymbol{\sigma})\,(\mathbf{p}\cdot\boldsymbol{\sigma}) - (\mathbf{p}\cdot\boldsymbol{\sigma})\,(\nabla\varphi\cdot\boldsymbol{\sigma})\right]\ .\end{aligned}$$

We have here $(T + e\,\varphi)$ *symmetrically* commuted with $(\mathbf{p}\cdot\boldsymbol{\sigma})$, once to the left, once to the right, and then added the two equivalent results. The factor $1/2$ guarantees the equality. For a further evaluation, we use once more the vector identity (5.238):

$$\begin{aligned}&(\nabla\varphi\cdot\boldsymbol{\sigma})\,(\mathbf{p}\cdot\boldsymbol{\sigma}) - (\mathbf{p}\cdot\boldsymbol{\sigma})\,(\nabla\varphi\cdot\boldsymbol{\sigma}) \\ &\quad = (\nabla\varphi\cdot\mathbf{p})\,\mathbb{1}_2 - (\mathbf{p}\cdot\nabla\varphi)\,\mathbb{1}_2 + i\,\boldsymbol{\sigma}\cdot(\nabla\varphi\times\mathbf{p}) - i\,\boldsymbol{\sigma}\cdot(\mathbf{p}\times\nabla\varphi) \\ &\quad = \sum_{i\,=\,1}^{3}\left[\frac{\partial\varphi}{\partial x_i}, p_i\right]_-\mathbb{1}_2 + 2i\,\boldsymbol{\sigma}\cdot(\nabla\varphi\times\mathbf{p}) \\ &\quad = -\frac{\hbar}{i}\,\Delta\varphi\,\mathbb{1}_2 + 2i\,\boldsymbol{\sigma}\cdot(\nabla\varphi\times\mathbf{p})\ .\end{aligned}$$

Convince yourself (Exercise 5.3.6) that indeed $(\nabla\varphi \times \mathbf{p}) = -(\mathbf{p} \times \nabla\varphi)$, which we have exploited for the transition from the second to the third line. With these reformulations we eventually get from (5.250):

$$\left(1 + \frac{\mathbf{p}^2}{8m_e^2\,c^2}\right)(T + e\,\varphi)|\eta\rangle \approx \frac{\mathbf{p}^2}{2m_e}\left(1 - \frac{\mathbf{p}^2}{8m_e^2\,c^2}\right)|\eta\rangle + \left[\frac{e\,\hbar^2}{8m_e^2\,c^2}\Delta\varphi - \frac{e\,\hbar}{4m_e^2\,c^2}(\nabla\varphi \times \mathbf{p}) \cdot \boldsymbol{\sigma}\right]|\eta\rangle \ .$$

We multiply this equation by $\left(1 + (p^2/8m_e^2\,c^2)\right)^{-1}$, expand it according to formula (5.246), and neglect terms of the order of magnitude v^4/c^4. Therewith we have then formally constructed, similar to as in the last section, a *two-component theory* as *non-relativistic limiting case* of the Dirac-theory, and that, too, in form of the following eigen-value equation:

$$H_{\rm nr}|\eta\rangle = E|\eta\rangle \ . \tag{5.251}$$

The *non-relativistic* Dirac operator $H_{\rm nr}$ is composed of several characteristic terms:

$$H_{\rm nr} = m_e\,c^2 + \frac{\mathbf{p}^2}{2m_e} - \frac{\mathbf{p}^4}{8m_e^3\,c^2} - e\,\varphi(\mathbf{r}) + V_{\rm D} + H_{\rm SO} \ . \tag{5.252}$$

The first three terms are the rest energy of the electron, the *normal* kinetic energy, and the first relativistic correction to the kinetic energy. These are nothing else but the three leading terms of the expansion of the relativistic kinetic energy $(m_e^2\,c^4 + c^2\,p^2)^{1/2}$ in powers of v/c. Their appearance in $H_{\rm nr}$ is therefore not astonishing. The same holds for the potential energy $(-e\,\varphi(\mathbf{r}))$ of the electron in the electrostatic field of the nucleus. On the other hand, the operator $V_{\rm D}$ is intuitively very difficult to explain. This so-called *Darwin term*,

$$V_{\rm D} = \frac{e\,\hbar^2}{8m_e^2\,c^2}\,\Delta\varphi \ , \tag{5.253}$$

can be interpreted as the first relativistic correction to the potential energy of the electron.

As to our original intention, the last term in (5.252) is the most important one,

$$H_{\rm SO} = -\frac{e\,\hbar}{4m_e^2\,c^2}(\nabla\varphi \times \mathbf{p}) \cdot \boldsymbol{\sigma} \ , \tag{5.254}$$

because it represents a *spin-orbit interaction*. If we use in (5.254) the spin operator $\mathbf{S} = (\hbar/2)\,\boldsymbol{\sigma}$, and if we assume, as for our classical estimation in (5.241), a spherical-symmetric potential of the nucleus,

$$\nabla\varphi = \frac{1}{r}\,\frac{d\varphi}{dr}\,\mathbf{r} \ ,$$

then we get:

$$H_{\mathrm{SO}} = \lambda(\mathbf{L}\cdot\mathbf{S})\,; \quad \lambda = -\frac{e}{2m_e^2\,c^2}\left(\frac{1}{r}\,\frac{d\varphi}{dr}\right)\,. \tag{5.255}$$

We see that our classical result $H_{\mathrm{SO}}^{\mathrm{kl}}$ (5.241) was indeed already correct except for a factor 1/2. As a plausible approximation one may write $\varphi(r) \sim 1/r$, and therewith $\lambda \sim 1/r^3$. The spin-orbit interaction thus decreases with the third power of the distance from the nucleus.

The operator H_{SO} brings about that, even in the absence of an external magnetic field, orbital angular momentum $\mathbf{L}$ and spin $\mathbf{S}$ do no longer commute with the Hamilton operator of the electron, if this is subject to a nuclear potential $\varphi(\mathbf{r}) \neq 0$. It namely holds (Exercise 5.3.5):

$$[\mathbf{L}\cdot\mathbf{S},\mathbf{L}]_- = i\,\hbar(\mathbf{L}\times\mathbf{S}) = -\,[\mathbf{L}\cdot\mathbf{S},\mathbf{S}]_-\ . \tag{5.256}$$

The total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$, however, which we introduced at the end of Sect. 5.3.2, commutes obviously with H_{SO},

$$[H_{\mathrm{SO}},\mathbf{J}]_- = 0\,, \tag{5.257}$$

and, consequently, with the total Hamilton operator (*integral of motion*). Furthermore, we prove in Exercise 5.3.5 the following commutation relations:

$$[H_{\mathrm{SO}},\mathbf{L}^2]_- = [H_{\mathrm{SO}},\mathbf{S}^2]_- = [H_{\mathrm{SO}},\mathbf{J}^2]_- = 0\,. \tag{5.258}$$

Hence, there must exist common eigen-states,

$$|x;j\,l\,S\,m_j\rangle\,,$$

for the operators H_{D}, $\mathbf{J}^2$, $\mathbf{L}^2$, $\mathbf{S}^2$ and J_z, which we can specify by the angular-momentum-quantum numbers j, l, S and m_j. m_j is here the *magnetic quantum number* of the total angular momentum ($J_z|x;j\,l\,S\,m_j\rangle = \hbar\,m_j|x;j\,l\,S\,m_j\rangle$; $-j \leq m_j \leq +j$). In x we gather all the quantum numbers, which have nothing to do with angular momenta, but are necessary via H_{D} for the identification of the states. The explicit appearance of the *total angular momentum* $\mathbf{J}$ in the *maximal set of compatible observables* for the preparation of the pure states of the atomic electron raise the question, important also in other connections, what we know about the correct *addition of angular momenta*, which we will therefore deal with extensively in the following Sect. 5.4.

The probably most important consequence of the spin-orbit interaction leads to a

fine structure of the energy levels

which are available for the electrons in atoms (molecules). We anticipate here the detailed considerations in Chap. 6, by which we want to give reasons for the classically incomprehensible stationary electron states in the atom. We will be able to show that, without spin-orbit interaction and without external magnetic

field, the electrons in the atom will take *discrete* energies E_{xl}. These will then get after the *switching on* of the spin-orbit interaction $H_{\rm SO}$, because of

$$\mathbf{L}\cdot\mathbf{S} = \frac{1}{2}\left(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2\right) ,$$

a *fine structure*, i.e., they split once more:

$$\begin{aligned} E_{xljs} &= \langle x; j\, l\, S\, m_j | H | x; j\, l\, S\, m_j\rangle \\ &= E_{xl} + \langle x; j\, l\, S\, m_j | H_{\rm SB} | x; j\, l\, S\, m_j\rangle \\ &= E_{xl} + \frac{1}{2}\lambda\hbar^2\,\left[\, j(j+1) - l(l+1) - S(S+1)\right] . \end{aligned} \tag{5.259}$$

Because of the factor $1/c^2$ in λ the splitting is very small. It is, however, with the today spectroscopic means definitely observable!

We want to finish our considerations on the relativistic theory of the electron with a **final remark**. In lowest order v/c Dirac-theory and Pauli two-component theory are equivalent. The transition from the *four-* to the *two-component theory* succeeds relatively simply by a decoupling of the *large* and the *small component* of the Dirac spinor. In contrast, the justification of the spin-orbit interaction, presented in this section, proves to be substantially more involved, since it is a *relativistic effect* of higher order. Nevertheless, one can of course derive by a systematic development of the exact equations (5.233) and (5.234) the required *relativistic corrections*. An essentially more elegant procedure represents the so-called *Foldy-Wouthuysen transformation* (L.L. Foldy, S.A. Wouthuysen, Phys. Rev. **78**, 29(1950)). It is about a rather subtle unitary transformation of the operators and spinors in the Dirac-theory, which takes care in each order of v/c for a complete decoupling of the *large* and the *small component*, so that one can simply disregard the latter reaching therewith directly a *two-component theory*. A detailed investigation of this ansatz, though, exceeds the limit of this ground course.

5.3.5 Exercises

Exercise 5.3.1
Show that the Dirac matrices (5.205)

$$\widehat{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix} \; ; \quad \widehat{\beta} = \begin{pmatrix} \mathbb{1}_2 & 0 \\ 0 & -\mathbb{1}_2 \end{pmatrix}$$

fulfill the conditions (5.197):

$$[\widehat{\alpha}_i, \widehat{\alpha}_j]_+ = 2\delta_{ij}\,\mathbb{1}_4 \; ; \quad [\widehat{\alpha}_i, \widehat{\beta}\,]_+ = 0 \; ; \quad \widehat{\beta}^2 = \mathbb{1}_4 \; .$$

Exercise 5.3.2
Show that the Cartesian components of the Dirac spin operator (5.215),

$$\widehat{\mathbf{S}} = \frac{\hbar}{2}\begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix} \; ; \quad (\boldsymbol{\sigma}: \text{ Pauli spin operator}) ,$$

fulfill the fundamental commutation relations (5.14):

$$[\widehat{S}_x, \widehat{S}_y]_- = i\,\hbar\,\widehat{S}_z, \ldots \text{ and cyclic} .$$

Exercise 5.3.3
Calculate for a *free Dirac electron* the commutators

1. $[\widehat{\mathbf{S}}, H_{\mathrm{D}}^{(0)}]_-$;

2. $[\mathbf{L}, H_{\mathrm{D}}^{(0)}]$,

where $\widehat{\mathbf{S}}$ is the Dirac spin operator and $\mathbf{L}$ the operator of the orbital angular momentum.

Exercise 5.3.4
Calculate for a (relativistic) electron in an external electromagnetic field (vector potential $\mathbf{A}(\mathbf{r}, t)$, scalar potential $\varphi(\mathbf{r}, t)$) the equations of motion of the observables *position* $\mathbf{r}$ and *mechanical momentum* $\mathbf{p}_m = \mathbf{p} + e\,\mathbf{A}$ (Heisenberg representation!). Show that the time-dependent operators fulfill the classical Lorentz-force law

$$\frac{d}{dt}\,\mathbf{p}_m = -e[\mathbf{E} + \dot{\mathbf{r}} \times \mathbf{B}] .$$

(Ehrenfest theorem!)

Exercise 5.3.5
Calculate for the operator of the spin-orbit interaction

$$H_{\mathrm{SO}} = \lambda(\mathbf{L} \cdot \mathbf{S})$$

the following commutators:

1. $[H_{\mathrm{SO}}, \mathbf{L}]_-$,

2. $[H_{\mathrm{SO}}, \mathbf{S}]_-$,

3. $[H_{\mathrm{SO}}, \mathbf{L}^2]_-$,

4. $[H_{\mathrm{SO}}, \mathbf{S}^2]$,

5. $[H_{\mathrm{SO}}, \mathbf{J}^2]_-$ $\qquad (\mathbf{J} = \mathbf{L} + \mathbf{S})$.

Exercise 5.3.6
Prove the relation, which was needed for the derivation of (5.251),

$$(\nabla\varphi \times \mathbf{p}) = -\,(\mathbf{p} \times \nabla\varphi) \ ,$$

in which $\mathbf{p}$ represents the momentum of the particle, and $\varphi(\mathbf{r}, t)$ the (twofold continuously differentiable) scalar electric potential, in which the particle moves.

5.4 Addition of Angular Momenta

5.4.1 Total Angular Momentum

We have seen in the last section that occasionally it can become necessary to combine two individual angular momenta, whose eigen-values and eigen-states are known, to a **total angular momentum**. For instance, according to (5.256) and (5.257), neither the spin $\mathbf{S}$ nor the orbital angular momentum $\mathbf{L}$ of the electron are integrals of motion, but, in contrast, the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is a constant of motion. Considerations are therefore of course interesting, how one can derive the properties of $\mathbf{J}$ from those of $\mathbf{L}$ and $\mathbf{S}$. In the following we will get to know further examples, which are concerned with the necessity of *adding angular momenta*. The problem shall therefore be discussed, at first, very generally, in order to be applied then in the form of exercises to concrete problems.

Starting point shall be two vector operators $\mathbf{J}_1$ and $\mathbf{J}_2$, which commute with each other,

$$[\mathbf{J}_1, \mathbf{J}_2]_- = 0 \; , \tag{5.260}$$

and whose components are Hermitian operators. They are assumed to fulfill the fundamental commutation relations (5.14), so that, according to our previous definition, $\mathbf{J}_1$ and $\mathbf{J}_2$ are *angular momenta* with all the properties derived in Sect. 5.1.4. In this sense, $\mathbf{J}_i^2$ and J_{iz} $(i = 1, 2)$ possess common eigen-states $|j_i\, m_i\rangle$:

$$\mathbf{J}_{1,2}^2 |j_{1,2}\, m_{1,2}\rangle = \hbar^2 j_{1,2}\,(j_{1,2}+1) |j_{1,2}\, m_{1,2}\rangle \; , \tag{5.261}$$

$$J_{1,2\,z} |j_{1,2}\, m_{1,2}\rangle = \hbar\, m_{1,2} |j_{1,2}\, m_{1,2}\rangle \; . \tag{5.262}$$

We interpret $\mathbf{J}_1$ and $\mathbf{J}_2$ as the angular momenta of two partial systems 1 and 2. The states of the system, which is composed by 1 and 2, can then be symbolized by

$$|\gamma; j_1\, j_2; m_1\, m_2\rangle \; ,$$

where γ gathers all quantum numbers, which are indispensable for the definition of a pure state, but which have nothing to do with the angular momenta. They are therefore the eigen-values of observables Γ_i, which build together with

$$\mathbf{J}_1^2, \mathbf{J}_2^2, J_{1z}, J_{2z} \tag{5.263}$$

a *complete set of compatible observables*, i.e. in particular, they commute with the angular momenta. For each γ, the eigen-states of the operator set (5.263) thus span a subspace $\mathcal{H}_\gamma$, where each subspace $\mathcal{H}_\gamma$ can be treated separately. Since we are interested here only in properties of the angular momentum, we restrict our considerations to a fixed $\mathcal{H}_\gamma$ and drop from now on, for simplifying the paperwork, the index γ from the state symbols. In the subspace $\mathcal{H}_\gamma$, already the operators (5.263) build a *complete set*. Their common eigen-states can be built up as product states of the $|j_{1,2}\, m_{1,2}\rangle$ in (5.261) and (5.262):

$$|j_1\, j_2; m_1\, m_2\rangle \equiv |j_1\, m_1\rangle |j_2\, m_2\rangle \; . \tag{5.264}$$

We call the vector sum of the two angular momenta $\mathbf{J}_1$ and $\mathbf{J}_2$

total angular momentum

$$\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2 \ . \tag{5.265}$$

The fact that $\mathbf{J}$ is really an angular momentum, is easily shown. Using (5.260) one calculates, for instance:

$$\begin{aligned} [J_x, J_y]_- &= [J_{1x} + J_{2x}, J_{1y} + J_{2y}]_- = [J_{1x}, J_{1y}]_- + [J_{2x}, J_{2y}]_- \\ &= i\,\hbar\, J_{1z} + i\,\hbar\, J_{2z} = i\,\hbar\, J_z \ . \end{aligned}$$

Analogously, one checks the two other fundamental commutator relation (5.14). $\mathbf{J}$ is thus an angular momentum!

One now realizes immediately that the states (5.264) are also eigen-states of the z-component J_z of the total angular momentum:

$$\begin{aligned} J_z|j_1 j_2; m_1 m_2\rangle &= (J_{1z} + J_{2z})|j_1 m_1\rangle|j_2 m_2\rangle \\ &= \hbar(m_1 + m_2)|j_1 j_2; m_1 m_2\rangle \ . \end{aligned} \tag{5.266}$$

They are, though, not eigen-states of $\mathbf{J}^2$. Because

$$\mathbf{J}^2 = \mathbf{J}_1^2 + \mathbf{J}_2^2 + 2\mathbf{J}_1 \cdot \mathbf{J}_2 \tag{5.267}$$

$\mathbf{J}^2$ does not commute with J_{1z} and J_{2z}:

$$\begin{aligned} [\mathbf{J}^2, J_{1z}]_- &= 2[J_{1x}J_{2x} + J_{1y}J_{2y}, J_{1z}]_- \\ &= 2[J_{1x}, J_{1z}]_- J_{2x} + 2[J_{1y}, J_{1z}]_- J_{2y} \\ &= 2i\,\hbar(\mathbf{J}_1 \times \mathbf{J}_2)_z = -[\mathbf{J}^2, J_{2z}]_- \ . \end{aligned} \tag{5.268}$$

On the other hand, we have:

$$[\mathbf{J}^2, J_z]_- = [\mathbf{J}^2, \mathbf{J}_1^2]_- = [\mathbf{J}^2, \mathbf{J}_2^2]_- = 0 \ . \tag{5.269}$$

The observables

$$\mathbf{J}^2, J_z, \mathbf{J}_1^2, \mathbf{J}_2^2 \tag{5.270}$$

thus represent also a *maximal set of commuting observables*. When we recall once more the example of the electron, then we remember that $\mathbf{J}^2$, J_z, $\mathbf{J}_1^2 = \mathbf{L}^2, \mathbf{J}_2^2 = \mathbf{S}^2$ are the actual constants of motion. Their common eigen-states,

$$|j_1 j_2; j\, m_j\rangle \qquad (-j \le m_j \le +j) \ ,$$

are therefore possibly more interesting than the product states (5.264). They are subject to the usual eigen-value equations of angular momenta:

$$\mathbf{J}^2|j_1 j_2; j\, m_j\rangle = \hbar^2 j(j+1)|j_1 j_2; j\, m_j\rangle \ , \tag{5.271}$$

$$J_z|j_1 j_2; j\, m_j\rangle = \hbar\, m_j|j_1 j_2; j\, m_j\rangle \ , \tag{5.272}$$

$$\mathbf{J}_{1,2}^2|j_1 j_2; j\, m_j\rangle = \hbar^2 j_{1,2}\,(j_{1,2}+1)|j_1 j_2; j\, m_j\rangle \ . \tag{5.273}$$

The product states (5.264) build in $\mathcal{H}_\gamma$ an orthonormal basis. Hence, the states $|j_1 j_2; j\, m_j\rangle$ can in any case be expanded in these basis states:

$$|j_1 j_2; j\, m_j\rangle = \sum_{j_1' j_2'} \sum_{m_1' m_2'} |j_1' j_2'; m_1' m_2'\rangle \langle j_1' j_2'; m_1' m_2' | j_1 j_2; j\, m_j\rangle \,. \tag{5.274}$$

It is now easy to realize that the expansion coefficients can be unequal zero only if $j_1 = j_1'$ and $j_2 = j_2'$. For the proof one uses that $\mathbf{J}_1^2$, $\mathbf{J}_2^2$ are Hermitian operators with positive quantum numbers j_1, j_2:

$$\begin{aligned} 0 &= \langle j_1' j_2'; m_1' m_2' | \left(\mathbf{J}_i^2 - \mathbf{J}_i^2\right) | j_1 j_2; j\, m_j\rangle \\ &= \hbar^2 \left[j_i'(j_i'+1) - j_i(j_i+1)\right] \langle j_1' j_2'; m_1' m_2' | j_1 j_2; j\, m_j\rangle \,. \end{aligned}$$

For $j_i \neq j_i'$ the matrix element must therefore vanish. The quadruple sum thus simplifies to a double sum:

$$|j_1 j_2; j\, m_j\rangle = \sum_{m_1 m_2} |j_1 j_2; m_1 m_2\rangle \langle j_1 j_2; m_1 m_2 | j_1 j_2; j\, m_j\rangle \,.$$

The amplitudes of this expansion are called

Clebsch-Gordan coefficients:

$$C_{j_1 j_2}\,(m_1 m_2; j\, m_j) \equiv \langle j_1 j_2; m_1 m_2 | j_1 j_2; j\, m_j\rangle \,. \tag{5.275}$$

Later they will be discussed in detail. Since, according to (5.274), states with different j_i *do not mix*, we can for the following considerations, without loss of information, besides γ fix also j_1 and j_2. Each subspace $\mathcal{H}_\gamma(j_1, j_2)$ of $\mathcal{H}_\gamma$ can be treated separately.

There remain two important questions to be clarified:

1. Which values can be adopted by j for given j_1, j_2?
2. How can the Clebsch-Gordan coefficients of the expansion law (5.274) be explicitly calculated?

Question 1. will be the subject of the next subsection, while question 2. will be answered in Sect. 5.4.3.

5.4.2 Quantum Numbers of the Total Angular Momentum

We first ask about the possible values of the magnetic quantum number m_j. Since J_z is a Hermitian operator, and both sets of states are, according to (5.266) and (5.272), eigen-states of J_z, we see that:

$$\begin{aligned} 0 &= \langle j_1 j_2; m_1 m_2 | (J_z - J_z) | j_1 j_2; j\, m_j\rangle \\ &= \hbar \left[(m_1 + m_2) - m_j \right] \langle j_1 j_2; m_1 m_2 | j_1 j_2; j\, m_j\rangle \,. \end{aligned}$$

Here we have let J_z act once *to the left* on the bra-state and once *to the right* on the ket-state. We recognize that only for

$$m_j = m_1 + m_2 \tag{5.276}$$

the Clebsch-Gordan coefficient can be unequal zero. The multiple sum in the expansion (5.274) therewith simplifies once more and becomes a simple sum. By a given m_1 the value for $m_2 = m_j - m_1$ is fixed. Applying then J_z to the state (5.274) makes clear that besides (5.276) no further values for m_j exist.

The determination of the possible quantum numbers j proves to be more difficult. It is sure, according to the general properties of the angular momentum, that $j \geq 0$ and that there belong to each j-value altogether $(2j + 1)$ magnetic quantum numbers m_j. All *conceivable* m_j are, on the other hand, contained in (5.276), i.e., being given by the $(2j_1+1)\,(2j_2+1)$ possible (m_1, m_2)-combinations. These combinations are of course not all pairwise different. We therefore think, at first, about the *degrees of degeneracy* $g(m_j)$ of the various m_j-values, i.e., about the number of different (m_1, m_2)-pairs, which fulfill (5.276) for a given m_j.

For the counting, the diagram sketched in Fig. 5.3 may provide a useful visual help. We plot on the abscissa m_1 and on the ordinate m_2. Each (m_1, m_2)-pair is then represented by a point in the (m_1, m_2)-plane. The *allowed* (m_1, m_2)-pairs build a rectangle with the *edge lengths* $(2j_1 + 1)$ and $(2j_2 + 1)$.

In Fig. 5.3 a situation is represented for which both j_2 and j_1 are half-integer.

The points on the dashed diagonals differ by $\Delta m_1 = -\Delta m_2$, having thus the same m_j-value. The number of points on such a diagonal thus corresponds to the degree of degeneracy $g(m_j)$. m_j increases thereby from diagonal to diagonal in each step by $+1$, starting at $-(j_1 + j_2)$ in the *left lower corner* up to $+(j_1 + j_2)$ in the *right upper corner*.

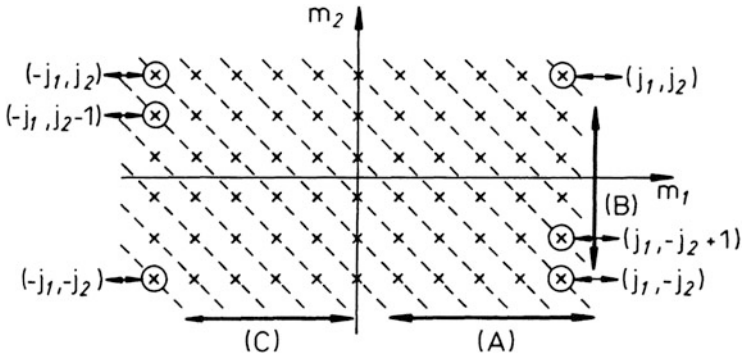

Figure 5.3: Scheme for the determination of the degree of degeneracy of the magnetic quantum number of a total angular momentum composed by two single angular momenta

It holds for the diagonals in the region (A) in the sketched case ($j_1 > j_2$):

$$j_2 - j_1 \leq m_j \leq j_1 - j_2 \ ,$$

or more generally:

$$-|j_1 - j_2| \leq m_j \leq |j_1 - j_2| \ . \tag{A}$$

On these diagonals we always find the same number of points, namely $2j_2 + 1$, or more generally:

$$g_{\mathrm{A}}(m_j) = j_1 + j_2 - |j_1 - j_2| + 1 \ .$$

This is just the *length* of the smaller edge of the rectangle in units of the point spacing. For the points in the region (B) we obviously have $j_1 + j_2 \geq m_j \geq j_1 - j_2 + 1$, or more general:

$$j_1 + j_2 \geq m_j > |j_1 - j_2| \ . \tag{B}$$

The *degree of degeneracy* increases in this region (B) from *top right* to *down left* in each step by the value 1, starting with $g_{\mathrm{B}} = 1$ for $m_j = j_1 + j_2$:

$$g_{\mathrm{B}}(m_j) = j_1 + j_2 - m_j + 1 \ .$$

Completely analogously we find for the situation in the region (C):

$$-|j_1 - j_2| > m_j \geq -(j_1 + j_2)$$

$$g_{\mathrm{C}}(m_j) = j_1 + j_2 + m_j + 1 \ . \tag{C}$$

Let us collect all the results once more in the form of a table:

$$\begin{aligned}
m_j &< -(j_1 + j_2) : && g(m_j) = 0 \ , \\
-(j_1 + j_2) \leq m_j &< -|j_1 - j_2| : && g(m_j) = j_1 + j_2 + m_j + 1 \ , \\
-|j_1 - j_2| \leq m_j &\leq |j_1 - j_2| : && g(m_j) = j_1 + j_2 - |j_1 - j_2| + 1 \ , \\
|j_1 - j_2| < m_j &\leq j_1 + j_2 : && g(m_j) = j_1 + j_2 - m_j + 1 \ , \\
j_1 + j_2 &< m_j && : \quad g(m_j) = 0 \ .
\end{aligned} \tag{5.277}$$

By means of this table we are now able to suggest the possible values of j. Let us assume that for a given j there were $n(j)$ sequences, each consisting of $2j + 1$ states $|j_1 j_2; j\, m_j\rangle$. Certainly $n(j)$ will take only the values 0 or 1. In each of these sequences m_j appears exactly once, if only $j \geq |m_j|$. Hence it follows for the *degree of degeneracy*:

$$g(m_j) = \sum_{j' \geq |m_j|} n(j') \ ,$$

what is in particular valid for the maximal value $m_j = j$. Therewith we can fix $n(j)$:

$$g(m_j = j) - g(m_{j+1} = j + 1) = n(j) \ .$$

When we still take into consideration that j cannot be negative then we read off from the table (5.277):

$$\begin{array}{ll} 0 \le j < |j_1 - j_2| \; ; & n(j) = 0 \; , \\ |j_1 - j_2| \le j \le j_1 + j_2 : & n(j) = 1 \; , \\ j_1 + j_2 < j : & n(j) = 0 \; . \end{array}$$

The values of j, to which states $|j_1 j_2; j\, m_j\rangle$ exist, fulfill the

triangle inequality

$$|j_1 - j_2| \le j \le j_1 + j_2 \; . \tag{5.278}$$

In principle, that is a plausible result, because it corresponds exactly to the classical **vector model** (Fig. 5.4). The parallel orientation of the vectors $\mathbf{j}_1$ and $\mathbf{j}_2$ means $j = j_1 + j_2$, the antiparallel orientation $j = |j_1 - j_2|$.

We now know the quantum numbers of the total angular momentum and want to calculate finally with this knowledge the total number N of states $|j_1 j_2; j\, m_j\rangle$. To each j there are $2j + 1$ different m_j-values. Therewith, N is calculated as follows:

$$\begin{aligned} N &= \sum_{j\,=\,|j_1 - j_2|}^{j_1 + j_2} (2j + 1) \\ &= \frac{1}{2}(j_1 + j_2 - |j_1 - j_2| + 1)\; [2(j_1 + j_2) + 1 + 2|j_1 - j_2| + 1] \\ &= (j_1 + j_2 + 1)^2 - |j_1 - j_2|^2 = (2j_1 + 1)\,(2j_2 + 1) \; . \end{aligned} \tag{5.279}$$

But this corresponds exactly to the dimension of the subspace $\mathcal{H}_\gamma(j_1, j_2)$. Since the states $|j_1 j_2; j\, m_j\rangle$ are surely linearly independent, they thus build, as the $|j_1 j_2; m_1 m_2\rangle$, a basis of the $\mathcal{H}_\gamma(j_1 j_2)$. The transition (5.274) from the one to the other basis is done by a **unitary transformation**. The elements of the transformation matrix are the Clebsch-Gordan coefficients (5.275), which we will treat in more detail in the next section.

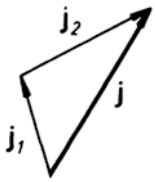

Figure 5.4: Vector model for the addition of two quantum-mechanical angular momenta

5.4.3 Clebsch-Gordan Coefficients

As before, the further considerations are also thought for fixed given quantum numbers j_1 and j_2. We can therefore simplify a bit the state symbols,

$$|j_1 j_2; j\, m_j\rangle \;\longrightarrow\; |j\, m_j\rangle\;; \quad |j_1 j_2; m_1 m_2\rangle \;\longrightarrow\; |m_1 m_2\rangle\;,$$

in order to save paperwork.

We investigate the relation (5.274):

$$|j\, m_j\rangle = \sum_{m_1,\, m_2}^{m_1 + m_2 = m_j} \langle m_1 m_2 | j\, m_j\rangle |m_1 m_2\rangle\;. \tag{5.280}$$

Many properties of the Clebsch-Gordan coefficients $\langle m_1 m_2 | j\, m_j\rangle$ result already from the fact that they are, as stated at the end of the last subsection, the elements of a unitary matrix of the rank $(2j_1 + 1)\,(2j_2 + 1)$. So it follows from the orthonormality of the columns,

$$\sum_{m_1 m_2} \langle m_1 m_2 \big| j\, m_j\rangle \langle m_1 m_2 \big| j'\, m_j'\rangle^* = \delta_{jj'}\, \delta_{m_j m_j'}\;, \tag{5.281}$$

and from the orthonormality of the rows:

$$\sum_{j\, m_j} \langle m_1 m_2 \big| j\, m_j\rangle \langle m_1' m_2' \Big| j\, m_j\rangle^* = \delta_{m_1 m_1'}\, \delta_{m_2 m_2'}\;. \tag{5.282}$$

By a proper choice of the phases of the states $|j\, m_j\rangle$ one can always make the Clebsch-Gordan coefficients real:

$$\langle m_1 m_2 \big| j\, m_j\rangle = \langle j\, m_j \big| m_1 m_2\rangle\;. \tag{5.283}$$

We now want to think about how these Clebsch-Gordan coefficients can explicitly be calculated. The procedure consists of two essential partial steps:

(I) Let the starting point be, at first, $j = j_1 + j_2$ and $m_j = j_1 + j_2$, i.e., the highest possible j with maximal magnetic quantum number m_j. The sum in (5.280) can then consist only of one summand, because only the combination $m_1 = j_1$ and $m_2 = j_2$ is possible. Since all participating states are normalized to one, and the phase is fixed by (5.283), we have to assume:

$$|j_1 + j_2\;\, j_1 + j_2\rangle = |j_1 j_2\rangle\;. \tag{5.284}$$

By means of the operator $J_- = J_{1-} + J_{2-}$, which we apply, according to the rules (5.64) in Sect. 5.1.4, to both sides of the equation, all states to $j = j_1 + j_2$ and $-j \le m_j \le +j$ can now be derived step by step. Let us perform that explicitly here: From the left side of (5.284) we get after application of J_-,

$$J_- |j_1 + j_2\;\, j_1 + j_2\rangle = \hbar\sqrt{2(j_1 + j_2)}\, |j_1 + j_2\;\, j_1 + j_2 - 1\rangle\;,$$

and from the right side:

$$\begin{aligned} J_-|j_1 j_2\rangle &= (J_{1-} + J_{2-})|j_1 j_2\rangle \\ &= \hbar\sqrt{2j_1}|j_1 - 1\, j_2\rangle + \hbar\sqrt{2j_2}|j_1 j_2 - 1\rangle \,. \end{aligned}$$

By equalizing these two equations it follows:

$$|j_1 + j_2\ j_1 + j_2 - 1\rangle = \sqrt{\frac{j_1}{j_1 + j_2}}|j_1 - 1\, j_2\rangle + \sqrt{\frac{j_2}{j_1 + j_2}}|j_1\, j_2 - 1\rangle \,. \tag{5.285}$$

We have therewith already found the first Clebsch-Gordan coefficient:

$$\begin{aligned} \langle m_1 m_2|j_1 + j_2\ j_1 + j_2 - 1\rangle &= \sqrt{\frac{j_1}{j_1 + j_2}}\,\delta_{m_1 j_1 - 1}\,\delta_{m_2 j_2} \\ &\quad + \sqrt{\frac{j_2}{j_1 + j_2}}\,\delta_{m_1 j_1}\,\delta_{m_2 j_2 - 1} \,. \end{aligned} \tag{5.286}$$

The procedure can be continued in this manner. *As an exercising demonstration* we still execute the next step by applying J_- to both sides of the Eq. (5.285):

$$J_-|j_1 + j_2\ j_1 + j_2 - 1\rangle = \hbar\sqrt{2(2j_1 + 2j_2 - 1)}|j_1 + j_2\, j_1 + j_2 - 2\rangle \,.$$

This is to be equated with

$$\begin{aligned} &\sqrt{\frac{j_1}{j_1 + j_2}}\,(J_{1-} + J_{2-})|j_1 - 1\, j_2\rangle + \sqrt{\frac{j_2}{j_1 + j_2}}\,(J_{1-} + J_{2-})|j_1\, j_2 - 1\rangle \\ = \ &\hbar\sqrt{\frac{j_1}{j_1 + j_2}}\,\left(\sqrt{2(2j_1 - 1)}|j_1 - 2\, j_2\rangle + \sqrt{2j_2}|j_1 - 1\, j_2 - 1\rangle\right) \\ &+\hbar\sqrt{\frac{j_2}{j_1 + j_2}}\,\left(\sqrt{2j_1}|j_1 - 1\, j_2 - 1\rangle + \sqrt{2(2j_2 - 1)}|j_1\, j_2 - 2\rangle\right) \,. \end{aligned}$$

We therewith obtain the representation of the state $|j_1 + j_2\ j_1 + j_2 - 2\rangle$ in the basis $\{|m_1 m_2\rangle\}$ with the following Clebsch-Gordan coefficients:

$$\begin{aligned} &\langle m_1 m_2|j_1 + j_2\ j_1 + j_2 - 2\rangle \\ &\quad = \sqrt{\frac{j_1(2j_1 - 1)}{(j_1 + j_2)\,(2j_1 + 2j_2 - 1)}}\,\delta_{m_1\, j_1 - 2}\,\delta_{m_2 j_2} \\ &\quad +2\sqrt{\frac{j_1 j_2}{(j_1 + j_2)\,(2j_1 + 2j_2 - 1)}}\,\delta_{m_1\, j_1 - 1}\,\delta_{m_2\, j_2 - 1} \\ &\quad +\sqrt{\frac{j_2(2j_2 - 1)}{(j_1 + j_2)\,(2j_1 + 2j_2 - 1)}}\,\delta_{m_1 j_1}\,\delta_{m_2\, j_2 - 2} \,. \end{aligned} \tag{5.287}$$

The procedure can obviously be continued in this way until all $2(j_1 + j_2) + 1$ states $|j_1 + j_2\, m_j\rangle$ are calculated.

(II) In the next step one investigates the states with $j = j_1 + j_2 - 1$ and starts again with the highest possible magnetic quantum number m_j. According to (5.280), this state consists of two summands:

$$|j_1 + j_2 - 1\ j_1 + j_2 - 1\rangle = \alpha|j_1 - 1\, j_2\rangle + \beta|j_1\, j_2 - 1\rangle\ .$$

α and β are Clebsch-Gordan coefficients. The states $|j\, m_j\rangle$ are orthonormalized. The scalar product $\langle j_1 + j_2\ j_1 + j_2 - 1|j_1 + j_2 - 1\ j_1 + j_2 - 1\rangle$ must therefore be zero, what leads with (5.285) to a conditional equation for α and β:

$$\alpha\sqrt{\frac{j_1}{j_1 + j_2}} + \beta\sqrt{\frac{j_2}{j_1 + j_2}} = 0\ .$$

The in the intermediate result,

$$|j_1 + j_2 - 1\ j_1 + j_2 - 1\rangle = \gamma\left(\sqrt{j_2}|j_1 - 1\, j_2\rangle - \sqrt{j_1}|j_1\, j_2 - 1\rangle\right)\ ,$$

still remaining constant γ is fixed by the normalization ($\to \gamma^2((j_1 + j_2) = 1)$:

$$|j_1 + j_2 - 1\ j_1 + j_2 - 1\rangle = \sqrt{\frac{j_2}{j_1 + j_2}}|j_1 - 1\ j_2\rangle - \sqrt{\frac{j_1}{j_1 + j_2}}|j_1\, j_2 - 1\rangle\ . \qquad (5.288)$$

We have therewith derived two further Clebsch-Gordan coefficients:

$$\begin{aligned}\langle m_1 m_2|j_1 + j_2 - 1\ j_1 + j_2 - 1\rangle \quad &= \quad \sqrt{\frac{j_2}{j_1 + j_2}}\ \delta_{m_1\, j_1 - 1}\,\delta_{m_2 j_2} \\ &\quad -\sqrt{\frac{j_1}{j_1 + j_2}}\ \delta_{m_1 j_1}\,\delta_{m_2\, j_2 - 1}\ . \qquad (5.289)\end{aligned}$$

One obtains the other states $|j_1 + j_2 - 1\ m_j\rangle$ now again according to the procedure (I), i.e., by repeated application of $J_- = J_{1-} + J_{2-}$ to Eq. (5.288). The procedure can be continued in this way until the determination of all Clebsch-Gordan coefficients is completed. So one would make in the next step an ansatz for the state $|j_1 + j_2 - 2\ j_1 + j_2 - 2\rangle$, corresponding to (5.280), and then one would fix the coefficients via orthogonality and normalization conditions as described in (II). Then again procedure (I) comes into play to determine the *other* states $|j_1 + j_2 - 2\ m_j\rangle$ for $m_j = j_1 + j_2 - 3, \ldots, -(j_1 + j_2 - 2)$, and so on.

For the addition of angular momenta with high quantum numbers j_1, j_2 the procedure becomes of course computationally rather demanding. Fortunately, that does not bother us in the concrete case of our presentation here. The Clebsch-Gordan coefficients of the most important (j_1, j_2)-combinations are available in tabulated form, where such a tabulation strongly benefits from group-theoretical considerations.

5.4.4 Exercises

Exercise 5.4.1
Let $\mathbf{S}_1$ and $\mathbf{S}_2$ be the spin operators of two spin-1/2 particles, e.g. the two electrons in the He-atom.

1. Find the common eigen-states $|S_1\, S_2; S\, m_s\rangle$ of the total spin operator $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$, its z-component S_z, and $\mathbf{S}_1^2$ and $\mathbf{S}_2^2$.

2. Show that these states are also the eigen-states of the operator $\mathbf{S}_1 \cdot \mathbf{S}_2$. Determine the eigen-values.

3. Show that the operator

$$P = \frac{3}{4} + \frac{1}{\hbar^2}\, \mathbf{S}_1 \cdot \mathbf{S}_2$$

is a projection operator in the space of the spin states! Onto which subspace does P project?

Exercise 5.4.2
Let the Hamilton operator of two spin-1/2 particles be given by

$$H = -J\, \mathbf{S}_1 \cdot \mathbf{S}_2 + \mu(S_{1z} + S_{2z})\ .$$

Calculate the eigen-values and find the eigen-states in the basis $\{|S_1\, S_2; S m_s\rangle\}$.

Exercise 5.4.3
Calculate for the total angular momentum of the electron,

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \qquad \left(S = \frac{1}{2}, l \geq 1\right)\ ,$$

the common eigen-states $|l(1/2); j\, m_j\rangle \equiv |j\, m_j\rangle$ of the operators $\mathbf{J}^2, J_z, \mathbf{L}^2, \mathbf{S}^2$ as linear combinations of the eigen-states $|l(1/2); m_l\, m_s\rangle \equiv |l\, m_l\rangle|(1/2)\, m_s\rangle$ of the operators $\mathbf{L}^2$, $L_z, \mathbf{S}^2, S_z$. For this purpose perform the following steps:

1. Show that for the quantum number j only the values $l+(1/2)$ and $l-(1/2)$ are possible.

2. Verify for the eigen-states the following expressions:

$$\begin{aligned}\left|l \pm \frac{1}{2}\, m_j\right\rangle \;=\; & \sqrt{\frac{l \pm m_j + (1/2)}{2l+1}}\left|l\ m_j - \frac{1}{2}\right\rangle|+\rangle \\ & \pm\sqrt{\frac{l \mp m_j + (1/2)}{2l+1}}\left|l\ m_j + \frac{1}{2}\right\rangle|-\rangle\ .\end{aligned}$$

Exercise 5.4.4
Two angular momenta $\mathbf{J}_1$, $\mathbf{J}_2$ couple to a total angular momentum $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$. Calculate for $j_1 = j_2 = 1$ all Clebsch-Gordan coefficients!

Exercise 5.4.5
Two angular momenta $\mathbf{J}_1$ and $\mathbf{J}_2$ with the quantum numbers $j_1 = 1/2$ and $j_2 = 3/2$ are given.

1. Which quantum numbers j and m_j are possible for the square and for the z-component of the operator of the total angular momentum

$$\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2 \ ?$$

2. Calculate, for the maximum value of j and all non-negative m_j, all Clebsch-Gordan coefficients!

5.5 Self-Examination Questions

To Section 5.1

1. Why is the classical angular momentum not a genuine property of the particle?
2. Why is it not possible to measure two components of the orbital angular momentum precisely at the same time?
3. How does the generalized uncertainty relation read for L_x and L_z?
4. Is it possible to measure precisely and simultaneously the observables $\mathbf{L}^2$ and L_y?
5. How are the ladder operators $L_\pm$ defined?
6. What is the result of the commutator of L_+ with L_-?
7. Which are the essential properties of the classical rotation matrix?
8. Why must the rotation operator $\widehat{D}$ be unitary?
9. What does one have to understand, pictorially, by the rotation of an observable?
10. Which connection exists between the rotation operator and the operator of the orbital angular momentum?
11. Let $\mathbf{A}$ be a vector operator. What can be said about the commutators $[L_z, A_z]_-$ and $[L_z, A_x]_-$?
12. In a central field, why should the operators H, $\mathbf{L}^2$ and L_z possess a common set of eigen-states?

13. Which properties of the angular-momentum operator are needed for the solution of its eigen-value problem?

14. Let $|j\,m\rangle$ be an eigen-state of $\mathbf{J}^2$ and J_z. In which manner does the application of J_+ or J_- change this state?

15. Which are the eigen-values of $\mathbf{J}^2$ and J_z? Which numerical values are possible for j and m?

16. What does one understand by *directional degeneracy*?

17. Which eigen-values do the operators J_x and J_y have?

18. What is meant by *directional quantization*?

19. How can we understand the properties of the quantum-mechanical angular momentum in the framework of the so-called *vector model*?

20. Which properties of the quantum-mechanical angular momentum are classically completely incomprehensible?

21. How do we get the matrix elements of the operators J_+ and J_- in the $\{|j\,m\rangle\}$-representation?

22. Let $\mathbf{J}^2$ have the eigen-value $12\hbar^2$. Which eigen-values are then possible for J_z?

23. How does the position representation of the Cartesian components of the orbital angular momentum look like?

24. Which structure does L_z have when spherical coordinates are applied?

25. When spherical coordinates are applied, what is the connection between the square of the angular momentum $\mathbf{L}^2$ and the Laplace operator, ?

26. Why, at least for the general case, do $\mathbf{L}^2$ and L_z not represent a complete set of compatible operators?

27. Why should the quantum number l of the orbital angular momentum be an integer?

28. With which well-known differential equation can the eigen-value equation of $\mathbf{L}^2$ be identified?

29. To which mathematical functions do the eigen-functions of $\mathbf{L}^2$ and L_z correspond?

30. Which parity does the special eigen-function $Y_{3-2}(\vartheta, \varphi)$ of the orbital angular momentum have?

To Section 5.2

1. How is the magnetic moment of a local current density $\mathbf{j}$ defined in Classical Electrodynamics?
2. How can the classical magnetic moment of a particle be derived from its energy?
3. How is the observable *magnetic moment* defined in Quantum Mechanics?
4. What is the canonically conjugate variable to the position $\mathbf{r}$ of a particle of mass m and charge $\hat{q}$ in the electromagnetic field?
5. What does *central-field approximation* mean?
6. Which structure does the Hamilton operator of a particle with p electrons (spin still excluded) have? How does the corresponding magnetic moment look like?
7. Which term of the magnetic moment causes diamagnetism, and which paramagnetism?
8. Which kind of splitting of energy levels is to be expected in the magnetic field, when the magnetic moment of an atom is exclusively caused by the orbital angular momenta of its electrons?
9. Which experimental observations enforce the introduction of the spin?
10. Which numerical values can be adopted by the spin quantum number S?
11. Is S changeable for a certain quantum-mechanical particle?
12. Explain, why the operator of the orbital angular momentum and that of the spin commute.
13. What does one understand by a spinor?
14. Are the components $\widehat{\mu}_x$, $\widehat{\mu}_y$ of the magnetic moment simultaneously precisely measurable?
15. Which important elementary particles possess a spin $S = 1/2$?
16. How are the Pauli spin matrices defined?
17. What can be said about the anticommutator $[S_x, S_z]_+$ for a spin $S = 1/2$?
18. Why is $(S_+)^2 = 0$ an operator identity in $\mathcal{H}_{S=1/2}$?
19. Which meaning do the squares of the absolute values $|\psi_\pm(\mathbf{r})|^2$ of the components of the spinor $|\psi_{1/2}(\mathbf{r})\rangle$ have?
20. What is $\|\psi_{1/2}(\mathbf{r})\|^2$?

21. What is the dimension of the spin space $\mathcal{H}_{S=1/2}$?
22. Which magnetic moment is generated by the spin?
23. In what do the spin moments of different spin-1/2 particles vary? Which common features do they have?
24. What does one understand by the Landé factor of the electron?
25. What is the paramagnetic total moment of the electron? Which additional term in the Hamilton operator is due to this moment after switching on a homogeneous magnetic field?
26. Which form does the time-dependent Schrödinger equation of the two-component spinor $|\psi_{1/2}(\mathbf{r},t)\rangle$ have for an electron in the potential $V(\mathbf{r})$ and a homogeneous magnetic field $\mathbf{B}$?

To Section 5.3

1. How does the relativistic, classical energy law read for a free electron?
2. What does one understand by *covariance* of relativistic equations?
3. How can the *rule of correspondence* be written in relativistic-covariant form for the transition of classical equations into Quantum Mechanics?
4. How does one get the *Klein-Gordon equation*? Which basic problems arise when solving it?
5. By which procedure does the Dirac equation of the free particle (electron) follow from the classical energy law?
6. In which respect does the Dirac equation reflect the equivalence of space and time coordinates, which is typical for the theory of relativity?
7. How does the Dirac equation of the electron in the electromagnetic field read?
8. How are the *Dirac matrices* $\widehat{\boldsymbol{\alpha}}$ and $\widehat{\beta}$ built up?
9. Which structure does the eigen-solution function $|\psi(\mathbf{r},t)\rangle$ of the Dirac operator $H_{\mathrm{D}}^{(0)}$ for the free particle have?
10. What are the energy-eigen values of $H_{\mathrm{D}}^{(0)}$? What is their degree of degeneracy?
11. What is the definition of the Dirac spin operator $\widehat{\mathbf{S}}$?
12. Which component of $\widehat{\mathbf{S}}$ commutes with $H_{\mathrm{D}}^{(0)}$?

13. Which eigen-values are found for this component?
14. With the aid of this component of the Dirac spin operator, how can one explain the degeneracy of the energy-eigen values of $H_{\mathrm{D}}^{(0)}$?
15. Which property characterizes the (relativistic) electron besides mass m_e and charge $q = -e$?
16. Is the orbital angular momentum $\mathbf{L}$ of the *free Dirac-electron* an integral of motion?
17. Which angular momentum commutes with $H_{\mathrm{D}}^{(0)}$?
18. How is the *Pauli-theory* of the electron related to the fully relativistic Dirac-theory?
19. What do we understand by the notations *small* and *large component* of the Dirac spinor?
20. By which considerations does the existence of the angular momentum *spin*, the spin moment, and the Landé factor $g = 2$ follow from the Dirac-theory of the electron?
21. How can one find *classical reasons* for the spin-orbit coupling?
22. Up to what order of v/c has the *non-relativistic limiting case* of the Dirac-theory to be correct, in order to exhibit the spin-orbit interaction?
23. Is it possible to find the spin-orbit interaction within the framework of the Pauli's *two-component theory*?
24. What is known as Darwin term?
25. How does the operator H_{SO} of the spin-orbit interaction look like?
26. Do orbital angular momentum $\mathbf{L}$ and spin $\mathbf{S}$ commute with H_{SO}?
27. Which important consequences of the spin-orbit interaction you know?

To Section 5.4

1. Let $\mathbf{J}_1$ and $\mathbf{J}_2$ be the commuting angular momentum operators of two partial systems. Which complete sets of commuting angular momenta exist for the composite system?
2. How does one show that the vector sum $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$ is also an angular momentum?
3. What is a Clebsch-Gordan coefficient?

4. How can we derive the magnetic quantum number m_j of the total angular momentum $\mathbf{J}$ in relation to those of the single angular momenta $\mathbf{J}_1$, $\mathbf{J}_2$?

5. How does the *triangle inequality* look like for the possible quantum numbers j of the total angular momentum? How can the inequality be physically justified?

6. How can one explicitly calculate the Clebsch-Gordan coefficients?

Chapter 6

Central Potential

After the rather abstract considerations of the preceding chapter concerning the observable *angular momentum*, now follows again a chapter, in which we want to work out, by the use of concrete and important examples, practical solution methods. The basic theoretical problem in Quantum Mechanics always consists in solving the Schrödinger equation, i.e. in solving the eigen-value problem of the Hamilton operator. The Schrödinger equation is normally a partial differential equation of second order, and therewith, *hardly ever* rigorously solvable. In the case of one-dimensional problems, however, the partial differential equation turns into an ordinary differential equation, which can be mathematically treated very much easier, and was indeed exactly solved in Chap. 4 (Vol. 6) for some simple model systems. A sometimes successful solution method therefore tries to decompose complicated multi-dimensional Schrödinger equations, by a clever choice of variables, into several independent ordinary differential equations. This procedure is called *'separation of the variables'*, which, by the way, we have already used in many places of this ground course in *Theoretical Physics*. Needless to say that not all problems can be *separated*. That succeeds, though, in particular for particle motions in a **central field**. By a central field we understand a spherically symmetric potential,

$$V(\mathbf{r}) = V(r) \ , \tag{6.1}$$

in which the potential energy of a particle depends only on its distance $r = |\mathbf{r}|$ from a fixedly given center of force, and not on the special direction of the position vector $\mathbf{r}$, if the origin of coordinates coincides with the center of force. We will demonstrate in Sect. 6.1 how the application of **spherical coordinates** reduces each central-field problem to a one-dimensional **radial equation**.

In the development and the structure of Quantum Mechanics, the theory of the **hydrogen atom** has played a very decisive role. In our *inductive reasons* of Quantum Mechanics in Chap. 1 (Vol. 6) we have discussed this fact in detail. The incontrovertible experimental statements, e.g. about the discrete stationary

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energy levels, which were experimentally reflected in the spectroscopic combination principle ((1.102), Vol. 6), stood, at the beginning of the twentieth century, in blatant contradiction to the *classical understanding of physics*. The main objective of the protagonists of the *pre-quantum-mechanical time* therefore consisted indeed in the development of a *new theory*, by which especially the properties of the hydrogen atom could be understood and explained. The H-atom consists of an electron and a positively charged nucleus (proton), the interaction of which follows the Coulomb law of Electrostatics. If one considers the approximately 2000-times heavier nucleus as *point charge at rest*, then the electron moves in a **central potential** ($V(r) \sim 1/r$), to which in Sect. 6.2 we will dedicate a relatively broad space, because of the mentioned *historical importance*. As an example for a short-range central potential, the **spherically symmetric potential well** will be discussed in Sect. 6.3, whose understanding will become important above all for the scattering theory presented in Chap. 9.

6.1 General Statements

6.1.1 Radial Equation

The special symmetry of the central potential $V(\mathbf{r}) = V(r)$ suggests of course the choice of spherical coordinates r, ϑ, φ (5.76), because then the potential energy of the particle becomes a function of one single independent variable. For the Hamilton operator of a particle of mass m in such a central potential,

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) = -\frac{\hbar^2}{2m}\,\Delta + V(r)\,, \tag{6.2}$$

it remains then to formulate, in particular, the Laplace operator Δ in spherical coordinates. This we have already done in (5.83),

$$\Delta = \frac{1}{r^2}\,\frac{\partial}{\partial r}\left(r^2\,\frac{\partial}{\partial r}\right) + \Delta_{\vartheta\varphi}\,, \tag{6.3}$$

and we had found thereby that the angular part $\Delta_{\vartheta\varphi}$ can be expressed in a simple manner by the operator of the square of the orbital angular momentum $\mathbf{L}^2$:

$$\Delta_{\vartheta\varphi} = -\frac{1}{r^2\hbar^2}\,\mathbf{L}^2\,. \tag{6.4}$$

The Hamilton operator therewith reads:

$$H = -\frac{\hbar^2}{2m}\,\frac{1}{r^2}\,\frac{\partial}{\partial r}\left(r^2\,\frac{\partial}{\partial r}\right) + \frac{1}{2m\,r^2}\,\mathbf{L}^2 + V(r)\,. \tag{6.5}$$

The operators (6.2) and (6.5) are equivalent, but of course only without the *critical point* $r = 0$. Since, according to (5.80) and (5.82), the operators of angular momentum $\mathbf{L}^2$ and L_z act only on the angles ϑ, φ, we recognize immediately the important statement:

$$[H,\, L_z]_- = [H, \mathbf{L}^2]_- = 0\,. \tag{6.6}$$

The three operators L_z, $\mathbf{L}^2$ and H will thus possess a common set of eigen-states. This means in particular that $\mathbf{L}^2$ and L_z are constants of motion (3.194) (Vol. 6), which, anyway, does not surprise, though, because already in Classical Mechanics the orbital angular momentum $\mathbf{L}$ remains, under the influence of central forces, constant with respect to direction and magnitude. The Poisson brackets of all components of $\mathbf{L}$ with the classical Hamilton function therefore vanish, which, in turn, according to the principle of correspondence (Sect. 3.5, Vol. 6), transfers to the corresponding quantum-mechanical commutators, finally leading to (6.6). But let us also recall once more the considerations in Sect. 5.1.3. Since H is, in the case of a central potential, a scalar operator invariant with respect to rotations, it must be commutable, according to (5.47) with each component of the orbital angular momentum.

In order to illustrate the analogy to the corresponding classical problem, we try to ascribe also a descriptive meaning to the first term in (6.5). This succeeds with the aid of the **radial momentum** p_r. This is defined in Classical Mechanics as the radial component of the particle momentum ($m\dot{r} = (\mathbf{r}/r) \cdot \mathbf{p}$). With the transition to Quantum Mechanics we have to bear in mind that $\mathbf{p}$ and $\mathbf{r}$ are non-commutable operators. The classical expression therefore has to be *symmetrized*, according to the prescriptions, developed in Chap. 2 (Vol. 6):

$$p_r = \frac{1}{2}\left(\frac{\mathbf{r}}{r} \cdot \mathbf{p} + \mathbf{p} \cdot \frac{\mathbf{r}}{r}\right) . \tag{6.7}$$

We prove as Exercise 6.1.1 that p_r is the canonical-conjugate momentum to the spherical coordinate r,

$$[r, p_r]_- = i\,\hbar\,, \tag{6.8}$$

which has in the position representation the following form:

$$p_r = \frac{\hbar}{i}\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) = \frac{\hbar}{i}\,\frac{1}{r}\,\frac{\partial}{\partial r}\,r\,. \tag{6.9}$$

It is a Hermitian operator if one allows only for such functions $\psi(\mathbf{r})$ which fulfill the following two conditions (Exercise 6.1.1):

$$\lim_{r \to 0} r\,\psi(\mathbf{r}) = 0\,, \tag{6.10}$$

$$\lim_{r \to \infty} r\,\psi(\mathbf{r}) = 0\,. \tag{6.11}$$

The second requirement is trivially fulfilled by square integrable wave functions. (6.10) is somewhat more stringent. For this reason, the operator p_r is in the strict sense **not** an observable, because the eigen-value problem of p_r has no solution in the Hilbert space of the wave functions, which fulfill (6.10) and (6.11) (see Exercise 6.1.3).

When we build according to (6.9) the square of the radial momentum,

$$\begin{aligned} p_r^2 &= -\hbar^2 \left(\frac{\partial}{\partial r} + \frac{1}{r}\right)\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) \\ &= -\hbar^2 \left(\frac{\partial^2}{\partial r^2} - \frac{1}{r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\right) \\ &= -\hbar^2 \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) = -\hbar^2 \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) , \end{aligned} \tag{6.12}$$

then the comparison with (6.3) and (6.4) leads to the **operator identity**,

$$\mathbf{p}^2 = p_r^2 + \frac{\mathbf{L}^2}{r^2} \qquad (r \neq 0) , \tag{6.13}$$

which is independent of the special potential, and can be also derived directly from the representation-independent definitions of p_r and $\mathbf{L}$ (Exercise 6.1.2). With (6.13) the **Hamilton operator** of the particle in the central field now reads:

$$H = \frac{1}{2m}\left(p_r^2 + \frac{1}{r^2}\mathbf{L}^2\right) + V(r) \qquad (r \neq 0) . \tag{6.14}$$

This expression strongly reminds of the energy law of Classical Mechanics ((2.260), Vol. 1), which can be broken down completely analogously. The kinetic energy consists of a radial *translation energy* $p_r^2/2m$ and a *rotation energy* $\mathbf{L}^2/2m\,r^2$. The term $m\,r^2$ is identical to the moment of inertia with respect to the origin of coordinates. Additionally we still have the potential energy $V(r)$.

The goal consists, also in the case of the central potentials, of solving the **time-independent Schrödinger equation**, i.e., seeking out the eigen-values and the eigen-states of the Hamilton operator:

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\mathbf{L}^2}{2m\,r^2} + V(r)\right]\psi(\mathbf{r}) = E\,\psi(\mathbf{r}) . \tag{6.15}$$

However, we can accept as solutions only those wave functions which fulfill the condition (6.10). (6.15) is equivalent to the Schrödinger equation $H\,\psi = E\,\psi$ only for these functions in the **entire** space, the critical point $r = 0$ included. For the practical solution of (6.15) the fact is helpful that because of (6.6) $\psi(\mathbf{r})$ must be simultaneous eigen-function of H, $\mathbf{L}^2$ and L_z. Since the angle contribution in (6.15) is exclusively due to $\mathbf{L}^2$, the following **separation ansatz** appears to be promising:

$$\psi(\mathbf{r}) = R(r)\,Y_{lm_l}(\vartheta,\varphi) . \tag{6.16}$$

The $Y_{lm_l}(\vartheta,\varphi)$ are the spherical harmonics, introduced in Sect. 5.1.6 as common eigen-functions of $\mathbf{L}^2$ and L_z. There is therefore of course no need to determine them, instead they can be presumed to be known:

$$\begin{aligned} \mathbf{L}^2\,Y_{lm_l}(\vartheta,\varphi) &= \hbar^2 l(l+1)\,Y_{lm_l}(\vartheta,\varphi) , \\ L_z\,Y_{lm_l}(\vartheta,\varphi) &= \hbar\,m_l\,Y_{lm_l}(\vartheta,\varphi) . \end{aligned}$$

Using the ansatz (6.16) in (6.15) we can replace the operator $\mathbf{L}^2$ by its eigenvalue $\hbar^2 l(l+1)$ and subsequently divide the equation by $Y_{lm_l}(\vartheta, \varphi)$. What is left is a differential equation for $R(r)$, which is referred to as the *radial equation*:

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\frac{\hbar^2 l(l+1)}{2m\,r^2}+V(r)\right] R(r) = E\,R(r)\ . \tag{6.17}$$

We see that the *magnetic quantum number* m_l does not appear anywhere. The resulting eigen-energies E will thus be in any case, i.e., for any arbitrary central field, $(2l+1)$-fold degenerate, corresponding to the number of possible m_l-values (5.63). As a rule, however, they will depend on the quantum number l. The **Coulomb potential** ($\sim 1/r$), however, represents an exception because the related energy levels are degenerate even with respect to l (*accidental degeneracy*, see Sect. 6.2).

In some cases it is still recommendable to substitute,

$$u(r) = r\,R(r)\ , \tag{6.18}$$

so that, because of

$$\frac{d^2}{dr^2}\,(r\,R(r)) = \frac{d}{dr}\,(R(r)+r\,R'(r)) = 2R'(r)+r\,R''(r)\ ,$$

the radial equation (6.17) becomes a formally simple, one-dimensional Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}+V_{\text{eff}}(r)\right] u(r) = E\,u(r)\ , \tag{6.19}$$

which describes a particle of mass m in the *effective central potential*

$$V_{\text{eff}}(r) = V(r)+\frac{\hbar^2 l(l+1)}{2m\,r^2}\ . \tag{6.20}$$

One denotes the second summand as *centrifugal barrier*, which is in any case repulsive, and which decreases quadratically with the distance from the center of force (Fig. 6.1).

The structure of the *effective* potential deviates in general rather drastically from the *true* potential. The concept of the *effective* potential in connection with central-force problems has proven to be useful also in Classical Mechanics. With this effective potential, the energy law for the three-dimensional motion got mathematically the same structure as that of the always integrable one-dimensional motion. The effective central potential ((2.255), Vol. 1) thereby had just the form (6.20), where only $\hbar^2 l(l+1)$ is of course to be replaced by the classical square of the angular momentum $\mathbf{L}^2 = \text{const}$.

The condition (6.10) for solving for the wave function $\psi(\mathbf{r})$ transfers with (6.16) and (6.18) to $u(r)$ in the form:

$$u(0) = 0\ . \tag{6.21}$$

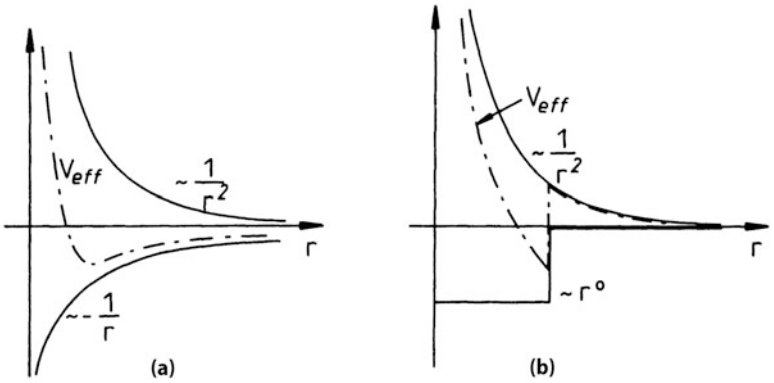

Figure 6.1: Two examples for the r-dependence of effective central potentials: **(a):** Coulomb potential; **(b):** well potential

Furthermore, $\psi(\mathbf{r})$ has to be square integrable, at least for bound states. Because of (5.103),

$$\int d\Omega |Y_{lm_l}(\vartheta,\varphi)|^2 = 1 \ ,$$

this means for $u(r)$:

$$\int d^3r |\psi(\mathbf{r})|^2 = \int_0^\infty dr\, r^2 |R(r)|^2 = \int_0^\infty dr |u(r)|^2 < \infty \ . \tag{6.22}$$

This condition, which is sharper than (6.11), requires that $|u(r)|$ approaches zero for $r \to \infty$ stronger than $1/\sqrt{r}$.

With the important boundary condition (6.21), the eigen-value problem (6.19) obviously becomes completely equivalent to the solution of a **one-dimensional** Schrödinger equation with the potential:

$$\widehat{V}(q) = \begin{cases} V_{\text{eff}}(q) & \text{for } q > 0 \ , \\ \infty & \text{for } q \le 0 \end{cases} \tag{6.23}$$

Many of the statements, derived in Chap. 4 (Vol. 6) for one-dimensional potential problems, can therefore be directly adopted.

6.1.2 Structure of the Solution

Before discussing in detail some special and concrete central potentials, we try to provide ourselves a first, a general overview of the structures of the solutions to be expected. We want to presume, though, that the potential rapidly vanishes at infinity, at least like $1/r$, and is at the zero point either regular or maybe

divergent, but weaker than $-1/r^2 \to -\infty$. For all $0 < r < \infty$, $V(r) \leq 0$:

$$\begin{aligned} \lim_{r \to \infty} r\, V(r) &= 0 \qquad \text{(or const)}\,, \\ \lim_{r \to 0} r^2 V(r) &= 0\,. \end{aligned} \tag{6.24}$$

For the most of the central potentials interesting to us, these are realistic assumptions. The oscillator potential $c\, r^2$, however, drops out. Because of the first condition, due to our general considerations in Sect. 4.1 (Vol. 6), we have to expect for $E > 0$ a continuous spectrum. Bound states with discrete energy-eigen values can appear only for $E < 0$.

1. *Behavior for* $r \to 0$

   In the effective potential (6.20) for $r \to 0$, because of (6.24), the centrifugal term dominates, so that we have to solve approximately, instead of (6.19), the following differential equation:

   $$\left(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} \right) u(r) = 0\,.$$

   This has two linearly independent solutions:

   $$u_1(r) \sim r^{l+1}\,; \qquad u_2(r) \sim r^{-l}\,.$$

   With $u_2(r)$, however, the boundary condition (6.21) cannot be fulfilled for $l > 0$. This solution therefore drops out (*irregular* solution). Even for $l = 0$ $u_2(r)$ is unusable, because then the corresponding wave function ($\psi(\mathbf{r}) \sim (1/r)\, u(r)$) would contain a $1/r$-term, by which, because of $\Delta(1/r) = -4\pi\, \delta(\mathbf{r})$ ((1.69), Vol. 3), the Schrödinger equation might not be satisfiable. There remains therefore what is called the *regular solution*:

   $$r \to 0 \;:\quad u(r) \sim r^{l+1}\,. \tag{6.25}$$

2. *Behavior for* $r \to \infty$

   In this case the full effective potential becomes negligible, and (6.19) simplifies to:

   $$\left(\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + E \right) u(r) = 0\,.$$

   With the abbreviation

   $$\kappa^2 = \frac{2m}{\hbar^2}\,(-E) \tag{6.26}$$

   we get the two linearly independent solutions:

   $$u_1(r) \sim e^{-\kappa r}\,; \quad u_2(r) \sim e^{+\kappa r}\,.$$

   According to our assumptions (6.24) for the potential $V(r)$, bound states can be expected only for $E < 0$. κ is then positive-real, and $u_2(r)$ diverges

for $r \to \infty$. The solution $u_2(r)$ thus violates the normalization condition (6.22):

$$r \to \infty \; : \quad u(r) \sim e^{-\kappa r} \qquad (E < 0) \; . \tag{6.27}$$

For bound states ($E < 0$) the two asymptotic solutions (6.25) and (6.27) suggest the following **ansatz** for the complete solution:

$$u(r) = e^{-\kappa r} \, r^{l+1} \, P(r) \; , \tag{6.28}$$

$$P(r) = \sum_{\mu} \alpha_\mu \, r^\mu \; . \tag{6.29}$$

We will come back to this ansatz in the next section when we treat the Coulomb potential. Thereby it will have to be investigated, in particular, whether or not the series $P(r)$ terminates after a finite number of terms. The argumentation will refer to the *Sommerfeld's polynomial method*, which we have introduced in Sect. 4.4.5 (Vol 6) in connection with the discussion of the harmonic oscillator.

For $E > 0$ the wave function can no longer be normalized in the strict sense. It exhibits an oscillatory behavior (Sect. 4.1, Vol. 6: *classically allowed* region up to $r \to \infty$). The correct complete solution must be found, as performed several times in Chap. 4 (Vol. 6), by *continuous fitting* to the for $r \to 0$ regular solution (6.25).

6.1.3 Exercises

Exercise 6.1.1
The classical definition of the *radial momentum*

$$p_r^{\rm cl} = \frac{1}{r} \, (\mathbf{r} \cdot \mathbf{p})$$

has to be *symmetrized* for the transition to Quantum Mechanics because of the non-commutability of the operators $\mathbf{r}$ and $\mathbf{p}$:

$$p_r = \frac{1}{2} \left(\frac{\mathbf{r}}{r} \cdot \mathbf{p} + \mathbf{p} \cdot \frac{\mathbf{r}}{r} \right) \; .$$

1. Show that the radial momentum can be written as:

$$p_r = \frac{\hbar}{i} \left(\frac{\partial}{\partial r} + \frac{1}{r} \right) = \frac{\hbar}{i} \, \frac{1}{r} \, \frac{\partial}{\partial r} \, r \; .$$

2. Verify that p_r is the canonical-conjugate momentum to $r = |\mathbf{r}|$.

3. Show that p_r is Hermitian. Which conditions must then be fulfilled by the wave functions?

Exercise 6.1.2
Verify, by using the general definitions of the orbital angular momentum $\mathbf{L}$ and the radial momentum p_r,

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \; ; \quad p_r = \frac{1}{2} \left[\frac{1}{r} (\mathbf{r} \cdot \mathbf{p}) + (\mathbf{p} \cdot \mathbf{r}) \frac{1}{r} \right] ,$$

the following operator identities:

1. $\mathbf{L}^2 = i\,\hbar\,(\mathbf{r} \cdot \mathbf{p}) + \mathbf{r}^2\mathbf{p}^2 - (\mathbf{r} \cdot \mathbf{p})^2$,
2. $p_r = \dfrac{1}{r}\,(\mathbf{r} \cdot \mathbf{p}) + \dfrac{\hbar}{i}\,\dfrac{1}{r}$,
3. $\mathbf{p}^2 = p_r^2 + \dfrac{1}{r^2}\,\mathbf{L}^2$.

Exercise 6.1.3
Give reasons why the radial momentum p_r can not be interpreted as observable. For this purpose investigate the eigen-value problem of the operator p_r.

Exercise 6.1.4

1. Prove the following assertion:

   If H is a Hamilton operator with a discrete spectrum, bounded below, then the state $|\psi\rangle$, which makes the expectation value

   $$\langle H \rangle = \langle \psi | H | \psi \rangle$$

   minimal, is just the eigen-state of H with the lowest eigen-value.

2. A particle moves in a central potential. The bounded eigen-states are distinguished by the quantum number l of the orbital angular momentum. Let E_l^* be the minimal eigen-value for a fixed l. With the use of part 1. show that for $l_1 < l_2$, $E_{l_1}^* < E_{l_2}^*$ is always valid.

6.2 Coulomb Potential (H-Atom)

After our general considerations on the central potential we will now investigate, as a first concrete application, the stationary states of an electron in the Coulomb potential. For this purpose we insert into the Hamilton operator (6.5) and into the radial equation (6.17) or (6.19), explicitly the potential energy:

$$V(r) = -\frac{Z\,e^2}{4\pi\,\varepsilon_0\,r} \; . \tag{6.30}$$

e is the elementary charge. For $Z = 1$ (nucleus = single positively charged proton) we have the situation of the **hydrogen atom**, and for $Z > 1$ that of the so-called **hydrogen-like ions** (He^+, Li^{++}, ...), which also possess only

one electron. We assume, at first, that the atomic nucleus is, as positive point charge ($q = Z\,e$), *at rest*, at the origin of coordinates. In the form of (6.30), the Coulomb potential fulfills all pre-conditions, which we used in Sect. 6.1.2 for the general discussion of the *solution structure*. In particular, *bound states* can be expected only for $E < 0$. We are going to investigate these states in the following section!

6.2.1 Discrete Energy Spectrum

We disregard, at first, the spin of the electron. Since the Hamilton operator (6.5) does not contain any spin-dependent terms, the resulting wave function will anyway factorize into a spin and a spatial part, where the spin part can be assumed to be known according to the considerations in Sect. 5.2.4.

Following our pre-considerations in Sect. 6.1 we are obliged to solve the following radial equation (m_e: electron mass):

$$\left[-\frac{\hbar^2}{2m_e}\,\frac{d^2}{dr^2} - \frac{Z\,e^2}{4\pi\varepsilon_0 r} + \frac{\hbar^2 l(l+1)}{2m_e\,r^2} - E\right] u(r) = 0\,. \tag{6.31}$$

This corresponds to (6.19) with (6.30) for $V(r)$. The notation is of course the same as in the preceding section. A scale transformation is recommendable:

$$\rho = Z\,\frac{r}{a_\mathrm{B}}\,; \quad a_\mathrm{B} = \frac{4\pi\,\varepsilon_0\hbar^2}{m_e\,e^2} = 0.529\,\text{Å}\,. \tag{6.32}$$

a_B is the *Bohr radius*, which can be considered as the typical atomic length scale. The corresponding characteristic energy scale is the **Rydberg energy** (1.118):

$$E_\mathrm{R} = \frac{\hbar^2}{2m_e\,a_\mathrm{B}^2} = \frac{m_e\,e^4}{2\hbar^2(4\pi\,\varepsilon_0)^2} = 13.605\,\text{eV}\,. \tag{6.33}$$

We multiply the differential equation (6.31) by

$$\frac{2m_e\,a_\mathrm{B}^2}{Z^2\,\hbar^2} = \frac{1}{Z^2\,E_\mathrm{R}}$$

and further write for abbreviation with κ from (6.26):

$$\eta = \frac{1}{Z}\,\kappa\,a_\mathrm{B} = \frac{1}{Z}\,\sqrt{-\frac{E}{E_\mathrm{R}}} \qquad (E < 0)\,. \tag{6.34}$$

This yields the following equation:

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho} - \frac{l(l+1)}{\rho^2} - \eta^2\right] u(\rho) = 0\,. \tag{6.35}$$

For the moment we are interested only in the discrete spectrum ($E < 0$). η is therefore positive-real. Our reflections in Sect. 6.1.2 on the asymptotic behavior of the solution function u make the following ansatz to be promising:

$$u(\rho) = e^{-\eta\rho}\,\rho^{l+1}\,P(\rho)\,. \tag{6.36}$$

Our further procedure now corresponds literally to the **Sommerfeld's polynomial method**, introduced in Sect. 4.4.5 (Vol. 6) for the case of the harmonic oscillator. In the first step we transform (6.35) with (6.36) into a differential equation for $P(\rho)$:

$$P''(\rho) + 2P'(\rho)\left(\frac{l+1}{\rho} - \eta\right) + P(\rho)\,\frac{2}{\rho}\,[1 - \eta(l+1)] = 0\,. \tag{6.37}$$

Into this expression we insert the ansatz

$$P(\rho) = \sum_{\mu=0}^{?} \alpha_\mu\,\rho^\mu \tag{6.38}$$

and sort the individual terms according to powers of ρ. That leads after simple manipulations to:

$$\sum_{\mu=0}^{?} \{\alpha_{\mu+1}\,(\mu+1)\,[\mu + 2(l+1)] + 2\alpha_\mu\,[1 - \eta(\mu + l + 1)]\}\,\rho^{\mu-1} = 0\,.$$

This relation, in turn, can be fulfilled only when each summand by itself vanishes. This yields the following recursion formula for the coefficients α_μ:

$$\alpha_{\mu+1} = 2\,\frac{\eta(l+\mu+1) - 1}{(\mu+1)\,(\mu+2l+2)}\,\alpha_\mu\;; \quad \mu = 0, 1, 2, \ldots \tag{6.39}$$

In the next step we check whether we can consider $P(\rho)$ in (6.38) as an **infinite** series with the so determined coefficients α_μ, without violating thereby elementary boundary conditions for $u(\rho)$ such as (6.21) and (6.22). That (6.21): $u(0) = 0$ is fulfilled, is already guaranteed by the ansatz (6.36). The normalization condition (6.22) in this connection is more problematic. Just like for the harmonic oscillator (Sect. 4.4.5, Vol. 6), we therefore test at first the asymptotic behavior of $P(\rho)$. The high powers of ρ dominate for $\rho \to \infty$. The corresponding coefficients can, according to (6.39), be represented to a good approximation by

$$\frac{\alpha_{\mu+1}}{\alpha_\mu} \approx \frac{2\eta}{\mu}\;; \quad \mu \gg l, 1\,.$$

The same inspection we perform for the exponential function,

$$e^{2\eta\rho} = \sum_{\mu=0}^{\infty} \frac{(2\eta)^\mu}{\mu!}\,\rho^\mu \equiv \sum_{\mu=0}^{\infty} \beta_\mu\,\rho^\mu\;,$$

and find that it exhibits the same asymptotic behavior of its coefficients:

$$\frac{\beta_{\mu+1}}{\beta_\mu} = \frac{2\eta}{\mu+1} \underset{\mu \gg 1}{\longrightarrow} \frac{2\eta}{\mu}\,.$$

From that we conclude that, in the case of a non-terminating series $P(\rho)$, for $\rho \to \infty$ the series would proceed like exp $(2\eta\,\rho)$. But then, however, according to (6.36),

$$u(\rho) \underset{\rho\to\infty}{\sim} e^{\eta\rho}\,\rho^{l+1} \qquad (\eta > 0)$$

would no longer be normalizable, because $u(\rho)$ has to, at infinity, drop to zero stronger than $1/\sqrt{\rho}$. This problem enforces the conclusion that $P(\rho)$ cannot contain arbitrarily many summands, but instead has to terminate at a **finite** $\mu = \mu_0$. Then for $\rho \to \infty$, the exponential function dominates in the ansatz (6.36) and takes care for the correct asymptotic behavior. The recursion formula (6.39), however, now makes it clear that such a truncation of the series $P(\rho)$,

$$\alpha_{\mu_0} \neq 0\,; \quad \alpha_{\mu_0+1} = \alpha_{\mu_0+2} = \ldots = 0\,,$$

at a finite μ_0 is possible only for very definite η-values:

$$\eta \overset{!}{=} \frac{1}{\mu_0 + l + 1}\,. \tag{6.40}$$

This transfers, according to (6.34), to the eigen-energies E, which thus build a **discrete spectrum**. The so-called *radial quantum number* μ_0, like the quantum number of the orbital angular momentum l, is of course an integer ($\mu_0 = 0, 1, 2, \ldots$). This holds then also for the whole denominator in (6.40), which for a given l can pass through the values

$$n \equiv \mu_0 + l + 1 = l + 1,\, l + 2, \ldots\,. \tag{6.41}$$

It has become conventional to use for the indexing of the energy levels primarily the

principal quantum number

$$n = 1, 2, 3, \ldots \tag{6.42}$$

We then get with (6.40) and (6.34) for the energy levels the important result:

$$E_n = -\frac{Z^2\,E_\mathrm{R}}{n^2}\,; \qquad n = 1, 2, 3, \ldots \tag{6.43}$$

Between the **ground-state energy**

$$E_1 = -Z^2\,E_\mathrm{R} \tag{6.44}$$

and $E = 0$ there are countably infinitely many discrete energies E_n, where the distances between neighboring levels become smaller and smaller with increasing principal quantum number. They accumulate at $E = 0$.

The eigen-energies E_n depend only on n, but not on the

secondary (orbital angular momentum) quantum number

$$l = 0, 1, 2, \ldots, n-1 \tag{6.45}$$

which for a fixed n can take, according to (6.41), one of the listed values. All states with different l, but the same n, have the same energy. This degeneracy with respect to l is a peculiarity of the Coulomb potential, and is not observed for other central potentials. It vanishes, by the way, already for smallest deviations of the Coulomb potential from the pure $1/r$-form (see Exercise 6.2.2). Sometimes one speaks therefore of *accidental degeneracy*, because there is apparently no compelling physical reason. The degeneracy with respect to the

magnetic quantum number

$$m_l = -l, -l+1, \ldots, l-1, l \ , \tag{6.46}$$

however, is typical for all central potentials. When we still add that the electron has two different possibilities for the spin orientation ($m_s = \pm(1/2)$), which are also degenerate in the Coulomb field, then the **total degree of degeneracy** g_n of the energy level E_n amounts to:

$$g_n = 2 \sum_{l=0}^{n-1} (2l + 1) = 2n^2 \ . \tag{6.47}$$

The Quantum Theory therefore provides, without any additional postulate, simply from the requirement of physically reasonable solutions of the Schrödinger equation (unique, normalizable, ...), the classically incomprehensible quantization of the energy. In particular, the existence of a finite ground-state energy E_1 for the atomic electron has been substantiated. Classically, arbitrarily low energies would be thinkable, at least in principle, because of $V(r) \underset{r \to 0}{\longrightarrow} -\infty$.

Let us add some further **discussion remarks**. For a complete evaluation and interpretation of the results of this section, however, we have to refer the reader to the special literature on atomic physics.

1) Term scheme

The hydrogen spectrum (Fig. 6.2), following from (6.43) with $Z = 1$, is completely consistent with the semi-classical Bohr theory (Sect. 1.5.2, Vol. 6). The principal quantum number n defines an *electron shell*, for which, first and foremost in X-ray spectroscopy, the following notation is conventional:

$$\begin{aligned} n &= 1: \quad \text{K-shell}, \\ n &= 2: \quad \text{L-shell}, \\ n &= 3: \quad \text{M-shell}, \\ n &= 4: \quad \text{O-shell}. \end{aligned}$$

This is different from the classification of the **(s, p, d, f, ...)-orbitals**, introduced at the end of Sect. 5.1.6, which differ from each other by the secondary quantum number $l = (0, 1, 2, 3, \ldots)$.

Transitions between the various energy levels explain the **spectral series**, already discussed in Chap. 1 (Vol. 6), (Lyman ((1.98), Vol. 6), Balmer ((1.99),

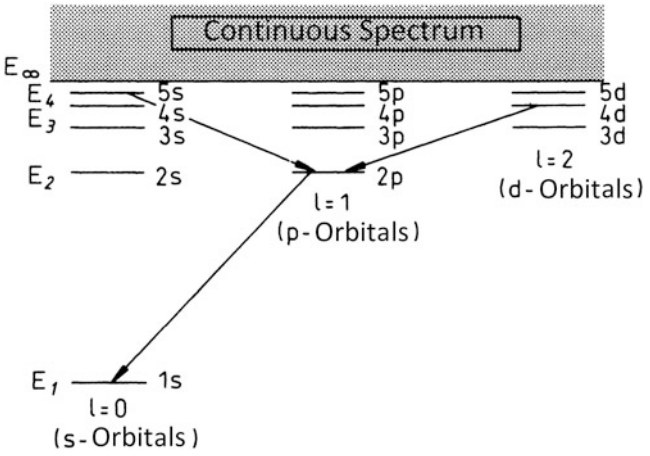

Figure 6.2: Schematic representation of the energy spectrum of the hydrogen atom

Vol. 6), Paschen ((1.100), Vol. 6), Brackett ((1.101), Vol. 6)). The **Ritz's combination principle** ((1.102), Vol. 6), which was at first postulated on the basis of experimental facts, turns out to be exact. At the transition of the electron in the H-atom from an energetically higher to an energetically lower level, the energy difference is emitted in form of a light quantum (photon) of the energy

$$h\,\nu_{nm} = -E_{\mathrm{R}}\left(\frac{1}{n^2} - \frac{1}{m^2}\right) .$$

Vice versa, the atom can of course also absorb a corresponding light quantum. The electron is thereby elevated into an energy-richer level, and the atom is then in an *excited state*.

Of course, the electron will not leave a *stationary state* without being forced to do that. It must somehow be *disturbed*. In this connection, however, we will restrict ourselves only to the remark that for light emission and light absorption, respectively, this disturbance is caused by the coupling of the electron charge to the electromagnetic field, known from Electrodynamics.

2) Fine structure

The quantum-mechanical theory of the hydrogen atom, which we developed in this section, comes out in remarkably excellent agreement with experiment, but it is not yet really exact. It is a non-relativistic theory, which is therefore unable to explain the *fine structure* of the energy terms. The latter is mainly caused by the **spin-orbit interaction** found in Sect. 5.3.4, which we have got to know as purely relativistic effect. As we could estimate with (5.259), it is a very small, nevertheless measurable correction of the order of magnitude $E_n/m\,c^2 \approx 10^{-4} - 10^{-5}$. The spin itself of course does not appear in the

non-relativistic Quantum Mechanics. We had to justify its existence in Sect. 5.3 with the aid of the relativistic Dirac-theory.

A further order of magnitude smaller, but also measurable with the today spectroscopic facilities, is the *hyperfine structure* which results from an interaction between electron spin and the spin of the nucleus. Furthermore, the corrections are due to the fact that the assumption of an atomic nucleus *at rest* at the origin of coordinates, strictly speaking, is of course no longer tenable. The *hydrogen problem* is, as a matter of course, a *two-body problem*. The modifications due to the co-motion of the nucleus are, however, not typically of quantum-mechanical nature. We have discussed them already in connection with the semi-classical Bohr atom theory in Chap. 1 (Vol. 6). The main point is simply to replace in the above formulas the bare electron mass m_e by the *reduced mass* $\mu = (m_e\, M)/(m_e + M)$, where M is the mass of the nucleus. We will inspect the two-body problem separately once more in Sect. 6.2.5.

3) Multiple-electron atoms

Multiple-particle systems are the matter of the considerations in Chap. 8. Here, to begin with, we want to present only a few qualitative remarks. Because of the electron-electron interaction, the potential, to which a single electron is subjected, is of course not a pure $1/r$-potential. The *accidental degeneracy* with respect to the secondary quantum number l will in any case be removed. The degeneracy with respect to m_l is, however, lifted only when the spherical symmetry is disturbed, e.g., by external magnetic fields. As a general rule, however, the l-splitting remains small compared to the level splitting given by (6.43), so that the term scheme maintains essentially its structure. The so-called *central field approximation* represents a useful starting point for the theoretical treatment of the multiple-electron atom, which simulates the complicated electron-electron interactions together with the $1/r$-Coulomb potential of the nucleus by an effective central potential $V_{\text{eff}}(r)$ (*Hartree potential*, Sect. 7.1.3). The electrons then move in this effective field practically independent of each other. According to the **Pauli principle**, explicitly introduced only in Chap. 8, each resulting energy state is occupied by at most one electron. The ground state of a Z-electron system then corresponds to the situation where the Z electrons are distributed over the Z energetically lowest energy levels.

4) Periodic table

The periodic table is better understandable now, on the basis of the in the meantime known shell-structure of the electronic states in the atoms, together with the at present still anticipated Pauli principle, than the picture of Chap. 1 (Vol. 6), which was based on *pre-quantum-mechanical*, semi-classical theories. In a *period* of the periodic table the atomic number Z increases by 1 from element to element (*from the left to the right*) and therewith the number of orbital electrons, up to $2n^2$ steps until the n-the shell is completely filled. Therewith, $2n^2$ is exactly the number of elements per period. Completely filled electron shells

are distinguished by spherically symmetric charge distributions which prove to be especially stable against external disturbances. The physical-chemical properties of the elements are therefore almost exclusively determined by the electrons in the outermost, not completely filled shells. That explains why the properties of the elements, ordered in the periodic table one below the other in a *column*, are so similar. All elements within such a column have the same number of electrons in the *not closed*, outermost shell. That this principle of construction is interrupted at certain positions of the periodic table (transition elements, rare earths, ...) has special reasons. To understand the deep connection, we have to refer to the special literature of atomic physics.

6.2.2 Eigen-Functions of the Bound States

We now want to look at the eigen-functions which belong to the spectrum (6.43). Thereby we already know that the series $P(\rho)$ in the ansatz (6.36) terminates at a finite μ_0:

$$P(\rho) = \sum_{\mu=0}^{\mu_0} \alpha_\mu \, \rho^\mu \; ; \quad \mu_0 = n - (l+1) \; . \tag{6.48}$$

The coefficients α_μ are determined by the recursion formula (6.39), which can be reformulated with $\eta = 1/n$ as follows:

$$\begin{aligned} \alpha_{\mu+1} &= -\frac{2}{n} \, \frac{n-(l+\mu+1)}{(\mu+1)\,(\mu+2l+2)} \, \alpha_\mu \\ &= \left(-\frac{2}{n}\right)^{\mu+1} \alpha_0 \left[\frac{n-(l+\mu+1)}{(\mu+1)\,(\mu+2l+2)} \cdot \frac{n-(l+\mu)}{\mu(\mu+2l+1)} \cdots \frac{n-(l+1)}{2l+2} \right] . \end{aligned}$$

From this one reads off:

$$\alpha_\mu = \alpha_0 \, (-1)^\mu \left(\frac{2}{n}\right)^\mu \frac{(2l+1)!\,(n-(l+1))!}{\mu!\,(\mu+2l+1)!(n-(l+\mu+1))!} \; .$$

α_0 remains, at first, undetermined. The homogeneous differential equation (6.37) fixes $P(\rho)$ of course only up to a constant factor, by which we will later fulfill the normalization condition of the resulting wave function. When we recall the definitions (6.32) and (6.34) of ρ and η, respectively,

$$\eta \, \rho = \frac{r \, Z}{n \, a_{\mathrm{B}}} = \kappa \, r \; , \tag{6.49}$$

we can write for the polynomial $P(r)$:

$$P(r) = \alpha_0 \sum_{\mu=0}^{n-(l+1)} (-1)^\mu \, (2\kappa \, r)^\mu \, \frac{(2l+1)!(n-(l+1))!}{\mu!(\mu+2l+1)!(n-(l+\mu+1))!} \; . \tag{6.50}$$

Let us recall once more the *'mathematically somewhat sloppy'* way of writing, which we agreed upon, namely, to use for functions, even after substitution

of variables, the same letter (here: $P(\rho) \to P(r)$), as long as there are no misinterpretations. The sum on the right-hand side of (6.50) is, except of a constant factor, just the *associated Laguerre polynomial*,

$$L_p^k(z) = (-1)^k \sum_{\mu=0}^{p-k} (-1)^\mu \frac{(p!)^2}{(p-k-\mu)!\,(k+\mu)!\,\mu!}\, z^\mu \,, \tag{6.51}$$

for $p = n + l$ and $k = 2l + 1$. In the next subsection we will gather some properties of the Laguerre polynomials, which are extensively discussed in the mathematical textbooks. Here we will, however, at first, follow through the just started line of thought. The sought-after radial function is with

$$P(r) \sim L_{n+l}^{2l+1}(2\kappa r)$$

as well as the ansatzes (6.18) and (6.28) already determined except for a constant:

$$R_{nl}(r) = D_{nl}\, e^{-\kappa r}\, (2\kappa r)^l\, L_{n+l}^{2l+1}(2\kappa r) \,. \tag{6.52}$$

Since $R_{nl}(r)$ has to fulfill (6.22),

$$\int_0^\infty dr\, r^2 |R_{nl}(r)|^2 = 1 \,, \tag{6.53}$$

we can fix D_{nl} via the normalization integral of the Laguerre polynomials, which we take over here, without proof, from mathematics literature:

$$\int_0^\infty dz\, z^{k+1}\, e^{-z}\, \left[L_p^k(z)\right]^2 = \frac{(2p-k+1)\,(p!)^3}{(p-k)!} \,. \tag{6.54}$$

The normalization condition (6.53) reads, if we assume the D_{nl} to be real:

$$1 = \frac{D_{nl}^2}{(2\kappa)^3} \int_0^\infty dz\, e^{-z}\, z^{2l+2}\, \left[L_{n+l}^{2l+1}(z)\right]^2 \,.$$

It follows with (6.54):

$$D_{nl} = \pm \left(\frac{Z}{a_\mathrm{B}}\right)^{3/2} \frac{2}{n^2 (n+l)!} \sqrt{\frac{(n-l-1)!}{(n+l)!}} \,. \tag{6.55}$$

With the separation ansatz (6.16) we have now found with (6.52) and (6.55) the complete system of eigen-functions of the bound states ($E < 0$) for the Coulomb potential:

$$\begin{aligned} \psi_{nlm_l}(\mathbf{r}) &= D_{nl} \exp\left(-\frac{Z\,r}{n\,a_\mathrm{B}}\right) \left(\frac{2Z\,r}{n\,a_\mathrm{B}}\right)^l L_{n+l}^{2l+1}\left(\frac{2Z\,r}{n\,a_\mathrm{B}}\right) Y_{lm_l}(\vartheta,\varphi) \\ &\equiv R_{nl}(r)\, Y_{lm_l}(\vartheta,\varphi) \,. \end{aligned} \tag{6.56}$$

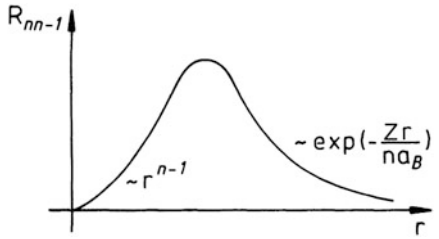

Figure 6.3: Qualitative behavior of the radial function for the case of a maximal secondary quantum number $l = n - 1$

As eigen-functions of a Hermitian operator they are orthogonal; the normalization also we have ensured:

$$\int d^3r\, \psi^*_{n'l'm_{l'}}(\mathbf{r})\, \psi_{nlm_l}(\mathbf{r}) = \delta_{nn'}\, \delta_{ll'}\, \delta_{m_l m_{l'}} \ . \tag{6.57}$$

Because of

$$L^p_p(z) = (-1)^p\, p! \tag{6.58}$$

the radial function exhibits an especially simple structure when the secondary quantum number l takes its maximal value $n - 1$ (Fig. 6.3):

$$R_{n\,n-1}(r) = \mp \left(\frac{2Z}{n\,a_{\mathrm{B}}}\right)^{3/2} \sqrt{\frac{1}{(2n)!}}\, e^{-(Z\,r)/(n\,a_{\mathrm{B}})} \left(\frac{2Z\,r}{n\,a_{\mathrm{B}}}\right)^{n-1} . \tag{6.59}$$

$R_{n\,n-1}(r)$ does not have a zero (Fig. 6.3). Because the associated Laguerre polynomial $L^k_p(z)$ possesses in the region $z > 0 \quad p-k$ zeros, the radial function $R_{nl}(r)$ has $(n-1-l)$ **zeros** on the positive-real r-axis. We choose the positive sign in (6.59).

We show explicitly the first few radial functions, where, according to (6.56), the corresponding spherical harmonics are listed in (5.108)–(5.113):

$$R_{10}(r) = 2 \left(\frac{Z}{a_{\mathrm{B}}}\right)^{3/2} e^{-Z\,r/a_{\mathrm{B}}} , \tag{6.60}$$

$$R_{20}(r) = 2 \left(\frac{Z}{2a_{\mathrm{B}}}\right)^{3/2} \left(1 - \frac{Z\,r}{2a_{\mathrm{B}}}\right) e^{-Z\,r/2a_{\mathrm{B}}} , \tag{6.61}$$

$$R_{21}(r) = \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_{\mathrm{B}}}\right)^{3/2} \frac{Z\,r}{a_{\mathrm{B}}}\, e^{-Z\,r/2a_{\mathrm{B}}} , \tag{6.62}$$

$$R_{30}(r) = 2 \left(\frac{Z}{3a_{\mathrm{B}}}\right)^{3/2} \left(1 - \frac{2Z\,r}{3a_{\mathrm{B}}} + \frac{2(Z\,r)^2}{27a^2_{\mathrm{B}}}\right) e^{-Z\,r/3a_{\mathrm{B}}} , \tag{6.63}$$

$$R_{31}(r) = \frac{4\sqrt{2}}{3} \left(\frac{Z}{3a_{\mathrm{B}}}\right)^{3/2} \frac{Z\,r}{a_{\mathrm{B}}} \left(1 - \frac{Z\,r}{6a_{\mathrm{B}}}\right) e^{-Z\,r/3a_{\mathrm{B}}} , \tag{6.64}$$

$$R_{32}(r) = \frac{2\sqrt{2}}{27\sqrt{5}} \left(\frac{Z}{3a_{\mathrm{B}}}\right)^{3/2} \left(\frac{Z\,r}{a_{\mathrm{B}}}\right)^2 e^{-Z\,r/3a_{\mathrm{B}}} . \tag{6.65}$$

It is a remarkable fact that all radial functions R_{nl} with $l = 0$ (s-states) are unequal zero at $r = 0$, while all R_{nl} with $l > 0$ vanish at this point. That means, in particular, that the electron in the s-state has a finite probability density at the position of the nucleus!

6.2.3 Laguerre Polynomials

Let us briefly interrupt our considerations on the Coulomb potential, in order to list, as an insertion, some properties of the Laguerre polynomials, which we did not meet so far in this ground course of *Theoretical Physics*. The strict mathematical derivations, however, we have to leave, to a large extent, to the special literature of mathematical physics.

The **ordinary Laguerre polynomials** $L_p(z)$ are defined by

$$L_p(z) = e^z \frac{d^p}{dz^p} \left(z^p\, e^{-z}\right) ; \quad p = 0, 1, \dots \ . \tag{6.66}$$

One recognizes that this expression starts with the lowest power $p!z^0$, when one performs the p differentiations on the first factor z^p , and ends with the highest power $(-1)^p z^p$, when the exponential function is p-times differentiated. $L_p(z)$ is thus a polynomial of the degree p. Equivalent to (6.66) there is the representation by the **generating function**:

$$\frac{1}{1-t} \exp\left(-z\,\frac{t}{1-t}\right) = \sum_{p=0}^{\infty} L_p(z)\,\frac{t^p}{p!} \ . \tag{6.67}$$

The **associated Laguerre polynomials** are derived from the ordinary ones by k-fold differentiation:

$$L_p^k(z) = \frac{d^k}{dz^k}\, L_p(z) \ ; \quad k \le p \ . \tag{6.68}$$

One easily verifies (complete induction) with the aid of (6.66):

$$L_p^k(z) = \frac{p!}{(p-k)!}\, e^z\, \frac{d^p}{dz^p} \left(z^{p-k} e^{-z}\right) \ . \tag{6.69}$$

From that immediately follows, in particular, the special case (6.58). $L_p^k(z)$ is a polynomial of $(p-k)$-th degree with just as many zeros on the positive-real axis.

When one differentiates (6.67) with respect to t,

$$\frac{1}{(1-t)^2} \left(1 - \frac{z}{1-t}\right) \exp\left(-z\,\frac{t}{1-t}\right) = \sum_{p=1}^{\infty} L_p(z)\,\frac{t^{p-1}}{(p-1)!} = \sum_{p=0}^{\infty} L_{p+1}(z)\,\frac{t^p}{p!} \ ,$$

and uses for the left-hand side once more (6.67),

$$\sum_{p=0}^{\infty} L_p(z)\,\frac{t^p}{p!}\,(1-t-z) = \sum_{p=0}^{\infty} L_{p+1}(z)\,\frac{t^p}{p!}\,(1-t)^2 \ ,$$

then one obtains by arranging according to powers of t an expression,

$$\sum_{p=0}^{\infty} \frac{t^p}{p!} \left[L_{p+1}(z) - (2p+1-z)\, L_p(z) + p^2\, L_{p-1}(z) \right] = 0 \,,$$

which in this form can be valid only if each summand by itself vanishes. This yields a useful **recursion formula** for the ordinary Laguerre polynomials:

$$L_{p+1}(z) - (2p+1-z)\, L_p(z) + p^2\, L_{p-1}(z) = 0 \,. \tag{6.70}$$

One easily gets a second recursion formula from the definition equation (6.66), if one differentiates this once with respect to z:

$$\frac{d}{dz} L_p(z) = L_p(z) + e^z \frac{d^{p+1}}{dz^{p+1}} (z^p\, e^{-z}) = p\, e^z \frac{d^p}{dz^p} (z^{p-1}\, e^{-z}) \,.$$

It namely follows therewith:

$$\frac{d}{dz} L_p(z) - p \left(\frac{d}{dz} L_{p-1}(z) - L_{p-1}(z) \right) = 0 \,. \tag{6.71}$$

We show in Exercise 6.2.1 that one obtains by combination of the two recursion formulas (6.70) and (6.71) the following **Laguerre differential equation**:

$$\left[z \frac{d^2}{dz^2} + (1-z) \frac{d}{dz} + p \right] L_p(z) = 0 \,. \tag{6.72}$$

This equation has the special peculiarity to change, after a further differentiation with respect to z, into a differential equation of the same kind for the derivative of $L_p(z)$, with only slightly changed coefficients:

$$\left[z \frac{d^2}{dz^2} + (2-z) \frac{d}{dz} + (p-1) \right] \frac{d}{dz} L_p(z) = 0 \,.$$

The procedure can obviously be arbitrarily continued and yields after k-fold differentiation together with (6.68) a **differential equation for the associated Laguerre polynomials**:

$$\left[z \frac{d^2}{dz^2} + (k+1-z) \frac{d}{dz} + (p-k) \right] L_p^k(z) = 0 \,. \tag{6.73}$$

We now will find out that the conditional equation (6.37) for the polynomial $P(\rho)$ is exactly of the type (6.73). To see this we substitute in (6.37)

$$\overline{\rho} = 2\rho\,\eta = 2\kappa\, r$$

and obtain then, at first:

$$4\eta^2\, P''(\overline{\rho}) + 4\eta\, P'(\overline{\rho}) \left(\frac{2\eta(l+1)}{\overline{\rho}} - \eta \right) + P(\overline{\rho})\, \frac{4\eta}{\overline{\rho}} \left[1 - \eta(l+1) \right] = 0 \,.$$

We multiply this equation by $\overline{\rho}/4\eta^2$ and exploit $\eta = 1/n$:

$$\left[\overline{\rho}\,\frac{d^2}{d\overline{\rho}^2} + (2l+2-\overline{\rho})\,\frac{d}{d\overline{\rho}} + (n-l-1)\right] P(\overline{\rho}) = 0\ . \tag{6.74}$$

This differential equation is now indeed, for $k = 2l+1$ and $p = n+l$, identical to (6.73). We have therewith reproduced, in a different way, the **old** solution (6.52):

$$P(\overline{\rho}) \sim L_{n+l}^{2l+1}(\overline{\rho}) = L_{n+l}^{2l+1}(2\kappa\, r)\ .$$

6.2.4 Probabilities, Expectation Values

The probability density of the electron in the volume element d^3r at $\mathbf{r}$ in the case of the Coulomb potential is also of course given by the square of the absolute value of the wave function corresponding to the quantum state n, l, m_l:

$$|\psi_{nlm_l}(\mathbf{r})|^2 d^3r\ .$$

Sometimes it is convenient to introduce a *radial position probability* as the probability to find the particle, independently of the angle, at the distance between r and $r+dr$ from the origin. For this purpose one integrates the *normal* probability density over its angle part:

$$w_{nl}(r)\,dr = r^2\,dr \int_0^\pi \sin\vartheta d\vartheta \int_0^{2\pi} d\varphi |\psi_{nlm_l}(\mathbf{r})|^2 = r^2 dr |R_{nl}(r)|^2\ . \tag{6.75}$$

The zeros of the R_{nl} define spherical surfaces with certain radii, on which the position probability of the electron is zero. These are called *nodal planes*. Their number is identical to the radial quantum number $\mu_0 = n-l-1$. Between these nodal planes $w_{nl}(r)$ has $n-l$ *humps*. For $l = n-1$ (maximal secondary quantum number) the radial position probability does not possess any node. According to (6.59) it behaves like:

$$w_{n\,n-1}(r) \sim r^{2n} \exp\left(-\frac{2\,Z\,r}{n\,a_\mathrm{B}}\right)\ .$$

We obtain the maximum of this special radial distribution by setting the first derivative equal to zero. It is at

$$(r_{n\,n-1})_\mathrm{max} = \frac{n^2\,a_\mathrm{B}}{Z}\ , \tag{6.76}$$

and increases quadratically with the principal quantum number. Classically, the orbital angular momentum L determines the semiminor axes of the elliptic paths. Maximal L leads to circular paths. When one evaluates (6.76) for the ground state ($n = 1$, $l = 0$) of the hydrogen atom ($Z = 1$), then $(r_{10})_\mathrm{max}$ is identical to the Bohr radius a_B. This corresponds to the semi-classical Bohr-theory (Sect. 1.5.2, (Vol. 6)), according to which in the ground state the electron moves on a stationary circular path of the radius a_B.

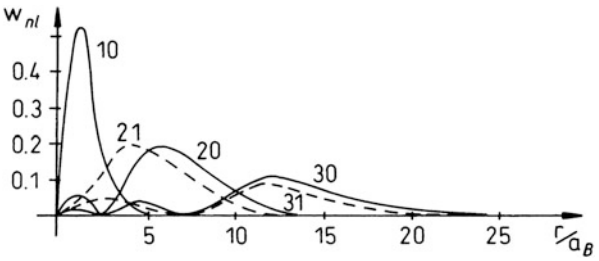

Figure 6.4: Radial probability density of the electron in the hydrogen atom as function of the distance from the nucleus

Figure 6.4 shows some *lower-indexed* radial position probabilities. One recognizes that with increasing n the distributions shift to larger r-values.

The expectation values of some powers of r in the bound states turn out to be rather revealing. They are defined by:

$$\langle r^k \rangle_{nl} = \int_0^\infty dr\, r^{2+k}\, [R_{nl}(r)]^2 \ . \tag{6.77}$$

In this context we derive the rather useful *Kramers relation* as Exercise 6.2.7:

$$\begin{aligned} \frac{k+1}{n^2}\langle r^k\rangle_{nl} - (2k\,+\,1)\,\frac{a_\mathrm{B}}{Z}\langle r^{k-1}\rangle_{nl} \quad &+ \quad \frac{k}{4}\,[(2l+1)^2 - k^2]\,\frac{a_\mathrm{B}^2}{Z^2}\langle r^{k-2}\rangle_{nl} = 0\ , \\ k \quad &+ \quad 2l+1 > 0\ . \end{aligned} \tag{6.78}$$

From this, if one inserts subsequently $k = 0, 1, 2$, one gets:

$$\langle r^{-1}\rangle_{nl} = \frac{Z}{a_\mathrm{B}\, n^2}\ , \tag{6.79}$$

$$\langle r\rangle_{nl} = \frac{a_\mathrm{B}}{2Z}\,[3n^2 - l(l+1)]\ , \tag{6.80}$$

$$\langle r^2\rangle_{nl} = \frac{n^2\, a_\mathrm{B}^2}{2Z^2}\,[5n^2 - 3l(l+1) + 1]\ . \tag{6.81}$$

The *orbit radii* $\langle r\rangle_{nl}$ are of special interest, where the term *path (orbit)* is of course somewhat problematic, because, according to (6.75), the probability density $w_{nl}(r)$ of the electron is, except for the nodal planes, in principle in the entire space unequal zero. The average distance $\langle r\rangle_{nl}$ of the electron from the nucleus increases quadratically with the principal quantum number n, which we already realized in the $w_{nl}(r)$-Fig. 6.4. The decrease proportional to $1/Z$ explains itself by the increasing attractive force of the nucleus with rising Z. For the maximum angular momentum $l = n-1$ it holds in particular:

$$\langle r\rangle_{n\,n-1} = \frac{a_\mathrm{B}}{2Z}\,(2n^2 + n)\ . \tag{6.82}$$

The average value is thus not identical to the maximal value $(r_{n\,n-1})_\mathrm{max}$ in (6.76).

We interpret, as radial uncertainty of the particle position, the **mean square deviation** of the particle-nucleus distance:

$$\Delta r_{nl} \equiv \sqrt{\langle r^2 \rangle_{nl} - \langle r \rangle_{nl}^2} \, .$$

This can be calculated with (6.80) and (6.81):

$$\Delta r_{nl} = \frac{a_\mathrm{B}}{2Z} \sqrt{n^2(n^2+2) - l^2(l+1)^2} \, . \tag{6.83}$$

The mean square deviation for the special case $l = n-1$, corresponding to the classical circular paths,

$$\Delta r_{n\,n-1} = \frac{n\,a_\mathrm{B}}{2Z} \sqrt{2n+1} \, ,$$

grows with n beyond all limits. The relative fluctuation, however, becomes negligible for large n:

$$\frac{\Delta r_{n\,n-1}}{\langle r \rangle_{n\,n-1}} = \frac{1}{\sqrt{2n+1}} \underset{n\to\infty}{\longrightarrow} 0 \, . \tag{6.84}$$

This fits the rule of correspondence (Sect. 1.5.3), according to which for large quantum numbers the classical concept of a path should become acceptable.

By the use of (6.79) it is eventually possible to make an interesting statement on the expectation value of the potential energy in the eigen-states of the Coulomb-Hamilton operator:

$$\langle V \rangle_{nl} = -\frac{Z\,e^2}{4\pi\,\varepsilon_0} \left\langle \frac{1}{r} \right\rangle_{nl} = -\frac{Z\,e^2}{4\pi\,\varepsilon_0} \frac{Z}{a_\mathrm{B}\,n^2} \, .$$

With the definitions (6.32) for the Bohr radius a_B and (6.33) for the Rydberg energy E_R it follows:

$$\langle V \rangle_{nl} = -2\,\frac{Z^2\,\mathrm{E_R}}{n^2} = 2E_n \, . \tag{6.85}$$

Therefore for all stationary states in the Coulomb field, the energy-eigen value E_n is equal to the half of the expectation value of the potential energy. When one still uses $E_n = \langle H \rangle_{nl} = \langle T \rangle_{nl} + \langle V \rangle_{nl}$, then it follows with

$$\langle T \rangle_{nl} = -\frac{1}{2} \langle V \rangle_{nl} \tag{6.86}$$

the analog to the classical virial theorem ((3.39), Vol. 1).

So far we have discussed only the *radial position probability* $w_{nl}(r)$. The angle distribution of the eigen-functions $\psi_{nlm_l}(\mathbf{r})$ is also interesting. In analogy to (6.75) one integrates for this purpose the full probability density $|\psi_{nlm_l}(\mathbf{r})|^2$ with respect to the radial component r:

$$\hat{w}_{lm_l}(\vartheta,\varphi)\,d\Omega = d\Omega \int_0^\infty r^2\,dr |\psi_{nlm_l}(\mathbf{r})|^2 = d\Omega |Y_{lm_l}(\vartheta,\varphi)|^2 \, . \tag{6.87}$$

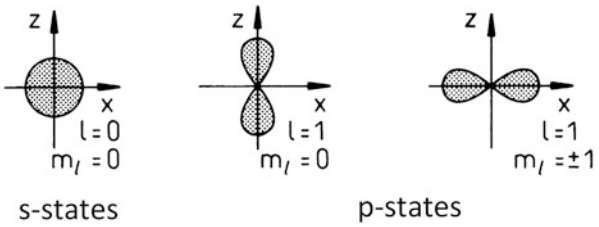

Figure 6.5: Polar diagrams for s- and p-states of the electron in the hydrogen atom as illustration of the angular distribution of the position probability

$d\Omega = \sin\vartheta\, d\vartheta\, d\varphi$ is the solid angle element. In (6.87) we have already exploited the normalization (6.53) of the radial function $R_{nl}(r)$. Because of (5.103) we can also write:

$$\begin{aligned} \hat{w}_{l\,m_l}(\vartheta,\varphi) &= N_{l\,m_l}|P_l^{m_l}(\cos\vartheta)|^2 \equiv \hat{w}_{l\,m_l}(\vartheta)\ , \\ N_{l\,m_l} &= \frac{2l+1}{4\pi}\,\frac{(l-m_l)!}{(l+m_l)!}\ . \end{aligned} \tag{6.88}$$

There is no φ-dependence; the angle distributions are rotational-symmetric around the z-axis! Because of (5.104) it further follows:

$$\hat{w}_{l\,m_l}(\vartheta) = \hat{w}_{l-m_l}(\vartheta)\ . \tag{6.89}$$

For the representation of such angle distributions (probability densities) one uses the so-called *polar diagrams*, in which the quantity $\hat{w}_{l\,m_l}$ is plotted as radius vector.

The **s-states** ($l = 0$, $m_l = 0$) are because of (5.108),

$$\hat{w}_{00}(\vartheta) \equiv \frac{1}{4\pi}\ , \tag{6.90}$$

distinguished by spherical symmetry (Fig. 6.5). There does not exist a corresponding semi-classical Bohr orbit. $l = 0$ would classically mean a straight-line motion through the center of force.

For the **p-states** ($l = 1$, $m_l = 0, \pm 1$) we have because of (5.109) and (5.110):

$$\hat{w}_{10}(\vartheta) = \frac{3}{4\pi}\cos^2\vartheta\ ; \quad \hat{w}_{1\pm1}(\vartheta) = \frac{3}{8\pi}\sin^2\vartheta\ . \tag{6.91}$$

The agreement with the semi-classical *Bohr paths* consists in the fact that these are running for $m_l = \pm 1$ in the xy-plane ($\vartheta = \pi/2$) and for $m_l = 0$ in the zy-plane ($\vartheta = 0$), i.e., there, where $\hat{w}_{1\,m_l}(\vartheta)$ becomes maximal (Fig. 6.5).

For the **d-states** ($l = 2$, $m_l = 0, \pm 1, \pm 2$) we take from ((5.111) to (5.113)):

$$\hat{w}_{20}(\vartheta) = \frac{5}{16\pi}\,(3\cos^2\vartheta - 1)^2\ , \tag{6.92}$$

$$\hat{w}_{2\,\pm1}(\vartheta) = \frac{15}{8\pi}\sin^2\vartheta\cos^2\vartheta\ , \tag{6.93}$$

$$\hat{w}_{2\,\pm2}(\vartheta) = \frac{15}{32\pi}\sin^4\vartheta\ . \tag{6.94}$$

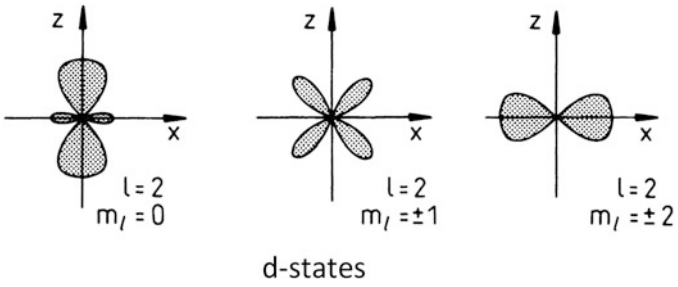

Figure 6.6: Polar diagrams as in Fig. 6.5, but here for d-states

Generally, all the distributions $\hat{w}_{l\,m_l=\pm l}(\vartheta)$ are tightly concentrated around the xy-plane (Fig. 6.6).

At the end, let us recall once more that we have restricted the discussion of the Coulomb potential, so far, exclusively to the case $E < 0$. For $E > 0$ one finds a **continuous energy spectrum**. This one realizes already by inspecting the asymptotic behavior (6.27) of the radial function. For $E > 0$ κ is purely imaginary so that the radial function $R(r) \approx \exp(\pm i|\kappa|r)$ exhibits asymptotically an oscillatory behavior. Since the differential equations to be solved are for $E > 0$ of course the same as for $E < 0$, one can naturally try the same ansatzes for the solution, which, however, here do not lead to a truncation condition for the series $P(\rho)$ because η is, according to (6.34), purely imaginary. We do not want to follow this aspect here, though, but content ourselves with the statement that there are for $E > 0$ no selection criteria for the energy. The spectrum is thus continuous.

6.2.5 Co-Motion of the Nucleus; Two-Body Problem

For the discussion of the electron motion in the Coulomb potential we have, up to now, assumed that the nucleus as the center of force is at rest at the origin of coordinates. This is certainly an acceptable approximation because in comparison to the electron mass m_e, the mass of the nucleus $m_\mathrm{N} \approx 1836\, m_e$ is relatively large. However, the assumption is of course not exact. The hydrogen-like atom presents, strictly speaking, just like the planetary motion of Classical Mechanics, a two-body problem. How **many-particle systems** are to be treated is described in Chap. 8, and especially in Vol. 9 of this ground course in *Theoretical Physics*. But let us work out, already now, the issue a bit with the present relatively simple two-particle problem. The *full* Hamilton operator of the hydrogen-like particle reads:

$$H = \frac{\mathbf{p}_\mathrm{N}^2}{2m_\mathrm{N}} + \frac{\mathbf{p}_\mathrm{e}^2}{2m_e} + V(\mathbf{r}_\mathrm{N}, \mathbf{r}_\mathrm{e})\,. \tag{6.95}$$

The indexes N and e refer to the nucleus and the electron, respectively. V is the Coulomb potential which depends only on the position distance:

$$V(\mathbf{r}_\mathrm{N}, \mathbf{r}_\mathrm{e}) \equiv V(|\mathbf{r}_\mathrm{N} - \mathbf{r}_\mathrm{e}|) = -\frac{Z\,e^2}{4\pi\,\varepsilon_0 |\mathbf{r}_\mathrm{N} - \mathbf{r}_\mathrm{e}|}\ . \tag{6.96}$$

When we continue to neglect, as hitherto, any spin-orbit interaction, then we can presume, in this case also, that the spin parts of the resulting wave function can be separated. It is therefore sufficient to discuss only the orbital motion. Using the position representation we then get the following time-independent Schrödinger equation:

$$\left(-\frac{\hbar^2}{2m_\mathrm{N}}\,\Delta_\mathrm{N} - \frac{\hbar^2}{2m_e}\,\Delta_\mathrm{e} - \frac{Z\,e^2}{4\pi\,\varepsilon_0 |\mathbf{r}_\mathrm{N} - \mathbf{r}_\mathrm{e}|}\right)\,\psi(\mathbf{r}_\mathrm{N}, \mathbf{r}_\mathrm{e}) = E\,\psi(\mathbf{r}_\mathrm{N}, \mathbf{r}_\mathrm{e})\ . \tag{6.97}$$

The wave function will in any case of course depend on the coordinates of both the particles, so that the eigen-value problem to be solved looks rather complicated. In Classical Mechanics we could solve the analogous problem quite elegantly by introducing *relative coordinates* and *center-of-mass coordinates* ((3.41) and (3.42), Vol. 1). It thus suggests itself to try the same procedure here:

$$\begin{aligned} \mathbf{R} &= \frac{1}{M}\,(m_\mathrm{N}\,\mathbf{r}_\mathrm{N} + m_e\,\mathbf{r}_\mathrm{e}) \equiv (X, Y, Z)\ , \\ \mathbf{r} &= \mathbf{r}_\mathrm{N} - \mathbf{r}_\mathrm{e} \equiv (x, y, z)\ . \end{aligned} \tag{6.98}$$

M denotes the total mass

$$M = m_\mathrm{N} + m_e\ .$$

We recognize that the potential V (6.96) depends only on the relative coordinate $\mathbf{r}$. With the resolution of (6.98) for $\mathbf{r}_\mathrm{N}$ and $\mathbf{r}_\mathrm{e}$,

$$\mathbf{r}_\mathrm{N} = \mathbf{R} + \frac{m_e}{M}\,\mathbf{r}\ ; \quad \mathbf{r}_\mathrm{e} = \mathbf{R} - \frac{m_\mathrm{N}}{M}\,\mathbf{r}\ , \tag{6.99}$$

the wave function ψ can be formulated with the coordinates $\mathbf{r}$ and $\mathbf{R}$:

$$\psi(\mathbf{r}_\mathrm{N}, \mathbf{r}_\mathrm{e}) = \psi[\mathbf{r}_\mathrm{N}(\mathbf{r}, \mathbf{R}), \mathbf{r}_\mathrm{e}(\mathbf{r}, \mathbf{R})] \equiv \widehat{\psi}(\mathbf{r}, \mathbf{R})\ .$$

That, of course, makes sense only if we can also transform the Laplace operators in (6.97),

$$\Delta_\mathrm{N,e} = \frac{\partial^2}{\partial x_\mathrm{N,e}^2} + \frac{\partial^2}{\partial y_\mathrm{N,e}^2} + \frac{\partial^2}{\partial z_\mathrm{N,e}^2}\ ,$$

to the new set of coordinates. For this purpose we can apply the known rules for the transformation of variables (Vol. 1) or, in the present simple case, we can perform the transformation simply directly step by step. So we obtain, e.g., with the chain rule:

$$\frac{\partial}{\partial x_\mathrm{e}} = \frac{\partial X}{\partial x_\mathrm{e}}\,\frac{\partial}{\partial X} + \frac{\partial x}{\partial x_\mathrm{e}}\,\frac{\partial}{\partial x} = \frac{m_e}{M}\,\frac{\partial}{\partial X} - \frac{\partial}{\partial x}\ .$$

This leads in the next step to

$$\begin{aligned}\frac{\partial^2}{\partial x_{\mathrm{e}}^2} &= \frac{m_e}{M}\left(\frac{\partial X}{\partial x_{\mathrm{e}}}\frac{\partial^2}{\partial X^2}+\frac{\partial x}{\partial x_{\mathrm{e}}}\frac{\partial^2}{\partial x\,\partial X}\right)-\frac{\partial X}{\partial x_{\mathrm{e}}}\frac{\partial^2}{\partial X\,\partial x}-\frac{\partial x}{\partial x_{\mathrm{e}}}\frac{\partial^2}{\partial x^2}\\ &= \frac{m_e^2}{M^2}\frac{\partial^2}{\partial X^2}-2\,\frac{m_e}{M}\frac{\partial^2}{\partial X\,\partial x}+\frac{\partial^2}{\partial x^2}\,.\end{aligned}$$

Analogous expressions come out for the other two components so that it follows altogether:

$$\Delta_{\mathrm{e}}=\frac{m_e^2}{M^2}\,\Delta_{\mathrm{R}}-2\,\frac{m_e}{M}\,(\nabla_{\mathrm{r}}\cdot\nabla_{\mathrm{R}})+\Delta_{\mathrm{r}}\,. \tag{6.100}$$

In the same way we find Δ_{N}:

$$\Delta_{\mathrm{N}}=\frac{m_{\mathrm{N}}^2}{M^2}\,\Delta_{\mathrm{R}}+2\frac{m_{\mathrm{N}}}{M}\,(\nabla_{\mathrm{r}}\cdot\nabla_{\mathrm{R}})+\Delta_{\mathrm{r}}\,. \tag{6.101}$$

Here Δ_{R} and Δ_{r} are the Laplace operators acting, respectively, on the center-of-mass and the relative coordinate, while ∇_{R}, ∇_{r} are the corresponding gradients. When inserting (6.100) and (6.101) into the Schrödinger equation (6.97), the *mixed* terms drop out:

$$\left(-\frac{\hbar^2}{2M}\,\Delta_{\mathrm{R}}-\frac{\hbar^2}{2\mu}\,\Delta_{\mathrm{r}}-\frac{Z\,e^2}{4\pi\,\varepsilon_0 r}\right)\,\widehat{\psi}(\mathbf{r},\mathbf{R})=E\,\widehat{\psi}(\mathbf{r},\mathbf{R})\,. \tag{6.102}$$

μ is the *reduced mass*:

$$\mu=\frac{m_{\mathrm{N}}\,m_e}{m_{\mathrm{N}}+m_e}\,. \tag{6.103}$$

Equation (6.102) corresponds to a Hamilton operator of the form:

$$H = \frac{\mathbf{P}^2}{2M}+\frac{\mathbf{p}^2}{2\mu}+V(r)\,, \tag{6.104}$$

$$\mathbf{P} = M\,\dot{\mathbf{R}}\,,\quad \mathbf{p}=\mu\,\dot{\mathbf{r}}\,. \tag{6.105}$$

It can quite easily be shown (Exercise 6.2.10) that the components of $\mathbf{P}$ and $\mathbf{R}$ as well as those of $\mathbf{p}$ and $\mathbf{r}$ are indeed canonically conjugate variables, which ultimately justifies the position representation (6.102).

Since the differential operators, which act on the coordinates $\mathbf{r}$ and $\mathbf{R}$, respectively, do not *mix*, but rather appear additively in the Schrödinger equation (6.102), a **separation ansatz** for $\widehat{\psi}$ would be appropriate:

$$\widehat{\psi}(\mathbf{r},\mathbf{R})=\chi(\mathbf{R})\,\varphi(\mathbf{r})\,. \tag{6.106}$$

When one inserts this ansatz into (6.102) and multiplies *from the left* by $\widehat{\psi}^{-1}$, then one gets:

$$\frac{1}{\chi(\mathbf{R})}\left(-\frac{\hbar^2}{2M}\,\Delta_{\mathrm{R}}\,\chi(\mathbf{R})\right)=-\frac{1}{\varphi(\mathbf{r})}\left(-\frac{\hbar^2}{2\mu}\,\Delta_{\mathrm{r}}+V(r)\right)\,\varphi(\mathbf{r})+E\,.$$

The left-hand side depends only on $\mathbf{R}$ and the right-hand side only on $\mathbf{r}$. In similar situations, we have already used several times the conclusion that, in such a case, both sides by themselves must already be constant:

$$-\frac{\hbar^2}{2M}\,\Delta_{\mathrm{R}}\,\chi(\mathbf{R}) \;=\; \lambda\,\chi(\mathbf{R})\;, \tag{6.107}$$

$$\left(-\frac{\hbar^2}{2\mu}\,\Delta_{\mathrm{r}} + V(r)\right)\varphi(\mathbf{r}) \;=\; (E-\lambda)\,\varphi(\mathbf{r})\;. \tag{6.108}$$

The center-of-mass motion and the relative motion are therewith completely decoupled. In addition, we have already solved the corresponding eigen-value problems. The center-of-mass motion is especially simple:

$$\lambda = \frac{\hbar^2\mathbf{K}^2}{2M}\;; \qquad \chi(\mathbf{R}) = \exp(i\,\mathbf{K}\cdot\mathbf{R})\;. \tag{6.109}$$

The wave number $\mathbf{K}$ is by $\hbar\mathbf{K} = \mathbf{P}$ connected to the center-of-mass momentum. The center-of-mass motion therefore corresponds to that of a *free* particle.

The remaining effective one-particle problem (6.108) comprises the motion of a particle of the charge $(-e)$ and the mass **mass** μ in the Coulomb field of a nucleus of the charge $(+Z\,e)$ **fixed in space**, where the position vector of the particle is given by the relative coordinate $\mathbf{r}$. The respective eigen-value problem we have completely solved just in the preceding subsections. We can therefore take over all the results, where we have simply to replace everywhere the electron mass m_e by the reduced mass μ. We thus obtain as eigen-energies:

$$E_n = \frac{\hbar^2\mathbf{K}^2}{2M} + \widehat{E}_n\;. \tag{6.110}$$

$\widehat{E}_n$ are the energies (6.43), where only in the Rydberg energy $E_{\mathrm{R}}\;m_e$ is substituted by μ:

$$\widehat{E}_n \;=\; -\frac{Z^2\,\widehat{E}_{\mathrm{R}}}{n^2}\;; \quad n = 1, 2, 3, \ldots\;, \tag{6.111}$$

$$\widehat{E}_{\mathrm{R}} \;=\; \frac{\mu\,e^4}{2\hbar^2\,(4\pi\,\varepsilon_0)^2}\;. \tag{6.112}$$

The *co-motion correction* treated here is of course not at all a typical quantum-mechanical effect. We have already in Chap. 1 (Vol. 6), in the framework of the semi-classical Bohr theory, corrected the Rydberg constant (1.125) and pointed out that actually due to this correction the *heavy hydrogen isotope 'deuterium'* was discovered. Because of $m_{\mathrm{N}} \approx 1836\,m_e$ μ is for the hydrogen atom of course only slightly different from m_e. This changes, however, enormously when the masses of the two interaction partners are of the same order of magnitude.

It goes without saying that the simple decoupling of a two-particle problem into two effective one-particle problems, as presented in this subsection, cannot always be executed so smoothly. We will therefore have to come back to the relevant considerations in Chap. 8 and to deepen them.

6.2.6 Exercises

Exercise 6.2.1
Derive with the recursion formulas (6.70) and (6.71) for the ordinary Laguerre polynomials $L_p(z)$ the Laguerre differential equation (6.72).

Exercise 6.2.2
Calculate the eigen-energies of an electron in the central potential

$$V(r) = -\frac{Z\,e^2}{4\pi\,\varepsilon_0 r} + \frac{\hat{c}}{r^2}\,; \quad \hat{c} = \frac{\hbar^2}{2m_e}\,c\,!$$

Let the second term thereby be a weak correction to the actual Coulomb potential ($c \ll 1$). Show that this additional term removes the *accidental* degeneracy of the Coulomb potential with respect to the secondary quantum number l.

Exercise 6.2.3
Let the electron in the H-atom be in the eigen-state $|n\,l\,m_l\,m_s\rangle$ with the energy-eigen value E_n.

1. How do the eigen-state and the eigen-value change, when a constant magnetic field $\mathbf{B}$ is applied in z-direction? Spin-orbit interaction and diamagnetic contributions are to be disregarded.

2. How high are the degrees of degeneracy before and after the switching on of the magnetic field?

Exercise 6.2.4
Given

$$\psi(r,\vartheta,\varphi) = \alpha\,r\exp\left(-\frac{r}{2a_{\mathrm{B}}}\right)\,Y_{11}(\vartheta,\varphi)\;.$$

Show by a direct solution of the time-independent Schrödinger equation that $\psi(r,\vartheta,\varphi)$ is an eigen-function of the (spinless) electron in the hydrogen atom. Find the corresponding energy-eigen value. By which quantum numbers is the state of the electron specified?

$$a_{\mathrm{B}} = \frac{4\pi\,\varepsilon_0\,\hbar^2}{m_e\,e^2} \qquad \textit{(Bohr radius)}\;.$$

Exercise 6.2.5
Let the electron (mass m, charge -e) of the hydrogen atom be in the eigen-state $\psi_{nlm_l}(\mathbf{r})$.

1. Calculate the current density due to the electron. Disregard the spin of the electron!

2. Determine the magnetic moment produced by this current!

Exercise 6.2.6
Let the electron of the hydrogen atom be in a state which is described by the wave function

$$\psi(\mathbf{r}) = \frac{1}{5}(3\psi_{100}(\mathbf{r}) - 2\psi_{211}(\mathbf{r}) + \sqrt{12}\psi_{21-1}(\mathbf{r})) \; .$$

Calculate the expectation value of the energy in units of Rydberg energy E_R as well as the expectation values of $\mathbf{L}^2$ and L_z. ($\psi_{nlm_l}(\mathbf{r})$: hydrogen eigenfunctions)

Exercise 6.2.7
Prove the Kramers relation (6.78):

$$\frac{k+1}{n^2}\langle r^k\rangle_{nl} - (2k+1)\frac{a_\mathrm{B}}{Z}\langle r^{k-1}\rangle_{nl} + \frac{k}{4}[(2l+1)^2 - k^2]\left(\frac{a_\mathrm{B}}{Z}\right)^2\langle r^{k-2}\rangle_{nl} = 0$$
$$(2l+k+1 > 0) \; .$$

It might be recommendable to start with the radial equation (6.35), and to multiply this by

$$\left[\rho^{k+1}\,u'(\rho) - \frac{1}{2}\,(k+1)\,\rho^k\,u(\rho)\right]$$

and then to integrate from 0 to ∞ over ρ!

Exercise 6.2.8
Consider the electron in the hydrogen atom, disregarding spin and relativistic corrections. Calculate for the ground state

1. the most probable value for the distance of the electron from the nucleus,
2. the expectation value and the mean square deviation of this distance,
3. the probability to find the electron at a distance $r > a_B$,
4. the most probable value for the magnitude of the momentum.

Exercise 6.2.9
A particle of charge q moves in a central potential $V(r)$. The operator of the electric dipole moment is defined by

$$\hat{p} = q\,z = q\,r\cos\vartheta \; .$$

Let $\psi_{nlm_l}(\mathbf{r}) = R_{nl}(r)\,Y_{lm_l}(\vartheta,\varphi)$ be the eigen-states of the Hamilton operator.

1. Show:
$$\int d^3r\,\psi^*_{nlm_l}(\mathbf{r})\cdot\hat{p}\cdot\psi_{nlm_l}(\mathbf{r}) = 0 \; .$$
2. For which pairs $l'm'_l;\; l, m_l$ is the matrix element
$$\int d^3r\,\psi_{nl'm'_l}(\mathbf{r})\cdot\hat{p}\cdot\psi_{nlm_l}(\mathbf{r})$$

unequal zero? Which meaning do these transitions have? Use the recursion formula for the associated Legendre polynomials:

$$(2l+1)\,z\,P_l^{m_l}(z) = (l+1-m_l)\,P_{l+1}^{m_l}(z) + (l+m_l)\,P_{l-1}^{m_l}(z) (0 \le m_l \le l-1)\,.$$

3. With the known eigen-functions of the hydrogen atom construct an eigenstate to $n = 2$, for which the expectation value of $\hat{p}$ **does not** vanish (contradiction to 1.?) and calculate this value!

Exercise 6.2.10
Show that the relative momentum (6.105) of the two-body problem (Sect. 6.2.5),

$$\mathbf{p} = \mu\,\dot{\mathbf{r}}\,; \qquad \mu = \left(\frac{1}{m_1} + \frac{1}{m_2}\right)^{-1}\,,$$

and the relative coordinate,

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2\,,$$

are canonical-conjugate variables. Demonstrate the same for the center-of-mass coordinate $\mathbf{R}$ (6.98) and the center-of-mass momentum $\mathbf{P} = M\,\dot{\mathbf{R}}$ (6.105).

Exercise 6.2.11

1. For the Hamilton operator of the electron in the hydrogen atom calculate the commutator
$$\frac{i}{\hbar}\,[H, \mathbf{r}\cdot\mathbf{p}]_- \quad !$$
2. Let $\langle T\rangle = \langle\psi|T|\psi\rangle$ and $\langle V\rangle = \langle\psi|V|\psi\rangle$ be the expectation values of the kinetic energy T and the potential energy V in an eigen-state $|\psi\rangle$ of the hydrogen atom. Use 1. to justify the so-called *virial theorem*
$$2\langle T\rangle + \langle V\rangle = 0\,.$$
Give explicit expressions for $\langle T\rangle$ and $\langle V\rangle$!
3. How does the virial theorem read for the spherical harmonic oscillator?

6.3 Spherical Symmetric Potential Well

6.3.1 Radial Equation

As a further example of a central potential we now investigate the spherically symmetric potential well (Fig. 6.7):

$$V(r) = \begin{cases} -V_0 & \text{for } r \le a\,, \\ 0 & \text{for } r > a\,. \end{cases} \tag{6.113}$$

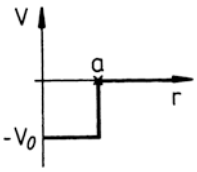

Figure 6.7: Radial form of the spherical-symmetric of the potential well

We have elaborately discussed in Sect. 4.2 (Vol. 6) the one-dimensional analog. The potential well is a simple model for short-range attractive forces, as for instance the nuclear forces.

We have of course already done, for the solution of this problem, a lot of preparatory work. So we can directly start with the radial equation (6.17), which is valid for all central potentials:

$$\left\{-\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{l(l+1)}{r^2}\right)+V(r)-E\right\}R(r)=0\,.$$

The potential is piecewise-constant. Therefore

$$k^2=\frac{2m}{\hbar^2}\left(E-V(r)\right)$$

is also in principle a constant. The space-dependence only concerns the discontinuity at $r=a$. With the exception of this point we can therefore substitute in the radial equation $z=k\,r$:

$$\left[\frac{d^2}{dz^2}+\frac{2}{z}\frac{d}{dz}-\frac{l(l+1)}{z^2}+1\right]R(z)=0\,. \tag{6.114}$$

We therewith have to deal again with a differential equation, which is extensively discussed in the textbooks of mathematical physics, the solutions of which are therefore well-known. It is the **Bessel differential equation**, with which we will first familiarize ourselves a bit in the next subsection.

The explicit solution of the problem will then later be carried out in the same manner as that for the one-dimensional potential well in Sect. 4.2 (Vol. 6). At first, we will seek general solutions in the regions $0\le r<a$ and $r>a$, and thereby take into account in particular the behavior for $r\to 0$ and $r\to\infty$, and subsequently *fit* properly the partial solutions by the use of the continuity conditions for wave functions and their derivatives.

6.3.2 Bessel Functions

We discuss some partial aspects of the differential equation (6.114), of course focused on that which is of importance for the following physical considerations.

We present this discussion in form of a list:
1) Inflection point
When we take $u(z) = z\,R(z)$, then:

$$u''(z) = 2R'(z) + z\,R''(z)\ .$$

(6.114) becomes therewith:

$$u''(z) + \left(1 - \frac{l(l+1)}{z^2}\right) u(z) = 0\ . \tag{6.115}$$

But this means that $u(z) = z\,R(z)$ has an inflection point at $z = \sqrt{l(l+1)}$.
2) Special case: $l = 0$
In this case, (6.115) can easily be solved:

$$u_0''(z) + u_0(z) = 0 \implies u_0(z) \sim \sin z, \cos z\ .$$

For the radial function this means:

$$R_0(z) \sim \frac{\sin z}{z}\ ; \quad R_0(z) \sim \frac{\cos z}{z}\ . \tag{6.116}$$

The first solution is regular at the origin ($z \to 0$), the second diverges at this point.
3) Explicit solution
We want to trace back in the following the solutions of the Bessel differential equation (6.114) by a recursion formula to $R_0(z)$. Thereby the following ansatz helps:

$$R_l(z) = z^l\, f_l(z)\ . \tag{6.117}$$

With

$$\begin{aligned}
\frac{2}{z}\frac{d}{dz} R_l(z) &= z^l \left(\frac{2l}{z^2} f_l(z) + \frac{2}{z}\frac{d}{dz} f_l(z)\right)\ , \\
\frac{d^2}{dz^2} R_l(z) &= z^l \left(\frac{l(l-1)}{z^2} f_l(z) + \frac{2l}{z}\frac{d}{dz} f_l(z) + \frac{d^2}{dz^2} f_l(z)\right)
\end{aligned}$$

we can rewrite (6.114) at first into a differential equation for $f_l(z)$:

$$\left[\frac{d^2}{dz^2} + \frac{2(l+1)}{z}\frac{d}{dz} + 1\right] f_l(z) = 0\ . \tag{6.118}$$

In order to get a recursion formula, we differentiate (6.118) once more with respect to z:

$$\left[\frac{d^3}{dz^3} + \frac{2(l+1)}{z}\frac{d^2}{dz^2} + \left(1 - \frac{2(l+1)}{z^2}\right)\frac{d}{dz}\right] f_l(z) = 0\ .$$

When we insert

$$\frac{d}{dz} f_l(z) = z\, g(z)$$

into this equation, then we reach eventually a differential equation for $g(z)$:

$$\left[\frac{d^2}{dz^2} + \frac{2(l+2)}{z}\,\frac{d}{dz} + 1\right] g(z) = 0\,.$$

Comparing this with (6.118) we recognize that $g(z)$ must be proportional to $f_{l+1}(z)$:

$$g(z) = \frac{1}{z}\,\frac{d}{dz}\,f_l(z) \sim f_{l+1}(z)\,.$$

This can be iterated and leads then to:

$$f_l(z) \sim \left(\frac{1}{z}\,\frac{d}{dz}\right)^l f_0(z)\,.$$

$f_0(z)$ is according to (6.117) identical to $R_0(z)$, and is therewith known. There is an expression, which is regular at the origin, and another one which is irregular. We obtain hence with (6.117) for the radial function the two special solutions:

$$j_l(z) = (-z)^l \left(\frac{1}{z}\,\frac{d}{dz}\right)^l \frac{\sin z}{z} \tag{6.119}$$

spherical Bessel function ,

$$n_l(z) = -(-z)^l \left(\frac{1}{z}\,\frac{d}{dz}\right)^l \frac{\cos z}{z} \tag{6.120}$$

spherical Neumann function .

The sign factors are of course arbitrary. The above choice, however, is the convention. The Bessel functions $j_l(z)$ are regular at the origin, but the Neumann functions $n_l(z)$ are not. They are linearly independent sets of functions. The general solution of the radial equation (6.114) therefore reads:

$$R_l(z) = a_l\, j_l(z) + b_l\, n_l(z)\,. \tag{6.121}$$

The coefficients a_l, b_l have to be fixed by boundary conditions.

4) Behavior for $z \to 0$

Let us analyze the solutions (6.120) and (6.121) further in some detail. The behavior at the origin turns out to be important. This is most easily investigated by the use of the series expansions of the trigonometric functions:

$$\frac{\sin z}{z} = \sum_{s=0}^{\infty} (-1)^s\,\frac{z^{2s}}{(2s+1)!}\,,$$

$$\frac{\cos z}{z} = \sum_{s=0}^{\infty} (-1)^s\,\frac{z^{2s-1}}{(2s)!}\,.$$

We apply to these expressions the operator $((1/z)\,(d/dz))^l$ and sort out the term

which dominates in the limit $z \to 0$:

$$\left(\frac{1}{z}\frac{d}{dz}\right)^l \frac{\sin z}{z} = \sum_{s=0}^{\infty} (-1)^s \frac{2s(2s-2)\cdots(2s-2l+2)}{(2s+1)!} z^{2s-2l}$$
$$\underset{z\to 0}{\longrightarrow} (-1)^l \frac{2l(2l-2)\cdots 2}{(2l+1)!} + \mathcal{O}(z^2) ,$$
$$\left(\frac{1}{z}\frac{d}{dz}\right)^l \frac{\cos z}{z} = \sum_{s=0}^{\infty} (-1)^s \frac{(2s-1)(2s-3)\cdots[2s-(2l-1)]}{(2s)!} z^{2s-(2l+1)}$$
$$\underset{z\to 0}{\longrightarrow} (-1)^l (2l-1)(2l-3)\cdots 1 \cdot z^{-(2l+1)} (1+\mathcal{O}(z^2)) .$$

In the last expression we have taken out the for $z \to 0$ *most divergent* summand ($s = 0$). With the definition of the so-called *double factorial*,

$$(2l+1)!! = 1 \cdot 3 \cdot 5 \cdots (2l+1) , \tag{6.122}$$

one then finds the following asymptotic behavior patterns for the solutions (6.120) and (6.121):

$$j_l(z) \underset{z\to 0}{\longrightarrow} \frac{z^l}{(2l+1)!!}(1+\mathcal{O}(z^2)) , \tag{6.123}$$
$$n_l(z) \underset{z\to 0}{\longrightarrow} -\frac{(2l+1)!!}{(2l+1)z^{l+1}}(1+\mathcal{O}(z^2)) . \tag{6.124}$$

By taking into consideration the next terms of the above expansions, one can of course easily extend these formulas to higher accuracy.

5) Behavior for $z \to \infty$

For $z \to \infty$ such terms in $j_l(z)$ and $n_l(z)$, respectively, dominate, for which all the l differentiations are applied to the sine and the cosine, respectively. Because of

$$\cos z = -\sin\left(z - \frac{\pi}{2}\right)$$

we can estimate,

$$\left(\frac{1}{z}\frac{d}{dz}\right)^l \frac{\sin z}{z} \underset{z\to\infty}{\longrightarrow} (-1)^l \frac{\sin(z-(l\pi/2))}{z^{l+1}} ,$$

and because of

$$\sin z = \cos\left(z - \frac{\pi}{2}\right)$$

it follows:

$$\left(\frac{1}{z}\frac{d}{dz}\right)^l \frac{\cos z}{z} \underset{z\to\infty}{\longrightarrow} (-1)^l \frac{\cos(z-(l\pi/2))}{z^{l+1}} .$$

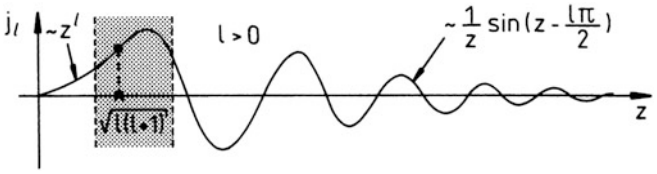

Figure 6.8: Qualitative curve of the spherical Bessel function for $l > 0$

The Bessel and Neumann functions therefore exhibit the following asymptotic behavior:

$$j_l(z) \underset{z\to\infty}{\longrightarrow} \frac{1}{z}\sin\left(z-\frac{l\pi}{2}\right), \tag{6.125}$$

$$n_l(z) \underset{z\to\infty}{\longrightarrow} -\frac{1}{z}\cos\left(z-\frac{l\pi}{2}\right). \tag{6.126}$$

6) Examples

For the spherical Bessel function we now expect a curve as qualitatively plotted in Fig. 6.8. Essential deviations from the asymptotic behavior appear only in the region around the inflection point $z = \sqrt{l(l+1)}$ of $z\,j_l(z)$. (6.125) can be used to represent $j_l(z)$, without remarkable mistake, already for $z > 2l$, which turns out to be advantageous for respective estimations. The $l = 0$ Bessel function, however, is in the region of small z, different from the others. It starts for $z = 0$ at the value 1.

The following examples of Bessel and Neumann functions are directly derived from (6.120) and (6.121):

$$\begin{aligned}
j_0(z) &= \frac{\sin z}{z}, \\
n_0(z) &= -\frac{\cos z}{z}, \\
j_1(z) &= \frac{\sin z}{z^2} - \frac{\cos z}{z}, \\
n_1(z) &= -\frac{\cos z}{z^2} - \frac{\sin z}{z}, \\
j_2(z) &= \left(\frac{3}{z^3} - \frac{1}{z}\right)\sin z - \frac{3}{z^2}\cos z, \\
n_2(z) &= -\left(\frac{3}{z^3} - \frac{1}{z}\right)\cos z - \frac{3}{z^2}\sin z.
\end{aligned}$$

7) Hankel functions

Another fundamental system for the solution of the Bessel differential equation (6.114) is represented by the *Hankel functions of the first and the second kind*, which are defined as follows:

$$h_l^{(\pm)}(z) = j_l(z) \pm i\,n_l(z) = \mp i\,(-z)^l \left(\frac{1}{z}\frac{d}{dz}\right)^l \frac{e^{\pm iz}}{z}. \tag{6.127}$$

Instead of (6.121) we can use as ansatz for the solution of (6.114) just as well:

$$R_l(z) = \alpha_l^{(+)}\, h_l^{(+)}(z) + \alpha_l^{(-)}\, h_l^{(-)}(z)\ . \tag{6.128}$$

The actual choice of the ansatz, (6.121) or (6.128), is of course decided, according to expedience, by the boundary conditions to be fulfilled.

The behavior of the Hankel functions for $z \to 0$ corresponds to that of the Neumann functions, diverging at the origin. On the other hand, it holds for large z:

$$h_l^{(\pm)}(z) \underset{z\to\infty}{\longrightarrow} \mp i\,\frac{1}{z}\, e^{\pm i(z-(l\pi/2))}\ . \tag{6.129}$$

We list some examples:

$$\begin{aligned}
h_0^{(+)}(z) &= -\frac{i}{z}\, e^{iz} = \left(h_0^{(-)}(z)\right)^*\ , \\
h_1^{(+)}(z) &= -\frac{1}{z}\, e^{iz}\left(1+\frac{i}{z}\right) = \left(h_1^{(-)}(z)\right)^*\ , \\
h_2^{(+)}(z) &= \frac{i}{z}\, e^{iz}\left(1+\frac{3i}{z}-\frac{3}{z^2}\right) = \left(h_2^{(-)}(z)\right)^*\ .
\end{aligned}$$

Further formulas in connection with the Bessel differential equation are collected in Sect. 7.4.6.

6.3.3 Bound States

After this mathematical interlude we now come back again to the actual physical problem and search at first for the *bound states* in the spherically symmetric potential well. It is clear that these can exist only for

$$-V_0 < E < 0\ .$$

We write

$$k^2 = \begin{cases} k_0^2 = \frac{2m}{\hbar^2}\,(E+V_0) & \text{for } r < a\ , \\ -\kappa^2 = \frac{2m}{\hbar^2}\,E & \text{for } r > a \end{cases} \tag{6.130}$$

and solve the eigen-value problem, in principle, by using the same algorithm that was already applied successfully in connection with the one-dimensional potentials in Chap. 4 (Vol. 6).

r < a

In this region: $k^2 = k_0^2$. We have to require that the radial function is regular at the origin of coordinates, which is guaranteed only by the Bessel function. The solution ansatz (6.121) is therefore appropriate, where the coefficients b_l must all be zero:

$$R_l(r) = a_l j_l(k_0 r)\ . \tag{6.131}$$

r > a

This is the *classically forbidden region*. The wave number k is purely imaginary: $k = i\,\kappa$. We must expect an exponential decay of the wave function. Only the Hankel function of the first kind (6.129) offers this. Therefore we choose here the ansatz (6.128) for the radial function, where it is clear, right from the start, that all the $\alpha_l^{(-)}$ vanish, because $h_l^{(-)}(i\,\kappa\,r)$ diverges for $r \to \infty$:

$$R_l(r) = \alpha_l^{(+)}\, h_l^{(+)}\,(i\,\kappa\,r)\;. \tag{6.132}$$

The radial function and its derivative have to be *continuously matched*:

$$a_l\, j_l\,(k_0 a) \;\stackrel{!}{=}\; \alpha_l^{(+)}\, h_l^{(+)}\,(i\,\kappa\,a)\;, \tag{6.133}$$

$$a_l\, \frac{d}{dr}\, j_l\,(k_0 r)|_{r=a} \;\stackrel{!}{=}\; \alpha_l^{(+)}\, \frac{d}{dr}\, h_l^{(+)}\,(i\,\kappa\,r)|_{r=a}\;. \tag{6.134}$$

These two conditions can be combined as follows:

$$k_0\, \frac{d}{dz} \ln j_l(z)|_{z=k_0 a} \;\stackrel{!}{=}\; i\,\kappa\, \frac{d}{dz} \ln h_l^{(+)}(z)|_{z=i\,\kappa\,a}\;, \tag{6.135}$$

from which we get a rather complicated transcendental equation, which, for given V_0 and l, can be fulfilled only for a definite E. According to (6.130) E appears in k_0 and κ. A general analytic solution, though, is not possible. We therefore restrict our further considerations to the special case $l = 0$ (**s-state**). The evaluation for $l = 1$ is performed as Exercise 6.3.2.

When we insert

$$\begin{aligned} j_0(z) &= \frac{\sin z}{z}\;; \quad j_0'(z) = \frac{1}{z^2}\,(z\cos z - \sin z)\;, \\ h_0^{(+)}(z) &= \frac{e^{iz}}{i\,z}\;; \qquad \left(h_0^{(+)}(z)\right)' = \frac{z+i}{z^2}\,e^{iz} \end{aligned} \tag{6.136}$$

into (6.135), we obtain after simple manipulations

$$k_0 \cot k_0\, a = -\kappa\;. \tag{6.137}$$

This is an energy condition, which we got, in exactly the same form, for the one-dimensional potential well (Sect. 4.2, Vol. 6). There it was the energy condition for the **antisymmetric** solution wave functions. The agreement of (4.43) (Vol. 6) and (6.137) is not accidental! We had already realized in connection with (6.23) that the solution of the radial equation for central potentials is equivalent to a **one-dimensional** Schrödinger equation, if one only replaces $V(r)$ by

$$\widehat{V}(q) = \begin{cases} V(q) + \dfrac{\hbar^2 l(l+1)}{2m\,q^2} & \text{for } q > 0\;, \\ \infty & \text{for } q \le 0 \end{cases}$$

(We had always used in Chap. 4 (Vol. 6) the letter q for the one-dimensional position variable.) For $l = 0$, however, on the positive axis, $\widehat{V}$ is identical

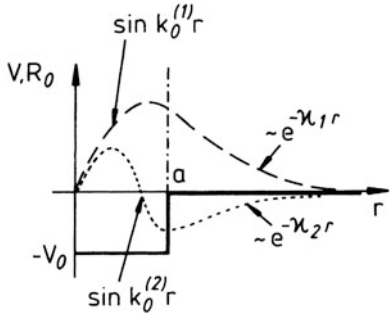

Figure 6.9: Two possible solutions for the radial function of the spherical-symmetric potential well, which correspond to bound states

to V, while the condition $\widehat{V} \equiv \infty$ for $q = r \leq 0$ restricts, in the equivalent one-dimensional potential problem, the solution ansatz to the antisymmetric eigen-functions, because only those vanish for $q = 0$.

The further analysis of (6.137) can be taken over from Sect. 4.3 (Vol. 6) almost without any modification. Here also holds, e.g., the statement (4.49) (Vol. 6), according to which a bound state can exist only if the *depth of the well* V_0 exceeds a certain minimal value V_0^*:

$$V_0 > V_0^* = \frac{\pi^2 \hbar^2}{8m\,a^2} \,. \tag{6.138}$$

In Fig. 6.9 there are plotted, qualitatively, two solutions of the radial function, where for $(k_0^{(1)}, \kappa_1)$ V_0 permits just one bound state, and for $(k_0^{(2)}, \kappa_2)$ two bound states are possible.

In Exercise 6.3.4 we investigate the limiting case of the very deep spherically symmetric potential well, for which the energy spectrum of the bound states can be estimated for arbitrary l.

6.3.4 Continuum States

We finally discuss the case

$$E > 0 \,,$$

for which the entire r-axis represents the *classically allowed region*. The solution-wave function will exhibit oscillatory behavior everywhere. We write

$$q = \sqrt{\frac{2m\,E}{\hbar^2}} \,; \quad k_0 = \sqrt{\frac{2m}{\hbar^2}\,(E + V_0)} \,, \tag{6.139}$$

and choose for the entire r-axis the solution ansatz (6.121). Hee also, of course, the regularity of the radial function at the origin has to be respected:

$$\begin{aligned} r < a \;:&\qquad R_l(r) = a_l\, j_l(k_0 r) \,, \\ r > a \;:&\qquad R_l(r) = \alpha_l\, j_l(q\,r) + \beta_l\, n_l(qr) \,. \end{aligned} \tag{6.140}$$

The continuity conditions at $r = a$ now deliver conditions for the coefficients in these solutions, i.e., ultimately there exists for **each** energy E a possible wave function and there are no selection conditions for the energy itself. We thus obtain a **continuous energy spectrum**. The explicit evaluation of the fitting condition

$$k_0 \left.\frac{(d/dz)\, j_l(z)}{j_l(z)}\right|_{z=k_0 a} = q \left(\frac{\alpha_l\,(d/dz)\, j_l(z) + \beta_l\,(d/dz)\, n_l(z)}{\alpha_l\, j_l(z) + \beta_l\, n_l(z)}\right)_{z=q\,a} , \quad (6.141)$$

is somewhat cumbersome. We therefore restrict ourselves here again to the special case $l = 0$ (**s-state**). With (6.136) we find for the left-hand side of equation (6.141):

$$k_0 \left.\frac{(d/dz)\, j_l(z)}{j_l(z)}\right|_{z=k_0 a} = \frac{1}{a}\,(k_0 a \cot k_0 a - 1) .$$

For the right-hand side we still need:

$$n_0(z) = -\frac{\cos z}{z} ; \quad n_0'(z) = \frac{1}{z^2}\,(z \sin z + \cos z) .$$

Therewith we have:

$$q \left(\frac{\alpha_0\, j_0'(z) + \beta_0\, n_0'(z)}{\alpha_0\, j_0(z) + \beta_0\, n_0(z)}\right)_{z=q\,a} = \frac{1}{a} \left(q\,a\, \frac{\cos q\,a + x_0 \sin q\,a}{\sin q\,a - x_0 \cos q\,a} - 1\right) .$$

Here we have written for abbreviation:

$$x_0 = \frac{\beta_0}{\alpha_0} = -\tan\delta_0 . \quad (6.142)$$

We get therewith the following $l = 0$-fitting condition:

$$k_0 \cot k_0 a = q\, \frac{\cos q\,a\ \cos\delta_0 - \sin q\,a\ \sin\delta_0}{\sin q\,a\ \cos\delta_0 + \cos q\,a\ \sin\delta_0} = q\, \frac{\cos(q\,a + \delta_0)}{\sin(q\,a + \delta_0)} = q \cot(q\,a + \delta_0) .$$

The phase δ_0 determines, according to (6.142) the ratio of the coefficients β_0/α_0:

$$\delta_0 = \arctan\left(\frac{q}{k_0} \tan k_0\, a\right) - q\,a = \delta_0\,(E, V_0) . \quad (6.143)$$

The physical meaning of the phase δ_0, one understands as follows: For $V_0 = 0$ it is of course $q = k_0$ and therewith $\delta_0 = 0$. Because of the still to be fulfilled condition of regularity at $r = 0$ we have:

$$R_0^{(0)}(r) \sim j_0(q\,r) \underset{q\,r \gg l}{\longrightarrow} \frac{1}{q\,r} \sin q\,r . \quad (6.144)$$

For $V_0 \neq 0$ and $r > a$ it holds according to (6.140), (6.125), (6.126):

$$R_0(r) \sim j_0(q\,r) + x_0\, n_0(q\,r) \underset{q\,r \gg l}{\longrightarrow} \frac{1}{q\,r}\,[\sin(q\,r) - x_0 \cos(q\,r)]$$

$$\sim \frac{1}{q\,r}\,[\sin(q\,r)\cos\delta_0 + \cos(q\,r)\sin\delta_0] .$$

It therefore results the following asymptotic behavior:

$$R_0(r) \longrightarrow \frac{1}{q\,r}\sin(q\,r+\delta_0)\;. \tag{6.145}$$

When we compare this result with (6.144), then we recognize that the *asymptotic influence* of the potential well on the radial function consists in a phase shift $\delta_0(E,V_0)$ with respect to the *free* solution. We have calculated this phase in (6.143).

These considerations are not restricted, of course, only to $l=0$, but are valid for arbitrary l,

$$R_l(r) \longrightarrow \frac{1}{q\,r}\sin\left(q\,r-\frac{l\pi}{2}+\delta_l\right)\;. \tag{6.146}$$

The point is, however, that the phase

$$\delta_l=\delta_l(E,V_0)$$

is no longer so easily calculated for $l\geq 1$ (see Chap. 9: *scattering theory*).

6.3.5 Exercises

Exercise 6.3.1
A particle of mass m moves freely in a spherical hollow. The potential reads correspondingly:

$$V(r)=\begin{cases}0 & \text{for } r\leq a\;,\\ \infty & \text{for } r>a\;.\end{cases}$$

1. Calculate the energy-eigen functions.
2. Which condition determines the energy-eigen values? Discuss these values for $l=0$.
3. How do the energy-eigen values look like for $k\,a\gg l$ $\left(k^2=(2m/\hbar^2)E\right)$?

Exercise 6.3.2
A particle moves in the spherical potential well:

$$V(r)=\begin{cases}-V_0,\;V_0>0 & \text{for } r<a\;,\\ 0 & \text{for } r\geq a\;.\end{cases}$$

Which equation determines the energy-eigen values of the bound states for $l=1$?

Exercise 6.3.3
A particle of the mass m moves in the field of the central potential

$$V(r)=\frac{c}{r^2}+\frac{1}{2}\,m\,\omega^2 r^2\;;\quad c>0\;.$$

Solve the corresponding time-independent Schrödinger equation $H\,\psi = E\,\psi$, where the angle part is given by the spherical harmonics $Y_{lm_l}(\vartheta,\varphi)$, and is therefore already known:

$$\psi(\mathbf{r}) = R(r)\,Y_{lm_l}(\vartheta,\varphi)\ .$$

1. Formulate the radial equation and discuss it for $r \to 0$ and $r \to \infty$. Show that
$$u(r) = r\,R(r) = r^x\,e^{-\gamma r^2}\,g(r)$$
is a suitable ansatz, which accommodates these limiting cases. What are the meanings of x and γ?

2. With the ansatz from 1. derive a conditional equation for $g(r)$.

3. Choose for $g(r)$ the ansatz
$$g(r) = \sum_{\mu} \alpha_\mu\,r^\mu$$
and give reasons why the series must terminate at a finite μ_0.

4. Determine the spectrum of the energy-eigen values!

5. For which value of r is the density of the position probability maximal in the ground state? Does this coincide with the minimum of the potential?

Exercise 6.3.4
Calculate, for the limiting case of a very deep spherically symmetric potential well, approximately the energy spectrum of the bound states. Investigate for this purpose the *fitting condition* (6.135) for the case $k_0 a \gg l$.

Exercise 6.3.5
A particle of mass m and charge $\hat{q}$ moves in a constant magnetic field $\mathbf{B}$, whose vector potential is given, by the use of cylindrical coordinates ρ, φ, z, by

$$A_\varphi = \frac{1}{2}B\,\rho\ , \quad A_\rho = A_z = 0\ .$$

1. For this problem find the time-independent Schrödinger equation written in cylindrical coordinates.

2. Which equation is fulfilled by the radial parts of the eigen-functions?

3. What are the energy-eigen values?

Exercise 6.3.6
A particle of the mass m moves in an attractive, at infinity sufficiently fast decaying *cylindrical potential*:

$$V(\mathbf{r}) \equiv V(\rho) = -\frac{c}{\rho^\alpha}\ ; \quad \alpha > 1 \quad (\rho,\varphi,z:\ \text{cylindrical coordinates})\ .$$

1. Write down the time-independent Schrödinger equation!
2. Decompose this equation into an axial, a radial, and an angular equation!
3. The radial equation has the structure:

$$\left(\frac{d^2}{d\rho^2} + \frac{1}{\rho}\,\frac{d}{d\rho} + F(\rho)\right) R(\rho) = 0\ .$$

   By which substitution for $R(\rho)$ can the linear term $(1/\rho)\,(d/d\rho)$ be eliminated?
4. Discuss the behavior of the radial function of a bound state for $\rho \to 0$ and $\rho \to \infty$, where $1 < \alpha < 2$.

Exercise 6.3.7
The potential of a molecule with a long extension in z-direction can be approximately represented as independent of z, when one uses cylindrical coordinates (ρ, φ, z):

$$V(\mathbf{r}) = V(\rho) = -\frac{Z\,e^2}{4\pi\,\varepsilon_0 \rho} \quad (Ze: \quad \text{charge of the molecule})\ .$$

Calculate the eigen-functions and the energy-eigen values of an electron bound by this potential.

Exercise 6.3.8
An electron (spin 1/2) occupies a bound state in the field of a central potential. Let the radial function $R(r)$ of this state be known. Moreover, one knows that the wave function $\psi(\mathbf{r})$ is an eigen-function of the operators $\mathbf{L}^2$, $\mathbf{J}^2$ and J_z $(\mathbf{J} = \mathbf{L} + \mathbf{S})$. Determine $\psi(\mathbf{r})$!

6.4 The Free Particle

We want to complete this chapter with the discussion of a special case, which will become important later, namely, for the scattering theory in Chap. 9. Here we get it, in a certain sense, as a bi-product. Let us investigate the free particle:

$$H_0\,\psi_0(\mathbf{r}) = E\,\psi_0(\mathbf{r})\ ; \quad H_0 = \frac{\mathbf{p}^2}{2m}\ ; \quad E > 0\ .$$

The solution of the eigen-value problem is of course well-known. The (non-normalized) plane wave,

$$\psi_0(\mathbf{r}) = e^{i\,\mathbf{k}\cdot\mathbf{r}}\ ; \quad E = \frac{\hbar^2 k^2}{2m}\ , \tag{6.147}$$

is a common eigen-function of the components p_x, p_y, p_z of the operator of the momentum, and therewith also an eigen-function of the Hamilton operator H_0.

In this state the particle has a precise momentum $\hbar\,\mathbf{k}$ and a precise energy E, but, on the other hand, not a well-defined angular momentum.

However, we can consider the *free* particle motion formally also as the limiting case of a motion in a *'central potential of the strength zero'*, and can therefore directly apply the so far derived results of the present chapter. So it is clear that with

$$k = \sqrt{\frac{2m\,E}{\hbar^2}}\;; \quad z = k\,r$$

the radial equation (6.114) remains valid:

$$\left(\frac{d^2}{dz^2} + \frac{2}{z}\,\frac{d}{dz} + 1 - \frac{l(l+1)}{z^2}\right) R_l(z) = 0\;.$$

The potential $V(r)$ is zero but the centrifugal barrier (6.20) is still present. The general solution of this *Bessel equation* is given in (6.121), where, because of the required regularity at the origin, all the coefficients of the Neumann functions must be zero:

$$R_l(r) \sim j_l(k\,r)\;.$$

The angle part of the wave function is, according to (6.16), a spherical harmonic $Y_{lm_l}(\vartheta,\varphi)$. We have therewith found for the *free* particle with

$$j_l(k\,r)\,Y_{lm_l}(\vartheta,\varphi) \qquad (\mathbf{r} : r,\vartheta,\varphi)$$

a common eigen-function of the operators H_0, $\mathbf{L}^2$ and L_z. These functions build a complete system. The plane wave (6.147) can therefore be expanded in these functions:

$$\psi_0(\mathbf{r}) = \sum_{l=0}^{\infty}\;\sum_{m_l=-l}^{+l} c_{lm_l}\,j_l(k\,r)\,Y_{lm_l}(\vartheta,\varphi)\;. \tag{6.148}$$

The remaining task consists in fixing the coefficients c_{lm_l}. For this purpose we consider at first the special case that the direction of the wave vector $\mathbf{k}$ defines the z-axis of the system of coordinates. The left-hand side of the equation (6.148) then no longer contains the angle φ ($\mathbf{k}\cdot\mathbf{r} = k\,r\cos\vartheta$). The same must therefore hold for the right-hand side, and that has the consequence that $m_l = 0$ or

$$c_{lm_l} = c_l\,\delta_{m_l 0}\;.$$

Since, according to (5.103), the $m_l = 0$-spherical harmonics are proportional to the Legendre polynomials,

$$Y_{l0}(\vartheta,\varphi) = \sqrt{\frac{2l+1}{4\pi}}\,P_l(\cos\vartheta)\;,$$

we have the intermediate result:

$$e^{ikr\cos\vartheta} = \sum_{l=0}^{\infty}\sqrt{\frac{2l+1}{4\pi}}\,c_l\,j_l(k\,r)\,P_l(\cos\vartheta)\;. \tag{6.149}$$

It follows, with the orthogonality relation (5.98) for Legendre polynomials, when we multiply the last equation by $P_n(x)$ and then integrate over $x = \cos\vartheta$ from -1 to $+1$:

$$\frac{2n+1}{2}\int_{-1}^{+1} dx\, e^{ikrx}\, P_n(x) = c_n\sqrt{\frac{2n+1}{4\pi}}\, j_n(k\,r)\ . \tag{6.150}$$

The actual goal is the determination of the c_n, which are independent of r. We can therefore, during the evaluation, ascribe the coordinate r to an especially *'handy'* region, for instance to the asymptotic limit $r \to \infty$. The left-hand side of the above equation can then be estimated as follows:

$$\begin{aligned}\int_{-1}^{+1} dx\, e^{ikrx}\, P_n(x) &= \frac{1}{ikr}\left[e^{ikrx}\, P_n(x)\right]_{-1}^{+1} - \frac{1}{ikr}\int_{-1}^{+1} dx\, e^{ikrx}\, P_n'(x) \\ &= \frac{1}{ikr}\left[e^{ikrx}\, P_n(x)\right]_{-1}^{+1} + \mathcal{O}\left(\frac{1}{r^2}\right)\ .\end{aligned}$$

The last step one understands when one integrates $e^{ikrx}\, P_n'(x)$ once more by parts. With $P_n(\pm 1) = (\pm 1)^n$ one thus can write:

$$\begin{aligned}\int_{-1}^{+1} dx\, e^{ikrx}\, P_n(x) &= \frac{1}{ikr}\left(e^{ikr} - (-1)^n\, e^{-ikr}\right) + \mathcal{O}\left(\frac{1}{r^2}\right) \\ &= \frac{i^n}{ikr}\left(e^{i(kr\,-\,n(\pi/2))} - e^{-i(kr\,-\,n(\pi/2))}\right) + \mathcal{O}\left(\frac{1}{r^2}\right) \\ &= \frac{2i^n}{kr}\sin\left(k\,r - n\frac{\pi}{2}\right) + \mathcal{O}\left(\frac{1}{r^2}\right)\ .\end{aligned} \tag{6.151}$$

The comparison with (6.125) shows that the integral behaves for large r almost like the spherical Bessel function:

$$\int_{-1}^{+1} dx\, e^{ikrx}\, P_n(x) \approx 2i^n\, j_n(k\,r)\ .$$

With (6.150) the coefficients c_n are then determined:

$$c_n = i^n\sqrt{4\pi(2n+1)}$$

Inserting them into (6.149) we finally get the following expansion of the plane wave:

$$e^{ikr\cos\vartheta} = \sum_{l\,=\,0}^{\infty} i^l(2l+1)\, j_l(k\,r)\, P_l(\cos\vartheta)\ . \tag{6.152}$$

When we still apply, at the end, the addition theorem for spherical harmonics ((2.161), Vol. 3),

$$\begin{aligned} P_l(\cos\gamma) &= \frac{4\pi}{2l+1}\sum_{m_l} Y^*_{lm_l}(\vartheta_k,\varphi_k)\, Y_{lm_l}(\vartheta_r,\varphi_r)\,, \\ \gamma &= \sphericalangle(\mathbf{r},\mathbf{k})\,, \end{aligned}$$

in which ϑ_k, φ_k are the polar angles of $\mathbf{k}$ and ϑ_r, φ_r those of $\mathbf{r}$, then we can generalize our result for the plane wave to arbitrary space directions of the wave vector $\mathbf{k}$:

$$\psi_0(\mathbf{r}) = e^{i\,\mathbf{k}\cdot\mathbf{r}} = 4\pi\sum_{l,m_l} i^l\, j_l(k\,r)\, Y^*_{lm_l}(\vartheta_k,\varphi_k)\, Y_{lm_l}(\vartheta_r,\varphi_r)\,. \tag{6.153}$$

6.5 Self-Examination Questions

To Section 6.1

1. What is the physical reason for the fact that in the case of a central potential the Hamilton operator H commutes with $\mathbf{L}^2$ and L_z?
2. How is the radial momentum p_r defined in Quantum Mechanics? Which form does this operator take in the position representation?
3. Under which conditions is p_r Hermitian?
4. Why, in a strict sense, p_r is not an observable?
5. What is the connection between particle momentum $\mathbf{p}$, radial momentum p_r and square of the angular momentum $\mathbf{L}^2$?
6. Which separation ansatz recommends itself for the wave function $\psi(\mathbf{r})$ of a particle in a central field?
7. What is understood by the *radial equation*?
8. With respect to which quantum number are the energies of a particle in an arbitrary central field in any case degenerate?
9. What does one understand by the *centrifugal barrier*?

To Section 6.2

1. What is the potential energy of an electron in a *hydrogen-like* ion?
2. Which structure does the radial equation have for the electron in the hydrogen atom?
3. Which ansatz is recommendable for the solution function of the radial equation?

4. Illustrate on the example of the H-atom *the idea* of the Sommerfeld's polynomial method!
5. Which discrete energy levels come into question for the electron in the H-atom?
6. To what degree are these degenerate? How does one calculate the degree of degeneracy?
7. Which ground state energy does the electron possess in the hydrogen atom? Give the approximate numerical value in eV!
8. How is the principal quantum number defined?
9. Which values can the secondary quantum number assume?
10. What is called *accidental degeneracy*?
11. Explain the term *electron shell* for the H-atom.
12. What is an L-shell and what is a d-orbital?
13. How can the Ritz's combination principle be explained by the example of the hydrogen atom?
14. Which type of function determines the radial part of the bound states in the Coulomb potential?
15. How many zeros does the radial function $R_{nl}(r)$ possess in the Coulomb potential?
16. Which of the $R_{nl}(r)$ are unequal zero at $r = 0$?
17. What does one understand by *radial position probability*?
18. What are *nodal planes*?
19. Where does one find the maximum of the radial position probability for the electron in the ground state ($n = 1$, $l = 0$) of the hydrogen atom?
20. How does the maximum of the density of the radial position probability shift with increasing principal quantum number and maximal secondary quantum number $l = n - 1$?
21. How do the *orbital radii* $\langle r \rangle_{nl}$ in the bound states of the Coulomb potential behave as functions of the principal quantum number n and the atomic number Z?
22. In which sense does the quantum-mechanical treatment of the electron motion in the Coulomb potential fulfill the rule of correspondence, according to which for large quantum numbers n the classical concept of a path (an orbit) should be approximately valid?

23. For the Coulomb potential, how does the quantum-mechanical analog of the classical virial theorem read?

24. How does one plot a *polar diagram*?

25. By which special symmetry are the s-states characterized?

26. Which angle distribution characterizes p-states?

27. Why is the *hydrogen problem* actually a two-body problem? By which *'trick'* can it be reduced to an effective one-particle problem?

28. How do the solutions of the hydrogen problem differ, when, on the one hand, one considers the nucleus to be *'at rest'*, and on the other hand, when one includes its motion?

29. What is the canonically conjugate momentum which belongs to the relative coordinate $\mathbf{r}$?

30. How does the center of gravity of the hydrogen atom move, when the Coulomb attraction between the proton and the electron is the only force acting?

To Section 6.3

1. For which type of forces can the spherically symmetric potential well serve as a simple model?

2. Which structure does the Bessel differential equation have?

3. Which special sets of functions solve the Bessel differential equation?

4. How do the spherical Bessel and Neumann functions ($j_l(z)$, $n_l(z)$) behave close to the origin of coordinates $z = 0$? Which curve do they exhibit for $z \to \infty$?

5. Which connection exists between the Hankel functions of first and second kind and the spherical Bessel and Neumann functions?

6. How do the Hankel functions behave for large z?

7. Why should the radial function of a bound state, within the spherically symmetric potential well, behave like a spherical Bessel function?

8. Why does the energy condition for bound s-states ($l = 0$) in the spherically symmetric potential well agree with that for antisymmetric eigen-functions of the one-dimensional potential well?

9. Are bound states possible for arbitrary depths V_0 of the spherically symmetric potential well?

10. How does the presence of the potential well asymptotically influence the radial functions of the continuum states?

To Section 6.4

1. In which manner are the general results for the problems of central potentials transferable to the case of the non-interacting (*free*) particle?

2. Does the *centrifugal barrier* exist also for the *free* particle?

3. What is the structure of the common eigen-functions of the operators H_0, $\mathbf{L}^2$ and L_z in the case of the *free* particle?

Chapter 7

Approximation Methods

Only very few problems of Theoretical Physics can be really solved in a mathematically rigorous sense. In order to be able to understand experimental observations and to describe them realistically the theoretician needs an as wide as possible repertoire of approximation methods. He (she) is obliged to replace not achievable exact solutions by well-founded approximations, which do not adulterate the essential *physical aspects*. He (she) will therefore try to free the original problem from unnecessary *'baggage'*. i.e., to stress the important facts, and to suppress *marginal phenomena* in favor of mathematical simplicity. It would be desirable, but unfortunately not always satisfactorily accessible, to find a way to estimate the *error*, which by definition is always associated with such an approximation.

