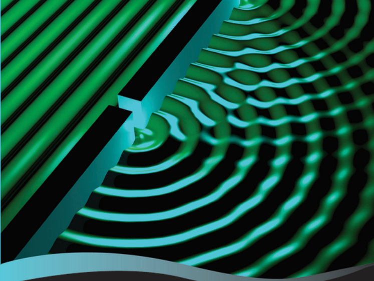

Practical Quantum Mechanics

Modern Tools and Applications

Efstratios Manousakis

OXFORD GRADUATE TEXTS

PRACTICAL QUANTUM MECHANICS

Practical Quantum Mechanics

Modern Tools and Applications

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Department of Physics, Florida State University, USA

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Dedicated to the loving memory of Jacob Manousakis

Preface

I found that writing these lecture notes was not a terribly difficult task for the following reasons. These notes are based on a two semester graduate level course in quantum mechanics. The course has, as a prerequisite, two semesters of undergraduate quantum mechanics. This means that, because of lack of time, I felt forced to assume that the time to ask questions on the fundamental issues of quantum mechanics, such as questions on interpretation of quantum mechanics, has "passed" for the students in this graduate class. The goal of the lectures is limited to teach students what I call "practical quantum mechanics," namely, how to use the formalism to solve problems and to give them the formal training to be able to follow other graduate courses and to tackle real problems in their research. This does not mean that when a student had such questions, in class or outside class, I did not try to answer them.

There are undoubtedly errata in this edition of these notes. Every time I read them, I feel that they can be improved further and I was hesitant to publish the document. However, I realized that I have done this in the past; namely, I have written notes on other subjects which I did not publish for this same reason, and because I was hoping that one day I would go back and make the needed improvements. However, this never happened, that is, I never found the time needed to go back to improve the notes for publication. More recently, I felt that writing extensive notes on a given subject and spending a few years working seriously to improve them for my class and not making them available to others may be, to some extent, a waste of human resources.

These notes contain some parts—some sections, examples, problems, derivations, and perspectives—which are not available in other books on quantum mechanics. Some parts or their emphasis have been inspired by relatively recent (i.e., during the last 25 years) advances in various areas of physics. For example, we begin by putting the Schrödinger equation on a spatial discrete lattice, something inspired by Hamiltonian lattice gauge theories (HLGT), which, I believe, allows us to better understand what we are doing by using a natural regularization scheme to circumvent the infinities associated with a continuum. We also discuss the path integral formulation of quantum mechanics; this choice was inspired both by the HLGT and by recent advances in simulations of quantum many-body systems. For example, we used the path-integral representation of the imaginary-time evolution operator to analytically show that, starting from a wavepacket as initial state, we can project the exact ground state wavefunction of the Harmonic oscillator. While this is analytical, it was inspired by numerical ground-state projection techniques, such as the so-called Green's function Monte Carlo method. We also emphasize the adiabatic time evolution in the case of a time-dependent Hamiltonian, the inclusion of which was motivated by real-time evolution studies in the area of cold atoms in optical lattices. As an example of how to use symmetry in quantum mechanics, we treat one-dimensional periodic potentials both exactly (when possible) and perturbatively. The inclusion of this area was inspired by condensed matter physics. We also discuss atoms and molecules using mean-field-like treatment, such as the Hartree–Fock approximation (including a discussion on how to go beyond mean-field theory), viewed as a variational technique. Motivated by the rather intense recent activity in condensed matter and atomic physics to study the so-called Hubbard model, the electron–electron correlations in the hydrogen molecule are taken into account with a simple, first quantized formulation of the two-site Hubbard model, which is solved analytically. Again inspired by HLGT, we also use the canonical Hamiltonian quantization of quantum electrodynamics (with no Fermions) by finding the normal modes, in a straightforward analogy with the treatment of the normal modes of an array of atoms; the photons emerge as the quanta of such normal modes, in the same way as the phonons emerge in the treatment of the normal modes of the coupled array of atoms. This Hamiltonian quantization of the electromagnetic field is used later to treat its interaction with atomic matter, without having to follow the usual semiclassical treatment.

There is some degree of redundancy in these notes. Namely, when the reader studies a chapter and we need to refer to an equation in a previous chapter, for convenience and for no interruption of the flow of thought, in some cases the equation is rewritten. Our personal experience with reading other physics books is that asking the reader to go back to another chapter to try to find the equation unnecessarily interrupts the continuity of the thought process. This set of lecture notes is intended to be used as a textbook mainly, that is, as a teaching tool, not as a reference book. Furthermore, this being an electronic document, the added volume does not add significantly to the cost.

Of course these lecture notes are by no means a substitute for any of the classic books on quantum mechanics. There are numerous such classic books and a number of recently published books. The purpose of the present lecture notes is to make available to others some examples, maybe some different derivations, and, in some cases, different sections and a different emphasis on the subject of practical quantum mechanics.

For further reading the following books are recommended:

1. P.A.M. Dirac, *The Principles of Quantum Mechanics*, 3rd Edn., The Clarendon Press, Oxford, (1947).

2. L.I. Schiff, *Quantum Mechanics*, McGraw-Hill Book Co, New York (1968).

3. D. Bohm, *Quantum Theory*, Dover Books, New York (1989).

4. H.A. Bethe and R. Jackiw, *Intermediate Quantum Mechanics*, Benjamin-Cummings, New York (1986).

5. L.D. Landau and E.M. Lifshitz, *Quantum Mechanics, Non-Relativistic Theory*, Vol. 3 of Course of Theoretical Physics. Elsevier Butterworth-Heinemann, Oxford (1977).

6. R.P. Feynmann and A.R. Hibbs, *Quantum Mechanics and Path Integrals*, McGraw-Hill, New York (1965).

7. E. Merzbacher, *Quantum Mechanics*, J. Wiley and Sons, New York (1970).

8. A. Messiah, *Quantum Mechanics*, Volumes I and II, North Holland, Amsterdam (1967).

9. G. Baym, *Lectures on Quantum Mechanics*, Benjamin, New York, (1969).

10. R.P. Feynmann, *Statistical Mechanics*, Benjamin, New York, (1972).

It would make a very long list if I were to name those who, through various discussions over the course of many years, have helped me better understand and teach quantum mechanics. I especially wish to thank the graduate students in my classes who helped me find several errors in the first draft of the present document and for their comments.

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1

Schrödinger equation on a lattice

In this chapter, we begin by studying the one-dimensional (1D) time-dependent Schrödinger equation. In order to do that we discretize the spatial coordinates and, thus, the differential equation becomes a set of coupled difference equations first order in time. Dealing with a finite number or a numerable set of states makes it easier to understand the concepts of Hilbert space, its measure, and the overlap between states. Furthermore, we only have to deal with the Kronecker symbol as opposed to the Dirac delta function. Later, in chapter 3, we will consider the continuum limit where we will naturally recover the Schrödinger differential equation, the state normalization condition as an integration condition, and the delta function.

1.1 Discretizing the spatial continuum

We may gain a clearer understanding of the problem by considering the 1D time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = \Big[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x,t)\Big]\psi(x,t), \tag{1.1}$$

on a discretized space.

First, let us consider a particle moving on a circle of a large radius R as illustrated in Fig. 1.1. We discretize the perimeter of the circle into N equal intervals of length $a = L/N$ (where $L = 2\pi R$ is the perimeter of the circle), which are defined by points x_n where $n = 1, 2, ..., N$ and $x_n = na$.

We will use a notation in which the $|n\rangle$ represents the state in which the particle is in the interval $(x_n - a/2, x_n + a/2)$. At the end of all of our calculations we will consider two limits, the limit of $R \to \infty$ and the continuum limit, that is, $a \to 0$. In the former limit, the circle becomes very large, its curvature goes to zero and becomes locally flat, as our familiar Euclidean space.

In order to express the Schrödinger equation on a discrete lattice, we need to express the first and second derivative of the wavefunction with respect to x on the discrete mesh, as the limit $a \to 0$ of the following expressions:

$$\frac{\partial\psi}{\partial x}\Big|_{x=x_n+\frac{a}{2}} = \frac{\psi_{n+1}-\psi_n}{a}, \qquad \frac{\partial\psi}{\partial x}\Big|_{x=x_n-\frac{a}{2}} = \frac{\psi_n-\psi_{n-1}}{a}$$

$$\frac{\partial^2\psi}{\partial x^2}\Big|_{x=x_n} = \frac{1}{a}\Big[\frac{\partial\psi}{\partial x}\Big|_{x+\frac{a}{2}} - \frac{\partial\psi}{\partial x}\Big|_{x-\frac{a}{2}}\Big] = \frac{\psi_{n+1}+\psi_{n-1}-2\psi_n}{a^2},$$

where $\psi_n = \psi(x_n)$. By mere substitution the Schrödinger equation is obtained as the $a \to 0$ limit of the following expression:

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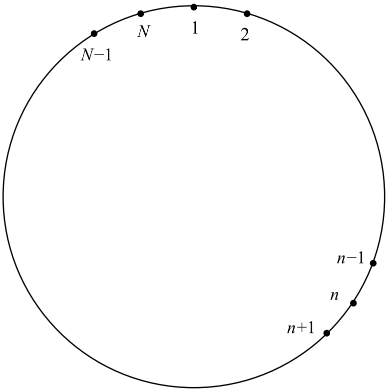

Fig. 1.1

$$i\hbar\frac{\partial}{\partial t}\psi_n = (\frac{\hbar^2}{ma^2} + V_n)\psi_n - \frac{\hbar^2}{2ma^2}(\psi_{n+1} + \psi_{n-1}), \tag{1.2}$$

where again $V_n = V(x_n)$.

1.2 The Schrödinger equation in a matrix form

Eq. 1.2 shows that we have N coupled independent equations for the coefficients $\psi_n(t)$. These equations can be cast in a matrix form as follows

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{H}|\psi\rangle \tag{1.3}$$

where $|\psi\rangle$ is an N-component vector of the form

$$|\psi\rangle = \begin{pmatrix} \psi_1 \\ \psi_2 \\ . \\ . \\ . \\ \psi_{n-1} \\ \psi_n \\ \psi_{n+1} \\ . \\ . \\ . \\ \psi_N \end{pmatrix}. \tag{1.4}$$

In the above, we have followed Dirac's notation for the case of an N-component vector. We will review the Dirac notation in the following chapter using an example of a two-dimensional space. Here, $\hat{H}$ is an $N \times N$ tri-diagonal matrix of the following form

$$\hat{H} = \begin{pmatrix} D_1 & T & 0 & 0 & ... & 0 & 0 & 0 & T \\ T & D_2 & T & 0 & 0 & ... & 0 & 0 & 0 \\ 0 & T & D_3 & T & 0 & ... & 0 & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & ... & 0 & T & D_n & T & 0 & ... & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & ... & 0 & T & D_{N-3} & T & 0 \\ 0 & 0 & 0 & ... & 0 & 0 & T & D_{N-1} & T \\ T & 0 & 0 & ... & 0 & 0 & 0 & T & D_N \end{pmatrix}, \tag{1.5}$$

Namely, the matrix elements are given as follows:

$$H_{n,n} = \frac{\hbar^2}{ma^2} + V_n \equiv D_n, \tag{1.6}$$

$$H_{n,n+1} = H_{n+1,n} = -\frac{\hbar^2}{2ma^2} \equiv T. \tag{1.7}$$

Notice that because of the periodic boundary conditions, that is,

$$|n + N\rangle = |n\rangle, \qquad n = 1, 2, ..., N, \tag{1.8}$$

we also have that

$$\begin{aligned} H_{N+1,N} &= H_{1,N} = -\frac{\hbar^2}{2ma^2}, \\ H_{N,N+1} &= H_{N,1} = -\frac{\hbar^2}{2ma^2}. \end{aligned} \tag{1.9}$$

All the other matrix elements of the $N \times N$ matrix $\hat{H}$ are zero. It is straightforward to show the above (see Problem 2 of this chapter) by carrying out the matrix multiplication implied in Eq. 1.3 to obtain Eq. 1.2.

Another way of writing the vector $|\psi\rangle$ is to express it as a linear combination of a basis set of vectors $|n\rangle$ with $n = 1, 2, ..., N$:

$$|\psi\rangle = \sum_{n=1}^{N} \psi_n |n\rangle. \tag{1.10}$$

Here, we can also think that each basis vector $|n\rangle$ represents a possible state of the particle. When the particle is in state $|n\rangle$, it is with certainty in the interval $(x_n - a/2, x_n + a/2)$. Notice that all N basis vectors $|n\rangle$ are linearly independent, unlike the case of all positions in ordinary space. Here, the position label is just a pointer to label a different potentiality: The potentiality that the particle can be in the interval $(x_n - a/2, x_n + a/2)$, which is conceptually entirely different from being in a different interval, say $(x_m - a/2, x_m + a/2)$ (with $m \neq n$), and, thus, the states $|n\rangle$ and $|m\rangle$ are considered to be orthogonal and, in a linear space, this means that these states have nothing to do with each other:

$$\langle n|m\rangle = \delta_{n,m}. \tag{1.11}$$

Now, the Schrödinger problem became a linear algebra problem in an N-dimensional vector space. In the next chapter, in order to gain more experience with the Dirac notation, we will discuss the case of two-dimensional Hilbert space. After that, we will return to the problem discussed here, that is, the Schrödinger equation on the lattice, for further discussion.

1.3 Problems

Problem 1

Carry out the matrix multiplication implied in Eq. 1.3 to obtain Eq. 1.2.

Problem 2

Consider the discretized version of the one-dimensional Schrödinger equation on a circle, but with only three sites as shown in the figure below.

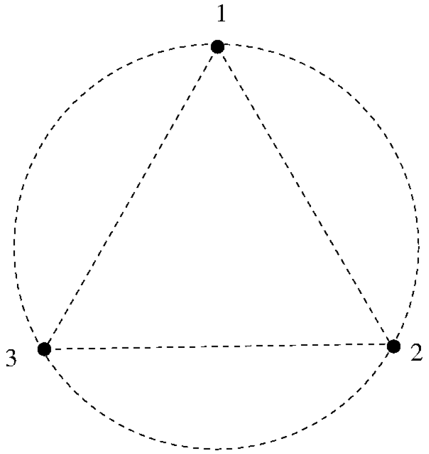

Fig. 1.2

Namely, only the three position eigenstates $|1\rangle$, $|2\rangle$, and $|3\rangle$ are possible. In this case, the free particle Hamiltonian becomes a 3×3 matrix:

$$\hat{H} = \begin{pmatrix} D & -T & -T \\ -T & D & -T \\ -T & -T & D \end{pmatrix}, \tag{1.12}$$

where the constants $D = \frac{\hbar^2}{ma^2}$ and $T = \frac{\hbar^2}{2ma^2}$, as we have shown, where a is the lattice spacing and m is the mass. Here, we treat them as given constants.

(a) Explicitly verify that the following three states are the three eigenstates of the matrix $\hat{H}$ above

$$|k\rangle = \frac{1}{\sqrt{3}}\Big(e^{ik}|1\rangle + e^{i2k}|2\rangle + e^{i3k}|3\rangle\Big), \tag{1.13}$$

or equivalently,

$$|k\rangle = \frac{1}{\sqrt{3}} \begin{pmatrix} e^{ik} \\ e^{i2k} \\ e^{i3k} \end{pmatrix}, \tag{1.14}$$

with k taking the values, 0, $2\pi/3$, and $4\pi/3$ and corresponding eigenstates:

$$E_k = D - 2T\cos(k), \tag{1.15}$$

that is,

$$E_0 = D - 2T, \tag{1.16}$$

$$E_{\frac{2\pi}{3}} = E_{-\frac{2\pi}{3}} = D + T. \tag{1.17}$$

Helpful formulas:
i) Notice that in the expression for the last two eigenstates, the phase $e^{\pm i\frac{6\pi}{3}} = 1$.
ii) It is also true that

$$e^{i\frac{2\pi}{3}} = \cos(\frac{2\pi}{3}) + i\sin(\frac{2\pi}{3}) = -\frac{1}{2} + i\frac{\sqrt{3}}{2}, \tag{1.18}$$

$$e^{i\frac{4\pi}{3}} = e^{i\frac{6\pi}{3}}e^{-i\frac{2\pi}{3}} = e^{-i\frac{2\pi}{3}}. \tag{1.19}$$

(b) Show that these three eigenstates form an orthonormal set.