In this chapter we present four conceptionally rather different methods, the variational method (Sect. 7.1), the time-independent Schrödinger perturbation theory (Sect. 7.2), the Dirac (time-dependent) perturbation theory (Sect. 7.3) as well as the quasi-classical WKB-method (**W**entzel, **K**ramers, **B**rillouin). All these approximation procedures can rather easily be abstract-theoretically understood; the application to actual problems, however, may sometimes turn out to be somewhat more demanding. Therefore, especially in this chapter, the offer of exercises should be accepted by the reader for an in-depth understanding of the underlying theory.

The **variational method** can be especially used sometimes for astonishingly excellent estimations of the ground-state energy of a physical system. It is based on a general extremal principle, according to which each state $|\varphi\rangle$, for which the expectation value $\langle\varphi|A|\varphi\rangle$ of the Hermitian operator A is extremal, is an eigen-state of A.

The **time-independent Schrödinger perturbation theory** is specific to systems, the Hamilton operator of which can be additively decomposed into an *unperturbed* operator H_0 and a *perturbation* H_1. The eigen-value problem for H_0 shall thereby be exactly solvable, while H_1 represents a *relatively small quantity*.

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Systematic expansions of physically relevant terms in powers of the *perturbation* can then be terminated approximately after a finite number of summands.

The statement of the problem for the **Dirac perturbation theory** is somewhat different. This theory is focused on the temporal evolution of a physical system under the influence of a time-dependent external perturbation. For realistic systems, however, that is again only approximately determinable.

While *perturbation theory* is applied to problems, for which the solution to be found differs *only slightly* from that of a known, precisely tractable problem, the **WKB-method** can be used always when the quantum-mechanical system is still rather similar to the corresponding classical $\hbar \to 0$-*limiting case*. That presumes an only weakly position-dependent de Broglie-wave length. In particular, the de Broglie wavelength should be small compared to all the geometric dimensions, over which the potential of the system changes appreciably. For *bound states* the wave length scales with the distance of the nodes. For large quantum numbers there are many nodes, and the system then behaves *quasi-classically*. There lies the scope of application of the WKB-method.

7.1 Variational Method

Let A be an arbitrary Hermitian operator (observable), whose eigen-value problem,

$$A|a\rangle = a|a\rangle \ ,$$

is too complicated for an exact solution to be available. We therefore have to be content with an approximate solution. One possibility to find such an approximate solution represents the variational method, which is based on a generally valid extremal principle.

7.1.1 Extremal Principle

Let $\mathcal{H}$ be the Hilbert space of the considered physical system and $|\varphi\rangle \in \mathcal{H}$ a state with a finite norm. Then one can interpret the expectation value of A in the state $|\varphi\rangle$,

$$\langle A\rangle_\varphi \equiv \frac{\langle\varphi|A|\varphi\rangle}{\langle\varphi|\varphi\rangle} \ , \tag{7.1}$$

as a functional of the state vector $|\varphi\rangle$. First we want to investigate how $\langle A\rangle_\varphi$ reacts on a variation of $|\varphi\rangle$, i.e., on an infinitesimal change of $|\varphi\rangle$ onto $|\varphi + d\varphi\rangle$. The variation of a functional is mathematically treated in the same manner as the *normal* differentiation (see *calculus of variation*: Sect. 1.3.2, Vol. 2):

$$\begin{aligned}
\delta\langle A\rangle_\varphi &= \frac{1}{\langle\varphi|\varphi\rangle}\,\delta\langle\varphi|A|\varphi\rangle - \frac{1}{\langle\varphi|\varphi\rangle^2}\,\langle\varphi|A|\varphi\rangle\delta\langle\varphi|\varphi\rangle \\
&= \frac{1}{\langle\varphi|\varphi\rangle}\,\left[\langle\delta\varphi|(A - \langle A\rangle_\varphi \mathbb{1})|\varphi\rangle + \langle\varphi|(A - \langle A\rangle_\varphi \mathbb{1})|\delta\varphi\rangle\right] \ .
\end{aligned}$$

The **extremal behavior** of $\langle A\rangle_\varphi$ is especially important:

$$\delta\langle A\rangle_\varphi \stackrel{!}{=} 0 \,. \tag{7.2}$$

Condition for this is obviously:

$$\langle\delta\varphi|(A - \langle A\rangle_\varphi \mathbb{1})|\varphi\rangle + \langle\varphi|(A - \langle A\rangle_\varphi \mathbb{1})|\delta\varphi\rangle = 0 \,. \tag{7.3}$$

$|\delta\varphi\rangle$ and $\langle\delta\varphi|$, which are variations of the dual ket- and bra-vectors $|\varphi\rangle$ und $\langle\varphi|$, are certainly not independent of each other. So we cannot conclude immediately that the two summands in (7.3) by themselves are already zero. Nevertheless, the conclusion is correct. $|\delta\varphi\rangle$ is an infinitesimally small *state deviation*. The same holds of course also for $i|\delta\varphi\rangle = |\delta(i\,\varphi)\rangle$. Any **arbitrary** infinitesimal deviation from the extremum of $\langle A\rangle_\varphi$ leads to (7.2), thus also $|\delta(i\,\varphi)\rangle$. Because of

$$|\delta(i\,\varphi)\rangle = i|\delta\varphi\rangle \;; \quad \langle\delta(i\,\varphi)| = -i\langle\delta\varphi|$$

it follows then instead of (7.3):

$$-i\langle\delta\varphi|(A - \langle A\rangle_\varphi \mathbb{1})|\varphi\rangle + i\langle\varphi|(A - \langle A\rangle_\varphi \mathbb{1})|\delta\varphi\rangle = 0 \,.$$

If one multiplies this equation by i and, respectively, adds it to (7.3) and subtracts it from (7.3), then one recognizes that indeed both the summands in (7.3) by themselves are already zero. But that is equivalent to :

$$(A - \langle A\rangle_\varphi \mathbb{1})|\varphi\rangle = 0 \;; \quad \langle\varphi|(A - \langle A\rangle_\varphi \mathbb{1}) = 0 \,. \tag{7.4}$$

The second equation is identical to

$$(A^+ - \langle A\rangle_\varphi^* \mathbb{1})|\varphi\rangle = 0 \,.$$

A is Hermitian according to the premises. In addition, the expectation values of Hermitian operators are always real ((3.64), Vol. 6). The two equations in (7.4) are therefore identical. We have therewith derived the important **extremal principle**:
Each state $|\varphi\rangle$ of the Hilbert space, for which the expectation value $\langle A\rangle_\varphi$ of the Hermitian operator A becomes extremal,

$$\delta\langle A\rangle_\varphi = 0 \,,$$

is an eigen-state of A. The eigen-values of A are just the extremal values of the functional $\langle A\rangle_\varphi$.

By this generally valid principle, practical methods for the approximate determination of eigen-values and eigen-states can be developed. This may happen, for instance, by restricting the space of the states from $\mathcal{H}$, which are allowed to participate in the variation, to those for which the extremal condition (7.2) is mathematically easy to evaluate. Is the actual eigen-state **not** within this *restricted space*, then the evaluation of (7.2) will result in an approximate solution. The disadvantage of such methods lies on hand. It is not always possible to judge the quality of the approximation, i.e., to estimate its deviation from the exact solution.

7.1.2 Ritz's Method

Variational procedures concerning the eigen-value problem of the Hamilton operator ($A = H$) of course are of special interest. The so-called Ritz's method aims at the approximate calculation of the levels of the discrete spectrum and can lead, in particular, to astonishingly close to the exact results for the ground-state energy. If the spectrum is bounded below, i.e., if there is a **ground-state energy** E_0, then we have for **arbitrary 'test states'** $|\varphi\rangle \in \mathcal{H}$:

$$\langle H\rangle_\varphi = \frac{\langle\varphi|H|\varphi\rangle}{\langle\varphi|\varphi\rangle} \geq E_0 \ . \tag{7.5}$$

We have presented the proof already as solution to Exercise 6.1.4. If we use

$$H|E_n\rangle = E_n|E_n\rangle \ ; \quad E_n \geq E_0 \ ; \quad |\varphi\rangle = \sum_n \alpha_n|E_n\rangle \ ,$$

then we can easily estimate:

$$\begin{aligned} \langle H\rangle_\varphi &= \frac{\sum\limits_{n,m} \alpha_n^* \alpha_m \langle E_n|H|E_m\rangle}{\sum\limits_{n,m} \alpha_n^* \alpha_m \langle E_n|E_m\rangle} = \frac{\sum\limits_n E_n|\alpha_n|^2}{\sum\limits_n |\alpha_n|^2} \\ &\geq E_0 \frac{\sum\limits_n |\alpha_n|^2}{\sum\limits_n |\alpha_n|^2} = E_0 \end{aligned}$$

We obtain therewith the important statement that $\langle H\rangle_\varphi$ in any case represents an upper bound for the ground-state energy. In the case of $A = H$ the extremum of $\langle A\rangle_\varphi$ is thus a minimum.

Ritz's method is based on (7.5):

1. One chooses a *test state*,

$$|\varphi\rangle = f\left(|\chi_1\rangle, \ldots, |\chi_m\rangle;\ \alpha_1, \ldots, \alpha_n\right) \ , \tag{7.6}$$

   as function of certain fixedly given states $|\chi_1\rangle, \ldots, |\chi_m\rangle$, which need not necessarily be orthogonal to each other. They should not be, though, mathematically too complicated, so that $\langle H\rangle_\varphi$ can be *relatively easily* calculated with them. On the other hand, one tries to fit them as well as possible to the actual physical problem by taking into account, e.g., obvious **symmetries** of the system, special **boundary conditions** (asymptotic or zero-point behavior) or precisely solvable **limiting cases**. The $|\chi_i\rangle$ are fixedly given, and are thus not to be varied.

   In addition, the *test state* $|\varphi\rangle$ contains a set of real, independent parameters $\alpha_1, \ldots, \alpha_n$ as the actual variational variables.

2. One calculates with the ansatz (7.6) the energy functional,

$$\langle H\rangle_\varphi = \frac{\langle\varphi|H|\varphi\rangle}{\langle\varphi|\varphi\rangle} \equiv g(\alpha_1,\ldots,\alpha_n)\ , \tag{7.7}$$

which then becomes a function of the parameters $\alpha_1,\ldots,\alpha_n$.

3. By the requirement

$$\frac{\partial}{\partial\alpha_i}\langle H\rangle_\varphi \stackrel{!}{=} 0\ ; \qquad i=1,2,\ldots,n \tag{7.8}$$

one gets a system of equations by which an *optimal set of parameters*

$$\alpha_1^*,\ \alpha_2^*,\ldots,\alpha_n^*$$

can be derived. It is quite possible that there exist more than one solution ansatzes for (7.8). One chooses then the one which leads to the lowest $\langle H\rangle_\varphi$.

4. Finally, with these parameters one calculates

$$|\varphi^*\rangle = f\left(|\chi_1\rangle,\ldots,|\chi_m\rangle;\ \alpha_1^*,\ldots,\alpha_n^*\right) \tag{7.9}$$

as approximation for the ground state and

$$\langle H\rangle_{\varphi*} = g\left(\alpha_1^*,\ \alpha_2^*,\ldots,\alpha_n^*\right) \geq E_0 \tag{7.10}$$

as an estimation for the ground-state energy.

It is clear, according to (7.5) that the estimation (7.10) is the better the lower $\langle H\rangle_{\varphi*}$ is. With a large number of variational parameters astonishingly good approximate values for the ground-state energy can be achieved by this method. For the ground state wave function itself, however, the procedure is normally far from being as good.

The variational technique becomes especially simple for the frequently applied special case that the *test state* $|\varphi\rangle$ in (7.6) depends linearly on the α_i:

$$|\varphi\rangle = \sum_{i=1}^{m} \alpha_i|\chi_i\rangle\ . \tag{7.11}$$

The extremal condition (7.8) can then be further evaluated:

$$\frac{\partial}{\partial\alpha_i}\left(\langle H\rangle_\varphi\,\langle\varphi|\varphi\rangle\right) = \langle H\rangle_\varphi\,\frac{\partial}{\partial\alpha_i}\langle\varphi|\varphi\rangle = \frac{\partial}{\partial\alpha_i}\langle\varphi|H|\varphi\rangle\ .$$

When one inserts here (7.11),

$$\frac{\partial}{\partial\alpha_i}\sum_{n,m}\alpha_n\,\alpha_m\,\left(\langle\chi_n|H|\chi_m\rangle - \langle H\rangle_\varphi\,\langle\chi_n|\chi_m\rangle\right) = 0\ ,$$

then there results a linear homogeneous system of equations,

$$\sum_n \alpha_n \left(\mathrm{Re}\langle\chi_n|H|\chi_m\rangle - \langle H\rangle_\varphi \ \mathrm{Re}\ \langle\chi_n|\chi_m\rangle \right) = 0 \ ,$$

the solution of which requires the vanishing of the secular determinant:

$$\det\{\mathrm{Re}\langle\chi_n|H|\chi_m\rangle - \langle H\rangle_\varphi \, \mathrm{Re}\langle\chi_n|\chi_m\rangle\} \stackrel{!}{=} 0 \ . \tag{7.12}$$

From all the possible solutions of this relation one again picks up the one with the minimal $\langle H\rangle_\varphi$. When one inserts this into the above homogeneous system of equations, the *optimal* α_i^* are also determined, which lead via (7.11) to an approximation for the ground state $|E_0\rangle$.

It should also be mentioned that with the Ritz's variational method one can find approximate solutions also for excited states and their energies. When one starts from the spectral representation of the Hamilton operator,

$$H = \sum_n E_n |E_n\rangle\langle E_n| \ , \tag{7.13}$$

then one can define an Hermitian operator H_1 by:

$$H_1 = H - E_0|E_0\rangle\langle E_0| \ . \tag{7.14}$$

If now E_0 and $|E_0\rangle$ are **exactly** known, then the Ritz's method delivers according to the extremal principle an upper bound for the first *excited* energy level E_1:

$$\langle H_1\rangle_\varphi \geq E_1 \ . \tag{7.15}$$

As a rule, though, the exact solutions for E_0 and $|E_0\rangle$ will not be available, but rather, if at all, approximations, e.g. from a preceding variational procedure. If one uses such approximations, then, of course, the statement (7.15) that $\langle H_1\rangle_\varphi$ represents in any case an upper bound for E_1, is no longer proven. The by far most applications of the variational method are therefore focused on the determination of the ground-state energy only.

We still want to talk a bit about a variant of the Ritz's method, which consists in the fact that in the test state $|\varphi\rangle$ not the real parameters α_i, but the states $|\chi_i\rangle$ are to be considered as the free variables (7.6). The extremal principle then yields a system of equations for *optimal* $|\chi_i\rangle$. A practically important example of application, which leads to the so-called *Hartree equations* for many-electron systems, explains, in the next section, details about the procedure.

7.1.3 Hartree Equations

The subject matter of the following considerations is a system of $N > 2$ electrons. They can be the shell electrons of an atom, but also can be the electrons in an energy band of a solid. We describe them by the Hamilton operator:

$$H_N = \sum_{i=1}^{N} \left(\frac{\mathbf{p}_i^2}{2m} + V_i(\mathbf{r}_i) \right) + \frac{1}{2} \sum_{i,\,j}^{i \neq j} \frac{e^2}{4\pi\,\varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \ . \tag{7.16}$$

$\mathbf{r}_i$ and $\mathbf{p}_i$ are position and momentum of the ith particle. Let $V_i(\mathbf{r}_i)$ be the potential energy of the electron in the field of the positively charged nucleus and in the field of periodically arranged lattice ions, respectively. An exact solution of the eigen-value problem for $N > 2$ is prevented by the second summand in (7.16), which represents the interaction of the electrons with each other. We look for a *well approximated* value of the ground-state energy of the N-electron system.

The special form of the Hamilton operator makes the position representation to be convenient. Let $\psi_i(\mathbf{r}_i)$ be the wave function of the ith electron with

$$\int d^3r_i \, \psi_i^* \left(\mathbf{r}_i\right) \psi_i \left(\mathbf{r}_i\right) = 1 \qquad \forall i \; . \tag{7.17}$$

For simplicity we disregard the spin of the electron since we are here more interested in the representation of the technical algorithm, and not so much in the details of the physical result. Of course, the inclusion of the spin according to Sect. 5.2.4 would not create any principle problem.

The product of the N one-particle wave functions presents itself as simplest *test wave function*:

$$\varphi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \equiv \psi_1 \left(\mathbf{r}_1\right) \psi_2 \left(\mathbf{r}_2\right) \cdots \psi_N \left(\mathbf{r}_N\right) \; , \tag{7.18}$$

$$\int d^3r_1 \ldots d^3r_N \, \varphi^* \left(\mathbf{r}_1, \ldots, \mathbf{r}_N\right) \varphi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = 1 \; . \tag{7.19}$$

Because of the interaction term in the Hamilton operator, φ is surely not an eigen-function of H_N. However, we will frequently meet such **product wave functions** in Chap. 8, where we treat systematically the *quantum theory of many-particle systems*. It is a matter of course that the ansatz for our variational procedure must contain the coordinates of all the N electrons. We want to achieve with this ansatz an estimation for the ground-state energy by choosing an *optimal set* of one-particle functions in (7.18). For this purpose we build the *energy functional*:

$$\begin{aligned} \langle H_N \rangle_\varphi &= \int d^3r_1 \ldots d^3r_N \, \varphi^* \, H_N \varphi \\ &= \sum_{i=1}^{N} \int d^3r_i \, \psi_i^* \left(\mathbf{r}_i\right) \left\{ -\frac{\hbar^2}{2m} \, \Delta_i + V_i \left(\mathbf{r}_i\right) \right\} \psi_i \left(\mathbf{r}_i\right) \\ &\quad + \frac{1}{2} \sum_{i,\, j}^{i \neq j} \int d^3r_i \, d^3r_j \, \psi_i^* \left(\mathbf{r}_i\right) \psi_j^* \left(\mathbf{r}_j\right) \frac{e^2}{4\pi \, \varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \, \psi_j \left(\mathbf{r}_j\right) \psi_i \left(\mathbf{r}_i\right) \; . \end{aligned} \tag{7.20}$$

Here we have already exploited the normalization (7.17). In order to find the *optimal* one-particle wave functions we vary the *energy functional* with respect to $\psi_i^* \left(\mathbf{r}\right)$ and set the first variation equal to zero. $\psi_i^* \left(\mathbf{r}\right)$ possesses, as a complex function with its real and imaginary parts, in principle two independent variational degrees of freedom. That we can exploit also in such a way that we consider $\psi_i^* \left(\mathbf{r}\right)$ and $\psi_i \left(\mathbf{r}\right)$ as independent variational variables. But then we

have to still incorporate the boundary conditions (7.17) for $i = 1, 2, \ldots, N$ into the main variational equation by the use of Lagrange multipliers λ_i (as to the *method of Lagrange multipliers* see Vol. 2, Sect. 1.2.5):

$$\delta \left(\langle H_N \rangle_\varphi - \sum_{i=1}^{N} \lambda_i \int d^3 r \, \psi_i^* (\mathbf{r}) \, \psi_i (\mathbf{r}) \right) \stackrel{!}{=} 0 \, . \tag{7.21}$$

This means with (7.20):

$$\sum_{i=1}^{N} \int d^3 r_i \, \delta\psi_i^* (\mathbf{r}_i) \left[-\frac{\hbar^2}{2m} \Delta_i + V_i (\mathbf{r}_i) \right.$$
$$\left. + \sum_{j}^{\neq i} \int d^3 r_j \, \psi_j^* (\mathbf{r}_j) \, \frac{e^2}{4\pi \, \varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \, \psi_j (\mathbf{r}_j) - \lambda_i \right] \psi_i (\mathbf{r}_i) \stackrel{!}{=} 0 \, .$$

The factor $1/2$ in front of the third term in the bracket vanishes because ψ_i^* appears twice in the double sum (7.20). After coupling the boundary conditions by the multipliers λ_i the variations $\delta\psi_i^*$ are completely arbitrary. We can, e.g., put all $\delta\psi_n^* (\mathbf{r}_n) = 0$ for $n \neq i$, and furthermore assume the $\mathbf{r}_i$-dependence of the $\delta\psi_i^*$ to be arbitrary. That leads then to the **Hartree equations**:

$$\left[-\frac{\hbar^2}{2m} \Delta_i + V_i (\mathbf{r}_i) \right.$$
$$\left. + \sum_{j}^{\neq i} \int d^3 r_j \, \psi_j^* (\mathbf{r}_j) \, \frac{e^2}{4\pi \, \varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \, \psi_j (\mathbf{r}_j) - \lambda_i \right] \psi_i (\mathbf{r}_i) = 0 \, ;$$
$$i = 1, 2, \ldots, N \, . \tag{7.22}$$

These have the form of eigen-value equations where the Lagrange multipliers λ_i play the role of the energy-eigen values and the *optimal* $\psi_i (\mathbf{r}_i)$ that of the eigen-functions:

$$\left[-\frac{\hbar^2}{2m} \Delta_i + V_i (\mathbf{r}_i) + V_{\text{eff}}^{(i)} (\mathbf{r}_i) \right] \psi_i (\mathbf{r}) = \lambda_i \, \psi_i (\mathbf{r}_i) \, ,$$
$$i = 1, 2, \ldots, N \, . \tag{7.23}$$

The meaning of the terms can be easily interpreted. The first term is the kinetic energy of the ith electron, the second its potential energy in the external potential (nuclear potential or periodic lattice potential). The third summand represents a **repulsive** potential which arises from the interaction with the $N-1$ other electrons:

$$V_{\text{eff}}^{(i)} (\mathbf{r}_i) = \frac{e^2}{4\pi \, \varepsilon_0} \sum_{j}^{\neq i} \int d^3 r_j \, \frac{|\psi_j (\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|} \, . \tag{7.24}$$

It is about an *effective* potential, which is actually determined by the still to be found one-electron wave functions, and therefore, as one says, has to be calculated *self-consistently*. This is effected by iteration. One first solves the problem without the repulsive term $V_{\text{eff}}^{(i)}$ and obtains therewith in *zeroth order* $\psi_i^{(0)}(\mathbf{r}_i)$, $\lambda_i^{(0)}$, for instance just the solutions of the hydrogen problem from Sect. 6.2. With the $\psi_i^{(0)}(\mathbf{r}_i)$ one calculates then $V_{\text{eff}}^{(i)}(\mathbf{r}_i)$ and solves subsequently the eigen-value anew. The procedure is continued until the solutions, within certain pre-given accuracy-limits, do no longer change (*'method of the self-consistent field'*). It goes without saying that the practical execution needs a high-power computer. After finishing the iteration one obtains as an estimation for the **ground-state energy**, when one multiplies from the left the Hartree equations (7.22) by $\psi_i^*(\mathbf{r}_i)$, integrates over $\mathbf{r}_i$, sums over i, and finally compares the result with (7.20):

$$E_0 \leq \langle H_N \rangle_\varphi = \sum_{i=1}^{N} \lambda_i \; - \\ -\frac{e^2}{8\pi\,\varepsilon_0} \sum_{i,\,j}^{i\neq j} \iint d^3r_i\, d^3r_j\, \psi_i^*(\mathbf{r}_i)\, \psi_j^*(\mathbf{r}_j)\, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\, \psi_j(\mathbf{r}_j)\, \psi_i(\mathbf{r}_i)\,. \tag{7.25}$$

The approximate ground state comes out by insertion of the *optimal* $\psi_i(\mathbf{r}_i)$ into the product ansatz (7.18).

It will be clearly demonstrated in Chap. 8, though, that the *Hartree ansatz* (7.18) is acceptable actually only for the *spinless* and the so-called *distinguishable* particles. Electrons are neither the one nor the other. They obey the fundamental **Pauli principle**, which requires an antisymmetrized N-particle wave function built up by pairwise-different one-particle functions. This fact is taken into account by the later to be discussed **Hartree-Fock method** (Sect. 8.4.1). We therefore cannot expect that the wave function (7.18), determined by the Hartree method, will turn out to be *physically convincing*. On the other hand, the estimation of the ground-state energy by (7.25) appears pretty much more realistic!

7.1.4 Exercises

Exercise 7.1.1
A particle moves in the potential

$$V(q) = \begin{cases} \frac{1}{2}\, m\, \omega^2 q^2 & \text{for } q > 0\,, \\ \infty & \text{for } q \leq 0\,. \end{cases}$$

1. Verify (without explicit calculation!) that the exact ground-state energy amounts to $E_0 = (3/2)\,\hbar\,\omega$.

2. Use the variational ansatz

$$\varphi(q) = \begin{cases} 0 & \text{for } q \le 0 \,, \\ c\, q\, e^{-\alpha q} & \text{for } q > 0 \end{cases}$$
$$(\alpha = \text{ variational parameter}) \,,$$

in order to estimate, according to the Ritz's variational procedure, the ground-state energy. Discuss the choice of this ansatz.

3. What would be the result with the variational ansatz:

$$\varphi(q) = \begin{cases} 0 & \text{for } q < 0 \,, \\ c\, q\, e^{-\alpha q^2} & \text{for } q \ge 0 \,? \end{cases}$$

Formulas:

$$\int_0^\infty dq\, q^n\, e^{-\gamma q} = \frac{\Gamma(n+1)}{\gamma^{n+1}} \,,$$
$$\int_0^\infty dq\, q^n\, e^{-\gamma q^2} = \frac{(1/2)\,\Gamma\left((n+1)/2\right)}{\gamma^{(n+1)/2}} \,,$$
$$\Gamma(n+1) = n\,\Gamma(n) \,; \quad \Gamma(1) = 1 \,; \quad \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi} \,.$$

Exercise 7.1.2
Use the Ritz's variational method for the estimation of the ground-state energy of the linear harmonic oscillator by means of the ansatz:

$$\varphi(q) = \frac{1}{\alpha^2 + q^2} \,.$$

Formulas:

$$\int_0^\infty \frac{dq}{(\alpha^2+q^2)^2} = \frac{\pi}{4\alpha^3} \,; \quad \int_0^\infty dq\, \frac{q^2}{(\alpha^2+q^2)^2} = \frac{\pi}{4\alpha} \,,$$
$$\int_0^\infty \frac{dq}{(\alpha^2+q^2)^3} = \frac{3\pi}{16\alpha^5} \,; \quad \int_0^\infty dq\, \frac{q^2}{(\alpha^2+q^2)^4} = \frac{\pi}{32\alpha^5} \,.$$

Exercise 7.1.3
A linear harmonic oscillator

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 q^2$$

is in a force field of the form:

$$F(q) = f - 2\gamma\, q \,; \quad (f, \gamma: \text{ real constants})$$

1. With the variational ansatz (α: variation parameter),

$$\varphi(q) = c \exp\left(-\frac{1}{2}\alpha q^2\right) ,$$

find an estimation for the ground-state energy!

2. Try to solve exactly the eigen-value problem and compare the ground-state energy with the variational result from part 1.

Exercise 7.1.4

1. For the ground state of the hydrogen atom we choose the normalized test-wave function

$$\psi_\alpha(\mathbf{r}) = \left(\frac{\alpha}{\pi}\right)^{\frac{3}{4}} \exp\left(-\frac{1}{2}\alpha r^2\right) .$$

Calculate therewith, according to the variational principle, an upper bound for the ground-state energy. Compare this with the exact result!

2. What would the ansatz

$$\psi_\beta(\mathbf{r}) = \gamma \exp(-\beta r)$$

yield? (γ: normalization constant, β: variational parameter)

Exercise 7.1.5
We describe the interaction between a neutron and a proton, at a distance r, by an attractive Yukawa potential

$$V(r) = -V_0 \frac{\exp(-r/a)}{r/a} \qquad (V_0 > 0) .$$

1. Formulate the time-independent Schrödinger equation and separate this equation with respect to relative and center-of-mass coordinates (cf. Sect. 6.2.5).

2. Solve the equation for the center-of-mass motion and find the angle-dependence of the eigen-functions of the relative motion.

3. Choose and motivate the variational ansatz

$$\varphi(\mathbf{r}) = c \exp\left(-\alpha\frac{r}{a}\right)$$

and calculate the energy functional.

4. At which value of α is this energy functional minimal (Ritz's variational method!)?

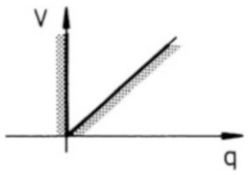

Figure 7.1: Simple one-dimensional potential curve with linear space-dependence for $q > 0$ and infinitely high wall for $q < 0$

5. For $a = 1.4 \cdot 10^{-13}\,\mathrm{cm}$, $V_0 = 50\,\mathrm{MeV}$, $q = 2\mu\, V_0\, a^2/\hbar^2 = 2.46$ (μ: reduced mass), the *optimal* α from 4. has the numerical value 0.85. Estimate therewith the binding energy of the deuterium.

6. Define, as *reasonably as possible*, the average radius of the deuterium, and calculate this radius by the use of the numerical values given in part 5.

Exercise 7.1.6
A particle of mass m performs a one-dimensional motion in the potential (Fig. 7.1)

$$V(q) = \begin{cases} \gamma\, q & \text{for } q \geq 0\,, \\ +\infty & \text{for } q < 0 \end{cases}$$

1. With the variational ansatz

$$\varphi(q) = \begin{cases} q\, e^{-\alpha q} & \text{for } q \geq 0\,, \\ 0 & \text{for } q < 0 \end{cases}$$

calculate the energy functional $\langle H \rangle_\varphi$. Give reasons for the ansatz.

2. Find by means of the Ritz's variational method an upper bound for the ground-state energy.

Exercise 7.1.7
A particle of mass m moves in a one-dimensional potential $V = V(q)$. Let this be a homogeneous function of q of the degree n, i.e.,

$$V(\alpha q) = \alpha^n V(q) \qquad \forall\, \alpha \in \mathbb{R}.$$

Prove by means of the extremal principle of the variational method that for the expectation values of the kinetic and potential energy, built with energy-eigen states, the *'quantum-mechanical virial theorem'* is valid:

$$2\langle T \rangle = n \cdot \langle V \rangle$$

(T: kinetic energy).
Hint: Let $|\psi(q)\rangle$ be a normalized eigen-state of $H = T + V$. Investigate the energy functional $\langle H \rangle_{\psi(\alpha q)}$!

7.2 Time-Independent Perturbation Theory

The **Schrödinger perturbation theory** aims at systems, whose Hamilton operators can be decomposed in such a way,

$$H = H_0 + H_1 \ , \tag{7.26}$$

that the eigen-value problem of H_0 is exactly solvable, and the *perturbation* H_1 represents only a small correction term. The goal is to find for the not exactly solvable *full* problem,

$$H\,|E_n\rangle = E_n|E_n\rangle \ , \tag{7.27}$$

as good an approximation as possible. For this purpose, in the first step, one rigorously solves the *unperturbed* problem:

$$H_0|E_n^{(0)}\rangle = E_n^{(0)}|E_n^{(0)}\rangle \tag{7.28}$$

The eigen-states of the Hermitian operator H_0 represent a complete orthonormal system:

$$\langle E_n^{(0)} \Big| E_m^{(0)}\rangle = \delta\,(n,m) \ , \tag{7.29}$$

$$\mathbb{1} = \sum\!\!\!\!\!\!\int_n |E_n^{(0)}\rangle\langle E_n^{(0)}| \ . \tag{7.30}$$

We have introduced the symbol $\delta(n,m)$ in (3.49) (Vol. 6). In the discrete part of the spectrum it has the meaning of the Kronecker-delta δ_{nm}, and in the continuum part it represents the δ-function $\delta\left(E_n^{(0)} - E_m^{(0)}\right)$. For the following we will assume that the eigen-value, whose shift due to the *perturbation* H_1 shall be investigated, is **discrete**, which, however, need not necessarily be the case for the entire spectrum of H_0.

Since, according to (7.27), the eigen-states $|E_n\rangle$, we are looking for, are fixed except for an arbitrary constant factor, we can agree upon the following **special normalization**:

$$\langle E_n^{(0)} \Big| E_n\rangle \stackrel{!}{=} 1 \ . \tag{7.31}$$

After having completed the perturbative procedure the resulting state $|E_n\rangle$ can of course be easily re-normalized.

The concept of the **Schrödinger perturbation theory** is based on the idea that the *perturbation* H_1 *is switched on* by means of a real parameter $0 \le \lambda \le 1$:

$$H_1 \ \longrightarrow \ \lambda\, H_1 \ . \tag{7.32}$$

For that it is presumed that it holds for $\lambda \to 0$ (Fig. 7.2):

$$\begin{aligned} E_{n\alpha} \ &\longrightarrow \ E_n^{(0)} \ , \\ |E_{n\alpha}\rangle \ &\longrightarrow \ |E_n^{(0)}\rangle \ . \end{aligned}$$

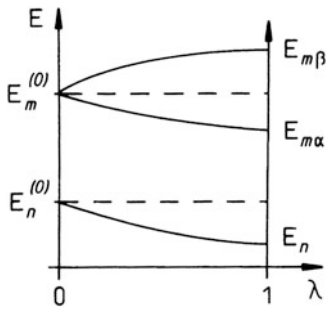

Figure 7.2: Schematic behavior of the eigen-energies of the Hamilton operator of a physical system, which can be treated by the Schrödinger perturbation theory, in dependence of a continuous switching on of the perturbation

The systems, described by H and H_0, respectively, will, because of the *perturbation*, in general quantitatively differ, but they should **qualitatively** be rather similar. This fact is, however, not at all always guaranteed. Certain phenomena, as e.g. superconductivity, for which the transition from the unperturbed to the perturbed system can **not** be achieved by a continuous change of the parameter λ, and therefore can not be treated perturbatively. The *perturbation* H_1 can possibly lift, though, certain degeneracies in the *unperturbed* system.

The parameter λ in (7.32) can, in concrete cases, also be a *real physical quantity (coupling constant)*. For the following rather abstract considerations, however, it is introduced only due to expedience. The method consists namely in the expansion of the unknown quantities E_n and $|E_n\rangle$ as power series in λ with coefficients which are built up exclusively by the known *unperturbed* quantities $E_n^{(0)}$ and $|E_n^{(0)}\rangle$. By sorting with respect to the powers of λ one can, in a convenient manner, expand the approximation in powers of the *perturbation* H_1 up to the desired accuracy. At the end of the calculation, of course one takes $\lambda = 1$. Thereby the convergence of the series will always be implicitly assumed, though without any explicit proof!

7.2.1 Perturbation of a Non-degenerate Energy Level

We assume at first that the level $E_n^{(0)}$, which we want to investigate, is **not degenerate**. This presumption concerns only this level, and need not necessarily be valid for all the other levels of the system. We start with the following expansions:

$$E_n = E_n^{(0)} + \lambda\, E_n^{(1)} + \lambda^2\, E_n^{(2)} + \ldots \tag{7.33}$$

$$|E_n\rangle = |E_n^{(0)}\rangle + \lambda |E_n^{(1)}\rangle + \lambda^2 |E_n^{(2)}\rangle + \ldots \tag{7.34}$$

Because of the special normalization (7.31) and because of (7.29) we have:

$$\lambda \langle E_n^{(0)} \Big| E_n^{(1)}\rangle + \lambda^2 \langle E_n^{(0)} \Big| E_n^{(2)}\rangle + \ldots = 0\,.$$

This, in turn, has the consequence

$$\langle E_n^{(0)} \Big| E_n^{(j)} \rangle = \delta_{0j} \; . \tag{7.35}$$

We now insert the ansatz-functions (7.33) and (7.34) into the exact eigen-value equation (7.27):

$$\begin{aligned} H|E_n\rangle &= H_0|E_n^{(0)}\rangle + \lambda \left(H_1|E_n^{(0)}\rangle + H_0|E_n^{(1)}\rangle \right) \\ &\quad +\lambda^2 \left(H_1|E_n^{(1)}\rangle + H_0|E_n^{(2)}\rangle \right) + \ldots \\ &= H_0|E_n^{(0)}\rangle + \sum_{p=1}^{\infty} \lambda^p \left(H_1|E_n^{(p-1)}\rangle + H_0|E_n^{(p)}\rangle \right) , \\ E_n|E_n\rangle &= E_n^{(0)}|E_n^{(0)}\rangle + \lambda \left(E_n^{(1)}|E_n^{(0)}\rangle + E_n^{(0)}|E_n^{(1)}\rangle \right) \\ &\quad +\lambda^2 \left(E_n^{(2)}|E_n^{(0)}\rangle + E_n^{(1)}|E_n^{(1)}\rangle + E_n^{(0)}|E_n^{(2)}\rangle \right) + \ldots \\ &= E_n^{(0)}|E_n^{(0)}\rangle + \sum_{p=1}^{\infty} \lambda^p \left\{ \sum_{j=0}^{p} E_n^{(j)}|E_n^{(p-j)}\rangle \right\} \; . \end{aligned}$$

By arranging with respect to powers of λ we get the different *orders* of the Schrödinger perturbation theory. In the zeroth order ($\sim \lambda^0$) we obtain the *unperturbed* eigen-value equation (7.28), which we consider as already solved. For $p \geq 1$ it follows from the last two equations:

$$H_1|E_n^{(p-1)}\rangle + H_0|E_n^{(p)}\rangle = \sum_{j=0}^{p} E_n^{(j)}|E_n^{(p-j)}\rangle \; . \tag{7.36}$$

When we multiply this expression from the left by the bra-state $\langle E_n^{(0)}|$, and take into consideration (7.35) as well as

$$\langle E_n^{(0)}|H_0|E_n^{(p)}\rangle = E_n^{(0)} \langle E_n^{(0)} \Big| E_n^{(p)}\rangle = 0 \qquad (p \geq 1) \; ,$$

then we get the following general expression for the

energy correction

$$E_n^{(p)} = \langle E_n^{(0)}|H_1|E_n^{(p-1)}\rangle \; . \tag{7.37}$$

In order to find also the *state corrections*, we multiply (7.36) from the left by $\langle E_m^{(0)}|$, where $m \neq n$:

$$\begin{aligned} \langle E_m^{(0)}|(H_0 - E_n^{(0)})|E_n^{(p)}\rangle &= (E_m^{(0)} - E_n^{(0)}) \langle E_m^{(0)} \Big| E_n^{(p)}\rangle \\ &= -\langle E_m^{(0)}|H_1|E_n^{(p-1)}\rangle + \sum_{j=1}^{p} E_n^{(j)} \langle E_m^{(0)} \Big| E_n^{(p-j)}\rangle \end{aligned}$$

As presumed, the level $E_n^{(0)}$ is not degenerate. We therefore can divide the last equation by $\left(E_m^{(0)} - E_n^{(0)}\right)$, and can further exploit the completeness of the *unperturbed* eigen-states (7.30):

$$|E_n^{(p)}\rangle = \sum\!\!\!\!\!\!\int_m |E_m^{(0)}\rangle\langle E_m^{(0)}| \, E_n^{(p)}\rangle \; .$$

One realizes that, because of (7.35), the $m = n$-summand of this expansion vanishes ($p \geq 1$). Therewith we get the following expression for the
state correction

$$|E_n^{(p)}\rangle = \sum\!\!\!\!\!\!\int_{\substack{m \\ (m \neq n)}} |E_m^{(0)}\rangle \frac{\left\langle E_m^{(0)} \middle| H_1 \middle| E_n^{(p-1)} \right\rangle}{E_n^{(0)} - E_m^{(0)}} - \sum_{j=1}^{p} E_n^{(j)} \sum\!\!\!\!\!\!\int_{\substack{m \\ (m \neq n)}} |E_m^{(0)}\rangle \frac{\left\langle E_m^{(0)} \middle| E_n^{(p-j)} \right\rangle}{E_n^{(0)} - E_m^{(0)}} \; . \tag{7.38}$$

With (7.37) and (7.38) the corrections can be calculated successively up to arbitrary order. However, with increasing order the expressions become very soon so complicated that for concrete applications one has to normally restrict oneself for the energy levels to the first two corrections, and for the states to the first one. We therefore write down, at the end of these considerations, explicitly the first two orders.

The **perturbation theory of first order** delivers to the *unperturbed* eigenvalues $E_n^{(0)}$ and eigen-states $|E_n^{(0)}\rangle$ the following corrections:

$$E_n^{(1)} = \langle E_n^{(0)}|H_1|E_n^{(0)}\rangle \; , \tag{7.39}$$

$$|E_n^{(1)}\rangle = \sum\!\!\!\!\!\!\int_m^{1 \neq n} |E_m^{(0)}\rangle \frac{\langle E_m^{(0)}|H_1|E_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}} \; . \tag{7.40}$$

The expectation value of the perturbation operator H_1 in the *unperturbed* eigenstate $|E_n^{(0)}\rangle$ thus yields already the energy correction of first order. This means especially for the ground state ($n = 0$), according to the variational principle (7.5), that $E_0^{(0)} + E_0^{(1)}$ represents an upper bound for the *true* ground-state energy. If the second order perturbation theory shall lead to an improvement in this respect, then $E_0^{(2)}$ should not be positive. As to the state correction (7.40), it is often sufficient, because of the energy-denominator, to include in the expansion only those levels which are closely adjacent to $E_n^{(0)}$.

The **perturbation theory of second order** accounts for the following correction:

$$E_n^{(2)} = \sum_m^{\neq p} \frac{|\langle E_m^{(0)}|H_1|E_n^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}} , \tag{7.41}$$

$$|E_n^{(2)}\rangle = \sum_m^{\neq p} \sum_q^{\neq p} |E_m^{(0)}\rangle \frac{\langle E_m^{(0)}|H_1|E_q^{(0)}\rangle\langle E_q^{(0)}|H_1|E_n^{(0)}\rangle}{(E_n^{(0)} - E_m^{(0)})(E_n^{(0)} - E_q^{(0)})} - E_n^{(1)} \sum_m^{\neq p} |E_m^{(0)}\rangle \frac{\langle E_m^{(0)}|H_1|E_n^{(0)}\rangle}{(E_n^{(0)} - E_m^{(0)})^2} . \tag{7.42}$$

We recognize that the second order correction $E_0^{(2)}$ of the ground-state energy is indeed negative.

Unfortunately, there exist hardly any useful criteria to judge the quality of the perturbation approximation, i.e., to predict at which order the required degree of accuracy is reached. But it can be expected that one can be content with (7.42), if one finds for all m:

$$|\langle E_m^{(0)}|H_1|E_n^{(0)}\rangle| \ll |E_n^{(0)} - E_m^{(0)}| . \tag{7.43}$$

Hence, the *perturbation* H_1 should be *as small as possible* and the distance of the levels *as large as possible*.

7.2.2 Perturbation of a Degenerate Level

Our considerations so far hold only for the non-degenerate *unperturbed* energy levels. If, in contrast, the level $E_n^{(0)}$ is degenerate, then the up to now developed theory has obviously to be extended, because the correction terms (7.40) to (7.42) would be divergent in such a case.

We still assume that the energy level $E_n^{(0)}$ belongs to the discrete part of the spectrum, but that it is now g_n-fold degenerate:

$$(H_0 - E_n^{(0)})|E_{n\alpha}^{(0)}\rangle = 0 , \quad \alpha = 1, 2, \ldots, g_n . \tag{7.44}$$

Since each linear combination of the $|E_{n\alpha}^{(0)}\rangle$ is also an eigen-state of H_0 with the eigen-value $E_n^{(0)}$, it is not at all clear from the beginning, which are the **'correct' states of zeroth order** for the perturbation theory. When we evaluate the *basic formula* (7.36) for $p = 1$,

$$H_1|E_n^{(0)}\rangle + H_0|E_n^{(1)}\rangle = E_n^{(0)}|E_n^{(1)}\rangle + E_n^{(1)}|E_n^{(0)}\rangle , \tag{7.45}$$

then it remains at first undetermined what is to be inserted for $|E_n^{(0)}\rangle$. Now that will be investigated in more detail.

Let $\{|E^{(0)}_{n\alpha}\rangle\}$ be an orthonormal basis of the g_n-dimensional eigen-space of the eigen-value $E^{(0)}_n$. A general state of this space can then be written as a linear combination:

$$|E^{(0)}_n\rangle = \sum_{\alpha=1}^{g_n} c_\alpha |E^{(0)}_{n\alpha}\rangle \; . \tag{7.46}$$

Let us for the moment assume that this state is the 'correct' state of zeroth order. Then it must fulfill (7.45):

$$\sum_\alpha c_\alpha \left(H_1 - E^{(1)}_n\right) |E^{(0)}_{n\alpha}\rangle + \left(H_0 - E^{(0)}_n\right) |E^{(1)}_n\rangle = 0 \; .$$

When we multiply this expression *from the left* by the bra-state $\langle E^{(0)}_{n\beta}|$ then the second summand vanishes because of the degeneracy:

$$\sum_\alpha c_\alpha \left(H^{\beta\alpha}_{1n} - E^{(1)}_n \, \delta_{\beta\alpha}\right) = 0 \; . \tag{7.47}$$

$H^{\beta\alpha}_{1n}$ is here an element of the so-called **perturbation matrix**:

$$H^{\beta\alpha}_{1n} \equiv \langle E^{(0)}_{n\beta}|H_1|E^{(0)}_{n\alpha}\rangle \; . \tag{7.48}$$

Equation (7.47) represents a linear homogeneous system of equations for the *'correct'* expansion coefficients c_α in (7.46). It has a non-trivial solution only if the **secular determinant** vanishes:

$$\det(H^{\beta\alpha}_{1n} - E^{(1)}_n \, \delta_{\beta\alpha}) = 0 \; . \tag{7.49}$$

This is a polynomial of g_nth degree with respect to $E^{(1)}_n$, with g_n possibly different solutions:

$$E^{(1)}_n \;\longrightarrow\; E^{(1)}_{nx} \; ; \quad x = 1, 2, \ldots, g_n \; . \tag{7.50}$$

In the next step we now solve for each x the homogeneous system of equations (7.47):

$$c_\alpha \;\longrightarrow\; c_{\alpha x} \; ; \quad x = 1, 2, \ldots, g_n \; . \tag{7.51}$$

Then two cases are to be distinguished:

1. *All $E^{(1)}_{nx}$ pair-wise different, degeneracy completely removed.*
2. *$E^{(1)}_{nx}$ still totally or partially degenerate.*

Let us treat case 1 at first. The $c_{\alpha x}$ then uniquely define the *'correct'* states of zeroth order:

$$|E^{(0)}_{nx}\rangle = \sum_{\alpha=1}^{g_n} c_{\alpha x} |E^{(0)}_{n\alpha}\rangle \; . \tag{7.52}$$

Equation (7.47) represents, ultimately, the eigen-value equation of the operator H_1 in the eigen-space of $E_n^{(0)}$. The $|E_{nx}^{(0)}\rangle$ and $E_{nx}^{(1)}$ are the corresponding eigen-states and eigen-values, respectively. As eigen-states of a Hermitian operator the $|E_{nx}^{(0)}\rangle$ can be seen as orthonormalized:

$$\langle E_{nx}^{(0)} \Big| E_{ny}^{(0)} \rangle = \sum_{\alpha=1}^{g_n} c_{\alpha x}^* \, c_{\alpha y} = \delta_{xy} \; . \tag{7.53}$$

In particular, H_1 is of course diagonal in these *'correct'* states:

$$\langle E_{nx}^{(0)} | H_1 | E_{ny}^{(0)} \rangle = E_{nx}^{(1)} \, \delta_{xy} \; . \tag{7.54}$$

Up to the first order of *degenerate* perturbation theory we now have found the following energy-eigen value of the *full* problem:

$$E_{nx} \approx E_n^{(0)} + E_{nx}^{(1)} \; . \tag{7.55}$$

Let us now still derive the state corrections of first order and the energy corrections of second order.

Since the *unperturbed* energy-states build a complete system, one can start with:

$$|E_{nx}^{(1)}\rangle = \sum_{m,y}^{\neq n} |E_{my}^{(0)}\rangle \left\langle E_{my}^{(0)} \Big| \; E_{nx}^{(1)} \right\rangle + \sum_{y}^{\neq x} |E_{ny}^{(0)}\rangle \left\langle E_{ny}^{(0)} \Big| \; E_{nx}^{(1)} \right\rangle \; . \tag{7.56}$$

Because of the special agreement (7.35) on the normalization, the $(x = y)$-term in the second summand drops out. When we multiply (7.45),

$$(H_0 - E_n^{(0)})|E_{nx}^{(1)}\rangle = (E_{nx}^{(1)} - H_1)|E_{nx}^{(0)}\rangle \; ,$$

from the left by $\langle E_{my}^{(0)}|$ then it follows for $m \neq n$:

$$\langle E_{my}^{(0)} \Big| E_{nx}^{(1)} \rangle = \frac{\langle E_{my}^{(0)} | H_1 | E_{nx}^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \; . \tag{7.57}$$

The first summand in (7.56) is therewith completely determined.

To get also the second summand under control, we have to evaluate (7.36) for $p = 2$:

$$H_1|E_{nx}^{(1)}\rangle + H_0|E_{nx}^{(2)}\rangle = E_n^{(0)}|E_{nx}^{(2)}\rangle + E_{nx}^{(1)}|E_{nx}^{(1)}\rangle + E_{nx}^{(2)}|E_{nx}^{(0)}\rangle \; . \tag{7.58}$$

This is multiplied *from the left* by $\langle E_{nz}^{(0)}|$:

$$\langle E_{nz}^{(0)}|H_1|E_{nx}^{(1)}\rangle - E_{nx}^{(1)} \langle E_{nz}^{(0)} \Big| E_{nx}^{(1)} \rangle = E_{nx}^{(2)} \delta_{xz} \; . \tag{7.59}$$

We now insert into this equation the ansatz (7.56):

$$\sum\!\!\!\!\!\!\int_{\substack{m,\,y\\(m\neq n)}} \left\langle E_{nz}^{(0)}\right| H_1 \left|E_{my}^{(0)}\right\rangle \left\langle E_{my}^{(0)}\right| E_{nx}^{(1)}\right\rangle + \sum_{y}^{\neq x} \left\langle E_{nz}^{(0)}\right| H_1 \left|E_{ny}^{(0)}\right\rangle \left\langle E_{ny}^{(0)}\right| E_{nx}^{(1)}\right\rangle$$

$$-E_{nx}^{(1)} \left(\sum\!\!\!\!\!\!\int_{\substack{m,\,y\\(m\neq n)}} \left\langle E_{nz}^{(0)}\right| E_{my}^{(0)}\right\rangle \left\langle E_{my}^{(0)}\right| E_{nx}^{(1)}\right\rangle + \sum_{y}^{\neq x} \left\langle E_{nz}^{(0)}\right| E_{ny}^{(0)}\right\rangle \left\langle E_{ny}^{(0)}\right| E_{nx}^{(1)}\right\rangle \right)$$

$$= \quad E_{nx}^{(2)}\,\delta_{xz}\ .$$

Because of (7.53) and (7.54), this expression further simplifies substantially:

$$\sum\!\!\!\!\!\!\int_{\substack{m,\,y\\(m\neq n)}} \left\langle E_{nz}^{(0)}\right| H_1 \left|E_{my}^{(0)}\right\rangle \left\langle E_{my}^{(0)}\right| E_{nx}^{(1)}\right\rangle + (E_{nz}^{(1)} - E_{nx}^{(1)}) \left\langle E_{nz}^{(0)}\right| E_{nx}^{(1)}\right\rangle = E_{nx}^{(2)}\,\delta_{xz}\ . \tag{7.60}$$

For $x = z$ it follows immediately with (7.57) the **energy correction of second order**:

$$E_{nz}^{(2)} = \sum\!\!\!\!\!\!\int_{\substack{m,\,y\\(m\neq n)}} \frac{\left|\left\langle E_{my}^{(0)}\right| H_1 \left|E_{nz}^{(0)}\right\rangle\right|^2}{E_n^{(0)} - E_m^{(0)}}\ . \tag{7.61}$$

This expression agrees formally with the result (7.41) of the non-degenerate perturbation theory of second order.

For the state correction of first order we still need the second summand in (7.56). This we get from (7.60) for $x \neq z$:

$$\left\langle E_{nz}^{(0)}\right| E_{nx}^{(1)}\right\rangle = \frac{1}{E_{nx}^{(1)} - E_{nz}^{(1)}} \sum\!\!\!\!\!\!\int_{\substack{m,\,y\\(m\neq n)}} \frac{\left\langle E_{nz}^{(0)}\right| H_1 \left|E_{my}^{(0)}\right\rangle \left\langle E_{my}^{(0)}\right| H_1 \left|E_{nx}^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}}\ . \tag{7.62}$$

When one inserts this, together with (7.57), into (7.56), then the state correction of first order, too, is completely determined. We have used thereby in (7.62) that in first order perturbation theory the energy degeneracy is completely removed. Otherwise we could not have divided by $E_{nx}^{(1)} - E_{nz}^{(1)}$.

It can also be (case 2.), though, that the *perturbation* H_1 removes the degeneracy in first order only partially or even not at all. The energy-eigen value $E_n^{(0)} + E_{nx}^{(1)}$ thus remains to be g_{nx}-fold ($1 \leq g_{nx} \leq g_n$) degenerate. Then the g_{nx} *correct* states of zeroth order belonging to the eigen-value $E_n^{(0)}$ remain undetermined. The removal of this indeterminacy needs the second or even a still higher order perturbation theory. It can of course also be that in no order the degeneracy is completely lifted. The eigen-value E_n of the *full* problem (7.27) itself can be degenerate.

Let us finally inspect briefly the special case where the **degeneracy** is still **completely retained** in first order. The *correct* states of zeroth order have even now to fulfill (7.54). They represent a basis of the eigen-space. But because all of the $E_{nx}^{(1)}$ are equal, **each** state of the eigen-space is also eigen-state of H_1. **Each** arbitrary basis of the eigen-space diagonalizes H_1. The *correct* states of zeroth order, however, have to now fulfill additionally, besides (7.57), also (7.60) in the form

$$E_{nx}^{(2)}\,\delta_{xz} = \sum\!\!\!\!\!\!\int_{\substack{m,\,y\\(m\neq n)}} \frac{\left\langle E_{nz}^{(0)}\right| H_1 \left|E_{my}^{(0)}\right\rangle \left\langle E_{my}^{(0)}\right| H_1 \left|E_{nx}^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}}\,. \tag{7.63}$$

If, however, the degeneracy is completely removed in second order then only a very special basis of the $E_n^{(0)}$-eigen space can provide that. Its elements are then the sought-after *correct* states of zeroth order, by the use of which, in addition, $E_{nx}^{(2)}$ takes again exactly the form (7.61).

These last considerations have, however, shown that with increasing order, in particular in the presence of degeneracies, the Schrödinger perturbation theory can become very soon rather complicated.

Let us finally add some further **remarks**:
For the evaluation of the secular determinant (7.49) it is recommendable to exploit the free choice of the basis $\{|E_{n\alpha}^{(0)}\rangle\}$ of the eigen-space of the degenerate eigen-value $E_n^{(0)}$ in such a way that the perturbation matrix (7.48) becomes especially simple, i.e., that as many elements as possible of the matrix are zero. By a skillful utilizing of the symmetries of the considered physical system (group-theoretical considerations!) the calculation effort can be sometimes substantially lowered. In particular, such situations are convenient for which one can find an observable A, which commutes with H_0 as well as with H_1. In such a case, one represents the perturbation matrix advantageously by using as basis the common eigen-states of H_0 and A.

If A has in the eigen-space of $E_n^{(0)}$ several different eigen-values a_{1n}, a_{2n}, $a_{3n}, \ldots,$, then the perturbation matrix will *split* into several *blocks* because it holds:

$$0 = \langle E_{n\alpha}^{(0)}|[A, H_1]_-|E_{n\beta}^{(0)}\rangle = (a_{\alpha n} - a_{\beta n})\, H_{1n}^{\alpha\beta}\,. \tag{7.64}$$

For $a_{\alpha n} \neq a_{\beta n}$ $H_{1n}^{\alpha\beta}$ thus must be zero:

$$(H_{1n}^{\alpha\beta}) \equiv \begin{pmatrix} \square & & & 0 \\ & \square & & \\ & & \square & \\ 0 & & & \ddots \end{pmatrix} \begin{matrix} \longleftarrow a_{1n} \\ \longleftarrow a_{2n} \\ \longleftarrow a_{3n} \\ \vdots \end{matrix}\,.$$

Since the full Hamilton operator H commutes with A, it will be possible to classify also the *full* eigen-states $|E_n\rangle$ with respect to the corresponding eigen-values of A. In a way, it suffices then to perform the perturbative calculations separately in the subspaces belonging to the given different eigen-values of A. These subspaces are orthogonal to each other.

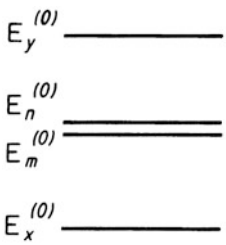

Figure 7.3: Energy spectrum of an unperturbed system with two quasi-degenerate levels

7.2.3 Quasi-Degeneracy

An energy level $E_n^{(0)}$, which is not degenerate in the *unperturbed* system, will be shifted by the *perturbation* H_1 in the second order perturbation theory according to (7.39) and (7.41) as follows:

$$E_n \approx E_n^{(0)} + \langle E_n^{(0)}|H_1|E_n^{(0)}\rangle + \sum_{\substack{m \\ (m \neq n)}} \frac{|\langle E_n^{(0)}|H_1|E_m^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}} \,. \tag{7.65}$$

In most cases the expansion can not be driven very much further. The decisive question therefore is, whether these first correction terms are sufficient at all to yield a reasonable approximation for $(E_n - E_n^{(0)})$. For that we had found a rough criterion with (7.43). The *perturbation* H_1 should be *as small as possible* and the level distance $|E_n^{(0)} - E_m^{(0)}|$ *as large as possible.*

But how should one treat systems, which are in the *unperturbed case* indeed not degenerate, but for which certain levels lie so closely together (Fig. 7.3) that the energy denominator in the perturbation correction of second order is so small that the concept of perturbation theory becomes questionable? Such cases obviously need a special treatment. The first order correction of the eigenvalue $E_n^{(0)}$ is still brought about by the corresponding eigen-state $|E_n^{(0)}\rangle$ itself and is independent of the other levels. The second order correction, on the other hand, contains, in **additive** form, contributions of all the other levels. Let us assume that the energies of two *unperturbed states*

$$|E_n^{(0)}\rangle \,, \; |E_m^{(0)}\rangle \,,$$

lie very closely to each other, while the energies of the other states are *energetically far away*, then we can neglect the latter, at least to a good approximation. We therefore choose for the quasi-degenerate effective two-level system the following ansatz,

$$|E\,\rangle = \alpha_n|E_n^{(0)}\rangle + \alpha_m|E_m^{(0)}\rangle \,, \tag{7.66}$$

and determine the coefficients by the requirement that $|E\rangle$ is an eigen-state of the *full* Hamilton operator $H = H_0 + H_1$:

$$H|E\,\rangle = E|E\,\rangle\ . \tag{7.67}$$

With the abbreviations

$$\begin{aligned} H_{xy} &= \langle E_x^{(0)}|H|E_y^{(0)}\rangle = E_x^{(0)}\,\delta_{xy} + H_1^{xy}\ , \\ H_1^{xy} &= \langle E_x^{(0)}|H_1|E_y^{(0)}\rangle \end{aligned}$$

we get from (7.67) a linear system of equations, when we insert (7.66) and multiply *from the left* by the bra-states $\langle E_n^{(0)}|$ and $\langle E_m^{(0)}|$:

$$\begin{aligned} (H_{nn} - E)\,\alpha_n + H_{nm}\,\alpha_m &= 0\ , \\ H_{mn}\,\alpha_n + (H_{mm} - E)\,\alpha_m &= 0\ . \end{aligned}$$

The vanishing of the secular determinant

$$\det\begin{pmatrix} H_{nn} - E & H_{nm} \\ H_{mn} & H_{mm} - E \end{pmatrix} = 0\ ,$$

fixes the corrected energy-eigen values:

$$E_\pm = \frac{1}{2}\left((H_{nn} + H_{mm}) \pm \sqrt{(H_{nn} - H_{mm})^2 + 4|H_{nm}|^2}\right)\ . \tag{7.68}$$

The mapping

$$E_n^{(0)} \iff E_+\ ; \quad E_m^{(0)} \iff E_-$$

becomes clear by the limiting process $H_1 \to 0$, where we assume, w.l.o.g., $E_n^{(0)} > E_m^{(0)}$. The splitting of E_+ and E_- is possibly distinctly larger than that of $E_n^{(0)}$ and $E_m^{(0)}$.

Also the coefficients α_n and α_m of the ansatz (7.66) are now fixed by (7.68). From

$$(H_{nn} - E_\pm)\,\alpha_n^{(\pm)} + H_{nm}\,\alpha_m^{(\pm)} = 0$$

it follows:

$$|\alpha_n^{(\pm)}|^2 = \frac{|H_{nm}|^2}{(H_{nn} - E_\pm)^2}\,|\alpha_m^{(\pm)}|^2\ .$$

The normalization of the state $|E\rangle$ yields:

$$|\alpha_m^{(\pm)}|^2 = 1 - |\alpha_n^{(\pm)}|^2 \tag{7.69}$$

This leads eventually to:

$$|\alpha_n^{(\pm)}|^2 = \frac{|H_{nm}|^2}{(H_{nn} - E_\pm)^2 + |H_{nm}|^2}\ . \tag{7.70}$$

The states $|E_\pm\rangle$ and the *corrected* energies $E_\pm$ are therewith completely determined. In order to demonstrate that the so found results represent good **interpolation formulas** for the transition *degeneracy* $\Longleftrightarrow$ *non-degeneracy*, we discuss two limiting cases:

1) $|\boldsymbol{H_{nn} - H_{mm}}| \gg |\boldsymbol{H_{nm}}| = |\boldsymbol{H_1^{nm}}|$

This can be realized for instance by a level distance $E_n^{(0)} - E_m^{(0)}$, which is still small compared to the distances to the other levels, but already large in comparison to the off-diagonal elements of the perturbation matrix. But then the *non-degenerate* perturbation theory of Sect. 7.2.1 should work. We expand the root in (7.68):

$$\begin{aligned} E_+ &= \frac{1}{2}\left(H_{nn}+H_{mm}\right) + \frac{1}{2}\left(H_{nn}-H_{mm}\right)\left(1+\frac{4|H_{nm}|^2}{(H_{nn}-H_{mm})^2}\right)^{1/2} \\ &\approx \frac{1}{2}\left(H_{nn}+H_{mm}\right) + \frac{1}{2}\left(H_{nn}-H_{mm}\right)\left(1+\frac{2|H_{nm}|^2}{(H_{nn}-H_{mm})^2}\right) \\ &= H_{nn} + \frac{|H_{nm}|^2}{(H_{nn}-H_{mm})} \; . \end{aligned}$$

In this limit we thus have:

$$E_+ \approx E_n^{(0)} + \langle E_n^{(0)}|H_1|E_n^{(0)}\rangle + \frac{|\langle E_n^{(0)}|H_1|E_m^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}} \; .$$

In the denominator of the third summand we still could neglect $\left(H_1^{nn} - H_1^{mm}\right)$ in relation to $\left(E_n^{(0)} - E_m^{(0)}\right)$. The result indeed corresponds to the *non-degenerate* perturbation theory of second order (7.41) for a two-level system, and also for an arbitrary system in the case that the other levels are *far away*.

The weight factors can be estimated in this case as follows:

$$|\alpha_n^{(+)}|^2 \approx \frac{1}{\dfrac{|H_{nm}|^2}{(H_{nn}-H_{mm})^2} + 1} \approx 1 \; ; \quad |\alpha_m^{(+)}|^2 \approx 0 \; .$$

The *admixture* of the state $|E_m^{(0)}\rangle$ thus becomes unimportant. (That one can also consider as a retroactive justification for the neglect of *'farther'* levels in the ansatz.) The same considerations can be applied to E_- and $|E_-\rangle$ with fully analogous results.

2) Degeneracy: $\boldsymbol{E_n^{(0)} = E_m^{(0)}}$

In this case, because of

$$\begin{aligned} H_{nn} + H_{mm} \quad &\longrightarrow \quad 2E_n^{(0)} + H_1^{nn} + H_1^{mm} \; , \\ H_{nn} - H_{mm} \quad &\longrightarrow \quad H_1^{nn} - H_1^{mm} \; , \end{aligned}$$

one can directly read off from (7.68):

$$E_\pm \longrightarrow E_n^{(0)} + \frac{1}{2}\left((H_1^{nn} + H_1^{mm}) \pm \sqrt{(H_1^{nn} - H_1^{mm})^2 + 4|H_1^{nm}|^2}\right) \; .$$

That is exactly the result of the perturbation theory of first order for a twofold degenerate level (see Exercise 7.2.9).

The results (7.68)–(7.70) for $E_\pm$ and $|E_\pm\rangle$, respectively, are obviously good interpolation formulas for quasi-degenerate levels.

7.2.4 Perturbation-Theoretical Basic Formula

The so far applied perturbation ansatzes are not the only possible ones. The problem can be also formulated more generally. That will be demonstrated in this and the next subsections. We presume thereby that the system to be investigated is **non-degenerate** and lies in the **discrete part of the spectrum**. Furthermore, also now the special normalization (7.31) shall be valid.

From the eigen-value equations (7.27) and (7.28) it follows by multiplication by the bra-state $\langle E_n|$ taking into account (7.31):

$$\begin{aligned} \langle E_n|H_0|E_n^{(0)}\rangle &= E_n^{(0)}\langle E_n\Big|E_n^{(0)}\rangle = E_n^{(0)} \,, \\ \langle E_n|H|E_n^{(0)}\rangle &= E_n\langle E_n\Big|E_n^{(0)}\rangle = E_n \,. \end{aligned}$$

From these equations one gets the still exact **level shift**:

$$E_n - E_n^{(0)} = \langle E_n|H_1|E_n^{(0)}\rangle = \langle E_n^{(0)}|H_1|E_n\rangle \,. \tag{7.71}$$

This is so of course not yet directly evaluable because of the unknown eigen-state $|E_n\rangle$ on the right-hand side.

We define the **projection operator**,

$$P_n = |E_n^{(0)}\rangle\langle E_n^{(0)}| \,, \tag{7.72}$$

for which, because of the special normalization (7.31), it holds:

$$P_n|E_n\rangle = |E_n^{(0)}\rangle \,. \tag{7.73}$$

Hence, P_n projects the *full* eigen-state onto the corresponding eigen-state of the *unperturbed* system. Analogously to that, we still need the **orthogonal projector**

$$Q_n = \mathbb{1} - P_n = \sum_{\substack{m \\ (m\neq n)}}{}' |E_m^{(0)}\rangle\langle E_m^{(0)}| \,. \tag{7.74}$$

P_n commutes with H_0 and the same holds also for Q_n:

$$[P_n,\, H_0]_- = [Q_n,\, H_0]_- = 0 \,. \tag{7.75}$$

We can now rewrite the eigen-value equation (7.27) at first with an arbitrary real constant D as follows:

$$(D - H_0)|E_n\rangle = (D - H + H_1)|E_n\rangle = (D - E_n + H_1)|E_n\rangle \,.$$

The operator $(D - H_0)$ possesses a unique inverse operator if H_0 does not have as eigen-value just the constant D:

$$|E_n\rangle = \frac{1}{D - H_0}\,(D - E_n + H_1)|E_n\rangle\ .$$

We use now for a further rearranging the above introduced projection operators

$$|E_n\rangle = P_n|E_n\rangle + Q_n|E_n\rangle = |E_n^{(0)}\rangle + Q_n\,\frac{1}{D - H_0}\,(D - E_n + H_1)|E_n\rangle\ .$$

This equation can obviously be iterated and then leads to the

perturbation-theoretical basic formula

$$|E_n\rangle = \sum_{m\,=\,0}^{\infty}\left\{Q_n\,\frac{1}{D - H_0}\,Q_n\,(D - E_n + H_1)\right\}^m |E_n^{(0)}\rangle\ . \tag{7.76}$$

Here we have exploited the commutability of Q_n with $(D - H_0)^{-1}$ as well as the idempotency $Q_n^2 = Q_n$ of the projector. This representation makes us aware that for the choice of the constant D we do not have to exclude all eigen-values of H_0. $D = E_n^{(0)}$ is, because of (7.74), obviously allowed (see (7.78)). On the right hand side there still appear only the *unperturbed* states $|E_n^{(0)}\rangle$, however also the unknown eigen-value E_n. On the other hand, the constant D is still free. Insertion of the basic formula into (7.71) yields the **level shift**:

$$E_n - E_n^{(0)} = \sum_{m\,=\,0}^{\infty}\langle E_n^{(0)}|H_1\left\{Q_n\,\frac{1}{D - H_0}\,Q_n\,(D - E_n + H_1)\right\}^m |E_n^{(0)}\rangle\ . \tag{7.77}$$

The formulas (7.76) and (7.77) are still exact. The relationship to the **Schrödinger perturbation theory** we get by the choice

$$D = E_n^{(0)}\ . \tag{7.78}$$

Then it follows, for instance, for the state correction in first order:

$$\begin{aligned}
|E_n\rangle &= |E_n^{(0)}\rangle + Q_n\,\frac{1}{E_n^{(0)} - H_0}\,Q_n\,\left(E_n^{(0)} - E_n + H_1\right)|E_n^{(0)}\rangle \\
&= |E_n^{(0)}\rangle + \sum_{\substack{m \\ (m\,\neq\,n)}}\!\!\!\!\!\!\sum\quad Q_n|E_m^{(0)}\rangle\langle E_m^{(0)}|\,\frac{E_n^{(0)} - E_n + H_1}{E_n^{(0)} - E_m^{(0)}}|E_n^{(0)}\rangle \\
&= |E_n^{(0)}\rangle + \sum_{\substack{m \\ (m\,\neq\,n)}}\!\!\!\!\!\!\sum\quad |E_m^{(0)}\rangle\,\frac{\langle E_m^{(0)}|H_1|E_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}\ .
\end{aligned}$$

But this is exactly the result (7.40) for the state correction in the Schrödinger theory. In the same manner we obtain for the level shift:

$$\begin{aligned}
&E_n - E_n^{(0)} \\
&= \langle E_n^{(0)}|H_1|E_n^{(0)}\rangle + \langle E_n^{(0)}|H_1\, Q_n \frac{1}{E_n^{(0)} - H_0} Q_n \left(E_n^{(0)} - E_n + H_1\right)|E_n^{(0)}\rangle \\
&= \langle E_n^{(0)}|H_1|E_n^{(0)}\rangle \\
&\quad + \sum\!\!\!\!\!\!\int_{\substack{m \\ (m \neq n)}} \langle E_n^{(0)}|H_1\, Q_n \frac{1}{E_n^{(0)} - H_0}|E_m^{(0)}\rangle\langle E_m^{(0)}|\left(E_n^{(0)} - E_n + H_1\right)|E_n^{(0)}\rangle \\
&= \langle E_n^{(0)}|H_1|E_n^{(0)}\rangle + \sum\!\!\!\!\!\!\int_{\substack{m \\ (m \neq n)}} \frac{|\langle E_n^{(0)}|H_1|E_m^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}} \,.
\end{aligned}$$

This agrees with (7.39) and (7.41). We have therewith shown, at least for the lowest orders, that the choice (7.78) for the constant D reproduces the results of the Schrödinger perturbation theory. With

$$\Delta E_n = E_n - E_n^{(0)} \tag{7.79}$$

this can thus be represented, according to (7.76) and (7.77), as follows in a compact form:

$$|E_n\rangle = \sum_{m=0}^{\infty} \left\{ Q_n \frac{1}{E_n^{(0)} - H_0} Q_n \left(H_1 - \Delta E_n\right)\right\}^m |E_n^{(0)}\rangle \,, \tag{7.80}$$

$$\Delta E_n = \sum_{m=0}^{\infty} \langle E_n^{(0)}|H_1 \left\{ Q_n \frac{1}{E_n^{(0)} - H_0} Q_n \left(H_1 - \Delta E_n\right)\right\}^m |E_n^{(0)}\rangle \,. \tag{7.81}$$

However, we can now construct also additional procedures by other choices of the constant D!

7.2.5 Brillouin-Wigner Perturbation Series

If one inserts into the perturbation-theoretical basic formula (7.76) and into the level shift (7.77) for the still free constant D,

$$D = E_n \,, \tag{7.82}$$

then one gets the following perturbation series:

$$|E_n\rangle = \sum_{m=0}^{\infty} \left\{ Q_n \frac{1}{E_n - H_0} Q_n H_1 \right\}^m |E_n^{(0)}\rangle \,, \tag{7.83}$$

$$E_n - E_n^{(0)} = \sum_{m=0}^{\infty} \langle E_n^{(0)}|H_1 \left\{ Q_n \frac{1}{E_n - H_0} Q_n H_1 \right\}^m |E_n^{(0)}\rangle \,. \tag{7.84}$$

They represent the starting point of the *Brilloui-Wigner perturbation theory*. We evaluate the level shift up to the second order:

$$E_n - E_n^{(0)} = \langle E_n^{(0)}|H_1|E_n^{(0)}\rangle + \langle E_n^{(0)}|H_1\, Q_n\, \frac{1}{E_n - H_0}\, Q_n\, H_1|E_n^{(0)}\rangle$$
$$= \langle E_n^{(0)}|H_1|E_n^{(0)}\rangle + \sum_{\substack{m \\ (m \neq n)}}{}' \langle E_n^{(0)}|H_1|E_m^{(0)}\rangle\langle E_m^{(0)}|\frac{1}{E_n - H_0}\, Q_n\, H_1|E_n^{(0)}\rangle\ .$$

Here we have utilized the representation (7.74) for Q_n. Further, if we execute the application of H_0, then we obtain the result:

$$E_n - E_n^{(0)} = \langle E_n^{(0)}|H_1|E_n^{(0)}\rangle + \sum_{m \neq n}{}' \frac{|\langle E_n^{(0)}|H_1|E_m^{(0)}\rangle|^2}{E_n - E_m^{(0)}}\ . \tag{7.85}$$

The comparison with the *Schrödinger results* (7.39) and (7.41) shows as an important difference the energy-denominator in the second order term. In the version (7.85) frequently problems can be avoided, which appear with the degeneracy or quasi-degeneracy of certain *unperturbed* levels. However, (7.85) has to be still iterated, because on the right-hand side of the equation there appears the *full* eigen-energy E_n.

The derivation of the state corrections up to first order is done completely analogously:

$$|E_n\rangle = |E_n^{(0)}\rangle + \sum_{\substack{m \\ (m \neq n)}}{}' |E_m^{(0)}\rangle\, \frac{\langle E_m^{(0)}|H_1|E_n^{(0)}\rangle}{E_n - E_m^{(0)}}\ . \tag{7.86}$$

When we presume that both the perturbation series, the one according to Schrödinger and the other according to Brillouin-Wigner, converge, then they must of course lead to the same results. They, in the last analysis, are exact expressions. Though, that does not at all mean that the corrections of first and second order also must agree with each other. It is well-known that it is indeed possible that two series, which are built up of different terms, can nevertheless approach the same limiting value. Which of the two perturbation theories turns out to be reasonable and easier tractable, is decided by the actual nature of the problem.

7.2.6 Exercises

Exercise 7.2.1
For the simplified hydrogen problem (Sect. 6.2) the spatial extension of the nucleus is neglected. One can consider the nucleus, to a first approximation, as a homogeneously charged sphere with the radius R.

1. Formulate the Hamilton operator $H = H_0 + H_1$ for the atomic electron, where H_0 represents the well-known operator for the case of the point-like nucleus, and H_1 is the *perturbation* due to the spatial extension of the nucleus.

2. For the calculation in part 3. we need the integral:

$$\int_0^{x_0} dx\, e^{-x}\, x^n = n! \left(1 - e^{-x_0} \sum_{\mu=0}^{n} \frac{x_0^\mu}{\mu!} \right) .$$

   Prove this formula!

3. Calculate in first order perturbation theory the influence of the spatial extension of the nucleus on the ground-state energy of the atomic electron.

Exercise 7.2.2
The Hamilton operator of the linear, anharmonic oscillator is given by

$$H = H_0 + H_1 , \quad H_0 = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 q^2 ; \quad H_1 = \alpha \frac{m^2 \omega^2}{\hbar} q^4 ; \quad \alpha > 0 .$$

Which energy corrections appear in first order perturbation theory due to H_1?

Exercise 7.2.3
Let the Hamilton operator of the linear harmonic oscillator be given in the form

$$\begin{aligned} H &= H_0 + H_1 ; \quad H_0 = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 q^2 , \\ H_1 &= \alpha \frac{1}{2} m \omega^2 q^2 ; \quad |\alpha| < 1 . \end{aligned}$$

The perturbation-theoretical solution can in this case be compared to the exact solution.

1. Determine the energy correction of first order!

2. Calculate the state correction $|n\rangle^{(1)}$ in first order perturbation theory!

3. How does the energy correction of second order look like?

4. Compare the energy corrections in 1. and 3. with the exact result for the eigen-energy of the harmonic oscillator.

Exercise 7.2.4
A weak constant force F acts on a linear harmonic oscillator what leads to the following Hamilton operator:

$$H = H_0 + H_1 ; \quad H_0 = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 q^2 , \quad H_1 = -F q .$$

1. With H_1 as *perturbation* calculate in first order perturbation theory the eigen-state $|n\rangle$ of the oscillator.

2. What are the energy corrections of first and second order?

3. Solve the eigen-value problem exactly and compare the result for the energy with 2.!

4. Does the energy correction of third order vanish?

Exercise 7.2.5
The one-dimensional harmonic oscillator is subject to the perturbation:

$$H_1 = \lambda \left(\hat{q} \cdot \hat{p} + \hat{p} \cdot \hat{q} \right) \ .$$

Calculate the states in first order and the energies up to second order perturbation theory!

Exercise 7.2.6
Let the Hamilton operator of the two-dimensional, anharmonic oscillator be given by $H = H_0 + H_1$,

$$\begin{aligned} H_0 &= \frac{1}{2m}(p_x^2 + p_y^2) + \frac{1}{2} m\omega^2 (q_x^2 + q_y^2) \\ H_1 &= \gamma \, q_x^2 \cdot q_y^2 \ . \end{aligned}$$

1. Calculate the energy corrections of first and second order for the ground state of H_0!

2. Calculate the first order energy corrections of the two lowest excited levels.

Exercise 7.2.7
In first order perturbation theory calculate the influence of the Darwin term (5.253) on the ground-state energy of the electron in the hydrogen atom.

Exercise 7.2.8
A particle of mass m moves on the surface of a sphere with the radius R.

1. Formulate the Hamilton operator and solve the still *unperturbed* eigenvalue problem. What is the present degeneracy?

2. As *perturbation* the homogeneous gravitational field acts. Find an observable which commutes with H_0 as well as with H_1.

3. Find the *correct* states of zeroth order. Use for this purpose the considerations from part 2.

4. Calculate the energy correction of first order. Is the degeneracy removed?

5. What comes out as the energy correction of second order?

Useful formula:

$$\cos\vartheta\, Y_{lm_l}(\vartheta,\varphi) = \sqrt{\frac{(l+1)^2-m_l^2}{(2l+1)(2l+3)}}\, Y_{l+1\,m_l}(\vartheta,\varphi) + \sqrt{\frac{l^2-m_l^2}{(2l+1)(2l-1)}}\, Y_{l-1\,m_l}(\vartheta,\varphi)\,.$$

Exercise 7.2.9
Consider a twofold degenerate *unperturbed* energy level $E_n^{(0)}$:

$$H_0|E_{n\alpha}^{(0)}\rangle = E_n^{(0)}|E_{n\alpha}^{(0)}\rangle\,; \quad \alpha = 1,2\,.$$

Determine the energy correction of first order and the *correct* states of zeroth order of the *'full'* Hamilton operator $H = H_0 + H_1$.

Exercise 7.2.10
Let us discuss a hydrogen atom in the homogeneous electric field (*Stark effect*):

$$\mathbf{F} = F\,\mathbf{e}_z\,.$$

Consider this field as perturbation.

1. Find the Hamilton operator and show that it commutes with the z-component L_z of the orbital angular momentum.

2. Let $|n\,l\,m_l\rangle$ be the eigen-states of the *field-free* system. Show generally:

$$\langle n'l'm_{l'}|H_1|n\,l\,m_l\rangle \neq 0$$
$$\text{at most for } m_{l'} = m_l\,; \quad l' = l \pm 1\,.$$

3. Calculate for $n = 1$ and $n = 2$ the energy corrections of first order.

4. According to 1. it suffices to perform the perturbation calculation in a subspace belonging to a given eigen-value of L_z. Calculate for $m_l = 0$ and $n = 2$ the *correct* states of zeroth order.

Exercise 7.2.11
Consider an atom with the nuclear charge Z, which is $(Z-1)$-fold ionized. Let the remaining electron be in the state $|nlm_l\rangle_Z$. The index Z shall thereby indicate the charge Ze of the nucleus. The electron spin may not play any role. As a consequence of a certain process, the nuclear charge changes by αe!

1. Calculate in first order perturbation theory the energy change of the state $|nlm_l\rangle_Z$. For that use the virial theorem from Exercise 7.1.7.

2. Compare the result from 1. with the exact energy of the state $|nlm_l\rangle_{Z+\alpha}$. For which values of α is the perturbation calculation reasonable?

Exercise 7.2.12
Consider the one-dimensional motion of a particle of mass m in a periodic potential $V(z)$. Let the period length be a ($V(z+a) = V(z)$).

1. Take $V(z)$ as perturbation and find the *unperturbed* eigen-energies $E_0(k)$ and eigen-functions $\varphi_k(z)$. Normalize the latter in the *volume* $L = N\,a$ with periodic boundary conditions:

$$\varphi_k\,(z + N\,a) = \varphi_k(z)\ .$$

2. How large is the degree of degeneracy of the *unperturbed* energies $E_0(k)$? Which wave numbers contribute to the Fourier expansion of $V(z)$?

3. Which necessary condition must be fulfilled by k and k' in order to give

$$\langle\varphi_k|V|\varphi_{k'}\rangle \neq 0\ ?$$

Which of these states $|\varphi_k\rangle,\ |\varphi_{k'}\rangle$ have in addition the same energy?

4. Calculate the energy corrections in first order perturbation theory and the *correct* states of zeroth order.

5. Which relation exists to the energy-band model of the solid (Sect. 4.3.5, Vol. 6)?

Exercise 7.2.13
Let the lattice of a solid be built up by two interpenetrating, chemically equivalent sublattices A and B. At each lattice site there is a magnetic moment $\mathbf{m}_i$. The moments order themselves in each of the sublattices ferromagnetically, but with antiparallel orientation in A and B (antiferromagnet!). Quasi-freely moving electrons in a partially filled energy band interact with these moments and are therefore subject to the following strongly simplified model-Hamilton operator:

$$\begin{aligned} H &= H_0 + H_1 \\ H_0 &= \sum_{\substack{\mathbf{k},\sigma \\ \alpha,\beta}} \varepsilon_{\alpha\beta}(\mathbf{k})\,|\mathbf{k}\sigma\alpha\rangle\langle\mathbf{k}\sigma\beta| \\ H_1 &= -\frac{1}{2}J\sum_{\mathbf{k}\sigma\alpha} z_\sigma m_\alpha |\mathbf{k}\sigma\alpha\rangle\langle\mathbf{k}\sigma\alpha| \quad \left(z_\sigma = \delta_{\sigma\uparrow} - \delta_{\sigma\downarrow}\right). \end{aligned}$$

α, β denote the two chemically equivalent, ferromagnetic sublattices A, B. m_α is the average (temperature-dependent) magnetic moment per lattice site, where it must hold because of the antiferromagnetic ordering:

$$m_{\mathrm{A}} = -m_{\mathrm{B}} \equiv m$$

$|\mathbf{k}\sigma\alpha\rangle$ marks the state of an electron with the wave vector $\mathbf{k}$ and the spin $\sigma = \uparrow, \downarrow$ in the sublattice α. The so-called Bloch energies $\varepsilon_{\alpha,\beta}(\mathbf{k})$,

$$\varepsilon_{\mathrm{AA}}(\mathbf{k}) = \varepsilon_{\mathrm{BB}}(\mathbf{k}) \equiv \varepsilon(\mathbf{k})\ ; \quad \varepsilon_{\mathrm{AB}}(\mathbf{k}) = \varepsilon^*_{\mathrm{BA}}(\mathbf{k}) \equiv t(\mathbf{k})\ ,$$

are assumed to be known. Although it is unimportant for the solution of the exercise, it is still mentioned that **k** is, due to the periodic boundary conditions, a discrete wave number of the so-called first Brillouin zone. Details should be taken from the textbooks on solid state physics.

1. Find the eigen-values and the eigen-states of the *'unperturbed'* operator H_0.
2. Write the *'perturbation'* H_1 by using as basis the H_0-eigen states!
3. Solve exactly the full eigen-value problem of $H = H_0 + H_1$!
4. In the sense of the Schrödinger perturbation theory, consider H_1 as the *'perturbation'* and calculate the energy corrections up to second order. Compare these with the exact result from part 3.!
5. Calculate the energy correction up to second order by the use of the Brillouin-Wigner perturbation theory. Compare this also with the exact result !

7.3 Time-Dependent (Dirac) Perturbation Theory

7.3.1 Basic Ideas

The **time-independent perturbation theory** presumes that the system to be investigated is represented by a time-independent Hamilton operator. It is an approximation method for the solution of the energy-eigen value problem. The idea is to come to a good approximation of the actual, not exactly solvable eigen-value equation via the exactly known solution of a simpler but *similar as possible* problem (*'free system'*). As soon as one has found the stationary states $|E_n\rangle$, the time-dependence of an arbitrary state of the system is completely determined by the given initial conditions:

$$|\psi(t)\rangle = e^{-(i/\hbar)Ht}|\psi(0)\rangle = \sum\!\!\!\!\!\!\int_n e^{-(i/\hbar)E_n t}|E_n\rangle\langle E_n|\psi(0)\rangle$$

Very often, though, the physical statement of the problem is different. One is, for instance, interested how the system reacts on a *time-dependent perturbation*. In most of these cases this is connected to *external fields* which are applied to the system. The time-dependence then comes already into play by switching on and off processes, in addition to an optionally existing direct time-variation of the field. For instance, one can think of a periodically alternating electromagnetic field. The task then consists in finding out how the states and the measured values develop in time under the influence of the *perturbation*. Since the Hamilton operator

$$H = H_0 + H_{1t} \equiv H_t \tag{7.87}$$

is now explicitly time-dependent, the energy of the system can no longer be a conserved quantity. We indicate the explicit time-dependence, caused by the perturbation, as index in order to distinguish it from the *dynamical* time-dependences (Heisenberg, Dirac picture). There do not exist stationary states so that a completely different statement of problem is present compared to the one we discussed in the framework of the time-independent perturbation theory. We have to realize again, though, that for practically all realistic situations, exact and complete solutions are not achievable. The **time-dependent perturbation theory** represents a method, by which one can determine, under certain conditions, **approximately**, the time-evolution of a physical system, characterized by parameters such as **transition probabilities** (Sect. 7.3.2) and **transition rates**.

Let a Hamilton operator of the form (7.87) be the starting point, where we assume here also that the solution of the H_0*-problem* is entirely known. H_0 itself is time-independent:

$$H_0|E_n^{(0)}\rangle = E_n^{(0)}|E_n^{(0)}\rangle \; . \tag{7.88}$$

It is clear that, because of the time-dependence of the Hamilton operator, the time-dependent perturbation theory cannot be developed on the basis of the time-independent Schrödinger equation (7.27) of the *perturbed* system. One could start, however, with the time-dependent Schrödinger equation,

$$i\,\hbar\,\frac{\partial}{\partial t}|\psi(t)\rangle = H_t|\psi(t)\rangle \; , \tag{7.89}$$

and try to solve it. Since the eigen-states $|E_n^{(0)}\rangle$ build a complete system (7.30), the following ansatz might offer itself:

$$|\psi(t)\rangle = \sum\!\!\!\!\!\!\int_m a_m(t)|E_m^{(0)}\rangle \; . \tag{7.90}$$

This we insert into the Schrödinger equation (7.89):

$$\sum\!\!\!\!\!\!\int_m i\,\hbar\,\dot{a}_m(t)|E_m^{(0)}\rangle = \sum\!\!\!\!\!\!\int_m a_m(t)\,(E_m^{(0)} + H_{1t})|E_m^{(0)}\rangle \; .$$

When we now multiply this equation *from the left* by the bra-state $\langle E_n^{(0)}|$, we have:

$$\left(i\,\hbar\,\frac{\partial}{\partial t} - E_n^{(0)}\right)\,a_n(t) = \sum\!\!\!\!\!\!\int_m a_m(t)\langle E_n^{(0)}|H_{1t}|E_m^{(0)}\rangle \; . \tag{7.91}$$

This is a set of differential equations of first order, for the solution of which the initial conditions,

$$|\psi(t_{\rm i})\rangle = \sum\!\!\!\!\!\!\int_m a_m(t_{\rm i})|E_m^{(0)}\rangle \; ,$$

must be known. Thereby we want to assume that the perturbation is switched on at the time t_i. Obviously we already obtain all that is essential when we assume that, before the *switching on of the perturbation* ($t < t_\mathrm{i}$), the system was in an eigen-state $|E_\mathrm{i}^{(0)}\rangle$ of H_0. This means:

$$a_m(t_\mathrm{i}) = \delta_{m\mathrm{i}} \; . \tag{7.92}$$

We can now proceed very similarly as we did for the time-independent Schrödinger perturbation theory in Sect. 7.2, by replacing H_{1t} by λH_{1t} ($0 \leq \lambda \leq 1$), and by choosing for the coefficients $a_m(t)$ a power-series ansatz in λ. By sorting with respect to powers of λ the *time-dependent perturbation theory of first, second, third, ... order* is then gradually developed (see Exercise 7.3.1).

We want to take here, however, another path, which is more formal but also more consistent. We did the essential preparatory work already in Sect. 3.4.4 (Vol. 6), where we discussed the Dirac picture (interaction representation). In the Dirac picture the dynamical time-dependence of the states is determined by the operator of the interaction. According to (3.206) (Vol. 6) the Schrödinger equation reads:

$$i\,\hbar|\dot{\psi}_\mathrm{D}(t)\rangle = H_{1t}^\mathrm{D}(t)|\psi_\mathrm{D}(t)\rangle \; . \tag{7.93}$$

On the other hand, the dynamics of the observables is due to H_0:

$$H_{1t}^\mathrm{D}(t) = \exp\left(\frac{i}{\hbar}\,H_0\,(t-t_0)\right)\,H_{1t}\exp\left(-\frac{i}{\hbar}\,H_0\,(t-t_0)\right) \; . \tag{7.94}$$

As in Sect. 3.4.4 (Vol. 6) we will mark states and observables of the Dirac picture by the index D. *'Index-free'* quantities are meant to belong to the Schrödinger picture. At the point of time t_0 both the representations shall coincide. We can choose $t_0 = t_\mathrm{i}$ and get therewith:

$$|\psi_\mathrm{D}\,(t_\mathrm{i})\rangle = |\psi\,(t_\mathrm{i})\rangle \overset{(7.92)}{=} |E_\mathrm{i}^{(0)}\rangle \; . \tag{7.95}$$

It is asked for $|\psi_\mathrm{D}(t)\rangle$ at $t > t_\mathrm{i}$. The answer is given by the **time evolution operator** $U_\mathrm{D}\,(t,t_\mathrm{i})$,

$$|\psi_\mathrm{D}(t)\rangle = U_\mathrm{D}\,(t,t_\mathrm{i})|\psi_\mathrm{D}\,(t_\mathrm{i})\rangle \; , \tag{7.96}$$

for which we could find in Sect. 3.4.4 (Vol. 6) with the **Dyson series** ((3.210), (3.172) (Vol. 6)) a formal integral representation:

$$U_\mathrm{D}\,(t,t_\mathrm{i}) = \mathbb{1} + \sum_{n\,=\,1}^{\infty} U_\mathrm{D}^{(n)}\,(t,t_\mathrm{i}) \; , \tag{7.97}$$

$$\begin{aligned} &U_\mathrm{D}^{(n)}\,(t,t_\mathrm{i}) \\ &= \left(-\frac{i}{\hbar}\right)^n \int\limits_{t_\mathrm{i}}^{t} dt_1 \int\limits_{t_\mathrm{i}}^{t_1} dt_2 \cdots \int\limits_{t_\mathrm{i}}^{t_{n\,-\,1}} dt_n\, H_{1t_1}^\mathrm{D}\,(t_1)\, H_{1t_2}^\mathrm{D}\,(t_2) \cdots H_{1t_n}^\mathrm{D}\,(t_n) \; . \end{aligned} \tag{7.98}$$

The time-behavior of the Dirac state $|\psi_{\mathrm{D}}(t)\rangle$ is therewith completely determined. However, for real problems it will not be possible to sum up the Dyson series in a closed form. On the other hand, (7.97) is obviously an excellent initial basis for *perturbation-theoretical* approximations because (7.97) is already sorted *with respect to powers of the perturbation* H_{1t}. When the perturbation is *small*—what that actually means we, of course, still have to think about—then one can terminate the series (7.97) after a finite number of summands. Consequently, one can speak of

time-dependent perturbation theory of nth order ,

if the evaluation comprises the first n summands of the Dyson series. Because the basic idea traces back to the Dirac representation, one speaks, by the way, also of the

Dirac perturbation theory ,

For the calculation of the integrals in (7.98), though, a change into the Schrödinger picture is recommendable. We agree upon the following abbreviations:

$$E^{(0)}_{nm} = E^{(0)}_n - E^{(0)}_m \,, \tag{7.99}$$

$$H_{nm}(t) = \langle E^{(0)}_n | H_{1t} | E^{(0)}_m \rangle \,. \tag{7.100}$$

Between each pair of perturbation operators in (7.98) we now insert the identity operator $\mathbb{1}$ in form of the completeness relation

$$\mathbb{1} = \sum\!\!\!\!\!\!\int_m |E^{(0)}_m\rangle\langle E^{(0)}_m| \,.$$

Because of (7.94) the dynamical time-dependence then becomes trivial:

$$\langle E^{(0)}_m | H^{\mathrm{D}}_{1t_n}(t_n) | E^{(0)}_n \rangle = H_{mn}(t_n)\, e^{(i/\hbar) E^{(0)}_{mn}(t_n - t_0)} \,.$$

The matrix element of the nth term in the Dyson series for the time-evolution operator now has the following structure:

$$\begin{aligned}\langle E^{(0)}_{\mathrm{f}} | U^{(n)}_{\mathrm{D}}(t,t_{\mathrm{i}}) | E^{(0)}_{\mathrm{i}} \rangle = \left(-\frac{i}{\hbar}\right)^n \int_{t_{\mathrm{i}}}^{t} dt_1 \cdots \int_{t_{\mathrm{i}}}^{t_{n-1}} dt_n \sum\!\!\!\!\!\!\int_{m_1} \cdots \sum\!\!\!\!\!\!\int_{m_{n-1}} H_{\mathrm{f}m_1}(t_1) \\ \cdot H_{m_1 m_2}(t_2) \cdots H_{m_{n-1} a}(t_n) \exp\left[\frac{i}{\hbar} E^{(0)}_{\mathrm{f}m_1}(t_1 - t_{\mathrm{i}})\right] \\ \cdot \exp\left[\frac{i}{\hbar} E^{(0)}_{m_1 m_2}(t_2 - t_{\mathrm{i}})\right] \cdots \exp\left[\frac{i}{\hbar} E^{(0)}_{m_{n-1}\mathrm{i}}(t_n - t_{\mathrm{i}})\right] \,.\end{aligned} \tag{7.101}$$

In order to be allowed to terminate the series after the nth summand one has to require that the $(n+1)$th term can be neglected compared to the nth term.

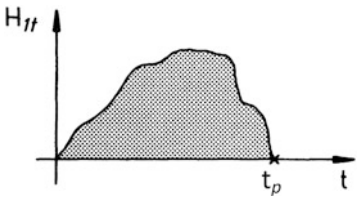

Figure 7.4: Schematic representation of a perturbation which is switched on for a finite time interval

These two members of the series differ, according to (7.101), by a factor of the type:

$$\left| -\frac{i}{\hbar} \int_{t_\mathrm{i}}^{t} dt_n \sum\!\!\!\!\!\!\int_n H_{mn}\left(t_n\right) \exp\left[\frac{i}{\hbar} E_{mn}^{(0)}\left(t_n - t_\mathrm{i}\right)\right] \right| \leq \frac{1}{\hbar} \int_{t_\mathrm{i}}^{t} dt_n \sum\!\!\!\!\!\!\int_n \left|H_{mn}\left(t_n\right)\right| \ .$$

One has to therefore require, as a *rough criterion* for a Dirac perturbation theory of **finite** order that

$$x_{mn}(t') \equiv (t - t_\mathrm{i}) |\langle E_m^{(0)} | H_{1t'} | E_n^{(0)} \rangle| \tag{7.102}$$

is for all m, n and $t' \in [t_\mathrm{i}, t]$ very much smaller than $\hbar$. The product of the *interaction strength* ($\sim |\langle E_m^{(0)} | H_{1t'} | E_n^{(0)} \rangle|$) and the *duration of interaction* ($\sim (t - t_\mathrm{i})$) should thus be a very small quantity.

7.3.2 Transition Probability

We assume that at a time t_i a perturbation H_{1t} is switched on, and that the system up to this point of time was in an eigen-state $|E_\mathrm{i}^{(0)}\rangle$ of H_0. *Transition probabilities* are then of special interest, which indicate, with what probability the system is found by a measurement at a later point of time $t > t_\mathrm{i}$ in another eigen-state $|E_\mathrm{f}^{(0)}(t)\rangle$ of H_0. Possible transitions are the results of the influence of the perturbation, which in a certain sense *shakes* the system. For $H_{1t} \neq 0$, as a rule, $|E_\mathrm{i}^{(0)}\rangle$ is no longer an eigen-state. The cases, for which the perturbation acts for a finite time t_p, are the most interesting. That may be an external field switched on for a certain span of time, or one can think of the perturbation to be provoked by the *fly by* of a charged particle (Fig. 7.4). Since H_0 itself is time-independent, the precise point of time of the switching on will not be decisive, but rather the time duration t_p of the perturbation. We therefore can choose, without further ado, t_i arbitrarily, for instance $t_\mathrm{i} = 0$. For $0 \leq t \leq t_\mathrm{p}$ the perturbation H_{1t} is operative, while outside this time interval, the total energy remains a constant of motion. We now define as

transition probability

$$w_\mathrm{if}(t) \equiv |\langle E_\mathrm{f}^{(0)} | U_\mathrm{D}(t, 0) | E_\mathrm{i}^{(0)} \rangle|^2 \ . \tag{7.103}$$

This formula should further be commented on a bit. Let $|\psi(t)\rangle$ be the state in the Schrödinger picture, which under the influence of $H = H_0 + H_{1t}$ develops from $|E_{\mathrm{i}}^{(0)}(0)\rangle$:

$$|\psi(t)\rangle = U(t,0)|E_{\mathrm{i}}^{(0)}\rangle \; . \tag{7.104}$$

$U(t,0)$ is the time-evolution operator in the Schrödinger picture. According to (3.200) (Vol. 6) we have the relation

$$U_{\mathrm{D}}(t,t') = e^{(i/\hbar)H_0(t-t_0)}\, U(t,t')\, e^{-(i/\hbar)H_0(t'-t_0)} \; .$$

t_0 is the point of time, at which the various *pictures* shall coincide. This point can be freely chosen. We take $t_0 = 0$. But then we have:

$$U_{\mathrm{D}}(t,0) = e^{(i/\hbar)H_0 t}\, U(t,0) \; .$$

When we insert this relation into (7.103), then the transition probability takes, in the Schrödinger picture, the *somewhat more familiar* form:

$$w_{\mathrm{if}}(t) = |\langle E_{\mathrm{f}}^{(0)}(t)|\psi(t)\rangle|^2 = |a_{\mathrm{f}}(t)|^2 \tag{7.105}$$

Plausibly, this is identical to the square of the absolute value of the expansion coefficient $a_{\mathrm{f}}(t)$ from (7.90). t is thereby the **point of time of the measurement**! If $w_{\mathrm{if}}(t)$ is to be the probability of a *real transition*, then we have in particular to presume, of course, that initial state and final state are indeed different, $|E_{\mathrm{i}}^{(0)}\rangle \neq |E_{\mathrm{f}}^{(0)}\rangle$. As the eigen-states of H_0, they are also orthogonal. With (7.97) inserted into (7.103) we then obtain:

$$w_{\mathrm{if}}(t) = \left| \sum_{n=1}^{\infty} \langle E_{\mathrm{f}}^{(0)}|U_{\mathrm{D}}^{(n)}(t,0)|E_{\mathrm{i}}^{(0)}\rangle \right|^2 \; . \tag{7.106}$$

Sometimes one defines for $|E_{\mathrm{i}}^{(0)}\rangle = |E_{\mathrm{f}}^{(0)}\rangle$ a *residence probability* $\hat{w}_{\mathrm{aa}}(t)$, for which it must of course hold

$$\hat{w}_{\mathrm{ii}}(t) = |\langle E_{\mathrm{i}}^{(0)}|U_{\mathrm{D}}(t,0)|E_{\mathrm{i}}^{(0)}\rangle|^2 = 1 - \sum_{f}^{\neq \mathrm{i}} w_{\mathrm{if}}(t) \; . \tag{7.107}$$

For the first two terms in (7.106) the matrix elements read according to (7.101):

$$\langle E_{\mathrm{f}}^{(0)}|U_{\mathrm{D}}^{(1)}(t,0)|E_{\mathrm{i}}^{(0)}\rangle = \left(-\frac{i}{\hbar}\right) \int_0^t dt_1\, H_{\mathrm{fi}}(t_1)\, e^{(i/\hbar)E_{\mathrm{fi}}^{(0)}\, t_1} \; , \tag{7.108}$$

$$\begin{aligned} \langle E_{\mathrm{f}}^{(0)}|U_{\mathrm{D}}^{(2)}(t,0)|E_{\mathrm{i}}^{(0)}\rangle &= \left(-\frac{i}{\hbar}\right)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \sum_m H_{\mathrm{f}m}(t_1)\, H_{m\mathrm{i}}(t_2) \cdot \\ &\quad \cdot \exp\left[\frac{i}{\hbar}\left(E_{\mathrm{f}m}^{(0)}\, t_1 + E_{m\mathrm{i}}^{(0)}\, t_2\right)\right] \; . \end{aligned} \tag{7.109}$$

We see that the expressions are becoming already in second order rather involved. In the orders $n \geq 2$ the system develops, illustratively, from the **real** initial state $|E_{\mathrm{i}}^{(0)}\rangle$ into the **real** final state via so-called **virtual intermediate states**. These are called *virtual*, since they are as the results of a formal expansion not really undertaken by the system. So they cannot be actually observed, i.e., they cannot be directly measured. Real transitions into such intermediate states would, by the way, in general, violate the energy conservation law. However, formulas like (7.109) convey the impression, *as if* the system would *indeed* reach the final state $|E_{\mathrm{f}}^{(0)}\rangle$ starting at the initial state $|E_{\mathrm{i}}^{(0)}\rangle$ via such intermediate states. They can therefore sometimes provide expedient help in illustrating and interpreting.

Generally one has to be content, as far as the transition probability is concerned, with the first order perturbation theory, for which, according to (7.106) and (7.108), it is left to calculate:

$$w_{\mathrm{if}}^{(1)}(t) = \frac{1}{\hbar^2}\left|\int_0^t dt_1 \langle E_{\mathrm{f}}^{(0)}|H_{1t_1}|E_{\mathrm{i}}^{(0)}\rangle \exp\left(\frac{i}{\hbar}\left(E_{\mathrm{f}}^{(0)} - E_{\mathrm{i}}^{(0)}\right)t_1\right)\right|^2 . \qquad (7.110)$$

The second order becomes important above all when the transition probability vanishes in the first order, i.e., when for instance the matrix element in the integrand of (7.110) equals zero. In such a case $w_{\mathrm{if}}^{(2)}(t)$ is directly be given by the square of the absolute value of the expression (7.109). If $\langle E_{\mathrm{f}}^{(0)}|H_{1t}|E_{\mathrm{i}}^{(0)}\rangle$ does not vanish, then we have to build, according to (7.106), for $w_{\mathrm{if}}^{(2)}(t)$ the square of the absolute value of a sum of two terms. We want to confine our considerations here, however, to the first order perturbation theory (7.110).

For $t < t_{\mathrm{p}}$, i.e., when the measurement takes place during the time of active perturbation, $w_{\mathrm{if}}^{(1)}(t)$ will be time-dependent. If, however, the perturbation is already *switched off* at the point of time of the measurement, i.e., $t > t_{\mathrm{p}}$, then we can replace in the integral in (7.110) the upper bound of integration t by t_{p}. The transition probability $w_{\mathrm{if}}^{(1)}$ is then time-independent. Each measurement yields for $t > t_{\mathrm{p}}$ the same $w_{\mathrm{if}}^{(1)}$. The system for $t > t_{\mathrm{p}}$ is again in a state, which obeys the *unperturbed*, time-independent Schrödinger equation. This state, though, must no longer be identical to $|E_{\mathrm{i}}^{(0)}\rangle$.

Let us further analyze the case $t > t_{\mathrm{p}}$. At first we can shift in (7.110) the bounds of integration to $\pm\infty$, because $H_{\mathrm{fi}}(t_1) = 0$ for $-\infty < t_1 < 0$ and $t_{\mathrm{p}} < t_1 < +\infty$:

$$(t \geq t_{\mathrm{p}}) \qquad w_{\mathrm{if}}^{(1)} = \frac{1}{\hbar^2}\left|\int_{-\infty}^{+\infty} dt_1\, H_{\mathrm{fi}}(t_1)\, e^{(i/\hbar)E_{\mathrm{fi}}^{(0)}\, t_1}\right|^2 .$$

On the right hand side there stands essentially the Fourier integral of the perturbation ((4.190), Vol. 3):

$$H_{\mathrm{fi}}(t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dE\, H_{\mathrm{fi}}(E)\, e^{-(i/\hbar)\, Et} , \tag{7.111}$$

$$H_{\mathrm{fi}}(E) = \int_{-\infty}^{+\infty} dt\, H_{\mathrm{fi}}(t)\, e^{(i/\hbar)\, Et} . \tag{7.112}$$

We have therewith found for the transition probability in the first order perturbation theory:

$$w_{\mathrm{if}}^{(1)} = \frac{1}{\hbar^2} |H_{\mathrm{fi}}(E_{\mathrm{fi}}^{(0)})|^2 . \tag{7.113}$$

$w_{\mathrm{if}}^{(1)}$ is therefore only then unequal zero when the energy $E_{\mathrm{f}}^{(0)} - E_{\mathrm{i}}^{(0)} = E_{\mathrm{fi}}^{(0)}$ belongs to the Fourier spectrum of the perturbation. The transition therefore has **resonance character**!

Before we continue the discussion in the next two subsections in somewhat more concrete form, we should remind ourselves once more that, because of (7.102), these perturbative results for the transition probability are reasonable only for $w_{\mathrm{if}}^{(1)} \ll 1$. Only when the transitions are still rather unlikely, we can be content with perturbation theory of first order!

7.3.3 Fermi's Golden Rule

We now want to discuss the transition probability for the important special case where the perturbation, which is switched on at the time $t = 0$, remains constant up to the switching off at $t = t_{\mathrm{p}}$ (Fig. 7.5):

$$H_{1t} \equiv H_1 \Theta(t)\, \Theta(t_{\mathrm{p}} - t) . \tag{7.114}$$

The *period of perturbation* t_{p} shall be long enough, so that special turning-on and turning-off processes can be neglected. Then the integral in (7.110) can easily be calculated:

$$w_{\mathrm{if}}^{(1)}(t) = \frac{1}{\hbar^2} |\langle E_{\mathrm{f}}^{(0)} | H_1 | E_{\mathrm{i}}^{(0)} \rangle|^2\, F_t\, (E_{\mathrm{fi}}^{(0)}) . \tag{7.115}$$

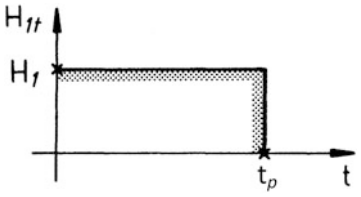

Figure 7.5: Simplest form of a perturbation, which acts for a finite time

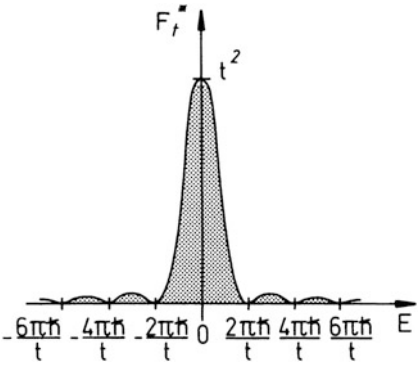

Figure 7.6: Energy-dependence of the weight factor in the transition probability of first order

The transition probability is thus determined by two terms, namely, firstly by the **transition matrix element** $\langle E_{\mathrm{f}}^{(0)}|H_1|E_{\mathrm{i}}^{(0)}\rangle$ and secondly by the time-dependent **weight factor** $F_t\big(E_{\mathrm{fi}}^{(0)}\big) = F_t\left(E_{\mathrm{f}}^{(0)} - E_{\mathrm{i}}^{(0)}\right)$. The latter we want to investigate now in some more detail:

$$F_t(E) = \Theta(t)\left[\Theta(t_{\mathrm{p}} - t)\, F_t^*(E) + \Theta(t - t_{\mathrm{p}})\, F_{t_{\mathrm{p}}}^*(E)\right] . \tag{7.116}$$

The function $F_t^*(E)$,

$$F_t^*(E) = \left|\int_0^t dt_1\, e^{(i/\hbar)E\,t_1}\right|^2 = \left|\frac{e^{(i/\hbar)Et} - 1}{(i/\hbar)E}\right|^2 = 2\hbar^2\,\frac{1 - \cos\left((E/\hbar)t\right)}{E^2} \tag{7.117}$$

has zeros at $E = n\,(2\pi\hbar/t)$; $n = \pm 1, \pm 2, \ldots$ and has a pronounced maximum at $E = 0$ (Fig. 7.6). By means of l'Hospital's rule ((1.96), Vol. 1) one finds the function value $F_t^*\,(E = 0)$:

$$F_t^*(0) = \lim_{E\to 0} 2\hbar^2\,\frac{(d^2/dE^2)\;(1 - \cos(E/\hbar)\,t)}{(d^2/dE^2)\,E^2} = t^2 . \tag{7.118}$$

The full width at half maximum can be estimated to be about $2\pi\hbar/t$. The peak thus becomes more and more pronounced with increasing time. We still calculate the following integral:

$$\frac{1}{2\pi\,\hbar\,t}\int_{-\infty}^{+\infty} dE\, F_t^*(E) = \frac{1}{\pi}\int_{-\infty}^{+\infty} dy\,\frac{1 - \cos y}{y^2} = \frac{1}{\pi}\int_{-\infty}^{+\infty} dy\,\frac{\sin y}{y} .$$

In the second step we have substituted $E = (\hbar/t)\,y$, and finally in the third step integrated by parts. The remaining integral can be evaluated by the use of the

residue theorem (see second example in Sect. 4.4.5, Vol. 3). It has the value π. This leads to:

$$\frac{1}{2\pi\,\hbar\,t}\int\limits_{-\infty}^{+\infty} dE\,F_t^*(E) = 1\,. \tag{7.119}$$

Eventually, it can be estimated for $E \neq 0$ by the use of (7.117):

$$\frac{F_t^*(E)}{2\pi\,\hbar\,t} \leq \frac{2\hbar}{\pi\,E^2 t} \underset{t\to\infty}{\longrightarrow} 0\,. \tag{7.120}$$

We recognize by (7.118)–(7.120) that the function $F_t^*(E)/2\pi\,\hbar\,t$ becomes for $t \to \infty$ a δ-function (see (1.2) and (1.3), Vol. 3):

$$\lim_{t\to\infty} \frac{1}{2\pi\,\hbar\,t}\,F_t^*(E) = \delta(E)\,. \tag{7.121}$$

We can draw now from these mathematical properties of the *weight function* $F_t^*(E)$ (Fig. 7.6) some far-reaching conclusions for the transition probability in (7.115):

1. Transitions take place predominantly between states with energy differences within the region:

$$\Delta E_t \approx \frac{2\pi\,\hbar}{t}\,. \tag{7.122}$$

2. For $E_{\mathrm{fi}}^{(0)} \neq 0$ the transition probability oscillates as function of t with the period

$$\tau = \frac{2\pi\,\hbar}{E_{\mathrm{fi}}^{(0)}}\,.$$

3. In a system, which is exposed practically infinitely long to a constant perturbation,

$$t, t_{\mathrm{p}} \to \infty\,,$$

transitions are induced at most between degenerate levels $\left(E_{\mathrm{fi}}^{(0)} = 0\right)$. This one recognizes by insertion of (7.121) into (7.115):

$$w_{\mathrm{if}}^{(1)}(t) \underset{\substack{t,t_{\mathrm{p}}\\ \text{'large'}}}{\approx} \frac{2\pi\,t}{\hbar}\,|\langle E_{\mathrm{f}}^{(0)}|H_1|E_{\mathrm{i}}^{(0)}\rangle|^2\,\delta\left(E_{\mathrm{f}}^{(0)} - E_{\mathrm{i}}^{(0)}\right)\,. \tag{7.123}$$

The δ-function expresses energy conservation. Frequently one still introduces as **transition rate** the transition probability per time unit:

$$\Gamma_{\mathrm{if}}^{(1)} \equiv \frac{w_{\mathrm{if}}^{(1)}(t)}{t} \approx \frac{2\pi}{\hbar}\,|\langle E_{\mathrm{f}}^{(0)}|H_1|E_{\mathrm{i}}^{(0)}\rangle|^2\delta(E_{\mathrm{f}}^{(0)} - E_{\mathrm{i}}^{(0)})\,. \tag{7.124}$$

According to a proposal of E. Fermi, one calls this formula, or the still to be discussed version (7.128), which is versatilely applied, and that with great success, because of its usefulness, the **golden rule**.

4. The indisputable success of the *golden rule*, however, appears to be more than astounding, if one carefully inspects the various steps which finally led to the rule. For its derivation we had to use several presumptions, which are partly seriously contradicting each other. The following points of criticism are evidently debatable:

   a) The *perturbation period* t_{p}, according to (7.102), should be *small* to let perturbation theory of the first order be reasonably applicable at all. On the other hand, it should also be *large* in order to justify the insertion of the mathematical limiting case (7.121) into (7.115).

   b) A *probability*, which according to (7.123) grows linearly with the time beyond all limits, appears highly absurd.

   c) *Probabilities* and *transition rates*, which are, as in (7.123) and (7.124), proportional to δ-functions, contradict *common sense* drastically.

   It is of course clear that the reason for the mentioned inconsistencies must be ascribed to the mistake, which is brought in by the deficiency of perturbation theory of first order. An exact, infinite series is actually approximated by only its first term. But then, why are (7.123) and (7.124) in many cases nevertheless rather useful formulas?

   As to the points a) and b) one often argues that t and t_{p}, respectively, are indeed macro-physically small, but also large in comparison to microphysical activation times, so that (7.121) can approximately be used in (7.115). The somewhat *vague* terms *'large', 'small' times* , used already several times, therefore have to be concretized very carefully in each single case.

5. One circumvents the objection c) normally in such a way that the formulas (7.123) and (7.124) are, strictly speaking, acceptable only for transitions into a **continuous spectrum**. When the final states are quasi-densely arranged, then one should appropriately not ask the transition into a special level, but that into a certain finite **interval** of the energy $E_{\mathrm{f}}^{(0)}$, $E_{\mathrm{f}}^{(0)} + \Delta E_{\mathrm{f}}$. The probability is then equal to the sum of the individual probabilities:

$$w_{\mathrm{i}\,\Delta\mathrm{f}}^{(1)}(t) = \sum_{\Delta E_{\mathrm{f}}} w_{\mathrm{if}}^{(1)}(t) \; .$$

   If the final states indeed build a continuum, then we have to write:

$$w_{\mathrm{i}\,\Delta\mathrm{f}}^{(1)}(t) = \int_{\Delta E_{\mathrm{f}}} dE_{\mathrm{f}}^{(0)}\, \rho_0\,(E_{\mathrm{f}}^{(0)})\, w_{\mathrm{if}}^{(1)}(t) \; . \tag{7.125}$$

   $\rho_0(E)$ is thereby the **density of states** of the *unperturbed* system. It is defined by the following statement:

$\rho_0(E)dE$ = number of the *unperturbed* eigen-states with energy values in the interval E, $E + dE$.

The density of states is a very useful quantity which appears at many places in Theoretical Physics.

We know from the preceding considerations of this chapter that for *large times* t and t_p the function $w^{(1)}_{\mathrm{if}}(t)$ is very sharply concentrated around $E^{(0)}_{\mathrm{fi}} = 0$. We could estimate the full width at half maximum of the central peak to be $2\pi\hbar/t$. If the energy interval ΔE_f is now distinctly broader than the peak,

$$\Delta E_\mathrm{f} \gg \frac{2\pi\hbar}{t}\,, \tag{7.126}$$

then we can confidently let the integral in (7.125) run from $-\infty$ to $+\infty$. Furthermore it should be allowed to draw the normally continuous density of states and the matrix element of the *perturbation operator* at the point $E^{(0)}_\mathrm{f} = E^{(0)}_\mathrm{i}$ as constants in front of the integral:

$$\begin{aligned} w^{(1)}_{\mathrm{i}\,\Delta\mathrm{f}}(t) &\overset{(7.115)}{\approx} \rho_0\left(E^{(0)}_\mathrm{i}\right)\frac{1}{\hbar^2}|\langle E^{(0)}_\mathrm{f}|H_1|E^{(0)}_\mathrm{i}\rangle|^2 \int\limits_{-\infty}^{+\infty} dE\, F^*_t(E) \\ &\overset{(7.119)}{=} \frac{2\pi}{\hbar}\,\rho_0\,(E^{(0)}_\mathrm{i})|\langle E^{(0)}_\mathrm{f}|H_1|E^{(0)}_\mathrm{i}\rangle|^2\, t\,. \end{aligned} \tag{7.127}$$

For the **transition rate** we have now instead of (7.124):

$$\Gamma^{(1)}_{\mathrm{i}\,\Delta\mathrm{f}} = \frac{2\pi}{\hbar}\,\rho_0\,(E^{(0)}_\mathrm{i})|\langle E^{(0)}_\mathrm{f}|H_1|E^{(0)}_\mathrm{i}\rangle|^2\,. \tag{7.128}$$

This version of the **golden rule** looks, with respect to the preceding critical discussion, after the elimination of the δ-function, *essentially more reasonable* than that in (7.124).

7.3.4 Periodic Perturbations

The assumption of a perturbation H_1, constant in the time interval $0 \le t \le t_\mathrm{p}$, led in the last subsection to a transition probability, which is finite only for transitions with energy conservation. However, characteristic *transient processes* must be taken into consideration, if the perturbation acts only for a finite time t_p.

We now aim to treat a further important, relatively simply calculable special case, for which H_{1t} is now a periodic function of time, realized, e.g., by a monochromatic electromagnetic field:

$$H_{1t} \equiv H_1 \cos\omega\, t\,\Theta(t)\,. \tag{7.129}$$

We assume that this perturbation is also switched on at the time $t_\mathrm{i} = 0$, but we let the *duration of the perturbation* t_p become infinitely large. For the calculation

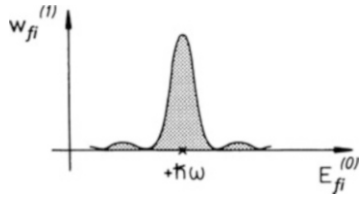

Figure 7.7: Transition probability, after absorption of monochromatic electromagnetic radiation, as function of the level separation

of the transition probability we use Eq. (7.110):

$$\begin{aligned} w_{\mathrm{if}}^{(1)}(t) &= \frac{1}{\hbar^2}\left|\int_0^t dt_1\, H_{\mathrm{fi}}(t_1)\, e^{i/\hbar E_{\mathrm{fi}}^{(0)}\, t_1}\right|^2 \\ &= \frac{|H_{\mathrm{fi}}|^2}{4\hbar^2}\left|\int_0^t dt_1\, e^{i/\hbar\left(E_{\mathrm{fi}}^{(0)}+\hbar\omega\right)t_1} + \int_0^t dt_1\, e^{i/\hbar\left(E_{\mathrm{fi}}^{(0)}-\hbar\omega\right)t_1}\right|^2 \\ &= \frac{1}{4}|H_{\mathrm{fi}}|^2\left|\frac{\exp\left[i/\hbar\left(E_{\mathrm{fi}}^{(0)}+\hbar\omega\right)t\right]-1}{E_{\mathrm{fi}}^{(0)}+\hbar\omega}\right. \\ &\qquad \left. + \frac{\exp\left[i/\hbar\left(E_{\mathrm{fi}}^{(0)}-\hbar\omega\right)t\right]-1}{E_{\mathrm{fi}}^{(0)}-\hbar\omega}\right|^2 . \end{aligned} \tag{7.130}$$

Each of the two summands has a structure similar to that of the function $F_t^*(E)$ in (7.117). For sufficiently large times t the first summand delivers a contribution which is concentrated around $E_{\mathrm{fi}}^{(0)} = -\hbar\omega$, while that of the second summand produces a sharp maximum at $E_{\mathrm{fi}}^{(0)} = +\hbar\omega$. When multiplying out the square of the absolute value, the *mixed* terms therefore play only a negligible role. The transition probability is thus composed essentially of two separate parts, which can easily be interpreted.

1) $E_{\mathrm{f}}^{(0)} > E_{\mathrm{i}}^{(0)}$; $\omega > 0$

In this case the second summand dominates, especially for such final state energies $E_{\mathrm{f}}^{(0)}$, for which (Fig. 7.7)

$$E_{\mathrm{f}}^{(0)} \approx E_{\mathrm{i}}^{(0)} + \hbar\omega\ . \tag{7.131}$$

In this energy region one can neglect the first summand, and one then obtains for the transition probability a similar expression as in (7.123):

$$w_{\mathrm{if}}^{(1)}(t) \overset{(7.117)}{\approx} \frac{|H_{\mathrm{fi}}|^2}{4\hbar^2}\, F_t^*\left(E_{\mathrm{fi}}^{(0)} - \hbar\omega\right) \overset{(7.121)}{\approx} \frac{\pi}{2\hbar}|H_{\mathrm{fi}}|^2\, t\, \delta\left(E_{\mathrm{fi}}^{(0)} - \hbar\omega\right) . \tag{7.132}$$

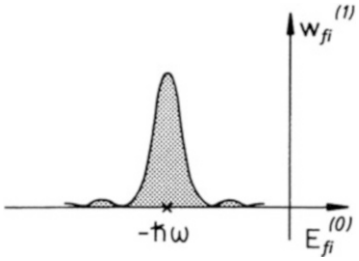

Figure 7.8: Transition probability, after emission of monochromatic electromagnetic radiation, as function of the level separation

With the same considerations as in the last subsection, we then find for the **transition rate** into the continuum:

$$\Gamma^{(1)}_{\mathrm{i}\,\Delta\mathrm{f}} \approx \frac{\pi}{2\hbar}\,\rho_0\,(E_{\mathrm{i}}^{(0)} + \hbar\,\omega)|\langle E_{\mathrm{f}}^{(0)}|H_1|E_{\mathrm{i}}^{(0)}\rangle|^2\ . \tag{7.133}$$

When the frequency ω of the perturbation corresponds just to an exact excitation energy $E_{\mathrm{fi}}^{(0)} = E_{\mathrm{f}}^{(0)} - E_{\mathrm{i}}^{(0)}$ of the *unperturbed* system, transitions become especially probable. It is thereby a typical **resonance phenomenon**. An important example of application is the atomic system, which is shined on by an electromagnetic field of the frequency ω. (7.131) corresponds in this case to Bohr's frequency condition ((1.103), Vol. 6). The *unperturbed* system (atom) absorbs an energy quantum $\hbar\,\omega$ (photon) and therewith goes into a higher level, i.e., into an **excited state**. We had already pointed out earlier that transitions between **stationary** states in the atom would not happen without being forced by *external perturbations.*

2) $\boldsymbol{E_{\mathrm{f}} < E_{\mathrm{i}}\ ;\ \omega > 0}$

Now the first summand in (7.130) dominates with a sharp peak at $E_{\mathrm{fi}}^{(0)} \approx -\hbar\omega$ (Fig. 7.8), i.e., for final states energies with:

$$E_{\mathrm{f}}^{(0)} \approx E_{\mathrm{i}}^{(0)} - \hbar\,\omega\ . \tag{7.134}$$

The *perturbing* monochromatic wave induces the system in this case to **emit** the energy $\hbar\omega$. By using the same considerations as for (7.133) we now find as transition rate:

$$\Gamma^{(1)}_{\mathrm{a}\,\Delta\mathrm{e}} \approx \frac{\pi}{2\hbar}\,\rho_0\,(E_{\mathrm{i}}^{(0)} - \hbar\,\omega)|\langle E_{\mathrm{f}}^{(0)}|H_1|E_{\mathrm{i}}^{(0)}\rangle|^2\ . \tag{7.135}$$

In the case of the **resonance** $\left(E_{\mathrm{fi}}^{(0)} \stackrel{!}{=} \pm\hbar\,\omega\right)$ the monochromatic *perturbation wave* can enforce both absorption 1) as well as emission 2).

7.3.5 Exercises

Exercise 7.3.1
A perturbation H_{1t} is turned on at the time $t = 0$ and acts on a system which is described by the Hamilton operator H_0. Immediately before the switching on of the perturbation, the system is in the eigen-state $|E_i^{(0)}\rangle$ of H_0. Expand the state $|\psi(t)\rangle$ for $t > 0$ in the complete system $\left\{|E_n^{(0)}\rangle\right\}$ (see (7.90)) and determine the expansion coefficients in first order perturbation theory.

Exercise 7.3.2
A linear harmonic oscillator of mass m and charge q experiences an alternating electric field:

$$\mathbf{F}(t) = F\,\mathbf{e}_z \cos\omega\, t$$
$$(\mathbf{e}_z : \text{ unit vector in } z\text{-direction}) .$$

Calculate in first order perturbation theory the dependence of the expectation value of the electric dipole moment

$$\langle \hat{p} \rangle = \langle \psi | q\, z | \psi \rangle$$

on the frequency ω. Assume thereby that, before the switching on of the field at the time $t = 0$, the oscillator is in the eigen-state $|E_n^{(0)}\rangle = |n\rangle$.

Exercise 7.3.3
Let a linear harmonic oscillator be in its ground state $\varphi_0(q, t)$. At the time $t = 0$ the force constant k of its restoring force ($F = -k\,q$) is abruptly brought to a new value k'. What is the probability that at $t > 0$ the oscillator is in its *new* ground state?

Hint: Take into consideration that the formulas of the *ordinary* time-dependent perturbation theory describe transitions between states of the *unperturbed* system, and therefore are here *not directly* applicable.

Exercise 7.3.4
A linear harmonic oscillator is in its ground state. At the time $t = 0$ an additional constant force F is applied to the oscillator. What is the probability for a transition into the *new* nth eigen-state at $t > 0$?

Exercise 7.3.5
An electron is within the attractive region of a Z-fold positively charged nucleus, which can be described as point charge of the strength Ze. At $t = 0$ the nuclear charge is changed by $+e$, e.g. by β-decay. At $t > 0$, what is the probability for a transition from the *old* $1s$-state into the *new* $2s$-state of the hydrogen-like ion?

Exercise 7.3.6
Let a physical system be for $t \leq 0$ in the state $|\varphi_1^{(0)}\rangle$ of a twofold degenerate level $E^{(0)}$. At $t = 0$ a constant *perturbation* is switched on.

1. According to the theory from Sect. 7.3.3, in the first order perturbation theory for $t > 0$, what is the probability for the transition into the other state $|\varphi_2^{(0)}\rangle$ of the same *unperturbed* energy?

2. The same problem is now to be solved, for comparison, in another way:

   2a) Calculate at first by means of time-independent perturbation theory the energy correction of first order $E^{(1)}$ and the *correct* states of zeroth order $|\varphi_\pm^{(0)}\rangle$, for which in first approximation

   $$H|\varphi_\pm^{(0)}\rangle \approx \left(E^{(0)} + E_\pm^{(1)}\right)|\varphi_\pm^{(0)}\rangle$$

   may be assumed ($H = H_0 + H_1$).

   2b) In the corresponding approximation determine the time evolution of the state of the system $|\varphi_1^{(0)}\rangle$ for $t > 0$, i.e., the evolution under the influence of the *perturbation*.

   2c) Define now as transition probability

   $$\widetilde{w}_{12}(t) \equiv \left|\left\langle \varphi_2^{(0)} \middle|\, \varphi_1^{(0)}(t)\right\rangle\right|^2$$

   and calculate it.

   2d) Compare the result with the expression from part 1.

Exercise 7.3.7
A linear harmonic oscillator of the mass m and the charge q is at the time $t_\mathrm{i} = -\infty$ in its ground state. At the point of time t_i a homogeneous, time-dependent electric field is applied:

$$\mathbf{F}(t) = F\, e^{-\alpha t^2}\, \mathbf{e}_z$$
$$(\mathbf{e}_z : \text{ unit vector in } z\text{-direction},\ \alpha > 0)\ .$$

1. For $t \to \infty$ calculate the *residence probability* $\hat{w}_{00}^{(1)}(\infty)$ of the oscillator in its ground state.

2. Under which conditions is perturbation theory of first order applicable?

Exercise 7.3.8
A linear harmonic oscillator of the mass m and the frequency ω is in its ground state $|0\rangle^{(0)}$ at times $t < 0$. For $t \geq 0$ the perturbation

$$H_{1t} = c\,\left(a^2 + a^{\dagger 2}\right)\, e^{-\gamma t}\ ; \quad c > 0, \gamma > 0\ .$$

acts on it. In the first order perturbation theory calculate the transition probability into an *unperturbed* excited state $|n\rangle^{(0)}$ at the time $t > 0$!

Exercise 7.3.9
A system is described by the Hamilton operator

$$H = H_0 + H_{1t}$$

with a time-dependent perturbation H_{1t}. Consider the Hilbert space which is spanned by the eigen-states $|1\rangle$, $|2\rangle$ of the *free* operator H_0:

$$H_0 \, |n\rangle = \varepsilon_n |n\rangle \;\; ; \;\; n = 1, 2 \;\; ; \;\; \varepsilon_2 > \varepsilon_1 \; .$$

In this space it holds for the *perturbation*:

$$H_{1t} = (\langle n \, | H_{1t} | \, n' \rangle) = \hbar\omega_0 \begin{pmatrix} 0 & e^{i\omega t} \\ e^{-i\omega t} & 0 \end{pmatrix} \; .$$

1. Determine the time-dependence of the *free* eigen-states $|n(t)\rangle$!
2. Solve the time-dependent Schrödinger equation in the space of the two *free* states $|n(t)\rangle$ with the initial condition $|\psi(0)\rangle = |1\rangle$! Interpret the occupation probabilities
$$|\alpha_n(t)|^2 = |\langle n \, | \, \psi(t) \rangle|^2 \; .$$
3. Calculate the transition $1 \to 2$ in first order perturbation theory! Compare this result with the exact expression from part 2.!

Exercise 7.3.10
A quantum-mechanical system,

$$H = H_0 + H_{1t},$$

is subject to the time-dependent perturbation

$$H_{1t} = \widehat{B} \, f(t) \; .$$

$\widehat{B}$ is thereby an observable and $f(t)$ a time-dependent real-valued function. Let $\widehat{A}$ be a not explicitly time-dependent observable. Investigate how the expectation value $\langle \widehat{A} \rangle$ in an arbitrary (mixed) state reacts to the perturbation H_{1t}. There are

ρ_0 : statistical operator of the free system
ρ_t : statistical operator of the interacting system,

both in the Schrödinger picture. The interaction is switched on at a certain point of time, so that

$$\lim_{t \to -\infty} \rho_t = \rho_0$$

can be assumed.

1. Show that it holds in the interaction representation (Dirac picture) for the statistical operator:

$$\rho_t^{\mathrm{D}}(t) = e^{\frac{i}{\hbar}H_0 t}\rho_t e^{-\frac{i}{\hbar}H_0 t} = \rho_0 - \frac{i}{\hbar}\int\limits_{-\infty}^{t} dt'[H_{1t'}^{\mathrm{D}}(t'), \rho_{t'}^{\mathrm{D}}(t')]_-$$

   Interpret the different time-dependences.

2. Find the formal solution

$$\rho_t^{\mathrm{D}}(t) = \rho_0 + \sum_{n=1}^{\infty} \rho_t^{\mathrm{D}(n)}(t) \ .$$

3. What results explicitly for $\rho_t^{\mathrm{D}}(t)$ in the first order perturbation theory? Use the result in order to calculate the change of the expectation value:

$$\Delta A_t = \langle \widehat{A} \rangle_t - \langle \widehat{A} \rangle_0$$

   Show that (*'linear response'*):

$$\Delta A_t = -\frac{i}{\hbar}\int\limits_{-\infty}^{t} \mathrm{t}' \, f(t')\langle[\widehat{A}^{\mathrm{D}}(t), \widehat{O}^{\mathrm{D}}(t')]_-\rangle_0 \ .$$

7.4 Quasi-Classical Approximation (WKB-Method)

In Chap. 2 (Vol. 6), using analogy arguments with the help of the classical *Hamilton-Jacobi theory* (keyword: *waves of action* $\longrightarrow$ *matter waves*), we justified (motivated) the wave mechanics of Schrödinger or at least made it appear plausible

The procedure was based on the idea that *Classical Mechanics* can be interpreted, in some way, as a limiting case of the super-ordinate *Quantum Mechanics*. Hints for the transition

wave mechanics $\longleftrightarrow$ classical mechanics

were derived from the known relationship:

wave optics $\longleftrightarrow$ geometrical (ray) optics

An essential difference between Classical Mechanics and Quantum Mechanics is connected with the classical concept of the *particle path*. This requires the simultaneous precise determination of *position* and *momentum* of the particle, which is basically impossible in Quantum Mechanics. One encounters a similar problem with the *ray-concept* of geometrical optics, which is acceptable for the exact *wave optics* also at most as a limiting case. The approximate transition

from the general wave optics to the special ray optics can be justified only if the spatial variation $|\nabla n(\mathbf{r})|$ of the index of refraction $n(\mathbf{r})$ is small compared to n/λ, where λ is the vacuum-wave length of light. We will see that the analogous requirement in wave mechanics aims at an only weak space-dependence of the potential $V(\mathbf{r})$, which is equivalent to a weak space-dependence of the *de Broglie wave length*

$$\lambda(\mathbf{r}) = \frac{2\pi\,\hbar}{\sqrt{2m(E - V(\mathbf{r}))}}\,.$$

In such a case one recognizes a *correspondence* between the laws and equations of Classical Mechanics and those of Quantum Mechanics (see Sects. 1.5.3 and 3.5 in Vol. 6).

We will pick up this thought here once more, and show explicitly that the classical **Hamilton-Jacobi differential equation** (2.1) (Vol. 6) can be considered as the limiting case of the **time-dependent Schrödinger equation**. This consideration will then become the background for a general method of solution, the development of which is the actual objective of this chapter. It is the so-called

WKB-method

which was proposed in 1926 by the scientists **W**entzel, **K**ramers and **B**rillouin, independently of each other.

7.4.1 The $\hbar \to 0$-Limiting Case of Wave Mechanics

The Hamilton-Jacobi theory is underlain by the concept of the *canonical transformation* (see Sect. 2.1.1 (Vol. 6), Sect. 2.5 (Vol. 2)) By means of a generating function, the so-called *action function* $S(\mathbf{q}, \bar{\mathbf{p}}, t)$, an *old* set of canonical variables $(\mathbf{q}, \mathbf{p})$ is transformed onto a *new* set $(\bar{\mathbf{q}}, \bar{\mathbf{p}})$, and that too in such a way that the *new* variables $\bar{q}_i$ and $\bar{p}_i$ $(i = 1, 2, \ldots, s)$ already are all integrals of motion. That is guaranteed when the action function S fulfills the Hamilton-Jacobi differential equation (2.1) (Vol. 6) (H = Hamilton function):

$$H\left(q_1, \ldots, q_s, \frac{\partial S}{\partial q_1}, \ldots, \frac{\partial S}{\partial q_s}, t\right) = -\frac{\partial S}{\partial t}\,.$$

It holds in particular for a particle of mass m in the potential $V(\mathbf{r}, t)$ ((3.185), Vol. 2):

$$\begin{aligned} \mathbf{p} &= \nabla S\,, \\ \frac{1}{2m}(\nabla S)^2 + V(\mathbf{r}, t) &= -\frac{\partial S}{\partial t}\,. \end{aligned} \tag{7.136}$$

Let us recall the concrete meaning of the action function:

1. Because of $\mathbf{p} = \nabla S$, the particles move in the phase space on paths, which are oriented perpendicular to the S = const-planes.

2. The **continuity equation** (*particle-number conservation*),

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho\,\mathbf{v}) = 0\ ,$$

can be expressed by S:

$$\frac{\partial \rho}{\partial t} + \frac{1}{m}\,(\nabla\rho\cdot\nabla S + \rho\,\Delta S) = 0\ . \tag{7.137}$$

We now want to assure ourselves that under certain limiting conditions the time-dependent Schrödinger equation leads to analogous results. For this purpose we choose the following ansatz for the wave function:

$$\psi(\mathbf{r},t) = \exp\left[\frac{i}{\hbar}\,S(\mathbf{r},t)\right]\ . \tag{7.138}$$

Let the function S have, as $\hbar$, the dimension *action*, being, however, otherwise not yet further specified. With (7.138) the Schrödinger equation becomes a non-linear, partial differential equation for S:

$$-\frac{\partial S}{\partial t} = \frac{1}{2m}\,(\nabla S)^2 + V(\mathbf{r},t) - \frac{i\,\hbar}{2m}\,\Delta S\ . \tag{7.139}$$

In order to come to a *systematic* approximate solution of this equation we expand S in powers of $\hbar$:

$$S(\mathbf{r},t) = \sum_{n=0}^{\infty} (i\,\hbar)^n\,S_n(\mathbf{r},t)\ ;\quad S_n \text{ real}\ . \tag{7.140}$$

This ansatz, whose convergence we presume without checking, is inserted into (7.139) and the resulting equation is sorted with respect to the powers of $\hbar$:

$$\begin{aligned}
&-\left\{\frac{\partial S_0}{\partial t} + i\,\hbar\,\frac{\partial S_1}{\partial t} - \hbar^2\,\frac{\partial S_2}{\partial t} + \cdots\right\}\\
&\quad= \frac{1}{2m}\,\left\{(\nabla S_0)^2 - \hbar^2(\nabla S_1)^2 + \hbar^4(\nabla S_2)^2 + \cdots + 2i\,\hbar\,(\nabla S_0\cdot\nabla S_1)\right.\\
&\qquad\left. - 2\hbar^2\,(\nabla S_0\cdot\nabla S_2) - 2i\,\hbar^3\,(\nabla S_1\cdot\nabla S_2) + \cdots\right\} + V(\mathbf{r},t)\\
&\qquad -\frac{i\hbar}{2m}\,\left\{\Delta S_0 + i\,\hbar\,\Delta S_1 - \hbar^2\Delta S_2 + \cdots\right\}.
\end{aligned}$$

We assume that this expression is satisfied separately by each power of $\hbar$. Then we obtain the following system of equations:

$$(\sim\hbar^0): \qquad -\frac{\partial S_0}{\partial t} = \frac{1}{2m}\,(\nabla S_0)^2 + V(\mathbf{r},t)\ , \tag{7.141}$$

$$(\sim\hbar^1): \qquad -\frac{\partial S_1}{\partial t} = \frac{1}{m}\,(\nabla S_0\cdot\nabla S_1) - \frac{1}{2m}\,\Delta S_0\ , \tag{7.142}$$

$$(\sim\hbar^2): \qquad -\frac{\partial S_2}{\partial t} = \frac{1}{2m}\,(\nabla S_1)^2 + \frac{1}{m}\,(\nabla S_0\cdot\nabla S_2)^2 - \frac{1}{2m}\,\Delta S_1,$$

$$\cdots$$

We recognize that in zeroth order ($\sim \hbar^0$) the Hamilton-Jacobi differential equation (7.136) is reproduced. The equation of first order (7.142) we still rearrange a bit. It holds approximatively for the **density of the position probability** $\rho(\mathbf{r},t) = |\psi(\mathbf{r},t)|^2$:

$$\begin{aligned}\rho &= \exp\left[\frac{i}{\hbar}\left(S_0 + i\,\hbar\,S_1 - \hbar^2 S_2 + \ldots\right)\right]\exp\left[-\frac{i}{\hbar}\left(S_0 - i\,\hbar\,S_1 - \hbar^2 S_2 + \ldots\right)\right] \\ &= \exp\left(-2S_1 + \mathcal{O}\left(\hbar^2\right)\right) .\end{aligned}$$

This means:

$$\frac{\partial\rho}{\partial t} \approx -2\,\frac{\partial S_1}{\partial t}\,\rho\,; \quad \nabla\rho \approx -2\nabla S_1\rho\,.$$

When we now multiply (7.142) by 2ρ, it follows with

$$\frac{\partial\rho}{\partial t} = -\frac{1}{m}\left(\nabla S_0 \cdot \nabla\rho\right) - \frac{1}{m}\,\rho\Delta\,S_0$$

just the continuity equation (7.137), if one inserts for S the first term (*'$\hbar \to 0$-term'*) of the expansion (7.140). The Schrödinger equation thus leads in zeroth order to the same results as the classical Hamilton-Jacobi differential equation, if we choose the wave function as in (7.138) and expand the phase $S(\mathbf{r},t)$ as done in (7.140). In this sense we can interpret

Classical Mechanics as '$\hbar \to 0$'-limiting case of Quantum Mechanics .

On the other hand, these considerations suggest an iterative quantum-mechanical method of solving by taking into consideration successively more and more *higher* terms in the expansion of S for the evaluation of the exact differential equation (7.139).

7.4.2 WKB-Method

The connection between Classical Mechanics and Quantum Mechanics, as described in the preceding subsection, does not only confirm the *principle of correspondence*, but can also be expanded, as mentioned, to a practical, iterative method for solving quantum-mechanical eigen-value problems. This method is especially clearly presentable and applicable for (effectively) one-dimensional problems, which satisfy a time-independent Schrödinger equation of the form:

$$\begin{aligned}u''(\rho) + k^2(\rho)\,u(\rho) &= 0\,, \\ k^2(\rho) &= \frac{2m}{\hbar^2}\left(E - \overline{V}(\rho)\right)\,. \end{aligned} \tag{7.143}$$

This concerns the really one-dimensional systems (Chap. 4, Vol. 6),

$$\rho = q\,; \quad \overline{V}(\rho) = V(q)\,; \quad u(\rho) = \psi(q)\,,$$

but also, for instance, the three-dimensional systems in central fields ((6.18), (6.19)), for which the actual problem lies in the determination of the radial part $R(r)$ of the wave function:

$$\rho = r \; ; \quad \overline{V}(\rho) = V(r) + \frac{\hbar^2 l(l+1)}{2m\, r^2} \; ; \quad u(\rho) = r\, R(r) \; .$$

We begin with an ansatz, completely analogously to (7.138), where we already split off, however, the trivial time-dependence ($S(\rho, t) = W(\rho) - E\, t$; see (2.3), Vol. 6):

$$u(\rho) = c \exp\left(\frac{i}{\hbar}\, W(\rho)\right) \; . \tag{7.144}$$

In (7.143) we need the second derivative of $u(\rho)$:

$$u''(\rho) = \left(\frac{i}{\hbar}\, W'(\rho)\, u(\rho)\right)' = \frac{i}{\hbar}\, W''(\rho)\, u(\rho) - \frac{1}{\hbar^2}\, (W'(\rho))^2\, u(\rho) \; .$$

The time-independent Schrödinger equation is therewith transferred into an inhomogeneous non-linear differential equation of second order for W:

$$(W'(\rho))^2 - (i\,\hbar)\, W''(\rho) = \hbar^2 k^2(\rho) \; . \tag{7.145}$$

Without the second summand on the left-hand side one would have the strict analog to the *eikonal equation* of geometrical optics ((3.198), Vol. 2). Starting from the idea, discussed in the last subsection, that Classical Mechanics should correspond to the '$\hbar \to 0$'-limiting case of Quantum Mechanics, an expansion of the *phase* W in powers of $(i\,\hbar)$ as in (7.140) appears to be reasonable:

$$W(\rho) = \sum_{n=0}^{\infty} (i\,\hbar)^n\, W_n(\rho) \tag{7.146}$$

This we insert into (7.145) and sort again by powers of $\hbar$:

$$(W_0'^2 - \hbar^2 k^2) + i\,\hbar\,(2W_0'\,W_1' - W_0'') - \hbar^2\,(W_1'^2 + 2W_0'W_2' - W_1'') + \mathcal{O}(\hbar^3) = 0 \; . \tag{7.147}$$

($\hbar^2 k^2(\rho) = 2m\,(E - \overline{V}(\rho))$ is thereby of course not a $\hbar^2$-term, but a $\hbar^0$-term.) In zeroth order ($\sim \hbar^0$) one therefore gets

$$W_0'(\rho) = \pm\hbar\, k(\rho) \implies W_0\,(\rho) = \pm\hbar \int^{\rho} k(\rho')\, d\rho' \tag{7.148}$$

with an at first still undetermined lower bound of integration. $W_0(\rho)$, fixed in such a way, corresponds to the *action function* (or the *characteristic function*) of Classical Mechanics (see (3.73), Vol. 2) warranting therewith the expected '$\hbar \to 0$'-limiting case.

The terms $\sim \hbar^1$ in (7.147) yield the following conditional equation:

$$W_1'(\rho) = \frac{1}{2}\,\frac{W_0''(\rho)}{W_0'(\rho)} = \frac{1}{2}\,\frac{k'(\rho)}{k(\rho)}\ .$$

This determines $W_1(\rho)$, except for an integration constant:

$$W_1(\rho) = \ln\sqrt{k(\rho)}\ . \tag{7.149}$$

For the next higher order ($\sim \hbar^2$ in (7.147)) we evaluate

$$W_1'^2(\rho) + 2W_0'(\rho)\,W_2'(\rho) - W_1''(\rho) = 0$$

and obtain:

$$W_2'(\rho) = \frac{W_1''(\rho)}{2W_0'(\rho)} - \frac{W_1'^2(\rho)}{2W_0'(\rho)} = \pm\frac{1}{4\hbar}\left(\frac{k''(\rho)}{k^2(\rho)} - \frac{3}{2}\,\frac{k'^2(\rho)}{k^3(\rho)}\right)\ .$$

Here we have already exploited the preceding partial results:

$$W_2(\rho) = \pm\frac{1}{4\hbar}\int^{\rho} d\rho'\,\left(\frac{k''(\rho')}{k^2(\rho')} - \frac{3}{2}\,\frac{k'^2(\rho')}{k^3(\rho')}\right) \tag{7.150}$$

Again an integration constant, at first, remains free. The procedure can now in principle be arbitrarily continued step by step according to this scheme, where the *higher* terms of the expansion (7.146) can be found from the already calculated ones, each by differentiations and elementary rearrangements.

When inserting (7.148)–(7.150) into the ansatz (7.144), the W_1-contribution (7.149) can be directly evaluated and becomes then the pre-factor:

$$u_\pm(\rho) \approx \frac{c_\pm}{\sqrt{k(\rho)}}\exp\left[\pm\frac{i}{\hbar}\int^{\rho} d\rho'\,\left(\hbar\,k(\rho') - \frac{\hbar}{4}\,\frac{k''(\rho')}{k^2(\rho')} + \frac{3}{8}\,\hbar\,\frac{k'^2(\rho')}{k^3(\rho')}\right)\right]\ . \tag{7.151}$$

In higher orders there arise, alternately, corrections of the pre-factor and the exponent. The **WKB-approximation** now consists in cutting the expansion after the term (W_1) linear in $\hbar$, where the complete solution must of course be written as a linear combination of the two linearly independent partial solutions:

$$\hat{u}(\rho) \equiv \frac{d_+}{\sqrt{k(\rho)}}\exp\left(i\int^{\rho} d\rho'\,k(\rho')\right) + \frac{d_-}{\sqrt{k(\rho)}}\exp\left(-i\int^{\rho} d\rho'\,k(\rho')\right)\ . \tag{7.152}$$

The constants $d_\pm$ and the lower bounds of integration in the exponents are still to be fixed by boundary conditions. Of course, only two of them can really be independent of each other, since $\hat{u}(\rho)$ is the solution of a differential equation of second order (7.143). (We will later identify, more or less arbitrarily, the still open bound of integration with a *classical turning point*.)

The approximate result (7.152) does indeed appear plausible. If, for instance, the potential $\overline{V}(\rho)$ were constant everywhere, which transfers of course to $k(\rho)$, the WKB-solution would correspond to the plane wave $e^{\pm ik\rho}$ and therewith to the exact result. For a slowly changing potential, one might then expect in first approximation instead of the phase $k\rho$ the term $\int^{\rho} k(\rho')d\rho'$, i.e., a *plane wave* with weakly space-dependent phase. Also the appearance of the factor $(k(\rho))^{-1/2}$ can easily be explained. The position probability of the particle in the interval $(\rho, \rho + d\rho)$ is proportional to $|u(\rho)|^2$ and therewith, according to the WKB-approximation (7.152), is essentially given by $1/k(\rho) \sim 1/p(\rho)$. But that is exactly what one would indeed expect from a (quasi-) classical particle. Its average duration of stay in the interval is surely inversely proportional to its velocity $v(\rho) = 1/m\, p(\rho)$.

The essentially new feature of the WKB-solution compared to the solutions of the classical Hamilton-Jacobi differential equation, though, consists in (7.152) being not restricted to the *classically allowed region* ($E > \overline{V}(\rho)$), but being applicable also in the *classically forbidden region*

$$E < \overline{V}(\rho)\ ; \quad k(\rho) = i|k(\rho)|\ .$$

The exponential functions then get real arguments:

$$\begin{aligned} \hat{u}(\rho) \;=\; & \frac{\overline{d}_+}{\sqrt{|k(\rho)|}} \exp\left(+ \int^{\rho} |k(\rho')| d\rho' \right) \\ & + \frac{\overline{d}_-}{\sqrt{|k(\rho)|}} \exp\left(- \int^{\rho} |k(\rho')| d\rho' \right)\ . \end{aligned} \tag{7.153}$$

The demand for correct asymptotic behavior (*exponential decay* of the wave function, (Sect. 4.1.1, Vol. 6)) sometimes sees to it that the two coefficients $\overline{d}_+$ and $\overline{d}_-$ can not be simultaneously equal to zero.

Before we further concretize and interpret these results in the next subsection, we want to give thought to the range of validity of the WKB-approximation.

7.4.3 Classical Turning Points

The WKB-solution (7.152) is of course only an approximation. It is therefore rather instructive to think about how the differential equation of second order has to look like so that (7.152) represents a **rigorous** mathematical solution.

For this purpose we differentiate (7.152) twice with respect to ρ:

$$\begin{aligned}
&\left[\frac{d_\pm}{\sqrt{k(\rho)}}\exp\left(\pm i\int^\rho d\rho'\,k(\rho')\right)\right]'' \\
&= \left[\left(-\frac{1}{2}\,\frac{k'(\rho)}{k(\rho)} \pm i\,k(\rho)\right)\,\frac{d_\pm}{\sqrt{k(\rho)}}\exp\left(\pm i\int^\rho d\rho'\,k(\rho')\right)\right]' \\
&= \left[\frac{3}{4}\,\frac{k'^2(\rho)}{k^2(\rho)} - k^2(\rho) - \frac{1}{2}\,\frac{k''(\rho)}{k(\rho)}\right]\left[\frac{d_\pm}{\sqrt{k(\rho)}}\exp\left(\pm i\int^\rho d\rho'\,k(\rho')\right)\right] .
\end{aligned}$$

(7.152) is therewith the solution of the following differential equation:

$$\hat{u}''(\rho) + \left(k^2(\rho) + \frac{1}{2}\,\frac{k''(\rho)}{k(\rho)} - \frac{3}{4}\,\frac{k'^2(\rho)}{k^2(\rho)}\right)\hat{u}(\rho) = 0 . \tag{7.154}$$

The comparison with (7.143) traces out the range of validity of the WKB-approximation. Obviously it must be required

$$\left|\frac{\frac{1}{2}\,\frac{k''(\rho)}{k(\rho)} - \frac{3}{4}\,\frac{k'^2(\rho)}{k^2(\rho)}}{k^2(\rho)}\right| \ll 1 , \tag{7.155}$$

which applies especially to weakly changing $k(\rho)$. With (7.148) and (7.150) follows the equivalent formulation:

$$\left|2\hbar^2\,\frac{W_2'(\rho)}{W_0'(\rho)}\right| \ll 1 .$$

If one additionally requires that in (7.155) already each summand by itself is small compared to 1, then it follows for instance from the second term with (7.148):

$$\left|3\hbar^2\,\left(\frac{W_1'(\rho)}{W_0'(\rho)}\right)^2\right| \ll 1 .$$

Both the two last inequalities include the plausible requirement that in the series expansion (7.146) for $W(\rho)$ the corrections of first and second order exhibit a distinctly weaker ρ-dependence than $W_0(\rho)$. But if now really

$$\left|\frac{3}{4}\,\frac{k'^2(\rho)}{k^4(\rho)}\right| \ll 1 ,$$

then it holds of course also:

$$\left|\frac{k'(\rho)}{k^2(\rho)}\right| = \left|\frac{d}{d\rho}\,\frac{1}{k(\rho)}\right| \ll 1 .$$

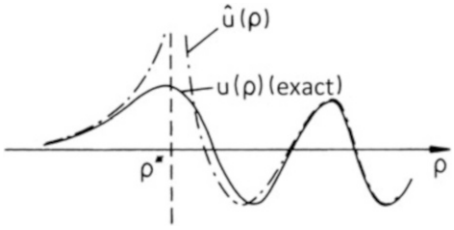

Figure 7.9: Demonstration of the failure of the WKB-solution at the classical turning point

Over a distance of $\Delta\rho$ the **de Broglie wave length** $\lambda(\rho) = 2\pi/k(\rho)$ should therefore change only by an amount, which is small compared to $\Delta\rho$:

$$\left|\frac{d}{d\rho}\lambda(\rho)\right| \overset{!}{\ll} 1 \,. \tag{7.156}$$

The WKB-theory should thus represent a usable concept for the case that the potential $\overline{V}(\rho)$ and therewith also the de Broglie wave length are only weakly space-dependent. But that is now indeed analogous to the condition for the classical transition between wave optics and geometrical (ray) optics, which requires an only weak spatial change of the index of refraction (see the discussion after (2.11), Vol. 6).

But the criterion of validity (7.155) also lays bare an obvious weak point of the WKB-approximation. Near the **classical turning point** ρ^* ((4.8), Vol. 6),

$$k^2(\rho^*) = 0 \iff E = \overline{V}(\rho^*) \,,$$

the inequality (7.155) is not satisfiable. There the solving function (7.152) diverges in any case and is therefore unusable. The WKB-theory is acceptable as physically reasonable approximation only *far away* from any turning point (Fig. 7.9).

There is another disagreeable consequence of the singular behavior of $\hat{u}(\rho)$ at the point $\rho = \rho^*$. In connection with the practical calculation of wave functions, which as solutions of a differential equation of second order always contain free parameters, we could fix these parameters by requirements on the continuity of the wave function and its first derivative. This possibility can not be exploited in the WKB-method. Because of the divergence, the coefficients d_+, d_- and $\overline{d}_+$, $\overline{d}_-$ can not be determined by *continuous fitting* of the partial solutions (7.152) and (7.153) at $\rho = \rho^*$. In this sense, the quasi-classical WKB-method actually appears only a little promising. However, we can help ourselves with the following *trick*:

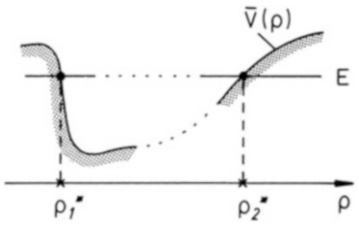

Figure 7.10: Definition of *left-hand* and *right-hand* turning points

In the immediate neighborhood of a classical turning point ρ^* $k^2(\rho)$ can be linearized:

$$\begin{aligned} k^2(\rho) &= \frac{2m}{\hbar^2}\,(E - \overline{V}(\rho^*)) - \frac{2m}{\hbar^2}\,(\rho - \rho^*)\,\overline{V}'(\rho^*) + \ldots \\ &= c\,(\rho - \rho^*) + \mathcal{O}\left[(\rho - \rho^*)^2\right], \\ c &= -\frac{2m}{\hbar^2}\,\overline{V}'\,(\rho^*)\,. \end{aligned} \tag{7.157}$$

With this form of $k^2(\rho)$ the Schrödinger equation (7.143) can be **exactly** solved. In the *classically forbidden region* ($\overline{V}(\rho) > E$) the WKB-function (7.153) and in the *classically allowed region* ($\overline{V}(\rho) < E$) the function (7.152) are *continuously fitted* to the solution which is exact in the *'turning region'*. The unknown parameters are therewith fixed. An algorithm of this kind, going back to R. E. Langer, will be illustrated in the next subsection in detailed single steps. With this procedure one achieves that the function, which is correct in the *'turning region'* and agrees *asymptotically* with the WKB-approximations, so that the parameter-fitting becomes unique.

7.4.4 Langer Procedure

It is advisable for the following considerations to distinguish *'left-hand'* and *'right-hand'* turning points. We speak of a *'left-hand'* turning point, if, as at ρ_1^* in Fig. 7.10, *to the left* of this point ($\rho < \rho_1^*$) we find *classically forbidden region* and *to the right* of this point ($\rho > \rho_1^*$) *classically allowed region*. For a *'right-hand'* turning point (ρ_2^* in Fig. 7.10) it is just the opposite.

Let ρ^* now be any *classical turning point*, which separates *classical allowed region* from *classical forbidden region*. According to a method of Langer (R. E. Langer, Phys. Rev. **51**, 669 (1937)) we aim to fit *physically reasonably* the two WKB-partial solutions (7.152) and (7.153) with respect to ρ^*. The not yet specified lower bound of integration in the exponents in (7.152) and (7.153) we set arbitrarily equal to ρ^*, but without restricting the general validity of the following considerations. The solutions (7.152) and (7.153) can therewith also

be seen as functions of a new variable α:

$$\alpha \equiv \begin{cases} \int\limits_{\rho^*}^{\rho} k(\rho')d\rho' \,, & \text{if } \rho^* \textit{ left-hand} \,, \\ \int\limits_{\rho}^{\rho^*} k(\rho')\,d\rho' \,, & \text{if } \rho^* \textit{ right-hand} \,, \end{cases} \tag{7.158}$$

The bounds of integration were thereby chosen so that for both types of turning points it equally holds:

$$\begin{aligned} E > \overline{V}(\rho) \quad &\Longrightarrow \quad \alpha > 0 \qquad \text{(classically allowed)} \,, \\ E < \overline{V}(\rho) \quad &\Longrightarrow \quad \alpha = -i|\alpha| \quad \text{(classically forbidden)} \,. \end{aligned} \tag{7.159}$$

The WKB-partial solutions (7.152) and (7.153) read with the new variable α:

$$\begin{aligned} \hat{u}(\alpha) &= \frac{1}{\sqrt{k(\alpha)}} \left(\gamma_+ \, e^{i\alpha} + \gamma_- \, e^{-i\alpha}\right) \text{ for } E > V \,, \\ \hat{u}(\alpha) &= \frac{1}{\sqrt{|k(\alpha)|}} \left(\delta_+ \, e^{|\alpha|} + \delta_- \, e^{-|\alpha|}\right) \text{ for } E < V \,. \end{aligned} \tag{7.160}$$

The turning point $\rho = \rho^*$ corresponds to $\alpha = 0$!

The now following considerations require *substantial calculational effort* and therefore, for a clearer picture, will be divided into several single steps. For this purpose we agree upon:

a) ρ^*: *left-hand* turning point,

b) $-\infty < \rho < \rho^*$: *classically forbidden region.*

The considerations can be done completely analogously for a corresponding *right-hand* turning point and lead then with the agreement (7.158) for α to formally exactly the same results. (It is surely a helpful exercise to check this step by step!). That, by the way, is the reason why α was defined in (7.158) for *right-hand* and *left-hand* turning points somewhat differently.

Because of the presumption b) the wave function must exponentially approach zero for $\rho \to -\infty$. But that is guaranteed only for

$$\delta_+ = 0 \,. \tag{7.161}$$

This point still has to be commented on later.

1) Schrödinger equation:

The differentiation with respect to the new variable α,

$$d\alpha = k \, d\rho \iff \frac{d}{d\rho} = k \, \frac{d}{d\alpha} \,,$$

will be marked by a point in order to distinguish it from that with respect to ρ:

$$u'' = \frac{d^2}{d\rho^2} \, u = k \, \frac{d}{d\alpha} \left(k \, \dot{u}\right) = k \, \dot{k} \, \dot{u} + k^2 \ddot{u} \,.$$

The exact Schrödinger equation (7.143) for $u = u(\alpha)$ then reads:

$$\ddot{u} + \frac{\dot{k}}{k}\,\dot{u} + u = 0\,. \tag{7.162}$$

In the next step we rewrite the *WKB-equation* (7.154) also by using the new variable α.

2) WKB-equation:
For this purpose we insert

$$k' = k\,\dot{k}\;; \quad k'' = k\,\dot{k}^2 + k^2\ddot{k}$$

into (7.154):

$$k\,\dot{k}\,\dot{\hat{u}} + k^2\,\ddot{\hat{u}} + \left(k^2 + \frac{1}{2}\,\dot{k}^2 + \frac{1}{2}\,k\,\ddot{k} - \frac{3}{4}\,\dot{k}^2\right)\hat{u} = 0\,.$$

After division by k^2 there results a differential equation,

$$\ddot{\hat{u}} + \frac{\dot{k}}{k}\,\dot{\hat{u}} + \left(1 - \frac{1}{4}\,\frac{\dot{k}^2}{k^2} + \frac{1}{2}\,\frac{\ddot{k}}{k}\right)\hat{u} = 0\,, \tag{7.163}$$

for which the WKB-function (7.160), which fulfills the Schrödinger equation (7.162) only approximately, represents an **exact** solution.

3) Linearization in the region of the turning point:
In the immediate neighborhood of the *turning point* ρ^* the linearization (7.157),

$$k^2(\rho) \sim (\rho - \rho^*)\,, \quad \alpha \sim (\rho - \rho^*)^{3/2}\,,$$

takes care for the following relatively simple relations:

$$k(\alpha) \sim \alpha^{1/3}\;; \quad \frac{\dot{k}}{k} = \frac{1}{3\alpha}\;; \quad \frac{\ddot{k}}{k} = -\frac{2}{9\alpha^2}\,.$$

In the turning region the Schrödinger equation (7.162) then reads,

$$\ddot{u} + \frac{1}{3\alpha}\,\dot{u} + u = 0\,, \tag{7.164}$$

while the WKB-equation (7.163) there takes the form

$$\ddot{\hat{u}} + \frac{1}{3\alpha}\,\dot{\hat{u}} + \left(1 - \frac{5}{36\alpha^2}\right)\hat{u} = 0\,. \tag{7.165}$$

The last summand is responsible for the *disturbing* singularity at the turning point $\alpha = 0$. On the other hand, the solution of the linearized Schrödinger equation (7.164) is regular at $\alpha = 0$. The *trick* now consists in not to solve

(7.164) directly, which would be in principle quite possible, but to seek a version, which makes the connection with the WKB-approximation become essentially simple.

4) 'Corrected' WKB-equation:

We modify the WKB-equation (7.163) such that the $(\alpha \to 0)$-singularity disappears. The comparison of (7.164) and (7.165) provides the hint as to what must be done:

$$\ddot{v} + \frac{\dot{k}}{k}\,\dot{v} + \left(1 - \frac{\dot{k}^2}{4k^2} + \frac{\ddot{k}}{2k} + \frac{5}{36\alpha^2}\right) v = 0\,. \tag{7.166}$$

The solution $v(\alpha)$ of this equation has the following remarkable properties:

$$\text{a)} \qquad v(\alpha) \underset{\alpha \to 0}{\longrightarrow} u(\alpha)\,.$$

In the turning region the differential equation (7.166) is identical to the linearized Schrödinger equation (7.164), and thus delivers there the same solutions. This means in particular that without any problem $v(\alpha)$ can be continued from the *classically allowed region* into the *classically forbidden region*.

$$\text{b)} \qquad v(\alpha) \underset{|\alpha| \gg 1}{\longrightarrow} \hat{u}(\alpha)\,.$$

Asymptotically (7.166) agrees with (7.163), so that $v(\alpha)$ turns for $|\alpha| \gg 1$ into the WKB-solution $\hat{u}(\alpha)$. One should bear in mind that the estimations for $k(\alpha)$, which lead to (7.164), are in the limit $|\alpha| \gg 1$ of course no longer valid.

5) Solution of the 'corrected' WKB-equation:

Because of a) and b) $v(\alpha)$ is obviously suitable to guarantee a *physically reasonable piecing together* of the two WKB-partial solutions (7.160). We will therefore try to solve the differential equation (7.166), in order to then fix the constants of integration in (7.160) by fitting the WKB-functions for $|\alpha| \gg 1$ to $v(\alpha)$. It turns out to be successful to use the ansatz

$$v(\alpha) = \sqrt{\frac{\alpha}{k}}\, x(\alpha)\,, \tag{7.167}$$

by which, after simple manipulations, a differential equation for $x(\alpha)$ results from (7.166), which is extensively investigated in the textbooks on mathematical physics:

$$\ddot{x}(\alpha) + \frac{1}{\alpha}\,\dot{x}(\alpha) + \left(1 - \frac{1}{9\alpha^2}\right) x(\alpha) = 0\,. \tag{7.168}$$

It concerns the so-called **general Bessel equation**:

$$y''(z) + \frac{1}{z}\,y'(z) + \left(1 - \frac{\nu^2}{z^2}\right) y(z) = 0 \tag{7.169}$$

for $\nu = \pm 1/3$. Solutions are the **Bessel functions of first kind** $J_{\pm\nu}(z)$, the mathematical behavior of which is very precisely known. Some of the special properties of the general Bessel equation and its solutions are listed in Sect. 7.4.6, as for instance the relationship to the **spherical Bessel equation** used in Sect. 6.3.2.

Since ν enters (7.168) quadratically, this equation is solved by both J_ν and $J_{-\nu}$. For non-integer ν, as in our case here, J_ν and $J_{-\nu}$ are linearly independent so that the general solution of the corrected WKB-equation (7.166) takes the following form:

$$v(\alpha) = \sqrt{\frac{\alpha}{k}}\,(a\,J_{1/3}(\alpha) + b\,J_{-1/3}(\alpha))\ . \tag{7.170}$$

The solution is regular at the turning point $\alpha = 0$ (see Exercise 7.4.2).

6) Fitting conditions for $E < \overline{V}(\rho)$:

According to our agreement on the turning point ρ^*, the solving function must decay exponentially in the *classically forbidden region* ($k^2(\rho) < 0$). Therefore $\delta_+ = 0$. One of the two constants of integration is therewith already determined. Here we thus exploit a precognition about the sought-after wave function. It will turn out that without such a precognition one of the free parameters in the WKB-solution would have to remain undetermined (see Exercise 7.4.3). Hence we can write, according to (7.160), for the WKB-solution in the *classically forbidden region*:

$$\hat{u}(\alpha) = \frac{\delta_-}{\sqrt{|k(\alpha)|}}\,e^{-|\alpha|}\ . \tag{7.171}$$

For the *Langer solution* (7.170) it holds at first with (7.159):

$$v(\alpha) = \sqrt{\frac{-i|\alpha|}{i|k|}}\,[a\,J_{1/3}\,(-i|\alpha|\,) + b\,J_{-1/3}\,(-i|\alpha|)]\ .$$

The Bessel functions with an imaginary argument lead to the so-called **modified Bessel functions** $I_{\pm\nu}$ (see (7.206) with (7.207)):

$$J_{\pm 1/3}\,(-i|\alpha|) = (-i)^{\pm 1/3}\,I_{\pm 1/3}\,(|\alpha|)\ .$$

When we still use

$$i(-i)^{1/3} = -1\ ; \quad i(-i)^{-1/3} = +1\ ,$$

it follows as intermediate result:

$$v(\alpha) = \sqrt{\left|\frac{\alpha}{k}\right|}\,(-a\,I_{1/3}(|\alpha|) + b\,I_{-1/3}(|\alpha|))\ . \tag{7.172}$$

For $|\alpha| \gg 1$ $v(\alpha)$ should comply with the WKB-solution (7.171), i.e., in particular it should decay exponentially. The asymptotic behavior of the modified

Bessel functions, however, fulfills this only by very special combinations ((7.208) and (7.213)):

$$I_{1/3}(|\alpha|) - I_{-1/3}(|\alpha|) = -\frac{2\sin(1/3\pi)}{\pi} K_{1/3}(|\alpha|)$$
$$\underset{|\alpha|\gg 1}{\longrightarrow} -\frac{2\sin(1/3\pi)}{\pi}\sqrt{\frac{\pi}{2|\alpha|}}\, e^{-|\alpha|} .$$

We have therefore to choose in (7.172) $a = b$ ($\sin\frac{\pi}{3} = \frac{1}{2}\sqrt{3}$):

$$v(\alpha) \underset{|\alpha|\gg 1}{\longrightarrow} a\sqrt{\frac{3}{2\pi|k|}}\, e^{-|\alpha|} . \tag{7.173}$$

The requirement that $v(\alpha)$ approaches for large $|\alpha|$ the WKB-solution $\hat{u}(\alpha)$, is according to (7.171) equivalent with:

$$\delta_- = a\sqrt{\frac{3}{2\pi}} . \tag{7.174}$$

7) Fitting conditions for $E > \overline{V}(\rho)$:

In the *classically allowed region* ($k^2(\rho) > 0$) we have $\alpha > 0$. We conclude from the asymptotic behavior of the Bessel functions (7.195),

$$J_\nu(\alpha) \underset{\alpha\gg 1}{\longrightarrow} \sqrt{\frac{2}{\pi\alpha}}\cos\left(\alpha - \frac{\pi}{4} - \nu\frac{\pi}{2}\right) ,$$

with (7.170) and the result $a = b$ derived in point 6):

$$v(\alpha) \underset{\alpha\gg 1}{\longrightarrow} a\sqrt{\frac{2}{\pi\, k}}\left[\cos\left(\alpha - \frac{\pi}{4} - \frac{\pi}{6}\right) + \cos\left(\alpha - \frac{\pi}{4} + \frac{\pi}{6}\right)\right]$$
$$= 2a\sqrt{\frac{2}{\pi\, k}}\cos\left(\alpha - \frac{\pi}{4}\right)\cos\frac{\pi}{6} = a\sqrt{\frac{6}{\pi\, k}}\cos\left(\alpha - \frac{\pi}{4}\right) . \tag{7.175}$$

We have here applied the addition theorem

$$\cos(x \mp y) = \cos x\cos y \pm \sin x\sin y$$

and $\cos(\pi/6) = (1/2)\sqrt{3}$. This result we have to now compare with the WKB-solution for the *classically allowed region* in (7.160). Obviously one has to choose for the coefficients in (7.160)

$$\gamma_\pm = \frac{1}{2}\,\gamma\, e^{\mp i(\pi 4)} \tag{7.176}$$

in order to get for $\hat{u}(\alpha)$ the same structure as that of the *asymptotic* $v(\alpha)$ in (7.175):

$$\hat{u}(\alpha) = \frac{\gamma}{\sqrt{k}}\cos\left(\alpha - \frac{\pi}{4}\right) . \tag{7.177}$$

The equating of (7.175) and (7.177) then yields immediately:

$$\gamma = a\sqrt{\frac{6}{\pi}}\,. \tag{7.178}$$

When we now, in the last step, combine the expressions (7.174) and (7.178),

$$\delta_- = \frac{1}{2}\gamma\,, \tag{7.179}$$

then all constants of integration in the WKB-solution (7.160), except one, are fixed. The remaining unknown can serve as normalization constant. We write down once more explicitly the complete result:

$\boldsymbol{E < \overline{V}(\rho)}$: $(\rho < \rho^*)$

$$\hat{u}(\rho) = \frac{\gamma}{2\sqrt{|k(\rho)|}} \exp\left\{ -\int_{\rho}^{\rho^*} |k(\rho')| d\rho' \right\}\,, \tag{7.180}$$

$\boldsymbol{E > \overline{V}(\rho)}$: $(\rho^* < \rho)$

$$\hat{u}(\rho) = \frac{\gamma}{\sqrt{k(\rho)}} \cos\left\{ \int_{\rho^*}^{\rho} d\rho'\, k(\rho') - \frac{\pi}{4} \right\}\,. \tag{7.181}$$

One should note with (7.180) that it holds for the here considered *left-hand* turning point according to (7.158)

$$\begin{aligned} |\alpha| &= \left| \int_{\rho^*}^{\rho} k(\rho')\, d\rho' \right| = \left| i \int_{\rho^*}^{\rho} |k(\rho')| d\rho' \right| \\ &= \left| \int_{\rho^*}^{\rho} |k(\rho')| d\rho' \right| \underset{\rho < \rho^*}{\rightarrow} = \int_{\rho}^{\rho^*} |k(\rho')| d\rho'\,. \end{aligned}$$

Let us finally add some remarks to the just performed Langer procedure:

1. The *Langer procedure* serves only to piece together the WKB-solutions of the *classically allowed region* and the *classically forbidden region* in a *physically reasonable manner*, in order to fix therewith the at first undetermined constants of integration. The singularities of the WKB-wave functions at the *classical turning points*, however, of course do not disappear therewith. The solution remains unusable there.

2. The concrete single steps of the above considerations refer to a *left-hand* turning point ρ^*, for which the **entire** region $-\infty < \rho < \rho^*$ is *classically forbidden*. The definition of the variable α in (7.158), though, was so chosen that the results (7.171), (7.177) and (7.178) remain exactly the

same for a *right-hand* turning point $\overline{\rho}^*$, when in this case the **entire** region $\overline{\rho}^* < \rho < +\infty$ is *classically forbidden*. The explicit evaluation of the mentioned equations then yields:

$\boldsymbol{E > \overline{V}(\rho)}$: $(\rho < \overline{\rho}^*)$

$$\hat{u}(\rho) = \frac{\overline{\gamma}}{\sqrt{k(\rho)}} \cos\left\{ \int_{\rho}^{\overline{\rho}^*} d\rho'\, k(\rho') - \frac{\pi}{4} \right\} , \tag{7.182}$$

$\boldsymbol{E < \overline{V}(\rho)}$: $(\overline{\rho}^* < \rho)$

$$\hat{u}(\rho) = \frac{\overline{\gamma}}{2\sqrt{|k(\rho)|}} \exp\left\{ -\int_{\overline{\rho}^*}^{\rho} d\rho' |k(\rho')| \right\} . \tag{7.183}$$

But here also, the condition is again important that the *classically forbidden region*, which is attached *to the right* to $\overline{\rho}^*$, extends up to $+\infty$. It is therewith guaranteed as in (7.161) that in the *non-oscillating* WKB-partial solution (7.160) one of the coefficients is zero.

3. For the general case, for which in the *classically forbidden region*, which is attached to the *turning point*, in the WKB-solution besides the decreasing also the increasing exponential function is to be taken into consideration, the *Langer method* leads to the following result:

   $\boldsymbol{E > \overline{V}(\rho)}$

   $$\hat{u}(\alpha) = \frac{\widehat{\gamma}}{\sqrt{k}} \cos\left(\alpha - \frac{\pi}{4} + \varphi\right) , \tag{7.184}$$

   $\boldsymbol{E < \overline{V}(\rho)}$

   $$\hat{u}(\alpha) = \frac{\widehat{\gamma}}{\sqrt{|k|}} \left(\frac{1}{2} \cos\varphi\, e^{-|\alpha|} + \sin\varphi\, e^{|\alpha|} \right) . \tag{7.185}$$

   The variable α is defined as in (7.158). $\widehat{\gamma}$ and φ are complex constants. In contrast to the solutions (7.180)–(7.183) φ represents an additional constant of integration, which can be more precisely specified only if certain *advance information* about the solution is available. In the cases of the above examples that was just the exponential decrease of the wave function to be required in the *classically forbidden region*, which brought about $\varphi = 0$, as the comparison of (7.171) and (7.177) with (7.184) and (7.185) points out. We perform the proof to (7.184) and (7.185) as Exercise 7.4.3!

4. The WKB-procedure finds important applications as approximation method in connection with all conceivable **tunneling processes** of quantum-mechanical particles through *classically impenetrable* potential barriers of complicated, realistic shape (Fig. 7.11). Although the situation

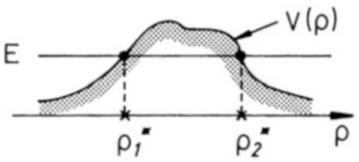

Figure 7.11: Tunneling of quantum-mechanical particles through classically impenetrable potential walls

described in part 3) is present, sometimes rather concrete statements can be derived. So one finds for the **transmission coefficient** $T(E)$ (4.56) (Vol. 6) of a particle of mass m through a potential wall $V(\rho)$ with $V(\rho \to \pm\infty) < E$ and only two turning points ρ_1^* and ρ_2^* (Fig. 7.11):

$$T(E) \approx \exp\left(-\frac{2}{\hbar} \int_{\rho_1^*}^{\rho_2^*} \sqrt{2m(V(\rho) - E)}\, d\rho \right) . \tag{7.186}$$

This useful formula, which we derive in Exercise 7.4.4, we have already made plausible, under strongly simplifying assumptions, in Sect. 4.3.3 (Vol. 6), where such important phenomena as the *α-radioactivity* (Sect. 4.3.4 (Vol. 6)) or the *field emission* (Exercise 4.3.4 (Vol. 6)) could be explained.

7.4.5 Phase-Integral Quantization

We want to derive now by means of the WKB-method a formula for an important special case which provides the way to calculate the discrete energy spectrum of bound states. We consider a potential curve, for which a particle of mass m and energy E can classically reach neither $+\infty$ nor $-\infty$. There exists a *left-hand* and a *right-hand* turning point. The interval $\rho_1^* < \rho < \rho_2^*$ represents a *classically allowed region*, while the regions $-\infty < \rho < \rho_1^*$ as well as $\rho_2^* < \rho < +\infty$ are *classically forbidden* (Fig. 7.12). For the *left-hand* turning point ρ_1^* the formulas (7.180) and (7.181) are valid and for the *right-hand* turning point ρ_2^* (7.182) and (7.183). Within the *classically allowed interval* $\rho_1^* < \rho < \rho_2^*$ the two solutions

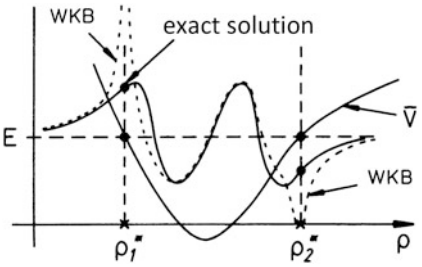

Figure 7.12: Schematic representation of the exact solution (*solid line*) and the WKB-approximation (*broken line*) for a particle motion with two classical turning points

(7.181) and (7.182) must of course coincide. This obviously requires that the two constants γ and $\overline{\gamma}$ differ at most by the sign, and furthermore

$$\begin{aligned}
\cos\left\{\int_{\rho_1^*}^{\rho} d\rho'\, k(\rho') - \frac{\pi}{4}\right\} &\stackrel{!}{=} \pm\cos\left\{\int_{\rho}^{\rho_2^*} d\rho'\, k(\rho') - \frac{\pi}{4}\right\} \\
&= \pm\cos\left\{-\int_{\rho}^{\rho_2^*} d\rho'\, k(\rho') + \frac{\pi}{4}\right\} \\
&= \pm\cos\left\{-\int_{\rho_1^*}^{\rho_2^*} d\rho'\, k(\rho') + \frac{\pi}{4} + \int_{\rho_1^*}^{\rho} d\rho'\, k(\rho')\right\} \\
&= \pm\cos\left\{\int_{\rho_1^*}^{\rho} d\rho'\, k(\rho') - \frac{\pi}{4} - \left(\int_{\rho_1^*}^{\rho_2^*} d\rho'\, k(\rho') - \frac{\pi}{2}\right)\right\}
\end{aligned}$$

This requirement is equivalent to:

$$\begin{aligned}
\gamma &\stackrel{!}{=} (-1)^n\,\overline{\gamma}\,, \\
\int_{\rho_1^*}^{\rho_2^*} d\rho'\, k(\rho') &\stackrel{!}{=} \left(n+\frac{1}{2}\right)\pi\,; \quad n\in\mathbb{N}\,.
\end{aligned} \tag{7.187}$$

The left-hand side is positive definite, so that for n only non-negative integers come into question. This relation turns out to be eminently useful because it can help to calculate, for a known potential $\overline{V}(\rho)$, the **energy-eigen values of the bound states** (see Exercise 7.4.1).

For a full circulation ($\rho_1^* \leftrightarrow \rho_2^*$) of a periodic motion (7.184) reads, if one takes into consideration that the momentum $p = \hbar k$ reverses its sign on the *way back*:

$$\oint p \, d\rho = 2\pi \hbar \left(n + \frac{1}{2} \right) \; ; \quad n \in \mathbb{N} \, . \tag{7.188}$$

This corresponds to the semi-classical **phase-integral quantization** (1.131) (Vol. 6). Here it is the result of an approximate quantum-mechanical consideration and must therefore no longer be seen as a pure postulate. The only difference to the famous **Bohr-Sommerfeld quantization rule** consists in the additive constant 1/2!

Because of the failure of the WKB-method in the *turning point regions* the results (7.187) and (7.188) are the more trustworthy the more oscillations the wave function carries out in the *classically allowed region*. One reaches the asymptotic region then *'faster'*, with respect to α from (7.158). According to the *law of nodes* (Sect. 4.1.3 (Vol. 6)) **large quantum numbers** n are thus convenient for this quasi-classical approximate procedure, which corresponds to the **principle of correspondence** discussed in Sect. 1.5.3 (Vol. 6).

7.4.6 Mathematical Supplement: Bessel Differential Equation

In this subsection we will collect some formulas and mathematical laws, which played a role in the preceding subsections. The strict mathematical proofs, though, can not all be performed in the framework of an ground course on Theoretical Physics. In this connection, the reader must be referred to the special textbooks.

In the **general Bessel differential equation**,

$$y''(z) + \frac{1}{z} \, y'(z) + \left(1 - \frac{\nu^2}{z^2} \right) y(z) = 0 \, , \tag{7.189}$$

let ν be an arbitrary **real** number and z an in general complex variable. One speaks of the **special** Bessel differential equation when ν is an integer. The **solutions** of (7.189) are generally called **cylindrical functions**. One distinguishes several types:

1) Bessel functions of the first kind

These are defined as follows:

$$J_\nu(z) = \left(\frac{z}{2} \right)^\nu \sum_{k=0}^{\infty} \frac{(-1)^k}{k! \Gamma(k + \nu + 1)} \left(\frac{z}{2} \right)^{2k} \, . \tag{7.190}$$

One immediately recognizes the symmetry relation:

$$J_\nu(-z) = (-1)^\nu \, J_\nu(z) \, . \tag{7.191}$$

In (7.190) Γ is the *gamma-function*:

$$\Gamma(\nu+1) = \int_0^\infty dt\, e^{-t}\, t^\nu \ . \tag{7.192}$$

As long as ν is not integral, $J_\nu(z)$ and $J_{-\nu}(z)$ are linearly independent. The general solution of (7.189) then reads

$$Z_\nu(z) = \alpha\, J_\nu(z) + \beta\, J_{-\nu}(z) \tag{7.193}$$

with any constants α and β.

The **asymptotic behavior** is important:

$$J_\nu(z) \underset{z\to 0}{\longrightarrow} \frac{1}{\Gamma(\nu+1)} \left(\frac{z}{2}\right)^\nu \ . \tag{7.194}$$

ν is here non-negative or, if it is negative, then not integral:

$$J_\nu(z) \underset{|z|\to\infty}{\longrightarrow} \sqrt{\frac{2}{\pi\, z}}\, \cos\left(z - \frac{\pi}{4} - \frac{\nu\pi}{2}\right) \ . \tag{7.195}$$

If $\nu = n$ is an integer, then J_ν and $J_{-\nu}$ are no longer linearly independent. Instead one recognizes with (7.190) (Exercise 7.4.5):

$$J_{-n}(z) = (-1)^n\, J_n(z) \ . \tag{7.196}$$

In such a case a second linearly independent solution must be found. These are the

2) Bessel functions of the second kind,

which are also called *Neumann functions*:

$$N_\nu(z) = \frac{1}{\sin\nu\,\pi} \left(J_\nu(z)\cos\nu\,\pi - J_{-\nu}(z)\right) . \tag{7.197}$$

This definition is, because of (7.196), to be read for integral ν as limiting value (l'Hospital). The $N_\nu(z)$ and $J_\nu(z)$ are for each real ν linearly independent. The general solution of (7.189) can therefore always be written as

$$Z_\nu(z) = \overline{\alpha}\, J_\nu(z) + \overline{\beta}\, N_\nu(z) \ . \tag{7.198}$$

In the case of non-integral ν both (7.193) as well as (7.198) are general solutions, for integral ν only (7.198).

The Neumann functions are singular at the origin:

$$N_\nu(z) \underset{z\to 0}{\longrightarrow} \begin{cases} \frac{2}{\pi}\left[\ln\left(\frac{z}{2}\right) + 0.5772 + \ldots\right] \ ; & \nu = 0 \ , \\ -\frac{1}{\pi}\Gamma(\nu)\left(\frac{z}{2}\right)^{-\nu} \ ; & \nu > 0 \ , \end{cases} \tag{7.199}$$

$$N_\nu(z) \underset{|z|\to\infty}{\longrightarrow} \sqrt{\frac{2}{\pi z}}\, \sin\left(z - \frac{\pi}{4} - \frac{\nu\,\pi}{2}\right) \ . \tag{7.200}$$

There still exists a third fundamental system. These are the

3) Bessel functions of the third kind,

which are also called *Hankel functions*:

$$H_\nu^{(1)}(z) = J_\nu(z) + i\,N_\nu(z)\,; \quad H_\nu^{(2)}(z) = J_\nu(z) - i\,N_\nu(z)\,. \tag{7.201}$$

Their introduction is sometimes reasonable in order to achieve a suitable asymptotic behavior:

$$H_\nu^{(1,2)}(z) \underset{|z|\to\infty}{\longrightarrow} \sqrt{\frac{2}{\pi\,z}}\exp\left[\pm i\left(z - \left(\nu+\frac{1}{2}\right)\frac{\pi}{2}\right)\right]\,. \tag{7.202}$$

For $z \to 0$ they are of course determined by the singular behavior of the Neumann functions.

We present at the end still some useful **recursion formulas**, which are fulfilled in the same manner by the functions $J_\nu(z)$, $N_\nu(z)$, $H_\nu^{(1,2)}(z)$ (Exercise 7.4.7):

$$y_{\nu-1}(z) + y_{\nu+1}(z) = \frac{2\nu}{z}\,y_\nu(z)\,, \tag{7.203}$$

$$y_{\nu-1}(z) - y_{\nu+1}(z) = 2\,\frac{d}{dz}\,y_\nu(z)\,, \tag{7.204}$$

$$y'_\nu(z) = y_{\nu-1}(z) - \frac{\nu}{z}\,y_\nu(z) = -y_{\nu+1}(z) + \frac{\nu}{z}\,y_\nu(z)\,. \tag{7.205}$$

Besides the general differential equation one still knows the **modified Bessel differential equation**:

$$y''(z) + \frac{1}{z}\,y'(z) - \left(1 + \frac{\nu^2}{z^2}\right)\,y(z) = 0\,. \tag{7.206}$$

The partial solutions $I_\nu(z)$ and $K_\nu(z)$, which are linearly independent for all real ν, are related to the already introduced Bessel functions as follows:

$$I_\nu(z) = (-i)^\nu\,J_\nu(i\,z)\,, \tag{7.207}$$

$$K_\nu(z) = \frac{\pi}{2}\,i^{\nu+1}\,H_\nu^{(1)}\,(i\,z) = \frac{\pi}{2}\,\frac{I_{-\nu}(z) - I_\nu(z)}{\sin(\nu\,\pi)} = K_{-\nu}(z)\,. \tag{7.208}$$

For non-integral ν also $I_\nu(z)$ and $I_{-\nu}(z)$ are linearly independent. In the case of integral $\nu = n$, however, it holds in agreement with (7.196):

$$I_{-n}(z) = I_n(z) \quad n \in \mathbb{N}\,. \tag{7.209}$$

For $\nu = n$ the second part in (7.208) has again to be read as a limiting process.

In the limit of *small* z, the *modified Bessel functions* behave as follows:

$$I_\nu(z) \underset{z\to 0}{\longrightarrow} \frac{1}{\Gamma(\nu+1)}\left(\frac{z}{2}\right)^\nu\,; \quad \nu \neq -n\,,\ n \in \mathbb{N} \tag{7.210}$$

$$K_\nu(z) \underset{z\to 0}{\longrightarrow} \begin{cases} -\left(\ln\dfrac{z}{2} + 0.5772 + \ldots\right)\,; & \nu = 0\,, \\ \frac{1}{2}\,\Gamma(\nu)\left(\dfrac{2}{z}\right)^\nu\,; & \nu \neq 0\,. \end{cases} \tag{7.211}$$

These functions are asymptoticly ($|z| \to \infty$) to first approximation even ν-independent:

$$I_\nu(z) \quad \underset{|z|\to\infty}{\longrightarrow} \quad \frac{1}{\sqrt{2\pi\, z}}\, e^z \;, \tag{7.212}$$

$$K_\nu(z) \quad \underset{|z|\to\infty}{\longrightarrow} \quad \sqrt{\frac{\pi}{2z}}\, e^{-z} \;. \tag{7.213}$$

Besides the *general* and the *modified* Bessel differential equation there exists still a third variant, namely, the one, discussed extensively in Sect. 6.3.2, the

spherical Bessel differential equation

$$R''(z) + \frac{2}{z}\, R'(z) + \left(1 - \frac{n(n+1)}{z^2}\right) R(z) = 0 \;, \quad n \in \mathbb{Z} \;, \tag{7.214}$$

which by the substitution $y(z) = \sqrt{z}\, R(z)$ turns into the *general* equation (7.189) for $\nu = n + 1/2$. Solutions of (7.214) are the **spherical Bessel, Neumann, Hankel functions**, for which we therefore have:

$$j_n(z) \;=\; \sqrt{\frac{\pi}{2z}}\, J_{n+1/2}(z) \;, \tag{7.215}$$

$$n_n(z) \;=\; \sqrt{\frac{\pi}{2z}}\, N_{n+1/2}(z) \;, \tag{7.216}$$

$$h_n^{(1,2)}(z) \;=\; \sqrt{\frac{\pi}{2z}}\, H_{n+1/2}(z) \;. \tag{7.217}$$

The properties of these functions, in particular their asymptotic behavior (see (6.120)–(6.126)), we got to know already in Sect. 6.3.2.

7.4.7 Exercises

Exercise 7.4.1
By means of the WKB-procedure calculate the energy-eigen values of the harmonic oscillator.

Exercise 7.4.2
Show that the *Langer-solution* (7.170),

$$v(\alpha) = \sqrt{\frac{\alpha}{k}}\, \left(a\, J_{1/3}(\alpha) + b\, J_{-1/3}(\alpha)\right) \;,$$

remains finite at the *turning point* $\alpha = 0$.

Exercise 7.4.3
Let ρ^* be a *classical turning point*, which separates the *classically forbidden region* ($E < \overline{V}(\rho)$) and the *classically allowed region* ($E > \overline{V}(\rho)$). Consider, in extension of the theory in Sect. 7.4.4, the general case, for which there does not exist a *precognition* of any sort about the wave function, neither in the *classically allowed region* nor in the *classically forbidden region*.

1. Show that in the *classically forbidden region* the WKB-solution (7.160) has the structure (7.184):

$$\hat{u}(\alpha) = \frac{\widehat{\gamma}}{\sqrt{k}} \cos\left(\alpha - \frac{\pi}{4} + \varphi\right) .$$

   α is here defined as in (7.158), while $\widehat{\gamma}$ and φ are complex constants. What is the relation between φ, $\widehat{\gamma}$ and the constants $\gamma_{\pm}$ in (7.160)?

2. Express the coefficients a and b in (7.170) by $\widehat{\gamma}$ and φ by an *asymptotic piecing together* of the WKB-solution from part 1. and the *Langer-solution* $v(\alpha)$.

3. Show that the *Langer-solution* (7.170) behaves in the *classically forbidden region* asymptoticly like

$$v(\alpha) \underset{|\alpha| \to \infty}{\longrightarrow} \frac{1}{2\sqrt{2\pi|k|}} \left[\sqrt{3}(a+b)\, e^{-|\alpha|} - 2(a-b)\, e^{|\alpha|}\right] .$$

4. Finally confirm the WKB-solution (7.185), again by an *asymptotic piecing together*, in the *classically forbidden region*:

$$\hat{u}(\alpha) = \frac{\widehat{\gamma}}{\sqrt{|k|}} \left(\frac{1}{2} \cos\varphi\, e^{-|\alpha|} + \sin\varphi\, e^{|\alpha|}\right) .$$

Exercise 7.4.4
A particle of mass m and energy E moves towards a broad potential wall $V(\rho)$, for which $V(\rho \to \pm\infty) < E$, where, as in Fig. 7.11, two turning points ($\rho_1^* < \rho_2^*$) exist.

1. How do the WKB-solutions with respect to ρ_1^* read, if one can approximately assume that, because of the width of the wall, only a negligible fraction of the particle wave can permeate the wall?

2. Calculate with part 1. the *incident* current density j_{in} in direction towards the potential wall.

3. How does the WKB-solution with respect to ρ_2^* read? Exploit the fact that from infinity ($\rho \to +\infty$) no part of the wave will be reflected.

4. Calculate the *outgoing* current density j_{out}, which permeates the wall.

5. Calculate the transmission coefficient

$$T(E) = \left|\frac{j_{\text{out}}}{j_{\text{in}}}\right| .$$

   Confirm the result (7.186).

Exercise 7.4.5
Use the properties of the gamma-function,

1.
$$\Gamma(n+1) = n! \quad \text{for} \quad n = 0, 1, 2, \ldots$$

2.
$$\Gamma(z) \text{ singular at } z = -n \quad (n = 0, 1, 2, \ldots) \quad \text{with the residues} \quad \frac{(-1)^n}{n!} ,$$

in order to derive from (7.190) the property (7.196),

$$J_{-n}(z) = (-1)^n J_n(z) \qquad\qquad n = 0, 1, 2, \ldots ,$$

of Bessel functions of the first kind with integral indexes!

Exercise 7.4.6
Derive directly from the definition (7.190) the two Bessel functions of the first kind with the indexes $\nu = +1/2$ and $\nu = -1/2$!

Exercise 7.4.7
Consider in the following exclusively the Bessel functions of the first kind with integral indexes $\nu = n \in \mathbb{Z}$.

1. Prove the relationship:
$$\exp\left(\frac{z}{2}\left(t - \frac{1}{t}\right)\right) = \sum_{n=-\infty}^{+\infty} J_n(z)\, t^n .$$
One calls the function on the left-hand side the *generating function* of the Bessel functions of the first kind.

2. Utilize the result from 1., in order to derive the recursion formula (7.203):
$$J_{n-1}(z) + J_{n+1}(z) = \frac{2n}{z} J_n(z) .$$

3. Verify the recursion formula (7.204):
$$J_{n-1}(z) - J_{n+1}(z) = 2\frac{d}{dz} J_n(z) .$$

4. Prove the recursion formula (7.205):
$$\frac{d}{dz} J_n(z) = J_{n-1}(z) - \frac{n}{z} J_n(z) = -J_{n+1}(z) + \frac{n}{z} J_n(z) .$$

5. Derive the following relations:
$$\frac{d}{dz}\left(z^n J_n(z)\right) = z^n J_{n-1}(z) ; \quad \frac{d}{dz}\left(z^{-n} J_n(z)\right) = -z^{-n} J_{n+1}(z) .$$

7.5 Self-Examination Questions

To Section 7.1

1. What is the statement of the *extremal principle*?
2. In which way can approximation methods be developed with the *extremal principle*?
3. On the basis of which generally valid statement does the Ritz's variational method work?
4. How does the Ritz's method operate for the calculation of the ground state energy?
5. What is normally better determined by the Ritz's method, the ground state or the ground-state energy?
6. How can, at least in principle, even *excited* states and their energies be determined by the Ritz's method?
7. Which variational ansatz underlies the Hartree-procedure?

To Section 7.2

1. To which physical problems is the Schrödinger perturbation theory tailored?
2. In the Schrödinger perturbation theory a parameter λ is *artificially* extracted from the interaction H_1. Which purpose does it serve?
3. How does one calculate the energy correction of first order for a non-degenerate level?
4. Which *rough* criterion should be fulfilled in order to make it reasonable to terminate the expansions for the eigen-energies and the eigen-states after a few terms in the *non-degenerate* perturbation theory?
5. What is to be taken into consideration when treating the *perturbation correction* of a degenerate energy level?
6. How are the energy corrections of first order to be determined for an degenerate energy level?
7. Which problems with respect to Schrödinger's perturbation expansion arise for the case of very closely adjacent (*quasi-degenerate*) energy levels?
8. Does the *quasi-degeneracy* represents a problem for the energy correction of first order also?
9. How can the perturbation of a twofold quasi-degenerate system be approximately treated?

10. Which *idea* leads to the perturbation-theoretical basic formula?
11. How does one get from this basic formula the perturbation series of Schrödinger and Brillouin-Wigner, respectively?
12. What could be an advantage, what could be a disadvantage of the Brillouin-Wigner perturbation theory compared to that of Schrödinger?

To Section 7.3

1. To which type of physical problem is the time-dependent perturbation theory tailored?
2. Which are the essential differences in the objectives of time-independent and time-dependent perturbation theory?
3. Which advantages do the Dirac representation offer for the development of the time-dependent perturbation theory?
4. What does one understand by the Dyson series?
5. Formulate a *rough criterion* for the applicability of time-dependent perturbation theory!
6. How is the *transition probability* defined?
7. What does one understand by *virtual intermediate states*?
8. What is to be calculated in first order for the transition probability?
9. To which range of values is the transition probability $w_{\mathrm{if}}^{(1)}$ restricted in first order perturbation theory?
10. Which terms dominate the transition probability $w_{\mathrm{if}}^{(1)}$, when a constant perturbation is switched on in the time interval $0 \leq t \leq t_{\mathrm{p}}$?
11. Which statement is made by the *Fermi's golden rule*?
12. What can be said about the range of validity of the *golden rule*?
13. What is a density of states?
14. What is meant when one says that the transition probability has a *resonance character*?

To Section 7.4

1. In which sense can Classical Mechanics be regarded as the '$\hbar \to 0$'-limiting case of Quantum Mechanics?
2. With which ansatz for the wave function does the WKB-method start? On which problems the method is focused in particular?

3. Which structure does the wave function in WKB-approximation have? How does it look like for the special case of a constant potential everywhere?

4. What do you know about the range of validity of the WKB-approximation?

5. In which regions is the WKB-solution definitely unusable?

6. Why can the WKB-solutions and their derivatives from the *classically forbidden* and from the *classically allowed region* not, as otherwise usual, continuously be fitted at the *classical turning point*?

7. How does one nevertheless reach a physically convincing piecing together by the WKB-procedure?

8. What is the objective of the Langer procedure?

9. Let a one-dimensional potential problem have a *lower* and an *upper* classical turning point. By the use of which relation can the energy-eigen values of the bound states be calculated in the WKB-approximation?

10. Which relationship exists between the semi-classical Bohr-Sommerfeld quantization rule and the WKB-approximation?

11. Which form does the general Bessel differential equation have?

12. What is the connection between the general and the spherical Bessel differential equation?

Chapter 8

Many-Particle Systems

Our considerations in the preceding chapters were valid for systems which consist of just one particle. We learned how such **one-particle systems** are to be described quantum-mechanically. Now we have to give thought to the question what is to take into consideration additionally when treating **many-particle systems**. It will turn out as necessary to strictly separate the so-called **distinguishable particles** from the indistinguishable ones, i.e., from the so-called **identical particles**. **Distinguishable** means that there exists some physical property (mass, charge, spin, ...), by which the single particles set themselves apart from the other ones, so that it is in principle possible, to identify the particles by an appropriate measurement. On the other hand, *identical particles* have all their properties same, and can thus be distinguished from each other by no measurement. In this sense, electrons and protons are distinguishable because of their different masses and different charges, while the electrons among themselves as well as the protons among themselves are *identical*.

At first, we want to begin in Sect. 8.1 with the discussion of systems of N distinguishable particles. Their description orients itself, in principle, directly along the line of the general postulates of Quantum Mechanics which are already known to us. However, that does not reduntantize that we have to very carefully think about which Hilbert space and which observables are to be ascribed to these systems. It will turn out that operators, which act on different particles, are in any case commutable. It is therefore, for instance, possible to measure simultaneously and precisely the position of particle i and the momentum of particle $j\,(\neq i)$.

When describing **identical particles** we will meet a completely new principle (Sect. 8.2), to which there does not exist any classical analog, and by which symmetry-requirements are to be placed on the Hilbert-space vectors. This **principle of indistinguishability** of identical particles has very far-reaching consequences. An immediate result is the **Pauli principle**, by which, in the last analysis, the entire buildup of the matter is regulated.

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The *ordinary* description of many-particle systems proves to be extremely troublesome, but gets a strong and elegant simplification by the **formalism of second quantization** (Sect. 8.3). A typical feature of this formalism is the introduction of **creation and annihilation operators**.

We will close this chapter with a few concrete examples of application, which clearly demonstrate the impact of the principle of indistinguishability. The Hartree-Fock equations (Sect. 8.4.1) are important basic equations for the determination of the electron-density distribution in atoms, molecules and solids. In connection with two-electron systems, **hydrogen molecule** (Sect. 8.4.2) and **helium atom** (Sect. 8.4.3), we will get to know the classically incomprehensible **exchange interaction**, on which such important phenomena as, e.g.,the **chemical bond** or the wide region of **collective magnetism** are based.

8.1 Distinguishable Particles

In this first section, at first we want to look for a representation of such systems, which consist of N particles, which do not agree in all their properties, and are therefore pairwise **distinguishable**. **Distinguishable** particle can in particular be *numbered consecutively* ($i = 1, 2, \ldots, N$). All the essentials can be demonstrated already by the relatively easily manageable case of $N = 2$, with which we therefore want to start our considerations.

8.1.1 Hilbert Space of Two Distinguishable Particles

How does one describe a system of two distinguishable particles? For simplicity we want at first to presume that the two particles do not interact with each other. We will of course soon be able to remove this restriction. To such a system there is classically ascribed a Hamilton function of the form

$$H = \sum_{i=1}^{2} H^{(i)} , \tag{8.1}$$

$$H^{(i)} = \frac{\mathbf{p}_i^2}{2m_i} + V_i(\mathbf{q}_i) , \tag{8.2}$$

where V_i represents the interaction of the ith particle with a possibly present external field. According to the principle of correspondence, therefrom we get the Hamilton **operator**, when we change the particle variables in the well-known manner to operators. With $H^{(1)}$ and $H^{(2)}$ there are then the time-independent Schrödinger equations to be fulfilled:

$$H^{(1)}|\varepsilon^{(1)}\rangle = \varepsilon^{(1)}|\varepsilon^{(1)}\rangle \; ; \quad H^{(2)}|\eta^{(2)}\rangle = \eta^{(2)}|\eta^{(2)}\rangle \; . \tag{8.3}$$

The eigen-states thereby belong to the respective one-particle Hilbert spaces:

$$|\varepsilon^{(1)}\rangle \in \mathcal{H}_1^{(1)} \; ; \quad |\eta^{(2)}\rangle \in \mathcal{H}_1^{(2)} \; . \tag{8.4}$$

The lower index of the Hilbert-space symbols $\mathcal{H}$ refer to the number of particles in the system ($\mathcal{H}_N \iff N$-particle system); the upper index marks the distinguishable and therefore denumerable particles. Because of the missing interaction the eigen-energies of the total Hamilton operator H of course are just the sum of the two partial energies in (8.3):

$$E = \varepsilon^{(1)} + \eta^{(2)} \; . \tag{8.5}$$

But now, how do the eigen-states of the total Hamilton operator look like? We remember that we have solved a similar problem already once in Sect. 5.2.3 when we had to incorporate the particle spin in addition to the orbital motion into our theoretical framework. This succeeded by means of the **direct product states** (5.138). It therefore suggests itself to try the same here, i.e., to write the two-particle state, we are looking for,

$$|\varepsilon\,\eta\rangle \equiv |\varepsilon^{(1)}\rangle|\eta^{(2)}\rangle = |\eta^{(2)}\rangle|\varepsilon^{(1)}\rangle \; , \tag{8.6}$$

formally as (commutative) product of the two one-particle states. Because of

$$\begin{aligned} H|\varepsilon\,\eta\rangle &= \left(H^{(1)} + H^{(2)}\right)\left|\varepsilon^{(1)}\right\rangle\left|\eta^{(2)}\right\rangle \\ &= \left(H^{(1)}\left|\varepsilon^{(1)}\right\rangle\right)\left|\eta^{(2)}\right\rangle + \left(H^{(2)}\left|\eta^{(2)}\right\rangle\right)\left|\varepsilon^{(1)}\right\rangle \\ &= \left(\varepsilon^{(1)} + \eta^{(2)}\right)\left|\varepsilon^{(1)}\right\rangle\left|\eta^{(2)}\right\rangle = E|\varepsilon\,\eta\rangle \end{aligned} \tag{8.7}$$

they are indeed the required eigen-states, if we reasonably presume that the operator $H^{(i)}$ $(i = 1, 2)$, defined only in $\mathcal{H}_1^{(i)}$, consequently acts only on the elements of this subspace and leaves the states of the other subspace uninfluenced. We will come back to this point once more in the next subsection.

The states (8.6) are of course neither elements of $\mathcal{H}_1^{(1)}$ nor of $\mathcal{H}_1^{(2)}$, but rather of the so-called **product space**

$$\mathcal{H}_2 = \mathcal{H}_1^{(1)} \otimes \mathcal{H}_1^{(2)} \; . \tag{8.8}$$

This space consists of all the product states, which can be built up, as in (8.6), by the elements of the two one-particle Hilbert spaces $\mathcal{H}_1^{(i)}$, as well as of all conceivable linear combinations of these product states with complex coefficients. For an arbitrary element $|\varphi_2\rangle$ of the $\mathcal{H}_2$ it can thus always be written:

$$\begin{aligned} |\varphi_2\rangle &= \sum\!\!\!\!\!\!\int_i \sum\!\!\!\!\!\!\int_j \alpha_{ij}(\varphi)|\overline{\varphi}_i\,\widehat{\varphi}_j\rangle = \sum\!\!\!\!\!\!\int_i \sum\!\!\!\!\!\!\int_j \alpha_{ij}(\varphi)|\overline{\varphi}_i^{(1)}\rangle|\widehat{\varphi}_j^{(2)}\rangle \; , \\ &\qquad |\overline{\varphi}_i^{(1)}\rangle \in \mathcal{H}_1^{(1)} \; ; \quad |\widehat{\varphi}_j^{(2)}\rangle \in \mathcal{H}_1^{(2)} \; ; \quad \alpha_{ij}(\varphi) \in \mathbb{C} \; . \end{aligned} \tag{8.9}$$

The summation symbol $\sum\!\!\!\!\!\!\int$ indicates that we allow proper as well as improper states (elements). Each product state of the type (8.6) is an element of $\mathcal{H}_2$. The reverse, however, does not hold. The relation (8.9) makes clear that not every

state of $\mathcal{H}_2$ can be written as a simple product state. It is just this fact, which allows for the inclusion of interactions into the formalism. It makes immediate sense that in the presence of interactions (8.6) can no longer be an eigen-state of H. But it is self-evident to assume that the mentioned state can be expanded in the eigen-states of the *free* system, in order to be therewith an element of the $\mathcal{H}_2$.

For $\mathcal{H}_2$ to be a unitary vector space we still have to explain the scalar product. As in (5.140) we trace this back to the corresponding scalar products in the partial spaces $\mathcal{H}_1^{(i)}$. It surely makes sense to combine states only out of the same partial space. For the pure product states,

$$|\chi\,\rho\rangle = |\chi^{(1)}\rangle|\rho^{(2)}\rangle\;; \quad |\overline{\chi}\,\overline{\rho}\rangle = |\overline{\chi}^{(1)}\rangle|\overline{\rho}^{(2)}\rangle\;,$$

which build a proper subset of the $\mathcal{H}_2$, it should be valid:

$$\langle\overline{\chi}\,\overline{\rho}|\chi\,\rho\rangle = \langle\overline{\chi}^{(1)}|\chi^{(1)}\rangle\langle\overline{\rho}^{(2)}|\rho^{(2)}\rangle\;. \tag{8.10}$$

Consistently therewith, general states $|\varphi_2\rangle$, $|\psi_2\rangle \in \mathcal{H}_2$, which are built as in (8.9), are *scalarly multiplied* as follows:

$$\langle\psi_2|\varphi_2\rangle = \sum_{k,l}\sum_{i,j}{}' \alpha^*_{kl}(\psi)\,\alpha_{ij}(\varphi)\;\langle\overline{\psi}^{(1)}_k|\overline{\varphi}^{(1)}_i\rangle\langle\widehat{\psi}^{(2)}_l|\widehat{\varphi}^{(2)}_j\rangle\;. \tag{8.11}$$

We prove as Exercise 8.1.1 that this definition indeed fulfills all the axioms of a scalar product.

Now let

$$\left\{|a^{(1)}_n\rangle\right\}\;; \quad \left\{|b^{(2)}_m\rangle\right\}$$

be eigen-states of complete sets of commuting observables in $\mathcal{H}_1^{(1)}$ and $\mathcal{H}_1^{(2)}$, respectively, building the orthonormalized bases of these spaces. Then the product states

$$\left\{|a_n\,b_m\rangle = |a^{(1)}_n\rangle|b^{(2)}_m\rangle\right\} \tag{8.12}$$

represent a continuous or discrete **orthonormalized** basis of the $\mathcal{H}_2$. Let us control this:

1. *Orthonormality*

$$\langle a_{n'}\,b_{m'}|a_n\,b_m\rangle = \langle a^{(1)}_{n'}|a^{(1)}_n\rangle\langle b^{(2)}_{m'}|b^{(2)}_m\rangle = \delta(n',n)\delta(m',m)\;. \tag{8.13}$$

We had introduced the δ-symbol in (3.49) (Vol. 6). It means the Kronecker-delta in the case of discrete states and the δ-function for improper (Dirac) states.

2. *Completeness*
Let $|\varphi_2\rangle$ be an arbitrary state of $\mathcal{H}_2$, for which the representation (8.9) holds. Then we can at first expand the one-particle states $|\overline{\varphi}_i^{(1)}\rangle$, $|\widehat{\varphi}_j^{(2)}\rangle$ respectively in complete bases $\{|a_n^{(1)}\rangle\}$ and $\{|b_m^{(2)}\rangle\}$ in their one-particle spaces $\mathcal{H}_1^{(1,2)}$:

$$\begin{aligned} |\overline{\varphi}_i^{(1)}\rangle &= \sum\!\!\!\!\!\!\int_n c_n^{(i)} |a_n^{(1)}\rangle \,, \\ |\widehat{\varphi}_j^{(2)}\rangle &= \sum\!\!\!\!\!\!\int_m d_m^{(j)} |b_m^{(2)}\rangle \,. \end{aligned}$$

This we insert into (8.9):

$$\begin{aligned} |\varphi_2\rangle &= \sum\!\!\!\!\!\!\int_{i,\,j} \sum\!\!\!\!\!\!\int_{n,m} \alpha_{ij}(\varphi)\, c_n^{(i)}\, d_m^{(j)} |a_n^{(1)}\rangle |b_m^{(2)}\rangle = \sum\!\!\!\!\!\!\int_{m,n} \gamma_{nm}(\varphi) |a_n\, b_m\rangle \,, \\ \gamma_{nm}(\varphi) &= \sum\!\!\!\!\!\!\int_{i,\,j} \alpha_{ij}(\varphi)\, c_n^{(i)}\, d_m^{(j)} \in \mathbb{C} \,. \end{aligned} \tag{8.14}$$

Each arbitrary state of the $\mathcal{H}_2$ can therefore be written as a linear combination of the product states (8.12). That demonstrates the completeness, which can also be expressed by

$$\sum\!\!\!\!\!\!\int_{n,m} |a_n\, b_m\rangle\langle a_n\, b_m| = \mathbb{1}_2 \,. \tag{8.15}$$

$\mathbb{1}_2$ is the identity in the two-particle Hilbert space $\mathcal{H}_2$. If $\mathcal{H}_1^{(1,2)}$ are finite-dimensional spaces, then the dimension of $\mathcal{H}_2$ is obviously equal to the product of the dimensions of the one-particle spaces $\mathcal{H}_1^{(1)}$ and $\mathcal{H}_1^{(2)}$. One can of course also find other basis systems for the product space, whose elements are then not necessarily the direct products of one state from $\mathcal{H}_1^{(1)}$ and one from $\mathcal{H}_1^{(2)}$. So we have recognized in Sect. 6.2.5 that in the case of two-particle systems with a distance-dependent interaction $V = V(|\mathbf{r}_1 - \mathbf{r}_2|)$, it can be convenient to choose center-of-mass and relative coordinates, $\mathbf{R}$ and $\mathbf{r}$ (6.98). It is evident that the two-particle states $|\mathbf{R}\,\mathbf{r}\rangle$ can not be written as direct products of states from $\mathcal{H}_1^{(1)}$ and $\mathcal{H}_1^{(2)}$. We met another example when we discussed in Sect. 5.4 the addition of angular momenta. In the product space of two single angular momenta $\mathbf{j}_1$ and $\mathbf{j}_2$, it can turn out to be reasonable to choose as basis the eigen-states $|j_1 j_2; j\, m_j\rangle$ of the total angular momentum.

The components $\gamma_{nm}(\varphi)$ of the general state $|\varphi_2\rangle$ in (8.14) must be understood as projections of $|\varphi_2\rangle$ onto the corresponding basis states $|a_n\, b_m\rangle$:

$$\gamma_{nm}(\varphi) = \langle a_n\, b_m|\varphi_2\rangle \,. \tag{8.16}$$

If we presume that $|\varphi_2\rangle$ is normalized, then we can apply exactly the same probability interpretations to the two-particle states as to the one-particle states. The respective statements in Chap. 2 (Vol. 6) can be adopted almost word-for-word. In this sense,

$$|\gamma_{nm}(\varphi)|^2 \equiv |\langle a_n\, b_m|\varphi_2\rangle|^2 \tag{8.17}$$

represents the probability that in a measurement on the two-particle system $|\varphi_2\rangle$ particle 1 is found in the state $|a_n^{(1)}\rangle$ and particle 2 in the state $|b_m^{(2)}\rangle$. In particular it holds with (8.15):

$$\sum\!\!\!\!\!\!\int_{n,m} |\gamma_{nm}(\varphi)|^2 = \langle\varphi_2|\varphi_2\rangle = 1\ . \tag{8.18}$$

8.1.2 Observables in the Product Space

We still have to give thought to the mode of action of the operators in the product space, where, however, fortunately, we can adopt almost all what we have worked out in Sect. 3.2 (Vol. 6) for the operators in $\mathcal{H}_1$. As a first point, also for many-particle systems only the **linear operators** (Sect. 3.25, Vol. 6) are interesting. Let

$$\begin{aligned} \{A_1^{(1)}\} \quad &\text{be the observables of the } \mathcal{H}_1^{(1)}\ , \\ \{B_1^{(2)}\} \quad &\text{be the observables of the } \mathcal{H}_1^{(2)}\ , \end{aligned}$$

then **the observables of $\boldsymbol{\mathcal{H}_2}$** will be some operator functions of the $A_1^{(1)}$ and $B_1^{(2)}$, just in the same sense with which we have introduced operator functions in Sect. 3.2.7 (Vol. 6) (sums, products, powers, power series, ...):

$$D_2 = \mathcal{F}\left(A_1^{(1)},\, B_1^{(2)}\right)\ . \tag{8.19}$$

When we take as basis of the $\mathcal{H}_2$ the product states (8.12), then we find by means of (8.15) the following decomposition of the operator D_2:

$$D_2 = \mathbb{1}_2\, D_2\, \mathbb{1}_2 = \sum\!\!\!\!\!\!\int_{n,m}\ \sum\!\!\!\!\!\!\int_{p,\,q} |a_n\, b_m\rangle\langle a_n\, b_m|D_2|a_p\, b_q\rangle\langle a_p\, b_q|\ . \tag{8.20}$$

In the integrand there appears the **matrix element** of the operator D_2 with respect to the basis $\{|a_n\, b_m\rangle\}$:

$$(D_2)_{nm,pq} \equiv \langle a_n\, b_m|D_2|a_p\, b_q\rangle\ . \tag{8.21}$$

The index pair n, m numbers the rows, and the index pair p, q the columns of the D_2-matrix. The representation becomes therewith, compared to that in $\mathcal{H}_1$, a bit more complicated, but does not really offer any novel facts. The application of the operator D_2 on the state $|\varphi_2\rangle \in \mathcal{H}_2$,

$$D_2|\varphi_2\rangle = |\psi_2\rangle \in \mathcal{H}_2\ ,$$

leads with (8.16), (8.20) and (8.21) to the following system of equations for the expansion coefficients $\gamma_{nm}(\psi)$ of the state $|\psi_2\rangle$:

$$\gamma_{nm}(\psi) = \sum\!\!\!\!\!\!\int_{p,\,q} (D_2)_{nm,pq}\,\gamma_{pq}(\varphi)\ . \tag{8.22}$$

The operators $A_1^{(1)}$, $B_1^{(2)}$, which act exclusively in one of the two subspaces $\mathcal{H}_1^{(i)}$, assume a certain exceptional position. For these we write in $\mathcal{H}_2$ according to (8.20):

$$A_1^{(1)} = \sum\!\!\!\!\!\!\int_{n,\,p} |a_n^{(1)}\rangle\langle a_n^{(1)}|A_1^{(1)}|a_p^{(1)}\rangle\langle a_p^{(1)}| \left(\sum\!\!\!\!\!\!\int_{m,\,q} |b_m^{(2)}\rangle\langle b_m^{(2)}|b_q^{(2)}\rangle\langle b_q^{(2)}|\right)\ .$$

The term in the bracket represents, because of the orthonormality of the one-particle states $\big(\langle b_m^{(2)}|b_q^{(2)}\rangle = \delta(m,q)\big)$, just the identity in $\mathcal{H}_1^{(2)}$:

$$\mathbb{1}_1^{(2)} = \sum\!\!\!\!\!\!\int_{m} |b_m^{(2)}\rangle\langle b_m^{(2)}|\ . \tag{8.23}$$

It thus remains for $A_1^{(1)}$:

$$A_1^{(1)} = \left[\sum\!\!\!\!\!\!\int_{n,\,p} |a_n^{(1)}\rangle\langle a_n^{(1)}|A_1^{(1)}|a_p^{(1)}\rangle\langle a_p^{(1)}|\right] \cdot \mathbb{1}_1^{(2)}\ . \tag{8.24}$$

The dot on the right-hand side does not at all indicate a scalar product, but simply expresses that $A_1^{(1)}$ does not act in $\mathcal{H}_1^{(1)}$, but in $\mathcal{H}_2 = \mathcal{H}_1^{(1)} \otimes \mathcal{H}_1^{(2)}$. (Sometimes one uses also the sign $\times$). An analogous relation is found for $B_1^{(2)}$:

$$B_1^{(2)} = \mathbb{1}_1^{(1)} \cdot \left[\sum\!\!\!\!\!\!\int_{m,\,q} |b_m^{(2)}\rangle\langle b_m^{(2)}|B_1^{(2)}|b_q^{(2)}\rangle\langle b_q^{(2)}|\right]\ . \tag{8.25}$$

As a rule, though, one refrains from explicitly writing down the identities $\mathbb{1}_1^{(1)}$ and $\mathbb{1}_1^{(2)}$, respectively.

If we now let the one-particle operator $A_1^{(1)}$ act on a basis product state,

$$\begin{aligned} A_1^{(1)}|a_n\,b_m\rangle &= |\tilde{a}_n\,b_m\rangle = |\tilde{a}_n^{(1)}\rangle|b_m^{(2)}\rangle\ , \\ |\tilde{a}_n^{(1)}\rangle &= \sum\!\!\!\!\!\!\int_{p} |a_p^{(1)}\rangle\langle a_p^{(1)}|A_1^{(1)}|a_n^{(1)}\rangle\ , \end{aligned} \tag{8.26}$$

then, according to (8.24), the state $|b_m^{(2)}\rangle$ obviously remains unaffected. Analogously, $B_1^{(2)}$ does not change the state $|a_n^{(1)}\rangle$:

$$\begin{aligned} B_1^{(2)}|a_n\,b_m\rangle &= |a_n\,\tilde{b}_m\rangle = |a_n^{(1)}\rangle|\tilde{b}_m^{(2)}\rangle\ , \\ |\tilde{b}_m^{(2)}\rangle &= \sum\!\!\!\!\!\!\int_{q} |b_q^{(2)}\rangle\langle b_q^{(2)}|B_1^{(2)}|b_m^{(2)}\rangle\ . \end{aligned} \tag{8.27}$$

This has an important consequence:

$$B_1^{(2)}\, A_1^{(1)}|a_n\, b_m\rangle = B^{(2)}|\tilde{a}_n\, b_m\rangle = |\tilde{a}_n\, \tilde{b}_m\rangle = A_1^{(1)}|a_n\, \tilde{b}_m\rangle = A_1^{(1)}\, B_1^{(2)}|a_n\, b_m\rangle \ .$$

Since $|a_n\, b_m\rangle$ is an **arbitrary** basis state, this relation leads to the operator identity:

$$\left[A_1^{(1)}, B_1^{(2)}\right]_- = 0 \ . \tag{8.28}$$

One-particle operators, which refer to different particles, commute in any case!

At the beginning of this section, we presumed that the two considered particles do not interact with each other. Therewith it was easier to justify our first steps into the field of many-particle systems. However, the effort would not have been necessary, if we had to restrict ourselves just to this special case. One can indeed realize that the considerations performed so far retain their validity even for interacting particles. At first we have to extend the Hamilton operator (8.1) by an interaction term:

$$H = H^{(1)} + H^{(2)} + H^{(1,2)} \ . \tag{8.29}$$

(In principle we should of course have written here $H_2 = H_1^{(1)} \cdot \mathbb{1}_1^{(2)} + \mathbb{1}_1^{(1)} \cdot H_1^{(2)} + H_2^{(1,2)}$!) The energy-eigen value is therewith no longer so simple as in (8.5), namely, surely not simply the sum of the two *free* one-particle energies. It is actually important, however, that the interaction, too, as an operator function, will depend only on the dynamical variables of the two particles, for instance

$$H_2^{(1,2)} = H_2^{(1,2)}\,(\mathbf{r}_1, \mathbf{r}_2) \ .$$

This is valid also for all the other observables of the two-particle system, which all have the structure of D_2 in (8.19). In this sense, all that has been stated up to now remains valid. The $\mathcal{H}_2$ is, even in the presence of interactions, the *suitable* Hilbert space. The time-independent Schrödinger equation,

$$H|\varphi_2(E)\rangle = E|\varphi_2(E)\rangle \ , \tag{8.30}$$

will in general, however, no longer be solved by pure product states as in (8.6). The eigen-states $|\varphi_2(E)\rangle$ will be expandable, though, according to (8.14) always in such product states, and are therefore elements of the $\mathcal{H}_2$. We had already mentioned that the interaction operators are responsible for the fact that the set of direct product states of the type (8.6), which represent a **real** subset of $\mathcal{H}_2$, is not sufficient for the description of general two-particle systems.

The dynamics of the composed system follows a formally unchanged, time-dependent Schrödinger equation:

$$i\,\hbar|\dot{\varphi}_2(E)\rangle = H|\varphi_2(E)\rangle \ . \tag{8.31}$$

The explicit calculation of the energy-eigen values and eigen-states as well as their time-dependences will, however, in almost all interesting and realistic cases, make it necessary to apply approximation methods (Chap. 7).

8.1.3 Systems of N Distinguishable Particles

There is a further step still to be done, namely, the generalization from the so far discussed two-particle system to such systems which consist of arbitrarily many $((N > 2))$ particles. The necessary extension of our hitherto theory, though, does not represent any real problem. The frame is built in line with (8.8) by the following product space:

$$\mathcal{H}_N = \mathcal{H}_1^{(1)} \otimes \mathcal{H}_1^{(2)} \otimes \ldots \otimes \mathcal{H}_1^{(N)} \; . \tag{8.32}$$

It contains all direct

N-particle product states

$$|\varphi_{\alpha_1}\, \varphi_{\alpha_2} \ldots \varphi_{\alpha_N}\rangle \equiv |\varphi_{\alpha_1}^{(1)}\rangle |\varphi_{\alpha_2}^{(2)}\rangle \ldots |\varphi_{\alpha_N}^{(N)}\rangle \; , \tag{8.33}$$

and all linear combinations of these states, where the product states are built up by the one-particle states of the spaces $\mathcal{H}_1^{(i)}$ $(i = 1, 2, \ldots, N)$. Their sequence in (8.33) is of course arbitrary. The usage of the same letter φ shall not at all imply that the one-particle bases are all the same. But just as before, we are considering distinguishable particles.

If the $\{|\varphi_{\alpha_i}^{(i)}\rangle\}$ are the common eigen-states of a complete set of commuting observables of the ith particle, they build an orthonormal basis of the $\mathcal{H}_1^{(i)}$. If this is true for all i, then the product states (8.33) can be taken as an orthonormal basis of the $\mathcal{H}_N$, in which any arbitrary N-particle state can be expanded:

$$|\psi_N\rangle = \sum\!\!\!\!\!\!\int_{\alpha_1 \ldots \alpha_N} \gamma_{\alpha_1 \ldots \alpha_N}(\psi) |\varphi_{\alpha_1} \ldots \varphi_{\alpha_N}\rangle \; . \tag{8.34}$$

The course of proof for orthonormality and completeness of the $|\varphi_{\alpha_1} \ldots \varphi_{\alpha_N}\rangle$ is carried out completely analogously to that in Sect. 8.1.1 for the two-particle system. So it follows, e.g., from the orthonormality, for the expansion coefficients in (8.34):

$$\gamma_{\alpha_1 \ldots \alpha_N}(\psi) = \langle \varphi_{\alpha_1}\, \varphi_{\alpha_2} \ldots \varphi_{\alpha_N} | \psi_N \rangle \; . \tag{8.35}$$

The scalar product is also a direct generalization of that in (8.11):

$$\begin{aligned} \langle \chi_N | \psi_N \rangle \;&=\; \sum\!\!\!\!\!\!\int_{\beta_1 \ldots \beta_N} \; \sum\!\!\!\!\!\!\int_{\alpha_1 \ldots \alpha_N} \gamma^*_{\beta_1 \ldots \beta_N}(\chi)\, \gamma_{\alpha_1 \ldots \alpha_N}(\psi) \\ &\qquad \cdot \langle \varphi_{\beta_1}^{(1)} | \varphi_{\alpha_1}^{(1)} \rangle \langle \varphi_{\beta_2}^{(2)} | \varphi_{\alpha_2}^{(2)} \rangle \ldots \langle \varphi_{\beta_N}^{(N)} | \varphi_{\alpha_N}^{(N)} \rangle \\ &=\; \sum\!\!\!\!\!\!\int_{\alpha_1 \ldots \alpha_N} \gamma^*_{\alpha_1 \ldots \alpha_N}(\chi)\, \gamma_{\alpha_1 \ldots \alpha_N}(\psi) \; . \end{aligned} \tag{8.36}$$

Especially the norm of a general N-particle state is given by

$$\| \psi_N \|^2 = \langle \psi_N | \psi_N \rangle = \sum\!\!\!\!\!\!\int_{\alpha_1 \ldots \alpha_N} |\gamma_{\alpha_1 \ldots \alpha_N}(\psi)\, .|^2 \tag{8.37}$$

In normal cases we normalize the states of the $\mathcal{H}_N$ to 1, so that their *statistical interpretation* can consistently be generalized from that of the one-particle states. As an example:

$$|\gamma_{\alpha_1 \ldots \alpha_N}(\psi)|^2 =$$

probability(density) to find by a measurement on the N-particle system in the state $|\psi_N\rangle$ *the eigen-value belonging to* $|\varphi_{\alpha_1} \ldots \varphi_{\alpha_N}\rangle$*, i.e., to find particle 1 in the state* $|\varphi_{\alpha_1}\rangle$*, particle 2 in the state* $|\varphi_{\alpha_2}\rangle, \ldots$.
From that we get for instance the special case:

$$\sum\!\!\!\!\!\!\int_{\alpha_2 \ldots \alpha_N} |\gamma_{\alpha_1 \ldots \alpha_N}(\psi)|^2 =$$

probability(density) to find particle 1 in the state $|\varphi_{\alpha_1}\rangle$*, when the N-particle system is in the state* $|\psi_N\rangle$.

Let us remark right at this stage that any question which singles out a particular particle, as for instance the above case where the probability for particle 1 is asked, of course makes sense only for distinguishable particles. For *identical particles*, which we will discuss in the next section, such a question is basically not answerable.

The observables of the $\mathcal{H}_N$ are operator functions of the observables $A_1^{(i)}$ of the one-particle spaces $\mathcal{H}_1^{(i)}$:

$$X_N = \mathcal{F}\big(A_1^{(1)},\, B_1^{(2)}, \ldots, K_1^{(N)}\big) \tag{8.38}$$

By the use of the basis (8.33) they possess the representation:

$$\begin{aligned} X_N \;=\; & \sum\!\!\!\!\!\!\int_{\alpha_1 \ldots \alpha_N} \; \sum\!\!\!\!\!\!\int_{\beta_1 \ldots \beta_N} |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle \\ & \cdot \langle \varphi_{\alpha_1} \cdots \varphi_{\alpha_N} | X_N | \varphi_{\beta_1} \cdots \varphi_{\beta_N} \rangle \langle \varphi_{\beta_1} \cdots \varphi_{\beta_N}| \end{aligned} \tag{8.39}$$

The operators, which are exclusively ascribed to a particular single particle, assume also here an exceptional position:

$$A_1^{(i)} = \left[\sum\!\!\!\!\!\!\int_{\alpha_i,\, \beta_i} |\varphi_{\alpha_i}^{(i)}\rangle \langle \varphi_{\alpha_i}^{(i)}| A_1^{(i)} |\varphi_{\beta_i}^{(i)}\rangle \langle \varphi_{\beta_i}^{(i)}| \right] \cdot \mathbb{1}_{N-1}^{(i)} \,. \tag{8.40}$$

$\mathbb{1}_{N-1}^{(i)}$ means here the identity of the $(N-1)$-particle product space, in which, compared to the $\mathcal{H}_N$, the $\mathcal{H}_1^{(i)}$ *is absent*. In the same way as shown in (8.28) for the special case $N = 2$, one can prove generally that one-particle operators, which refer to different particles, do commute in any case:

$$\Big[A_1^{(i)},\, B_1^{(j)}\Big]_- = 0 \,. \tag{8.41}$$

The dynamics of the N-particle systems follows from the **time-dependent Schrödinger equation**,

$$i\,\hbar|\dot{\psi}_N\rangle = H_N|\psi_N\rangle\ , \tag{8.42}$$

in which H_N means the Hamilton operator related to the N-particle system.

In summary we realize that the treatment of many-particle systems, in the case of particle-distinguishability, do not require novel concepts with regard to the *Quantum Theory of the single particle*, which we developed in the preceding chapters. Only the computational and procedural effort increases tremendously. In Classical Mechanics also the transition from the one- to the many-particle problem is not in any way different. In the case of indistinguishable particles, however, completely new and classically not understandable aspects will play a decisive role!

8.1.4 Exercises

Exercise 8.1.1
Show that by the description (8.11) for two-particle states of the $\mathcal{H}_2$ the general axioms of a scalar product are fulfilled.

Exercise 8.1.2
Let the two Hilbert spaces $\mathcal{H}_1^{(1)}$ and $\mathcal{H}_1^{(2)}$ be two-dimensional (e.g., spin-(1/2)-particles!). By the use of the bases $\{|a_n^{(1)}\rangle\}$ and $\{|b_m^{(2)}\rangle\}$ the observables $A_1^{(1)}$ and $B_1^{(2)}$ possess the matrix representation $\left(A_1^{(1)}\right)_{ij} = \alpha_{ij}$ and $\left(B_1^{(2)}\right)_{ij} = \beta_{ij}$, respectively.

1. Find the matrix representation of $A_1^{(1)}$ in the product basis $\{|a_n\, b_m\rangle\}$ of the space $\mathcal{H}_2 = \mathcal{H}_1^{(1)} \otimes \mathcal{H}_1^{(2)}$.

2. How does the matrix representation of $B_1^{(2)}$ look like in $\mathcal{H}_2$?

3. Derive explicitly the product matrix $A_1^{(1)} \cdot B_1^{(2)}$ and verify the commutativity of the two operators!

8.2 Identical Particles

At first glance, it appears as if the theory of Sect. 8.1 is really complete for arbitrary many-particle systems. Upon closer inspection, however, there are distinct hints even in our *physical everyday world* that there is something which does not yet really fit the above considerations. There are phenomena to observe, which obviously go beyond the limits of the so far developed Quantum Theory. For the heuristic reasoning of the structure of the atomic electron shell, and, following from that, the buildup-principle of the periodic table in the framework of the semi-classical *pre-Quantum Mechanics* (Bohr, Sommerfeld, ..., see Chap. 1

(Vol. 6)), we had to assume, e.g., that the stationary energy levels of an atom can not be occupied by arbitrarily many shell electrons. Today we know that this phenomenon is a consequence of the fundamental **Pauli principle**, according to which two electrons can never simultaneously occupy one and the same state. Therewith, the Pauli principle makes even interaction-free electrons not completely independent of each other. In our quantum-mechanical considerations so far there was no indication leading to the discovery the Pauli principle. We will be able to show in this chapter that this principle is an immediate consequence of the **categorical indistinguishability of identical particles**!

8.2.1 Principle of Indistinguishability

What are actually *identical particles*? In order to prevent misunderstandings let us at first strictly distinguish the genuine **particle properties** from the **measured values of the particle observables**. A *particle property* (e.g., mass, spin, charge, magnetic moment, moment of inertia) is an in principle unchangeable characteristic of the particle. As soon as such a quantity is nevertheless changed by some *drastic course of action*, then the particle looses in a certain sense its identity. The *measured values of the particle observables* (e.g., position, momentum, angular momentum, spin projection), on the other hand, can change in the course of time.

Definition 8.2.1

'Identical particles' have all their particle properties identically same!

They behave themselves under similar conditions completely equivalently, and can therefore not be distinguished from each other by any objective measurement. The measured values of the particle observables in a system of identical particles can of course be different. The *identical* electrons in an energy band of a solid have, for instance, different energies and different momenta. However, **every** electron comes into question for **each** energy state. It is impossible to find out which of the identical particles occupies which state.

Identical particles of course exist also in Classical Physics. However, one can perform at a point of time t_0 a position and momentum measurement for them, and from that one can calculate in advance by means of the Hamilton equations of motion (Sect. 2.2.1, Vol. 2) their phase-space point $(\mathbf{r}, \mathbf{p})(t)$ for every later time (Fig. 8.1). The $(\mathbf{r}, \mathbf{p})$-measurement at a single point of time t_0

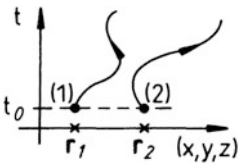

Figure 8.1: Paths of motion of classical (identical) particles

makes it possible to identify out of an ensemble of classical identical particles each individual uniquely at every later point of time. By the measurement one has attached, in a certain sense, *labels* to the particles, which make them for all times recognizable in spite of identical properties.

Just this *labeling* is basically impossible for quantum-mechanical identical particles. The deep reason for this lies in the statistical character of the particle state, which we have discussed extensively in Chaps. 2 and 3 of Vol. 6. We remember that for a measurement of the observable A it can, in general, not be precisely predicted, which measured value will actually be observed. It is only ensured that it will be one of the eigen-values of A. Apart from that, only the probability can be found, with which a certain eigen-value will really appear as the measured value. Think of the above discussed measurement of the position of a classical particle, which observes that at the time t_0 particle 1 is at $\mathbf{r}_1$ and particle 2 at $\mathbf{r}_2$. When now at a later point of time a measurement at $\mathbf{r}$ receives a signal, then, quantum-mechanically, we can not say with full certainty, whether the signal comes from particle 1 or particle 2. The density of the position probability of both the particles $\rho_{1,2}(\mathbf{r},t) = |\psi_{1,2}(\mathbf{r},t)|^2$, if at all reasonably definable, is for **both** particles unequal zero at $\mathbf{r}$. Furthermore, since the particles are identical, the unchangeable particle properties can contribute in no way to distinguish them.

Although these considerations do not prove the

principle of indistinguishability ,

they make it at least plausible. It must be incorporated into the framework of Quantum Mechanics as a further postulate:

Identical particles are basically indistinguishable. Therefore they do not possess any individuality!

This postulate leads to a series of far-reaching consequences, which we will analyze point by point.

As a start, assignments of the kind

$$(\text{particle})_i \iff \text{state } |\varphi^{(i)}\rangle$$

become meaningless and have to be replaced by the *more sweeping* assignment

$$\{(\text{particle})_i\,; \quad i = 1, 2, \ldots, N\} \iff N\text{-particle state } |\varphi_N\rangle\,.$$

Each question, which aims at the observation of a single particle, is for systems of identical particles not only forbidden but also completely meaningless.

Up to now we do not know the states which are acceptable for N identical particles. We can, however, assume that they must be special combinations of the direct products of one-particle states discussed in Sect. 8.1. Let us use for them in the following tentatively the symbol:

$$|\varphi_N\rangle \equiv \left|\varphi^{(1)}_{\alpha_1}\,\varphi^{(2)}_{\alpha_2}\cdots\varphi^{(N)}_{\alpha_N}\right\rangle\,. \tag{8.43}$$

In a manner, which we still have to work out, the one-particle states $|\varphi_{\alpha_1}\rangle, |\varphi_{\alpha_2}\rangle, \ldots, |\varphi_{\alpha_N}\rangle$ are involved in the N-particle state $|\varphi_N\rangle$. The lower indexes in the symbol (8.43) refer, in this regard, to (sets of) quantum numbers, by which these one-particle states are uniquely characterized, and the upper indexes refer to the particles which are somehow distributed over the one-particle states.

Let us try to concretize the above train of thoughts, i.e., to bring it into a mathematically evaluable form! As we now know, such observables are not admitted in a system of N identical particles, which are focused on a certain individual. For distinguishable particles, in contrast, that is surely possible (see 8.40). Expressions of the form

$$\langle\varphi_N|A_1^{(i)}|\varphi_N\rangle$$

are acceptable only for distinguishable particles. If they could provide relevant statements also for identical particles, then we would have a means to single out the particle i amongst the other particles by measuring the observable $A_1^{(i)}$, and therewith to label it.

Reasonable measured quantities, as for instance expectation values of observables, are surely to be related only to the total *collective*. Therefore, as *acceptable* observables only such come into question which explicitly depend on the coordinates of **all** the particles, and that too in an equally weighted *symmetric* manner:

$$\left\langle \varphi_{\alpha_1}^{(1)} \cdots \varphi_{\alpha_N}^{(N)} \right| A_N(1,2,\ldots,N) \left| \varphi_{\alpha_1}^{(1)} \cdots \varphi_{\alpha_N}^{(N)} \right\rangle \ .$$

This representation, however, already reveals the actual problem. Because of purely calculatory reasons we are forced to perform something like a *particle numbering*, for instance for the discrimination of variables in multiple integrals and sums, or for the correct assignment of the one-particle states, which build up the states $|\varphi_N\rangle$, to *their* Hilbert spaces $\mathcal{H}_1^{(i)}$. If such a numbering is indeed from practical reasons unavoidable, then it must be done, in order not to violate the principle of indistinguishability, in such a way that **physically relevant statements** remain unaffected by the kind of numbering, i.e. in particular, being invariant with respect to changes in the performed numbering. All that, which is in some way accessible to the experiment (expectation values, eigenvalues, scalar products, matrix elements, ...) is *physically relevant*. The *bare* operators and states, by the way, do not belong to this. For the expectation value of an *allowed* observable in an *allowed* state of a system of N identical particles, we have therefore to require, for instance:

$$\begin{aligned} &\left\langle \cdots \varphi_{\alpha_i}^{(i)} \cdots \varphi_{\alpha_j}^{(j)} \cdots \right| A_N \left| \cdots \varphi_{\alpha_i}^{(i)} \cdots \varphi_{\alpha_j}^{(j)} \cdots \right\rangle \\ &\quad \stackrel{!}{=} \left\langle \cdots \varphi_{\alpha_i}^{(j)} \cdots \varphi_{\alpha_j}^{(i)} \cdots \right| A_N \left| \cdots \varphi_{\alpha_i}^{(j)} \cdots \varphi_{\alpha_j}^{(i)} \cdots \right\rangle \ . \end{aligned} \tag{8.44}$$

The interchange of the particle indexes at the state symbols should not change the actual measured value! We will be able to derive in the next subsection some important conclusions from this symmetry requirement alone.

8.2.2 Observables and States

We will now take advantage of the condition (8.44), in order to obtain concrete information about the *allowed* observables and states of a system of identical particles.

We define at first the **permutation operator** $\mathcal{P}$ by its mode of action on the N-particle state (8.43):

$$\mathcal{P}\left|\varphi_{\alpha_1}^{(1)}\,\varphi_{\alpha_2}^{(2)}\cdots\varphi_{\alpha_N}^{(N)}\right\rangle = \left|\varphi_{\alpha_1}^{(i_1)}\,\varphi_{\alpha_2}^{(i_2)}\cdots\varphi_{\alpha_N}^{(i_N)}\right\rangle \,. \tag{8.45}$$

$\mathcal{P}$ acts on the particle indexes, and changes the distribution of the particles over the N one-particle states. $(i_1, i_2, \ldots, i_N)$ is the permuted N-tuple $(1, 2, \ldots, N)$. The particle, which is placed *before* at the jth site changes into the i_jth position. Each permutation can be traced back to a product of pairwise interchanges of two particles. We therefore define the **transposition operator** P_{ij},

$$P_{ij}\left|\cdots\varphi_{\alpha_i}^{(i)}\cdots\varphi_{\alpha_j}^{(j)}\cdots\right\rangle = \left|\cdots\varphi_{\alpha_i}^{(j)}\cdots\varphi_{\alpha_j}^{(i)}\cdots\right\rangle \,, \tag{8.46}$$

which interchanges the particles at the ith and the jth positions. P_{ij} is of course a special permutation. We look at a simple example:

$$\begin{aligned} P_{23}\,P_{12}\left|\varphi_{\alpha_1}^{(1)}\,\varphi_{\alpha_2}^{(2)}\,\varphi_{\alpha_3}^{(3)}\right\rangle &= P_{23}\left|\varphi_{\alpha_1}^{(2)}\,\varphi_{\alpha_2}^{(1)}\,\varphi_{\alpha_3}^{(3)}\right\rangle = \left|\varphi_{\alpha_1}^{(2)}\,\varphi_{\alpha_2}^{(3)}\,\varphi_{\alpha_3}^{(1)}\right\rangle \,, \\ P_{12}\,P_{23}\left|\varphi_{\alpha_1}^{(1)}\,\varphi_{\alpha_2}^{(2)}\,\varphi_{\alpha_3}^{(3)}\right\rangle &= P_{12}\left|\varphi_{\alpha_1}^{(1)}\,\varphi_{\alpha_2}^{(3)}\,\varphi_{\alpha_3}^{(2)}\right\rangle = \left|\varphi_{\alpha_1}^{(3)}\,\varphi_{\alpha_2}^{(1)}\,\varphi_{\alpha_3}^{(2)}\right\rangle \,. \end{aligned}$$

The example gives evidence that in general the transposition operators are not commutable. Twofold application of the same transition operator obviously leads back to the initial state:

$$P_{ij}^2 = \mathbb{1}_N \iff P_{ij} = P_{ij}^{-1} \,. \tag{8.47}$$

The mappings (8.45) and (8.46) must not change, because of the indistinguishability of the particles, in particular the norm of the state. $\mathcal{P}$ and P_{ij} are therefore unitary in $\mathcal{H}_N$, P_{ij} in addition, because of (8.47) is also Hermitian:

$$\mathcal{P}^+ = \mathcal{P}^{-1}\,; \quad P_{ij}^+ = P_{ij}^{-1} = P_{ij} \,. \tag{8.48}$$

Because of the non-commutability of the transpositions the general permutation operator is not Hermitian in $\mathcal{H}_N$.

We can now bring the basic requirement (8.44) into the following form:

$$\langle\varphi_N|A_N|\varphi_N\rangle \stackrel{!}{=} \langle P_{ij}\,\varphi_N|A_N|P_{ij}\,\varphi_N\rangle = \langle\varphi_N|P_{ij}^+\,A_N\,P_{ij}|\varphi_N\rangle \,.$$

This relation must be valid for **all** states of the system of identical particles. If it is fulfilled then the analogous relation holds even for arbitrary matrix elements,

$$\langle\varphi_N|A_N|\psi_N\rangle \stackrel{!}{=} \langle\varphi_N|P_{ij}^+\,A_N\,P_{ij}|\psi_N\rangle \,, \tag{8.49}$$

because these can always be decomposed into expectation values of the above form:

$$\langle\varphi_N|A_N|\psi_N\rangle = \frac{1}{4}\{\langle\varphi_N+\psi_N|A_N|\varphi_N+\psi_N\rangle - \langle\varphi_N-\psi_N|A_N|\varphi_N-\psi_N\rangle \\ +i\langle\varphi_N-i\,\psi_N|A_N|\varphi_N-i\,\psi_N\rangle - i\langle\varphi_N+i\,\psi_N|A_N|\varphi_N+i\,\psi_N\rangle\}$$

In the state space for identical particles, which is so far, though, still unknown to us, it must therefore hold the operator identity

$$A_N = P_{ij}^{+}\, A_N\, P_{ij}\ . \tag{8.50}$$

Multiplying this identity *from the left* by P_{ij} and taking account of (8.48), we recognize that all *allowed* observables of the N-particle system must be commutable with all transposition operators and consequently also with all permutation operators:

$$[A_N, P_{ij}]_- = 0 \quad \forall i,j\ ; \quad [A_N, \mathcal{P}]_- = 0\ . \tag{8.51}$$

Therewith we have got to know a very important characteristic of the observables of identical particles.

What can now be said about the states which are *allowed* in the sense of the principle of indistinguishability? Let $|\varphi_N\rangle$ be such a state, then the projection operator $|\varphi_N\rangle\langle\varphi_N|$ represents an observable, for which (8.50) is valid:

$$|\varphi_N\rangle\langle\varphi_N| = P_{ij}^{+}|\varphi_N\rangle\langle\varphi_N|P_{ij} = |P_{ij}^{+}\,\varphi_N\rangle\langle P_{ij}^{+}\,\varphi_N| = |P_{ij}\,\varphi_N\rangle\langle P_{ij}\,\varphi_N|\ .$$

The state $|P_{ij}\,\varphi_N\rangle$ creates therewith the same subspace as $|\varphi_N\rangle$. This, however, is possible only if the two Hilbert-space vectors are *parallel*, i.e., if $|\varphi_N\rangle$ is an eigen-state of P_{ij}:

$$P_{ij}|\varphi_N\rangle = \lambda_{ij}|\varphi_N\rangle\ .$$

Because of (8.47) for all i and j only $\lambda_{ij} = \pm 1$ can come into consideration. This means:

$$P_{ij}\left|\varphi_N^{(\pm)}\right\rangle = \pm\left|\varphi_N^{(\pm)}\right\rangle \quad \forall i,\, j\ . \tag{8.52}$$

The states of a system of identical particles are either symmetric or antisymmetric with respect to an interchange of two particle indexes!

All these states are of course, additionally, elements of the product space $\mathcal{H}_N$ (8.32), which we have constructed in Sect. 8.1 for systems of distinguishable particles. For systems of identical particles this space turns out to be too large, because not all elements of $\mathcal{H}_N$ comply with the symmetry requirements (8.52) due to the *principle of indistinguishability*. We will have to still discuss the corresponding subspaces.

We want to list some further basic properties of the states of identical particles:

1. A first important conclusion results from the fact that Eq. (8.51) is true in particular for the Hamilton operator of the system:

$$[H_N, P_{ij}]_- = 0 \; .$$

Since the time evolution operator U ((3.177), Vol. 6) reads for not explicitly time-dependent H_N

$$U(t, t_0) = \exp\left[-\frac{i}{\hbar} H_N (t - t_0)\right] \; ,$$

U also commutes with P_{ij}:

$$[U, P_{ij}]_- = 0 \; . \tag{8.53}$$

This statement, by the way, remains valid even for time-dependent H_N (proof as Exercise 8.2.1)! When the state $|\varphi_N\rangle$ has at any point of time t_0 a particular symmetry,

$$P_{ij}|\varphi_N(t_0)\rangle = \pm|\varphi_N(t_0)\rangle \; ,$$

it will exhibit this symmetry for all other times also:

$$\begin{aligned} P_{ij}|\varphi_N(t)\rangle &= P_{ij}\, U(t, t_0)|\varphi_N(t_0)\rangle \overset{(8.53)}{=} U(t, t_0)\, P_{ij}|\varphi_N(t_0)\rangle \\ &= \pm U(t, t_0)|\varphi_N(t_0)\rangle = \pm|\varphi_N(t)\rangle \; . \end{aligned}$$

The states of a system of identical particles thus retain their symmetry character for all times!

2. Symmetric and antisymmetric states are orthogonal to each other:

$$\begin{aligned} \left\langle \varphi_N^{(+)} \middle| \psi_N^{(-)} \right\rangle &= \left\langle \varphi_N^{(+)} \middle| \mathbb{1}_N \middle| \psi_N^{(-)} \right\rangle = \left\langle \varphi_N^{(+)} \middle| P_{ij}^+ P_{ij} \middle| \psi_N^{(-)} \right\rangle \\ &= -\left\langle \varphi_N^{(+)} \middle| \psi_N^{(-)} \right\rangle = 0 \; . \end{aligned} \tag{8.54}$$

3. There does not exist an observable, which can map a symmetric onto an antisymmetric state, and vice versa:

$$\langle \varphi_N^{(+)}|A_N|\psi_N^{(-)}\rangle = 0 \quad \forall A_N \tag{8.55}$$

(see Exercise 8.2.2).

4. The states of a certain system of identical particles belong either all to the $\mathcal{H}_N^{(+)}$ or all to the $\mathcal{H}_N^{(-)}$. If one and the same system could be in states with different symmetry behavior, then a linear combination of these states, which must also be a possible state, would be neither symmetric nor antisymmetric.

8.2.3 Hilbert Space

The time-independent symmetry character and the orthogonality of the symmetric and the antisymmetric states of identical particles make the following division appear reasonable:
$\mathcal{H}_N^{(+)}$: Space of the symmetric states $|\varphi_N^{(+)}\rangle \in \mathcal{H}_N$ with

$$P_{ij} \left|\varphi_N^{(+)}\right\rangle = \left|\varphi_N^{(+)}\right\rangle \quad \forall i,j \; .$$

$\mathcal{H}_N^{(-)}$: Space of the antisymmetric states $|\varphi_N^{(-)}\rangle \in \mathcal{H}_N$ with

$$P_{ij} \left|\varphi_N^{(-)}\right\rangle = - \left|\varphi_N^{(-)}\right\rangle \quad \forall i,j \; .$$

The spaces $\mathcal{H}_N^{(\pm)}$ are subspaces of the product space $\mathcal{H}_N$, defined in (8.32). They contain from the elements of $\mathcal{H}_N$ just those with the proper symmetry behavior.

But how can we now find these, respectively, *totally symmetric* and *totally antisymmetric* N-particle states? Equation (8.43) is up to now only an abstract, and not further specified symbol.

Since the sought-after (anti)symmetric states must in any case be elements of the $\mathcal{H}_N$, it suggests itself to start from one of the basis states of the product space:

$$|\varphi_{\alpha_1}\, \varphi_{\alpha_2} \cdots \varphi_{\alpha_N}\rangle = \left|\varphi_{\alpha_1}^{(1)}\right\rangle \left|\varphi_{\alpha_2}^{(2)}\right\rangle \cdots \left|\varphi_{\alpha_N}^{(N)}\right\rangle \; .$$

If we succeed to (anti)symmetrize this state by a proper operation, then it will not be difficult to transfer this method to any arbitrary element of the $\mathcal{H}_N$.

We introduce a new operator,

$$S_N^{(\pm)} = \frac{1}{N!} \sum_{\mathcal{P}} (\pm)^p \, \mathcal{P} \; , \tag{8.56}$$

which we call the **symmetrization operator** and the **antisymmetrization operator**, respectively. The sum runs over all conceivable permutations of the N-tuple $(1, 2, \ldots, N)$, including the identity. p is the number of transpositions, by which $\mathcal{P}$ is built up. Let us consider whether indeed with $S_N^{(\pm)}$ the required (anti)symmetrizations of the basis states can be done, and therewith ultimately those of all states of the $\mathcal{H}_N$.

If one multiplies any $\mathcal{P}$ of the sum (8.56) by any transposition P_{ij}, then it results obviously in another permutation $\mathcal{P}'$ with a by one different number of transpositions $p' = p \pm 1$. Since the sum in (8.56) contains all permutations, $\mathcal{P}'$ also appears as one of the summands:

$$\begin{aligned} P_{ij}\, S_N^{(\pm)} &= \frac{1}{N!} \sum_{\mathcal{P}} (\pm)^p \, P_{ij}\, \mathcal{P} = (\pm)\, \frac{1}{N!} \sum_{\mathcal{P}'} (\pm)^{p'} \, \mathcal{P}' \\ &= \pm S_N^{(\pm)} \; \left(= S_N^{(\pm)}\, P_{ij}\right) \; . \end{aligned} \tag{8.57}$$

This result transfers immediately to general permutations:

$$\mathcal{P}\, S_N^{(\pm)} = S_N^{(\pm)}\, \mathcal{P} = (\pm)^p\, S_N^{(\pm)} \ . \tag{8.58}$$

When we thus apply $S_N^{(\pm)}$ to a non-symmetrized product state of the $\mathcal{H}_N$, then we can be sure that the resulting state is an element of the $\mathcal{H}_N^{(\pm)}$:

$$\begin{aligned} |\varphi_N^{(\pm)}\rangle &\equiv |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(\pm)} = S_N^{(\pm)} |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle \\ &= \frac{1}{N!} \sum_{\mathcal{P}} (\pm)^p\, \mathcal{P} |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle \ . \end{aligned} \tag{8.59}$$

One should strictly bear in mind the different meanings of $|\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle$ and $|\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(\pm)}$! Because of (8.57) and (8.58) we have in every case for the so constructed states:

$$P_{ij} \left|\varphi_N^{(\pm)}\right\rangle = \pm \left|\varphi_N^{(\pm)}\right\rangle \ ; \quad \mathcal{P} \left|\varphi_N^{(\pm)}\right\rangle = (\pm)^p \left|\varphi_N^{(\pm)}\right\rangle \ . \tag{8.60}$$

This means in particular:

$$S_N^{(\pm)} \left|\varphi_N^{(\pm)}\right\rangle = \frac{1}{N!} \sum_{\mathcal{P}} (\pm)^p\, \mathcal{P} \left|\varphi_N^{(\pm)}\right\rangle = \left|\varphi_N^{(\pm)}\right\rangle \ . \tag{8.61}$$

The (anti)symmetrized states $|\varphi_N^{(\pm)}\rangle$ are of course again elements of the $\mathcal{H}_N$. By application of $S_N^{(\pm)}$ to **every single** state in $\mathcal{H}_N$ we obtain **all** (anti)symmetrized states of the $\mathcal{H}_N$. The already symmetric or antisymmetric elements of the product space will be mapped on themselves according to (8.61). $S_N^{(\pm)}$ acts in $\mathcal{H}_N$ as an **projection operator**:

$$S_N^{(\pm)} : \ \mathcal{H}_N \ \longrightarrow \ \mathcal{H}_N^{(\pm)} \ .$$

Its idempotency is easily demonstrated:

$$\begin{aligned} \left[S_N^{(\pm)}\right]^2 |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle &= S_N^{(\pm)} |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(\pm)} = |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(\pm)} \\ &= S_N^{(\pm)} |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle \ . \end{aligned}$$

This is true for arbitrary states $|\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle$ of the $\mathcal{H}_N$. It is hence:

$$\left[S_N^{(\pm)}\right]^2 = S_N^{(\pm)} \ . \tag{8.62}$$

According to (8.48) $\mathcal{P}^+ = \mathcal{P}^{-1}$. Since $\mathcal{P}$ represents a product of transpositions, $\mathcal{P}^{-1}$ is, because of (8.47), just that permutation, in which the transpositions appear in the opposite sequence. Particularly, the number of transpositions is the same for $\mathcal{P}$ and $\mathcal{P}^{-1}$. In expressions like (8.56) the summation can of course be performed, instead over all $\mathcal{P}$, also over all $\mathcal{P}^{-1}$. This means:

$$\begin{aligned} \left(S_N^{(\pm)}\right)^+ &= \frac{1}{N!} \sum_{\mathcal{P}} (\pm)^p\, \mathcal{P}^+ = \frac{1}{N!} \sum_{\mathcal{P}^{-1}} (\pm)^p\, \mathcal{P}^{-1} \\ &= \frac{1}{N!} \sum_{\mathcal{P}'} (\pm)^{p'}\, \mathcal{P}' = S_N^{(\pm)} \ . \end{aligned} \tag{8.63}$$

$S_N^{(+)}$ and $S_N^{(-)}$ are therefore idempotent and Hermitian, and possess therewith the properties of projection operators (Sect. 3.2.7, Vol. 6). It holds for arbitrary states $|\varphi_N\rangle$, $|\psi_N\rangle$ of the $\mathcal{H}_N$:

$$\langle\psi_N|\, S_N^{(+)}\, S_N^{(-)}\, |\varphi_N\rangle = \left\langle \psi_N^{(+)} \middle|\, \varphi_N^{(-)} \right\rangle \overset{(8.54)}{=} 0\,.$$

$S_N^{(+)}$ and $S_N^{(-)}$ thus project onto orthogonal subspaces of the $\mathcal{H}_N$:

$$S_N^{(+)}\, S_N^{(-)} = S_N^{(-)}\, S_N^{(+)} = 0\,. \tag{8.64}$$

Already for $N > 2$ the sum of $S_N^{(+)}$ and $S_N^{(-)}$ is no longer the identity $\mathbb{1}_N$. The subspaces, created by $S_N^{(+)}$ and $S_N^{(-)}$, therefore do not cover the whole $\mathcal{H}_N$. If one defines the operator $S_N^{(0)}$ by

$$S_N^{(+)} + S_N^{(-)} + S_N^{(0)} = \mathbb{1}_N\,, \tag{8.65}$$

then it can be shown that it is also a projection operator. It projects onto a subspace $\mathcal{H}_N^{(0)}$, which is orthogonal to the spaces, which are created by $S_N^{(+)}$ and $S_N^{(-)}$. The three spaces $\mathcal{H}_N^{(+)}$, $\mathcal{H}_N^{(-)}$, $\mathcal{H}_N^{(0)}$ together build, because of (8.65), the entire product space $\mathcal{H}_N$. The Hermiticity of $S_N^{(0)}$ is, because of (8.63), immediately clear. From

$$S_N^{(0)}\, S_N^{(\pm)} = \left(\mathbb{1}_N - S_N^{(+)} - S_N^{(-)}\right) S_N^{(\pm)} \overset{(8.64)}{=} S_N^{(\pm)} - \left[S_N^{(\pm)}\right]^2 \overset{(8.62)}{=} 0 \tag{8.66}$$

it follows the orthogonality of $\mathcal{H}_N^{(0)}$ to the two other spaces, and from

$$\left[S_N^{(0)}\right]^2 = S_N^{(0)} \left(\mathbb{1}_N - S_N^{(+)} - S_N^{(-)}\right) = S_N^{(0)} \tag{8.67}$$

the idempotency of the operator $S_N^{(0)}$.

8.2.4 Basis States

We have now to find out which basis can come into consideration for the (anti)symmetrized spaces $\mathcal{H}_N^{(\pm)}$. In the product space $\mathcal{H}_N$, suitable for a system of N distinguishable particles, the N-particle basis states can be written as direct products (8.33) of one-particle basis states. If we gather together by $\widehat{\varphi}$ a complete set of commutable one-particle observables, then the eigen-states $\{|\varphi_{\alpha_i}\rangle\}$ build an orthonormal basis of the one-particle Hilbert space:

$$\widehat{\varphi}|\varphi_{\alpha_i}\rangle = \varphi_{\alpha_i}|\varphi_{\alpha_i}\rangle\,, \tag{8.68}$$

$$\langle\varphi_{\alpha_i}|\varphi_{\alpha_j}\rangle = \delta(\alpha_i, \alpha_j)\,, \tag{8.69}$$

$$\sum\!\!\!\!\!\!\int_{\alpha_i} |\varphi_{\alpha_i}\rangle\langle\varphi_{\alpha_i}| = \mathbb{1}_1 \tag{8.70}$$

The product states (8.33), built by these one-particle basis states, represent then a basis for the N-particle space $\mathcal{H}_N$, so that each state of $\mathcal{H}_N$ can be expanded as follows:

$$|\psi_N\rangle = \sum\!\!\!\!\!\!\int_{\alpha_1 \cdots \alpha_N} |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle\langle\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}|\psi_N\rangle \; . \tag{8.71}$$

Since the (anti)symmetrized states of the subspaces $\mathcal{H}_N^{(\pm)}$ belong to the elements of $\mathcal{H}_N$, they can of course also be expanded as in (8.71):

$$|\psi_N^{(\pm)}\rangle = \sum\!\!\!\!\!\!\int_{\alpha_1 \cdots \alpha_N} |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle\langle\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}|\psi_N^{(\pm)}\rangle \; . \tag{8.72}$$

The scalar product in the integrand is rearranged as follows:

$$\begin{aligned} \langle\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}|\psi_N^{(\pm)}\rangle &\overset{(8.61)}{=} \langle\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}|S_N^{(\pm)}|\psi_N^{(\pm)}\rangle \\ &\overset{(8.63)}{=} {}^{(\pm)}\langle\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}|\psi_N^{(\pm)}\rangle \; . \end{aligned} \tag{8.73}$$

When we insert this into the above equation (8.72) and apply once more to both sides the operator $S_N^{(\pm)}$, then we have, because of (8.59) and (8.61),:

$$|\psi_N^{(\pm)}\rangle = \sum\!\!\!\!\!\!\int_{\alpha_1 \cdots \alpha_N} |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(\pm)\,(\pm)}\langle\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}|\psi_N^{(\pm)}\rangle \; . \tag{8.74}$$

This relation is valid for arbitrary states from $\mathcal{H}_N^{(\pm)}$. The (anti)symmetrized product states,

$$\begin{aligned} |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(\pm)} &= \frac{1}{N!}\sum_{\mathcal{P}} (\pm)^p \, \mathcal{P}|\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle \\ &= \frac{1}{N!}\sum_{\mathcal{P}} (\pm)^p \, \mathcal{P}\left(\left|\varphi_{\alpha_1}^{(1)}\right\rangle \cdots \left|\varphi_{\alpha_N}^{(N)}\right\rangle\right) \; , \end{aligned} \tag{8.75}$$

thus build a basis of the $\mathcal{H}_N^{(\pm)}$, and comply thereby with the **completeness relation**:

$$\sum\!\!\!\!\!\!\int_{\alpha_1 \cdots \alpha_N} |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(\pm)\,(\pm)}\langle\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}| = \mathbb{1}_N \; . \tag{8.76}$$

An interesting specialty arises for the basis states of the antisymmetrized space $\mathcal{H}_N^{(-)}$, which obviously can be written as determinant:

$$|\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(-)} = \frac{1}{N!}\begin{vmatrix} |\varphi_{\alpha_1}^{(1)}\rangle & |\varphi_{\alpha_1}^{(2)}\rangle & \cdots & |\varphi_{\alpha_1}^{(N)}\rangle \\ |\varphi_{\alpha_2}^{(1)}\rangle & |\varphi_{\alpha_2}^{(2)}\rangle & \cdots & |\varphi_{\alpha_2}^{(N)}\rangle \\ \vdots & \vdots & & \vdots \\ |\varphi_{\alpha_N}^{(1)}\rangle & |\varphi_{\alpha_N}^{(2)}\rangle & \cdots & |\varphi_{\alpha_N}^{(N)}\rangle \end{vmatrix} \; . \tag{8.77}$$

This expression is denoted as **Slater determinant**. If in the N-particle state two sets of quantum numbers are equal ($\alpha_i = \alpha_j$ for $i \neq j$), then this means that two rows of the determinant are equal, and that means that the determinant vanishes. The (density of the) probability for the situation that in an N-particle state of the $\mathcal{H}_N^{(-)}$ two of the identical particles have all their quantum numbers same is thus equal to zero. This is just the statement of the fundamental **Pauli principle**, to which we will come back once more in Sect. 8.2.6. An analogous restriction for the states of the $\mathcal{H}_N^{(+)}$, according to (8.75), obviously does not exist!

In order to be able to really work in the space $\mathcal{H}_N^{(\pm)}$, we have to still think about the scalar product between (anti)symmetrized basis states. With (8.73) we can directly write this down:

$$\begin{aligned}
&{}^{(\pm)}\langle\varphi_{\beta_1}\cdots\varphi_{\beta_N}|\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}\rangle^{(\pm)} = \langle\varphi_{\beta_1}\cdots\varphi_{\beta_N}|\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}\rangle^{(\pm)} \\
= \;& \frac{1}{N!}\sum_{\mathcal{P}}(\pm)^p\left[\left\langle\varphi_{\beta_1}^{(1)}\right|\left\langle\varphi_{\beta_2}^{(2)}\right|\cdots\left\langle\varphi_{\beta_N}^{(N)}\right|\mathcal{P}\left(\left|\varphi_{\alpha_1}^{(1)}\right\rangle\left|\varphi_{\alpha_2}^{(2)}\right\rangle\cdots\left|\varphi_{\alpha_N}^{(N)}\right\rangle\right)\right] \\
= \;& \frac{1}{N!}\sum_{\mathcal{P}_\alpha}(\pm)^{p_\alpha}\,\mathcal{P}_\alpha\left[\left\langle\varphi_{\beta_1}^{(1)}\right|\left|\varphi_{\alpha_1}^{(1)}\right\rangle\cdots\left\langle\varphi_{\beta_N}^{(N)}\right|\left|\varphi_{\alpha_N}^{(N)}\right\rangle\right] \\
\overset{(8.69)}{=} \;& \frac{1}{N!}\sum_{\mathcal{P}_\alpha}(\pm)^{p_\alpha}\,\mathcal{P}_\alpha\left[\delta(\beta_1,\alpha_1)\cdots\delta(\beta_N,\alpha_N)\right]\,. \qquad (8.78)
\end{aligned}$$

That is the consistent generalization of the one-particle scalar product (8.69) for the (anti)symmetrized N-particle states. The index α at the $\mathcal{P}$-symbol shall indicate that after forming the scalar products in the respective one-particle spaces $\mathcal{H}_1^{(i)}$ the permutation aims exclusively at the quantum numbers α_i. As soon as the one-particle scalar products are formed, the particle index has become superfluous, because the Hilbert spaces $\mathcal{H}_1^{(i)}$ of the identical particles, and therewith in particular also the scalar products in these spaces, are of course completely equivalent. The particle indexes only serve for the *correct assignment* of the one-particle states.

By the use of the completeness relation (8.76), each observable A_N can be expressed by its matrix elements in the (anti)symmetrized N-particle basis:

$$\begin{aligned}
A_N &= \mathbb{1}_N\, A_N\, \mathbb{1}_N \\
&= \sum\!\!\!\!\!\!\int_{\alpha_1\cdots\alpha_N}\;\sum\!\!\!\!\!\!\int_{\beta_1\cdots\beta_N} |\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}\rangle^{(\pm)} \\
&\qquad .\,{}^{(\pm)}\langle\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}|A_N|\varphi_{\beta_1}\cdots\varphi_{\beta_N}\rangle^{(\pm)(\pm)}\langle\varphi_{\beta_1}\cdots\varphi_{\beta_N}|\,. \qquad (8.79)
\end{aligned}$$

8.2.5 Occupation Number Representation

The situation where the (anti)symmetrized N-particle states are built up by elements of a **discrete one-particle basis** allows for a special, sometimes remarkably useful representation. Let us first consider the normalization of the

N-particle states:

$$
\begin{aligned}
&{}^{(\pm)}\langle\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}|\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}\rangle^{(\pm)} \qquad (8.80)\\
&\overset{(8.73)}{=} \frac{1}{N!}\sum_{\mathcal{P}}(\pm)^p\left(\left\langle\varphi_{\alpha_1}^{(1)}\right|\left\langle\varphi_{\alpha_2}^{(2)}\right|\cdots\left\langle\varphi_{\alpha_N}^{(N)}\right|\right)\mathcal{P}\left(\left|\varphi_{\alpha_1}^{(1)}\right\rangle\left|\varphi_{\alpha_2}^{(2)}\right\rangle\cdots\left|\varphi_{\alpha_N}^{(N)}\right\rangle\right).
\end{aligned}
$$

Before we evaluate this expression we introduce the term

occupation number n_{α_i}

which will be used frequently later. It is defined as the frequency of occurrence, with which the one-particle state $|\varphi_{\alpha_i}\rangle$ appears in the considered N-particle state. More illustrative, one could denote n_α as the number of identical particles, which occupy the one-particle state $|\varphi_{\alpha_i}\rangle$. It holds obviously:

$$
\begin{aligned}
\sum_i n_{\alpha_i} &= N\,,\\
n_{\alpha_i} &= 0,1 \qquad \text{for states in } \mathcal{H}_N^{(-)}\,,\\
n_{\alpha_i} &= 0,1,2,\ldots \qquad \text{for states in } \mathcal{H}_N^{(+)}\,.
\end{aligned}
$$

Because of the orthonormality of the one-particle basis states, only such permutations of the sum in (8.80) yield a finite contribution, which interchange exclusively particles in the n_{α_i} identical one-particle states. These are altogether

$$n_{\alpha_1}!\,n_{\alpha_2}!\cdots n_{\alpha_N}!$$

possible permutations. Each summand of this kind is equal to 1:

$${}^{(\pm)}\langle\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}|\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}\rangle^{(\pm)} = \frac{1}{N!}\prod_{i=1}^{N} n_{\alpha_i}! \qquad (8.81)$$

Because of $0! = 1! = 1$ the right-hand side simplifies distinctly for antisymmetrized states, which only permit $n_{\alpha_i} = 0, 1$. It is then just $1/N!$. The in the form of (8.75) constructed basis states of the $\mathcal{H}_N^{(\pm)}$ are thus not normalized to one. That can of course be easily caught up in (8.75), if desired or even necessary, by introducing the normalization constant:

$$C_+ = \left\{\frac{1}{N!}\prod_{i=1}^{N} n_{\alpha_i}!\right\}^{-1/2} \quad ; \quad C_- = \sqrt{N!} \qquad (8.82)$$

Note, however, that then the completeness relation (8.76), if it is written with the normalized states, must get a corresponding additional factor.

We now come back to the above-mentioned alternative representation, which one calls the

occupation number representation.

It traces back to the following idea: One realizes with (8.75) that for a fixedly given one-particle basis $\{|\varphi_{\alpha_i}\rangle\}$ the (anti)symmetrized N-particle state is completely defined by the specification of the occupation numbers n_{α_i}. In the non-symmetrized direct product $|\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle$, on the other hand, the sequence of the one-particle states is in principle arbitrary. It must only once be fixedly preset, and that for ever. We thus can choose the initial order as we want, i.e. according to convenience. At the first position we put the n_{α_1} states $|\varphi_{\alpha_1}\rangle$, then come the n_{α_2} states $|\varphi_{\alpha_2}\rangle$, and so on:

$$C_{\pm}\,\frac{1}{N!}\sum_{\mathcal{P}}(\pm)^p\,\mathcal{P}\left\{\underbrace{\left|\varphi_{\alpha_1}^{(1)}\right\rangle\left|\varphi_{\alpha_1}^{(2)}\right\rangle\cdots}_{n_{\alpha_1}}\;\cdots\;\underbrace{\left|\varphi_{\alpha_i}^{(p)}\right\rangle\left|\varphi_{\alpha_i}^{(p+1)}\right\rangle\cdots}_{n_{\alpha_i}}\right\}\cdots$$
$$\equiv\left|N;\,n_{\alpha_1}\,n_{\alpha_2}\cdots n_{\alpha_i}\cdots n_{\alpha_j}\cdots\right\rangle^{(\pm)}\,. \tag{8.83}$$

With this arrangement the occupation numbers uniquely define the state. It is important, though, that **all** occupation numbers are given in the ket-symbol. Unoccupied one-particle states get $n_\alpha = 0$. The representation (8.83) is obviously realizable only for discrete bases. The orthonormality of these so-called **Fock states** can directly be read off from (8.78), (8.81), and (8.83):

$${}^{(\pm)}\langle N;\cdots n_{\alpha_i}\cdots|\widehat{N};\cdots\hat{n}_{\alpha_i}\cdots\rangle^{(\pm)}=\delta_{N\,\widehat{N}}\prod_i\delta_{n_{\alpha_i}\,\hat{n}_{\alpha_i}}\,. \tag{8.84}$$

They build, in the so-called **Fock space**, a complete basis:

$$\sum_{n_{\alpha_1}}\sum_{n_{\alpha_2}}\cdots\sum_{n_{\alpha_i}}\cdots|N;\,n_{\alpha_1}\,n_{\alpha_2}\cdots n_{\alpha_i}\cdots\rangle^{(\pm)}\,{}^{(\pm)}\langle N;n_{\alpha_1}\,n_{\alpha_2}\cdots n_{\alpha_i}\cdots|=\mathbb{1}_N\,. \tag{8.85}$$

It is summed over all *allowed* occupation numbers with the constraint: $\sum_i n_{\alpha_i} = N$. We will come back to the occupation number representation in the next section.

8.2.6 Pauli Principle

Finally, it still remains to clarify the important question which type of identical particles is to be described in which of the two spaces $\mathcal{H}_N^{(+)}$ and $\mathcal{H}_N^{(-)}$. How can we, for a given particle system, decide, whether its states are elements of the $\mathcal{H}_N^{(+)}$ or of the $\mathcal{H}_N^{(-)}$? This question can not be answered, though, by the means of Quantum Mechanics. The so-called **spin-statistics theorem**, which is decisive here, was formulated in 1925 by W. Pauli, at first purely empirically, for the theoretical explanation of experimentally found atomic spectra. The same author was then later (1940) able to strictly prove the theorem in the framework of the *relativistic quantum field theory* (Phys. Rev. **58**, 716 (1940)). According to the theorem the **particle spin** decides, which space, $\mathcal{H}_N^{(+)}$ or $\mathcal{H}_N^{(-)}$,

is in charge of the respective system of identical particles:

$\mathcal{H}_N^{(+)}$: *Space of the totally symmetric states of identical particles with* ***integral spin*** *($S = 0, 1, 2, \ldots$).*

These particles are called

bosons

Examples:
π-mesons ($S = 0$), photons ($S = 1$), phonons ($S = 1$), magnons ($S = 1$), α-particles ($S = 0$), ...

$\mathcal{H}_N^{(-)}$: *Space of the totally antisymmetric states of identical particles with* ***half-integral spin*** *($S = 1/2, 3/2, 5/2, \ldots$).*

These particles are called

fermions

Examples:
electrons ($S = 1/2$), positrons ($S = 1/2$), neutrons ($S = 1/2$), protons ($S = 1/2$), ... The statement, which we formulated in connection with the representation of the antisymmetric N-particle basis states as Slater determinants (8.77), turns out to be the fundamental **Pauli principle**:

In a system of identical fermions two particles can not have, in a measurement, all their quantum numbers same!

Two electrons in one and the same atom can therefore not possess the same set of quantum numbers n, l, m_l, m_s. Two protons with parallel spin projections can not occupy the same space point. Two spin-parallel electrons of the same energy band of a solid can not have the same momentum (the same wave number). Pauli's *exclusion principle* has the remarkable consequence that even interaction-free fermions are not fully independent of each other. **Such an exclusion principle does not exist for bosons!**

Important consequences of the Pauli principle are the *shell structure of the electron density in an atom* and the *periodic table of the elements*. Anticipating the Pauli principle, we have commented on both phenomena already at the end of Sect. 6.2.1, so here we can restrict ourselves to a passing remark. The direct consequences of the Pauli principle are surely known to the reader also from elementary atomic physics.

The results of this section urge us to think once more whether the manner, with which we practiced Quantum Mechanics up to now, namely essentially as a *one-particle theory*, was reasonable at all. Would it not be actually mandatory, for the theoretical-physical description of nature, to include in the formulation *all identical particles of this world*? When we intend, e.g., to calculate the electronic structure of a ferromagnetic Ni-crystal, can we then restrict ourselves to the small piece of Ni in the lab or have we to take into consideration also the

electrons anywhere in the near and farther surroundings? Can the electrons of two hydrogen atoms, the one localized in Berlin, the other in New York, with parallel spin projections, actually be both in the ground state without violating the Pauli principle?

The answer to the last question is the simpler one. The answer is: yes! There are two different one-particle ground states, since the hydrogen nuclei are located at different sites. In Chap. 6, when we calculated the hydrogen spectrum, we have identified the position of the nucleus with the origin of coordinates. That we can do in our example here of course only for one of the two hydrogen atoms, either the one in Berlin or the one in New York, but not for both. One easily convinces oneself that in the position representation the hydrogen-wave functions strongly depend on the position of the nucleus.

The other question, whether or not we actually have to (anti)symmetrize states, which incorporate **all** identical particles, we have to rack our brain about, because the answer is: in principle yes! Luckily, though, this is actually necessary only *'in principle'*! To see this, let us consider the just-mentioned example of the two hydrogen electrons in Berlin and New York. The wave functions, in particular their squares of the absolute values, decay exponentially with the distance to the nucleus center. The overlap of the *American* and the *German* H-wave function is therefore immeasurably small. The corresponding one-particle states ($|\varphi_{\mathrm{N}}\rangle$ and $|\varphi_{\mathrm{B}}\rangle$ with $\langle\varphi_{\mathrm{N,B}}|\varphi_{\mathrm{N,B}}\rangle = 1$) are thus factually orthogonal:

$$\langle\varphi_{\mathrm{N}}|\varphi_{\mathrm{B}}\rangle = \int d^3r\, \langle\varphi_{\mathrm{N}}|\mathbf{r}\rangle\langle\mathbf{r}|\varphi_{\mathrm{B}}\rangle = \int d^3r\, \varphi^*_{\mathrm{N}}(\mathbf{r})\, \varphi_{\mathrm{B}}(\mathbf{r}) \approx 0\,. \tag{8.86}$$

This is the first important point. We now perform on the two-electron system a measurement of the two-particle observable A_2, where we will exclusively be interested in the *German* results. The question, which we want to clarify thereby, is, whether we then can *quite simply forget* the hydrogen atom in New York, or whether it somehow influences substantially the measurement in Berlin.

Without antisymmetrization the system would be described by a product state of the type

$$|\varphi_{\mathrm{N}}\,\varphi_{\mathrm{B}}\rangle = |\varphi^{(1)}_{\mathrm{N}}\rangle|\varphi^{(2)}_{\mathrm{B}}\rangle\,,$$

if we assume, despite knowing better, that the two electrons are after all distinguishable in some way. The index 1 can then be ascribed to the electron in New York, and the index 2 to the electron in Berlin. In this case we of course expect an independence of the measurements in America and Germany. In order to show this, we calculate the probability for the appearance of the measured value a_{B} in the *German lab* as eigen-value of the (non-symmetrized) eigen-state

$$|a_{\mathrm{N}}\,a_{\mathrm{B}}\rangle = \left|a^{(1)}_{\mathrm{N}}\right\rangle \left|a^{(2)}_{\mathrm{B}}\right\rangle$$

of the observable A_2. The *American contributions to the measurement* do not interest here. It is therefore summed over the respective terms:

$$\begin{aligned} w &= \sum_{a_\mathrm{N}} |\langle a_\mathrm{N}\, a_\mathrm{B}|\varphi_\mathrm{N}\, \varphi_\mathrm{B}\rangle|^2 = |\langle a_\mathrm{B}|\varphi_\mathrm{B}\rangle|^2 \sum_{a_\mathrm{N}} |\langle a_\mathrm{N}|\varphi_\mathrm{N}\rangle|^2 \\ &= |\langle a_\mathrm{B}|\varphi_\mathrm{B}\rangle|^2 \sum_{a_\mathrm{N}} \langle\varphi_\mathrm{N}|a_\mathrm{N}\rangle\langle a_\mathrm{N}|\varphi_\mathrm{N}\rangle = |\langle a_\mathrm{B}|\varphi_\mathrm{B}\rangle|^2 \langle\varphi_\mathrm{N}|\varphi_\mathrm{N}\rangle \\ &= |\langle a_\mathrm{B}|\varphi_\mathrm{B}\rangle|^2 \,. \end{aligned} \tag{8.87}$$

As expected, it comes out a *purely German* result, completely independent of the H-atom in New York.

But what happens now in the case of correct antisymmetrization? The two electrons are indistinguishable fermions:

$$|\varphi_\mathrm{N}\, \varphi_\mathrm{B}\rangle^{(-)} = \frac{1}{\sqrt{2}} \left(\left|\varphi_\mathrm{N}^{(1)}\right\rangle \left|\varphi_\mathrm{B}^{(2)}\right\rangle - \left|\varphi_\mathrm{N}^{(2)}\right\rangle \left|\varphi_\mathrm{B}^{(1)}\right\rangle \right) . \tag{8.88}$$

The factor $1/\sqrt{2}$ takes care for the correct normalization (8.82). The eigen-state $|a_\mathrm{N}\, a_\mathrm{B}\rangle^{(-)}$ is analogously built up. We can now exploit for the evaluation the quasi-orthogonality (8.86) of the N- and B-states:

$$\begin{aligned} & {}^{(-)}\langle a_\mathrm{N}\, a_\mathrm{B}|\varphi_\mathrm{N}\, \varphi_\mathrm{B}\rangle^{(-)} \\ = \; & \frac{1}{2} \Big[\langle a_\mathrm{N}^{(1)}|\varphi_\mathrm{N}^{(1)}\rangle\langle a_\mathrm{B}^{(2)}|\varphi_\mathrm{B}^{(2)}\rangle + \langle a_\mathrm{N}^{(2)}|\varphi_\mathrm{N}^{(2)}\rangle\langle a_\mathrm{B}^{(1)}|\varphi_\mathrm{B}^{(1)}\rangle - \\ & \quad - \langle a_\mathrm{N}^{(1)}|\varphi_\mathrm{B}^{(1)}\rangle\langle a_\mathrm{B}^{(2)}|\varphi_\mathrm{N}^{(2)}\rangle - \langle a_\mathrm{N}^{(2)}|\varphi_\mathrm{B}^{(2)}\rangle\langle a_\mathrm{B}^{(1)}|\varphi_\mathrm{N}^{(1)}\rangle \Big] \\ \approx \; & \frac{1}{2} \Big[\langle a_\mathrm{N}^{(1)}|\varphi_\mathrm{N}^{(1)}\rangle\langle a_\mathrm{B}^{(2)}|\varphi_\mathrm{B}^{(2)}\rangle + \langle a_\mathrm{N}^{(2)}|\varphi_\mathrm{N}^{(2)}\rangle\langle a_\mathrm{B}^{(1)}|\varphi_\mathrm{B}^{(1)}\rangle \Big] \,. \end{aligned}$$

Because of the identity of the particles both the summands yield the same contribution!

In a thought experiment, we then perform the same measurement of the observable A_2 as above, where again the *American* partial results are not interesting for us:

$$\begin{aligned} w &= \sum_{a_\mathrm{N}} \left| {}^{(-)}\langle a_\mathrm{N}\, a_\mathrm{B}|\varphi_\mathrm{N}\, \varphi_\mathrm{B}\rangle^{(-)} \right|^2 \\ &= |\langle a_\mathrm{B}|\varphi_\mathrm{B}\rangle|^2 \sum_{a_\mathrm{N}} |\langle a_\mathrm{N}|\varphi_\mathrm{N}\rangle|^2 = |\langle a_\mathrm{B}|\varphi_\mathrm{B}\rangle|^2 \,. \end{aligned} \tag{8.89}$$

That is exact the same result as that of the, in principle, not correct one of the non-symmetrized representation. In particular it is clear therewith that, if we are not interested in the *American measured values*, we can *'forget'* the far away electron, without any drawback for the results we are actually interested in. That is extraordinarily calming, because it *'saves'* the procedure which was considered so far always as reasonable. The (anti)symmetrized formulation is, strictly speaking, the only correct one, but need not always be strictly obeyed.

When the identical particles, however, are microscopically close to each other, then novel phenomena appear, which can be encompassed only by the correct (anti)symmetrized representation.

8.2.7 Exercises

Exercise 8.2.1
Show that for a system of identical particles the time-evolution operator $U(t, t_0)$ commutes with each transposition operator. Prove therewith that (8.53) is valid even if the Hamilton operator is explicitly time-dependent!

Exercise 8.2.2
Show that there does not exist an observable A_N, which is able to transfer a state from the $\mathcal{H}_N^{(+)}$ into the $\mathcal{H}_N^{(-)}$:

$$\left\langle \varphi_N^{(+)} \right| A_N \left| \psi_N^{(-)} \right\rangle \stackrel{!}{=} 0 \,.$$

Exercise 8.2.3
Investigate whether for

1. $N = 2$,

2. $N = 3$

the basis states of the $\mathcal{H}_N^{(-)}$ together with those of the $\mathcal{H}_N^{(+)}$ span the entire product space $\mathcal{H}_N$.

Exercise 8.2.4
Show that the permutation operator $\mathcal{P}$ is Hermitian in the (anti)symmetrized space $\mathcal{H}_N^{(\pm)}$.

Exercise 8.2.5
Two identical particles move interaction-free in a one-dimensional potential well with infinitely high walls:

$$V(q) = \begin{cases} 0 & \text{for } |q| < q_0 \,, \\ \infty & \text{for } |q| \geq q_0 \,. \end{cases}$$

Let the spin state of the two-particle system be symmetric with respect to a particle interchange. The two single spins are *parallel*, so that both particles have the same magnetic quantum number m_s.

1. Formulate the Hamilton operator of the two-particle system. Show that the energy-eigen states separate into a space and a spin part. Of which symmetry should the space part of the total state be, if the two particles are both fermions and both bosons, respectively?

2. Calculate the possible eigen-states and eigen-energies for bosons and fermions, respectively!

3. Find the ground-state energy for two bosons and two fermions, respectively!

Exercise 8.2.6
A system of two identical fermions is described by a Hamilton operator, which does **not** depend on the spins of the two fermions, but may be, e.g., explicitly time-dependent. The eigen-states therefore factorize into a space and a spin part:

$$\left|\psi_2^{(S)}\right\rangle = \left|q^{(+)}\right\rangle |S\, m_S\rangle^{(-)} \qquad \left|\psi_2^{(T)}\right\rangle = \left|q^{(-)}\right\rangle |S\, m_S\rangle^{(+)} \ .$$

The upper indexes $(\pm)$ refer to the symmetry character of the particle states.

1. Let P_{12} be the transposition operator. What is

$$P_{12} \left|\psi_2^{(S,T)}\right\rangle \ ?$$

2. Decompose P_{12} into a space and a spin part,

$$P_{12} = P_{12}^{(q)} \cdot P_{12}^{(S)} = P_{12}^{(S)} \cdot P_{12}^{(q)} \ ,$$

   and give reasons why $P_{12}^{(q)}$ commutes with H.

3. Show that the time-evolution operator $U(t, t_0)$ also commutes with $P_{12}^{(q)}$, even if H were explicitly time-dependent.

4. Explain by the use of the preceding partial results, why in the temporal development of a state of the two-fermion system no transitions between $|\psi_2^{(S)}\rangle$ and $|\psi_2^{(T)}\rangle$ can happen, although both have the same symmetry character.

Exercise 8.2.7
Starting point is a system of two spin-1/2 particles. The transposition operator P_{12} is defined by its action on the common eigen-states,

$$|m_1 m_2\rangle = |m_1\rangle^{(1)} |m_2\rangle^{(2)} \ ; \quad m_{1,2} = \pm\frac{1}{2} \ ,$$

of the spin operators $\mathbf{S}_1^2$, $\mathbf{S}_2^2$, $\mathbf{S}_1^z$, $\mathbf{S}_2^z$ in the product space $H_2 = H_1^{(1)} \otimes H_1^{(2)}$ of the two spin-1/2 Hilbert spaces $H_1^{(1,2)}$:

$$\begin{aligned} P_{12}|m_1 m_2\rangle &= P_{12}|m_1\rangle^{(1)}|m_2\rangle^{(2)} \\ &= |m_1\rangle^{(2)}|m_2\rangle^{(1)} \\ &= |m_2\rangle^{(1)}|m_1\rangle^{(2)} \\ &= |m_2 m_1\rangle. \end{aligned}$$

1. Confirm the known relations:

$$P_{12}^{-1} = P_{12}^{+} = P_{12}$$

   P_{12} possesses only the eigen-values ± 1.

2. Give reasons why the common eigen-states of

$$\mathbf{S}_1^2\,,\quad \mathbf{S}_2^2\,,\quad \mathbf{S}^2\,,\quad \mathbf{S}^z\qquad (\mathbf{S}=\mathbf{S}_1+\mathbf{S}_2)$$

are also the eigen-states of P_{12}.

3. Show that

$$P_{12}\mathbf{S}_1P_{12}^+=\mathbf{S}_2\;;\quad P_{12}\mathbf{S}_2P_{12}^+=\mathbf{S}_1\;.$$

4. Verify the representation

$$P_{12}=\frac{1}{2}[\mathbb{1}+\frac{4}{\hbar^2}\mathbf{S}_1\cdot\mathbf{S}_2]\;.$$

Exercise 8.2.8
The symmetrization operator

$$S_N^{(\pm)}=\frac{1}{N!}\sum_{\mathcal{P}}(\pm1)^p\mathcal{P}$$

projects the product space H_N onto the subspace $H_N^{(\pm)}$ of the (anti)symmetrized states $|\varphi_N^{(\pm)}\rangle$ of a system of N identical particles. Let it be a system of interaction-free particles in the non-degenerate particle-energy states $|n\rangle$:

$$H|n\rangle=(\alpha\cdot n+\varepsilon_0)|n\rangle\;;\quad n=0,1,2,\ldots\;;\quad \alpha>0\;;\quad \varepsilon_0>0\;.$$

1. Express $S_2^{(-)}$ and $S_3^{(+)}$ by the transposition operators P_{ij}!

2. Let the system consist of $N=3$ noninteraction bosons. How do the ground state $|E_0^{(+)}\rangle$ and the ground-state energy $E_0^{(+)}$ of the three-boson system look like?

3. Let the system consist of $N=2$ noninteraction fermions. Find the ground state $|E_0^{(-)}\rangle$ and the ground-state energy $E_0^{(-)}$ of the two-fermion system.

4. Determine for the three-boson system in 2. the first excited state $|E_1^{(+)}\rangle$.

Exercise 8.2.9
Let N interaction-free identical particles be encased in a cuboid of the volume $V=L^3$:

1. Determine for the case of periodic boundary conditions (Sect. 2.2.5, Vol. 6): $\psi(x,y,z)=\psi(x+L,y,z)=\psi(x,y+L,z)=\psi(x,y,z+L)$) the one-particle wave function and the one-particle energies.

2. Consider the ground state for the case of bosons and fermions ($S=1/2$), respectively. Calculate the maximal absolute value of the one-particle momentum!

3. Calculate the ground-state energy of the N-particle system.

Exercise 8.2.10
Three noninteraction identical particles with spin $S = 0$ move in a one-dimensional potential well with infinitely high walls (see Exercise 8.2.5):

$$V(q) = \begin{cases} 0 & \text{for } |q| < q_0 \ , \\ \infty & \text{for } |q| \geq q_0 \ . \end{cases}$$

Determine the wave functions of the ground state and the first excited state of the three-particle system. Find also the corresponding energies.

8.3 Second Quantization

The considerations in the preceding Sects. 8.1 and 8.2 have revealed how troublesome the description of many-particle systems can be. The formalism of **second quantization**, which we will now deal with, means ultimately, though, only a redrafting of the many-body problem and does not at all represent a method of complete solution. The introduction of so-called

creation and annihilation operators

is typical for the *second quantization*, which makes the troublesome construction of (anti)symmetrized products of one-particle states superfluous. The wealth of consequences of the *principle of indistinguishability*, which we gathered in the last two sections, can then be traced back to a few fundamental **(anti)commutator relations** between these so-called *construction operators*. Formally, the theory becomes independent of the particle number. Interaction processes are expressed by *creation* and *annihilation* of particles. That may appear, at first, rather peculiar, is , however, in principle, a *highly illustrative* way of description. When a particle hops from the position $\mathbf{R}_i$ to the position $\mathbf{R}_j$, then one can interpret that also as if the particle is *annihilated* at $\mathbf{R}_i$ and subsequently created at $\mathbf{R}_j$. Interaction processes change the states of the interacting partners. That can be understood illustratively as an *annihilation* of the two particles in their *old* states and subsequent *creation* in their *new* states (Fig. 8.2).

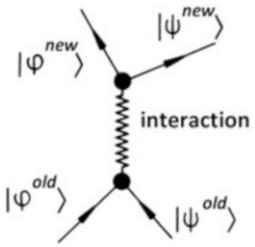

Figure 8.2: Symbolic representation of an interaction process

The formalism of *second quantization* has proven as so advantageous that it has found today a very broad application in the research literature. One has therefore to master it, in order to at least be able to read corresponding publications. We will apply it in Vol. 9 **(Fundamentals of Many-body Physics)** almost exclusively, and will therefore repeat there once more some of the following most important considerations.

To the nomenclature *second quantization* one should not attach too much importance; it is indeed widely considered as more or less inappropriate. The most elegant derivation of the formalism is provided by the *quantum field theory*, which is not a part of our program, and which is based on the quantization of Schrödinger's matter field. Since Schrödinger's Quantum Theory exhibits already a *first quantization*, one thought to have to speak now of a *second quantization*. It can be shown that this *reasoning of the notation* rests actually on a misinterpretation. However, that does not change the fact that the nomenclature is now absolutely established.

8.3.1 Creation and Annihilation Operators

For the set-up of the (anti)symmetrized basis states (8.75) of the Hilbert space $\mathcal{H}_N^{(\pm)}$ we define a special operator, which creates them step by step out of the so-called

vacuum state

$$|0\rangle\ ; \quad \langle 0|0\rangle = 1\ . \tag{8.90}$$

This so-called

creation operator

$$a^+_{\varphi_\alpha} \equiv a^+_\alpha$$

has the special property to connect Hilbert spaces of different particle numbers:

$$a^+_\alpha :\ \mathcal{H}_N^{(\pm)} \ \longrightarrow\ \mathcal{H}_{N+1}^{(\pm)}\ . \tag{8.91}$$

Apart from that it is uniquely defined by its mode of action:

$$\begin{aligned} a^+_{\alpha_1}|0\rangle &= \sqrt{1}|\varphi_{\alpha_1}\rangle \in \mathcal{H}_1^{(\pm)}\ , \\ a^+_{\alpha_2}|\varphi_{\alpha_1}\rangle &= \sqrt{2}|\varphi_{\alpha_2}\,\varphi_{\alpha_1}\rangle^{(\pm)} \in \mathcal{H}_2^{(\pm)}\ , \\ a^+_{\alpha_3}|\varphi_{\alpha_2}\,\varphi_{\alpha_1}\rangle^{(\pm)} &= \sqrt{3}|\varphi_{\alpha_3}\,\varphi_{\alpha_2}\,\varphi_{\alpha_1}\rangle^{(\pm)} \in \mathcal{H}_3^{(\pm)} \\ &\ldots \end{aligned}$$

The state $|0\rangle$ thus characterizes a *system without a particle* (vacuum). In general the assignment holds:

$$a^+_\beta|\underbrace{\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}}_{\in\,\mathcal{H}_N^{(\pm)}}\rangle^{(\pm)} = \sqrt{N+1}\,|\underbrace{\varphi_\beta\,\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}}_{\in\,\mathcal{H}_{N+1}^{(\pm)}}\rangle^{(\pm)}\ . \tag{8.92}$$

The *creation operator* a_β^+ adds to the N-particle state a further particle in the one-particle state $|\varphi_\beta\rangle$. This *new* state $|\varphi_\beta\rangle$ is put, according to an agreement, at the first place in the initial order of the one-particle states. The relation (8.92) can of course also be reversed:

$$|\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}\rangle^{(\pm)} = \frac{1}{\sqrt{N!}}\, a_{\alpha_1}^+\, a_{\alpha_2}^+\cdots a_{\alpha_N}^+|0\rangle\ . \tag{8.93}$$

Since a change of the initial ordering of the one-particle states in $|\varphi_{\alpha_1}\cdots\cdots\varphi_{\alpha_N}\rangle^{(\pm)}$ can for fermions cause a sign change (8.60), the sequence of the operators in (8.93) is important. If we want to change this order, we must know the commutation relation of the operators. This we get by the following consideration:

$$\begin{aligned} a_{\alpha_1}^+\, a_{\alpha_2}^+|\underbrace{\varphi_{\alpha_3}\cdots\varphi_{\alpha_N}}_{\in\,\mathcal{H}_{N-2}^{(\pm)}}\rangle^{(\pm)} &= \sqrt{N\,(N-1)}|\underbrace{\varphi_{\alpha_1}\,\varphi_{\alpha_2}\,\varphi_{\alpha_3}\cdots\varphi_{\alpha_N}}_{\in\,\mathcal{H}_N^{(\pm)}}\rangle^{(\pm)}\ , \\ a_{\alpha_2}^+\, a_{\alpha_1}^+|\varphi_{\alpha_3}\cdots\varphi_{\alpha_N}\rangle^{(\pm)} &= \sqrt{N(N-1)}|\varphi_{\alpha_2}\,\varphi_{\alpha_1}\,\varphi_{\alpha_3}\cdots\varphi_{\alpha_N}\rangle^{(\pm)} \\ &= \pm\sqrt{N(N-1)}|\varphi_{\alpha_1}\,\varphi_{\alpha_2}\,\varphi_{\alpha_3}\cdots\varphi_{\alpha_N}\rangle^{(\pm)}\ . \end{aligned}$$

Interchange of two adjacent one-particle symbols in the N-particle ket-vector $|\cdots\rangle^{(\pm)}$ changes for the antisymmetrized state the sign. The above two equations hold for arbitrary basis states. They lead after subtraction and addition, respectively, therefore to the following operator identities:

$$\left[a_{\alpha_1}^+, a_{\alpha_2}^+\right]_\mp \equiv a_{\alpha_1}^+\, a_{\alpha_2}^+ \mp a_{\alpha_2}^+\, a_{\alpha_1}^+ \equiv 0\ . \tag{8.94}$$

The upper sign ($[\ldots,\ldots]_-$: *commutator*) holds in the space $\mathcal{H}_N^{(+)}$, the lower sign ($[\ldots,\ldots]_+$: *anti-commutator*) in the space $\mathcal{H}_N^{(-)}$. **Creation operators for bosons commute, those for fermions anti-commute!**

We now introduce the to a_α^+ adjoint operator and call this already now, for reasons, which will become clear very soon, the

annihilation operator

$$a_{\varphi_\alpha} \equiv \left(a_{\varphi_\alpha}^+\right)^+ \ \longleftrightarrow\ a_\alpha \equiv (a_\alpha^+)^+\ .$$

According to (8.92) and (8.93) we have, as a start, for the corresponding bra-states:

$$\begin{aligned} {}^{(\pm)}\langle\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}|a_\gamma &= \sqrt{N+1}\,{}^{(\pm)}\langle\varphi_\gamma\,\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}|\ , \qquad (8.95) \\ {}^{(\pm)}\langle\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}| &= \frac{1}{\sqrt{N!}}\langle 0|\left(a_{\alpha_1}^+\cdots a_{\alpha_N}^+\right)^+ \\ &= \frac{1}{\sqrt{N!}}\langle 0|a_{\alpha_N}\,a_{\alpha_{N-1}}\cdots a_{\alpha_1}\ . \qquad (8.96) \end{aligned}$$

Which meaning and which functionality does the so introduced *annihilation operator* have? We find the answer by evaluating the following matrix element:

$$
\begin{aligned}
&{}^{(\pm)}\langle \underbrace{\varphi_{\beta_2}\cdots\varphi_{\beta_N}}_{\in\mathcal{H}_{N-1}^{(\pm)}} |a_\gamma| \underbrace{\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}}_{\in\mathcal{H}_N^{(\pm)}}\rangle^{(\pm)} \\
&\overset{(8.95)}{=} \sqrt{N}\,{}^{(\pm)}\langle\varphi_\gamma\,\varphi_{\beta_2}\cdots\varphi_{\beta_N}|\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}\rangle^{(\pm)} \\
&\overset{(8.78)}{=} \frac{\sqrt{N}}{N!}\sum_{\mathcal{P}_\alpha}(\pm)^{p_\alpha}\,\mathcal{P}_\alpha\left[\delta(\gamma,\alpha_1)\,\delta(\beta_2,\alpha_2)\cdots\delta(\beta_N,\alpha_N)\right] \\
&= \frac{1}{\sqrt{N}}\,\frac{1}{(N-1)!}\Bigg\{\delta(\gamma,\alpha_1)\sum_{\mathcal{P}_\alpha}(\pm)^{p_\alpha}\,\mathcal{P}_\alpha\left[\delta(\beta_2,\alpha_2)\cdots\delta(\beta_N,\alpha_N)\right] \\
&\quad +(\pm)^1\,\delta(\gamma,\alpha_2)\sum_{\mathcal{P}_\alpha}(\pm)^{p_\alpha}\,\mathcal{P}_\alpha\left[\delta(\beta_2,\alpha_1)\,\delta(\beta_3,\alpha_3)\cdots\delta(\beta_N,\alpha_N)\right] \\
&\quad +\ldots \\
&\quad +(\pm)^{(N-1)}\,\delta(\gamma,\alpha_N)\sum_{\mathcal{P}_\alpha}(\pm)^{p_\alpha}\,\mathcal{P}_\alpha\left[\delta(\beta_2,\alpha_1)\,\delta(\beta_3,\alpha_2)\cdots\delta(\beta_N,\alpha_{N-1})\right]\Bigg\} \\
&\overset{(8.78)}{=} \frac{1}{\sqrt{N}}\Big\{\delta(\gamma,\alpha_1)\,{}^{(\pm)}\langle\varphi_{\beta_2}\ldots\varphi_{\beta_N}|\varphi_{\alpha_2}\cdots\varphi_{\alpha_N}\rangle^{(\pm)} \\
&\quad +(\pm)^1\,\delta(\gamma,\alpha_2)\,{}^{(\pm)}\langle\varphi_{\beta_2}\cdots\varphi_{\beta_N}|\varphi_{\alpha_1}\,\varphi_{\alpha_3}\cdots\varphi_{\alpha_N}\rangle^{(\pm)} \\
&\quad +\ldots \\
&\quad +(\pm)^{(N-1)}\,\delta(\gamma,\alpha_N)\,{}^{(\pm)}\langle\varphi_{\beta_2}\cdots\varphi_{\beta_N}|\varphi_{\alpha_1}\,\varphi_{\alpha_2}\cdots\varphi_{\alpha_{N-1}}\rangle^{(\pm)}\Big\}\,.
\end{aligned}
$$

The $(N-1)$-particle bra-state ${}^{(\pm)}\langle\varphi_{\beta_2}\cdots\varphi_{\beta_N}|$ is the same in all summands, and also on the left-hand side of the equation. It is furthermore a completely arbitrary basis state of the $\mathcal{H}_{N-1}^{(\pm)}$. We can therefore write:

$$
\begin{aligned}
&a_\gamma|\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}\rangle^{(\pm)} \\
&= \frac{1}{\sqrt{N}}\Big\{\delta(\gamma,\alpha_1)|\varphi_{\alpha_2}\cdots\varphi_{\alpha_N}\rangle^{(\pm)} \\
&\quad +(\pm)^1\,\delta(\gamma,\alpha_2)|\varphi_{\alpha_1}\,\varphi_{\alpha_3}\cdots\varphi_{\alpha_N}\rangle^{(\pm)} \\
&\quad \cdots \\
&\quad +(\pm)^{N-1}\,\delta(\gamma,\alpha_N)|\varphi_{\alpha_1}\,\varphi_{\alpha_2}\cdots\varphi_{\alpha_{N-1}}\rangle^{(\pm)}\Big\}\,.
\end{aligned}
\tag{8.97}
$$

If the one-particle state $|\varphi_\gamma\rangle$ is found among the states $|\varphi_{\alpha_1}\rangle$ to $|\varphi_{\alpha_N}\rangle$, which, according to (8.75), build up the (anti)symmetrized state $|\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}\rangle^{(\pm)}$, it results after application of a_γ an $(N-1)$-particle state, in which $|\varphi_\gamma\rangle$, compared to the initial state, is eliminated (*annihilated*). If $|\varphi_\gamma\rangle$ does not appear among the N one-particle states, then the application of a_γ will make the state $|\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}\rangle^{(\pm)}$ to vanish. The vacuum state does *not contain a particle at all*. It therefore holds for this state, independently of γ (or φ_γ):

$$
a_\gamma|0\rangle = 0\,. \tag{8.98}
$$

Because of

$$[a_{\alpha_1}, a_{\alpha_2}]_{\mp} = \left([a^+_{\alpha_2}, a^+_{\alpha_1}]_{\mp}\right)^+$$

the fundamental commutation relation for the annihilation operators follows directly from that of the *creation operators* (8.94). **Annihilation operators commute in the case of bosons, and anti-commute in the case of fermions**:

$$[a_{\alpha_1}, a_{\alpha_2}]_{\mp} = 0 \,. \tag{8.99}$$

It still remains to derive as a third fundamental commutation relation the one between *creators* and *annihilators*. Let $|\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(\pm)}$ be again an arbitrary basis state of the $\mathcal{H}_N^{(\pm)}$. One after the other, we apply to this state the two operators a_β and a^+_γ:

$$\begin{aligned}
&a_\beta\big(a^+_\gamma |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(\pm)}\big) \\
&= \sqrt{N+1}\, a_\beta |\varphi_\gamma\, \varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(\pm)} \\
&= \delta(\beta,\gamma)|\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(\pm)} \\
&\quad +(\pm)^1\, \delta(\beta,\alpha_1)|\varphi_\gamma\, \varphi_{\alpha_2} \cdots \varphi_{\alpha_N}\rangle^{(\pm)} \\
&\quad +\ldots \\
&\quad +(\pm)^N\, \delta(\beta,\alpha_N)|\varphi_\gamma\, \varphi_{\alpha_1} \cdots \varphi_{\alpha_{N-1}}\rangle^{(\pm)} \,.
\end{aligned}$$

A somewhat different result is found when one lets the operators act in the reverse order:

$$\begin{aligned}
&a^+_\gamma \left(a_\beta |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(\pm)}\right) \\
&= \delta(\beta,\alpha_1)|\varphi_\gamma\, \varphi_{\alpha_2} \cdots \varphi_{\alpha_N}\rangle^{(\pm)} \\
&\quad +(\pm)^1\, \delta(\beta,\alpha_2)|\varphi_\gamma\, \varphi_{\alpha_1}\, \varphi_{\alpha_3} \cdots \varphi_{\alpha_N}\rangle^{(\pm)} \\
&\quad +\ldots \\
&\quad +(\pm)^{N-1}\, \delta(\beta,\alpha_N)|\varphi_\gamma\, \varphi_{\alpha_1} \cdots \varphi_{\alpha_{N-1}}\rangle^{(\pm)} \,.
\end{aligned}$$

When we multiply the last equation by ± 1, and then subtract it from the preceding one, then all terms except for the first summand of the first equation are canceling each other:

$$\big(a_\beta\, a^+_\gamma \mp a^+_\gamma\, a_\beta\big)|\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(\pm)} = \delta(\beta,\gamma)|\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(\pm)} \,.$$

With the usual reasoning, we can read this equation as operator identity:

$$\left[a_\beta, a^+_\gamma\right]_{\mp} = \delta(\beta,\gamma) \,. \tag{8.100}$$

The commutator refers to bosons, and the anti-commutator to fermions.

By the relations (8.93) and (8.97) we succeeded to trace all N-particle states back to the vacuum state $|0\rangle$. The mode of action of the annihilation operator on the vacuum state is very simple (8.98).

We have gotten rid of the cumbersome *(anti)symmetrization* of the N-particle states by the introduction of the new operators. The corresponding effect is absorbed now by the three formally simple, fundamental commutation relations (8.94), (8.99), and (8.100). They prescribe the manner, in which the sequence of *construction operators* can be changed.

The derivation so far presented of the creation and annihilation operators and their modes of action is likewise valid for discrete (proper) and continuous (improper) one-particle basis states. In the *discrete case*, though, the *Fock states* (8.83) of the occupation number representation from Sect. 8.2.5 are by a far more common starting point than the general (anti)symmetrized basis states (8.75). The corresponding derivation follows more or less exactly the same line as the one just discussed, however, unfortunately with somewhat modified normalization factors.

One writes instead of (8.92):

$$\begin{aligned} a^+_{\alpha_r}|N;\cdots n_{\alpha_r}\cdots\rangle^{(\pm)} &= a^+_{\alpha_r}\, C_\pm|\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}\rangle^{(\pm)} \\ &\equiv \sqrt{N+1}\, C_\pm|\varphi_{\alpha_r}\underbrace{\varphi_{\alpha_1}\cdots}_{n_{\alpha_1}}\cdots\underbrace{\varphi_{\alpha_r}\cdots}_{n_{\alpha_r}}\cdots\rangle^{(\pm)} \\ &= (\pm)^{N_r}\sqrt{N+1}\, C_\pm|\cdots\underbrace{\varphi_{\alpha_r}\,\varphi_{\alpha_r}\cdots}_{n_{\alpha_r}+1}\cdots\rangle^{(\pm)}\,. \end{aligned}$$

N_r corresponds thereby to the number of pairwise interchanges, which are necessary to permute the one-particle state $|\varphi_{\alpha_r}\rangle$, which is at first *created at the first position*, to its *correct position*, namely to the already present n_{α_r} states of the same kind:

$$N_r = \sum_{i=1}^{r-1} n_{\alpha_i}\,. \tag{8.101}$$

The creation operator shall act on the Fock states as follows:

$$a^+_{\alpha_r}|N;\cdots n_{\alpha_r}\cdots\rangle^{(\pm)} = (\pm)^{N_r}\sqrt{n_{\alpha_r}+1}\,|N+1;\cdots n_{\alpha_r}+1\cdots\rangle^{(\pm)}\,. \tag{8.102}$$

That differs indeed from (8.92) by the normalization factor. For the representation (8.102) one has, however, to bear in mind that the occupation restriction for fermions is not directly recognizable. It is therefore sometimes recommendable to itemize the expression according to fermions and bosons:

Bosons

$$\begin{aligned} &a^+_{\alpha_r}|N;\cdots n_{\alpha_r}\cdots\rangle^{(+)} = \sqrt{n_{\alpha_r}+1}|N+1;\cdots n_{\alpha_r}+1\cdots\rangle^{(+)}\,, \\ &n_{\alpha_r} = 0,1,2,\ldots \end{aligned} \tag{8.103}$$

Fermions

$$a^+_{\alpha_r}|N;\cdots n_{\alpha_r}\cdots\rangle^{(-)} = (-1)^{N_r}\,\delta_{n_{\alpha_r},0}|N+1;\cdots n_{\alpha_r}+1\cdots\rangle^{(-)}\,. \tag{8.104}$$

We can also here, of course, develop each Fock state out of the vacuum state $|0\rangle$ by repeated application of the creation operator,

$$|N; n_{\alpha_1} \cdots n_{\alpha_r} \cdots\rangle^{(\ afterpm)} = \prod_r \frac{\left(a^+_{\alpha_r}\right)^{n_{\alpha_r}}}{\sqrt{n_{\alpha_r}!}} (\pm)^{N_r} |0\rangle \ , \tag{8.105}$$

where, though, again the occupation restriction for fermions ($n_{\alpha_r} = 0, 1$; $n_{\alpha_r}! = 0! = 1! = 1$) is to be taken into consideration.

The **annihilation operator** a_{α_r} is of course also now defined as the adjoint operator of the creation operator. Its mode of action we get to know with a similar consideration as that after (8.96):

$$\begin{aligned}
&{}^{(\pm)}\langle N; \cdots n_{\alpha_r} \cdots | a_{\alpha_r} | \overline{N}; \cdots \overline{n}_{\alpha_r} \cdots\rangle^{(\pm)} \\
&\overset{(8.102)}{=} (\pm)^{N_r} \sqrt{n_{\alpha_r}+1}\, {}^{(\pm)}\langle N+1; \cdots n_{\alpha_r}+1 \cdots | \overline{N}; \cdots \overline{n}_{\alpha_r} \cdots\rangle^{(\pm)} \\
&\overset{(8.84)}{=} (\pm)^{N_r} \sqrt{n_{\alpha_r}+1}\, \delta_{N+1,\overline{N}} \left(\delta_{n_{\alpha_1}\overline{n}_{\alpha_1}} \cdots \delta_{n_{\alpha_r}+1,\overline{n}_{\alpha_r}} \cdots\right) \\
&= (\pm)^{N_r} \sqrt{\overline{n}_{\alpha_r}}\, \delta_{N,\overline{N}-1} \left(\delta_{n_{\alpha_1}\overline{n}_{\alpha_1}} \cdots \delta_{n_{\alpha_r},\overline{n}_{\alpha_r}-1} \cdots\right) \\
&= (\pm)^{N_r} \sqrt{\overline{n}_{\alpha_r}}\, {}^{(\pm)}\langle N; n_{\alpha_1} \cdots n_{\alpha_r} \cdots | \overline{N}-1; \cdots \overline{n}_{\alpha_r}-1 \cdots\rangle^{(\pm)} \ .
\end{aligned}$$

The product of the Kronecker-deltas sees to it that

$$N_r = \sum_{i=1}^{r-1} n_{\alpha_i} = \sum_{i=1}^{r-1} \overline{n}_{\alpha_i} = \overline{N}_r \ .$$

When one compares the first with the last line in the above chain of equations and takes into consideration that it was chosen as bra-state ${}^{(\pm)}\langle \cdots |$ an arbitrary basis state of the Fock space, then one comes to the conclusion:

$$a_{\alpha_r} |N; \cdots n_{\alpha_r} \cdots\rangle^{(\pm)} = (\pm)^{N_r} \sqrt{n_{\alpha_r}} |N-1; \cdots n_{\alpha_r}-1 \cdots\rangle^{(\pm)} \ . \tag{8.106}$$

We should formulate also this relation once more explicitly and separately for bosons and fermions:

Bosons

$$\begin{aligned}
a_{\alpha_r} |N; \cdots n_{\alpha_r} \cdots\rangle^{(+)} &= \sqrt{n_{\alpha_r}} |N-1; \cdots n_{\alpha_r}-1 \cdots\rangle^{(+)} \ , \\
n_{\alpha_r} &= 0, 1, 2, \ldots
\end{aligned} \tag{8.107}$$

Fermions

$$a_{\alpha_r} |N; \cdots n_{\alpha_r} \cdots\rangle^{(-)} = (-1)^{N_r} \delta_{n_{\alpha_r},1} |N-1; \cdots n_{\alpha_r}-1 \cdots\rangle^{(-)} \ . \tag{8.108}$$

By means of the equations (8.103), (8.104), (8.107), and (8.108) one finds the **fundamental commutation relations** of the creation and annihilation operators in the Fock space (see Exercise 8.3.1):

$$\left[a_{\alpha_r}, a_{\alpha_s}\right]_\mp = \left[a^+_{\alpha_r}, a^+_{\alpha_s}\right]_\mp = 0 \ , \tag{8.109}$$

$$\left[a_{\alpha_r}, a^+_{\alpha_s}\right]_\mp = \delta_{rs} \ . \tag{8.110}$$

They are of course identical to (8.94), (8.99), and (8.100). The commutators refer again to bosons, and the anti-commutators to fermions.

8.3.2 Operators in Second Quantization

We have been able in the preceding sections to trace back all (anti)symmetrized N-particle states ultimately to the vacuum state $|0\rangle$, by having replaced the complicated process of (anti)symmetrization by the application of creation and annihilation operators, which obey a rather simple algebra, which manifests itself exclusively in three fundamental commutation relations. The whole procedure, however, makes of course sense only if it is possible to express also the observables of the N-particle system by creation and annihilation operators, so that their actions on the states can be calculable exclusively on the basis of the commutation relations.

Starting point for the following considerations is the representation (8.79) of the general N-particle observable A_N, where we can express the basis states, according to (8.93) and (8.96), already by *creators* and *annihilators*:

$$A_N = \frac{1}{N!} \sum\!\!\!\!\!\!\int_{\alpha_1 \cdots \alpha_N} \sum\!\!\!\!\!\!\int_{\beta_1 \cdots \beta_N} a^+_{\alpha_1} \cdots a^+_{\alpha_N} |0\rangle \, {}^{(\pm)}\langle \varphi_{\alpha_1} \cdots | A_N | \varphi_{\beta_1} \cdots \rangle^{(\pm)} \langle 0 | a_{\beta_N} \cdots a_{\beta_1} \, . \tag{8.111}$$

In all physically relevant cases such an operator consists of a one-particle and a two-particle part:

$$A_N = \sum_{i=1}^{N} A_1^{(i)} + \frac{1}{2} \sum_{i,\,j}^{i \neq j} A_2^{(i,\,j)} \, . \tag{8.112}$$

By a careful inspection of the matrix element (8.111) one can reach some further substantial simplifications. This we show at first for the one-particle part. For that purpose we still reshape the matrix element a bit:

$$\begin{aligned}
&{}^{(\pm)}\langle \varphi_{\alpha_1} \cdots \varphi_{\alpha_N} | \sum_i A_1^{(i)} | \varphi_{\beta_1} \cdots \varphi_{\beta_N} \rangle^{(\pm)} \\
&\overset{(8.59)}{=} \langle \varphi_{\alpha_1} \cdots \varphi_{\alpha_N} | S_N^{(\pm)} \sum_i A_1^{(i)} | \varphi_{\beta_1} \cdots \varphi_{\beta_N} \rangle^{(\pm)} \\
&\overset{(8.51),(8.61)}{=} \langle \varphi_{\alpha_1} \cdots \varphi_{\alpha_N} | \sum_{i=1}^{N} A_1^{(i)} | \varphi_{\beta_1} \cdots \varphi_{\beta_N} \rangle^{(\pm)} \\
&= \frac{1}{N!} \sum_{\mathcal{P}_\beta} (\pm)^{p_\beta} \, \mathcal{P}_\beta \left[\left\langle \varphi^{(1)}_{\alpha_1} \right| A_1^{(1)} \left| \varphi^{(1)}_{\beta_1} \right\rangle \left\langle \varphi^{(2)}_{\alpha_2} \right| \left. \varphi^{(2)}_{\beta_2} \right\rangle \cdots \right. \\
&\quad \left. \cdots \left\langle \varphi^{(N)}_{\alpha_N} \right| \left. \varphi^{(N)}_{\beta_N} \right\rangle + \ldots + \left\langle \varphi^{(1)}_{\alpha_1} \right| \left. \varphi^{(1)}_{\beta_1} \right\rangle \cdots \left\langle \varphi^{(N)}_{\alpha_N} \right| A_1^{(N)} \left| \varphi^{(N)}_{\beta_N} \right\rangle \right] \, .
\end{aligned}$$

This expression must now be inserted into (8.111), where the following simplifying measures are possible:

1. Each term of the sum over the permutations $\mathcal{P}_\beta$ yields in (8.111) the same contribution, because each by $\mathcal{P}_\beta$ permuted ordering of the $|\varphi^{(i)}_{\beta_i}\rangle$ can be led back into the initial order by

   a) a renaming of the integration (summation) variables β_i and

   b) a subsequent respective interchange of the *annihilators* in the product $a_{\beta_N} \cdots a_{\beta_1}$.

   The step b) yields according to (8.99) a factor $(\pm)^{p_\beta}$, which, together with the identical factor already present in the above representation of the matrix element, leads to $(\pm)^{2p_\beta} = +1$. The sum yields therefore in (8.111) $N!$ equal contributions.

2. Each summand in the square bracket contributes also the same value. It is thereby important to remember that the particle indexes serve only to combine to scalar products the *right* one-particle states in the *right* Hilbert spaces. The Hilbert spaces $\mathcal{H}^{(i)}_1$ as such are of course for all i completely equivalent. In order to see then that, for instance, the first and the last summand in the square bracket of the above equation contribute the same to (8.111), we replace in the last term β_N by β_1 and α_N by α_1. This renaming of the variables is allowed, because in (8.111) it is summed and integrated, respectively, over all the quantum numbers. After the renaming, though, the *creators* and the *annihilators* are no longer in their original order. To bring them back to this original order, an equal number of interchanges between the a's and between the a^+'s are necessary, which in turn yields simply a factor $+1$.

We are now able to formulate an intermediate result:

$$\begin{aligned}
\sum_{i=1}^{N} A^{(i)}_1 \;&=\; \frac{N}{N!} \sum\!\!\!\!\!\!\int_{\alpha_1 \cdots \alpha_N} \sum\!\!\!\!\!\!\int_{\beta_1 \cdots \beta_N} a^+_{\alpha_1} \cdots a^+_{\alpha_N} |0\rangle \\
&\qquad \cdot \left\{ \left\langle \varphi^{(1)}_{\alpha_1} \right| A^{(1)}_1 \left| \varphi^{(1)}_{\beta_1} \right\rangle \delta(\alpha_2, \beta_2) \cdots \delta(\alpha_N, \beta_N) \right\} \langle 0 | a_{\beta_N} \cdots a_{\beta_1} \\
&=\; \sum\!\!\!\!\!\!\int_{\alpha_1} \sum\!\!\!\!\!\!\int_{\beta_1} \left\langle \varphi^{(1)}_{\alpha} \right| A^{(1)}_1 \left| \varphi^{(1)}_{\beta} \right\rangle a^+_{\alpha_1} \\
&\qquad \cdot \left\{ \frac{1}{(N-1)!} \sum\!\!\!\!\!\!\int_{\alpha_2 \cdots \alpha_N} a^+_{\alpha_2} \cdots a^+_{\alpha_N} |0\rangle\langle 0| a_{\alpha_N} \cdots a_{\alpha_2} \right\} a_{\beta_1} \; .
\end{aligned}$$

The curly bracket represents just the identity of the $\mathcal{H}^{(\pm)}_{N-1}$ (8.76). We are therewith left with the remarkably simple final result:

$$\sum_{i=1}^{N} A^{(i)}_1 = \sum\!\!\!\!\!\!\int_{\alpha} \sum\!\!\!\!\!\!\int_{\beta} \langle \varphi_\alpha | A_1 | \varphi_\beta \rangle a^+_\alpha \, a_\beta \; . \tag{8.113}$$

For a given one-particle basis the matrix element is normally easily calculable. One should note that on the right-hand side the particle number N does not explicitly appear. It is hidden in the identity $\mathbb{1}_{N-1}$, which we have to actually insert into the space between a_α^+ and a_β.

Let us now inspect the two-particle part in (8.112). For this we have to calculate the following matrix element, in order to insert it then into (8.111):

$$
\begin{aligned}
&{}^{(\pm)}\langle\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}|\frac{1}{2}\sum_{i,\,j}^{i\neq j}A_2^{(i,\,j)}|\varphi_{\beta_1}\cdots\varphi_{\beta_N}\rangle^{(\pm)}\\
&\overset{(8.59)}{=}\langle\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}|S_N^{(\pm)}\,\frac{1}{2}\sum_{i,\,j}^{i\neq j}A_2^{(i,\,j)}|\varphi_{\beta_1}\cdots\varphi_{\beta_N}\rangle^{(\pm)}\\
&\overset{(8.51),(8.61)}{=}\langle\varphi_{\alpha_1}\cdots\varphi_{\alpha_N}|\frac{1}{2}\sum_{i,\,j}^{i\neq j}A_2^{(i,\,j)}|\varphi_{\beta_1}\cdots\varphi_{\beta_N}\rangle^{(\pm)}\\
&=\frac{1}{2N!}\sum_{\mathcal{P}_\beta}(\pm)^{p_\beta}\,\mathcal{P}_\beta\,\Big[\Big\langle\varphi_{\alpha_1}^{(1)}\Big|\Big\langle\varphi_{\alpha_2}^{(2)}\Big|A_2^{(1,2)}\Big|\varphi_{\beta_1}^{(1)}\Big\rangle\Big|\varphi_{\beta_2}^{(2)}\Big\rangle\\
&\quad\cdot\Big\langle\varphi_{\alpha_3}^{(3)}\Big|\varphi_{\beta_3}^{(3)}\Big\rangle\cdots\Big\langle\varphi_{\alpha_N}^{(N)}\Big|\varphi_{\beta_N}^{(N)}\Big\rangle+\Big\langle\varphi_{\alpha_1}^{(1)}\Big|\Big\langle\varphi_{\alpha_3}^{(3)}\Big|A_2^{(1,3)}\Big|\varphi_{\beta_1}^{(1)}\Big\rangle\Big|\varphi_{\beta_3}^{(3)}\Big\rangle\\
&\quad\cdot\Big\langle\varphi_{\alpha_2}^{(2)}\Big|\varphi_{\beta_2}^{(2)}\Big\rangle\Big\langle\varphi_{\alpha_4}^{(4)}\Big|\varphi_{\beta_4}^{(4)}\Big\rangle\cdots\Big\langle\varphi_{\alpha_N}^{(N)}\Big|\varphi_{\beta_N}^{(N)}\Big\rangle+\cdots\Big]\ .
\end{aligned}
$$

The square bracket contains $N(N-1)$ summands. Exactly the same reasoning as that, which we just presented elaborately for the one-particle part, shows that all $N!$ permutations $\mathcal{P}_\beta$, and also all the $N(N-1)$ terms in the square bracket in (8.111) deliver the same contribution 1. Thereby it is again co-decisive that the particle index only adjusts the correct assignment of the one-particle states. As soon as this assignment has been done, the particle index can of course be omitted. It remains therewith for the two-particle part in (8.111):

$$
\begin{aligned}
&\frac{1}{2}\sum_{i,\,j}^{i\neq j}A_2^{(i,\,j)}\\
&=\frac{1}{2}\sum\!\!\!\!\!\!\int_{\alpha_1,\,\alpha_2}\sum\!\!\!\!\!\!\int_{\beta_1,\,\beta_2}\langle\varphi_{\alpha_1}\,\varphi_{\alpha_2}|A_2^{(1,2)}|\varphi_{\beta_1}\,\varphi_{\beta_2}\rangle\\
&\quad\cdot a_{\alpha_1}^+\,a_{\alpha_2}^+\left\{\frac{1}{(N-2)!}\sum\!\!\!\!\!\!\int_{\alpha_3\ldots\,\alpha_N}a_{\alpha_3}^+\cdots a_{\alpha_N}^+|0\rangle\langle 0|a_{\alpha_N}\cdots a_{\alpha_3}\right\}a_{\beta_2}\,a_{\beta_1}\ .
\end{aligned}
$$

In the curly bracket there stands the identity of the $(N-2)$-particle Hilbert space $\mathcal{H}_{N-2}^{(\pm)}$. We see that also the two-particle operator is formally independent of the particle number:

$$
\frac{1}{2}\sum_{i,\,j}^{i\neq j}A_2^{(i,\,j)}=\frac{1}{2}\sum\!\!\!\!\!\!\int_{\alpha_1\alpha_2\beta_1\beta_2}\langle\varphi_{\alpha_1}\,\varphi_{\alpha_2}|\,A_2^{(1,2)}\,|\varphi_{\beta_1}\,\varphi_{\beta_2}\rangle\,a_{\alpha_1}^+\,a_{\alpha_2}^+\,a_{\beta_2}\,a_{\beta_1}\ . \tag{8.114}
$$

Notice the *β-indexing*, which is at the operators just in the opposite order compared to that in the matrix element. According to our derivation, the latter must be built with non-symmetrized two-particle states. One easily realizes, however, that the four terms which arise, when one takes the (anti)symmetrized states instead, are identical in the four-fold sum (four-fold integral) (8.114), so that the normalization factor $1/(2!)^2$ takes care for the fact that the application of the (anti)symmetrized two-particle state for building the matrix element is equivalent to the application of the non-symmetrized state. One can use, simply according to expedience, for the calculation of the matrix element (anti)symmetrized or non-symmetrized states.

We had found out in Sect. 8.2.5 that in the case of a discrete one-particle basis the *occupation number (Fock) representation* appears to be especially convenient. The creation and annihilation operators fulfill the same fundamental commutation relations (8.109) and (8.110) as the operators of the *general* representation (8.94), (8.99) and (8.100). Even the representation of a general observable A_N is in the Fock space the same as in (8.113) and (8.114), only the matrix elements of the two-particle operator have then to be built in any case with non-symmetrized two-particle states. The reason for this is the special normalization (8.83), which was chosen for the Fock states. But this is really the only difference.

What, in the end, did we achieve? By the introduction of creation and annihilation operators we could replace the troublesome (anti)symmetrizing of the N-particle states by the application of a certain product of these operators to the vacuum state $|0\rangle$. The symmetry requirements, in the last analysis following from the principle of indistinguishability, are accounted for by three simple commutation relations. By this, in particular, the *in principle not allowed (not reasonable)* particle numbering is dropped. The observables also could be expressed by *creators* and *annihilators*. The matrix elements, which *physically characterize* the operator, are in normal cases easily calculable. In addition, they have to be determined only once, fixing the operator then for all times. It turns out to be a special advantage that the complete one-particle basis, for which there exist in general several realizations, can be chosen purely according to convenience.

8.3.3 Special Operators

As a start, we want to exercise the just developed formalism of second quantization by an example of application. Let us consider thereto a system of N identical (spinless) particles with an only distance-dependent pair interaction:

$$V_2^{(i,\,j)} \equiv v\left(\left|\mathbf{r}^{(i)} - \mathbf{r}^{(j)}\right|\right) \ .$$

The Hamilton operator therefore in the *normal* quantum-mechanical formulation reads:

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2} + \frac{1}{2} \sum_{i,j}^{i \neq j} v\left(\left|\mathbf{r}^{(i)} - \mathbf{r}^{(j)}\right|\right) . \tag{8.115}$$

The (continuous) momentum or wave number representation appears to be convenient:

$$|\mathbf{k}\rangle \longleftrightarrow \langle \mathbf{r}|\mathbf{k}\rangle = \frac{1}{(2\pi)^{3/2}} e^{i\,\mathbf{k}\cdot\mathbf{r}} \quad \text{(plane wave)} ,$$

because in this representation the one-particle operator (*kinetic energy*) becomes diagonal. The pre-factor in the plane wave is for continuous wave numbers $\mathbf{k}$ different from that in the case of discrete $\mathbf{k}$-values (*periodic boundary conditions*, (2.38), (2.78), (Vol. 6)). It is chosen such that the one-particle states $|\mathbf{k}\rangle$ are normalized *to δ-functions*:

$$\langle \mathbf{k}'|\mathbf{k}\rangle = \int d^3r \langle \mathbf{k}'|\mathbf{r}\rangle\langle \mathbf{r}|\mathbf{k}\rangle = \frac{1}{(2\pi)^3} \int d^3r\, e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} = \delta(\mathbf{k}' - \mathbf{k}) . \tag{8.116}$$

For the kinetic energy we use the formula (8.113):

$$\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} = \iint d^3k\, d^3k' \langle \mathbf{k}|\frac{\mathbf{p}^2}{2m}|\mathbf{k}'\rangle a_{\mathbf{k}'}^{+} a_{\mathbf{k}} .$$

The matrix element is quickly calculated:

$$\langle \mathbf{k}|\frac{\mathbf{p}^2}{2m}|\mathbf{k}'\rangle = \frac{\hbar^2\mathbf{k}'^2}{2m} \langle \mathbf{k}|\mathbf{k}'\rangle = \frac{\hbar^2\mathbf{k}'^2}{2m} \delta(\mathbf{k} - \mathbf{k}') .$$

The one-particle part of the Hamilton operator (8.115) therewith reads:

$$\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} = \int d^3k \frac{\hbar^2\mathbf{k}^2}{2m} a_{\mathbf{k}}^{+} a_{\mathbf{k}} . \tag{8.117}$$

The interaction-matrix element must be calculated of course also in the one-particle basis $\{|\mathbf{k}\rangle\}$. The position representation would actually be more convenient. We therefore insert at *proper* positions the identity in the form

$$\mathbb{1}_1 = \int d^3r |\mathbf{r}\rangle\langle \mathbf{r}| ; \tag{8.118}$$

a *trick*, which we have already used for the calculation of (8.116):

$$\begin{aligned}
&\langle \mathbf{k}_1\,\mathbf{k}_2|\, V_2^{(1,2)}\,|\mathbf{k}_3\,\mathbf{k}_4\rangle \;=\; \left\langle \mathbf{k}_1^{(1)}\right| \left\langle \mathbf{k}_2^{(2)}\right| V_2^{(1,2)} \left|\mathbf{k}_3^{(1)}\right\rangle \left|\mathbf{k}_4^{(2)}\right\rangle \\
&= \int\cdots\int d^3r_1\cdots d^3r_4\, \left(\left\langle \mathbf{k}_1^{(1)}\right|\left.\mathbf{r}_1^{(1)}\right\rangle \left\langle \mathbf{r}_1^{(1)}\right|\right) \\
&\quad\cdot \left(\left\langle \mathbf{k}_2^{(2)}\right|\left.\mathbf{r}_2^{(2)}\right\rangle \left\langle \mathbf{r}_2^{(2)}\right|\right) V_2^{(1,2)} \left(\left|\mathbf{r}_3^{(1)}\right\rangle \left\langle \mathbf{r}_3^{(1)}\right|\left.\mathbf{k}_3^{(1)}\right\rangle\right) \left(\left|\mathbf{r}_4^{(2)}\right\rangle \left\langle \mathbf{r}_4^{(2)}\right|\left.\mathbf{k}_4^{(2)}\right\rangle\right) \\
&= \int\cdots\int d^3r_1\cdots d^3r_4\; v\,(|\mathbf{r}_3-\mathbf{r}_4|) \left\langle \mathbf{k}_1^{(1)}\right|\left.\mathbf{r}_1^{(1)}\right\rangle \\
&\quad\cdot \left\langle \mathbf{k}_2^{(2)}\right|\left.\mathbf{r}_2^{(2)}\right\rangle \left\langle \mathbf{r}_3^{(1)}\right|\left.\mathbf{k}_3^{(1)}\right\rangle \left\langle \mathbf{r}_4^{(2)}\right|\left.\mathbf{k}_4^{(2)}\right\rangle \left\langle \mathbf{r}_1^{(1)}\right|\left.\mathbf{r}_3^{(1)}\right\rangle \left\langle \mathbf{r}_2^{(2)}\right|\left.\mathbf{r}_4^{(2)}\right\rangle \\
&= \iint d^3r_1\, d^3r_2\; v\,(|\mathbf{r}_1-\mathbf{r}_2|)\; (2\pi)^{-6}\, e^{i(\mathbf{k}_3-\mathbf{k}_1)\cdot\mathbf{r}_1}\, e^{i(\mathbf{k}_4-\mathbf{k}_2)\cdot\mathbf{r}_2}\;.
\end{aligned}$$

The further evaluation recommends the transition to relative and center-of-mass coordinates,

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2\;; \quad \mathbf{R} = \frac{1}{2}\,(\mathbf{r}_1+\mathbf{r}_2)\;,$$

which with the representation (8.116) of the δ-function leads to

$$\langle \mathbf{k}_1\,\mathbf{k}_2|V_2^{(1,2)}|\mathbf{k}_3\,\mathbf{k}_4\rangle = v(\mathbf{k}_1-\mathbf{k}_3)\,\delta(\mathbf{k}_1-\mathbf{k}_3+\mathbf{k}_2-\mathbf{k}_4)\;.$$

It is thereby

$$v(\mathbf{q}) = \frac{1}{(2\pi)^3}\int d^3r\; v(\mathbf{r})\; e^{i\,\mathbf{q}\cdot\mathbf{r}} = v(-\mathbf{q}) \tag{8.119}$$

the Fourier transform of the interaction potential. With the substitutions

$$\mathbf{k}_1 \to \mathbf{k}+\mathbf{q}\;; \quad \mathbf{k}_2 \to \mathbf{p}-\mathbf{q}\;; \quad \mathbf{k}_3 \to \mathbf{k}\;; \quad \mathbf{k}_4 \to \mathbf{p}$$

it eventually comes out as interaction operator:

$$\frac{1}{2}\sum_{i,\,j}^{i\neq j} V_2^{(i,\,j)} = \frac{1}{2}\iiint d^3k\, d^3p\, d^3q\; v(\mathbf{q}) a^+_{\mathbf{k}+\mathbf{q}}\, a^+_{\mathbf{p}-\mathbf{q}}\, a_{\mathbf{p}}\, a_{\mathbf{k}}\;. \tag{8.120}$$

The operator combination describes *illustratively* the interaction process as an *annihilation* of two particles with the wave numbers $\mathbf{p}$ and $\mathbf{k}$ (*incoming* arrows in Fig. 8.3) and subsequent *creation* of two particles with the wave numbers $\mathbf{k}+\mathbf{q}$ and $\mathbf{p}-\mathbf{q}$ (*outgoing* arrows in Fig. 8.3). The momentum $\hbar\,\mathbf{q}$ is thereby exchanged and the interaction energy $v(\mathbf{q})$ expended. (The *discrete* analog to (8.120) is calculated as Exercise 8.3.7!)

At the end of this subsection we will introduce some special operators, which are typical for the formalism of second quantization.

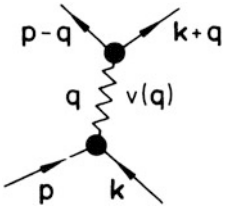

Figure 8.3: Representation of an interaction process by annihilation (*incoming arrows*) and creation (*outgoing arrows*) of two particles with momentum and energy exchange

1) Occupation density operator

$$\hat{n}_\alpha = a_\alpha^+ \, a_\alpha \; . \tag{8.121}$$

A **continuous** one-particle basis (e.g. position-eigen states) is presumed. The mode of action results from (8.92) and (8.97):

$$\begin{aligned}
&\hat{n}_\alpha |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(\pm)} = \\
&= \Big[\delta(\alpha - \alpha_1)|\varphi_\alpha \, \varphi_{\alpha_2} \cdots\rangle^{(\pm)} + \\
&\quad + (\pm)^1 \, \delta(\alpha - \alpha_2)|\varphi_\alpha \, \varphi_{\alpha_1} \, \varphi_{\alpha_3} \cdots\rangle^{(\pm)} \; + \\
&\quad + \ldots + \\
&\quad + (\pm)^{N-1} \, \delta(\alpha - \alpha_N)|\varphi_\alpha \, \varphi_{\alpha_1} \, \varphi_{\alpha_2} \cdots \varphi_{\alpha_{N-1}}\rangle^{(\pm)}\Big] = \\
&= \left[\sum_{i=1}^{N} \delta(\alpha - \alpha_i)\right] |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(\pm)} \; .
\end{aligned} \tag{8.122}$$

(Note that we interchanged in the second line φ_α into the second position with a factor $(\pm)^1$. In the fifth line we brought φ_α to the Nth position with a factor $(\pm)^{N-1}$.) The basis states of the $\mathcal{H}_N^{(\pm)}$ are eigen-states of the *occupation density operator* $\hat{n}_\alpha$. The corresponding eigen-value is the *microscopic occupation density* $\sum_{i=1}^{N} \delta(\alpha - \alpha_i)$.

2) Occupation number operator

$$\hat{n}_{\alpha_r} = a_{\alpha_r}^+ \, a_{\alpha_r} \; . \tag{8.123}$$

This operator is for the case of a **discrete** one-particle basis the analog to (8.121). The Fock states (8.83) are eigen-states, where one finds according to (8.103) and (8.107):

$$\hat{n}_{\alpha_r} |N; \cdots n_{\alpha_r} \cdots\rangle^{(\pm)} = n_{\alpha_r} |N; \cdots n_{\alpha_r} \cdots\rangle^{(\pm)} \; . \tag{8.124}$$

The occupation number n_{α_r} appears as eigen-value.

3) Particle number operator

$$\widehat{N} = \int d\alpha\, \hat{n}_\alpha \quad \text{(continuous)} \tag{8.125}$$

$$= \sum_r \hat{n}_{\alpha_r} \quad \text{(discrete)} . \tag{8.126}$$

$\widehat{N}$ has obviously the same eigen-states as $\hat{n}_\alpha$ and $\hat{n}_{\alpha_r}$, respectively. The eigenvalue is in both cases the particle number N:

$$N = \int d\alpha \sum_{i=1}^{N} \delta(\alpha - \alpha_i) \quad \text{(continuous)}$$

$$= \sum_r n_{\alpha_r} \quad \text{(discrete)} .$$

8.3.4 Exercises

Exercise 8.3.1
Prove the fundamental commutation relations,

$$[a_{\alpha_r}, a_{\alpha_s}]_\mp = [a^+_{\alpha_r}, a^+_{\alpha_s}]_\mp = 0 ,$$
$$[a_{\alpha_r}, a^+_{\alpha_s}]_\mp = \delta_{rs} ,$$

for creation and annihilation operators in the *discrete* Fock space ((8.109) and (8.110)).

Exercise 8.3.2
Let $|0\rangle$ be the normalized vacuum state, and a^+_α and a_α creation and annihilation operators for a particle in the one-particle state $|\varphi_\alpha\rangle$. By the use of the fundamental commutation relations derive the expression:

$$\langle 0|a_{\beta_N} \cdots a_{\beta_1}\, a^+_{\alpha_1} \cdots a^+_{\alpha_N}|0\rangle = \sum_{\mathcal{P}_\alpha} (\pm)^{p_\alpha}\, \mathcal{P}_\alpha\, [\delta(\beta_1, \alpha_1) \cdots \delta(\beta_N, \alpha_N)]$$

$\mathcal{P}_\alpha$ is the permutation operator which acts on the state-indexes α_i.

Exercise 8.3.3
For the occupation density operator calculate the commutators:

$$1) \quad [\hat{n}_\alpha, a^+_\beta]_- ; \qquad 2) \quad [\hat{n}_\alpha, a_\beta]_- .$$

Are there differences for bosons and fermions?

Exercise 8.3.4
For the occupation number operator calculate the commutators:

$$1) \quad [\hat{n}_{\alpha_r}, a^+_{\alpha_s}]_- ; \qquad 2) \quad [\hat{n}_{\alpha_r}, a_{\alpha_s}]_- .$$

Are there differences for bosons and fermions?

Exercise 8.3.5
For fermions show that the following relations are valid:

1.
$$(a_\alpha)^2 = 0 \;\; ; \;\; \left(a_\alpha^+\right)^2 = 0$$

2.
$$(\hat{n}_\alpha)^2 = \hat{n}_\alpha$$

3.
$$a_\alpha \, \hat{n}_\alpha = a_\alpha \;\; ; \;\; a_\alpha^+ \, \hat{n}_\alpha = 0$$

4.
$$\hat{n}_\alpha \, a_\alpha = 0 \;\; ; \;\; \hat{n}_\alpha \, a_\alpha^+ = a_\alpha^+ \; .$$

Exercise 8.3.6
The (anti)symmetrized basis states $|\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(\pm)}$ of the $\mathcal{H}_N^{(\pm)}$ are constructed from *continuous* one-particle basis states. They are eigen-states of the particle number operator $\widehat{N}$. Show that then

$$1) \quad a_\beta^+ |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(\pm)} \; ; \qquad 2) \quad a_\beta |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(\pm)}$$

are also eigen-states of $\widehat{N}$, and calculate the eigen-values!

Exercise 8.3.7
N electrons in the volume $V = L^3$ exert on each other the Coulomb interaction:

$$V_2 = \frac{1}{2} \sum_{i,\,j}^{i \neq j} V_2^{(i,\,j)} \; ; \quad V_2^{(i,\,j)} = \frac{e^2}{4\pi \, \varepsilon_0} \, \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|}$$

$\hat{\mathbf{r}}_i$, $\hat{\mathbf{r}}_j$ are the position operators of the ith and the jth electron, respectively. Formulate the Hamilton operator of the system in second quantization. Use as one-particle basis plane waves with discrete wave vectors $\mathbf{k}$ due to periodic boundary conditions on $V = L^3$.

Exercise 8.3.8
For a system of N electrons the operator of the electron density is given by

$$\widehat{\rho}(\mathbf{r}) = \sum_{i\,=\,1}^{N} \delta(\mathbf{r} - \hat{\mathbf{r}}_i) \; .$$

($\widehat{\rho}$ and $\hat{\mathbf{r}}_i$ are operators, while $\mathbf{r}$ is as a variable a so-called c-number, i.e., not an operator.) How does $\widehat{\rho}(\mathbf{r})$ read in second quantization? Use, as in Exercise 8.3.7, as one-particle basis plane waves with discrete wave vectors $\mathbf{k}$.

Exercise 8.3.9
For the construction of the states and the observables of an N electron system one uses as one-particle basis that of the noninteraction system:

$$\begin{aligned} |\mathbf{k}\sigma\rangle &= |\mathbf{k}\rangle\,|\sigma\rangle \quad ; \quad \mathbf{k}: \text{ discrete wave number} \\ |\uparrow\rangle &= \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad |\downarrow\rangle = \begin{pmatrix} 0 \end{pmatrix} . \end{aligned}$$

Find therewith the following operators in second quantization:

1. Total momentum;

$$\mathbf{P} = \sum_{i=1}^{N} \mathbf{p}_i$$

2. Total spin (x-component)

$$S^x = \sum_{i=1}^{N} s_i^x$$

3. Calculate with the results from 1. and 2. the commutator

$$[S^x, \mathbf{P}]_- \ .$$

Exercise 8.3.10
Show that the Hamilton operator of the interacting N-electron system, calculated in Exercise 8.3.7,

$$H_N = \sum_{\mathbf{k}\sigma} \varepsilon_0(\mathbf{k})\, a^+_{\mathbf{k}\sigma}\, a_{\mathbf{k}\sigma} + \frac{1}{2} \sum_{\substack{\mathbf{k},\mathbf{p},\mathbf{q} \\ \sigma\sigma'}} v_0(\mathbf{q})\, a^+_{\mathbf{k}+\mathbf{q}\sigma}\, a^+_{\mathbf{p}-\mathbf{q}\sigma'}\, a_{\mathbf{p}\sigma'}\, a_{\mathbf{k}\sigma}$$

commutes with the particle number operator,

$$\widehat{N} = \sum_{\mathbf{k}\sigma} a^+_{\mathbf{k}\sigma}\, a_{\mathbf{k}\sigma} \ .$$

What does that physically mean?

Exercise 8.3.11
$a^+_{i\sigma}$ and $a_{i\sigma}$ are the creation and annihilation operators of an electron with spin σ ($\sigma = \uparrow, \downarrow$) at the lattice site $\mathbf{R}_i$. The commutation relations for fermions (8.109), (8.110) are valid:

$$\left[a^+_{i\sigma},\, a_{j\sigma'}\right]_+ = \left[a^+_{i\sigma},\, a^+_{j\sigma'}\right]_+ = 0 \qquad \left[a_{i\sigma},\, a^+_{j\sigma'}\right]_+ = \delta_{ij}\delta_{\sigma\sigma'} \ .$$

Show that by

$$\begin{aligned} S_i^z &= \frac{\hbar}{2}\,(n_{i\uparrow} - n_{i\downarrow}) \quad ; \quad n_{i\sigma} = a_{i\sigma}^+ a_{i\sigma} \\ S_i^+ &= \hbar\, a_{i\uparrow}^+ a_{i\downarrow} \\ S_i^- &= \hbar\, a_{i\downarrow}^+ a_{i\uparrow} \end{aligned}$$

'quite normal' spin operators are defined. For this purpose, verify the commutation relations for spin operators!

8.4 Applications

We want to demonstrate in this section by a few concrete examples of application the impact of the principle of indistinguishability. We begin with the derivation of the so-called **Hartree-Fock equations**, which must be reckoned practically important, numerically evaluable basic equations for the determination of the electron distributions in atoms, molecules, and solids. Subsequently we inspect two relatively simple, but revealing two-electron systems, namely the hydrogen molecule and the helium atom. Thereby we will get to know the so-called **exchange interaction**, upon which important phenomena are based such as the *chemical bond* or the entire field of *magnetism*.

8.4.1 Hartree-Fock Equations

As an example of application of the *variational procedure* we have derived the Hartree equations in Sect. 7.1.3. They serve to fix optimal one-particle states for the description of many-particle systems. The Hartree-Fock equations, which we will now derive, fulfill the same purpose, but start with a physically more correct ansatz. To be concrete we will in this subsection think of a **many-electron atom**, whose Hamilton operator

$$H_N = \sum_{i=1}^{N} H_1^{(i)} + \frac{1}{2} \sum_{i,\,j}^{i \neq j} H_2^{(i,\,j)} \tag{8.127}$$

is composed by a one-particle operator, which incorporates the kinetic energy of the electrons and their potential energy in the Coulomb field of the Z-fold positively charged nucleus,

$$H_1^{(i)} = \frac{\mathbf{p}_i^2}{2m} - \frac{Z\,e^2}{4\pi\,\varepsilon_0\,r_i}\,, \tag{8.128}$$

and a two-particle part, which represents the Coulomb repulsion of the shell electrons among each other:

$$H_2^{(i,\,j)} = \frac{e^2}{4\pi\,\varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|}\,. \tag{8.129}$$

$\mathbf{r}_i$, $\mathbf{r}_j$ are the electron positions. Let the origin of coordinates coincide with the position of the nucleus, which is assumed to be point-like and *at rest*. We neglect all spin-dependent effects, in particular the *spin-orbit interaction*. For the *Hartree procedure* in Sect. 7.1.3 we had chosen as *test wave function* for the N-electron system a simple product ansatz of N one-particle wave functions (7.18). In the meantime we have learned how systems of identical particles are to be correctly treated, and we know therefore that the product ansatz does not comply with the necessary symmetry requirements. Electrons as fermions are to be described by antisymmetrized states. That is the new aspect of the Hartree-Fock procedure, which also uses the variational method, but applies Slater determinants (8.77) as *test functionals* $|\mathrm{HF}\rangle^{(-)}$ for the to be varied one-particle states, in order to bring into play from the beginning the correct symmetry:

$$|\mathrm{HF}\rangle^{(-)} = \frac{1}{\sqrt{N!}} \sum_{\mathcal{P}} (-1)^p \, \mathcal{P} \left(\left|\varphi_{\alpha_1}^{(1)}\right\rangle \left|\varphi_{\alpha_2}^{(2)}\right\rangle \cdots \left|\varphi_{\alpha_N}^{(N)}\right\rangle \right) . \tag{8.130}$$

This state is, according to (8.82), already suitably normalized. The sets of quantum numbers α_i now contain in particular the projection ($\sigma = \uparrow$ or $\downarrow$) of the electron spin:

$$|\varphi_\alpha\rangle \longleftrightarrow \begin{pmatrix} |\varphi_{\nu\uparrow}\rangle \\ |\varphi_{\nu\downarrow}\rangle \end{pmatrix} . \tag{8.131}$$

The task now is, as in the Hartree procedure, to find optimal one-particle states $|\varphi_{\alpha_i}\rangle$, which we will presume are orthonormalized:

$$\langle \varphi_{\alpha_i} | \varphi_{\alpha_j} \rangle = \delta_{ij} . \tag{8.132}$$

This is a constraint, which we will include later into the variational procedure by means of *Lagrange multipliers* (Sect. 1.2.6, Vol. 2). Initially, however, one has to calculate the functional

$$\langle H_N \rangle_{\mathrm{HF}} = \frac{{}^{(-)}\langle \mathrm{HF} | H_N | \mathrm{HF} \rangle^{(-)}}{{}^{(-)}\langle \mathrm{HF} | \mathrm{HF} \rangle^{(-)}} = {}^{(-)}\langle \mathrm{HF} | H_N | \mathrm{HF} \rangle^{(-)} . \tag{8.133}$$

in order to vary it then with respect to the one-particle states.