2

Dirac notation

In this chapter we review the Dirac notation. In the simplest realization of quantum mechanics, we consider a two state system, that is, a problem which requres a Hilbert space spanned by a basis of just two states.

2.1 The bit and the q-bit

In this section we will consider a two state system in order to review the Dirac notation in the simplest realization of quantum mechanics, that is, a Hilbert space spanned by a basis of just two states.

There are numerous physical systems which can be represented by such a two-state Hilbert space. Two such examples are: a) a spin-1/2 particle and b) a very simplified model of a two-atom molecule (or the H_2^+ ion; see chapter 26 for this example) where the two atoms share a single electron in the outer orbital $|1\rangle$ of the first atom, and in the outer orbital $|2\rangle$ of the second atom; the state of the electron can be approximated by a linear superposition $|\psi\rangle = a_1|1\rangle + a_2|2\rangle$.

A bit in a computer is a memory element which can be either in state 1 or in state 0, and is used to store information. We can represent the instantaneous state of the bit formally as $|1\rangle$ and $|0\rangle$. Computations on a classical computer consist of operations which transform the state of the various bits. For example, the NOT operation is the operation which converts the state $|1\rangle$ to $|0\rangle$, and the state $|0\rangle$ to $|1\rangle$. Using a long series of a few such basic operations and an algorithm, a classical computer can provide the solution to a given problem.

In a quantum computer, the analogous element of memory or state is a quantum mechanical superposition of two such possibilities. The state of a q-bit (or qubit), is thus represented by

$$|q\rangle = q_0|0\rangle + q_1|1\rangle, \tag{2.1}$$

$$|q_0|^2 + |q_1|^2 = 1, \tag{2.2}$$

and both q_0 and q_1 are complex numbers representing probability amplitudes. Here, $|q_n|^2$ is the probability, if a measurement on this q-bit is performed, to find the q-bit in the state $|n\rangle$.

In order to carry out the quantum computation, there should also be a pool of a few fundamental operations which can be used to apply a series of consecutive operations on the q-bit. The series of these consecutive operations is the quantum algorithm to solve a particular problem. The final result of the quantum computation consists of measuring another operator which represents the question which we wish to find an answer to using the quantum computer.

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2.2 Dirac notation

Here, we would like to review the Dirac notation as a convenient tool to use to facilitate the language and symbolic manipulations needed in computations in quantum mechanics. We can survive without the Dirac notation, but it is a useful tool to have at our disposal.

We really want to describe a linear space, which in the case of our example is spanned by two basis vectors which we denote as

$$|0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \text{and,} \quad |1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{2.3}$$

This means that any state in this space can be written as linear superposition of these two basis states:

$$|\psi\rangle = \psi_0|0\rangle + \psi_1|\psi_1\rangle = \begin{pmatrix} \psi_0 \\ \psi_1 \end{pmatrix}. \tag{2.4}$$

For any given "ket," there is a corresponding "bra," namely

$$|\psi\rangle \to \langle\psi|, \tag{2.5}$$

which, in standard linear algebra notation, means

$$\begin{pmatrix} \psi_0 \\ \psi_1 \end{pmatrix} \to (\psi_0^*, \psi_1^*). \tag{2.6}$$

The language of "bra" and "ket" is used because the meaning of a "bracket," such as $\langle\phi|\psi\rangle$ between the states

$$|\phi\rangle = \begin{pmatrix} \phi_0 \\ \phi_1 \end{pmatrix} \quad \text{and} \quad |\psi\rangle = \begin{pmatrix} \psi_0 \\ \psi_1 \end{pmatrix}, \tag{2.7}$$

is taken to be that of the familiar inner product

$$\langle\psi|\psi\rangle = \phi_0^*\psi_0 + \phi_1^*\psi_1 \tag{2.8}$$

which is the result of multiplying a 1 × 2 with a 2 × 1 matrix to obtain an 1 × 1 matrix, that is, a number which is the inner product as follows

$$(\phi_0^*, \phi_1^*) \begin{pmatrix} \psi_0 \\ \psi_1 \end{pmatrix} = \phi_0^*\psi_0 + \phi_1^*\psi_1. \tag{2.9}$$

From these definitions, it follows that

$$\langle\psi|\psi\rangle = 1, \quad \langle 0|0\rangle = 1, \quad \langle 1|1\rangle = 1, \quad \langle 0|1\rangle = 0. \tag{2.10}$$

The last three equations which can be summarized as

$$\langle n|m\rangle = \delta_{n,m}, \tag{2.11}$$

where n and m take two possible values 0 and 1. This is the formal statement that we have an orthonormal basis.

2.3 Outer product

The *outer product* (which refers to the *tensor product* of two vectors) between a "ket" and a "bra" is defined to be the result of multiplying the "ket" which is a 2×1 matrix with a "bra" which is a 1×2 matrix to obtain the following 2×2 matrix

$$|\psi\rangle\langle\phi| = \begin{pmatrix} \psi_0 \\ \\ \psi_1 \end{pmatrix} (\phi_0^* \quad , \quad \phi_1^*) = \begin{pmatrix} \psi_0\phi_0^* \ \psi_0\phi_1^* \\ \\ \psi_1\phi_0^* \ \psi_1\phi_1^* \end{pmatrix} . \tag{2.12}$$

Below, we list a few examples for the reader to practice:

$$|0\rangle\langle 0| = \begin{pmatrix} 1 \\ 0 \end{pmatrix} (1, 0) = \begin{pmatrix} 1 \ 0 \\ 0 \ 0 \end{pmatrix} , \tag{2.13}$$

$$|1\rangle\langle 1| = \begin{pmatrix} 0 \\ 1 \end{pmatrix} (0, 1) = \begin{pmatrix} 0 \ 0 \\ 0 \ 1 \end{pmatrix} , \tag{2.14}$$

$$|0\rangle\langle 1| = \begin{pmatrix} 1 \\ 0 \end{pmatrix} (0, 1) = \begin{pmatrix} 0 \ 1 \\ 0 \ 0 \end{pmatrix} , \tag{2.15}$$

$$|1\rangle\langle 0| = \begin{pmatrix} 0 \\ 1 \end{pmatrix} (1, 0) = \begin{pmatrix} 0 \ 0 \\ 1 \ 0 \end{pmatrix} . \tag{2.16}$$

Now let us consider the outer product as defined by Eq. 2.12 which is a 2×2 matrix to operate on a vector

$$|w\rangle = \begin{pmatrix} w_0 \\ \\ w_1 \end{pmatrix} , \tag{2.17}$$

by multiplying the matrix and the vector in the familiar fashion. The result is, $(\langle\phi|w\rangle)|\psi\rangle$, that is, a vector parallel to the vector $|\psi\rangle$, which can be written as

$$(|\psi\rangle\langle\phi|)|w\rangle = |\psi\rangle\langle\phi|w\rangle. \tag{2.18}$$

which means that we can just drop the parenthesis on the left-hand-side. This is another convenience brought by the Dirac notation.