We determine at first the contribution of the one-particle part in the Hamilton operator (8.127):

$$\begin{aligned} &{}^{(-)}\langle \mathrm{HF} | \sum_i H_1^{(i)} | \mathrm{HF} \rangle^{(-)} \\ &\quad = \frac{1}{N!} \sum_{\mathcal{P}\,\mathcal{P}'} (-1)^{p+p'} \, \langle \varphi_{\alpha_1} \cdots \varphi_{\alpha_N} | \mathcal{P}^+ \sum_i H_1^{(i)} \mathcal{P}' | \varphi_{\alpha_1} \cdots \varphi_{\alpha_N} \rangle . \end{aligned}$$

To the double sum only the terms $\mathcal{P}' = \mathcal{P}$ contribute, since the one-particle states are orthogonal and each of them appears exactly once in the N-particle

state. For $\mathcal{P}' \neq \mathcal{P}$ there exists at least one scalar product with $\langle \varphi_{\alpha_\mu}^{(j)} | \varphi_{\alpha_\nu}^{(j)} \rangle = 0$ because of $\mu \neq \nu$:

$$ {}^{(-)}\langle \mathrm{HF}| \sum_i H_1^{(i)} |HF\rangle^{(-)} = \sum_i \frac{1}{N!} \sum_{\mathcal{P}} \langle \varphi_{\alpha_1} \cdots \varphi_{\alpha_N} | \mathcal{P}^+ H_1^{(i)} \mathcal{P} | \varphi_{\alpha_1} \cdots \varphi_{\alpha_N} \rangle \, . $$

The $(N-1)!$ permutations, which let the ith particle fixed, but permute the $(N-1)$ others, deliver the same contribution:

$$ {}^{(-)}\langle \mathrm{HF}| \sum_i H_1^{(i)} |\mathrm{HF}\rangle^{(-)} = \frac{(N-1)!}{N!} \sum_i \sum_{\mu=1}^{N} \left\langle \varphi_{\alpha_\mu}^{(i)} \right| H_1^{(i)} \left| \varphi_{\alpha_\mu}^{(i)} \right\rangle \, . $$

We can now exploit again the equivalence of the one-particle Hilbert spaces getting therewith the remarkable result that the summation over the particle indexes is replaced by a summation over the different one-particle states, which appear in the Slater determinant $|\mathrm{HF}\rangle^{(-)}$, where only *one-particle expectation values* remain to be calculated:

$$ {}^{(-)}\langle \mathrm{HF}| \sum_{i=1}^{N} H_1^{(i)} |\mathrm{HF}\rangle^{(-)} = \sum_{\mu=1}^{N} \left\langle \varphi_{\alpha_\mu}^{(1)} \right| H_1^{(1)} \left| \varphi_{\alpha_\mu}^{(1)} \right\rangle \, . \tag{8.134} $$

The particle-indexing on the right-hand side has, of course, actually become redundant.

In the same manner we now treat the two-particle term in the Hamilton operator (8.127):

$$ \begin{aligned} &{}^{(-)}\langle \mathrm{HF}| \frac{1}{2} \sum_{i,j}^{i \neq j} H_2^{(i,j)} |\mathrm{HF}\rangle^{(-)} \\ &\quad = \frac{1}{2} \sum_{i,j}^{i \neq j} \frac{1}{N!} \sum_{\mathcal{P},\mathcal{P}'} (-1)^{p+p'} \langle \varphi_{\alpha_1} \cdots | \mathcal{P}^+ H_2^{(i,j)} \mathcal{P}' | \varphi_{\alpha_1} \cdots \rangle \, . \end{aligned} $$

Because of (8.132) only the permutations $\mathcal{P}' = \mathcal{P}$ and $\mathcal{P}' = P_{ij}\,\mathcal{P}$ yield contributions unequal zero. For the number of transpositions in $\mathcal{P}'$ only $p' = p$ or $p' = p \pm 1$ are then possible:

$$ \begin{aligned} &{}^{(-)}\langle \mathrm{HF}| \frac{1}{2} \sum_{i,j}^{i \neq j} H_2^{(i,j)} |\mathrm{HF}\rangle^{(-)} \\ &= \frac{1}{2} \sum_{i,j}^{i \neq j} \frac{1}{N!} \sum_{\mathcal{P}} \Big\{ \langle \varphi_{\alpha_1} \cdots | \mathcal{P}^+ H_2^{(i,j)} \mathcal{P} | \varphi_{\alpha_1} \cdots \rangle \\ &\quad - \langle \varphi_{\alpha_1} \cdots | \mathcal{P}^+ H_2^{(i,j)} P_{ij} \mathcal{P} | \varphi_{\alpha_1} \cdots \rangle \Big\} \\ &= \frac{1}{2N(N-1)} \sum_{i,j}^{i \neq j} \sum_{\nu,\mu=1}^{N} \Big\{ \left\langle \varphi_{\alpha_\nu}^{(i)} \, \varphi_{\alpha_\mu}^{(j)} \right| H_2^{(i,j)} \left| \varphi_{\alpha_\nu}^{(i)} \, \varphi_{\alpha_\mu}^{(j)} \right\rangle \\ &\quad - \left\langle \varphi_{\alpha_\nu}^{(i)} \, \varphi_{\alpha_\mu}^{(j)} \right| H_2^{(i,j)} \left| \varphi_{\alpha_\nu}^{(j)} \, \varphi_{\alpha_\mu}^{(i)} \right\rangle \Big\} \, . \end{aligned} $$

In the last step we have exploited, analogous to the line of thought which led to (8.134), that the $(N-2)!$ permutations $\mathcal{P}$, which keep the particles i and j fixed, lead to identical summands. In the curly bracket there are non-symmetrized two-particle states, whose contributions of course do not really depend on the particle-indexes i and j. The expression can therefore be further simplified:

$$
\begin{aligned}
&{}^{(-)}\langle \mathrm{HF}| \frac{1}{2} \sum_{i,\,j}^{i\neq j} H_2^{(i,\,j)} |\mathrm{HF}\rangle^{(-)} \qquad (8.135)\\
&= \frac{1}{2} \sum_{\nu,\,\mu}^{\nu\neq\mu} \left\{ \left\langle \varphi_{\alpha_\nu}^{(1)}\, \varphi_{\alpha_\mu}^{(2)} \right| H_2^{(1,2)} \left| \varphi_{\alpha_\nu}^{(1)}\, \varphi_{\alpha_\mu}^{(2)} \right\rangle - \left\langle \varphi_{\alpha_\nu}^{(1)}\, \varphi_{\alpha_\mu}^{(2)} \right| H_2^{(1,2)} \left| \varphi_{\alpha_\nu}^{(2)}\, \varphi_{\alpha_\mu}^{(1)} \right\rangle \right\} .
\end{aligned}
$$

With (8.134) and (8.135) the functional $\langle H_N\rangle_{\mathrm{HF}}$ is calculated. The further evaluation is then conveniently performed by using the **position representation**, where, however, the electron spin must now be taken into account. Since the spin-orbit interaction remains out of consideration, spin and position parts will factorize in the basis states:

$$
|\mathbf{r}\, m_s\rangle \;=\; |\mathbf{r}\rangle |m_s\rangle \;,
$$

$$
\left| m_s = +\frac{1}{2} \right\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad ; \qquad \left| m_s = -\frac{1}{2} \right\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} .
$$

It follows with (8.131) for the one-particle state $|\varphi_\alpha\rangle$ in the *position representation*:

$$
\begin{aligned}
\langle \mathbf{r}\, m_s|\varphi_\alpha\rangle &\equiv \varphi_{\nu\sigma}(\mathbf{r})\, \delta_{\sigma\, m_s} \;; \quad \alpha = (\nu,\sigma) \;, && (8.136)\\
\langle \mathbf{r}|\varphi_{\nu\sigma}\rangle &\equiv \varphi_{\nu\sigma}(\mathbf{r}) \;; \quad \sigma = \uparrow, \downarrow \;. && (8.137)
\end{aligned}
$$

The identity in the one-particle Hilbert space can then be written in the basis $\{|\mathbf{r}\, m_s\rangle\}$ as:

$$
\mathbb{1}_1 = \sum_{m_s} \int d^3r |\mathbf{r}\, m_s\rangle\langle \mathbf{r}\, m_s| \;. \qquad (8.138)
$$

We reformulate (8.134) by a suitable *inserting of the identity* ($\alpha_\mu \equiv (\mu,\sigma_\mu)$):

$$
\begin{aligned}
\langle \varphi_{\alpha_\mu}|H_1|\varphi_{\alpha_\mu}\rangle &= \sum_{m_s} \int d^3r \langle \varphi_{\alpha_\mu}|\mathbf{r}\, m_s\rangle\langle \mathbf{r}\, m_s|H_1|\varphi_{\alpha_\mu}\rangle \\
&= \int d^3r\, \langle \varphi_{\mu\,\sigma_\mu}|\mathbf{r}\rangle\langle \mathbf{r}|H_1|\varphi_{\mu\,\sigma_\mu}\rangle \\
&= \int d^3r\, \varphi^*_{\mu\,\sigma_\mu}(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\Delta - \frac{Z\,e^2}{4\pi\,\varepsilon_0 r} \right) \varphi_{\mu\,\sigma_\mu}(\mathbf{r}) \;.
\end{aligned}
$$

Here we have at first used that H_1 is spin-independent, and then we switched into the position representation *according to the general rule* (see (3.253), Vol. 6).

The matrix elements in (8.135) are rearranged in the same manner:

$$\begin{aligned}
&\left\langle \varphi^{(1)}_{\alpha_\nu}\,\varphi^{(2)}_{\alpha_\mu}\right| H_2^{(1,2)} \left|\varphi^{(1)}_{\alpha_\nu}\,\varphi^{(2)}_{\alpha_\mu}\right\rangle \\
&= \sum_{m_s}\sum_{m_s'} \iint d^3r\, d^3r' \left\langle \varphi^{(1)}_{\alpha_\nu}\,\varphi^{(2)}_{\alpha_\mu}\right| (\mathbf{r}\, m_s)^{(1)}\,(\mathbf{r}'\, m_s')^{(2)}\Big\rangle \\
&\quad \cdot \left\langle (\mathbf{r}\, m_s)^{(1)}\,(\mathbf{r}'\, m_s')^{(2)}\right| H_2^{(1,2)} \left|\varphi^{(1)}_{\alpha_\nu}\,\varphi^{(2)}_{\alpha_\mu}\right\rangle \\
&= \iint d^3r\, d^3r'\, \varphi^*_{\nu\,\sigma_\nu}(\mathbf{r})\,\varphi^*_{\mu\sigma_\mu}(\mathbf{r}')\,\frac{e^2}{4\pi\,\varepsilon_0|\mathbf{r}-\mathbf{r}'|}\,\varphi_{\nu\,\sigma_\nu}(\mathbf{r})\,\varphi_{\mu\,\sigma_\mu}(\mathbf{r}')\,.
\end{aligned}$$

Completely analogously one finds for the second summand in (8.135):

$$\begin{aligned}
&\left\langle \varphi^{(1)}_{\alpha_\nu}\,\varphi^{(2)}_{\alpha_\mu}\right| H_2^{(1,2)} \left|\varphi^{(2)}_{\alpha_\nu}\,\varphi^{(1)}_{\alpha_\mu}\right\rangle \\
&= \delta_{\sigma_\nu\sigma_\mu} \iint d^3r\, d^3r'\, \varphi^*_{\nu\,\sigma_\nu}(\mathbf{r})\,\varphi^*_{\mu\,\sigma_\mu}(\mathbf{r}')\,\frac{e^2}{4\pi\,\varepsilon_0|\mathbf{r}-\mathbf{r}'|}\,\varphi_{\nu\,\sigma_\nu}(\mathbf{r}')\,\varphi_{\mu\,\sigma_\mu}(\mathbf{r})\,.
\end{aligned}$$

The Kronecker delta for the spin variable results, because of (8.136), from the *particle interchange* in the ket-state. It concerns here obviously an interaction exclusively between electrons with **parallel** spins.

All in all we have found for the energy functional (8.133) the following expression:

$$\begin{aligned}
\langle H_N\rangle_{\mathrm{HF}} \;=\; &\sum_{\mu\sigma}\int d^3r\,\varphi^*_{\mu\sigma}(\mathbf{r})\left(-\frac{\hbar^2}{2m}\Delta - \frac{Z\,e^2}{4\pi\,\varepsilon_0 r}\right)\varphi_{\mu\sigma}(\mathbf{r}) \\
&+\frac{1}{2}\,\frac{e^2}{4\pi\,\varepsilon_0}\sum_{\substack{\mu,\nu\\ \sigma,\sigma'}}^{(\mu,\sigma)\neq(\nu,\sigma')} \iint d^3r\, d^3r'\,\varphi^*_{\mu\sigma}(\mathbf{r})\,\varphi^*_{\nu\sigma'}(\mathbf{r}')\,\frac{1}{|\mathbf{r}-\mathbf{r}'|} \\
&\cdot\big(\varphi_{\mu\sigma}(\mathbf{r})\,\varphi_{\nu\sigma'}(\mathbf{r}') - \delta_{\sigma\sigma'}\,\varphi_{\mu\sigma'}(\mathbf{r}')\,\varphi_{\nu\sigma}(\mathbf{r})\big)\,. \qquad (8.139)
\end{aligned}$$

Together with the still to be respected constraints (8.132) we have now to vary this relation with respect to the one-particle wave functions and to put the first variation equal to zero:

$$\delta\Big(\langle H_N\rangle_{\mathrm{HF}} - \sum_{\substack{\mu\nu\\ \sigma}}\varepsilon_{\mu\nu\sigma}\int d^3r\,\varphi^*_{\mu\sigma}(\mathbf{r})\,\varphi_{\nu\sigma}(\mathbf{r})\Big) \stackrel{!}{=} 0\,.$$

The $\varepsilon_{\mu\nu\sigma}$ are **Lagrange multipliers**. The performance of the procedure follows exactly the same line as for the Hartree equations (7.22). We can therefore restrict ourselves here simply to present the results:

Hartree-Fock equations

$$\begin{aligned}
&\left(-\frac{\hbar^2}{2m}\,\Delta - \frac{Z\,e^2}{4\pi\,\varepsilon_0 r}\right)\varphi_{\mu\sigma}(\mathbf{r}) + \frac{e^2}{4\pi\,\varepsilon_0}\sum_{\nu,\sigma'}^{(\mu\sigma)\neq(\nu\sigma')}\int d^3r'\,\varphi^*_{\nu\sigma'}(\mathbf{r}')\,\frac{1}{|\mathbf{r}-\mathbf{r}'|} \\
&\cdot\big(\varphi_{\mu\sigma}(\mathbf{r})\varphi_{\nu\sigma'}(\mathbf{r}') - \delta_{\sigma\sigma'}\,\varphi_{\mu\sigma'}(\mathbf{r}')\,\varphi_{\nu\sigma}(\mathbf{r})\big) - \sum_{\nu}\varepsilon_{\mu\nu\sigma}\,\varphi_{\nu\sigma}(\mathbf{r}) \stackrel{!}{=} 0\,. \qquad (8.140)
\end{aligned}$$

It is common to diagonalize the last term by a suitable unitary transformation,

$$\varepsilon_{\mu\nu\sigma} \xrightarrow{U} \varepsilon_{\mu\sigma}\,\delta_{\mu\nu}\ ,$$

whereby of course also the wave functions $\varphi_{\nu\sigma}(\mathbf{r})$ transform into corresponding linear combinations. Since we do not have these functions to our disposal yet, and actually intend to determine them, we still utilize the same letter for them. That yields the following, more frequently used form of the

Hartree-Fock equations

$$\Big[-\frac{\hbar^2}{2m}\Delta - \frac{Z\,e^2}{4\pi\,\varepsilon_0 r} + \frac{e^2}{4\pi\,\varepsilon_0}\sum_{\nu,\sigma'}^{(\mu\sigma)\neq(\nu\sigma')}\int d^3r'\,\frac{|\varphi_{\nu\sigma'}(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} - \widehat{A}_{\mu\sigma}(\mathbf{r})\Big]\,\varphi_{\mu\sigma}(\mathbf{r}) = \varepsilon_{\mu\sigma}\,\varphi_{\mu\sigma}(\mathbf{r})\ . \tag{8.141}$$

The Hartree-Fock equations differ from the Hartree equations (7.22) by the so-called **exchange term**

$$\widehat{A}_{\mu\sigma}(\mathbf{r}) = \sum_{\nu}^{\nu\neq\mu}\int d^3r'\,\frac{e^2}{4\pi\,\varepsilon_0|\mathbf{r}-\mathbf{r}'|}\,\frac{\varphi^*_{\nu\sigma}(\mathbf{r}')\varphi_{\mu\sigma}(\mathbf{r}')\,\varphi_{\nu\sigma}(\mathbf{r})}{\varphi_{\mu\sigma}(\mathbf{r})}\ , \tag{8.142}$$

which is exclusively caused by electrons, whose spins are parallel to that of the singled out (μ,σ)-electron. One denotes this term as **non-local** because there appears in the integrand $\varphi_{\mu\sigma}$ with the argument $\mathbf{r}' \neq \mathbf{r}$. Not the least of this fact, the integral-differential equations (8.141) are in general analytically unsolvable. For realistic problems one needs a powerful computer.

The *Hartree-Fock equations* have the form of eigen-value equations for the Lagrange multipliers $\varepsilon_{\mu\sigma}$ and the one-particle wave functions $\varphi_{\mu\sigma}(\mathbf{r})$. The following terms determine these:

1. kinetic energy,
2. Coulomb attraction by the Z-fold positively charged nucleus,
3. (*selfconsistent*) repulsion by *the other* electrons,
4. *effective* attraction by *other* electrons with parallel spins, due to the *exchange term*.

In comparison to the Hartree equations point 4. is new. It is an immediate consequence of the *antisymmetrization principle*, and therewith *classically not understandable*. It conveys the impression, as if there would exist, for the singled out electron in the state $|\varphi_{\mu\sigma}\rangle$, an *additional effective* interaction. One has given to this term the name *exchange interaction*. We know that the **Pauli principle** is equivalent to the *antisymmetrization principle*, according to which electrons with parallel spins *draw each other aside*. Any mechanism, however, which *keeps*

at bay likely charged particles, leads otherwise to a lowering of the potential energy, and is therefore equivalent to an *effective attractive* interaction.

The just mentioned influence of the Pauli principle is of course particularly large when as many as possible electrons orient their spins *spontaneously* parallel, i.e. without any external enforcement. This fact explains the phenomenon of *band-ferromagnetism* in certain solids. On the other hand, the fact that not all metallic solids are *ferromagnetic*, is also a consequence of the Pauli principle. Because of the parallel spin orientation, the electrons have to enter higher and higher energy levels. In a certain sense, their *kinetic energy* increases. When the lowering of the potential energy is stronger than the increase of the kinetic energy, then the electron spins will be *spontaneously* parallel. The magnetic spin moments (5.240) then take care for a *spontaneous finite magnetization* of the solid. In the opposite case it is energetically more convenient for the system to contain an equal number of $\sigma = \uparrow$- and $\sigma = \downarrow$-electrons. The magnetic moments (vectors!) compensate each other. The solid is then *non-magnetic (paramagnetic)*.

The solution of the *Hartree-Fock equations* (8.141) is carried out by iteration, in the same way as explained in connection with the *Hartree equations* after Eq. (7.24). The results are *optimal* one-particle states $\varphi_{\mu\sigma}(\mathbf{r})$, by which an estimation (upper bound) of the ground-state energy E_0 is possible. The comparison of (8.141) and (8.139) yields, together with the variational principle (7.5):

$$E_0 \leq \langle H_N \rangle_{\mathrm{HF}} = \sum_{\mu\sigma} \varepsilon_{\mu\sigma} - \frac{1}{2} \sum_{\substack{\mu,\nu \\ \sigma,\sigma'}}^{(\mu\sigma)\neq(\nu\sigma')} \left(C_{\mu\sigma}^{\nu\sigma'} - A_{\mu\sigma}^{\nu\sigma}\, \delta_{\sigma\sigma'} \right) . \tag{8.143}$$

Here we have used the following abbreviations:

Coulomb integral

$$C_{\mu\sigma}^{\nu\sigma'} = \frac{e^2}{4\pi\,\varepsilon_0} \iint d^3r\, d^3r' \, \frac{|\varphi_{\mu\sigma}(\mathbf{r})|^2\, |\varphi_{\nu\sigma'}(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} , \tag{8.144}$$

exchange integral

$$A_{\mu\sigma}^{\nu\sigma} = \frac{e^2}{4\pi\,\varepsilon_0} \iint d^3r\, d^3r' \, \frac{\varphi_{\mu\sigma}^*(\mathbf{r})\, \varphi_{\nu\sigma}^*(\mathbf{r}')\, \varphi_{\mu\sigma}(\mathbf{r}')\, \varphi_{\nu\sigma}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} . \tag{8.145}$$

The Hartree-Fock energy is lower than the Hartree energy, and represents therewith, according to the variational principle, a better approach to the ground-state energy. However, it is of course also not an exact result, either, because the Slater determinant (8.130) does agree with the real ground state only in the case of **non**interacting electrons.

8.4.2 Hydrogen Molecule

In this subsection we want to demonstrate by means of a simple model calculation (*Heitler-London method*) that the **covalent (homopolar, chemical)**

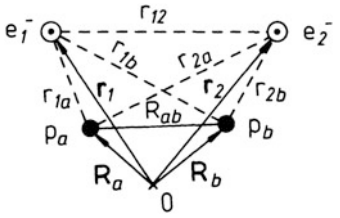

Figure 8.4: Distances in the hydrogen molecule

bond of the H_2-molecule is a direct consequence of the *antisymmetrization principle* for systems of identical fermions. What concerns the hydrogen molecule, it of course is actually a four-particle problem, because it is composed of two electrons (e_1^-, e_2^-) and two protons (p_a, p_b). However, the proton mass is about 2000-times larger than the electron mass. We therefore can neglect, as a first rather well justifiable approximation, the co-motion of the nuclei, and fix the protons with a constant distance at $\mathbf{R}_a$ and $\mathbf{R}_b$. What is then left is effectively a *two-electron problem*.

As a further simplification we will incorporate in the Hamilton operator only Coulomb interactions, and take the spin of the electrons into consideration only for the classification of the states. Figure 8.4 illustrates, which terms are relevant:

$$H = \sum_{i=1}^{2} \left[\frac{\mathbf{p}_i^2}{2m} - \frac{e^2}{4\pi\,\varepsilon_0} \left(\frac{1}{r_{i\,a}} + \frac{1}{r_{i\,b}} \right) \right] + \frac{e^2}{4\pi\,\varepsilon_0} \left(\frac{1}{r_{12}} + \frac{1}{R_{ab}} \right) . \tag{8.146}$$

Besides the kinetic energy of the two electrons and their Coulomb attraction by the two protons,

$$r_{i\,a} = |\mathbf{r}_i - \mathbf{R}_a| \; ; \quad r_{i\,b} = |\mathbf{r}_i - \mathbf{R}_b| \; , \quad (i = 1, 2) \; , \tag{8.147}$$

we still have to include their mutual repulsion, and the analogous repulsion between the protons:

$$r_{12} = |\mathbf{r}_1 - \mathbf{r}_2| \; ; \quad R_{ab} = |\mathbf{R}_a - \mathbf{R}_b| \; . \tag{8.148}$$

The eigen-states and the eigen-values of the total Hamilton operator will have to be considered as functions of the distance R_{ab} between the protons, which in our model is a parameter and not at all a dynamical variable.

The Hamilton operator (8.146) is, as required by the general theory, symmetric in the indexes 1 and 2 of the two identical fermions. H does not contain any spin-parts, and does therefore commute with the square of the absolute value as well as with the z-component of the total spin operator $\mathbf{S}$ of the two-electron system. The common eigen-states will therefore factorize in a space-part $|q\rangle$ and a spin-part:

$$|\psi_2\rangle = |q\rangle |S\, m_s\rangle \; .$$

We can exactly write down the spin part. For, from Sect. 5.4.4 we know that the two spin-(1/2) particles can couple to a total spin $S = 0$ or $S = 1$. We have calculated the corresponding four possible spin states,

$$|0\,0\rangle\,; \quad |1\,-1\rangle,\, |1\,0\rangle,\, |1\,1\rangle\,,$$

as Exercise 5.4.1. It results a singlet,

$$|0\;0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\rangle^{(1)}|\downarrow\rangle^{(2)} - |\uparrow\rangle^{(2)}|\downarrow\rangle^{(1)}\right), \tag{8.149}$$

and a triplet:

$$\begin{aligned} |1\,-1\rangle &= |\downarrow\rangle^{(1)}|\downarrow\rangle^{(2)}\,, \\ |1\,0\rangle &= \frac{1}{\sqrt{2}}\left(|\uparrow\rangle^{(1)}|\downarrow\rangle^{(2)} + |\uparrow\rangle^{(2)}|\downarrow\rangle^{(1)}\right), \\ |1\,1\rangle &= |\uparrow\rangle^{(1)}|\uparrow\rangle^{(2)}\,. \end{aligned} \tag{8.150}$$

The singlet state is obviously antisymmetric with respect to particle interchange, while the triplet state is symmetric. Since the total state $|\psi_2\rangle$ of the two-electron system has to be in any case antisymmetric, $|0\,0\rangle$ couples with a symmetric space-part, and $|1\,m_s\rangle$ with an antisymmetric one:

$$\left|\psi_2^{(S)}\right\rangle = \left|q^{(+)}\right\rangle |0\,0\rangle\;; \quad \left|\psi_2^{(T)}\right\rangle = \left|q^{(-)}\right\rangle |1\,m_s\rangle\;. \tag{8.151}$$

Here a remarkable correlation between the symmetry of the space-wave function and the spin S betokens itself. If it turned out that different energies belong to $|q^{(+)}\rangle$ and $|q^{(-)}\rangle$, then a certain spin orientation would be energetically favored, and that, although the Hamilton operator itself is spin-independent.

The space-part $|q^{(\pm)}\rangle$ can not be calculated exactly. Here we will be content with a very simple estimation, which, however, reproduces already rather well the physically important aspects. For the limiting case $R_{\rm ab} \to \infty$, in which the two protons with *their 'own' electron* are infinitely far away from each other, the scope of work goes over into that of the *normal* hydrogen problem, known from Sect. 6.2, whose solution is already available:

$$\begin{aligned} \left(\frac{\mathbf{p}_1^2}{2m} - \frac{e^2}{4\pi\,\varepsilon_0 r_{1\rm a}}\right)\left|\varphi_{\rm a}^{(1)}\right\rangle &= E_{\rm a}\left|\varphi_{\rm a}^{(1)}\right\rangle\,, \\ \left(\frac{\mathbf{p}_2^2}{2m} - \frac{e^2}{4\pi\,\varepsilon_0 r_{2\rm b}}\right)\left|\varphi_{\rm b}^{(2)}\right\rangle &= E_{\rm b}\left|\varphi_{\rm b}^{(2)}\right\rangle\,. \end{aligned}$$

We use the eigen-states following from these equations as one-particle states for the construction of correctly antisymmetrized two-particle states:

$$\begin{aligned} \left|q^{(\pm)}\right\rangle &= S_2^{(\pm)}\,|\varphi_{\rm a}\,\varphi_{\rm b}\rangle \overset{(8.56)}{=} \frac{1}{2!}\,(\mathbb{1}_2 \pm P_{12})\left(\left|\varphi_{\rm a}^{(1)}\right\rangle\left|\varphi_{\rm b}^{(2)}\right\rangle\right) \\ &= \frac{1}{2}\left(\left|\varphi_{\rm a}^{(1)}\right\rangle\left|\varphi_{\rm b}^{(2)}\right\rangle \pm \left|\varphi_{\rm a}^{(2)}\right\rangle\left|\varphi_{\rm b}^{(1)}\right\rangle\right)\,. \end{aligned} \tag{8.152}$$

This is the exact eigen-state of course only if the two hydrogen atoms are infinitely far away from each other. The approximation (*Heitler-London method*) consists in applying the two-electron state $|q^{(\pm)}\rangle$ nevertheless even for finite $R_{\rm ab}$ as *approximate* eigen-state, in order to calculate with it the expectation value of the Hamilton operator as an estimation for the system energy:

$$E_\pm = \frac{\left\langle q^{(\pm)}\right| H \left|q^{(\pm)}\right\rangle}{\left\langle q^{(\pm)}\right| \left.q^{(\pm)}\right\rangle} \ . \tag{8.153}$$

We therewith put up with the fact that the ansatz (8.152) neglects *polar states* of the form

$$\left|\varphi^{(1)}_{\rm i_1}\right\rangle \left|\varphi^{(2)}_{\rm i_2}\right\rangle \ ; \quad \left|\varphi^{(1)}_{\rm b_1}\right\rangle \left|\varphi^{(2)}_{\rm b_2}\right\rangle \ ,$$

which concerns situations, in which both electrons are to be found at one and the same proton. With the focus on the *chemical bond*, at the qualitative understanding of which this model calculation aims, they would be a measure for the *rest ionicity*.

We are mainly interested in an estimation of the ground-state energy. It seems then of course obvious to consider $|\varphi_{\rm a}\rangle$ and $|\varphi_{\rm b}\rangle$ as the two ground states of the electrons in the hydrogen atoms ($\sim 1s$-wave functions). Since the states belong to two different nuclei, the Pauli principle need not be obeyed. The electrons can occupy the ground states even with the same spin projections. According to the *variational principle* (7.5), (8.153) represents in any case an upper bound for the ground-state energy.

At first we will not make explicit use of the fact that $|\varphi_{\rm a}\rangle$, $|\varphi_{\rm b}\rangle$ are ground states, but permit arbitrary eigen-states of the hydrogen atom. These shall be normalized, but cannot be assumed to be orthogonal to each other. The so-called *overlap integral*,

$$L_{\rm ab} \equiv \left\langle \varphi^{(1,2)}_{\rm a}\right| \left.\varphi^{(1,2)}_{\rm b}\right\rangle = \int d^3r\, \varphi^*_{\rm a}(\mathbf{r})\, \varphi_{\rm b}(\mathbf{r}) \ = L^*_{\rm ba} \ , \tag{8.154}$$

will always be unequal zero, because the hydrogen-eigen functions are centered around **different** nuclear positions. $L_{\rm ab}$ will decrease fast, though, with increasing distance $R_{\rm ab}$ of the nuclei. It determines the normalization of the *test state* $|q^{(\pm)}\rangle$:

$$\left\langle q^{(\pm)}\right| \left.q^{(\pm)}\right\rangle = \frac{1}{2}\left(1 \pm |L_{\rm ab}|^2\right) \ . \tag{8.155}$$

For the numerator in (8.153) the following terms are to be calculated:

$$\begin{aligned}
&\left\langle \varphi_{\mathrm{a}}^{(1)} \right| \left\langle \varphi_{\mathrm{b}}^{(2)} \right| H \left| \varphi_{\mathrm{a}}^{(1)} \right\rangle \left| \varphi_{\mathrm{b}}^{(2)} \right\rangle = \left\langle \varphi_{\mathrm{a}}^{(2)} \right| \left\langle \varphi_{\mathrm{b}}^{(1)} \right| H \left| \varphi_{\mathrm{a}}^{(2)} \right\rangle \left| \varphi_{\mathrm{b}}^{(1)} \right\rangle \\
&= E_{\mathrm{a}} + E_{\mathrm{b}} + \frac{e^2}{4\pi\,\varepsilon_0 R_{\mathrm{ab}}} \\
&\quad + \frac{e^2}{4\pi\,\varepsilon_0} \left\langle \varphi_{\mathrm{a}}^{(1)} \right| \left\langle \varphi_{\mathrm{b}}^{(2)} \right| \left(\frac{1}{r_{12}} - \frac{1}{r_{1\mathrm{b}}} - \frac{1}{r_{2\mathrm{a}}} \right) \left| \varphi_{\mathrm{a}}^{(1)} \right\rangle \left| \varphi_{\mathrm{b}}^{(2)} \right\rangle \\
&= E_{\mathrm{a}} + E_{\mathrm{b}} + \frac{e^2}{4\pi\,\varepsilon_0} \left[\frac{1}{R_{\mathrm{ab}}} - \left\langle \varphi_{\mathrm{a}}^{(1)} \right| \frac{1}{r_{1\mathrm{b}}} \left| \varphi_{\mathrm{a}}^{(1)} \right\rangle \right. \\
&\quad \left. - \left\langle \varphi_{\mathrm{b}}^{(2)} \right| \frac{1}{r_{2\mathrm{a}}} \left| \varphi_{\mathrm{b}}^{(2)} \right\rangle + \left\langle \varphi_{\mathrm{a}}^{(1)} \right| \left\langle \varphi_{\mathrm{b}}^{(2)} \right| \frac{1}{r_{12}} \left| \varphi_{\mathrm{a}}^{(1)} \right\rangle \left| \varphi_{\mathrm{b}}^{(2)} \right\rangle \right] ,
\end{aligned}$$

$$\begin{aligned}
&\left\langle \varphi_{\mathrm{a}}^{(1)} \right| \left\langle \varphi_{\mathrm{b}}^{(2)} \right| H \left| \varphi_{\mathrm{a}}^{(2)} \right\rangle \left| \varphi_{\mathrm{b}}^{(1)} \right\rangle = \left(\left\langle \varphi_{\mathrm{a}}^{(2)} \right| \left\langle \varphi_{\mathrm{b}}^{(1)} \right| H \left| \varphi_{\mathrm{a}}^{(1)} \right\rangle \left| \varphi_{\mathrm{b}}^{(2)} \right\rangle \right)^* \\
&= \left(E_{\mathrm{a}} + E_{\mathrm{b}} + \frac{e^2}{4\pi\,\varepsilon_0 R_{\mathrm{ab}}} \right) |L_{\mathrm{ab}}|^2 - \frac{e^2}{4\pi\,\varepsilon_0} \left(\left\langle \varphi_{\mathrm{a}}^{(1)} \right| \frac{1}{r_{1\mathrm{b}}} \left| \varphi_{\mathrm{b}}^{(1)} \right\rangle L_{\mathrm{ab}}^* \right. \\
&\quad \left. + \left\langle \varphi_{\mathrm{b}}^{(2)} \right| \frac{1}{r_{2\mathrm{a}}} \left| \varphi_{\mathrm{a}}^{(2)} \right\rangle L_{\mathrm{ab}} \right) + \frac{e^2}{4\pi\,\varepsilon_0} \left\langle \varphi_{\mathrm{a}}^{(1)} \right| \left\langle \varphi_{\mathrm{b}}^{(2)} \right| \frac{1}{r_{12}} \left| \varphi_{\mathrm{a}}^{(2)} \right\rangle \left| \varphi_{\mathrm{b}}^{(1)} \right\rangle .
\end{aligned}$$

One now defines, something differently from that in the Hartree-Fock equations in (8.144), as **Coulomb integral**:

$$\begin{aligned}
C_{\mathrm{ab}} \;=\; & \frac{e^2}{4\pi\,\varepsilon_0} \left[\frac{1}{R_{\mathrm{ab}}} - \int d^3 r_1 \, \frac{|\varphi_{\mathrm{a}}(\mathbf{r}_1)|^2}{|\mathbf{r}_1 - \mathbf{R}_{\mathrm{b}}|} - \int d^3 r_2 \, \frac{|\varphi_{\mathrm{b}}(\mathbf{r}_2)|^2}{|\mathbf{r}_2 - \mathbf{R}_{\mathrm{a}}|} \right. \\
& \left. + \iint d^3 r_1 \, d^3 r_2 \, \frac{|\varphi_{\mathrm{a}}(\mathbf{r}_1)|^2 \, |\varphi_{\mathrm{b}}(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] . \qquad (8.156)
\end{aligned}$$

The terms are easily (*classically*) interpretable. The first results from the Coulomb repulsion of the two protons, the second from the attraction of the electron, which belongs to nucleus a, by the nucleus b, the third from the attraction of the electron, which belongs to nucleus b, by the nucleus a, and the fourth from the repulsion of the two electrons with each other.

On the other hand, the terms of the **exchange integral** are *classically not interpretable*:

$$\begin{aligned}
A_{\mathrm{ab}} \;=\; & \frac{e^2}{4\pi\,\varepsilon_0} \left[\frac{1}{R_{\mathrm{ab}}} |L_{\mathrm{ab}}|^2 - \mathrm{Re} \left(L_{\mathrm{ab}}^* \int d^3 r_1 \, \frac{\varphi_{\mathrm{a}}^*(\mathbf{r}_1) \, \varphi_{\mathrm{b}}(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{R}_{\mathrm{b}}|} \right. \right. \\
& \left. + L_{\mathrm{ab}} \int d^3 r_2 \, \frac{\varphi_{\mathrm{b}}^*(\mathbf{r}_2) \, \varphi_{\mathrm{a}}(\mathbf{r}_2)}{|\mathbf{r}_2 - \mathbf{R}_{\mathrm{a}}|} \right) \\
& \left. + \mathrm{Re} \iint d^3 r_1 \, d^3 r_2 \, \frac{\varphi_{\mathrm{a}}^*(\mathbf{r}_1) \, \varphi_{\mathrm{b}}^*(\mathbf{r}_2) \, \varphi_{\mathrm{a}}(\mathbf{r}_2) \, \varphi_{\mathrm{b}}(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] . \qquad (8.157)
\end{aligned}$$

When $|\varphi_{\mathrm{a}}\rangle$ and $|\varphi_{\mathrm{b}}\rangle$ are the ground states of the two hydrogen atoms, then all quantities in (8.157) are real. In addition, the second and the third summand are then identical.

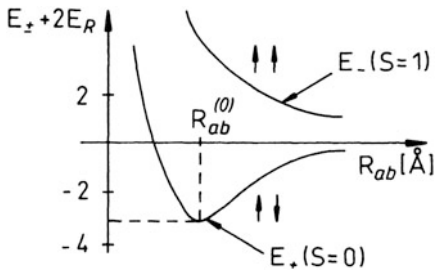

Figure 8.5: Singlet and triplet ground-state energies for the hydrogen molecule as function of the distance of the protons, according to the Heitler-London method

When we now insert the at last calculated partial results into (8.153) then we have:

$$E_{\pm} = E_{\mathrm{a}} + E_{\mathrm{b}} + \frac{C_{\mathrm{ab}} \pm A_{\mathrm{ab}}}{1 \pm |L_{\mathrm{ab}}|^2} \,. \tag{8.158}$$

The energy E_+ belongs to the singlet state $|\psi_2^{(S)}\rangle$, the energy E_- to the triplet state $|\psi_2^{(T)}\rangle$ (8.151). The integrals L_{ab}, C_{ab}, A_{ab} are easily evaluated, at least with a computer, with the known eigen-functions of the hydrogen atom (see (6.60)–(6.65)). The first analytical calculation traces back to W. Heitler and F. London (Z. Phys. **44**, 455 (1927)) as well as Y. Suguira (Z. Phys. **45**, 485 (1927)), where the ground-state wave functions of the hydrogen atoms, centered around $\mathbf{R}_{\mathrm{a}}$ and $\mathbf{R}_{\mathrm{b}}$, were applied. The numerical values of the integrals strongly depend on the distance R_{ab} of the nuclei (Fig. 8.5). The important result is that one finds for not too small distances: $|L_{\mathrm{ab}}| \ll 1$ and $A_{\mathrm{ab}} < 0$. This means:

$$E_+ < E_- \,. \tag{8.159}$$

For the singlet state with the energy E_+ there exists an energetically most convenient **finite (!)** distance of the nuclei $R_{\mathrm{ab}}^{(0)}$ (Fig. 8.5). That explains the *chemical bond* of the hydrogen molecule, since the system aims of course to reach the state with minimal energy. The triplet state $|\psi_2^{(T)}\rangle$, to which the antisymmetric position-wave function belongs, is obviously non-bonding.

Even though a simple ansatz is used, the agreement of the model results with experimental data is rather satisfying:

$$\begin{array}{lll} \text{model:} & R_{\mathrm{ab}}^{(0)} = 0.869\,\text{Å}\,; & (E_+ + 2E_{\mathrm{R}})^{(0)} = -3.14\,\text{eV}\,, \\ \text{experiment:} & R_{\mathrm{ab}}^{(0)} \approx 0.74\,\text{Å}\,; & (E_+ + 2E_{\mathrm{R}})^{(0)} \approx -4.73\,\text{eV}\,. \end{array}$$

8.4.3 Helium Atom

The Helium atom is the simplest many-electron atom of the periodic table, but nevertheless not exactly solvable. The focus is here therefore only to illustrate

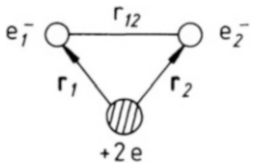

Figure 8.6: Schematic arrangement of electrons and nucleus in the Helium atom

by means of simple approximations, which consequences result from the fact that the two Helium-electrons are about two identical particles. We will see that the *principle of indistinguishability* leads to some interesting, classically not to be expected effects.

We neglect, as we did in the case of the hydrogen molecule, the co-motion of the nucleus and put the origin of coordinates at the twofold positively charged nucleus. We assume, furthermore, that spin-dependent interactions (spin-orbit interaction, magnetic interactions, ...) do not play any role, so that the spin comes up only for the classification of the states. The Coulomb interactions, which come into consideration, can directly be taken from Fig. 8.6:

$$H = H_1^{(1)} + H_1^{(2)} + H_2^{(1,2)} = \sum_{i=1}^{2} \left(\frac{\mathbf{p}_i^2}{2m} - \frac{2e^2}{4\pi\,\varepsilon_0\, r_i} \right) + \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \ . \quad (8.160)$$

The first two terms are one-particle operators representing the *undisturbed problem* of an electron in the Coulomb field of a point charge $Z\,e$ ($Z = 2$). We know the solution from Sect. 6.2. The third summand is as electron-electron interaction a two-particle operator. Since H does not contain spin-parts, the eigenstates will factorize, as for the H_2-molecule (Sect. 8.4.2), into a space (orbital) and a spin part. The spin states are of course, as in (8.149) and (8.150), a singlet ($S = 0$)-state and a triplet ($S = 1$)-state. Therefore we can start, as in (8.151), with:

$$\begin{aligned} \left|\psi_2^{(\mathrm{S})}\right\rangle &= \left|q^{(+)}\right\rangle |0,0\rangle \ ; \\ \left|\psi_2^{(\mathrm{T})}\right\rangle &= \left|q^{(-)}\right\rangle |1\,m_s\rangle \ . \end{aligned} \quad (8.161)$$

Both total states $|\psi_2^{(\mathrm{S,T})}\rangle$ are antisymmetric with respect to particle interchange, so that at first nothing speaks against possible transitions between these states. The transposition operator P_{12} can formally be written as the product of two transposition operators, $P_{12} = P_{12}^{\text{position}}\, P_{12}^{\text{spin}}$, by which the one interchanges the particles only with respect to their space-states, and the other with respect to their spin states. Because of its spin-independence, the Hamilton operator commutes already with P_{12}^{position}. With the same considerations as after (8.53) (see also Exercise 8.2.1) it can then be concluded that the space-part $|q^{(\pm)}\rangle$ retains its symmetry character for all times. This means that transitions between $|\psi_2^{(S)}\rangle$ and $|\psi_2^{(T)}\rangle$ are impossible (*prohibition of inter-combinations*)

(see Exercise 8.2.6). Transitions require:

$$\Delta S = 0\,. \tag{8.162}$$

It appears that, and this is a first important consequence of the principle of indistinguishability, there were two sorts of Helium, the one with $S = 0$ and the other with $S = 1$. For these, special nomenclatures have been established:

$$\begin{aligned} \left|\psi_2^{(S)}\right\rangle &\longleftrightarrow S = 0 \longleftrightarrow \textbf{para-Helium,} \\ \left|\psi_2^{(T)}\right\rangle &\longleftrightarrow S = 1 \longleftrightarrow \textbf{ortho-Helium.} \end{aligned} \tag{8.163}$$

It is clear that the *exact* He-Hamilton operator will not be completely spin-independent, so that prohibition on the transition will not be valid without exception. But certainly, transitions with $\Delta S = 0$ will dominate very strongly. It is, however, interesting in any case that the fact, already observed for the H_2-molecule, namely, the principle of indistinguishability gives rise to dramatic spin effects although the model-Hamilton operator itself is not spin-dependent!

In the following we want to get a general qualitative idea about the energy spectrum of the Helium. This we do in three stages:

1) 'Undisturbed' Helium spectrum

At first, let us *switch off* the electron-electron interaction ($H_2^{(1,2)} \equiv 0$). If, however, the two electrons disregard each other, then what is left is nothing but the *normal* Coulomb problem ($Z = 2$) solved in Sect. 6.2. The eigen-states will be (anti)symmetrized products of the one-electron states $|\varphi_{nlm_l}\rangle$:

$$\left|q^{(\pm)}\right\rangle^{(0)} \equiv \left|\varphi_{nlm_l}\,\varphi_{n'l'm_l'}\right\rangle^{(\pm)} = A\left(\left|\varphi^{(1)}_{nlm_l}\right\rangle\left|\varphi^{(2)}_{n'l'm_l'}\right\rangle \pm \left|\varphi^{(2)}_{nlm_l}\right\rangle\left|\varphi^{(1)}_{n'l'm_l'}\right\rangle\right)\,. \tag{8.164}$$

n, l, m_l are the principal quantum number, the azimuthal quantum number, and the magnetic quantum number. The normalization constant A is equal to $1/2$ for $(n\,l\,m_l) = (n'\,l'\,m_l')$, otherwise equal to $1/\sqrt{2}$. The one-particle states $|\varphi_{n\,l\,m_l}\rangle$ are the $Z = 2$-solutions, known from (6.56) and (6.60) to (6.65):

$$\left(H_1^{(1)} + H_1^{(2)}\right)\left|\varphi_{n\,l\,m_l}\,\varphi_{n'\,l'\,m_l'}\right\rangle^{(\pm)} = \left(E_n^{(0)} + E_{n'}^{(0)}\right)\left|\varphi_{n\,l\,m_l}\,\varphi_{n'\,l'\,m_l'}\right\rangle^{(\pm)}.$$

For the energies $E^{(0)}_{n,n'}$ it holds with (6.43):

$$E^{(0)}_{n^{(\prime)}} = -\frac{4E_{\mathrm{R}}}{n^{(\prime)2}}\,; \quad n^{(\prime)} = 1, 2, 3, \ldots$$

E_{R} is the *Rydberg energy* defined in (6.33). The states are in total $n^2 \cdot n'^2$-fold degenerate with respect to l, m_l, l', m_l'. For ortho-Helium there comes in addition the threefold degeneracy according to m_s. The symmetric states of the para-Helium $|\varphi_{n\,l\,m_l}\,\varphi_{n'\,l'\,m_l'}\rangle^{(+)}$ can be built for all combinations of quantum numbers, and therefore also for $n' = n$, $l' = l$, $m_l' = m_l$. But the latter are

obviously absent in the spectrum of the ortho-Helium. The corresponding states are, according to (8.164), identical to zero. This means that in particular the *undisturbed* ground state,

$$|E^{(0)}_{100,\,100}\rangle \equiv |\varphi_{100}\,\varphi_{100}\rangle^{(+)} \,,$$

must be ascribed to the para-Helium:

$$E^{(0)}_{100,\,100} = 2E^{(0)}_1 = -8E_{\mathrm{R}} \approx -108.8\,\mathrm{eV} \,. \tag{8.165}$$

The first excited state of the *unperturbed* two-electron system has the energy:

$$E^{(0)}_{100,\,2lm_l} = -5E_{\mathrm{R}} \approx -68.0\,\mathrm{eV} \,. \tag{8.166}$$

That means that one of the two particles remains in the *undisturbed* ground state, while the other goes into the first excited state. For the case that both the electrons enter the first excited state one finds:

$$E^{(0)}_{2l\,m_l,\,2l'm_{l'}} = -2E_{\mathrm{R}} \approx -27.2\,\mathrm{eV} \,. \tag{8.167}$$

This corresponds to an excitation energy of

$$E^{(0)}_{2l\,m_l,\,2l'm_{l'}} - E^{(0)}_{100,100} = 6E_{\mathrm{R}} \approx 81.6\,\mathrm{eV} \,.$$

It is interesting to compare this value with the so-called *ionization energy* $E^{(0)}_{\mathrm{ion}}$. That is the energy which must be provided in order to shift one of the electrons from the ground state into the continuum $\left(E^{(0)}_{n=\infty} = 0\right)$:

$$E^{(0)}_{\mathrm{ion}} = E^{(0)}_{100,\infty} - E^{(0)}_{100,100} = -4E_{\mathrm{R}} + 8E_{\mathrm{R}} \approx 54.4\,\mathrm{eV} \,. \tag{8.168}$$

One recognizes that the excitation energy for the state $|\varphi_{2l\,m_l}\,\varphi_{2l'm_{l'}}\rangle$ is already substantially larger than the ionization energy. This state thus lies already in the continuum of the spectrum of $H_0 = H^{(1)}_1 + H^{(2)}_1$. If such a state is excited by absorption of radiation, the subsequent *de-excitation* must not necessarily occur into the ground state or any other state of the He-spectrum. It can also be a singly ionized Helium (He^+) together with a free electron, where the energy law determines the kinetic energy of the electron. One calls this process *autoionization*. For all the discrete states below the *continuum limit* (ionization limit) one of the two He-electrons stays in the one-particle ground state $|\varphi_{100}\rangle$. To their characterization the specification of the quantum numbers of the *other* electron $(n\,l\,m_l)$ is therefore completely sufficient. They accumulate for $n \to \infty$ at the continuum limit. We have plotted in the schematic Fig. 8.7 only the discrete levels for $n = 1, 2, 3$.

2) Influence of the electron-electron interaction on the ground state
The ground state

$$|\varphi_{100}\,\varphi_{100}\rangle^{(+)} = |\varphi^{(1)}_{100}\rangle|\varphi^{(2)}_{100}\rangle$$

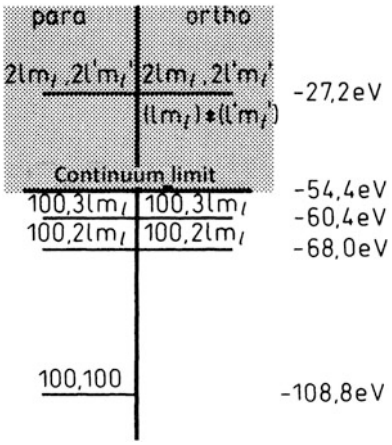

Figure 8.7: Energy spectrum of ortho- and para-Helium

belongs to para-Helium and is not degenerate. Let us calculate in the first order perturbation theory the energy shift, which is to be expected due to the Coulomb repulsion. According to (7.39) this means to evaluate the expectation value of the interaction operator $H_2^{(1,2)}$ in the *unperturbed* ground state:

$$\Delta E^{(1)}_{100,100} = {}^{(+)}\langle\varphi_{100}\,\varphi_{100}|H_2^{(1,2)}|\varphi_{100}\,\varphi_{100}\rangle^{(+)} \,. \tag{8.169}$$

The easiest way to do it, is using the position representation. For this purpose we insert into suitable spots the identity,

$$\mathbb{1} = \int d^3r |\mathbf{r}\rangle\langle\mathbf{r}| \,,$$

where $|\mathbf{r}\rangle$ is an eigen-state of the position operator:

$$\begin{aligned}\Delta E^{(1)}_{100,100} &= \iint d^3r_1\, d^3r_2 \left\langle\varphi^{(1)}_{100}\right| \left\langle\varphi^{(2)}_{100}\right| H_2^{(1,2)} \left(\left|\mathbf{r}_1^{(1)}\right\rangle \left\langle\mathbf{r}_1^{(1)}\right| \varphi^{(1)}_{100}\right\rangle\right) \\ &\quad \cdot \left(\left|\mathbf{r}_2^{(2)}\right\rangle \left\langle\mathbf{r}_2^{(2)}\right| \varphi^{(2)}_{100}\right\rangle\right) \\ &= \frac{e^2}{4\pi\,\varepsilon_0} \iint d^3r_1\, d^3r_2\, \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} |\langle\varphi_{100}|\mathbf{r}_1\rangle|^2 |\langle\varphi_{100}|\mathbf{r}_2\rangle|^2 \,.\end{aligned}$$

It holds for the one-particle wave function according to (6.56) and (6.60) with $Z = 2$:

$$\varphi_{100}(\mathbf{r}) = \langle\mathbf{r}|\varphi_{100}\rangle = \sqrt{\frac{8}{\pi\, a_{\mathrm{B}}^3}}\, \exp\left(-\frac{2r}{a_{\mathrm{B}}}\right).$$

a_{B} is the *Bohr radius* (6.32):

$$2a_{\mathrm{B}}\, E_{\mathrm{R}} = \frac{e^2}{4\pi\,\varepsilon_0} \,. \tag{8.170}$$

For the energy correction of first order it remains then to be calculated:

$$\Delta E^{(1)}_{100,100} = E_{\mathrm{R}}\,\frac{128}{\pi^2 a_{\mathrm{B}}^5}\iint d^3r_1\,d^3r_2\,\frac{\exp\left[-(4/a_{\mathrm{B}})\,(r_1+r_2)\right]}{|\mathbf{r}_1-\mathbf{r}_2|}\;. \tag{8.171}$$

For the $\mathbf{r}_2$-integration we consider $\mathbf{r}_1$ as the polar axis, and can assume, because of the symmetry of the integrand, that $r_2 \geq r_1$, where the result is to be multiplied by a factor 2:

$$\begin{aligned}
\Delta E^{(1)}_{100,100} &= E_{\mathrm{R}}\,\frac{8^3}{\pi\,a_{\mathrm{B}}^5}\,Q\;,\\
Q &= \int d^3r_1\,e^{-(4/a_{\mathrm{B}})\,r_1}\,D_{r_1}\;,\\
D_{r_1} &= \int\limits_{r_1}^{\infty} dr_2\,r_2^2\,e^{-(4/a_{\mathrm{B}})\,r_2}\,I_{r_1\leq r_2}\;.
\end{aligned}$$

$I_{r_1\leq r_2}$ includes the integration over the polar angles of the $\mathbf{r}_2$-integral, for which it holds because of $r_2 \geq r_1$:

$$I_{r_1\leq r_2} = \int\limits_{-1}^{+1}\frac{dx}{\sqrt{r_1^2+r_2^2-2r_1r_2x}} = \frac{2}{r_2}\;.$$

Therewith we calculate D_{r_1}:

$$\begin{aligned}
D_{r_1} &= 2\int\limits_{r_1}^{\infty} dr_2\,r_2\,e^{-(4/a_{\mathrm{B}})\,r_2} = 2\left[-\frac{d}{d\lambda}\int\limits_{r_1}^{\infty} dr_2\,e^{-\lambda r_2}\right]_{\lambda=(4/a_{\mathrm{B}})}\\
&= \frac{1}{2}\,a_{\mathrm{B}}\left(r_1+\frac{1}{4}\,a_{\mathrm{B}}\right)\,e^{-(4/a_{\mathrm{B}})\,r_1}\;.
\end{aligned}$$

This is inserted into the expression for Q, and then evaluated with the known integral formula,

$$\int\limits_0^{\infty} dx\,x^n e^{-ax} = \frac{n!}{a^{n+1}}\;,$$

to give:

$$Q = 2\pi\,a_{\mathrm{B}}\int\limits_0^{\infty} dr_1\,\left(r_1^3+\frac{1}{4}\,a_{\mathrm{B}}\,r_1^2\right)\,e^{-\frac{8}{a_{\mathrm{B}}}\,r_1} = \frac{5}{2}\,\frac{\pi\,a_{\mathrm{B}}^5}{8^3}.$$

The energy correction is therewith determined:

$$\Delta E^{(1)}_{100,100} = \frac{5}{2}\,E_{\mathrm{R}} \approx 34\,\mathrm{eV}\;. \tag{8.172}$$

The electrostatic repulsion of the two electrons enhances the energy of the system rather substantially. Together with (8.165), the ground-state energy of the Helium atom, *corrected* by first order perturbation theory, is obtained asz:

$$E^{(1)}_{100,100} = -\frac{11}{2}\, E_{\mathrm{R}} \approx -74.8\,\mathrm{eV}\ . \tag{8.173}$$

When one compares this with the experimental value,

$$E^{\mathrm{exp}}_{100,100} = -78.98\,\mathrm{eV}\ , \tag{8.174}$$

then the agreement is actually not extremely convincing. As a reason for the discrepancy one can suppose the *screening* of the nucleus, according to which each of the two electrons *does not see*, because of the presence of the other electron, the full $Z = 2$-charge of the nucleus, but rather an effectively somewhat smaller one. This can nicely be demonstrated by a variational calculation, which we perform explicitly as Exercise 8.4.3. In the variational ansatz, *suggested by* $\langle \mathbf{r}_1|\varphi_{100}\rangle\, \langle \mathbf{r}_2|\varphi_{100}\rangle$, Z^* can be interpreted as *effective* nuclear charge

$$\psi_{Z^*}\,(\mathbf{r}_1, \mathbf{r}_2) = \exp\left[-\frac{Z^*}{a_{\mathrm{B}}}\,(r_1 + r_2)\right]\ . \tag{8.175}$$

The variation of the energy functional

$$\langle H\rangle_{Z^*} = \frac{\langle \psi_{Z^*}|H|\psi_{Z^*}\rangle}{\langle \psi_{Z^*}|\psi_{Z^*}\rangle}\ ,$$

yields an *optimal* Z^*_0:

$$Z^*_0 = \frac{27}{16} = 2 - \frac{5}{16}\ .$$

This indeed corresponds to an effective reduction of the nuclear charge due to *screening* by $(5/16)\, e$. The energy bound,

$$\langle H\rangle_{Z^*_0} \approx -5.7\, E_{\mathrm{R}} \approx -77.49\,\mathrm{eV}\ ,$$

approaches the experimental value already essentially better than the perturbative result.

We still remark that the so calculated *screening* of the nucleus holds for the ground state. If the electrons are in excited states, then they will experience *different screenings*.

3) Energy shift of the excited states

In the third and the last step we still want to work out a qualitative picture of the influence of the electron-electron interaction on the excited states. It is to be expected that the degeneracies with respect to the secondary (orbital angular momentum) quantum number l are removed. As we have discussed after (6.45) it is in any case about an *accidental* degeneracy, which appears exclusively in the *pure* Coulomb field. Due to the presence of the second electron the Coulomb field

of the nucleus is, however, disturbed. In contrast, the m_l-degeneracy remains because of

$$\left[H_2^{(1,2)},\, L_z\right]_- = 0\,. \tag{8.176}$$

For simplicity, in the following we will always put $m_l = 0$.

We are interested here only in the discrete part of the spectrum, i.e., in states, whose excitation energies are smaller than the ionization energy. We had seen that then only one of the two electrons is really excited, while the other stays in the ground state. We estimate the energy shift of the excited states by the expectation value of the interaction operator in the corresponding *undisturbed* energy states:

$$\begin{aligned}
\Delta E^{\substack{\text{para}\\ \text{ortho}}}_{100,\,nl0} &\equiv {}^{(\pm)} \quad \langle \varphi_{100}\,\varphi_{nl0}|\, H_2^{(1,2)}\, |\varphi_{100}\,\varphi_{nl0}\rangle^{(\pm)} \\
&= \quad \frac{1}{2}\,\Big\{ \Big\langle \varphi^{(1)}_{100}\Big| \Big\langle \varphi^{(2)}_{nl0}\Big| H_2^{(1,2)} \Big|\varphi^{(1)}_{100}\Big\rangle \Big|\varphi^{(2)}_{nl0}\Big\rangle \\
&\quad + \Big\langle \varphi^{(2)}_{100}\Big| \Big\langle \varphi^{(1)}_{nl0}\Big| H_2^{(1,2)} \Big|\varphi^{(2)}_{100}\Big\rangle \Big|\varphi^{(1)}_{nl0}\Big\rangle \\
&\quad \pm \Big\langle \varphi^{(1)}_{100}\Big| \Big\langle \varphi^{(2)}_{nl0}\Big| H_2^{(1,2)} \Big|\varphi^{(2)}_{100}\Big\rangle \Big|\varphi^{(1)}_{nl0}\Big\rangle \\
&\quad \pm \Big\langle \varphi^{(2)}_{100}\Big| \varphi^{(1)}_{nl0}\Big| H_2^{(1,2)} \Big| \varphi^{(1)}_{100}\Big\rangle \Big|\varphi^{(2)}_{nl0}\Big\rangle \Big\}\,.
\end{aligned}$$

The first two and the last two summands yield both the same contribution. For abbreviation we write:

$$\Delta E^{\text{para}}_{100,\,nl0} = C^{nl}_{10} + A^{nl}_{10}\,, \tag{8.177}$$

$$\Delta E^{\text{ortho}}_{100,\,nl0} = C^{nl}_{10} - A^{nl}_{10}\,. \tag{8.178}$$

Here are C^{nl}_{10} and A^{nl}_{10} Coulomb and exchange integrals, which are defined closely analogously to those of the *Hartree-Fock method*, (8.144) and (8.145):

Coulomb integral:

$$C^{nl}_{10} = \frac{e^2}{4\pi\,\varepsilon_0} \iint d^3r_1\, d^3r_2\, \frac{|\varphi_{100}(\mathbf{r}_1)|^2\, |\varphi_{nl0}(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\,. \tag{8.179}$$

Exchange integral:

$$A^{nl}_{10} = \frac{e^2}{4\pi\,\varepsilon_0} \iint d^3r_1\, d^3r_2\, \frac{\varphi^*_{100}(\mathbf{r}_1)\,\varphi^*_{nl0}(\mathbf{r}_2)\,\varphi_{100}(\mathbf{r}_2)\,\varphi_{nl0}(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|}\,. \tag{8.180}$$

One finds:

$$C^{nl}_{10} \geq 0\,; \quad A^{nl}_{10} \geq 0\,. \tag{8.181}$$

That the Coulomb integrals are non-negative, one directly reads off from (8.179). The electrostatic interaction energy between two charge densities of equal sign

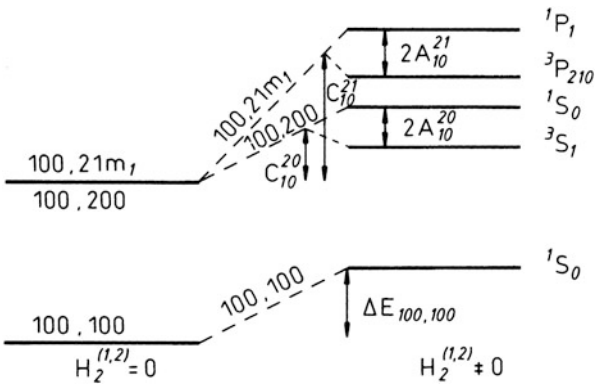

Figure 8.8: Schematic representation of the lowest part of the He-energy spectrum without and with the Coulomb interaction of the two electrons. Removal of the degeneracy by the interaction

must of course be positive. That the exchange integral, too, is non-negative, can be realized immediately only for $l = n-1$ (see Exercise 8.4.4). Apart from that, this comes out only by an explicit calculation of A_{10}^{nl}. The Coulomb integrals are in general one order of magnitude larger than the exchange integrals (see Exercise 8.4.7).

We recognize that the physically important effects, namely the energetic separation of ortho- and para-He states, is again due to the *classically not understandable* exchange integrals. The triplet states of the ortho-Helium lie energetically deeper than the singlet states of the para-Helium. To the triplet states of the ortho-Helium there belong antisymmetric space-states, for which, as we had already seen for the H_2-molecule, the electrons are separated stronger from each other (*antibonding in the case of* H_2) than in the symmetric states. Effects, which keep like charged particles *at bay*, lower the total energy!

Let us, at the end, schematically (not true to scale) plot the lowest part of the He-term scheme (Fig. 8.8). The states $|\varphi_{100}\,\varphi_{200}\rangle^{(\pm)}$ $(1s,\,2s)$ and $|\varphi_{100}\,\varphi_{210}\rangle^{(\pm)}$ $(1s,\,2p)$, which without interaction are degenerate and build the lowest excited state, split due to the electron-electron interaction according to (8.177) and (8.178). We calculate explicitly the corresponding exchange and Coulomb integrals in the exercises 8.4.5, 8.4.7, and 8.4.8:

$$\begin{aligned} C_{10}^{20} &\approx 11.42\,\text{eV}\,; \quad C_{10}^{21} \approx 13.21\,\text{eV}\,, \\ A_{10}^{20} &\approx 1.19\,\text{eV}\,; \quad A_{10}^{21} \approx 0.93\,\text{eV}\,. \end{aligned} \tag{8.182}$$

For the *disturbed* states we have applied in the right part of Fig. 8.8 the usual spectroscopic notation

$$^{2S+1}L_J$$

$(L = 0, 1, 2, \ldots \longleftrightarrow S, P, D, \ldots)$. The ortho-states belong to the total spin $S = 1$ and can therefore for $L \geq 1$, according to the spin-orbit interaction, which

is neglected in the present treatment, additionally split threefold ($J = L-1$, L, $L+1$) (see (5.259)). For the para-states it is always $J = L$. They are therefore uninfluenced by the spin-orbit interaction.

At this stage we have to pass up, though, a further detailed discussion of the He-spectrum, and have instead to refer the reader to the special literature of atom physics.

8.4.4 Exercises

Exercise 8.4.1
For an approximate calculation of the ground-state energy of the H_2-molecule use the variational procedure with the *test state*:

$$|q\rangle = c_1 \left|\varphi_{\mathrm{a}}^{(1)}\right\rangle \left|\varphi_{\mathrm{b}}^{(2)}\right\rangle + c_2 \left|\varphi_{\mathrm{a}}^{(2)}\right\rangle \left|\varphi_{\mathrm{b}}^{(1)}\right\rangle \; ; \quad c_1,\, c_2 \text{ real.}$$

Determine the *optimal* coefficients c_1, c_2 and compare the result to that from Sect. 8.4.2.

Exercise 8.4.2
The Hamilton operator of the H_2-molecule, used in Eq. (8.146), does not contain any spin-dependent terms. The total state of the two-electron system therefore factorizes in a space-part $|q^{(\pm)}\rangle$ and a spin-part $|S\, m_s\rangle^{(\pm)}$. The model Hamilton operator acts only on $|q^{(\pm)}\rangle$:

$$\frac{\langle q^{(\pm)}|H|q^{(\pm)}\rangle}{\langle q^{(\pm)}|q^{(\pm)}\rangle} = E_{\pm} \; .$$

Construct with the spin operators $\mathbf{S}_1$ and $\mathbf{S}_2$ of the two electrons an equivalent Hamilton operator $\widehat{H}$, which acts only on the spin-part and yields the energy-eigen values $E_{\pm}$:

$$\widehat{H}|S\, m_s\rangle^{(\mp)} = E_{\pm}|S\, m_s\rangle^{(\mp)} \; .$$

Exercise 8.4.3
Calculate with the variational anstz

$$\psi_{Z^*}(r_1, \mathbf{r}_2) = \exp\left[-\frac{Z^*}{a_{\mathrm{B}}}(r_1 + r_2)\right]$$

an upper bound of the ground-state energy of Helium. Z^* can be considered as *effective* nuclear charge, which is *noticed* by one of the electrons due to the *screening* of the nucleus by the other electron. Determine the *optimal* Z^*.

Exercise 8.4.4
Show that the exchange integrals (8.180), which are responsible for the energetic separation of the ortho- and the para-states of Helium, can be written in the following form:

$$A_{10}^{nl} = \frac{e^2}{4\pi\,\varepsilon_0(2l+1)} \int_0^\infty dr_1\, r_1^2 \int_0^\infty dr_2\, r_2^2\, \frac{r_<^l}{r_>^{l+1}}\, R_{10}(r_1)\, R_{nl}(r_2)\, R_{10}(r_2)\, R_{nl}(r_1) \; .$$

The $R_{nl}(r)$ are thereby the radial functions of the Coulomb-eigen functions $\varphi_{nlm}(\mathbf{r})$ (see (6.56)). Furthermore:

$$r_> = \max(r_1, r_2); \quad r_< = \min(r_1, r_2).$$

Give reasons, why for $l = n - 1$ the exchange integrals cannot be negative.

Exercise 8.4.5
Calculate the energy splitting of the $(1s)(2s)$-state ($\sim |\varphi_{100}\,\varphi_{200}\rangle^{(\pm)}$) in the Helium spectrum, due to the electron-electron interaction.

Exercise 8.4.6
Show that the Coulomb integrals (8.179) can be written in the following form:

$$C_{10}^{nl} = \frac{e^2}{4\pi\,\varepsilon_0} \int_0^\infty dr_1\, r_1^2 \int_0^\infty dr_2\, r_2^2\, \frac{1}{r_>}\, R_{10}^2(r_1)\, R_{nl}^2(r_2).$$

The nomenclatures are the same as in Exercise 8.4.4.

Exercise 8.4.7
Calculate the Coulomb integral C_{10}^{20} and compare its order of magnitude with that of the corresponding exchange integral A_{10}^{20} (see Exercise 8.4.5).

Exercise 8.4.8
Calculate the energy shift $\Delta E^{(21)}_{\substack{\text{para}\\\text{ortho}}}$ of the $(1s)(2p)$-state ($\sim |\varphi_{100}\,\varphi_{210}\rangle^{(\pm)}$), which appears as consequence of the Coulomb interaction between the two Helium-electrons!

8.5 Self-Examination Questions

To Section 8.1

1. What is the type of the solutions of the time-independent Schrödinger equation for a system of two distinguishable particles, which do not interact with each other?
2. Which states does the product space $\mathcal{H}_2 = \mathcal{H}_1^{(1)} \otimes \mathcal{H}_1^{(2)}$ contain, when $\mathcal{H}_1^{(1,2)}$ are the Hilbert spaces of particle 1 and particle 2?
3. How is the scalar product defined in the product space $\mathcal{H}_2$?
4. How does one find an orthonormal basis of the $\mathcal{H}_2$?
5. Let $|\varphi_2\rangle \in \mathcal{H}_2$, and $|a_n\, b_m\rangle = |a_n^{(1)}\rangle |b_m^{(2)}\rangle$ be a basis state of the $\mathcal{H}_2$. What does then $|\langle a_n\, b_m|\psi_2\rangle|^2$ mean?
6. The eigen-states $|a_n^{(1)}\rangle$ of the operator $A_1^{(1)}$ are a basis of the $\mathcal{H}_1^{(1)}$. What is then the spectral representation of $A_1^{(1)}$ in the product space $\mathcal{H}_2 = \mathcal{H}_1^{(1)} \otimes \mathcal{H}_1^{(2)}$?

7. Let particle 1 and 2 be distinguishable. Is it then possible to precisely measure simultaneously the momentum of particle 1 and the position of particle 2? Explain!

8. How does the Hilbert space $\mathcal{H}_N$ of a system of N distinguishable particles look like?

9. How does one find an orthonormal basis in the $\mathcal{H}_N$?

10. What can be said about the statistical interpretation of an N-particle state $|\psi_N\rangle$?

To Section 8.2

1. What are *identical particles*?

2. Are there *identical particles* in Classical Physics also?

3. How does the *principle of indistinguishability* read?

4. Which basic presumptions must be fulfilled by the observables of a system of N identical particles?

5. Describe the mode of action of the permutation and the transposition operator!

6. Are transposition operators generally commutable?

7. Is the permutation (transposition) operator Hermitian in the product space $\mathcal{H}_N$?

8. Which fundamental requirement must be fulfilled by observables of a system of identical particles?

9. Which important symmetry requirement is to be addressed to the states of a system of identical particles?

10. Is the product space $\mathcal{H}_N = \mathcal{H}_1^{(1)} \otimes \mathcal{H}_1^{(2)} \otimes \ldots \otimes \mathcal{H}_1^{(N)}$ suitable for the description of N identical particles?

11. Why does the symmetry character of the states of identical particles do not change in the course of time?

12. How are the spaces $\mathcal{H}_N^{(\pm)}$ defined?

13. What is the result of the scalar product of a state of the $\mathcal{H}_N^{(+)}$ with the one of the $\mathcal{H}_N^{(-)}$?

14. Why can a system of identical particles not possess simultaneously symmetrized as well as antisymmetrized states?

15. How does one get from a non-symmetrized product state $|\varphi_N\rangle \in \mathcal{H}_N$ an (anti)symmetrized state of the $\mathcal{H}_N^{(\pm)}$?

16. What comes out when one applies the symmetrization operator $S_N^{(\pm)}$ to an already (anti)symmetrized state $|\varphi_N^{(\pm)}\rangle$?

17. Is the unification of the partial spaces $\mathcal{H}_N^{(+)}$ and $\mathcal{H}_N^{(-)}$ identical to the product space $\mathcal{H}_N$?

18. Which basis states span the $\mathcal{H}_N^{(\pm)}$?

19. What is a Slater determinant?

20. What does one understand by the occupation number n_{α_i}? Which values can it take in $\mathcal{H}_N^{(-)}$, and which in $\mathcal{H}_N^{(+)}$?

21. How does the scalar product between the (anti)symmetrized basis states of the $\mathcal{H}_N^{(\pm)}$ read?

22. What does one understand by *occupation number representation*?

23. Which particle type is described in the Hilbert space $\mathcal{H}_N^{(+)}$, and which type in the Hilbert space $\mathcal{H}_N^{(-)}$?

24. What is expressed by the *spin-statistics theorem*?

25. What are bosons, what are fermions?

26. To which type of particles does the Pauli principle apply?

27. Can the two electrons of two hydrogen atoms, one here on earth, the other on the moon, simultaneously be with parallel spins in the ground state?

To Section 8.3

1. Which Hilbert spaces are connected by the creation operator a_α^+?

2. In which way can the (anti)symmetrized N-particle state $|\varphi_{\alpha_1} \cdots \cdots \varphi_{\alpha_N}\rangle^{(\pm)}$ be *created* out of the vacuum state $|0\rangle$ by means of creation operators?

3. How does the fundamental commutation relation read for creation operators of bosons and fermions, respectively?

4. Which meaning and functionality does the *annihilation operator* have?

5. What results, when the *annihilation operator* a_γ is applied to an N-particle state, in which the one-particle state $|\varphi_\gamma\rangle$ does not occur?

6. How does the fundamental commutation relation for annihilation operators read?

7. Which commutation relation holds between creation and annihilation operators?

8. How is the mode of action of a_r^+ on a Fock state $|N; n_{\alpha_1} \cdots n_{\alpha_r} \ldots\rangle^{(\pm)}$ defined? How does the annihilation operator act?

9. Which general structure does a one-particle operator in the formalism of second quantization have?

10. How do two-particle operators look like in second quantization?

11. How is the occupation density (occupation number) operator defined? Which are its eigen-states and eigen-energies?

12. How is the particle number operator defined? Which are its eigen-states and eigen-energies?

To Section 8.4

1. What is the objective of the Hartree-Fock procedure?

2. In which way do the Hartree and the Hartree-Fock methods differ?

3. By which term do the Hartree-fock equations differ from the Hartree equations? How can this additional term physically be interpreted?

4. What does one understand by *exchange interaction*?

5. By which Hamilton operator is the hydrogen molecule described in the *Heitler-London method*?

6. What can be said for the H_2-molecule about the connection between the total electron spin and the symmetry of the position wave function?

7. How can one understand that a special relative spin orientation of the two electrons is energetically favored, although the model-Hamilton operator of the H_2-molecule is spin-independent?

8. By which state-ansatz is the ground-state energy estimated in the Heitler-London theory?

9. In which respect does the model calculation for the H_2-molecule according to the Heitler-London theory contribute to the understanding of the *chemical bond*?

10. What does one understand in the case of the Helium atom by *prohibition of inter-combination*?

11. What is the difference between ortho- and para-Helium?

12. How can one explain the strong spin effects of Helium, although it is described, to a good approximation, by a spin-independent Hamilton-operator?

13. To which *type* of Helium (para or ortho) does the ground state belong?

14. How can one explain the *autoionization* of Helium?

15. What is the order of magnitude (in eV) of the electrostatic repulsion-energy of the two He-electrons in the ground state?

16. Which *quantity* is responsible for the energetic separation of the excited ortho- and para-states?

Chapter 9

Scattering Theory

The theoretical investigation and description of **scattering (collision) processes** of atomic particles represents an important field of application of Quantum Mechanics. One can gain therewith valuable information about particle interactions (e.g., nuclear forces), about elementary interaction potentials, about the structure of matter (e.g., crystal structures), and so on. The energetic structure of atoms and molecules, however, is *spectroscopically* investigated, where by any kind of energy supply the particle is transferred from its ground state into an excited state. The energy, which is emitted with the return into the ground state, e.g. in form of a photon, is analyzed. Initial and final state of the process stem from the discrete spectrum of the Hamilton operator (*bound states*). In contrast, it is typical for scattering processes that the initial and final state of the considered system both lie in the continuous part of the eigen-value spectrum. The scattered particle comes from infinity into the sphere of action of the *scatterer*, in order to be detected after the collision again asymptotically at infinity. The particle is therefore **not** in a bound state.

An example of how one can draw conclusions from scattering processes about the physical properties of atomic and subatomic particles, we have already got to know in connection with the *classical* Rutherford-scattering in Sect. 1.3.3 (Vol. 6). Its analysis led to a first, already rather realistic *nuclear model*. We had seen there that in Classical Physics the collision between two particles can uniquely be described by their velocities and the *impact parameter*. Although the latter could not be precisely given, so that we were forced to revert to means of Statistics, nevertheless the total *classical process* remained of course in principle deterministic. That is now different, though, in Quantum Mechanics, since concepts like *path*, *impact parameter* have lost their meaning. Accordingly, quantum-mechanically, for a scattering process, only probability statements are possible. In the following, we will have to concentrate ourselves on the question, with which probability particles are deflected (*scattered*) at the angle (ϑ, φ) relative to the original direction of motion, as a consequence of their interaction

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with *collision partners*. That will lead to the concept of the

(differential) cross-section

(Sect. 9.1). This is directly accessible by the experiment. For this purpose, one shoots a particle beam onto a *target* and counts by the use of a detector the number of particles, which are scattered by the angle (ϑ, φ) into the solid-angle element $d\Omega$. Relative to the total number of *incident* particles this yields directly the cross-section. The objective of the theory consists now of the task of bringing the cross-section into contact with basic interaction potentials, in order to get by comparison with the experimental findings concrete statements about these potentials. In this chapter some procedures are introduced, which allow to construct, at least approximately, such a connection.

9.1 Basic Concepts

We want to try in this chapter, at first, to transfer our *classical visualization* of the course of a scattering process into a *quantum-mechanical formulation*.

9.1.1 Model of the Scattering Process

The scattering process is a **dynamical** event, for the description of which only the **time-dependent Schrödinger equation** can come into consideration. The picture that at a certain point of time from some position a particle is *dispatched* in the direction of a scattering center makes the representation of the particle as **wave packet** of the kind, as we have discussed in Sect. 2.2.3 (Vol. 6), necessary. One can then consider the total scattering process as decomposed into the following partial steps:

1) Before the scattering:

Let the wave packet, which represents the particle, move with the group velocity $\mathbf{v}_g = v_g\,\mathbf{e}_z$ along the z-axis onto the scattering center (Fig. 9.1). We consider this process in the *laboratory system*, i.e. in a reference system, whose origin of coordinates is defined by the position of the scattering center. We

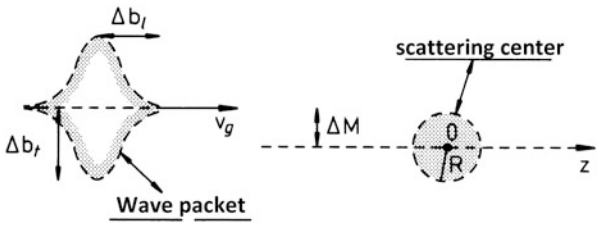


Figure 9.1: Exemplary representation of the scattering process **before** the actual scattering act

assume that the *scatterer* is a particle very much heavier than the incident particle or a particle in a space-fixed target. In both the cases the motion of the scatterer is not of special interest.

We assume that the domain of action of the scattering center is concentrated on a narrow space region around the origin of coordinates, so that the *incident* particle is influenced only within the *reach* R (Fig. 9.1). At larger distances from the scatterer the wave packet will therefore move *free of forces* and will be describable by the wave function (2.49) (Vol. 6):

$$\begin{aligned} \psi(\mathbf{r},t) &= \int d^3k\, \widehat{\psi}(\mathbf{k})\, e^{i(\mathbf{k}\cdot\mathbf{r}\,-\,\omega(\mathbf{k})t)}\ , \\ \omega(k) &= \frac{\hbar\, k^2}{2m}\ . \end{aligned} \tag{9.1}$$

The amplitude function $\widehat{\psi}(\mathbf{k})$ *compresses* the wave packet to a longitudinal (transverse) width $\Delta b_{\mathrm{l(t)}}$. The so prepared packet is indeed the solution of the time-dependent Schrödinger equation, but not an eigen-state of the *force-free* Hamilton operator. It does therefore possess neither a sharp momentum nor a precisely defined energy. The extensions Δb_{t} and Δb_{l} are measures for the corresponding position-indeterminacies. They should be very much larger than the average de Broglie wavelength λ of the packet, in order to guarantee that momentum and energy of the particle are still reasonably well defined:

$$\lambda \ll \Delta b_{\mathrm{t}}, \Delta b_{\mathrm{l}}\ . \tag{9.2}$$

On the other hand, in order to be able to remain also in the particle picture, the packet should of course be sufficiently sharply bunched. With considerations as those in Sect. 2.2.3 (Vol. 6) one can find out that even for atomic particles these two running counter requirements can be absolutely conciliated.

It goes without saying that in a real experiment one will not be able to send a single particle onto another single particle, but one has to deal with particle beams, i.e. with many wave packets of the just discussed kind. However, we let the particle density be so small that the interaction among the *incident* particles can be neglected, and the whole procedure can be considered as a sum of independent single processes.

2) The actual scattering act:

In the second step the particle enters the region of influence of the *scatterer*, when the transverse extension Δb_{t} of the *scatterer* is not smaller than the perpendicular distance ΔM of the packet-center of gravity from the origin of coordinates. For $\Delta M + R > \Delta b_{\mathrm{t}}$ the particle of course *ignores'* the *scatterer* (see Fig. 9.2). To avoid that the special structure of the wave packet influences the scattering process too much, the packet should completely cover the scattering region:

$$R \ll \Delta b_{\mathrm{t}},\ \Delta b_{\mathrm{l}}\ . \tag{9.3}$$

We furthermore assume that the scattering is **elastic**, so that the scattered particle changes only its direction, but not its kinetic energy. We exclude therewith

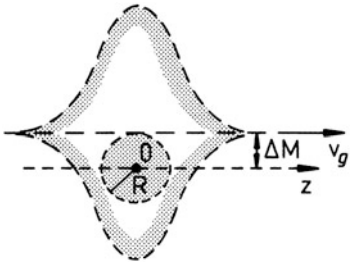


Figure 9.2: Exemplary representation of the actual scattering act

inner excitations of the collision partners. In the case of *inelastic scattering* the problem would of course become much more complicated, since then the initial state of the *scatterer* would play a non-negligible role. In the case of *elastic scattering* the presence of the *scatterer* can be represented by a *scattering potential* $V(\mathbf{r})$, which we will assume to be a spherically symmetric central potential $V(\mathbf{r}) = V(r)$.

It is clear that in the experiment normally the scattering is not affected by a single atom. However, let the target be *sufficiently thin*, so that only single-scatterings play a role. For this purpose, in particular, the interatomic distance must be large compared to the wavelength λ of the *incident* particles, large compared to the range R of the potential, and large compared to the extension of the wave packet. These assumptions are not always well fulfilled, sometimes, however, even not intended. In crystal-structure investigations (see Sect. 1.4.3 (Vol. 6)), *diffraction phenomena* in beams of electrons, photons, or thermal neutrons are intentionally exploited as the source of information. If, however, the above assumptions, together with those listed under 1), are fulfilled, then the total scattering process represents a sum of independent single events, which can be treated as spherically symmetric two-body problems.

3) After the scattering:

Because of the assumed short range of the potential, the particle, after the scattering, again enters the force-free region. As we still have to justify in detail, the wave function consists, due to the scattering process, of two components, a *traversing* uninfluenced wave packet and a *scattered* part, which is composed of spherical waves outgoing in all directions. The situation is completely equivalent to the behavior of reflection and transmission of waves at one-dimensional potential barriers, which we investigated in the Sects. 4.2 and 4.3 in Vol. 6. The observation of the scattered particle takes place by means of a suitable detector at the distance D from the scattering center. This must stand so far away that the condition of the force-free motion is realized, and the packet is no longer influenced by the scattering zone:

$$R,\, \lambda \ll D\ . \tag{9.4}$$

On the other hand, though, the detector should also be close enough, in order to keep the force-free *diffluence* of the wave packet, discussed in Sect. 2.2.3 of Vol. 6, within limits. We had estimated as condition for that in part 2. of Exercise 2.2.3 (Vol. 6):

$$\sqrt{\frac{\lambda\, D}{2\pi}} \ll \Delta b_{\mathrm{l}} \,. \tag{9.5}$$

It will not be possible to separate the freely traversing wave and the wave scattered in the forward direction. In order to avoid that the traversing wave switches on the detector, the measurement should finally take place at sufficiently large angles ϑ:

$$\Delta b_{\mathrm{t}} \ll D \sin\vartheta \,. \tag{9.6}$$

The considerations of this section show that it is possible to transfer our illustrative understanding of a scattering process into the formalism of Quantum Mechanics. On the other hand, because of the rather restrictive boundary conditions, this succeeds lastly more or less only *asymptotically*. All the following investigations are therefore to be understood under this aspect. We will certainly beware of trying to calculate explicitly the precise path of the particle, for instance within the scattering zone. In order to get the actually required information, fortunately, this will also prove to be not necessary.

9.1.2 Formulation of the Scattering Problem

As described in the preceding section, we assume that a particle beam with *sufficiently sharp* $(\mathbf{p}, E)$ impinged onto a target with N_{T} scattering centers per cm^2. Let the scattering be elastic, where it is a bunch of incoherent single processes, so that the problem to be solved can be reduced to a **two-body problem**. The interaction potential is presumed as spherically symmetric and short range:

$$r\, V(r) \underset{r\to\infty}{\longrightarrow} 0 \,. \tag{9.7}$$

The bare Coulomb potential does not fulfill this requirement and must therefore be considered separately. The *incident* particle should be actually described as wave packet. This can, however, always, as in (9.1), be represented as superposition of plane waves with suitable amplitude functions $\widehat{\psi}(\mathbf{k})$. It therefore suffices to calculate the scattering of a single plane wave. In order to avoid contradictions and misunderstandings, however, we will have to include at times the *wave-packet picture* in our argumentation. As an example the plane wave is characterized by a sharp momentum and a sharp energy, and therewith by a completely undetermined position. The plane wave is therefore *'everywhere existing'* and consequently also *'never far away'* from the scattering center. The requirement, which leads to (9.6), that the traversed wave does not affect the detector, is of course by the plane wave not satisfiable, either. From time to time we will therefore have to implicitly utilize in the following that the amplitude function $\widehat{\psi}(\mathbf{k})$ in (9.1) guarantees that the plane waves, which are to be investigated, *destructively interfere among themselves* everywhere except for a

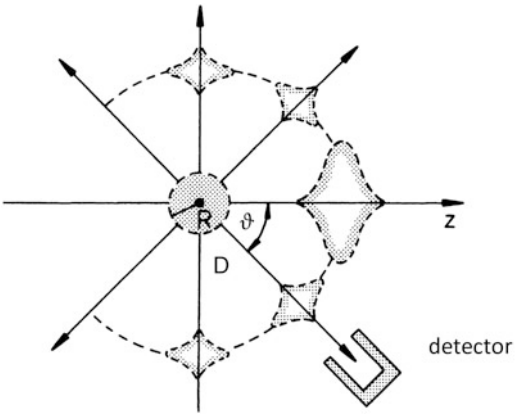


Figure 9.3: Exemplary representation of the scattering process **after** the actual scattering act

small space region (Fig. 9.3). Of course, the consistent description of the scattering process by wave packets would also be possible, but would turn out to be mathematically very much more involved.

The plane wave is an energy-eigen state, and the energy does not change by the *elastic* scattering. All expectation values become time-independent (*stationary scattering problem!*). Distinctly before the scattering zone, the plane wave is a solution of the *force-free*, time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\,\Delta\,\varphi_0(\mathbf{r}) = E\,\varphi_0(\mathbf{r})\ .$$

The direction of incidence defines the z-direction:

$$\begin{aligned} \mathbf{p} &= \hbar\,\mathbf{k}_0 = \hbar\,k_0\,\mathbf{e}_z\ ; \quad E = \frac{\hbar^2 k_0^2}{2m}\ , \\ \varphi_0(\mathbf{r}) &= e^{i\,k_0 z}\ . \end{aligned}$$

If n_0 is the particle density in the *incident* beam, then we have with ((2.27), Vol. 6) the following time-independent (*stationary*) current density:

$$\mathbf{j}_0 = n_0\,\frac{\hbar}{2m\,i}\,(\varphi_0^*(\mathbf{r})\,\nabla\,\varphi_0(\mathbf{r}) - \varphi_0(\mathbf{r})\,\nabla\,\varphi_0^*(\mathbf{r})) = n_0\,\frac{\hbar\,\mathbf{k}_0}{m}\ . \tag{9.8}$$

We had found in Sect. 6.4 a special representation of the plane wave, which turns out to be extremely useful for our further considerations, namely the expansion (6.152) in eigen-functions of the orbital angular momentum:

$$e^{ikz} = e^{ikr\cos\vartheta} = \sum_{l=0}^{\infty} i^l (2l+1)\,j_l(k\,r)\,P_l(\cos\vartheta)\ .$$

This is convenient because the scattering potential is spherically symmetric and therefore conserves the angular momentum. That means that for the resulting wave function after the scattering process it appears appropriate to also use such an expansion in eigen-functions of the angular momentum. (One should remember at this stage once more the results from Sect. 6.4). For the following the result (6.125) is especially important, according to which one can consider the plane wave as composed asymptotically by an outgoing and an incoming spherical wave. This results from the corresponding behavior of the spherical Bessel function:

$$j_l(k\,r) \underset{\text{large } r}{\longrightarrow} \frac{1}{2\,ikr}\left(e^{i(k\,r\,-\,l\,\pi/2)} - e^{-i(k\,r\,-\,l\,\pi/2)}\right) . \tag{9.9}$$

The actual *scattering problem* now consists in the solution of the Schrödinger equation,

$$\left[\frac{\mathbf{p}^2}{2m} + V(r)\right]\,\varphi(\mathbf{r}) = E\,\varphi(\mathbf{r}) , \tag{9.10}$$

with $E > 0$ and

$$\varphi(\mathbf{r}) = \varphi_0(\mathbf{r}) + \varphi_{\rm s}(\mathbf{r}) . \tag{9.11}$$

At the center of scattering the *incident* wave $\varphi_0(\mathbf{r})$ creates a **scattered wave** $\varphi_{\rm s}(\mathbf{r})$. Since this part is *created* just there, it must contain of course only *outgoing* parts. If one takes into consideration that for $r \to \infty$ again a *force-free* motion sets in, it must be expected for $\varphi(\mathbf{r})$ asymptotically a form as in (9.9) with a *proper* modification of the *outgoing* part. For the scattered wave the following ansatz therewith suggests itself:

$$\varphi_{\rm s}(\mathbf{r}) \underset{r\,\to\,\infty}{\longrightarrow} f(\vartheta)\,\frac{e^{ikr}}{r} . \tag{9.12}$$

That the pre-factor depends only on ϑ, and not on φ, is of course due to the special symmetry, which we have chosen for the scattering process. One calls $f(\vartheta)$ the **scattering amplitude**, which contains the full information about the scattering potential.

The mathematical solutions of (9.10) will be normally degenerate. Only by the physical boundary condition that $\varphi(\mathbf{r})$ must be built up by an *incident* plane wave and an *outgoing* spherical wave with angle-dependent amplitude, the matter becomes unique. It would of course also be possible to construct an *incident* scattered wave as a solution of (9.10). But that would be *unphysical*.

In the next step let us calculate the current density $\mathbf{j}_{\rm s}$ of the scattered wave. With the representation of the nabla operator in spherical coordinates (r, ϑ, φ), derived as Eq. (1.395) in Vol. 1, ,

$$\nabla \equiv \mathbf{e}_r\,\frac{\partial}{\partial r} + \mathbf{e}_\vartheta\,\frac{1}{r}\,\frac{\partial}{\partial \vartheta} + \mathbf{e}_\varphi\,\frac{1}{r\sin\vartheta}\,\frac{\partial}{\partial \varphi} ,$$

one easily finds:

$$\varphi_s^*(\mathbf{r})\,\nabla\,\varphi_s(\mathbf{r}) = \mathbf{e}_r\,\frac{|f(\vartheta)|^2}{r}\,\left(\frac{i\,k}{r}-\frac{1}{r^2}\right)+\mathbf{e}_\vartheta\,\frac{1}{r^3}\,f^*(\vartheta)\,\frac{\partial f(\vartheta)}{\partial\vartheta}\;.$$

$\varphi_s(\mathbf{r})\,\nabla\,\varphi_s^*(\mathbf{r})$ is just the conjugate-complex hereof. Therewith it follows as current density of the scattered wave:

$$\begin{aligned}\mathbf{j}_s(\mathbf{r}) &= n_0\,\frac{\hbar}{2\,m\,i}\,\left(\varphi_s^*(\mathbf{r})\,\nabla\,\varphi_s(\mathbf{r})-\varphi_s(\mathbf{r})\,\nabla\,\varphi_s^*(\mathbf{r})\right)\\ &= n_0\,\frac{\hbar\,k}{m}\,\frac{|f(\vartheta)|^2}{r^2}\,\mathbf{e}_r+\mathcal{O}\left(\frac{1}{r^3}\right)\;.\end{aligned}\tag{9.13}$$

The second summand can be neglected asymptotically. $\mathbf{j}_s$ has then only a radial component. The radial particle current through the surface of a sphere of the radius r,

$$\iint d\varphi\,d\cos\vartheta\,r^2\,(\mathbf{e}_r\cdot\mathbf{j}_s)\;\longrightarrow\;\text{const}>0\;,$$

is independent of r and positive, corresponding to the fact that $\varphi_s(\mathbf{r})$ is an **outgoing** spherical wave.

If we would take the ansatz (9.11) really in every sense as serious, then the above considerations were of course not completely correct. The current density of the solving solution $\varphi(\mathbf{r})$ is naturally not simply the sum of the current density of the *incident* and the *scattered* wave. There will appear interference terms. In order to justify the separate calculation of $\mathbf{j}_s$, we have rather to recall again the picture of the wave packet, according to which the *incident* beam has only a minor transversal expansion. We are interested, however, only in the current density, which falls onto the detector. Because of (9.6) contributions of the *incident* wave are excluded from that. The total current density, seen by the detector, will therefore be composed only of scattering contributions.

Let us finally try to get contact to the experiment. That succeeds by means of the **cross-section**, which is generally defined as

$$\frac{\textbf{number of processes per unit time}}{\textbf{incident particle current density}}$$

The process, which we are interested in here, is the traversing of a particle through the area $d\mathbf{F}$ which is covered by the detector (Fig. 9.4). With

$$d\mathbf{F}=r^2 d\Omega\,\mathbf{e}_r\qquad(d\Omega=\sin\vartheta\,d\vartheta\,d\varphi)$$

one finds for the number of the particles, which are scattered into the solid-angle element $d\Omega$, and which penetrate per second the surface $d\mathbf{F}$:

$$\mathbf{j}_s\cdot d\mathbf{F}=n_0\,\frac{\hbar\,k}{m}\,|f(\vartheta)|^2\,d\Omega+\mathcal{O}\left(\frac{1}{r}\right)\;.$$

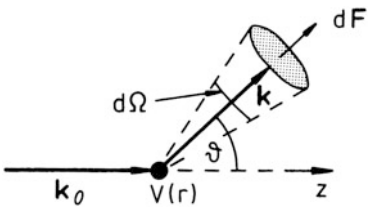


Figure 9.4: Angle relations for fixing the cross-section

This yields the **differential cross-section**

$$d\sigma(\vartheta) = \frac{\mathbf{j}_\mathrm{s} \cdot d\mathbf{F}}{|\mathbf{j}_0|} = |f(\vartheta)|^2 \, d\Omega \,, \tag{9.14}$$

where we have used (9.8) and $k = k_0$ (elastic scattering). The cross-section is thus completely determined by the scattering amplitude. $d\sigma$ has the dimension of an area. The unit, in use for nuclear physical scattering experiments, is $1\,\mathrm{barn} = 10^{-24}\,\mathrm{cm}^2$. When one integrates (9.14) over the total solid angle, then one gets the **total cross-section**

$$\sigma = \int d\Omega \, \frac{d\sigma}{d\Omega} = 2\pi \int_0^\pi d\vartheta \, \sin\vartheta |f(\vartheta)|^2 \,. \tag{9.15}$$

In the experiment N_0 is the number of particles, which impinge on the target per second and per cm^2, N_T the number of atomic scatterers in the target per cm^2, and $dn(\vartheta)$ the number of the particles, which are scattered per second into the angle element $d\Omega$. All the three quantities are measurable and therefore also the **differential cross-section**:

$$d\sigma(\vartheta) = \frac{dn(\vartheta)}{N_\mathrm{T} \, N_0} \,. \tag{9.16}$$

This means lastly that $|f(\vartheta)|^2$ can be experimentally determined. The task of the theory is, consequently, to bring $|f(\vartheta)|^2$ into contact with the interaction potential $V(r)$.

9.1.3 Exercises

Exercise 9.1.1
Calculate the current density of the wave function composed by the *incident* plane wave $\varphi_0(\mathbf{r})$ and the *scattered wave* $\varphi_\mathrm{s}(\mathbf{r})$ (9.11):

$$\begin{aligned} \varphi(\mathbf{r}) &= \varphi_0(\mathbf{r}) + \varphi_\mathrm{s}(\mathbf{r}) \,, \\ \varphi_0(\mathbf{r}) &= e^{ikr\cos\vartheta} \,, \\ \varphi_\mathrm{s}(\mathbf{r}) &= f(\vartheta) \, \frac{e^{ikr}}{r} \,. \end{aligned}$$

Which terms of interference appear in the current density?

Exercise 9.1.2
Show that the asymptotic solution (9.11) of the scattering problem,

$$\varphi(\mathbf{r}) = e^{ikz} + f(\vartheta)\,\frac{e^{ikr}}{r} \qquad \left(k^2 = \frac{2m\,E}{\hbar^2}\right) ,$$

fulfills the Schrödinger equation, if the scattering potential for $r \to \infty$ decreases stronger than $1/r$.

9.2 Partial Wave Method

9.2.1 Decomposition in Partial Waves

The Hamilton operator (9.10) of the full scattering problem commutes with the angular momentum operators $\mathbf{L}^2$ and L_z. Therefore it is natural to expand the solution in eigen-functions of angular momentum, i.e., in spherical harmonics. According to the agreed arrangement, the scattering problem possesses azimuthal symmetry ($m_l = 0$), i.e., no dependence on the angle φ. The spherical harmonics are then reduced to Legendre polynomials (5.103),

$$Y_{l0}\,(\vartheta, \varphi) = \sqrt{\frac{2l+1}{4\pi}}\,P_l(\cos\vartheta)\ .$$

We therefore choose the ansatz

$$\varphi(\mathbf{r}) = \sum_{l\,=\,0}^{\infty} \frac{u_l(\mathbf{r})}{r}\,P_l(\cos\vartheta)\ . \tag{9.17}$$

As exemplified in detail in connection with Eq. (6.19), the time-independent Schrödinger equation leads with such an ansatz to the following differential equation for $u_l(r)$:

$$u_l''(r) + \left(k^2 - v_{\text{eff}}(r)\right)\,u_l(r) = 0\ . \tag{9.18}$$

Thereby we have used, as already done often earlier, the abbreviation:

$$k^2 = \frac{2m}{\hbar^2}\,E$$

The effective potential contains the *centrifugal part* (6.20):

$$v_{\text{eff}}(r) = \frac{2m}{\hbar^2}\,V_{\text{eff}}(r) = \frac{2m}{\hbar^2}\,\left[V(r) + \frac{\hbar^2 l(l+1)}{2m\,r^2}\right]\ . \tag{9.19}$$

We have solved in Sect. 6.4 a completely analogous problem for the *free* particle, i.e., for the special case $V = 0$. The solution (6.152) indeed has the structure of (9.17) with

$$u_l^{(0)}(r) = i^l\,(2l+1)\,r\,j_l\,(k\,r)\ .$$

At this point the asymptotic behavior ($k\,r \gg l$) of the Bessel function (6.125) is important:

$$u_l^{(0)}(r) \sim \frac{1}{k}\, i^l (2l+1) \sin\left(k\,r - \frac{l\,\pi}{2}\right) . \tag{9.20}$$

The wave function $\varphi(\mathbf{r})$ of the *full* scattering problem must also be asymptotically describable as a solution of a force-free motion, because, according to the presumption (9.7), the potential $V(r)$ is of sufficiently short range. Therefore one can safely assume that the influence of the potential will asymptotically manifest itself essentially by a phase shift:

$$u_l(r) \sim \alpha_l \sin\left(k\,r - \frac{l\,\pi}{2} + \delta_l\right) . \tag{9.21}$$

One calls δ_l the **scattering phase of the lth partial wave**. It is of course characteristic of the respective potential $V(r)$, and will be a function of the energy E via k.

With the **ansatz** (9.21), the solution (9.17) can be asymptotically written as an incoming and an outgoing spherical wave:

$$\varphi(\mathbf{r}) \sim \left(\frac{e^{ikr}}{r} \sum_l \frac{\alpha_l}{2i}\, e^{i\delta_l}\, e^{-i(l\,\pi/2)}\, P_l(\cos\vartheta) + \frac{e^{-ikr}}{r} \sum_l \frac{\alpha_l}{2i}\, e^{-i\delta_l}\, e^{i(l\,\pi/2)}\, P_l(\cos\vartheta) \right) .$$

The sums run in principle over **all** quantum numbers of the angular momentum. One has to therefore ask oneself, whether and how, for $l \to \infty$, the presumption $kr \gg l$ can be fulfilled for the asymptotic behavior. At the end of this section, though, we will convince ourselves that for a short-range potential $V(r)$ only the lowest quantum numbers l must be taken into consideration, for which $k\,r \gg l$ is always realizable.

The above asymptotic form of the solution $\varphi(\mathbf{r})$, however, has to now have the structure (9.11), (9.12), i.e., it should also hold with (9.20):

$$\begin{aligned} \varphi(\mathbf{r}) \quad \sim \quad & \left\{ \frac{e^{ikr}}{r} \left[\frac{1}{k} \sum_l \frac{i^l}{2i}\, (2l+1)\, e^{-i(l\,\pi/2)}\, P_l(\cos\vartheta) + f(\vartheta) \right] \right. \\ & \left. + \frac{e^{-ikr}}{r}\, \frac{1}{k} \sum_l \frac{i^l}{2i}\, (2l+1)\, e^{i(l\,\pi/2)}\, P_l(\cos\vartheta) \right\} . \end{aligned}$$

Here we find, among other points, the fact that only the outgoing spherical wave can be influenced by the scattering center. In order to guarantee that, in contrast, the incoming wave part can be exclusively ascribed to the plane wave, it must obviously hold in our ansatz

$$\alpha_l = \frac{1}{k}\, i^l (2l+1)\, e^{i\delta_l} = \frac{1}{k} (2l+1)\, e^{i(\delta_l + (l\,\pi/2))} . \tag{9.22}$$

But then, by comparison of the two asymptotic expressions for $\varphi(\mathbf{r})$, the scattering amplitude $f(\vartheta)$ is also fixed:

$$\begin{aligned} f(\vartheta) &= \frac{1}{k}\sum_l (2l+1)\,\frac{1}{2i}\left(e^{2i\,\delta_l}-1\right)\,P_l(\cos\vartheta) \\ &= \frac{1}{k}\sum_l (2l+1)\,e^{i\,\delta_l}\sin\delta_l\,P_l(\cos\vartheta)\;. \end{aligned} \tag{9.23}$$

If we know the scattering phases δ_l, the scattering amplitude $f(\vartheta)$ is then calculable, which in turn determines the cross-section (9.14). At first glance, however, it looks as if we would not have gained very much. Quite the contrary, instead of **one** sought-after function we now have to determine **infinitely many** partial waves. The representation (9.23) becomes useful surely only when, because of some reasons, the l-sum can be terminated after a few terms ($l \le l_0$). As already agreed upon, only then the *asymptotic* ($k\,r \gg l$) *ansatz* (9.21) can strictly be justified. At the end of this section we will try to estimate the *really efficient* angular momentum quantum numbers $l \le l_0$ by an analogy-consideration to the *classical* scattering process.

With the scattering amplitude in the forward-direction $f(\vartheta = 0)$ a **sum-rule for scattering phases** can be formulated:

$$f(0) = \frac{1}{k}\sum_l (2l+1)\,e^{i\,\delta_l}\sin\delta_l\;. \tag{9.24}$$

The *differential cross-section* (9.14) can now also be expressed with (9.23) by the scattering phases:

$$\frac{d\sigma}{d\Omega} = \frac{1}{k^2}\sum_{l,\,l'}(2l+1)\,(2l'+1)\sin\delta_l\sin\delta_{l'}\,e^{i(\delta_l\,-\,\delta_{l'})}\,P_l(\cos\vartheta)\,P_{l'}(\cos\vartheta)\;. \tag{9.25}$$

For the calculation of the *total cross-section* (9.15) we use the orthogonality relation (5.98) of the Legendre polynomials:

$$\sigma = 2\pi\int_{-1}^{+1} d\cos\vartheta\,\frac{d\sigma}{d\Omega} = \frac{4\pi}{k^2}\sum_l (2l+1)\sin^2\delta_l\;. \tag{9.26}$$

The comparison of this expression with (9.24) yields an interesting relation, which is called the **optical theorem**:

$$\sigma = \frac{4\pi}{k}\;\mathrm{Im}\;f(0)\;. \tag{9.27}$$

This theorem can be qualitatively understood as follows: The scattering process does not change the particle number. Therefore, all that the total cross-section registers as *scattered* intensity, should have been *interfered away* from the incident wave. Interference is possible, however, only with the wave scattered in

forward-direction ($\vartheta = 0$).This interference is responsible, in primary beam direction, for a *particle shadow*, which just corresponds to the newly added scattering current. The fact that only the imaginary part of $f(0)$ appears in the *optical theorem* must be justified by a more detailed consideration, which we have to skip here.

We already mentioned that the problem seems, at first, to have become more complicated with the introduction of the partial waves. Only when the series for σ and $d\sigma/d\Omega$ are quickly converging, so that only few scattering phases play a role, the *decomposition with respect to partial waves*, done in (9.23), (9.25) and (9.26), can be of practical use. But under which conditions can we count with such a quick convergence? Let us try to answer this question by an analogy consideration from Classical Mechanics.

From a classical point of view, scattering can not happen, when the *impact parameter* b (Fig. 9.5) is larger than the effective range R_0 of the potential $V(r)$. We remember that the *impact parameter* is defined as the perpendicular distance, with which the *incident* particle would pass the *scatterer* if no potential force influenced the flight path. (To avoid confusion with the momentum we use here (Fig. 9.5) for the impact parameter the letter b instead of p as in Sect. 1.3.3 (Vol. 6)).

Since the particle is scattered by a central potential, the classical angular momentum is an integral of motion:

$$|\mathbf{L}| = |\mathbf{r} \times \mathbf{p}| = \text{const} = b\, p_\infty = b\, \sqrt{2m\, E}\ .$$

p_∞ is the absolute value of the particle momentum at a large distance from the scattering center. The condition that for a *scattering* the impact parameter must be smaller than the range of the potential, does obviously, for given particle energy E, not permit arbitrarily large angular momenta:

$$|\mathbf{L}| \leq R_0\, \sqrt{2m\, E}\ . \tag{9.28}$$

If we transfer now this consideration, in the sense of the *principle of correspondence* (Sect. 3.5 (Vol. 6)), into Quantum Mechanics, then it has to be required correspondingly

$$l \leq \sqrt{l(l+1)} \leq \frac{1}{\hbar}\, R_0\, \sqrt{2m\, E} = k\, R_0\ . \tag{9.29}$$

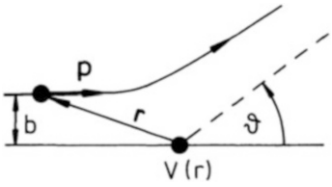


Figure 9.5: Definition of the impact parameter for a classical scattering process

We can therefore assume that the sums (9.23), (9.25) and (9.26) can be terminated at a maximal angular momentum quantum number l_0 of the order of magnitude $k\,R_0$. In the next subsections we will substantiate this supposition by some examples.

One denotes the contribution to $l = 0$ as *s-scattering*, the one to $l = 1$ as *p-scattering*, and so on, in analogy to the corresponding orbital nomenclature which we introduced in Sect. 5.1.6. According to (9.29) we expect for small particle energies and very short-range potentials *pure s-scattering* with a spherically symmetric cross-section:

$$\frac{d\sigma}{d\Omega} \underset{s\text{-scattering}}{\longrightarrow} \frac{1}{k^2}\sin^2\delta_0\ . \tag{9.30}$$

We will be able to confirm this in the next section by an explicit evaluation of the scattering at a simple idealized potential.

In principle we can of course solve the radial equation (9.18) for a given potential $V(r)$ and for arbitrary quantum numbers of the angular momentum l with the aid of a computer. For r-values, which are outside the reach of the potential, the comparison of the numerical solution with (9.21), (9.22) should determine the scattering phases δ_l. The explicit *analytic* calculation of scatterings at simple potentials, however, is to be preferred here, because they lead to a better understanding of the intrinsic physical connections.

9.2.2 Scattering by a Hard Sphere

Let us demonstrate the method of scattering phases at first for the simple model of a *hard sphere*:

$$V(r) = \begin{cases} \infty & \text{for } r \le R_0\ , \\ 0 & \text{for } r > R_0\ . \end{cases} \tag{9.31}$$

One can simulate by this potential, as a very simple approximation, the scattering of microscopic particles by an atomic nucleus. The *range* R_0 of the potential would then correspond to the *nuclear radius*.

The wave function ($\varphi(\mathbf{r})$), to be determined, obviously has to fulfill the boundary condition

$$\varphi(\mathbf{r}) \equiv 0 \quad \text{for } r \le R_0\ . \tag{9.32}$$

For $r > R_0$ the potential vanishes. The particle then moves, in a certain sense, in a *central field of the strength zero*, as we have discussed it in Sect. 6.4. The potential V is zero, but the *centrifugal barrier* (6.20) $(\hbar^2 l(l+1))/(2mr^2)$ still acts. Therefore an ansatz as that in (6.16) and (9.17), respectively, is recommended, where we can already exploit again the azimuthal symmetry of the scattering process:

$$\varphi(\mathbf{r}) = \sum_{l=0}^{\infty} R_l(r)\,P_l(\cos\vartheta)\ . \tag{9.33}$$

As explained in detail in Chap. 6, the radial part $R_l(r)$ has to fulfill also here the Bessel differential equation (6.114). The general solution can be formulated

by the spherical Bessel functions (j_l) and the spherical Neumann functions (n_l) ((6.120), (6.121)),

$$R_l(r) = a_l\, j_l(k\,r) + b_l\, n_l(k\,r) \qquad \left(k = \sqrt{\frac{2m\,E}{\hbar^2}}\right) ,$$

or also with the Hankel functions defined in (6.127):

$$R_l(r) = c_l\, h_l^{(+)}(k\,r) + d_l\, h_l^{(-)}(k\,r) .$$

$\varphi(r)$ must of course possess, first of all, the solution structure (9.11), i.e., it must be composed of a plane wave $\varphi_0(\mathbf{r})$ and a scattered wave $\varphi_\mathrm{s}(\mathbf{r})$. According to (9.12) the latter must asymptotically behave like an outgoing spherical wave. Of all the four types of solution (j_l, n_l, $h_l^{(+)}$, $h_l^{(-)}$) this is guaranteed only by the Hankel function $h_l^{(+)}(k\,r)$ (see (6.129)):

$$h_l^{(+)}(k\,r) \sim -\frac{i}{k\,r}\, e^{i(k\,r\,-\,(l\,\pi/2))} .$$

Together with the expansion of the plane wave (6.152) it follows therewith an ansatz for the solution, which is, compared to (9.33), already essentially more detailed:

$$\varphi(\mathbf{r}) = \sum_l (2l+1)\, i^l \left[j_l(k\,r) + \gamma_l\, h_l^{(+)}(k\,r)\right] P_l(\cos\vartheta) . \tag{9.34}$$

In this form $\varphi(\mathbf{r})$ has the right asymptotic behavior, and the radial part solves the Bessel differential equation (6.114). The coefficients are still to be fixed by the boundary condition (9.32):

$$\gamma_l = -\frac{j_l(k\,R_0)}{h_l^{(+)}\,(k\,R_0)} = -\frac{j_l\,(k\,R_0)}{j_l\,(k\,R_0) + i\,n_l\,(k\,R_0)} . \tag{9.35}$$

$\varphi(\mathbf{r})$ is therewith completely determined for the entire space, i.e., not only asymptotically.

The second summand in (9.34) represents the scattered wave $\varphi_\mathrm{s}(\mathbf{r})$. Its behavior for $r \to \infty$ must, according to (9.12), fix the scattering amplitude $f(\vartheta)$:

$$\begin{aligned} f(\vartheta) &= \sum_l (2l+1)\, i^l\, \gamma_l \left(-\frac{i}{k}\, e^{-i(l\,\pi/2)}\right) P_l(\cos\vartheta) \\ &= \frac{1}{k} \sum_l (2l+1)\,(-i)\,\gamma_l\, P_l(\cos\vartheta) . \end{aligned}$$

If we equate this expression with the *scattering phase representation* (9.23) for $f(\vartheta)$, then it follows, because of the orthogonality of the Legendre polynomials, that the equality must already be valid for each single summand:

$$\gamma_l = i\, e^{i\delta_l} \sin\delta_l = \frac{1}{2}\left(e^{2i\delta_l} - 1\right) . \tag{9.36}$$

Via (9.35) and (9.36) we now have the possibility to represent all scattering phases δ_l as functions of the energy E (in k) and the *potential range* R_0:

$$\tan 2\delta_l = \frac{\sin 2\delta_l}{\cos 2\delta_l} = \frac{2\ \mathrm{Im}\ \gamma_l}{2\ \mathrm{Re}\ \gamma_l + 1} = \frac{2 j_l\,(k\,R_0)\,n_l\,(k\,R_0)}{n_l^2\,(k\,R_0) - j_l^2\,(k\,R_0)}\ .$$

The comparison with

$$\tan 2\delta_l = \frac{2\tan\delta_l}{1-\tan^2\delta_l}$$

leads to:

$$\tan\delta_l = \frac{j_l\,(k\,R_0)}{n_l\,(k\,R_0)}\ . \tag{9.37}$$

There is with $\tan\delta_l = -n_l\,(k\,R_0)/\ j_l\,(k\,R_0)$ still another mathematical solution, which, however, violates the *physical boundary condition*, that for $R_0 \to 0$ all scattering phases must vanish.

If we now insert

$$\sin^2\delta_l = \frac{\tan^2\delta_l}{1+\tan^2\delta_l}$$

into Eq. (9.26), using (9.37), then we can find the exact expression for the **cross-section for the scattering by a hard sphere**:

$$\sigma = \frac{4\pi}{k^2}\sum_l (2l+1)\,\frac{j_l^2\,(k\,R_0)}{n_l^2\,(k\,R_0) + j_l^2\,(k\,R_0)}\ . \tag{9.38}$$

We will comment a bit on this result concerning its limiting behavior:

1) Limiting case: $k\,R_0 \ll 1$

Let us at first assume that the de Broglie wave length of the scattered particle is very much larger than the range of the potential. According to our *semi-classical* estimation (9.29) we expect in this limit almost pure *s-scattering* with an isotropic cross-section (9.30).

Using the approximation formulas (6.123) and (6.124) for the Bessel and Neumann functions with small argument, it can be estimated:

$$\begin{aligned} l = 0: &\quad \tan\delta_0 \approx -k\,R_0 \approx \sin\delta_0\ , \\ l \geq 1: &\quad \tan\delta_l \approx -\frac{(k\,R_0)^{2l+1}}{(2l-1)!!\,(2l+1)!!} \approx \sin\delta_l\ . \end{aligned}$$

We recognize here that with increasing quantum number l of the angular momentum the scattering phases become very quickly very small or lie very closely to an integral multiple of π,

$$\frac{\sin^2\delta_{l+1}}{\sin^2\delta_l} \approx \frac{\tan^2\delta_{l+1}}{\tan^2\delta_l} \approx \frac{(k\,R_0)^4}{(2l+1)^2\,(2l+3)^2} \ll 1\ , \tag{9.39}$$

so that in fact almost *pure s-scattering* is present. In the sum (9.26) the $l = 0$-term dominates:

$$\sigma \approx \frac{4\pi}{k^2}\,\sin^2\delta_0 \approx 4\pi\,R_0^2\ . \tag{9.40}$$

The cross-section is thus in the limit of large de Broglie wave lengths just the fourfold of the geometric cross-section of the sphere.

2) Limiting case: $k\,R_0 \gg 1$

Since in this limit the de Broglie wave length is very much smaller than the linear extensions of the scattering center, the quantum-mechanical cross-section should approach its classical counterpart $\sigma_{cl} = \pi\,R_0^2$. At least one should suppose this according to the principle of correspondence.

The boundary conditions, which lead to (9.37), are independent of $k\,R_0$. Equation (9.37) is therefore also valid in the present limit, but where we now have to apply the asymptotic forms (6.125) and (6.126) of the Bessel and Neumann functions:

$$\tan\delta_l \underset{k\,R_0 \gg l}{\longrightarrow} -\tan\left(k\,R_0 - \frac{l\,\pi}{2}\right) .$$

By this we can read off the scattering phase δ_l, at least except for an integral multiple of π:

$$\delta_l \longrightarrow -k\,R_0 + l\,\frac{\pi}{2}\,(+n\,\pi) . \tag{9.41}$$

Presuming the validity of our semi-classical estimation (9.29) we will approximately terminate the *sum of partial waves* (9.26) for the total cross-section at an angular momentum quantum number l_0. This number is the maximal positive integer, for which

$$\sqrt{l_0(l_0+1)} \le k\,R_0 . \tag{9.42}$$

It is therefore certainly $l_0 \gg 1$, so that σ can be calculated as follows:

$$\begin{aligned}
\sigma \quad &\approx \quad \frac{4\pi}{k^2}\sum_{l=0}^{l_0}(2l+1)\sin^2\delta_l \\
&\overset{(9.41)}{\approx} \quad \frac{4\pi}{k^2}\sum_{l=0}^{l_0}\left[(l+1)\cos^2\left(k\,R_0-(l+1)\,\frac{\pi}{2}\right)+l\sin^2\left(k\,R_0-l\,\frac{\pi}{2}\right)\right] \\
&= \quad \frac{4\pi}{k^2}\sum_{l'=1}^{l_0} l'\left[\cos^2\left(k\,R_0-l'\frac{\pi}{2}\right)+\sin^2\left(k\,R_0-l'\,\frac{\pi}{2}\right)\right] \\
&\qquad +\frac{4\pi}{k^2}\,(l_0+1)\cos^2\left[k\,R_0-(l_0+1)\,\frac{\pi}{2}\right] \\
&= \quad \frac{4\pi}{k^2}\sum_{l'=1}^{l_0} l' + \mathcal{O}(l_0) .
\end{aligned}$$

The sum has the value $(1/2)\,l_0(l_0+1)$, so that we can estimate the cross-section, because of $l_0 \gg 1$ and with (9.42), to be:

$$\sigma \approx \frac{2\pi}{k^2}\,l_0^2 \approx 2\pi\,R_0^2 . \tag{9.43}$$

Contrary to our expectations, the cross-section is for high energies (small wave lengths) of the *incident* particle **twice as large** as the classical cross-section, which is identical to the geometric cross-section πR_0^2 of the sphere. The reason is the same as that which explains the *optical theorem* (9.27). The cross-section consists of two terms, a real *scattering term*, which exactly corresponds to the *classical expectation*, and a *diffraction term*, which is concentrated in forward direction and takes care for the *shadow* behind the hard sphere. As already thought through in connection with the *optical theorem*, the cancellation of the *incident* wave intensity in the *shadow region* of the sphere by the in forward direction *scattered* wave corresponds exactly to the scattered intensity reflected by finite angles, because the particle number can not change by the scattering process. The scattering intensity in forward direction ($\vartheta = 0$) thus is exactly as large as the residual scattering intensity. But because the *classical* cross-section registers only the really scattered radiation, it is just half as large as the *total* quantum-mechanical cross-section, which also incorporates the *diffraction term*.

9.2.3 Scattering of Slow Particles by a Potential Well

As a further example of application we look at the scattering on a three-dimensional *potential well*:

$$V(r) = \begin{cases} -V_0 & \text{if } r < a\,, \\ 0 & \text{if } r \geq a \end{cases}$$

We have already worked on this potential problem in Sect. 6.3, and thereby investigated especially the *bound states* (Sect. 6.3.3) for energies $-V_0 < E < 0$. Here we are interested in the case $E > 0$, which we could only shortly broach in Sect. 6.3.4. We use in the following the abbreviations:

$$\begin{aligned} q^2 &= \begin{cases} k_0^2 & \text{for } r < a\,, \\ k^2 & \text{for } r \geq a\,, \end{cases} \\ k^2 &= \frac{2m}{\hbar^2} E\,; \quad k_0^2 = \frac{2m}{\hbar^2}(E + V_0)\,. \end{aligned} \tag{9.44}$$

According to (6.17) and (6.114) we have to search for the solution of the *radial equation*

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} + \left(q^2 - \frac{l(l+1)}{r^2}\right)\right] R_l(r) = 0\,.$$

This type of differential equation we have evaluated often enough in the meantime. We are therefore able to directly display the structure of the solution. With the requirement that $R_l(r)$ is regular in the origin, it remains only the choice (see (6.140)):

$$R_l(r) = \begin{cases} a_l\, j_l(k_0 r) & \text{for } r < a\,, \\ \alpha_l\, j_l(k\,r) + \beta_l\, n_l\,(k\,r) & \text{for } r \geq a\,. \end{cases} \tag{9.45}$$

j_l and n_l are here of course again the Bessel and Neumann functions. Once more, the asymptotic ($r \to \infty$)-behavior of the particle wave will be important for the following considerations. With (6.125) and (6.126) the ansatz (9.45) for the radial function in this limit has the form:

$$R_l(r) \;\longrightarrow\; \frac{1}{k\,r}\left[\alpha_l \sin\left(k\,r - \frac{l\,\pi}{2}\right) - \beta_l \cos\left(k\,r - \frac{l\,\pi}{2}\right)\right] .$$

On the other hand, it is, very generally, because of (9.21) and (9.22), to require:

$$\begin{aligned} R_l(r) \;&\longrightarrow\; i^l(2l+1)\,\frac{1}{k\,r}\sin\left(k\,r - \frac{l\,\pi}{2} + \delta_l\right)\, e^{i\delta_l} \\ &= i^l(2l+1)\,\frac{e^{i\delta_l}}{k\,r}\left[\sin\left(k\,r - \frac{l\,\pi}{2}\right)\cos\delta_l + \cos\left(k\,r - \frac{l\,\pi}{2}\right)\sin\delta_l\right] . \end{aligned}$$

The comparison of the last two equations provides the relationship between the coefficients α_l, β_l and the scattering phases δ_l:

$$\begin{aligned} \alpha_l &= i^l(2l+1)\,e^{i\delta_l}\cos\delta_l\ , \\ \beta_l &= -i^l(2l+1)\,e^{i\delta_l}\sin\delta_l\ . \end{aligned}$$

The ratio of the amplitudes

$$\frac{\beta_l}{\alpha_l} = -\tan\delta_l \tag{9.46}$$

has already been found in (6.142) for the special case $l = 0$. Further statements on the quotient β_l/α_l can be derived from the continuity conditions for the radial function $R_l(r)$ and its derivative $(d/dr)\,R_l(r)$ at the discontinuity of the potential at $r = a$. These two requirements can be combined to yield the *fitting condition*:

$$\frac{1}{R_l(r)}\,\frac{d}{dr}\,R_l(r)\bigg|_{r\,=\,a} \qquad \text{continuous!}$$

The coefficients a_l of the ansatz (9.45) drop out. But for our purposes here, they are in fact unimportant and can later be post-determined, if necessary, via the normalization of the solution:

$$k_0\,\frac{j_l'\,(k_0 a)}{j_l\,(k_0 a)} \stackrel{!}{=} k\,\frac{\alpha_l\,j_l'\,(k\,a) + \beta_l\,n_l'\,(k\,a)}{\alpha_l\,j_l\,(k\,a) + \beta_l\,n_l\,(k\,a)}\ . \tag{9.47}$$

The prime means differentiation with respect to the full argument. We further reformulate (9.47) a bit,

$$k_0\,j_l'\,(k_0 a)\left[j_l\,(k\,a) + \frac{\beta_l}{\alpha_l}\,n_l\,(k\,a)\right] = k\,j_l\,(k_0 a)\left[j_l'\,(k\,a) + \frac{\beta_l}{\alpha_l}\,n_l'\,(k\,a)\right] ,$$

and solve it for β_l/α_l. It follows then with (9.46):

$$\tan\delta_l = \frac{k\,j_l'\,(k\,a)\,j_l\,(k_0 a) - k_0\,j_l'\,(k_0 a)\,j_l\,(k\,a)}{k\,n_l'\,(k\,a)\,j_l\,(k_0 a) - k_0\,j_l'\,(k_0 a)\,n_l\,(k\,a)}\ . \tag{9.48}$$

Therewith all the scattering phases $\delta_l = \delta_l(E, V_0)$ are completely determined. The right-hand side looks complicated, but can be evaluated without problem on a computer. We want to provide here, however, only a certain overview of the *physical content* of (9.48) and consider for this *slow particles*, i.e., the limiting case

$$k\,a \ll 1\ .$$

Of course, this need not necessarily also mean $k_0\,a \ll 1$. We can therefore apply in (9.48) the approximate formulas (6.123) and (6.124) for the Bessel and Neumann functions in fact only for small arguments $k\,a$:

$$\begin{aligned} j_l(z) &\approx \frac{z^l}{(2l+1)!!} \longrightarrow j_l'(z) \approx \frac{l\,z^{l-1}}{(2l+1)!!}\ , \\ n_l(z) &\approx -\frac{(2l+1)!!}{(2l+1)\,z^{l+1}} \longrightarrow n_l'(z) \approx \frac{(l+1)\,(2l+1)!!}{(2l+1)\,z^{l+2}}\ . \end{aligned}$$

After a few simple rearrangements we obtain therewith instead of (9.48):

$$\tan\delta_l = \frac{2l+1}{[(2l+1)!!]^2}\,(k\,a)^{2l+1}\,\widehat{P}_l(k_0 a)\ . \tag{9.49}$$

where we have used the abbreviation:

$$\widehat{P}_l(k_0 a) = \left(\frac{l\,j_l(z) - z\,j_l'(z)}{(l+1)\,j_l(z) + z\,j_l'(z)}\right)_{z\,=\,k_0 a}\ . \tag{9.50}$$

If the denominator is not zero,—an interesting special case, which we will investigate in the next subsection—then $\widehat{P}_l\,(k_0 a)$ will behave *'reasonably'* as function of the particle energy, i.e., will not show any peculiarities. Because of $k\,a \ll 1$, then $\tan\delta_l$ also must be very small. We will have reasons to assume $\tan^2\delta_l \approx \sin^2\delta_l$, finding therewith

$$\frac{\sin^2\delta_{l+1}}{\sin^2\delta_l} \approx \frac{(k\,a)^4}{(2l+1)^2\,(2l+3)^2} \ll 1 \tag{9.51}$$

an estimation, which agrees exactly with that for the *hard sphere* (see (9.39)), if the radii of the sphere and the well are equal ($R_0 = a$). As was done there, we can conclude that in the expansion (9.26) for the total cross-section σ the s-term ($l = 0$) dominates. For the slow (low-energy) particles we have, in the case of the potential well also, almost pure isotropic ***s*-scattering**:

$$\sigma \approx \frac{4\pi}{k^2}\sin^2\delta_0\ . \tag{9.52}$$

This holds, though, under the above assumption that $\widehat{P}_l(k_0 a)$ is well-behaved, i.e., first of all it must not become singular as a function of E.

The scattering phase δ_0 needed in (9.52) can be calculated with (9.48). The direct calculation of the $l = 0$-scattering phase is even simpler, as we did it in

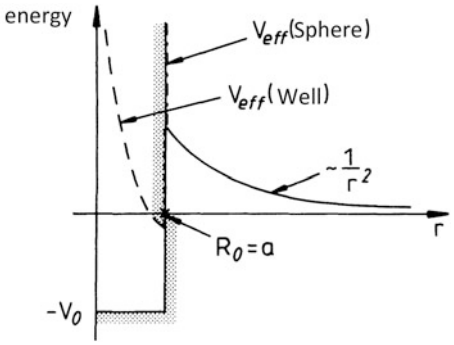


Figure 9.6: Distance-dependence of the effective potentials for the hard sphere and the potential well, respectively

Sect. 6.3.4. We can take the result (6.143), which is exactly valid, i.e., without restriction to small $k\,a$:

$$\delta_0 = \arctan\left(\frac{k}{k_0}\tan k_0 a\right) - k\,a \quad (+n\,\pi)\ . \tag{9.53}$$

The scattering phase is of course determined only except for an integral multiple of π. In Sect. 9.2.5 we will pick up once more the discussion of the s-scattering by the potential well.

At first glance, the similarity of the results (9.51), (9.52) for the potential well with those for the *hard sphere* ((9.39), (9.40)) may be a bit puzzling, but can be explained relatively simply. The cause is the **centrifugal barrier** ($\sim \hbar^2 l(l+1)/2m\,r^2$ (6.20)), which for $l \geq 1$, for low energies prevents the wave from approaching the region of action of the bare potential too closely. The wave is obviously not able to penetrate the *'centrifugal barrier'*. For $r > R_0 = a$, however, the effective scattering potential $V_{\text{eff}}(r) = V(r) + \hbar^2 l(l+1)/2m\,r^2$ is the same for the hard sphere and for the potential well (see Fig. 9.6). The result

$$\tan\delta_l \sim (k\,a)^{2l+1} \tag{9.54}$$

at low particle energies is therefore typical for all potentials of finite range. One speaks of **potential scattering** in such a case, from which we have seen that it is s-like for all potentials of this kind. For s-scattering, though, the centrifugal barrier vanishes. This partial scattering is therefore determined by the *bare* potential only.

9.2.4 Resonance Scattering

For the analysis of the scattering result (9.49) so far we have always presumed that the term $\widehat{P}_l(k_0 a)$, defined in (9.50), is *well behaved*. In a certain sense that is the basic precondition for *potential scattering*. It is now definitely possible

that at certain particle energies E the denominator of $\widehat{P}_l(k_0 a)$ becomes zero. Then, in particular, the estimation (9.51) is simply wrong. In the region of the so-called *resonance energy* E_R, which solves the following equation,

$$0 \stackrel{!}{=} \left[(l+1)\, j_l(k_0 a) + k_0 a\, j_l'(k_0 a)\right]_{E=E_\mathrm{R}} \ , \tag{9.55}$$

another type of scattering appears, which is called **resonance scattering**. $\widehat{P}_l(k_0 a)$ diverges at $E = E_\mathrm{R}$. In order to see what is *physically* the reason for this singularity, let us approximately evaluate (9.55) for the special case of a very deep potential well

$$k_0 a \gg l \qquad (l \geq 1) \ .$$

In this case we can apply for the spherical Bessel function $j_l(k_0 a)$ the asymptotic form (6.125):

$$\begin{aligned} j_l(k_0 a) &\approx \frac{1}{k_0 a} \sin\left(k_0 a - \frac{l\,\pi}{2}\right) \ , \\ j_l'\,(k_0 a) &\approx -\frac{1}{(k_0 a)^2} \sin\left(k_0 a - \frac{l\,\pi}{2}\right) + \frac{1}{k_0 a} \cos\left(k_0 a - \frac{l\,\pi}{2}\right) \ . \end{aligned}$$

Therewith (9.55) becomes:

$$\begin{aligned} 0 &\stackrel{!}{=} \frac{l}{k_0 a} \sin\left(k_0 a - \frac{l\,\pi}{2}\right) + \cos\left(k_0 a - \frac{l\,\pi}{2}\right) \\ &= \frac{l}{k_0 a} \cos\left[k_0 a - (l+1)\,\frac{\pi}{2}\right] - \sin\left[k_0 a - (l+1)\,\frac{\pi}{2}\right] \ . \end{aligned}$$

This means:

$$\tan\left[k_0 a - (l+1)\,\frac{\pi}{2}\right] = \frac{l}{k_0 a} \ll 1 \ .$$

Since the right-hand side is very small, the tangent must be, except for an integral multiple of π, approximately equal to its argument:

$$k_0 a - l\,\frac{\pi}{2} \approx \left(n + \frac{1}{2}\right) \pi + \frac{l}{k_0 a} \qquad (n = 0, 1, 2, \ldots) \ . \tag{9.56}$$

Negative values of n are, because of $k_0 a \gg l$, out of question. Without the last summand, which as per presumption is small compared to 1, (9.56) represents just the condition for a bound state (discrete level) in the (very deep) three-dimensional potential well (see the solution of Exercise 6.3.4). Always when the energy of the *incident* particle corresponds to the energy of such a bound state (Fig. 9.7) **resonance scattering** sets in. In the *resonance* $\tan\delta_l$ diverges according to (9.49) and (9.50). Since in the region of *potential scattering* $\tan\delta_l \ll 1$, so that δ_l lies close to an integral multiple of π, the δ_l must, as a function of E, obviously have jump in the neighborhood of E_R, abruptly from $m\,\pi$ to $(m \pm 1)\,\pi$, thereby traversing in the resonance the value

$$\delta_l(E = E_\mathrm{R}) = m\,\pi \pm \frac{\pi}{2} \ . \tag{9.57}$$

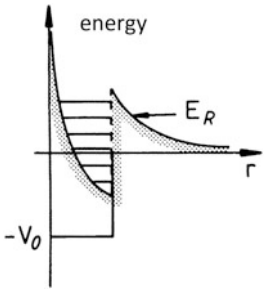


Figure 9.7: Illustration of the resonance scattering at the potential well

We should investigate in a bit more detail the energy region around E_{R}. At first, the numerator of $\widehat{P}_l(k_0 a)$ can be expanded as a Taylor series around E_{R}, which we cut off after the linear term:

$$\begin{aligned}&(l+1)\, j_l\,(k_0 a) + k_0 a\, j_l'\,(k_0 a)\\ &= 0 + (E - E_{\mathrm{R}})\,\left[(l+1)\,\frac{d}{dE}\, j_l\,(k_0 a) + \frac{d}{dE}\,\left(k_0 a\, j_l'\,(k_0 a)\right)\right]_{E\,=\,E_{\mathrm{R}}}\\ &\qquad + \mathcal{O}\left[(E - E_{\mathrm{R}})^2\right]\ .\end{aligned}$$

In the numerator of $\widehat{P}_l(k_0 a)$ we can directly replace E by E_{R}. With the definition

$$\gamma_l = \frac{2l+1}{[(2l+1)!!]^2}\,\left[\frac{l\, j_0\,(k_0 a) - k_0 a\, j_l'(k_0 a)}{(l+1)\,(d/dE)\, j_l\,(k_0 a) + (d/dE)\,(k_0 a\, j_l'\,(k_0 a))}\right]_{E\,=\,E_{\mathrm{R}}} \tag{9.58}$$

in the immediate surrounding of the resonance we then have:

$$\tan\delta_l \approx \gamma_l\,\frac{(k\,a)^{2l\,+\,1}}{E - E_{\mathrm{R}}}\ . \tag{9.59}$$

If one assumes that δ_l as function of E increases monotonically from 0 to π (or from $m\pi$ to $(m+1)\pi$) and takes at E_R the value $\pi/2$ (or $(m+1/2)\pi$), then it must obviously be $\gamma_l < 0$. The *partial cross-section* σ_l (l-contribution to the cross-section σ (9.26)),

$$\sigma_l = \frac{4\pi(2l+1)}{k^2}\,\sin^2\delta_l = \frac{4\pi(2l+1)}{k^2}\,\frac{\tan^2\delta_l}{1+\tan^2\delta_l}\ ,$$

gets therewith a *Lorentzian profile*:

$$\sigma_l = \frac{4\pi(2l+1)}{k^2}\,\frac{\gamma_l^2\,(k\,a)^{4l\,+\,2}}{(E - E_{\mathrm{R}})^2 + \gamma_l^2\,(k\,a)^{4l\,+\,2}}\ . \tag{9.60}$$

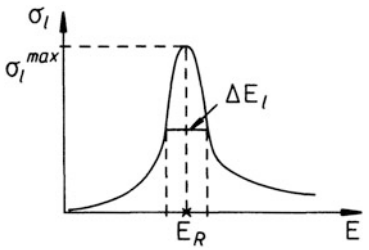


Figure 9.8: Resonance behavior of the partial cross-section

This relation is called **Breit-Wigner formula**. In the resonance $E = E_{\mathrm{R}}$ σ_l takes its maximal value

$$\sigma_l^{\max} = \frac{4\pi(2l+1)}{k^2} \; . \tag{9.61}$$

When we define as *half width* ΔE_l the distance between the points on the E-axis, at which σ_l drops to half of its maximal value (Fig. 9.8),

$$\Delta E_l = 2|\gamma_l| \, (k\,a)^{2l+1} \; , \tag{9.62}$$

then we recognize that, because of $k\,a \ll 1$, it is an extremely sharp resonance. The other partial cross-sections $\sigma_{l'}$, whose quantum numbers l' do **not** fulfill the resonance condition (9.56), lie in the region of *potential scattering* and are then negligible compared to σ_l.

Outside the *resonance* an $l \geq 1$-partial wave experiences only an unimportant scattering, and can not significantly penetrate the potential region, either. The scattering features turn out as almost independent of the actual potential. In the region of the *resonance* the corresponding partial wave obviously tunnels to a great part into the centrifugal barrier, and occupies there a quasi-bound state, which can be calculated via a relation like (9.56). After a relatively long time span the particle is then re-emitted, which is the reason for the high scattering cross-section. The particle thus spend only a *finite lifetime* τ inside the potential. The resonance is therefore in fact not a real bound state (*metastable*). According to the energy-time uncertainty relation (3.221) (Vol. 6) it possesses an energy-indeterminacy of the order of magnitude $\Delta E = \hbar/\tau$.

9.2.5 S-Scattering by the Potential Well

The considerations and interpretations of the last subsection excluded s-scattering, because for $l = 0$ the centrifugal barrier does not exist. We therefore now consider this case separately.

The scattering phase δ_0 we already know. The version (9.53) is valid even for all particle energies. For low energies and for the case that $\tan k_0 a$ is not right diverging ($k_0 a \neq (\hat{n} + 1/2)\,\pi$; $\hat{n} \stackrel{!}{=} \mathbb{Z}$), we can replace the arc tangent by its argument:

$$\delta_0 \approx \frac{k}{k_0} \tan k_0 a - k\, a + n\, \pi \; . \tag{9.63}$$

One defines as **scattering length** the expression

$$a_\mathrm{s} = a \left(1 - \frac{\tan k_0 a}{k_0 a} \right) \tag{9.64}$$

and can write therewith:

$$\delta_0 \approx n\, \pi - k\, a_\mathrm{s} \; . \tag{9.65}$$

This means for the cross-section ($l = 0$):

$$\sigma_0 \approx \frac{4\pi}{k^2} \sin^2 k\, a_\mathrm{s} \approx 4\pi\, a_\mathrm{s}^2 \; . \tag{9.66}$$

It can be shown that the first corrections to this result are of the order of magnitude k^2.

In order to get further information about the scattering phase δ_0 and the partial cross-section σ_0, let us consider the relation (9.53) in the form

$$\frac{\tan(k\, a + \delta_0)}{\tan k_0 a} = \frac{k}{k_0} = \frac{k}{\sqrt{k^2 + 2m\, V_0/\hbar^2}} \; . \tag{9.67}$$

The right-hand side is a positive, monotonically from 0 to 1 increasing function of k. Consequently it holds for the left-hand side:

$$\lim_{k \to \infty} \frac{\tan(k\, a + \delta_0)}{\tan k_0 a} = \lim_{k \to \infty} \frac{\tan(k\, a + \delta_0)}{\tan k\, a} \stackrel{!}{=} 1 \; . \tag{9.68}$$

We can conclude from (9.65) and (9.68) that for $k \to 0$ as well as for $k \to \infty$ the scattering phase δ_0 must be an integral multiple of π. On the other hand, scattering phases are by definition (9.21) afflicted with an arbitrariness *modulo* π. We have therefore the freedom to lift this arbitrariness by the following convention: When $k_0 a$ lies in the interval

$$\pi \left(\hat{n} - \frac{1}{2} \right) < k_0 a < \pi \left(\hat{n} + \frac{1}{2} \right) \; ; \quad \hat{n} = 0, 1, 2, \ldots \; , \tag{9.69}$$

we require that this is also the case for $k\, a + \delta_0$. According to (9.68) it must then obviously be for $k \to \infty$

$$\lim_{k \to \infty} \delta_0(k) = 0 \; , \tag{9.70}$$

and because of (9.69) for $k \to 0$:

$$\lim_{k \to 0} \delta_0(k) = \hat{n}\,\pi\ . \tag{9.71}$$

In order to see the meaning of the non-negative integer $\hat{n}$, we investigate (9.69) for $k \to 0$. Then k_0 there is to be replaced by

$$k_0^0 = k_0\,(k=0) = \sqrt{\frac{2m\,V_0}{\hbar^2}}\,. \tag{9.72}$$

(9.69) is therewith for $V_0 = 0$ fulfilled by $\hat{n} = 0$. It is plausible that for this limiting case the scattering phase vanishes. If we enhance the depth of the potential well so far that $k_0^0 a > \pi/2$, then $\hat{n}$ jumps onto the value 1 and $\delta_0(0)$ is equal to π. But on the other hand, $k_0^0 a > \pi/2$ also means

$$V_0 > \frac{\pi^2\hbar^2}{8m\,a^2}\ ,$$

and that is, in turn, according to (6.138), the condition for a first bound state in the potential well. With increasing V_0 more and more bound states appear, whose number N_- is calculated according to (6.137) and according to the considerations in connection with (4.48) in Vol. 6:

$$N_- = \left[\frac{1}{\pi}\sqrt{\frac{2m\,V_0 a^2}{\hbar^2}} - \frac{1}{2}\right] = \left[\frac{k_0^0\,a}{\pi} - \frac{1}{2}\right]$$

($[x]$ is the first integer above x.) Equation (9.69) can be read as:

$$\hat{n} - 1 < \frac{k_0^0\,a}{\pi} - \frac{1}{2} < \hat{n}.$$

The number $\hat{n}$ in (9.71) is thus equal to the number of bound states in the potential well of the depth V_0. It is therewith uniquely fixed. Let us assume for the moment that the depth V_0 of the potential well is just so that $\hat{n} = 3$ bound states appear, then it follows from (9.70) and (9.71) for (continuous) δ_0 as function of k, and therewith as function of the particle energy E, qualitatively a curve shape as sketched in Fig. 9.9. With (9.66) the $k \to 0$-value of the cross-section σ_0,

$$\sigma_0 = \frac{4\pi}{k^2}\sin^2\delta_0\ ,$$

is known, so that we obtain for σ_0 even as function of the particle energy E quite a detailed picture. There arise typical oscillations (*resonances*) as a function of the energy of the *incident* particle.

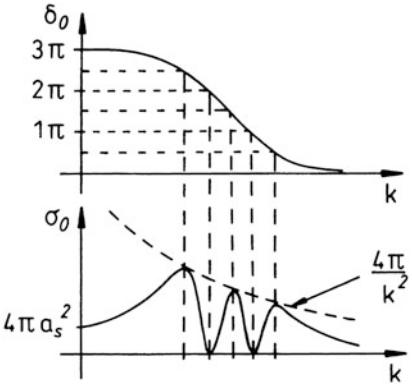


Figure 9.9: Connection between scattering phase and cross-section for s-scattering at the potential well

9.2.6 Integral-Representation for Scattering Phases

The calculation of scattering phases is in general rather complicated and normally possible only under strongly restrictive assumptions. Different representations offer different starting points for approximations, what can be of great importance for the treatment of scattering problems. We therefore want to derive in this subsection an alternative integral-representation of the scattering phases.

The general ansatz (9.17) for the solution $\varphi(\mathbf{r})$, which respects the symmetry of the scattering problem, leads to the differential equation (9.18) for the radial function $u_l(r) = r\,R_l(r)$, which we want to apply in the following form:

$$u_l''(r) + \left[k^2 - \frac{2m}{\hbar^2}\,V(r) - \frac{l(l+1)}{r^2}\right] u_l(r) = 0\,. \tag{9.73}$$

$u_l(r)$ solves this equation with the boundary condition (6.21)

$$u_l(0) = 0\,,$$

and exhibits, according to (9.21), (9.22) for $r \to \infty$ the asymptotic behavior

$$u_l(r) \sim \frac{1}{k} i^l (2l+1)\, e^{i\delta_l} \sin\left(k\,r - \frac{l\,\pi}{2} + \delta_l\right)\,.$$

In the limiting case of vanishing interaction potential the differential equation, analogous to (9.73), reads:

$$u_l^{\prime\prime(0)}(r) + \left[k^2 - \frac{l(l+1)}{r^2}\right] u_l^{(0)}(r) = 0\,. \tag{9.74}$$

The solution, which belongs to the boundary condition $u_l^{(0)}(0) = 0$, is already known to us (9.20):

$$u_l^{(0)}(r) = i^l\,(2l+1)\,r\,j_l\,(k\,r) \underset{r\to\infty}{\sim} \frac{1}{k}\,i^l\,(2l+1)\sin\left(k\,r - \frac{l\,\pi}{2}\right).$$

We now multiply (9.73) by $u_l^{(0)}(r)$ and (9.74) by $u_l(r)$, subtract the two equations from each other, and integrate over all r:

$$\int_0^\infty dr\left(u_l''(r)\,u_l^{(0)}(r) - u_l^{(0)\prime\prime}(r)\,u_l(r)\right) = \frac{2m}{\hbar^2}\int_0^\infty dr\,V(r)\,u_l(r)\,u_l^{(0)}(r)\ .$$

We further evaluate the left-hand side using integration by parts, where we apply the two boundary conditions for u_l und $u_l^{(0)}$:

$$\begin{aligned}
&\int_0^\infty dr\left(u_l''(r)\,u_l^{(0)}(r) - u_l^{(0)\prime\prime}(r)\,u_l(r)\right)\\
&= \left(u_l'(r)\,u_l^{(0)}(r) - u_l^{(0)\prime}(r)\,u_l(r)\right)\Big|_0^\infty - \int_0^\infty dr\left(u_l'(r)\,u_l^{(0)\prime}(r) - u_l^{(0)\prime}(r)\,u_l'(r)\right)\\
&= \lim_{r\to\infty}\left(u_l'(r)\,u_l^{(0)}(r) - u_l^{(0)\prime}(r)\,u_l(r)\right)\ .
\end{aligned}$$

By inserting in the next step the asymptotic solution profiles, we bring into play the scattering phases δ_l, which we are actually interested in:

$$\begin{aligned}
&\lim_{r\to\infty}\left(u_l'\,u_l^{(0)} - u_l^{(0)\prime}\,u_l\right)\\
&= \left(\frac{1}{k}\,(2l+1)\,i^l\right)^2 e^{i\delta_l}\lim_{r\to\infty}\left[k\cos\left(k\,r - \frac{l\,\pi}{2} + \delta_l\right)\sin\left(k\,r - \frac{l\,\pi}{2}\right)\right.\\
&\quad \left. -k\sin\left(k\,r - \frac{l\,\pi}{2} + \delta_l\right)\cos\left(k\,r - \frac{l\,\pi}{2}\right)\right]\\
&= k\left(\frac{1}{k}\,(2l+1)\,i^l\right)^2 e^{i\delta_l}\lim_{r\to\infty}\left[\cos\left(k\,r - \frac{l\,\pi}{2}\right)\cos\delta_l\right.\\
&\quad \cdot\sin\left(k\,r - \frac{l\,\pi}{2}\right) - \sin^2\left(k\,r - \frac{l\,\pi}{2}\right)\sin\delta_l\\
&\quad \left. - \sin\left(k\,r - \frac{l\,\pi}{2}\right)\cos\delta_l\cos\left(k\,r - \frac{l\,\pi}{2}\right) - \cos^2\left(k\,r - \frac{l\,\pi}{2}\right)\sin\delta_l\right]\\
&= -k\left(\frac{1}{k}\,(2l+1)\,i^l\right)^2 e^{i\delta_l}\sin\delta_l\ .
\end{aligned}$$

We have therewith found an exact integral-representation for the scattering phases δ_l:

$$i^l(2l+1)\,e^{i\delta_l}\sin\delta_l = -\frac{2m}{\hbar^2}\int_0^\infty dr\,V(r)\,\left[k\,r\,j_l(k\,r)\right]\,u_l(r)\ . \tag{9.75}$$

This relation reveals the close entanglement of scattering phases and interaction potential. However, it of course does not yet represent a solution of the scattering problem, because there appears on the right-hand side the *full*, unknown solution function $u_l(r)$.

If the interaction potential $V(r)$ is sufficiently weak, the *full* solution $u_l(r)$ will differ only slightly from the *free* solution $u_l^{(0)}(r)$. Simultaneously, the scattering phases δ_l, aside from an integral multiple of π, will be very small. We therefore will not make too large a mistake, when we replace on the right-hand side of (9.75) $u_l(r)$ by $u_l^{(0)}(r)$, and furthermore approximate on the left-hand side $e^{i\delta_l} \sin\delta_l$ by δ_l:

$$\delta_l \approx -\frac{2m}{\hbar^2} \frac{1}{k} \int_0^\infty dr\, V(r) \left[k\, r\, j_l(k\, r)\right]^2 \ . \tag{9.76}$$

One calls this the **Born approximation for scattering phases**.

We will try to estimate the rating of this approximation and its region of validity, respectively. The steps, which led to (9.76), illustrate that only *weak* scattering processes can come into consideration. The scattering phases δ_l must be small, consequently also the right-hand side of (9.76).

1) Small energies $\longleftrightarrow$ small k

We know from Sect. 6.3.2 that the function $z\, j_l(z)$ has an inflection point at $z = \sqrt{l(l+1)}$ and increases up to this point like z^{l+1}. In order to guarantee that the integral in (9.76) is small, $k\, r\, j_l(k\, r)$ has to stay small within the effective range R_0 of the potential. The latter is valid up to

$$r \leq \frac{1}{k} \sqrt{l(l+1)} \ .$$

The right-hand side of this inequality is just the quantum-mechanical analog, discussed in Sect. 9.2.1, to the classical impact parameter (9.28). For small k the approximation (9.76) can then be good at most if it can be assumed:

$$k\, R_0 \leq \sqrt{l(l+1)}$$

On the other hand, however, this condition is just fulfilled by those quantum-numbers l of the angular momentum, which may be unimportant for the scattering process (see (9.299)). For small particle energies the Born approximation (9.76) therefore appears rather questionable.

2) High energies $\longleftrightarrow$ large k

The term $[k\, r\, j_l(k\, r)]^2$ is bound for all values of the argument (see Sect. 6.3.2). The right-hand side of (9.76) is therefore in any case small, if one assumes

$$\frac{2m}{\hbar^2 k} \int_0^\infty dr |V(r)| \ll 1 \ . \tag{9.77}$$

For higher particle energies and weak interaction potentials the Born approximation is thus acceptable for all quantum numbers l of the angular momentum. At high energy the *incident* particle hardly *feels* the weak potential. The approximation $u_l(r) \approx u_l^{(0)}(r)$ obviously becomes appropriate.

9.2.7 Exercises

Exercise 9.2.1
It has been measured for pure s-scattering the differential cross-section

$$\frac{d\sigma}{d\Omega} = a \; ; \quad a > 0 \; .$$

Determine the complex scattering amplitude $f(\vartheta)$!

Exercise 9.2.2
For elastic scattering at the central potential

$$V(\mathbf{r}) = V(r) = \frac{c}{r^2} \; ; \quad c > 0$$

the scattering phases $\delta_l(k)$ are to be determined under the simplifying assumption

$$c \ll \frac{\hbar^2}{2m} \; .$$

Furthermore, the scattering amplitude is to be found.
Useful formula:

$$\sum_{l=0}^{\infty} P_l(\cos\vartheta) = \frac{1}{2\sin(\vartheta/2)} \; .$$

Exercise 9.2.3
Consider the s-scattering at a spherical potential well with the radius a:

$$V(r) = \begin{cases} V_0 > 0 & \text{for } r < a \; , \\ 0 & \text{for } r \geq a \; . \end{cases}$$

1. Find for the case $E < V_0$ a conditional equation for the scattering phase δ_0.
2. Estimate for small energies E of the *incident* particle the scattering phase δ_0 and determine the partial cross-section σ_0. Investigate also the limiting case $V_0 \to \infty$.

Exercise 9.2.4
Consider the scattering at a centrally symmetric, δ-like potential:

$$V(r) = V_0 \, \delta(r - R) \; ; \quad (V_0 > 0) \; .$$

The incorporated energies are all so low that one can restrict oneself to pure s-scattering.

1. Derive a conditional equation for the scattering phase δ_0, i.e., calculate $\tan\delta_0$!

2. Show that in the neighborhood of resonances $\tan\delta_0$ takes the form of (9.59):
$$\tan\delta_{0,n} = \gamma_n \frac{kR}{E - E_n} \; ; \quad (n = 1, 2, \ldots)$$
$E_n = \hbar^2 k_n^2/2m$ are here the resonance energies, of which there exist possibly more than one. Which sign do the γ_n have?

3. Estimate for strong couplings $V_0 R \gg 1$ the resonance energies E_n and discuss the results!

4. Show that for strong coupling the following approximate relation exists between the coefficients γ_n and the resonance energies E_n:
$$\gamma_n \approx -\frac{1}{2} E_n \left(\frac{\hbar^2}{mV_0 R}\right)^2 .$$

Exercise 9.2.5
The differential cross-section $d\sigma/d\Omega$ for elastic scattering can be expressed by scattering phases δ_l (9.25). Therewith, the integrals
$$\int d\Omega \frac{d\sigma}{d\Omega} \quad \text{and} \quad \int d\Omega \cos\vartheta \frac{d\sigma}{d\Omega}$$
are to be calculated, and it is to be found out, how these integrals influence an expansion of $d\sigma/d\Omega$ in Legendre polynomials.

9.3 Integral-Equations for Scattering Problems

At high particle energies many scattering phases contribute to the cross-section and the scattering amplitude, respectively, so that the practicability of the method of partial waves appears to be rather questionable. We therefore now consider another approach to the scattering amplitude $f(\vartheta)$, the determination of which solves, as we know, the scattering problem. We try to reformulate the problem by integration of the Schrödinger equation, hoping therewith to get via the corresponding integral equation hints of new, perhaps promising approximations.

9.3.1 Integral Form of the Scattering Amplitude

For the calculation of the scattering amplitude $f(\vartheta)$ the solution of the time-independent Schrödinger equation (9.10) is necessary, which we can bring, with the abbreviations
$$k^2 = \frac{2m\,E}{\hbar^2} \; ; \quad v(\mathbf{r}) = \frac{2m}{\hbar^2} V(\mathbf{r}) \; .$$

into the following form:

$$(\Delta_r + k^2)\,\varphi(\mathbf{r}) = v(\mathbf{r})\,\varphi(\mathbf{r}) \tag{9.78}$$

The assumption that $V(\mathbf{r})$ is a central potential, will be brought into play only later. We want to transform the linear inhomogeneous differential equation (9.78) into an integral equation, which incorporates already explicitly the boundary conditions.

Let $\varphi_0(\mathbf{r})$ be the solution of the associated homogeneous differential equation:

$$\left(\Delta_r + k^2\right)\,\varphi_0(\mathbf{r}) = 0\ . \tag{9.79}$$

But then each solution of the **integral equation**

$$\varphi(\mathbf{r}) = \varphi_0(\mathbf{r}) + \int d^3r'\,G(\mathbf{r}-\mathbf{r}')\,v(\mathbf{r}')\,\varphi(\mathbf{r}') \tag{9.80}$$

is also a solution of the Schrödinger equation (9.78), if the so-called

Green's function $G(\mathbf{r}-\mathbf{r}')$

fulfills the equation

$$\left(\Delta_r + k^2\right)\,G(\mathbf{r}-\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')\ . \tag{9.81}$$

In a certain sense, $G(\mathbf{r}-\mathbf{r}')$ is the solution of the scattering problem for a *fictitious* point-like scattering source at $\mathbf{r}'$. The *method of the Green's function* we already got to know in Electrodynamics (Sects. 2.3.3 and 4.5.1, Vol. 3). The procedure is here completely analogous.

In (9.80) we have to fix $\varphi_0(\mathbf{r})$ and $G(\mathbf{r}-\mathbf{r}')$ regarding the boundary conditions. That is uniquely and simply done for $\varphi_0(\mathbf{r})$:

$$\varphi_0(\mathbf{r}) = e^{ikz} \qquad (\mathbf{r} = (x,y,z))\ . \tag{9.82}$$

In order to find $G(\mathbf{r}-\mathbf{r}')$, we solve (9.81) by Fourier transformation:

$$\begin{aligned} G(\mathbf{r}-\mathbf{r}') &= \frac{1}{(2\pi)^{3/2}} \int d^3q\, e^{i\,\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}\,G(\mathbf{q})\ , \\ \delta(\mathbf{r}-\mathbf{r}') &= \frac{1}{(2\pi)^3} \int d^3q\, e^{i\,\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}\ . \end{aligned}$$

If one inserts both expressions into (9.81), then a conditional equation for $G(\mathbf{q})$ is obtained:

$$\int d^3q\, e^{i\,\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}\,\left[(2\pi)^{3/2}\,G(\mathbf{q})\,(k^2-q^2)-1\right] = 0\ .$$

It follows after Fourier inversion:

$$G(\mathbf{q}) = \frac{1}{(2\pi)^{3/2}}\,\frac{1}{k^2-q^2}\ .$$

On the right-hand side one could of course still add the solution

$$[a_+(q)\,\delta(q+k) + a_-(q)\,\delta(q-k)]$$

of the *homogeneous* relation $G(\mathbf{q})\,(k^2-q^2)=0$ (see (4.330), Vol. 3). However, one recognizes very soon that then the *physical* boundary conditions would be violated. Therewith, we have found:

$$G(\mathbf{r}-\mathbf{r}') = \frac{1}{(2\pi)^3}\int d^3q\,\frac{e^{i\,\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}}{k^2-q^2}\;. \tag{9.83}$$

With the direction of $(\mathbf{r}-\mathbf{r}')$ as polar axis the angle integrations can easily be done:

$$\int\limits_{-1}^{+1} dx\,e^{i\,q|\mathbf{r}-\mathbf{r}'|x} = \frac{2\sin(q|\mathbf{r}-\mathbf{r}'|)}{q|\mathbf{r}-\mathbf{r}'|}\;.$$

We obtain as intermediate result:

$$G(\mathbf{r}-\mathbf{r}') = \frac{1}{2\pi^2}\int\limits_0^\infty dq\,\frac{\sin(q|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}\,\frac{q}{k^2-q^2}\;.$$

For the further evaluation a slight rearranging is recommendable:

$$\begin{aligned}
&\int\limits_0^\infty dq\sin\left(q\,|\mathbf{r}-\mathbf{r}'|\right)\,\frac{q}{k^2-q^2}\\
&= \frac{1}{4i}\int\limits_0^\infty dq\,\left(\frac{1}{k-q}-\frac{1}{k+q}\right)\,e^{i\,q|\mathbf{r}-\mathbf{r}'|}\\
&\quad -\frac{1}{4i}\int\limits_0^{-\infty} d(-q)\,\left(\frac{1}{k+q}-\frac{1}{k-q}\right)\,e^{i\,q|\mathbf{r}-\mathbf{r}'|}\\
&= \frac{1}{4i}\int\limits_{-\infty}^{+\infty} dq\,\left(\frac{1}{k-q}-\frac{1}{k+q}\right)\,e^{i\,q|\mathbf{r}-\mathbf{r}'|}\;.
\end{aligned}$$

With the definition

$$J_\pm \equiv \int\limits_{-\infty}^{+\infty} dq\,e^{i\,q|\mathbf{r}-\mathbf{r}'|}\,\frac{1}{q\pm k} \tag{9.84}$$

the Green's function can now be written as:

$$G(\mathbf{r}-\mathbf{r}') = \frac{i}{8\pi^2|\mathbf{r}-\mathbf{r}'|}\,(J_+ + J_-)\;. \tag{9.85}$$

We evaluate $J_\pm$ by complex integration by means of the *residue theorem* ((4.424), Vol. 3). The integration path C is closed by a semi-circle in the upper

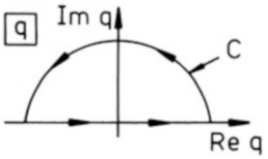
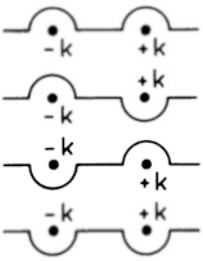


Figure 9.10: Integration path C in the complex q-plane for the calculation of the Green's function of the scattering problem

half-plane at infinity (Fig. 9.10), where, because of the exponential function, no finite contribution appears. There are four possibilities to circumscribe the poles at $\pm k$. The related arbitrariness will later be removed by the physical boundary condition. With the residue theorem we find the following solutions for J_+ and J_-:



1) $J_+ = J_- = 0$

2) $J_+ = 0\,; \quad J_- = 2\pi\, i\; e^{i\,k|\mathbf{r}-\mathbf{r}'|}$

3) $J_+ = 2\pi\, i\; e^{-ik|\mathbf{r}-\mathbf{r}'|}\,; \quad J_- = 0$

4) $J_\pm = 2\pi\, i\; e^{\mp ik|\mathbf{r}-\mathbf{r}'|}$

This yields for the Green's function:

$$G(\mathbf{r}-\mathbf{r}') = \frac{-1}{4\pi|\mathbf{r}-\mathbf{r}'|} \begin{cases} 0 & (1)\,, \\ e^{i\,k|\mathbf{r}-\mathbf{r}'|} & (2)\,, \\ e^{-ik|\mathbf{r}-\mathbf{r}'|} & (3)\,, \\ 2\cos\left(k|\mathbf{r}-\mathbf{r}'|\right) & (4)\,. \end{cases}$$

(2) and (3) are linearly independent solutions. Since the scattering part of the solution $\varphi(\mathbf{r})$ (second summand in (9.80)) must asymptotically behave like an outgoing spherical wave, only (2) can come into consideration as the *physically correct* Green's function: When we insert (2) together with (9.82) into (9.80), then the to be solved **integral equation**, which now contains already the correct boundary conditions being therewith equivalent to the Schrödinger equation **with** boundary conditions, reads:

$$\varphi(\mathbf{r}) = e^{ikz} - \frac{m}{2\pi\,\hbar^2} \int d^3r'\, V(\mathbf{r}')\, \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\, \varphi(\mathbf{r}')\,. \tag{9.86}$$

We want to verify once more, whether this solution really possesses the right asymptotic behavior, and thereby we want to find the explicit integral representation of the scattering amplitude. We will come from the general presumption, agreed upon in Sect. 9.1.1, that the scattering potential has a finite effective

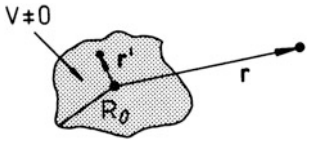


Figure 9.11: Scattering potential of finite range

range (Fig. 9.11). We observe the scattered wave at a distance $r \gg R_0$. The integrand (9.86) is unequal zero only if $\mathbf{r}'$ remains in the sphere of influence of the potential ($r' \leq R_0$). It is therefore also $r' \ll r$. We can thus certainly approximate the denominator by

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} \approx \frac{1}{r} \,.$$

In the exponential function (oscillations!) we have to perform the approximation more carefully:

$$|\mathbf{r}-\mathbf{r}'| = \sqrt{r^2 + r'^2 - 2\,\mathbf{r}\cdot\mathbf{r}'} \approx r\left(1 - \frac{2\,\mathbf{r}\cdot\mathbf{r}'}{r^2}\right)^{1/2} \approx r - \frac{\mathbf{r}\cdot\mathbf{r}'}{r} = r - \mathbf{e}_r\cdot\mathbf{r}' \,.$$

Hence, asymptotically (9.86) changes into:

$$\varphi(\mathbf{r}) \;\longrightarrow\; e^{ikz} - \frac{e^{ikr}}{r}\,\frac{m}{2\pi\,\hbar^2}\int d^3r'\,V(\mathbf{r}')\,\varphi(\mathbf{r}')\,e^{-ik(\mathbf{e}_r\cdot\mathbf{r}')} \,. \tag{9.87}$$

The boundary condition (9.12) is obviously fulfilled. Simultaneously, we have found therewith a (so far still exact) integral equation for the **scattering amplitude**:

$$f(\vartheta,\varphi) = -\frac{m}{2\pi\,\hbar^2}\int d^3r'\,V(\mathbf{r}')\,\varphi(\mathbf{r}')\,e^{-ik(\mathbf{e}_r\cdot\mathbf{r}')} \,. \tag{9.88}$$

At no point we had to assume that $V(\mathbf{r})$ is a central potential. In general, f will therefore depend on both the angles ϑ and φ. (Distinguish *angle* φ from *wave function* $\varphi(\mathbf{r}')$!) In the case of a central-symmetric potential $V(\mathbf{r}') = V(r')$ there remains only the ϑ-dependence.

9.3.2 Born's Series

The exact results (9.86) and (9.88) of the last subsection suggest an iterative procedure. The formal solution of (9.86) is called **Born's series**:

$$\begin{aligned}
\varphi(\mathbf{r}) &= \sum_{n=0}^{\infty} \varphi^{(n)}(\mathbf{r}) \,, \\
\varphi^{(0)}(\mathbf{r}) &= e^{ikz} \,, \\
\varphi^{(n)}(\mathbf{r}) &= -\frac{m}{2\pi\,\hbar^2}\int d^3r'\,V(\mathbf{r}')\,\frac{e^{i\,k|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\,\varphi^{(n-1)}(\mathbf{r}') \,.
\end{aligned} \tag{9.89}$$

By insertion of the Born's series into the exact expression (9.88) for the scattering amplitude one has the possibility to follow up an approximation procedure:

$$f(\vartheta,\varphi) = -\frac{m}{2\pi\,\hbar^2}\sum_{n=0}^{\infty}\int d^3r'\,V(\mathbf{r}')\,e^{-ik(\mathbf{e}_r\cdot\mathbf{r}')}\,\varphi^{(n)}(\mathbf{r}')\;. \tag{9.90}$$

One speaks of the **nth Born approximation**, if the series for $\varphi(\mathbf{r})$ is terminated after the nth summand, and the series for $f(\vartheta,\varphi)$ after the $(n-1)$-st summand. In practice, however, one uses almost exclusively the

first Born approximation

$$\begin{aligned} f^{(1)}(\vartheta,\varphi) &= -\frac{m}{2\pi\,\hbar^2}\int d^3r'\,V(\mathbf{r}')\,e^{-ik(\mathbf{e}_r-\mathbf{e}_z)\cdot\mathbf{r}'} \\ \big(z' &= \mathbf{r}'\cdot\mathbf{e}_z\;;\quad \vartheta = \sphericalangle(\mathbf{e}_r,\mathbf{e}_z)\big)\;. \end{aligned} \tag{9.91}$$

In the first approximation the scattering amplitude is, essentially, equal to the Fourier transform $V(\mathbf{K})$ $\big(\mathbf{K} = k(\mathbf{e}_r-\mathbf{e}_z)\big)$ of the interaction potential. For the further evaluation, if we restrict ourselves now to **centrally symmetric potentials**

$$V(\mathbf{r}') = V(r')\;,$$

then we can explicitly perform the angle integrations in (9.91). We take from Fig. 9.12:

$$\begin{aligned} \mathbf{K} &= k(\mathbf{e}_r-\mathbf{e}_z)\;; \\ K &= 2k\sin\frac{\vartheta}{2}\;. \end{aligned} \tag{9.92}$$

When we orient the polar axis parallel to $\mathbf{r}'$, then it follows for the integral in (9.91):

$$\begin{aligned} &\int d^3r'\,V(r')\,e^{-ik(\mathbf{e}_r-\mathbf{e}_z)\cdot\mathbf{r}'} \\ &= 2\pi\int_0^{\infty} dr'\,r'^2\,V(r')\int_{-1}^{+1} dx\,e^{-iKr'x} = \frac{4\pi}{K}\int_0^{\infty} dr'\,r'\,V(r')\sin(K\,r')\;. \end{aligned}$$

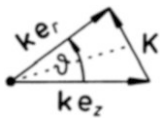


Figure 9.12: Angle-relations for the calculation of the scattering amplitude in the first Born approximation

The scattering amplitude $f^{(1)}(\vartheta)$ therewith depends only on the momentum transfer K :

$$f^{(1)}(\vartheta) = -\frac{2m}{\hbar^2}\,\frac{1}{K}\int\limits_0^\infty dr'\, r'\, V(r')\sin(K\,r')\ . \tag{9.93}$$

We recognize immediately one shortcoming of the first Born approximation by the fact that $f^{(1)}(\vartheta)$ is **real**, which means the *optical theorem* (9.27) is violated. The approximation (9.93) can therefore be accepted of course only for *weak* scattering processes.

It is not so easy to mark out the **region of validity** of the Born approximation. However, it is certainly a necessary precondition for the applicability of (9.91) and (9.93) that

$$|\varphi^{(1)}(\mathbf{r})| \ll |\varphi^{(0)}(\mathbf{r})| = 1\ .$$

This is equivalent to

$$\frac{m}{2\pi\,\hbar^2}\left|\int d^3r'\,V(r')\,\frac{e^{i\,k|\mathbf{r}\,-\,\mathbf{r}'|}}{|\mathbf{r}\,-\,\mathbf{r}'|}\,e^{ikz'}\right| \ll 1\ .$$

Because of $r \gg R_0 \geq r'$ the term $1/(|\mathbf{r}-\mathbf{r}'|)$ represents something like a *damping factor* for the scattering potential. The validity-condition is thus fulfilled only when it is satisfied for $r = 0$. After elimination of the angle integrations,

$$\int d^3r'\,V(r')\,\frac{1}{r'}\,e^{ikr'(1\,+\,\cos\vartheta')} = \frac{2\pi}{i\,k}\int\limits_0^\infty dr'\,V(r')\,e^{ikr'}\,\left(e^{ikr'}\,-\,e^{-ikr'}\right)\ ,$$

it then remains the requirement:

$$\left|\int\limits_0^\infty dr\,V(r)\,\left(e^{2ikr}\,-\,1\right)\right| \ll \frac{\hbar^2 k}{m}\ . \tag{9.94}$$

In order to see, whether or not the condition is actually satisfiable, we investigate two limiting cases:

1) High energies: $k\,R_0 \gg 1$

In this case the exponential function oscillates very rapidly, so that for a *'more or less' continuous* potential $V(r)$ the first summand on the left-hand side of the inequality (9.94) can be neglected:

$$\left|\int\limits_0^\infty dr\,V(r)\right| \ll \frac{\hbar^2 k}{m}\ . \tag{9.95}$$

When $V(r)$ has approximately the *shape of a well* with an *effective* Radius R_0 and an *effective* depth V_0 (Fig. 9.13), then (9.95) can further be simplified:

$$V_0\,R_0 \ll \frac{\hbar^2 k}{m}\ .$$

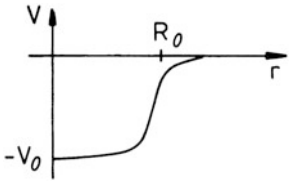


Figure 9.13: Typical sketch of a potential with the 'shape of a well', for which effective range and effective depth are still definable

For high particle energies and weak scattering potential (9.95) is fulfilled. The Born approximation (9.93) should then be trustworthy. $f^{(1)}(\vartheta)$ in this limit is only a small quantity, and therewith also the total cross-section $\sigma^{(1)}$. We have come to practically the same result as in (9.95) with (9.77) where we estimated the region of validity of the *Born approximation* for scattering phases in Sect. 9.2.6.

2) Low energies: $k\,R_0 \ll 1$

In this case we can expand the exponential function in (9.94) up to the linear term:

$$\left| \int_0^\infty dr\, r\, V(r) \right| \ll \frac{\hbar^2}{2m} \,. \tag{9.96}$$

This condition means for a *well-like* $V(r)$:

$$V_0\, R_0^2 \ll \frac{\hbar^2}{m} \,.$$

The requirement (9.96) is indeed rather restrictive. The scattering potential has to be even very much smaller than the already rather small particle energy!

All in all we have found that the Born approximation is very much better for high particle energies ($k\,R_0 \gg 1$) than for small ones ($k\,R_0 \ll 1$). The same conclusion was reached in Sect. 9.2.6 in connection with the scattering phases. We prove the equivalence of the Born approximations for the scattering phases in (9.76), and for the scattering amplitude in (9.91) as Exercise 9.3.5.

9.3.3 Exercises

Exercise 9.3.1

A particle of mass m is scattered by the screened Coulomb potential

$$V(r) = \frac{\alpha}{r} \exp\left(-\frac{r}{R_0}\right) \,, \quad \alpha > 0 \quad (\textit{Yukawa potential}) \,.$$

1. Calculate in the first Born approximation the scattering amplitude $f(\vartheta)$ and the differential cross-section $d\sigma/d\Omega$.

2. In which range of values for α and R_0, respectively, does the Born approximation represent a reasonable approximation at low energies?

3. What comes out for the limiting case of the Coulomb potential?

Exercise 9.3.2
A particle of mass m is scattered at the potential

$$V(r) = -V_0\, e^{-r/R_0}\ , \quad V_0 > 0\ .$$

1. Calculate in the first Born approximation the scattering amplitude $f(\vartheta)$.

2. Evaluate the general criterion of validity (9.94) for the Born approximation.

3. With the result from part 1. determine the phase δ_0 for s-scattering.

4. Determine the phase δ_1 for p-scattering.

Exercise 9.3.3
A particle of mass m is scattered at the potential well:

$$V(r) = \begin{cases} -V_0 & \text{for } r < R_0 \\ 0 & \text{for } r > R_0, \end{cases} \qquad V_0 > 0$$

1. Calculate in the first Born approximation the scattering amplitude $f(\vartheta)$.

2. Find the differential cross-section $d\sigma/d\Omega$ and discuss this for low particle energies ($k\,R_0 \ll 1$).

3. Under which conditions, according to the criterion of validity (9.94), is the Born approximation allowed? Consider in particular the limits of low ($k\,R_0 \ll 1$) and high particle energies ($k\,R_0 \gg 1$).

4. Let the potential well be so deep that at least one bound state can exist. What can then be said about the Born approximation for low-energy particle scattering?

Exercise 9.3.4
Discuss the scattering of electrons by neutral hydrogen atoms. Consider thereby exclusively single scattering processes. Each electron is scattered by exactly one H-atom. The hydrogen atoms are in their ground states.

1. Write down the scattering potential. Demonstrate in particular that it is a central potential.

2. Calculate the scattering amplitude in the first Born approximation!

3. Determine with 2. the differential cross-section.

4. Derive the total cross-section!

5. What is the condition for the validity of the first Born approximation?

Formulas:

$$\int_0^{x_0} dx\, e^{-\alpha x}\, x^n = \frac{n!}{\alpha^{n+1}} \left(1 - e^{-\alpha x_0} \sum_{\nu=0}^{n} \frac{(\alpha\, x_0)^\nu}{\nu!} \right) ,$$

$$\int_{x_0}^{\infty} dx\, e^{-\alpha x}\, x^n = \frac{n!}{\alpha^{n+1}}\, e^{-\alpha x_0} \sum_{\nu=0}^{n} \frac{(\alpha\, x_0)^\nu}{\nu!} .$$

Exercise 9.3.5
Prove the equivalence of the Born approximation for scattering phases (9.76),

$$\delta_l \approx -\frac{2m}{\hbar^2}\, \frac{1}{k} \int_0^{\infty} dr\, V(r)\, [k\, r\, j_l\, (k\, r)]^2 ,$$

and the Born approximation for the scattering amplitude (9.91),

$$f^{(1)}(\vartheta) = -\frac{m}{2\pi\, \hbar^2} \int d^3r'\, V(r')\, e^{-ik(\mathbf{e}_r - \mathbf{e}_z)\cdot \mathbf{r}'} .$$

9.4 Formal Scattering Theory

So far we have formulated the scattering problem exclusively in the *illustrative* position representation. The *incident* particle was interpreted as a wave packet. Since this is built up by plane waves, we could focus the full theory on the investigation of an *incident plane wave*. Furthermore, since, in contrast to the wave packet, the plane wave is an energy-eigen state of the *free* Hamilton operator, the scattering problem became *stationary*. In this section we will now look for more abstract representations, in order to have the freedom to choose a particular realization which is most suitable for evaluation.