An arbitrary state $|\psi\rangle$ from this two-state space can be expanded in the basis $|0\rangle$ and $|1\rangle$ as shown by Eq. 2.4. Taking the inner product of both sides of this equation with the bra $\langle 0|$ first and, then, with the bra $\langle 1|$, we find that

$$\psi_0 = \langle 0|\psi\rangle, \qquad \psi_1 = \langle 1|\psi\rangle. \tag{2.19}$$

This means that we can write

$$|\psi\rangle = \langle 0|\psi\rangle|0\rangle + \langle 1|\psi\rangle|1\rangle. \tag{2.20}$$

Using the properties of the outer product, we can rewrite the above equation as follows:

$$|\psi\rangle = |0\rangle\langle 0|\psi\rangle + |1\rangle\langle 1|\psi\rangle| = (|0\rangle\langle 0| + |1\rangle\langle 1|)|\psi\rangle. \tag{2.21}$$

This equation implies that the following operator is the identity operator or the identity matrix:

$$|0\rangle\langle 0| + |1\rangle\langle 1| = \hat{1}. \tag{2.22}$$

2.4 Matrices and matrix elements

Consider a general 2×2 matrix which we assume is written in the basis spanned by $|0\rangle$ and $|1\rangle$.

$$\hat{O} = \begin{pmatrix} O_{00} & O_{01} \\ O_{10} & O_{11} \end{pmatrix}. \tag{2.23}$$

We can easily show that

$$O_{mn} = \langle m|\hat{O}|n\rangle, \tag{2.24}$$

where m and n each independently take the values 0 and 1. The above notation means that we obtain the matrix element labeled O_{mn} by first operating with the matrix $\hat{O}$ on the state $|n\rangle$ and, then, by taking the inner product of the result with the bra $\langle m|$. This is easily shown by evaluating $\hat{O}|0\rangle$:

$$\hat{O}|0\rangle = \begin{pmatrix} O_{00} & O_{01} \\ O_{10} & O_{11} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} O_{00} \\ O_{10} \end{pmatrix}, \tag{2.25}$$

from which we find that

$$\langle 1|\hat{O}|0\rangle = (0,1) \begin{pmatrix} O_{00} \\ O_{10} \end{pmatrix} = O_{10}, \tag{2.26}$$

$$\langle 0|\hat{O}|0\rangle = (1,0) \begin{pmatrix} O_{00} \\ O_{10} \end{pmatrix} = O_{00}. \tag{2.27}$$

Similarly, we can show that this is also true for the other two matrix elements.

This allows us to write the matrix as follows

$$\hat{O} = \begin{pmatrix} \langle 0|\hat{O}|0\rangle & \langle 0|\hat{O}|1\rangle \\ \langle 1|\hat{O}|0\rangle & \langle 1|\hat{O}|1\rangle \end{pmatrix}. \tag{2.28}$$

2.5 Quantum gates

A quantum gate (or quantum logic gate) is a basic quantum circuit operating on a small number of q-bits. They are the building blocks of quantum circuits, like classical logic gates are for conventional digital circuits. Quantum logic gates are represented by unitary matrices.

An example of a commonly used gate which acts on a single q-bit is the **Pauli-X gate**. It is the quantum equivalent of a NOT gate. It maps $|0\rangle$ to $|1\rangle$ and $|1\rangle$ to $|0\rangle$. It is represented by the x-component of the Pauli matrix:

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{2.29}$$

An example of a gate which acts on a pair of q-bits is the controlled NOT gate (or CNOT). A pair of q-bits is a state of the form $|\alpha\rangle|\beta\rangle$ where both α and β take the values 0 and 1. It also be represented by a 4-component vector where the first two components represent the components of the first q-bit and the other two components of the 4-component vector are the components of the second q-bit. The transformation CNOT performs the NOT operation on the second q-bit only when the first q-bit is $|1\rangle$, and otherwise leaves it unchanged. It is represented by the matrix

$$\mathrm{CNOT} = \begin{pmatrix} 1\,0\,0\,0 \\ 0\,1\,0\,0 \\ 0\,0\,0\,1 \\ 0\,0\,1\,0 \end{pmatrix}. \tag{2.30}$$

2.6 Rotation

Consider an arbitrary state in the basis $|0\rangle$, $|1\rangle$,

$$|\psi\rangle = \begin{pmatrix} \psi_0 \\ \psi_1 \end{pmatrix} = \psi_0|0\rangle + \psi_1|1\rangle = \langle 0|\psi\rangle|0\rangle + \langle 1|\psi\rangle|1\rangle. \tag{2.31}$$

Let us rotate the basis by an angle θ, as illustrated in Fig. 2.1.

In terms of the new (rotated) unit vectors $|0'\rangle$ and $|1'\rangle$, we can express the old basis vectors as follows

$$|0\rangle = \cos\theta|0'\rangle - \sin\theta|1'\rangle \tag{2.32}$$

$$|1\rangle = \sin\theta|0'\rangle + \cos\theta|1'\rangle. \tag{2.33}$$

Now, let us expand the same vector $|\psi\rangle$ in the new basis:

$$|\psi\rangle = \begin{pmatrix} \psi'_0 \\ \psi'_1 \end{pmatrix} = \psi'_0|0'\rangle + \psi'_1|1'\rangle = \langle 0'|\psi\rangle|0'\rangle + \langle 1'|\psi\rangle|1'\rangle. \tag{2.34}$$

Inserting the unit operator $\hat{1} = |0\rangle\langle 0| + |1\rangle\langle 1|$ we obtain:

$$\langle 0'|\psi\rangle = \langle 0'|0\rangle\langle 0|\psi\rangle + \langle 0'|1\rangle\langle 1|\psi\rangle, \tag{2.35}$$

$$\langle 1'|\psi\rangle = \langle 1'|0\rangle\langle 0|\psi\rangle + \langle 1'|1\rangle\langle 1|\psi\rangle. \tag{2.36}$$

This can be written as a matrix-vector multiplication as

$$\begin{pmatrix} \langle 0'|\psi\rangle \\ \\ \langle 1'|\psi\rangle \end{pmatrix} = \begin{pmatrix} \langle 0'|0\rangle & \langle 0'|1\rangle \\ \\ \langle 1'|0\rangle & \langle 1'|1\rangle \end{pmatrix} \begin{pmatrix} \langle 0|\psi\rangle \\ \\ \langle 1|\psi\rangle \end{pmatrix}. \tag{2.37}$$

We define the rotation matrix or transformation operator as

$$\hat{R}(\theta) = \begin{pmatrix} \langle 0'|0\rangle & \langle 0'|1\rangle \\ \\ \langle 1'|0\rangle & \langle 1'|1\rangle \end{pmatrix}, \tag{2.38}$$

in terms of which we transform the old basis to the new basis

$$\begin{pmatrix} \langle 0'|\psi\rangle \\ \\ \langle 1'|\psi\rangle \end{pmatrix} = \hat{R}(\theta) \begin{pmatrix} \langle 0|\psi\rangle \\ \\ \langle 1|\psi\rangle \end{pmatrix}. \tag{2.39}$$

We can easily compute the matrix $\hat{R}(\theta)$ using the transformation (2.33) and we obtain:

$$\hat{R}(\theta) = \begin{pmatrix} \cos\theta & \sin\theta \\ \\ -\sin\theta & \cos\theta \end{pmatrix}. \tag{2.40}$$

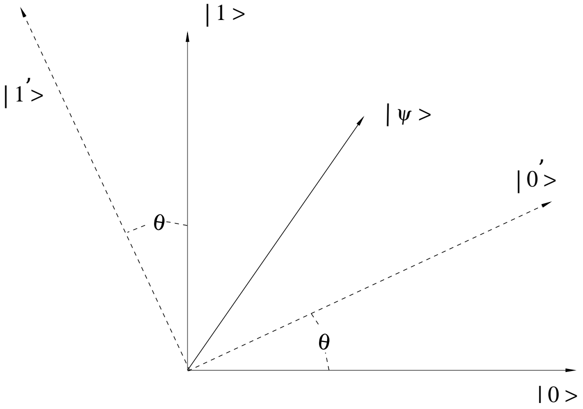

Fig. 2.1

We can show that the eigenstates of $\hat{R}(\theta)$ are the following states, that is,

$$|+\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix}, \qquad |-\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix}, \tag{2.41}$$

with corresponding eigenvalues $e^{\pm i\theta}$.

In addition, we can show that the above rotation operator can be written in the following form:

$$\hat{R}(\theta) = \cos\theta\hat{1} + i\sin\theta\hat{S}, \tag{2.42}$$

where

$$\hat{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \hat{S} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}. \tag{2.43}$$

2.7 Functions of operators

In general, when we write down a function $f(\hat{O})$ of an operator $\hat{O}$, we mean the following. The scalar function $f(\lambda)$ is a known function of the variable λ, for example

$f(\lambda) = e^{\lambda}$. When we say that the function $f(\lambda)$ is known, we mean that we know its Tayor-series expansion:

$$f(\lambda) = f(0) + f'(0)\lambda + \frac{1}{2}f''(0)\lambda^2 + ... = \sum_0^{\infty} \frac{1}{n!} f^{(n)}(0)\lambda^n, \tag{2.44}$$

where $f^{(n)}(0)$ is the nth derivative of $f(\lambda)$ evaluated at $\lambda = 0$. Knowing the function $f(\lambda)$ means that we know $f^{(n)}(0)$ for all n. When we use the symbol $f(\hat{O})$ we will mean the following

$$\begin{aligned} f(\hat{O}) &= f(0)\hat{1} + f'(0)\hat{O} + \frac{1}{2}f''(0)\hat{O}^2 + ... \\ &= \sum_0^{\infty} \frac{1}{n!} f^{(n)}(0)\hat{O}^n, \end{aligned} \tag{2.45}$$

with the additional convention that $\hat{O}^0 = \hat{1}$, that is, the unit operator in the space in which the operator $\hat{O}$ is defined. If this is an N-dimensional space, then $\hat{1}$ is an $N \times N$ diagonal matrix with all of its diagonal elements equal to unity.

The above expression makes sense because all powers of the $N \times N$ matrix $\hat{O}$ are also $N \times N$ matrices and they can be added together.

2.8 Generator of planar rotations

Using the discussion of the previous section, it is straightforward to show that

$$\hat{R}(\theta) = e^{i\theta\hat{S}}, \tag{2.46}$$

by using the identity

$$\hat{S}^2 = \hat{1}. \tag{2.47}$$

The property specified by Eq. 2.46 means that the operator $\hat{S}$ is the so-called *generator* of infinitesimal planar rotations. A more in-depth analysis about generators of infinitesimal rotations is discussed in chapter 18.

2.9 Problems

Problem 1

Consider a general operator $\hat{O}$ which in the basis of the two basis vectors $|i\rangle$, $i = 1, 2$ is the following 2×2 matrix

$$\hat{O} = \begin{pmatrix} O_{11} & O_{12} \\ O_{21} & O_{22} \end{pmatrix}, \tag{2.48}$$

$$O_{ij} = \langle i|\hat{O}|j\rangle. \tag{2.49}$$

a) Show that

$$\langle\Phi|\hat{O}|\Psi\rangle^* = \langle\Psi|\hat{O}^\dagger|\Phi\rangle, \tag{2.50}$$

for any two states $|\Phi\rangle$ and $|\Psi\rangle$ which, in general, are linear combinations of $|1\rangle$ and $|2\rangle$, that is,

$$|\Phi\rangle = \Phi_1|1\rangle + \Phi_2|2\rangle, \tag{2.51}$$

$$|\Psi\rangle = \Psi_1|1\rangle + \Psi_2|2\rangle. \tag{2.52}$$

b) Show that if $|\Psi\rangle$ is chosen such as

$$\hat{O}|\Psi\rangle = \lambda|\Psi\rangle, \tag{2.53}$$

then necessarily the following follows from that

$$\langle\Psi|\hat{O}^\dagger = \lambda^*\langle\Psi|. \tag{2.54}$$

c) Show that the transformation from one basis to another is a unitary transformation.

d) Show that the matrix $|\Phi\rangle\langle\Phi|$ is Hermitian.

Problem 2

Consider the rotation operator discussed in this chapter

$$\hat{R}(\theta) = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}. \tag{2.55}$$

a) Show that its eigenstates are the following,

$$|+\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix}, \qquad |-\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix}, \tag{2.56}$$

with corresponding eigenvalues $e^{\pm i\theta}$.

b) Show that the above rotation operator can be written in the following form:

$$\hat{R}(\theta) = \cos\theta\hat{1} + i\sin\theta\hat{S}, \tag{2.57}$$

where

$$\hat{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \qquad \hat{S} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}. \tag{2.58}$$

c) Show that

$$\hat{R}(\theta) = e^{i\theta\hat{S}}, \tag{2.59}$$

by using the identity

$$\hat{S}^2 = \hat{1}. \tag{2.60}$$

Problem 3

The trace of an operator $\hat{O}$ in an n-dimensional linear space is the sum of all the diagonal elements of the $n \times n$ matrix O_{nm} which represents the operator $\hat{O}$ in a given basis.

Show that the trace of any such matrix representing an operator is independent of the choice of the basis.

3

Back to the Schrödinger equation on a lattice

In this chapter we go back to the discrete lattice in order to transform the basis to momentum eigenstates. In addition, we take the continuum limit of space and we recover known relations.

3.1 Lattice states

Let us apply the Dirac notation in the case of the 1D Schrödinger equation on the discrete lattice. In this case the basis consists of N states $|n\rangle$, with $n = 1, 2, ..., N$, which are orthonormal, that is, they obey Eq. 1.11, and they form a complete basis, namely,

$$\sum_{n=1}^{N} |n\rangle\langle n| = \hat{1}. \tag{3.1}$$

This means that an arbitrary state $|\psi\rangle$ can be expanded in this basis as shown by Eq. 1.10.

3.2 Transformation of basis: momentum states

We consider the following set of states

$$|k\rangle = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{ikna} |n\rangle. \tag{3.2}$$

While $|n\rangle$ describes the state of a particle which is located in the interval $[na - a/2, na + a/2)$, the above state describes the state in which the probability amplitude for a particle to be in a particular small interval $[na - a/2, na + a/2)$ is given by a phase factor e^{ikna}, which is characterized by a wavevector k, very analogous to the amplitude of an ordinary wave. Next, we address a set of questions and statements which further illuminate the nature of this state.

What is the range of k? First notice that the following identity is valid

$$|k + \frac{2\pi}{a}\rangle = |k\rangle. \tag{3.3}$$

Thus, we only need to restrict the values of k in an interval of size $2\pi/a$, such as the interval $[-\pi/a, \pi/a)$ which is known as the **first Brillouin zone**.

Practical Quantum Mechanics. First Edition. Efstratios Manousakis.

How many values of k give different solutions? The periodic boundary condition (Eq. 1.8) implies that

$$e^{ikNa} = 1 \rightarrow k = \frac{2\pi}{Na} m, \qquad m = 0, \pm 1, \pm 2, ... \tag{3.4}$$

Now, if we restrict k in the first Brillouin zone, the possible values of m are the following N:

$$-\frac{n}{2} \leq m < \frac{n}{2}. \tag{3.5}$$

Therefore, there are only N-different states $|k\rangle$ as expected from a transformation. Namely, we start from a basis of N states, $|n\rangle$ $(n = 1, 2, ..., N)$ and we transform the basis to the N different states given by the transformation described by Eq. 3.2.

The transformation is unitary. It is straightforward to show that this transformation which changes the basis from the set of N states $|n\rangle$ to the states given by Eq. 3.2 is a unitary transformation. A unitary transformation $\hat{U}$ is one which satisfies the following equation:

$$\hat{U}\hat{U}^{\dagger} = U^{\dagger}U = \hat{1}, \tag{3.6}$$

and $U^{\dagger}$ is the adjoint operator of U, i.e., its matrix elements, $(U^{\dagger})_{ij} = U^{*}_{ji}$.

In order to show this, we need to make use of the following identity

$$\frac{1}{N}\sum_{n=1}^{N} e^{ikna} = \delta_{k,0}. \tag{3.7}$$

It is straightforward to show this identity: First, notice that when $k = 0$, the left-hand-side is 1, while when $k \neq 0$, the left-hand-side can be summed up as a geometric series which becomes zero on the account of the fact that $e^{ikNa} = 1$ for any k of the form $k = [2\pi/(Na)]m$, with m integer.