9.4.1 Lippmann-Schwinger Equation

Let the particle (system), which undergoes the scattering process, be described in the Schrödinger picture by the time-dependent state $|\varphi(t)\rangle$. Its time-behavior under the influence of the Hamilton operator

$$H = H_0 + H_1$$

contains of course the full information about the scattering process, if H_1 is the operator of the interaction between particle and scattering center. Let the *free* operator $H_0 = \mathbf{p}^2/2m$, which alone acts *far away from the scattering center*, have a continuous eigen-value spectrum:

$$H_0 \left| E_n^{(0)} \right\rangle = E_n^{(0)} \left| E_n^{(0)} \right\rangle .$$

n is thereby a set of quantum numbers, as for instance the Cartesian wave-number components k_x, k_y, k_z. Let the eigen-states $|E_n^{(0)}\rangle$ be complete and orthonormalized to δ-functions:

$$\int dn \left| E_n^{(0)} \right\rangle \left\langle E_n^{(0)} \right| = \mathbb{1} \; ; \quad \left\langle E_n^{(0)} \middle| \, E_m^{(0)} \right\rangle = \delta(n-m) \; .$$

When we, at first, *switch off* the interaction and prepare the particle state at the time $t = 0$, e.g., as wave packet,

$$|\varphi_0(0)\rangle = \int dn \, \alpha_n \left| E_n^{(0)} \right\rangle \; ; \quad \int dn \, |\alpha_n|^2 = 1 \; ,$$

then it would hold for the time t:

$$|\varphi_0(t)\rangle = e^{-(i/\hbar)H_0 t} \int dn \, \alpha_n \left| E_n^{(0)} \right\rangle = \int dn \, \alpha_n \, e^{-(i/\hbar)E_n^{(0)} t} \left| E_n^{(0)} \right\rangle \; . \quad (9.97)$$

The expansion coefficients α_n can thereby be considered as known. For the *switched on* interaction, though, $|\varphi_0(t)\rangle$ can be an exact eigen-state only for $t \to -\infty$ (*the time long before the scattering*). By means of Schrödinger's time evolution operator ((3.177), Vol. 6) we can, however, find a formally exact relation between $|\varphi_0(t \to -\infty)\rangle$ and the general scattering state $|\varphi(t)\rangle$:

$$\begin{aligned} |\varphi(t)\rangle &= \lim_{t' \to -\infty} e^{-(i/\hbar)H(t-t')} \, |\varphi_0(t')\rangle \\ &= e^{-(i/\hbar)Ht} \lim_{t' \to -\infty} \int dn \, \alpha_n \, e^{-(i/\hbar)(E_n^{(0)} - H)t'} \left| E_n^{(0)} \right\rangle \; . \end{aligned} \quad (9.98)$$

We have of course to ask ourselves how to perform such a limiting process. We want to presume here without explicit proof that the limiting value does indeed exist for *reasonable* scattering potentials. Then the following consideration will help: Let $f(t)$ be a function with a limiting value for $t \to -\infty$:

$$\begin{aligned} f(-\infty) &= f(-\infty) \int_{-\infty}^{0} dx \, e^x = \lim_{\eta \to 0^+} \int_{-\infty}^{0} dx \, e^x \, f\left(\frac{x}{\eta}\right) \\ &= \lim_{\eta \to 0^+} \eta \int_{-\infty}^{0} dt \, e^{\eta t} \, f(t) \; . \end{aligned} \quad (9.99)$$

Note in the second partial step that, because of the special limits of integration, x is always negative. The limiting process thus leads indeed to $f(-\infty)$. With (9.99) we calculate the limiting process in (9.98):

$$\begin{aligned} &\lim_{t' \to -\infty} e^{-(i/\hbar)(E_n^{(0)} - H)t'} \left| E_n^{(0)} \right\rangle = \lim_{\eta \to 0^+} \eta \int_{-\infty}^{0} dt \, e^{-(i/\hbar)(E_n^{(0)} - H + i\hbar\eta)t} \left| E_n^{(0)} \right\rangle \\ &= \lim_{\eta \to 0^+} \eta \, \frac{1}{-(i/\hbar)\,(E_n^{(0)} - H + i\,\hbar\,\eta)} \left| E_n^{(0)} \right\rangle = \frac{i\,0^+}{E_n^{(0)} - H + i\,0^+} \left| E_n^{(0)} \right\rangle \; . \end{aligned} \quad (9.100)$$

With the *new* state vector

$$\left|E_n^{(+)}\right\rangle = \lim_{t'\to-\infty} e^{-(i/\hbar)(E_n^{(0)}-H)t'}\left|E_n^{(0)}\right\rangle = \frac{i\,0^+}{E_n^{(0)}-H+i\,0^+}\left|E_n^{(0)}\right\rangle \quad (9.101)$$

we are now able to write (9.98) as follows:

$$|\varphi(t)\rangle = e^{-(i/\hbar)Ht}\int dn\,\alpha_n|E_n^{(+)}\rangle\,. \quad (9.102)$$

This expression can be further manipulated, as soon as we have shown that $|E_n^{(+)}\rangle$ is an eigen-state of the Hamilton operator H. But one realizes that immediately when one applies to both sides of the definition equation (9.101) the operator $(E_n^{(0)}-H+i\,0^+)$:

$$\left(E_n^{(0)}-H+i\,0^+\right)\left|E_n^{(+)}\right\rangle = i\,0^+\left|E_n^{(0)}\right\rangle \iff \left(E_n^{(0)}-H\right)\left|E_n^{(+)}\right\rangle = 0\,. \quad (9.103)$$

The states $|E_n^{(+)}\rangle$ are thus eigen-states of H with the eigen-values $E_n^{(0)}$ of the *free* system. We can therefore write instead of (9.102):

$$|\varphi(t)\rangle = \int dn\,\alpha_n\,e^{-(i/\hbar)E_n^{(0)}t}\left|E_n^{(+)}\right\rangle\,. \quad (9.104)$$

The states $|E_n^{(+)}\rangle$ obviously solve the scattering problem, whose time-dependence has already been separated off in (9.104).

If one exploits in (9.101) that the number $E_n^{(0)}$ of course commutes with the operator H ($e^A\,e^B = e^{A+B}$ only if $[A,B]_- = 0$!), then $|E_n^{(+)}\rangle$ can be cast into the form,

$$\left|E_n^{(+)}\right\rangle = \lim_{t'\to-\infty} e^{(i/\hbar)Ht'}\,e^{-(i/\hbar)E_n^{(0)}t'}\left|E_n^{(0)}\right\rangle = \lim_{t'\to-\infty} e^{(i/\hbar)Ht'}\,e^{-(i/\hbar)H_0t'}\left|E_n^{(0)}\right\rangle,$$

from which we can read off the later needed *orthonormalization* of these states. It is identical to that of the *free* states:

$$\left\langle E_m^{(+)}\right|\left.E_n^{(+)}\right\rangle = \left\langle E_m^{(0)}\right|\left.E_n^{(0)}\right\rangle = \delta(m-n)\,. \quad (9.105)$$

The according to (9.104) remaining task now consists in the determination of $|E_n^{(+)}\rangle$. At first, it follows from the definition (9.101):

$$\left|E_n^{(+)}\right\rangle = \frac{1}{E_n^{(0)}-H+i\,0^+}\left[i\,0^+ + \left(E_n^{(0)}-H_0\right)\right]\left|E_n^{(0)}\right\rangle\,;.$$

This is equivalent to:

$$\frac{1}{E_n^{(0)}-H_0+i\,0^+}\left(E_n^{(0)}-H+i\,0^+\right)\left|E_n^{(+)}\right\rangle$$
$$= \left(1\!\!1 - \frac{1}{E_n^{(0)}-H_0+i\,0^+}H_1\right)\left|E_n^{(+)}\right\rangle = \left|E_n^{(0)}\right\rangle\,.$$

We define:

Green operator to $\boldsymbol{H}_0$

$$R_n^{(\pm)} = \frac{1}{E_n^{(0)} - H_0 \pm i\,0^+} \,. \tag{9.106}$$

We do not need the operator $R_n^{(-)}$ before the next subsection. But here it is simply co-introduced. From the last equation we get, with the definition of the Green operator, the

Lippmann-Schwinger equation

$$\left|E_n^{(+)}\right\rangle = \left|E_n^{(0)}\right\rangle + R_n^{(+)}\, H_1 \left|E_n^{(+)}\right\rangle \,, \tag{9.107}$$

which turns out to be fundamental for the formal scattering theory. This equation can be iterated,

$$\left|E_n^{(+)}\right\rangle = \sum_{m=0}^{\infty} \left|E_n^{(m)}\right\rangle \,, \tag{9.108}$$

$$\left|E_n^{(m=0)}\right\rangle = \left|E_n^{(0)}\right\rangle \,; \quad \left|E_n^{(m)}\right\rangle = R_n^{(+)}\, H_1 \left|E_n^{(m-1)}\right\rangle \,, \tag{9.109}$$

and strongly resembles **Born's series** (9.89) in Sect. 9.3.2. This similarity is not by chance. The Born's series is just the position representation of the abstract Lippmann-Schwinger equation. This we will now check.

At first, we can reformulate Eq. (9.107) by an arbitrary complete system $\{|\rho\rangle\}$ of the Hilbert space:

$$\left\langle \rho \middle| E_n^{(+)} \right\rangle = \left\langle \rho \middle| E_n^{(0)} \right\rangle + \iint d\rho'\, d\rho'' \left\langle \rho \middle| R_n^{(+)} \middle| \rho' \right\rangle \langle \rho' |\, H_1 \,| \rho'' \rangle \left\langle \rho'' \middle| E_n^{(+)} \right\rangle \,. \tag{9.110}$$

In the special position representation the interaction H_1 is diagonal:

$$\langle \mathbf{r}' |\, H_1 \,| \mathbf{r}'' \rangle = V(\mathbf{r}')\delta(\mathbf{r}' - \mathbf{r}'') \,.$$

If we specify the set of quantum numbers to $n = (k_x,\, k_y\, k_z) = \mathbf{k}$, then

$$\left\langle \mathbf{r} \middle| E_n^{(0)} \right\rangle \Longrightarrow \varphi_{\mathbf{k}}^{(0)}(\mathbf{r}) = e^{i\,\mathbf{kr}}$$

denotes the (not normalized) plane wave. It is then

$$\left\langle \mathbf{r} \middle| E_n^{(+)} \right\rangle \implies \varphi_{\mathbf{k}}^{(+)}(\mathbf{r})$$

the solution wave function:

$$\varphi_{\mathbf{k}}^{(+)}(\mathbf{r}) = \varphi_{\mathbf{k}}^{(0)}(\mathbf{r}) + \int d^3r'\, \langle \mathbf{r} |\, R_{\mathbf{k}}^{(+)} | \mathbf{r}' \rangle V(\mathbf{r}')\, \varphi_{\mathbf{k}}^{(+)}(\mathbf{r}') \,. \tag{9.111}$$

We now show that, except for an unimportant factor, the position representation of the Green **operator** $R_{\mathbf{k}}^{(+)}$ agrees with the Green's **function** (9.83). When inserting

$$H_0 = \frac{\hbar^2}{2m}\,\hat{\mathbf{k}}^2\;; \quad E_n^{(0)} = \frac{\hbar^2}{2m}\,\mathbf{k}^2$$

we have to take into consideration that $\hat{\mathbf{k}}$ is the operator of the wave number $\mathbf{k}$, while the latter is a c-number, and not an operator:

$$\begin{aligned}
\langle \mathbf{r}|R_{\mathbf{k}}^{(+)}|\mathbf{r}'\rangle &= \langle \mathbf{r}|\frac{1}{E_n^{(0)} - H_0 + i\,0^+}\,|\mathbf{r}'\rangle \\
&= \frac{2m}{\hbar^2}\langle \mathbf{r}|\frac{1}{\mathbf{k}^2 - \hat{\mathbf{k}}^2 + i\,0^+}|\mathbf{r}'\rangle \\
&= \frac{2m}{\hbar^2}\int d^3q \langle \mathbf{r}|\frac{1}{\mathbf{k}^2 - \hat{\mathbf{k}}^2 + i\,0^+}|\mathbf{q}\rangle\langle \mathbf{q}|\mathbf{r}'\rangle \\
&= \frac{2m}{\hbar^2}\int d^3q\,\frac{\langle \mathbf{r}|\mathbf{q}\rangle\langle \mathbf{q}|\mathbf{r}'\rangle}{\mathbf{k}^2 - \mathbf{q}^2 + i\,0^+}\;.
\end{aligned}$$

$\langle \mathbf{r}|\mathbf{q}\rangle = (2\pi)^{-3/2}\exp(i\,\mathbf{q}\cdot\mathbf{r})$ is the normalized plane wave:

$$\langle \mathbf{r}|R_{\mathbf{k}}^{(+)}|\mathbf{r}'\rangle = \frac{2m}{\hbar^2}\,\frac{1}{(2\pi)^3}\int d^3q\,\frac{e^{i\,\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}}{\mathbf{k}^2 - \mathbf{q}^2 + i\,0^+}\;. \tag{9.112}$$

Except for the factor $2m/\hbar^2$ this is now just the Green's function $G(\mathbf{r}-\mathbf{r}')$ (9.83). The factor can be explained by the integral equation (9.80), which defines $G(\mathbf{r}-\mathbf{r}')$. There we had taken instead of the real potential the *renormalized* potential $v(\mathbf{r}) = 2m/\hbar^2\,V(\mathbf{r})$. The integrand in (9.112) has poles at the positions

$$q = \pm\sqrt{\mathbf{k}^2 + i\,0^+} = \pm(k + i\,0^+)\;.$$

The infinitesimal $+i\,0^+$ in (9.112) has therefore the same effect as the *'circumscribing' of the poles*, which we discussed after Eq. (9.85) in connection with the evaluation of the Green's function. It just corresponds to the path 2) of integration, which we denoted there as the *physically correct one*. The integral equations (9.111) and (9.80) are therefore identical. The Lippmann-Schwinger equation (9.107), for which (9.111) is a special realization, now still allows, according to (9.110), also for other representations. That can mean a rather significant advantage for the practical solution of a scattering problem.

Let us finally try to also find for the important **scattering amplitude** a generalized, abstract representation. For this purpose we reformulate (9.88):

$$\begin{aligned}
f_{\mathbf{k}}(\vartheta,\varphi) &= \frac{-m}{2\pi\,\hbar^2}\,(2\pi)^3\int d^3r'\int d^3r''\,V(\mathbf{r}')\,\delta(\mathbf{r}'-\mathbf{r}'')\langle k\,\mathbf{e}_r|\mathbf{r}'\rangle\langle \mathbf{r}''|E_{\mathbf{k}}^{(+)}\rangle \\
&= -\frac{4\pi^2 m}{\hbar^2}\int d^3r'\int d^3r''\langle k\,\mathbf{e}_r|\mathbf{r}'\rangle\langle \mathbf{r}'|H_1|\mathbf{r}''\rangle\langle \mathbf{r}''|E_{\mathbf{k}}^{(+)}\rangle\;.
\end{aligned}$$

The direction of $\mathbf{k}$ defines the polar axis; ϑ, φ are the spherical angles of the unit vector $\mathbf{e}_r$:

$$f_{\mathbf{k}}(\vartheta, \varphi) = -\frac{4\pi^2 m}{\hbar^2} \langle k\, \mathbf{e}_r | H_1 | E_{\mathbf{k}}^{(+)} \rangle \; . \tag{9.113}$$

In this form also other representations can be applied for the calculation of the scattering amplitude.

9.4.2 *S*- and *T*-Matrix

The considerations of the last subsection can further be generalized. They provide an abstract access to scattering theory via the important **scattering matrix** (**S-matrix)**, whose elements can be interpreted as *transition probabilities* between given *initial states* and well-defined *final states*. The scattering matrix therefore holds a close relationship to *basic quantities* of the scattering theory, as, e.g., the cross-section or the scattering amplitude. The corresponding connections are the topic of this concluding section.

The task of the preceding section was focused on the calculation of the state $|\varphi(t)\rangle$ of the system from the *free* state,

$$|\varphi_0(t)\rangle \; = \int dn\, \alpha_n\, e^{-(i/\hbar) E_n^{(0)} t} \left| E_n^{(0)} \right\rangle \; ,$$

which for $t \to -\infty$, i.e., *long before* the actual act of scattering, is identical with the actual state. The expansion coefficients α_n can be considered as known. The determination of the state $|\varphi(t)\rangle$ for finite times t,

$$|\varphi(t)\rangle \; = \lim_{t' \to -\infty} \; e^{-(i/\hbar) H (t - t')} \; |\varphi_0(t')\rangle \; ,$$

solves the scattering problem, and can be traced back with (9.104) to the determination of the time-**in**dependent *scattering state* $|E_n^{(+)}\rangle$ (9.101).

The total scattering formalism in this section, though, was conceived *asymptotically*. *Finite times* t up to now were not the matter of our investigations. Instead of $|\varphi(t)\rangle$ we are actually more interested in transition probabilities between the *force-free* states *long time before* ($t \to -\infty$) and *long time after* ($t \to +\infty$) the actual scattering process. In this direction we will modify the procedure of Sect. 9.4.1. At first, it is advisable to expand the initial state as well as the final state in the complete set of the eigen-states $|E_n^{(0)}\rangle$ of the *free* Hamilton operator H_0:

$$\lim_{t \to -\infty} |\varphi(t)\rangle \quad = \quad \lim_{t \to -\infty} \int dn\, \alpha_n\, e^{-(i/\hbar) E_n^{(0)} t} \left| E_n^{(0)} \right\rangle \; , \tag{9.114}$$

$$\lim_{t \to +\infty} |\varphi(t)\rangle \quad = \quad \lim_{t \to +\infty} \int dn\, \beta_n\, e^{-(i/\hbar) E_n^{(0)} t} \left| E_n^{(0)} \right\rangle \; . \tag{9.115}$$

We postulate again that these limiting values do exist for *physically reasonable* scattering potentials. The α_n of the initial state (9.114) are known (by

preparation). The main problem therefore consists in the determination of the coefficients β_n of the final state (9.115) in terms of the given α_n.

It proves to be advantageous to use for the following considerations the *interaction representation* (*Dirac picture*, Sect. 3.4.4 (Vol. 6)), in which the time-dependence of the states is due to the interaction H_1 and that of the operators due to H_0. Since the particle moves for $t \to \pm\infty$ outside the interaction domain ($H_1 \neq 0$), the limiting processes (9.114) and (9.115) become very simple in the Dirac picture. We mark in the following the states of the Dirac picture by the index D and assume that they coincide with those of the Schrödinger picture (without index) at the time $t = 0$ ((3.196), Vol. 6). Then it holds in particular ((3.198), Vol. 6):

$$|\varphi_{\mathrm{D}}(t)\rangle = e^{(i/\hbar)H_0 t}\, |\varphi(t)\rangle \ .$$

For the *time evolution operator* $U_{\mathrm{D}}(t, t')$,

$$|\varphi_{\mathrm{D}}(t)\rangle = U_{\mathrm{D}}(t, t')\, |\varphi_{\mathrm{D}}(t')\rangle \ ,$$

we had found in ((3.200), Vol. 6):

$$U_{\mathrm{D}}(t, t') = e^{(i/\hbar)H_0 t}\, e^{-(i/\hbar)H(t-t')}\, e^{-(i/\hbar)H_0 t'} \ . \tag{9.116}$$

Without interaction ($H_1 = 0$), U_{D} is the identity.

The limiting processes in (9.114) and (9.115), respectively, substantially simplify in the interaction representation:

$$\begin{aligned} \lim_{t \to -\infty} |\varphi_{\mathrm{D}}(t)\rangle &= \lim_{t \to -\infty} e^{(i/\hbar)H_0 t}\, |\varphi(t)\rangle \\ &= \lim_{t \to -\infty} e^{(i/\hbar)H_0 t} \int dn\, \alpha_n\, e^{-(i/\hbar)E_n^{(0)} t} \left| E_n^{(0)} \right\rangle \\ &= \int dn\, \alpha_n \left| E_n^{(0)} \right\rangle \ . \end{aligned} \tag{9.117}$$

In the same manner one shows:

$$\lim_{t \to +\infty} |\varphi_{\mathrm{D}}(t)\rangle = \int dn\, \beta_n \left| E_n^{(0)} \right\rangle \ . \tag{9.118}$$

The probability amplitude for the situation that the particle is at the time t in a *free* energy-eigen state $|E_m^{(0)}\rangle$, when it at the time t' occupied the state $|\varphi_{\mathrm{D}}(t')\rangle$, corresponds to the scalar product:

$$\begin{aligned} \left\langle E_m^{(0)} \middle| \varphi_{\mathrm{D}}(t) \right\rangle &= \left\langle E_m^{(0)} \middle| U_{\mathrm{D}}(t, t')\, |\varphi_{\mathrm{D}}(t')\rangle \right. \\ &= \int dn\, \left\langle E_m^{(0)} \middle| U_{\mathrm{D}}(t, t') \middle| E_n^{(0)} \right\rangle \left\langle E_n^{(0)} \middle| \varphi_{\mathrm{D}}(t') \right\rangle \ . \end{aligned} \tag{9.119}$$

This expression, for which we have exploited in the last step the completeness relation of the $|E_n^{(0)}\rangle$, represents the probability amplitudes for transitions at

arbitrary times t and t', especially for $t \to +\infty$ and $t' \to -\infty$. Because of (9.117) and (9.118) we also have:

$$\begin{aligned} \lim_{t\to+\infty} \left\langle E_m^{(0)} \middle| \varphi_{\mathrm{D}}(t) \right\rangle &= \beta_m \,, \\ \lim_{t'\to-\infty} \left\langle E_n^{(0)} \middle| \varphi_{\mathrm{D}}(t') \right\rangle &= \alpha_n \,. \end{aligned}$$

This we use in (9.119):

$$\beta_m = \int dn \left\langle E_m^{(0)} \middle| U_{\mathrm{D}}(+\infty,-\infty) \middle| E_n^{(0)} \right\rangle \alpha_n \,.$$

For that one writes in brief,

$$\beta_m = \int dn\, S_{mn}\, \alpha_n \,, \tag{9.120}$$

and defines by

$$S_{mn} \equiv \left\langle E_m^{(0)} \middle| U_{\mathrm{D}}(+\infty,-\infty) \middle| E_n^{(0)} \right\rangle \tag{9.121}$$

the (m,n)-element of the so-called

scattering matrix (S-matrix) $U_{\mathbf{D}}(+\infty,-\infty)$.

The physical meaning of the S-matrix elements is evident. They correspond to the *asymptotic* transition-probability amplitudes between the *free* states $|E_n^{(0)}\rangle$ and $|E_m^{(0)}\rangle$. With (9.116) we rearrange S_{mn} a bit:

$$\begin{aligned} S_{mn} &= \lim_{t\to+\infty} \lim_{t'\to-\infty} \left\langle E_m^{(0)} \middle| U_{\mathrm{D}}(t,t') \middle| E_n^{(0)} \right\rangle \\ &= \lim_{t\to+\infty} \lim_{t'\to-\infty} \left\langle E_m^{(0)} \middle| e^{(i/\hbar)(E_m^{(0)}-H)t}\, e^{-(i/\hbar)(E_n^{(0)}-H)t'} \middle| E_n^{(0)} \right\rangle \,. \end{aligned} \tag{9.122}$$

For the calculation of these limiting values we can apply the same procedure as that in the preceding subsection. The relation (9.100) for the transition $t \to -\infty$ can even be directly taken over. For $t \to +\infty$ we argue completely analogously as for (9.99). If the function $f(t)$ has such a limiting value, one can write:

$$\begin{aligned} \lim_{t\to+\infty} f(t) &= f(\infty) \int_0^\infty dx\, e^{-x} = \lim_{\eta\to 0^+} \int_0^\infty dx\, e^{-x}\, f\left(\frac{x}{\eta}\right) \\ &= \lim_{\eta\to 0^+} \eta \int_0^\infty dt'\, e^{-\eta t'}\, f(t') \,. \end{aligned}$$

This formula interests us in the following context:

$$\lim_{t\to+\infty} e^{-(i/\hbar)(E_m^{(0)}-H)t} \left| E_m^{(0)} \right\rangle = \lim_{\eta\to 0^+} \eta \int_0^\infty dt'\, e^{-(i/\hbar)(E_m^{(0)}-H-i\hbar\eta)t'} \left| E_m^{(0)} \right\rangle$$

$$= \lim_{\eta\to 0^+} \frac{-\eta}{-(i/\hbar)\left(E_m^{(0)} - H - i\,\hbar\,\eta\right)} \left| E_m^{(0)} \right\rangle = \frac{-i\,0^+}{E_m^{(0)} - H - i\,0^+} \left| E_m^{(0)} \right\rangle \,.$$

This distinctly resembles the result (9.101). We therefore combine both the limiting values by the following definition:

$$\left|E_n^{(\pm)}\right\rangle = \lim_{t \to \mp\infty} e^{-(i/\hbar)(E_n^{(0)} - H)t} \left|E_n^{(0)}\right\rangle = \frac{\pm i\, 0^+}{E_n^{(0)} - H \pm i\, 0^+} \left|E_n^{(0)}\right\rangle \ . \quad (9.123)$$

$|E_n^{(-)}\rangle$ is exactly as $|E_n^{(+)}\rangle$ an eigen-state of the *full* Hamilton operator H with the eigen-value $E_n^{(0)}$ of the *free* Hamilton operator H_0. The explanatory statement is the same as that to (9.103):

$$H \left|E_n^{(\pm)}\right\rangle = E_n^{(0)} \left|E_n^{(\pm)}\right\rangle \ . \quad (9.124)$$

Even the normalization of the states $|E_n^{(-)}\rangle$ is identical to that for the $|E_n^{(+)}\rangle$ (9.105):

$$\left\langle E_m^{(\pm)} \middle| E_n^{(\pm)} \right\rangle = \delta(m-n) \ . \quad (9.125)$$

If we finally still replace in the derivation of (9.107) everywhere $i\, 0^+$ by $-i\, 0^+$, $|E_n^{(+)}\rangle$ by $|E_n^{(-)}\rangle$, and $R_n^{(+)}$ by $R_n^{(-)}$, then we get for $|E_n^{(-)}\rangle$, compared to (9.107), a formally unchanged

Lippmann-Schwinger equation

$$\left|E_n^{(\pm)}\right\rangle = \left|E_n^{(0)}\right\rangle + R_n^{(\pm)}\, H_1 \left|E_n^{(\pm)}\right\rangle \ . \quad (9.126)$$

For the following conclusions, however, a *second version* of the Lippmann-Schwinger equation is also interesting and useful, which applies instead of $R_n^{(\pm)}$ the

Green operator to H

$$G_n^{(\pm)} = \frac{1}{E_n^{(0)} - H \pm i\, 0^+} \ . \quad (9.127)$$

In contrast to the definition (9.106) of the operators $R_n^{(\pm)}$, there appears here in the denominator the *full* Hamilton operator H. Starting at (9.123) we find:

$$\begin{aligned} \left|E_n^{(\pm)}\right\rangle &= \frac{1}{E_n^{(0)} - H \pm i\, 0^+} \left[\left(E_n^{(0)} - H \pm i\, 0^+\right) + \left(H_0 + H_1 - E_n^{(0)}\right)\right] \left|E_n^{(0)}\right\rangle \\ &= \left[\mathbb{1} + G_n^{(\pm)}\, H_1\right] \left|E_n^{(0)}\right\rangle \ . \end{aligned}$$

The following expression for the *scattering states* $|E_n^{(\pm)}\rangle$ is therefore equivalent to (9.126):

$$\left|E_n^{(\pm)}\right\rangle = \left|E_n^{(0)}\right\rangle + G_n^{(\pm)}\, H_1 \left|E_n^{(0)}\right\rangle \ . \quad (9.128)$$

We now come back to the *scattering matrix*, whose investigation we interrupted after Eq. (9.122). Instead of (9.122), we can now write with (9.123):

$$S_{mn} = \left\langle E_m^{(-)} \middle| E_n^{(+)} \right\rangle \ . \quad (9.129)$$

For a further rearrangement we apply (9.128):

$$\left|E_m^{(-)}\right\rangle - \left|E_m^{(+)}\right\rangle = \left(G_m^{(-)} - G_m^{(+)}\right) H_1 \left|E_m^{(0)}\right\rangle .$$

We multiply this equation scalarly by the bra-state $\langle E_n^{(+)}|$ and respect the normalization condition (9.125):

$$S_{mn}^* = \left\langle E_n^{(+)} \middle| E_m^{(-)} \right\rangle = \delta(n-m) + \left\langle E_n^{(+)} \middle| \left(G_m^{(-)} - G_m^{(+)}\right) H_1 \middle| E_m^{(0)} \right\rangle .$$

H_1 is Hermitian, and it holds for the Green operator (9.127):

$$\left[G_m^{(\pm)}\right]^+ = G_m^{(\mp)} .$$

This means:

$$S_{mn} = \delta(n-m) + \left\langle E_m^{(0)} \middle| H_1 \left(G_m^{(+)} - G_m^{(-)}\right) \middle| E_n^{(+)} \right\rangle .$$

$|E_n^{(+)}\rangle$ is eigen-state of H with the eigen-value $E_n^{(0)}$. We thus know also the action of the Green operators on this state:

$$\begin{aligned} \left(G_m^{(+)} - G_m^{(-)}\right) \left|E_n^{(+)}\right\rangle &= \left(\frac{1}{E_m^{(0)} - E_n^{(0)} + i\,0^+} - \frac{1}{E_m^{(0)} - E_n^{(0)} - i\,0^+}\right) \left|E_n^{(+)}\right\rangle \\ &= \frac{-2i\,0^+}{\left(E_m^{(0)} - E_n^{(0)}\right)^2 + (0^+)^2} \left|E_n^{(+)}\right\rangle . \end{aligned}$$

Using the special representation of the δ-function ((1.7), Vol. 3),

$$\delta(x) = \lim_{\eta \to 0^+} \frac{1}{\pi} \frac{\eta}{x^2 + \eta^2} ,$$

we find a form of the scattering matrix, which turns out to be fundamental for the abstract scattering theory:

Basic formula of scattering theory

$$S_{mn} = \delta(m-n) - 2\pi\, i\, \delta\left(E_m^{(0)} - E_n^{(0)}\right) \left\langle E_m^{(0)} \middle| H_1 \middle| E_n^{(+)} \right\rangle . \tag{9.130}$$

Note that the two δ-functions are **not** equivalent!

In practice one defines besides the S-matrix also a so-called

Transfermatrix (T-matrix)

$$T^{(n)} \equiv H_1 \left(\mathbb{1} + G_n^{(+)} H_1\right) , \tag{9.131}$$

for which one finds because of (9.128):

$$H_1 \left|E_n^{(+)}\right\rangle = H_1 \left(\mathbb{1} + G_n^{(+)} H_1\right) \left|E_n^{(0)}\right\rangle = T^{(n)} \left|E_n^{(0)}\right\rangle . \tag{9.132}$$

The *basic formula* (9.130) takes therewith the following equivalent form:

$$S_{mn} = \delta(m-n) - 2\pi\, i\, \delta\left(E_m^{(0)} - E_n^{(0)}\right) \left\langle E_m^{(0)} \left| T^{(n)} \right| E_n^{(0)} \right\rangle \ . \tag{9.133}$$

In the case that the T-matrix is known, the state after the scattering is completely determined. If we insert namely (9.133) into (9.120), then we can calculate the coefficients β_m of the *asymptotic final state* (9.118) out of the coefficients α_n of the *asymptotic initial state* (9.117):

$$\beta_m = \alpha_m - 2\pi\, i \int dn\ \delta\left(E_m^{(0)} - E_n^{(0)}\right) \alpha_n \left\langle E_m^{(0)} \left| T^{(n)} \right| E_n^{(0)} \right\rangle \ . \tag{9.134}$$

The first term on the right-hand side must be ascribed to the *traversing wave*. When there is no interaction ($H_1 = 0 \implies T^{(n)} = 0$), then the initial and the final state should of course be identical ($\beta_m = \alpha_m$). Even when the interaction is *switched on*, there exists a *traversing* part. The second term in (9.134) describes the scattered wave, where the δ-function takes care for energy conservation (elastic scattering!). At first glance, this *energy conservation* may be a bit puzzling, namely if one asks oneself, at which point of the preceding derivation could it actually have entered the considerations. That has happened indeed *somewhat hiddenly*, namely by the fact that we have investigated from the beginning only the states of the *scattered* particle. Thereby it was implicitly presumed that the scattering center does not experience any internal excitations. Only for this reason, the scattering center could be simulated by a potential $V(r)$ (remember the considerations subsequent to (9.3)). But when there does not exist a partner for energy exchange, the scattering must be **elastic** in order to fulfill the energy conservation law. In the case of inelastic scattering, the Hamilton operator of the total system ($\cong$ *scattering* particle plus *scattered* particle) with its eigen-states and eigen-values should have been included in the theory. Energy conservation in the total system would have been to be required, which then would **not** exclude energy **exchange** between the two particles.

The T-matrix, according to (9.134), obviously is the decisive operator for the scattering. Its matrix elements $\langle E_m^{(0)}|T^{(n)}|E_n^{(0)}\rangle$ determine the *strength* of the scattering. $T^{(n)}$ will not always be precisely calculable for realistic problems. We will therefore need approximate methods for the determination of the T-matrix. In this respect, the *integral equation*, which we derive in the following, may be a good starting basis. We begin with the definition equation (9.131):

$$\begin{aligned} T^{(n)} &= \left(\mathbb{1} + H_1\, G_n^{(+)}\right) H_1 = \left(E_n^{(0)} - H + i\,0^+ + H_1\right) G_n^{(+)}\, H_1 \\ &= \left(R_n^{(+)}\right)^{-1} \left[\left(R_n^{(+)}\right)^{-1} - H_1\right]^{-1} H_1 = \left(\mathbb{1} - H_1\, R_n^{(+)}\right)^{-1} H_1 \ . \end{aligned}$$

From this we read off the useful relation

$$T^{(n)} = H_1 + H_1\, R_n^{(+)}\, T^{(n)} \ , \tag{9.135}$$

which can formally be solved by iteration:

$$\begin{aligned} T^{(n)} &= \sum_{m=0}^{\infty} \left[T^{(n)}\right]^{(m)} , \\ \left[T^{(n)}\right]^{(0)} &= H_1 , \\ \left[T^{(n)}\right]^{(m)} &= H_1 \, R_n^{(+)} \left[T^{(n)}\right]^{m-1} . \end{aligned} \tag{9.136}$$

Let us finally represent the scattering matrix in the special basis of the

eigen-states of the momentum operator $|\mathbf{k}\rangle$.

($n \to \mathbf{k}$; $m \to \mathbf{k}'$). The particle, which *comes in* in the direction of $\mathbf{k}$, is scattered into the direction of $\mathbf{k}'$. We need in (9.130) and (9.133), respectively:

$$\begin{aligned} \delta\left(E_m^{(0)} - E_n^{(0)}\right) \quad &\longrightarrow \quad \delta\left(\frac{\hbar^2 k'^2}{2m} - \frac{\hbar^2 k^2}{2m}\right) = \frac{2m}{\hbar^2}\,\delta(k'^2 - k^2) \\ &= \quad \frac{2m}{\hbar^2}\,\frac{1}{2k}\,\left[\delta\left(k' + k\right) + \delta\left(k' - k\right)\right] = \frac{m}{\hbar^2 k}\,\delta\left(k' - k\right) . \end{aligned}$$

Because of $k,\, k' > 0$ $\delta(k' + k)$ vanishes. Therewith the scattering matrix reads:

$$\begin{aligned} S_{\mathbf{k}'\mathbf{k}} &= \delta(\mathbf{k}' - \mathbf{k}) - 2\pi\, i\, \frac{m}{\hbar^2 k}\,\delta(k - k')\left\langle \mathbf{k}' \middle| H_1 \middle| E_{\mathbf{k}}^{(+)} \right\rangle \\ &= \delta(\mathbf{k}' - \mathbf{k}) - 2\pi\, i\, \frac{m}{\hbar^2 k}\,\delta(k - k')\left\langle \mathbf{k}' \middle| T^{(\mathbf{k})} \middle| \mathbf{k} \right\rangle . \end{aligned} \tag{9.137}$$

Notice that in the argument of the first δ-function there appear the **vectors** $\mathbf{k}$ and $\mathbf{k}'$, but in the argument of the second δ-function only the **magnitudes** k, k'. The comparison of (9.137) with (9.113),

$$\left\langle \mathbf{k}' \middle| T^{(\mathbf{k})} \middle| \mathbf{k} \right\rangle = -\frac{\hbar^2}{4\pi^2 m}\, f_{\mathbf{k}}(\vartheta, \varphi) , \tag{9.138}$$

shows that in the momentum representation, the elements of the T-matrix are equivalent to the centrally important **scattering amplitude** $f_{\mathbf{k}}(\vartheta, \varphi)$, which was extensively discussed in the preceding (sub)sections. The direction of $\mathbf{k}$ defines thereby the polar axis, and ϑ, φ are the polar angles of the *scattering direction* $\mathbf{k}'/k$. The abstract operator relations (9.135) and (9.136), respectively, obviously correspond in the momentum representation to the **Born series** (9.90) for the scattering amplitude. That emphasizes once more the importance of the T-matrix.

9.4.3 Møller Operators

In this subsection we concern ourselves with an alternative and complementary representation of the scattering process, in order to understand better the statements of the abstract formalism of the last subsection. Starting point is again a Hamilton operator of the form

$$H = H_0 + H_1 ,$$

where H_1 describes the interaction of the particle with the scattering center. We decompose the Hilbert space into two partial spaces,

$$\mathcal{H} = \mathcal{H}_d + \mathcal{H}_S \ , \tag{9.139}$$

where $\mathcal{H}_d$ is spanned by the (bound) states of the discrete spectrum of H. These can of course **not** come into consideration for the description of scattering processes. $\mathcal{H}_S$ contains all those states, which are orthogonal to $\mathcal{H}_d$, and represents therewith the space of the scattering states. The states in $\mathcal{H}_S$ belong to the *continuous* spectrum of H. Only these are here interesting to us.

Let us consider once more the *'scattering process'*. An arbitrary state $|\psi\rangle \in \mathcal{H}_S$, which one can imagine in the position representation as a somehow prepared wave packet, will be modified in the interaction zone by H_1, where its time-dependence is given, according to ((3.156)) and ((3.177)) in Vol. 6, by

$$|\psi(t)\rangle = \exp\left(-\frac{i}{\hbar}Ht\right)|\psi(0)\rangle \ . \tag{9.140}$$

It is now illustratively clear that the wave packet travels, for $t \to +\infty$, eventually out of the region of influence of the scattering potential H_1, and moves then practically as a free, only by H_0 determined wave packet. Thus it should hold for *'sufficiently large'* times t_0 and $t > t_0$:

$$\begin{aligned} |\psi(t)\rangle &\approx \exp\left(-\frac{i}{\hbar}H_0(t-t_0)\right)\left(\exp\left(-\frac{i}{\hbar}Ht_0\right)\Big|\psi\Big\rangle\right) \\ &= \exp\left(-\frac{i}{\hbar}H_0t\right)\left[\exp\left(\frac{i}{\hbar}H_0t_0\right)\Big|\psi(t_0)\Big\rangle\right] \ . \end{aligned} \tag{9.141}$$

The state in the square bracket may surely exist for *'normal'* scattering potentials as an element of $\mathcal{H}$. Consequently, it is a state $|\varphi\rangle$ from $\mathcal{H}$, which develops in the course of time under the action only of H_0 asymptotically in the same manner as the scattering state $|\psi\rangle$ under the influence of the full Hamilton operator H. In general, of course, $|\varphi\rangle$ will be different from $|\psi\rangle$.

The same considerations are of course also valid for very early times, when the wave packet has not yet entered the region of influence of the scattering potential, i.e., when its time-evolution is still exclusively due to H_0. Summarized, there should therefore exist to each $|\psi\rangle \in \mathcal{H}_S$ limiting states $|\varphi_\mp\rangle$ as elements of $\mathcal{H}$ [1]:

$$|\varphi_\mp\rangle = \lim_{t\to\pm\infty} \exp\left(\frac{i}{\hbar}H_0t\right)\exp\left(-\frac{i}{\hbar}Ht\right)|\psi\rangle \ \in \mathcal{H} \ . \tag{9.142}$$

That can be formulated also as follows:

$$\lim_{t\to\pm\infty}\left\|\exp\left(-\frac{i}{\hbar}H_0t\right)\varphi_\mp - \exp\left(-\frac{i}{\hbar}Ht\right)\psi\right\| = 0 \ . \tag{9.143}$$

[1] The perhaps somewhat contra-intuitive indexing of the states $|\varphi_\mp\rangle$ was chosen here intentionally to be in accordance with the indexing in Sect. 9.4.1. The limiting state, which is ascribed to the *incoming* wave packet, gets the plus sign, that for the *outgoing* wave packet the minus sign.

When we indeed assume that the states $|\varphi_\mp\rangle$ exist as elements of the Hilbert space $\mathcal{H}$,—the exact, rather involved mathematical proof we have to skip here—then it should be possible to expand them in plane waves $|\boldsymbol{k}\rangle$, which represent as eigen-states of H_0 a complete orthonormal system:

$$\begin{aligned} \exp\left(-\frac{i}{\hbar}H_0 t\right)|\varphi_\mp\rangle &= \exp\left(-\frac{i}{\hbar}H_0 t\right)\int d^3k\,\widehat{\varphi}_\mp(\mathbf{k})\,|\mathbf{k}\rangle \\ &= \int d^3k\,\widehat{\varphi}_\mp(\mathbf{k})\,\exp\left(-i\frac{\hbar k^2}{2m}t\right)|\mathbf{k}\rangle\,. \end{aligned} \tag{9.144}$$

In the position representation,

$$\varphi_\mp(\mathbf{r}) \equiv \langle \mathbf{r}|\varphi_\mp\rangle\,; \quad \langle \mathbf{r}|\mathbf{k}\rangle = \frac{1}{(2\pi)^{3/2}}\,e^{i\mathbf{k}\cdot\mathbf{r}}\,, \tag{9.145}$$

this reads:

$$\exp\left(-\frac{i}{\hbar}H_0 t\right)\varphi_\mp(\mathbf{r}) = \frac{1}{(2\pi)^{3/2}}\int d^3k\,\left(\widehat{\varphi}_\mp(\mathbf{k})\,\exp\left(-i\frac{\hbar k^2}{2m}t\right)\right)\,e^{i\mathbf{k}\cdot\mathbf{r}}\,. \tag{9.146}$$

On the right-hand side we have a free propagating wave packet, fixed by the wave-number distribution $\widehat{\varphi}_\mp(\boldsymbol{k})$ (see (2.49), Vol. 6). Because of (9.143), it belongs to each $|\psi\rangle \in \mathcal{H}_S$ for $t \to -\infty$ an incoming and for $t \to +\infty$ an outgoing *free* wave packet. But that corresponds precisely to the scattering process: $\widehat{\varphi}_+(\mathbf{k})$ identifies a free incoming wave packet before the scattering act, which is then influenced in the interaction zone by the scattering potential, and which, after leaving this zone, moves asymptotically again as a free wave packet, but that in general with a modified momentum distribution $\widehat{\varphi}_-(\mathbf{k})$. The task thus is to find out for a distribution $\widehat{\varphi}_+(\mathbf{k})$, prepared at $t \to -\infty$, whether and with what probability the distribution $\widehat{\varphi}_-(\mathbf{k})$ appears in the scattered wave packet.

The actual goal is therefore the determination of scattering states $|\psi_\pm\rangle \in \mathcal{H}_S$, which *asymptotically* correspond to pre-given distributions $\widehat{\varphi}_\pm(\mathbf{k})$:

$$\lim_{t\to\pm\infty}\left\| e^{-\frac{i}{\hbar}H_0 t}\,\varphi_\mp - e^{-\frac{i}{\hbar}Ht}\,\psi_\mp\{\widehat{\varphi}_\mp(\mathbf{k})\}\right\| = 0\,. \tag{9.147}$$

In the *Schrödinger picture* the scattering state changes with the time under the influence of H,

$$\exp\left(-\frac{i}{\hbar}Ht\right)\,\left|\psi_\mp\,\{\widehat{\varphi}_\mp(\mathbf{k})\}\,\right\rangle\,,$$

and under compliance of the boundary conditions for $t \to \pm\infty$. In the *Heisenberg picture* the scattering state is time-**in**dependent. $|\psi_\mp\,\{\widehat{\varphi}_\mp(\mathbf{k})\}\rangle$ then corresponds to, respectively, the *'incoming'* and the *'outgoing situation'*. Therewith

$$\left|\left\langle \psi_+\,\{\widehat{\varphi}_+(\mathbf{k})\}\,\middle|\,\psi_-\,\{\widehat{\varphi}_-(\mathbf{k})\}\,\right\rangle\right|^2$$

is the probability to measure, long time after the scattering, a wave packet with the amplitude function $\widehat{\varphi}_-(\mathbf{k})$, if, long time before the scattering, a wave packet with the amplitude function $\widehat{\varphi}_+(\mathbf{k})$ were prepared.

So far we have argued that to each scattering state from $\mathcal{H}_S$ there can be ascribed asymptotically a free wave packet. In a certain sense, however, the *'reversal'* should also be valid. In principle, any arbitrary distribution (amplitude function) $\widehat{\varphi}(\boldsymbol{k})$ can be prepared, and, as such, can be sent into the scattering zone. But in the case of a *'sufficiently normal'* scattering potential, there should then also exist for each wave packet $|\varphi\rangle$, scattering states $|\psi_\mp\rangle \in \mathcal{H}_S$, which behave for $t \to \pm\infty$ like $|\varphi\rangle$. It should therefore hold, analogous to (9.143)

$$\lim_{t\to\pm\infty} \left\| \exp\left(-\frac{i}{\hbar}H_0 t\right)\varphi - \exp\left(-\frac{i}{\hbar}Ht\right)\psi_\mp \right\| = 0 \,, \tag{9.148}$$

and equivalently therewith, the limiting value

$$\lim_{t\to\pm\infty} \exp\left(\frac{i}{\hbar}Ht\right)\exp\left(-\frac{i}{\hbar}H_0 t\right)|\varphi\rangle \tag{9.149}$$

should, for each $|\varphi\rangle \in \mathcal{H}$, lead to a scattering state of $\mathcal{H}_S$.

Our hitherto performed considerations can be summarized as follows: For *'normal'* scattering potentials the so-called

Møller operators $\mathbf{M}_\pm, \widehat{M}_\pm$

should exist:

$$M_\pm \equiv \lim_{t\to\mp\infty} \exp\left(\frac{i}{\hbar}Ht\right)\exp\left(-\frac{i}{\hbar}H_0 t\right) \;; \quad M_\pm : \mathcal{H} \subseteq \mathcal{H}_S \tag{9.150}$$

$$\widehat{M}_\pm \equiv \lim_{t\to\mp\infty} \exp\left(\frac{i}{\hbar}H_0 t\right)\exp\left(-\frac{i}{\hbar}Ht\right) P_S \;; \quad \widehat{M}_\pm : \mathcal{H}_{(S)} \subseteq \mathcal{H} \tag{9.151}$$

P_S is the projection operator onto the partial space $\mathcal{H}_S$ of the scattering states.

Let us list some obvious properties of the Møller operators.

- It follows directly from the definition (9.151), because of $P_S^2 = P_S$:

$$\widehat{M}_\pm P_S = \widehat{M}_\pm \tag{9.152}$$

- Because $e^{-i/\hbar\, H_0 t}$ and $e^{-i/\hbar\, Ht}$ are unitary operators, it follows immediately:

$$\|M_\pm\varphi\| = \|\varphi\| \quad \forall\, |\varphi\rangle \in \mathcal{H} \,. \tag{9.153}$$

The reasoning is indeed very simple:

$$\begin{aligned}
\|M_\pm\varphi\|^2 &= \langle M_\pm\varphi | M_\pm\varphi\rangle \\
&= \lim_{t\to\mp\infty} \left\langle e^{\frac{i}{\hbar}Ht}e^{-\frac{i}{\hbar}H_0 t}\varphi \,\middle|\, e^{\frac{i}{\hbar}Ht}e^{-\frac{i}{\hbar}H_0 t}\varphi \right\rangle \\
&= \lim_{t\to\mp\infty} \left\langle e^{-\frac{i}{\hbar}H_0 t}\varphi \middle| e^{-\frac{i}{\hbar}Ht}e^{\frac{i}{\hbar}Ht} \,\middle|\, e^{-\frac{i}{\hbar}H_0 t}\varphi \right\rangle \\
&= \lim_{t\to\mp\infty} \left\langle \varphi \middle| e^{\frac{i}{\hbar}H_0 t}e^{-\frac{i}{\hbar}H_0 t} \middle| \varphi \right\rangle \\
&= \langle\varphi|\varphi\rangle = \|\varphi\|^2 \,.
\end{aligned}$$

- Since the projection operator is Hermitian but not unitary ($P_S^+ P_S \neq \mathbb{1}$), it holds for the *other* Møller operator:

$$\left\| \widehat{M}_\pm \varphi \right\| = \| P_S \varphi \| \quad \forall\, |\varphi\rangle \in \mathcal{H} \,. \tag{9.154}$$

Also this is easily understood:

$$\begin{aligned} \left\| \widehat{M}_\pm \varphi \right\|^2 &= \langle \widehat{M}_\pm \varphi | \widehat{M}_\pm \varphi \rangle \\ &= \lim_{t \to \mp\infty} \left\langle e^{\frac{i}{\hbar} H_0 t} e^{-\frac{i}{\hbar} H t} P_S \varphi \,\middle|\, e^{\frac{i}{\hbar} H_0 t} e^{-\frac{i}{\hbar} H t} P_S \varphi \right\rangle \\ &= \lim_{t \to \mp\infty} \langle P_S \varphi \,|P_S \varphi\rangle \\ &= \| P_S \varphi \|^2 \end{aligned}$$

- In the next step we prove the following connection between the two Møller operators:

$$M_\pm^+ = \widehat{M}_\pm \,. \tag{9.155}$$

Let $|\varphi_1\rangle$ and $|\varphi_2\rangle$ be two arbitrary states of $\mathcal{H}$. With them we get:

$$\begin{aligned} \left\langle \varphi_1 \middle| \widehat{M}_\pm \middle| \varphi_2 \right\rangle &= \lim_{t \to \mp\infty} \left\langle \varphi_1 \left| e^{\frac{i}{\hbar} H_0 t} e^{-\frac{i}{\hbar} H t} \, P_S \right| \varphi_2 \right\rangle \\ &= \lim_{t \to \mp\infty} \left\langle P_S e^{\frac{i}{\hbar} H t} e^{-\frac{i}{\hbar} H_0 t} \, \varphi_1 \right| \varphi_2 \Big\rangle \\ &= \Big\langle P_S \underbrace{M_\pm \varphi_1}_{\in \mathcal{H}_S} \Big| \varphi_2 \Big\rangle \\ &= \left\langle M_\pm \varphi_1 \middle| \varphi_2 \right\rangle \\ &= \left\langle \varphi_1 \middle| M_\pm^+ \middle| \varphi_2 \right\rangle . \end{aligned}$$

That proves the assertion (9.155).

- The relation

$$M_\pm^+ \, M_\pm = \mathbb{1} \tag{9.156}$$

represents a further important property, which can be derived as follows: For an arbitrary state $|\varphi\rangle$ in $\mathcal{H}$ it holds:

$$\begin{aligned} \left\| \left(M_\pm^+ \, M_\pm - \mathbb{1} \right) \varphi \right\|^2 &= \left\langle \left(M_\pm^+ \, M_\pm - \mathbb{1} \right) \varphi \,\middle|\, \left(M_\pm^+ \, M_\pm - \mathbb{1} \right) \varphi \right\rangle \\ &= \left\langle M_\pm^+ \, M_\pm \varphi \,\middle|\, M_\pm^+ \, M_\pm \varphi \right\rangle + \langle \varphi | \varphi \rangle \\ &\quad - \left\langle \varphi \,\middle|\, M_\pm^+ \, M_\pm \varphi \right\rangle - \left\langle M_\pm^+ \, M_\pm \varphi \middle|\, \varphi \right\rangle \end{aligned}$$

$$
\begin{aligned}
&= \left\| M_\pm^+ \, M_\pm \varphi \right\|^2 + \|\varphi\|^2 - 2 \left\langle M_\pm \varphi \,\middle|\, M_\pm \varphi \right\rangle \\
&= \left\| M_\pm^+ \, M_\pm \varphi \right\|^2 + \|\varphi\|^2 - 2 \left\| M_\pm \varphi \right\|^2 \\
\|M_\pm \varphi\|^2 &\overset{(9.153)}{=} \|\varphi\|^2 \\
\left\| M_\pm^+ \underbrace{M_\pm \varphi}_{=|\psi\rangle \in \mathcal{H}_S} \right\|^2 &= \left\| M_\pm^+ \psi \right\|^2 \overset{(9.155)}{=} \left\| \widehat{M}_\pm \psi \right\|^2 \overset{(9.154)}{=} \|P_S \psi\|^2 \\
&= \|\psi\|^2 = \|M_\pm \varphi\|^2 \overset{(9.153)}{=} \|\varphi\|^2 \\
\curvearrowright \quad \left\| \left(M_\pm^+ \, M_\pm - \mathbb{1} \right) \varphi \right\|^2 &= 0 \, .
\end{aligned}
$$

Since $|\varphi\rangle$ is an arbitrary state of $\mathcal{H}$, the last line proves (9.156).

- In the same manner one shows:

$$M_\pm \, M_\pm^+ = P_S \, . \tag{9.157}$$

We choose again an arbitrary element $|\varphi\rangle \in \mathcal{H}$:

$$
\begin{aligned}
\left\| \left(M_\pm \, M_\pm^+ - P_S \right) \varphi \right\|^2 &= \left\| M_\pm \, M_\pm^+ \varphi \right\|^2 + \|P_S \varphi\|^2 \\
&\quad - \left\langle M_\pm \, M_\pm^+ \varphi \,\middle|\, P_S \varphi \right\rangle - \left\langle P_S \varphi \,\middle|\, M_\pm \, M_\pm^+ \varphi \right\rangle \\
\left\| M_\pm \, M_\pm^+ \varphi \right\|^2 &= \left\langle M_\pm \, M_\pm^+ \varphi \,\middle|\, M_\pm \, M_\pm^+ \varphi \right\rangle \\
&= \left\langle M_\pm^+ \varphi \,\middle|\, M_\pm^+ M_\pm \, M_\pm^+ \varphi \right\rangle \\
&\overset{(9.156)}{=} \left\langle M_\pm^+ \varphi \,\middle|\, M_\pm^+ \varphi \right\rangle \overset{(9.155)}{=} \left\| \widehat{M}_\pm \varphi \right\|^2 \\
&\overset{(9.154)}{=} \|P_S \varphi\|^2 \\
\left\langle M_\pm \, M_\pm^+ \varphi \,\middle|\, P_S \varphi \right\rangle &= \left\langle M_\pm^+ \varphi \,\middle|\, M_\pm^+ P_S \varphi \right\rangle \\
&\overset{\substack{(9.155) \\ (9.152)}}{=} \left\langle \widehat{M}_\pm \varphi \,\middle|\, \widehat{M}_\pm \varphi \right\rangle = \left\| \widehat{M}_\pm \varphi \right\|^2 \\
&\overset{(9.154)}{=} \|P_S \varphi\|^2 \\
\left\langle P_S \varphi \,\middle|\, M_\pm \, M_\pm^+ \varphi \right\rangle &= \left\langle M_\pm \, M_\pm^+ \varphi \,\middle|\, P_S \varphi \right\rangle^* \\
&= \|P_S \varphi\|^2 \\
\curvearrowright \quad \left\| \left(M_\pm M_\pm^+ - P_S \right) \varphi \right\|^2 &= 0 \, .
\end{aligned}
$$

The property (9.157) is therewith verified.

- The up to now derived properties show that the Møller operators ascribe to each element from $\mathcal{H}$ one and only one element of $\mathcal{H}_S$, i.e., in (9.150) already the equality sign is correct:

$$M_\pm : \mathcal{H} = \mathcal{H}_S \, . \tag{9.158}$$

- We derive a further important relation by the following consideration:

$$\begin{aligned} e^{-\frac{i}{\hbar}Ht_0}\,M_\pm &= \lim_{t\to\mp\infty} e^{\frac{i}{\hbar}H(t-t_0)}e^{-\frac{i}{\hbar}H_0(t-t_0)}e^{-\frac{i}{\hbar}H_0t_0} \\ &= \lim_{t'\to\mp\infty} e^{\frac{i}{\hbar}Ht'}e^{-\frac{i}{\hbar}H_0t'}e^{-\frac{i}{\hbar}H_0t_0} \\ &= M_\pm\, e^{-\frac{i}{\hbar}H_0t_0}\,. \end{aligned}$$

Since t_0 can be chosen arbitrarily, this equation must be valid for each summand in the exponential function:

$$H^n\,M_\pm = M_\pm\,H_0^n\,;\quad n\in\mathbb{N}\,. \tag{9.159}$$

This is true especially for $n=1$:

$$H\,M_\pm = M_\pm\,H_0\,. \tag{9.160}$$

When one eventually goes over to the Hermitian conjugate, then (9.159) reads:

$$M_\pm^+\,H^n = H_0^n\,M_\pm^+\,;\quad n\in\mathbb{N}\,. \tag{9.161}$$

9.4.4 Scattering Operator

We will now try to establish, with the aid of the Møller operators, the connection to the time-independent scattering theory of Sect. 9.3. For this purpose, we bring, at first, the operators in a form convenient for the following. That succeeds by means of limiting-value representations, which we have got to know and have justified in connection with (9.99) and (9.122):

$$M_\pm = \lim_{\eta\to0^+}(\mp\eta)\int_0^{\mp\infty} dt\,e^{\pm\eta t}\,e^{\frac{i}{\hbar}Ht}\,e^{-\frac{i}{\hbar}H_0t} \tag{9.162}$$

$$\widehat{M_\pm} = M_\pm^+ = \lim_{\eta\to0^+}(\mp\eta)\int_0^{\mp\infty} dt\,e^{\pm\eta t}\,e^{\frac{i}{\hbar}H_0t}\,e^{-\frac{i}{\hbar}Ht}\,. \tag{9.163}$$

These expressions can further be rewritten. For that we consider the operator function

$$f(t) = e^{\frac{i}{\hbar}Ht}\,e^{-\frac{i}{\hbar}H_0t}\,;\quad f(t=0)=\mathbb{1}\,. \tag{9.164}$$

It obeys the differential equation

$$\frac{d}{dt}f(t) = \frac{i}{\hbar}\,e^{\frac{i}{\hbar}Ht}(H-H_0)e^{-\frac{i}{\hbar}H_0t} = \frac{i}{\hbar}e^{\frac{i}{\hbar}Ht}H_1e^{-\frac{i}{\hbar}H_0t}\,. \tag{9.165}$$

We exploit this for a new representation of the Møller operators. For (9.162) we get:

$$\begin{aligned} M_\pm &= \lim_{\eta\to 0^+} (\mp\eta) \int_0^{\mp\infty} dt\, e^{\pm\eta t}\, f(t) \\ &= -\lim_{\eta\to 0^+} \int_0^{\mp\infty} dt \left(\frac{d}{dt} e^{\pm\eta t}\right) f(t) \\ &= -\lim_{\eta\to 0^+} \left\{ \left(e^{\pm\eta t}\, f(t)\right)_0^{\mp\infty} - \int_0^{\mp\infty} dt\, e^{\pm\eta t}\, \frac{df}{dt} \right\} . \end{aligned}$$

It follows then with (9.164) and (9.165):

$$M_\pm = \mathbb{1} + \frac{i}{\hbar} \lim_{\eta\to 0^+} \int_0^{\mp\infty} dt\, e^{\pm\eta t}\, e^{\frac{i}{\hbar}Ht}\, H_1\, e^{-\frac{i}{\hbar}H_0 t} \tag{9.166}$$

$$\widehat{M_\pm} = M_\pm^+ = \mathbb{1} - \frac{i}{\hbar} \lim_{\eta\to 0^+} \int_0^{\mp\infty} dt\, e^{\pm\eta t}\, e^{\frac{i}{\hbar}H_0 t}\, H_1\, e^{-\frac{i}{\hbar}Ht} . \tag{9.167}$$

As elements of $\mathcal{H}$, the limiting states $|\varphi_\mp\rangle$ (9.142) can be expanded in eigenstates of H_0,

$$|\varphi\{\widehat{\varphi}(\boldsymbol{k})\}\rangle = \int d^3k\, \widehat{\varphi}(\boldsymbol{k}) \left|E_{\boldsymbol{k}}^{(0)}\right\rangle \tag{9.168}$$

$$H_0 \left|E_{\boldsymbol{k}}^{(0)}\right\rangle = E_{\boldsymbol{k}}^{(0)} \left|E_{\boldsymbol{k}}^{(0)}\right\rangle ; \quad \left\langle E_{\boldsymbol{k}}^{(0)} \middle| E_{\boldsymbol{k}'}^{(0)}\right\rangle = \delta(\boldsymbol{k}-\boldsymbol{k}') , \tag{9.169}$$

We therefore consider at first a special eigen-vector of the *free* part H_0 of the Hamilton operator and define to that vector *incoming* and *outgoing* states:

$$\left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle = M_\pm \left|E_{\boldsymbol{k}}^{(0)}\right\rangle . \tag{9.170}$$

It follows additionally, with (9.156):

$$\left|E_{\boldsymbol{k}}^{(0)}\right\rangle = M_\pm^+ \left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle . \tag{9.171}$$

One recognizes that these *new* states are normalized to δ-functions:

$$\begin{aligned} \left\langle E_{\boldsymbol{k}'}^{(\pm)} \middle| E_{\boldsymbol{k}}^{(\pm)}\right\rangle &= \left\langle E_{\boldsymbol{k}'}^{(0)} \middle| M_\pm^+ M_\pm \middle| E_{\boldsymbol{k}}^{(0)}\right\rangle \\ &\overset{(9.156)}{=} \left\langle E_{\boldsymbol{k}'}^{(0)} \middle| E_{\boldsymbol{k}}^{(0)}\right\rangle = \delta(\boldsymbol{k}-\boldsymbol{k}') . \end{aligned} \tag{9.172}$$

Moreover, they are eigen-states of the full Hamilton operator H with eigenenergies, which correspond to those of H_0:

$$\begin{aligned} H \left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle &= H\, M_\pm \left|E_{\boldsymbol{k}}^{(0)}\right\rangle \overset{(9.160)}{=} M_\pm\, H_0 \left|E_{\boldsymbol{k}}^{(0)}\right\rangle \\ &= E_{\boldsymbol{k}}^{(0)}\, M_\pm \left|E_{\boldsymbol{k}}^{(0)}\right\rangle = E_{\boldsymbol{k}}^{(0)} \left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle . \end{aligned} \tag{9.173}$$

The Eqs. (9.172) and (9.173) correspond exactly to (9.124) and (9.125). The special scattering states $\left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle$, introduced in (9.170), are thus just the state vectors, discussed in connection with (9.101) and (9.123) in Sect. 9.4.1.

For a general scattering state in $\mathcal{H}_S$ (Heisenberg picture) it now follows with (9.169)

$$\begin{aligned}\left|E^{(\pm)}\{\widehat{\varphi}(\boldsymbol{k})\}\right\rangle &= M_{\pm}\,|\varphi\{\widehat{\varphi}(\boldsymbol{k})\}\rangle \\ &= M_{\pm}\int d^3k\,\widehat{\varphi}(\boldsymbol{k})\,\left|E_{\boldsymbol{k}}^{(0)}\right\rangle \\ &= \int d^3k\,\widehat{\varphi}(\boldsymbol{k})\,\left(M_{\pm}\left|E_{\boldsymbol{k}}^{(0)}\right\rangle\right) \\ &= \int d^3k\,\widehat{\varphi}(\boldsymbol{k})\,\left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle \end{aligned} \tag{9.174}$$

with a time-dependence,

$$e^{-\frac{i}{\hbar}Ht}\,\left|E^{(\pm)}\{\widehat{\varphi}(\boldsymbol{k}))\}\right\rangle = \int d^3k\,\widehat{\varphi}(\boldsymbol{k})\,e^{-\frac{i}{\hbar}E_{\mathbf{k}}^{(0)}t}\,\left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle\ ,$$

which agrees with that in (9.104). Since the wave-number distribution (amplitude function) $\widehat{\varphi}(\mathbf{k})$ can be assumed as given, the determination of the $\left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle$ obviously solves the full scattering problem.[2] To show this, we now insert (9.166) into (9.170):

$$\left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle = \left|E_{\boldsymbol{k}}^{(0)}\right\rangle + \frac{i}{\hbar}\lim_{\eta\to 0^+}\int_0^{\mp\infty} dt\,\exp\left(\frac{i}{\hbar}\left(H - E_{\boldsymbol{k}}^{(0)} \mp i\eta\hbar\right)t\right)H_1\left|E_{\boldsymbol{k}}^{(0)}\right\rangle\ .$$

The integration can be easily performed, where the integrated part vanishes at the upper limit because of $\eta > 0$:

$$\begin{aligned}\left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle &= \left|E_{\boldsymbol{k}}^{(0)}\right\rangle - \frac{1}{H - E_{\boldsymbol{k}}^{(0)} \mp i0^+}\,H_1\left|E_{\boldsymbol{k}}^{(0)}\right\rangle \\ &= \left|E_{\boldsymbol{k}}^{(0)}\right\rangle + \frac{1}{E_{\boldsymbol{k}}^{(0)} - H \pm i0^+}\,H_1\left|E_{\boldsymbol{k}}^{(0)}\right\rangle\ . \end{aligned} \tag{9.175}$$

We recognize on the right-hand side the Green operator to $H\,G_{\mathbf{k}}^{(\pm)}$ from (9.127):

$$\left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle = \left|E_{\boldsymbol{k}}^{(0)}\right\rangle + G_{\boldsymbol{k}}^{(\pm)}\,H_1\,\left|E_{\boldsymbol{k}}^{(0)}\right\rangle\ . \tag{9.176}$$

That is exactly the Lippmann-Schwinger equation in the form (9.128).

[2] This justifies by the way the treatment of the scattering problem in Sect. 9.4.1.

In order to confirm also the other version (9.126) of the Lippmann-Schwinger equation, we now insert (9.167) into (9.171):

$$\begin{aligned}
\left|E_{\boldsymbol{k}}^{(0)}\right\rangle &= \left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle - \frac{i}{\hbar}\lim_{\eta\to 0^+}\int_0^{\mp\infty} dt\, e^{\pm\eta t}\, e^{\frac{i}{\hbar}H_0 t}\, H_1\, e^{-\frac{i}{\hbar}Ht}\left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle \\
&\overset{(9.173)}{=} \left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle - \frac{i}{\hbar}\lim_{\eta\to 0^+}\int_0^{\mp\infty} dt\, e^{\frac{i}{\hbar}\left(H_0 - E_{\boldsymbol{k}}^{(0)} \mp i\eta\hbar\right)t}\, H_1\left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle \\
&= \left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle + \frac{1}{H_0 - E_{\boldsymbol{k}}^{(0)} \mp i0^+}\, H_1\left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle \\
&= \left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle - R_{\boldsymbol{k}}^{(\pm)}\, H_1\left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle .
\end{aligned}$$

In the last step we have inserted the Green operator to H_0 from (9.106). We have indeed reproduced therewith the Lippmann-Schwinger equation in the form (9.126):

$$\left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle = \left|E_{\boldsymbol{k}}^{(0)}\right\rangle + R_{\boldsymbol{k}}^{(\pm)}\, H_1\left|E_{\boldsymbol{k}}^{(\pm)}\right\rangle . \tag{9.177}$$

Using the position representation we had found in Sect. 9.4.1 a special realization of the Lippmann-Schwinger equation (9.111), and we could identify it with Born's series (9.90), which we derived by another method. Obviously we have succeeded in finding via the representation-independent Lippmann-Schwinger equation the link-up to the time-independent treatment of the scattering problem in the position representation (Sect. 9.3).

We will finally construct the connection between the Møller operators and the fundamental scattering matrix (9.121). We want to show that the definition

$$S \equiv M_-^+\, M_+ \tag{9.178}$$

as *scattering operator* or *S-operator* is compatible with the expressions (9.129) and (9.121) for the elements of the scattering matrix.

$$\begin{aligned}
\left\langle E_m^{(0)}\right| S \left|E_n^{(0)}\right\rangle &= \left\langle E_m^{(0)}\right| M_-^+\, M_+ \left|E_n^{(0)}\right\rangle \\
&\overset{(9.170)}{=} \left\langle E_m^{(-)}\right| \left|E_n^{(+)}\right\rangle \\
&\overset{(9.129)}{\equiv} S_{mn} .
\end{aligned} \tag{9.179}$$

If one uses, on the other hand, the expressions (9.150), (9.155), and (9.151) for

the Møller operators, it also follows

$$\begin{aligned}
\left\langle E_m^{(0)} \middle| S \middle| E_n^{(0)} \right\rangle &= \left\langle E_m^{(0)} \middle| M_-^+ M_+ \middle| E_n^{(0)} \right\rangle \\
&= \lim_{t\to+\infty} \left\langle E_m^{(0)} \middle| e^{\frac{i}{\hbar}H_0 t}\, e^{-\frac{i}{\hbar}Ht} \underbrace{P_S\, M_+}_{\equiv M_+} \middle| E_n^{(0)} \right\rangle \\
&= \lim_{t\to+\infty} \lim_{t'\to-\infty} \left\langle E_m^{(0)} \middle| e^{\frac{i}{\hbar}H_0 t}\, e^{-\frac{i}{\hbar}Ht}\, e^{\frac{i}{\hbar}Ht'}\, e^{-\frac{i}{\hbar}H_0 t'} \middle| E_n^{(0)} \right\rangle \\
&\overset{(9.116)}{=} \lim_{t\to+\infty} \lim_{t'\to-\infty} \left\langle E_m^{(0)} \middle| U_D(t,t') \middle| E_n^{(0)} \right\rangle \\
&= \left\langle E_m^{(0)} \middle| U_D(+\infty,-\infty) \middle| E_n^{(0)} \right\rangle \\
&\overset{(9.121)}{\equiv} S_{mn}\ . \qquad (9.180)
\end{aligned}$$

The ansatz (9.178) for the scattering operator appears reasonable. In the basis of the eigen-states of the *free* Hamilton operator H_0 the matrix elements of the scattering operator agree with the previously introduced elements of the scattering matrix ((9.121), (9.129)). They correspond thus to the asymptotic transition probabilities between two *free* energy-eigen states.

The following two properties of the scattering operator (9.178) are still important. At first, the operator turns out to be unitary in $\mathcal{H}$:

$$S\,S^+ = S^+\,S = \mathbb{1}\ . \qquad (9.181)$$

That can easily be proven with our earlier considerations:

$$\begin{aligned}
S\,S^+ &= M_-^+ M_+ M_+^+ M_- \overset{(9.157)}{=} M_-^+ P_S M_- \overset{(9.150)}{=} M_-^+ M_- \overset{(9.156)}{=} \mathbb{1} \\
S^+\,S &= M_+^+ M_- M_-^+ M_+ \overset{(9.157)}{=} M_+^+ P_S M_+ \overset{(9.150)}{=} M_+^+ M_+ \overset{(9.156)}{=} \mathbb{1}\ .
\end{aligned}$$

In addition one also realizes that the scattering operator commutes with the *free* Hamilton operator:

$$[S,\, H_0]_- = 0\ . \qquad (9.182)$$

We perform the explicit proof as Exercise 9.4.3. The matrix elements (9.179) of the scattering operator and the scattering matrix, respectively, can thus be different from zero only if $E_n^{(0)} = E_m^{(0)}$:

$$\begin{aligned}
[S,\, H_0]_- = 0 \quad &\curvearrowright \quad \left\langle E_n^{(0)} \middle| [S,\, H_0]_- \middle| E_m^{(0)} \right\rangle = 0 \\
&\curvearrowright \quad \left(E_m^{(0)} - E_n^{(0)}\right) \left\langle E_n^{(0)} \middle| S \middle| E_m^{(0)} \right\rangle = 0 \\
\left\langle E_n^{(0)} \middle| S \middle| E_m^{(0)} \right\rangle \neq 0 \quad &\curvearrowright \quad E_m^{(0)} = E_n^{(0)}\ .
\end{aligned}$$

Physically that means of course nothing else but the initially presumed **elastic** scattering.[3]

[3] Note hereto also the remarks subsequent to (9.134).

The further considerations up to the *basic formula of scattering theory* (9.130) are identical with those in Sect. 9.4.2. There is therefore no need to repeat them here once more.

9.4.5 Exercises

Exercise 9.4.1
Show that the Green operators $R_n^{(\pm)}$ (9.106) and $G_n^{(\pm)}$ (9.127) fulfill the *Dyson equation*

$$G_n^{(\pm)} = R_n^{(\pm)} + R_n^{(\pm)}\, H_1\, G_n^{(\pm)}$$

Exercise 9.4.2
Show that (9.128) represents a formal solution of the Lippmann-Schwinger equation (9.126). For that use the Dyson equation from Exercise 9.4.1.

Exercise 9.4.3
Show that the scattering operator S commutes with the *interaction-free* Hamilton operator H_0:

$$[S,\, H_0]_- = 0\ .$$

Exercise 9.4.4
Differently from (9.178) the scattering operator is sometimes also defined as

$$\widehat{S} = M_+\, M_-^+\ .$$

Confirm the following properties of this operator:

1. $$\widehat{S}\widehat{S}^+ = \widehat{S}^+\widehat{S} = P_S \quad (= \mathbb{1} \text{ in } \mathcal{H}_S)$$

2. $$[\widehat{S},\, H]_- = 0$$

3. $$\widehat{S}\left|E_n^{(-)}\right\rangle = \left|E_n^{(+)}\right\rangle\ .$$

9.5 Self-Examination Questions

To Section 9.1

1. Which information can be derived from scattering processes?
2. For the scattering process the *incoming* particle is described, before the actual scattering act, as a wave packet. Which demands have to be placed to the longitudinal and the transversal extensions of the wave packet?
3. Under which preconditions can the scattering center be represented by a potential?

4. Which boundary conditions must be fulfilled with respect to the position of the detector, which counts the scattered particles?
5. Which asymptotic shape should the scattered wave possess when scattered by a central potential $V(r)$?
6. How is the scattering amplitude $f(\vartheta)$ defined?
7. How is $f(\vartheta)$ connected to the current density $\mathbf{j}_\mathrm{s}$ of the scattered wave?
8. What is the general definition of the cross-section ?
9. What is the relation between the differential cross-section and the scattering amplitude?

To Section 9.2

1. Why is an expansion in spherical harmonics recommendable for the wave function of the scattering problem?
2. How does the influence of the scattering potential on the wave function of the scattering problem manifest itself asymptotically ($k\,r \gg 1$)?
3. What does one understand by the *scattering phase of the lth partial wave*? By which quantities are they essentially determined?
4. What do we understand by the *optical theorem*? How can we physically interpret it?
5. How can we estimate, which partial waves play a role for the scattering of a particle of energy E at a potential of the effective range R_0?
6. What is meant by s- or p-scattering?
7. Under which conditions is *pure s-scattering* to be expected?
8. For the scattering at the *hard sphere*, how do the scattering phases δ_l depend on the radius of the sphere R_0, and on the particle energy E?
9. What is the relationship in a scattering process at the *hard sphere* between the cross-section σ and the geometric cross-sectional area of the sphere ($= \pi\,R_0^2$) in the case of large de Broglie wavelength ($k\,R_0 \ll 1$) of the incident particle?
10. How can it be explained that for the scattering at the *hard sphere* in the limit $k\,R_0 \gg 1$ the cross-section σ is just twice the geometric cross-sectional area of the sphere?
11. How can we explain the relative similarity of the scattering processes of slow particles at **all** potentials of finite range?
12. What does one understand by *potential scattering*?

13. When does *resonance scattering* appear for the scattering at the potential well?

14. What happens with the scattering phase δ_l in the resonance?

15. How does the *partial cross-section* σ_l qualitatively look like in the neighborhood of the resonance?

16. For low particle energies, how are the phase δ_0 and the partial cross-section σ_0 for s-scattering at the potential well connected with the scattering length a_s?

17. What can be said about the scattering phase δ_0 for $E \to 0$ and $E \to \infty$?

18. Which arbitrariness (indeterminacy) remains when fixing scattering phases?

19. The indeterminacy of δ_0 is removed in such a way that $\lim_{k\to 0}\, \delta_0(k) = \hat{n}\,\pi,\ \lim_{k\to\infty}\, \delta_0(k) = 0$. Which physical meaning does the integer $\hat{n}$ have?

20. How does σ_0 for $\hat{n} = 3$ qualitatively look like as function of k?

21. Which preconditions and assumptions enter Born's approximation for the scattering phases?

22. What is the region of validity of Born's approximation for scattering phases?

To Section 9.3

1. Which differential equation is fulfilled by the *Green's function* of the scattering problem?

2. Which structure does the exact integral equation for the scattering amplitude $f(\vartheta, \varphi)$ have? How does the interaction potential $V(\mathbf{r})$ enter the equation?

3. Which condition must be fulfilled by $V(\mathbf{r})$, in order that the scattering amplitude depends only on the angle ϑ?

4. What does one understand by *Born's series*?

5. How is the *nth Born approximation* defined?

6. In which way in first Born approximation, the scattering amplitude is connected to the wave number-dependent Fourier transform of the interaction potential?

7. Does the first Born approximation fulfill the *optical theorem*?

8. What can be said about the region of validity of the first Born approximation?

To Section 9.4

1. How is the Green operator $R_n^{(\pm)}$ defined?
2. Formulate and interpret the Lippmann-Schwinger equation.
3. What is the relation between the Lippmann-Schwinger equation and the Born's series?
4. How are Green operator and Green's function related?
5. How is the scattering matrix defined?
6. Which physical meaning does the (m, n)-element of the scattering matrix have?
7. How is the Green operator $G_n^{(\pm)}$ defined?
8. What is the difference between the Green operators $R_n^{(\pm)}$ and $G_n^{(\pm)}$?
9. What is the relationship of the *scattering states* $|E_n^{(\pm)}\rangle$ with the scattering matrix?
10. How do the Lippmann-Schwinger equations differ for $|E_n^{(+)}\rangle$ and $|E_n^{(-)}\rangle$?
11. What is the adjoint operator of $G_n^{(+)}$ and $R_n^{(+)}$, respectively?
12. What can be considered as the *basic formula* of the abstract scattering theory?
13. How is the T-matrix defined?
14. How are the T-matrix and the scattering amplitude related?

Appendix A
Solutions of the Exercises

Section 5.1.7

Solution 5.1.1

For the unit vectors $\mathbf{e}_i$ of the space-fixed system of coordinates $\sum$, we have in the co-rotated system $\overline{\sum}$:

$$\mathbf{e}_i = \sum_j \overline{x}_j^{(i)} \overline{\mathbf{e}}_j \quad \longrightarrow \quad \overline{x}_j^{(i)} = (\overline{\mathbf{e}}_j \cdot \mathbf{e}_i) \overset{(5.27)}{=} D_{ij} \ .$$

It follows:

$$\mathbf{e}_i = \sum_j D_{ij}\, \overline{\mathbf{e}}_j \ .$$

Orthonormalization of the basis vectors:

$$\begin{aligned} \delta_{ij} = \mathbf{e}_i \cdot \mathbf{e}_j &= \sum_{km} D_{ik}\, D_{jm}\, (\overline{\mathbf{e}}_k \cdot \overline{\mathbf{e}}_m) = \sum_{km} D_{ik}\, D_{jm}\, \delta_{km} \\ &= \sum_k D_{ik}\, D_{jk} \end{aligned}$$

Solution 5.1.2

1. Rows and columns of the matrix are obviously orthonormalized. We check the determinant:

$$\det D = \begin{vmatrix} -\frac{1}{2}\sqrt{2} & 0 & -\frac{1}{2}\sqrt{2} \\ 0 & 1 & 0 \\ \frac{1}{2}\sqrt{2} & 0 & -\frac{1}{2}\sqrt{2} \end{vmatrix} = \frac{2}{4} + 0 + 0 + \frac{2}{4} - 0 - 0 = 1 \ .$$

Thus, it is a rotation

$$D_{ij} = (\mathbf{e}_i \cdot \hat{\mathbf{e}}_j) = \cos\varphi_{ij} \ .$$

W. Nolting, *Theoretical Physics 7*, DOI 10.1007/978-3-319-63324-4

φ_{ij}: angle between ith axis (before) and jth axis (after). That means here:

$$\cos\varphi_{11} = \cos\varphi_{33} = -\frac{1}{2}\sqrt{2} \quad \curvearrowright \quad \varphi_{11} = \varphi_{33} = 135^\circ \,.$$

It is therefore a rotation around the y-axis by 135°.

2.

$$\hat{\mathbf{a}} = D\begin{pmatrix} 0 \\ -2 \\ 1 \end{pmatrix} = \begin{pmatrix} -\frac{1}{2}\sqrt{2} & 0 & -\frac{1}{2}\sqrt{2} \\ 0 & 1 & 0 \\ \frac{1}{2}\sqrt{2} & 0 & -\frac{1}{2}\sqrt{2} \end{pmatrix}\begin{pmatrix} 0 \\ -2 \\ 1 \end{pmatrix} = \begin{pmatrix} -\frac{1}{2}\sqrt{2} \\ -2 \\ -\frac{1}{2}\sqrt{2} \end{pmatrix}$$

$$\hat{\mathbf{b}} = D\begin{pmatrix} 3 \\ 5 \\ -4 \end{pmatrix} = \begin{pmatrix} -\frac{1}{2}\sqrt{2} & 0 & -\frac{1}{2}\sqrt{2} \\ 0 & 1 & 0 \\ \frac{1}{2}\sqrt{2} & 0 & -\frac{1}{2}\sqrt{2} \end{pmatrix}\begin{pmatrix} 3 \\ 5 \\ -4 \end{pmatrix} = \begin{pmatrix} \frac{1}{2}\sqrt{2} \\ 5 \\ \frac{7}{2}\sqrt{2} \end{pmatrix}$$

Scalar product:

- before:

$$\mathbf{a}\cdot\mathbf{b} = \begin{pmatrix} 0 & -2 & 1 \end{pmatrix}\begin{pmatrix} 3 \\ 5 \\ -4 \end{pmatrix} = -14$$

- after:

$$\hat{\mathbf{a}}\cdot\hat{\mathbf{b}} = \begin{pmatrix} -\frac{1}{2}\sqrt{2} & -2 & -\frac{1}{2}\sqrt{2} \end{pmatrix}\begin{pmatrix} \frac{1}{2}\sqrt{2} \\ 5 \\ \frac{7}{2}\sqrt{2} \end{pmatrix} = -14$$

Therefore, the scalar product remains unchanged after the rotation.

3. Notations as in (5.26):

$$\hat{x}_i = \sum_{j=1}^{3} D_{ij}\, x_j$$

'length':

$$\begin{aligned} \sum_{1=1}^{3} \hat{x}_i^2 &= \sum_{ijk} D_{ij} D_{ik}\, x_j x_k \\ &= \sum_{jk} \underbrace{\left(\sum_i D_{ij} D_{ik}\right)}_{\delta_{jk}} x_j x_k = \sum_j x_j^2 \end{aligned}$$

Here we have exploited the orthonormality of the columns of a rotation matrix. The *'lengths'* of vectors thus remain uninfluenced by the rotation!

Solution 5.1.3

For each component (5.12) is valid; ε_{imn} is real:

$$\begin{aligned} L_i^+ &= \sum_{m,n} \varepsilon_{imn}\,(x_m\,p_n)^+ = \sum_{m,n} \varepsilon_{imn}\,p_n^+\,x_m^+ \\ &= \sum_{m,n} \varepsilon_{imn}\,p_n\,x_m = \sum_{m,n} \varepsilon_{imn}\,x_m\,p_n = L_i\ . \end{aligned}$$

The last step is allowed, because $m \neq n$ can be assumed. For $m = n$ we have $\varepsilon_{imn} = 0$!

Solution 5.1.4

1.

$$\begin{aligned} [L_x, L_y]_- &= [y\,p_z - z\,p_y, z\,p_x - x\,p_z]_- = [y\,p_z, z\,p_x]_- + [z\,p_y, x\,p_z]_- \\ &= y[p_z, z]_- p_x + x[z, p_z]_- p_y = -i\hbar y\,p_x + i\hbar x p_y = i\hbar(x p_y - y p_x) \\ &= i\,\hbar\,L_z\ , \end{aligned}$$

$$\begin{aligned} [L_y, L_z]_- &= [z\,p_x - x\,p_z, x\,p_y - y\,p_x]_- = [z\,p_x, x\,p_y]_- + [x\,p_z, y\,p_x]_- \\ &= z[p_x, x]_-\,p_y + y[x, p_x]_-\,p_z = -i\,\hbar\,z\,p_y + i\,\hbar\,y\,p_z \\ &= i\,\hbar(y\,p_z - z\,p_y) = i\,\hbar\,L_x\ , \end{aligned}$$

$$\begin{aligned} [L_z, L_x]_- &= [x\,p_y - y\,p_x, y\,p_z - z\,p_y]_- = [x\,p_y, y\,p_z]_- + [y\,p_x, z\,p_y]_- \\ &= x[p_y, y]_-\,p_z + z[y, p_y]_-\,p_x = -i\,\hbar\,x\,p_z + i\,\hbar\,z\,p_x \\ &= i\,\hbar(z\,p_x - x\,p_z) = i\,\hbar\,L_y\ . \end{aligned}$$

2.

$$\begin{aligned} [\mathbf{L}^2, L_x]_- &= [L_x^2, L_x]_- + [L_y^2, L_x]_- + [L_z^2, L_x]_- \\ &= 0 + L_y\,[L_y, L_x]_- + [L_y, L_x]\,L_y + L_z\,[L_z, L_x]_- + [L_z, L_x]\,L_z \\ &= -i\,\hbar\,L_y\,L_z - i\,\hbar\,L_z\,L_y + i\,\hbar\,L_z\,L_y + i\,\hbar\,L_y\,L_z = 0\ . \end{aligned}$$

Analogously, since symmetric in x, y, z:

$$[\mathbf{L}^2, L_y]_- = [\mathbf{L}^2, L_z]_- = 0\ .$$

3.

$$\begin{aligned} [L_x, \mathbf{r}^2]_- &= [y\,p_z - z\,p_y, x^2 + y^2 + z^2]_- \\ &= [y\,p_z, z^2]_- - [z\,p_y, y^2]_- = y[p_z, z^2]_- - z[p_y, y^2]_- \\ &= y\,z[p_z, z]_- + y[p_z, z]_- z - z\,y[p_y, y]_- - z[p_y, y]_- y \\ &= -i\,\hbar\,y\,z - i\,\hbar\,y\,z + i\,\hbar\,z\,y + i\,\hbar\,z y = 0\ . \end{aligned}$$

4.

$$\begin{aligned}[L_y, \mathbf{p}^2]_- &= [z\,p_x - x\,p_z, p_x^2 + p_y^2 + p_z^2]_- = [z\,p_x, p_z^2]_- - [x\,p_z, p_x^2]_- \\ &= [z, p_z^2]_-\,p_x - [x, p_x^2]_-\,p_z = p_z[z, p_z]_-\,p_x + [z, p_z]\,p_z p_x - \\ &\quad -p_x[x, p_x]_-\,p_z - [x, p_x]_-\,p_x p_z \\ &= i\,\hbar\,p_z\,p_x + i\,\hbar\,p_z\,p_x - i\,\hbar\,p_x\,p_z - i\,\hbar\,p_x\,p_z = 0\,.\end{aligned}$$

5.

$$[L_z, x]_- = [x\,p_y - y\,p_x, x]_- = -[y\,p_x, x]_- = -y[p_x, x] = i\,\hbar\,y$$

$$\begin{aligned}[L_z, p_x]_- &= [x\,p_y - y\,p_x, p_x]_- \\ &= [x\,p_y, p_x]_- = [x, p_x]_- p_y = i\,\hbar\,p_y\,.\end{aligned}$$

6.

$$\begin{aligned}[L_i, x_j]_- &\overset{(5.12)}{=} \sum_{mn} \varepsilon_{imn}[x_m p_n, x_j]_- \\ &= \sum_{mn} \varepsilon_{imn} x_m [p_n, x_j]_- \\ &= -i\hbar \sum_{mn} \varepsilon_{imn} x_m\,\delta_{nj} \\ &= -i\hbar \sum_{m} \varepsilon_{imj}\,x_m \\ &= i\hbar \sum_{m} \varepsilon_{ijm}\,x_m \quad (5.19)\end{aligned}$$

$$\begin{aligned}[L_i, p_j]_- &\overset{(5.12)}{=} \sum_{mn} \varepsilon_{imn}[x_m p_n, p_j]_- \\ &= \sum_{mn} \varepsilon_{imn}[x_m, p_j]_- p_n \\ &= i\hbar \sum_{mn} \varepsilon_{imn} p_n\,\delta_{mj} \\ &= i\hbar \sum_{n} \varepsilon_{ijn}\,p_n \quad (5.20)\,.\end{aligned}$$

Solution 5.1.5

$$[L_i, L_j]_- = i\,\hbar\,L_k\,; \quad (i, j, k) \text{ cyclic from } (1, 2, 3)\,.$$

Let A be an operator with

$$[L_i, A]_- = [L_j, A]_- = 0\,.$$

Then it follows:

$$\begin{aligned}[L_k, A]_- &= \frac{1}{i\,\hbar}\,[[L_i, L_j]_-, A]_- = \frac{1}{i\,\hbar}\,\{[L_i\,L_j, A]_- - [L_j\,L_i, A]\} \\ &= \frac{1}{i\,\hbar}\,\{L_i[L_j, A]_- + [L_i, A]_- L_j - L_j[L_i, A]_- - [L_j, A]L_i\} \\ &= \frac{1}{i\,\hbar}\{0 + 0 - 0 - 0\} = 0\end{aligned}$$

Solution 5.1.6

$$\begin{aligned}L_+\,L_- &= (L_x + i\,L_y)\,(L_x - i\,L_y) = L_x^2 + L_y^2 + i\,[L_y, L_x]_- = \mathbf{L}^2 - L_z^2 + \hbar\,L_z, \\ L_-\,L_+ &= (L_x - i\,L_y)\,(L_x + i\,L_y) = L_x^2 + L_y^2 + i\,[L_x, L_y]_- = \mathbf{L}^2 - L_z^2 - \hbar\,L_z.\end{aligned}$$

Solution 5.1.7

1. It follows directly from (5.19):

$$[L_z, z]_- = 0\,,$$

$$\begin{aligned}[L_z, x \pm i\,y]_- &= [L_z, x]_- \pm i[L_z, y]_- = i\,\hbar\,y \pm i(-i\,\hbar\,x) \\ &= i\,\hbar\,y \pm \hbar\,x = \pm\hbar(x \pm i\,y)\,.\end{aligned}$$

2. We use once more (5.19):

$$\begin{aligned}[\mathbf{L}^2, x]_- &= [L_y^2, x]_- + [L_z^2, x]_- \\ &= L_y\,[L_y, x]_- + [L_y, x]_-\,L_y + L_z\,[L_z, x]_- + [L_z, x]_-\,L_z \\ &= i\,\hbar\{-L_y\,z - z\,L_y + L_z\,y + y\,L_z\}\,.\end{aligned}$$

In the same manner the other components are calculated:

$$[\mathbf{L}^2, y]_- = i\,\hbar\{L_x\,z + z\,L_x - L_z\,x - x\,L_z\}\,,$$

$$[\mathbf{L}^2, z]_- = i\,\hbar\{L_y\,x + x\,L_y - L_x\,y - y\,L_x\}\,.$$

Therewith we derive now the given commutator relation for the x-component:

$$\begin{aligned}\big[\mathbf{L}^2, [\mathbf{L}^2, x]_-\big]_- &= i\hbar[\mathbf{L}^2, -L_y z - zL_y + L_z y + yL_z]_- \\ &= i\hbar\Big\{ - L_y[\mathbf{L}^2, z]_- - [\mathbf{L}^2, z]_- L_y + L_z[\mathbf{L}^2, y]_- + [\mathbf{L}^2, y]_- L_z\Big\} \\ &= -\hbar^2\Big\{ - L_y(L_y x + xL_y - L_x y - yL_x) \\ &\quad -(L_y x + xL_y - L_x y - yL_x)L_y \\ &\quad +L_z(L_x z + zL_x - L_z x - xL_z) \\ &\quad +(L_x z + zL_x - L_z x - xL_z)L_z\Big\}\end{aligned}$$

$$
\begin{aligned}
&= -\hbar^2\Big\{ -2L_y^2 x - L_y\,[x,L_y]_- + 2L_y y L_x + [L_y,L_x]_-\, y \\
&\quad -2xL_y^2 - [L_y,x]_- L_y + 2L_x y L_y + y\,[L_x,L_y]_- \\
&\quad +2L_z z L_x + L_z\,[L_x,z]_- - 2L_z^2 x - L_z\,[x,L_z]_- \\
&\quad +2L_x z L_z + [z,L_x]_- L_z - 2xL_z^2 - [L_z,x]_- L_z\Big\} \\
&= 2\hbar^2\Big\{(L_y^2+L_z^2)x + x(L_y^2+L_x^2)\Big\} \\
&\quad -2\hbar^2\Big\{(L_y y + L_z z)L_x + L_x(L_y y + L_z z)\Big\} \\
&\quad -\hbar^2(+i\hbar)\Big\{ -L_y z - L_z y + z L_y + y L_z \\
&\quad -L_z y + L_z y + y L_z - y L_z\Big\} \\
&= 2\hbar^2\Big\{\mathbf{L}^2\, x - L_x^2\, x + x\,\mathbf{L}^2 - x\,L_x^2\Big\} \\
&\quad -2\hbar^2\Big\{(\mathbf{L}\cdot\mathbf{r})\,L_x - L_x x L_x + L_x\,(\mathbf{L}\cdot\mathbf{r}) - L_x^2 x\Big\} \\
&\quad +i\hbar^3\Big\{[L_y,z]_- - [y,L_z]_-\Big\}\,.
\end{aligned}
$$

Now it is according to (5.19)

$$L_x x = x L_x \quad \text{and} \quad [L_y,z]_- = [y,L_z]_-\ .$$

Because of $\mathbf{r}\cdot\mathbf{L} = \mathbf{L}\cdot\mathbf{r} = 0$ it follows then the assertion:

$$\big[\mathbf{L}^2,[\mathbf{L}^2,x]_-\big]_- = 2\hbar^2\Big\{\mathbf{L}^2\, x + x\,\mathbf{L}^2\Big\}\,.$$

Analogously one proves the commutator relations for the two other components.

Solution 5.1.8

1. We take $m = j - x$ with $x = 0,1,2,\ldots,2j$. Then it remains to be proved:

$$(J_-)^x|j\ j\rangle = \hbar^x\sqrt{\frac{(2j)!x!}{(2j-x)!}}\,|j\ j-x\rangle\ .$$

We use full induction:
$x = 1$:

$$J_-|j\ j\rangle \overset{(5.64)}{=} \hbar\sqrt{2j}|j\ j-1\rangle\ .$$

Induction step from x to $x+1$:

$$
\begin{aligned}
(J_-)^{x+1}|j\ j\rangle &= \hbar^x\sqrt{\frac{(2j)!x!}{(2j-x)!}}\,J_-|j\ j-x\rangle \\
&\overset{(5.64)}{=} \hbar^x\sqrt{\frac{(2j)!x!}{(2j-x)!}}\,\hbar\sqrt{(2j-x)\,(x+1)}\,|j\ j-x-1\rangle \\
&= \hbar^{x+1}\sqrt{\frac{(2j)!(x+1)!}{[2j-(x+1)]!}}\,|j\ j-(x+1)\rangle
\end{aligned}
$$

2. We take $m = -j + x$ with $x = 0, 1, \ldots, 2j$, and then we have to verify:

$$(J_+)^x |j\ -j\rangle = \hbar^x \sqrt{\frac{(2j)!x!}{(2j-x)!}}\, |j\ \ -j+x\rangle\ .$$

We again use full induction:
$x = 1$:

$$J_+|j\ -j\rangle \overset{(5.64)}{=} \hbar\sqrt{2j}|j\ \ -j+1\rangle\ .$$

Induction step from x to $x+1$:

$$\begin{aligned}
(J_+)^{x+1}|j\ -j\rangle &= \hbar^x \sqrt{\frac{(2j)!x!}{(2j-x)!}}\, J_+|j\ \ -j+x\rangle \\
&\overset{(5.64)}{=} \hbar^x \sqrt{\frac{(2j)!x!}{(2j-x)!}}\, \hbar\sqrt{(2j-x)(x+1)}\, |j\ \ -j+x+1\rangle \\
&= \hbar^{x+1} \sqrt{\frac{(2j)!(x+1)!}{[2j-(x+1)]!}}\, |j\ \ -j+x+1\rangle
\end{aligned}$$

Solution 5.1.9

$$\begin{aligned}
J_x &= \frac{1}{i\,\hbar}\,[J_y, J_z]_-\ ; \quad J_y = \frac{1}{i\,\hbar}\,[J_z, J_x]_-\ , \\
\langle j\,m|J_x|j\,m\rangle &= \frac{1}{i\,\hbar}\,(\langle j\,m|J_y\,J_z|j\,m\rangle - \langle j\,m|J_z\,J_y|j\,m\rangle) \\
&= -i\,m\,(\langle j\,m|J_y|j\,m\rangle - \langle j\,m|J_y|j\,m\rangle) = 0\ .
\end{aligned}$$

Here we have exploited that J_z is a Hermitian operator:

$$J_z|j\,m\rangle = \hbar\,m|j\,m\rangle\ ; \quad \langle j\,m|J_z = \hbar\,m\langle j\,m|\ .$$

Analogously one shows:

$$\langle j\,m|J_y|j\,m\rangle = 0\ .$$

Mean square deviations:

$$\begin{aligned}
J_x^2 &= \frac{1}{4}\,(J_+ + J_-)^2 = \frac{1}{4}\,(J_+^2 + J_-^2 + J_+\,J_- + J_-\,J_+) \\
\Longrightarrow\ \langle j\,m|J_x^2|j\,m\rangle &= \frac{1}{4}\langle j\,m|(J_+\,J_- + J_-\,J_+)|j\,m\rangle \\
&\overset{(5.58),(5.59)}{=} \frac{1}{4}\langle j\,m|2(\mathbf{J}^2 - J_z^2)|j\,m\rangle = \frac{1}{2}\,\hbar^2\left[j(j+1) - m^2\right], \\
J_y^2 &= -\frac{1}{4}(J_+ - J_-)^2 = -\frac{1}{4}(J_+^2 + J_-^2 - J_+J_- - J_-J_+) \\
\Longrightarrow\ \langle j\,m|J_y^2|j\,m\rangle &= \langle j\,m|J_x^2|j\,m\rangle = \frac{1}{2}\,\hbar^2\left[j(j+1) - m^2\right]\ .
\end{aligned}$$

Therewith it follows eventually:

$$\Delta J_{x,y} = \sqrt{\langle j\,m|J_{x,y}^2|j\,m\rangle - \langle j\,m|J_{x,y}|j\,m\rangle^2} = \hbar\sqrt{\frac{1}{2}\,[j(j+1)-m^2]}\,.$$

Solution 5.1.10

m	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$
(j-m) (j+m+1)	0	3	4	3
(j+m) (j-m+1)	3	4	3	0

Because of $2j+1=4$ the operators are represented by 4×4-matrices:

$$\begin{aligned}
J_+ &= \hbar\begin{pmatrix} 0 & \sqrt{3} & 0 & 0\\ 0 & 0 & 2 & 0\\ 0 & 0 & 0 & \sqrt{3}\\ 0 & 0 & 0 & 0 \end{pmatrix}, \\
J_- &= \hbar\begin{pmatrix} 0 & 0 & 0 & 0\\ \sqrt{3} & 0 & 0 & 0\\ 0 & 2 & 0 & 0\\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}, \\
J_x &= \frac{1}{2}\,(J_+ + J_-) = \frac{\hbar}{2}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0\\ \sqrt{3} & 0 & 2 & 0\\ 0 & 2 & 0 & \sqrt{3}\\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}, \\
J_y &= \frac{1}{2i}\,(J_+ - J_-) = \frac{\hbar}{2i}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0\\ -\sqrt{3} & 0 & 2 & 0\\ 0 & -2 & 0 & \sqrt{3}\\ 0 & 0 & -\sqrt{3} & 0 \end{pmatrix}, \\
J_z &= \hbar\begin{pmatrix} \frac{3}{2} & 0 & 0 & 0\\ 0 & \frac{1}{2} & 0 & 0\\ 0 & 0 & -\frac{1}{2} & 0\\ 0 & 0 & 0 & -\frac{3}{2} \end{pmatrix}.
\end{aligned}$$

Solution 5.1.11

1.

$$\begin{aligned}
(\Delta J_x)^2 &= \langle J_x^2\rangle - \langle J_x\rangle^2 \quad (\langle \dots\rangle \equiv \langle jm|\dots|jm\rangle)\\
(\Delta J_y)^2 &= \langle J_y^2\rangle - \langle J_y\rangle^2\\
J_x &= \frac{1}{2}(J_+ + J_-)\\
J_y &= \frac{1}{2i}(J_+ - J_-)
\end{aligned}$$

$$\begin{aligned}\langle jm|J_\pm|jm\rangle &= \hbar\sqrt{j(j+1)-m(m\pm1)}\cdot\underbrace{\langle jm|jm\pm1\rangle}_{=0}\\ &= 0\\ \langle J_\pm\rangle = 0 &\implies \langle J_x\rangle = \langle J_y\rangle = 0\end{aligned}$$

Furthermore:

$$\begin{aligned}J_x^2 &= \frac{1}{4}\left(J_+^2+J_-^2+J_+J_-+J_-J_+\right)\\ J_y^2 &= -\frac{1}{4}\left(J_+^2+J_-^2-J_+J_--J_-J_+\right)\end{aligned}$$

As above, it can be shown

$$\begin{aligned}\langle J_\pm^2\rangle &= 0\\ \implies \langle J_x^2\rangle = \langle J_y^2\rangle &= \frac{1}{4}\langle J_+J_-+J_-J_+\rangle\end{aligned}$$

According to (5.58), (5.59):

$$\begin{aligned}J_+J_- &= \mathbf{J}^2-J_z^2+\hbar J_z\\ J_-J_+ &= \mathbf{J}^2-J_z^2-\hbar J_z\end{aligned}$$

$$\begin{aligned}\implies J_+J_-+J_-J_+ &= 2\left(\mathbf{J}^2-J_z^2\right)\\ \implies \langle J_x^2\rangle &= \langle J_y^2\rangle = \frac{1}{2}\hbar^2\left(j(j+1)-m^2\right)\\ \implies \Delta J_x = \Delta J_y &= \hbar\sqrt{\frac{1}{2}(j(j+1)-m^2)}\end{aligned}$$

'Smallest indeterminacy' for $m=\pm j$, i.e., in the states:

$$|jj\rangle\,;\quad |j-j\rangle$$

with

$$(\Delta J_x)_{\min} = (\Delta J_y)_{\min} = \hbar\sqrt{\frac{1}{2}j}$$

2. Yes, for

$$|jm\rangle = |00\rangle$$

namely then according to 1. because of $j=m=0$

$$\Delta J_x = \Delta J_y = 0\,,$$

In addition of course $\Delta J_z = 0$.
Alternatively:

$$\begin{aligned}(\Delta J_x)^2 &= \langle\psi|(J_x-\langle J_x\rangle)^2|\psi\rangle\\ (\Delta J_y)^2 &= \langle\psi|(J_y-\langle J_y\rangle)^2|\psi\rangle\\ (\Delta J_z)^2 &= \langle\psi|(J_z-\langle J_z\rangle)^2|\psi\rangle\end{aligned}$$

If the three components possess precise values, it must be:

$$\begin{aligned} \Delta J_x &= 0 \iff J_x|\psi\rangle = \alpha_x|\psi\rangle \\ \Delta J_y &= 0 \iff J_y|\psi\rangle = \alpha_y|\psi\rangle \\ \Delta J_z &= 0 \iff J_z|\psi\rangle = \alpha_z|\psi\rangle \end{aligned}$$

$|\psi\rangle$ is eigen-state of all the three components:

$$[J_i, J_j]_-|\psi\rangle = (\alpha_i\alpha_j - \alpha_j\alpha_i)|\psi\rangle = 0 = i\hbar J_k|\psi\rangle$$

$$\begin{aligned} J_k|\psi\rangle &= 0 \quad \text{for} \quad k = x, y, z \\ \mathbf{J}^2|\psi\rangle &= (J_x^2 + J_y^2 + J_z^2)|\psi\rangle = 0 \end{aligned}$$

$$\begin{aligned} \Longrightarrow \ |\psi\rangle &\sim |j = 0m\rangle \\ j = 0 \Longrightarrow m &= 0 \Longrightarrow |\psi\rangle \sim |00\rangle \end{aligned}$$

Solution 5.1.12

1. J_x, J_y, J_z are the completely equivalent Cartesian components of the operator of the angular momentum $\mathbf{J}$. This means that the sets of operators $(\mathbf{J}^2, J_x)$ and $(\mathbf{J}^2, J_y)$ have of course the same eigen-values as $(\mathbf{J}^2, J_z)$. The corresponding derivations go exactly as those for $(\mathbf{J}^2, J_z)$ in Sect. 5.1.4. This means here:

$$\begin{aligned} \mathbf{J}^2|1\, m_x\rangle &= 2\hbar^2|1\, m_x\rangle \ , \\ J_x|1\, m_x\rangle &= \hbar\, m_x|1\, m_x\rangle \\ &\quad \text{with} \quad m_x = 1, 0, -1 \ , \\ |1\, m_x\rangle &= \sum_{m_z}^{1,0,-1} \gamma(1, m_z)|1\, m_z\rangle \ . \end{aligned}$$

But also:

$$|1\, m_z\rangle = \sum_{m_x}^{1,0,-1} \alpha(1, m_x)|1\, m_x\rangle \ .$$

2. Probabilities:

$$w(m_x) = \left|\, \langle 1\, m_x|1\, m_z\rangle \,\right|^2 = |\gamma(1, m_z)|^2 \ .$$

For the explicit evaluation we need the eigen-states $|1\, m_x\rangle$ of the operator J_x in the $(\mathbf{J}^2, J_z)$-representation!

The matrix representation of J_x for $j = 1$ has been derived at the end of Sect. 5.1.4:

$$\text{general state } |\psi\rangle \quad = \quad \begin{pmatrix} \psi_x \\ \psi_y \\ \psi_z \end{pmatrix} \; ; \quad J_x = \frac{\hbar}{2} \begin{pmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{pmatrix}$$

$$\Longrightarrow \quad J_x|\psi\rangle = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} \psi_y \\ \psi_x + \psi_z \\ \psi_y \end{pmatrix} .$$

Eigen-value equations:

a) $m_x = 1$:

$$J_x|1\, m_x = 1\rangle = \hbar|1\, m_x = 1\rangle = \hbar \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

$$\Longrightarrow \quad \frac{\hbar}{\sqrt{2}} \begin{pmatrix} b \\ a + c \\ b \end{pmatrix} \stackrel{!}{=} \hbar \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

$$\Longrightarrow \quad b = \sqrt{2}\, a \; ; \quad a + c = \sqrt{2}\, b \; ; \quad b = \sqrt{2}\, c \; .$$

It follows therewith:

$$|1\, m_x = 1\rangle = b \begin{pmatrix} \frac{1}{\sqrt{2}} \\ 1 \\ \frac{1}{\sqrt{2}} \end{pmatrix} .$$

Normalization $\Longrightarrow$ $b^2 = 1/2$:

$$|1\, m_x = 1\rangle = \frac{1}{2} \begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix} .$$

b) $m_x = 0$:

$$\begin{aligned} J_x|1\, m_x = 0\rangle \quad &= \quad 0 \\ \Longrightarrow \begin{pmatrix} b \\ a + c \\ b \end{pmatrix} \quad &= \quad 0 \;\Longrightarrow\; b = 0 \; ; \quad a = -c \, , \\ |1\, m_x = 0\rangle \quad &= \quad a \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} . \end{aligned}$$

Normalization $\Longrightarrow$ $a^2 = 1/2$:

$$|1\, m_x = 0\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} .$$

c) $m_x = -1$:

$$J_x|1\,m_x=-1\rangle = -\hbar|1\,m_x=-1\rangle$$

$$\Longrightarrow \frac{\hbar}{\sqrt{2}}\begin{pmatrix} b \\ a+c \\ b \end{pmatrix} = -\hbar\begin{pmatrix} a \\ b \\ c \end{pmatrix} \Longrightarrow b = -\sqrt{2}\,a; a+c = -\sqrt{2}\,b\,; b = -\sqrt{2}\,c,$$

$$|1m_x=-1\rangle = -b\begin{pmatrix} \frac{1}{\sqrt{2}} \\ -1 \\ \frac{1}{\sqrt{2}} \end{pmatrix}\,.$$

Normalization $\Longrightarrow\ b^2 = 1/2$:

$$\Longrightarrow\ |1\,m_x=-1\rangle = \frac{1}{2}\begin{pmatrix} -1 \\ \sqrt{2} \\ -1 \end{pmatrix}\,.$$

Now the probabilities can be calculated:

$\alpha)$ $m_z = +1$:

$$\begin{aligned} w(1) &= \left|\langle 1\,m_x=1|1\,m_z=1\rangle\right|^2 = \frac{1}{4}\,, \\ w(0) &= \frac{1}{2}\,, \\ w(-1) &= \frac{1}{4}\,. \end{aligned}$$

$\beta)$ $m_z = 0$:

$$w(1) = \frac{1}{2}\,; \quad w(0) = 0\,; \quad w(-1) = \frac{1}{2}\,.$$

$\gamma)$ $m_z = -1$:

$$w(1) = \frac{1}{4}\,; \quad w(0) = \frac{1}{2}\,; \quad w(-1) = \frac{1}{4}\,.$$

3. After the measurement of J_x the pure state $|1\,m_z\rangle$ has changed now to be the pure state $|1\,m_x\rangle$. An anew measurement of J_z then yields with the probability

$$\left|\langle 1\,m_z|1\,m_x\rangle\right|^2$$

the measuring value $\hbar\,m_z$. But these are just the probabilities, which have been calculated in part 2.!

Solution 5.1.13

1. $j = 1$:

$$|\varphi\rangle = \sum_m |1m\rangle\langle 1m|\varphi\rangle \qquad \left(\mathbb{1} = \sum_m |1m\rangle\langle 1m|\right)$$

$$\begin{aligned} \Longrightarrow \quad -1\hbar &\stackrel{!}{=} \langle\varphi|J_z|\varphi\rangle \\ &= \sum_{m,m'} \langle\varphi|1m\rangle\langle 1m|J_z|1m'\rangle\langle 1m'|\varphi\rangle \\ &= \sum_{m,m'} \hbar m' \langle\varphi|1m\rangle \underbrace{\langle 1m|1m'\rangle}_{=\delta_{mm'}} \langle 1m'|\varphi\rangle \\ &= \sum_m \hbar m \left|\langle\varphi|1m\rangle\right|^2 \end{aligned}$$

Normalization:

$$\begin{aligned} 1 \stackrel{!}{=} \langle\varphi|\varphi\rangle &= \sum_{m,m'} \langle\varphi|1m\rangle \underbrace{\langle 1m|1m'\rangle}_{=\delta_{mm'}} \langle 1m'|\varphi\rangle \\ &= \sum_m \left|\langle\varphi|1m\rangle\right|^2 \end{aligned}$$

Combination:

$$\begin{aligned} 0 &= \langle\varphi|J_z|\varphi\rangle + \hbar\langle\varphi|\varphi\rangle \\ &= \sum_m \hbar(m+1)\left|\langle\varphi|1m\rangle\right|^2 \end{aligned}$$

Because of $j = 1$ it is $(m+1) \geq 0 \quad \forall m$
$\Longrightarrow$ all summands non-negative
$\Longrightarrow$ each summand on its own already zero
$\Longrightarrow$ $\langle\varphi|1m\rangle \neq 0$ at most for $m = -1$

$$\Longrightarrow \quad |\varphi\rangle = \sum_m |1m\rangle\langle 1m|\varphi\rangle \sim |1-1\rangle$$

$\Longrightarrow$ $|\varphi\rangle$ is eigen-state of J_z

$$\begin{aligned} J_+|\varphi\rangle &\sim \hbar\sqrt{1(1+1) - m(m+1)}|10\rangle \\ &\sim \hbar\sqrt{2}|10\rangle \\ J_-|\varphi\rangle &= 0 \end{aligned}$$

$$J_x = \frac{1}{2}(J_+ + J_-)\,; \quad J_y = \frac{1}{2i}(J_+ - J_-)$$

$$\begin{aligned} \Longrightarrow \quad \langle\varphi|J_x|\varphi\rangle &\sim \langle\varphi|J_+|\varphi\rangle \sim \langle 1-1|10\rangle = 0 \\ \langle\varphi|J_y|\varphi\rangle &\sim \langle\varphi|J_+|\varphi\rangle \sim \langle 1-1|10\rangle = 0 \end{aligned}$$

Alternatively:

$$\begin{aligned}\langle\varphi|J_x|\varphi\rangle &= \frac{1}{i\hbar}\langle\varphi|[J_y,J_z]_-|\varphi\rangle \\ &= \frac{1}{i\hbar}\left\{\langle\varphi|J_yJ_z|\varphi\rangle - \langle\varphi|J_zJ_y|\varphi\rangle\right\} \\ &= \frac{-\hbar}{i\hbar}\left\{\langle\varphi|J_y|\varphi\rangle - \langle\varphi|J_y|\varphi\rangle\right\} \\ &= 0\end{aligned}$$

Analogously: $\langle\varphi|J_y|\varphi\rangle = 0$

2. $|\psi\rangle$ **can** be eigen-state, e.g.

$$|\psi\rangle = |\frac{7}{2}\frac{3}{2}\rangle$$

$$\begin{aligned}\Longrightarrow\ \langle\psi|J_z|\psi\rangle &= \frac{3}{2}\hbar\langle\psi|\psi\rangle = \frac{3}{2}\hbar \\ \langle\psi|J_x|\psi\rangle &= \frac{1}{2}\langle\psi|J_+ + J_-|\psi\rangle \\ &= c_1\underbrace{\left\langle\frac{7}{2}\frac{3}{2}\middle|\frac{7}{2}\frac{5}{2}\right\rangle}_{=0} + c_2\underbrace{\left\langle\frac{7}{2}\frac{3}{2}\middle|\frac{7}{2}\frac{1}{2}\right\rangle}_{=0} \\ &= 0\end{aligned}$$

Analogously: $\langle\psi|J_y|\psi\rangle = 0$

$|\psi\rangle$ must, however, **not necessarily be** an eigen-state.

Counterexample:

$$|\psi\rangle = \sqrt{\frac{4}{5}}|\frac{7}{2}\frac{5}{2}\rangle + \sqrt{\frac{1}{5}}|\frac{7}{2}-\frac{5}{2}\rangle$$

Test:

$$\begin{aligned}\langle\psi|J_z|\psi\rangle &= \frac{4}{5}\langle\frac{7}{2}\frac{5}{2}|J_z|\frac{7}{2}\frac{5}{2}\rangle + \frac{1}{5}\langle\frac{7}{2}-\frac{5}{2}|J_z|\frac{7}{2}-\frac{5}{2}\rangle \\ &= \hbar\left(\frac{4}{5}\cdot\frac{5}{2} - \frac{1}{5}\cdot\frac{5}{2}\right) = \hbar\left(2-\frac{1}{2}\right) \\ &= \frac{3}{2}\hbar \\ \langle\psi|J_x|\psi\rangle &= c_1\underbrace{\left\langle\psi\middle|\frac{7}{2}\frac{7}{2}\right\rangle}_{=0} + c_2\underbrace{\left\langle\psi\middle|\frac{7}{2}\frac{3}{2}\right\rangle}_{=0} \\ &\quad + d_1\underbrace{\left\langle\psi\middle|\frac{7}{2}-\frac{3}{2}\right\rangle}_{=0} + d_2\underbrace{\left\langle\psi\middle|\frac{7}{2}-\frac{7}{2}\right\rangle}_{=0} \\ &= 0\end{aligned}$$

Analogously: $\langle\psi|J_y|\psi\rangle = 0$

All mentioned properties are fulfilled!
Nevertheless:

$$\begin{aligned} J_z|\psi\rangle &= \hbar\frac{5}{2}\sqrt{\frac{4}{5}}\left|\frac{7}{2}\frac{5}{2}\right\rangle - \hbar\frac{5}{2}\sqrt{\frac{1}{5}}\left|\frac{7}{2}-\frac{5}{2}\right\rangle \\ &\neq \alpha|\psi\rangle \end{aligned}$$

$\Longrightarrow$ $|\psi\rangle$ is **not** an eigen-state!

Solution 5.1.14

1.

$$\begin{aligned} L_x\,L_y &= -\hbar^2\left(-\sin\varphi\frac{\partial}{\partial\vartheta}-\cot\vartheta\cos\varphi\frac{\partial}{\partial\varphi}\right)\left(\cos\varphi\frac{\partial}{\partial\vartheta}-\cot\vartheta\sin\varphi\frac{\partial}{\partial\varphi}\right) \\ &= -\hbar^2\left[-\sin\varphi\cos\varphi\frac{\partial^2}{\partial\vartheta^2}-\frac{\sin^2\varphi}{\sin^2\vartheta}\,\frac{\partial}{\partial\varphi}\right. \\ &\quad +\cot\vartheta\sin^2\varphi\,\frac{\partial^2}{\partial\vartheta\,\partial\varphi}+\cot\vartheta\cos\varphi\sin\varphi\frac{\partial}{\partial\vartheta} \\ &\quad -\cot\vartheta\cos^2\varphi\,\frac{\partial^2}{\partial\varphi\,\partial\vartheta}+\cot^2\vartheta\cos^2\varphi\frac{\partial}{\partial\varphi} \\ &\quad \left.+\cot^2\vartheta\sin\varphi\cos\varphi\frac{\partial^2}{\partial\varphi^2}\right]\,, \\ L_y\,L_x &= -\hbar^2\left(\cos\varphi\frac{\partial}{\partial\vartheta}-\cot\vartheta\sin\varphi\frac{\partial}{\partial\varphi}\right)\left(-\sin\varphi\frac{\partial}{\partial\vartheta}-\cot\vartheta\cos\varphi\frac{\partial}{\partial\varphi}\right) \\ &= -\hbar^2\left[-\cos\varphi\sin\varphi\frac{\partial^2}{\partial\vartheta^2}+\frac{\cos^2\varphi}{\sin^2\vartheta}\,\frac{\partial}{\partial\varphi}\right. \\ &\quad -\cot\vartheta\cos^2\varphi\,\frac{\partial^2}{\partial\vartheta\,\partial\varphi}+\cot\vartheta\sin\varphi\cos\varphi\frac{\partial}{\partial\vartheta} \\ &\quad +\cot\vartheta\sin^2\varphi\frac{\partial^2}{\partial\varphi\,\partial\vartheta}-\cot^2\vartheta\sin^2\varphi\frac{\partial}{\partial\varphi} \\ &\quad \left.+\cot^2\vartheta\sin\varphi\cos\varphi\frac{\partial^2}{\partial\varphi^2}\right]\,. \end{aligned}$$

It follows:

$$\begin{aligned} &[L_x, L_y]_- \\ &= -\hbar^2\left[-\frac{\sin^2\varphi}{\sin^2\vartheta}+\cot^2\vartheta\cos^2\varphi-\frac{\cos^2\varphi}{\sin^2\vartheta}+\cot^2\vartheta\sin^2\varphi\right]\frac{\partial}{\partial\varphi} \\ &= -\hbar^2\left[-\frac{1}{\sin^2\vartheta}+\cot^2\vartheta\right]\frac{\partial}{\partial\varphi} = \hbar^2\frac{\partial}{\partial\varphi} = i\,\hbar\left(\frac{\hbar}{i}\,\frac{\partial}{\partial\varphi}\right) = i\,\hbar\,L_z \end{aligned}$$

2. L_y does not contain r-parts, thus commutes with $\mathbf{r}^2 = r^2$!

3. For Eq. (5.82) in Sect. 5.1.5 we have already calculated:

$$L_+ L_- = -\hbar^2 \left[\frac{\partial^2}{\partial\vartheta^2} + i\,\frac{\partial}{\partial\varphi} + \cot\vartheta \frac{\partial}{\partial\vartheta} + \cot^2\vartheta\,\frac{\partial^2}{\partial\varphi^2} \right] .$$

We therefore still need:

$$\begin{aligned} L_- L_+ &= \hbar^2\, e^{-i\varphi} \left(-\frac{\partial}{\partial\vartheta} + i\cot\vartheta\,\frac{\partial}{\partial\varphi} \right) e^{i\varphi} \left(\frac{\partial}{\partial\vartheta} + i\cot\vartheta\,\frac{\partial}{\partial\varphi} \right) \\ &= \hbar^2 \left(-\frac{\partial^2}{\partial\vartheta^2} + \frac{i}{\sin^2\vartheta}\,\frac{\partial}{\partial\varphi} - i\cot\vartheta\,\frac{\partial^2}{\partial\vartheta\,\partial\varphi} \right. \\ &\quad - \cot\vartheta\,\frac{\partial}{\partial\vartheta} + i\cot\vartheta\,\frac{\partial^2}{\partial\varphi\,\partial\vartheta} \\ &\quad \left. -i\cot^2\vartheta\,\frac{\partial}{\partial\varphi} - \cot^2\vartheta\,\frac{\partial^2}{\partial\varphi^2} \right) \\ &= -\hbar^2 \left(\frac{\partial^2}{\partial\vartheta^2} - i\,\frac{\partial}{\partial\varphi} + \cot\vartheta\,\frac{\partial}{\partial\vartheta} + \cot^2\vartheta\,\frac{\partial^2}{\partial\varphi^2} \right) . \end{aligned}$$

It follows from that:

$$[L_+, L_-]_- = -2i\,\hbar^2\,\frac{\partial}{\partial\varphi} = 2\hbar \left(\frac{\hbar}{i}\,\frac{\partial}{\partial\varphi} \right) = 2\hbar\, L_z$$

Solution 5.1.15

1. The normalization integral reads (c_l real!):

$$\begin{aligned} 1 &= c_l^2 \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\vartheta\, d\vartheta \sin^{2l}\vartheta = c_l^2\, 2\pi \int_{-1}^{+1} d\cos\vartheta\, (1-\cos^2\vartheta)^l \\ \Longrightarrow\ c_l &= \frac{1}{\sqrt{2\pi}} \left[\int_{-1}^{+1} dz\, \left(1-z^2\right)^l \right]^{-1/2} , \end{aligned}$$

$$\begin{aligned} x_l &= \int_{-1}^{+1} dz\, \left(1-z^2\right)^l = \int_{-1}^{+1} dz\, \left(1-z^2\right)^{l-1} - \int_{-1}^{+1} dz\, z^2\, \left(1-z^2\right)^{l-1} \\ &= x_{l-1} + \frac{1}{2l} \int_{-1}^{+1} dz\, z\, \frac{d}{dz}\, \left(1-z^2\right)^l \\ &= x_{l-1} + \left[\frac{1}{2l}\, z\, \left(1-z^2\right)^l \right]_{-1}^{+1} - \frac{1}{2l} \int_{-1}^{+1} dz\, \left(1-z^2\right)^l . \end{aligned}$$

$l \geq 1$:

$$x_l \left(1 + \frac{1}{2l}\right) = x_{l-1}$$

$$\begin{aligned} \Longrightarrow \quad x_l &= \frac{2l}{2l+1}\, x_{l-1} = \frac{2l}{2l+1}\,\frac{2(l-1)}{2l-1}\, x_{l-2}\,, \\ x_0 &= 2\,. \end{aligned}$$

This can be written as follows:

$$x_l = \frac{2l\,2l\,2(l-1)\,2(l-1)\,2(l-2)\cdots 2}{(2l+1)\,2l\,(2l-1)\,(2l-2)\,(2l-3)\cdots 1} = \frac{2\,2^l\,2^l\,l!\,l!}{(2l+1)!}\,.$$

Therewith we get the sought normalization constants:

$$c_l = \sqrt{\frac{(2l+1)!}{4\pi}}\,\frac{1}{2^l\,l!}\,.$$

2.

$$\begin{aligned} \mathbf{L}^2\, Y_{l-l}(\vartheta,\varphi) &= -\frac{\hbar^2}{\sin^2\vartheta}\left(\sin\vartheta\,\frac{\partial}{\partial\vartheta}\sin\vartheta\,\frac{\partial}{\partial\vartheta} + \frac{\partial^2}{\partial\varphi^2}\right) Y_{l-l}(\vartheta,\varphi) \\ &= \frac{-\hbar^2 c_l}{\sin^2\vartheta}\left[\sin\vartheta\,\frac{\partial}{\partial\vartheta}\,(l\cos\vartheta\sin^l\vartheta) - l^2\sin^l\vartheta\right] e^{-il\varphi} \\ &= \frac{-\hbar^2 c_l}{\sin^2\vartheta}\,(-l\sin^2\vartheta\sin^l\vartheta + l^2\cos^2\vartheta\sin^l\vartheta - l^2\sin^l\vartheta)\,e^{-il\varphi} \\ &= \frac{-\hbar^2}{\sin^2\vartheta}\,(-l\sin^2\vartheta - l^2\sin^2\vartheta)\,Y_{l-l}(\vartheta,\varphi) \\ \Longrightarrow \quad & \mathbf{L}^2 Y_{l-l}(\vartheta,\varphi) = \hbar^2 l(l+1)\,Y_{l-l}(\vartheta,\varphi) \end{aligned}$$

Solution 5.1.16

1. Spherical harmonics (5.108)–(5.110) are eigen-states of the orbital angular momentum:

$$\begin{aligned} Y_{00}(\vartheta,\varphi) &= \frac{1}{\sqrt{4\pi}} \cong |0\,0\rangle \\ Y_{10}(\vartheta,\varphi) &= \sqrt{\frac{3}{4\pi}}\,\cos\vartheta \cong |1\,0\rangle \\ Y_{1\pm1}(\vartheta,\varphi) &= \mp\sqrt{\frac{3}{8\pi}}\,\sin\vartheta\,e^{\pm i\varphi} \cong |1\;\pm 1\rangle\,. \end{aligned}$$

This means:

$$\begin{aligned}
Y_{11}(\vartheta,\varphi)+Y_{1-1}(\vartheta,\varphi) &= -\sqrt{\frac{3}{8\pi}}\,\sin\vartheta\left(e^{+i\varphi}-e^{-i\varphi}\right)\\
&= -2i\sqrt{\frac{3}{8\pi}}\,\sin\vartheta\,\sin\varphi\\
Y_{11}(\vartheta,\varphi)-Y_{1-1}(\vartheta,\varphi) &= -\sqrt{\frac{3}{8\pi}}\,\sin\vartheta\left(e^{+i\varphi}+e^{-i\varphi}\right)\\
&= -2\sqrt{\frac{3}{8\pi}}\,\sin\vartheta\,\cos\varphi\\
\curvearrowright\quad \sin\vartheta\,\cos\varphi &= -\sqrt{\frac{2\pi}{3}}\,(Y_{11}(\vartheta,\varphi)-Y_{1-1}(\vartheta,\varphi))\\
\sin\vartheta\,\sin\varphi &= i\sqrt{\frac{2\pi}{3}}\,(Y_{11}(\vartheta,\varphi)+Y_{1-1}(\vartheta,\varphi))\\
\sqrt{3}\,\cos\vartheta &= \sqrt{4\pi}Y_{10}(\vartheta,\varphi)\\
\sin\vartheta\,\cos\varphi+\sin\vartheta\,\sin\varphi &= \sqrt{\frac{2\pi}{3}}\Big((i-1)Y_{11}(\vartheta,\varphi)+(i+1)Y_{1-1}(\vartheta,\varphi)\Big).
\end{aligned}$$

Therewith:

$$|\psi\rangle=\alpha\sqrt{\frac{2\pi}{3}}\Big((i-1)\,|1\,1\rangle+\sqrt{6}\,|1\,0\rangle+(i+1)\,|1\,-1\rangle\Big)\,.$$

Normalization:

$$\langle\psi|\psi\rangle\stackrel{!}{=}1=\alpha^2\frac{2\pi}{3}(2+6+2)\quad\curvearrowright\ \alpha=\sqrt{\frac{3}{20\pi}}\,.$$

Rotator state expanded in eigen-functions of the orbital angular momentum:

$$|\psi\rangle=\frac{1}{2}\sqrt{\frac{2}{5}}\Big((i-1)\,|1\,1\rangle+\sqrt{6}\,|1\,0\rangle+(i+1)\,|1\,-1\rangle\Big)\,.$$

2.

$$\mathbf{L}^2\,|l\,m\rangle=\hbar^2 l(l+1)\,|l\,m\rangle\,.$$

The eigen-value $2\hbar^2$ belongs to $l=1$. $|\psi\rangle$ is obviously the eigen-state with $l=1$. The probability to find with a measurement of $\mathbf{L}^2$ the value $2\hbar^2$ is therewith equal to 1.

3.

$$W(2\hbar^2,0)=|\langle 1\,0|\psi\rangle|^2=\left|\frac{1}{2}\sqrt{\frac{2}{5}}\sqrt{6}\right|^2=\frac{3}{5}\,.$$

Solution 5.1.17

1.
$$H|l\,m\rangle = E_{lm}|l\,m\rangle\ ,\ E_{lm} = \frac{1}{2J}\,\hbar^2 l\,(l+1)\ .$$
Because of the indeterminacy of m each eigen-value is $(2l+1)$-fold degenerate!
Eigen-functions:
$$\langle\vartheta\varphi|l\,m\rangle = Y_{lm}(\vartheta,\varphi) \quad \text{spherical harmonics}\ .$$

2.
$$\psi(\vartheta,\varphi) = \alpha\left(\cos^2\vartheta + \sin^2\vartheta\cos\varphi\right)\ .$$
According to (5.108) and (5.111) it is
$$\cos^2\vartheta = \frac{\sqrt{4\pi}}{3}\left[\sqrt{\frac{4}{5}}\,Y_{20}(\vartheta,\varphi) + Y_{00}(\vartheta,\varphi)\right]$$
and from (5.113) it follows:
$$\sin^2\vartheta\cos 2\varphi = \sqrt{\frac{8\pi}{15}}\,\left[Y_{22}(\vartheta,\varphi) + Y_{2-2}(\vartheta,\varphi)\right]\ .$$
The state of the system $|\psi\rangle$ can therewith be expressed by eigen-functions of the angular momentum:
$$|\psi\rangle = \alpha\sqrt{4\pi}\left(\sqrt{\frac{2}{15}}|2\,2\rangle + \sqrt{\frac{2}{15}}|2\,-2\rangle + \frac{1}{3}\sqrt{\frac{4}{5}}|2\,0\rangle + \frac{1}{3}|0\,0\rangle\right)\ .$$
We normalize $|\psi\rangle$ and exploit thereby the orthonormality of the $|l\,m\rangle$ (α real!):
$$\langle\psi|\psi\rangle = 1 \quad\Longrightarrow\quad \alpha^{-2} = \frac{8\,\pi}{15} + \frac{8\,\pi}{15} + \frac{16\,\pi}{45} + \frac{4\,\pi}{9} = \frac{28\,\pi}{15} \quad\Longrightarrow\quad \alpha = \sqrt{\frac{15}{28\,\pi}}$$
$$\Longrightarrow\quad |\psi\rangle = \sqrt{\frac{2}{7}}|2\,2\rangle + \sqrt{\frac{2}{7}}|2\,-2\rangle + \frac{1}{3}\sqrt{\frac{12}{7}}|2\,0\rangle + \frac{1}{3}\sqrt{\frac{15}{7}}|0\,0\rangle\ .$$
Probabilities for the measurement of $\mathbf{L}^2$:
$$\begin{aligned} w(6\,\hbar^2) &= \sum_{m\,=\,-2}^{+2} |\langle 2\,m|\psi\rangle|^2 = \frac{2}{7} + \frac{2}{7} + \frac{4}{21} = \frac{16}{21}\ , \\ w(2\,\hbar^2) &= \sum_{m\,=\,-1}^{+1} |\langle 1\,m|\psi\rangle|^2 = 0\ , \\ w(0) &= |\langle 0\,0|\psi\rangle|^2 = \frac{5}{21}\ . \end{aligned}$$

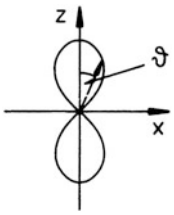


Figure A.1:

3. Simultaneous measurement of $\mathbf{L}^2$ and L_z:

$$w(6\,\hbar^2, -2\,\hbar) = |\langle 2-2|\psi\rangle|^2 = \frac{2}{7}\,.$$

Solution 5.1.18

1. In a so-called *polar diagram* one plots

$$\left|Y_{lm}(\vartheta,\varphi)\right|^2 = \left|\Theta_{lm}(\vartheta)\right|^2$$

as a function of ϑ (Fig. A.1). Because of the lacking φ-dependence these representations exhibit rotational symmetry around the z-axis. Diagrams for m and $-m$ are therefore identical.

$$\begin{aligned} (5.109) \implies Y_{10}(\vartheta,\varphi) &= \sqrt{\tfrac{3}{4\pi}}\cos\vartheta\,, \\ |Y_{10}|^2 &= \tfrac{3}{4\pi}\cos^2\vartheta\,. \end{aligned}$$

2. We now choose the x-axis as the symmetry-axis. For the *new* density of the position probability it holds according to the presumption:

$$|f(\alpha)|^2 = \frac{3}{4\pi}\cos^2\alpha\,.$$

The angle α (Fig. A.2) must be expressed by ϑ and φ. It is:

$$\begin{aligned} x &= r\cos\alpha\,, \\ x &= r\sin\vartheta\cos\varphi\,. \end{aligned}$$

This means:

$$\cos\alpha = \sin\vartheta\cos\varphi\,.$$

It holds according to (5.110):

$$\begin{aligned} Y_{11}(\vartheta,\varphi) - Y_{1-1}(\vartheta,\varphi) &= -\sqrt{\frac{3}{8\pi}}\sin\vartheta\left(e^{i\varphi}+e^{-i\varphi}\right) = -\sqrt{\frac{3}{2\pi}}\sin\vartheta\cos\varphi \\ \implies \sin\vartheta\cos\varphi &= \sqrt{\frac{2\pi}{3}}\left[Y_{1-1}(\vartheta,\varphi) - Y_{11}(\vartheta,\varphi)\right]. \end{aligned}$$

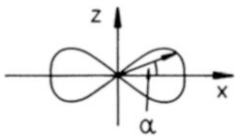


Figure A.2:

This means for the *new* density of the position probability:

$$|f(\alpha)|^2 = \frac{1}{2}\left(Y_{1-1}(\vartheta,\varphi) - Y_{11}(\vartheta,\varphi)\right)^2 \ .$$

Solution 5.1.19

Because of $L_x^2 + L_y^2 = \mathbf{L}^2 - L_z^2$ we can also write:

$$H = B\,\mathbf{L}^2 + (A-B)\,L_z^2 \ .$$

Therefore the eigen-functions are the spherical harmonics:

$$\begin{aligned} & H\,Y_{lm}(\vartheta,\varphi) = \hbar^2\left[B\,l(l+1) + (A-B)\,m^2\right]\,Y_{lm}(\vartheta,\varphi) \\ \Longrightarrow\ & \text{eigen-values:}\quad E_{lm} = \hbar^2\left[B\,l(l+1) + (A-B)\,m^2\right] \ . \end{aligned}$$

The eigen-functions are, however, not real except for $m = 0$. We construct by means of (5.104) the following real combinations:

$$\begin{aligned} \widehat{Y}^{+}_{lm}(\vartheta,\varphi) &= \alpha\left[Y_{lm}(\vartheta,\varphi) + Y^*_{lm}(\vartheta,\varphi)\right] = \alpha\left[Y_{lm}(\vartheta,\varphi) + (-1)^m\,Y_{l\,-m}(\vartheta,\varphi)\right] \ , \\ \widehat{Y}^{-}_{lm}(\vartheta,\varphi) &= i\,\beta\left[Y_{lm}(\vartheta,\varphi) - Y^*_{lm}(\vartheta,\varphi)\right] = i\beta\left[Y_{lm}(\vartheta,\varphi) - (-1)^m\,Y_{l\,-m}(\vartheta,\varphi)\right] . \end{aligned}$$

Obviously it holds:

$$\begin{aligned} \mathbf{L}^2\,\widehat{Y}^{\pm}_{lm}(\vartheta,\varphi) &= \hbar^2 l(l+1)\,\widehat{Y}^{(\pm)}_{lm}(\vartheta,\varphi) \ , \\ L_z^2\,\widehat{Y}^{(\pm)}_{lm}(\vartheta,\varphi) &= \hbar^2 m^2\,\widehat{Y}^{(\pm)}_{lm}(\vartheta,\varphi) \ , \end{aligned}$$

and therewith:

$$H\,\widehat{Y}^{(\pm)}_{lm}(\vartheta,\varphi) = E_{lm}\,\widehat{Y}^{(\pm)}_{lm}(\vartheta,\varphi) \ .$$

Solution 5.1.20

Position representation of the orbital angular momentum (5.81)

$$L_{\pm} = \hbar\,e^{\pm i\varphi}\left(\pm\frac{\partial}{\partial\vartheta} + i\cot\vartheta\frac{\partial}{\partial\varphi}\right) \ .$$

Eigen-functions for $(L_z, \mathbf{L}^2)$:

$$Y_{lm}(\vartheta,\varphi) = \Theta_{lm}(\vartheta)\,e^{im\varphi} \ .$$

1. Hypothesis: $l = \frac{1}{2}$
   This means for $l = m$:

$$\begin{aligned} L_+ Y_{ll}(\vartheta,\varphi) &= 0 \\ \curvearrowright \quad \hbar\, e^{i\varphi}\left(\frac{\partial}{\partial\vartheta} + i\cot\vartheta\frac{\partial}{\partial\varphi}\right)\Theta_{ll}(\vartheta)\, e^{il\varphi} &= 0 \\ \curvearrowright \quad \left(\frac{\partial}{\partial\vartheta} - l\cot\vartheta\right)\Theta_{ll}(\vartheta) &= 0 \\ \curvearrowright \quad \Theta_{ll}(\vartheta) &\propto \sin^l\vartheta\ . \end{aligned}$$

   This yields as *'possible'* eigen-function

$$\widehat{Y}_{\frac{1}{2}\frac{1}{2}}(\vartheta,\varphi) = \left\langle \vartheta\varphi \middle| \frac{1}{2}\ \frac{1}{2} \right\rangle \propto \sqrt{\sin\vartheta}\, \exp\left(i\frac{\varphi}{2}\right)\ .$$

2. If $\widehat{Y}_{\frac{1}{2}\frac{1}{2}}(\vartheta,\varphi)$ is really an eigen-function, then we should have, because m is maximal:

$$L_+\, \widehat{Y}_{\frac{1}{2}\frac{1}{2}}(\vartheta,\varphi) = 0\ .$$

   That is indeed fulfilled:

$$\begin{aligned} L_+\, \widehat{Y}_{\frac{1}{2}\frac{1}{2}}(\vartheta,\varphi) &\propto \hbar\, e^{i\varphi}\left(\frac{\partial}{\partial\vartheta} + i\cot\vartheta\frac{\partial}{\partial\varphi}\right)\sqrt{\sin\vartheta}\, \exp\left(i\frac{\varphi}{2}\right) \\ &\propto \left(\frac{\partial}{\partial\vartheta} - \frac{1}{2}\cot\vartheta\right)\sqrt{\sin\vartheta} \\ &= \frac{1}{2}\,\frac{\cos\vartheta}{\sqrt{\sin\vartheta}} - \frac{1}{2}\frac{\cos\vartheta}{\sin\vartheta}\sqrt{\sin\vartheta} = 0\ . \end{aligned}$$

   Actually, this serves here only as a checking, because lastly we have derived $\widehat{Y}_{\frac{1}{2}\frac{1}{2}}(\vartheta,\varphi)$ from the relation $L_+\, \widehat{Y}_{\frac{1}{2}\frac{1}{2}}(\vartheta,\varphi) \stackrel{!}{=} 0$.

3. It must also hold

$$L_-^2\, \widehat{Y}_{\frac{1}{2}\frac{1}{2}}(\vartheta,\varphi) = 0\ .$$

   This is then an appropriate criterion:

$$\begin{aligned} L_-\, \widehat{Y}_{\frac{1}{2}\frac{1}{2}}(\vartheta,\varphi) &\propto \hbar\, e^{-i\varphi}\left(-\frac{\partial}{\partial\vartheta} + i\cot\vartheta\frac{\partial}{\partial\varphi}\right)\sqrt{\sin\vartheta}\, \exp\left(i\frac{\varphi}{2}\right) \\ &= \hbar\, e^{-i\frac{\varphi}{2}}\left(-\frac{\partial}{\partial\vartheta} - \frac{1}{2}\cot\vartheta\right)\sqrt{\sin\vartheta} \\ &= \hbar\, e^{-i\frac{\varphi}{2}}\left(-\frac{\cos\vartheta}{2\sqrt{\sin\vartheta}} - \frac{\cos\vartheta}{2\sqrt{\sin\vartheta}}\right) \\ &= -\hbar\,\frac{\cos\vartheta}{\sqrt{\sin\vartheta}}\, e^{-i\frac{\varphi}{2}} \not\equiv 0 \end{aligned}$$

$$
\begin{aligned}
L_-^2\,\widehat{Y}_{\frac{1}{2}\frac{1}{2}}(\vartheta,\varphi) &\propto -\hbar^2\,e^{-i\varphi}\left(-\frac{\partial}{\partial\vartheta}+i\cot\vartheta\frac{\partial}{\partial\varphi}\right)\frac{\cos\vartheta}{\sqrt{\sin\vartheta}}\,e^{-i\frac{\varphi}{2}}\\
&\propto e^{-i\frac{3\varphi}{2}}\left(-\frac{\partial}{\partial\vartheta}+\frac{1}{2}\cot\vartheta\right)\frac{\cos\vartheta}{\sqrt{\sin\vartheta}}\\
&= e^{-i\frac{3\varphi}{2}}\left(\frac{\sin\vartheta\sqrt{\sin\vartheta}-\frac{\cos^2\vartheta}{2\sqrt{\sin\vartheta}}}{\sin\vartheta}+\frac{\cos^2\vartheta}{2\sin\vartheta\sqrt{\sin\vartheta}}\right)\\
&= e^{-i\frac{3\varphi}{2}}\sqrt{\sin\vartheta}\\
&\not\equiv 0\,.
\end{aligned}
$$

From this reason $\widehat{Y}_{\frac{1}{2}\frac{1}{2}}(\vartheta,\varphi)$ **can not** be an eigen-function of $(\mathbf{L}^2, L_z)$.

Section 5.2.5

Solution 5.2.1

1. It is $S_+|+\rangle = S_-|-\rangle = 0$ and therewith $(S_\pm)^2 \equiv 0$. It follows then with $S_\pm = S_x \pm i\,S_y$:

$$
\begin{aligned}
0 &= S_+^2 = S_x^2 - S_y^2 + i\,(S_x\,S_y + S_y\,S_x)\,,\\
0 &= S_-^2 = S_x^2 - S_y^2 - i\,(S_x\,S_y + S_y\,S_x)\,.
\end{aligned}
$$

   Subtraction of these two equations:

$$
0 = 2i\,(S_x\,.S_y + S_y\,S_x) = 2i\,[S_x, S_y]_+
$$

2. Addition of the two equations for S_+^2 and S_-^2 from 1.:

$$
\begin{aligned}
0 &= 2\,(S_x^2 - S_y^2) \implies S_x^2 = S_y^2\,,\\
\mathbf{S}^2|\pm\rangle &= \frac{3}{4}\,\hbar^2|\pm\rangle\,;\quad S_z^2|\pm\rangle = \frac{\hbar^2}{4}|\pm\rangle\,.
\end{aligned}
$$

   The states $|+\rangle$ and $|-\rangle$ build in $\mathcal{H}_{S=1/2}$ a complete basis. For this reason we have in $\mathcal{H}_{S=1/2}$ the operator identities:

$$
\begin{aligned}
&\mathbf{S}^2 = \frac{3}{4}\,\hbar^2\,\mathbb{1}_2\,;\quad S_z^2 = \frac{1}{4}\,\hbar^2\,\mathbb{1}_2\\
\implies\quad &\mathbf{S}^2 - S_z^2 = \frac{2}{4}\,\hbar^2\,\mathbb{1}_2 = S_x^2 + S_y^2\\
\implies\quad &S_x^2 = S_y^2 = S_z^2 = \frac{1}{4}\,\hbar^2\,\mathbb{1}_2\,.
\end{aligned}
$$

3. It follows from 1.:

$$
\begin{aligned}
S_x\,S_y &= -S_y\,S_x\\
\implies [S_x, S_y]_- = 2S_x\,S_y &= i\,\hbar\,S_z \implies S_x\,S_y = i\,\frac{\hbar}{2}\,S_z\,.
\end{aligned}
$$

4. With 3.:

$$S_x\,S_y\,S_z = i\,\frac{\hbar}{2}\,S_z^2 \overset{2)}{=} i\,\frac{\hbar^3}{8}\,\mathbb{1}_2\ .$$

Solution 5.2.2

1. Commutation relations (5.14):

$$[S_i, S_j]_- = i\,\hbar\sum_k \varepsilon_{ijk}\,S_k\ . \qquad (*)$$

According to part 1. of Exercise 5.2.1:

$$[S_x, S_y]_+ = 0\ . \qquad (**)$$

Furthermore:

$$\begin{aligned} S_z\,S_x|\pm\rangle &= S_z\,\frac{1}{2}\,(S_+ + S_-)|\pm\rangle = \frac{1}{2}\,S_z\,S_\mp|\pm\rangle \\ &= \frac{1}{2}\,S_z|\mp\rangle = \mp\frac{\hbar}{4}|\mp\rangle\ , \\ & S_x\,S_z|\pm\rangle = \pm\frac{\hbar}{2}\,S_x|\pm\rangle = \pm\frac{\hbar}{4}\,S_\mp|\pm\rangle = \pm\frac{\hbar}{4}|\mp\rangle \\ \Longrightarrow\quad & S_z\,S_x|\pm\rangle = -S_x\,S_z|\pm\rangle\ , \end{aligned}$$

$$\begin{aligned} \{|+\rangle, |-\rangle\} \quad & \text{complete basis of the } \mathcal{H}_{S=1/2} \\ \Longrightarrow \quad & \text{operator identity in } \mathcal{H}_{S=1/2}\text{:} \\ & S_z\,S_x = -S_x\,S_z\ . \end{aligned}$$

Analogously one shows:

$$S_z\,S_y = -S_y\,S_z\ .$$

Altogether it follows with (**) and part 2. of Exercise 5.2.1:

$$[S_i, S_j]_+ = \frac{\hbar^2}{2}\,\delta_{ij}\,\mathbb{1}_2\ .$$

This is added to (*):

$$S_i\,S_j = \frac{\hbar^2}{4}\,\delta_{ij}\,\mathbb{1}_2 + i\,\frac{\hbar}{2}\sum_k \varepsilon_{ijk}\,S_k\ .$$

This means for the Pauli spin matrices:

$$\begin{aligned} \boldsymbol{\sigma} &= \frac{2}{\hbar}\,\mathbf{S}\ , \\ \sigma_i\sigma_j &= \delta_{ij}\,\mathbb{1}_2 + i\sum_k \varepsilon_{ijk}\,\sigma_k \end{aligned}$$

2. Because of the assumed commutability it is:

$$\begin{aligned}(\boldsymbol{\sigma}\cdot\mathbf{a})\,(\boldsymbol{\sigma}\cdot\mathbf{b}) &= \sum_{i,\,j} a_i b_j\,\sigma_i\sigma_j \overset{1.}{=} \sum_{i,\,j} a_i\,b_j\,\left(\delta_{ij}\,\mathbb{1}_2 + i\sum_k \varepsilon_{ijk}\,\sigma_k\right)\\ &= \left(\sum_i a_i\,b_i\right)\mathbb{1}_2 + i\sum_{ijk}\varepsilon_{ijk}\,a_i\,b_j\,\sigma_k = (\mathbf{a}\cdot\mathbf{b})\mathbb{1}_2 + i\mathbf{a}\cdot(\mathbf{b}\times\boldsymbol{\sigma})\end{aligned}$$

(see formula (1.197), Vol. 1 for the scalar triple product) ,

$$\begin{aligned}\mathbf{a}\cdot(\mathbf{b}\times\boldsymbol{\sigma}) &= (\mathbf{a}\times\mathbf{b})\cdot\boldsymbol{\sigma}\\ &= \boldsymbol{\sigma}\cdot(\mathbf{a}\times\mathbf{b})\,, \quad \text{since } \boldsymbol{\sigma} \text{ commutes with } \mathbf{a} \text{ and } \mathbf{b}.\end{aligned}$$

Therewith the assertion is proven!

Solution 5.2.3

1. We use the result from part 2. of Exercise 5.2.2:

$$(\mathbf{a}\cdot\boldsymbol{\sigma})(\mathbf{b}\cdot\boldsymbol{\sigma}) = \mathbf{a}\cdot\mathbf{b}\mathbb{1}_2 + i\,(\mathbf{a}\times\mathbf{b})\cdot\boldsymbol{\sigma}\,.$$

Therewith one finds:

$$\begin{aligned}\widehat{A}\cdot\widehat{B} &= a_0b_0\mathbb{1}_2 + a_0\mathbf{b}\cdot\boldsymbol{\sigma} + b_0\mathbf{a}\cdot\boldsymbol{\sigma} + (\mathbf{a}\cdot\boldsymbol{\sigma})(\mathbf{b}\cdot\boldsymbol{\sigma})\\ &= \underbrace{(a_0b_0 + \mathbf{a}\cdot\mathbf{b})}_{x}\,\mathbb{1}_2 + \underbrace{(a_0\mathbf{b} + b_0\mathbf{a} + i(\mathbf{a}\times\mathbf{b}))}_{\mathbf{y}}\cdot\boldsymbol{\sigma}\,.\end{aligned}$$

2. Special choice:

$$\widehat{B} = \widehat{A}^{-1} \;\curvearrowright\; \widehat{A}\cdot\widehat{B} = \mathbb{1}_2\,.$$

This requires according to part 1.:

$$\begin{aligned}a_0b_0 + \mathbf{a}\cdot\mathbf{b} &\overset{!}{=} 1\\ a_0\mathbf{b} + b_0\mathbf{a} + i(\mathbf{a}\times\mathbf{b}) &\overset{!}{=} 0\,.\end{aligned}$$

The latter equation tells us that the vectors $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{a}\times\mathbf{b}$ are linearly dependent. But now it holds also

$$(\mathbf{a}\times\mathbf{b}) \perp \mathbf{a}, \mathbf{b}\,.$$

That means that the second conditional equation can be fulfilled only if

$$\mathbf{a}\times\mathbf{b} = 0 \quad \text{and} \quad a_0\mathbf{b} + b_0\mathbf{a} = 0\,.$$

That yields

$$\mathbf{b} = -\frac{b_0}{a_0}\mathbf{a}\,.$$

This we insert into the first conditional equation:

$$1 \stackrel{!}{=} a_0 b_0 + \mathbf{a}\cdot\left(-\frac{b_0}{a_0}\mathbf{a}\right) = \frac{b_0}{a_0}\left(a_0^2 - \mathbf{a}\cdot\mathbf{a}\right) \ .$$

The bracket is unequal to zero:

$$b_0 = \frac{a_0}{a_0^2 - \mathbf{a}\cdot\mathbf{a}} \qquad \mathbf{b} = -\frac{1}{a_0^2 - \mathbf{a}\cdot\mathbf{a}}\,\mathbf{a}\,.$$

The inverse matrix $\widehat{B} = \widehat{A}^{-1}$ is therewith determined:

$$\widehat{A}^{-1} = b_0 \mathbb{1}_2 + \mathbf{b}\cdot\boldsymbol{\sigma} = \frac{1}{a_0^2 - \mathbf{a}\cdot\mathbf{a}}\left(a_0\mathbb{1}_2 - \mathbf{a}\cdot\boldsymbol{\sigma}\right) \ .$$

Solution 5.2.4

$$\begin{aligned}
S_x|\alpha\rangle &= \frac{\hbar}{2}\begin{pmatrix}0&1\\1&0\end{pmatrix}\begin{pmatrix}\alpha_+\\\alpha_-\end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix}\alpha_-\\\alpha_+\end{pmatrix}\ ,\\
S_y|\alpha\rangle &= \frac{\hbar}{2}\begin{pmatrix}0&-i\\i&0\end{pmatrix}\begin{pmatrix}\alpha_+\\\alpha_-\end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix}-i\,\alpha_-\\i\,\alpha_+\end{pmatrix}\ ,\\
S_z|\alpha\rangle &= \frac{\hbar}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}\alpha_+\\\alpha_-\end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix}\alpha_+\\-\alpha_-\end{pmatrix}\\
\Longrightarrow\ \langle S_x\rangle &= \langle\alpha|S_x|\alpha\rangle = \frac{\hbar}{2}\left(\alpha_+^*\,\alpha_- + \alpha_-^*\,\alpha_+\right) = \hbar\ \mathrm{Re}\ \left(\alpha_+^*\,\alpha_-\right)\ ,\\
\langle S_y\rangle &= \langle\alpha|S_y|\alpha\rangle = \frac{\hbar}{2}\,i\left(-\alpha_+^*\,\alpha_- + \alpha_-^*\,\alpha_+\right) = \hbar\ \mathrm{Im}\ \left(\alpha_+^*\,\alpha_-\right)\ ,\\
\langle S_z\rangle &= \langle\alpha|S_z|\alpha\rangle = \frac{\hbar}{2}\left(|\alpha_+|^2 - |\alpha_-|^2\right)\ .
\end{aligned}$$

Solution 5.2.5

1.

$$S_x = \frac{\hbar}{2}\begin{pmatrix}0&1\\1&0\end{pmatrix}\ ;\quad S_y = \frac{\hbar}{2}\begin{pmatrix}0&-i\\i&0\end{pmatrix}$$

Eigen-value equations:

$$\begin{aligned}
&\begin{pmatrix}-\lambda_x & \frac{\hbar}{2}\\ \frac{\hbar}{2} & -\lambda_x\end{pmatrix}\begin{pmatrix}a_x\\b_x\end{pmatrix} \stackrel{!}{=} 0\\
0 \stackrel{!}{=} &\begin{vmatrix}-\lambda_x & \frac{\hbar}{2}\\ \frac{\hbar}{2} & -\lambda_x\end{vmatrix} = \lambda_x^2 - \frac{\hbar^2}{4} \quad\Longrightarrow\quad \lambda_x = \pm\frac{\hbar}{2}\\
&\begin{pmatrix}-\lambda_y & -i\frac{\hbar}{2}\\ i\frac{\hbar}{2} & -\lambda_y\end{pmatrix}\begin{pmatrix}a_y\\b_y\end{pmatrix} \stackrel{!}{=} 0\\
0 \stackrel{!}{=} &\begin{vmatrix}-\lambda_y & -i\frac{\hbar}{2}\\ i\frac{\hbar}{2} & -\lambda_y\end{vmatrix} = \lambda_y^2 - \frac{\hbar^2}{4} \quad\Longrightarrow\quad \lambda_y = \pm\frac{\hbar}{2}
\end{aligned}$$

Eigen-values as measured values(!) of course the same as for S_z!

2.

$$|1\ 0\rangle \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix}\ ;\ |0\ 1\rangle \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Eigen-states for S_x:

$$\begin{pmatrix} -\frac{\hbar}{2} & \frac{\hbar}{2} \\ \frac{\hbar}{2} & -\frac{\hbar}{2} \end{pmatrix} \begin{pmatrix} a_x^{(+)} \\ b_x^{(+)} \end{pmatrix} = 0$$

$$\Longrightarrow \frac{\hbar}{2}(-a_x^{(+)} + b_x^{(+)}) = 0 \quad \Longrightarrow a_x^{(+)} = b_x^{(+)}$$

Normalization (except for a phase factor):

$$a_x^{(+)} = b_x^{(+)} = \frac{1}{\sqrt{2}}$$

$$\Longrightarrow |x_+\rangle = \frac{1}{\sqrt{2}}(|1\ 0\rangle + |0\ 1\rangle)$$

$$\begin{pmatrix} \frac{\hbar}{2} & \frac{\hbar}{2} \\ \frac{\hbar}{2} & \frac{\hbar}{2} \end{pmatrix} \begin{pmatrix} a_x^{(-)} \\ b_x^{(-)} \end{pmatrix} = 0$$

$$\Longrightarrow \frac{\hbar}{2}(a_x^{(-)} + b_x^{(-)}) = 0 \quad \Longrightarrow a_x^{(-)} = -b_x^{(-)}$$

Normalization:

$$a_x^{(-)2} + b_x^{(-)2} = 1 \quad \Longrightarrow \quad a_x^{(-)} = -b_x^{(-)} = \frac{1}{\sqrt{2}}$$

$$\Longrightarrow |x_-\rangle = \frac{1}{\sqrt{2}}(|1\ 0\rangle - |0\ 1\rangle)$$

Eigen-states for S_y:

$$\begin{pmatrix} -\frac{\hbar}{2} & -i\frac{\hbar}{2} \\ i\frac{\hbar}{2} & -\frac{\hbar}{2} \end{pmatrix} \begin{pmatrix} a_y^{(+)} \\ b_y^{(+)} \end{pmatrix} = 0$$

$$\Longrightarrow -\frac{\hbar}{2}a_y^{(+)} - i\frac{\hbar}{2}b_y^{(+)} = 0 \quad \Longrightarrow a_y^{(+)} = -ib_y^{(+)}$$

Normalization:

$$|a_y^{(+)}|^2 + |b_y^{(+)}|^2 = 1$$

$$\Longrightarrow a_y^{(+)} = \frac{1}{\sqrt{2}}\ ;\ b_y^{(+)} = i\frac{1}{\sqrt{2}}$$

$$\Longrightarrow |y_+\rangle = \frac{1}{\sqrt{2}}(|1\ 0\rangle + i|0\ 1\rangle)$$

$$\begin{pmatrix} \frac{\hbar}{2} & -i\frac{\hbar}{2} \\ i\frac{\hbar}{2} & \frac{\hbar}{2} \end{pmatrix} \begin{pmatrix} a_y^{(-)} \\ b_y^{(-)} \end{pmatrix} = 0$$

$$\Longrightarrow \frac{\hbar}{2}a_y^{(-)} - i\frac{\hbar}{2}b_y^{(-)} = 0 \quad \Longrightarrow a_y^{(-)} = ib_y^{(-)}$$

Normalization:

$$\begin{aligned} |a_y^{(-)}|^2 + |b_y^{(-)}|^2 &= 1 \\ \Longrightarrow\ a_y^{(-)} &= \frac{1}{\sqrt{2}}\ ;\ b_y^{(-)} = -i\frac{1}{\sqrt{2}} \\ \Longrightarrow\ |y_-\rangle &= \frac{1}{\sqrt{2}}(|1\ 0\rangle - i|0\ 1\rangle) \end{aligned}$$

Solution 5.2.6

1.

$$\begin{aligned} (\boldsymbol{\sigma}\cdot\mathbf{e})^2 &= \sum_{ij}\sigma_i\sigma_j\, e_i e_j = \sum_i \sigma_i^2\, e_i^2 + \sum_{ij}^{i\neq j}\sigma_i\sigma_j\, e_i e_j \\ \sum_i \sigma_i^2\, e_i^2 &\overset{(5.166)}{=} \mathbb{1}_2 \sum_i e_i^2 = \mathbb{1}_2 \\ \sum_{ij}^{i\neq j}(\sigma_i\sigma_j)\,(e_i e_j) &= \sum_{ji}^{j\neq i}(\sigma_j\sigma_i)(e_j e_i) \overset{(5.167)}{=} \sum_{ij}^{i\neq j}(-\sigma_i\sigma_j)(e_i e_j) = 0. \end{aligned}$$ *herewith :*

$$(\sigma\cdot\mathbf{e})^2 = \mathbb{1}_2\ .$$

2. The uncertainty is then zero only when $|\psi\rangle$ is an eigen-state of $\mathbf{S}\cdot\mathbf{e}$. It is therefore to require:

$$(\mathbf{S}\cdot\mathbf{e})|\psi\rangle \overset{!}{=} \pm\frac{\hbar}{2}|\psi\rangle \quad\Leftrightarrow\quad (\sigma\cdot\mathbf{e})|\psi\rangle \overset{!}{=} \pm|\psi\rangle\ .$$

According to (5.175) we have:

$$\sigma_+|+\rangle = 0 = \sigma_-|-\rangle\ ;\ \sigma_+|-\rangle = 2|+\rangle\ ;\ \sigma_-|+\rangle = 2|-\rangle\ .$$

It follows therewith:

$$\begin{aligned} (\sigma\cdot\mathbf{e})|+\rangle &= (\sigma_x e_x + \sigma_y e_y + \sigma_z e_z)|+\rangle \\ &= e_x\frac{1}{2}(\sigma_+ + \sigma_-)|+\rangle + e_y\frac{1}{2i}(\sigma_+ - \sigma_-)|+\rangle + e_z\sigma_z|+\rangle \\ &= (e_x + ie_y)|-\rangle + e_z|+\rangle \\ (\sigma\cdot\mathbf{e})|-\rangle &= (e_x - ie_y)|+\rangle - e_z|-\rangle \end{aligned}$$

It remains as conditional equation:

$$\begin{aligned} \frac{1}{\sqrt{2}}\Big((e_x + ie_y)|-\rangle + e_z|+\rangle\Big) &+ \frac{1+i}{2}\Big((e_x - ie_y)|+\rangle - e_z|-\rangle\Big) \\ &\overset{!}{=} \pm\left(\frac{1}{\sqrt{2}}|+\rangle + \frac{1+i}{2}|-\rangle\right) \end{aligned}$$

$$\curvearrowright \qquad \left(\frac{1}{\sqrt{2}}(e_x + ie_y) - \frac{1+i}{2}e_z \mp \frac{1+i}{2}\right)|-\rangle + \left(\frac{1}{\sqrt{2}}e_z + \frac{1+i}{2}(e_x - ie_y) \mp \frac{1}{\sqrt{2}}\right)|+\rangle = 0$$

$|+\rangle$ and $|-\rangle$ are linearly independent. The corresponding pre-factors must therefore already vanish:

$$\begin{aligned}\left(\frac{1}{\sqrt{2}}e_x - \frac{1}{2}e_z \mp \frac{1}{2}\right) + i\left(\frac{1}{\sqrt{2}}e_y - \frac{1}{2}e_z \mp \frac{1}{2}\right) &= 0\\ \left(\frac{1}{\sqrt{2}}e_z + \frac{1}{2}e_x + \frac{1}{2}e_y \mp \frac{1}{\sqrt{2}}\right) + i\left(\frac{1}{2}e_x - \frac{1}{2}e_y\right) &= 0\,.\end{aligned}$$

Separation of real and imaginary parts:

$$\begin{aligned}\frac{1}{\sqrt{2}}e_x - \frac{1}{2}e_z \mp \frac{1}{2} &= 0\\ \frac{1}{\sqrt{2}}e_y - \frac{1}{2}e_z \mp \frac{1}{2} &= 0\\ \frac{1}{\sqrt{2}}e_z + \frac{1}{2}e_x + \frac{1}{2}e_y \mp \frac{1}{\sqrt{2}} &= 0\\ \frac{1}{2}e_x - \frac{1}{2}e_y &= 0\,.\end{aligned}$$

The last equation yields immediately $e_x = e_y$. The first two equations are therefore identical, while the second and the third simplify to:

$$\begin{aligned}e_x - \frac{1}{\sqrt{2}}e_z \mp \frac{1}{\sqrt{2}} &= 0\\ \frac{1}{\sqrt{2}}e_z + e_x \mp \frac{1}{\sqrt{2}} &= 0\,.\end{aligned}$$

By addition and subtraction, respectively, from these two equations we obtain immediately e_x and e_z:

$$e_x = e_y = \pm\frac{1}{\sqrt{2}}\;;\; e_z = 0 \;\curvearrowright\; \mathbf{e} = \pm\frac{1}{\sqrt{2}}(1,1,0)\,.$$

Solution 5.2.7

1. Hamilton operator:

$$H = \eta\,\sigma_x\,.$$

Time evolution operator:

$$U(t,0) = \exp\left(-\frac{i}{\hbar}Ht\right) = \exp\left(-\frac{i}{\hbar}\eta\sigma_x t\right) = \cos\left(\frac{\eta}{\hbar}\sigma_x t\right) - i\sin\left(\frac{\eta}{\hbar}\sigma_x t\right)\,.$$

Pauli spin matrices:

$$\begin{aligned} n \in \mathbb{N}: \quad \sigma_x^{2n} &= \left(\sigma_x^2\right)^n \overset{(5.166)}{=} \mathbb{1}_2^n = \mathbb{1}_2 \\ \curvearrowright \quad \sigma_x^{2n+1} &= \sigma_x \ . \end{aligned}$$

This means:

$$\begin{aligned} \cos\left(\frac{\eta}{\hbar}\sigma_x t\right) &= \cos\left(\frac{\eta}{\hbar}t\right)\, \mathbb{1}_2 \\ \sin\left(\frac{\eta}{\hbar}\sigma_x t\right) &= \sin\left(\frac{\eta}{\hbar}t\right)\, \sigma_x \\ \curvearrowright \quad U(t,0) &= \cos\left(\frac{\eta}{\hbar}t\right)\, \mathbb{1}_2 - i\, \sin\left(\frac{\eta}{\hbar}t\right)\, \sigma_x \ . \end{aligned}$$

2.
$$|\psi(t)\rangle = U(t,0)\,|\psi(0)\rangle = \left(\cos\left(\frac{\eta}{\hbar}t\right)\, \mathbb{1}_2 - i\, \sin\left(\frac{\eta}{\hbar}t\right)\, \sigma_x\right)\, |+\rangle \ .$$

It is

$$\sigma_x|+\rangle = \frac{1}{2}(\sigma_+ + \sigma_-)|+\rangle = |-\rangle$$

and therewith

$$|\psi(t)\rangle = \cos\left(\frac{\eta}{\hbar}t\right)\, |+\rangle - i\, \sin\left(\frac{\eta}{\hbar}t\right)\, |-\rangle \ .$$

Probability:

$$W_+(t) = |\langle +|\psi(t)\rangle|^2 = \cos^2\left(\frac{\eta}{\hbar}t\right) = \frac{1}{2}\left(1 + \cos\left(\frac{2\eta}{\hbar}t\right)\right) \ .$$

Periodic function with the periodic time $\tau = \pi\hbar/\eta$.

3. It is a similar problem like the one, which was treated in the second part of Exercise 5.2.6. Requirement:

$$(\sigma \cdot \mathbf{e})\,|\psi(t)\rangle \overset{!}{=} +|\psi(t)\rangle \ ; \quad (\mathbf{e} = (e_x, e_y, e_z)) \ .$$

We take from Exercise 5.2.6:

$$\begin{aligned} (\sigma \cdot \mathbf{e})\,|+\rangle &= (e_x + ie_y)\,|-\rangle + e_z\,|+\rangle \\ (\sigma \cdot \mathbf{e})\,|-\rangle &= (e_x - ie_y)\,|+\rangle - e_z\,|-\rangle \ . \end{aligned}$$

For the state $|\psi(t)\rangle$ from part 2. it is then to require:

$$\begin{aligned} (\sigma \cdot \mathbf{e})\,|\psi(t)\rangle &= \cos\left(\frac{\eta}{\hbar}t\right)\,(\sigma \cdot \mathbf{e})\,|+\rangle - i\, \sin\left(\frac{\eta}{\hbar}t\right)\,(\sigma \cdot \mathbf{e})\,|-\rangle \\ &= \cos\left(\frac{\eta}{\hbar}t\right)\,(e_x + ie_y)\,|-\rangle + \cos\left(\frac{\eta}{\hbar}t\right)\,e_z|+\rangle \\ &\quad -i\, \sin\left(\frac{\eta}{\hbar}t\right)\,(e_x - ie_y)\,|+\rangle + i\, \sin\left(\frac{\eta}{\hbar}t\right)\,e_z\,|-\rangle \\ &\overset{!}{=} \cos\left(\frac{\eta}{\hbar}t\right)\, |+\rangle - i\, \sin\left(\frac{\eta}{\hbar}t\right)\, |-\rangle \ . \end{aligned}$$

This can be sorted a bit:

$$\begin{aligned}
&\left\{\cos\left(\frac{\eta}{\hbar}t\right)(e_x+ie_y)+i\,\sin\left(\frac{\eta}{\hbar}t\right)e_z+i\,\sin\left(\frac{\eta}{\hbar}t\right)\right\}|-\rangle\\
&+\left\{\cos\left(\frac{\eta}{\hbar}t\right)e_z-i\,\sin\left(\frac{\eta}{\hbar}t\right)(e_x-ie_y)-\cos\left(\frac{\eta}{\hbar}t\right)\right\}|+\rangle\\
=\;& 0\,.
\end{aligned}$$

$|+\rangle$ and $|-\rangle$ are linearly independent. It must therefore hold already:

$$\begin{aligned}
\cos\left(\frac{\eta}{\hbar}t\right)(e_x+ie_y)+i\,\sin\left(\frac{\eta}{\hbar}t\right)e_z+i\,\sin\left(\frac{\eta}{\hbar}t\right) &= 0\\
\cos\left(\frac{\eta}{\hbar}t\right)e_z-i\,\sin\left(\frac{\eta}{\hbar}t\right)(e_x-ie_y)-\cos\left(\frac{\eta}{\hbar}t\right) &= 0\,.
\end{aligned}$$

These equations must be fulfilled separately for real and imaginary parts:

$$\cos\left(\frac{\eta}{\hbar}t\right)e_x=0 \tag{A.1}$$

$$\cos\left(\frac{\eta}{\hbar}t\right)e_y+\sin\left(\frac{\eta}{\hbar}t\right)e_z=-\sin\left(\frac{\eta}{\hbar}t\right) \tag{A.2}$$

$$\cos\left(\frac{\eta}{\hbar}t\right)e_z-\sin\left(\frac{\eta}{\hbar}t\right)e_y=\cos\left(\frac{\eta}{\hbar}t\right) \tag{A.3}$$

$$\sin\left(\frac{\eta}{\hbar}t\right)e_x=0\,. \tag{A.4}$$

From (A.1) and (A.4) it follows directly:

$$e_x(t)\equiv 0\,.$$

We multiply (A.2) by $\sin\left(\frac{\eta}{\hbar}t\right)$ and (A.3) by $\cos\left(\frac{\eta}{\hbar}t\right)$:

$$\begin{aligned}
\sin\left(\frac{\eta}{\hbar}t\right)\cos\left(\frac{\eta}{\hbar}t\right)e_y+\sin^2\left(\frac{\eta}{\hbar}t\right)e_z &= -\sin^2\left(\frac{\eta}{\hbar}t\right)\\
\cos^2\left(\frac{\eta}{\hbar}t\right)e_z-\cos\left(\frac{\eta}{\hbar}t\right)\sin\left(\frac{\eta}{\hbar}t\right)e_y &= \cos^2\left(\frac{\eta}{\hbar}t\right)\,.
\end{aligned}$$

We build the sum of these equations:

$$e_z(t)=\cos^2\left(\frac{\eta}{\hbar}t\right)-\sin^2\left(\frac{\eta}{\hbar}t\right)=\cos\left(2\frac{\eta}{\hbar}t\right)\,.$$

On the other hand, from the difference of these equations follows:

$$\begin{aligned}
&2\sin\left(\frac{\eta}{\hbar}t\right)\cos\left(\frac{\eta}{\hbar}t\right)e_y+\left(\sin^2\left(\frac{\eta}{\hbar}t\right)-\cos^2\left(\frac{\eta}{\hbar}t\right)\right)e_z\\
&=-\sin^2\left(\frac{\eta}{\hbar}t\right)-\cos^2\left(\frac{\eta}{\hbar}t\right)\\
\Leftrightarrow\;& \sin\left(2\frac{\eta}{\hbar}t\right)e_y-\cos\left(2\frac{\eta}{\hbar}t\right)e_z=-1\\
\Leftrightarrow\;& \sin\left(2\frac{\eta}{\hbar}t\right)e_y-\cos^2\left(2\frac{\eta}{\hbar}t\right)=-1\\
\Leftrightarrow\;& \sin\left(2\frac{\eta}{\hbar}t\right)e_y=-1+\cos^2\left(2\frac{\eta}{\hbar}t\right)=-\sin^2\left(2\frac{\eta}{\hbar}t\right)\\
\Leftrightarrow\;& e_y(t)=-\sin\left(2\frac{\eta}{\hbar}t\right)\,.
\end{aligned}$$

The tip of the unit vector thus precesses as function of time with the angular velocity $2\eta/\hbar$ (periodic time $\pi\hbar/\eta$, see part 2.) in the yz-plane:

$$\mathbf{e} = \left(0, -\sin\left(2\frac{\eta}{\hbar}t\right), \cos\left(2\frac{\eta}{\hbar}t\right)\right) .$$

Solution 5.2.8
Sufficient:
Let $|\varphi\rangle$ be an eigen-state of S_z:

$$\begin{aligned} |\varphi\rangle &= \left|\frac{3}{2}\,\frac{1}{2}\right\rangle \\ \Longrightarrow \langle\varphi|S_z|\varphi\rangle &= \frac{\hbar}{2} , \end{aligned}$$

$$\begin{aligned} S_x &= \frac{1}{2}\left(S_+ + S_-\right) , \\ S_y &= \frac{1}{2i}\left(S_+ - S_-\right) \end{aligned}$$

$\Longrightarrow$ because of the orthonormality of the states $|(3/2)\,m\rangle$:

$$\langle\varphi|S_x|\varphi\rangle = \langle\varphi|S_y|\varphi\rangle = 0 .$$

The eigen-state $|(3/2)\,(1/2)\rangle$ thus indeed leads to the given expectation values!
Necessary:
Counter-example:

$$|\varphi\rangle = a\left|\frac{3}{2}\,\frac{3}{2}\right\rangle + b\left|\frac{3}{2}\,-\frac{3}{2}\right\rangle ; \quad a, b \ \text{ real} , \quad \langle\varphi|\varphi\rangle = 1 .$$

At first it is:

$$\begin{aligned} \langle\varphi|S_\pm|\varphi\rangle &= 0 \\ \Longrightarrow \langle\varphi|S_x|\varphi\rangle &= \langle\varphi|S_y|\varphi\rangle = 0 , \\ \langle\varphi|S_z|\varphi\rangle &= \frac{3}{2}\,\hbar\,(a^2 - b^2) \stackrel{!}{=} \frac{\hbar}{2} \\ \Longrightarrow a^2 - b^2 &= \frac{1}{3} , \\ \text{Normalization:}\quad a^2 + b^2 &= 1 \\ \Longrightarrow a &= \sqrt{\frac{2}{3}} , \quad b = \sqrt{\frac{1}{3}} . \end{aligned}$$

The state

$$|\varphi\rangle = \sqrt{\frac{2}{3}}\left|\frac{3}{2}\,\frac{3}{2}\right\rangle + \sqrt{\frac{1}{3}}\left|\frac{3}{2}\,-\frac{3}{2}\right\rangle$$

has the expectation values

$$\langle\varphi|S_z|\varphi\rangle = \frac{\hbar}{2}\,; \quad \langle\varphi|S_x|\varphi\rangle = \langle\varphi|S_y|\varphi\rangle = 0\,,$$

but is not an eigen-state of S_z:

$$S_z|\varphi\rangle = \frac{3}{2}\,\hbar\left(\sqrt{\frac{2}{3}}\left|\frac{3}{2}\,\frac{3}{2}\right\rangle - \sqrt{\frac{1}{3}}\left|\frac{3}{2}-\frac{3}{2}\right\rangle\right) \neq c|\varphi\rangle\,.$$

Solution 5.2.9
Answer: yes
Reason:

$$\begin{aligned}\langle\psi|S_z|\psi\rangle &= \sum_{m,m'}\left\langle\psi|\frac{3}{2}\,m\right\rangle\left\langle\frac{3}{2}\,m\,|S_z|\,\frac{3}{2}\,m'\right\rangle\left\langle\frac{3}{2}\,m'|\psi\right\rangle\\ &= \sum_{m,m'}\hbar\,m'\,\delta_{mm'}\left\langle\psi|\frac{3}{2}\,m\right\rangle\left\langle\frac{3}{2}\,m'|\psi\right\rangle\\ &= \hbar\sum_m m\left|\left\langle\psi|\frac{3}{2}\,m\right\rangle\right|^2 \stackrel{!}{=} \frac{3}{2}\hbar\,.\end{aligned}$$

Normalization:

$$\langle\psi|\psi\rangle = \sum_m\left|\left\langle\psi|\frac{3}{2}\,m\right\rangle\right|^2 \stackrel{!}{=} 1\,.$$

Combination of the two equations:

$$\sum_m \underbrace{\left(m-\frac{3}{2}\right)}_{\leq 0}\left|\underbrace{\left\langle\psi|\frac{3}{2}\,m\right\rangle}_{\geq 0}\right|^2 = 0\,.$$

Satisfiable only if

$$\left\langle\psi|\frac{3}{2}\,m\right\rangle = 0 \quad \forall m \neq \frac{3}{2} \Longrightarrow\ |\psi\rangle \sim \left|\frac{3}{2}\,\frac{3}{2}\right\rangle\ :\ \text{eigen-state!}$$

Solution 5.2.10
Schrödinger equation for an electron in the electromagnetic field (5.191):

$$\begin{aligned}i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\psi_+(\mathbf{r},t)\\ \psi_-(\mathbf{r},t)\end{pmatrix} &= \left[\left(\frac{1}{2m}(\mathbf{p}+e\mathbf{A}(\mathbf{r},t))^2 - e\varphi(\mathbf{r},t)\right)\mathbb{1}_2\right.\\ &\qquad \left.+\mu_{\mathrm{B}}\,\sigma\cdot\mathbf{B}(t)\right]\begin{pmatrix}\psi_+(\mathbf{r},t)\\ \psi_-(\mathbf{r},t)\end{pmatrix}.\end{aligned}$$

Let the magnetic induction be homogeneous, but possibly time-dependent.