Furthermore, following the same approach, one can easily show the following identity:

$$\frac{1}{N}\sum_{k \in 1stBZ} e^{ikna} = \delta_{n,0}, \tag{3.8}$$

where the sum is over all the discrete values of k of the form $k = (2\pi/L)m$ which are within the first Brillouin zone.

Using the identity (3.7) we can show that

$$\langle k|k'\rangle = \delta_{k,k'}. \tag{3.9}$$

Furthermore, using the identity (3.8) it is straightforward to show that

$$\sum_{k \in 1stBZ} |k\rangle\langle k| = \hat{1}, \tag{3.10}$$

which means that the k-basis is complete.

The inverse transformation, that is, the one which transforms the k-basis states into the $|n\rangle$ basis states, is

$$|n\rangle = \frac{1}{\sqrt{N}} \sum_{k \in 1stBZ} e^{-ikna} |k\rangle, \qquad n = 1, 2, ..., N. \tag{3.11}$$

This can be shown by starting from the right-hand-side of this equation and by substituting our definition of $|k\rangle$, and then by applying the identity given by Eq. 3.7.

Conclusion: We have carried out a unitary transformation from the basis $|n\rangle$, which describes the N possibilities where the particle is the interval $[na - a/2, na + a/2)$, to a basis of N distinct states $|k\rangle$, in which the probability amplitude for a particle to be in state $|n\rangle$) is a phase factor e^{ikna}, which is characterized by a wavevector $k = m2\pi/L$ (m is a positive or negative integer including the value $m = 0$), very analogous to the case of the amplitude of a classical wave which is confined in a region of length L.

3.3 Continuum limit of space

In our attempt to take the continuum limit, we will need to relate ψ_n and the wavefunction $\Psi(x)$ on the one hand and the state $|n\rangle$ and the familiar continuum state $|x\rangle$ on the other.

Remember, first, that the absolute magnitude squared of the wavefunction gives the probability density, that is, $|\Psi(x)|^2 dx$ gives the probability for the particle to be in the interval $(x - dx/2, x + dx/2)$. Therefore, for sufficiently small value of a, we must require that $|\Psi(x_n)|^2 a = |\psi_n|^2$. This implies that

$$\psi_n = \sqrt{a}\Psi(x_n). \tag{3.12}$$

Second, as is customary, we need to define the state $|x\rangle$ is such a way that in the continuum limit Eq. 1.10 takes the form

$$|\Psi\rangle = \int dx \Psi(x) |x\rangle. \tag{3.13}$$

Going back one step in the process of taking the limit $a \to 0$, this equation should come as the limit of

$$|\Psi\rangle = \lim_{a \to 0} a \sum_{n=1}^{N} \Psi(x_n) |x\rangle, \tag{3.14}$$

which, by taking into account Eq. 3.12, is the same as

$$|\Psi\rangle = \lim_{a \to 0} \sqrt{a} \sum_{n=1}^{N} \psi_n |x\rangle. \tag{3.15}$$

Therefore, in order for Eq. 1.10 and Eq. 3.13 to agree, we need to choose

$$|x\rangle = \left\{ \begin{array}{cc} \frac{1}{\sqrt{a}}|n\rangle, \text{ for } na - a/2 < x < na + a/2, \\ 0 & \text{otherwise} \end{array} \right\}. \tag{3.16}$$

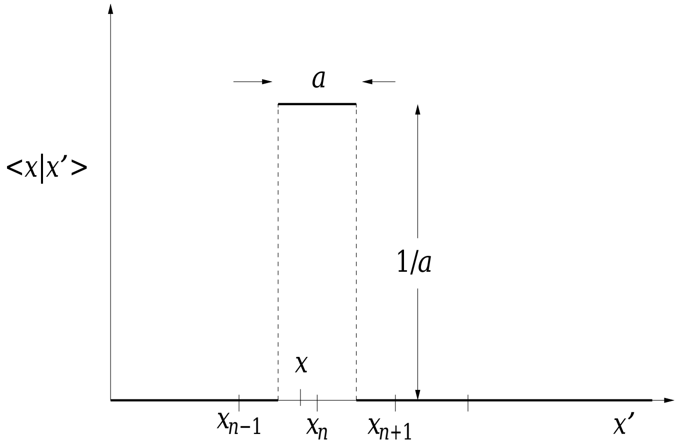

Fig. 3.1

The value of n in the above equation is uniquely determined from the given value of x, as follows:

$$n = [\frac{x}{a} + \frac{1}{2}], \tag{3.17}$$

where the brackets [] denote the integer part. In Fig. 3.1 we plot the function $\langle x|x'\rangle$ as a function of x'.

Using the above (and Fig. 3.1), it can be easily shown that

$$\langle x|x'\rangle = \delta(x - x'), \tag{3.18}$$

where $\delta(x - x')$ is the Dirac delta function.

Using the previous expressions it can be also shown that

$$\int dx|x\rangle\langle x| = \hat{1}, \tag{3.19}$$

where $\hat{1}$ is the unit operator.

Given two states which can be expanded in the basis $|x\rangle$ as follows

$$|\psi\rangle = \int dx\psi(x)|x\rangle, \tag{3.20}$$

$$|\phi\rangle = \int dx\phi(x)|x\rangle, \tag{3.21}$$

it follows from the above that their inner product is given by

$$\langle\phi|\psi\rangle = \int dx\phi^*(x)\psi(x), \tag{3.22}$$

and the normalization condition is

$$\langle\psi|\psi\rangle = \int dx|\psi(x)|^2. \tag{3.23}$$

3.4 Continuum limit of k-space

Here, our goal is to take the continuum limit in k-space. By continuum limit we mean the limit where $\Delta k = 2\pi/L \to 0$. This limit is the same as the infinite size limit ($L \to \infty$). For any finite value of L, however, the possible values of k which are consistent with the boundary condition is N, and are integer multiples of $\Delta k = 2\pi/L$. From now on, for these N states we will use the notation

$$|k_d\rangle = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{ik_d na} |n\rangle, \tag{3.24}$$

where we have added the subscript d to denote the fact that these states span a discrete set in order to distinguish this state from a state $|k\rangle$ where k can take continuous values.

First, let us expand an arbitrary state $|\psi\rangle$ using the basis $|k_d\rangle$, that is,

$$|\psi\rangle = \sum_{k_d \in 1stBZ} \tilde{\psi}_{k_d} |k_d\rangle, \qquad \tilde{\psi}_{k_d} = {}_d\langle k_d|\psi\rangle. \tag{3.25}$$

The normalization of this state is obtained as follows:

$$\langle\psi|\psi\rangle = 1 \to \sum_{k \in 1stBZ} |\tilde{\psi}_k|^2 = 1. \tag{3.26}$$

Multiplying and dividing by Δk we can write

$$\frac{1}{\Delta k} \Delta k \sum_{k \in 1stBZ} |\tilde{\psi}_k|^2 = 1. \tag{3.27}$$

In the limit where $\Delta k \to 0$ ($L \to \infty$), this equation becomes

$$L \int_{-\infty}^{\infty} \frac{dk}{2\pi} |\tilde{\psi}_k|^2 = 1. \tag{3.28}$$

Since $L \to \infty$ we can rescale $\tilde{\psi}_k$ and by defining the continuum wavefunction in momentum space as

$$\tilde{\Psi}(k) \equiv \sqrt{L}\tilde{\psi}_k, \tag{3.29}$$

we obtain the following normalization condition

$$\int_{-\infty}^{\infty} \frac{dk}{2\pi} |\tilde{\Psi}(k)|^2 = 1. \tag{3.30}$$

Using the same trick of multiplying and dividing by Δk, the expansion of $|\psi\rangle$ in k-space as given by Eq. 3.25 in the $\Delta k \to 0$

$$|\psi\rangle = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \tilde{\Psi}(k) |k\rangle, \tag{3.31}$$

where

$$|k\rangle = \begin{Bmatrix} \sqrt{L}|k_d\rangle, \text{ for } k_d - \pi/L < k < k_d + \pi/L \\ 0 \qquad\qquad\qquad \text{otherwise,} \end{Bmatrix} \tag{3.32}$$

where

$$k_d \equiv \left[\frac{k}{(2\pi)/L} + \frac{1}{2}\right]\frac{2\pi}{L}. \tag{3.33}$$

Now, in the interval of k defined as $k_d - \pi/L < k < k_d + \pi/L$ we obtain,

$$\langle k|k'\rangle = L\langle k_d|k'_d\rangle, \tag{3.34}$$

this can be considered as a function of k' for given fixed value of k. This function is illustrated in Fig. 3.2.