Separation ansatz for orbital and spin dynamics:

$$\begin{pmatrix} \psi_+(\mathbf{r},t) \\ \psi_-(\mathbf{r},t) \end{pmatrix} \equiv \left|\psi_{\frac{1}{2}}(\mathbf{r},t)\right\rangle = \eta(\mathbf{r},t)\,\left|\chi_{\frac{1}{2}}(t)\right\rangle \quad ; \quad \left|\chi_{\frac{1}{2}}(t)\right\rangle = \begin{pmatrix} \chi_+(t) \\ \chi_-(t) \end{pmatrix} .$$

Insertion into the Schrödinger equation:

$$\begin{aligned} \left(i\hbar\frac{\partial}{\partial t}\eta(\mathbf{r},t)\right)\left|\chi_{\frac{1}{2}}(t)\right\rangle \qquad & +i\hbar\eta(\mathbf{r},t)\frac{d}{dt}\left|\chi_{\frac{1}{2}}(t)\right\rangle \\ = \quad & \left(\frac{1}{2m}(\mathbf{p}+e\mathbf{A}(\mathbf{r},t))^2\eta(\mathbf{r},t)\right)\left|\chi_{\frac{1}{2}}(t)\right\rangle \\ & -e\varphi(\mathbf{r},t)\eta(\mathbf{r},t)\,\left|\chi_{\frac{1}{2}}(t)\right\rangle \\ & +\mu_{\mathrm{B}}\,\eta(\mathbf{r},t)\,\sigma\cdot\mathbf{B}(t)\,\left|\chi_{\frac{1}{2}}(t)\right\rangle . \end{aligned}$$

Division by η:

$$\begin{aligned} & \frac{1}{\eta(\mathbf{r},t)}\left[\left(\frac{1}{2m}(\mathbf{p}+e\mathbf{A}(\mathbf{r},t))^2-e\varphi(\mathbf{r},t)\right)\eta(\mathbf{r},t)-\left(i\hbar\frac{\partial}{\partial t}\eta(\mathbf{r},t)\right)\right]\left|\chi_{\frac{1}{2}}(t)\right\rangle \\ & =\left(i\hbar\frac{d}{dt}-\mu_{\mathrm{B}}\,\sigma\cdot\mathbf{B}(t)\right)\left|\chi_{\frac{1}{2}}(t)\right\rangle . \end{aligned}$$

The right-hand side of the equation is dependent only on t. The pre-factor of the spinor on the left-hand side must therefore also be a pure time-function:

$$D(t)\equiv\frac{1}{\eta(\mathbf{r},t)}\left[\left(\frac{1}{2m}(\mathbf{p}+e\mathbf{A}(\mathbf{r},t))^2-e\varphi(\mathbf{r},t)\right)\eta(\mathbf{r},t)-\left(i\hbar\frac{\partial}{\partial t}\eta(\mathbf{r},t)\right)\right] .$$

It the remains to be solved:

$$D(t)\,\left|\chi_{\frac{1}{2}}(t)\right\rangle=\left(i\hbar\frac{d}{dt}-\mu_{\mathrm{B}}\,\sigma\cdot\mathbf{B}(t)\right)\,\left|\chi_{\frac{1}{2}}(t)\right\rangle .$$

That succeeds with the ansatz:

$$\left|\chi_{\frac{1}{2}}(t)\right\rangle=|\widehat{\chi}(t)\rangle\,\exp\left(-\frac{i}{\hbar}\int_0^t D(t')\,dt'\right) .$$

Insertion:

$$\begin{aligned} D(t)\,|\widehat{\chi}(t)\rangle\,e^{-\frac{i}{\hbar}\int_0^t D(t')\,dt'} \quad = \quad & i\hbar\left(-\frac{i}{\hbar}D(t)\right)|\widehat{\chi}(t)\rangle\,e^{-\frac{i}{\hbar}\int_0^t D(t')\,dt'} \\ & +\left(i\hbar\frac{d}{dt}\,|\widehat{\chi}(t)\rangle\right)e^{-\frac{i}{\hbar}\int_0^t D(t')\,dt'} \\ & -\mu_{\mathrm{B}}\,\sigma\cdot\mathbf{B}(t)\,|\widehat{\chi}(t)\rangle\,e^{-\frac{i}{\hbar}\int_0^t D(t')\,dt'} . \end{aligned}$$

$|\widehat{\chi}(t)\rangle$ thus has to fulfill the following differential equation which is independent of $D(t)$:

$$\left(i\hbar\frac{d}{dt} - \mu_{\mathrm{B}}\,\sigma\cdot\mathbf{B}(t)\right)\,|\widehat{\chi}(t)\rangle = 0\,. \tag{A.5}$$

Otherwise it must be:

$$D(t)\,\eta(\mathbf{r},t) = \left(\frac{1}{2m}(\mathbf{p}+e\mathbf{A}(\mathbf{r},t))^2 - e\varphi(\mathbf{r},t)\right)\eta(\mathbf{r},t) - i\hbar\frac{\partial}{\partial t}\eta(\mathbf{r},t)\,.$$

For the solution we choose a similar ansatz as that above for the spin-spinor:

$$\eta(\mathbf{r},t) = \widehat{\eta}(\mathbf{r},t)\,\exp\left(+\frac{i}{\hbar}\int\limits_0^t D(t')\,dt'\right)\,.$$

That leads to:

$$\begin{aligned} D(t)\,\widehat{\eta}(\mathbf{r},t)\,e^{\frac{i}{\hbar}\int_0^t D(t')\,dt'} \quad = \quad & \left(\frac{1}{2m}(\mathbf{p}+e\mathbf{A}(\mathbf{r},t))^2 - e\varphi(\mathbf{r},t)\right)\widehat{\eta}(\mathbf{r},t)\,e^{\frac{i}{\hbar}\int_0^t D(t')\,dt'} \\ & -i\hbar\left(\frac{\partial}{\partial t}\widehat{\eta}(\mathbf{r},t)\right)\,e^{\frac{i}{\hbar}\int_0^t D(t')\,dt'} \\ & -i\hbar\left(\frac{i}{\hbar}D(t)\right)\widehat{\eta}(\mathbf{r},t)\,e^{\frac{i}{\hbar}\int_0^t D(t')\,dt'} \end{aligned}$$

Therewith what is left is a differential equation which is independent of $D(t)$:

$$\left(i\hbar\frac{\partial}{\partial t} - \frac{1}{2m}(\mathbf{p}+e\mathbf{A}(\mathbf{r},t))^2 + e\varphi(\mathbf{r},t)\right)\,\widehat{\eta}(\mathbf{r},t) = 0\,. \tag{A.6}$$

Spin and orbital part of the two-component spinor can therefore be determined independently of each other via (A.5) and (A.6). Because of

$$\left|\psi_{\frac{1}{2}}(\mathbf{r},t)\right\rangle = \eta(\mathbf{r},t)\,\left|\chi_{\frac{1}{2}}(t)\right\rangle = \widehat{\eta}(\mathbf{r},t)\,|\widehat{\chi}(t)\rangle$$

the problem is therewith solved.

Solution 5.2.11

We introduce for abbreviation the *Larmor-frequency of the electron*:

$$\omega_{\mathrm{L}} = \frac{\mu_{\mathrm{B}}}{\hbar}\,B\,.$$

Heisenberg's equation of motion ((3.191), Vol. 6):

$$
\begin{aligned}
i\hbar \dot{S}_{\substack{z\\y\\x}}(t) &= \left[S_{\substack{z\\y\\x}}, H \right]_- (t) = 2\frac{\omega_\mathrm{L}}{B} \left[S_{\substack{z\\y\\x}}, S_x B_x + S_y B_y + S_z B_z \right]_- \\
&= i\hbar 2\frac{\omega_\mathrm{L}}{B} \begin{cases} S_y B_x - S_x B_y \\ -S_z B_x + S_x B_z \\ S_z B_y - S_y B_z \end{cases} = i\hbar 2\frac{\omega_\mathrm{L}}{B} \begin{cases} -(\mathbf{S}\times\mathbf{B})_z \\ -(\mathbf{S}\times\mathbf{B})_y \\ -(\mathbf{S}\times\mathbf{B})_x \end{cases} .
\end{aligned}
$$

The equation of motion therefore reads:

$$
\dot{\mathbf{S}}(t) = -2\frac{\omega_\mathrm{L}}{B} (\mathbf{S}\times\mathbf{B})(t) = (\boldsymbol{\mu}_S \times \mathbf{B})(t) .
$$

The operator of the time-differentiated spin thus corresponds to the torque, which is exerted by the field $\mathbf{B}$ on the magnetic spin moment (see (3.53), Vol. 3). According to Ehrenfest's theorem ((3.211), Vol. 6) the equation of motion of the expectation values of observables is formally same in all the three pictures. Therefore we can directly conclude from the last equation, which uses the Heisenberg picture:

$$
\frac{d}{dt}\langle \mathbf{S} \rangle_t = -2\frac{\omega_\mathrm{L}}{B} (\langle \mathbf{S} \rangle_t \times \mathbf{B}) .
$$

We now take: $\mathbf{B} = B\,\mathbf{e}_z$. The equations of motion then read one by one:

$$
\begin{aligned}
\frac{d}{dt}\langle S_x \rangle_t &= -2\omega_\mathrm{L} \langle S_y \rangle_t , \\
\frac{d}{dt}\langle S_y \rangle_t &= 2\omega_\mathrm{L} \langle S_x \rangle_t , \\
\frac{d}{dt}\langle S_z \rangle_t &= 0 .
\end{aligned}
$$

By one more differentiation of the first two equations we find a familiar differential equation,

$$
\frac{d^2}{dt^2}\langle S_{x,y} \rangle_t + (2\omega_\mathrm{L})^2 \langle S_{x,y} \rangle_t = 0,
$$

which can easily be integrated:

$$
\begin{aligned}
\langle S_x \rangle_t &= a \sin 2\omega_\mathrm{L}\, t + b \cos 2\omega_\mathrm{L}\, t , \\
\langle S_y \rangle_t &= \hat{a} \sin 2\omega_\mathrm{L}\, t + \hat{b} \cos 2\omega_\mathrm{L}\, t .
\end{aligned}
$$

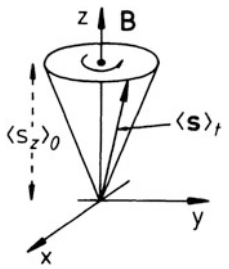


Figure A.3:

With the initial conditions,

$$\begin{aligned} \langle S_x\rangle_{t=0} &= b\,, \\ \frac{d}{dt}\,\langle S_x\rangle_t\Big|_{t=0} &= 2\omega_{\mathrm{L}}\,a = -2\omega_{\mathrm{L}}\langle S_y\rangle_{t=0}\,, \\ \langle S_y\rangle_{t=0} &= \hat{b}\,, \\ \frac{d}{dt}\,\langle S_y\rangle_t\Big|_{t=0} &= 2\omega_{\mathrm{L}}\,\hat{a} = 2\omega_{\mathrm{L}}\langle S_x\rangle_{t=0}\,, \end{aligned}$$

we have the complete solutions:

$$\begin{aligned} \langle S_x\rangle_t &= \langle S_y\rangle_{t=0}\sin 2\omega_{\mathrm{L}}\,t + \langle S_x\rangle_{t=0}\cos 2\omega_{\mathrm{L}}\,t\,, \\ \langle S_y\rangle_t &= -\langle S_x\rangle_{t=0}\sin 2\omega_{\mathrm{L}}\,t + \langle S_y\rangle_{t=0}\cos 2\omega_{\mathrm{L}}\,t\,, \\ \langle S_z\rangle_t &= \langle S_z\rangle_{t=0}\,. \end{aligned}$$

The expectation value $\langle\mathbf{S}\rangle_t$ of the spin operator thus precesses with twice the Larmor frequency around the magnetic field $\mathbf{B}$ (Fig. A.3). The angular aperture of the precession cone is found by the initial conditions $\langle S_x\rangle_{t=0}$ and $\langle S_y\rangle_{t=0}$.

Solution 5.2.12

In the *S_z-representation* S_x and S_y read:

$$S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\;;\quad S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\,,$$

and therewith A:

$$A = \alpha\,\frac{\hbar}{2}\begin{pmatrix} 0 & 1-i \\ 1+i & 0 \end{pmatrix}\,.$$

Eigen-values from the secular determinant:

$$\begin{aligned} &\det\left(A - \lambda\,\mathbb{1}_2\right) \stackrel{!}{=} 0\,, \\ &\det\begin{pmatrix} -\lambda & (1-i)\,\alpha\,\frac{\hbar}{2} \\ (1+i)\,\alpha\,\frac{\hbar}{2} & -\lambda \end{pmatrix} = \lambda^2 - \alpha^2\,\frac{\hbar^2}{4}\,2 \\ &\Longrightarrow\;\; \lambda_\pm = \pm\frac{\alpha\,\hbar}{\sqrt{2}}\,. \end{aligned}$$

Eigen-states from:

$$\begin{aligned} A|\lambda_\pm\rangle = \pm\frac{\alpha\,\hbar}{\sqrt{2}}|\lambda_\pm\rangle\,; \quad |\lambda_\pm\rangle &= \begin{pmatrix} a_\pm \\ b_\pm \end{pmatrix} \\ \iff \begin{pmatrix} \mp\sqrt{2} & 1-i \\ 1+i & \mp\sqrt{2} \end{pmatrix} \begin{pmatrix} a_\pm \\ b_\pm \end{pmatrix} &\stackrel{!}{=} 0 \end{aligned}$$

$$\begin{aligned} \implies \mp\sqrt{2}\,a_\pm + (1-i)\,b_\pm &= 0\,, \\ (1+i)\,a_\pm \mp \sqrt{2}\,b_\pm &= 0 \\ \implies b_\pm &= \pm\frac{1+i}{\sqrt{2}}\,a_\pm\,. \end{aligned}$$

Normalization: $|b_\pm|^2 + |a_\pm|^2 \stackrel{!}{=} 1$

$$\implies 1 = |a_\pm|^2 \left(\frac{2}{2}+1\right)\,.$$

Choose the phase so that $a_\pm$ real:

$$a_\pm = \frac{1}{\sqrt{2}}\,; \quad b_\pm = \pm\frac{1}{2}\,(1+i)\,.$$

Therewith the eigen-states in the *S_z-representation* read:

$$|\lambda_+\rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{2}\,(1+i) \end{pmatrix}\,; \quad |\lambda_-\rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{2}\,(1+i) \end{pmatrix}\,.$$

Probabilities:

$$\left|\langle - |\lambda_+\rangle\right|^2 = \left|\frac{1}{2}\,(1+i)\right|^2 = \frac{1}{2}\,; \quad \left|\langle - |\lambda_-\rangle\right|^2 = \frac{1}{2}\,.$$

Solution 5.2.13

Hamilton operator in the S_z-representation:

$$H = -\mu_s\,\frac{\hbar}{2}\,(\sigma_x\,B_x + \sigma_y\,B_y + \sigma_z\,B_z) = -\mu_s\,\frac{\hbar}{2}\begin{pmatrix} B_0 & B_1\,e^{i\omega t} \\ B_1\,e^{-i\omega t} & -B_0 \end{pmatrix}\,.$$

Schrödinger equation for the general state:

$$\begin{aligned} |\psi(t)\rangle &= \begin{pmatrix} a_+(t) \\ a_-(t) \end{pmatrix}\,, \\ i\,\hbar \begin{pmatrix} \dot{a}_+(t) \\ \dot{a}_-(t) \end{pmatrix} &= -\mu_s\,\frac{\hbar}{2}\begin{pmatrix} B_0\,a_+(t) + B_1\,e^{i\omega t}\,a_-(t) \\ B_1\,e^{-i\omega t}\,a_+(t) - B_0\,a_-(t) \end{pmatrix}\,. \end{aligned}$$

We differentiate the equation for $a_-(t)$ once more with respect to time:

$$\begin{aligned}
\ddot{a}_-(t) &= \frac{i\,\mu_s}{2}\left(-i\,\omega\,B_1\,e^{-i\omega t}\,a_+(t) + B_1\,e^{-i\omega t}\,\dot{a}_+(t) - B_0\,\dot{a}_-(t)\right) \\
&= \frac{i\,\mu_s}{2}\left[-i\,\omega\left(-i\,\frac{2}{\mu_s}\,\dot{a}_-(t) + B_0\,a_-(t)\right)\right. \\
&\quad + B_1\,e^{-i\omega t}\,\frac{i\,\mu_s}{2}\left(B_0\,a_+(t) + B_1\,e^{i\omega t}\,a_-(t)\right) \\
&\quad \left. - B_0\,\frac{i\,\mu_s}{2}\left(B_1\,e^{-i\omega t}\,a_+(t) - B_0\,a_-(t)\right)\right] \\
&= -i\,\omega\,\dot{a}_-(t) + a_-(t)\left[\frac{1}{2}\,\omega\,\mu_s\,B_0 - \frac{1}{4}\,\mu_s^2\,\left(B_1^2 + B_0^2\right)\right] .
\end{aligned}$$

Solution ansatz :

$$\begin{aligned}
a_-(t) &\sim e^{i\alpha t} \\
\Longrightarrow\; -\alpha^2 &= \alpha\,\omega + \left[-\left(\frac{1}{2}\,\mu_s\,B_0 - \frac{1}{2}\,\omega\right)^2 + \frac{1}{4}\,\omega^2 - \frac{1}{4}\,\mu_s^2\,B_1^2\right] \\
\Longleftrightarrow\; \frac{1}{4}\left[(\mu_s\,B_0 - \omega)^2 + \mu_s^2\,B_1^2\right] &= \left(\alpha + \frac{1}{2}\,\omega\right)^2 .
\end{aligned}$$

We abbreviate:

$$\Delta = \frac{1}{2}\sqrt{(\mu_s\,B_0 - \omega)^2 + \mu_s^2\,B_1^2} .$$

It follows therewith:

$$\alpha_\pm = -\frac{1}{2}\,\omega \pm \Delta .$$

The general solution for $a_-(t)$ therefore reads:

$$a_-(t) = e^{-(i/2)\omega t}\,\left[A\,e^{i\,\Delta t} + B\,e^{-i\,\Delta t}\right] .$$

Initial conditions:

$$\begin{aligned}
a_-(t=0) &= 0\,; \quad a_+(t=0) = 1 \\
\Longrightarrow\; A &= -B\,, \\
\dot{a}_-(t=0) &= i\,\Delta\,[A - B] = 2i\,\Delta\,A \stackrel{!}{=} \frac{i\,\mu_s}{2}\,B_1 \\
\Longrightarrow\; A &= \frac{\mu_s}{4\,\Delta}\,B_1 .
\end{aligned}$$

Solution:

$$a_-(t) = \frac{i\,\mu_s}{2\,\Delta}\,B_1\,e^{-\frac{i}{2}\omega t}\,\sin\Delta t .$$

Transition probability:

$$w_-(t) = |a_-(t)|^2 = \frac{\mu_s^2\,B_1^2}{(\mu_s\,B_0 - \omega)^2 + \mu_s^2\,B_1^2}\,\sin^2\frac{1}{2}\,\sqrt{(\mu_s\,B_0 - \omega)^2 + \mu_s^2\,B_1^2}\;t\;.$$

This probability is in general very small, since in the experiment $B_0 \gg B_1$ must be chosen. But when the frequency ω of the alternating field approaches $\mu_s B_0$, then the pre-factor will be of the order of magnitude 1:

$$w_-(t) \underset{\omega \to \mu_s B_0}{\longrightarrow} \sin^2\left(\frac{1}{2}\mu_s B_1 t\right) .$$

At the points of time

$$t_n = \frac{(2n+1)\pi}{\mu_s B_1} ; \quad n = 0, 1, 2, \ldots$$

the transition probability even becomes 1. In the field the energies of the states $|+\rangle$ and $|-\rangle$ differ by the energy $\Delta E \approx \hbar \mu_s B_0$. Since this energy must be taken from the applied field, the resonance frequency $\omega_0 = \mu_s B_0$ is precisely observable by the energy absorption. This procedure (*paramagnetic resonance*) allows for the determination of the magnetic moment μ_s.

Solution 5.2.14

1. Homogeneous magnetic field:

$$\mathbf{B} = \frac{B}{\sqrt{2}}(0, 1, 1) .$$

Vector potential

$$\begin{aligned} \mathbf{B} &\overset{!}{=} \text{curl}\mathbf{A} \\ 0 &\overset{!}{=} \text{div}\mathbf{A} \ \text{(Coulomb gauge!)} . \end{aligned}$$

This means:

$$\begin{aligned} 0 &= \frac{\partial}{\partial y}A_z - \frac{\partial}{\partial z}A_y \\ \frac{1}{\sqrt{2}}B &= \frac{\partial}{\partial z}A_x - \frac{\partial}{\partial x}A_z \\ \frac{1}{\sqrt{2}}B &= \frac{\partial}{\partial x}A_y - \frac{\partial}{\partial y}A_x . \end{aligned}$$

Possible choice:

$$\mathbf{A}(\mathbf{r}) = \frac{1}{2\sqrt{2}} B\,(z - y, x, -x) .$$

It holds also:

$$\mathbf{B} \times \mathbf{r} = \frac{1}{\sqrt{2}} B\,(z - y, x, -x) \quad \curvearrowright \quad \mathbf{A}(\mathbf{r}) = \frac{1}{2}(\mathbf{B} \times \mathbf{r}) .$$

Canonical momentum:

$$\mathbf{p} = m\dot{\mathbf{r}} + q\mathbf{A}(\mathbf{r}) .$$

Hamilton function:

$$H = \frac{1}{2m}\left(\mathbf{p} - q\mathbf{A}(\mathbf{r})\right)^2 + qEx\,.$$

Now quantization, whereby p_i and x_i become operators. It follows as Hamilton operator:

$$H = \frac{1}{2m}\left(\mathbf{p}^2 + q^2\mathbf{A}^2(\mathbf{r}) - q\mathbf{p}\cdot\mathbf{A}(\mathbf{r}) - q\mathbf{A}(\mathbf{r})\cdot\mathbf{p}\right) + qEx\,.$$

Position representation and Coulomb gauge:

$$\mathbf{p}\cdot\mathbf{A}(\mathbf{r}) = \frac{\hbar}{i}(\nabla\cdot\mathbf{A}(\mathbf{r}) + \mathbf{A}(\mathbf{r})\cdot\nabla) = \frac{\hbar}{i}\mathbf{A}(\mathbf{r})\cdot\nabla = \mathbf{A}(\mathbf{r})\cdot\mathbf{p}\,.$$

In the Coulomb gauge $\mathbf{A}$ and $\mathbf{p}$ commute.

$$\begin{aligned} H &= \left(\frac{1}{2m}\mathbf{p}^2 + qEx\right) + \frac{1}{2m}q^2\mathbf{A}^2(\mathbf{r}) - \frac{q}{m}\mathbf{A}(\mathbf{r})\cdot\mathbf{p} \\ \frac{1}{2m}q^2\mathbf{A}^2(\mathbf{r}) &= \frac{q^2}{16m}\left((z-y)^2 + 2x^2\right)\mathbf{B}^2 \\ \frac{q}{m}\mathbf{A}(\mathbf{r})\cdot\mathbf{p} &= \frac{q}{2m}(\mathbf{B}\times\mathbf{r})\cdot\mathbf{p} = \frac{q}{2m}(\mathbf{r}\times\mathbf{p})\cdot\mathbf{B} = \frac{q}{2m}\mathbf{L}\cdot\mathbf{B}\,. \end{aligned}$$

$\mathbf{L}$ is the orbital angular momentum. We are left with the

$$H = \left(\frac{1}{2m}\mathbf{p}^2 + qEx\right) - \frac{q}{2m}\mathbf{L}\cdot\mathbf{B} + \frac{q^2}{16m}\left((z-y)^2 + 2x^2\right)\mathbf{B}^2\,.$$

Operator of the magnetic moment

$$\boldsymbol{\mu} = -\nabla_{\mathrm{B}}H = \frac{q}{2m}\mathbf{L} - \frac{q^2}{8m}\left((z-y)^2 + 2x^2\right)\mathbf{B}\,.$$

The first term represents a *permanent* magnetic moment (if $\mathbf{L} \neq 0$), whereas the second summand obviously vanishes after switching off the magnetic field. It thus represents an *induced* moment, oppositely directed to the exciting field (induction effect, Lenz's law).

2. It follows because of $B_x = 0$:

$$\begin{aligned} \mu_x &= \frac{q}{2m}L_x \\ \mu_y &= \frac{q}{2m}L_y - \frac{q^2}{8\sqrt{2}m}\left((z-y)^2 + 2x^2\right)B\,. \end{aligned}$$

We calculate therewith:

- $$[\mu_x,\, p_x]_- = \frac{q}{2m}\,[L_x,\, p_x]_-\ .$$

We use the vector formula (5.43)

$$[\mathbf{e}_i \cdot \mathbf{L},\, \mathbf{e}_j \cdot \mathbf{A}]_- = i\hbar(\mathbf{e}_i \times \mathbf{e}_j) \cdot \mathbf{A} \; .$$

$\mathbf{A}$ is thereby an arbitrary vector operator. We choose $\mathbf{A} = \mathbf{p}$:

$$[\mu_x,\, p_x]_- = \frac{q}{2m}\,[L_x,\, p_x]_- = \frac{q}{2m} i\hbar(\mathbf{e}_x \times \mathbf{e}_x) \cdot \mathbf{p} = 0 \; .$$

- $$[\mu_y,\, p_x]_- = \frac{q}{2m}\,[L_y,\, p_x]_- - \frac{q^2}{8\sqrt{2}m}\left[2x^2\, B,\, p_x\right]_- \; .$$

  We use again the above vector formula:

$$\begin{aligned} [L_y,\, p_x]_- &= i\hbar(\mathbf{e}_y \times \mathbf{e}_x) \cdot \mathbf{p} = -i\hbar p_z \\ \left[2x^2\, B,\, p_x\right]_- &= 2B\left(x\,[x,\, p_x]_- + [x,\, p_x]_-\, x\right) = 4i\hbar B x \\ \curvearrowright \quad [\mu_y,\, p_x]_- &= -i\hbar\frac{q}{2m}\left(p_z + \frac{1}{\sqrt{2}} qBx\right) \; . \end{aligned}$$

- $$\begin{aligned} [\mu_x,\, p_y]_- &= \frac{q}{2m}\,[L_x,\, p_y]_- = \frac{q}{2m} i\hbar(\mathbf{e}_x \times \mathbf{e}_y) \cdot \mathbf{p} = i\hbar\frac{q}{2m} p_z \\ \curvearrowright \quad \left[[\mu_x,\, p_y]_-\,,\, z\right]_- &= i\hbar\frac{q}{2m}\,[p_z,\, z]_- = \hbar^2\frac{q}{2m} \end{aligned}$$

Solution 5.2.15

1. Neutrons are spin-$\frac{1}{2}$-particles. It is therefore according to (5.164):

$$\langle\sigma_x\rangle = \langle\sigma_z\rangle = \frac{1}{2} \;\; ; \;\; \langle\sigma_y\rangle = 0 \; .$$

Statistical operator ρ:

a) Formula from Exercise 3.3.9 in Vol. 6:

$$\rho = \frac{1}{2}\left(\mathbb{1} + \langle\boldsymbol{\sigma}\rangle \cdot \boldsymbol{\sigma}\right) \; .$$

Thereby it is:

$$\langle\boldsymbol{\sigma}\rangle \cdot \boldsymbol{\sigma} = \frac{1}{2}(\sigma_x + \sigma_z) = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \; .$$

That yields:

$$\rho = \frac{1}{4}\begin{pmatrix} 3 & 1 \\ 1 & 1 \end{pmatrix} \; .$$

b) Alternative solution by direct calculation:

i.

$$\langle\sigma_x\rangle = \frac{1}{2} = \mathrm{Tr}(\rho\sigma_x) = \mathrm{Tr}\begin{pmatrix} \rho_{12} & \rho_{11} \\ \rho_{22} & \rho_{21} \end{pmatrix} = \rho_{12} + \rho_{21} \; .$$

ii.

$$\langle\sigma_z\rangle = \frac{1}{2} = \mathrm{Tr}(\rho\sigma_z) = \mathrm{Tr}\begin{pmatrix} \rho_{11} & -\rho_{12} \\ \rho_{21} & -\rho_{22} \end{pmatrix} = \rho_{11} - \rho_{22} \; .$$

iii.

$$\langle\sigma_y\rangle = 0 = \mathrm{Tr}(\rho\sigma_y) = \mathrm{Tr}\begin{pmatrix} i\rho_{12} & -i\rho_{11} \\ i\rho_{22} & -i\rho_{21} \end{pmatrix} = i(\rho_{12} - \rho_{21}) \; .$$

iv.

$$\mathrm{Tr}\rho = 1 = \rho_{11} + \rho_{22} \; .$$

$$\begin{aligned} \text{(iii)} \quad &\curvearrowright \rho_{12} &&= \rho_{21} \\ \text{(i)} \quad &\curvearrowright \rho_{12} &&= \rho_{21} = \frac{1}{4} \\ \text{(ii)} + \text{(iv)} \quad &\curvearrowright \rho_{11} &&= \frac{3}{4} \\ \text{(iv)} \quad &\curvearrowright \rho_{22} &&= \frac{1}{4} \; . \end{aligned}$$

Therewith we get again:

$$\rho = \frac{1}{4}\begin{pmatrix} 3 & 1 \\ 1 & 1 \end{pmatrix} \; .$$

2. Arbitrary space-direction:

$$\mathbf{e} = (\sin\vartheta\cos\varphi, \sin\vartheta\sin\varphi, \cos\vartheta) \; .$$

Component of the spin in the direction of $\mathbf{e}$:

$$(\boldsymbol{\sigma}\cdot\mathbf{e}) = \begin{pmatrix} \cos\vartheta & e^{-i\varphi}\sin\vartheta \\ e^{i\varphi}\sin\vartheta & -\cos\vartheta \end{pmatrix} \; .$$

Polarization:

$$\begin{aligned} \langle\boldsymbol{\sigma}\cdot\mathbf{e}\rangle &= \mathrm{Tr}(\rho(\boldsymbol{\sigma}\cdot\mathbf{e})) \\ &= \frac{1}{4}\mathrm{Tr}\begin{pmatrix} 3 & 1\&1 \end{pmatrix}\begin{pmatrix} \cos\vartheta & e^{-i\varphi}\sin\vartheta \\ e^{i\varphi}\sin\vartheta & -\cos\vartheta \end{pmatrix} \\ &= \frac{1}{4}\left(3\cos\vartheta + e^{i\varphi}\sin\vartheta + e^{-i\varphi}\sin\vartheta - \cos\vartheta\right) \\ &= \frac{1}{2}(\cos\vartheta + \sin\vartheta\cos\varphi) \; . \end{aligned}$$

Especially it was given:

$$\left(\vartheta = \frac{\pi}{3}, \varphi = \frac{\pi}{6}\right) \curvearrowright \cos\vartheta = \frac{1}{2}\,;\ \sin\vartheta = \frac{1}{2}\sqrt{3}\,;\ \cos\varphi = \frac{1}{2}\sqrt{3}\,.$$

This means for the polarization in the given direction:

$$\langle \boldsymbol{\sigma}\cdot\mathbf{e}\rangle = \frac{1}{2}\left(\frac{1}{2} + \frac{3}{4}\right) = \frac{5}{8}\,.$$

3. Mean square deviation:

$$(\Delta\sigma_e)^2 \equiv \left\langle (\boldsymbol{\sigma}\cdot\mathbf{e})^2\right\rangle - \langle \boldsymbol{\sigma}\cdot\mathbf{e}\rangle^2 \qquad \langle \boldsymbol{\sigma}\cdot\mathbf{e}\rangle^2 = \frac{25}{64}\,.$$

We need:

$$\begin{aligned}(\boldsymbol{\sigma}\cdot\mathbf{e})^2 &= \begin{pmatrix} \cos\vartheta & e^{-i\varphi}\sin\vartheta \\ e^{i\varphi}\sin\vartheta & -\cos\vartheta \end{pmatrix}\cdot\begin{pmatrix} \cos\vartheta & e^{-i\varphi}\sin\vartheta \\ e^{i\varphi}\sin\vartheta & -\cos\vartheta \end{pmatrix} \\ &= \begin{pmatrix} \cos^2\vartheta + \sin^2\vartheta & e^{-i\varphi}\cos\vartheta\sin\vartheta - e^{-i\varphi}\sin\vartheta\cos\vartheta \\ e^{i\varphi}\sin\vartheta\cos\vartheta - e^{i\varphi}\cos\vartheta\sin\vartheta & \sin^2\vartheta + \cos^2\vartheta \end{pmatrix} \\ &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \mathbb{1}_2\,.\end{aligned}$$

Therewith it is:

$$\left\langle (\boldsymbol{\sigma}\cdot\mathbf{e})^2\right\rangle = \mathrm{Tr}\left(\rho(\boldsymbol{\sigma}\cdot\mathbf{e})^2\right) = \mathrm{Tr}\,(\rho) = 1\,.$$

Uncertainty of the spin measurement:

$$\Delta\sigma_e = \sqrt{1 - \frac{25}{64}} = \frac{1}{8}\sqrt{39}\,.$$

Section 5.3.5

Solution 5.3.1

One recognizes immediately:

$$\widehat{\alpha}_i\,\widehat{\alpha}_j = \begin{pmatrix} \sigma_i\,\sigma_j & 0 \\ 0 & \sigma_i\,\sigma_j \end{pmatrix}\,.$$

With the commutation relations (5.167) oft the Pauli's spin matrices σ_i, where $i = x, y, z$, it follows then:

$$\begin{aligned}[\widehat{\alpha}_i, \widehat{\alpha}_j]_+ &= \begin{pmatrix} [\sigma_i, \sigma_j]_+ & 0 \\ 0 & [\sigma_i, \sigma_j]_+ \end{pmatrix} \\ &= 2\delta_{ij}\begin{pmatrix} \mathbb{1}_2 & 0 \\ 0 & \mathbb{1}_2 \end{pmatrix} = 2\delta_{ij}\,\mathbb{1}_4\,.\end{aligned}$$

Furthermore, one calculates:

$$\begin{aligned}
\widehat{\alpha}_i\,\widehat{\beta} &= \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix}\begin{pmatrix} \mathbb{1}_2 & 0 \\ 0 & -\mathbb{1}_2 \end{pmatrix} = \begin{pmatrix} 0 & -\sigma_i \\ \sigma_i & 0 \end{pmatrix}\,, \\
\widehat{\beta}\,\widehat{\alpha}_i &= \begin{pmatrix} \mathbb{1}_2 & 0 \\ 0 & -\mathbb{1}_2 \end{pmatrix}\begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix} = \begin{pmatrix} 0 & \sigma_i \\ -\sigma_i & 0 \end{pmatrix}
\end{aligned}$$

$$\Longrightarrow \left[\widehat{\alpha}_i, \widehat{\beta}\right]_+ = 0\,,$$

$$\widehat{\beta}^2 = \begin{pmatrix} \mathbb{1}_2 & 0 \\ 0 & -\mathbb{1}_2 \end{pmatrix}\begin{pmatrix} \mathbb{1}_2 & 0 \\ 0 & -\mathbb{1}_2 \end{pmatrix} = \begin{pmatrix} \mathbb{1}_2 & 0 \\ 0 & \mathbb{1}_2 \end{pmatrix} = \mathbb{1}_4\,.$$

The conditions (5.197) are therewith obviously fulfilled.

Solution 5.3.2

The path of solution is the same as in the preceding exercise:

$$\begin{aligned}
[S_i, S_j]_- &= \frac{\hbar^2}{4}\begin{pmatrix} [\sigma_i,\sigma_j]_- & 0 \\ 0 & [\sigma_i,\sigma_j]_- \end{pmatrix} \overset{(5.171)}{=} \frac{\hbar^2}{4}\begin{pmatrix} 2i\sum_k \varepsilon_{ijk}\,\sigma_k & 0 \\ 0 & 2i\sum_k \varepsilon_{ijk}\,\sigma k \end{pmatrix} \\
&= i\,\frac{\hbar^2}{2}\sum_k \varepsilon_{ijk}\begin{pmatrix} \sigma_k & 0 \\ 0 & \sigma_k \end{pmatrix} = i\,\hbar\sum_k \varepsilon_{ijk}\,S_k\,.
\end{aligned}$$

That corresponds precisely to (5.14)!

Solution 5.3.3

$$H_{\mathrm{D}}^{(0)} = c\,\widehat{\boldsymbol{\alpha}}\cdot\mathbf{p} + \widehat{\beta}\,m_{\mathrm{e}}\,c^2\,.$$

1. $\widehat{\mathbf{S}}$ commutes with the momentum $\mathbf{p}$:

$$\begin{aligned}
\widehat{S}_i\,\widehat{\alpha}_j &= \frac{\hbar}{2}\begin{pmatrix} \sigma_i & 0 \\ 0 & \sigma_i \end{pmatrix}\begin{pmatrix} 0 & \sigma_j \\ \sigma_j & 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 0 & \sigma_i\sigma_j \\ \sigma_i\sigma_j & 0 \end{pmatrix} \\
\Longrightarrow \left[\widehat{S}_i, \widehat{\alpha}_j\right]_- &= \frac{\hbar}{2}\begin{pmatrix} 0 & [\sigma_i,\sigma_j]_- \\ [\sigma_i\sigma_j]_- & 0 \end{pmatrix} \\
&\overset{(5.171)}{=} \frac{\hbar}{2}\begin{pmatrix} 0 & 2i\sum\limits_k \varepsilon_{ijk}\,\sigma_k \\ 2i\sum\limits_k \varepsilon_{ijk}\,\sigma_k & 0 \end{pmatrix} \\
&= i\,\hbar\sum_k \varepsilon_{ijk}\begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix} = i\,\hbar\sum_k \varepsilon_{ijk}\,\widehat{\alpha}_k\,.
\end{aligned}$$

This means:

$$\begin{aligned}
\left[\widehat{S}_i, \widehat{\boldsymbol{\alpha}}\cdot\mathbf{p}\right]_- &= i\,\hbar\sum_{jk}\varepsilon_{ijk}\,p_j\,\widehat{\alpha}_k = i\,\hbar(\mathbf{p}\times\widehat{\boldsymbol{\alpha}})_i\,, \\
\left[\widehat{\mathbf{S}}, \widehat{\boldsymbol{\alpha}}\cdot\mathbf{p}\right]_- &= i\,\hbar\,(\mathbf{p}\times\widehat{\boldsymbol{\alpha}})\,.
\end{aligned}$$

In addition it holds:

$$\begin{aligned}\widehat{S}_i \cdot \widehat{\beta} &= \frac{\hbar}{2}\begin{pmatrix}\sigma_i & 0\\ 0 & \sigma_i\end{pmatrix}\begin{pmatrix}\mathbb{1}_2 & 0\\ 0 & -\mathbb{1}_2\end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix}\sigma_i & 0\\ 0 & -\sigma_i\end{pmatrix}\\ &= \widehat{\beta}\cdot\widehat{S}_i \implies \left[\widehat{\mathbf{S}},\widehat{\beta}\right]_- = 0\,.\end{aligned}$$

It remains:

$$\left[\widehat{\mathbf{S}}, H_{\mathrm{B}}^{(0)}\right]_- = i\,\hbar\,c\,(\mathbf{p}\times\widehat{\boldsymbol{\alpha}})\ .$$

2. According to (5.20):

$$\begin{aligned}[L_i, p_j]_- &= i\,\hbar\sum_k \varepsilon_{ijk}\,p_k\\ \implies [L_i, \widehat{\boldsymbol{\alpha}}\cdot\mathbf{p}]_- &= i\,\hbar\sum_{jk}\varepsilon_{ijk}\,\widehat{\alpha}_j\,p_k = i\,\hbar\,(\widehat{\boldsymbol{\alpha}}\times\mathbf{p})_i\ .\end{aligned}$$

Because of

$$\left[L_i, \widehat{\beta}\right]_- = 0$$

it is then left:

$$\left[\mathbf{L}, H_{\mathrm{B}}^{(0)}\right]_- = i\,\hbar\,c\,(\widehat{\boldsymbol{\alpha}}\times\mathbf{p})\ .$$

Solution 5.3.4

$$H_{\mathrm{D}} = c\,\widehat{\boldsymbol{\alpha}}\cdot(\mathbf{p}+e\,\mathbf{A}) + \widehat{\beta}\,m_{\mathrm{e}}\,c^2 - e\,\varphi\ .$$

Heisenberg's equation of motion:

$$\begin{aligned}i\,\hbar\frac{d}{dt}\mathbf{r} &= [\mathbf{r}, H_{\mathrm{D}}]_- = c\,[\mathbf{r},\mathbf{p}]\cdot\widehat{\boldsymbol{\alpha}} = i\,\hbar\,\widehat{\boldsymbol{\alpha}}\,c\\ &\implies \dot{\mathbf{r}}(t) = c\,\widehat{\boldsymbol{\alpha}}\ ,\\ i\,\hbar\frac{d}{dt}(\mathbf{p}+e\,\mathbf{A}) &= [(\mathbf{p}+e\,\mathbf{A}), H_{\mathrm{D}}]_- + i\,\hbar\frac{\partial}{\partial t}(\mathbf{p}+e\,\mathbf{A})\\ &= c\,e\,[\mathbf{p},\widehat{\boldsymbol{\alpha}}\cdot\mathbf{A}]_- - e\,[\mathbf{p},\varphi]_-\\ &\quad + e\,c\,[\mathbf{A},\widehat{\boldsymbol{\alpha}}\cdot\mathbf{p}]_- + i\,\hbar\,e\frac{\partial\mathbf{A}}{\partial t}\\ &= e\,c\frac{\hbar}{i}\,[-\widehat{\boldsymbol{\alpha}}\cdot\nabla\mathbf{A} + \nabla(\widehat{\boldsymbol{\alpha}}\cdot\mathbf{A})]\\ &\quad - e\frac{\hbar}{i}\nabla\varphi + i\,\hbar\,e\frac{\partial\mathbf{A}}{\partial t}\\ &\overset{\text{(sol. 1.7.13, Vol. 3)}}{=} e\,c\frac{\hbar}{i}\,(\widehat{\boldsymbol{\alpha}}\times(\nabla\times\mathbf{A})) - e\frac{\hbar}{i}\nabla\varphi + i\,\hbar\,e\frac{\partial\mathbf{A}}{\partial t}\\ \implies \frac{d}{dt}(\mathbf{p}+e\,\mathbf{A}) &= -e\,c\,(\widehat{\boldsymbol{\alpha}}\times\mathbf{B}) + e\left(\nabla\varphi + \frac{\partial\mathbf{A}}{\partial t}\right).\end{aligned}$$

With

$$\mathbf{E} = -\nabla\boldsymbol{\varphi} - \frac{\partial\mathbf{A}}{\partial t}$$

it follows eventually:

$$\frac{d}{dt}\left(\mathbf{p} + e\,\mathbf{A}\right) = -e\left(\dot{\mathbf{r}} \times \mathbf{B} + \mathbf{E}\right) .$$

On the right-hand side we find the Lorentz force.

Solution 5.3.5

1.

$$\begin{aligned}
[H_{\mathrm{SO}}, L_i]_- &= \sum_{j=1}^{3} \lambda\,[L_j\,S_j, L_i]_- = \sum_{j=1}^{3} \lambda\,[L_j, L_i]_-\,S_j \\
&= \sum_{j=1}^{3} \lambda \sum_{k} \varepsilon_{jik}\,L_k\,S_j\,i\hbar = i\,\hbar\,\lambda \sum_{jk} \varepsilon_{kji}\,L_k\,S_j \\
&= i\,\hbar\,\lambda\,(\mathbf{L} \times \mathbf{S})_i\ , \\
\Longrightarrow\ [H_{\mathrm{SO}}, \mathbf{L}]_- &= i\,\hbar\,\lambda\,(\mathbf{L} \times \mathbf{S})\ .
\end{aligned}$$

2.

$$\begin{aligned}
[H_{\mathrm{SO}}, S_i]_- &= \sum_{j=1}^{3} \lambda\,[L_j\,S_j, S_i]_- = \lambda \sum_{j=1}^{3} L_j\,[S_j, S_i]_- \\
&= \lambda \sum_{j=1}^{3} L_j\,i\,\hbar \sum_{k} \varepsilon_{jik}\,S_k = i\,\hbar\,\lambda \sum_{jk} \varepsilon_{kji}\,S_k\,L_j \\
&= i\,\hbar\,\lambda\,(\mathbf{S} \times \mathbf{L})_i \\
\Longrightarrow\ [H_{\mathrm{SO}}, \mathbf{S}]_- &= i\,\hbar\,\lambda\,(\mathbf{S} \times \mathbf{L})\ .
\end{aligned}$$

3.

$$\left[H_{\mathrm{SO}}, \mathbf{L}^2\right]_- = \sum_{i=1}^{3} \lambda\,[L_i\,S_i, \mathbf{L}^2]_- = \sum_{i=1}^{3} \lambda\,[L_i, \mathbf{L}^2]_-\,S_i = 0\ .$$

4.

$$\left[H_{\mathrm{SO}}, \mathbf{S}^2\right]_- = \lambda \sum_{i=1}^{3} L_i\,[S_i, \mathbf{S}^2]_- = 0\ .$$

5. It follows from 1. and 2.:

$$\begin{aligned}
[H_{\mathrm{SO}}, J_i]_- &= 0 \quad \text{for } i = x, y, z \\
\Longrightarrow\ \left[H_{\mathrm{SO}}, \mathbf{J}^2\right]_- &= \sum_{i} \left[H_{\mathrm{SO}}, J_i^2\right]_- = 0\ .
\end{aligned}$$

Solution 5.3.6

We calculate the ith component:

$$\begin{aligned}(\nabla\varphi\times\mathbf{p})_i &= \sum_{jk}\varepsilon_{ijk}\frac{\partial\varphi}{\partial x_j}\cdot\frac{\hbar}{i}\frac{\partial}{\partial x_k}\\ &= \frac{\hbar}{i}\sum_{jk}\varepsilon_{ijk}\left(\frac{\partial}{\partial x_k}\frac{\partial\varphi}{\partial x_j}-\frac{\partial^2\varphi}{\partial x_k\partial x_j}\right).\end{aligned}$$

Continuous differentiability of the scalar product:

$$\begin{aligned}\sum_{jk}\varepsilon_{ijk}\frac{\partial^2\varphi}{\partial x_k\partial x_j}\overset{k\leftrightarrow j}{=}\sum_{jk}\varepsilon_{ikj}\frac{\partial^2\varphi}{\partial x_j\partial x_k} &= \sum_{jk}\varepsilon_{ikj}\frac{\partial^2\varphi}{\partial x_k\partial x_j}\\ &= -\sum_{jk}\varepsilon_{ijk}\frac{\partial^2\varphi}{\partial x_k\partial x_j}\\ &= 0\,.\end{aligned}$$

It thus remains:

$$\begin{aligned}(\nabla\varphi\times\mathbf{p})_i &= \frac{\hbar}{i}\sum_{jk}\varepsilon_{ijk}\frac{\partial}{\partial x_k}\frac{\partial\varphi}{\partial x_j}\\ &= \frac{\hbar}{i}\sum_{jk}\varepsilon_{ikj}\frac{\partial}{\partial x_j}\frac{\partial\varphi}{\partial x_k}\\ &= -\sum_{jk}\varepsilon_{ijk}\left(\frac{\hbar}{i}\frac{\partial}{\partial x_j}\right)\frac{\partial\varphi}{\partial x_k}\\ &= -\left(\mathbf{p}\times\nabla\varphi\right)_i\,.\end{aligned}$$

Therewith the assertion is proved!

Section 5.4.4

Solution 5.4.1

1. For the sought spin states we have according to (5.280):

$$|S_1\,S_2;S\,m_s\rangle=\sum_{m_{s_1},m_{s_2}}\langle m_{s_1}\,m_{s_2}|S\,m_s\rangle|S_1\,S_2;m_{s_1}\,m_{s_2}\rangle\,.$$

The states

$$|S_1\,S_2;m_{s_1}\,m_{s_2}\rangle=|S_1\,m_{s_1}\rangle|S_2\,m_{s_2}\rangle$$

are the product states of the spinors known from Sect. 5.2.4.

Triangle inequality (5.278):

$$\begin{aligned}&\left|\frac{1}{2}-\frac{1}{2}\right|\le S\le\frac{1}{2}+\frac{1}{2}\\ &\Longrightarrow\ S=1,0\ \text{possible!}\,.\end{aligned}$$

There are the following four eigen-states:

$$|S_1\, S_2; S\, m_s\rangle \equiv |S\, m_s\rangle = |1\,1\rangle, |1\,0\rangle, |1\,-1\rangle, |0\,0\rangle\ .$$

These states can easily be derived from the results in Sect. 5.4.3:

(5.284) $\Longrightarrow$ $|1\,1\rangle = \left|S_1\, S_2; \frac{1}{2}\,\frac{1}{2}\right\rangle = |+\rangle_1|+\rangle_2$
We use for the spin states the symbols $|+\rangle, |-\rangle$ from Sect. 5.2.4. Let the lower index denote the particles 1 and 2,

(5.286) $\Longrightarrow$ Clebsch-Gordan coefficients:

$$\begin{aligned}\langle m_{s_1}\, m_{s_2}|1\,0\rangle &= \frac{1}{\sqrt{2}}\,\delta_{m_{s_1}-1/2}\,\delta_{m_{s_2}\,1/2} + \frac{1}{\sqrt{2}}\,\delta_{m_{s_1}\,1/2}\,\delta_{m_{s_2}-1/2}\\ \Longrightarrow\ |1\,0\rangle &= \frac{1}{\sqrt{2}}\,(|-\rangle_1|+\rangle_2 + |+\rangle_1|-\rangle_2)\ ,\end{aligned}$$

(5.287) $\Longrightarrow$ $|1\,-1\rangle = |-\rangle_1|-\rangle_2$,

(5.289) $\Longrightarrow$ Clebsch-Gordan coefficients:

$$\begin{aligned}\langle m_{s_1}\, m_{s_2}|0\,0\rangle &= \frac{1}{\sqrt{2}}\,\delta_{m_{s_1}-1/2}\,\delta_{m_{s_2}1/2} - \frac{1}{\sqrt{2}}\,\delta_{m_{s_1}1/2}\,\delta_{m_{s_2}-1/2}\\ \Longrightarrow\ |0\,0\rangle &= \frac{1}{\sqrt{2}}\,(|-\rangle_1|+\rangle_2 - |+\rangle_1|-\rangle_2)\ .\end{aligned}$$

2.

$$\mathbf{S}^2 = (\mathbf{S}_1+\mathbf{S}_2)^2 \ \Longrightarrow\ \mathbf{S}_1\cdot\mathbf{S}_2 = \frac{1}{2}\,(\mathbf{S}^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2)\ .$$

The eigen-states $|S_1\, S_2; S\, m_s\rangle$ are common eigen-states of the operators

$$\mathbf{S}^2, S^z, \mathbf{S}_1^2, \mathbf{S}_2^2$$

and therewith also of $\mathbf{S}_1\cdot\mathbf{S}_2$:

$$\mathbf{S}_1\cdot\mathbf{S}_2|1\,m_s\rangle = \frac{\hbar^2}{2}\left(2-\frac{3}{4}-\frac{3}{4}\right)|1\,m_s\rangle = \frac{1}{4}\,\hbar^2|1\,m_s\rangle$$

$$\text{eigen-value}: \frac{1}{4}\,\hbar^2 \text{ (three-fold degenerate)},$$

$$\mathbf{S}_1\cdot\mathbf{S}_2|0\,0\rangle = \frac{\hbar^2}{2}\left(0-\frac{3}{4}-\frac{3}{4}\right)|0\,0\rangle = -\frac{3}{4}\,\hbar^2|0\,0\rangle$$

$$\text{eigen-value}: -\frac{3}{4}\,\hbar^2.$$

3. P is Hermitian because the spin operators $\mathbf{S}_1$ and $\mathbf{S}_2$ are Hermitian and commute with each other. Furthermore:

$$\begin{aligned}P|1\,m_s\rangle &= \left(\frac{3}{4}+\frac{1}{4}\right)|1\,m_s\rangle = |1\,m_s\rangle\ ,\\ P|0\,0\rangle &= \left(\frac{3}{4}-\frac{3}{4}\right)|0\,0\rangle = 0\\ \Longrightarrow\ & P^2|S\,m_s\rangle = P|S\,m_s\rangle\ .\end{aligned}$$

P projects onto the subspace of the so-called *triplet states* $|1\,m_s\rangle$.

Solution 5.4.2

We use the partial results of the preceding exercise:

$$\begin{aligned} \mathbf{S}_1 \cdot \mathbf{S}_2 = \frac{1}{2}\left(\mathbf{S}^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2\right) &= \frac{1}{2}\left(\mathbf{S}^2 - \frac{3}{2}\hbar^2 \mathbb{1}\right) , \\ S_{1z} + S_{2z} &= S_z . \end{aligned}$$

Therewith the Hamilton operator reads:

$$H = -\frac{1}{2} J \left(\mathbf{S}^2 - \frac{3}{2}\hbar^2 \mathbb{1}\right) + \mu S_z .$$

The common eigen-states

$$|1\,1\rangle, |1\,0\rangle, |1\,-1\rangle, |0\,0\rangle$$

of $\mathbf{S}^2$, S_z, $\mathbf{S}_1^2$, $\mathbf{S}_2^2$, which we have calculated in the preceding exercise, are thus also the eigen-states of H:

$$H|1\,m_s\rangle = \left\{-\frac{1}{2} J \left(2\hbar^2 - \frac{3}{2}\hbar^2\right) + \mu\, m_s\right\} |1\,m_s\rangle$$

$$\begin{aligned} \Longrightarrow E_{11} &= -\frac{1}{4} J\hbar^2 + \mu , \\ E_{10} &= -\frac{1}{4} J\hbar^2 , \\ E_{1-1} &= -\frac{1}{4} J\hbar^2 - \mu , \\ H\,|0\,0\rangle &= -\frac{1}{2} J \left(0 - \frac{3}{2}\hbar^2\right) |0\,0\rangle \\ \Longrightarrow E_{00} &= +\frac{3}{4}\hbar^2 J . \end{aligned}$$

Solution 5.4.3

1. Triangle inequality (5.278):

$$\begin{aligned} \left|l - \frac{1}{2}\right| &\leq j \leq l + \frac{1}{2} , \\ l = 0 &\Longrightarrow j = \frac{1}{2} , \\ l \geq 1 \Longrightarrow j &= l + \frac{1}{2}, l - \frac{1}{2} . \end{aligned}$$

2. We use for the proof full induction and start with $|l + 1/2\, m_j\rangle$. For $m_j = l + 1/2$ the assertion reads:

$$\left|l + \frac{1}{2}\ \ l + \frac{1}{2}\right\rangle = |l\,l\rangle|+\rangle \quad \left(|+\rangle \equiv \left|\frac{1}{2}\,\frac{1}{2}\right\rangle\right) .$$

This agrees with (5.284). We now check the case $m_j = l - (1/2)$:

$$\left| l + \frac{1}{2} \;\; l - \frac{1}{2} \right\rangle = \sqrt{\frac{2l}{2l+1}} \, |l \, l-1\rangle |+\rangle + \sqrt{\frac{1}{2l+1}} \, |l \, l\rangle |-\rangle \, .$$

This is identical to (5.285). We now assume that the formula for m_j is correct, and conclude for $m_j - 1$:

$$J_- = J_- \, |l + 1/2 \, m_j\rangle \overset{(5.64)}{=} \hbar \sqrt{(l+1/2+m_j) \; (l+1/2-m_j+1)} \; |l + 1/2 \, m_j - 1\rangle \, ,$$

$$\begin{aligned} J_- \left| l \, m_j - \frac{1}{2} \right\rangle |+\rangle &= \hbar \left| l \, m_j - \frac{1}{2} \right\rangle |-\rangle \\ &\quad + \hbar \sqrt{\left(l + m_j - \frac{1}{2} \right) \left(l - m_j + \frac{3}{2} \right)} \left| l \, m_j - \frac{3}{2} \right\rangle |+\rangle \, , \\ J_- \left| l \, m_j + \frac{1}{2} \right\rangle |-\rangle &= \hbar \sqrt{\left(l + m_j + \frac{1}{2} \right) \left(l - m_j + \frac{1}{2} \right)} \; |l \, m_j - 1\rangle \, |-\rangle \, . \end{aligned}$$

It follows:

$$\begin{aligned} &\left| l + \frac{1}{2} \, m_j - 1 \right\rangle \\ &= \left| l \, m_j - \frac{1}{2} \right\rangle |-\rangle \left\{ \sqrt{\frac{1}{(2l+1) \, (l - m_j + \frac{3}{2})}} \right. \\ &\left. + \frac{l - m_j + 1/2}{\sqrt{(2l+1) \; (l - m_j + 3/2)}} \right\} + \left| l \, m_j - \frac{3}{2} \right\rangle |+\rangle \sqrt{\frac{l + m_j - 1/2}{2l+1}} \\ &= \sqrt{\frac{l - m_j + 3/2}{2l+1}} \; |l \, m_j - 1/2\rangle \, |-\rangle + \sqrt{\frac{l + m_j - 1/2}{2l+1}} \left| l m_j - \frac{3}{2} \right\rangle |+\rangle . \end{aligned}$$

This is the assertion for $m_j - 1$. The relation for $|l + 1/2 \, m_j\rangle$ is therewith proven. We now investigate the state $|l - 1/2 \, m_j\rangle$: For $m_j = l - 1/2$ the assertion reads:

$$\left| l - \frac{1}{2} \;\; l - \frac{1}{2} \right\rangle = + \sqrt{\frac{1}{2l+1}} \, |l \, l-1\rangle |+\rangle - \sqrt{\frac{2l}{2l+1}} \, |l \, l\rangle |-\rangle \, .$$

This is the exact result (5.288). We conclude again from m_j to $m_j - 1$:

$$J_- \left| l - \frac{1}{2} \;\; m_j \right\rangle = \hbar \sqrt{\left(l - \frac{1}{2} + m_j \right) \left(l + \frac{1}{2} - m_j \right)} \left| l - \frac{1}{2} \;\; m_j - 1 \right\rangle \, ,$$

$$
\begin{aligned}
J_- \left| l\, m_j - \frac{1}{2} \right\rangle |+\rangle &= \hbar \left| l\, m_j - \frac{1}{2} \right\rangle |-\rangle \\
&+ \hbar \sqrt{\left(l + m_j - \frac{1}{2}\right)\left(l - m_j + \frac{3}{2}\right)} \left| l\, m_j - \frac{3}{2} \right\rangle |+\rangle \,, \\
J_- \left| l\, m_j + \frac{1}{2} \right\rangle |-\rangle &= \hbar \sqrt{\left(l + m_j + \frac{1}{2}\right)\left(l - m_j + \frac{1}{2}\right)} \left| l\, m_j - \frac{1}{2} \right\rangle |-\rangle .
\end{aligned}
$$

This can again be gathered, since we assume the correctness of the formula for $|l - 1/2\, m_j\rangle$:

$$
\begin{aligned}
\left| l - \frac{1}{2}\ m_j - 1 \right\rangle &= \sqrt{\frac{1}{(2l+1)\ (l + m_j - 1/2)}} \left| l\, m_j - \frac{1}{2} \right\rangle |-\rangle \\
&+ \sqrt{\frac{l - m_j + 3/2}{2l+1}} \left| l\, m_j - \frac{3}{2} \right\rangle |+\rangle \\
&- \sqrt{\frac{(l + m_j + 1/2)^2}{(2l+1)\ (l + m_j - 1/2)}} \left| l\, m_j - \frac{1}{2} \right\rangle |-\rangle \\
&= \sqrt{\frac{l - m_j + 3/2}{2l+1}} \left| l\, m_j - \frac{3}{2} \right\rangle |+\rangle \ - \\
&- \sqrt{\frac{l + m_j - 1/2}{2l+1}} \left| l\, m_j - \frac{1}{2} \right\rangle |-\rangle \,.
\end{aligned}
$$

This is the assertion for $m_j - 1$. The proof is therewith complete!

Solution 5.4.4

Triangle inequality:

$$0 \le j \le 2 \implies j = 0, 1, 2 \text{ possible.}$$

1. $\boldsymbol{j = 2}$

$$
\begin{aligned}
\langle m_1\, m_2 | 2\, 2 \rangle &= \delta_{m_1 1}\, \delta_{m_2 1} \ \text{(see (5.284))} \,, \\
\langle m_1\, m_2 | 2\, 1 \rangle &= \frac{1}{\sqrt{2}}\, \delta_{m_1 0}\, \delta_{m_2 1} + \frac{1}{\sqrt{2}}\, \delta_{m_1 1}\, \delta_{m_2 0} \ \text{(s. 5.286)} \,, \\
\langle m_1\, m_2 | 2\, 0 \rangle &= \frac{1}{\sqrt{6}}\, \delta_{m_1 -1}\, \delta_{m_2 1} + \frac{2}{\sqrt{6}}\, \delta_{m_1 0} \delta_{m_2 0} + \frac{1}{\sqrt{6}} \delta_{m_1 1} \delta_{m_2 -1} \ \text{(see 5.287)}.
\end{aligned}
$$

We have taken these relations directly from the text. However,we still have to derive the missing Clebsch-Gordan coefficients. At first we have:

$$|2\, 0\rangle = \frac{1}{\sqrt{6}} \left(|-1\, 1\rangle + 2|0\, 0\rangle + |1 - 1\rangle \right) .$$

To this we apply $J_- = J_{1-} + J_{2-}$:

$$\begin{aligned} J_-|2\,0\rangle &= \hbar\sqrt{6}\,|2-1\rangle\ , \\ J_-|-1\,1\rangle &= \hbar\sqrt{2}\,|-1\,0\rangle\ , \\ J_-|1-1\rangle &= \hbar\sqrt{2}\,|0-1\rangle \\ J_-|00\rangle &= \hbar\sqrt{2}\,\left(|0-1\rangle + |-1\,0\rangle\right)\ . \end{aligned}$$

From that it follows:

$$|2-1\rangle = \frac{1}{\sqrt{2}}\left(|-1\,0\rangle + |0-1\rangle\right)\ .$$

J_-, once more applied, eventually yields:

$$|2-2\rangle = |-1-1\rangle\ .$$

The still missing Clebsch-Gordan coefficients thus read:

$$\begin{aligned} \langle m_1\,m_2|2-1\rangle &= \frac{1}{\sqrt{2}}\left(\delta_{m_1-1}\,\delta_{m_2 0} + \delta_{m_1 0}\,\delta_{m_2-1}\right)\ , \\ \langle m_1\,m_2|2-2\rangle &= \delta_{m_1-1}\,\delta_{m_2-1}\ . \end{aligned}$$

2. $\boldsymbol{j=1}$
We take from (5.288):

$$|1\,1\rangle = \frac{1}{\sqrt{2}}\left(|0\,1\rangle - |1\,0\rangle\right)\ .$$

To that we apply $J_- = J_{1-} + J_{2-}$:

$$\begin{aligned} J_-|1\,1\rangle &= \hbar\sqrt{2}\,|1\,0\rangle\ , \\ J_-|0\,1\rangle &= \hbar\sqrt{2}\,\left(|-1\,1\rangle + |0\,0\rangle\right)\ , \\ J_-|1\,0\rangle &= \hbar\sqrt{2}\,\left(|0\,0\rangle + |1-1\rangle\right)\ . \end{aligned}$$

This yields:

$$|1\,0\rangle = \frac{1}{\sqrt{2}}\left(|-1\,1\rangle - |1-1\rangle\right)\ .$$

J_-, once more applied, leads to:

$$|1-1\rangle = \frac{1}{\sqrt{2}}\left(|-1\,0\rangle - |0-1\rangle\right)\ .$$

We can therewith list all the Clebsch-Gordan coefficients for $j=1$:

$$\begin{aligned} \langle m_1\,m_2|1\,1\rangle &= \frac{1}{\sqrt{2}}\left(\delta_{m_1 0}\,\delta_{m_2 1} - \delta_{m_1 1}\,\delta_{m_2 0}\right)\ , \\ \langle m_1\,m_2|1\,0\rangle &= \frac{1}{\sqrt{2}}\left(\delta_{m_1-1}\,\delta_{m_2 1} - \delta_{m_1 1}\,\delta_{m_2-1}\right)\ , \\ \langle m_1\,m_2|1-1\rangle &= \frac{1}{\sqrt{2}}\left(\delta_{m_1-1}\,\delta_{m_2 0} - \delta_{m_1 0}\,\delta_{m_2-1}\right)\ . \end{aligned}$$

3. $\boldsymbol{j = 0}$

Because of $m_j = m_1 + m_2 \stackrel{!}{=} 0$ the following ansatz holds:

$$|0\,0\rangle = \alpha|-1\,1\rangle + \beta|0\,0\rangle + \gamma|1\,-1\rangle \ .$$

We exploit orthogonality and normalization:

$$\begin{aligned}
\langle 0\,0|0\,0\rangle \stackrel{!}{=} 1 &= \alpha^2 + \beta^2 + \gamma^2 \ , \\
\langle 2\,0|0\,0\rangle \stackrel{!}{=} 0 &= \frac{1}{\sqrt{6}}\,(\alpha + 2\beta + \gamma) \ , \\
\langle 1\,0|0\,0\rangle \stackrel{!}{=} 0 &= \frac{1}{\sqrt{2}}\,(\alpha - \gamma) \\
\Longrightarrow\ \alpha = \gamma &= -\beta = \frac{1}{\sqrt{3}} \\
\Longrightarrow\ |0\,0\rangle &= \frac{1}{\sqrt{3}}\,(|-1\,1\rangle - |0\,0\rangle + |1\,-1\rangle) \ .
\end{aligned}$$

Clebsch-Gordan coefficient:

$$\langle m_1\,m_2|0\,0\rangle = \frac{1}{\sqrt{3}}\,\left(\delta_{m_1,-1}\,\delta_{m_2,1} - \delta_{m_1,0}\,\delta_{m_2,0} + \delta_{m_1,1}\,\delta_{m_2,-1}\right) \ .$$

Solution 5.4.5

1. Triangle inequality (5.278):

$$|j_1 - j_2| \le j \le j_1 + j_2 \ .$$

Because of $j_1 = 1/2$ and $j_2 = 3/2$ we thus have:

$$j = 1, 2 \quad \text{with} \quad m_{j=1} = -1, 0, +1 \ ; \ m_{j=2} = -2, -1, 0, +1, +2$$

2.

$$j = j_{\max} = 2 \quad \curvearrowright \quad -2 \le m_j \le +2 \ .$$

We investigate here only $m_{j=2} = 0, 1, 2$. According to (5.276) and (5.280) it must be:

$$\begin{aligned}
m_j &= m_1 + m_2 \\
m_1 &= +\frac{1}{2}, -\frac{1}{2} \\
m_2 &= +\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2} \\
|2\,m_{j=2}\rangle &= \sum_{\substack{m_1 \\ m_2 = m_{j=2} - m_1}} |m_1 m_2\rangle \underbrace{\langle m_1 m_2|2\,m_{j=2}\rangle}_{\text{Clebsch-Gordan coefficient}} \ .
\end{aligned}$$

Let all the states be normalized!

(a)

$$j = 2\ ,\ \ m_j = 2\ .$$

This is possible only if $m_1 = +1/2$ and $m_2 = +3/2$. This means:

$$|jm_j\rangle = |22\rangle = |m_1 m_2\rangle = \left|\frac{1}{2}\frac{3}{2}\right\rangle\ .$$

This yields the *Clebsch-Gordan coefficient*:

$$\langle m_1 m_2|\, 22\rangle = \delta_{m_1 1/2}\delta_{m_2 3/2}$$

(b)

$$j = 2\ ,\ \ m_j = 1\ .$$

One finds with (5.64):

$$\begin{aligned}
J_-\,|22\rangle &= \hbar\sqrt{2(2+1)-2(2-1)}\,|21\rangle = 2\hbar\,|21\rangle \\
(J_{1-}+J_{2-})\left|\frac{1}{2}\frac{3}{2}\right\rangle &= \hbar\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}-1\right)}\left|-\frac{1}{2}\frac{3}{2}\right\rangle \\
&\quad +\hbar\sqrt{\frac{3}{2}\left(\frac{3}{2}+1\right)-\frac{3}{2}\left(\frac{3}{2}-1\right)}\left|\frac{1}{2}\frac{1}{2}\right\rangle \\
&= \hbar\left|-\frac{1}{2}\frac{3}{2}\right\rangle + \hbar\sqrt{3}\left|\frac{1}{2}\frac{1}{2}\right\rangle \\
\curvearrowright\ \ |j=2\ m_j=1\rangle &= \frac{1}{2}\left(\left|-\frac{1}{2}\frac{3}{2}\right\rangle + \sqrt{3}\left|\frac{1}{2}\frac{1}{2}\right\rangle\right)\ .
\end{aligned}$$

Clebsch-Gordan coefficient:

$$\langle m_1\, m_2|21\rangle = \frac{1}{2}\,\delta_{m_1-\frac{1}{2}}\,\delta_{m_2\frac{3}{2}} + \frac{1}{2}\,\sqrt{3}\,\delta_{m_1\frac{1}{2}}\,\delta_{m_2\frac{1}{2}}$$

(c)

$$j = 2\ \ ,\ \ m_j = 0\ .$$

Again with (5.64) one finds:

$$\begin{aligned}
& J_-\,|2\,1\rangle = \hbar\sqrt{2(2+1)-1(1-1)}|20\rangle = \hbar\sqrt{6}\,|2\,0\rangle \\
& (J_{1-}+J_{2-})\ \frac{1}{2}\left(\left|-\frac{1}{2}\frac{3}{2}\right\rangle + \sqrt{3}\left|\frac{1}{2}\frac{1}{2}\right\rangle\right) \\
= \ & \frac{1}{2}\left(0+\sqrt{3}\hbar\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}-1\right)}\left|-\frac{1}{2}\frac{1}{2}\right\rangle\right) \\
& +\frac{1}{2}\left(\hbar\sqrt{\frac{3}{2}\left(\frac{3}{2}+1\right)-\frac{3}{2}\left(\frac{3}{2}-1\right)}\left|-\frac{1}{2}\frac{1}{2}\right\rangle\right. \\
& \left.+\sqrt{3}\hbar\sqrt{\frac{3}{2}\left(\frac{3}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}-1\right)}\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle\right)
\end{aligned}$$

$$
\begin{aligned}
&= \hbar\frac{\sqrt{3}}{2}\left|-\frac{1}{2}\,\frac{1}{2}\right\rangle + \hbar\frac{\sqrt{3}}{2}\left|-\frac{1}{2}\,\frac{1}{2}\right\rangle + \hbar\frac{\sqrt{3}}{2}\,4\left|\frac{1}{2}\,-\frac{1}{2}\right\rangle \\
\curvearrowright \quad |j=2\; m_j=0\rangle &= \frac{1}{\sqrt{2}}\left|-\frac{1}{2}\,\frac{1}{2}\right\rangle + \sqrt{2}\left|\frac{1}{2}\,-\frac{1}{2}\right\rangle .
\end{aligned}
$$

Clebsch-Gordan coefficient:

$$
\langle m_1\, m_2|2\,0\rangle = \frac{1}{\sqrt{2}}\,\delta_{m_1-\frac{1}{2}}\,\delta_{m_2\frac{1}{2}} + \sqrt{2}\,\delta_{m_1\frac{1}{2}}\,\delta_{m_2-\frac{1}{2}} .
$$

Section 6.1.3

Solution 6.1.1

1.

$$
\begin{aligned}
p_{\rm r} &= \frac{1}{2}\sum_{i=1}^{3}\left(p_i\,\frac{x_i}{r} + \frac{x_i}{r}\,p_i\right) = \frac{\hbar}{2i}\sum_{i=1}^{3}\left(\frac{\partial}{\partial x_i}\,\frac{x_i}{r} + \frac{x_i}{r}\,\frac{\partial}{\partial x_i}\right) \\
&= \frac{\hbar}{2i}\sum_{i=1}^{3}\left(\frac{1}{r} - \frac{x_i}{r^2}\,\frac{\partial r}{\partial x_i} + 2\,\frac{x_i}{r}\,\frac{\partial}{\partial x_i}\right) = \frac{\hbar}{2i}\sum_{i=1}^{3}\left(\frac{1}{r} - \frac{x_i^2}{r^3} + 2\,\frac{x_i}{r}\,\frac{\partial}{\partial x_i}\right) \\
&= \frac{\hbar}{2i}\left(\frac{3}{r} - \frac{r^2}{r^3} + 2\,\frac{\mathbf{r}}{r}\cdot\nabla\right) .
\end{aligned}
$$

Gradient in spherical coordinates (5.78):

$$
\nabla \equiv \mathbf{e}_{\rm r}\,\frac{\partial}{\partial r} + \mathbf{e}_\vartheta\,\frac{1}{r}\,\frac{\partial}{\partial\vartheta} + \mathbf{e}_\varphi\frac{1}{r\sin\vartheta}\,\frac{\partial}{\partial\varphi} \Longrightarrow \frac{\mathbf{r}}{r}\cdot\nabla = \frac{\partial}{\partial r} .
$$

It remains:

$$
p_{\rm r} = \frac{\hbar}{i}\left(\frac{1}{r} + \frac{\partial}{\partial r}\right) = \frac{\hbar}{i}\,\frac{1}{r}\,\frac{\partial}{\partial r}\,r .
$$

2.

$$
\begin{aligned}
[p_{\rm r}, r]_-\;\psi(\mathbf{r}) &= \frac{\hbar}{i}\left[\frac{1}{r}\,\frac{\partial}{\partial r}\,r, r\right]_-\psi(\mathbf{r}) = \frac{\hbar}{i}\left(\frac{1}{r}\,\frac{\partial}{\partial r}\,r^2\psi(\mathbf{r}) - \frac{\partial}{\partial r}\,r\,\psi(\mathbf{r})\right) \\
&= \frac{\hbar}{i}\left(2\psi(\mathbf{r}) + r\,\frac{\partial}{\partial r}\,\psi(\mathbf{r}) - \psi(\mathbf{r}) - r\,\frac{\partial}{\partial r}\,\psi(\mathbf{r})\right) = \frac{\hbar}{i}\,\psi(\mathbf{r}) ,
\end{aligned}
$$

$$
\psi(\mathbf{r}) \text{ arbitrary} \quad\Longrightarrow\quad [p_{\rm r}, r]_- = \frac{\hbar}{i}
$$

3. p_r Hermitian?

$$\begin{aligned}
&\Longleftrightarrow \quad \int d^3r\, \varphi^*(\mathbf{r}) \left(\frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}\, r\,\psi(\mathbf{r})\right) \stackrel{!}{=} -\frac{\hbar}{i}\int d^3r \left(\frac{1}{r}\frac{\partial}{\partial r}\, r\,\varphi(\mathbf{r})\right)^* \psi(\mathbf{r}) \\
&\Longleftrightarrow \quad \int d^3r \left[\varphi^*(\mathbf{r})\frac{\partial}{\partial r}\psi(r) + \psi(r)\frac{\partial}{\partial r}\varphi^*(\mathbf{r}) + \frac{2}{r}\varphi^*(\mathbf{r})\,\psi(\mathbf{r})\right] \stackrel{!}{=} 0 \\
&\Longleftrightarrow \quad \int d\Omega \int_0^\infty dr\, \frac{\partial}{\partial r}\left[r^2\varphi^*(\mathbf{r})\,\psi(\mathbf{r})\right] \stackrel{!}{=} 0 \\
&\Longleftrightarrow \quad \int d\Omega\, \left[r^2\varphi^*(\mathbf{r})\,\psi(\mathbf{r})\right]_0^\infty \stackrel{!}{=} 0\,.
\end{aligned}$$

p_r is therewith Hermitian, if the wave function fulfills the following two conditions:

$$\begin{aligned}
&\text{a)} \qquad \lim_{r\to 0} r\,\psi(\mathbf{r}) = 0\,, \\
&\text{b)} \qquad \lim_{r\to\infty} r\,\psi(\mathbf{r}) = 0\,.
\end{aligned}$$

Solution 6.1.2

1.

$$\mathbf{L}^2 = \sum_{i=1}^{3} L_i^2 = \sum_i \sum_{m,n} \varepsilon_{imn}\, x_m\, p_n \sum_{q,r} \varepsilon_{iqr}\, x_q p_\mathrm{r}\,.$$

With

$$\sum_i \varepsilon_{imn}\,\varepsilon_{iqr} = \delta_{mq}\,\delta_{nr} - \delta_{mr}\,\delta_{nq}$$

it follows:

$$\begin{aligned}
\mathbf{L}^2 &= \sum_{m,n} x_m\, p_n\,(x_m\, p_n - x_n\, p_m) \\
&= \sum_{m,n}\left[x_m\left(\frac{\hbar}{i}\,\delta_{mn}\, p_n + x_m\, p_n^2\right) - x_m\, p_n\,(i\,\hbar\,\delta_{nm} + p_m\, x_n)\right] \\
&= \frac{\hbar}{i}\,(\mathbf{r}\cdot\mathbf{p}) + \mathbf{r}^2\,\mathbf{p}^2 - i\,\hbar(\mathbf{r}\cdot\mathbf{p}) - (\mathbf{r}\cdot\mathbf{p})\,(\mathbf{p}\cdot\mathbf{r})\,.
\end{aligned}$$

We still need:

$$\mathbf{p}\cdot\mathbf{r} = \sum_i p_i\, x_i = \sum_i \left(\frac{\hbar}{i} + x_i\, p_i\right) = 3\frac{\hbar}{i} + \mathbf{r}\cdot\mathbf{p}\,.$$

It is left therewith for the square of the orbital angular momentum:

$$\begin{aligned}
\mathbf{L}^2 &= 2\frac{\hbar}{i}(\mathbf{r}\cdot\mathbf{p}) + \mathbf{r}^2\mathbf{p}^2 - (\mathbf{r}\cdot\mathbf{p})^2 - 3\frac{\hbar}{i}(\mathbf{r}\cdot\mathbf{p}) \\
&= i\,\hbar(\mathbf{r}\cdot\mathbf{p}) + \mathbf{r}^2\mathbf{p}^2 - (\mathbf{r}\cdot\mathbf{p})^2
\end{aligned}$$

2.

$$p_{\mathrm{r}} = \frac{1}{2}\left[\frac{1}{r}(\mathbf{r}\cdot\mathbf{p}) + (\mathbf{p}\cdot\mathbf{r})\frac{1}{r}\right] .$$

It holds as special case of Exercise 2.3.5 (Vol. 6):

$$\begin{aligned}
\left[p_i, \frac{1}{r}\right]_- &= \frac{\hbar}{i}\frac{\partial}{\partial x_i}\frac{1}{r} = -\frac{\hbar}{i}\frac{x_i}{r^3} \\
\Longrightarrow\ \mathbf{p}\,\frac{1}{r} &= \frac{1}{r}\,\mathbf{p} - \frac{\hbar}{i}\frac{\mathbf{r}}{r^3} , \\
(\mathbf{p}\cdot\mathbf{r})\,\frac{1}{r} = \frac{1}{r}(\mathbf{p}\cdot\mathbf{r}) - \frac{\hbar}{i}\frac{1}{r} &\overset{1)}{=} 2\,\frac{\hbar}{i}\frac{1}{r} + \frac{1}{r}(\mathbf{r}\cdot\mathbf{p}) .
\end{aligned}$$

This we insert into the definition equation for p_{r}:

$$p_{\mathrm{r}} = \frac{1}{r}(\mathbf{r}\cdot\mathbf{p}) + \frac{\hbar}{i}\frac{1}{r} .$$

3. We build at first:

$$p_{\mathrm{r}}^2 = \frac{1}{r}(\mathbf{r}\cdot\mathbf{p})\,\frac{1}{r}(\mathbf{r}\cdot\mathbf{p}) + \frac{\hbar}{i}\frac{1}{r}(\mathbf{r}\cdot\mathbf{p})\,\frac{1}{r} + \frac{\hbar}{i}\frac{1}{r^2}\,(\mathbf{r}\cdot\mathbf{p}) - \hbar^2\,\frac{1}{r^2} .$$

As in 2. one shows:

$$\begin{aligned}
(\mathbf{r}\cdot\mathbf{p})\,\frac{1}{r} &= \frac{1}{r}\,(\mathbf{r}\cdot\mathbf{p}) - \frac{\hbar}{i}\frac{1}{r} \\
\Longrightarrow\ p_{\mathrm{r}}^2 &= \frac{1}{r}\left[\frac{1}{r}\,(\mathbf{r}\cdot\mathbf{p}) - \frac{\hbar}{i}\frac{1}{r}\right](\mathbf{r}\cdot\mathbf{p}) + \frac{\hbar}{i}\frac{1}{r^2}\,(\mathbf{r}\cdot\mathbf{p}) + \hbar^2\,\frac{1}{r^2} \\
&\quad + \frac{\hbar}{i}\frac{1}{r^2}\,(\mathbf{r}\cdot\mathbf{p}) - \hbar^2\,\frac{1}{r^2} \\
&= \frac{1}{r^2}\left[(\mathbf{r}\cdot\mathbf{p})^2 - i\,\hbar\,(\mathbf{r}\cdot\mathbf{p})\right] .
\end{aligned}$$

It then follows with the result from part 1.:

$$\mathbf{L}^2 = -r^2 p_{\mathrm{r}}^2 + r^2\mathbf{p}^2 \ \Longrightarrow\ \mathbf{p}^2 = p_{\mathrm{r}}^2 + \frac{1}{r^2}\,\mathbf{L}^2$$

Solution 6.1.3

Eigen-value problem:

$$\begin{aligned}
p_{\mathrm{r}}\,\varphi(\mathbf{r}) &= \frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}\,[r\,\varphi(\mathbf{r})] \overset{!}{=} \alpha\,\varphi(\mathbf{r}) \\
\Longleftrightarrow\ \frac{\partial}{\partial r}\,(r\,\varphi(\mathbf{r})) &= \frac{i}{\hbar}\,\alpha\,(r\,\varphi(\mathbf{r})) \\
\Longrightarrow\ r\,\varphi(\mathbf{r}) &\sim \exp\left(\frac{i}{\hbar}\alpha\, r\right) , \\
\varphi(\mathbf{r}) &\sim \frac{1}{r}\exp\left(\frac{i}{\hbar}\,\alpha\, r\right) .
\end{aligned}$$

The solution function $\varphi(\mathbf{r})$ does not fulfill the condition

$$\lim_{r \to 0} r\,\varphi(\mathbf{r}) = 0$$

(see part 3. of Exercise 6.1.1). In the space of the wave functions, in which p_r is Hermitian, the eigen-value problem of p_r has **no** solution. Therefore the operator p_r can **not** be interpreted as an observable.

Solution 6.1.4

1. $$H|E_n\rangle = E_n|E_n\rangle\ .$$

   The states $|E_n\rangle$ build a complete, orthonormalized system of eigen-states with eigen-values:

   $$E_0 \le E_1 \le E_2 \le \ldots\ .$$

   Let $|\psi\rangle$ be an arbitrary normalized state:

   $$\begin{aligned} |\psi\rangle &= \sum_n \alpha_n |E_n\rangle\ ; \quad \sum_n |\alpha_n|^2 = 1 \\ \Longrightarrow \langle\psi|H|\psi\rangle &= \sum_{n,m} \alpha_n^*\,\alpha_m \langle E_n|H|E_m\rangle \\ &= \sum_{n,m} \alpha_n^*\,\alpha_m\,E_m \langle E_n|E_m\rangle \\ &= \sum_n E_n|\alpha_n|^2 \ge E_0 \sum_n |\alpha_n|^2 = E_0\ . \end{aligned}$$

   The equality sign is correct only if in the expansion of $|\psi\rangle$ all $\alpha_n = 0$ except for α_0. But then $|\psi\rangle = |E_0\rangle$. The statement remains valid also in the case of a degenerate ground state!

2. We read the radial equation (6.17) as eigen-value equation of the operator

   $$\begin{aligned} H_l &= R + \frac{\hbar^2 l(l+1)}{2m\,r^2}\ , \\ R &= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\,\frac{\partial}{\partial r}\right) + V(r)\ . \end{aligned}$$

   Let $\psi_l(\mathbf{r})$ and $\psi_{l+1}(\mathbf{r})$ now be the wave functions to the lowest eigen-values E_l^* and E_{l+1}^*:

   $$\begin{aligned} E_l^* &= \int d^3r\,\psi_l^*(\mathbf{r})\left(R + \frac{\hbar^2 l(l+1)}{2m\,r^2}\right)\psi_l(\mathbf{r})\ , \\ E_{l+1}^* &= \int d^3r\,\psi_{l+1}^*(\mathbf{r})\left(R + \frac{\hbar^2 (l+1)\,(l+2)}{2m\,r^2}\right)\psi_{l+1}(\mathbf{r})\ . \end{aligned}$$

   According to part 1. it holds for any arbitrary wave function $\psi(\mathbf{r})$:

   $$\int d^3r\,\psi^*(\mathbf{r})\left(R + \frac{\hbar^2 l(l+1)}{2m\,r^2}\right)\psi^*(r) \ge E_l^*\ .$$

We now can write:

$$\begin{aligned} E^*_{l+1} &= A + B \,, \\ A &= \int d^3r\, \psi^*_{l+1}(\mathbf{r}) \left(R + \frac{\hbar^2 l\,(l+1)}{2m\,r^2} \right) \psi_{l+1}(\mathbf{r}) \geq E^*_l \,, \end{aligned}$$

$$\begin{aligned} B &= \int d^3r\, \psi^*_{l+1}(\mathbf{r})\, \frac{\hbar^2}{m\,r^2}\,(l+1)\,\psi_{l+1}(\mathbf{r}) \\ &= \int d^3r\, \frac{\hbar^2}{m\,r^2}\,(l+1)|\psi_{l+1}(\mathbf{r})|^2 > 0 \\ &\Longrightarrow\ E^*_{l+1} > E^*_l \end{aligned}$$

Section 6.2.6

Solution 6.2.1

(6.70) $\Longrightarrow$

$$\begin{aligned} L^{'}_{p+1} - L_{p+1} &= (2p+1-z)\left(L^{'}_p - L_p\right) - L_p - p^2\left(L^{'}_{p-1} - L_{p-1}\right) \\ &\overset{(6.71)}{=} (p+1-z)\,L^{'}_p - (2p+2-z)\,L_p \,. \end{aligned}$$

(6.71) $\Longrightarrow$

$$L'_{p+1} = (p+1)\,\left(L'_p - L_p\right) \,. \qquad (*)$$

Combination of these two equations yields:

$$L_{p+1} = z\,L'_p + (p+1-z)\,L_p \,.$$

Further differentiation gives:

$$L'_{p+1} = z\,L''_p + L'_p + (p+1-z)\,L'_p - L_p \,.$$

It follows with $(*)$

$$(p+1)\,(L'_p - L_p) = z\,L''_p + (p+2-z)\,L'_p - L_p$$

and from that:

$$0 = z\,L''_p + (1-z)\,L'_p + p\,L_p$$

Solution 6.2.2

Starting point now is the radial equation (6.31), which now takes the form:

$$\left(-\frac{\hbar^2}{2m_{\mathrm{f}}}\,\frac{d^2}{dr^2} - \frac{Z\,e^2}{4\pi\,\varepsilon_0 r} + \frac{\hat{c}}{r^2} + \frac{\hbar^2 l\,(l+1)}{2m_{\mathrm{f}}\,r^2} - E \right) u(r) = 0 \,.$$

When we define

$$\hat{l}\,\left(\hat{l}+1\right) \equiv l\,(l+1) + c \,,$$

then it follows, with the definitions (6.32)–(6.34) for ρ, E_{R} and η, a differential equation, which is formally identical with (6.35):

$$\left(\frac{d^2}{d\rho^2} + \frac{2}{\rho} - \frac{\hat{l}(\hat{l}+1)}{\rho^2} - \eta^2 \right) u(\rho) = 0 \, .$$

The path of solution is therefore exactly the same as that in Sect. 6.2.1. We obtain a truncation-condition in analogy to (6.40):

$$\eta \stackrel{!}{=} \frac{1}{\mu_0 + \hat{l} + 1} = \frac{1}{n - l + \hat{l}} \, .$$

This leads to the eigen-energies:

$$E_{nl} = -\frac{Z^2 \, E_{\mathrm{R}}}{(n - l + \hat{l})^2} \; ; \quad n = 1, 2, \ldots \, .$$

We estimate ($c \ll 1$):

$$\begin{aligned} \hat{l}(\hat{l}+1) &= l(l+1) + c \\ \Longrightarrow \left(\hat{l} + \frac{1}{2}\right)^2 &= \left(l + \frac{1}{2}\right)^2 + c \\ \Longrightarrow \hat{l} + \frac{1}{2} &\approx \left(l + \frac{1}{2}\right) \left[1 + \frac{1}{2} \, \frac{c}{(l+1/2)^2}\right] \\ \Longrightarrow \hat{l} &\approx l + \frac{c}{(2l+1)} \, . \end{aligned}$$

The *accidental* degeneracy with respect to l is thus removed:

$$E_{nl} \approx -\frac{Z^2 \, E_{\mathrm{R}}}{\left(n + \dfrac{c}{2l+1}\right)^2} \; ; \quad n = 1, 2, 3, \ldots \, .$$

Solution 6.2.3

1. H_0 : Hamilton operator without field. According to (5.187) it holds with field:

$$H = H_0 + H_m \; ; \quad H_m = \frac{\mu_{\mathrm{B}}}{\hbar} \, (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B} = \frac{1}{\hbar} \, \mu_{\mathrm{B}} \, B(L_z + 2S_z) \, .$$

$|n \, l \, m_l \, m_s\rangle$ is also eigen-state of L_z and S_z. The state thus does not change!

$$H|n \, l \, m_l \, m_s\rangle = [E_n + \mu_{\mathrm{B}} \, B(m_l + 2m_s)] \, |n \, l \, m_l \, m_s\rangle \, .$$

New eigen-energies:

$$\widehat{E}_{n m_l m_s} = E_n + \mu_{\mathrm{B}} \, B(m_l + 2m_s) \, .$$

2. Before: degree of degeneracy $g_n = 2n^2$ (6.47). By the field $\mathbf{B}$ the degeneracy with respect to m_l and m_s is removed. It is left only that with respect to l, where, however, only the values $l \geq |m_l|$ are allowed:

$$g_{nm_lm_s} = \sum_{l=|m_l|}^{n-1} 1 = n - |m_l| \; .$$

Solution 6.2.4

Hamilton operator in position representation:

$$H = -\frac{\hbar^2}{2m_\mathrm{e}}\Delta - \frac{e^2}{4\pi\,\varepsilon_0 r} = -\frac{\hbar^2}{2m_\mathrm{e}}\left(\Delta + \frac{2}{a_\mathrm{B}\,r}\right) \; .$$

Laplace operator:

$$\begin{aligned}
\Delta &= \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\mathbf{L}^2}{\hbar^2 r^2} \\
\Longrightarrow\ \Delta\,\psi &= \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{1\cdot 2}{r^2}\right)\psi \; , \\
\frac{d}{dr}\,r\,e^{-r/2a_\mathrm{B}} &= \left(1 - \frac{r}{2a_\mathrm{B}}\right) e^{-r/2a_\mathrm{B}} \; , \\
\frac{d^2}{dr^2}\,r\,e^{-\frac{r}{2a_\mathrm{B}}} &= \left(-\frac{1}{2a_\mathrm{B}} - \frac{1}{2a_\mathrm{B}} + \frac{r}{4a_\mathrm{B}^2}\right) e^{-\frac{r}{2a_\mathrm{B}}} \\
\Longrightarrow\ \Delta\psi &= \left(-\frac{1}{a_\mathrm{B}r} + \frac{1}{4a_\mathrm{B}^2} + \frac{2}{r^2} - \frac{1}{a_\mathrm{B}r} - \frac{2}{r^2}\right)\psi = \left(-\frac{2}{a_\mathrm{B}r} + \frac{1}{4a_\mathrm{B}^2}\right)\psi \\
\Longrightarrow\ H\,\psi &= -\frac{\hbar^2}{2m_\mathrm{f}}\,\frac{1}{4a_\mathrm{B}^2}\,\psi \overset{(6.33)}{=} -\frac{E_\mathrm{R}}{4}\,\psi \ \Longrightarrow\ \psi \text{ is eigen-state!}
\end{aligned}$$

Energy-eigen value:

$$E_2 = -\frac{E_\mathrm{R}}{4} \; .$$

Quantum numbers:

$$n = 2,\, l = 1,\, m_l = 1: \quad \psi = \psi_{211}(\mathbf{r}) \; .$$

Solution 6.2.5

$$\psi_{nlm_l}(\mathbf{r}) = R_{nl}(r)Y_{lm_l}(\vartheta,\varphi)$$

Radial contribution $R_{nl}(r)$: real!

$$Y_{lm_l}(\vartheta,\varphi) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-m_l)!}{(l+m_l)!}}P_l^{m_l}(\cos\vartheta)e^{im_l\varphi}$$

$P_l^{m_l}(\cos\vartheta)$: real!

1. Current density of the electron:

$$\mathbf{j} = (-e)\frac{\hbar}{2mi}(\psi^*\nabla\psi - \psi\nabla\psi^*)$$

Spherical coordinates:

$$\nabla = \left(\frac{\partial}{\partial r}, \frac{1}{r}\frac{\partial}{\partial\vartheta}, \frac{1}{r\sin\vartheta}\frac{\partial}{\partial\varphi}\right) .$$

Component-by-component:

$$\begin{aligned} j_r &= -\frac{e\hbar}{2mi}|Y_{lm_l}(\vartheta,\varphi)|^2 \underbrace{(R^*_{nl}\frac{\partial}{\partial r}R_{nl} - R_{nl}\frac{\partial}{\partial r}R^*_{nl})}_{=0,\ \text{since}\ R_{nl}\equiv R^*_{nl}} = 0 \\ j_\vartheta &= -\frac{e\hbar}{2mi}R^2_{nl}(r)\frac{2l+1}{4\pi}\frac{(l-m_l)!}{(l+m_l)!}\frac{1}{r} \\ &\quad \underbrace{\times (P_l^{m_l\,*}(\cos\vartheta)\frac{\partial}{\partial\vartheta}P_l^{m_l}(\cos\vartheta) - P_l^{m_l}(\cos\vartheta)\frac{\partial}{\partial\vartheta}P_l^{m_l\,*}(\cos\vartheta))}_{=0,\ \text{since}\ P_l^{m_l}\equiv P_l^{m_l\,*}} = 0 . \end{aligned}$$

That is illustratively clear, because for $j_r \neq 0$, e.g., charge would flow apart or would concentrate itself in the nucleus.

$$\begin{aligned} j_\varphi &= -\frac{e\hbar}{2mi}R^2_{nl}(r)\frac{2l+1}{4\pi}\frac{(l-m_l)!}{(l+m_l)!}(P_l^{m_l}(\cos\vartheta))^2\frac{1}{r\sin\vartheta} \\ &\quad \underbrace{\times (e^{-im_l\varphi}\frac{\partial}{\partial\varphi}e^{im_l\varphi} - e^{im_l\varphi}\frac{\partial}{\partial\varphi}e^{-im_l\varphi})}_{=2im_l} \\ &= -\frac{e\hbar}{m}m_l\frac{1}{r\sin\vartheta}R^2_{nl}(r)|Y_{lm_l}(\vartheta,\varphi)|^2 \end{aligned}$$

$\Longrightarrow$ current density

$$\mathbf{j}(\mathbf{r}) = -\frac{e\hbar}{m}m_l\frac{1}{r\sin\vartheta}R^2_{nl}(r)|Y_{lm_l}(\vartheta,\varphi)|^2\mathbf{e}_\varphi .$$

2. Magnetic moment
Electrodynamics: Current, which flows around the area F, creates a magnetic moment

$$d\mu_z = F\,dI_\varphi .$$

With $F = \pi r^2\sin^2\vartheta$ (Fig. A.4):

$$\begin{aligned} \Longrightarrow\ d\mu_z &= -\frac{e\hbar}{m}m_l\frac{1}{r\sin\vartheta}|\psi_{nlm_l}(\mathbf{r})|^2\pi r^2\sin^2\vartheta\,df \\ &= -\frac{e\hbar}{2m}m_l|\psi_{nlm_l}(\mathbf{r})|^2 \underbrace{(2\pi r\sin\vartheta)df}_{\text{volume of the thread of current}} . \end{aligned}$$

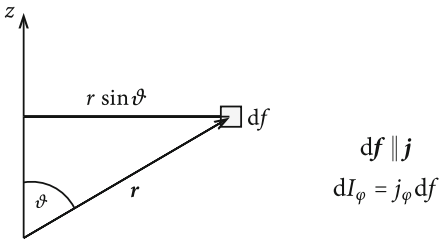


Figure A.4:

Summation over *'all'* threads of current;
$|\psi_{nlm_l}|^2$: φ independent, normalized

$$\begin{aligned} \Longrightarrow \quad \boldsymbol{\mu} &= \mu_z \mathbf{e}_z \\ \mu_z &= -\mu_{\mathrm{B}} m_l \end{aligned}$$

μ_{B}: Bohr magneton.

Solution 6.2.6

$$\begin{aligned} H\psi_{100}(\mathbf{r}) &= -E_R\,\psi_{100}(\mathbf{r}) \\ H\psi_{211}(\mathbf{r}) &= -\frac{E_R}{4}\psi_{211}(\mathbf{r}) \\ H\psi_{21-1}(\mathbf{r}) &= -\frac{E_R}{4}\psi_{21-1}(\mathbf{r}) \end{aligned}$$

$$\begin{aligned} \mathbf{L}^2\psi_{100}(\mathbf{r}) &= 0\,; & L_z\psi_{100}(\mathbf{r}) &= 0 \\ \mathbf{L}^2\psi_{211}(\mathbf{r}) &= 2\hbar^2\psi_{211}(\mathbf{r})\,; & L_z\psi_{211}(\mathbf{r}) &= \hbar\psi_{211}(\mathbf{r}) \\ \mathbf{L}^2\psi_{21-1}(\mathbf{r}) &= 2\hbar^2\psi_{21-1}(\mathbf{r})\,; & L_z\psi_{21-1}(\mathbf{r}) &= -\hbar\psi_{21-1}(\mathbf{r})\,. \end{aligned}$$

Expectation values:

$$\begin{aligned} \langle\psi|H|\psi\rangle &= \frac{1}{25}(9\langle 100|H|100\rangle + 4\langle 211|H|211\rangle + 12\langle 21-1|H|21-1\rangle) \\ &= -\frac{E_R}{25}\left(9\cdot 1 + 4\cdot\frac{1}{4} + 12\cdot\frac{1}{4}\right) = -\frac{13}{25}E_R \\ \langle\psi|\mathbf{L}^2|\psi\rangle &= \frac{1}{25}(9\cdot 0 + 4\cdot 2\hbar^2 + 12\cdot 2\hbar^2) = \frac{32}{25}\hbar^2 \\ \langle\psi|L_z|\psi\rangle &= \frac{1}{25}(9\cdot 0 + 4\hbar - 12\hbar) = -\frac{8}{25}\hbar\,. \end{aligned}$$

Solution 6.2.7

Starting point is the radial equation (6.35). For simplicity we drop, at first, the indexes n, l in the function $u(\rho)$. We multiply (6.35) by

$$\left[\rho^{k+1}\,u'(\rho) - \frac{1}{2}(k+1)\,\rho^k\,u(\rho)\right]$$

and write:

$$\overline{\rho^k} \equiv \int_0^\infty d\rho\, \rho^k\, u^2(\rho) \overset{(6.32)}{\longrightarrow} \left(\frac{Z}{a_\mathrm{B}}\right)^{k+1} \langle r^k \rangle \,.$$

Then it follows at first:

$$(1)+(2)+(3) = (k+1)\,\overline{\rho^{k-1}} - \frac{1}{2}(k+1)l(l+1)\,\overline{\rho^{k-2}} - \frac{1}{2}\,(k+1)\,\eta^2\,\overline{\rho^k}\,,$$

$$\begin{aligned}
(1) &= \int_0^\infty d\rho\, u''(\rho)\, u'(\rho)\, \rho^{k+1}\,, \\
(2) &= -\frac{1}{2}(k+1)\int_0^\infty d\rho\, u''(\rho)\, u(\rho)\, \rho^k\,, \\
(3) &= \int_0^\infty d\rho\, u'(\rho) u(\rho)\, \left[2\rho^k - l(l+1)\,\rho^{k-1} - \eta^2\,\rho^{k+1}\right]\,.
\end{aligned}$$

For the following partial integrations we exploit (6.28):

$$\begin{aligned}
&\rho \to \infty: \; u(\rho) \to 0\,; \quad u'(\rho) \to 0\,, \\
&\rho \to 0: \; u(\rho) \sim \rho^{l+1}\,; \quad u'(\rho) \sim \rho^l, \\
(1) &= \int_0^\infty d\rho\, \rho^{k+1}\, \frac{1}{2}\left[(u'(\rho))^2\right]' \\
&= \underbrace{\rho^{k+1}\,\frac{1}{2}\,(u'(\rho))^2}_{=0,\;\text{if}\;\; 2l\,+\,k\,+\,1\,>\,0}\Bigg|_0^\infty - \frac{1}{2}\,(k+1)\int_0^\infty d\rho\,\rho^k\,\left(u'(\rho)\right)^2\,, \\
(2) &= -\frac{1}{2}\,(k+1)\int_0^\infty d\rho\,\left(u(\rho)\,\rho^k\right)\,u''(\rho) \\
&= \underbrace{-\frac{1}{2}\,(k+1)\,u(\rho)\,u'(\rho)\,\rho^k}_{=0,\;\text{if}\;\; 2l+k+1>0}\Bigg|_0^\infty \\
&\quad + \frac{1}{2}\,(k+1)\int_0^\infty d\rho\, u'(\rho)\,\left(k\,u\,(\rho)\,\rho^{k-1} + u'(\rho)\,\rho^k\right)\,.
\end{aligned}$$

This yields:

$$(1)+(2) = \frac{1}{2}\,k\,(k+1)\int_0^\infty d\rho\,\rho^{k-1}\,u'(\rho)\,u(\rho)\,.$$

That can be combined with (3):

$$\begin{aligned}
& (1)+(2)+(3) \\
= & \int_0^\infty d\rho\,\frac{1}{2}\,(u^2(\rho))'\,\left[2\rho^k+\left\{\frac{1}{2}\,k(k+1)-l(l+1)\right\}\,\rho^{k-1}-\eta^2\,\rho^{k+1}\right] \\
= & \underbrace{\frac{1}{2}\,u^2(\rho)[\ldots]}_{=0,\ \text{if}\ 2l+k+1>0}\Bigg|_0^\infty-\frac{1}{2}\int_0^\infty d\rho\,u^2(\rho)\,\left[2k\,\rho^{k-1}\right. \\
& \left.+(k-1)\,\left\{\frac{1}{2}\,k(k+1)-l(l+1)\right\}\,\rho^{k-2}-\eta^2(k+1)\,\rho^k\right] \\
= & \frac{1}{2}\,(k+1)\,\eta^2\,\overline{\rho^k}-k\,\overline{\rho^{k-1}}-\frac{1}{2}\,(k-1)\,\left\{\frac{1}{2}\,k(k+1)-l(l+1)\right\}\,\overline{\rho^{k-2}}\,.
\end{aligned}$$

All in all we have found:

$$\begin{aligned}
& (k+1)\eta^2\overline{\rho^k}-(2k+1)\overline{\rho^{k-1}} \\
& +\left[-\frac{1}{4}k(k^2-1)+\frac{1}{2}(k-1)\,l\,(l+1)+\frac{1}{2}(k+1)\,l\,(l+1)\right]\,\overline{\rho^{k-2}}=0\,.
\end{aligned}$$

It follows eventually with $\eta=1/n$:

$$\frac{k+1}{n^2}\,\overline{\rho^k}-(2k+1)\,\overline{\rho^{k-1}}+\frac{k}{4}\,\left[(2l+1)^2-k^2\right]\,\overline{\rho^{k-2}}=0\,.$$

We now multiply this equation with $(a_{\rm B}/Z)^{k+1}$ and introduce again the so far suppressed indexes n, l of the expectation values:

$$\frac{k+1}{n^2}\langle r^k\rangle_{nl}-(2k+1)\,\frac{a_{\rm B}}{Z}\langle r^{k-1}\rangle_{nl}+\frac{k}{4}\,\left[(2l+1)^2-k^2\right]\,\left(\frac{a_{\rm B}}{Z}\right)^2\langle r^{k-2}\rangle_{nl}=0\,.$$

Solution 6.2.8

Ground state wave function

$$\begin{aligned}
\psi_{100}(\mathbf{r}) &= R_{10}(r)\cdot Y_{00}(\vartheta,\varphi) \\
&= \frac{2}{a_{\rm O}^{3/2}}\exp(-\frac{r}{a_{\rm O}})\,\frac{1}{\sqrt{4\pi}}\,.
\end{aligned}$$

1. Radial position probability:

$$\begin{aligned}
w_{nl}(r)dr &= r^2dr\int d\Omega\,|\psi_{nlm_l}(\mathbf{r})|^2 \\
&= r^2dr\,|R_{nl}(r)|^2\,.
\end{aligned}$$

Most probable value = maximum of $w_{10}(r)$

$$\begin{aligned} w_{10}(r) &= \frac{4}{a_{\mathrm{B}}^3}\exp(-\frac{2r}{a_{\mathrm{B}}})r^2 \\ \Longrightarrow \frac{dw_{10}}{dr} &= \frac{4}{a_{\mathrm{B}}^3}\left(2r-\frac{2r^2}{a_{\mathrm{B}}}\right)\exp\left(-\frac{2r}{a_{\mathrm{B}}}\right) \stackrel{!}{=} 0 \\ \Longrightarrow (r)_{10}^{\max} &= a_{\mathrm{O}}\ . \end{aligned}$$

2. Expectation values in the ground state

$$\begin{aligned} \langle r^k\rangle_{10} &= \int d^3r\, r^k|\psi_{100}(\mathbf{r})|^2 = \int\limits_0^\infty dr\, r^{2+k}|R_{10}(r)|^2 \\ &= \int\limits_0^\infty dr\, r^k w_{10}(r) = \frac{4}{a_{\mathrm{B}}^3}\int\limits_0^\infty dr\, r^{2+k}e^{-\frac{2r}{a_{\mathrm{B}}}}\ . \end{aligned}$$

For abbreviation $\rho = 2\frac{r}{a_{\mathrm{B}}}$:

$$\begin{aligned} \langle r^k\rangle_{10} &= \frac{a_{\mathrm{B}}^k}{2^{k+1}}\int\limits_0^\infty d\rho\,\rho^{k+2}e^{-\rho} = \frac{a_{\mathrm{B}}^k}{2^{k+1}}\underbrace{\Gamma(k+3)}_{=(k+2)!} \\ \Longrightarrow \langle r^k\rangle_{10} &= \frac{(k+2)!}{2^{k+1}}a_{\mathrm{B}}^k\ , \quad k=-2,-1,0,1,\ldots \end{aligned}$$

Especially:

$$\begin{aligned} k=1: &\quad \langle r\rangle_{10} = \tfrac{3}{2}a_{\mathrm{B}} \\ k=2: &\quad \langle r^2\rangle_{10} = \tfrac{4!}{8}a_{\mathrm{B}}^2 = 3a_{\mathrm{B}}^2 \end{aligned}$$

$$\Longrightarrow \Delta r_{10} = a_{\mathrm{B}}\sqrt{3-\frac{9}{4}} = \frac{\sqrt{3}}{2}a_{\mathrm{B}}\ .$$

3.

$$\begin{aligned} W &= \int\limits_{a_{\mathrm{B}}}^\infty dr\, w_{10}(r) = \frac{4}{a_{\mathrm{B}}^3}\int\limits_{a_{\mathrm{B}}}^\infty dr\, r^2 e^{-\frac{2r}{a_{\mathrm{B}}}} = \frac{1}{2}\int\limits_2^\infty d\rho\,\rho^2 e^{-\rho} \\ &= \frac{1}{2}\{-\rho^2e^{-\rho}|_2^\infty + (-2\rho e^{-\rho})\big|_2^\infty + 2\int\limits_2^\infty d\rho\, e^{-\rho}\} \\ &= \frac{1}{2}\cdot 10\, e^{-2} \approx 0.6767\ . \end{aligned}$$

4. Analogous to 1.

$$\bar{w}(p)dp = p^2dp\int d\Omega_p\,|\bar{\psi}_{100}(\mathbf{p})|^2\ .$$

Now:

$$\begin{aligned}
\bar{\psi}_{100}(\mathbf{p}) &= \frac{1}{(2\pi\hbar)^{3/2}} \int d^3r\, e^{-\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}}\, \psi_{100}(\mathbf{r}) \\
&= \frac{1}{\sqrt{4\pi}} \frac{2}{(2\pi\hbar a_{\mathrm{B}})^{3/2}} \int_0^\infty dr\, r^2 e^{-\frac{r}{a_{\mathrm{B}}}} \int_0^{2\pi} d\varphi \underbrace{\int_{-1}^{+1} d\cos\vartheta\, e^{-\frac{i}{\hbar}p\,r\cos\vartheta}}_{=\frac{1}{-\frac{i}{\hbar}pr}\left(e^{-\frac{i}{\hbar}pr} - e^{\frac{i}{\hbar}pr}\right)} \\
&= \frac{2}{\sqrt{4\pi}} \frac{2\pi}{(2\pi\hbar a_{\mathrm{B}})^{3/2}} \frac{i\hbar}{p} \Big(\int_0^\infty dr\, r\, e^{-(\frac{1}{a_{\mathrm{B}}}+\frac{ip}{\hbar})r} - \int_0^\infty dr\, r\, e^{-(\frac{1}{a_{\mathrm{B}}}-\frac{ip}{\hbar})r} \Big) \\
&= \frac{1}{\pi\sqrt{2\hbar}} \frac{i}{p\, a_{\mathrm{B}}^{3/2}} \Big(\frac{1}{\frac{1}{a_{\mathrm{B}}}+\frac{ip}{\hbar}} \int_0^\infty dr\, e^{-(\frac{1}{a_{\mathrm{B}}}+\frac{ip}{\hbar})r} \\
&\qquad - \frac{1}{\frac{1}{a_{\mathrm{B}}}-\frac{ip}{\hbar}} \int_0^\infty dr\, e^{-(\frac{1}{a_{\mathrm{B}}}-\frac{ip}{\hbar})r} \Big) \\
&\qquad \text{(actually a complex integration!)} \\
&= \frac{i}{\pi\sqrt{2\hbar}p\, a_{\mathrm{B}}^{3/2}} \Big(\frac{1}{(\frac{1}{a_{\mathrm{B}}}+\frac{ip}{\hbar})^2} - \frac{1}{(\frac{1}{a_{\mathrm{B}}}-\frac{ip}{\hbar})^2} \Big) \\
&= \frac{\frac{4}{\hbar\, a_{\mathrm{B}}}}{\pi\sqrt{2\hbar}\, a_{\mathrm{B}}^{3/2}} \frac{1}{(\frac{1}{a_{\mathrm{B}}^2}+\frac{p^2}{\hbar^2})^2} \\
&\Longrightarrow \bar{\psi}_{100}(\mathbf{p}) = \frac{(\frac{2a_{\mathrm{B}}}{\hbar})^{3/2}}{\pi(1+\frac{a_{\mathrm{B}}^2 p^2}{\hbar^2})^2} \,.
\end{aligned}$$

No angle-dependence:

$$\bar{w}(p) = 4\pi p^2 |\bar{\psi}_{100}(\mathbf{p})|^2 = \frac{32}{\pi} \Big(\frac{\hbar}{a_{\mathrm{B}}}\Big)^5 \frac{p^2}{(p^2+\frac{\hbar^2}{a_{\mathrm{B}}^2})^4} \,.$$

Position of the maximum:

$$\begin{aligned}
\frac{d\bar{w}}{dp} \stackrel{!}{=} 0 \quad &= \quad \frac{32}{\pi} \Big(\frac{\hbar}{a_{\mathrm{B}}}\Big)^5 \frac{(p^2+\frac{\hbar^2}{a_{\mathrm{B}}^2})^4 2p - 4p^2 \cdot 2p(p^2+\frac{\hbar^2}{a_{\mathrm{B}}^2})^3}{(p^2+\frac{\hbar^2}{a_{\mathrm{B}}^2})^8} \\
&\Longleftrightarrow \quad (p^2+\frac{\hbar^2}{a_{\mathrm{B}}^2}) = 4p^2 \\
\Longrightarrow\ p_{10}^{\max} \quad &= \quad \frac{1}{\sqrt{3}} \frac{\hbar}{a_{\mathrm{B}}} \approx 0.5774 \frac{\hbar}{a_{\mathrm{B}}}
\end{aligned}$$

is the most probable value of the magnitude of the momentum!

Solution 6.2.9

1.

$$\int d^3r\, \psi^*_{nlm_l}(\mathbf{r})\, \hat{p}\, \psi_{nlm_l}(\mathbf{r}) = q \int_0^\infty dr\, r^3\, R^*_{nl}(r)\, R_{nl}(r) \int_0^{2\pi} d\varphi\, I_{lm_l} \ ,$$

$$I_{lm_l} \equiv \int_{-1}^{+1} d\cos\vartheta \cos\vartheta |Y_{lm_l}(\vartheta,\varphi)|^2 \overset{(5.103)}{=} \frac{(2l+1)\,(l-m_l)!}{4\pi\,(l+m_l)!}\, Q_{lm_l} \ ,$$

$$Q_{lm_l} = \int_{-1}^{+1} d\cos\vartheta \cos\vartheta\, |P_l^{m_l}(\cos\vartheta)|^2 \ .$$

According to (5.95) and (5.96):

$$\begin{aligned} & P_l^{m_l}(-\cos\vartheta) = (-1)^{l+m_l} P_l^{m_l}(\cos\vartheta) \\ \Longrightarrow \quad & |P_l^{m_l}(\cos\vartheta)|^2 \text{ even function of } \cos\vartheta \\ \Longrightarrow \quad & Q_{lm_l} = 0 \ . \end{aligned}$$

2. At first, it surely must be

$$m'_l = m_l \ ,$$

because $\hat{p}$ does not depend on φ:

$$\begin{aligned} & \int d^3r\, \psi^*_{nl'm_l}(\mathbf{r})\, \hat{p}\, \psi_{nlm_l}(\mathbf{r}) \sim \widehat{Q}_{l'l} \\ \widehat{Q}_{l'l} \quad = \quad & \int_{-1}^{+1} d\cos\vartheta \cos\vartheta\, P_{l'}^{m_l}(\cos\vartheta)\, P_l^{m_l}(\cos\vartheta) \ . \end{aligned}$$

Because of (5.95),

$$P_l^{-m_l}(z) = (-1)^{m_l} \frac{(l-m_l)!}{(l+m_l)!} P_l^{m_l}(z),$$

we can assume $m_l \geq 0$. The matrix element vanishes for $l = l'$. We therefore take w.l.o.g.:

$$l' \leq l-1 \ .$$

But then it must also be

$$0 \leq m_l \leq l-1;\, .$$

So we can use the recursion formula:

$$z\, P_l^{m_l}(z) = \alpha_{lm_l} P_{l+1}^{m_l}(z) + \beta_{lm_l} P_{l-1}^{m_l}(z) \ .$$

Because of the orthogonality of the Legendre polynomials (5.101) it follows therewith

$$\widehat{Q}_{l'l} \neq 0 \text{ only for } l' = l+1 \text{ and } l' = l-1.$$

The matrix element of the operator of the dipole moment is therefore unequal zero only for

$$\begin{aligned} m_l' &= m_l \,, \\ l' &= l \pm 1 \,. \end{aligned}$$

It describes electric dipole transitions!

3.

$$\langle\psi|\hat{p}|\psi\rangle \overset{!}{\neq} 0, \qquad |\psi\rangle \quad \text{eigen-state to } n=2.$$

Because of 1. $|\psi\rangle$ must then be a linear combination of several $|2l\,m_l\rangle$:

$$|\psi\rangle = \frac{1}{\sqrt{2}}\left(|200\rangle + |210\rangle\right) \,.$$

This ansatz is an eigen-state only for the special case of the Coulomb potential with its *accidental* degeneracy with respect to l. For other central potentials this is not true!

$$\begin{aligned} \langle\psi|\hat{p}|\psi\rangle &= \frac{1}{2}\left(\langle 200|\hat{p}|210\rangle + \langle 210|\hat{p}|200\rangle\right) \,, \\ |200\rangle &\mathrel{\widehat{=}} \frac{1}{2\sqrt{2\pi\, a_{\mathrm{B}}^3}}\left(1 - \frac{r}{2a_{\mathrm{B}}}\right) e^{-r/2a_{\mathrm{B}}} \quad (\text{(6.61) and (5.108)}) \,, \\ |210\rangle &\mathrel{\widehat{=}} \frac{1}{4\sqrt{2\pi\, a_{\mathrm{B}}^5}} \cos\vartheta\, r\, e^{-r/2a_{\mathrm{B}}} \quad (\text{(6.62) and (5.109)}) \,, \end{aligned}$$

$$\begin{aligned} \langle 200|\hat{p}|210\rangle &= \frac{q}{16\pi\, a_{\mathrm{B}}^4}\, 2\pi \int_0^\infty r^2\, dr \int_{-1}^{+1} d\cos\vartheta \left(1 - \frac{r}{2a_{\mathrm{B}}}\right) r^2 \cos^2\vartheta\, e^{-r/a_{\mathrm{B}}} \\ &= \frac{q}{12\, a_{\mathrm{B}}^4} \int_0^\infty dr \left(r^4 - \frac{r^5}{2a_{\mathrm{B}}}\right) e^{-r/a_{\mathrm{B}}} \\ &= \frac{q}{12}\, a_{\mathrm{B}} \int_0^\infty d\rho \left(\rho^4 - \frac{1}{2}\,\rho^5\right) e^{-\rho} \\ &= \frac{q}{12}\, a_{\mathrm{B}} \left(\Gamma(5) - \frac{1}{2}\,\Gamma(6)\right) = \frac{1}{12}\, q\, a_{\mathrm{B}} \left(4! - \frac{1}{2}\, 5!\right) = -3q\, a_{\mathrm{B}} \end{aligned}$$

$$\Longrightarrow \quad \langle\psi|\hat{p}|\psi\rangle = -3q\, a_{\mathrm{B}} \,.$$

Solution 6.2.10

We perform the proof for the x-component:

$$\begin{aligned} p_x &= \mu\dot{x} = \mu\,(\dot{x}_1 - \dot{x}_2) \\ \Longrightarrow\ [x, p_x]_- &= [x_1 - x_2,\ \mu(\dot{x}_1 - \dot{x}_2)]_- = \mu\ ([x_1, \dot{x}_1]_- + [x_2, \dot{x}_2]_-) \\ &= \mu\left(\frac{1}{m_1}\,[x_1, m_1\dot{x}_1]_- + \frac{1}{m_2}\,[x_2, m_2\dot{x}_2]_-\right)\,. \end{aligned}$$

In the bracket there appear the fundamental commutators of the x-components of the position vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ with the *normal* momenta $\mathbf{p}_{1,2} = m_{1,2}\,\dot{\mathbf{r}}_{1,2}$:

$$[x, p_x]_- = \mu\left(\frac{1}{m_1}\,i\,\hbar + \frac{1}{m_2}\,i\,\hbar\right) = i\,\hbar\,.$$

Analogously, the proof for the other components.

In the case of the center-of-mass coordinates we have:

$$\begin{aligned} [X, P_x]_- &= \left[\frac{1}{M}\,(m_1x_1 + m_2x_2),\ M\,\frac{1}{M}\,(m_1\dot{x}_1 + m_2\dot{x}_2)\right]_- \\ &= \frac{1}{M}\ (m_1\,[x_1, m_1\dot{x}_1]_- + m_2\,[x_2, m_2\dot{x}_2]_-) \\ &= \frac{1}{M}\,(m_1 + m_2)\,i\,\hbar = i\,\hbar\,. \end{aligned}$$

Solution 6.2.11

1. Hamilton operator:

$$H = T + V = \frac{\mathbf{p}^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r}\,.$$

It is to be calculated:

$$\begin{aligned} [H,\,\mathbf{r}\cdot\mathbf{p}]_- &= [H,\,\mathbf{r}]_-\cdot\mathbf{p} + \mathbf{r}\cdot[H,\,\mathbf{p}]_- \\ [H,\,\mathbf{r}]_- &= \left[\frac{\mathbf{p}^2}{2m},\,\mathbf{r}\right]_- = \frac{1}{2m}\sum_i \left(p_i\,[p_i,\,\mathbf{r}]_- + [p_i,\,\mathbf{r}]_-\,p_i\right) \\ &= \frac{1}{2m}\sum_i \left(p_i\,[p_i,\,x_i]_-\,\mathbf{e}_i + [p_i,\,x_i]_-\,\mathbf{e}_i p_i\right) \\ &= \frac{1}{2m}\sum_i \left(\frac{\hbar}{i}p_i\mathbf{e}_i + \frac{\hbar}{i}\mathbf{e}_i p_i\right) \\ &= \frac{\hbar}{im}\mathbf{p} \\ [H,\,\mathbf{p}]_- &= [V(\mathbf{r}),\,\mathbf{p}]_- = -\frac{\hbar}{i}\nabla V(\mathbf{r})\,. \end{aligned}$$

It holds therewith, still quite generally:

$$\frac{i}{\hbar}\left[H, \mathbf{r}\cdot\mathbf{p}\right]_- = \frac{1}{m}\mathbf{p}^2 - \left(\mathbf{r}\cdot\nabla\right)V(\mathbf{r}) \ .$$

Because of

$$-\left(\mathbf{r}\cdot\nabla\right)V(\mathbf{r}) = -r\frac{\partial}{\partial r}V(\mathbf{r}) = -r\frac{e^2}{4\pi\varepsilon_0 r^2} = V(\mathbf{r})$$

it finally follows for the hydrogen atom:

$$\frac{i}{\hbar}\left[H, \mathbf{r}\cdot\mathbf{p}\right]_- = 2T + V \ .$$

2. $|\psi\rangle$ is eigen-state of H:

$$H|\psi\rangle = E|\psi\rangle \ .$$

Together with the fact that H is Hermitian, this is exploited for the calculation of the following expectation value:

$$\begin{aligned}\langle\psi|\left[H, \mathbf{r}\cdot\mathbf{p}\right]_-|\psi\rangle &= \langle\psi|H\,\mathbf{r}\cdot\mathbf{p}|\psi\rangle - \langle\psi|\mathbf{r}\cdot\mathbf{p}\,H|\psi\rangle \\ &= E\left(\langle\psi|\mathbf{r}\cdot\mathbf{p}|\psi\rangle - \langle\psi|\mathbf{r}\cdot\mathbf{p}|\psi\rangle\right) \\ &= 0 \ .\end{aligned}$$

With 1. it follows then the *'virial theorem'*:

$$2\langle T\rangle + \langle V\rangle = 0 \ .$$

This can further be analyzed when one uses the result (6.43):

$$\langle H\rangle = \langle T\rangle + \langle V\rangle = -\frac{E_\mathrm{R}}{n^2} \ .$$

Subtraction of the last two equations yields:

$$\langle T\rangle = \frac{E_\mathrm{R}}{n^2} \ \ ; \ \ \langle V\rangle = -2\frac{E_\mathrm{R}}{n^2} \ .$$

3. Spherical harmonic oscillator:

$$H = \frac{\mathbf{p}^2}{2m} + \frac{1}{2}m\omega^2 r^2 \ .$$

As in 1. we have at first:

$$\frac{i}{\hbar}\left[H, \mathbf{r}\cdot\mathbf{p}\right]_- = \frac{1}{m}\mathbf{p}^2 - r\frac{\partial}{\partial r}V(\mathbf{r}) = \frac{1}{m}\mathbf{p}^2 - 2V(\mathbf{r}) = 2T - 2V \ .$$

Because of $H|\psi\rangle = E|\psi\rangle$ we can use again:

$$\langle\psi|\left[H, \mathbf{r}\cdot\mathbf{p}\right]_-|\psi\rangle = 0 \ .$$

This means

$$\langle T\rangle = \langle V\rangle \ .$$

Section 6.3.5

Solution 6.3.1

1. Starting point is the Bessel differential equation (6.114):

$$\left[\frac{d^2}{dz^2}+\frac{2}{z}\frac{d}{dz}-\frac{l(l+1)}{z^2}+1\right]R(z)=0\,,\qquad z=k\,r\,,$$

Wave function: $\psi(\mathbf{r})=R(r)\,Y_{lm_l}(\vartheta\varphi)$,
Boundary conditions:

$$\begin{aligned} a)\quad & \psi(\mathbf{r})\equiv 0 \quad \text{for } r>a,\\ b)\quad & V(r)\equiv 0 \quad \text{for } r\le a\\ & \Longrightarrow\ k^2=\frac{2m}{\hbar^2}E\,,\\ c)\quad & \psi(\mathbf{r}) \text{ regular at the origin.}\end{aligned}$$

General solution (6.121):

$$\begin{aligned} R_l(z) &= a_l\,j_l(z)+b_l\,n_l(z)\,,\\ b_l &= 0 \text{ because of c)}\\ \Longrightarrow\ \psi_{lm_l}(\mathbf{r}) &= a_l\,j_l(k\,r)\,Y_{lm_l}(\vartheta,\varphi)\,.\end{aligned}$$

2. Boundary condition a):

$$j_l(k\,a)=0\,.$$

The zeros of the Bessel function are known. From these one takes for a given l the *'allowed'* values for $k\,a$, and therewith for the energy E!

$l=0$

$$j_0(z)=\frac{\sin z}{z}\,.$$

No zero at $z=0$:

$$\begin{aligned} \lim_{z\to 0} j_0(z) &= \lim_{z\to 0}\frac{\cos z}{1}=1 \qquad \text{(l'Hospital's rule)}\,,\\ j_0(k_0 a) &\stackrel{!}{=} 0 \Longrightarrow k_{0,\mu}=\mu\,\pi\,\frac{1}{a}\,,\\ \mu &= 1,2,3,\ldots\\ \Longrightarrow\ E_{0,\mu} &= \frac{\hbar^2\pi^2}{2m\,a^2}\,\mu^2\,.\end{aligned}$$

3. Asymptotic solutions:

$$\begin{aligned} z &\gg \sqrt{l(l+1)}\gtrsim l\,,\\ j_l(z) &\sim \frac{1}{z}\sin\left(z-\frac{l\,\pi}{2}\right)\,,\\ j_l(k\,a) &\stackrel{!}{=} 0 \Longleftrightarrow k_{l,\mu}\,a=\mu\,\pi+\frac{l\,\pi}{2}\\ \Longrightarrow\ E_{l,\mu} &= \frac{\hbar^2\pi^2}{2m\,a^2}\left(\mu+\frac{l}{2}\right)^2\,.\end{aligned}$$

Solution 6.3.2

General condition equation (6.135):

$$
\begin{aligned}
k\,\frac{(d/dz)\,j_l(z)}{j_l(z)}\bigg|_{z=k\,a} &\stackrel{!}{=} i\,\kappa\,\frac{(d/dz)\,h_l^{(+)}(z)}{h_l^{(+)}(z)}\bigg|_{z=i\kappa a}\,,\\
j_1(z) &= \frac{\sin z}{z^2}-\frac{\cos z}{z}=\frac{1}{z^2}\,(\sin z - z\cos z)\,,\\
h_1^{(+)}(z) &= -\frac{e^{iz}}{z}\left(1+\frac{i}{z}\right)\,,\\
\frac{d}{dz}\,j_1(z) &= \frac{1}{z^2}\left[2\cos z+\sin z\left(z-\frac{2}{z}\right)\right]\\
\Longrightarrow\; k\,\frac{(d/dz)\,j_1(z)}{j_1(z)}\bigg|_{z=k\,a} &= \frac{1}{a}\,\frac{2\,k\,a\cos k\,a+\sin k\,a\,(k^2a^2-2)}{\sin k\,a-k\,a\cos k\,a}\,,\\
\frac{d}{dz}\,h_1^{(+)}(z) &= -\frac{e^{iz}}{z}\left(i-\frac{2}{z}-\frac{2i}{z^2}\right)\\
\Longrightarrow\; i\,\kappa\,\frac{(d/dz)\,h_1^{(+)}(z)}{h_1^{(+)}(z)}\bigg|_{z=i\,k\,a} &= -\frac{1}{a}\,\frac{(\kappa\,a+1)^2+1}{\kappa\,a+1}\,.
\end{aligned}
$$

Conditional equation for $l=1$:

$$
\begin{aligned}
-2+\frac{k^2a^2\sin k\,a}{\sin k\,a-k\,a\cos k\,a} &\stackrel{!}{=} -2-\frac{\kappa^2a^2}{\kappa\,a+1}\\
\Longleftrightarrow\; \frac{k^2}{\kappa^2}\,(\kappa\,a+1)\sin k\,a &= k\,a\cos k\,a-\sin k\,a\\
\Longleftrightarrow\; \frac{k^2}{\kappa^2}\,(\kappa\,a+1) &\stackrel{!}{=} k\,a\cot k\,a-1\,.
\end{aligned}
$$

This equation fixes with

$$
k^2=\frac{2m}{\hbar^2}\,(E+V_0)\,;\quad \kappa^2=-\frac{2m}{\hbar^2}\,E
$$

the *'allowed'* energy values for $l=1$!

Solution 6.3.3

1. As in (6.19) we find the radial equation:

$$
\left[\frac{d^2}{dr^2}+\frac{2m}{\hbar^2}\left(E-\frac{1}{2}\,m\,\omega^2r^2-\frac{D}{r^2}\right)\right]\,u(r)=0\,,
$$

$$
D=c+\frac{\hbar^2}{2m}\,l(l+1)\,.
$$

Limiting cases:

a) $r \to 0$:

$$\left(\frac{d^2}{dr^2} - \frac{2m\,D}{\hbar^2 r^2}\right) u(r) \approx 0$$

$\Longrightarrow$ $u(r) \sim r^x$ with x from:

$$x(x-1) = \frac{2m\,c}{\hbar^2} + l(l+1)\;.$$

Since $u(r)$ must be zero at the origin of coordinates, $x > 0$ has to be required!

b) $r \to \infty$:

$$\left(\frac{d^2}{dr^2} - 4\gamma^2\, r^2\right) u(r) \approx 0\;; \quad \gamma = \frac{m\,\omega}{2\hbar}\;.$$

We take:

$$u(r) \sim e^{-\gamma r^2}$$

$$\Longrightarrow u''(r) \sim \frac{d}{dr}\left(-2\gamma\, r\, e^{-\gamma r^2}\right) = \left(-2\gamma + 4\gamma^2 r^2\right)\, e^{-\gamma r^2} \underset{r\to\infty}{\longrightarrow} 4\gamma^2 r^2\, e^{-\gamma r^2}.$$

The ansatz is thus an approximate solution of the asymptotic radial equation.

The two limiting cases make the following general ansatz appear to be reasonable:

$$u(r) = r^x\, e^{-\gamma r^2}\, g(r)\;.$$

Above, x and γ are uniquely given!

2. For the radial equation we need the first and the second derivative of $u(r)$:

$$\begin{aligned} u'(r) &= \left(x\, r^{x-1}\, g(r) + r^x\, g'(r) - 2\gamma\, r^{x+1}\, g(r)\right)\, e^{-\gamma r^2}\;, \\ u''(r) &= \left[g(r)\,\left\{x(x-1)\, r^{x-2} - 2\gamma\, x\, r^x - 2\gamma(x+1)\, r^x + 4\gamma^2\, r^{x+2}\right\}\right. \\ &\quad \left. + g'(r)\,\left\{2x\, r^{x-1} - 4\gamma\, r^{x+1}\right\} + g''(r)\, r^x\right]\, e^{-\gamma r^2}\;. \end{aligned}$$

This is inserted into the radial equation:

$$\begin{aligned} g''(r) \;+\; & 2g'(r)\,\left(\frac{x}{r} - 2\gamma\, r\right) + g(r)\,\left\{\frac{x(x-1)}{r^2} - 2\gamma\,(2x+1) + 4\gamma^2 r^2\right. \\ & \left. + \frac{2m}{\hbar^2}\,\left(E - \frac{D}{r^2}\right) - \frac{m^2\omega^2}{\hbar^2}\, r^2\right\} = 0\;. \end{aligned}$$

This expression further simplifies because of

$$4\gamma^2 = \frac{m^2\omega^2}{\hbar^2}\;; \quad \frac{2m}{\hbar^2}\, D = x\,(x-1)\;.$$

It is left therewith:

$$g''(r) + 2g'(r)\,\left(\frac{x}{r} - 2\gamma\, r\right) + g(r)\,\left[\frac{2m\,E}{\hbar^2} - 2\gamma\,(2x+1)\right] = 0\;.$$

3. Ansatz:

$$g(r) = \sum_{\mu} \alpha_\mu \, r^\mu \; .$$

Insertion into the differential equation for g:

$$\sum_{\mu} \alpha_\mu \left[(\mu(\mu-1) + 2x\,\mu)\; r^{\mu-2} + \left(\frac{2m}{\hbar^2}\, E - 2\gamma\,(2x+1) - 4\gamma\,\mu \right) r^\mu \right] = 0.$$

We change the indexing in the first term:

$$\sum_{\mu} \left\{ \alpha_{\mu+2}\; ((\mu+2)\,(\mu+1) + 2x\,(\mu+2)) \right.$$
$$\left. + \alpha_\mu \left(\frac{2m}{\hbar^2}\, E - 2\gamma\,(2x+1) - 4\gamma\,\mu \right) \right\} r^\mu = 0 \; .$$

This can be correct only if each summand by itself already vanishes:

$$\alpha_{\mu+2} = \frac{2\gamma\,(2x+1) + 4\gamma\,\mu - (2m/\hbar^2)\,E}{(\mu+2)\,(\mu+1) + 2x\,(\mu+2)}\, \alpha_\mu \; .$$

We estimate for larger indexes μ:

$$\frac{\alpha_{\mu+2}}{\alpha_\mu} \underset{\mu\to\infty}{\longrightarrow} \frac{4\gamma}{\mu} \; .$$

For comparison:

$$e^{4\gamma r^2} = \sum_{\nu=0}^{\infty} \frac{(4\gamma)^\nu}{\nu!}\, r^{2\nu} = \sum_{\nu=0}^{\infty} \beta_\nu \, r^{2\nu} \; .$$

$\alpha_{\mu+2}$ and α_μ in the above expression are the coefficients of $r^{\mu+2}$ and r^μ. This corresponds in the expansion of the exponential equation to a rise of the summation index by 1:

$$\frac{\beta_{\nu+1}}{\beta_\nu} = \frac{4\gamma}{\nu+1} \underset{\nu\gg 1}{\longrightarrow} \frac{4\gamma}{\nu} \; .$$

In the case of a not terminated series, $g(r)$ for large r, when the high powers dominate, would behave like $\exp(4\gamma\, r^2)$. The function $u(r)$ would then no longer be normalizable as required in (6.22). We have to therefore assume that the series terminates at a finite μ_0:

$$\alpha_{\mu_0} \neq 0 \; ; \quad \alpha_{\mu_0+1} = \alpha_{\mu_0+2} = \ldots = 0 \; .$$

4. The truncation-condition yields the discrete energy spectrum:

$$E_{\mu_0} \mathrel{\widehat{=}} \frac{\hbar^2}{2m}\, [2\gamma(2\mu_0 + 2x + 1)] \; .$$

It follows with the meaning of γ and x ($x > 0$):

$$E_{\mu_0 l} = \hbar\,\omega \left(\mu_0 + 1 + \sqrt{\frac{2m\,c}{\hbar^2} + \left(l + \frac{1}{2}\right)^2} \right) , \qquad \mu_0 = 0, 1, 2, 3, \ldots .$$

For $c \to 0$ we get the known eigen-functions of the three-dimensional harmonic oscillator with the ground-state energy $(3/2)\,\hbar\,\omega$ ((4.186), Vol. 6).

5. Ground state: $\mu_0 = l = 0$
In this case:

$$g_0(r) \equiv \alpha_0 = \text{const} \implies u_0(r) = \alpha_0\, r^x\, e^{-\gamma r^2} .$$

Ground-state wave function:

$$\begin{aligned} \psi_0(\mathbf{r}) &= \frac{1}{r}\, u_0(r)\, Y_{00}\,(\vartheta, \varphi) \\ \implies |\psi_0(\mathbf{r})|^2 &= \frac{|\alpha_0|^2}{4\pi}\, r^{2(x_0-1)}\, e^{-2\gamma r^2} . \end{aligned}$$

Maximal density of the position probability:

$$\begin{aligned} \frac{d}{dr}|\psi_0(\mathbf{r})|^2 \stackrel{!}{=} 0 &= \frac{|\alpha_0|^2}{4\pi} \left[2(x-1)\, r_0^{2x-3} - 4\gamma\, r_0^{2x-1} \right] e^{-2\gamma\, r_0^2} \\ &\implies r_0^2 = \frac{1}{2}\, \frac{x_0 - 1}{\gamma} , \\ x_0 &= x\,(l=0) = \frac{1}{2} \left(1 + \sqrt{1 + \frac{8m\,c}{\hbar^2}} \right) \\ \implies r_0^2 &= \frac{\hbar}{2m\,\omega} \left(\sqrt{1 + \frac{8m\,c}{\hbar^2}} - 1 \right) \underset{c \text{ small}}{\longrightarrow} \frac{2c}{\hbar\,\omega} . \end{aligned}$$

Minimum of the potential:

$$\begin{aligned} \frac{d}{dr}\, V(r) &= -2\,\frac{c}{r_{\min}^3} + m\,\omega^2\, r_{\min} \stackrel{!}{=} 0 \\ &\implies r_{\min}^2 = \frac{1}{\omega} \sqrt{\frac{2c}{m}} . \end{aligned}$$

The maximum of the density of position probability does not coincide with the minimum of the potential!

Solution 6.3.4

We can apply in (6.135), because of $k_0 a \gg l$, for $j_l(z)$ the asymptotic form (6.125):

$$\begin{aligned} \frac{d}{dz}\, j_l(z) &\approx -\frac{1}{z^2} \sin\left(z - \frac{l\,\pi}{2} \right) + \frac{1}{z} \cos\left(z - \frac{l\,\pi}{2} \right) \\ \implies \frac{d}{dz} \ln j_l(z) &\approx -\frac{1}{z} + \cot\left(z - \frac{l\,\pi}{2} \right) . \end{aligned}$$

The fitting condition then reads:

$$\begin{aligned} -\frac{1}{a} \quad + \quad & k_0 \cot\left(k_0\, a - \frac{l\,\pi}{2}\right) = i\,\kappa\,\frac{d}{dz}\ln\, h_l^{(+)}(z)\Big|_{z\,=\,i\,\kappa\,a}\,, \\ k_0^2 \quad = \quad & \frac{2m}{\hbar^2}\,(E+V_0)\,; \quad \kappa^2 = -\frac{2m}{\hbar^2}\,E\,. \end{aligned}$$

The right-hand side does not depend on V_0. That must then hold for $V_0 \to \infty$ also for the left-hand side. Because of $k_0 \to \infty$, the cotangent must then take care for the vanishing of the second summand in the above conditional equation:

$$k_0\, a - \frac{l\,\pi}{2} \approx \left(n + \frac{1}{2}\right)\pi\,; \quad n \in \mathbb{N}\,.$$

$n \gg 1$, in order that $k_0\, a \gg l$ remains fulfilled.

$$\Longrightarrow\; E_{nl} = \frac{\hbar^2\pi^2}{2m\,a^2}\left(n + \frac{l}{2} + \frac{1}{2}\right)^2 - V_0\,.$$

Solution 6.3.5

Cylindrical coordinates (Sect. 1.7.3, Vol. 1):

$$\begin{aligned} x &= \rho\cos\varphi\,, \\ y &= \rho\sin\varphi\,, \\ z &= z\,. \end{aligned}$$

Gradient ((1.388), Vol. 1):

$$\nabla_\rho = \frac{\partial}{\partial\rho}\,; \quad \nabla_\varphi = \frac{1}{\rho}\,\frac{\partial}{\partial\varphi}\,; \quad \nabla_z = \frac{\partial}{\partial z}\,.$$

Divergence:

$$\mathrm{div}\mathbf{a} = \frac{1}{\rho}\,\frac{\partial}{\partial\rho}\,(\rho\, a_\rho) + \frac{1}{\rho}\,\frac{\partial}{\partial\varphi}\,a_\varphi + \frac{\partial}{\partial z}\,a_z\,.$$

Laplace operator:

$$\Delta \equiv \frac{1}{\rho}\,\frac{\partial}{\partial\rho}\left(\rho\,\frac{\partial}{\partial\rho}\right) + \frac{1}{\rho^2}\,\frac{\partial^2}{\partial\varphi^2} + \frac{\partial^2}{\partial z^2}\,.$$

1. Hamilton operator

$$\begin{aligned} H \quad &= \quad \frac{1}{2m}\,(\mathbf{p} - \hat{q}\,\mathbf{A}(\mathbf{r}))^2 \\ &= \quad \frac{1}{2m}\,\mathbf{p}^2 - \frac{\hat{q}}{2m}\,(\mathbf{p}\cdot\mathbf{A}(\mathbf{r}) + \mathbf{A}(\mathbf{r})\cdot\mathbf{p}) + \frac{\hat{q}^2}{2m}\,\mathbf{A}^2(\mathbf{r})\,, \end{aligned}$$

$$\begin{aligned} \mathrm{div}\mathbf{A}(\mathbf{r}) \quad &= \quad \frac{1}{\rho}\,\frac{\partial}{\partial\rho}\,(\rho\, A_\rho) + \frac{1}{\rho}\,\frac{\partial}{\partial\varphi}\,A_\varphi + \frac{\partial}{\partial z}\,A_z = 0 \\ \Longrightarrow\; \mathbf{p}\cdot\mathbf{A}(\mathbf{r}) \quad &= \quad \mathbf{A}(\mathbf{r})\cdot\mathbf{p} = \frac{\hbar}{i}\,A_\varphi(\mathbf{r})\,\frac{1}{\rho}\,\frac{\partial}{\varphi} = \frac{\hbar}{2i}\,B\,\frac{\partial}{\partial\varphi}\,. \end{aligned}$$

Hamilton operator in position representation:

$$H = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{1}{\rho^2}\frac{\partial^2}{\partial\varphi^2} + \frac{\partial^2}{\partial z^2}\right) + i\,\hbar\,\frac{\hat{q}\,B}{2m}\frac{\partial}{\partial\varphi} + \frac{\hat{q}^2\,B^2}{8m}\,\rho^2 \ .$$

With $k^2 = (2m/\hbar^2)\,E$ the time-independent Schrödinger equation in cylindrical coordinates then reads:

$$\left[\left\{\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} - \left(\frac{\hat{q}\,B}{2\hbar}\right)^2\rho^2 + k^2\right\} + \left\{\frac{1}{\rho^2}\frac{\partial^2}{\partial\varphi^2} - i\,\frac{\hat{q}\,B}{\hbar}\frac{\partial}{\partial\varphi}\right\} + \frac{\partial^2}{\partial z^2}\right]\psi(\rho,\varphi,z) = 0 \ .$$

2. The structure of the equation suggests a separation ansatz:

$$\psi(\rho,\varphi,z) = R(\rho)\,f(\varphi)\,g(z) \ .$$

Insertion into the Schrödinger equation and division by ψ:

$$\frac{1}{R(\rho)}\left\{\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} - \left(\frac{\hat{q}\,B}{2\hbar}\right)^2\rho^2 + k^2\right\}R(\rho) + \frac{1}{f(\varphi)}\left\{\frac{1}{\rho^2}\frac{\partial^2}{\partial\varphi^2} - \frac{i}{\hbar}\,\hat{q}\,B\,\frac{\partial}{\partial\varphi}\right\}f(\varphi) + \frac{1}{g(z)}\frac{\partial^2}{\partial z^2}\,g(z) = 0 \ .$$

Useful ansatz:

$$g(z) \sim \exp(i\,k_z\,z) \ ; \quad f(\varphi) \sim \exp(i\,m^*\varphi) \ .$$

We write for abbreviation

$$k^{*2} = k^2 - k_z^2 + \frac{m^*\,\hat{q}\,B}{\hbar} \ ; \quad F = \left(\frac{\hat{q}\,B}{2\hbar}\right)^2 \ .$$

It then remains:

$$\left\{\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} - F\,\rho^2 + k^{*2} - \frac{m^{*2}}{\rho^2}\right\}R(\rho) = 0 \ .$$

The following substitution is still recommendable:

$$\begin{aligned} u(\rho) &= \sqrt{\rho}\,R(\rho) \\ \Longrightarrow\ \sqrt{\rho}\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho}\right)R(\rho) &= \left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{4\rho^2}\right)u(\rho) \ . \end{aligned}$$

This yields the following radial equation:

$$\left\{\frac{d^2}{d\rho^2} + k^{*2} - F\,\rho^2 - \frac{m^{*2} - 1/4}{\rho^2}\right\}u(\rho) = 0 \ .$$

3. This differential equation is, according to its structure, identical to the solution of Exercise 6.3.3 (1). We can therefore take the results derived there, when we agree upon the following assignments:

$$\begin{aligned} \frac{2m}{\hbar^2}\,E &\iff k^{*2}\,, \\ \frac{m^2\omega^2}{\hbar^2} &\iff F\,, \\ \frac{2m}{\hbar^2}\,D = \frac{2mc}{\hbar^2} + l(l+1) &\iff m^{*2} - \frac{1}{4}\,. \end{aligned}$$

The eigen-energies from part 4. of Exercise 6.3.3,

$$E_{\mu_0 l} = \hbar\,\omega\,\left(\mu_0 + 1 + \sqrt{\frac{2m\,c}{\hbar^2} + \left(l + \frac{1}{2}\right)^2}\right),$$

now turn into:

$$\begin{aligned} \frac{\hbar^2}{2m}\left(k^2 - k_z^2 + m^*\,\frac{\hat{q}\,B}{\hbar}\right) &= \frac{\hbar^2}{m}\,\frac{\hat{q}\,B}{2\hbar}\left(\mu_0 + 1 + \sqrt{m^{*2}}\right) \\ \Longrightarrow\; E_{\mu_0,m^*} = \frac{\hbar^2 k^2}{2m} &= \frac{\hbar^2 k_z^2}{2m} + \hbar\frac{\hat{q}\,B}{2m}\,(\mu_0+1) \equiv E_{\mu_0}\,, \\ \mu_0 &= 0, 1, 2, \ldots \end{aligned}$$

Solution 6.3.6

1. Cylindrical coordinates, see Exercise 6.3.5.
Schrödinger equation:

$$\left(-\frac{\hbar^2}{2m}\,\Delta + V(\rho) - E\right)\,\psi(\rho,\varphi,z) = 0$$

$$\Longrightarrow \quad \left\{\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\,\frac{\partial}{\partial\rho} - \frac{2m}{\hbar^2}\,\left(V(\rho) - E\right)\right\}\,\psi(\rho,\varphi,z) + \frac{1}{\rho^2}\,\frac{\partial^2}{\partial\varphi^2}\,\psi(\rho,\varphi,z) + \frac{\partial^2}{\partial z^2}\,\psi(\rho,\varphi,z) = 0\,.$$

2. The following separation ansatz suggests itself:

$$\psi(\rho,\varphi,z) = R(\rho)\,f(\varphi)\,g(z)\,.$$

Insert into 1. and subsequently divide by ψ:

$$\frac{1}{R(\rho)}\,\left\{\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\,\frac{\partial}{\partial\rho} - \frac{2m}{\hbar^2}\,\left(V(\rho) - E\right)\right\}\,R(\rho) + \frac{1}{f(\varphi)}\,\frac{1}{\rho^2}\,\frac{\partial^2}{\partial\varphi^2}\,f(\varphi) + \frac{1}{g(z)}\,\frac{\partial^2}{\partial z^2}\,g(z) = 0\,.$$

The last summand only depends on z, the other two, however, do not. The last term as well as the sum of the two first terms therefore have to be constant by themselves. It follows from that:

Axial equation

$$\frac{\partial^2}{\partial z^2}\, g(z) = -k_z^2\, g(z) \implies g(z) = e^{ik_z z}\ .$$

This we insert into the above Schrödinger equation:

$$\frac{1}{R(\rho)}\left\{\rho^2\,\frac{\partial^2}{\partial\rho^2} + \rho\frac{\partial}{\partial\rho} - \left[\frac{2m}{\hbar^2}\,(V(\rho)-E) + k_z^2\right]\rho^2\right\} R(\rho) + \frac{1}{f(\varphi)}\frac{\partial^2}{\partial\varphi^2} f(\varphi) = 0.$$

The same argumentation as above now leads immediately to

the angle equation

$$\frac{\partial^2}{\partial\varphi^2}\, f(\varphi) = -m^{*2}\, f(\varphi) \implies f(\varphi) = e^{im^*\varphi}\ .$$

The uniqueness of the wave function still requires:

$$m^* \in \mathbb{Z}\ .$$

It remains therewith eventually as

the radial equation

$$\left\{\frac{d^2}{d\rho^2} + \frac{1}{\rho}\,\frac{d}{d\rho} - \left[\frac{2m}{\hbar^2}\,(V(\rho)-E) + k_z^2 + \frac{m^{*2}}{\rho^2}\right]\right\} R(\rho) = 0\ .$$

3. Ansatz:

$$\begin{aligned} R(\rho) &= \rho^n\, u(\rho) \\ \implies R'(\rho) &= n\,\rho^{n-1}\, u(\rho) + \rho^n\, u'(\rho)\ , \\ R''(\rho) &= n(n-1)\,\rho^{n-2}\, u(\rho) + 2n\,\rho^{n-1}\, u'(\rho) + \rho^n\, u''(\rho)\ . \end{aligned}$$

When we define

$$F(\rho) = \left[\frac{2m}{\hbar^2}\,(V(\rho)-E) + k_z^2 + \frac{m^{*2}}{\rho^2}\right],$$

then it follows:

$$\rho^n\left\{\frac{n(n-1)}{\rho^2} + \frac{2n}{\rho}\,\frac{d}{d\rho} + \frac{d^2}{d\rho^2} + \frac{n}{\rho^2} + \frac{1}{\rho}\,\frac{d}{d\rho} - F(\rho)\right\} u(\rho) = 0\ .$$

This is equivalent to:

$$\left\{\frac{d^2}{d\rho^2}+\frac{2n+1}{\rho}\,\frac{d}{d\rho}+\frac{n^2}{\rho^2}-F(\rho)\right\}u(\rho)=0\;.$$

The choice $n=-1/2$ let the linear term disappear:

$$u(\rho)=\sqrt{\rho}\,R(\rho)\;,$$
$$\left\{\frac{d^2}{d\rho^2}-\left[\frac{2m}{\hbar^2}\,(V(\rho)-E)+k_z^2+\frac{m^{*2}-1/4}{\rho^2}\right]\right\}u(\rho)=0\;.$$

4a) $\rho\to 0$: In this limit it holds approximately:

$$\left(\frac{d^2}{d\rho^2}-\frac{m^{*2}-1/4}{\rho^2}\right)u(\rho)=0\;.$$

General solution:

$$\begin{aligned}
u(\rho) &= A\,\rho^{\nu+1}+B\,\rho^{-\nu}\;,\\
u(0) &= 0 \implies B=0\;,\\
(\nu+1)\,\nu &\stackrel{!}{=} m^{*2}-\frac{1}{4} \iff \left(\nu+\frac{1}{2}\right)^2=m^{*2}\\
\implies u(\rho) &\sim \rho^{|m^*|+1/2} \quad \text{for } \rho\to 0.
\end{aligned}$$

4b) $\rho\to\infty$:

$$\begin{aligned}
&\left[\frac{d^2}{d\rho^2}+\left(\frac{2m}{\hbar^2}\,E-k_z^2\right)\right]u(\rho)=0\\
\implies\quad &u(\rho)\sim e^{-\gamma\rho}\;;\quad \gamma=\sqrt{k_z^2-\frac{2m}{\hbar^2}\,E}\;,\\
&E<0,\ \text{bound state!}
\end{aligned}$$

Solution 6.3.7

The problem here a special case of the more general problem discussed in the preceding exercise. We can therefore adopt:

$$\psi(\mathbf{r})=R(\rho)\,e^{im^*\varphi}\,e^{ik_z\,z}\;.$$

For $u(\rho)=\sqrt{\rho}\,R(\rho)$ the following differential equation is to be solved:

$$\left[\frac{d^2}{d\rho^2}-\left(\gamma^2-\frac{\varepsilon}{\rho}+\frac{m^{*2}-1/4}{\rho^2}\right)\right]u(\rho)=0\;,$$
$$\gamma^2=k_z^2-\frac{2m_{\rm f}}{\hbar^2}\,E\;;\quad \varepsilon=\frac{2m_{\rm f}}{\hbar^2}\,\frac{Z\,e^2}{4\pi\,\varepsilon_0}\;.$$

Part 4. from Exercise 6.3.6 leads to the following solution ansatz:

$$\begin{aligned} u(\rho) &= \rho^{|m^*|+1/2}\, e^{-\gamma\rho}\, P(\rho)\ , \\ P(\rho) &= \sum_{\mu=0}^{?} a_\mu\, \rho^\mu\ , \end{aligned}$$

$$\begin{aligned} \Longrightarrow\ u'(\rho) &= e^{-\gamma\rho}\left[\left(|m^*|+\frac{1}{2}\right)\rho^{|m^*|-1/2}\, P(\rho)\right. \\ &\quad \left. -\gamma\rho^{|m^*|+1/2}\, P(\rho) + \rho^{|m^*|+1/2}\, P'(\rho)\right] \\ \Longrightarrow\ u''(\rho) &= \rho^{|m^*|+1/2}\, e^{-\gamma\rho}\left[P''(\rho) + \left(\frac{2|m^*|+1}{\rho} - 2\gamma\right) P'(\rho)\right. \\ &\quad \left. + \left(\frac{m^{*2}-1/4}{\rho^2} - 2\gamma\,\frac{|m^*|+1/2}{\rho} + \gamma^2\right) P(\rho)\right]\ . \end{aligned}$$

Therewith the radial equation becomes a differential equation for $P(\rho)$:

$$\left\{\frac{d^2}{d\rho^2} + \left(\frac{2|m^*|+1}{\rho} - 2\gamma\right)\frac{d}{d\rho} + \frac{1}{\rho}\left[\varepsilon - 2\gamma\left(|m^*|+\frac{1}{2}\right)\right]\right\} P(\rho) = 0\ .$$

It follows with the series-ansatz for $P(\rho)$:

$$\textstyle\sum_{\mu=0}^{?}\left[\alpha_{\mu+1}\,(\mu+1)\,(\mu+2|m^*|+1) + \alpha_\mu\left(\varepsilon - 2\gamma\left(|m^*|+\frac{1}{2}\right) - 2\gamma\mu\right)\right]\rho^{\mu-1} = 0.$$

Each summand itself must already be zero. That leads to the recursion formula:

$$\alpha_{\mu+1} = \frac{2\gamma\,(|m^*|+1/2+\mu) - \varepsilon}{(\mu+1)\,(\mu+2|m^*|+1)}\,\alpha_\mu\ .$$

For $\mu \gg 1, |m^*|$ it holds approximately:

$$\frac{\alpha_{\mu+1}}{\alpha_\mu} \approx \frac{2\gamma}{\mu}\ .$$

With the same reasoning as in Sect. 6.2.1 we conclude that in the case that the series

$$P(\rho) \sim e^{2\gamma\rho}$$

does not terminate, the divergence of $u(\rho)$ for $\rho \to \infty$ would be the consequence. This problem can only be solved by the assumption that the series stops at a finite μ_0, for which it must be:

$$\mu_0 = \frac{\varepsilon}{2\gamma} - \left(|m^*|+\frac{1}{2}\right)\ .$$

After insertion of the definitions of γ and ε we obtain the energy spectrum:

$$E_n = -\frac{Z^2\, E_\mathrm{R}}{(n+1/2)^2} + \frac{\hbar^2\, k_z^2}{2m_\mathrm{f}}\ .$$

E_{R} is the *Rydberg energy* defined in (6.33), and n is the quantum number

$$n = \mu_0 + |m^*| = 0, 1, 2, \dots \ .$$

We have then found for the eigen-functions:

$$\psi_{nm^*}(\mathbf{r}) = e^{-\gamma\rho} \left(\sum_{\mu=0}^{n-|m^*|} \alpha_\mu \, \rho^{\mu+|m^*|} \right) e^{im^*\varphi} \, e^{ik_z z} \ .$$

The coefficients α_μ result from the above recursion formula and the normalization condition for $\psi_{nm^*}(\mathbf{r})$.

Solution 6.3.8
Ansatz:

$$\psi(\mathbf{r}) = R(r) \left(f_\uparrow(\vartheta,\varphi) \begin{pmatrix} 1 \\ 0 \end{pmatrix} + f_\downarrow(\vartheta,\varphi) \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right) \ .$$

$R(r)$ is assumed to be known.

1. $\psi(\mathbf{r})$ *eigen-function of* $J_z = L_z + S_z$*:*
   J_z is diagonal in the spin space:

   $$J_z \equiv \begin{pmatrix} L_z + \frac{\hbar}{2} & 0 \\ 0 & L_z - \frac{\hbar}{2} \end{pmatrix} \ ; \quad L_z = \frac{\hbar}{i} \frac{\partial}{\partial\varphi} \ .$$

   Requirement: $J_z \, \psi \stackrel{!}{=} \hbar \, m_j \, \psi$:

   $$\begin{pmatrix} \left(\frac{\hbar}{i} \frac{\partial}{\partial\varphi} + \frac{\hbar}{2} \right) f_\uparrow(\vartheta,\varphi) \\ \left(\frac{\hbar}{i} \frac{\partial}{\partial\varphi} - \frac{\hbar}{2} \right) f_\downarrow(\vartheta,\varphi) \end{pmatrix} \stackrel{!}{=} \hbar \, m_j \begin{pmatrix} f_\uparrow(\vartheta,\varphi) \\ f_\downarrow(\vartheta,\varphi) \end{pmatrix}$$

   $$\begin{aligned} f_\uparrow(\vartheta,\varphi) &\sim \exp\left[i \left(m_j - \frac{1}{2} \right) \varphi \right] \ , \\ f_\downarrow(\vartheta,\varphi) &\sim \exp\left[i \left(m_j + \frac{1}{2} \right) \varphi \right] \ . \end{aligned}$$

   Because of the uniqueness of the wave function, m_j must be half-integral. The *triangle inequality* (5.278) allows only for

   $$j = l \pm \frac{1}{2} \ .$$

   m_j is therefore automatically half-integral.

2. $\psi(\mathbf{r})$ *eigen-function of* $\mathbf{L}^2$: This means together with the result 1.:

   $$\begin{aligned} f_\uparrow(\vartheta,\varphi) &= a_\uparrow \, Y_{l,m_j-1/2}(\vartheta,\varphi) \ , \\ f_\downarrow(\vartheta,\varphi) &= a_\downarrow \, Y_{l,m_j+1/2}(\vartheta,\varphi) \ . \end{aligned}$$

   It is possible that the coefficients $a_{\uparrow\downarrow}$ still depend on the quantum numbers l, j, m_j.

3. $\psi(\mathbf{r})$ *eigen-function of* $\mathbf{J}^2$*:*

$$\mathbf{J}^2 = (\mathbf{L}+\mathbf{S})^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{L}\cdot\mathbf{S}\,.$$

In the spin space:

$$\mathbf{J}^2 \equiv \begin{pmatrix} \mathbf{L}^2+\mathbf{S}^2+\hbar L_z & \hbar L_- \\ \hbar L_+ & \mathbf{L}^2+\mathbf{S}^2-\hbar L_z \end{pmatrix}\,.$$

It holds according to (5.64):

$$\begin{aligned} L_\pm|l,m\rangle &= \hbar\sqrt{l(l+1)-m(m\pm1)}\,|l,m\pm1\rangle \\ \Longrightarrow\; L_-\,Y_{l,m_j+1/2}(\vartheta,\varphi) &= \hbar\sqrt{\left(l+\frac{1}{2}\right)^2-m_j^2}\;Y_{l,m_j-1/2}(\vartheta,\varphi)\,, \\ L_+\,Y_{l,m_j-1/2}(\vartheta,\varphi) &= \hbar\sqrt{\left(l+\frac{1}{2}\right)^2-m_j^2}\;Y_{l,m_j+1/2}(\vartheta,\varphi)\,. \end{aligned}$$

Eigen-value equation for $\mathbf{J}^2$:

$$\mathbf{J}^2\begin{pmatrix} f_\uparrow \\ f_\downarrow \end{pmatrix} = \begin{pmatrix} (L^2+S^2+\hbar L_z)\,f_\uparrow + \hbar L_-\,f_\downarrow \\ \hbar L_+\,f_\uparrow + (L^2+S^2-\hbar L_z)\,f_\downarrow \end{pmatrix} = \hbar^2 j(j+1)\begin{pmatrix} f_\uparrow \\ f_\downarrow \end{pmatrix}\,.$$

That yields for the coefficients the following conditional equations:

$$\begin{aligned} a_\uparrow\left(l(l+1)+\frac{3}{4}+\left(m_j-\frac{1}{2}\right)-j(j+1)\right)+a_\downarrow\sqrt{\left(l+\frac{1}{2}\right)^2-m_j^2} &= 0 \\ a_\uparrow\sqrt{\left(l+\frac{1}{2}\right)^2-m_j^2}+a_\downarrow\left(l(l+1)+\frac{3}{4}+\left(m_j+\frac{1}{2}\right)-j(j+1)\right) &= 0. \end{aligned}$$

Both equations lead to identical results:

$$\begin{aligned} a_\uparrow &= -\frac{\sqrt{\left(l+\frac{1}{2}\right)^2-m_j^2}}{(l+\frac{1}{2})^2+m_j-j(j+1)}\,a_\downarrow \\ &= -\frac{(l+\frac{1}{2})^2-m_j-j(j+1)}{\sqrt{\left(l+\frac{1}{2}\right)^2-m_j^2}}\,a_\downarrow\,. \end{aligned}$$

Together with the normalization condition this determines the coefficients $a_\uparrow$ and $a_\downarrow$.

Section 7.1.3

Solution 7.1.1

1. See Exercise 4.4.11 (Vol. 6):
   For $q > 0$ the eigen-functions $\varphi_n(q)$ are identical to those of the harmonic oscillator. For $q \leq 0$ it must necessarily be $\varphi_n(q) \equiv 0$. From continuity reasons only the oscillator-eigen functions with odd indexes come into consideration for $q > 0$. The exact ground-state energy thus is that for $n = 1$:
   $$E_0 = \frac{3}{2}\hbar\,\omega\ .$$

2. The ansatz is exact for $q \leq 0$ and makes for continuity at $q = 0$. Furthermore, the exponential function guarantees normalizability ($\alpha > 0$).

   Energy functional:
   $$\langle H\rangle_\varphi = \frac{\langle\varphi|H|\varphi\rangle}{\langle\varphi|\varphi\rangle}\ .$$

   Position representation:
   $$\begin{aligned}\langle\varphi|H|\varphi\rangle &= \int_{-\infty}^{+\infty} dq\,\langle\varphi|\ q\rangle\langle q|H|\varphi\rangle \\ &= \int_0^\infty dq\,\varphi^*(q)\,\left(-\frac{\hbar^2}{2m}\,\frac{d^2}{dq^2} + \frac{1}{2}\,m\,\omega^2 q^2\right)\,\varphi(q)\ ,\end{aligned}$$

   $$\frac{d^2}{dq^2}\,q\,e^{-\alpha q} = \frac{d}{dq}\,(1-\alpha\,q)\,e^{-\alpha q} = \left(-2\alpha + \alpha^2 q\right)\ e^{-\alpha q}\ ,$$

   $$\begin{aligned}\langle H\rangle_\varphi &= \frac{\int_0^\infty dq\,e^{-2\alpha q}\,\left[(\hbar^2/2m)\,\left(2\alpha\,q - \alpha^2 q^2\right) + (1/2)\,m\,\omega^2 q^4\right]}{\int_0^\infty dq\,q^2\,e^{-2\alpha q}} \\ &= \frac{(\hbar^2/2m)\,\left(2\alpha\,\left(1!/(2\alpha)^2\right) - \alpha^2\ \left(2!/(2\alpha)^3\right)\right) + \frac{1}{2}m\,\omega^2\,\left(4!/(2\alpha)^5\right)}{(2!/(2\alpha)^3)}\end{aligned}$$

   $$\Longrightarrow\ \langle H\rangle_\varphi = \frac{\hbar^2}{2m}\,\alpha^2 + \frac{3}{2}\,m\,\omega^2\,\frac{1}{\alpha^2}.$$

   Extremal condition:
   $$\begin{aligned}0 &\stackrel{!}{=} \frac{\partial}{\partial\alpha}\langle H\rangle_\varphi = \frac{\hbar^2}{m}\,\alpha - 3m\,\omega^2\,\frac{1}{\alpha^3} \\ \Longrightarrow\ (\alpha^*)^4 &= 3\,\frac{m^2\omega^2}{\hbar^2}\ .\end{aligned}$$

Approximate ground-state energy:

$$\begin{aligned}\langle H\,\rangle_{\varphi^*} &= \frac{\hbar^2}{2m}\sqrt{3}\,\frac{m\,\omega}{\hbar}+\frac{3}{2}\,m\,\omega^2\,\frac{\hbar}{\sqrt{3}\,m\,\omega}\\ &= \sqrt{3}\,\hbar\,\omega\approx 1.732\,\hbar\,\omega > E_0 = 1.5\,\hbar\omega\,.\end{aligned}$$

As approximation surely usable!

3. Energy functional:

$$\begin{aligned}\langle H\rangle_\varphi &= \frac{\langle\varphi|H|\varphi\rangle}{\langle\varphi|\varphi\rangle}\,,\\ \langle\varphi|H|\varphi\rangle &= |c|^2\int\limits_0^\infty dq\,q\,e^{-\alpha q^2}\,\left(-\frac{\hbar^2}{2m}\,\frac{d^2}{dq^2}+\frac{1}{2}\,m\,\omega^2 q^2\right)\,q\,e^{-\alpha\,q^2}\,,\\ \frac{d^2}{dq^2}\,q\,e^{-\alpha q^2} &= \frac{d}{dq}\,\left(1-2\alpha\,q^2\right)\,e^{-\alpha\,q^2} = \left(-6\alpha\,q+4\alpha^2 q^3\right)\,e^{-\alpha\,q^2}\\ \Longrightarrow\ \langle\varphi|H|\varphi\rangle &= |c|^2\int\limits_0^\infty dq\,e^{-2\alpha\,q^2}\,\left[\frac{\hbar^2}{2m}\,(6\alpha\,q^2-4\alpha^2 q^4)+\frac{1}{2}\,m\,\omega^2 q^4\right]\\ &= |c|^2\,\left[\frac{\hbar^2}{2m}\,\left(\frac{3\alpha}{(2\alpha)^{3/2}}\,\Gamma\left(\frac{3}{2}\right)-\frac{2\alpha^2}{(2\alpha)^{5/2}}\,\Gamma\,\left(\frac{5}{2}\right)\right)\right.\\ &\quad\left.+\frac{1}{2}\,m\,\omega^2\,\frac{1/2}{(2\alpha)^{5/2}}\,\Gamma\,\left(\frac{5}{2}\right)\right]\\ &= |c|^2\,\frac{(1/4)\sqrt{\pi}}{(2\alpha)^{3/2}}\,\left[\frac{\hbar^2}{2m}\,(6\alpha-3\alpha)+\frac{3}{8}\,m\,\omega^2\,\frac{1}{\alpha}\right]\,,\end{aligned}$$

$$\langle\varphi|\varphi\rangle = |c|^2\int\limits_0^\infty dq\,q^2\,e^{-2\alpha q^2} = |c|^2\,\frac{(1/4)\,\sqrt{\pi}}{(2\alpha)^{3/2}}\,.$$

It follows therewith for the energy functional:

$$\langle H\rangle_\varphi = \frac{3\hbar^2}{2m}\,\alpha+\frac{3m\,\omega^2}{8\alpha}\,.$$

Extremal condition:

$$0\stackrel{!}{=}\frac{\partial}{\partial\alpha}\langle H\rangle_\varphi = \frac{3\hbar^2}{2m}-\frac{3m\,\omega^2}{8\alpha^2}\ \Longrightarrow\ \alpha^* = \frac{m\,\omega}{2\hbar}\,.$$

This yields with

$$\langle H\rangle_{\varphi^*} = \frac{3}{2}\,\hbar\,\omega$$

the **exact** ground-state energy. That is a result of the fact that the variational ansatz has the same structure as the exact oscillator function!