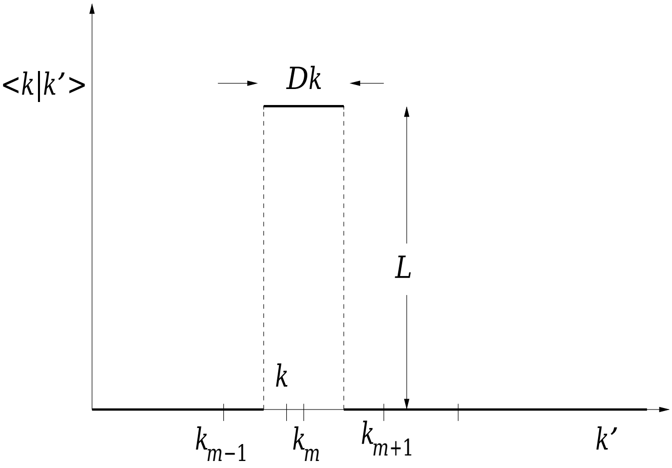

Fig. 3.2

Therefore, as $L \to \infty$ we obtain that,

$$\langle k|k'\rangle \to \infty, \qquad \text{if} \quad k = k', \tag{3.35}$$

$$\langle k|k'\rangle = 0, \qquad \text{if} \quad k \neq k', \tag{3.36}$$

and since

$$\int_{-\infty}^{\infty} dk' \langle k|k'\rangle = \frac{2\pi}{L} \times L = 2\pi, \tag{3.37}$$

we conclude that

$$\langle k|k'\rangle = 2\pi\delta(k - k'). \tag{3.38}$$

This identity can be derived in a different way, as follows: First, notice that

$$|k\rangle = \sqrt{L}|k_d\rangle = \int_{-\infty}^{\infty} dx e^{ikx}|x\rangle, \tag{3.39}$$

and, thus,

$$\begin{aligned}\langle k|k'\rangle &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx dx' e^{-ikx} e^{ik'x'}\langle x|x'\rangle \\ &= \int_{-\infty}^{\infty} dx e^{-i(k-k')x} = 2\pi\delta(k-k'). \end{aligned}\tag{3.40}$$

Using the same trick as above, the completeness relation of the $|k_d\rangle$ states given by Eq. 3.10 can be transformed to the following

$$\int_{-\infty}^{\infty} \frac{dk}{2\pi}|k\rangle\langle k| = \hat{1}. \tag{3.41}$$

3.5 Generalization in d-dimensions

All of the conclusions of this chapter for 1D can be straightforwardly generalized in higher dimensions as follows

$$|\vec{r}\rangle = |x\rangle|y\rangle|z\rangle... \tag{3.42}$$

$$\begin{aligned}\langle\vec{r}|\vec{r}'\rangle &= \langle x|x'\rangle\langle y|y'\rangle\langle z|z'\rangle... \\ &= \delta(x-x')\delta(y-y')\delta(z-z')... \end{aligned}\tag{3.43}$$

$$\int d^d r|\vec{r}\rangle\langle r| = \hat{1}, \tag{3.44}$$

and an arbitrary normalized state can be expanded as

$$|\psi\rangle = \int d^d r \psi(\vec{r})|\vec{r}\rangle, \tag{3.45}$$

$$\psi(\vec{r}) = \langle\vec{r}|\psi\rangle. \tag{3.46}$$

Similarly in k-space, that is,

$$|\vec{k}\rangle = |k_x\rangle|k_y\rangle|k_z\rangle..., \tag{3.47}$$

which is related to $|\vec{r}\rangle$ by the transformation:

$$|\vec{k}\rangle = \int d^d r e^{i\vec{k}\cdot\vec{r}}|\vec{r}\rangle, \tag{3.48}$$

$$\langle\vec{r}|\vec{k}\rangle = e^{i\vec{k}\cdot\vec{r}}, \tag{3.49}$$

we have the corresponding relations

$$|\psi\rangle = \int \frac{d^d k}{(2\pi)^d} \tilde{\psi}(\vec{k})|\vec{k}\rangle, \tag{3.50}$$

$$\begin{aligned}\langle\vec{k}|\vec{k}'\rangle &= \langle k_x|k'_x\rangle\langle k_y|k'_y\rangle\langle k_z|k'_z\rangle ...\\ &= (2\pi)^d \delta(k_x - k'_x)\delta(k_y - k'_y)\delta(k_z - k'_z)...\end{aligned} \tag{3.51}$$

and an arbitrary normalized state can be expanded as

$$|\psi\rangle = \int \frac{d^d k}{(2\pi)^d} \tilde{\psi}(\vec{k})|\vec{k}\rangle, \tag{3.52}$$

$$\tilde{\psi}(\vec{k}) = \langle\vec{k}|\psi\rangle. \tag{3.53}$$

3.6 Problems

Problem 1

Starting from the right-hand-side of Eq. 3.11 show that the inverse transformation for the state $|n\rangle$ in terms of the complete basis $|k\rangle$ is given by Eq. 3.11.

Problem 2

Consider the circular geometry we discussed in this chapter, where the perimeter is $L = Na$ and there are N discrete points on the circle.

a) When k is of the form $k = [2\pi/(Na)]m$ (N and m are integers), show the following identity

$$\frac{1}{N}\sum_{n=1}^{N} e^{ikna} = \delta_{k,0}. \tag{3.54}$$

b) Also show the following identity:

$$\frac{1}{N}\sum_{k\in 1stBZ} e^{ikna} = \delta_{n,0}, \tag{3.55}$$

where the sum is over all the discrete values of k of the form $k = (2\pi/L)m$ ($L = Na$ and m is an integer) and all values of k are within the first Brillouin zone.

c) Using the identity (3.54) show that

$$\langle k|k'\rangle = \delta_{k,k'}. \tag{3.56}$$

d) Use the identity (3.55) to show that

$$\sum_{k\in 1stBZ} |k\rangle\langle k| = \hat{1}. \tag{3.57}$$

Problem 3

Show that the transformation which changes the basis from the set of N states $|n\rangle$ to the states given by Eq. 3.2 is a unitary transformation.

4

Operator mechanics

In this chapter, we discuss the need to use operator in quantum mechanics and how the operators relate to observables.

4.1 Operators and observables

Quantum mechanics uses operators which represent observables. Here, we will assume that the student is already familiar from his undergraduate course work in quantum mechanics with the fact that the expectation value of an operator is the quantity that is experimentally measured. Next, we will give a qualitative argument to rationalize why this is the case.

An observable is represented by an operator because an operator represents the potential act of a measurement. A measurement is an operation, an action on the state of the system with the goal to measure a particular observable. This action may change the state of the system, much like an operator's action on a state changes the state of the system under consideration. The particular operator representing a given observable is constructed in such a way that when it acts on the state, it changes according to the meaning of the observable it represents.