Solution 7.1.2

$$\begin{aligned}\langle\varphi|H|\varphi\rangle &= \int\limits_{-\infty}^{+\infty} dq\,\varphi^*(q)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dq^2}+\frac{1}{2}\,m\,\omega^2 q^2\right)\varphi(q)\,,\\ \frac{d^2}{dq^2}\,\varphi(q) &= \frac{d}{dq}\,\frac{-2q}{(\alpha^2+q^2)^2}=\frac{-2}{(\alpha^2+q^2)^2}+\frac{8q^2}{(\alpha^2+q^2)^3}\,.\end{aligned}$$

It is therewith to calculate:

$$\begin{aligned}\langle\varphi|H|\varphi\rangle &= \frac{\hbar^2}{m}\int\limits_{-\infty}^{+\infty}\frac{dq}{(\alpha^2+q^2)^3}-\frac{4\hbar^2}{m}\int\limits_{-\infty}^{+\infty}dq\,\frac{q^2}{(\alpha^2+q^2)^4}+\frac{1}{2}\,m\,\omega^2\int\limits_{-\infty}^{+\infty}dq\frac{q^2}{(\alpha^2+q^2)^2}\\ &= 2\,\frac{\hbar^2}{m}\,\frac{3\pi}{16\,\alpha^5}-\frac{8\hbar^2}{m}\,\frac{\pi}{32\,\alpha^5}+m\,\omega^2\,\frac{\pi}{4\alpha}\,,\\ \langle\varphi|H|\varphi\rangle &= \frac{\hbar^2\pi}{8m\,\alpha^5}+\frac{\pi\,m\,\omega^2}{4\alpha}\,.\end{aligned}$$

It is further to determine:

$$\langle\varphi|\varphi\rangle=\int\limits_{-\infty}^{+\infty}dq\,\frac{1}{(\alpha^2+q^2)^2}=\frac{\pi}{2\alpha^3}\,.$$

The energy functional then reads:

$$\langle H\rangle_\varphi=\frac{\hbar^2}{4m\,\alpha^2}+\frac{1}{2}\,m\,\omega^2\alpha^2\,.$$

Extremal condition:

$$0\stackrel{!}{=}\frac{\partial}{\partial\alpha}\langle H\rangle_\varphi=-\frac{\hbar^2}{2m\,\alpha^3}+m\,\omega^2\alpha\implies(\alpha^*)^4=\frac{\hbar^2}{2m^2\omega^2}\,.$$

That yields:

$$\langle H\rangle_{\varphi^*}=\frac{\sqrt{2}}{2}\,\hbar\,\omega>E_0=\frac{1}{2}\,\hbar\,\omega\,.$$

Solution 7.1.3

1.

$$F(q)=f-2\gamma\,q=-\frac{d}{dq}V(q)\quad\curvearrowright\ V(q)=-fq+\gamma q^2\,.$$

Hamilton operator:

$$H=\frac{p^2}{2m}+\frac{1}{2}m\omega^2q^2-fq+\gamma q^2=\frac{p^2}{2m}+\frac{1}{2}m\widehat{\omega}^2q^2-fq$$

with

$$\frac{1}{2}m\omega^2+\gamma\stackrel{!}{=}\frac{1}{2}m\widehat{\omega}^2\quad\curvearrowright\ \widehat{\omega}^2=\omega^2+\frac{2\gamma}{m}\,.$$

Energy functional:

$$\langle H\rangle_\alpha = \frac{\int\limits_{-\infty}^{+\infty} dq e^{-1/2\alpha q^2}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dq^2}+\frac{1}{2}m\widehat{\omega}^2q^2-fq\right)e^{-1/2\alpha q^2}}{\int\limits_{-\infty}^{+\infty} dq e^{-\alpha q^2}} .$$

The evaluation succeeds with:

$$\begin{aligned}
\frac{d^2}{dq^2}\,e^{-1/2\alpha q^2} &= \frac{d}{dq}\left(-\alpha q\, e^{-1/2\alpha q^2}\right) = (-\alpha+\alpha^2q^2)e^{-1/2\alpha q^2}\\
\int\limits_{-\infty}^{+\infty} dq\, e^{-\alpha q^2} &= \sqrt{\frac{\pi}{\alpha}}\\
\int\limits_{-\infty}^{+\infty} dq\, \underbrace{q e^{-\alpha q^2}}_{\text{odd}} &= 0\\
\int\limits_{-\infty}^{+\infty} dq\, q^2 e^{-\alpha q^2} &= -\frac{d}{d\alpha}\sqrt{\frac{\pi}{\alpha}} = \frac{1}{2\pi}\left(\frac{\pi}{\alpha}\right)^{\frac{3}{2}} .
\end{aligned}$$

Energy functional:

$$\begin{aligned}
\langle H\rangle_\alpha &= \sqrt{\frac{\alpha}{\pi}}\left(\frac{\hbar^2\alpha}{2m}\sqrt{\frac{\pi}{\alpha}}+\left(-\frac{\hbar^2\alpha^2}{2m}+\frac{1}{2}m\widehat{\omega}^2\right)\frac{1}{2\pi}\left(\frac{\pi}{\alpha}\right)^{\frac{3}{2}}-f\cdot 0\right)\\
&= \frac{\hbar^2\alpha}{2m}+\left(-\frac{\hbar^2\alpha^2}{2m}+\frac{1}{2}m\widehat{\omega}^2\right)\frac{1}{2\pi}\frac{\pi}{\alpha}\\
&= \frac{\hbar^2\alpha}{4m}+\frac{m\widehat{\omega}^2}{4\alpha} .
\end{aligned}$$

Variational condition:

$$\frac{d}{d\alpha}\langle H\rangle_\alpha\Big|_{\alpha=\alpha^*} \stackrel{!}{=} 0 = \frac{\hbar^2}{4m}-\frac{m\widehat{\omega}^2}{4\alpha^{\star 2}} \;\curvearrowright\; \alpha^* = \frac{m\widehat{\omega}}{\hbar} .$$

That yields the energy boundary:

$$E_0 \le \langle H\rangle_{\alpha^*} = \frac{\hbar\widehat{\omega}}{2}$$

2. Hamilton operator:

$$\begin{aligned}
H &= \frac{p^2}{2m}+\frac{1}{2}m\widehat{\omega}^2q^2-fq\\
&= \frac{p^2}{2m}+\frac{1}{2}m\widehat{\omega}^2\left(q^2-\frac{2f}{m\widehat{\omega}^2}q\right)\\
&= \frac{p^2}{2m}+\frac{1}{2}m\widehat{\omega}^2\left(q-\frac{f}{m\widehat{\omega}^2}\right)^2-\frac{f^2}{2m\widehat{\omega}^2} .
\end{aligned}$$

Substitution:

$$\widehat{q} = q - \frac{f}{m\widehat{\omega}^2} \quad \curvearrowright \quad \widehat{p} = \frac{\hbar}{i}\frac{d}{d\widehat{q}} = \frac{\hbar}{i}\frac{d}{dq} = p \; .$$

This means

$$H = \left(\frac{\widehat{p}^2}{2m} + \frac{1}{2}m\widehat{\omega}^2\widehat{q}^2\right) - \frac{f^2}{2m\widehat{\omega}^2} \; .$$

In the bracket there appears the Hamilton operator of the harmonic $(m, \widehat{\omega})$-oscillator, whose eigen-values are known. The second term is a constant. It holds therefore for the ground-state energy:

$$E_0 = \frac{1}{2}\hbar\widehat{\omega} - \frac{f^2}{2m\widehat{\omega}^2} < \langle H \rangle_{\alpha^*} \; .$$

Solution 7.1.4

1. Variational principle:

$$E_0 \leq \langle \psi_\alpha \, | H | \, \psi_\alpha \rangle \; .$$

Hamilton operator:

$$H = \frac{\mathbf{p}^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r} \; .$$

- Kinetic energy:

$$\begin{aligned}
\langle \psi_\alpha \left| \frac{\mathbf{p}^2}{2m} \right| \psi_\alpha \rangle &= \frac{1}{2m}\langle \mathbf{p}\psi_\alpha | \mathbf{p}\psi_\alpha \rangle \\
&= \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \frac{\hbar^2}{2m} \int d^3r \left| \nabla e^{-\frac{\alpha}{2}r^2} \right|^2 \\
&= \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \frac{\hbar^2}{2m} \int d^3r \left| -\alpha r e^{-\frac{\alpha}{2}r^2} \right|^2 \\
&= 4\pi\alpha^2 \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \frac{\hbar^2}{2m} \int_0^\infty dr \, r^4 e^{-\alpha r^2} \\
&= 4\pi\alpha^2 \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \frac{\hbar^2}{2m} \frac{d^2}{d\alpha^2} \underbrace{\int_0^\infty dr \, e^{-\alpha r^2}}_{\frac{1}{2}\sqrt{\frac{\pi}{\alpha}}} \\
&= 4\pi\alpha^2 \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \frac{\hbar^2}{2m} \frac{3}{8}\sqrt{\pi}\frac{1}{\alpha^{\frac{5}{2}}} \\
&= \frac{3\hbar^2}{4m}\alpha \; .
\end{aligned}$$

- Potential energy:

$$\begin{aligned}
\langle\psi_\alpha\left|\frac{-e^2}{4\pi\varepsilon_0 r}\right|\psi_\alpha\rangle &= \frac{-e^2}{4\pi\varepsilon_0}\left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}}\int d^3r\frac{1}{r}e^{-\alpha r^2} \\
&= \frac{-e^2}{\varepsilon_0}\left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}}\int_0^\infty dr\, r e^{-\alpha r^2} \\
&= \frac{e^2}{\varepsilon_0}\left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}}\frac{1}{2\alpha}\int_0^\infty dr\,\frac{d}{dr}e^{-\alpha r^2} \\
&= -\frac{e^2}{2\pi\varepsilon_0}\sqrt{\frac{\alpha}{\pi}}\,.
\end{aligned}$$

- Energy functional

$$E(\alpha) \equiv \langle\psi_\alpha\,|H|\,\psi_\alpha\rangle = \frac{3\hbar^2}{4m}\alpha - \frac{e^2}{2\pi\varepsilon_0}\sqrt{\frac{\alpha}{\pi}}\,.$$

- Extremal condition:

$$\begin{aligned}
&\frac{dE(\alpha)}{d\alpha} \stackrel{!}{=} 0 = \frac{3\hbar^2}{4m} - \frac{e^2}{4\pi\varepsilon_0}\sqrt{\frac{1}{\pi}}\frac{1}{\sqrt{\alpha^*}} \\
\curvearrowright \qquad &\alpha^* = \frac{1}{\pi}\left(\frac{me^2}{3\pi\hbar^2\varepsilon_0}\right)^2 = \frac{1}{\pi}\left(\frac{4}{3a_\mathrm{B}}\right)^2 \\
&a_\mathrm{B} = \frac{4\pi\varepsilon_0\hbar^2}{me^2} \quad \text{Bohr radius}\,.
\end{aligned}$$

- Upper limit of the ground-state energy:

$$\begin{aligned}
E(\alpha^*) &= \frac{3\hbar^2}{4m}\frac{1}{\pi}\left(\frac{4}{3a_\mathrm{B}}\right)^2 - \frac{e^2}{2\pi\varepsilon_0}\frac{1}{\sqrt{\pi}}\frac{1}{\sqrt{\pi}}\left(\frac{4}{3a_\mathrm{B}}\right) \\
&= -\frac{4}{3}\frac{\hbar^2}{\pi m a_\mathrm{B}^2} \\
&= -\frac{8}{3\pi}E_\mathrm{R} \approx -0.849\,E_\mathrm{R} \\
E_\mathrm{R} &= \frac{\hbar^2}{2ma_\mathrm{B}^2} \quad \text{Rydberg energy}\,.
\end{aligned}$$

The ground-state energy amounts to $E_0 = -E_\mathrm{R}$. $E(\alpha^*)$ is therewith an upper bound of the ground-state energy, and differs by about 15 % from the exact value.

2. - Energy functional

$$E(\beta) = \frac{\langle\psi_\beta\,|H|\,\psi_\beta\rangle}{\langle\psi_\beta\,|\,\psi_\beta\rangle} = \frac{\int d^3r\, e^{-\beta r}He^{-\beta r}}{\int d^3r\, e^{-2\beta r}}\,.$$

- Normalization:

$$\begin{aligned}\int d^3r\, e^{-2\beta r} &= 4\pi \int_0^\infty dr\, r^2 e^{-2\beta r} \\ &= \frac{1}{(2\beta)^3} 4\pi \underbrace{\int_0^\infty dy\, y^2 e^{-y}}_{\Gamma(3)=2!} \\ &= \frac{\pi}{\beta^3} \\ \curvearrowright \langle \psi_\beta \,|\, \psi_\beta \rangle &= |\gamma|^2 \frac{\pi}{\beta^3} \,.\end{aligned}$$

- Kinetic energy

$$\begin{aligned}\langle \psi_\beta \left| \frac{\mathbf{p}^2}{2m} \right| \psi_\beta \rangle &= |\gamma|^2 \frac{\hbar^2}{2m} \int d^3r \, \left| \nabla e^{-\beta r} \right|^2 \\ &= |\gamma|^2 \beta^2 \frac{\hbar^2}{2m} 4\pi \int_0^\infty dr\, r^2 e^{-2\beta r} \\ &= |\gamma|^2 \beta^2 \frac{\hbar^2}{2m} 4\pi \, \frac{1}{4\beta^3} \\ &= |\gamma|^2 \frac{\hbar^2}{2m} \pi \frac{1}{\beta} \,.\end{aligned}$$

- Potential energy

$$\begin{aligned}\langle \psi_\beta \left| \frac{-e^2}{4\pi\varepsilon_0 r} \right| \psi_\beta \rangle &= |\gamma|^2 \frac{-e^2}{4\pi\varepsilon_0} \int d^3r \, \frac{1}{r} e^{-\beta r} \\ &= |\gamma|^2 \frac{-e^2}{\varepsilon_0} \int_0^\infty dr\, r\, e^{-2\beta r} \\ &= |\gamma|^2 \frac{-e^2}{\varepsilon_0} \frac{1}{4\beta^2} \underbrace{\int_0^\infty dy\, y\, e^{-y}}_{\Gamma(2)=1!=1} \\ &= |\gamma|^2 \frac{-e^2}{\varepsilon_0} \frac{1}{4\beta^2} \,.\end{aligned}$$

- Energy functional

$$E(\beta) = \frac{\beta^3}{\pi} \left(\frac{\hbar^2}{2m} \pi \frac{1}{\beta} - \frac{e^2}{\varepsilon_0} \frac{1}{4\beta^2} \right) = \frac{\hbar^2}{2m} \beta^2 - \frac{e^2}{4\pi\varepsilon_0} \beta \,.$$

- Extremal condition

$$\begin{aligned}\frac{dE(\beta)}{d\beta} \stackrel{!}{=} 0 &= \frac{\hbar^2}{m} \beta^* - \frac{e^2}{4\pi\varepsilon_0} \\ \curvearrowright \quad \beta^* &= \frac{me^2}{4\pi\varepsilon_0 \hbar^2} = \frac{1}{a_\mathrm{B}}\end{aligned}$$

$$\curvearrowright \quad E(\beta^*) = \frac{\hbar^2}{2ma_\mathrm{B}^2} - \frac{e^2}{4\pi\varepsilon_0 a_\mathrm{B}} = E_\mathrm{R} - \frac{\hbar^2}{ma_\mathrm{B}^2} = E_\mathrm{R} - 2E_\mathrm{R}$$
$$\curvearrowright \quad E(\beta^*) = -E_\mathrm{R} = E_0 \; .$$

The energy functional thus corresponds to the exact ground-state energy. Consequently, the exact ground state wave function belongs in this case to the set of test functions which are admitted to the variation.

Solution 7.1.5

1.

$\mathbf{r}_\mathrm{p}$: position operator of the proton,
$\mathbf{r}_\mathrm{n}$: position operator of the neutron.

Schrödinger equation:

$$\left\{ -\frac{\hbar^2}{2m_\mathrm{n}} \Delta_\mathrm{n} - \frac{\hbar^2}{2m_\mathrm{p}} \Delta_\mathrm{p} + V\left(|\mathbf{r}_\mathrm{n} - \mathbf{r}_\mathrm{p}|\right) \right\} \psi(\mathbf{r}_\mathrm{n}, \mathbf{r}_\mathrm{p}) = E\, \psi(\mathbf{r}_\mathrm{n}, \mathbf{r}_\mathrm{p}) \; .$$

Relative coordinate:

$$\mathbf{r} = \mathbf{r}_\mathrm{n} - \mathbf{r}_\mathrm{p} \; .$$

Center-of-mass coordinate:

$$\mathbf{R} = \frac{1}{M} \left(m_\mathrm{n}\, \mathbf{r}_\mathrm{n} + m_\mathrm{p}\, \mathbf{r}_\mathrm{p} \right) \; ; \quad M = m_\mathrm{n} + m_\mathrm{p} \; .$$

Exactly the same line of thought as in Sect. 6.2.5 leads then to the *new* Schrödinger equation:

$$\left\{ -\frac{\hbar^2}{2M} \Delta_\mathrm{R} - \frac{\hbar^2}{2\mu} \Delta_\mathrm{r} + V(r) \right\} \psi(\mathbf{r}, \mathbf{R}) = E\, \psi(\mathbf{r}, \mathbf{R}) \; ,$$
$$\mu = \frac{m_\mathrm{n}\, m_\mathrm{p}}{m_\mathrm{n} + m_\mathrm{p}} \; : \text{ reduced mass.}$$

Separation ansatz:

$$\psi(\mathbf{r}, \mathbf{R}) = \chi(\mathbf{R})\, \varphi(\mathbf{r}) \; .$$

Inserting and multiplying *from the left* by ψ^{-1}:

$$-\frac{1}{\chi(\mathbf{R})} \frac{\hbar^2}{2M} \Delta_\mathrm{R}\, \chi(\mathbf{R}) = \frac{1}{\varphi(\mathbf{r})} \frac{\hbar^2}{2\mu} \Delta_\mathrm{r}\, \varphi(\mathbf{r}) - V(r) + E \; .$$

The left-hand side is only dependent on $\mathbf{R}$, the right-hand side only on $\mathbf{r}$, therefore the *usual* conclusion:

$$-\frac{\hbar^2}{2M} \Delta_\mathrm{R}\, \chi(\mathbf{R}) = \lambda \chi(\mathbf{r}) \; ,$$
$$\left(-\frac{\hbar^2}{2\mu} \Delta_\mathrm{r} + V(r) \right) \varphi(\mathbf{r}) = (E - \lambda)\, \varphi(\mathbf{r}) \; .$$

2. *Free* movement of the center-of-mass:

$$\begin{aligned} \chi(\mathbf{R}) &= e^{i\,\mathbf{K}\cdot\mathbf{R}} \\ \Longrightarrow\ \lambda &= \frac{\hbar^2 K^2}{2M}\ . \end{aligned}$$

It remains the *equivalent* one-body problem:

$$\begin{aligned} \left(-\frac{\hbar^2}{2\mu}\,\Delta_{\mathrm{r}} + V(r)\right)\,\varphi(\mathbf{r}) &= \varepsilon\,\varphi(\mathbf{r})\ , \\ \varepsilon &= E - \frac{\hbar^2 K^2}{2M}\ . \end{aligned}$$

That is obviously a central-force problem. The general statements of Sect. 6.1 can directly be adopted, for instance (6.16):

$$\varphi(\mathbf{r}) = R(r)\,Y_{lm_l}\,(\vartheta,\varphi)\ .$$

3. The ansatz corresponds to the ground-state wave function of the hydrogen atom (6.60), and offers itself, because for $1/a \to 0$ the Yukawa potential turns into the Coulomb potential. Because of $Y_{00}(\vartheta,\varphi) = 1/\sqrt{4\pi}$ the ansatz is spherically symmetric.

We find with (6.17) and $\mathbf{L}^2\varphi(\mathbf{r}) = 0$:

$$\begin{aligned} \langle\varphi|H|\varphi\rangle &= \int d^3r\,\varphi^*(\mathbf{r})\,H\,\varphi(\mathbf{r}) \\ &= 4\pi|c|^2\int_0^\infty dr\,r^2\,e^{-\alpha(r/a)}\left[-\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dr^2}+\frac{2}{r}\,\frac{d}{dr}\right)\right]e^{-\alpha(r/a)} \\ &\quad -4\pi|c|^2\,V_0\,a\int_0^\infty dr\,r\,e^{-(1+2\alpha)(r/a)} \\ &= 4\pi|c|^2\left\{-\frac{\hbar^2}{2\mu}\,\frac{\alpha^2}{a^2}\int_0^\infty dr\,r^2\,e^{-2\alpha(r/a)}\right. \\ &\quad \left.+\frac{\hbar^2}{2\mu}\,\frac{2\alpha}{a}\int_0^\infty dr\,r\,e^{-2\alpha(r/a)} - V_0\,a\int_0^\infty dr\,r\,e^{-(1+2\alpha)(r/a)}\right\}\ , \end{aligned}$$

$$\int_0^\infty dx\,x^n e^{-\gamma x} = n!\,\gamma^{-n-1}\ ,$$

$$\begin{aligned} \langle\varphi|H|\varphi\rangle &= 4\pi|c|^2\left\{-\frac{\hbar^2}{2\mu}\,\frac{\alpha^2}{a^2}\,2!\,\left(\frac{a}{2\alpha}\right)^3+\frac{\hbar^2}{2\mu}\,\frac{2\alpha}{a}\,\left(\frac{a}{2\alpha}\right)^2 - V_0\,a\,\left(\frac{a}{1+2\alpha}\right)^2\right\} \\ &= 4\pi|c|^2\left\{\frac{\hbar^2}{2\mu}\,\frac{a}{4\alpha} - \frac{V_0\,a^3}{(1+2\alpha)^2}\right\}\ . \end{aligned}$$

It still lacks the normalization integral:

$$\langle\varphi|\varphi\rangle = 4\pi|c|^2 \int_0^\infty dr\, r^2\, e^{-2\alpha(r/a)} = 4\pi|c|^2\, 2!\, \left(\frac{a}{2\alpha}\right)^3 .$$

Energy functional:

$$\langle H\rangle_\varphi = \frac{\langle\varphi|H|\varphi\rangle}{\langle\varphi|\varphi\rangle} = \frac{\hbar^2}{2\mu}\,\frac{\alpha^2}{a^2} - V_0\,\frac{4\alpha^3}{(1+2\alpha)^2} .$$

4. Extremal condition:

$$\begin{aligned}\frac{\partial}{\partial\alpha}\langle H\rangle_\varphi &= \frac{\hbar^2}{\mu}\,\frac{\alpha}{a^2} - 12\,V_0\,\frac{\alpha^2}{(1+2\alpha)^2} + V_0\,\frac{16\,\alpha^3}{(1+2\alpha)^3} \\ &= \frac{\hbar^2}{\mu\,a^2}\,\alpha - 4V_0\,\frac{\alpha^2(3+2\alpha)}{(1+2\alpha)^3} \stackrel{!}{=} 0 .\end{aligned}$$

This is equivalent to:

$$0 = 1 - 2q\,\frac{\alpha(3+2\alpha)}{(1+2\alpha)^3} ; \quad q = \frac{2\mu\,V_0\,a^2}{\hbar^2} .$$

This equation determines the *optimal* α.

5. Binding energy: $E_\mathrm{B} \le \langle H\rangle_\varphi$:

$$\begin{aligned}\langle H\rangle_\varphi &= \frac{V_0}{q}\,\alpha^2 - 4V_0\,\frac{\alpha^3}{(1+2\alpha)^2} \\ &\approx \left[20.28\cdot(0.85)^2 - 200\,\frac{(0.85)^3}{(1+1.7)^2}\right]\mathrm{MeV} \approx -2.19\,\mathrm{MeV} .\end{aligned}$$

Experiment:

$$E_\mathrm{B} \approx -2.23\,\mathrm{MeV} .$$

6. It appears reasonable to define as radius just half of the average distance of the two nucleons:

$$R = \frac{1}{2}\,\frac{\langle\varphi|r|\varphi\rangle}{\langle\varphi|\varphi\rangle} .$$

$\langle\varphi|\varphi\rangle$ has been calculated in 3.:

$$\begin{aligned}R &= \frac{1}{2}\,\frac{1}{2!\,(a/2\alpha)^3}\int_0^\infty dr\, r^3\, e^{-2\alpha\frac{r}{a}} = \frac{1}{4\,(a/2\alpha)^3}\,3!\,\left(\frac{a}{2\alpha}\right)^4 \\ \Longrightarrow\ R &= \frac{3a}{4\alpha} = 0.75\,\frac{1.4}{0.85}\cdot 10^{-13}\,\mathrm{cm} , \\ R &\approx 1.235\cdot 10^{-13}\,\mathrm{cm} .\end{aligned}$$

Solution 7.1.6

1. The exact wave function must vanish for $q < 0$. This, as well as the continuity at $q = 0$, is guaranteed by the ansatz. For each finite energy E the particle enters for $q \to \infty$ a *classically forbidden* region. The wave function must therefore decrease exponentially for large q. In this sense the ansatz appears to be reasonable!

$$\frac{d^2}{dq^2}\, q\, e^{-\alpha q} = (-2\alpha + \alpha^2 q)\, e^{-\alpha q} \quad \text{(see part 2. in solution 7.1.1)}\,,$$

$$\langle H\rangle_\varphi = \frac{\int_0^\infty dq\, e^{-2\alpha q}\, \left[(\hbar^2/2m)\,(2\alpha q - \alpha^2 q^2) + \gamma\, q^3\right]}{\int_0^\infty dq\, e^{-2\alpha q}\, q^2}\,,$$

$$\int_0^\infty dx\, x^n\, e^{-yx} = \frac{n!}{y^{n+1}}\,,$$

$$\langle H\rangle_\varphi = \frac{(\hbar^2/2m)\,\left(2\alpha\,\left(1/(2\alpha)^2\right) - \alpha^2\,\left(2!/(2\alpha)^3\right)\right) + \gamma\,\left(3!/(2\alpha)^4\right)}{(2!/(2\alpha)^3)},$$

$$\langle H\rangle_\varphi = \frac{\hbar^2}{2m}\,\alpha^2 + \frac{3\gamma}{2\alpha}\,.$$

2. Extremal condition:

$$\frac{\partial}{\partial\alpha}\langle H\rangle_\varphi = \frac{\hbar^2}{m}\,\alpha - \frac{3\gamma}{2\alpha^2} \stackrel{!}{=} 0$$

$$\Longrightarrow\ \alpha^* = \left(\frac{3\gamma\, m}{2\hbar^2}\right)^{1/3}\,.$$

Ground-state energy:

$$\langle H\rangle_{\varphi^*} = \frac{\hbar^2}{2m}\left(\frac{3\gamma\, m}{2\hbar^2}\right)^{2/3} + \frac{3}{2}\,\gamma\,\left(\frac{2\hbar^2}{3\gamma\, m}\right)^{1/3}$$

$$= \frac{3}{4}\left(\frac{2\gamma^2\hbar^2}{3m}\right)^{1/3} + \frac{3}{2}\left(\frac{2\gamma^2\hbar^2}{3m}\right)^{1/3}$$

$$= \frac{9}{4}\left(\frac{2\gamma^2\hbar^2}{3m}\right)^{1/3} \geq E_0\,.$$

Solution 7.1.7

$|\psi(q)\rangle$ eigen-state of H:

$$E(\alpha) = \langle H\rangle_{\psi(\alpha q)} = \frac{\langle\psi(\alpha q)|H|\psi(\alpha q)\rangle}{\langle\psi(\alpha q)|\psi(\alpha q)\rangle}$$

Normalization:

$$\begin{aligned}\langle\psi(\alpha q)|\psi(\alpha q)\rangle &= \int \underset{\cdot}{\mathrm{q}}\,\psi^*(\alpha q)\psi(\underbrace{\alpha q}_{x}) \\ &= \frac{1}{\alpha}\underbrace{\int \underset{\cdot}{\mathrm{x}}\,\psi^*(x)\psi(x)}_{=1} = \frac{1}{\alpha}\end{aligned}$$

Numerator:

$$\begin{aligned}\langle\psi(\alpha q)|H|\psi(\alpha q)\rangle &= \int dq\,\psi^*(\alpha q)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dq^2}\right)\psi(\alpha q) \\ &\quad + \int dq\,V(q)|\psi(\alpha q)|^2 \\ &= \frac{1}{\alpha}\alpha^2\int dx\,\psi^*(x)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\psi(x) \\ &\quad + \frac{1}{\alpha}\int dx\,V(\frac{x}{\alpha})|\psi(x)|^2 \\ &= \alpha\langle T\rangle + \frac{1}{\alpha}\frac{1}{\alpha^n}\int dx\,V(x)|\psi(x)|^2 \qquad : \text{ homogeneity} \\ &= \alpha\langle T\rangle + \frac{1}{\alpha^{n+1}}\langle V\rangle\ .\end{aligned}$$

Energy functional:

$$E(\alpha) = \alpha^2\langle T\rangle + \frac{1}{\alpha^n}\langle V\rangle\ .$$

Extremal principle: Since $|\psi(q)\rangle$ is eigen state of H, $E(\alpha)$ is extremal for $\alpha = 1$!

$$\begin{aligned}\longrightarrow\ 0 = \frac{d}{d\alpha}E(\alpha)\big|_{\alpha=1} &= (2\alpha\langle T\rangle - \frac{n}{\alpha^{n+1}}\langle V\rangle)_{\alpha=1} \\ &= 2\langle T\rangle - n\cdot\langle V\rangle \\ \longrightarrow\ 2\langle T\rangle &= n\cdot\langle V\rangle\end{aligned}$$

Examples:

1. Harmonic oscillator

$$V(q) = \frac{1}{2}m\omega^2 q^2 \quad \longrightarrow\ \langle T\rangle = \langle V\rangle$$

2. Particle in the Coulomb field (hydrogen atom)

$$V(q) \sim \frac{1}{q} \quad \longrightarrow\ 2\langle T\rangle = -\langle V\rangle\ .$$

Section 7.2.6

Solution 7.2.1

1. We calculate at first the electrostatic potential of a homogeneously charged sphere. That is a standard problem of Electrostatics, which can be solved by means of the Gauss theorem ((1.58), Vol. 3).

$$\begin{aligned}
&\text{charge: } Q = +e \,, \\
&\text{charge density: } \frac{Q}{(4\pi/3)\, R^3}\Theta(R-r) \,, \\
&\text{Maxwell equation: } \mathrm{div}\mathbf{D} = \varepsilon_0 \ \mathrm{div}\ \mathbf{E} = \rho \,, \\
&\text{symmetry: } \mathbf{E} = E(r)\cdot \mathbf{e}_{\mathrm{r}} \,.
\end{aligned}$$

r* ≤ *R

$$\begin{aligned}
\int\limits_v d^3r \ \mathrm{div}\ \mathbf{E} &= \int\limits_{S(v)} d\mathbf{f}\cdot\mathbf{E} = \frac{1}{\varepsilon_0}\int\limits_v d^3r\,\rho \,, \\
v &= \text{volume of a sphere of the radius } r \\
\Longrightarrow\ 4\pi\, r^2\, E(r) &= \frac{4\pi}{\varepsilon_0}\, Q\, \frac{3}{4\pi\, R^3}\int\limits_0^r dr'\, r'^2 = \frac{1}{\varepsilon_0}\, Q\, \left(\frac{r}{R}\right)^3 \,, \\
\Longrightarrow\ E(r) &= \frac{1}{4\pi\varepsilon_0}\, Q\, \frac{r}{R^3}
\end{aligned}$$

r* > *R

$$\begin{aligned}
4\pi\, r^2\, E(r) &= \frac{1}{\varepsilon_0}\, Q \\
\Longrightarrow\ E(r) &= \frac{1}{4\pi\,\varepsilon_0}\, Q\, \frac{1}{r^2} \,.
\end{aligned}$$

The sphere thus creates the following electrostatic potential ($\varphi(r \to \infty) = 0$):

$$\varphi(\mathbf{r}) = \begin{cases} -\frac{1}{8\pi\,\varepsilon_0}\, Q\, \frac{r^2}{R^3} + a & \text{for } \ r \le R, \\ +\frac{1}{4\pi\,\varepsilon_0}\, Q\, \frac{1}{r} & \text{for } \ r > R. \end{cases}$$

Continuity at $r = R$:

$$a = \frac{3}{2}\, \frac{1}{4\pi\,\varepsilon_0}\, \frac{Q}{R} \,.$$

Potential energy of the electron in the nuclear field:

$$V(\mathbf{r}) = -e\,\varphi(\mathbf{r}) = \begin{cases} -\frac{e^2}{4\pi\,\varepsilon_0 R}\left(\frac{3}{2} - \frac{1}{2}\,\frac{r^2}{R^2}\right) & \text{for } \ r \le R, \\ -\frac{e^2}{4\pi\,\varepsilon_0}\,\frac{1}{r} & \text{for } \ r > R. \end{cases}$$

Hamilton operator:

$$\begin{aligned} H &= H_0 + H_1 \,, \\ H_0 &= \frac{p^2}{2m_\mathrm{f}} - \frac{e^2}{4\pi\,\varepsilon_0 r} \,, \\ H_1 &= \begin{cases} -\frac{e^2}{4\pi\,\varepsilon_0 R}\left(\frac{3}{2} - \frac{R}{r} - \frac{r^2}{2R^2}\right) & \text{for } r \le R, \\ 0 & \text{for } r > R. \end{cases} \end{aligned}$$

2. Assertion:

$$I_n = \int\limits_0^{x_0} dx\, e^{-x}\, x^n = n!\left(1 - e^{-x_0} \sum_{\mu=0}^{n} \frac{x_0^\mu}{\mu!}\right) .$$

Proof by full induction:

$$\begin{aligned} I_0 &= \int\limits_0^{x_0} dx\ e^{-x} = -e^{-x}\big|_0^{x_0} = \left(1 - e^{-x_0}\right) \,, \\ I_1 &= \int\limits_0^{x_0} dx\, x\ e^{-x} = -x\, e^{-x}\big|_0^{x_0} + \int\limits_0^{x_0} dx\, e^{-x} = \left(1 - e^{-x_0} - x_0\, e^{-x_0}\right) . \end{aligned}$$

Conclusion from n to $n+1$:

$$\begin{aligned} I_{n+1} &= \int\limits_0^{x_0} dx\, x^{n+1}\, e^{-x} = -x^{n+1}\ e^{-x}\big|_0^{x_0} + (n+1)\int\limits_0^{x_0} dx\, x^n\, e^{-x_0} \\ &= -x_0^{n+1}\, e^{-x_0} + (n+1)\, I_n \\ &= -\frac{(n+1)!}{(n+1)!}\, x_0^{n+1}\, e^{-x_0} + (n+1)!\left(1 - e^{-x_0} \sum_{\mu=0}^{n} \frac{x_0^\mu}{\mu!}\right) \\ &= (n+1)!\left(1 - e^{-x_0} \sum_{\mu=0}^{n+1} \frac{x_0^\mu}{\mu!}\right) \end{aligned}$$

3. *Unperturbed* wave function:

$$\psi_{100}(\mathbf{r}) = R_{10}(r)\, Y_{00}(\vartheta,\varphi) \overset{(6.60)}{=} \frac{1}{\sqrt{\pi a_\mathrm{B}^3}} \exp\left(-\frac{r}{a_\mathrm{B}}\right) .$$

Energy correction:

$$\begin{aligned} E_{100}^{(1)} &= \int d^3r\, \psi_{100}^*(\mathbf{r})\, H_1\, \psi_{100}(\mathbf{r}) \\ &= -\frac{e^2}{\pi\,\varepsilon_0 R\, a_\mathrm{B}^3} \int\limits_0^R dr\, e^{-(2r/a_\mathrm{B})} \left(\frac{3}{2}r^2 - r\,R - \frac{r^4}{2R^2}\right) . \end{aligned}$$

Substitution:

$$x = \frac{2r}{a_\mathrm{B}} \; ; \quad x_0 = \frac{2R}{a_\mathrm{B}} \; ,$$

$$\begin{aligned} E^{(1)}_{100} &= \frac{-e^2}{\pi\,\varepsilon_0 R\,a_\mathrm{B}^3} \int\limits_0^{x_0} dx\,\frac{a_\mathrm{B}}{2}\,e^{-x}\left(\frac{3a_\mathrm{B}^2}{8}\,x^2 - \frac{R\,a_\mathrm{B}}{2}\,x - \frac{a_\mathrm{B}^4}{32\,R^2}\,x^4\right) \\ &= \frac{e^2}{4\pi\,\varepsilon_0}\left(\frac{a_\mathrm{B}^2}{16\,R^3}\,I_4 - \frac{3}{4R}\,I_2 + \frac{1}{a_\mathrm{B}}\,I_1\right) \; , \end{aligned}$$

$$\frac{a_\mathrm{B}^2}{16\,R^3}\,I_4 = \frac{3a_\mathrm{B}^2}{2R^3}\left\{1 - e^{-x_0}\left[1 + \frac{2R}{a_\mathrm{B}} + \frac{1}{2}\left(\frac{2R}{a_\mathrm{B}}\right)^2 + \frac{1}{6}\left(\frac{2R}{a_\mathrm{B}}\right)^3 + \frac{1}{24}\left(\frac{2R}{a_\mathrm{B}}\right)^4\right]\right\},$$

$$-\frac{3}{4R}\,I_2 = -\frac{3}{2R}\left\{1 - e^{-x_0}\left[1 + \frac{2R}{a_\mathrm{B}} + \frac{1}{2}\left(\frac{2R}{a_\mathrm{B}}\right)^2\right]\right\}.$$

$$\frac{1}{a_\mathrm{B}}\,I_1 = \frac{1}{a_\mathrm{B}}\left[1 - e^{-x_0}\left(1 + \frac{2R}{a_\mathrm{B}}\right)\right] \; .$$

Energy correction:

$$E^{(1)}_{100} = \frac{e^2}{4\pi\varepsilon_0\,a_\mathrm{B}}\left[\left(\frac{3a_\mathrm{B}^3}{2R^3} - \frac{3a_\mathrm{B}}{2R} + 1\right) - e^{-(2R/a_\mathrm{B})}\left(\frac{3a_\mathrm{B}^3}{2R^3} + \frac{3a_\mathrm{B}^2}{R^2} + \frac{3a_\mathrm{B}}{2R}\right)\right].$$

The Bohr radius a_B and the radius of the nucleus R are of different orders of magnitude

$$\frac{a_\mathrm{B}}{R} \approx 10^3 \; .$$

One can therefore expand the exponential function, and take into consideration in the bracket only terms up to the order $(R/a_\mathrm{B})^2$:

$$E^{(1)}_{100} \approx \frac{e^2}{4\pi\,\varepsilon_0\,a_\mathrm{B}}\,\frac{2}{5}\left(\frac{R}{a_\mathrm{B}}\right)^2 \overset{(6.33)}{=} \frac{4}{5}\,E_\mathrm{R}\left(\frac{R}{a_\mathrm{B}}\right)^2 = -\frac{4}{5}\,E^{(0)}_{100}\left(\frac{R}{a_\mathrm{B}}\right)^2 \; .$$

On the whole, the *corrected* ground-state energy then reads:

$$E_{100} \approx E^{(0)}_{100} + E^{(1)}_{100} = E^{(0)}_{100}\left[1 - \frac{4}{5}\left(\frac{R}{a_\mathrm{B}}\right)^2\right] \; .$$

The influence of the spatial extension of the nucleus is thus of the order of magnitude 10^{-6} and therewith surely negligible!

Solution 7.2.2

The occupation number representation turns out to be convenient. According to ((4.129), Vol. 6) it holds for the *unperturbed* Hamilton operator:

$$H_0 = -\frac{\hbar^2}{2m}\,\frac{d^2}{dq^2} + \frac{1}{2}\,m\,\omega^2 q^2 \equiv \hbar\,\omega\left(\hat{n} + \frac{1}{2}\right) \qquad \hat{n} = a^+\,a \; .$$

$|n\rangle$ are the *unperturbed* eigen-states ((4.145), Vol. 6) $\Longrightarrow$

$$\begin{aligned} H_0|n\rangle &= E_n^{(0)}|n\rangle\,; \quad n \in \mathbb{N}_0\,, \\ E_n^{(0)} &= \hbar\,\omega\left(n+\frac{1}{2}\right)\,. \end{aligned}$$

((4.139), (4.140), Vol. 6) $\Longrightarrow$

$$a^+|n\rangle = \sqrt{n+1}|n+1\rangle\,; \quad a|n\rangle = \sqrt{n}|n-1\rangle\,.$$

((4.127), Vol. 6) $\Longrightarrow$

$$q = \sqrt{\frac{\hbar}{2m\,\omega}}\,(a+a^+)\,.$$

Energy correction of first order:

$$\begin{aligned} E_n^{(1)} &= \langle n|H_1|n\rangle = \alpha\,\frac{m^2\omega^2}{\hbar}\langle n|q^4|n\rangle\,, \\ q^2 &= \frac{\hbar}{2m\,\omega}\,(a^2+a^{+2}+a\,a^+ + a^+a)\,, \end{aligned}$$

$$\begin{aligned} q^4 = \frac{\hbar^2}{4m^2\omega^2}\big(&a^4 + a^2\,a^{+2} + a^3a^+ + a^2a^+a \\ &+a^{+2}a^2 + a^{+4} + a^{+2}a\,a^+ + a^{+3}a + a\,a^+a^2 + a\,a^{+3} + a\,a^+a\,a^+ \\ &+a\,a^{+2}a + a^+a^3 + a^+a\,a^{+2} + a^+a^2a^+ + a^+a\,a^+a\big)\,. \end{aligned}$$

Because of $\langle n|m\rangle = \delta_{nm}$ not all the terms contribute to $E_n^{(1)}$:

$$\begin{aligned} &\langle n|q^4|n\rangle \\ &= \frac{\hbar^2}{4m^2\omega^2}\,\big(\langle n\,|a^2a^{+2}|\,n\rangle + \langle n\,|a^{+2}a^2|\,n\rangle + \langle n\,|a\,a^+a\,a^+|\,n\rangle \\ &\quad + \langle n\,|a\,a^{+2}a|\,n\rangle + \langle n\,|a^+a^2a^+|\,n\rangle + \langle n\,|\hat{n}^2|\,n\rangle\big) \\ &= \frac{\hbar^2}{4m^2\omega^2}\,\big[(n+1)\,(n+2) + n(n-1) + (n+1)^2 + n(n+1) \\ &\quad + (n+1)\,n + n^2\big] \\ &= \frac{\hbar^2}{4m^2\omega^2}\,(6n^2+6n+3) \end{aligned}$$

$$\Longrightarrow \quad E_n^{(1)} = \frac{3}{4}\,\hbar\,\alpha\,(2n^2+2n+1)\,.$$

Solution 7.2.3

We use, as in the last exercise, the occupation number representation:

$$H_0 = \hbar\,\omega\left(\hat{n}+\frac{1}{2}\right)\,.$$

1. As for the solution of the last exercise:

$$q^2 = \frac{\hbar}{2m\,\omega}\,\left(a^2 + a^{+2} + a\,a^+ + a^+ a\right) \overset{(4.120)}{=} \frac{\hbar}{2m\,\omega}\,\left(a^2 + a^{+2} + 2\hat{n} + 1\right)\,.$$

It follows therewith immediately:

$$E_n^{(1)} = \frac{1}{4}\,\alpha\,\hbar\,\omega\,(2n+1)\,.$$

2. State correction of first order:

$$\begin{aligned}
|n\rangle^{(1)} &= \sum_m^{\neq n} |m\rangle^{(0)}\,\frac{{}^{(0)}\langle m|H_1|n\rangle^{(0)}}{E_n^{(0)} - E_m^{(0)}}\,,\\
E_n^{(0)} - E_m^{(0)} &= \hbar\,\omega\,(n-m)\,,\\
{}^{(0)}\langle m\,|H_1|\,n\rangle^{(0)} &= \frac{1}{4}\,\alpha\,\hbar\,\omega\,{}^{(0)}\left\langle m\,\middle|\left(a^2 + a^{+2}\right)\right|\,n\right\rangle^{(0)}\\
&= \frac{1}{4}\,\alpha\,\hbar\,\omega\,\left\{\delta_{m\;n-2}\,\sqrt{n(n-1)} + \delta_{m\;n+2}\,\sqrt{(n+1)\,(n+2)}\right\}
\end{aligned}$$

$$\Longrightarrow\; |n\rangle^{(1)} = \frac{\alpha}{8}\,\left\{\sqrt{n\,(n-1)}|n-2\rangle^{(0)} - \sqrt{(n+1)\,(n+2)}|n+2\rangle^{(0)}\right\}\,.$$

3.

$$E_n^{(2)} = \sum_m^{m\neq n} \frac{\left|{}^{(0)}\langle m|H_1|n\rangle^{(0)}\right|^2}{E_n^{(0)} - E_m^{(0)}}\,.$$

According to part 2.:

$$\begin{aligned}
E_n^{(0)} - E_m^{(0)} &= \hbar\,\omega(n-m)\,,\\
\left|{}^{(0)}\langle m|H_1|n\rangle^{(0)}\right|^2 &= \frac{1}{16}\,\alpha^2\hbar^2\omega^2\,\left[n(n-1)\,\delta_{m\;n-2} + (n+1)(n+2)\,\delta_{m\;n+2}\right]\\
\Longrightarrow\; E_n^{(2)} &= \frac{\alpha^2}{16}\,\hbar\,\omega\,\left[\frac{1}{2}\,(n^2-n) - \frac{1}{2}\,(n^2+3n+2)\right]\,,\\
E_n^{(2)} &= -\frac{\alpha^2}{16}\,\hbar\,\omega\,(2n+1)\,.
\end{aligned}$$

4. Exact:

$$E_n = \hbar\,\widehat{\omega}\,\left(n + \frac{1}{2}\right)$$

with

$$\widehat{\omega} = \omega\,\sqrt{1+\alpha}\,.$$

Series expansion of the root:

$$E_n = \hbar\,\omega\,\left(n + \frac{1}{2}\right)\,\left(1 + \frac{1}{2}\,\alpha - \frac{1}{8}\,\alpha^2 + \ldots\right)\,.$$

Perturbation series is in any case exact up to the third term!

Solution 7.2.4

1.

$$
\begin{aligned}
|n\rangle &\approx |n\rangle^{(0)} + \sum_{m}^{\neq n} |m\rangle^{(0)} \, \frac{{}^{(0)}\langle m|H_1|n\rangle^{(0)}}{E_n^{(0)} - E_m^{(0)}} \, , \\
E_n^{(0)} - E_m^{(0)} &= \hbar\,\omega(n-m) \, , \\
((4.127), Vol.\ 6) \implies q &= \sqrt{\frac{\hbar}{2m\,\omega}}\,(a + a^{+}) \, , \\
{}^{(0)}\langle m|q|n\rangle^{(0)} &= \sqrt{\frac{\hbar}{2m\,\omega}}\,\left(\sqrt{n}\,\delta_{m\ n-1} + \sqrt{n+1}\,\delta_{m\ n+1}\right) \\
\implies |n\rangle &\approx |n\rangle^{(0)} - F\sqrt{\frac{1}{2\hbar\,m\,\omega^3}}\,\left(\sqrt{n}|n-1\rangle - \sqrt{n+1}|n+1\rangle\right) \, .
\end{aligned}
$$

2.

$$
\begin{aligned}
E_n^{(1)} &= -F\,{}^{(0)}\langle n|q|n\rangle^{(0)} = 0 \, , \\
E_n^{(2)} &= \sum_{m}^{m\neq n} \frac{\left|{}^{(0)}\langle m|H_1|n\rangle^{(0)}\right|^2}{E_n^{(0)} - E_m^{(0)}} \, , \\
\left|{}^{(0)}\langle m|H_1|n\rangle^{(0)}\right|^2 &= F^2\,\frac{\hbar}{2m\,\omega}\,\left(n\,\delta_{m\ n-1} + (n+1)\,\delta_{m\ n+1}\right) \\
\implies E_n^{(2)} &= \frac{F^2}{2m\,\omega^2}\,[n-(n+1)] = -\frac{F^2}{2m\,\omega^2} \, .
\end{aligned}
$$

3. Exact solution (see Exercise 4.4.14 (Vol. 6)) or Exercise 7.1.3:

$$
H = \frac{p^2}{2m} + \frac{1}{2}\,m\omega^2\,\left(q^2 - \frac{2F}{m\,\omega^2}\,q\right) \, .
$$

Substitution:

$$
\begin{aligned}
\overline{q} &= q - \frac{F}{m\,\omega^2} \, , \\
\frac{d}{d\overline{q}} &= \frac{d}{dq} \implies \overline{p} = p \, , \\
H &= \frac{\overline{p}^2}{2m} + \frac{1}{2}\,m\,\omega^2\,\overline{q}^2 - \frac{F^2}{2m\,\omega^2} \, .
\end{aligned}
$$

$\implies$ exact eigen-energies:

$$
E_n^{(\mathrm{ex})} = \hbar\,\omega\,\left(n + \frac{1}{2}\right) - \frac{F^2}{2m\,\omega^2} = E_n^{(0)} + E_n^{(2)} \, .
$$

The second order perturbation theory is already exact!

4. According to (7.37):

$$E_n^{(3)} = \left\langle E_n^{(0)} | H_1 | E_n^{(2)} \right\rangle \ .$$

We insert $|E_n^{(2)}\rangle$ according to (7.42) and exploit $E_n^{(1)} = 0$:

$$E_n^{(3)} = \sum_m^{\neq n} \sum_q^{\neq n} \frac{\left\langle E_n^{(0)} | H_1 | E_m^{(0)} \right\rangle \left\langle E_m^{(0)} | H_1 | E_q^{(0)} \right\rangle \left\langle E_q^{(0)} | H_1 | E_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)}\right) \left(E_n^{(0)} - E_q^{(0)}\right)} \ ,$$

$$\text{numerator} = -F^3 \left(\frac{\hbar}{2m\,\omega}\right)^{3/2} I_{nmq}\, L_{qn} \ ,$$

$$\begin{aligned}
I_{nmq} &= \left(\sqrt{m}\,\delta_{n\ m-1} + \sqrt{m+1}\,\delta_{n\ m+1}\right)\left(\sqrt{q}\,\delta_{m\ q-1} + \sqrt{q+1}\,\delta_{m\ q+1}\right) \ , \\
L_{qn} &= \left(\sqrt{n}\,\delta_{q\ n-1} + \sqrt{n+1}\,\delta_{q\ n+1}\right) \ , \\
I_{nmq} &= \Big(\sqrt{m\,q}\,\delta_{n\ m-1}\,\delta_{m\ q-1} + \sqrt{m(q+1)}\,\delta_{n\ m-1}\,\delta_{m\ q+1} \\
&\quad + \sqrt{q(m+1)}\,\delta_{n\ m+1}\,\delta_{m\ q-1} + \sqrt{(m+1)\,(q+1)}\,\delta_{n\ m+1}\,\delta_{m\ q+1}\Big) \\
&= \delta_{q\,n+2}\,(\sqrt{m\,q}\delta_{m\,q-1}) + \delta_{qn}\left(\sqrt{m(q+1)}\,\delta_{m\,q+1} + \sqrt{q(m+1)}\,\delta_{m\,q-1}\right) \\
&\quad + \delta_{q\ n-2}\left(\sqrt{(m+1)\,(q+1)}\,\delta_{m\ q+1}\right) \ .
\end{aligned}$$

L_{qn} is now unequal zero for $q = n-1$ and $q = n+1$.

$$\Longrightarrow\ I_{nmq}\, L_{qn} = 0 \ \Longrightarrow\ E_n^{(3)} = 0 \ .$$

Solution 7.2.5

According to (4.127) and (4.128) (Vol. 6) it holds:

$$\begin{aligned}
\hat{q} &= \sqrt{\frac{\hbar}{2m\omega}}\left(a + a^+\right) \ ; \ \hat{p} = -i\sqrt{\frac{1}{2}\hbar m\omega}\left(a - a^+\right) \\
\curvearrowright\ \hat{q}\cdot\hat{p} + \hat{p}\cdot\hat{q} &= -i\frac{\hbar}{2}\left((a+a^+)(a-a^+) + (a-a^+)(a+a^+)\right) \\
&= -i\hbar\left(a^2 - a^{+2}\right) \ .
\end{aligned}$$

- Matrix elements:

$$\begin{aligned}
{}^{(0)}\langle m|H_1|n\rangle^{(0)} &= -i\hbar\lambda\,{}^{(0)}\langle m|\left(a^2 - a^{+2}\right)|n\rangle^{(0)} \\
&= -i\hbar\lambda\left(\sqrt{n(n-1)}\,\delta_{m,n-2} - \sqrt{(n+1)(n+2)}\,\delta_{m,n+2}\right) \ .
\end{aligned}$$

- Energy correction of first order:

$$E_n^{(1)} = {}^{(0)}\langle n|H_1|n\rangle^{(0)} = 0 \ .$$

- State correction of first order:

$$\begin{aligned} |n\rangle^{(1)} &= \sum_m^{\neq 0} |m\rangle^{(0)} \frac{{}^{(0)}\langle m|H_1|n\rangle^{(0)}}{E_n^{(0)} - E_m^{(0)}} \\ &= -i\frac{\lambda}{2\omega}\left(\sqrt{n(n-1)}|n-2\rangle^{(0)} + \sqrt{(n+1)(n+2)}|n+2\rangle^{(0)}\right) . \end{aligned}$$

- Energy correction of second order:

$$\begin{aligned} E_n^{(2)} &= {}^{(0)}\langle n|H_1|n\rangle^{(1)} \\ &= -i\hbar\lambda\, {}^{(0)}\langle n|\left(a^2 - a^{+2}\right)|n\rangle^{(1)} \\ &= -\lambda^2\frac{\hbar}{2\omega}\left(\sqrt{n(n-1)}\,{}^{(0)}\langle n|\left(a^2 - a^{+2}\right)|n-2\rangle^{(0)}\right. \\ &\quad \left. + \sqrt{(n+1)(n+2)}\,{}^{(0)}\langle n|\left(a^2 - a^{+2}\right)|n+2\rangle^{(0)}\right) \\ &= -\lambda^2\frac{\hbar}{2\omega}\left(-\sqrt{n(n-1)}\sqrt{(n-1)n}\right. \\ &\quad \left. + \sqrt{(n+1)(n+2)}\sqrt{(n+2)(n+1)}\right) \\ &= -\lambda^2\frac{\hbar}{2\omega}\left(-n(n-1) + (n+2)(n+1)\right) \\ \curvearrowright\quad E_n^{(2)} &= -\lambda^2\frac{\hbar}{\omega}(2n+1) . \end{aligned}$$

Solution 7.2.6

Solution of the eigen-value problem of the *'unperturbed'* oscillator:

$$\begin{aligned} H_0|n_i n_j\rangle &= E^{(0)}_{n_i n_j}|n_i n_j\rangle \\ |n_i n_j\rangle &= |n_i\rangle^{(x)}|n_j\rangle^{(y)} ; \quad n_{i,j} = 0, 1, 2, \ldots \\ E^{(0)}_{n_i n_j} &= (n_i + n_j + 1)\hbar\omega . \end{aligned}$$

1. Ground state:

$$n_i = n_j = 0 ; \qquad \text{not degenerate!}$$

Matrix elements of the perturbation:

$$\langle n_i n_j|H_1|n'_i n'_j\rangle = \gamma\, {}^{(x)}\langle n_i|q_x^2|n'_i\rangle^{(x)}\,{}^{(y)}\langle n_j|q_y^2|n'_j\rangle^{(y)}$$

$$\begin{aligned} q &= \sqrt{\frac{\hbar}{2m\omega}}(a + a^+) \qquad \text{(4.127), Vol. 6} \\ q^2 &= \frac{\hbar}{2m\omega}(a^2 + \underbrace{a\,a^+ + a^+ a}_{2\hat{n}+1} + a^{+2}) \\ \langle n_i|q_x^2|n'_i\rangle^{(x)} &= \frac{\hbar}{2m\omega}\left(\sqrt{n'_i(n'_i-1)}\delta_{n_i n'_i-2}\right. \\ &\quad \left. +(2n'_i+1)\delta_{n_i n'_i} + \sqrt{(n'_i+1)(n'_i+2)}\delta_{n_i n'_i+2}\right) . \end{aligned}$$

Energy correction of first order:

$$E_0^{(1)} = \langle 0\,0|H_1|0\,0\rangle = \gamma\frac{\hbar^2}{4m^2\omega^2}\ .$$

Energy correction of second order:

$$\begin{aligned}
E_0^{(2)} &= \sum_{n_i,n_j}^{\neq(0,0)} \frac{|\langle 0\,0|H_1|n_i n_j\rangle|^2}{E_0^{(0)} - E_{n_i n_j}} \\
&\qquad {}^{(x)}\langle 0|q_x^2|n_i\rangle^{(x)} = \frac{\hbar}{2m\omega}\left(\sqrt{2}\,\delta_{n_i 2} + \delta_{n_i 0}\right) \\
E_0^{(2)} &= \frac{|\langle 0\,0|H_1|0\,2\rangle|^2}{\hbar\omega - 3\hbar\omega} + \frac{|\langle 0\,0|H_1|2\,0\rangle|^2}{\hbar\omega - 3\hbar\omega} + \frac{|\langle 0\,0|H_1|2\,2\rangle|^2}{\hbar\omega - 5\hbar\omega} \\
&= \frac{\gamma^2}{\hbar\omega}\left(\frac{\hbar}{2m\omega}\right)^4\left(\frac{(\sqrt{2}\cdot 1)^2}{-2} + \frac{(\sqrt{2}\cdot 1)^2}{-2} + \frac{(\sqrt{2}\cdot\sqrt{2})^2}{-4}\right) \\
&\qquad \Longrightarrow\ E_0^{(2)} = -3\frac{\gamma^2}{\hbar\omega}\left(\frac{\hbar}{2m\omega}\right)^4 .
\end{aligned}$$

2. First excitation energy:

$$n_i + n_j = 1 \qquad E_1^{(0)} = 2\hbar\omega$$

twofold degenerate: $|0\,1\rangle$, $|1\,0\rangle$.

Perturbation matrix:

$$\hat{H}_1 = \begin{pmatrix} \langle 1\,0|H_1|1\,0\rangle & \langle 1\,0|H_1|0\,1\rangle \\ \langle 0\,1|H_1|1\,0\rangle & \langle 0\,1|H_1|0\,1\rangle \end{pmatrix}$$

$$\begin{aligned}
\langle 1\,0|H_1|0\,1\rangle &= \langle 0\,1|H_1|1\,0\rangle = 0 \\
\langle 1\,0|H_1|1\,0\rangle &= \gamma\left(\frac{\hbar}{2m\omega}\right)^2(2\cdot 1 + 1)\cdot 1 \\
&= 3\gamma\left(\frac{\hbar}{2m\omega}\right)^2 = \langle 0\,1|H_1|0\,1\rangle
\end{aligned}$$

$$\Longrightarrow\ \hat{H}_1 = 3\gamma\left(\frac{\hbar}{2m\omega}\right)^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\ .$$

The matrix is already diagonal:

$$\Longrightarrow\ E_{11}^{(1)} = E_{12}^{(1)} = 3\gamma\left(\frac{\hbar}{2m\omega}\right)^2$$

Degeneracy is **not** removed!

$$E_1 \approx 2\hbar\omega + 3\gamma\left(\frac{\hbar}{2m\omega}\right)^2 .$$

Next excitation energy:

$$n_i + n_j = 2 \qquad E_2^{(0)} = 3\hbar\omega$$

threefold degenerate: $|0\,2\rangle$, $|1\,1\rangle$, $|2\,0\rangle$.

Perturbation matrix in the eigen-space to $E_2^{(0)}$:

$$\widehat{H}_1 = \begin{pmatrix} \langle 2\,0|H_1|2\,0\rangle & \langle 2\,0|H_1|1\,1\rangle & \langle 2\,0|H_1|0\,2\rangle \\ \langle 1\,1|H_1|2\,0\rangle & \langle 1\,1|H_1|1\,1\rangle & \langle 1\,1|H_1|0\,2\rangle \\ \langle 0\,2|H_1|2\,0\rangle & \langle 0\,2|H_1|1\,1\rangle & \langle 0\,2|H_1|0\,2\rangle \end{pmatrix}$$

$$\begin{aligned}
\langle 2\,0|H_1|2\,0\rangle &= \gamma\left(\frac{\hbar}{2m\omega}\right)^2 (2\cdot 2+1)\cdot 1 = 5\gamma\left(\frac{\hbar}{2m\omega}\right)^2 \\
\langle 2\,0|H_1|1\,1\rangle &= 0 \\
\langle 2\,0|H_1|0\,2\rangle &= \gamma\left(\frac{\hbar}{2m\omega}\right)^2 (\sqrt{2}\cdot\sqrt{2}) = 2\gamma\left(\frac{\hbar}{2m\omega}\right)^2 \\
\langle 1\,1|H_1|2\,0\rangle &= 0 \\
\langle 1\,1|H_1|1\,1\rangle &= \gamma\left(\frac{\hbar}{2m\omega}\right)^2 (3\cdot 3) = 9\gamma\left(\frac{\hbar}{2m\omega}\right)^2 \\
\langle 1\,1|H_1|0\,2\rangle &= 0 \\
\langle 0\,2|H_1|2\,0\rangle &= \gamma\left(\frac{\hbar}{2m\omega}\right)^2 (\sqrt{2}\cdot\sqrt{2}) = 2\gamma\left(\frac{\hbar}{2m\omega}\right)^2 \\
\langle 0\,2|H_1|1\,1\rangle &= 0 \\
\langle 0\,2|H_1|0\,2\rangle &= \gamma\left(\frac{\hbar}{2m\omega}\right)^2 \cdot 1\cdot(2\cdot 2+1) = 5\gamma\left(\frac{\hbar}{2m\omega}\right)^2 .
\end{aligned}$$

$\widehat{H}_1$ is of course Hermitian:

$$\hat{H}_1 = \gamma\left(\frac{\hbar}{2m\omega}\right)^2 \begin{pmatrix} 5 & 0 & 2 \\ 0 & 9 & 0 \\ 2 & 0 & 5 \end{pmatrix} .$$

It must be:

$$\det(\widehat{H}_1 - E_2^{(1)}\mathbb{1}) \stackrel{!}{=} 0 .$$

With

$$\alpha \equiv \gamma\left(\frac{\hbar}{2m\omega}\right)^2$$

$$\begin{aligned}
\Longrightarrow\ 0 \quad &\stackrel{!}{=} \quad (5\alpha - E_2^{(1)})^2(9\alpha - E_2^{(1)}) - 4\alpha^2(9\alpha - E_2^{(1)}) \\
&\Longrightarrow \quad E_{21}^{(1)} = 3\alpha\ ; \quad E_{22}^{(1)} = 7\alpha\ ; \quad E_{23}^{(1)} = 9\alpha\ .
\end{aligned}$$

The degeneracy is completely removed!

Solution 7.2.7

Relativistic Darwin term (5.253):

$$H_1 = V_\mathrm{B} = \frac{e\,\hbar^2}{8m_\mathrm{e}^2\,c^2}\,\Delta\varphi\ .$$

The point-like hydrogen atom creates the Coulomb field:

$$\varphi(\mathbf{r}) = \frac{e}{4\pi\,\varepsilon_0 r}\ .$$

According to (1.69) in Vol. 3:

$$\Delta\,\frac{1}{r} = -4\pi\,\delta(\mathbf{r})\ .$$

The *perturbation* reads therewith:

$$H_1 = -\frac{e^2\hbar^2}{8m_\mathrm{e}^2c^2\varepsilon_0}\,\delta(\mathbf{r})\ .$$

Ground-state wave function of the electron in the hydrogen atom:

$$\psi_{100}(\mathbf{r}) \overset{(6.60)}{=} \frac{1}{\sqrt{\pi\,a_\mathrm{B}^3}}\,\exp\left(-\frac{r}{a_\mathrm{B}}\right)\ .$$

Energy correction of first order:

$$\begin{aligned} E_{100}^{(1)} &= \int d^3r\,\psi_{100}^*(\mathbf{r})\,H_1\,\psi_{100}(\mathbf{r}) = -\frac{e^2\hbar^2}{8m_\mathrm{e}^2c^2\varepsilon_0}\,\frac{1}{\pi\,a_\mathrm{B}^3}\int d^3r\,e^{-(2r/a_\mathrm{B})}\,\delta(\mathbf{r}) \\ &= -\frac{e^2}{4\pi\,\varepsilon_0 m_\mathrm{e}c^2\,a_\mathrm{B}}\left(\frac{\hbar^2}{2m_\mathrm{f}\,a_\mathrm{B}^2}\right)\ , \end{aligned}$$

$$(6.33) \implies 1\,\mathrm{Ry} = \frac{\hbar^2}{2m_\mathrm{e}a_\mathrm{B}^2}\ ,$$

$$(6.32) \implies a_\mathrm{B} = \frac{4\pi\,\varepsilon_0\hbar^2}{m_\mathrm{e}e^2}$$

$$\implies E_{100}^{(1)} = -\left(\frac{e^2}{4\pi\,\varepsilon_0\hbar\,c}\right)^2\,[\mathrm{Ry}]\ .$$

In the bracket we find the *Sommerfeld fine structure constant*:

$$\alpha = \frac{e^2}{4\pi\,\varepsilon_0\hbar\,c} \approx \frac{1}{137} \implies E_{100}^{(1)} \approx -5.33\cdot 10^{-5}\,[\mathrm{Ry}]\ .$$

It represents a relatively small correction!

Solution 7.2.8

1. *Free* movement with the constraint:

$$H_0 = \frac{p^2}{2m} = -\frac{\hbar^2}{2m}\,\Delta\ .$$

The constraint is formulated most easily with spherical coordinates:

$$(6.3) \implies \Delta = \frac{1}{r^2}\,\frac{\partial}{\partial r}\left(r^2\,\frac{\partial}{\partial r}\right) - \frac{\mathbf{L}^2}{r^2\hbar^2}\ .$$

Constraint: $r \stackrel{!}{=} R = \text{const}$

$$\implies H_0 = \frac{\mathbf{L}^2}{2m\,R^2} = \frac{\mathbf{L}^2}{2J}\ ; \quad J = m\,R^2: \quad \text{moment of inertia.}$$

Eigen-functions are therefore the spherical harmonics:

$$H_0\,Y_{lm_l}(\vartheta,\varphi) = \frac{1}{2J}\,\mathbf{L}^2\,Y_{lm_l}(\vartheta,\varphi) = \frac{1}{2J}\,\hbar^2 l(l+1)\,Y_{lm}(\vartheta,\varphi)\ .$$

Eigen-values:

$$E_l^{(0)} = \frac{\hbar^2}{2J}\,l(l+1)\ .$$

The eigen-values are obviously $(2l+1)$-fold degenerate due to the magnetic quantum number m_l.

2.

$$\begin{aligned} H &= H_0 + H_1\ , \\ H_1 &= m\,g\,z = m\,g\,R\cos\vartheta\ . \end{aligned}$$

The particle remains bound to the surface of the sphere!
Because of (5.19), the z-component of the orbital angular momentum L_z commutes with H_1,

$$[H_1, L_z]_- = m\,g\,[z, L_z]_- = 0\ ,$$

and of course also with H_0:

$$[H_0, L_z]_- = 0\ .$$

3. L_z commutes with the total Hamilton operator. It will therefore be possible to classify also the full energy-eigen states by the quantum number m_l. But when we perform perturbation theory for an eigen-state (eigen-value) with a fixed m_l, then also the *'correct'* state of zeroth order must be chosen with this quantum number. It is therewith clear that the spherical harmonics from part 1. are already the *'correct'* states of zeroth order.

4. With the given formula it can be easily realized that all elements of the perturbation matrix are zero:

$$\langle l\, m_l|H_1|l\, m_l'\rangle = H_{1l}^{m_l m_l'} = 0\ .$$

The energy correction of first order therewith is of course also zero:

$$E_l^{(1)} = 0\ .$$

The degeneracy with respect to m_l is thus completely retained!

5. For the energy correction of second order we have (7.61) and (7.63), respectively:

$$E_{l\,m_l}^{(2)} = \sum_{\substack{l',\,m_{l'}\\(l'\neq l)}} \frac{\left|\langle l' m_{l'}|H_1|l\, m_l\rangle\right|^2}{E_l^{(0)} - E_{l'}^{(0)}}\ .$$

We calculate the matrix element using the given formula:

$$\begin{aligned}
&\langle l'\, m_{l'}|H_1|l\, m_l\rangle = \iint d\varphi\, d\cos\vartheta\, Y^*_{l' m_{l'}}(\vartheta,\varphi)\, m\, g\, R\cos\vartheta\, Y_{l m_l}(\vartheta,\varphi)\\
=&m\, g\, R\left\{\sqrt{\frac{(l+1)^2-m_l^2}{(2l+1)\,(2l+3)}}\iint d\varphi\, d\cos\vartheta\, Y^*_{l' m_{l'}}(\vartheta,\varphi)\, Y_{l+1\, m_l}(\vartheta,\varphi)\right.\\
&\left.+\sqrt{\frac{l^2-m_l^2}{(2l+1)\,(2l-1)}}\iint d\varphi\, d\cos\vartheta\, Y^*_{l' m_{l'}}(\vartheta,\varphi)\, Y_{l-1\, m_l}(\vartheta,\varphi)\right\}\\
\overset{(5.102)}{=}&\ mgR\delta_{m_{l'}m_l}\left\{\sqrt{\frac{(l+1)^2-m_l^2}{(2l+1)(2l+3)}}\delta_{l'l+1}+\sqrt{\frac{l^2-m_l^2}{(2l+1)(2l-1)}}\delta_{l'l-1}\right\}.
\end{aligned}$$

It is clear according to 2. and 3. that the matrix element can be unequal zero only for $m_l = m_{l'}$. This could have been assumed, actually from the beginning, in the above energy formula.

$$\begin{aligned}
E_{lm_l}^{(2)} &= \frac{2J}{\hbar^2}(m\, g\, R)^2\left[\frac{(l+1)^2-m_l^2}{(2l+3)\,(2l+1)}\,\frac{1}{l(l+1)-(l+1)\,(l+2)}\right.\\
&\quad\left.+\frac{l^2-m_l^2}{(2l-1)\,(2l+1)}\,\frac{1}{l(l+1)-(l-1)\,l}\right]\\
&= \frac{2J}{\hbar^2}\,\frac{(m\, g\, R)^2}{(2l+3)\,(2l+2)\,(2l+1)\,2l\,(2l-1)}\\
&\quad\cdot\left\{-m_l^2\,\left[(2l+3)\,(2l+2)-2l\,(2l-1)\right]\right.\\
&\quad\left.+\,l^2\,(2l+3)\,(2l+2)-(l+1)^2\,2l\,(2l-1)\right\}\ .
\end{aligned}$$

The degeneracy with respect to m_l is to a great part removed by the energy correction of second order:

$$E_{lm_l}^{(2)} = \frac{2J}{\hbar^2}(m\, g\, R)^2\,\frac{l(l+1)-3m_l^2}{(2l+3)\,(l+1)\,2l\,(2l-1)} = E_{l|m_l|}^{(2)}\ .$$

Each eigen-value, unless that of $m_l = 0$, is still twofold degenerate (m_l and $-m_l$).

Solution 7.2.9

We build with the degenerate states $|E_{n1}^{(0)}\rangle$, $|E_{n2}^{(0)}\rangle$ the elements

$$H_{1n}^{\alpha\beta} = \langle E_{n\alpha}^{(0)} | H_1 | E_{n\beta}^{(0)} \rangle$$

of the perturbation matrix, and calculate the secular determinant (7.49):

$$\begin{vmatrix} H_{1n}^{11} - E_n^{(1)} & H_{1n}^{12} \\ H_{1n}^{21} & H_{1n}^{22} - E_n^{(1)} \end{vmatrix} \stackrel{!}{=} 0 = \left(H_{1n}^{11} - E_n^{(1)} \right) \left(H_{1n}^{22} - E_n^{(1)} \right) - |H_{1n}^{12}|^2 \; .$$

$\Longrightarrow$ energy correction of first order:

$$E_{n\pm}^{(1)} = \frac{1}{2} \left\{ (H_{1n}^{11} + H_{1n}^{22}) \pm \sqrt{(H_{1n}^{11} - H_{1n}^{22})^2 + 4|H_{1n}^{12}|^2} \right\} \; .$$

If the root is different from zero, then the energy correction of first order leads to a *repulsion* of the originally degenerate levels!

'Correct' states of zeroth order:

$$\left| E_{n\pm}^{(0)} \right\rangle = c_1^{(\pm)} \left| E_{n1}^{(0)} \right\rangle + c_2^{(\pm)} \left| E_{n2}^{(0)} \right\rangle \; .$$

Linear, homogeneous system of equations:

$$\begin{pmatrix} H_{1n}^{11} - E_{n\pm}^{(1)} & H_{1n}^{12} \\ H_{1n}^{21} & H_{1n}^{22} - E_{n\pm}^{(1)} \end{pmatrix} \begin{pmatrix} c_1^{(\pm)} \\ c_2^{(\pm)} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\begin{aligned} \Longrightarrow \quad & \left(H_{1n}^{11} - E_{n\pm}^{(1)} \right) c_1^{(\pm)} + H_{1n}^{12} \, c_2^{(\pm)} = 0 \\ \Longrightarrow \quad & |c_1^{(\pm)}|^2 = \frac{|H_{1n}^{12}|^2}{\left(H_{1n}^{11} - E_{n\pm}^{(1)} \right)^2} \left| c_2^{(\pm)} \right|^2 \; . \end{aligned}$$

Normalization:

$$\begin{aligned} \left| c_2^{(\pm)} \right|^2 &= 1 - \left| c_1^{(\pm)} \right|^2 \\ \Longrightarrow \left| c_1^{(\pm)} \right|^2 &= \frac{\left| H_{1n}^{12} \right|^2}{\left(H_{1n}^{11} - E_{n\pm}^{(1)} \right)^2 + |H_{1n}^{12}|^2} = 1 - \left| c_2^{(\pm)} \right|^2 \; . \end{aligned}$$

Solution 7.2.10

1. Potential energy of the electron in the homogeneous electric field:

$$V(\mathbf{r}) = V(z) = +e\,F\,z,$$

because:

$$-\frac{d}{dz}\,V(z) = -e\,F$$

Hamilton operator:

$$\begin{aligned} H &= H_0 + H_1\ , \\ H_0 &: \textit{unperturbed}\ \text{hydrogen problem, solution known!} \\ H_1 &= e\,F\,z:\ \textit{perturbation}\ . \end{aligned}$$

Because of (5.19):

$$[H_1, L_z]_- = e\,F\,[z, L_z]_- = 0\ .$$

2. We have proven this statement, in another context, already as part 2. of Exercise 6.2.9. Repeat the path of solution!

3. *Unperturbed* hydrogen eigen-states:
(6.60) and (5.108):

$$|100\rangle \mathrel{\widehat{=}} \frac{1}{\sqrt{\pi\,a_{\mathrm{B}}^3}}\,e^{-r/a_{\mathrm{B}}}\ .$$

(6.61) and (5.108):

$$|200\rangle \mathrel{\widehat{=}} \frac{1}{2\sqrt{2\pi\,a_{\mathrm{B}}^3}}\left(1-\frac{r}{2a_{\mathrm{B}}}\right)e^{-r/2a_{\mathrm{B}}}\ .$$

(6.62) and (5.109):

$$|210\rangle \mathrel{\widehat{=}} \frac{1}{4\sqrt{2\pi\,a_{\mathrm{B}}^5}}\,\cos\vartheta\,r\,e^{-r/2a_{\mathrm{B}}}\ .$$

(6.62) and (5.110):

$$|21\pm1\rangle \mathrel{\widehat{=}} \frac{\mp1}{8\sqrt{\pi\,a_{\mathrm{B}}^5}}\,\sin\vartheta\,r\,e^{-r/2a_{\mathrm{B}}}\,e^{\pm i\,\varphi}\ .$$

Unperturbed eigen-energies:

$$E_n^{(0)} = -\frac{E_{\mathrm{R}}}{n^2},$$

without spin n^2-fold degenerate!

a) $n=1 \implies l=0,\, m_l=0$
no degeneracy!

$$E_1^{(1)} = \langle 100|H_1|100\rangle = 0 \quad \text{because of 2. .}$$

b)

$$\begin{aligned} n=2 \implies l=0,\, m_l &= 0\,, \\ l=1, m_l &= \pm 1, 0\,. \end{aligned}$$

Perturbation matrix:

$$\left(H_{12}^{\alpha\beta}\right) \equiv$$

$$\begin{pmatrix} \langle 200|H_1|200\rangle & \langle 200|H_1|210\rangle & \langle 200|H_1|211\rangle & \langle 200|H_1|21\,-1\rangle \\ \langle 210|H_1|200\rangle & \langle 210|H_1|210\rangle & \langle 210|H_1|211\rangle & \langle 210|H_1|21\,-1\rangle \\ \langle 211|H_1|200\rangle & \langle 211|H_1|210\rangle & \langle 211|H_1|211\rangle & \langle 211|H_1|21\,-1\rangle \\ \langle 21\,-1|H_1|200\rangle & \langle 21\,-1|H_1|210\rangle & \langle 21\,-1|H_1|211\rangle & \langle 21\,-1|H_1|21\,-1\rangle \end{pmatrix}$$

decomposes into blocks because of 1.:

$$\left(H_{12}^{\alpha\beta}\right) = \begin{pmatrix} 0 & \langle 200|H_1|210\rangle & 0 & 0 \\ \langle 210|H_1|200\rangle & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}.$$

Matrix element:

$$\begin{aligned} &\langle 200|H_1|210\rangle \\ =&\frac{e\,F\,2\pi}{16\,\pi\,a_{\mathrm{B}}^4} \int\limits_0^\infty r^2\,dr \int\limits_{-1}^{+1} d\cos\vartheta \left(1-\frac{r}{2a_{\mathrm{B}}}\right) e^{-r/2a_{\mathrm{B}}}\, r\cos\vartheta\cos\vartheta\, r\, e^{-r/2a_{\mathrm{B}}} \\ =&\frac{e\,F}{8a_{\mathrm{B}}^4}\,\frac{2}{3} \int\limits_0^\infty dr\, \left(r^4 - \frac{r^5}{2a_{\mathrm{B}}}\right) e^{-r/a_{\mathrm{B}}} \\ =&\frac{e\,F}{12\,a_{\mathrm{B}}^4}\,a_{\mathrm{B}} \int\limits_0^\infty dx\, \left(a_{\mathrm{B}}^4\,x^4 - \frac{1}{2}\,a_{\mathrm{B}}^4\,x^5\right) e^{-x} \\ =&\frac{1}{12}\,e\,F\,a_{\mathrm{B}}\,\left(\Gamma(5) - \frac{1}{2}\,\Gamma(6)\right) \\ =&\frac{1}{12}\,e\,F\,a_{\mathrm{B}}\,(24-60) = -3e\,a_{\mathrm{B}}\,F\,. \end{aligned}$$

Secular determinant:

$$0 \stackrel{!}{=} \begin{vmatrix} -E_2^{(1)} & -3e\,a_{\mathrm{B}}\,F & 0 & 0 \\ -3e\,a_{\mathrm{B}}\,F & -E_2^{(1)} & 0 & 0 \\ 0 & 0 & -E_2^{(1)} & 0 \\ 0 & 0 & 0 & -E_2^{(1)} \end{vmatrix}$$

Figure A.5:

The first two rows belong to $m_l = 0$, the third belongs to $m_l = 1$, and the fourth to $m_l = -1$.
The states $|21 \pm 1\rangle$ are in first order not disturbed:

$$E^{(1)}_{21\pm1} = 0 \, .$$

Energy correction for $m_l = 0$:

$$\begin{aligned} 0 \stackrel{!}{=} \begin{vmatrix} -E^{(1)}_2 & -3e\, a_\mathrm{B}\, F \\ -3e\, a_\mathrm{B}\, F & -E^{(1)}_2 \end{vmatrix} &= \left(E^{(1)}_2\right)^2 - (3e\, a_\mathrm{B}\, F)^2 \\ \Longrightarrow \; E^{(1)}_{2l\, m_l=0} &= \pm 3e\, a_\mathrm{B}\, F \, . \end{aligned}$$

The degeneracy of the energy level $E^{(0)}_2$ is partly lifted by the electric field (Fig. A.5). The levels split linearly with the field. One speaks of the *linear Stark effect*.

4. The degeneracy is completely removed in the $m_l = 0$-subspace. We can thus determine the *'correct'* states of zeroth order:

$$|2\, m_l = 0\rangle^{(\pm)} = c^{(\pm)}_0 |200\rangle + c^{(\pm)}_1 |210\rangle \, .$$

$E^{(1)}_{2l\, m_l=0} = +3a_\mathrm{B}\, e\, F$:

$$\begin{pmatrix} -3a_\mathrm{B}\, e\, F & -3a_\mathrm{B}\, e\, F \\ -3a_\mathrm{B}\, e\, F & -3a_\mathrm{B}\, e\, F \end{pmatrix} \begin{pmatrix} c^{(+)}_0 \\ c^{(+)}_1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\Longrightarrow \; c^{(+)}_0 = -c^{(+)}_1 = \frac{1}{\sqrt{2}} \quad \text{(with normalization)} \, .$$

$E^{(1)}_{2l\, m_l=0} = -3a_\mathrm{B}\, e\, F$:

$$\begin{pmatrix} 3a_\mathrm{B}\, e\, F & -3a_\mathrm{B}\, e\, F \\ -3a_\mathrm{B}\, e\, F & 3a_\mathrm{B}\, e\, F \end{pmatrix} \begin{pmatrix} c^{(-)}_0 \\ c^{(-)}_1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\Longrightarrow \; c^{(-)}_0 = c^{(-)}_1 = \frac{1}{\sqrt{2}} \quad \text{(with normalization)}$$

$$\Longrightarrow \; |2m_l = 0\rangle^{(\pm)} = \frac{1}{\sqrt{2}} \left(|200\rangle \mp |210\rangle\right) \, .$$

Solution 7.2.11

1. Nuclear charge Z:

$$H(Z) = \frac{\mathbf{p}^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 \cdot r} = T + V(Z)$$

Nuclear charge $Z + \alpha$:

$$\begin{aligned} H(Z+\alpha) &= \frac{\mathbf{p}^2}{2m} - \frac{(Z+\alpha)\,e^2}{4\pi\varepsilon_0 \cdot r} \\ \curvearrowright \quad H(Z+\alpha) &= H(Z) + H_1 \;\; ; \;\; H_1 = -\alpha \frac{e^2}{4\pi\varepsilon_0 \cdot r} \; . \end{aligned}$$

Energy correction of first order:

$$E^{(1)} = {}_Z\langle nlm_l|H_1|nlm_l\rangle_Z = -\frac{\alpha e^2}{4\pi\varepsilon_0}\, {}_Z\langle nlm_l|\frac{1}{r}|nlm_l\rangle_Z \; .$$

Comparison with $V(Z)$:

$$E^{(1)} = \frac{\alpha}{Z}\, {}_Z\langle nlm_l|V(Z)|nlm_l\rangle_Z \; .$$

We now exploit the virial theorem from Exercise 7.1.7. Since $|nlm_l\rangle_Z$ is eigen-state of $H(Z)$, it must follow:

$$2\, {}_Z\langle nlm_l|T|nlm_l\rangle_Z = n'\, {}_Z\langle nlm_l|V(Z)|nlm_l\rangle_Z = -\, {}_Z\langle nlm_l|V(Z)|nlm_l\rangle_Z \; .$$

Here it is used that for the Coulomb potential: $V \propto \frac{1}{r} \curvearrowright n' = -1$. It thus remains:

$${}_Z\langle nlm_l|H(Z)|nlm_l\rangle_Z = \left(-\frac{1}{2} + 1\right) {}_Z\langle nlm_l|V(Z)|nlm_l\rangle_Z \; .$$

Hydrogen problem:

$$\begin{aligned} {}_Z\langle nlm_l|H(Z)|nlm_l\rangle_Z &= -\frac{Z^2 E_\mathrm{R}}{n^2} \\ \curvearrowright \quad {}_Z\langle nlm_l|V(Z)|nlm_l\rangle_Z &= -2\frac{Z^2 E_\mathrm{R}}{n^2} \end{aligned}$$

Energy correction of first order:

$$E^{(1)} = -2\alpha \frac{Z E_\mathrm{R}}{n^2} \; .$$

or

$$E(Z+\alpha) \approx -\frac{E_\mathrm{R}}{n^2}\left(Z^2 + 2Z\alpha\right) \; .$$

2. Exact result:

$$E(Z+\alpha) = -\frac{E_\mathrm{R}}{n^2}(Z+\alpha)^2 = -\frac{E_\mathrm{R}}{n^2}\left(Z^2 + 2Z\alpha + \alpha^2\right) .$$

Perturbation theory is therefore reasonable if

$$\alpha^2 \ll 2Z\alpha \iff \alpha \ll 2Z .$$

Solution 7.2.12

1.

$$\begin{aligned} H_0 &= \frac{p^2}{2m} = -\frac{\hbar^2}{2m}\frac{d^2}{dz^2} , \\ H_0\varphi(z) &= E\,\varphi(z) \implies \varphi(z) \sim e^{ikz} . \end{aligned}$$

Normalization on $L = N\,a$: $1 = \int_0^L dz|\varphi(z)|^2$

$$\implies \varphi(z) = \frac{1}{\sqrt{L}}\,e^{ikz} ; \quad E_0(k) = \frac{\hbar^2 k^2}{2m}$$

Periodic boundary conditions:

$$\begin{aligned} \varphi(z + N\,a) \stackrel{!}{=} \varphi(z) \quad &\implies \quad k = \frac{2\pi}{N\,a}\,m ; \quad m \in \mathbb{Z} , \\ \varphi(z) \quad &\longrightarrow \quad \varphi_k(z) . \end{aligned}$$

2. $E_0(k) = E_0(-k) \implies$ each energy level is twofold degenerate!

$$\begin{aligned} V(z) &= \sum_K V_K\, e^{iKz} , \\ V(z): \ \text{real} \curvearrowright V_K &= V_{-K} \\ V(z+a) &= V(z) \implies K = \frac{2\pi}{a}\,n ; \quad n \in \mathbb{Z} , \\ K &: \quad \text{reciprocal lattice vector} . \end{aligned}$$

3.

$$\begin{aligned} \langle\varphi_k|V|\varphi_{k'}\rangle &= \frac{1}{L}\int_0^L dz\, e^{i(k'-k)z}\, V(z) \\ &= \sum_K V_K\,\frac{1}{L}\int_0^L dz\, e^{i(k'-k+K)z} = \sum_K V_K\,\delta_{k',\,k-K} . \end{aligned}$$

Necessary condition:

$$k - k' = K = \frac{2\pi}{a}\,n ; \quad n \in \mathbb{Z} .$$

Otherwise, it must also hold:

$$k - k' = \frac{2\pi}{N\,a}\,(m - m') \implies \frac{m - m'}{N} = n \in \mathbb{Z}\ .$$

The states of equal energy are of special interest:

$$k' = -k \iff m' = -m \implies \frac{2m}{N} = n \implies m = \frac{N}{2}\,n$$
$$\implies \text{condition for degeneracy: } k = \frac{\pi}{a}\,n = \frac{K}{2}\ .$$

4. Perturbation theory for twofold degenerate levels: Perturbation matrix:

$$V \equiv \begin{pmatrix} \langle\varphi_k|V|\varphi_k\rangle & \langle\varphi_k|V|\varphi_{-k}\rangle \\ \langle\varphi_{-k}|V|\varphi_k\rangle & \langle\varphi_{-k}|V|\varphi_{-k}\rangle \end{pmatrix}\ .$$

From part 3.:

$$\begin{aligned} \langle\varphi_k|V|\varphi_k\rangle &= \langle\varphi_{-k}|V|\varphi_{-k}\rangle = V_0\ , \\ \langle\varphi_{-k}|V|\varphi_k\rangle &= \sum_K V_K\,\delta_{k,\frac{1}{2}K} = \langle\varphi_k|V|\varphi_{-k}\rangle\ . \end{aligned}$$

Case-by case analysis:

a) $k \neq K/2$:

$$V \equiv \begin{pmatrix} V_0 & 0 \\ 0 & V_0 \end{pmatrix} \implies E^{(1)}(k) \equiv V_0\ .$$

Degeneracy is not removed. For such k-values even non-degenerate perturbation theory is applicable, because for $k' = -k$ the corresponding matrix elements vanish. With

$$\begin{aligned} |\langle\varphi_k|V|\varphi_{k'}\rangle|^2 &= \sum_{K,K'} V_K V_{K'}\,\delta_{k',k-K}\delta_{k,k'-K'} \\ &= \sum_K V_K V_{k'-k}\,\delta_{k',k-K} \\ &= \sum_K V_K V_{-K}\,\delta_{k',k-K} \\ &\overset{V_K = V_{-K}}{=} \sum_K V_K^2\,\delta_{k',k-K} \end{aligned}$$

it follows:

$$\begin{aligned} E(k) &\approx E_0(k) + V_0 + \sum_{k'}^{\neq k,\,-k} \frac{|\langle\varphi_{k'}|V|\varphi_k\rangle|^2}{E_0(k) - E_0(k')} \\ &= E_0(k) + V_0 + \sum_K^{\neq 0,2k} \frac{V_K^2}{E_0(k) - E_0(k-K)} \\ &= E_0(k) + V_0 + \frac{m}{\hbar^2} \sum_K^{\neq 0,2k} \frac{V_K^2}{K\left(k - \frac{K}{2}\right)}\ . \end{aligned}$$

b) $k = K/2$:

$$V \equiv \begin{pmatrix} V_0 & V_K \\ V_K & V_0 \end{pmatrix} \quad \Longrightarrow \quad \text{secular determinant:}$$

$$\begin{vmatrix} V_0 - E^{(1)} & V_K \\ V_K & V_0 - E^{(1)} \end{vmatrix} \stackrel{!}{=} 0 \quad \Longleftrightarrow \quad E_{\pm}^{(1)} = \pm V_K + V_0 \; .$$

Degeneracy is removed $\Longrightarrow$ *energy gap.*

'Correct' states of zeroth order:

a) $k \neq (1/2)\, K$:

$$|E_0(k)\rangle \;\longleftrightarrow\; \varphi_k(z) : \text{ propagating plane wave.}$$

b) $k = (1/2)\, K$:

$$|E_{\pm}(k)\rangle \;\longleftrightarrow\; c_1^{(\pm)}\, \varphi_k(z) + c_2^{(\pm)}\, \varphi_{-k}(z) \; ,$$

$$\begin{pmatrix} \mp V_K & V_K \\ V_K & \mp V_K \end{pmatrix} \begin{pmatrix} c_1^{(\pm)} \\ c_2^{(\pm)} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\Longrightarrow \; c_1^{(+)} = c_2^{(+)} \; ; \quad c_1^{(-)} = -c_2^{(-)} \; .$$

Normalization:

$$c_1^{(+)} = c_2^{(+)} = \frac{1}{\sqrt{2}} \; ; \quad c_1^{(-)} = -c_2^{(-)} = \frac{1}{\sqrt{2}}$$

$$\Longrightarrow \; |E_{\pm}(k)\rangle \;\longleftrightarrow\; \frac{1}{\sqrt{2L}} \left(e^{ikz} \pm e^{-ikz} \right) \; .$$

Standing waves:

$$|E_{+}(k)\rangle \;\longleftrightarrow\; \sqrt{\frac{2}{L}}\, cos \left(\frac{1}{2}\, K\, z \right) \; ,$$

$$|E_{-}(k)\rangle \;\longleftrightarrow\; i \sqrt{\frac{2}{L}}\, \sin \left(\frac{1}{2}\, K\, z \right) \; .$$

5. Band structure model (Fig. A.6): Condition of degeneracy in three dimensions:

$$\mathbf{k}^2 = (\mathbf{k} - \mathbf{K})^2 \;\Longleftrightarrow\; \mathbf{k} \cdot \mathbf{e}_K = \frac{1}{2}\, K \; ;$$

Bragg planes (Sect. 1.4.3, Vol. 6).

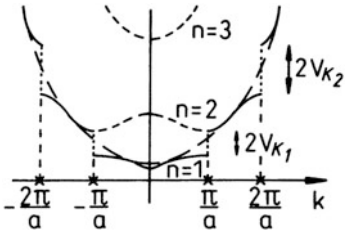


Figure A.6:

Solution 7.2.13

1. H_0 can be separated with respect to wave number and spin projection:

$$H_0 = \sum_{\substack{\mathbf{k},\sigma \\ \alpha,\beta}} \varepsilon_{\alpha\beta}(\mathbf{k})\,|\mathbf{k}\sigma\alpha\rangle\langle\mathbf{k}\sigma\beta| = \sum_{\mathbf{k}\sigma} \left(H_{\mathbf{k}\sigma}\right)^{(0)} .$$

In the basis of the $|\mathbf{k}\sigma\alpha\rangle$ for fixed $\mathbf{k},\sigma$ one has:

$$\left(H_{\mathbf{k}\sigma}\right)^{(0)} = \begin{pmatrix} \varepsilon(\mathbf{k}) & t(\mathbf{k}) \\ t^*(\mathbf{k}) & \varepsilon(\mathbf{k}) \end{pmatrix} .$$

Eigen-values:

$$\det \begin{pmatrix} \varepsilon(\mathbf{k}) - E & t(\mathbf{k}) \\ t^*(\mathbf{k}) & \varepsilon(\mathbf{k}) - E \end{pmatrix} \stackrel{!}{=} 0$$

$$\curvearrowright \quad E_{\pm}^{(0)}(\mathbf{k}\sigma) = \varepsilon(\mathbf{k}) \pm |t(\mathbf{k})| \equiv E_{\pm}^{(0)}(\mathbf{k}) .$$

No real spin-dependence!
Eigen-states:

$$|E_{\pm}^{(0)}(\mathbf{k}\sigma)\rangle = c_A^{\pm}|\mathbf{k}\sigma A\rangle + c_B^{\pm}|\mathbf{k}\sigma B\rangle$$

$$\curvearrowright \quad \begin{pmatrix} \varepsilon(\mathbf{k}) - E_{\pm}^{(0)} & t(\mathbf{k}) \\ t^*(\mathbf{k}) & \varepsilon(\mathbf{k}) - E_{\pm}^{(0)} \end{pmatrix} \begin{pmatrix} c_A^{\pm} \\ c_B^{\pm} \end{pmatrix} = 0 .$$

From this it follows

$$\mp|t(\mathbf{k})|\, c_A^{\pm} + t(\mathbf{k})\, c_B^{\pm} = 0$$

which, together with the normalization, leads to

$$c_A^{\pm} = \frac{\gamma}{\sqrt{2}} \;;\; c_B^{\pm} = \pm\frac{1}{\sqrt{2}} \;;\; \gamma = \frac{t(\mathbf{k})}{|t(\mathbf{k})|} .$$

The eigen-states in zeroth order therewith read:

$$\left|E_{\pm}^{(0)}(\mathbf{k})\right\rangle = \frac{1}{\sqrt{2}}\left(\gamma|\mathbf{k}\sigma A\rangle \pm |\mathbf{k}\sigma B\rangle\right) .$$

Note that, because of the symmetry $(\sigma, A) \leftrightarrow (-\sigma, B)$ of the antiferromagnet, the eigen-states do not exhibit a real spin-dependence.

2. Perturbation:

$$\begin{aligned} H_1 &= -\frac{1}{2}J\sum_{\mathbf{k}\sigma\alpha\beta} z_\sigma m_\alpha |\mathbf{k}\sigma\alpha\rangle\langle\mathbf{k}\sigma\beta|\delta_{\alpha\beta} = \sum_{\mathbf{k}\sigma} \left(H_{\mathbf{k}\sigma}\right)^{(1)} \\ m_A &= -m_B = m \qquad \left(z_\sigma = \delta_{\sigma\uparrow} - \delta_{\sigma\downarrow}\right). \end{aligned}$$

It holds in the basis of the initial states $|\mathbf{k}\sigma\alpha\rangle$:

$$\left(H_{\mathbf{k}\sigma}\right)^{(1)} = \begin{pmatrix} -\frac{1}{2}Jz_\sigma m & 0 \\ 0 & +\frac{1}{2}Jz_\sigma m \end{pmatrix}.$$

Perturbation matrix in the basis of the eigen-states of the *'unperturbed'* Hamilton operator:

$$\begin{aligned} \langle E_\pm^{(0)}| \left(H_{\mathbf{k}\sigma}\right)^{(1)} |E_\pm^{(0)}\rangle &= \frac{1}{2}\begin{pmatrix} \gamma^* & \pm 1 \end{pmatrix}\begin{pmatrix} -\frac{1}{2}Jz_\sigma m & 0 \\ 0 & +\frac{1}{2}Jz_\sigma m \end{pmatrix}\begin{pmatrix} \gamma \\ \pm 1 \end{pmatrix} \\ &= \frac{1}{2}\left(-\frac{1}{2}Jz_\sigma m|\gamma|^2 + \frac{1}{2}Jz_\sigma m\right) = 0 \\ \langle E_+^{(0)}| \left(H_{\mathbf{k}\sigma}\right)^{(1)} |E_-^{(0)}\rangle &= \frac{1}{2}\begin{pmatrix} \gamma^* & +1 \end{pmatrix}\begin{pmatrix} -\frac{1}{2}Jz_\sigma m & 0 \\ 0 & +\frac{1}{2}Jz_\sigma m \end{pmatrix}\begin{pmatrix} \gamma \\ -1 \end{pmatrix} \\ &= -\frac{1}{4}Jz_\sigma m(|\gamma|^2 + 1) = -\frac{1}{2}Jz_\sigma m \\ &= \langle E_-^{(0)}| \left(H_{\mathbf{k}\sigma}\right)^{(1)} |E_+^{(0)}\rangle. \end{aligned}$$

The perturbation operator in the basis of the H_0-eigen states therewith takes the following simple form:

$$\left(H_{\mathbf{k}\sigma}\right)^{(1)} = \begin{pmatrix} 0 & -\frac{1}{2}Jz_\sigma m \\ -\frac{1}{2}Jz_\sigma m & 0 \end{pmatrix}$$

3. Exact solution:
Total Hamilton operator in the H_0-basis:

$$\left(H_{\mathbf{k}\sigma}\right) = \begin{pmatrix} \varepsilon(\mathbf{k}) + |t(\mathbf{k})| & -\frac{1}{2}Jz_\sigma m \\ -\frac{1}{2}Jz_\sigma m & \varepsilon(\mathbf{k}) - |t(\mathbf{k})| \end{pmatrix}.$$

Eigen-values:

$$\det\begin{pmatrix} \varepsilon(\mathbf{k}) + |t(\mathbf{k})| - E & -\frac{1}{2}Jz_\sigma m \\ -\frac{1}{2}Jz_\sigma m & \varepsilon(\mathbf{k}) - |t(\mathbf{k})| - E \end{pmatrix} \stackrel{!}{=} 0.$$

It remains to be solved:

$$\left(\varepsilon(\mathbf{k}) - E\right)^2 - |t(\mathbf{k})|^2 = \frac{1}{4}J^2m^2.$$

That yields:

$$E_\pm(\mathbf{k}) = \varepsilon(\mathbf{k}) \pm \sqrt{\frac{1}{4}J^2m^2 + |t(\mathbf{k})|^2}$$

4. Schrödinger perturbation theory:
   Energy correction of first order:

$$\left\langle E_{\pm}^{(0)}(\mathbf{k}\sigma)\right| \left(H_{\mathbf{k}\sigma}\right)^{(1)} \left|E_{\pm}^{(0)}(\mathbf{k}\sigma)\right\rangle = 0 \;\curvearrowright\; E_{\pm}^{(1)}(\mathbf{k}\sigma) = 0 \,.$$

   Energy correction of second order:

$$E_{\pm}^{(2)}(\mathbf{k}\sigma) = \frac{\left|\left\langle E_{\mp}^{(0)}(\mathbf{k}\sigma)\right| \left(H_{\mathbf{k}\sigma}\right)^{(1)} \left|E_{\pm}^{(0)}(\mathbf{k}\sigma)\right\rangle\right|^2}{E_{\pm}^{(0)}(\mathbf{k}\sigma) - E_{\mp}^{(0)}(\mathbf{k}\sigma)} = \frac{\frac{1}{4}J^2m^2}{\pm 2|t(\mathbf{k})|} \equiv E_{\pm}^{(2)}(\mathbf{k}) \,.$$

   The perturbation theory thus yields:

$$E_{\pm}(\mathbf{k}) \approx \varepsilon(\mathbf{k}) \pm |t(\mathbf{k})| \pm \frac{J^2m^2}{8|t(\mathbf{k})|} \,.$$

   That corresponds to the first term of an expansion of the exact eigen-energies for $\frac{1}{2}Jm \ll |t(\mathbf{k}|$. Now there are, though, $\mathbf{k}$-vectors, for which the $|t(\mathbf{k})|$ can become very small or even zero (edge of the Brillouin zone!). In such cases the Schrödinger perturbation theory obviously becomes unusable.

5. Brillouin-Wigner perturbation theory:
   The energy correction of first order is the same as that given by the Schrödinger version, i.e., it vanishes.

   Energy correction of second order:

$$\begin{aligned} E_{\pm}(\mathbf{k}\sigma) &= E_{\pm}^{(0)}(\mathbf{k}) + E_{\pm}^{(1)}(\mathbf{k}) + \frac{\left|\left\langle E_{\mp}^{(0)}(\mathbf{k})\right| \left(H_{\mathbf{k}\sigma}\right)^{(1)} \left|E_{\pm}^{(0)}(\mathbf{k})\right\rangle\right|^2}{E_{\pm}(\mathbf{k}\sigma) - E_{\mp}^{(0)}(\mathbf{k})} \\ &= \varepsilon(\mathbf{k}) \pm |t(\mathbf{k})| + \frac{\frac{1}{4}J^2m^2}{E_{\pm}(\mathbf{k}\sigma) - \varepsilon(\mathbf{k}) \pm |t(\mathbf{k})|} \,. \end{aligned}$$

   This is a quadratic equation for the sought eigen-energies $E_{\pm}(\mathbf{k}\sigma)$ with the obvious spin-independent solution:

$$E_{\pm}(\mathbf{k}) = \varepsilon(\mathbf{k}) \pm \sqrt{\frac{1}{4}J^2m^2 + |t(\mathbf{k})|^2} \,.$$

   The Brillouin-Wigner perturbation theory thus already in second order yields the exact result!

Section 7.3.5

Solution 7.3.1

According to (7.104):

$$\begin{aligned} |\psi(t)\rangle = U(t,0)\left|E_i^{(0)}\right\rangle &= e^{-(i/\hbar)H_0 t}\, U_{\mathrm{D}}(t,0)\left|E_i^{(0)}\right\rangle \\ (t_i = t_0 &= 0) \,. \end{aligned}$$

Ansatz as in (7.90):

$$|\psi(t)\rangle = \sum\!\!\!\!\!\!\int_m a_m(t) \left|E_m^{(0)}\right\rangle \ .$$

Scalar multiplication by $\left\langle E_n^{(0)}\right|$ yields:

$$a_n(t) = e^{-(i/\hbar)E_n^{(0)}t} \left\langle E_n^{(0)}\right| U_{\rm D}(t,0) \left|E_i^{(0)}\right\rangle \ .$$

This is still exact and is in first order perturbation theory, according to (7.101), approximated by:

$$\begin{aligned} a_n^{(1)}(t) &= e^{-(i/\hbar)E_n^{(0)}t} \left\{ \delta_{ni} - \frac{i}{\hbar} \int_0^t dt_1 \, H_{ni}(t_1) \, e^{(i/\hbar)E_{ni}^{(0)}\, t_1} \right\} \ , \\ H_{ni}(t_1) &= \left\langle E_n^{(0)}\right| H_{1t_1} \left|E_i^{(0)}\right\rangle \ , \\ E_{ni}^{(0)} &= E_n^{(0)} - E_i^{(0)} \ . \end{aligned}$$

Solution 7.3.2
Unperturbed oscillator:

$$\begin{aligned} H_0 &= \frac{p^2}{2m} + \frac{1}{2}\, m\, \omega^2 z^2 \ , \\ H_0|m\rangle &= \hbar\, \omega_0 \left(m + \frac{1}{2}\right) |m\rangle \ , \end{aligned}$$

Perturbation:

$$H_{1t} = -q\, z\, F\, \cos\omega t \ .$$

Ansatz:

$$\begin{aligned} |\psi(t)\rangle &= \sum_m a_m(t) |m\rangle \ , \\ |\psi(t=0)\rangle &= |n\rangle \ . \end{aligned}$$

Dipole moment:

$$\langle \hat{p} \rangle = q \sum_{m,r} a_m^*(t)\, a_{\rm r}(t) \langle m|z|r\rangle \ .$$

According to ((4.127), Vol. 6) it holds:

$$\begin{aligned} \langle m|z|r\rangle &= \sqrt{\frac{\hbar}{2m\,\omega_0}} \, \langle m|(a + a^+)|r\rangle \\ &= \sqrt{\frac{\hbar}{2m\,\omega_0}} \, \left(\delta_{m\,r-1}\, \sqrt{r} + \delta_{m\,r+1}\, \sqrt{r+1}\right) \ . \end{aligned}$$

Intermediate result:

$$\langle \hat{p} \rangle = q\sqrt{\frac{\hbar}{2m\,\omega_0}} \sum_r a_{\rm r}(t) \left(\sqrt{r}\, a^*_{r-1}(t) + \sqrt{r+1}\, a^*_{r+1}(t) \right) \ .$$

Expansion coefficients in first order perturbation theory (see solution 7.3.1):

$$\begin{aligned} a^{(1)}_{\rm r}(t) &= e^{-(i/\hbar)E^{(0)}_{\rm r} t} \left\{ \delta_{rn} - \frac{i}{\hbar} \int_0^t dt_1\, H_{rn}(t_1)\, e^{(i/\hbar)\, E^{(0)}_{rn}\, t_1} \right\} \ , \\ H_{rn}(t_1) &= -q\, F \cos\omega\, t_1 \sqrt{\frac{\hbar}{2m\,\omega_0}} \left(\delta_{r\,n-1} \sqrt{n} + \delta_{r\,n+1} \sqrt{n+1} \right) \ . \end{aligned}$$

Up to the first order:

$$\begin{aligned} a_{\rm r}(t)\, a^*_{r-1}(t) &\approx e^{-(i/\hbar)E^{(0)}_{\rm r} t}\, \delta_{rn}\, a^{(1)*}_{r-1}(t) \\ &\quad + e^{(i/\hbar)\, E^{(0)}_{r-1} t}\, \delta_{r-1\,n}\, a^{(1)}_{\rm r}(t) \ , \\ a_{\rm r}(t)\, a^*_{r+1}(t) &\approx e^{-(i/\hbar)\, E^{(0)}_{\rm r} t}\, \delta_{rn}\, a^{(1)*}_{r+1}(t) \\ &\quad + e^{(i/\hbar)\, E^{(0)}_{r+1} t}\, \delta_{r+1\,n}\, a^{(1)}_{\rm r}(t) \ , \\ \delta_{r-1\,n}\, a^{(1)}_{\rm r}(t) &= +i\, \frac{q}{\hbar}\, F \sqrt{\frac{\hbar}{2m\,\omega_0}}\, \sqrt{n+1}\, e^{-(i/\hbar)E^{(0)}_{n+1} t} \\ &\quad \cdot \int_0^t dt_1 \cos\omega\, t_1\, e^{i\omega_0 t_1}\, \delta_{r\,n+1} \ , \\ \delta_{r+1\,n}\, a^{(1)}_{\rm r}(t) &= +i\, \frac{q}{\hbar}\, F \sqrt{\frac{\hbar}{2m\,\omega_0}}\, \sqrt{n}\, e^{-(i/\hbar)\, E^{(0)}_{n-1} t} \\ &\quad \cdot \int_0^t dt_1 \cos\omega\, t_1\, e^{-i\,\omega_0 t_1}\, \delta_{r\,n-1} \ , \\ \delta_{rn}\, a^{(1)*}_{r-1}(t) &= -i\, \frac{q}{\hbar}\, F \sqrt{\frac{\hbar}{2m\,\omega_0}}\, \sqrt{n}\, e^{+(i/\hbar)E^{(0)}_{n-1} t} \\ &\quad \cdot \int_0^t dt_1\ \cos\omega\, t_1\, e^{+i\omega_0 t_1}\, \delta_{rn} \ , \\ \delta_{rn}\, a^{(1)*}_{r+1}(t) &= -i\, \frac{q}{\hbar}\, F \sqrt{\frac{\hbar}{2m\,\omega_0}}\, \sqrt{n+1}\, e^{(i/\hbar)E^{(0)}_{n+1} t} \\ &\quad \cdot \int_0^t dt_1\ \cos\omega\, t_1\, e^{-i\omega_0 t_1} \delta_{rn} \ . \end{aligned}$$

By insertion we find a further intermediate result:

$$\begin{aligned}
\langle\hat{p}\rangle &= i\,\frac{q^2F}{2m\,\omega_0}\int\limits_0^t dt_1\cos\omega\,t_1\,\left(e^{i\omega_0(t_1-t)}-e^{i\omega_0(t-t_1)}\right)\\
&= \frac{q^2F}{m\,\omega_0}\int\limits_0^t dt_1\,\cos\omega\,t_1\sin\omega_0(t-t_1)\\
&= \frac{q^2F}{2m\,\omega_0}\left[\int\limits_0^t dt_1\sin[(\omega-\omega_0)t_1+\omega_0 t]+\int\limits_0^t dt_1\sin[-(\omega_0+\omega)\,t_1+\omega_0 t]\right]\\
&= \frac{q^2F}{2m\,\omega_0}\,(\cos\omega\,t-\cos\omega_0 t)\,\left(-\frac{1}{\omega-\omega_0}+\frac{1}{\omega_0+\omega}\right)\,.
\end{aligned}$$

Thereby we have utilized the addition theorem

$$2\sin x\cos y=\sin(x+y)+\sin(x-y)\,.$$

Finally we get:

$$\langle\hat{p}\rangle=\frac{q^2F}{m(\omega_0^2-\omega^2)}\,(\cos\omega t-\cos\omega_0 t)\,.$$

Solution 7.3.3

- $t<0$:
  Oscillator in the ground state:

  $$\varphi(q,t)=e^{-(i/\hbar)Ht}\,\varphi_0(q)=e^{-(i/2)\omega t}\,\varphi_0(q)\,.$$

  ((4.158), Vol. 6):

  $$\varphi_0(q)=\left(\frac{m\,\omega}{\hbar\,\pi}\right)^{1/4}\,e^{-(m\,\omega/2\hbar)\,q^2}\,.$$

- $t=0^-$:
  $\varphi(q,0^-)\equiv\varphi_0(q)$.

- $t=0$:
  Abrupt change of the force constant:

  $$k\;\longrightarrow\;k'\;\Longleftrightarrow\;\omega=\sqrt{\frac{k}{m}}\;\longrightarrow\;\omega'=\sqrt{\frac{k'}{m}}\,.$$

- $t=0^+$:
  The wave function can not have changed yet:

  $$\varphi(q,0^+)\equiv\varphi_0(q)\,.$$

But $\varphi_0(q)$ is not an eigen-state of the *new* Hamilton operator H':

$$\begin{aligned} H' &= \frac{p^2}{2m} + \frac{1}{2}\, m\omega'^2 q^2 \ , \\ H'\varphi'_n(q) &= E'_n\, \varphi'_n(q) \ . \end{aligned}$$

The *new* eigen-functions build a complete system:

$$\varphi_0(q) = \sum_n \alpha_n \varphi'_n(q) \ .$$

- $t > 0$:
  H' is time-independent for $t > 0$:

$$\varphi(q,t) = e^{-(i/\hbar)H't}\, \varphi(q,0^+) = \sum_n \alpha_n\, \varphi'_n(q)\, e^{-i\omega'(n+1/2)\,t} \ .$$

Therewith it results as probability to find the oscillator at the time $t > 0$ in the *new* eigen-state φ'_n:

$$w_n = \left| \int\limits_{-\infty}^{+\infty} dq\, \varphi(q,t)\, \varphi'^*_n(q,t) \right|^2 = |\alpha_n|^2 \ .$$

Especially for the ground state:

$$\begin{aligned} w_0 &= \left| \int\limits_{-\infty}^{+\infty} dq\, \varphi(q,t)\, \varphi'^*_0(q,t) \right|^2 = \left| \int\limits_{-\infty}^{+\infty} dq \varphi_0(q)\, \varphi'^*_0(q) \right|^2 \\ &= \frac{m}{\hbar\,\pi}\, \sqrt{\omega\,\omega'} \left| \int\limits_{-\infty}^{+\infty} dq \exp\left(-\frac{m}{2\hbar}\, (\omega + \omega')\, q^2 \right) \right|^2 \\ &= \frac{m}{\hbar\,\pi}\, \sqrt{\omega\,\omega'}\, \frac{1}{(m/2\hbar)(\omega+\omega')} \left| \int\limits_{-\infty}^{+\infty} dy\, e^{-y^2} \right|^2 \ . \end{aligned}$$

We have calculated the integral in the solution 2.2.1 (Vol. 6). It has the value $\sqrt{\pi}$:

$$w_0 = \frac{2}{\omega + \omega'}\, \sqrt{\omega\,\omega'} \quad (w_0 = 1 \text{ for } \omega = \omega'!) \ .$$

Solution 7.3.4

The same considerations about the transition probability as in the preceding exercise are valid here also:

$$\begin{aligned} w_n &= \left| \int_{-\infty}^{+\infty} dq\, \varphi_0(q)\, \varphi_n'^*(q) \right|^2 , \\ H' &= H - F\, q\, , \\ H &= \frac{p^2}{2m} + \frac{1}{2}\, m\, \omega^2 q^2\, . \end{aligned}$$

We have calculated $\varphi_n'(q)$ in Exercise 4.4.14 (Vol. 6):

$$\begin{aligned} \varphi_n'(q) &= \left(2^n\, n!\, q_0 \sqrt{\pi}\right)^{-1/2} \exp\left[-\frac{1}{2} \left(\frac{q-a}{q_0} \right)^2 \right] H_n\left(\frac{q-a}{q_0} \right) , \\ a &= \frac{F}{m\,\omega^2}\, ; \quad q_0 = \sqrt{\frac{\hbar}{m\,\omega}}\, . \end{aligned}$$

For the ground-state of H we have already used in the preceding exercise:

$$\varphi_0(q) = \left(q_0\, \sqrt{\pi}\right)^{-1/2} \exp\left[-\frac{1}{2} \left(\frac{q}{q_0} \right)^2 \right] .$$

We write for abbreviation:

$$y = \frac{q-a}{q_0}\, ; \quad y_0 = \frac{a}{q_0}\, .$$

It then follows with (4.163, Vol. 6),

$$H_n(y) = (-1)^n\, e^{y^2}\, \frac{d^n}{dy^n}\, e^{-y^2},$$

the following expression for w_n:

$$w_n = \left(2^n\, n!\, \pi\, q_0^2\right)^{-1} \left| q_0 \int_{-\infty}^{+\infty} dy\, e^{-(1/2)\left(y^2 + 2y\, y_0 + y_0^2 - y^2\right)}\, \frac{d^n}{dy^n}\, e^{-y^2} \right|^2 = \frac{e^{-y_0^2}}{2^n\, n!\, \pi}\, |I|^2\, .$$

The integral

$$I = \int_{-\infty}^{+\infty} dy\, e^{-y\, y_0}\, \frac{d^n}{dy^n}\, e^{-y^2}$$

can be n-times integrated by parts, where the integrated part always drops out:

$$\begin{aligned} I &= (-y_0)^n \int_{-\infty}^{+\infty} dy\, e^{-y\, y_0}\, e^{-y^2} \\ &= (-y_0)^n\, e^{(1/4)\, y_0^2} \int_{-\infty}^{+\infty} dz\, e^{-z^2} = \sqrt{\pi}\, (-y_0)^n\, e^{(1/4)\, y_0^2}\, . \end{aligned}$$

Transition probability:

$$w_n = \frac{a^{2n}}{q_0^{2n}\, 2^n\, n!} \exp\left[-\frac{1}{2}\left(\frac{a}{q_0}\right)^2\right] .$$

Solution 7.3.5

The considerations about the transition probability in solution 7.3.3 are again valid:

$$w_{1s\to 2s} = \left| \int d^3r\, \varphi_{100}^{(Z)*}(\mathbf{r})\, \varphi_{200}^{(Z+1)}(\mathbf{r}) \right|^2 .$$

(6.60):

$$\varphi_{100}^{(Z)}(\mathbf{r}) = \sqrt{\frac{Z^3}{\pi\, a_\mathrm{B}^3}} \exp\left(-\frac{Z\, r}{a_\mathrm{B}}\right) .$$

(6.61):

$$\varphi_{200}^{(Z+1)}(\mathbf{r}) = \frac{1}{2}\sqrt{\frac{(Z+1)^3}{2\pi\, a_\mathrm{B}^3}} \left(1 - \frac{(Z+1)r}{2a_\mathrm{B}}\right) \exp\left(-\frac{(Z+1)r}{2a_\mathrm{B}}\right) .$$

Insertion leads to:

$$\begin{aligned} w_{1s\to 2s} &= 16\,\pi^2\, \frac{Z^3}{\pi\, a_\mathrm{B}^3}\, \frac{1}{4}\, \frac{(Z+1)^3}{2\pi\, a_\mathrm{B}^3} \left| \int_0^\infty dr\, r^2 \left[1 - \frac{(Z+1)r}{2a_\mathrm{B}}\right] \cdot \right. \\ &\qquad \left. \cdot \exp\left\{-\frac{r}{a_\mathrm{B}} \left[Z + \frac{1}{2}(Z+1)\right]\right\} \right|^2 = \frac{2}{a_\mathrm{B}^6}\, Z^3 (Z+1)^3 |I_1 - I_2|^2 , \end{aligned}$$

$$I_1 = \int_0^\infty dr\, r^2 \exp\left[-\frac{r}{2a_\mathrm{B}}\,(3Z+1)\right] = \left(\frac{2a_\mathrm{B}}{3Z+1}\right)^3 \underbrace{\int_0^\infty dy\, y^2\, e^{-y}}_{=\Gamma(3)=2!} = 2\left(\frac{2a_\mathrm{B}}{3Z+1}\right)^3 ,$$

$$\begin{aligned} I_2 &= \frac{Z+1}{2a_\mathrm{B}} \int_0^\infty dr\, r^3 \exp\left[-\frac{r}{2a_\mathrm{B}}\,(3Z+1)\right] \\ &= \frac{Z+1}{2a_\mathrm{B}} \left(\frac{2a_\mathrm{B}}{3Z+1}\right)^4 \Gamma(4) = 3\,\frac{Z+1}{a_\mathrm{B}} \left(\frac{2a_\mathrm{B}}{3Z+1}\right)^4 . \end{aligned}$$

Transition probability:

$$w_{1s\to 2s} = 2^{11}\, \frac{Z^3 (Z+1)^3}{(3Z+1)^8} .$$

Solution 7.3.6

1. The formulas (7.115) and (7.118) yield:

$$w_{12}^{(1)}(t) = \frac{1}{\hbar^2}\left|\left\langle \varphi_1^{(0)}|H_1|\varphi_2^{(0)}\right\rangle\right|^2 t^2 \,.$$

2a) We have solved this problem as Exercise 7.2.9. Using the abbreviation

$$H_1^{\alpha\beta} \equiv \left\langle \varphi_\alpha^{(0)}|H_1|\varphi_\beta^{(0)}\right\rangle \;; \quad \alpha,\beta = 1,2,$$

we get:

$$\begin{aligned} E_\pm^{(1)} &= \frac{1}{2}\left\{H_1^{11}+H_1^{22} \pm \sqrt{\left(H_1^{11}-H_1^{22}\right)^2 + 4\left|H_1^{12}\right|^2}\right\} \,, \\ \left|\varphi_\pm^{(0)}\right\rangle &= c_1^{(\pm)}\left|\varphi_1^{(0)}\right\rangle + c_2^{(\pm)}\left|\varphi_2^{(0)}\right\rangle \,, \\ \left|c_1^{(\pm)}\right|^2 &= \frac{\left|H_1^{12}\right|^2}{\left(H_1^{11}-E_\pm^{(1)}\right)^2+\left|H_1^{12}\right|^2} = 1-\left|c_2^{(\pm)}\right|^2 \,. \end{aligned}$$

We presume real coefficients and respect the orthogonality of the states $|\varphi_\pm^{(0)}\rangle$:

$$\left\langle \varphi_+^{(0)}|\varphi_-^{(0)}\right\rangle = 0 = c_1^{(+)}\,c_1^{(-)} + c_2^{(+)}\,c_2^{(-)} \,.$$

If one still writes

$$\begin{aligned} \left|H_1^{12}\right|^2 &= \frac{1}{4}\left(\sqrt{\left(H_1^{11}-H_1^{22}\right)^2+4\left|H_1^{12}\right|^2}\right)^2 - \frac{1}{4}\left(H_1^{11}-H_1^{22}\right)^2 \\ &\equiv \frac{1}{4}A^2 - \frac{1}{4}\left(H_1^{11}-H_1^{22}\right)^2 \end{aligned}$$

and additionally

$$\begin{aligned} \left(H_1^{11}-E_\pm^{(1)}\right)^2 + \left|H_1^{12}\right|^2 &= \frac{1}{4}\left(H_1^{11}-H_1^{22}\mp A\right)^2 + \left|H_1^{12}\right|^2 \\ &= \frac{1}{4}\left(H_1^{11}-H_1^{22}\right)^2 + \frac{1}{4}A^2 \mp \frac{1}{2}A\left(H_1^{11}-H_1^{22}\right) + \left|H_1^{12}\right|^2 \\ &= \frac{1}{2}A\left(A\mp\left(H_1^{11}-H_1^{22}\right)\right) \end{aligned}$$

then it follows:

$$\left|c_1^{(\pm)}\right|^2 = \frac{\frac{1}{4}\left(A+\left(H_1^{11}-H_1^{22}\right)\right)\left(A-\left(H_1^{11}-H_1^{22}\right)\right)}{\frac{1}{2}A\left(A\mp\left(H_1^{11}-H_1^{22}\right)\right)} = \frac{1}{2A}\left(A\pm\left(H_1^{11}-H_1^{22}\right)\right).$$

This means for real $c_1^{(\pm)}$:

$$c_1^{(\pm)} = \left\{\frac{1}{2}\left(1\pm\frac{H_1^{11}-H_1^{22}}{\sqrt{\left(H_1^{11}-H_1^{22}\right)^2+4\left|H_1^{12}\right|^2}}\right)\right\}^{1/2} \,.$$

With

$$c_2^{(\pm)} = \pm c_1^{(\mp)}$$

orthogonality as well as normalization are then guaranteed!

2b) It holds obviously:

$$\left|\varphi_1^{(0)}\right\rangle = \frac{c_2^{(-)}\left|\varphi_+^{(0)}\right\rangle - c_2^{(+)}\left|\varphi_-^{(0)}\right\rangle}{c_1^{(+)}\,c_2^{(-)} - c_2^{(+)}\,c_1^{(-)}} \; .$$

The time-dependence of the *'correct'* states of zeroth order are, because of

$$H\left|\varphi_\pm^{(0)}\right\rangle \approx \left(E^{(0)} + E_\pm^{(1)}\right)\left|\varphi_\pm^{(0)}\right\rangle \; ,$$

relatively simple:

$$\left|\varphi_\pm^{(0)}(t)\right\rangle = e^{-(i/\hbar)\,H\,t}\left|\varphi_\pm^{(0)}\right\rangle \approx e^{-(i/\hbar)\left(E^{(0)}+E_\pm^{(1)}\right)t}\left|\varphi_\pm^{(0)}\right\rangle \; .$$

This means for the state of the system:

$$\begin{aligned}\left|\varphi_1^{(0)}(t)\right\rangle \;\; &= \;\; e^{-(i/\hbar)\,H\,t}\left|\varphi_1^{(0)}\right\rangle \approx \frac{e^{-(i/\hbar)\,E^{(0)}t}}{c_1^{(+)}\,c_2^{(-)} - c_2^{(+)}\,c_1^{(-)}} \times \\ &\times \left(c_2^{(-)}e^{-(i/\hbar)E_+^{(1)}t}\left|\varphi_+^{(0)}\right\rangle - c_2^{(+)}e^{-(i/\hbar)E_-^{(1)}t}\left|\varphi_-^{(0)}\right\rangle\right).\end{aligned}$$

2c) Because of

$$\left\langle\varphi_2^{(0)}\middle|\varphi_\pm^{(0)}\right\rangle = c_2^{(\pm)}$$

we have at first:

$$\left\langle\varphi_2^{(0)}\middle|\varphi_1(t)\right\rangle \approx e^{-(i/\hbar)E^{(0)}t}\frac{c_2^{(+)}c_2^{(-)}}{c_1^{(+)}c_2^{(-)} - c_2^{(+)}c_1^{(-)}}\left(e^{-(i/\hbar)E_+^{(1)}t} - e^{-(i/\hbar)E_-^{(1)}t}\right).$$

We need the square of the magnitude:

$$\begin{aligned}\left|c_2^{(+)}c_2^{(-)}\right|^2 &= \frac{1}{4}\left(1 - \frac{\left(H_1^{11} - H_1^{22}\right)^2}{\left(H_1^{11} - H_1^{22}\right)^2 + 4\left|H_1^{12}\right|^2}\right) \; , \\ \left|c_1^{(+)}\,c_2^{(-)} - c_2^{(+)}\,c_1^{(-)}\right|^2 &= \left|-\left(c_1^{(+)}\right)^2 - \left(c_2^{(+)}\right)^2\right|^2 = 1 \; , \\ \left|e^{-(i/\hbar)E_+^{(1)}t} - e^{-(i/\hbar)E_-^{(1)}t}\right|^2 &= \left|e^{-(i/\hbar)\left(E_+^{(1)} - E_-^{(1)}\right)t} - 1\right|^2 \\ &= \left\{\cos\left[\frac{1}{\hbar}\left(E_+^{(1)} - E_-^{(1)}\right)t\right] - 1\right\}^2 \\ &\quad + \sin^2\left[\frac{1}{\hbar}\left(E_+^{(1)} - E_-^{(1)}\right)t\right] \\ &= 2\left\{1 - \cos\left[\frac{1}{\hbar}\left(E_+^{(1)} - E_-^{(1)}\right)t\right]\right\} \; .\end{aligned}$$

After all, this yields the following transition probability:

$$\begin{aligned}\widetilde{w}_{12}(t) &= \frac{\left|H_1^{12}\right|^2}{\left(H_1^{11}-H_1^{22}\right)^2+4\left|H_1^{12}\right|^2} \\ &\quad\times\left[1-\cos\left(\frac{1}{\hbar}\sqrt{\left(H_1^{11}-H_1^{22}\right)^2+4\left|H_1^{12}\right|^2}\,t\right)\right] .\end{aligned}$$

It oscillates with the frequency:

$$\omega=\frac{1}{\hbar}\sqrt{\left(H_1^{11}-H_1^{22}\right)^2+4\left|H_1^{12}\right|^2} .$$

2d) Perturbation theory of first order is applicable only for *small perturbation times*. For $t \ll 1/\omega$ it holds approximately:

$$\widetilde{w}_{12}(t) \approx \frac{1}{\hbar^2}\left|H_1^{12}\right|^2 t^2 .$$

This agrees with the result for $w_{12}^{(1)}$ from part 1.!

Solution 7.3.7

1. $H = H_0 + H_{1t}$

$$\begin{aligned}H_0|n\rangle &= \hbar\,\omega\left(n+\frac{1}{2}\right)|n\rangle , \\ H_{1t} &= -q\,F\,e^{-\alpha t^2} z .\end{aligned}$$

Transition probability (7.110):

$$\begin{aligned}w_{0n}^{(1)}(\infty) &= \frac{1}{\hbar^2}\left|\int_{-\infty}^{+\infty} dt_1\,\langle n|H_{1\,t_1}|0\rangle\,e^{(i/\hbar)\hbar\,\omega\,n\,t_1}\right|^2 \\ &= \frac{q^2F^2}{\hbar^2}|\langle n|z|0\rangle|^2\left|\int_{-\infty}^{+\infty} dt_1\,\exp\left(-\alpha\,t_1^2+i\,\omega\,n\,t_1\right)\right|^2 .\end{aligned}$$

According to ((4.127), Vol. 6):

$$\langle n|z|0\rangle=\sqrt{\frac{\hbar}{2m\,\omega}}\langle n|(a+a^+)|0\rangle=\sqrt{\frac{\hbar}{2m\,\omega}}\,\delta_{n1} .$$

Evaluation of the integral:

$$\int_{-\infty}^{+\infty} dt_1 \, \exp\left(-\alpha\, t_1^2 + i\,\omega\, n\, t_1\right) = \int_{-\infty}^{+\infty} dt_1 \, \exp\left[-\alpha\left(t_1 - \frac{i\,\omega\, n}{2\alpha}\right)^2 - \frac{\omega^2 n^2}{4\alpha}\right]$$

$$= \exp\left(-\frac{\omega^2 n^2}{4\alpha}\right) \frac{1}{\sqrt{\alpha}} \int_{-\infty - i\,x}^{+\infty - i\,x} dy\, e^{-y^2} \; ; \quad x = \frac{\omega\, n}{2\sqrt{\alpha}} \; ,$$

$$\int_{-\infty - i\,x}^{+\infty - i\,x} dy\, e^{-y^2} = \sqrt{\pi} \quad \text{(see Exercise 2.2.2, Vol. 6)} \; .$$

It results therewith as transition probability:

$$w_{0n}^{(1)}(\infty) = \frac{q^2 F^2 \pi}{2m\,\alpha\,\hbar\,\omega}\, e^{-(n^2\omega^2/2\alpha)}\, \delta_{n1} \; .$$

Residence probability (7.107):

$$\hat{w}_{00}^{(1)}(\infty) = 1 - \sum_{n}^{\neq 0} w_{0n}^{(1)}(\infty) = 1 - \frac{q^2 F^2 \pi}{2m\,\alpha\,\hbar\,\omega}\, e^{-(\omega^2/2\alpha)} \; .$$

2. Requirement:

$$w_{0n}^{(1)}(\infty) \ll 1 \; ; \quad \hat{w}_{00}^{(1)}(\infty) \lesssim 1 \; .$$

This means:

$$\frac{q^2 F^2 \pi}{2m\,\alpha\,\hbar\,\omega}\, e^{-(\omega^2/2\alpha)} \ll 1 \; .$$

Solution 7.3.8

According to (7.110) it is to evaluate:

$$w_{n0}^{(1)}(t) = \frac{1}{\hbar^2} \left| \int_0^t dt' \, {}^{(0)}\langle n|H_{1t'}|0\rangle^{(0)} \exp\left(\frac{i}{\hbar}\left(E_n^{(0)} - E_0^{(0)}\right) t'\right) \right|^2 \; .$$

We utilize for this purpose:

$$\begin{aligned}
E_n^{(0)} - E_0^{(0)} &= n\hbar\omega \\
{}^{(0)}\langle n|H_{1t}|0\rangle^{(0)} &= c\, e^{-\gamma t}\, {}^{(0)}\langle n|\left(a^2 + a^{\dagger 2}\right)|0\rangle^{(0)} \\
a|0\rangle^{(0)} &= 0 \\
a^\dagger|0\rangle^{(0)} &= \sqrt{1}\,|1\rangle^{(0)} \\
a^{\dagger 2}|0\rangle^{(0)} &= \sqrt{1}\,\sqrt{2}\,|2\rangle^{(0)} \\
\curvearrowright \; {}^{(0)}\langle n|H_{1t}|0\rangle^{(0)} &= \sqrt{2}\, c\, e^{-\gamma t}\delta_{n2} \; .
\end{aligned}$$

It follows therewith:

$$\begin{aligned} w_{n0}^{(1)}(t) &= 2\frac{c^2}{\hbar^2}\left|\int_o^t dt'\, e^{-\gamma t'}\, e^{ni\omega t'}\right|^2 \delta_{n2} \\ &= 2\frac{c^2}{\hbar^2}\left|\frac{1}{-\gamma+ni\omega}\left(e^{(ni\omega-\gamma)t}-1\right)\right|^2 \delta_{n2} \\ &= 2\frac{c^2}{\hbar^2}\frac{1}{\gamma^2+n^2\omega^2}\left(e^{(ni\omega-\gamma)t}-1\right)\left(e^{(-ni\omega-\gamma)t}-1\right)\delta_{n2} \\ &= \frac{2c^2}{\hbar^2(\gamma^2+n^2\omega^2)}\left(e^{-2\gamma t}+1-e^{-\gamma t}\,2\cos(n\omega t)\right)\delta_{n2} \\ &= \frac{2c^2}{\hbar^2(\gamma^2+n^2\omega^2)}\,e^{-\gamma t}\,\left(2\cos\gamma t-2\cos(n\omega t)\right)\delta_{n2} \\ \curvearrowright\quad w_{n0}^{(1)}(t) &= \frac{4c^2}{\hbar^2(\gamma^2+n^2\omega^2)}\,e^{-\gamma t}\left(\cos\gamma t-\cos(n\omega t)\right)\delta_{n2}\,. \end{aligned}$$

Solution 7.3.9

1.

$$H_0\,|n\rangle = \varepsilon_n|n\rangle \;\;;\;\; n=1,2\,.$$

Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\,|n(t)\rangle = H_0\,|n(t)\rangle = \varepsilon_n|n(t)\rangle\,.$$

H_0 is time-independent. Therefore:

$$|n(t)\rangle = e^{-\frac{i}{\hbar}H_0 t}\,|n\rangle = e^{-\frac{i}{\hbar}\varepsilon t}\,|n\rangle\,.$$

$e^{-\frac{i}{\hbar}H_0 t}$ is the time evolution operator of the *'free'* system.

2. General state:

$$|\psi(t)\rangle = \sum_{n'=1}^{2}\alpha_{n'}(t)|n'(t)\rangle = \sum_{n'=1}^{2}\alpha_{n'}(t)\,e^{-\frac{i}{\hbar}\varepsilon_{n'}t}|n'\rangle$$

Time-dependent Schrödinger equation:

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\,|\psi(t)\rangle &= \sum_{n'=1}^{2}\left(i\hbar\dot{\alpha}_{n'}(t)+\varepsilon_{n'}\,\alpha_{n'}(t)\right)e^{-\frac{i}{\hbar}\varepsilon_{n'}t}|n'\rangle \\ &\stackrel{!}{=} \left(H_0+H_{1t}\right)\,|\psi(t)\rangle \\ &= \sum_{n'=1}^{2}\alpha_{n'}(t)\,e^{-\frac{i}{\hbar}\varepsilon_{n'}t}\left(\varepsilon_{n'}+H_{1t}\right)\,|n'\rangle \\ \curvearrowright\quad i\hbar\sum_{n'=1}^{2}\dot{\alpha}_{n'}(t)\,e^{-\frac{i}{\hbar}\varepsilon_{n'}t}|n'\rangle &= \sum_{n'=1}^{2}\alpha_{n'}(t)\,e^{-\frac{i}{\hbar}\varepsilon_{n'}t}\,H_{1t}\,|n'\rangle\,. \end{aligned}$$

Scalar multiplication from the left by $\langle n|$:

$$i\hbar\dot{\alpha}_n(t) = \sum_{n'=1}^{2} \alpha_{n'}(t)\, e^{\frac{i}{\hbar}(\varepsilon_n - \varepsilon_{n'})t} \langle n|H_{1t}\,|n'\rangle \ .$$

That yields a coupled system of equations:

$$\begin{aligned} i\hbar\dot{\alpha}_1(t) &= \hbar\omega_0\, e^{\frac{i}{\hbar}(\varepsilon_1-\varepsilon_2)t}\, \alpha_2(t)\, e^{i\omega t} \\ i\hbar\dot{\alpha}_2(t) &= \hbar\omega_0\, e^{\frac{i}{\hbar}(\varepsilon_2-\varepsilon_1)t}\, \alpha_1(t)\, e^{-i\omega t} \ . \end{aligned}$$

With the abbreviation

$$\hbar\overline{\omega} = \varepsilon_2 - \varepsilon_1 - \hbar\omega$$

it remains to be solved:

$$\begin{aligned} i\,\dot{\alpha}_1(t) &= \omega_0\, \alpha_2(t)\, e^{-i\overline{\omega}t} \\ i\,\dot{\alpha}_2(t) &= \omega_0\, \alpha_1(t)\, e^{i\overline{\omega}t} \ . \end{aligned}$$

From the second equation it follows:

$$\begin{aligned} i\,\ddot{\alpha}_2 &= \omega_0\dot{\alpha}_1(t)e^{i\overline{\omega}t} + i\overline{\omega}\omega_0\alpha_1(t)e^{i\overline{\omega}t} \\ &= -i\omega_0^2\alpha_2(t)e^{-i\overline{\omega}t}e^{i\overline{\omega}t} + i\overline{\omega}\omega_0\frac{i\dot{\alpha}_2(t)}{\omega_0}e^{-i\overline{\omega}t}e^{i\overline{\omega}t} \\ \curvearrowright \qquad & \ddot{\alpha}_2(t) - i\overline{\omega}\,\dot{\alpha}_2(t) + \omega_0^2\,\alpha_2(t) = 0 \ . \end{aligned}$$

Ansatz:

$$\begin{aligned} \alpha_2(t) &= A\, e^{\gamma t} \\ \curvearrowright\ \gamma^2 - i\overline{\omega}\gamma + \omega_0^2 &= 0 \\ \curvearrowright\ \gamma_\pm &= \frac{1}{2}i\overline{\omega} \pm id \quad ; \quad d^2 = \omega_0^2 + \frac{1}{4}\overline{\omega}^2 \\ \curvearrowright\ \alpha_2(t) &= e^{\frac{1}{2}i\overline{\omega}t}\left(A_+e^{idt} + A_-e^{-idt}\right) \ . \end{aligned}$$

Initial condition:

$$\alpha_2(0) \stackrel{!}{=} 0 = A_+ + A_- \qquad \curvearrowright\ A_+ = -A_- \ .$$

Therewith it follows:

$$\alpha_2(t) = A\sin(dt)\, e^{\frac{1}{2}i\overline{\omega}t} \quad (A = 2iA_+) \ .$$

The second coefficient is calculated from:

$$\alpha_1(t) = \frac{i}{\omega_0}\, e^{-i\overline{\omega}t}\, \dot{\alpha}_2(t) = \frac{i}{\omega_0}\, e^{-i\overline{\omega}t}\, A\, e^{\frac{1}{2}i\overline{\omega}t}\left(d\cos(dt) + \frac{1}{2}i\overline{\omega}\sin(dt)\right) \ .$$

Initial condition:

$$\alpha_1(0) \stackrel{!}{=} 1 = \frac{id}{\omega_0} A \qquad \curvearrowright \quad A = -i\frac{\omega_0}{d} .$$

That leads to the complete solution:

$$\begin{aligned} \alpha_1(t) &= e^{-\frac{1}{2}i\overline{\omega}t} \left(\cos(dt) + \frac{i\overline{\omega}}{2d} \sin(dt) \right) \\ \alpha_2(t) &= -i\frac{\omega_0}{d} \sin(dt)\, e^{\frac{1}{2}i\overline{\omega}t} \qquad d = \sqrt{\omega_0^2 + \frac{1}{4}\overline{\omega}^2} . \end{aligned}$$

Occupation probabilities:

$$\begin{aligned} |\alpha_1(t)|^2 &= \cos^2(dt) + \frac{\overline{\omega}^2}{4d^2} \sin^2(dt) \\ |\alpha_2(t)|^2 &= \frac{\omega_0^2}{d^2} \sin^2(dt) . \end{aligned}$$

Because of

$$d^2 = \omega_0^2 + \frac{1}{4}\overline{\omega}^2$$

it is obviously:

$$|\alpha_1(t)|^2 + |\alpha_2(t)|^2 = 1 .$$

The occupation probabilities are periodic functions of the time. At the points of time

$$t_n = 2n\pi\frac{1}{d}$$

the system is in the ground-state $|1\rangle$. A perturbation (e.g. light source), switched on at $t = 0$ and switched off at $t = t_n$ allows the system to be in the ground state!

3. Transition probability in first order perturbation theory:

$$\begin{aligned} w_{21}^{(1)}(t) &= \frac{1}{\hbar^2} \left| \int_0^t dt_1 \, \langle 2|H_{1t_1}|1\rangle \, e^{\frac{i}{\hbar}(\varepsilon_2 - \varepsilon_1)t_1} \right|^2 \\ &= \frac{1}{\hbar^2} \left| \int_0^t dt_1 \, \hbar\omega_0 \, e^{i\overline{\omega}t_1} \right|^2 \\ &= \frac{\omega_0^2}{\overline{\omega}^2} \left| e^{i\overline{\omega}t} - 1 \right|^2 \\ &= \frac{\omega_0^2}{\overline{\omega}^2} \left| e^{i\frac{1}{2}\overline{\omega}t} \left(e^{i\frac{1}{2}\overline{\omega}t} - e^{-i\frac{1}{2}\overline{\omega}t} \right) \right|^2 \\ w_{21}^{(1)}(t) &= 4\frac{\omega_0^2}{\overline{\omega}^2} \sin^2\left(\frac{1}{2}\overline{\omega}t \right) \end{aligned}$$

That can be compared with the exact expression for $|\alpha_2(t)|^2$ from part 2. For a weak perturbation

$$\omega_0 \ll |\overline{\omega}| \; ; \qquad d \approx \frac{1}{2}\overline{\omega}$$

the exact solution can be approximated:

$$|\alpha_2(t)|^2 = \frac{\omega_0^2}{d^2}\sin^2(dt) \approx \frac{4\omega_0^2}{\overline{\omega}^2}\sin^2\left(\frac{1}{2}\overline{\omega}t\right) \; .$$

In the case of weak perturbation the perturbation theory of first order thus becomes exact!

Solution 7.3.10

1. Schrödinger picture

$$\lim_{t\to-\infty}\rho_t = \rho_0$$

Dirac picture

$$\lim_{t\to-\infty}\rho_t^{\mathrm{D}}(t) = \rho_0 \qquad \text{(boundary condition)}$$

($\dot{\rho}_0 = 0 \;\rightarrow\; [\rho_0, H_0]_- = 0$).
Equation of motion (3.207), Vol. 6:

$$\dot{\rho}_t^{\mathrm{D}}(t) = \frac{i}{\hbar}[\rho_t^{\mathrm{D}}(t), H_{1t}^{\mathrm{D}}(t)]_-$$

Formal integration

$$\rho_t^{\mathrm{D}}(t) = \rho_0 - \frac{i}{\hbar}\int_{-\infty}^{t} \mathrm{t}'[H_{1t'}^{\mathrm{D}}(t'), \rho_{t'}^{\mathrm{D}}(t')]_- \; .$$

$\rho_t^{\mathrm{D}}(t)$: t as index refers to an explicit time-dependence due to an external perturbation means, while that in the argument refers to the 'dynamic' time-dependence in the Dirac picture.

2. Formal solution by iteration:

$$\begin{aligned}
\rho_t^{\mathrm{D}}(t) &= \rho_0 + \sum_{n=1}^{\infty}\rho_t^{\mathrm{D}(n)}(t) \\
\rho_t^{\mathrm{D}(n)}(t) &= (-\frac{i}{\hbar})^n \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \ldots \int_{-\infty}^{t_{n-1}} dt_n \\
&\quad \times [H_{1t_1}^{\mathrm{D}}(t_1), [H_{1t_2}^{\mathrm{D}}(t_2), [\ldots [H_{1t_n}^{\mathrm{D}}(t_n), \rho_0]_- \ldots]_-]_-]_- \; .
\end{aligned}$$

3. *Linear response*

$$\rho_t^{\mathrm{D}}(t) \approx \rho_0 - \frac{i}{\hbar}\int\limits_{-\infty}^{t} dt' [H_{1t'}^{\mathrm{D}}(t'), \rho_0]_-$$

$\rightarrow$ Schrödinger picture:

$$\rho_t = \rho_0 - \frac{i}{\hbar}\int\limits_{-\infty}^{t} dt' e^{-\frac{i}{\hbar}H_0 t}[H_{1t'}^{\mathrm{D}}(t'), \rho_0]_- e^{\frac{i}{\hbar}H_0 t} \; .$$

Expectation values:

$$\begin{aligned} \langle \widehat{A} \rangle_t &= \mathrm{Tr}(\rho_t \widehat{A}) \\ \langle \widehat{A} \rangle_0 &= \mathrm{Tr}(\rho_0 \widehat{A}) \; . \end{aligned}$$

We find:

$$\begin{aligned} \Delta A_t &= -\frac{i}{\hbar}\int\limits_{-\infty}^{t} dt' \, \mathrm{Tr}(e^{-\frac{i}{\hbar}H_0 t}[H_{1t'}^{\mathrm{D}}(t'), \rho_0]_- e^{\frac{i}{\hbar}H_0 t}\hat{A}) \\ &= -\frac{i}{\hbar}\int\limits_{-\infty}^{t} dt' \, f(t') \, \mathrm{Tr}\big(\underbrace{[B^{\mathrm{D}}(t'), \rho_0]_- A^{\mathrm{D}}(t)}_{= B\rho_0 A - \rho_0 B A} \big) \\ &= -\frac{i}{\hbar}\int\limits_{-\infty}^{t} dt' \, f(t') \, \mathrm{Tr}(\rho_0 [A^{\mathrm{D}}(t), B^{\mathrm{D}}(t')]_-) \\ &= -\frac{i}{\hbar}\int\limits_{-\infty}^{t} dt' \, f(t') \, \langle [A^{\mathrm{D}}(t), B^{\mathrm{D}}(t')]_- \rangle_0 \; . \end{aligned}$$

In the first and the second step we have utilized the cyclic invariance of the trace. The averaging in the last row is done in the free(!) system.

Section 7.4.7

Solution 7.4.1

It holds:

$$k(q) = \frac{\sqrt{2m}}{\hbar}\sqrt{E - V(q)} = \frac{1}{\hbar}\sqrt{2m\left(E - \frac{1}{2}m\,\omega^2 q^2\right)} \; .$$

Classical turning points:

$$q_{1,2}^* = \pm\sqrt{\frac{2E}{m\,\omega^2}} \; .$$

We calculate the integral

$$I = \int_{q_1^*}^{q_2^*} dq\, \frac{1}{\hbar} \sqrt{2m \left(E - \frac{1}{2}\, m\, \omega^2 q^2 \right)} = \frac{\sqrt{2m\, E}}{\hbar} \int_{q_1^*}^{q_2^*} dq \sqrt{1 - \frac{m\, \omega^2}{2E}\, q^2}$$

using the substitution

$$y = \sqrt{\frac{m}{2E}}\, \omega\, q \implies dq = \sqrt{\frac{2E}{m}}\, \frac{1}{\omega}\, dy,$$

which leads to a standard integral:

$$I = \frac{2E}{\hbar\, \omega} \int_{-1}^{+1} dy\, \sqrt{1 - y^2} = \frac{2E}{\hbar\, \omega}\, \frac{1}{2} \arcsin y \Big|_{-1}^{+1} = \frac{E\pi}{\hbar\, \omega}\ .$$

The WKB-condition (7.187) requires:

$$I \stackrel{!}{=} \left(n + \frac{1}{2} \right) \pi \implies E = \hbar\, \omega \left(n + \frac{1}{2} \right) \ ; \quad n \in \mathbb{Z}\ .$$

In this case the WKB-procedure is thus exact!

Solution 7.4.2

The $\alpha \to 0$-behavior of the Bessel function is known (7.194):

$$J_{1/3}(\alpha) \sim \alpha^{1/3}\ ; \quad J_{-1/3}(\alpha) \sim \alpha^{-1/3}\ .$$

Furthermore it holds near the turning point $\alpha = 0$:

$$k(\alpha) \sim \alpha^{1/3} \implies \sqrt{\frac{\alpha}{k}} \sim \alpha^{1/3}\ .$$

The two terms of the Langer solution thus behave as follows:

$$\sqrt{\frac{\alpha}{k}}\, J_{1/3}(\alpha) \sim \alpha^{2/3}\ ; \quad \sqrt{\frac{\alpha}{k}}\, J_{-1/3}(\alpha) \sim \alpha^{0}\ .$$

They therefore remain finite for $\alpha \to 0$.

Solution 7.4.3

1. According to (7.160) the WKB-solution reads in the *classically allowed* region:

$$\hat{u}(\alpha) = \frac{\gamma_+^*}{\sqrt{k}}\, e^{i(\alpha - \pi/4)} + \frac{\gamma_-^*}{\sqrt{k}}\, e^{-i(\alpha - \pi/4)}\ .$$

Here it turns out to be useful to split off the factors $e^{\pm i\pi/4}$:

$$\hat{u}(\alpha) = \frac{1}{\sqrt{k}} \left\{ \left(\gamma_+^* + \gamma_-^* \right) \cos\left(\alpha - \frac{\pi}{4} \right) + i \left(\gamma_+^* - \gamma_-^* \right) \sin\left(\alpha - \frac{\pi}{4} \right) \right\}\ .$$

With the ansatz

$$\gamma_{\pm}^{*} = \frac{1}{2}\,\widehat{\gamma}\,e^{\pm i\,\varphi}\;; \quad \widehat{\gamma},\varphi:\ \text{complex constants}$$

it follows:

$$\hat{u}(\alpha) = \frac{\widehat{\gamma}}{\sqrt{k}}\,\left\{\cos\varphi\cos\left(\alpha-\frac{\pi}{4}\right) - \sin\varphi\sin\left(\alpha-\frac{\pi}{4}\right)\right\}\ .$$

In the classically allowed region the WKB-solution therewith has the structure,

$$\hat{u}(\alpha) = \frac{\widehat{\gamma}}{\sqrt{k}}\,\cos\left(\alpha-\frac{\pi}{4}+\varphi\right)\ ,$$

where:

$$\gamma_{\pm} = \frac{1}{2}\,\widehat{\gamma}\,e^{\pm i(\varphi+\pi/4)}\ .$$

2. Asymptotically it holds with (7.195) for the Langer solution (7.170):

$$v(\alpha) \underset{\alpha\to\infty}{\longrightarrow} \sqrt{\frac{2}{\pi k}}\,\left\{(a+b)\cos\frac{\pi}{6}\cos\left(\alpha-\frac{\pi}{4}\right) + (a-b)\sin\frac{\pi}{6}\sin\left(\alpha-\frac{\pi}{4}\right)\right\},$$
$$\cos\frac{\pi}{6} = \frac{1}{2}\sqrt{3}\;; \quad \sin\frac{\pi}{6} = \frac{1}{2}\ .$$

Comparison with the WKB-solution yields:

$$\begin{aligned}\sqrt{\frac{3}{2\pi}}\,(a+b) &= \widehat{\gamma}\cos\varphi\ ,\\ \sqrt{\frac{1}{2\pi}}\,(a-b) &= -\widehat{\gamma}\sin\varphi\end{aligned}$$

or:

$$a+b = \sqrt{\frac{2\pi}{3}}\,\widehat{\gamma}\cos\varphi\;; \quad a-b = -\sqrt{2\pi}\,\widehat{\gamma}\sin\varphi\ .$$

3. For the *Langer solution* $v(\alpha)$ one finds, according to (7.172), in the *classically forbidden* regions:

$$\begin{aligned} v(\alpha) &= \sqrt{\left|\frac{\alpha}{k}\right|}\,\left(-a\,I_{1/3}\left(|\alpha|\right) + b\,I_{-1/3}\left(|\alpha|\right)\right)\\ &= \sqrt{\left|\frac{\alpha}{k}\right|}\,\left\{-\frac{1}{2}\,(a+b)\,\left(I_{\frac{1}{3}}\left(|\alpha|\right) - I_{-1/3}(|\alpha|)\right)\right.\\ &\qquad \left.-\frac{1}{2}\,(a-b)\,\left(I_{1/3}\left(|\alpha|\right) + I_{-1/3}\left(|\alpha|\right)\right)\right\}\ .\end{aligned}$$

Asymptotic behavior of the modified Bessel functions:

$$I_{1/3}(|\alpha|) + I_{-1/3}(|\alpha|) \underset{|\alpha|\to\infty}{\overset{(7.212)}{\longrightarrow}} \frac{2}{\sqrt{2\pi|\alpha|}}\, e^{|\alpha|}\,,$$

$$I_{1/3}(|\alpha|) - I_{-1/3}(|\alpha|) \overset{(7.208)}{=} -\frac{2}{\pi}\,\sin\frac{1}{3}\,\pi\, K_{-1/3}(|\alpha|) \underset{|\alpha|\to\infty}{\overset{(7.212)}{\longrightarrow}} -\sqrt{\frac{3}{2\pi|\alpha|}}\, e^{-|\alpha|}$$

$$\left(\sin\frac{1}{3}\pi = \frac{1}{2}\sqrt{3}\right)\,.$$

This means:

$$v(\alpha) \underset{|\alpha|\to\infty}{\longrightarrow} \frac{1}{\sqrt{|k|}}\left[\frac{1}{2}(a+b)\sqrt{\frac{3}{2\pi}}\, e^{-|\alpha|} - (a-b)\,\frac{1}{\sqrt{2\pi}}\, e^{|\alpha|}\right]\,.$$

4. WKB-solution (7.160) in the *classically forbidden* region:

$$\hat{u}(\alpha) = \frac{1}{\sqrt{|k|}}\left(\delta_+\, e^{|\alpha|} + \delta_-\, e^{-|\alpha|}\right)\,.$$

Asymptotic comparison with $v(\alpha)$:

$$\begin{aligned}\delta_+ &= -\frac{1}{\sqrt{2\pi}}\,(a-b) \overset{2)}{=} \widehat{\gamma}\sin\varphi\,,\\ \delta_- &= \frac{1}{2}\sqrt{\frac{3}{2\pi}}\,(a+b) \overset{2)}{=} \frac{1}{2}\,\widehat{\gamma}\cos\varphi\,.\end{aligned}$$

From that follows the assertion:

$$\hat{u}(\alpha) = \frac{\widehat{\gamma}}{\sqrt{|k|}}\left(\sin\varphi\, e^{|\alpha|} + \frac{1}{2}\cos\varphi\, e^{-|\alpha|}\right)\,.$$

Solution 7.4.4

1. ρ_1^* is a *right-hand* turning point. With the underlying assumptions the *classically forbidden* region $\rho_1^* < \rho$ can be approximately considered as reaching up to infinity so that (7.182) and (7.183) become valid:

$$\rho < \rho_1^*: \qquad \hat{u}(\rho) = \frac{\overline{\gamma}}{\sqrt{k}}\cos\left[\int_\rho^{\rho_1^*} d\rho' k(\rho') - \frac{\pi}{4}\right]\,,$$

$$\rho > \rho_1^*: \qquad \hat{u}(\rho) = \frac{\overline{\gamma}}{2\sqrt{k}}\exp\left[-\int_{\rho_1^*}^{\rho} d\rho'\,|k(\rho')|\right]\,.$$

2.

$$\rho < \rho_1^* : \ \hat{u}(\rho) = \frac{\overline{\gamma}}{2\sqrt{k}} \left\{ \exp\left[i \left(\int_\rho^{\rho_1^*} d\rho' k(\rho') - \frac{\pi}{4} \right) \right] + \exp\left[-i \left(\int_\rho^{\rho_1^*} d\rho' k(\rho') - \frac{\pi}{4} \right) \right] \right\} .$$

The second(!) summand represents the *incident* wave, the first summand the *reflected* wave:

$$\begin{aligned} \hat{u}_{\text{in}}(\rho) &= \frac{\overline{\gamma}}{2\sqrt{k}} \exp\left[-i \left(\int_\rho^{\rho_1^*} d\rho' k(\rho') - \frac{\pi}{4} \right) \right] \\ \Longrightarrow \frac{d}{d\rho} \hat{u}_{\text{in}}(\rho) &= \left(-\frac{1}{2} \frac{k'}{k} + i\, k \right) \hat{u}_{\text{in}}(\rho) \\ \Longrightarrow \hat{u}_{\text{in}}^*(\rho) \frac{d}{d\rho} \widehat{u}_{\text{in}}(\rho) &= \frac{1}{4} |\overline{\gamma}|^2 \left(-\frac{1}{2} \frac{k'}{k^2} + i \right) . \end{aligned}$$

Analogously one finds:

$$\hat{u}_{\text{in}}(\rho) \frac{d}{d\rho} \hat{u}_{\text{ein}}^*(\rho) = \frac{1}{4} |\overline{\gamma}|^2 \left(-\frac{1}{2} \frac{k'}{k^2} - i \right) .$$

Current density (4.55), Vol. 6:

$$\begin{aligned} j_{\text{in}} &= \frac{\hbar}{2m\, i} \left(\hat{u}_{\text{in}}^*(\rho) \frac{d}{d\rho} \hat{u}_{\text{in}}(\rho) - \hat{u}_{\text{in}}(\rho) \frac{d}{d\rho} \hat{u}_{\text{in}}^*(\rho) \right) \\ \Longrightarrow j_{\text{in}} &= \frac{\hbar}{4m} |\overline{\gamma}|^2 . \end{aligned}$$

3. At first, the general solutions (7.184) and (7.185) are valid. ρ_2^* is a *left-hand* turning point.

$\boldsymbol{\rho_2^* < \rho}$

$$\hat{u}(\rho) = \frac{\widehat{\gamma}}{2\sqrt{k}} \left\{ \exp\left[i \left(\int_{\rho_2^*}^{\rho} d\rho' k(\rho') - \frac{\pi}{4} + \varphi \right) \right] + \exp\left[-i \left(\int_{\rho_2^*}^{\rho} d\rho' k(\rho') - \frac{\pi}{4} + \varphi \right) \right] \right\} .$$

No reflection at $\rho = +\infty$ means:

$$\begin{aligned} \widehat{\gamma}\, e^{-i\varphi} \stackrel{!}{=} 0 \qquad &\Longrightarrow\ \widehat{\gamma}\cos\varphi = i\,\widehat{\gamma}\sin\varphi \quad (\widehat{\gamma}, \varphi \ \text{ complex}\,!) \\ &\Longrightarrow\ \widehat{\gamma}\, e^{+i\varphi} = 2i\,\widehat{\gamma}\sin\varphi\ . \end{aligned}$$

Outgoing wave:

$$\hat{u}_{\text{out}}(\rho) = i\frac{\widehat{\gamma}}{\sqrt{k}}\sin\varphi\exp\left[i\left(\int\limits_{\rho_2^*}^{\rho} d\rho' k(\rho') - \frac{\pi}{4}\right)\right]\ .$$

$\boldsymbol{\rho < \rho_2^*}$

$$\hat{u}(\rho) = \frac{\widehat{\gamma}}{\sqrt{|k|}}\sin\varphi\left(\frac{i}{2}\, e^{-|\alpha|} + e^{|\alpha|}\right)\ .$$

In the WKB-validity region the first term can in any case be neglected compared to the second summand:

$$\hat{u}(\rho) \approx \frac{\widehat{\gamma}}{\sqrt{|k|}}\sin\varphi\exp\left[\int\limits_{\rho}^{\rho_2^*} |k(\rho')|\, d\rho'\right]\ .$$

4. Calculation for j_{out} is equivalent to that for j_{in} in part 2.:

   $\boldsymbol{\rho_2^* < \rho}$

$$j_{\text{out}} = \frac{\hbar}{2m\,i}\left(\hat{u}_{\text{out}}^*\frac{d}{d\rho}\,\hat{u}_{\text{out}} - \hat{u}_{\text{out}}\frac{d}{d\rho}\,\hat{u}_{\text{out}}^*\right) = \frac{\hbar}{m}|\widehat{\gamma}|^2\sin^2\varphi\ .$$

5. According to the partial results 2. and 4. it follows at first:

$$T(E) = \left|\frac{j_{\text{out}}}{j_{\text{in}}}\right| = 4\left|\frac{\widehat{\gamma}}{\overline{\gamma}}\right|^2\sin^2\varphi\ .$$

The still missing connection between $\widehat{\gamma}$ and $\overline{\gamma}$ is given by the requirement that for $\rho_1^* < \rho < \rho_2^*$ the WKB-solution with respect to ρ_1^* must coincide with that for ρ_2^*. It holds according to 1. and 3.:

$$\begin{aligned} \frac{\overline{\gamma}}{2\sqrt{k}}\exp\left[-\int\limits_{\rho_1^*}^{\rho} d\rho'\,|k(\rho')|\right] \quad &\stackrel{!}{=} \quad \frac{\widehat{\gamma}}{\sqrt{|k|}}\sin\varphi\exp\left[\int\limits_{\rho}^{\rho_2^*}|k(\rho')|\,d\rho'\right] \\ \Longrightarrow\ \overline{\gamma} \quad &= \quad 2\,\widehat{\gamma}\sin\varphi\exp\left[\int\limits_{\rho_1^*}^{\rho_2^*}|k(\rho')|\,d\rho'\right]\ . \end{aligned}$$

This means:

$$T(E) = \exp\left[-2\int\limits_{\rho_1^*}^{\rho_2^*}|k(\rho')|\,d\rho'\right] \quad \text{(see 7.186)}\ .$$

Solution 7.4.5

$$\begin{aligned}
J_{-n}(z) &= \left(\frac{z}{2}\right)^{-n} \sum_{k=0}^{\infty} \frac{(-1)^k}{k!\,\Gamma(k-n+1)} \left(\frac{z}{2}\right)^{2k} \\
&= \left(\frac{z}{2}\right)^{n} \sum_{k=0}^{\infty} \frac{(-1)^k}{k!\,\Gamma(k-n+1)} \left(\frac{z}{2}\right)^{2(k-n)} \\
&= \left(\frac{z}{2}\right)^{n} \sum_{k'=-n}^{\infty} \frac{(-1)^{k'+n}}{(k'+n)!\,\Gamma(k'+1)} \left(\frac{z}{2}\right)^{2k'} \\
&= (-1)^n \left(\frac{z}{2}\right)^{n} \sum_{k'=0}^{\infty} \frac{(-1)^{k'}}{(k'+n)!\,\Gamma(k'+1)} \left(\frac{z}{2}\right)^{2k'} \\
&\quad -(-1)^n \left(\frac{z}{2}\right)^{n} \sum_{k'=-n}^{0} \frac{(-1)^{k'}}{(k'+n)!\,\Gamma(k'+1)} \left(\frac{z}{2}\right)^{2k'} .
\end{aligned}$$

Because of 2. the second sum vanishes.

$$\begin{aligned}
J_{-n}(z) &\overset{1.}{=} (-1)^n \left(\frac{z}{2}\right)^{n} \sum_{k'=0}^{\infty} \frac{(-1)^{k'}}{(k'+n)!\,k'!} \left(\frac{z}{2}\right)^{2k'} \\
&\overset{1.}{=} (-1)^n \left(\frac{z}{2}\right)^{n} \sum_{k'=0}^{\infty} \frac{(-1)^{k'}}{\Gamma(k'+n+1)\,k'!} \left(\frac{z}{2}\right)^{2k'} \\
&= (-1)^n\, J_n(z) .
\end{aligned}$$

Solution 7.4.6

- $$J_{1/2}(z) = \left(\frac{z}{2}\right)^{\frac{1}{2}} \sum_{k=0}^{\infty} \frac{(-1)^k}{k!\,\Gamma(k+\frac{1}{2}+1)} \left(\frac{z}{2}\right)^{2k} .$$

  We consider at first the denominator of this expression:

$$\begin{aligned}
2^{2k} k! \Gamma\left(k+\frac{1}{2}+1\right) &= (2k)!!2^k \left(k+\frac{1}{2}\right) \Gamma\left(k+\frac{1}{2}\right) \\
&= (2k)!!2^k \left(k+\frac{1}{2}\right)\left(k-1+\frac{1}{2}\right)\cdots\left(k-k+\frac{1}{2}\right)\Gamma\left(\frac{1}{2}\right) \\
&= \frac{1}{2}\,(2k)!!(2k+1)(2k-1)\cdots\cdot 1\sqrt{\pi} \\
&= \frac{1}{2}(2k)!!(2k+1)!!\sqrt{\pi} \\
&= \frac{1}{2}\sqrt{\pi}(2k+1)!
\end{aligned}$$

  It follows therewith:

$$\begin{aligned}
J_{1/2}(z) &= \left(\frac{1}{2z}\right)^{\frac{1}{2}} \frac{2}{\sqrt{\pi}} \sum_{k=0}^{\infty} \frac{(-1)^k}{(2k+1)!}\, z^{2k+1} \\
&= \sqrt{\frac{2}{\pi z}}\, \sin z
\end{aligned}$$

- $$J_{-1/2}(z) = \left(\frac{z}{2}\right)^{-\frac{1}{2}} \sum_{k=0}^{\infty} \frac{(-1)^k}{k!\,\Gamma(k-\frac{1}{2}+1)} \left(\frac{z}{2}\right)^{2k} .$$

  We consider at first again the denominator:

$$\begin{aligned} 2^{2k}k!\Gamma(k-\frac{1}{2}+1) &= (2k)!!2^k \left(k-\frac{1}{2}\right)\left(k-1-\frac{1}{2}\right)\cdots \\ &\quad \cdots\left(k-(k-1)-\frac{1}{2}\right)\Gamma\left(\frac{1}{2}\right) \\ &= (2k)!!(2k-1)!!\sqrt{\pi} = (2k)!\sqrt{\pi} . \end{aligned}$$

  It remains:

$$\begin{aligned} J_{-1/2}(z) &= \sqrt{\frac{2}{\pi z}} \sum_{k=0}^{\infty} \frac{(-1)^k}{(2k)!} z^{2k} \\ &= \sqrt{\frac{2}{\pi z}} \cos z . \end{aligned}$$

Solution 7.4.7

1. $$\begin{aligned} \exp\left(\frac{z}{2}\left(t-\frac{1}{t}\right)\right) &= \exp\left(\frac{zt}{2}\right)\exp\left(-\frac{z}{2t}\right) \\ &= \sum_{r=0}^{\infty} \frac{t^r}{r!}\left(\frac{z}{2}\right)^r \sum_{s=0}^{\infty} \frac{(-1)^s}{s!}\left(\frac{z}{2}\right)^s t^{-s} \\ &= \sum_{s=0}^{\infty}\sum_{r=0}^{\infty} \frac{(-1)^s}{s!\,r!}\left(\frac{z}{2}\right)^{r+s} t^{r-s} . \end{aligned}$$

   Take $n = r - s$, where n can take integral values between $-\infty$ and $+\infty$:

$$\begin{aligned} \exp\left(\frac{z}{2}\left(t-\frac{1}{t}\right)\right) &= \sum_{n=-\infty}^{+\infty} \left(\sum_{s=0}^{\infty} \frac{(-1)^s}{s!\,(n+s)!}\left(\frac{z}{2}\right)^{2s+n}\right) t^n \\ &\overset{(7.190)}{=} \sum_{n=-\infty}^{+\infty} J_n(z)\, t^n . \end{aligned}$$

2. Partial differentiation of the generating function with respect to t:

$$\begin{aligned} \frac{z}{2}\left(1+\frac{1}{t^2}\right)\exp\left(\frac{z}{2}\left(t-\frac{1}{t}\right)\right) &= \sum_{n=-\infty}^{+\infty} nJ_n(z)t^{n-1} \\ \curvearrowright \quad \frac{z}{2}\sum_{n=-\infty}^{+\infty} J_n(z)t^n + \frac{z}{2}\sum_{n=-\infty}^{+\infty} J_n(z)t^{n-2} &= \sum_{n=-\infty}^{+\infty} nJ_n(z)t^{n-1} \\ \curvearrowright \quad \frac{z}{2}\sum_{n=-\infty}^{+\infty} J_{n-1}(z)t^{n-1} + \frac{z}{2}\sum_{n=-\infty}^{+\infty} J_{n+1}(z)t^{n-1} &= \sum_{n=-\infty}^{+\infty} nJ_n(z)t^{n-1} . \end{aligned}$$

Comparison of the coefficients of equal powers of t:

$$\frac{z}{2}\left(J_{n-1}(z)+J_{n+1}(z)\right)=nJ_n(z)\ .$$

That is the assertion! It represents a very useful formula. When one has found J_0 and J_1 via the definition equation (7.190), then one can derive step-by-step all higher indexed Bessel functions by the use of this recursion formula.

3. Partial differentiation of the generating function with respect to z:

$$\begin{aligned}
\frac{1}{2}\left(t-\frac{1}{t}\right)\exp\left(\frac{z}{2}\left(t-\frac{1}{t}\right)\right) &= \sum_{n=-\infty}^{+\infty}\left(\frac{d}{dz}J_n(z)\right)t^n \\
\curvearrowright\ \frac{1}{2}\sum_{n=-\infty}^{+\infty}J_n(z)t^{n+1}-\frac{1}{2}\sum_{n=-\infty}^{+\infty}J_n(z)t^{n-1} &= \sum_{n=-\infty}^{+\infty}\left(\frac{d}{dz}J_n(z)\right)t^n \\
\curvearrowright\ \frac{1}{2}\sum_{n=-\infty}^{+\infty}J_{n-1}(z)t^{n}-\frac{1}{2}\sum_{n=-\infty}^{+\infty}J_{n+1}(z)t^{n} &= \sum_{n=-\infty}^{+\infty}\left(\frac{d}{dz}J_n(z)\right)t^n\ .
\end{aligned}$$

Comparison of coefficients:

$$\frac{1}{2}\left(J_{n-1}(z)-J_{n+1}(z)\right)=\frac{d}{dz}J_n(z)$$

4. Addition of the recursion formulas 2. (7.203) and 3. (7.204):

$$2J_{n-1}(z)=\frac{2n}{z}J_n(z)+2\frac{d}{dz}J_n(z)\ \curvearrowright\ \frac{d}{dz}J_n(z)=J_{n-1}(z)-\frac{n}{z}J_n(z)\ .$$

Subtraction of the two recursion formulas:

$$2J_{n+1}(z)=\frac{2n}{z}J_n(z)-2\frac{d}{dz}J_n(z)\ \curvearrowright\ \frac{d}{dz}J_n(z)=-J_{n+1}(z)+\frac{n}{z}J_n(z)$$

5. Multiplication of the recursion formula in 4. by z^n:

$$\begin{aligned}
z^n\frac{d}{dz}J_n(z) &= z^nJ_{n-1}(z)-nz^{n-1}J_n(z) \\
\curvearrowright\ \frac{d}{dz}\left(z^n\,J_n(z)\right) &= z^n\,J_{n-1}(z)\ .
\end{aligned}$$

Alternative derivation by multiplying the second version of the recursion formula in 4. by $-z^{-n}$:

$$\begin{aligned}
-z^{-n}\frac{d}{dz}J_n(z) &= +z^{-n}J_{n+1}(z)-nz^{-n-1}J_n(z) \\
\curvearrowright\ \frac{d}{dz}\left(z^{-n}\,J_n(z)\right) &= -z^{-n}\,J_{n+1}(z)\ .
\end{aligned}$$

Section 8.1.4

Solution 8.1.1

$$
\begin{aligned}
|\varphi_2\rangle &= \sum\!\!\!\!\!\!\int_{i,\,j} \alpha_{ij}(\varphi)\, \left|\overline{\varphi}_i^{(1)}\right\rangle \left|\widehat{\varphi}_j^{(2)}\right\rangle \,, \\
|\psi_2\rangle &= \sum\!\!\!\!\!\!\int_{i,\,j} \alpha_{ij}(\psi)\, \left|\overline{\psi}_i^{(1)}\right\rangle \left|\widehat{\psi}_j^{(2)}\right\rangle \,.
\end{aligned}
$$

It is convenient to expand the one-particle states on the right-hand side in the orthonormalized bases $\left\{|a_n^{(1)}\rangle\right\}$, $\left\{|b_m^{(2)}\rangle\right\}$ of the $\mathcal{H}_1^{(1)}$ and $\mathcal{H}_1^{(2)}$, respectively (see (8.14)):

$$
\begin{aligned}
|\varphi_2\rangle &= \sum\!\!\!\!\!\!\int_{n,\,m} \gamma_{nm}(\varphi)\, \left|a_n^{(1)}\right\rangle \left|b_m^{(2)}\right\rangle \,, \\
|\psi_2\rangle &= \sum\!\!\!\!\!\!\int_{n,\,m} \gamma_{nm}(\psi)\, \left|a_n^{(1)}\right\rangle \left|b_m^{(2)}\right\rangle \,.
\end{aligned}
$$

Equation (8.11) then reads:

$$
\begin{aligned}
\langle\psi_2|\varphi_2\rangle &= \sum\!\!\!\!\!\!\int_{n,\,m} \sum\!\!\!\!\!\!\int_{n',\,m'} \gamma_{nm}^*(\psi)\gamma_{n'm'}(\varphi) \left\langle a_n^{(1)}\middle|a_{n'}^{(1)}\right\rangle \left\langle b_m^{(1)}\middle|b_{m'}^{(1)}\right\rangle \\
&= \sum\!\!\!\!\!\!\int_{n,\,m} \gamma_{nm}^*(\psi)\gamma_{nm}(\varphi) \,.
\end{aligned}
$$

The axioms can therewith easily be verified:

1.
$$
\langle\psi_2|\varphi_2\rangle = \left(\sum\!\!\!\!\!\!\int_{n,\,m} \gamma_{nm}^*(\varphi)\gamma_{nm}(\psi)\right)^* = \langle\varphi_2|\psi_2\rangle^* \quad ((3.15), \text{Vol. 6}) \,.
$$

2.
$$
\langle\psi_2|\varphi_2+\chi_2\rangle = \sum\!\!\!\!\!\!\int_{n,m} \gamma_{nm}^*(\psi)\big(\gamma_{nm}(\varphi)+\gamma_{nm}(\chi)\big) = \langle\psi_2|\varphi_2\rangle + \langle\psi_2|\chi_2\rangle \quad ((3.16), \text{Vol. 6})
$$

3. $c \in \mathbb{C}$
$$
\begin{aligned}
\langle\psi_2|c\,\varphi_2\rangle &= \sum\!\!\!\!\!\!\int_{n,\,m} \gamma_{nm}^*(\psi)\ (c\,\gamma_{nm}(\varphi)) = \sum\!\!\!\!\!\!\int_{n,\,m} \left(c^*\gamma_{nm}(\psi)\right)^*\ \gamma_{nm}(\varphi) \\
&= c \sum\!\!\!\!\!\!\int_{n,\,m} \gamma_{nm}^*(\psi)\,\gamma_{nm}(\varphi) = \langle c^*\psi_2|\varphi_2\rangle = c\langle\psi_2|\varphi_2\rangle \quad ((3.17), \text{Vol. 6}) \,.
\end{aligned}
$$

4.
$$
\begin{aligned}
\langle\varphi_2|\varphi_2\rangle &= \sum\!\!\!\!\!\!\int_{n,\,m} |\gamma_{nm}(\varphi)|^2 \geq 0 \,, \\
\langle\varphi_2|\varphi_2\rangle = 0 \Longleftrightarrow \gamma_{nm}(\varphi) &= 0 \quad \forall n, m \Longleftrightarrow |\varphi_2\rangle = |0\rangle \quad ((3.18), \text{Vol. 6}) \,.
\end{aligned}
$$

Solution 8.1.2

1. Matrix elements of the operator $A_1^{(1)} = A_1^{(1)}\,\mathbb{1}_1^{(2)}$:

$$\left\langle a_n\, b_m \left| A_1^{(1)}\,\mathbb{1}_1^{(2)} \right| a_p\, b_q \right\rangle = \left\langle a_n^{(1)} \left| A_1^{(1)} \right| a_p^{(1)} \right\rangle \left\langle b_m^{(2)} | b_q^{(2)} \right\rangle = \alpha_{np}\,\delta_{mq}\ .$$

$$A_1^{(1)} \iff \begin{array}{c} nm \\ \downarrow \\ 11 \\ 12 \\ 21 \\ 22 \end{array} \begin{array}{c} pq \rightarrow \\ \begin{array}{cccc} 11 & 12 & 21 & 22 \end{array} \\ \begin{pmatrix} \alpha_{11} & 0 & \alpha_{12} & 0 \\ 0 & \alpha_{11} & 0 & \alpha_{12} \\ \alpha_{21} & 0 & \alpha_{22} & 0 \\ 0 & \alpha_{21} & 0 & \alpha_{22} \end{pmatrix} \end{array}$$

2. Matrix elements of the operator $B_1^{(2)} = \mathbb{1}_1^{(1)} \cdot B_1^{(2)}$:

$$\left\langle a_n\, b_m \left| \mathbb{1}_1^{(1)} \cdot B_1^{(2)} \right| a_p\, b_q \right\rangle = \left\langle a_n^{(1)} | a_p^{(1)} \right\rangle \left\langle b_m^{(2)} \left| B_1^{(2)} \right| b_q^{(2)} \right\rangle = \delta_{np}\,\beta_{mq}\ .$$

$$B_1^{(2)} \iff \begin{array}{c} nm \\ \downarrow \\ 11 \\ 12 \\ 21 \\ 22 \end{array} \begin{array}{c} pq \rightarrow \\ \begin{array}{cccc} 11 & 12 & 21 & 22 \end{array} \\ \begin{pmatrix} \beta_{11} & \beta_{12} & 0 & 0 \\ \beta_{21} & \beta_{22} & 0 & 0 \\ 0 & 0 & \beta_{11} & \beta_{12} \\ 0 & 0 & \beta_{21} & \beta_{22} \end{pmatrix} \end{array}$$

3. Matrix element of the operator $A_1^{(1)}\,B_1^{(2)}$:

$$\left\langle a_n\, b_m \left| A_1^{(1)}\, B_1^{(2)} \right| a_p\, b_q \right\rangle = \left\langle a_n^{(1)} \left| A_1^{(1)} \right| a_p^{(1)} \right\rangle \left\langle b_m^{(2)} \left| B_1^{(2)} \right| b_q^{(2)} \right\rangle = \alpha_{np}\,\beta_{mq}\ .$$

$$A_1^{(1)}\,B_1^{(2)} \iff \begin{array}{c} nm \\ \downarrow \\ 11 \\ 12 \\ 21 \\ 22 \end{array} \begin{array}{c} pq \rightarrow \\ \begin{array}{cccc} 11 & 12 & 21 & 22 \end{array} \\ \begin{pmatrix} \alpha_{11}\,\beta_{11} & \alpha_{11}\,\beta_{12} & \alpha_{12}\,\beta_{11} & \alpha_{12}\,\beta_{12} \\ \alpha_{11}\,\beta_{21} & \alpha_{11}\,\beta_{22} & \alpha_{12}\,\beta_{21} & \alpha_{12}\,\beta_{22} \\ \alpha_{21}\,\beta_{11} & \alpha_{21}\,\beta_{12} & \alpha_{22}\,\beta_{11} & \alpha_{22}\,\beta_{12} \\ \alpha_{21}\,\beta_{21} & \alpha_{21}\,\beta_{22} & \alpha_{22}\,\beta_{21} & \alpha_{22}\,\beta_{22} \end{pmatrix} \end{array}$$

This matrix is of course identical to the product of the two matrices from 1. and 2.!

Commutation of the operators $A_1^{(1)}$ and $B_1^{(2)}$ means only that in each matrix element the complex numbers α_{ij} and β_{ij} are to be interchanged. Because of $\alpha_{ij}\,\beta_{ij} = \beta_{ij}\,\alpha_{ij} \forall i,j$ it is also

$$A_1^{(1)}\,B_1^{(2)} = B_1^{(2)}\,A_1^{(1)}\ .$$

Section 8.2.7

Solution 8.2.1

It holds in general, according to ((3.169), Vol. 6), for the time evolution operator

$$i\,\hbar\,\frac{d}{dt}\,U(t,t_0) = H_N\,U\,(t,t_0)$$

with the boundary condition $U(t_0,t_0) = \mathbb{1}_N$. In any case:

$$[H_N,\,P_{ij}]_- = 0\,.$$

We multiply the above differential equation from the left as well as from the right by P_{ij}:

$$i\,\hbar\,\frac{d}{dt}\,P_{ij}\,U\,P_{ij} = P_{ij}\,H_N\,U\,P_{ij} = H_N\,P_{ij}\,U\,P_{ij}\,.$$

Boundary condition:

$$P_{ij}\,U(t_0,t_0)\,P_{ij} = P_{ij}^2 = \mathbb{1}_N\,.$$

We see that U as well as $P_{ij}\,U\,P_{ij}$ are solutions of the same differential equation of first order with identical boundary condition. Because of the uniqueness of the solution of such a differential equation we have to conclude

$$U = P_{ij}\,U\,P_{ij}\,.$$

Therefore:

$$U\,P_{ij} = P_{ij}\,U\,P_{ij}^2 = P_{ij}\,U \Longrightarrow\ [U,P_{ij}]_- = 0$$

Solution 8.2.2

$$\begin{aligned}\left\langle\varphi_N^{(+)}\,|A_N|\,\psi_N^{(-)}\right\rangle &\overset{(8.50)}{=} \left\langle\varphi_N^{(+)}\,\big|P_{ij}^{+}\,A_N\,P_{ij}\big|\,\psi_N^{(-)}\right\rangle\\ &\overset{(8.60)}{=} -\left\langle\varphi_N^{(+)}\,|A_N|\,\psi_N^{(-)}\right\rangle = 0\,.\end{aligned}$$

Solution 8.2.3

1. $N = 2$:

$$\begin{aligned} S_2^{(+)} &= \frac{1}{2}\,(\mathbb{1}_2 + P_{12})\,,\\ S_2^{(-)} &= \frac{1}{2}\,(\mathbb{1}_2 - P_{12})\\ \Longrightarrow\ S_2^{(+)} + S_2^{(-)} &= \mathbb{1}_2\,.\end{aligned}$$

$\mathcal{H}_2^{(+)}$ and $\mathcal{H}_2^{(-)}$ obviously build the entire $\mathcal{H}_2$.

2. $N = 3$:

$$\begin{aligned} S_3^{(+)} &= \frac{1}{6}\left(\mathbb{1}_3 + P_{12} + P_{13} + P_{23} + P_{12}\,P_{23} + P_{12}\,P_{13}\right) , \\ S_3^{(-)} &= \frac{1}{6}\left(\mathbb{1}_3 - P_{12} - P_{13} - P_{23} + P_{12}\,P_{23} + P_{12}\,P_{13}\right) \\ \Longrightarrow\ S_3^{(+)} + S_3^{(-)} &\neq \mathbb{1}_3 . \end{aligned}$$

$\mathcal{H}_3$ contains states with components, which belong neither to $\mathcal{H}_N^{(+)}$ nor to $\mathcal{H}_N^{(-)}$.

Solution 8.2.4

Let $|\varphi_N^{(\pm)}\rangle$, $|\psi_N^{(\pm)}\rangle$ be arbitrary elements of the $\mathcal{H}_N^{(\pm)}$:

$$\begin{aligned} \left\langle \varphi_N^{(\pm)} \left| \mathcal{P}^+ \right| \psi_N^{(\pm)} \right\rangle &= \left\langle \mathcal{P}\,\varphi_N^{(\pm)} \middle| \psi_N^{(\pm)} \right\rangle \overset{(8.60)}{=} (\pm)^p \left\langle \varphi_N^{(\pm)} \middle| \psi_N^{(\pm)} \right\rangle \\ &\overset{(8.60)}{=} \left\langle \varphi_N^{(\pm)} \middle| \mathcal{P}\,\psi_N^{(\pm)} \right\rangle = \left\langle \varphi_N^{(\pm)} \left| \mathcal{P} \right| \psi_N^{(\pm)} \right\rangle \\ &\Longrightarrow \quad \mathcal{P} = \mathcal{P}^+ \quad \text{in } \mathcal{H}_N^{(\pm)} . \end{aligned}$$

Solution 8.2.5

1.
$$H = H^{(1)} + H^{(2)} = -\frac{\hbar^2}{2m}\left(\frac{d^2}{dq_1^2} + \frac{d^2}{dq_2^2}\right) + V(q_1) + V(q_2) .$$

The Hamilton operator does not contain any spin contributions. Furthermore, H commutes of course with the total spin operators $\mathbf{S}^2$, S^z. Therefore there must exist common eigen-states, which factorize in position and spin states:

$$|E_2\rangle = |q\rangle|S,\, M_S\rangle^{(+)} .$$

According to the presumption, the spin state is symmetric. The position state $|q\rangle$ as well as the total state $|E_2\rangle$ must therefore be symmetric for bosons, and antisymmetric for fermions.

2. Non-symmetrized product state:

$$|\varphi_{\alpha_1}\,\varphi_{\alpha_2}\rangle = \left|\varphi_{\alpha_1}^{(1)}\right\rangle \left|\varphi_{\alpha_2}^{(2)}\right\rangle .$$

(Anti)symmetrized:

$$|\varphi_{\alpha_1}\,\varphi_{\alpha_2}\rangle^{(\pm)} = \frac{1}{\sqrt{2}}\left(\left|\varphi_{\alpha_1}^{(1)}\right\rangle \left|\varphi_{\alpha_2}^{(2)}\right\rangle \pm \left|\varphi_{\alpha_1}^{(2)}\right\rangle \left|\varphi_{\alpha_2}^{(1)}\right\rangle\right) .$$

The corresponding one-particle problem is solved as Exercise 4.2.1 in Vol. 6. We take over:

Quantum numbers:

$$\alpha \equiv (n, \gamma)\ ; \quad \gamma = \pm : \text{ parity.}$$

Position representation:

$$\begin{aligned}
\gamma = -: \ \varphi_{n-}(q) &= \frac{1}{\sqrt{q_0}} \sin\left(\frac{\pi}{q_0}\, n\, q\right)\ , \\
E_{n-} &= \frac{\hbar^2 \pi^2}{2m\, q_0^2}\, n^2\ , \qquad n = 1, 2, 3, \ldots \\
\gamma = +: \ \varphi_{n+}(q) &= \frac{1}{\sqrt{q_0}} \cos\left[\frac{\pi}{2q_0}\,(2n+1)\, q\right]\ , \\
E_{n+} &= \frac{\hbar^2 \pi^2}{8m\, q_0^2}\,(2n+1)^2 \qquad n = 0, 1, 2, \ldots\ .
\end{aligned}$$

It results for the position part

$$|q\rangle^{(\pm)} \implies \frac{1}{\sqrt{2}}\left\{\varphi_{n\gamma}(q_1)\,\varphi_{n'\gamma'}(q_2) \pm \varphi_{n\gamma}(q_2)\,\varphi_{n'\gamma'}(q_1)\right\}$$

with $(n, \gamma) \neq (n', \gamma')$ for fermions, because the spin quantum numbers are the same for both particles. In contrast, no restriction for bosons!

Eigen-energies:

$$E_{n\gamma, n'\gamma'} = E_{n\gamma} + E_{n'\gamma'}$$
with $(n, \gamma) \neq (n', \gamma')$ for fermions.

3. Ground-state energies:
Ground-state of the one-particle system:

$$E_{0+} = \frac{\hbar^2 \pi^2}{8m\, q_0^2}\ .$$

First excited state of the one-particle system:

$$E_{1-} = \frac{\hbar^2 \pi^2}{2m\, q_0^2}\ .$$

$\Longrightarrow$ Ground-state energy of

$$\begin{aligned}
&\text{two bosons:} && E_0^B = 2E_{0+}\ , \\
&\text{two fermions:} && E_0^F = E_{0+} + E_{1-}\ .
\end{aligned}$$

Solution 8.2.6

1. We have antisymmetric fermion-states. Therefore:

$$P_{12}\left|\psi_2^{(S,T)}\right\rangle = -\left|\psi_2^{(S,T)}\right\rangle\ .$$

2. In a system of identical particles each observable commutes with P_{12} (8.51). That holds also for H:

$$[H, P_{12}]_- = 0$$

H is spin-**independent** and commutes therefore with $P_{12}^{(S)}$:

$$0 = [H, P_{12}]_- = \left[P_{12}^{(S)} \cdot P_{12}^{(q)},\, H\right]_- = P_{12}^{(S)} \left[P_{12}^{(q)},\, H\right]_- .$$

Therefore

$$\left[P_{12}^{(q)},\, H\right]_- = 0 .$$

3. Equation of motion of the time evolution operator ((3.169), Vol. 6):

$$i\hbar \frac{\partial}{\partial t} U(t, t_0) = H\, U(t, t_0) \qquad \text{initial condition: } U(t_0, t_0) = \mathbb{1} .$$

We multiply the equation of motion from the left and from the right by $P_{12}^{(q)}$:

$$i\hbar \frac{\partial}{\partial t} P_{12}^{(q)} U(t, t_0) P_{12}^{(q)} = P_{12}^{(q)} H\, U(t, t_0) P_{12}^{(q)} = H P_{12}^{(q)}\, U(t, t_0) P_{12}^{(q)} .$$

Initial condition for this differential equation:

$$P_{12}^{(q)} U(t_0, t_0) P_{12}^{(q)} = P_{12}^{(q)}\, \mathbb{1}\, P_{12}^{(q)} = \left(P_{12}^{(q)}\right)^2 = \mathbb{1} .$$

We see that $U(t, t_0)$ and $P_{12}^{(q)} U(t, t_0) P_{12}^{(q)}$ fulfill the same differential equation of first order with the same initial condition. Thus they must be identical:

$$\begin{aligned} U(t, t_0) = \quad & P_{12}^{(q)} U(t, t_0) P_{12}^{(q)} \;\curvearrowright\; P_{12}^{(q)} U(t, t_0) = U(t, t_0) P_{12}^{(q)} \\ & \curvearrowright \left[U(t, t_0),\, P_{12}^{(q)}\right]_- = 0 . \end{aligned}$$

4. General state:

$$|\psi\rangle = |q\rangle\, |S\, m_S\rangle \ .$$

$\boldsymbol{t = t_0}$

$$P_{12}^{(q)}\ |\psi(t_0)\rangle = \pm\, |\psi(t_0)\rangle \ .$$

$\boldsymbol{t > t_0}$

$$\begin{aligned} P_{12}^{(q)}\ |\psi(t)\rangle &= P_{12}^{(q)}\, U(t, t_0)\, |\psi(t_0)\rangle \\ &= U(t, t_0)\, P_{12}^{(q)}\ |\psi(t_0)\rangle \\ &= \pm U(t, t_0)\ |\psi(t_0)\rangle \\ &= \pm\, |\psi(t)\rangle \end{aligned}$$

$|\psi(t)\rangle$ therefore retains its symmetry character for all times with respect to its *position part*. There are thus no transitions possible between $|\psi\rangle = \left|\psi_2^{(S)}\right\rangle$ and $|\psi\rangle = \left|\psi_2^{(T)}\right\rangle$!

Solution 8.2.7

1.

$$\begin{aligned} P_{12}^2|m_1m_2\rangle &= P_{12}|m_2m_1\rangle = |m_1m_2\rangle \quad \forall\,|m_1m_2\rangle \\ \Longrightarrow\ P_{12}^2 &= \mathbb{1} \Longrightarrow\ P_{12} = P_{12}^{-1}\ . \end{aligned}$$

$$\begin{aligned} \langle\hat{m}_1\hat{m}_2|P_{12}|m_1m_2\rangle &= \langle\hat{m}_1\hat{m}_2|m_2m_1\rangle \\ &= {}^{(1)}\langle\hat{m}_1|m_2\rangle^{(1)}\ {}^{(2)}\langle\hat{m}_2|m_1\rangle^{(2)} \\ &= \delta_{\hat{m}_1m_2}\delta_{\hat{m}_2m_1} \qquad \text{real} \\ &= {}^{(1)}\langle m_1|\hat{m}_2\rangle^{(1)}\ {}^{(2)}\langle m_2|\hat{m}_1\rangle^{(2)} \\ &= \langle m_1m_2|\hat{m}_2\hat{m}_1\rangle \\ &= (\langle m_1m_2|\hat{m}_2\hat{m}_1\rangle)^* \\ &= (\langle m_1m_2|P_{12}|\hat{m}_1\hat{m}_2\rangle)^* \end{aligned}$$

$$\Longrightarrow\ P_{12}^+ = P_{12}\ .$$

Eigen-values:

$$\begin{aligned} P_{12}|p\rangle &= c_{12}|p\rangle \qquad |p\rangle \in H_2 \qquad |p\rangle \neq 0 \\ P_{12}^2 &= \mathbb{1} \\ \Longrightarrow\ P_{12}^2|p\rangle &= c_{12}^2|p\rangle = |p\rangle \\ \Longrightarrow\ c_{12} &= \pm 1\ . \end{aligned}$$

2. Common eigen-states (Exercise 5.4.1):

$$S = 0, 1$$

$$\begin{aligned} |0\,0\rangle &= (|\tfrac{1}{2}\ -\tfrac{1}{2}\rangle - |-\tfrac{1}{2}\ \tfrac{1}{2}\rangle) \\ |1\,1\rangle &= |\tfrac{1}{2}\ \tfrac{1}{2}\rangle \\ |1\,0\rangle &= \frac{1}{\sqrt{2}}(|\tfrac{1}{2}\ -\tfrac{1}{2}\rangle + |-\tfrac{1}{2}\ \tfrac{1}{2}\rangle) \\ |1-1\rangle &= |-\tfrac{1}{2}\ -\tfrac{1}{2}\rangle\ . \end{aligned}$$

Obviously,

$$\begin{aligned} P_{12}|0\,0\rangle &= -|0\,0\rangle \\ P_{12}|1\,m_s\rangle &= |1\,m_s\rangle\ , \end{aligned}$$

are also eigen-states of P_{12}!

3. $|m_1 m_2\rangle$ arbitrary basis-state of the H_2:

$$\begin{aligned} P_{12}S_1^z P_{12}^+|m_1m_2\rangle &= P_{12}S_1^z P_{12}|m_1m_2\rangle \\ &= P_{12}S_1^z|m_2m_1\rangle \\ &= \hbar m_2 P_{12}|m_2m_1\rangle \\ &= \hbar m_2|m_1m_2\rangle \\ &= S_2^z|m_1m_2\rangle \end{aligned}$$

$$\begin{aligned} \Longrightarrow P_{12}S_1^z P_{12}^+ &= S_2^z \\ \text{analogously } P_{12}S_2^z P_{12}^+ &= S_1^z \ . \end{aligned}$$

Proof for x-, y-components:

$$S_i^x = \frac{1}{2}(S_i^+ + S_i^-)\ ; \quad S_i^y = \frac{1}{2i}(S_i^+ - S_i^-)\ .$$

It holds:

$$\begin{aligned} P_{12}S_1^\pm P_{12}^+|m_1m_2\rangle &= P_{12}S_1^\pm|m_2m_1\rangle \\ &= \hbar\sqrt{\frac{1}{2}(\frac{1}{2}+1) - m_2(m_2\pm 1)}P_{12}|m_2 \pm 1\, m_1\rangle \\ &= \hbar\sqrt{\frac{1}{2}(\frac{1}{2}+1) - m_2(m_2\pm 1)}\,|m_1 m_2 \pm 1\rangle \\ &= S_2^\pm|m_1m_2\rangle \end{aligned}$$

$$\begin{aligned} \Longrightarrow P_{12}S_1^\pm P_{12}^+ &= S_2^\pm \\ \text{analogously } P_{12}S_2^\pm P_{12}^+ &= S_1^\pm \ . \end{aligned}$$

Therewith we have:

$$\Longrightarrow\ P_{12}\mathbf{S}_1 P_{12}^+ = \mathbf{S}_2\ ; \quad P_{12}\mathbf{S}_2 P_{12}^+ = \mathbf{S}_1\ .$$

4.

$$\begin{aligned} P_{12} &= \frac{1}{2}[\mathbb{1} + \frac{4}{\hbar^2}\mathbf{S}_1\cdot\mathbf{S}_2] \\ &= \frac{1}{2}[\mathbb{1} + \frac{2}{\hbar^2}(S_1^+S_2^- + S_1^-S_2^+) + \frac{4}{\hbar^2}S_1^zS_2^z] \end{aligned}$$

(1) $|m_1m_2\rangle = |\frac{1}{2}\,\frac{1}{2}\rangle$:

$$\begin{aligned} P_{12}|m_1m_2\rangle &= \frac{1}{2}|\frac{1}{2}\frac{1}{2}\rangle + \frac{1}{\hbar^2}\underbrace{(S_1^+S_2^- + S_1^-S_2^+)|\frac{1}{2}\frac{1}{2}\rangle}_{=0} + \frac{2}{\hbar^2}\underbrace{S_1^zS_2^z|\frac{1}{2}\frac{1}{2}\rangle}_{\frac{\hbar^2}{4}|\frac{1}{2}\frac{1}{2}\rangle} \\ &= (\frac{1}{2}+\frac{1}{2})\,|\frac{1}{2}\,\frac{1}{2}\rangle = |\frac{1}{2}\,\frac{1}{2}\rangle = |m_2m_1\rangle \end{aligned}$$

(2) Analogously to (1) $|m_1 m_2\rangle = |-\frac{1}{2}\ -\frac{1}{2}\rangle$:

$$P_{12}|-\frac{1}{2}-\frac{1}{2}\rangle = |-\frac{1}{2}-\frac{1}{2}\rangle$$

(3) $|m_1 m_2\rangle = |\frac{1}{2}-\frac{1}{2}\rangle$:

$$\begin{aligned} P_{12}|m_1 m_2\rangle &= \frac{1}{2}|\frac{1}{2}-\frac{1}{2}\rangle + \frac{1}{\hbar^2}(S_1^+|\frac{1}{2}\rangle^{(1)})(S_2^-|-\frac{1}{2}\rangle^{(2)}) \\ &\quad + \frac{1}{\hbar^2}(S_1^-|\frac{1}{2}\rangle^{(1)})(S_2^+|-\frac{1}{2}\rangle^{(2)}) \\ &\quad + \frac{2}{\hbar^2}(S_1^z|\frac{1}{2}\rangle^{(1)})(S_2^z|-\frac{1}{2}\rangle^{(2)}) \\ &= \frac{1}{2}|\frac{1}{2}-\frac{1}{2}\rangle + 0 + (\sqrt{\frac{3}{4}+\frac{1}{4}}|-\frac{1}{2}\rangle^{(1)})(\sqrt{\frac{3}{4}+\frac{1}{4}}|\frac{1}{2}\rangle^{(2)}) \\ &\quad + \frac{2}{\hbar^2}(-\frac{\hbar^2}{4}|\frac{1}{2}-\frac{1}{2}\rangle) \\ &= |-\frac{1}{2}\,\frac{1}{2}\rangle = |m_2 m_1\rangle \end{aligned}$$

(4) $|m_1 m_2\rangle = |-\frac{1}{2}\,\frac{1}{2}\rangle$:

$$\begin{aligned} P_{12}|m_1 m_2\rangle &= \frac{1}{2}|-\frac{1}{2}\,\frac{1}{2}\rangle + \frac{1}{\hbar^2}(S_1^+|-\frac{1}{2}\rangle^{(1)})(S_2^-|\frac{1}{2}\rangle^{(2)}) \\ &\quad + \frac{1}{\hbar^2}(S_1^-|-\frac{1}{2}\rangle^{(1)})(S_2^+|\frac{1}{2}\rangle^{(2)}) \\ &\quad + \frac{2}{\hbar^2}(S_1^z|-\frac{1}{2}\rangle^{(1)})(S_2^z|\frac{1}{2}\rangle^{(2)}) \\ &= \frac{1}{2}|-\frac{1}{2}\,\frac{1}{2}\rangle + |\frac{1}{2}-\frac{1}{2}\rangle + 0 - \frac{1}{2}|-\frac{1}{2}\,\frac{1}{2}\rangle \\ &= |\frac{1}{2}-\frac{1}{2}\rangle = |m_2 m_1\rangle\ . \end{aligned}$$

All in all:

$$P_{12}|m_1 m_2\rangle = |m_2 m_1\rangle$$

Solution 8.2.8

1.

$$\begin{aligned} S_2^{(-)} &= \frac{1}{2}(\mathbb{1}_2 - P_{12}) \\ S_3^{(+)} &= \frac{1}{6}(\mathbb{1}_3 + P_{12} + P_{13} + P_{23} + P_{12}P_{23} + P_{12}P_{13}) \end{aligned}$$

2. No exclusion principle for bosons

$\rightarrow$ energetically lowest state, if all the three bosons occupy the one-particle ground state:

$$E_0^{(+)} = 3\varepsilon_0$$

$$\begin{aligned} |E_0^{(+)}\rangle &= S_3^{(+)}|0\,0\,0\rangle \\ &= S_3^{(+)}\big(|0\rangle^{(1)}\,|0\rangle^{(2)}\,|0\rangle^{(3)}\big) \\ &= |0\rangle^{(1)}\,|0\rangle^{(2)}\,|0\rangle^{(3)}\ . \end{aligned}$$

3. By reason of the Pauli principle it follows for the ground state: one fermion in $|0\rangle$, the other in $|1\rangle$:

$$E_0^{(-)} = \alpha + 2\varepsilon_0$$

$$\begin{aligned} |E_0^{(-)}\rangle &= S_2^{(-)}|0\,1\rangle = S_2^{(-)}\big(|0\rangle^{(1)}\,|1\rangle^{(2)}\big) \\ &= \frac{1}{2}\big(|0\rangle^{(1)}\,|1\rangle^{(2)} - |0\rangle^{(2)}\,|1\rangle^{(1)}\big) \\ &= \frac{1}{2}\begin{vmatrix} |0\rangle^{(1)} & |0\rangle^{(2)} \\ |1\rangle^{(1)} & |1\rangle^{(2)} \end{vmatrix} \end{aligned}$$

(not-normalized) Slater determinant .

4. First excited state $\widehat{=}$ 1 boson in $|1\rangle$, 2 bosons in $|0\rangle$:

$$E_1^{(+)} = \alpha + 3\varepsilon_0$$

$$\begin{aligned} |E_1^{(+)}\rangle &= S_3^{(+)}|0\,0\,1\rangle \\ &= S_3^{(+)}\big(|0\rangle^{(1)}\,|0\rangle^{(2)}\,|1\rangle^{(3)}\big) \\ &= \frac{1}{6}\big(|0\rangle^{(1)}\,|0\rangle^{(2)}\,|1\rangle^{(3)} + |0\rangle^{(2)}\,|0\rangle^{(1)}\,|1\rangle^{(3)} + |0\rangle^{(3)}\,|0\rangle^{(2)}\,|1\rangle^{(1)} \\ &\quad + |0\rangle^{(1)}\,|0\rangle^{(3)}\,|1\rangle^{(2)} + |0\rangle^{(3)}\,|0\rangle^{(1)}\,|1\rangle^{(2)} + |0\rangle^{(2)}\,|0\rangle^{(3)}\,|1\rangle^{(1)}\big) \\ &= \frac{1}{3}\big(|0\,0\,1\rangle + |0\,1\,0\rangle + |1\,0\,0\rangle\big) \qquad \text{(states not symmetrized).} \end{aligned}$$

Solution 8.2.9

1. Eigen-functions are plane waves:

$$\varphi_{\mathbf{k}}(\mathbf{r}) \sim e^{i\,\mathbf{k}\cdot\mathbf{r}}\ .$$

Periodic boundary conditions:

$$k_{x,y,z} = \frac{2\pi}{L}\,n_{x,y,z}\ ; \quad n_{x,y,z} \in \mathbb{Z}\ .$$

Energies:

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} = \frac{2\pi^2\hbar^2}{m\,L^2}\left(n_x^2 + n_y^2 + n_z^2\right)\ .$$

2. Ground state:

   a) Bosons:
   All particles are in the energetically lowest state,

   b) Fermions ($S = 1/2$):
   Each state can be occupied by at most two electrons of opposite spins ($m_s = \pm 1/2$) (Pauli principle)!

   Per *grid volume* $\Delta k = (2\pi/L)^3$ there is state in the $\mathbf{k}$-space one, which can at most be twofold occupied. In the ground-state, therefore N fermions enter all the states inside the so-called *Fermi sphere*, whose radius k_F (*Fermi wave vector*) is determined by the particle number N,

$$N = 2\,\frac{(4\pi/3)\,k_\mathrm{F}^3}{\Delta k} = \frac{L^3\,k_\mathrm{F}^3}{3\pi^2}\ ,$$

   in the form:

$$\Longrightarrow\ k_\mathrm{F} = \left(3\pi^2\,\frac{N}{V}\right)^{1/3}\ ;\quad p_\mathrm{F} = \hbar\,k_\mathrm{F}\ .$$

3. *Fermi energy*: maximal one-particle energy:

$$\varepsilon_\mathrm{F} = \frac{\hbar^2 k_\mathrm{F}^2}{2m}\ .$$

   Ground-state energy:

$$\begin{aligned} E_0^{(\mathrm{F})} &= 2\sum_{\mathbf{k}}^{k\le k_\mathrm{F}} \frac{\hbar^2k^2}{2m} = \frac{2}{\Delta k}\int\limits_{(k\le k_\mathrm{F})} d^3k\,\frac{\hbar^2k^2}{2m} = \frac{L^3}{4\pi^3}\,4\pi\int\limits_0^{k_\mathrm{F}} dk\,k^2\,\frac{\hbar^2k^2}{2m} \\ &= \frac{V\,\hbar^2}{2m\,\pi^2}\,\frac{k_\mathrm{F}^5}{5} = \frac{V\,\varepsilon_\mathrm{F}}{5\pi^2}\,k_\mathrm{F}^3 \end{aligned}$$

$$\Longrightarrow\ E_0^{(\mathrm{F})} = \frac{3}{5}\,N\,\varepsilon_\mathrm{F}\ .$$

   For bosons it is of course:

$$E_0^{(\mathrm{O})} = 0\ .$$

Solution 8.2.10

The Hamilton operator

$$H = H^{(1)} + H^{(2)} + H^{(3)} = \sum_{i\,=\,1}^{3}\left(-\frac{\hbar^2}{2m}\,\frac{d^2}{dq_i^2} + V(q_i)\right)$$

is spin-independent. Therefore the eigen-state separates in a position and a spin part. Since all the three particles possess the spin $S = 0$, the spin state is trivially symmetric with respect to particle interchange. Therefore we need to

discuss in the following only the position part. This also must be symmetric, because the particles are bosons.

One-particle problem (see solution of Exercise (8.2.5)) and ((4.2.1), Vol. 6):

$$\begin{aligned}
\varphi_{n-}(q) &= \frac{1}{\sqrt{q_0}} \sin\left(\frac{\pi}{q_0}\, n\, q\right) \\
E_{n-} &= \frac{\hbar^2\pi^2}{2m\, q_0^2}\, n^2\,, \qquad n = 1, 2, 3, \dots\,, \\
\varphi_{n+}(q) &= \frac{1}{\sqrt{q_0}} \cos\left[\frac{\pi}{2q_0}\,(2n+1)\, q\right]\,, \\
E_{n+} &= \frac{\hbar^2\pi^2}{8m\, q_0^2}\,(2n+1)^2 \qquad n = 0, 1, 2, \dots\,.
\end{aligned}$$

Hence, the two energetically lowest one-particle states are:

$$\begin{aligned}
|0\rangle \longleftrightarrow \varphi_{0+}(q) &= \frac{1}{\sqrt{q_0}} \cos\left(\frac{\pi}{2q_0}\, q\right)\,, \\
E_{0+} &= \frac{\hbar^2\pi^2}{8m\, q_0^2}\,, \\
|1\rangle \longleftrightarrow \varphi_{1-}(q) &= \frac{1}{\sqrt{q_0}} \sin\left(\frac{\pi}{q_0}\, q\right)\,, \\
E_{1-} &= \frac{\hbar^2\pi^2}{2m\, q_0^2}\,.
\end{aligned}$$

Ground state $|E_0\rangle^{(+)}$ of the three-particle system:

$$|E_0\rangle^{(+)} \overset{(8.84)}{=} \sqrt{\frac{3!}{3!}}\, S_3^{(+)} \left(|0\rangle^{(1)}|0\rangle^{(2)}|0\rangle^{(3)}\right)\,.$$

According to Solution 8.2.3:

$$\begin{aligned}
S_3^{(+)} &= \frac{1}{6}\,(\mathbb{1}_3 + P_{12} + P_{13} + P_{23} + P_{12}\,P_{23} + P_{12}\,P_{13}) \\
\Longrightarrow\ S_3^{(+)}|0\,0\,0\rangle &= \frac{1}{6}\,6\mathbb{1}_3|0\,0\,0\rangle = |0\rangle^{(1)}|0\rangle^{(2)}|0\rangle^{(3)} \\
\Longrightarrow\ |E_0\rangle^{(+)} &\leftrightarrow \frac{1}{\sqrt{q_0^3}} \cos\left(\frac{\pi}{2q_0}\, q_1\right) \cos\left(\frac{\pi}{2q_0}\, q_2\right) \cos\left(\frac{\pi}{2q_0}\, q_3\right)\,.
\end{aligned}$$

First excited state $|E_1\rangle^{(+)}$:

Two particles in the state $|0\rangle$, the third in the state $|1\rangle$

$$\begin{aligned} |E_1\rangle^{(+)} &= \frac{\sqrt{3!}}{\sqrt{2!\,1!}}\, S_3^{(+)} \left(|0\rangle^{(1)}|0\rangle^{(2)}|1\rangle^{(3)}\right) \\ &= \frac{\sqrt{3}}{6}\left(|0\,0\,1\rangle + |0\,0\,1\rangle + |1\,0\,0\rangle + |0\,1\,0\rangle + |1\,0\,0\rangle + |0\,1\,0\rangle\right) \\ &= \frac{1}{\sqrt{3}}\left(|0\,0\,1\rangle + |1\,0\,0\rangle + |0\,1\,0\rangle\right) \\ \Longrightarrow\ |E_1\rangle^{(+)} &\longleftrightarrow \frac{1}{\sqrt{3q_0^3}}\left[\cos\left(\frac{\pi}{2q_0}\,q_1\right)\cos\left(\frac{\pi}{2q_0}\,q_2\right)\sin\left(\frac{\pi}{q_0}\,q_3\right)\right. \\ &\quad + \sin\left(\frac{\pi}{q_0}\,q_1\right)\cos\left(\frac{\pi}{2q_0}\,q_2\right)\cos\left(\frac{\pi}{2q_0}\,q_3\right) \\ &\quad \left. + \cos\left(\frac{\pi}{2q_0}\,q_1\right)\sin\left(\frac{\pi}{q_0}\,q_2\right)\cos\left(\frac{\pi}{2q_0}\,q_3\right)\right]\,. \end{aligned}$$

Eigen-energies: $E_0 = 3E_{0+}$; $E_1 = 2E_{0+} + E_{1-}$.

Section 8.3.4

Solution 8.3.1
Bosons:

$$|\cdots n_{\alpha_r}\cdots n_{\alpha_s}\cdots\rangle^{(+)}\,:\ \textbf{arbitrary}\ \text{Fock state.}$$

***r* ≠ *s* :**

$$\begin{aligned} & a^+_{\alpha_r}\, a^+_{\alpha_s}\,|\cdots n_{\alpha_r}\cdots n_{\alpha_s}\cdots\rangle^{(+)} \\ = \ & \sqrt{n_{\alpha_r}+1}\,\sqrt{n_{\alpha_s}+1}\,|\cdots n_{\alpha_r}+1\cdots n_{\alpha_s}+1\cdots\rangle^{(+)} \\ = \ & a^+_{\alpha_s}\, a^+_{\alpha_r}\,|\cdots n_{\alpha_r}\cdots n_{\alpha_s}\cdots\rangle^{(+)} \\ \Longrightarrow \ & \left[a^+_{\alpha_r}, a^+_{\alpha_s}\right]_- = 0\,. \end{aligned}$$

For $r = s$ this relation is trivially fulfilled.

Because of

$$[a_{\alpha_r}, \alpha_{\alpha_s}]_- = \left(\left[a^+_{\alpha_s}, a^+_{\alpha_r}\right]_-\right)^+$$

it follows immediately:

$$[a_{\alpha_r}, a_{\alpha_s}]_- = 0\,.$$

***r* ≠ *s* :**

$$\begin{aligned} a_{\alpha_r}a^+_{\alpha_s}|\cdots n_{\alpha_r}\cdots n_{\alpha_s}\cdots\rangle^{(+)} &= \sqrt{n_{\alpha_r}}\sqrt{n_{\alpha_s}+1}|\cdots n_{\alpha_r}-1\cdots n_{\alpha_s}+1\cdots\rangle^{(+)} \\ &= a^+_{\alpha_s}a_{\alpha_r}|\cdots n_{\alpha_r}\cdots n_{\alpha_s}\cdots\rangle^{(+)}\,. \end{aligned}$$

r = s :

$$\begin{aligned} a_{\alpha_r}\, a^+_{\alpha_r} |\cdots n_{\alpha_r} \cdots\rangle^{(+)} &= a_{\alpha_r}\, \sqrt{n_{\alpha_r}+1}\, |\cdots n_{\alpha_r}+1 \cdots\rangle^{(+)} \\ &= (n_{\alpha_r}+1) |\cdots n_{\alpha_r} \cdots\rangle^{(+)} , \\ a^+_{\alpha_r}\, a_{\alpha_r} |\cdots n_{\alpha_r} \cdots\rangle^{(+)} &= \sqrt{n_{\alpha_r}}\, a^+_{\alpha_r} |\cdots n_{\alpha_r}-1 \cdots\rangle^{(+)} = n_{\alpha_r} |\cdots n_{\alpha_r} \cdots\rangle^{(+)} \end{aligned}$$

$$\Longrightarrow \; [a_{\alpha_r}, a^+_{\alpha_s}]_- = \delta_{r,s} \; .$$

Fermions:

$$\left(a^+_{\alpha_r}\right)^2 |\cdots n_{\alpha_r} \cdots\rangle^{(-)} = 0 \quad \textit{(Pauli principle!)} \quad (8.104)$$

r < s :

$$\begin{aligned} & a^+_{\alpha_r}\, a^+_{\alpha_s} |\cdots n_{\alpha_r} \cdots n_{\alpha_s} \cdots\rangle^{(-)} \\ = \;& a^+_{\alpha_r}\, (-1)^{N_s}\, \delta_{n_{\alpha_s},0} |\cdots n_{\alpha_r} \cdots n_{\alpha_s}+1 \cdots\rangle^{(-)} \\ = \;& (-1)^{N_r}\, (-1)^{N_s}\, \delta_{n_{\alpha_s},0}\, \delta_{n_{\alpha_r},0} |\cdots n_{\alpha_r}+1 \cdots n_{\alpha_s}+1 \cdots\rangle^{(-)} , \\ & a^+_{\alpha_s}\, a^+_{\alpha_r} |\cdots n_{\alpha_r} \cdots n_{\alpha_s} \cdots\rangle^{(-)} \\ = \;& (-1)^{N_r}\, \delta_{n_{\alpha_r},0}\, a^+_{\alpha_s} |\cdots n_{\alpha_r}+1 \cdots n_{\alpha_s} \cdots\rangle^{(-)} \\ = \;& (-1)^{N_r}\, (-)^{N'_s}\, \delta_{n_{\alpha_r},0}\, \delta_{n_{\alpha_s},0} |\cdots n_{\alpha_r}+1 \cdots n_{\alpha_s}+1 \cdots\rangle^{(-)} , \end{aligned}$$

$$\begin{aligned} N'_s &= N_s + 1 \\ \Longrightarrow \left(a^+_{\alpha_r}\, a^+_{\alpha_s} + a^+_{\alpha_s}\, a^+_{\alpha_r}\right) |\cdots n_{\alpha_r} \cdots n_{\alpha_s} \cdots\rangle^{(-)} &= 0 \\ \Longrightarrow \left[a^+_{\alpha_r}, a^+_{\alpha_s}\right]_+ &= 0 \; . \end{aligned}$$

Because of

$$[a_{\alpha_r}, a_{\alpha_s}]_+ = \left(\left[a^+_{\alpha_s}, a^+_{\alpha_r}\right]_+\right)^+$$

it follows again immediately the second anti-commutator relation:

$$[a_{\alpha_r}, a_{\alpha_s}]_+ = 0 \; .$$

r = s :

$$\begin{aligned} a_{\alpha_r}\, a^+_{\alpha_r} |\cdots n_{\alpha_r} \cdots\rangle^{(-)} &= a_{\alpha_r}\, (-1)^{N_r}\, \delta_{n_{\alpha_r},0} |\cdots n_{\alpha_r}+1 \cdots\rangle^{(-)} \\ &= (-1)^{2N_r}\, \delta_{n_{\alpha_r},0} |\cdots n_{\alpha_r} \cdots\rangle^{(-)} \\ &= \delta_{n_{\alpha_r},0} |\cdots n_{\alpha_r} \cdots\rangle^{(-)} , \\ a^+_{\alpha_r}\, a_{\alpha_r} |\cdots n_{\alpha_r} \cdots\rangle^{(-)} &= \delta_{n_{\alpha_r},1} |\cdots n_{\alpha_r} \cdots\rangle^{(-)} . \end{aligned}$$

Since in any case $n_{\alpha_r} = 0$ or 1:

$$\left(a_{\alpha_r}\, a^+_{\alpha_r} + a^+_{\alpha_r}\, a_{\alpha_r}\right) |\cdots n_{\alpha_r} \cdots\rangle^{(-)} = |\cdots n_{\alpha_r} \cdots\rangle^{(-)} \; .$$

$\boldsymbol{r < s}$ **:**

$$
\begin{aligned}
& a_{\alpha_r}\, a^+_{\alpha_s} |\cdots n_{\alpha_r} \cdots n_{\alpha_s} \cdots\rangle^{(-)} \\
= \;& a_{\alpha_r}\, (-1)^{N_s}\, \delta_{n_{\alpha_s},0} |\cdots n_{\alpha_r} \cdots n_{\alpha_s} + 1 \cdots\rangle^{(-)} \\
= \;& (-1)^{N_r+N_s}\, \delta_{n_{\alpha_r},1}\, \delta_{n_{\alpha_s},0} |\cdots n_{\alpha_r} - 1 \cdots n_{\alpha_s} + 1 \cdots\rangle^{(-)} \,, \\
& a^+_{\alpha_s}\, a_{\alpha_r} |\cdots n_{\alpha_r} \cdots n_{\alpha_s} \cdots\rangle^{(-)} \\
= \;& a^+_{\alpha_s}\, (-1)^{N_r}\, \delta_{n_{\alpha_r},1} |\cdots n_{\alpha_r} - 1 \cdots n_{\alpha_s} \cdots\rangle^{(-)} \\
= \;& (-1)^{N_r+N''_s}\, \delta_{n_{\alpha_r},1}\, \delta_{n_{\alpha_s},0} |\cdots n_{\alpha_r} - 1 \cdots n_{\alpha_s} + 1 \cdots\rangle^{(-)} \,,
\end{aligned}
$$

$$
\begin{aligned}
& & N''_s &= N_s - 1 \\
\Longrightarrow\; & \left(a_{\alpha_r}\, a^+_{\alpha_s} + a^+_{\alpha_s}\, a_{\alpha_r}\right) |\cdots n_{\alpha_r} \cdots n_{\alpha_s} \cdots\rangle^{(-)} &= 0 \,.
\end{aligned}
$$

Finally we have:

$$
\left[a_{\alpha_r}, a^+_{\alpha_s}\right]_+ = \delta_{r,s} \,.
$$

Solution 8.3.2

Proof by full induction:

$\boldsymbol{N = 1}$

$$
\begin{aligned}
\langle 0| a_{\beta_1}\, a^+_{\alpha_1} |0\rangle &= \left\langle 0\right| \left[\delta(\beta_1,\alpha_1) \pm a^+_{\alpha_1}\, a_{\beta_1}\right] |0\rangle \\
&= \delta(\beta_1,\alpha_1) \langle 0|0\rangle \pm \langle 0| a^+_{\alpha_1}\, a_{\beta_1} |0\rangle = \delta(\beta_1,\alpha_1) \\
\text{because of } a_{\beta_1}|0\rangle &= 0 \,.
\end{aligned}
$$

$\boldsymbol{N-1 \longrightarrow N}$

$$
\begin{aligned}
& \alpha_{\beta_1} : \textit{ pull to the right} \\
& \langle 0| a_{\beta_N} \cdots a_{\beta_1}\, a^+_{\alpha_1} \cdots a^+_{\alpha_N} |0\rangle \\
= \;& \delta(\beta_1,\alpha_1) \langle 0| a_{\beta_N} \cdots a_{\beta_2}\, a^+_{\alpha_2} \cdots a^+_{\alpha_N} |0\rangle \\
& +(\pm)^1 \delta(\beta_1,\alpha_2) \langle 0| a_{\beta_N} \cdots a_{\beta_2}\, a^+_{\alpha_1}\, a^+_{\alpha_3} \cdots a^+_{\alpha_N} |0\rangle \\
& + \cdots \\
& +(\pm)^{N-1}\, \delta(\beta_1,\alpha_N) \langle 0| a_{\beta_N} \cdots a_{\beta_2}\, a^+_{\alpha_1}\, a^+_{\alpha_2} \cdots a^+_{\alpha_{N-1}} |0\rangle \\
& \quad \textit{presumption of the induction} \\
= \;& \delta(\beta_1,\alpha_1) \sum_{\mathcal{P}_\alpha} (\pm)^{p_\alpha}\, \mathcal{P}_\alpha \left[\delta(\beta_2,\alpha_2) \cdots \delta(\beta_N,\alpha_N)\right] \\
& +(\pm)^1 \delta(\beta_1,\alpha_2) \sum_{\mathcal{P}_\alpha} (\pm)^{p_\alpha}\, \mathcal{P}_\alpha \left[\delta(\beta_2,\alpha_1)\delta(\beta_3,\alpha_3) \cdots \delta(\beta_N,\alpha_N)\right] \\
& + \ldots \\
& +(\pm)^{N-1}\, \delta(\beta_1,\alpha_N) \sum_{\mathcal{P}_\alpha} (\pm)^{p_\alpha}\, \mathcal{P}_\alpha \left[\delta(\beta_2,\alpha_1)\delta(\beta_3,\alpha_2) \cdots \delta(\beta_N,\alpha_{N-1})\right] \\
= \;& \sum_{\mathcal{P}_\alpha} (\pm)^{p_\alpha}\, \mathcal{P}_\alpha \left[\delta(\beta_1,\alpha_1)\delta(\beta_2,\alpha_2) \cdots \delta(\beta_N,\alpha_N)\right] \,.
\end{aligned}
$$

Solution 8.3.3

1.

$$\begin{aligned}[\hat{n}_\alpha, a_\beta^+]_- &= a_\alpha^+ a_\alpha a_\beta^+ - a_\beta^+ a_\alpha^+ a_\alpha = \delta(\alpha-\beta)\, a_\alpha^+ \pm a_\alpha^+ a_\beta^+ a_\alpha - a_\beta^+ a_\alpha^+ a_\alpha \\ &= \delta(\alpha-\beta)\, a_\alpha^+ + a_\beta^+ a_\alpha^+ a_\alpha - a_\beta^+ a_\alpha^+ a_\alpha = \delta(\alpha-\beta)\, a_\alpha^+ \,.\end{aligned}$$

2.

$$\begin{aligned}[\hat{n}_\alpha, a_\beta]_- &= a_\alpha^+ a_\alpha a_\beta - a_\beta a_\alpha^+ a_\alpha = a_\alpha^+ a_\alpha a_\beta - \delta(\beta-\alpha)\, a_\alpha \mp a_\alpha^+ a_\beta a_\alpha \\ &= a_\alpha^+ a_\alpha a_\beta - \delta(\beta-\alpha)\, a_\alpha - a_\alpha^+ a_\alpha a_\beta = -\delta(\alpha-\beta)\, a_\alpha \,.\end{aligned}$$

These relations are valid for fermions as well as bosons.

Solution 8.3.4

1.

$$\begin{aligned}[\hat{n}_{\alpha_r}, a_{\alpha_s}^+]_- &= a_{\alpha_r}^+ a_{\alpha_r} a_{\alpha_s}^+ - a_{\alpha_s}^+ a_{\alpha_r}^+ a_{\alpha_r} = a_{\alpha_r}^+ \delta_{rs} \pm a_{\alpha_r}^+ a_{\alpha_s}^+ a_{\alpha_r} - a_{\alpha_s}^+ a_{\alpha_r}^+ a_{\alpha_r} \\ &= a_{\alpha_r}^+ \delta_{rs} + a_{\alpha_s}^+ a_{\alpha_r}^+ a_{\alpha_r} - a_{\alpha_s}^+ a_{\alpha_r}^+ a_{\alpha_r} = \delta_{rs} a_{\alpha_r}^+ \,.\end{aligned}$$

2.

$$\begin{aligned}[\hat{n}_{\alpha_r}, a_{\alpha_s}]_- &= a_{\alpha_r}^+ a_{\alpha_r} a_{\alpha_s} - a_{\alpha_s} a_{\alpha_r}^+ a_{\alpha_r} \\ &= a_{\alpha_r}^+ a_{\alpha_r} a_{\alpha_s} - \delta_{rs} a_{\alpha_r} \mp a_{\alpha_r}^+ a_{\alpha_s} a_{\alpha_r} \\ &= a_{\alpha_r}^+ a_{\alpha_r} a_{\alpha_s} - \delta_{rs} a_{\alpha_r} - a_{\alpha_r}^+ a_{\alpha_r} a_{\alpha_s} = -\delta_{rs} a_{\alpha_r} \,.\end{aligned}$$

These relations are likewise valid for fermions as well as bosons. In the intermediate steps of the calculations the upper signs always hold for bosons and the lower ones for fermions.

Solution 8.3.5

1.

$$\begin{aligned}[a_\alpha, a_\beta]_+ &= 0 \;\curvearrowright\; [a_\alpha, a_\alpha]_+ = 2a_\alpha^2 = 0 \;\curvearrowright\; a_\alpha^2 = 0 \\ \left[a_\alpha^+, a_\beta^+\right]_+ &= 0 \;\curvearrowright\; \left[a_\alpha^+, a_\alpha^+\right]_+ = 2\left(a_\alpha^+\right)^2 = 0 \;\curvearrowright\; \left(a_\alpha^+\right)^2 = 0\end{aligned}$$

(Pauli principle!)

2.

$$\begin{aligned}\widehat{n}_\alpha^2 &= a_\alpha^+ a_\alpha a_\alpha^+ a_\alpha = a_\alpha^+ \left(1 - a_\alpha^+ a_\alpha\right) a_\alpha \\ &= a_\alpha^+ a_\alpha - \left(a_\alpha^+\right)^2 (a_\alpha)^2 \overset{1.}{=} \widehat{n}_\alpha \qquad \text{(Pauli principle!)}\end{aligned}$$

3.

$$\begin{aligned}a_\alpha \widehat{n}_\alpha &= a_\alpha a_\alpha^+ a_\alpha = \left(1 - a_\alpha^+ a_\alpha\right) a_\alpha \overset{1.}{=} a_\alpha \\ a_\alpha^+ \widehat{n}_\alpha &= a_\alpha^+ a_\alpha^+ a_\alpha \overset{1.}{=} 0\end{aligned}$$

4.

$$\begin{aligned}\widehat{n}_\alpha\, a_\alpha &= a_\alpha^+ a_\alpha a_\alpha \overset{1.}{=} 0 \\ \widehat{n}_\alpha\, a_\alpha^+ &= a_\alpha^+ a_\alpha a_\alpha^+ = a_\alpha^+ \left(1 - a_\alpha^+ a_\alpha\right) \overset{1.}{=} a_\alpha^+\end{aligned}$$

Solution 8.3.6

$$\widehat{N} = \int d\alpha\, \hat{n}_\alpha \ .$$

We calculate at first the following commutators:

$$[\widehat{N}, a^+_\beta]_- = \int d\alpha [\hat{n}_\alpha, a^+_\beta]_- \overset{\text{ex. } 8.3.3}{=} \int d\alpha\, a^+_\alpha\, \delta(\alpha - \beta) = a^+_\beta \ ,$$

$$[\widehat{N}, a_\beta]_- = \int d\alpha\, [\hat{n}_\alpha, a_\beta]_- \overset{\text{ex. } 8.3.3}{=} \int d\alpha\, [-\delta(\alpha - \beta)\, a_\alpha] = -a_\beta \ .$$

It thus holds:

$$\widehat{N}\, a^+_\beta = a^+_\beta\, (\widehat{N} + \mathbb{1}) \ ; \quad \widehat{N}\, a_\beta = a_\beta\, (\widehat{N} - \mathbb{1}) \ .$$

1.

$$\widehat{N}\, \left(a^+_\beta |\varphi_{\alpha_1} \cdots\rangle^{(\pm)}\right) = a^+_\beta\, (\widehat{N} + \mathbb{1}) |\varphi_{\alpha_1} \cdots\rangle^{(\pm)} = (N+1)\, \left(a^+_\beta |\varphi_{\alpha_1} \cdots\rangle^{(\pm)}\right) \ .$$

It is, as stated, an eigen-state. The eigen-value is $N+1$. The denotation *creator* for a^+_β is obviously reasonable!

2.

$$\widehat{N}\, \left(a_\beta |\varphi_{\alpha_1} \cdots\rangle^{(\pm)}\right) = a_\beta\, (\widehat{N} - \mathbb{1}) |\varphi_{\alpha_1} \cdots\rangle^{(\pm)} = (N-1)\, \left(a_\beta |\varphi_{\alpha_1} \cdots\rangle^{(\pm)}\right) \ .$$

$a_\beta |\varphi_{\alpha_1} \cdots\rangle^{(\pm)}$ is thus also an eigen-state of the particle number operator $\widehat{N}$ with the eigen-value $N-1$. The name *annihilator* for a_β becomes therewith plausible.

Solution 8.3.7

Plane wave:

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}}\, e^{i\, \mathbf{k}\cdot\mathbf{r}} = \langle \mathbf{r} | \mathbf{k} \rangle \ .$$

Periodic boundary conditions:

$$\begin{aligned} V &= L^3 \ , \\ \varphi_{\mathbf{k}}(x+L, y, z) \overset{!}{=} \varphi_{\mathbf{k}}(x, y+L, z) &\overset{!}{=} \varphi_{\mathbf{k}}(x, y, z+L) \overset{!}{=} \varphi_{\mathbf{k}}(x, y, z) \\ \Longrightarrow\ k_{x,y,z} = \frac{2\pi}{L}\, n_{x,y,z} \quad &; \qquad n_{x,\,y,\,z} \in \mathbb{Z} \ \text{ discrete!} \end{aligned}$$

Kinetic energy:
One-particle basis: $|\mathbf{k}\,\sigma\rangle = |\mathbf{k}\rangle|\sigma\rangle$

$$\begin{aligned}
\sigma &= \uparrow,\downarrow \longleftrightarrow\ m_{s=1/2} = +\frac{1}{2},\,-\frac{1}{2}\,, \\
5.172:\ |\uparrow\rangle &= \begin{pmatrix}1\\0\end{pmatrix}\ ;\quad |\downarrow\rangle = \begin{pmatrix}0\\1\end{pmatrix}\,, \\
\left\langle \mathbf{k}\,\sigma \left| \frac{\mathbf{p}^2}{2m} \right| \mathbf{k}'\,\sigma' \right\rangle &= \frac{\hbar^2 k'^2}{2m}\,\langle \mathbf{k}\,\sigma|\mathbf{k}'\sigma'\rangle = \frac{\hbar^2 k'^2}{2m}\,\delta_{\mathbf{k}\mathbf{k}'}\,\delta_{\sigma\sigma'} \\
\Longrightarrow \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} &= \sum_{\mathbf{k}\mathbf{k}'\sigma\sigma'} \left\langle \mathbf{k}\,\sigma \left| \frac{\mathbf{p}^2}{2m} \right| \mathbf{k}'\sigma' \right\rangle a^+_{\mathbf{k}\sigma}\,a_{\mathbf{k}'\sigma'} = \sum_{\mathbf{k}\sigma} \frac{\hbar^2 k^2}{2m}\,a^+_{\mathbf{k}\sigma}\,a_{\mathbf{k}\sigma}\,.
\end{aligned}$$

Interaction:

$$\begin{aligned}
&\left\langle \mathbf{k}_1\,\sigma_1, \mathbf{k}_2\,\sigma_2 \left| \frac{1}{|\hat{\mathbf{r}}^{(1)} - \hat{\mathbf{r}}^{(2)}|} \right| \mathbf{k}_3\,\sigma_3, \mathbf{k}_4\,\sigma_4 \right\rangle \\
&= \delta_{\sigma_1\sigma_3}\,\delta_{\sigma_2\sigma_4} \left\langle \mathbf{k}_1\,\mathbf{k}_2 \left| \frac{1}{|\hat{\mathbf{r}}^{(1)} - \hat{\mathbf{r}}^{(2)}|} \right| \mathbf{k}_3\,\mathbf{k}_4 \right\rangle\,.
\end{aligned}$$

The interaction is spin-independent. The spin parts of the one-particle states can therefore be directly evaluated leading to the two Kronecker-deltas. The two-particle states are non-symmetrized:

$$\begin{aligned}
&\left\langle \mathbf{k}_1\,\mathbf{k}_2 \left| \frac{1}{|\hat{\mathbf{r}}^{(1)} - \hat{\mathbf{r}}^{(2)}|} \right| \mathbf{k}_3\,\mathbf{k}_4 \right\rangle \\
&= \iint d^3r_1\,d^3r_2 \left\langle \mathbf{k}_1\,\mathbf{k}_2 \left| \frac{1}{|\hat{\mathbf{r}}^{(1)} - \hat{\mathbf{r}}^{(2)}|} \right| \mathbf{r}_1\,\mathbf{r}_2 \right\rangle \langle \mathbf{r}_1\,\mathbf{r}_2\,|\mathbf{k}_3\,\mathbf{k}_4\rangle \\
&= \iint d^3r_1\,d^3r_2\,\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \langle \mathbf{k}_1^{(1)}|\mathbf{r}_1^{(1)}\rangle \langle \mathbf{k}_2^{(2)}|\mathbf{r}_2^{(2)}\rangle \langle \mathbf{r}_1^{(1)}|\mathbf{k}_3^{(1)}\rangle \langle \mathbf{r}_2^{(2)}|\mathbf{k}_4^{(2)}\rangle \\
&= \frac{1}{V^2} \iint d^3r_1\,d^3r_2\,\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\,e^{i(\mathbf{k}_3 - \mathbf{k}_1)\cdot\mathbf{r}_1}\,e^{i(\mathbf{k}_4 - \mathbf{k}_2)\cdot\mathbf{r}_2} \\
&= \delta_{\mathbf{k}_1 + \mathbf{k}_2,\,\mathbf{k}_3 + \mathbf{k}_4}\,\frac{1}{V} \int d^3r\,\frac{1}{r}\,e^{i(\mathbf{k}_3 - \mathbf{k}_1)\cdot\mathbf{r}}\,.
\end{aligned}$$

The last step results from the introduction of relative and center-of-mass coordinates, likewise as in (8.119).

$\alpha > 0$: convergence generating factor

$$\begin{aligned}
\lim_{\alpha\to 0} \int d^3r\,\frac{1}{r}\,e^{i\,\mathbf{q}\cdot\mathbf{r}}\,e^{-\alpha r} &= \lim_{\alpha\to 0}\,2\pi \int_{-1}^{+1} dx \int_0^{\infty} dr\,r\,e^{iqrx}\,e^{-\alpha r} \\
= \lim_{\alpha\to 0}\,\frac{2\pi}{i\,q} \int_0^{\infty} dr\,\left(e^{iqr} - e^{-iqr}\right) e^{-\alpha r} &= \lim_{\alpha\to 0}\,\frac{4\pi}{q^2 + \alpha^2} = \frac{4\pi}{q^2}\,.
\end{aligned}$$

The interaction-matrix element is therewith calculated as follows:

$$\begin{aligned} & \left\langle \mathbf{k}_1\,\sigma_1, \mathbf{k}_2\,\sigma_2 \left| \frac{1}{\left|\hat{\mathbf{r}}^{(1)} - \hat{\mathbf{r}}^{(2)}\right|} \right| \mathbf{k}_3\,\sigma_3, \mathbf{k}_4\,\sigma_4 \right\rangle \\ = \;& \delta_{\sigma_1\sigma_3}\,\delta_{\sigma_2\sigma_4}\,\delta_{\mathbf{k}_1+\mathbf{k}_2,\mathbf{k}_3+\mathbf{k}_4}\,\frac{4\pi}{V\,|\mathbf{k}_3-\mathbf{k}_1|^2}\;. \end{aligned}$$

The interaction thus reads in second quantization:

$$\begin{aligned} & \frac{1}{2}\sum_{i,\,j}^{i\neq j}\frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} \\ = \;& \frac{1}{2}\sum_{\substack{\mathbf{k}_1\sigma_1,\,\mathbf{k}_2\sigma_2,\\ \mathbf{k}_3\sigma_3,\,\mathbf{k}_4\sigma_4}} \left\langle \mathbf{k}_1\,\sigma_1, \mathbf{k}_2\,\sigma_2 \left| \frac{1}{\left|\hat{\mathbf{r}}^{(1)} - \hat{\mathbf{r}}^{(2)}\right|} \right| \mathbf{k}_3\,\sigma_3, \mathbf{k}_4\,\sigma_4 \right\rangle \cdot \\ & \qquad \cdot a^+_{\mathbf{k}_1\sigma_1}\,a^+_{\mathbf{k}_2\sigma_2}\,a_{\mathbf{k}_4\sigma_4}\,a_{\mathbf{k}_3\sigma_3} \\ = \;& \frac{1}{2}\sum_{\substack{\mathbf{k}_1\sigma_1,\,\mathbf{k}_2\sigma_2\\ \mathbf{k}_3}} \frac{4\pi}{V|\mathbf{k}_3-\mathbf{k}_1|^2}\,a^+_{\mathbf{k}_1\sigma_1}\,a^+_{\mathbf{k}_2\sigma_2}\,a_{\mathbf{k}_1+\mathbf{k}_2-\mathbf{k}_3\sigma_2}\,a_{\mathbf{k}_3\sigma_1}\;. \end{aligned}$$

We put

$$\mathbf{k}_1 \to \mathbf{k}+\mathbf{q}\,; \quad \mathbf{k}_2 \to \mathbf{p}-\mathbf{q}\,; \quad \mathbf{k}_3 \to \mathbf{k}\,; \quad \sigma_1 \to \sigma\,; \quad \sigma_2 \to \sigma'$$

and have then, after all, the Hamilton operator of the N-electron system in second quantization:

$$\begin{aligned} H_N &= \sum_{\mathbf{k}\sigma}\varepsilon_0(\mathbf{k})\,a^+_{\mathbf{k}\sigma}\,a_{\mathbf{k}\sigma} + \frac{1}{2}\sum_{\substack{\mathbf{kpq}\\ \sigma\sigma'}} v_0(\mathbf{q})\,a^+_{\mathbf{k}+\mathbf{q}\sigma}\,a^+_{\mathbf{p}-\mathbf{q}\sigma'}\,a_{\mathbf{p}\sigma'}\,a_{\mathbf{k}\sigma}\;, \\ \varepsilon_0(\mathbf{k}) &= \frac{\hbar^2k^2}{2m}\;; \quad v_0(\mathbf{q}) = \frac{e^2}{\varepsilon_0 V\,q^2}\;. \end{aligned}$$

Solution 8.3.8

$\widehat{\rho}$ is a one-particle operator. According to (8.113) it must be:

$$\widehat{\rho}(\mathbf{r}) = \sum_{\substack{\mathbf{k},\,\mathbf{k}'\\ \sigma,\,\sigma'}} \langle \mathbf{k}\,\sigma|\delta(\mathbf{r}-\hat{\mathbf{r}}')|\mathbf{k}'\sigma'\rangle\,a^+_{\mathbf{k}\sigma}\,a_{\mathbf{k}'\sigma'}\;.$$

Matrix element:

$$\begin{aligned} & \langle \mathbf{k}\,\sigma|\delta(\mathbf{r}-\hat{\mathbf{r}}')|\mathbf{k}'\sigma'\rangle = \delta_{\sigma\sigma'}\langle\mathbf{k}|\delta(\mathbf{r}-\hat{\mathbf{r}}')|\mathbf{k}'\rangle \\ = \;& \delta_{\sigma\sigma'}\int d^3r''\langle\mathbf{k}|\delta(\mathbf{r}-\hat{\mathbf{r}}')|\mathbf{r}''\rangle\langle\mathbf{r}''|\mathbf{k}'\rangle \\ = \;& \delta_{\sigma\sigma'}\int d^3r''\,\delta(\mathbf{r}-\mathbf{r}'')\langle\mathbf{k}|\mathbf{r}''\rangle\langle\mathbf{r}''|\mathbf{k}'\rangle = \delta_{\sigma\sigma'}\,\frac{1}{V}\,e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}\;. \end{aligned}$$

$\mathbf{k}' \to \mathbf{k}+\mathbf{q}$:

$$\Longrightarrow\ \widehat{\rho}(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{k},\,\mathbf{q},\,\sigma} a^+_{\mathbf{k}\sigma}\, a_{\mathbf{k}+\mathbf{q}\sigma}\, e^{i\,\mathbf{q}\cdot\mathbf{r}}\ .$$

Solution 8.3.9

1.

$$\mathbf{P} \longrightarrow \sum_{\mathbf{k}\mathbf{k}'\sigma\sigma'} \langle \mathbf{k}\sigma|\,\mathbf{p}\,|\mathbf{k}'\sigma'\rangle\ a^+_{\mathbf{k}\sigma} a_{\mathbf{k}'\sigma'}\ .$$

Matrix element:

$$\langle \mathbf{k}\sigma|\,\mathbf{p}\,|\mathbf{k}'\sigma'\rangle = \langle \mathbf{k}|\,\hbar\,\widehat{\mathbf{k}}\,|\mathbf{k}'\rangle\,\langle\sigma|\ \sigma'\rangle = \delta_{\sigma\sigma'}\hbar\,\mathbf{k}'\,\langle \mathbf{k}|\ \mathbf{k}'\rangle = \delta_{\mathbf{k}\mathbf{k}'}\delta_{\sigma\sigma'}\,\hbar\mathbf{k}'\ .$$

It follows therewith:

$$\mathbf{P} = \sum_{\mathbf{k}\sigma} \hbar\,\mathbf{k}\, a^+_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma}\ .$$

2. x-component of the total spin:

$$S^x \longrightarrow \sum_{\mathbf{k}\mathbf{k}'\sigma\sigma'} \langle \mathbf{k}\sigma|\,s^x\,|\mathbf{k}'\sigma'\rangle\ a^+_{\mathbf{k}\sigma} a_{\mathbf{k}'\sigma'}\ .$$

Matrix element:

$$\begin{aligned}
\langle \mathbf{k}\sigma|\,s^x\,\big|\mathbf{k}'\sigma'\big\rangle &= \delta_{\mathbf{k}\mathbf{k}'}\,\langle\sigma|\,\frac{\hbar}{2}\begin{pmatrix} 0 & 1\\ 1 & 0\end{pmatrix}\big|\sigma'\big\rangle\\
&= \frac{\hbar}{2}\delta_{\mathbf{k}\mathbf{k}'}\left[\delta_{\sigma'\uparrow}\langle\sigma|\begin{pmatrix} 0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix} 1\\ 0\end{pmatrix} + \delta_{\sigma'\downarrow}\langle\sigma|\begin{pmatrix} 0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix} 0\\ 1\end{pmatrix}\right]\\
&= \frac{\hbar}{2}\delta_{\mathbf{k}\mathbf{k}'}\left[\delta_{\sigma'\uparrow}\langle\sigma|\downarrow\rangle + \delta_{\sigma'\downarrow}\langle\sigma|\uparrow\rangle\right]\\
&= \frac{\hbar}{2}\delta_{\mathbf{k}\mathbf{k}'}\left[\delta_{\sigma'\uparrow}\,\delta_{\sigma\downarrow} + \delta_{\sigma'\downarrow}\,\delta_{\sigma\uparrow}\right]\ .
\end{aligned}$$

It follows for the spin operator:

$$S^x = \frac{\hbar}{2}\sum_{\mathbf{k}}\left(a^+_{\mathbf{k}\downarrow}a_{\mathbf{k}\uparrow} + a^+_{\mathbf{k}\uparrow}a_{\mathbf{k}\downarrow}\right)\ .$$

3.

$$\begin{aligned}
\big[S^x,\,\mathbf{P}\big]_- &= \frac{\hbar}{2}\sum_{\mathbf{k}}\sum_{\mathbf{k}'\sigma}\hbar\mathbf{k}'\left[a^+_{\mathbf{k}\downarrow}a_{\mathbf{k}\uparrow} + a^+_{\mathbf{k}\uparrow}a_{\mathbf{k}\downarrow},\,a^+_{\mathbf{k}'\sigma}a_{\mathbf{k}'\sigma}\right]_-\\
&= \frac{\hbar}{2}\sum_{\mathbf{k}\mathbf{k}'\sigma}\hbar\mathbf{k}'\delta_{\mathbf{k}\mathbf{k}'}\left(\left[a^+_{\mathbf{k}\downarrow}a_{\mathbf{k}\uparrow},\,a^+_{\mathbf{k}\sigma}a_{\mathbf{k}\sigma}\right]_- + \left[a^+_{\mathbf{k}\uparrow}a_{\mathbf{k}\downarrow},\,a^+_{\mathbf{k}\sigma}a_{\mathbf{k}\sigma}\right]_-\right)\\
&= \frac{\hbar}{2}\sum_{\mathbf{k}\sigma}\hbar\mathbf{k}\left(\delta_{\sigma\uparrow}a^+_{\mathbf{k}\downarrow}a_{\mathbf{k}\sigma} - \delta_{\sigma\downarrow}a^+_{\mathbf{k}\sigma}a_{\mathbf{k}\uparrow} + \delta_{\sigma\downarrow}a^+_{\mathbf{k}\uparrow}a_{\mathbf{k}\sigma} - \delta_{\sigma\uparrow}a^+_{\mathbf{k}\sigma}a_{\mathbf{k}\downarrow}\right)\\
&= \frac{\hbar}{2}\sum_{\mathbf{k}}\hbar\mathbf{k}\left(a^+_{\mathbf{k}\downarrow}a_{\mathbf{k}\uparrow} - a^+_{\mathbf{k}\downarrow}a_{\mathbf{k}\uparrow} + a^+_{\mathbf{k}\uparrow}a_{\mathbf{k}\downarrow} - a^+_{\mathbf{k}\uparrow}a_{\mathbf{k}\downarrow}\right)\\
&= 0\ .
\end{aligned}$$

Solution 8.3.10

$$\hat{n}_{\mathbf{k}\sigma} = a^+_{\mathbf{k}\sigma}\, a_{\mathbf{k}\sigma} \implies \left[\hat{n}_{\mathbf{k}\sigma}, \hat{n}_{\mathbf{k}'\sigma'}\right]_- = 0\,.$$

The kinetic energy in any case commutes with $\widehat{N}$. The commutator with the interaction remains to be calculated:

$$\begin{aligned}
&\frac{1}{2}\sum_{\substack{\mathbf{k},\mathbf{p},\mathbf{q},\\ \sigma,\sigma',\mathbf{k}',\sigma''}} v_0(\mathbf{q})\left[a^+_{\mathbf{k}+\mathbf{q}\sigma}\, a^+_{\mathbf{p}-\mathbf{q}\sigma'}\, a_{\mathbf{p}\sigma'}\, a_{\mathbf{k}\sigma}, a^+_{\mathbf{k}'\sigma''}\, a_{\mathbf{k}'\sigma''}\right]_- \\
= \;& \frac{1}{2}\sum_{\substack{\mathbf{k},\,\mathbf{p},\,\mathbf{q}\\ \mathbf{k}',\,\sigma,\,\sigma',\,\sigma''}} v_0(\mathbf{q})\Big\{\delta_{\mathbf{k}\mathbf{k}'}\,\delta_{\sigma\sigma''}\, a^+_{\mathbf{k}+\mathbf{q}\sigma}\, a^+_{\mathbf{p}-\mathbf{q}\sigma'}\, a_{\mathbf{p}\sigma'}\, a_{\mathbf{k}'\sigma''} \\
&-\delta_{\mathbf{p},\,\mathbf{k}'}\,\delta_{\sigma'\sigma''}\, a^+_{\mathbf{k}+\mathbf{q}\sigma}\, a^+_{\mathbf{p}-\mathbf{q}\sigma'}\, a_{\mathbf{k}\sigma}\, a_{\mathbf{k}'\sigma''} \\
&+\delta_{\mathbf{p}-\mathbf{q}\mathbf{k}'}\delta_{\sigma'\sigma''} a^+_{\mathbf{k}'\sigma''} a^+_{\mathbf{k}+\mathbf{q}\sigma} a_{\mathbf{p}\sigma'} a_{\mathbf{k}\sigma} - \delta_{\mathbf{k}+\mathbf{q}\mathbf{k}'}\delta_{\sigma\sigma''} a^+_{\mathbf{k}'\sigma''} a^+_{\mathbf{p}-\mathbf{q}\sigma'} a_{\mathbf{p}\sigma'} a_{\mathbf{k}\sigma}\Big\} \\
= \;& \frac{1}{2}\sum_{\substack{\mathbf{k},\,\mathbf{p},\,\mathbf{q}\\ \sigma,\,\sigma'}} v_0(\mathbf{q})\Big\{a^+_{\mathbf{k}+\mathbf{q}\sigma}\, a^+_{\mathbf{p}-\mathbf{q}\sigma'}\, a_{\mathbf{p}\sigma'}\, a_{\mathbf{k}\sigma} - a^+_{\mathbf{k}+\mathbf{q}\sigma}\, a^+_{\mathbf{p}-\mathbf{q}\sigma'}\, a_{\mathbf{k}\sigma}\, a_{\mathbf{p}\sigma'} \\
&+a^+_{\mathbf{p}-\mathbf{q}\sigma'}\, a^+_{\mathbf{k}+\mathbf{q}\sigma}\, a_{\mathbf{p}\sigma'}\, a_{\mathbf{k}\sigma} - a^+_{\mathbf{k}+\mathbf{q}\sigma}\, a^+_{\mathbf{p}-\mathbf{q}\sigma'}\, a_{\mathbf{p}\sigma'}\, a_{\mathbf{k}\sigma}\Big\} = 0 \\
\implies \;& [H_N, \widehat{N}]_- = 0\,.
\end{aligned}$$

H_N and $\widehat{N}$ have common eigen-states. The particle number is a conserved quantity!

Solution 8.3.11

We have to show:

$$\left[S^+_i, S^-_j\right]_- = 2\hbar\,\delta_{ij}\, S^z_i \qquad \left[S^z_i, S^\pm_j\right]_- = \pm\hbar\,\delta_{ij}\, S^\pm_i$$

1.

$$\begin{aligned}
\left[S^+_i, S^-_j\right]_- &= \hbar^2\left[a^+_{i\uparrow}a_{i\downarrow},\, a^+_{j\downarrow}a_{j\uparrow}\right]_- \\
&= \hbar^2\delta_{ij}\left(a^+_{i\uparrow}a_{j\uparrow} - a^+_{j\downarrow}a_{i\downarrow}\right) \\
&= \hbar^2\delta_{ij}\left(n_{i\uparrow} - n_{i\downarrow}\right) \\
&= 2\hbar\,\delta_{ij}\, S^z_i
\end{aligned}$$

2.

$$\begin{aligned}
\left[S^z_i, S^+_j\right]_- &= \frac{\hbar^2}{2}\left[n_{i\uparrow} - n_{i\downarrow},\, a^+_{j\uparrow}a_{j\downarrow}\right]_- \\
&= \frac{\hbar^2}{2}\delta_{ij}\left(\left[n_{i\uparrow},\, a^+_{i\uparrow}a_{i\downarrow}\right]_- - \left[n_{i\downarrow},\, a^+_{i\uparrow}a_{i\downarrow}\right]_-\right) \\
&= \frac{\hbar^2}{2}\delta_{ij}\left(a^+_{i\uparrow}a_{i\downarrow} + a^+_{i\uparrow}a_{i\downarrow}\right) \\
&= \hbar^2\delta_{ij}\, a^+_{i\uparrow}a_{i\downarrow} \\
&= +\hbar\,\delta_{ij}\, S^+_i
\end{aligned}$$

3.

$$\begin{aligned}
\left[S_i^z, S_j^-\right]_- &= \frac{\hbar^2}{2}\left[n_{i\uparrow} - n_{i\downarrow},\, a_{j\downarrow}^+ a_{j\uparrow}\right]_- \\
&= \frac{\hbar^2}{2}\delta_{ij}\left(\left[n_{i\uparrow},\, a_{i\downarrow}^+ a_{i\uparrow}\right]_- - \left[n_{i\downarrow},\, a_{i\downarrow}^+ a_{i\uparrow}\right]_-\right) \\
&= \frac{\hbar^2}{2}\delta_{ij}\left(-a_{i\downarrow}^+ a_{i\uparrow} - a_{i\downarrow}^+ a_{i\uparrow}\right) \\
&= -\hbar^2\delta_{ij}\, a_{i\downarrow}^+ a_{i\uparrow} \\
&= -\hbar\,\delta_{ij}\, S_i^-
\end{aligned}$$

Section 8.4.4

Solution 8.4.1

Test state:

$$|q\rangle = c_1 \left|\varphi_{\mathrm{a}}^{(1)}\right\rangle \left|\varphi_{\mathrm{b}}^{(2)}\right\rangle + c_2 \left|\varphi_{\mathrm{a}}^{(2)}\right\rangle \left|\varphi_{\mathrm{b}}^{(1)}\right\rangle \;; \quad c_{1,2} \text{ real} .$$

Normalization:

$$\begin{aligned}
\langle q|q\rangle &= c_1^2 + c_2^2 + c_1\, c_2 \left(\left\langle\varphi_{\mathrm{a}}^{(1)}\middle|\varphi_{\mathrm{b}}^{(1)}\right\rangle \left\langle\varphi_{\mathrm{b}}^{(2)}\middle|\varphi_{\mathrm{a}}^{(2)}\right\rangle + \left\langle\varphi_{\mathrm{a}}^{(2)}\middle|\varphi_{\mathrm{b}}^{(2)}\right\rangle \left\langle\varphi_{\mathrm{b}}^{(1)}\middle|\varphi_{\mathrm{a}}^{(1)}\right\rangle\right) \\
&= c_1^2 + c_2^2 + 2c_1\, c_2 |L_{\mathrm{ab}}|^2 .
\end{aligned}$$

Furthermore we use the denotations (8.156) and (8.157):

$$\begin{aligned}
\left\langle\varphi_{\mathrm{a}}^{(1)}\middle|\left\langle\varphi_{\mathrm{b}}^{(2)}\middle| H \middle|\varphi_{\mathrm{a}}^{(1)}\right\rangle\middle|\varphi_{\mathrm{b}}^{(2)}\right\rangle &= \left\langle\varphi_{\mathrm{a}}^{(2)}\middle|\left\langle\varphi_{\mathrm{b}}^{(1)}\middle| H \middle|\varphi_{\mathrm{a}}^{(2)}\right\rangle\middle|\varphi_{\mathrm{b}}^{(1)}\right\rangle \\
&= E_{\mathrm{a}} + E_{\mathrm{b}} + C_{\mathrm{ab}} , \\
\left\langle\varphi_{\mathrm{a}}^{(1)}\middle|\left\langle\varphi_{\mathrm{b}}^{(2)}\middle| H \middle|\varphi_{\mathrm{a}}^{(2)}\right\rangle\middle|\varphi_{\mathrm{b}}^{(1)}\right\rangle &+ \left\langle\varphi_{\mathrm{a}}^{(2)}\middle|\left\langle\varphi_{\mathrm{b}}^{(1)}\middle| H \middle|\varphi_{\mathrm{a}}^{(1)}\right\rangle\middle|\varphi_{\mathrm{b}}^{(2)}\right\rangle \\
&= 2(E_{\mathrm{a}} + E_{\mathrm{b}})|L_{\mathrm{ab}}|^2 + 2A_{\mathrm{ab}} .
\end{aligned}$$

Therewith the energy functional reads:

$$\langle H\rangle_q = \frac{\langle q|H|q\rangle}{\langle q|q\rangle} = E_{\mathrm{a}} + E_{\mathrm{b}} + \frac{\left(c_1^2 + c_2^2\right)\, C_{\mathrm{ab}} + 2c_1\, c_2\, A_{\mathrm{ab}}}{c_1^2 + c_2^2 + 2c_1\, c_2 |L_{\mathrm{ab}}|^2} .$$

This expression is symmetric in c_1 and c_2. The variational condition reads:

$$\frac{\partial}{\partial c_1}\langle H\rangle_q \stackrel{!}{=} 0 = \frac{2c_2\left(C_{\mathrm{ab}}|L_{\mathrm{ab}}|^2 - A_{\mathrm{ab}}\right)}{\left(c_1^2 + c_2^2 + 2c_1\, c_2 |L_{\mathrm{ab}}|^2\right)^2}\left(c_1^2 - c_2^2\right) .$$

In general it is surely

$$C_{\mathrm{ab}}|L_{\mathrm{ab}}|^2 \neq A_{\mathrm{ab}} .$$

The above condition is thus satisfiable only if

$$c_1 = \pm c_2 .$$

We get therewith exactly the same result as in Sect. 8.4.2. The variational condition leads to the correct (anti)symmetrized test state $|q\rangle$!

Solution 8.4.2

We have shown in Exercise 5.4.1 that the four spin states ((8.149), (8.150)),

$$|S_1\, S_2;\, S\, m_s\rangle \equiv |S\, m_s\rangle = |1\,1\rangle, |1\,0\rangle, |1\,-1\rangle, |0\,0\rangle,$$

are common eigen-states of the operators

$$\mathbf{S}^2 = \left(\mathbf{S}_1 + \mathbf{S}_2\right)^2,\; S^z = \left(S_1^z + S_2^z\right),\; \mathbf{S}_1^2,\; \mathbf{S}_2^2$$

and because of

$$\mathbf{S}_1 \cdot \mathbf{S}_2 = \frac{1}{2}\left(\mathbf{S}^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2\right)$$

also eigen-states of $\mathbf{S}_1 \cdot \mathbf{S}_2$:

$$\begin{aligned}
(\mathbf{S}_1 \cdot \mathbf{S}_2)|0\,0\,\rangle &= \frac{1}{2}\left(0 - \frac{3}{4} - \frac{3}{4}\right)\hbar^2|0\,0\rangle = -\frac{3}{4}\,\hbar^2|0\,0\rangle\,, \\
(\mathbf{S}_1 \cdot \mathbf{S}_2)|1 m_s\rangle &= \frac{1}{2}\left(2 - \frac{3}{4} - \frac{3}{4}\right)\hbar^2|1 m_s\rangle = \frac{1}{4}\,\hbar^2|1 m_s\rangle\,.
\end{aligned}$$

Requirement:

$$\begin{aligned}
\widehat{H}|1 m_s\rangle^{(+)} &\stackrel{!}{=} E_-|1 m_s\rangle^{(+)}\,; \quad m_s = \pm 1, 0\,, \\
\widehat{H}|0\,0\rangle^{(-)} &\stackrel{!}{=} E_+|0\,0\rangle^{(-)}\,.
\end{aligned}$$

This is guaranteed by

$$\begin{aligned}
\widehat{H} &= E_0 - J_{12}\,(\mathbf{S}_1 \cdot \mathbf{S}_2)\,, \\
E_0 &= \frac{1}{4}\,(E_+ + 3E_-)\,; \quad J_{12} = \frac{1}{\hbar^2}\,(E_+ - E_-)\,.
\end{aligned}$$

Solution 8.4.3

We calculate at first the normalization integral:

$$\begin{aligned}
\langle\psi_{Z^*}|\psi_{Z^*}\rangle &= 16\,\pi^2 \int_0^\infty dr_1 \int_0^\infty dr_2\, r_1^2\, r_2^2\, e^{-(2Z^*/a_\mathrm{B})(r_1 + r_2)} \\
&= \left[4\pi \int_0^\infty dr\, r^2 \exp\left(-\frac{2Z^*}{a_\mathrm{B}}\, r\right)\right]^2 = \left[4\pi \cdot 2!\,\left(\frac{a_\mathrm{B}}{2Z^*}\right)^3\right]^2 = \frac{\pi^2\, a_\mathrm{B}^6}{Z^{*6}}\,,
\end{aligned}$$

$$\left(\int_0^\infty dx\, x^n\, e^{-ax} = \frac{1}{a^{n+1}}\,\Gamma(n+1) = \frac{n!}{a^{n+1}}\right)\,.$$

We need for the energy functional:

$$\begin{aligned}
&\left\langle \psi_{Z^*} \left| \left(H_1^{(1)} + H_1^{(2)} \right) \right| \psi_{Z^*} \right\rangle = 2 \left\langle \psi_{Z^*} \left| H_1^{(2)} \right| \psi_{Z^*} \right\rangle \\
= \;& 2 \int d^3 r_1 e^{-(2Z^*/a_\mathrm{B}) r_1} \int d^3 r_2 e^{-(Z^*/a_\mathrm{B}) r_2} \left(-\frac{\hbar^2}{2m} \Delta_2 - \frac{2e^2}{4\pi\varepsilon_0} \frac{1}{r_2} \right) e^{-(Z^*/a_\mathrm{B}) r_2} \\
= \;& \frac{2\pi a_\mathrm{B}^3}{Z^{*3}} 4\pi \int_0^\infty dr_2 r_2^2 e^{-(Z^*/a_\mathrm{B}) r_2} \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2} \frac{\partial}{\partial r_2} \right) - \frac{e^2}{2\pi\varepsilon_0} \frac{1}{r_2} \right] e^{-(Z^*/a_\mathrm{B}) r_2} \\
= \;& \frac{8\pi^2 a_\mathrm{B}^3}{Z^{*3}} \int_0^\infty dr_2 \, e^{-(2Z^*/a_\mathrm{B})\, r_2} \left[-\frac{\hbar^2}{2m} \left(\frac{Z^{*2}}{a_\mathrm{B}^2} r_2^2 - 2 \frac{Z^*}{a_\mathrm{B}} r_2 \right) - \frac{e^2 \, r_2}{2\pi \, \varepsilon_0} \right] \\
= \;& \frac{8\pi^2 \, a_\mathrm{B}^3}{Z^{*3}} \left\{ -\frac{\hbar^2}{2m} \left[\frac{Z^{*2}}{a_\mathrm{B}^2} 2! \left(\frac{a_\mathrm{B}}{2Z^*} \right)^3 - 2 \frac{Z^*}{a_\mathrm{B}} \left(\frac{a_\mathrm{B}}{2Z^*} \right)^2 \right] - \frac{e^2}{2\pi \, \varepsilon_0} \left(\frac{a_\mathrm{B}}{2Z^*} \right)^2 \right\} \\
= \;& \frac{8\pi^2 a_\mathrm{B}^3}{Z^{*3}} \left[\frac{\hbar^2 a_\mathrm{B}}{8m \, Z^*} - \frac{e^2 \, a_\mathrm{B}^2}{8\pi \, \varepsilon_0 \, Z^{*2}} \right] .
\end{aligned}$$

We exploit:

$$E_\mathrm{R} = \frac{e^2}{8\pi \, \varepsilon_0 a_\mathrm{B}} ; \quad a_\mathrm{B} = \frac{\hbar^2 4\pi \, \varepsilon_0}{m \, e^2} ; \quad \frac{\hbar^2}{m} = 2 a_\mathrm{B}^2 \, E_\mathrm{R} .$$

It follows therewith:

$$\begin{aligned}
\left\langle \psi_{Z^*} \left| \left(H_1^{(1)} + H_1^{(2)} \right) \right| \psi_{Z^*} \right\rangle &= \frac{8\pi^2 a_\mathrm{B}^6}{Z^{*3}} E_\mathrm{R} \left(\frac{1}{4Z^*} - \frac{1}{Z^{*2}} \right) , \\
\frac{\left\langle \psi_{Z^*} \left| \left(H_1^{(1)} + H_1^{(2)} \right) \right| \psi_{Z^*} \right\rangle}{\langle \psi_{Z^*} | \psi_{Z^*} \rangle} &= E_\mathrm{R} \left(2Z^{*2} - 8Z^* \right) .
\end{aligned}$$

The interaction part

$$\frac{\langle \psi_{Z^*} | H_2^{(1,2)} | \psi_{Z^*} \rangle}{\langle \psi_{Z^*} | \psi_{Z^*} \rangle}$$

can of course be calculated in the same manner as the perturbation correction of first order (8.169) and must agree with this for $Z^* = 2$:

$$\langle \psi_{Z^*} | H_2^{(1,\,2)} | \psi_{Z^*} \rangle = \frac{e^2}{4\pi \, \varepsilon_0} \iint d^3 r_1 \, d^3 r_2 \, \frac{e^{-(2Z^*/a_\mathrm{B})\,(r_1 + r_2)}}{|\mathbf{r}_1 - \mathbf{r}_2|} .$$

The integrand is fully symmetric in $\mathbf{r}_1$ and $\mathbf{r}_2$. Hence we can presume $r_2 \geq r_1$, when adding to the result a factor 2. With

$$\frac{e^2}{4\pi \, \varepsilon_0} = 2 a_\mathrm{B} \, E_\mathrm{R}$$

it is to be calculated:

$$\begin{aligned}\langle\psi_{Z^*}|H_2^{(1,2)}|\psi_{Z^*}\rangle &= 8\pi\, a_{\rm B}\, E_{\rm R}\, Q\ ,\\ Q &= \int d^3r_1\, e^{-(2Z^*/a_{\rm B})\, r_1}\, D_{r_1}\ ,\\ D_{r_1} &= \int\limits_{r_1}^{\infty} dr_2\, r_2^2\, e^{-(2Z^*/a_{\rm B})\, r_2}\, I_{r_1\le r_2}\ ,\end{aligned}$$

$$\begin{aligned}I_{r_1\le r_2} &= \int\limits_{-1}^{+1} \frac{dx}{\sqrt{r_1^2+r_2^2-2r_1r_2x}}\\ &= -\frac{1}{r_1r_2}\left(\sqrt{(r_1-r_2)^2}-\sqrt{(r_1+r_2)^2}\right)=\frac{2}{r_2}\ .\end{aligned}$$

It remains for D_{r_1} :

$$\begin{aligned}D_{r_1} &= 2\int\limits_{r_1}^{\infty} dr_2\, r_2\, \exp\left(-\frac{2Z^*}{a_{\rm B}}\, r_2\right) = -2\left[\frac{d}{d\lambda}\int\limits_{r_1}^{\infty} dr_2\, e^{-\lambda r_2}\right]_{\lambda=2Z^*/a_{\rm B}}\\ &= -2\left[\frac{d}{d\lambda}\,\frac{1}{\lambda}\, e^{-\lambda r_1}\right]_{\lambda=2Z^*/a_{\rm B}} = \left[\frac{a_{\rm B}^2}{2Z^{*2}}+\frac{r_1\, a_{\rm B}}{Z^*}\right]\exp\left(-\frac{2Z^*}{a_{\rm B}}\, r_1\right)\\ &= \frac{a_{\rm B}}{Z^*}\left(r_1+\frac{1}{2}\,\frac{a_{\rm B}}{Z^*}\right)\exp\left(-\frac{2Z^*}{a_{\rm B}}\, r_1\right)\ .\end{aligned}$$

We determine in the next step:

$$\begin{aligned}Q &= 4\pi\,\frac{a_{\rm B}}{Z^*}\int\limits_0^{\infty} dr_1\,\left(r_1^3+\frac{1}{2}\,\frac{a_{\rm B}}{Z^*}\, r_1^2\right)\exp\left(-\frac{4Z^*}{a_{\rm B}}\, r_1\right)\\ &= 4\pi\,\frac{a_{\rm B}}{Z^*}\left[3!\,\left(\frac{a_{\rm B}}{4Z^*}\right)^4+\frac{1}{2}\,\frac{a_{\rm B}}{Z^*}\, 2!\,\left(\frac{a_{\rm B}}{4Z^*}\right)^3\right]\\ &= 4\pi\left(\frac{a_{\rm B}}{Z^*}\right)^5\,\frac{1}{4^3}\,\left(\frac{3}{2}+1\right)=\frac{5\pi}{32}\left(\frac{a_{\rm B}}{Z^*}\right)^5\ .\end{aligned}$$

Finally this yields:

$$\frac{\left\langle\psi_{Z^*}\left|H_2^{(1,2)}\right|\psi_{Z^*}^{(1,2)}\right\rangle}{\langle\psi_{Z^*}|\psi_{Z^*}\rangle}=\frac{5}{4}\, Z^* E_{\rm R}\ .$$

Altogether the to be varied energy functional reads:

$$\langle H\rangle_{Z^*}=\frac{\langle\psi_{Z^*}|H|\psi_{Z^*}\rangle}{\langle\psi_{Z^*}|\psi_{Z^*}\rangle}=E_{\rm R}\left(2Z^{*2}-\frac{27}{4}\, Z^*\right)\ .$$

Variational condition:

$$0 \stackrel{!}{=} \frac{d}{dZ^*}\langle H\rangle_{Z^*} = E_{\mathrm{R}}\left(4Z^* - \frac{27}{4}\right) \Longrightarrow \; Z_0^* = \frac{27}{16} < 2\,.$$

Upper limit for the ground-state energy:

$$E_0 \leq \langle H\rangle_{Z_0^*} = -E_{\mathrm{R}}\,\frac{(27)^2}{128} \approx -5.7\,E_{\mathrm{R}} \approx -77.49\,\mathrm{eV}\,,$$

Z_0^* : *effective* nuclear charge. Because of the presence of the respective other electron the He-electrons *do not see* the full nuclear charge $Z = 2$.

Solution 8.4.4

Equation (2.169) in Vol. 3 proves to be very useful:

$$\begin{aligned}
\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} &= \frac{4\pi}{r_>}\sum_l \sum_{m=-l}^{+l} \frac{1}{2l+1}\left(\frac{r_<}{r_>}\right)^l Y_{lm}^*(\vartheta_1,\varphi_1)\,Y_{lm}(\vartheta_2,\varphi_2)\,,\\
\mathbf{r}_i &\equiv (r_i,\vartheta_i,\varphi_i)\,,\\
r_> &= \max\,(r_1,r_2)\,; \quad r_< = \min\,(r_1,r_2)\,.
\end{aligned}$$

With (5.108),

$$Y_{00}(\vartheta,\varphi) \equiv \frac{1}{\sqrt{4\pi}}\,,$$

it follows for the exchange integrals:

$$\begin{aligned}
A_{10}^{nl} &= \frac{e^2}{4\pi\,\varepsilon_0}\int_0^\infty r_1^2\,dr_1 \int_0^\infty r_2^2\,dr_2\,R_{10}(r_1)\,R_{nl}(r_2)\\
&\quad \cdot R_{10}(r_2)\,R_{nl}(r_1)\,\frac{1}{r_>}\sum_{l'm'}\frac{1}{2l'+1}\left(\frac{r_<}{r_>}\right)^{l'}\\
&\quad \cdot \int d\varphi_1\;d\cos\vartheta_1 \int d\varphi_2\;d\cos\vartheta_2\;Y_{l'm'}^*(\vartheta_1,\varphi_1)\\
&\quad \cdot Y_{l'm'}(\vartheta_2,\varphi_2)\,Y_{l0}^*(\vartheta_2,\varphi_2)\,Y_{l0}(\vartheta_1,\varphi_1)\,.
\end{aligned}$$

Orthogonality relation (5.102) of the spherical harmonics:

$$A_{10}^{nl} = \frac{e^2}{4\pi\,\varepsilon_0(2l+1)}\int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2\;R_{10}(r_1)\,R_{nl}(r_2)\,R_{10}(r_2)\,R_{nl}(r_1)\,\frac{r_<^l}{r_>^{l+1}}\,.$$

According to (6.59) the radial function with $l = n-1$ has **no** nodes. But then it must be

$$\begin{aligned}
R_{10}(r_1)\,R_{10}(r_2) &\geq 0\,,\\
R_{nl}(r_1)\,R_{nl}(r_2) &\geq 0 \quad (l = n-1)\,.
\end{aligned}$$

Consequently:

$$A_{10}^{n\,n-1} \geq 0 \,.$$

Solution 8.4.5

According to (8.177) and (8.178) the splitting is given by the corresponding exchange integral:

$$\Delta E = 2A_{10}^{20} \,.$$

For its calculation we use the formula from Exercise 8.4.4:

$$A_{10}^{20} = \frac{e^2}{4\pi\,\varepsilon_0} \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \, \frac{1}{r_>} \, R_{10}(r_1)\, R_{20}(r_2)\, R_{10}(r_2)\, R_{20}(r_1) \,,$$

$$(6.60): \quad R_{10}(r) = 2 \left(\frac{2}{a_\mathrm{B}}\right)^{3/2} e^{-2r/a_\mathrm{B}} \,,$$

$$(6.61): \quad R_{20}(r) = 2 \left(\frac{2}{2a_\mathrm{B}}\right)^{3/2} \left(1 - \frac{r}{a_\mathrm{B}}\right) e^{-r/a_\mathrm{B}} \,.$$

Substitution:

$$x_i = \frac{r_i}{a_\mathrm{B}} \,; \quad i = 1,2 \qquad\qquad \frac{e^2}{4\pi\varepsilon_0} = 2a_\mathrm{B}\, E_\mathrm{R}$$

$$\begin{aligned}
\Longrightarrow \; A_{10}^{20} &= 2^8\, E_\mathrm{R} \int_0^\infty x_1^2(1-x_1)\, dx_1 \int_0^\infty x_2^2(1-x_2)\, dx_2 \, \frac{e^{-3(x_1+x_2)}}{r_>/a_\mathrm{B}} \\
&= 2^8\, E_\mathrm{R} \int_0^\infty dx_1\, x_1^2(1-x_1)\, e^{-3x_1} \left[I_1 + I_2\right] , \\
I_1 &= \frac{1}{x_1} \int_0^{x_1} dx_2 \left(x_2^2 - x_2^3\right) e^{-3x_2} \\
&= \frac{1}{x_1} \int_0^{x_1} dx_2 \, \frac{1}{3} \, \frac{d}{dx_2}\, x_2^3\, e^{-3x_2} = \frac{1}{3}\, x_1^2\, e^{-3x_1} \,.
\end{aligned}$$

For the calculation of the other integral I_2 the formula from Exercise 7.2.1 is useful:

$$\begin{aligned}
\int_0^{x_0} dx\, e^{-x}\, x^n &= n! \left(1 - e^{-x_0} \sum_{\mu=0}^{n} \frac{x_0^\mu}{\mu!}\right) \\
\Longrightarrow \int_{x_0}^\infty dx\, e^{-x}\, x^n &= n!\, e^{-x_0} \sum_{\mu=0}^{n} \frac{x_0^\mu}{\mu!} \,,
\end{aligned}$$

$$
\begin{aligned}
I_2 &= \int_{x_1}^{\infty} dx_2 \left(x_2 - x_2^2\right) e^{-3x_2} = \frac{1}{3} \int_{3x_1}^{\infty} dy_2 \left(\frac{1}{3}\, y_2 - \frac{1}{9}\, y_2^2\right) e^{-y_2} \\
&= \frac{1}{9}\, e^{-3x_1} \left(1 + 3x_1\right) - \frac{2!}{27}\, e^{-3x_1} \left(1 + 3x_1 + \frac{9x_1^2}{2!}\right) \\
&= \frac{1}{9}\, e^{-3x_1} \left(\frac{1}{3} + x_1 - 3x_1^2\right) \\
\Longrightarrow \quad & I_1 + I_2 = \frac{1}{9}\, e^{-3x_1} \left(\frac{1}{3} + x_1\right) .
\end{aligned}
$$

It is left:

$$
\begin{aligned}
A_{10}^{20} &= \frac{2^8}{9}\, E_{\mathrm{R}} \int_0^{\infty} dx_1\, e^{-6x_1} \left(\frac{1}{3}\, x_1^2 + \frac{2}{3}\, x_1^3 - x_1^4\right) \\
&= \frac{2^8}{9}\, E_{\mathrm{R}} \left(\frac{1}{3}\, \frac{2!}{6^3} + \frac{2}{3}\, \frac{3!}{6^4} - \frac{4!}{6^5}\right) \\
\Longrightarrow \; A_{10}^{20} &= \left(\frac{2}{3}\right)^6 E_{\mathrm{R}} \approx 1.19\,\mathrm{eV} \;\Longrightarrow\; \Delta E \approx 2.38\,\mathrm{eV} .
\end{aligned}
$$

Solution 8.4.6

The path of solution is in principle the same as that for the exchange integrals in Exercise 8.4.4. We use for $1/|\mathbf{r}_1 - \mathbf{r}_2|$ the same expression as there:

$$
\begin{aligned}
C_{10}^{nl} &= \frac{e^2}{4\pi\,\varepsilon_0} \int_0^{\infty} r_1^2\, dr_1 \int_0^{\infty} r_2^2\, dr_2\, R_{10}^2(r_1)\, R_{nl}^2(r_2)\, \frac{1}{r_>} \\
&\quad \cdot \sum_{l'm'} \frac{1}{(2l'+1)} \left(\frac{r_<}{r_>}\right)^{l'} \int d\varphi_1\; d\cos\vartheta_1\; Y_{l'm'}^*\left(\vartheta_1, \varphi_1\right) \cdot \\
&\quad \cdot \int d\varphi_2\; d\cos\vartheta_2\; Y_{l'm'}(\vartheta_2, \varphi_2) |Y_{l0}(\vartheta_2\, \varphi_2)|^2 , \\
&\int d\varphi_1\, d\cos\vartheta_1\; Y_{l'm'}^*(\vartheta_1, \varphi_1) \\
= \;& \sqrt{4\pi} \int d\varphi_1\; d\cos\vartheta_1\; Y_{l'm'}^*(\vartheta_1\varphi_1)\, Y_{00}(\vartheta_1\varphi_1) = \sqrt{4\pi}\, \delta_{l'0}\, \delta_{m'0} .
\end{aligned}
$$

It follows therewith:

$$
\begin{aligned}
C_{10}^{nl} &= \frac{e^2}{4\pi\,\varepsilon_0} \int_0^{\infty} r_1^2\, dr_1 \int_0^{\infty} r_2^2\, dr_2\, R_{10}^2(r_1)\, R_{nl}^2(r_2)\, \frac{1}{r_>} \cdot \\
&\quad \cdot \sqrt{4\pi}\, \frac{1}{\sqrt{4\pi}} \int d\varphi_2\; d\cos\vartheta_2 |\, Y_{l0}(\vartheta_2, \varphi_2)|^2 \\
&= \frac{e^2}{4\pi\,\varepsilon_0} \int_0^{\infty} r_1^2\, dr_1 \int_0^{\infty} r_2^2\, dr_2\, R_{10}^2(r_1)\, R_{nl}^2(r_2)\, \frac{1}{r_>}
\end{aligned}
$$

Solution 8.4.7

We use for C_{10}^{20} the formula from Exercise 8.4.6:

$$C_{10}^{20} = 2a_{\mathrm{B}}\, E_{\mathrm{R}} \int_0^\infty r_1^2\, dr_1 \int_0^\infty r_2^2\, dr_2\, R_{10}^2(r_1)\, R_{20}^2(r_2)\, \frac{1}{r_>}\,.$$

With $R_{10}(r_1)$ according to (6.60) and $R_{20}(r_2)$ according to (6.61) as well as

$$x_i = \frac{r_i}{a_{\mathrm{B}}}, \quad i = 1, 2$$

it remains to be calculated:

$$C_{10}^{20} = 2^8\, E_{\mathrm{R}} \int_0^\infty dx_2 \left(x_2^2 - 2x_2^3 + x_2^4\right) e^{-2x_2} \left[J_1 + J_2\right].$$

We use again the integral formulas from solution 8.4.5:

$$\begin{aligned}
J_1 &= \frac{1}{x_2} \int_0^{x_2} dx_1\, x_1^2\, e^{-4x_1} \\
&= \frac{1}{4^3 x_2} \int_0^{4x_2} dy_1\, y_1^2\, e^{-y_1} = \frac{2!}{4^3 x_2} \left\{1 - e^{-4x_2} \left[1 + 4x_2 + \frac{1}{2!}\,(4x_2)^2\right]\right\} \\
&= \frac{1}{32\, x_2} - \frac{e^{-4x_2}}{16} \left(\frac{1}{2x_2} + 2 + 4x_2\right), \\
J_2 &= \int_{x_2}^\infty dx_1\, x_1\, e^{-4x_1} = \frac{1}{4^2} \int_{4x_2}^\infty dy_1\, y_1\, e^{-y_1} = \frac{e^{-4x_2}}{16}\,(1 + 4x_2)\,.
\end{aligned}$$

From that we get for the Coulomb integral:

$$\begin{aligned}
C_{10}^{20} &= 2^3\, E_{\mathrm{R}} \left[\int_0^\infty dx_2 \left(x_2 - 2x_2^2 + x_2^3\right) e^{-2x_2} - \int_0^\infty dx_2 \left(x_2 - 3x_2^3 + 2x_2^4\right) e^{-6x_2}\right] \\
&= 2^3\, E_{\mathrm{R}} \left[\frac{1}{2^2} - 2\,\frac{2!}{2^3} + \frac{3!}{2^4} - \frac{1}{6^2} + \frac{3 \cdot 3!}{6^4} - 2\,\frac{4!}{6^5}\right], \\
C_{10}^{20} &= \frac{68}{81}\, E_{\mathrm{R}} \approx 11.42\,\mathrm{eV}\,, \\
&\quad \text{solution 8.4.5} \implies A_{10}^{20} \approx 1.19\,\mathrm{eV}\,.
\end{aligned}$$

The Coulomb integral is larger by one order of magnitude!

Solution 8.4.8

$$\Delta E^{(21)}_{\substack{\text{para}\\ \text{ortho}}} = C_{10}^{21} \pm A_{10}^{21}\,.$$

We use for the calculation the formulas from the Exercises 8.4.4 and 8.4.6 with the radial functions according to (6.60) and (6.62):

$$\begin{aligned} R_{10}(r) &= 2\left(\frac{2}{a_\mathrm{B}}\right)^{3/2} e^{-2r/a_\mathrm{B}} , \\ R_{21}(r) &= \frac{1}{\sqrt{3}}\left(\frac{2}{2a_\mathrm{B}}\right)^{3/2} \frac{2r}{a_\mathrm{B}}\, e^{-r/a_\mathrm{B}} . \end{aligned}$$

With the substitutions

$$x_i = \frac{r_i}{a_\mathrm{B}}$$

it is then to calculate:

$$\begin{aligned} C_{10}^{21} &= \frac{2^8}{3} E_\mathrm{R} \int_0^\infty dx_1\, x_1^2 \int_0^\infty dx_2\, x_2^4\, \frac{1}{x_>}\, e^{-\left(4x_1+2x_2\right)} , \\ A_{10}^{21} &= \frac{2^8}{3^2} E_\mathrm{R} \int_0^\infty dx_1\, x_1^3 \int_0^\infty dx_2\, x_2^3\, \frac{r_<}{r_>^2}\, e^{-3\left(x_1+x_2\right)} . \end{aligned}$$

We start with the Coulomb integral:

$$C_{10}^{21} = \frac{2^8}{3} E_\mathrm{R} \int_0^\infty dx_2\, x_2^4\, e^{-2x_2}\,(J_1 + J_2) .$$

J_1 and J_2 are exactly the same integrals as those in the Solution 8.4.7. We thus can adopt directly the partial results:

$$\begin{aligned} J_1 &= \frac{1}{x_2}\int_0^{x_2} dx_1\, x_1^2\, e^{-4x_1} = \frac{1}{32\,x_2} - \frac{e^{-4x_2}}{16}\left(\frac{1}{2x_2} + 2 + 4x_2\right) , \\ J_2 &= \int_{x_2}^\infty dx_1\, x_1\, e^{-4x_1} = \frac{e^{-4x_2}}{16}\,(1+4x_2) . \end{aligned}$$

It remains to be calculated:

$$\begin{aligned} C_{10}^{21} &= \frac{2^8}{3} E_\mathrm{R}\left[\frac{1}{32}\int_0^\infty dx_2\, x_2^3\, e^{-2x_2} - \frac{1}{16}\int_0^\infty dx_2\, e^{-6x_2}\left(\frac{1}{2}\,x_2^3 + x_2^4\right)\right] \\ &= \frac{2^3}{3} E_\mathrm{R}\left[\frac{3!}{2^4} - \left(\frac{3!}{6^4} + 2\,\frac{4!}{6^5}\right)\right] = E_\mathrm{R}\left[1 - \frac{7}{243}\right] = \frac{236}{243} E_\mathrm{R} \\ &\Longrightarrow \quad C_{10}^{21} \approx 13.21\,\mathrm{eV} . \end{aligned}$$

We need for the exchange integral:

$$\begin{aligned}
A_{10}^{21} &= \frac{2^8}{3^2}\,E_{\mathrm{R}} \int\limits_0^\infty dx_1\, x_1^3\, e^{-3x_1}\,\left[I_1 + I_2\right]\,, \\
I_1 &= \frac{1}{x_1^2} \int\limits_0^{x_1} dx_2\, x_2^4\, e^{-3x_2} = \frac{1}{3^5\, x_1^2} \int\limits_0^{3x_1} dy_2\, y_2^4\, e^{-y_2} \\
&= \frac{4!}{3^5\, x_1^2}\left[1 - e^{-3x_1}\left(1 + 3x_1 + \frac{1}{2}\,(3x_1)^2 + \frac{1}{6}\,(3x_1)^3 + \frac{1}{24}\,(3x_1)^4\right)\right]\,, \\
I_2 &= x_1 \int\limits_{x_1}^\infty dx_2\, x_2\, e^{-3x_2} = \frac{x_1}{3^2} \int\limits_{3x_1}^\infty dy_2\, y_2\, e^{-y_2} = \frac{1}{3^2}\, x_1\, e^{-3x_1}\,(1 + 3x_1)\,.
\end{aligned}$$

For the calculation of I_1 and I_2 we have again applied the integral formulas from solution 8.4.5:

$$\begin{aligned}
A_{10}^{21} &= \frac{2^8}{3^6}\,E_{\mathrm{R}}\left[2^3 \int\limits_0^\infty dx_1\, x_1\, e^{-3x_1} - \int\limits_0^\infty dx_1\, e^{-6x_1}\,\left(8x_1 + 24\,x_1^2 + 36\,x_1^3 + 27\,x_1^4\right)\right] \\
&= \frac{2^8}{3^6}\,E_{\mathrm{R}}\left[8\,\frac{1}{3^2} - 8\,\frac{1}{6^2} - 24\,\frac{2}{6^3} - 36\,\frac{3!}{6^4} - 27\,\frac{4!}{6^5}\right] = \frac{2^8}{3^6}\,E_{\mathrm{R}}\,\frac{7}{36} = \frac{448}{6561}\,E_{\mathrm{R}} \\
&\Longrightarrow \quad A_{10}^{21} \approx 0.93\,\mathrm{eV}\,.
\end{aligned}$$

The exchange integral is smaller by one order of magnitude than the corresponding Coulomb integral:

$$\begin{aligned}
\Delta E_{\mathrm{para}}^{(21)} &\approx 14.14\,\mathrm{eV}\,, \\
\Delta E_{\mathrm{ortho}}^{(21)} &\approx 12.28\,\mathrm{eV}\,.
\end{aligned}$$

Section 9.1.3

Solution 9.1.1

$$\begin{aligned}
\mathbf{k} &= k\mathbf{e}_z\,, \quad \mathbf{k}\cdot\mathbf{r} = kz = kr\,\cos\delta\,, \\
\varphi^*\,\nabla\varphi &= \left(e^{-i\,\mathbf{k}\cdot\mathbf{r}} + \frac{f^*(\vartheta)}{r}\,e^{-ikr}\right)\,\nabla\left(e^{i\,\mathbf{k}\cdot\mathbf{r}} + \frac{f(\vartheta)}{r}\,e^{ikr}\right)\,, \\
\nabla\left(e^{i\,\mathbf{k}\cdot\mathbf{r}} + \frac{f(\vartheta)}{r}\,e^{ikr}\right) &= i\,\mathbf{k}\,e^{i\,\mathbf{k}\cdot\mathbf{r}} + \nabla\left(\frac{f(\vartheta)}{r}\,e^{ikr}\right)\,.
\end{aligned}$$

Gradient in spherical coordinates:

$$\nabla \equiv \mathbf{e}_r\,\frac{\partial}{\partial r} + \mathbf{e}_\vartheta\,\frac{1}{r}\,\frac{\partial}{\partial\vartheta} + \mathbf{e}_\varphi\,\frac{1}{r\sin\vartheta}\,\frac{\partial}{\partial\varphi}\,.$$

It follows therewith:

$$\nabla\left(\frac{f(\vartheta)}{r}\,e^{ikr}\right) = \mathbf{e}_r\,\left(-\frac{f(\vartheta)}{r^2} + i\,k\,\frac{f(\vartheta)}{r}\right)\,e^{ikr} + \mathbf{e}_\vartheta\,\frac{1}{r^2}\,\frac{\partial f}{\partial\vartheta}\,e^{ikr}\,.$$

We neglect terms of the order $1/r^3$ and take $\mathbf{k}\cdot\mathbf{r} = k\,r\cos\vartheta$:

$$\begin{aligned}\varphi^*\,\nabla\,\varphi &= i\,\mathbf{k} + i\,\mathbf{k}\,\frac{f^*(\vartheta)}{r}\,e^{-ikr\,(1-\cos\vartheta)} \\ &\quad +\mathbf{e}_r\,\left[-\frac{f(\vartheta)}{r^2}\,e^{ikr\,(1-\cos\vartheta)} + i\,k\,\frac{f(\vartheta)}{r}\,e^{ikr\,(1-\cos\vartheta)} + i\,k\,\frac{|f(\vartheta)|^2}{r^2}\right] \\ &\quad +\mathbf{e}_\vartheta\,\frac{1}{r^2}\,\frac{\partial f(\vartheta)}{\partial\vartheta}\,e^{ikr\,(1-\cos\vartheta)}\,.\end{aligned}$$

$\varphi\,\nabla\,\varphi^*$ is just the conjugate-complex of this expression:

$$\begin{aligned}&\varphi^*\,\nabla\,\varphi - \varphi\,\nabla\,\varphi^* \\ =\;& 2i\,\mathbf{k} + i\,\mathbf{k}\,\frac{1}{r}\,\left[f^*(\vartheta)\,e^{-ikr\,(1-\cos\vartheta)} + f(\vartheta)\,e^{ikr\,(1-\cos\vartheta)}\right] \\ &+\mathbf{e}_r\,\left[-\frac{1}{r^2}\,\left(f(\vartheta)\,e^{ikr\,(1-\cos\vartheta)} - f^*(\vartheta)\,e^{-ikr\,(1-\cos\vartheta)}\right)\right. \\ &\left.+\frac{i\,k}{r}\,\left(f(\vartheta)\,e^{ikr\,(1-\cos\vartheta)} + f^*(\vartheta)\,e^{-ikr\,(1-\cos\vartheta)}\right) + 2i\,k\,\frac{|f(\vartheta)|^2}{r^2}\right] \\ &+\mathbf{e}_\vartheta\,\frac{1}{r^2}\,\left[\frac{\partial f(\vartheta)}{\partial\vartheta}\,e^{ikr\,(1-\cos\vartheta)} - \frac{\partial f^*(\vartheta)}{\partial\vartheta}\,e^{-ikr\,(1-\cos\vartheta)}\right]\,.\end{aligned}$$

Current density:

$$\begin{aligned}\mathbf{j} &= \frac{\hbar}{2m\,i}\,\left(\varphi^*\nabla\,\varphi - \varphi\,\nabla\,\varphi^*\right) = \frac{\hbar\,\mathbf{k}}{m} + \frac{\hbar\,k}{m}\,\mathbf{e}_r\,\frac{|f(\vartheta)|^2}{r^2} \\ &\quad +\frac{\hbar\,k}{m}\,\frac{1}{r}\,(\mathbf{e}_r + \mathbf{e}_z)\;\mathrm{Re}\,\left(f(\vartheta)\,e^{ikr\,(1-\cos\vartheta)}\right) - \frac{\hbar}{m}\,\frac{1}{r^2}\,\mathbf{e}_r\;\mathrm{Im}\,\left(f(\vartheta)\,e^{ikr\,(1-\cos\vartheta)}\right) \\ &\quad +\frac{\hbar}{m}\,\frac{1}{r^2}\,\mathbf{e}_\vartheta\;\mathrm{Im}\,\left(\frac{\partial f(\vartheta)}{\partial\vartheta}\,e^{ikr\,(1-\cos\vartheta)}\right)\,.\end{aligned}$$

The last three summands are terms representing interference!

Solution 9.1.2

Schrödinger equation:

$$\begin{aligned}\left(-\frac{\hbar^2}{2m}\,\Delta + V(r)\right)\,\varphi(\mathbf{r}) &= E\,\varphi(\mathbf{r})\,, \\ E = \frac{\hbar^2 k^2}{2m} \;\Longrightarrow\; -\frac{\hbar^2}{2m}\,\Delta\,e^{ikz} &= E\,e^{ikz}\,.\end{aligned}$$

It remains to show for $r\to\infty$:

$$-\frac{\hbar^2}{2m}\,\Delta\,\left(f(\vartheta)\,\frac{e^{ikr}}{r}\right) + V(r)\,\left(e^{ikz} + f(\vartheta)\,\frac{e^{ikr}}{r}\right) = E\,f(\vartheta)\,\frac{e^{ikr}}{r}\,.$$

Since $V(r)$ vanishes stronger than $1/r$ at infinity, one can for $r\to\infty$ at first

neglect the potential term with respect to the $1/r$-terms:

$$\begin{aligned} -\frac{\hbar^2}{2m}\,\Delta\left(f(\vartheta)\,\frac{e^{ikr}}{r}\right) &= -\frac{\hbar^2}{2m}\Big(\Delta(f(\vartheta))\Big)\,\frac{e^{ikr}}{r} - \frac{\hbar^2}{2m}\,f(\vartheta)\left(\Delta\left(\frac{e^{ikr}}{r}\right)\right) \\ &= E\,f(\vartheta)\,\frac{e^{ikr}}{r}\;. \end{aligned}$$

Laplace operator in spherical coordinates (5.83):

$$\Delta = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\mathbf{L}^2}{\hbar^2 r^2}\;.$$

The operator of the square of the angular momentum $\mathbf{L}^2$ contains differentiations exclusively with respect to angles. That means:

$$-\frac{\hbar^2}{2m}\Big(\Delta(f(\vartheta))\Big)\,\frac{e^{ikr}}{r} \sim \mathcal{O}\left(\frac{1}{r^3}\right)\;.$$

This term, too, can thus be neglected for $r \to \infty$. That also holds for the following expression:

$$\frac{2}{r}\frac{\partial}{\partial r}\,\frac{e^{ikr}}{r} = \frac{2}{r}\left(-\frac{1}{r^2} + \frac{ik}{r}\right)\,e^{ikr} \sim \mathcal{O}\left(\frac{1}{r^2}\right)\;.$$

It still remains:

$$\frac{\partial^2}{\partial r^2}\,\frac{e^{ikr}}{r} = \left(-\frac{ik}{r^2} - \frac{k^2}{r} + \frac{2}{r^3} - \frac{ik}{r^2}\right)\,e^{ikr} \sim -k^2\,\frac{e^{ikr}}{r} + \mathcal{O}\left(\frac{1}{r^2}\right)\;.$$

The following equation must be asymptotically valid:

$$\frac{\hbar^2 k^2}{2m}\,f(\vartheta)\,\frac{e^{ikr}}{r} = E\,f(\vartheta)\,\frac{e^{ikr}}{r}\;.$$

This obviously succeeds with the above E!

Section 9.2.7

Solution 9.2.1

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= a = \text{const} \implies \sigma = \int d\Omega\,\frac{d\sigma}{d\Omega} = 4\pi\,a\;, \\ \frac{d\sigma}{d\Omega} &= |f(\vartheta)|^2 \implies a = [\text{Im}\;f(\vartheta)]^2 + [\text{Re}\;f(\vartheta)]^2\;. \end{aligned}$$

Pure s-scattering $\implies$ $l = 0$; $P_0(\cos\vartheta) = 1$:

$$\begin{aligned} (9.23) \quad &\implies \quad f(\vartheta) = \frac{1}{k}\,e^{i\delta_0}\sin\delta_0\;, \\ (9.24) \quad &\implies \quad f(0) = \frac{1}{k}\,e^{i\delta_0}\sin\delta_0 \equiv f(\vartheta)\;. \end{aligned}$$

Optical theorem (9.28):

$$\begin{aligned} \sigma = \frac{4\pi}{k}\ \mathrm{Im}\ f(0) &= \frac{4\pi}{k}\ \mathrm{Im}\ f(\vartheta) = 4\pi\, a \\ \Longrightarrow\ \mathrm{Im}\ f(\vartheta) &= k\, a\ . \end{aligned}$$

This means eventually:

$$\begin{aligned} a &= k^2 a^2 + [\mathrm{Re}\ f(\vartheta)]^2 \\ \Longrightarrow\ \mathrm{Re}\ f(\vartheta) &= \pm\sqrt{a(1 - a\, k^2)} \\ \Longrightarrow\ f(\vartheta) &= \pm\sqrt{a(1 - a\, k^2)} + i\, k\, a\ . \end{aligned}$$

Solution 9.2.2

Ansatz as in (9.33):

$$\varphi(\mathbf{r}) = \sum_{l=0}^{\infty} R_l(r)\, P_l(\cos\vartheta)\ .$$

Laplace operator in spherical coordinates (5.83):

$$\Delta = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\,\frac{\partial}{\partial r} - \frac{\mathbf{L}^2}{\hbar^2 r^2}\ .$$

Schrödinger equation:

$$\begin{aligned} \left(-\frac{\hbar^2}{2m}\,\Delta + \frac{c}{r^2}\right)\varphi(\mathbf{r}) &= E\,\varphi(\mathbf{r}) \\ k^2 &= \frac{2m}{\hbar^2}\,E \\ \Longrightarrow\ \left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\,\frac{\partial}{\partial r} + k^2 - \frac{1}{r^2}\left(l(l+1) + \frac{2m\,c}{\hbar^2}\right)\right] R_l(r) &= 0\ . \end{aligned}$$

We take

$$\begin{aligned} \lambda(\lambda+1) &= l(l+1) + \frac{2m\,c}{\hbar^2} \\ \rho &= k\, r \end{aligned}$$

and have to then solve the following differential equation:

$$\left(\frac{d^2}{d\rho^2} + \frac{2}{\rho}\,\frac{d}{d\rho} + 1 - \frac{\lambda(\lambda+1)}{\rho^2}\right) R_l(\rho) = 0\ .$$

If λ were integral, then this would be the spherical Bessel differential equation (7.214) with spherical Bessel (j_λ) and spherical Neumann functions (n_λ) as solutions. Because of

$$\frac{2m\,c}{\hbar^2} \ll 1$$

we write approximately

$$R_l(\rho) \longrightarrow j_\lambda(\rho) \,.$$

From the asymptotic behavior ((9.21) and (9.22)),

$$R_l(\rho) \longrightarrow \frac{1}{\rho} \sin\left(\rho - \frac{l\,\pi}{2} + \delta_l\right) e^{i\delta_l},$$

and (6.125),

$$j_\lambda(\rho) \longrightarrow \frac{1}{\rho} \sin\left(\rho - \frac{\lambda\,\pi}{2}\right),$$

we conclude with $e^{i\delta_l} \approx 1$:

$$\delta_l(k) \equiv \delta_l = \frac{\pi}{2}\,(l - \lambda) \,.$$

λ can be calculated as function of l:

$$\begin{aligned} \lambda^2 + \lambda &= l^2 + l + \frac{2m\,c}{\hbar^2} \\ \Longrightarrow\ \lambda &= -\frac{1}{2} + \sqrt{\left(l + \frac{1}{2}\right)^2 + \frac{2m\,c}{\hbar^2}} \\ \Longrightarrow\ \lambda &\approx l + \frac{m\,c}{\hbar^2}\,\frac{1}{l + 1/2} \,. \end{aligned}$$

It thus holds for the scattering phases:

$$\delta_l \approx -\frac{\pi\,m\,c}{(2l+1)\,\hbar^2} \ll 1 \,.$$

Scattering amplitude (9.23):

$$\begin{aligned} \delta_l \ll 1 \quad &\Longrightarrow \quad e^{i\delta_l} \approx 1\,; \quad \sin\delta_l \approx \delta_l \\ \Longrightarrow\ f(\vartheta) \quad &\approx \quad \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)\,\delta_l\,P_l(\cos\vartheta) \approx -\frac{\pi\,m\,c}{k\,\hbar^2}\sum_{l=0}^{\infty}P_l(\cos\vartheta) \\ &= \quad -\frac{\pi\,m\,c}{2k\,\hbar^2}\,\frac{1}{\sin\frac{\vartheta}{2}} \,. \end{aligned}$$

Solution 9.2.3

1. With the definitions

$$k = \sqrt{\frac{2m\,E}{\hbar^2}}\,; \quad k_0^2 = \frac{2m}{\hbar^2}\,(E - V_0) = -p^2 < 0\,, q^2 = \begin{cases} k^2 & \text{for } r \geq a\,, \\ k_0^2 = -p^2 & \text{for } r < a \end{cases}$$

we have to solve for s-scattering according to (9.18) the following differential equation:

$$\frac{d^2}{dr^2}\,u_0(r) + q^2\,u_0(r) = 0 \,.$$

q is imaginary for $r < a$. The solution function exhibits exponentially decaying behavior. Because of the additional boundary condition (6.21), $u_0(0) = 0$, it follows as ansatz:

$$r < a : \; u_0^<(r) = a_0 \sinh(p\,r) \; .$$

For $r > a$ the solution function must oscillate and has to simultaneously guarantee the asymptotic behavior (9.21). Therefore the ansatz should be of the form:

$$r > a : \; u_0^>(r) = b_0 \sin(k\,r + \delta_0) \; .$$

Fitting condition:

$$\left.\frac{(d/dr)\,u_0^<(r)}{u_0^<(r)}\right|_{r\,=\,a} \stackrel{!}{=} \left.\frac{(d/dr)\,u_0^>(r)}{u_0^>(r)}\right|_{r\,=\,a} \; .$$

This is easily evaluated:

$$p \coth(p\,a) = k \cot(k\,a + \delta_0) \; .$$

Conditional equation for δ_0:

$$\begin{aligned} \tan(k\,a + \delta_0) &= \frac{k}{p} \tanh(p\,a) \\ \delta_0 &= \arctan\left(\frac{k}{p} \tanh(p\,a)\right) - k\,a \; . \end{aligned}$$

Compare this result with (6.143)!

2. It always holds:

$$0 \le \tanh(p\,a) \le 1 \; .$$

For low particle energies ($k \to 0$) the arc tangent can in any case be replaced by its argument (modulo π):

$$\delta_0 \approx \frac{k}{p} \tanh(p\,a) - k\,a + n\,\pi \; .$$

With the definition,

$$a_s \equiv a\left(1 - \frac{\tanh p\,a}{p\,a}\right) : \; \textit{scattering length} \text{ (cf. (9.64))} \; ,$$

there results an expression which is completely analogous to (9.65):

$$\delta_0 \approx n\,\pi - k\,a_s \underset{k\,\to\,0}{\longrightarrow} n\,\pi \; .$$

Cross-section:

$$\sigma_0 = \frac{4\pi}{k^2} \sin^2 \delta_0 \approx \frac{4\pi}{k^2} \sin^2 k\,a_s \approx 4\pi\,a_s^2 \quad \text{(cf. (9.66))} \; .$$

Limiting case:

$$\begin{aligned} & V_0 \to \infty \quad (\textit{hard sphere}) \\ \Longrightarrow \quad & p \to \infty,\ \tanh p\,a \to 1 \implies a_s \to a,\ \delta_0 \to n\,\pi - k\,a \\ \Longrightarrow \quad & \sigma_0 \longrightarrow 4\pi\,a^2 \quad (\text{cf. (9.40)}) \,. \end{aligned}$$

Solution 9.2.4

1. We consider pure s-scattering ($l = 0$) at a central-symmetric potential $V(r)$. Therefore we have to solve a radial equation of the form (6.17) for $l = 0$, which, with the ansatz (6.18), $u_0(r) = rR_0(r)$, goes over into the Eq. (6.19),

$$u_0''(r) + k^2 u_0(r) = \frac{2m}{\hbar^2}\, V_0\, \delta(r - R)\, u_0(r) \,,$$

with

$$k^2 = \frac{2m}{\hbar^2} E \quad \text{and the boundary condition:} \quad u_0(0) = 0 \,.$$

The *classically allowed region* lies inside ($r < R$) and outside ($r > R$) the *'potential shell'*. The solution function will therefore exhibit there oscillatory behavior. A proper ansatz, which fulfills the above boundary condition and shows the correct asymptotic behavior, then might be:

$$u_0(r) = \begin{cases} \alpha \sin(kr) & \text{for} \quad r < R \\ \beta \sin(kr + \delta_0(k)) & \text{for} \quad r > R \end{cases} \,.$$

Continuity at $r = R$:

$$\alpha \sin(kR) \stackrel{!}{=} \beta \sin(kR + \delta_0(k)) \,.$$

Because of the δ-potential the first derivative of u_0 performs a jump at $r = R$ (see (4.107) or also Exercise 4.2.5 in Vol. 6):

$$u_0'(R + 0^+) - u_0'(R - 0^+) = \frac{2m}{\hbar^2}\, V_0\, u_0(R) \,.$$

That means here:

$$\beta k \cos(kR + \delta_0(k)) - \alpha k \cos(kR) = \frac{2m}{\hbar^2} V_0 \alpha \sin(kR) \,.$$

Division by the continuity condition results in:

$$k \cot(kR + \delta_0(k)) - k \cot(kR) = \frac{2m}{\hbar^2} V_0 \,.$$

That can be rearranged:

$$\tan(kR + \delta_0(k)) = \frac{\tan(kR)}{1 + \frac{2mV_0}{\hbar^2 k} \tan(kR)} = \frac{\tan(kR) + \tan(\delta_0(k))}{1 - \tan(kR)\tan(\delta_0(k))} \,.$$

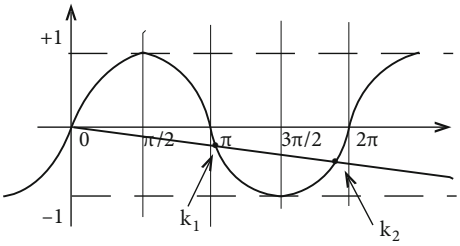


Figure A.7:

In the second step we have used the addition theorem for the tangent. Solving for $\tan(\delta_0(k))$ yields:

$$\tan(\delta_0(k)) = \frac{-\sin^2(kR)}{\frac{\hbar^2 k}{2mV_0} + \frac{1}{2}\sin(2kR)} \tag{A.7}$$

Thereby we used $\sin(kR)\cos(kR) = \frac{1}{2}\sin(2kR)$.

2. The zeros of the denominator in (A.7) can give rise to resonance scattering (Sect. 9.2.4). They can be taken from:

$$\sin(2kR) \stackrel{!}{=} -\frac{\hbar^2}{2mV_0R}(2kR) \tag{A.8}$$

As function of $2kR$ the solutions correspond to the intersection points of the sine function on the left-hand side, which oscillates between $+1$ and -1, and the straight line with negative(!) slope on the right-hand side. There can exist several intersection points k_n, and that the more the flatter the line runs, i.e., the stronger the coupling V_0R (Fig. A.7). Let us number them consecutively by $n = 1, 2, \ldots$ according to their magnitude. One can easily imagine, because of the known behavior of the sine, that for large V_0R the oddly indexed solutions $2k_{2\nu-1}R$ ($\nu = 1, 2, \ldots$) lie slightly above $(2\nu - 1)\pi$ and the evenly indexed ones $2k_{2\nu}R$ slightly below $2\nu\pi$.

We investigate the behavior of $\tan(\delta_0(k))$ in the neighborhoods of the *'resonances'* k_n. For this purpose we expand the denominator in (A.7) according to Taylor:

$$\textit{'denominator'} = 0 + \left(\frac{\hbar^2}{2mV_0} + R\cos(2k_nR)\right)(k - k_n) + \mathcal{O}\left((k - k_n)^2\right) .$$

In addition:

$$E - E_n = \frac{\hbar^2}{2m}\left(k^2 - k_n^2\right) = \frac{\hbar^2}{2m}(k + k_n)(k - k_n) \approx \frac{\hbar^2 k_n}{m}(k - k_n) .$$

Insertion:

$$\text{'denominator'} \approx \left(\frac{1}{2V_0k_n} + \frac{mR}{\hbar^2 k_n}\cos(2k_nR)\right)(E - E_n) .$$

We can therewith bring (A.7) for $k \approx k_n$ into the form of (9.59):

$$\tan\delta_{0,n} \approx \gamma_n \frac{kR}{E - E_n} \quad ; \quad (n = 1, 2, \ldots)$$

with

$$\gamma_n = \frac{-\sin^2(k_n R)}{\frac{R}{2V_0} + \frac{mR^2}{\hbar^2}\cos(2k_n R)} \,. \tag{A.9}$$

Finally, statements are still possible about the sign of γ_n. The right-hand and the left-hand side of the condition (A.8) have different slopes at the intersection points:

$$\begin{aligned} \textit{slope of the left-hand side}|_{k_n} &= 2R\cos(2k_n R) \\ \textit{slope of the right-hand side}|_{k_n} &= -\frac{\hbar^2}{mV_0} \,. \end{aligned}$$

One again realizes easily (Fig. A.7) that it holds for the, respectively, odd and even intersection points:

$$\begin{aligned} 2R\cos(2k_{2\nu-1}R) &< -\frac{\hbar^2}{mV_0} \quad \Leftrightarrow \quad \frac{mR^2}{\hbar^2}\cos(2k_{2\nu-1}R) < -\frac{R}{2V_0} \\ 2R\cos(2k_{2\nu}R) &> -\frac{\hbar^2}{mV_0} \quad \Leftrightarrow \quad \frac{mR^2}{\hbar^2}\cos(2k_{2\nu}R) > -\frac{R}{2V_0} \,. \end{aligned}$$

It then follows with (A.9):

$$\gamma_n : \begin{cases} > 0 & \text{for} \quad n \quad \text{odd} \\ < 0 & \text{for} \quad n \quad \text{even} \end{cases} .$$

This transfers to the scattering phase:

- n odd:

$$\tan\delta_0 : \begin{cases} < 0 & \text{for} \quad E \lesssim E_n \\ > 0 & \text{for} \quad E \gtrsim E_n \end{cases}$$

- n even:

$$\tan\delta_0 : \begin{cases} > 0 & \text{for} \quad E \lesssim E_n \\ < 0 & \text{for} \quad E \gtrsim E_n \end{cases} .$$

Since the phase δ_0 can be fixed only except for an integral multiple of π, we can restrict our considerations to the interval $[0, \pi]$. Solution (A.7) tells us that $\tan\delta_0 \to 0$ follows for $E \to 0$ as well as for $E \to \infty$. The phase then takes the value 0 or π. If one presumes that δ_0 is a monotonic function of the energy E, then the phase has to monotonically decrease from π for $E = 0$ to 0 for $E \to \infty$, with the value $\pi/2$ at $E = E_n$, in order to realize the above expressions of $\tan\delta_0$ with odd n. From a physical point of view, though, the phase should disappear at $E = 0$, because in this case no particle *'comes in'*, so that no scattering whatsoever can

take place. One will therefore suppose that the oddly indexed graphical solutions of Eq. (A.8) *do not represent real resonances*. We will therefore no longer discuss them in what follows.

For even n, however, the above expression for $\tan\delta_0$ can be realized by a phase, which vanishes at $E = 0$ and runs for $E \to \infty$ into the value π. For $E = E_n$ in this case also $\delta_0 = \pi/2$.

3. Determination of the resonance energies for strong couplings $V_0 R \gg 1$! Then the right-hand side of (A.8) is very small in magnitude. That means for the left-hand side:

$$2k_n R = n\pi + \alpha \;\; ; \;\; (|\alpha| \ll 1)$$

(see remark after (A.8)). It can therewith be estimated:

$$\begin{aligned} \sin(2k_n R) &= \sin(n\pi + \alpha) = \sin(n\pi)\cos\alpha + \cos(n\pi)\sin\alpha \\ &= (-1)^n \sin\alpha \approx (-1)^n \alpha \; . \end{aligned}$$

On the other hand:

$$\sin(2k_n R) \stackrel{!}{=} -\frac{\hbar^2}{2mV_0 R}(n\pi + \alpha) \approx -\frac{\hbar^2}{2mV_0 R}\, n\pi \; .$$

Equating the last two expressions:

$$\alpha \approx (-1)^{n+1} \frac{\hbar^2}{2mV_0 R}\, n\pi \; .$$

That means:

$$2k_n R \approx n\pi \left(1 + (-1)^{n+1} \frac{\hbar^2}{2mV_0 R}\right) .$$

Resonance energies:

$$E_n = \frac{\hbar^2 k_n^2}{2m} \approx \frac{\hbar^2}{8mR^2}\,(n\pi)^2 \left(1 + (-1)^{n+1} \frac{\hbar^2}{mV_0 R}\right) .$$

For the here interesting even $n = 2\nu$ $(\nu = 1, 2, 3, \ldots)$ this expression reads:

$$E_\nu \approx \frac{\hbar^2}{2mR^2}\,(\nu\pi)^2 \left(1 - \frac{\hbar^2}{mV_0 R}\right) = E_{0,\nu} \left(1 - \frac{\hbar^2}{mV_0 R}\right) . \qquad \text{(A.10)}$$

The pre-factor is identical to the $l = 0$-energies $E_{0,\nu}$ in the infinitely high spherical potential well (radius R), which were calculated in Exercise 6.3.1. That means that the resonance energies E_ν, which belong to the evenly indexed solutions k_n from (A.8), lie very close to the energies $E_{0,\nu}$ of the (bound) states in the spherical hollow-potential (cf. also the discussion after (9.56)).

4. For the coefficients γ_n with $n = 2\nu$ $(\nu = 1, 2, 3, \ldots)$, given in (A.9), we estimate for strong coupling $(V_0 R \gg 1)$:

$$\begin{aligned}
\sin(k_n R) &= \sin\left(\frac{n\pi}{2} + \frac{\alpha}{2}\right) \overset{(n=2\nu)}{=} \sin\left(\nu\pi - \frac{\hbar^2}{2mV_0 R}\nu\pi\right) \\
&= \sin(\nu\pi)\cos\left(\frac{\hbar^2}{2mV_0 R}\nu\pi\right) - \cos(\nu\pi)\sin\left(\frac{\hbar^2}{2mV_0 R}\nu\pi\right) \\
&= (-1)^{\nu+1}\sin\left(\frac{\hbar^2}{2mV_0 R}\nu\pi\right) \approx (-1)^{\nu+1}\frac{\hbar^2}{2mV_0 R}\nu\pi \\
\cos(2k_n R) &\approx \cos(n\pi) = (-1)^n \overset{(n=2\nu)}{=} +1 \,.
\end{aligned}$$

The estimations are of course valid only for not too large quantum numbers ν. We insert them now into(A.9):

$$\begin{aligned}
\gamma_n = \gamma_{2\nu} &= \frac{-\left(\frac{\hbar^2}{2mV_0 R}\right)^2 (\nu\pi)^2}{\frac{mR^2}{\hbar^2}\left(1 + \frac{\hbar^2}{2mV_0 R}\right)} \approx -\frac{\hbar^2}{mR^2}\left(\frac{\hbar^2}{2mV_0 R}\right)^2 (\nu\pi)^2 \\
&= -\frac{1}{2}E_{0,2\nu}\left(\frac{\hbar^2}{2mV_0 R}\right)^2 \\
E_{0,n} &\overset{(A.9)}{\approx} E_n\left(1 + \frac{\hbar^2}{mV_0 R}\right) \\
\curvearrowright\ \gamma_n &\approx -\frac{1}{2}E_n\left(1 + \frac{\hbar^2}{mV_0 R}\right)\left(\frac{\hbar^2}{2mV_0 R}\right)^2 \approx -\frac{1}{2}E_n\left(\frac{\hbar^2}{2mV_0 R}\right)^2 \,.
\end{aligned}$$

That was to be shown!

Solution 9.2.5

Equation (9.25) yields:

$$\frac{d\sigma}{d\Omega} = \frac{1}{k^2}\sum_{l,l'}(2l+1)(2l'+1)\sin\delta_l \sin\delta_{l'}\, e^{i(\delta_l - \delta_{l'})} P_l(\cos\vartheta) P_{l'}(\cos\vartheta) \,.$$

For a centrally symmetric scattering potential the differential cross-section, too, will show this symmetry. An expansion in Legendre polynomials therefore appears to be reasonable:

$$\frac{d\sigma}{d\Omega} = \sum_{\nu=0}^{\infty} a_\nu P_\nu(\cos\vartheta) \,.$$

With the orthogonality relation for Legendre polynomials (5.98)

$$\int_{-1}^{+1} d\cos\vartheta P_\nu(\cos\vartheta) P_\mu(\cos\vartheta) = \frac{2}{2\nu+1}\delta_{\nu\mu}$$

it follows immediately for the expansion coefficients:

$$a_\mu = \frac{2\mu+1}{2}\int\limits_{-1}^{+1} d\cos\vartheta\, P_\mu(\cos\vartheta)\frac{d\sigma}{d\Omega} = \frac{2\mu+1}{4\pi}\int\limits_{-1}^{+1} d\Omega\, P_\mu(\cos\vartheta)\frac{d\sigma}{d\Omega}\,.$$

The integrals, given in the problem, are, except for trivial pre-factors, identical to the expansion coefficients a_0 and a_1:

$$\begin{aligned} P_0(\cos\vartheta) = 1 \quad &\curvearrowright \quad a_0 = \frac{1}{4\pi}\int d\Omega \frac{d\sigma}{d\Omega} \\ P_1(\cos\vartheta) = \cos\vartheta \quad &\curvearrowright \quad a_1 = \frac{3}{4\pi}\int d\Omega \cos\vartheta \frac{d\sigma}{d\Omega}\,. \end{aligned}$$

The calculation of the coefficient a_0 is relatively simple:

$$\begin{aligned} a_0 &= \frac{2\pi}{4\pi k^2}\sum_{l,l'}(2l+1)(2l'+1)\sin\delta_l \sin\delta_{l'}\, e^{i(\delta_l-\delta_{l'})} \star \\ &\quad \star\int\limits_{-1}^{+1} d\cos\vartheta P_l(\cos\vartheta)P_{l'}(\cos\vartheta) \\ &= \frac{1}{2k^2}\sum_l (2l+1)^2\sin^2\delta_l \frac{2}{2l+1} \\ &= \frac{1}{k^2}\sum_l (2l+1)\sin^2\delta_l \overset{(9.26)}{=} \frac{1}{4\pi}\sigma\,. \end{aligned}$$

For the determination of a_1 we need expressions of the form

$$\cos\vartheta\, P_l(\cos\vartheta)P_{l'}(\cos\vartheta)\,.$$

The recursion formula from part 2. of Exercise 6.2.9 helps:

$$\cos\vartheta P_l(\cos\vartheta) = \frac{1}{2l+1}\Big((l+1)P_{l+1} + lP_{l-1}\Big) \quad \curvearrowright$$

$$\begin{aligned} \int\limits_{-1}^{+1} d\cos\vartheta\, \cos\vartheta P_l(\cos\vartheta)P_{l'}(\cos\vartheta) &= \frac{l+1}{2l+1}\int\limits_{-1}^{+1} d\cos\vartheta\, P_{l+1}(\cos\vartheta)P_{l'}(\cos\vartheta) \\ &\quad + \frac{l}{2l+1}\int\limits_{-1}^{+1} d\cos\vartheta\, P_{l-1}(\cos\vartheta)P_{l'}(\cos\vartheta) \\ &= \frac{2(l+1)\,\delta_{l'l+1}}{(2l+1)(2l+3)} + \frac{2l\,\delta_{l'l-1}}{(2l+1)(2l-1)}\,. \end{aligned}$$

Therewith it is:

$$\begin{aligned}
a_1 &= \frac{3}{4\pi}\frac{2\pi}{k^2}\sum_{l,l'}(2l+1)(2l'+1)\sin\delta_l\sin\delta_{l'}\,e^{i(\delta_l-\delta_{l'})}\ \star \\
&\quad \star\int_{-1}^{+1} d\cos\vartheta\cos\vartheta P_l(\cos\vartheta)P_{l'}(\cos\vartheta) \\
&= \frac{3}{2k^2}\sum_l(2l+1)(2l+3)\frac{l+1}{2l+1}\frac{2}{2l+3}\sin\delta_l\sin\delta_{l+1}\,e^{i(\delta_l-\delta_{l+1})} \\
&\quad +\frac{3}{2k^2}\sum_l(2l+1)(2l-1)\frac{l}{2l+1}\frac{2}{2l-1}\sin\delta_l\sin\delta_{l-1}\,e^{i(\delta_l-\delta_{l-1})} \\
&= \frac{3}{2k^2}\sum_{l=0}^{\infty}2(l+1)\sin\delta_l\sin\delta_{l+1}\,e^{i(\delta_l-\delta_{l+1})} \\
&\quad +\frac{3}{2k^2}\sum_{l=0}^{\infty}2l\sin\delta_l\sin\delta_{l-1}\,e^{i(\delta_l-\delta_{l-1})} \\
&= \frac{3}{k^2}\sum_{l=0}^{\infty}(l+1)\sin\delta_l\sin\delta_{l+1}\,\left(e^{i(\delta_l-\delta_{l+1})}+e^{i(\delta_{l+1}-\delta_l)}\right)\,.
\end{aligned}$$

It remains:

$$a_1 = \frac{6}{k^2}\sum_{l=0}^{\infty}(l+1)\sin\delta_l\sin\delta_{l+1}\,\cos(\delta_{l+1}-\delta_l)\,.$$

Section 9.3.3

Solution 9.3.1

1. We use the formula (9.93) for the calculation of the scattering amplitude:

$$\begin{aligned}
f^{(1)}(\vartheta) &= -\frac{2m}{\hbar^2 K}\,\alpha\int_0^{\infty}dr'\,e^{-r'/R_0}\sin(K\,r') \equiv -\frac{2m\,\alpha}{\hbar^2 K}\,J\,, \\
J &= \int_0^{\infty}dr'\,e^{-r'/R_0}\sin(K\,r') \\
&= -R_0\ e^{-r'/R_0}\sin(K\,r')\Big|_0^{\infty} + K\,R_0\int_0^{\infty}dr'\,e^{-r'/R_0}\cos(K\,r') \\
&= 0 - K\,R_0^2\ e^{-r'/R_0}\cos(K\,r')\Big|_0^{\infty} - K^2R_0^2\,J = K\,R_0^2 - K^2R_0^2\,J \\
\Longrightarrow\ J &= \frac{K\,R_0^2}{1+K^2R_0^2}\,.
\end{aligned}$$

Scattering amplitude:

$$f^{(1)}(\vartheta) = -\frac{2m\,\alpha}{\hbar^2}\,\frac{R_0^2}{1+4k^2R_0^2\sin^2(\vartheta/2)}\,.$$

($K = 2k\sin(\vartheta/2)$ inserted according to (9.92)!)
Differential cross-section:

$$\frac{d\sigma^{(1)}}{d\Omega} = |f^{(1)}(\vartheta)|^2 = \frac{4m^2\alpha^2}{\hbar^4}\,\frac{R_0^4}{\left(1+4k^2R_0^2\sin^2(\vartheta/2)\right)^2}\,.$$

2. Low energies: $k\,R_0 \ll 1$
Criterion (9.96) should be fulfilled:

$$\left|\int_0^\infty dr\,r\,V(r)\right| = \alpha\left|\int_0^\infty dr\,e^{-r/R_0}\right| = \alpha\,R_0\,.$$

Requirement:

$$\alpha\,R_0 \ll \frac{\hbar^2}{2m}\,.$$

3. The Coulomb potential represents the $R_0 \to \infty$-limiting case of the Yukawa potential, when one still chooses

$$\alpha = \frac{Z_1\,Z_2\,e^2}{4\pi\,\varepsilon_0}$$

($Z_1\,(Z_2)\,e$: charge of the scattered (scattering) particle).

($R_0 \to \infty$ contradicts, though, 2.!). According to part 1. we now have for the scattering amplitude:

$$f^{(1)}(\vartheta) = -\frac{m\,Z_1\,Z_2\,e^2}{4\pi\,\varepsilon_0\,\hbar^2}\,\frac{1}{2k^2\sin^2(\vartheta/2)}\,.$$

Differential cross-section:

$$\frac{d\sigma^{(1)}}{d\Omega} = |f^{(1)}(\vartheta)|^2 = \left(\frac{Z_1\,Z_2\,e^2}{4\pi\,\varepsilon_0}\,\frac{1}{4E}\right)^2\,\frac{1}{\sin^4(\vartheta/2)}\,.$$

This result agrees exactly with the *Rutherford scattering formula* ((1.67), Vol. 6) for the classical particle scattering. On the other hand, the scattering problem for the Coulomb potential can also be exactly treated. Surprisingly, it comes out again ((1.67), Vol. 6). The first Born approximation thus yields for $(d\sigma/d\Omega)$ already the exact result. That must be judged, though, as *only accidental*. It is not at all so that all higher Born approximations would vanish. The second Born approximation, for instance, diverges for $R_0 \to \infty$. The scattering amplitude $f^{(1)}(\vartheta)$ does not agree with the exact one, either. It differs from that by a phase factor, which is unimportant, though, for $(d\sigma/d\Omega)$.

Solution 9.3.2

1. We use formula (9.93) for the calculation of the scattering amplitude:

$$\begin{aligned} f^{(1)}(\vartheta) &= \frac{2m\,V_0}{\hbar^2}\,\frac{1}{K}\int\limits_0^\infty dr\,r\,e^{-\frac{r}{R_0}}\sin K\,r\;, \\ K &= 2k\sin\frac{\vartheta}{2}\;. \end{aligned}$$

Substitution:

$$\begin{aligned} x &= \frac{r}{R_0}\;; \quad q = K\,R_0 \\ \Longrightarrow\; f_1(\vartheta) &= \frac{2m\,V_0}{\hbar^2}\,\frac{R_0^3}{q}\underbrace{\int\limits_0^\infty dx\,x\,e^{-x}\sin q\,x}_{I(q)} \\ I(q) &= -\frac{d}{dq}\int\limits_0^\infty dx\,e^{-x}\cos(q\,x) = -\frac{d}{dq}\,\mathrm{Re}\int\limits_0^\infty dx\,e^{-x+iqx} \\ &= +\frac{d}{dq}\,\mathrm{Re}\,\frac{1}{-1+i\,q} = \frac{d}{dq}\,\frac{-1}{1+q^2} = \frac{2q}{(1+q^2)^2}\;. \end{aligned}$$

Scattering amplitude:

$$f^{(1)}(\vartheta) = \frac{4m\,V_0\,R_0^3}{\hbar^2}\,\frac{1}{\left(1+4k^2R_0^2\sin^2(\vartheta/2)\right)^2}\;.$$

2.

$$\left|\int\limits_0^\infty dr\,V_0\,e^{-r/R_0}\left(e^{2ikr}-1\right)\right| \overset{!}{\ll} \frac{\hbar^2 k}{m}$$

$$\begin{aligned} & V_0\left|\frac{-1}{-1/R_0+2i\,k}-R_0\right| = V_0\left|\frac{R_0}{1-2i\,k\,R_0}-R_0\right| = V_0\left|\frac{2i\,k\,R_0^2}{1-2i\,k\,R_0}\right| \\ = \;& V_0\,R_0\left|\frac{2i\,k\,R_0(1+2i\,k\,R_0)}{1+4k^2R_0^2}\right| = \frac{V_0R_0}{1+4k^2R_0^2}\,\sqrt{16\,k^4\,R_0^4+4k^2R_0^2} \\ = \;& \frac{2V_0\,k\,R_0^2}{\sqrt{1+4k^2R_0^2}} \overset{!}{\ll} \frac{\hbar^2 k}{m}\;. \end{aligned}$$

In particular it must be required:

$$\begin{aligned} k\,R_0 \gg 1: &\qquad V_0\,R_0 \overset{!}{\ll} \frac{\hbar^2 k}{m}\;, \\ k\,R_0 \ll 1: &\qquad V_0\,R_0^2 \overset{!}{\ll} \frac{\hbar^2}{2m}\;. \end{aligned}$$

3. With the exact expression (9.23)

$$f(\vartheta) = \frac{1}{k} \sum_{l=0}^{\infty} (2l+1)\, e^{i\delta_l} \sin\delta_l\, P_l(\cos\vartheta)$$

and the orthogonality relation (5.98) for Legendre polynomials

$$\int_{-1}^{+1} d\cos\vartheta\, P_l(\cos\vartheta)\, P_{l'}(\cos\vartheta) = \frac{2}{2l+1}\,\delta_{l\,l'}$$

it follows, at first very general:

$$2\sin\delta_l\, e^{i\delta_l} = k \int_{-1}^{+1} d\cos\vartheta\, f(\vartheta)\, P_l(\cos\vartheta)\ .$$

***s*-scattering:**

$$\begin{aligned}
\sin^2\frac{\vartheta}{2} &= \frac{1}{2}\,(1-\cos\vartheta)\ , \\
2\sin\delta_0\, e^{i\delta_0} &= \frac{4m\,V_0\,R_0^3}{\hbar^2}\, k \int_{-1}^{+1} \frac{d\cos\vartheta}{\left[1+2k^2\,R_0^2\,(1-\cos\vartheta)\right]^2} \\
&= \frac{2m\,V_0\,R_0}{\hbar^2 k} \int_{-1}^{+1} d\cos\vartheta\, \frac{d}{d\cos\vartheta}\, \frac{1}{1+2k^2R_0^2(1-\cos\vartheta)} \\
&= \frac{2m\,V_0\,R_0}{\hbar^2 k} \left(1 - \frac{1}{1+4k^2\,R_0^2}\right)\ , \\
2\sin\delta_0\, e^{i\delta_0} &= -i\big(e^{2i\delta_0}-1\big)\ .
\end{aligned}$$

This yields:

$$e^{2i\,\delta_0} = 1 + i\,\frac{8m\,V_0\,k\,R_0^3}{\hbar^2\ (1+4k^2\,R_0^2)}\ .$$

This relation can not be actually fulfilled, because on the right-hand side there stands a complex number with a magnitude larger than 1. It can be correct only approximately. In the sense of part 1. the imaginary part should be smaller than one:

$$\begin{aligned}
\cos 2\delta_0 &= 1\ , \\
\sin 2\delta_0 &= \frac{8m\,V_0\,k\,R_0^3}{\hbar^2\big(1+4k^2\,R_0^2\big)} \approx 2\delta_0\ , \\
\delta_0 &\approx \frac{4m\,V_0\,k\,R_0^3}{\hbar^2\,\big(1+4k^2\,R_0^2\big)}\ .
\end{aligned}$$

High particle energies ($k\,R_0 \gg 1$):

$$\delta_0 \approx \frac{m\,V_0\,R_0}{\hbar^2 k} \ll 1\,. \qquad \text{part 2.}$$

Low particle energies ($k\,R_0 \ll 1$):

$$\delta_0 \approx \frac{4m\,V_0\,k\,R_0^3}{\hbar^2} \ll 2k\,R_0 \ll 1 \qquad \text{part 2.}$$

In these limits the approximation is thus unambiguous.

4. To facilitate the paperwork we put:

$$y_0 = k\,R_0\,; \quad \cos\vartheta = z\,.$$

***p*-scattering:**

$$\begin{aligned}
P_1(\cos\vartheta) &= \cos\vartheta\,, \\
2\sin\delta_1\,e^{i\delta_1} &= \frac{4m\,V_0\,R_0^2}{\hbar^2}\,y_0 \underbrace{\int_{-1}^{+1} dz\,\frac{z}{\left[1+2y_0^2(1-z)\right]^2}}_{I}\,, \\
I &= \frac{(1/2y_0^2)\,z}{1+2y_0^2(1-z)}\bigg|_{-1}^{+1} - \frac{1}{2y_0^2}\int_{-1}^{+1}\frac{dz}{1+2y_0^2(1-z)} \\
&= \frac{1}{2y_0^2} + \frac{1}{2y_0^2}\,\frac{1}{1+4y_0^2} + \frac{1}{4y_0^4}\ln\frac{1}{1+4y_0^2} \\
&= \frac{1}{2y_0^2}\left[\frac{2+4y_0^2}{1+4y_0^2} - \frac{1}{2y_0^2}\ln\bigl(1+4y_0^2\bigr)\right] \\
\Longrightarrow\ 2\sin\delta_1\,e^{i\delta_1} &= \frac{4m\,V_0\,R_0^2}{\hbar^2\,y_0}\left[\frac{1+2y_0^2}{1+4y_0^2} - \frac{1}{4y_0^2}\ln\bigl(1+4y_0^2\bigr)\right]\,.
\end{aligned}$$

The conditional equation

$$e^{2i\,\delta_1} = 1 + i\,\frac{4m\,V_0\,R_0^2}{\hbar^2 y_0}\left[\frac{1+2y_0^2}{1+4y_0^2} - \frac{1}{4y_0^2}\ln\bigl(1+4y_0^2\bigr)\right]$$

is actually not satisfiable as in part 3.. With the same *'justification'* as there, ($\cos 2\delta_1 = 1$, $\sin 2\delta_1 \approx 2\delta_1 \ll 1$), we conclude:

$$\delta_1 \approx \frac{2m\,V_0\,R_0}{\hbar^2 k}\left[\frac{1+2k^2\,R_0^2}{1+4k^2\,R_0^2} - \frac{1}{4k^2\,R_0^2}\ln\bigl(1+4k^2\,R_0^2\bigr)\right]\,.$$

Solution 9.3.3

1. Starting point is formula (9.93):

$$\begin{aligned} f^{(1)}(\vartheta) &= \frac{2m\,V_0}{\hbar^2\,K}\int\limits_0^{R_0} dr'\,r'\sin(K\,r') = \frac{2m\,V_0}{\hbar^2\,K}\left(-\frac{d}{dK}\int\limits_0^{R_0} dr'\cos K\,r'\right) \\ &= -\frac{2m\,V_0}{\hbar^2 K}\,\frac{d}{dK}\,\frac{1}{K}\sin K\,R_0 \\ \Longrightarrow\ f^{(1)}(\vartheta) &= \frac{2m\,V_0}{\hbar^2 K^3}\left(\sin K\,R_0 - K\,R_0\cos K\,R_0\right), \\ & K = 2k\sin\frac{\vartheta}{2}\,. \end{aligned}$$

2.

$$\frac{d\sigma^{(1)}}{d\Omega} = \left|f^{(1)}(\vartheta)\right|^2 = \left(\frac{2m\,V_0\,R_0^3}{\hbar^2}\right)^2 \frac{\left(\sin K\,R_0 - K\,R_0\cos K\,R_0\right)^2}{(K\,R_0)^6}\,.$$

We investigate the limit of low particle energies. According to l'Hospital's rule it holds at first:

$$\lim_{x\to 0}\frac{\sin x - x\cos x}{x^3} = \lim_{x\to 0}\frac{\cos x - \cos x + x\sin x}{3x^2} = \lim_{x\to 0}\frac{\sin x}{3x} = \lim_{x\to 0}\frac{\cos x}{3} = \frac{1}{3}\,.$$

$k\,R_0 \ll 1$ also means $K\,R_0 \ll 1$. It thus follows for the differential cross-section at low energy of the *incident* particle:

$$\frac{d\sigma^{(1)}}{d\Omega} \approx \frac{1}{9}\,R_0^2\left(\frac{2m\,V_0\,R_0^2}{\hbar^2}\right)^2\,.$$

It turns out to be isotropic and energy-independent. The isotropy of the cross-section at low energies is typical for the scattering at short range potentials. That we have already realized at the end of Sect. 9.2.3.

Total cross-section:

$$\sigma^{(1)} \approx 4\pi\,R_0^2\,\frac{1}{9}\left(\frac{2m\,V_0\,R_0^2}{\hbar^2}\right)^2\,.$$

3.

$$\begin{aligned} &\left|\int\limits_0^\infty dr\,V(r)\left(e^{2ikr}-1\right)\right| = V_0\left|\frac{1}{2i\,k}\left(e^{2i\,k\,R_0}-1\right) - R_0\right| \\ =\ & \frac{V_0}{2k}\left|\left(\cos 2k\,R_0 - 1\right) + i\left(\sin 2k\,R_0 - 2k\,R_0\right)\right| \\ =\ & \frac{V_0}{2k}\sqrt{\left(\cos 2k\,R_0 - 1\right)^2 + \left(\sin 2k\,R_0 - 2k\,R_0\right)^2} \\ =\ & \frac{V_0}{2k}\sqrt{2\left(1-\cos 2k\,R_0\right) + 4k\,R_0\left(k\,R_0 - \sin 2k\,R_0\right)} \overset{!}{\ll} \frac{\hbar^2 k}{m}\,. \end{aligned}$$

$k\,R_0 \ll 1$

We develop the radicand in powers of $k\,R_0$:

$$\begin{aligned} & \sqrt{2(1-\cos 2k\,R_0)+4k\,R_0(k\,R_0-\sin 2k\,R_0)} \\ = & \left[2\left(\frac{1}{2}\,(2k\,R_0)^2-\frac{1}{4!}\,(2k\,R_0)^4\right)\right. \\ & \left.+4k\,R_0\,\left(k\,R_0-2k\,R_0+\frac{1}{3!}\,(2k\,R_0)^3\right)+\mathcal{O}\big((k\,R_0)^6\big)\right]^{1/2} \\ = & \sqrt{4(k\,R_0)^4+0\big[(k\,R_0)^6\big]} \approx 2(k\,R_0)^2\ . \end{aligned}$$

The criterion then reads:

$$V_0\,R_0^2 \ll \frac{\hbar^2}{m} \quad \text{(see discussion after (9.96))}\ .$$

$k\,R_0 \gg 1$

$$\sqrt{2(1-\cos 2k\,R_0)+4k\,R_0\,(k\,R_0-\sin 2k\,R_0)} \approx 2k\,R_0\ .$$

Criterion:

$$V_0\,R_0 \ll \frac{\hbar^2 k}{m} \quad \text{(see discussion after (9.95))}.$$

4. Condition for the bound state (6.138):

$$\begin{aligned} V_0 &> \frac{\pi^2\hbar^2}{8m\,R_0^2} \\ \Longrightarrow \quad \frac{m\,V_0\,R_0^2}{\hbar^2} &> \frac{\pi^2}{8} \approx 1.23 \end{aligned}$$

$\Longrightarrow$ criterion not fulfilled, Born approximation fails.

Solution 9.3.4

1. Let the *scattering* hydrogen atom be at the origin of coordinates. The probability density to find the orbital electron of the H-atom at the position r is given by

$$|\psi_{100}(\mathbf{r})|^2\ .$$

for the *incident* electron, the orbital electron creates the following potential at the position $\mathbf{r}_0$:

$$V_{\rm f}\,(\mathbf{r}_0) = \frac{e^2}{4\pi\,\varepsilon_0}\int d^3r\,\frac{|\psi_{100}(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{r}_0|}\ .$$

In addition there is the nuclear potential:

$$V_{\rm N}\,(\mathbf{r}_0) = -\frac{e^2}{4\pi\,\varepsilon_0\,r_0}\ .$$

The *incident* electron *sees* therefore the scattering potential:

$$V(\mathbf{r}_0) = \frac{e^2}{4\pi\,\varepsilon_0}\left\{\int d^3r\,\frac{|\psi_{100}(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{r}_0|} - \frac{1}{r_0}\right\}\,.$$

According to (6.60) and (5.108):

$$\psi_{100}(\mathbf{r}) = \frac{1}{\sqrt{\pi\,a_\mathrm{B}^3}}\,e^{-r/a_\mathrm{B}}\,.$$

We calculate therewith ($\mathbf{r}_0$: polar axis):

$$\begin{aligned}
\int d^3r\,\frac{|\psi_{100}(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{r}_0|} &= \frac{2\pi}{\pi\,a_\mathrm{B}^3}\int_0^\infty dr\,r^2\,e^{-2r/a_\mathrm{B}}\,I\,,\\
I \equiv \int_{-1}^{+1}\frac{dx}{\sqrt{r^2+r_0^2-2r\,r_0\,x}} &= -\frac{1}{r\,r_0}\sqrt{r^2+r_0^2-2r\,r_0\,x}\,\Big|_{-1}^{+1}\\
= -\frac{1}{r\,r_0}\left[|r-r_0|-(r+r_0)\right] &= \begin{cases}\frac{2}{r}\,, & \text{if } r\geq r_0\,,\\ \frac{2}{r_0}\,, & \text{if } r\leq r_0\end{cases}
\end{aligned}$$

$$\Longrightarrow\; V_\mathrm{f}(\mathbf{r}_0) = \frac{e^2}{4\pi\,\varepsilon_0}\,\frac{2}{a_\mathrm{B}^3}\left(\frac{2}{r_0}\int_0^{r_0} dr\,r^2\,e^{-2r/a_\mathrm{B}} + 2\int_{r_0}^\infty dr\,r\,e^{-2r/a_\mathrm{B}}\right)\,.$$

This we evaluate with the given formulas:

$$\begin{aligned}
V_\mathrm{f}(\mathbf{r}_0) &= \frac{e^2}{\pi\,\varepsilon_0\,a_\mathrm{B}^3}\left[\frac{1}{r_0}\,\frac{2}{(2/a_\mathrm{B})^3}\left(1-e^{-\frac{2r_0}{a_\mathrm{B}}}\left(1+\frac{2r_0}{a_\mathrm{B}}+\frac{2r_0^2}{a_\mathrm{B}^2}\right)\right)\right.\\
&\quad\left.+\,\frac{1}{(2/a_\mathrm{B})^2}\,e^{-2r_0/a_\mathrm{B}}\left(1+\frac{2r_0}{a_\mathrm{B}}\right)\right]\\
&= \frac{e^2}{\pi\,\varepsilon_0\,a_\mathrm{B}^3}\left[\frac{a_\mathrm{B}^3}{4r_0}+e^{-2r_0/a_\mathrm{B}}\left(\frac{a_\mathrm{B}^2}{4}+\frac{a_\mathrm{B}\,r_0}{2}-\frac{a_\mathrm{B}^3}{4r_0}-\frac{a_\mathrm{B}^2}{2}-\frac{a_\mathrm{B}\,r_0}{2}\right)\right]\\
&= \frac{e^2}{4\pi\,\varepsilon_0\,a_\mathrm{B}}\left[\frac{a_\mathrm{B}}{r_0}-e^{-2r_0/a_\mathrm{B}}\left(1+\frac{a_\mathrm{B}}{r_0}\right)\right]\,.
\end{aligned}$$

$\Longrightarrow$ scattering potential ($\mathbf{r}_0\to\mathbf{r}$):

$$V(\mathbf{r}) = -\frac{e^2}{4\pi\,\varepsilon_0}\,e^{-2r/a_\mathrm{B}}\left(\frac{1}{a_\mathrm{B}}+\frac{1}{r}\right)\,.$$

2. Scattering amplitude in first Born approximation:

$$\begin{aligned}
\frac{m\,e^2}{4\pi\varepsilon_0\,\hbar^2} &= \frac{1}{a_\mathrm{B}} \quad 6.32\,; \quad K = 2k\sin\frac{\vartheta}{2} \\
&\quad \text{(formula (9.93))}\,, \\
f^{(1)}(\vartheta) &= \frac{2}{a_\mathrm{B}K}\left[\frac{1}{a_\mathrm{B}}\int\limits_0^\infty dr\,r\,\frac{1}{2i}\left(e^{-(2/a_\mathrm{B}\,-\,i\,K)r} - e^{-(2/a_\mathrm{B}\,+\,i\,K)r}\right)\right. \\
&\quad \left. + \int\limits_0^\infty dr\,\frac{1}{2i}\left(e^{-(2/a_\mathrm{B}\,-\,i\,K)r} - e^{-(2/a_\mathrm{B}\,+\,i\,K)r}\right)\right] \\
&= \frac{1}{i\,a_\mathrm{B}\,K}\left[\left(-\frac{1}{a_\mathrm{B}}\,\frac{d}{d(2/a_\mathrm{B}\,-\,i\,K)} + 1\right)\int\limits_0^\infty dr\,e^{-(2/a_\mathrm{B}\,-\,i\,K)r}\right. \\
&\quad \left. - \left(-\frac{1}{a_\mathrm{B}}\,\frac{d}{d\,(2/a_\mathrm{B} + i\,K)} + 1\right)\int\limits_0^\infty dr\,e^{-(2/a_\mathrm{B}\,+\,i\,K)r}\right] \\
&= \frac{1}{i\,a_\mathrm{B}\,K}\left[\frac{1}{2/a_\mathrm{B} - i\,K} + \frac{1}{a_\mathrm{B}}\,\frac{1}{(2/a_\mathrm{B}\,-\,i\,K)^2} - \frac{1}{2/a_\mathrm{B} + i\,K}\right. \\
&\quad \left. - \frac{1}{a_\mathrm{B}}\,\frac{1}{(2/a_\mathrm{B} + i\,K)^2}\right] \\
&= \frac{1}{i\,a_\mathrm{B}\,K}\left[\frac{2i\,K}{4/a_\mathrm{B}^2 + K^2} + \frac{1}{a_\mathrm{B}}\,\frac{8i\,K/a_\mathrm{B}}{(4/a_\mathrm{B}^2 + K^2)^2}\right] \\
\Longrightarrow \quad & f^{(1)}(\vartheta) = \frac{2a_\mathrm{B}\left(8 + a_\mathrm{B}^2\,K^2\right)}{\left(4 + a_\mathrm{B}^2\,K^2\right)^2}\,.
\end{aligned}$$

3. Differential cross-section:

$$\begin{aligned}
K^2 &= 4k^2\sin^2\frac{\vartheta}{2} = 2k^2(1-\cos\vartheta)\,, \\
\frac{d\sigma^{(1)}}{d\vartheta} &= \left|f^{(1)}(\vartheta)\right|^2 = \frac{a_\mathrm{B}^2\,\left[4 + a_\mathrm{B}^2k^2(1-\cos\vartheta)\right]^2}{\left[2 + a_\mathrm{B}^2k^2\,(1-\cos\vartheta)\right]^4}\,.
\end{aligned}$$

4. Total cross-section:

$$\sigma^{(1)} = 2\pi\int\limits_{-1}^{+1} d\cos\vartheta\,\frac{d\sigma^{(1)}}{d\Omega}\,.$$

The angle-dependence is hidden in K:

$$x \equiv a_\mathrm{B}^2\,K^2 \implies dx = -2k^2\,a_\mathrm{B}^2\,d\cos\vartheta,$$

Abbreviation: $y = k\,a_{\rm B}$. It then remains to be calculated::

$$\begin{aligned}
\sigma^{(1)} &= -\frac{\pi}{y^2}\,4a_{\rm B}^2 \int\limits_{4y^2}^{0} dx\,\frac{(8+x)^2}{(4+x)^4} \\
&= \frac{4a_{\rm B}^2\,\pi}{y^2} \int\limits_{0}^{4y^2} dx\,\left[\frac{1}{(4+x)^2} + \frac{8}{(4+x)^3} + \frac{16}{(4+x)^4}\right] \\
&= \frac{4\pi\,a_{\rm B}^2}{y^2}\left[-\frac{1}{4+x} - \frac{4}{(4+x)^2} - \frac{16/3}{(4+x)^3}\right]_0^{4y^2} \\
&= \frac{4\pi\,a_{\rm B}^2}{y^2}\left[-\frac{1+2y^2+y^4+1+y^2+\frac{1}{3}}{4(1+y^2)^3} + \frac{7}{12}\right] \\
&= \frac{\pi\,a_{\rm B}^2}{y^2}\,\frac{(7/3)+7y^2+7y^4+(7/3)\,y^6-(7/3)-3y^2-y^4}{(1+y^2)^3}\,.
\end{aligned}$$

This leads to:

$$\sigma^{(1)} = \pi\,a_{\rm B}^2\,\frac{4+6k^2\,a_{\rm B}^2+(7/3)\,k^4\,a_{\rm B}^4}{\left(1+k^2\,a_{\rm B}^2\right)^3}\,.$$

Low particle energies: $k\,a_{\rm B} \ll 1$

$$\Longrightarrow\ \sigma^{(1)} \approx 4\pi\,a_{\rm B}^2 \quad \text{(see } \textit{hard sphere}\text{)}.$$

5. Criterion of validity (9.94):

$$\left|\int\limits_0^\infty dr\,\left(\frac{1}{a_{\rm B}}+\frac{1}{r}\right)\,e^{-2r/a_{\rm B}}\left(e^{2ikr}-1\right)\right| \overset{!}{\ll} \frac{\hbar^2 k}{m}\,\frac{4\pi\,\varepsilon_0}{e^2} = k\,a_{\rm B}\,.$$

We need for the evaluation an integral of the type:

$$\begin{aligned}
f(t) &= \int\limits_0^\infty dr\,\frac{1}{r}\left(e^{-(t\,-\,i\,\alpha)r} - e^{-tr}\right) \quad \text{with}\ \ f(t\to\infty)=0 \\
\Longrightarrow\ \frac{df}{dt} &= \int\limits_0^\infty dr\,\left(e^{-tr} - e^{-(t\,-\,i\,\alpha)r}\right) = \frac{1}{t} - \frac{1}{t\,-\,i\,\alpha}\,.
\end{aligned}$$

This yields with the correct boundary condition for $t\to\infty$:

$$f(t) = \ln\frac{t}{t\,-\,i\,\alpha}\,.$$

This we use with $t = 2/a_{\rm B},\ \alpha = 2k$ for the calculation of the integral in the criterion of validity:

$$|\ldots| = \left|\frac{1}{a_{\rm B}}\left(\frac{1}{2/a_{\rm B}-2i\,k} - \frac{1}{2/a_{\rm B}}\right) + \ln\frac{1}{1\,-\,i\,k\,a_{\rm B}}\right|\,.$$

The requirement for the validity of the Born approximation therefore reads:

$$\left|\frac{1}{2}\,\frac{i\,k\,a_\mathrm{B}}{1-i\,k\,a_\mathrm{B}} - \ln\bigl(1-i\,k\,a_\mathrm{B}\bigr)\right| \overset{!}{\ll} k\,a_\mathrm{B}\ .$$

We discuss the limiting cases:

$\boldsymbol{k\,a_\mathrm{B} \ll 1}$

$$\left|\frac{1}{2}\,i\,k\,a_\mathrm{B} + i\,k\,a_\mathrm{B}\right| \overset{!}{\ll} k\,a_\mathrm{B} \qquad \Longleftrightarrow\ \frac{3}{2} \overset{!}{\ll} 1\ .$$

The condition cannot be fulfilled. For low particle energies the Born approximation is obviously not useful!

$\boldsymbol{k\,a_\mathrm{B} \gg 1}$

$$\begin{aligned} &\left|-\frac{1}{2} - \ln(-i\,k\,a_\mathrm{B})\right| = \left|\frac{1}{2} + \ln\bigl(k\,a_\mathrm{B}\,e^{-i\pi/2}\bigr)\right| \\ = \ &\left|\frac{1}{2} - i\,\frac{\pi}{2} + \ln(k\,a_\mathrm{B})\right| \approx \left|\ln(k\,a_\mathrm{B})\right| \overset{!}{\ll} k\,a_\mathrm{B}\ . \end{aligned}$$

This condition is satisfiable. The Born approximation may be applicable for high particle energies.

Solution 9.3.5

$$\begin{aligned} \vartheta',\,\varphi' \ &: \quad \text{polar angle of the vector } \mathbf{r}', \\ \vartheta,\,\varphi \ &: \quad \text{polar angle of the unit vector } \mathbf{e}_r\ . \end{aligned}$$

We begin with the expression for $f^{(1)}(\vartheta)$ and use the formulas (6.152) and (6.153):

$$\begin{aligned} e^{ik\,\mathbf{r}'\cdot\mathbf{e}_z}\,e^{-ik\,\mathbf{r}'\cdot\mathbf{e}_r} &= \sum_l i^l\,\sqrt{4\pi(2l+1)}\,j_l(k\,r')\,Y_{l0}\,(\vartheta',\varphi') \\ \cdot\sum_{l'm'}(-i)^{l'}\,4\pi\,j_{l'}\,(k\,r') &\qquad \underbrace{Y_{l'm'}(\vartheta',\varphi')\,Y^*_{l'm'}\,(\vartheta,\varphi)}_{\overset{5.104}{=}\ (-1)^{2m'}\,Y^*_{l'\,-\,m'}\,(\vartheta',\varphi')\,Y_{l'\,-\,m'}\,(\vartheta,\varphi)}\ . \end{aligned}$$

Integration over the angles, as required in (9.91), yields together with the orthogonality relation (5.102) of the spherical harmonics:

$$\begin{aligned} &\int d\Omega' e^{-ik(\mathbf{e}_r\,-\,\mathbf{e}_z)\cdot\mathbf{r}'} \\ &\quad = \sum_{ll'm'} i^l(-i)^{l'}\sqrt{4\pi(2l+1)}\,4\pi\,j_l\,(k\,r')\,j_{l'}\,(k\,r')Y_{l'\,-\,m'}\,(\vartheta,\varphi)\,\delta_{ll'}\,\delta_{-m'0} \\ &\quad = 4\pi\sum_l \sqrt{4\pi(2l+1)}\,[j_l\,(k\,r')]^2\,Y_{l0}\,(\vartheta,\varphi) \\ &\quad \overset{(5.103)}{=}\ 4\pi\sum_l (2l+1)\,\bigl[j_l\,(k\,r')\bigr]^2\,P_l(\cos\vartheta)\ . \end{aligned}$$

It follows therewith for the scattering amplitude according to (9.91):

$$f^{(1)}(\vartheta,\,\varphi) = -\frac{2m}{\hbar^2}\,\sum_l (2l+1)\,P_l\,(\cos\vartheta)\,\int\limits_0^\infty dr'\,r'^2\,V(r')\,\left[j_l\,(k\,r')\right]^2\,.$$

We compare this with the exact expression (9.23):

$$\frac{1}{k}\,e^{i\delta_l}\,\sin\delta_l \approx -\frac{2m}{\hbar^2}\,\frac{1}{k^2}\,\int\limits_0^\infty dr'\,V(r')\,\left[k\,r'\,j_l(k\,r')\right]^2\,.$$

Because of $e^{i\delta_l}\sin\delta_l \approx \delta_l$ it results from that the Born approximation (9.76) for the scattering phase:

$$\delta_l \approx -\frac{2m}{\hbar^2}\,\frac{1}{k}\,\int\limits_0^\infty dr'\,V(r')\,\left[k\,r'\,j_l\,(k\,r')\right]^2\,.$$

Section 9.4.5

Solution 9.4.1

It holds:

$$\begin{aligned}
1 &= \left(E_n^{(0)} - H \pm i0^+\right)\,\frac{1}{E_n^{(0)} - H \pm i0^+} \\
&= \left(E_n^{(0)} - H_0 - H_1 \pm i0^+\right)\,\frac{1}{E_n^{(0)} - H \pm i0^+} \\
&= \frac{E_n^{(0)} - H_0 \pm i0^+}{E_n^{(0)} - H \pm i0^+} - H_1\,\frac{1}{E_n^{(0)} - H \pm ii0^+}\,.
\end{aligned}$$

This means:

$$\begin{aligned}
\frac{1}{E_n^{(0)} - H_0 \pm i0^+} &= \frac{1}{E_n^{(0)} - H \pm i0^+} - \frac{1}{E_n^{(0)} - H_0 \pm i0^+}\,H_1\,\frac{1}{E_n^{(0)} - H \pm i0^+} \\
\Leftrightarrow\; R_n^{(\pm)} &= G_n^{(\pm)} - R_n^{(\pm)}\,H_1\,G_n^{(\pm)} \\
\Leftrightarrow\; G_n^{(\pm)} &= R_n^{(\pm)} + R_n^{(\pm)}\,H_1\,G_n^{(\pm)}\,.
\end{aligned}$$

That was to be shown.

Solution 9.4.2

We insert (9.128) into (9.126) and demonstrate the identity:

$$\begin{aligned}
\left|E_n^{(0)}\right\rangle + G_n^{(\pm)}\,H_1\,\left|E_n^{(0)}\right\rangle &\stackrel{!}{=} \left|E_n^{(0)}\right\rangle + R_n^{(\pm)}\,H_1\,\left(\left|E_n^{(0)}\right\rangle + G_n^{(\pm)}\,H_1\,\left|E_n^{(0)}\right\rangle\right) \\
\Leftrightarrow\quad G_n^{(\pm)}\,H_1\,\left|E_n^{(0)}\right\rangle &\stackrel{!}{=} \left(R_n^{(\pm)}\,H_1 + R_n^{(\pm)}\,H_1\,G_n^{(\pm)}\,H_1\right)\,\left|E_n^{(0)}\right\rangle \\
\Leftrightarrow\quad G_n^{(\pm)}\,H_1 &\stackrel{!}{=} \left(R_n^{(\pm)} + R_n^{(\pm)}\,H_1\,G_n^{(\pm)}\right)\,H_1 = G_n^{(\pm)}\,H_1\,.
\end{aligned}$$

Solution 9.4.3

$$\begin{aligned}[S,\,H_0]_- &= M_-^+M_+H_0 - H_0M_-^+M_+ \\ &\overset{(9.161),(9.162)}{=} M_-^+HM_+ - M_-^+HM_+ \\ &= 0\,.\end{aligned}$$

Solution 9.4.4

1.

$$\begin{aligned}\widehat{S}\widehat{S}^+ &= M_+M_-^+M_-M_+^+ \overset{(9.156)}{=} M_+M_+^+ \overset{(9.157)}{=} P_S \\ \widehat{S}^+\widehat{S} &= M_-M_+^+M_+M_-^+ \overset{(9.156)}{=} M_-M_-^+ \overset{(9.157)}{=} P_S\,.\end{aligned}$$

2.

$$\begin{aligned}[\widehat{S},\,H]_- &= M_+M_-^+H - HM_+M_-^+ \\ &\overset{(9.161),(9.162)}{=} M_+H_0M_-^+ - M_+H_0M_-^+ \\ &= 0\,.\end{aligned}$$

3. With (9.156) and (9.170) it follows:

$$\begin{aligned}\widehat{S}\left|E_n^{(-)}\right\rangle &= M_+M_-^+\left|E_n^{(-)}\right\rangle \\ &= M_+M_-^+M_-\left|E_n^{(0)}\right\rangle \\ &= M_+\left|E_n^{(0)}\right\rangle \\ &= \left|E_n^{(+)}\right\rangle\,.\end{aligned}$$

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