The change an operator $\hat{O}$ causes on the state $|\psi\rangle$ of the system is evaluated by comparing the state $|\psi'\rangle \equiv \hat{O}|\psi\rangle$ produced by the action of the operator with the state of the system prior to the action of the operator. Namely, $\langle\psi|\psi'\rangle$, gives a measure of how much the state $|\psi\rangle$ is changed by the action of the operator. The inner product is a measure of how close to each other two vectors are. For example, when $\langle\psi|\psi'\rangle = 0$, the two vectors are orthogonal, and this means that this is the farthest distance from one another that they can possibly have. On the other hand, if for two normalized vectors $|\langle\psi|\psi'\rangle| \sim 1$, the two vectors are close to each other. Therefore, the expression

$$\langle\hat{O}\rangle = \langle\psi|\psi'\rangle = \langle\psi|\hat{O}|\psi\rangle, \tag{4.1}$$

gives a measure of the observable represented by $\hat{O}$. Fig. 4.1 (top) illustrates that the operation of measurement causes a change on the state of the apparatus and the result of the measurement is to compare the state of the apparatus before and after the measurement.

We would next like to give a simple example of how we define an operator based on what we need to measure. Fig. 4.1 (bottom) illustrates that when we want to figure out the parity of the function $f(x)$ on the left, (a) we apply the parity operator $\hat{\mathrm{P}}$ on the function to obtain the function on the right, that is, $g(x) = \hat{\mathrm{P}}f(x)$ and, then, (b) we compare the function $g(x) = f(-x)$ on the right to the function $f(x)$ on the left.

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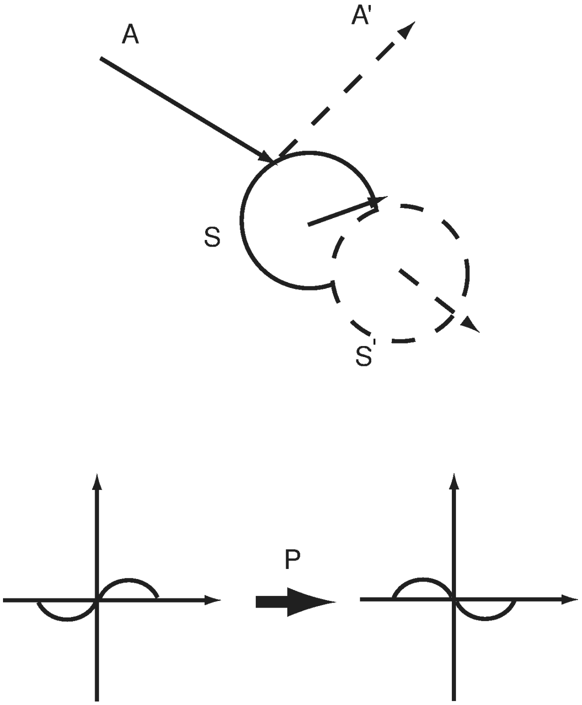

Fig. 4.1 (Top) The result of a measurement on the system S is obtained by comparing the state of the apparatus A′ after the intervention of the measurement to its state A before the measurement. (Bottom) To figure out the parity of the function on the left: (a) we apply the parity operator P to change the function to the one on the right and (b) we compare the function on the left to the function on the right to measure the parity of the function.

Since the result of a measurement in quantum mechanics is the expectation value of the operator which represents the observable, we can ask the following question: In general, what should be the mathematical nature of an operator in order to correctly represent a physical observable?

It turns out that if we use Hermitian (or self-adjoint) operators to represent physical observables, we can guarantee that the expectation value of the corresponding observable is a real number.

So, what is a Hermitian operator? In order to define the Hermitian operator, we need first to define the so-called adjoint (or Hermitian conjugate) of a given operator $\hat{A}$. The adjoint $\hat{A}^\dagger$ of the operator $\hat{A}$, is the operator whose matrix elements between any two given states $|\psi\rangle$ and $|\phi\rangle$ are given in terms of the matrix elements of $\hat{A}$ as follows:

$$\langle\psi|\hat{A}^\dagger|\phi\rangle \equiv \langle\phi|\hat{A}|\psi\rangle^*. \tag{4.2}$$

A Hermitian operator is one which is self-adjoint, that is, the same as its adjoint, that is,

$$\hat{A}^\dagger = \hat{A}. \tag{4.3}$$

It follows straightforwardly that the expectation value of a Hermitian operator is real.

4.2 Representation of operators

The position operator is diagonal in the position representation, that is, in 1D in the basis $|x\rangle$, namely,

$$\hat{x}|x\rangle = x|x\rangle. \tag{4.4}$$

In chapter 3 we discussed that the states $|k\rangle$, defined by the transformation given by Eq. (3.2), describe a particle in which the probability amplitude for the particle to be in state $|n\rangle$ is a phase factor e^{ikna}, which is characterized by a wavevector $k = m2\pi/L$ (where m is an integer). We also stated that this is analogous to the case of the amplitude of a classical wave which is confined in a region of length L. Therefore, in a similar way to our previous definition that the states $|n\rangle$ can be considered eigenstates of the position operator, we can define an operator $\hat{k}$, and we will call it, the "wavevector operator," which is diagonal in the $|k\rangle$ basis, that is,

$$\hat{k}|k\rangle \equiv k|k\rangle. \tag{4.5}$$

The difference between this operator and the usual momentum operator $\hat{p}$ is just a multiplicative (Planck's) constant, that is,

$$\hat{p} = \hbar k. \tag{4.6}$$

Thus, the momentum operator is also diagonal in the basis $|k\rangle$, namely,

$$\hat{p}|k\rangle = \hbar k|k\rangle. \tag{4.7}$$

The momentum operator can be expressed in the x-labeled basis, that is, given an arbitrary state $|\psi\rangle$

$$\langle x|\hat{p}|\psi\rangle = \hat{\mathcal{P}}\langle x|\psi\rangle, \tag{4.8}$$

and this is an equation defining the momentum operator $\hat{\mathcal{P}}$ in the position-labeled basis. Using this equation we can also determine the form of $\hat{\mathcal{P}}$ as follows: First we expand the arbitrary state $|\psi\rangle$ in the k-labeled basis, that is,

$$|\psi\rangle = \int \frac{dk}{2\pi}\tilde{\psi}(k)|k\rangle, \tag{4.9}$$

where the coefficient $\tilde{\psi}(k) = \langle k|\psi\rangle$ of the expansion can be found in terms of the coefficient $\psi(x)$ of the expansion of the same state in the position basis, that is,

$$|\psi\rangle = \int dx \psi(x) |x\rangle, \tag{4.10}$$

by projecting both sides of the above equation in the basis vector $|k\rangle$, that is,

$$\tilde{\psi}(k) = \langle k|\psi\rangle = \int dx \psi(x) e^{-ikx}, \tag{4.11}$$

and we have used the fact that $\langle k|x\rangle = e^{-ikx}$. Now, let us operate on both sides of Eq. (4.9) with the operator $\hat{p}$ as defined by Eq. (4.7).

$$\hat{p}|\psi\rangle = \int \frac{dk}{2\pi} \tilde{\psi}(k) \hat{p}|k\rangle = \hbar \int \frac{dk}{2\pi} \tilde{\psi}(k) k|k\rangle \tag{4.12}$$

and, by taking the inner product with state $|x\rangle$ in order to obtain the desired quantity, we find

$$\langle x|\hat{p}|\psi\rangle = \hbar \int \frac{dk}{2\pi} \tilde{\psi}(k) k e^{ikx} = -i\hbar \frac{d}{dx} \int \frac{dk}{2\pi} \tilde{\psi}(k) e^{ikx}. \tag{4.13}$$

Now, by projecting both sides of Eq. (4.9) onto the state $|x\rangle$ and using the fact that $\langle x|k\rangle = e^{ikx}$, we find that

$$\psi(x) = \int \frac{dk}{2\pi} \tilde{\psi}(k) e^{ikx}. \tag{4.14}$$

Using the last equation, we can rewrite the previous equation as

$$\langle x|\hat{p}|\psi\rangle = -i\hbar \frac{d}{dx} \langle x|\psi\rangle. \tag{4.15}$$

Therefore, we conclude that the position space representation of the momentum operator is the following:

$$\hat{\mathcal{P}} = -i\hbar \frac{d}{dx}. \tag{4.16}$$

4.3 The Hamiltonian operator

Here, we consider operators which can be functions of other operators, such as the Hamiltonian which is a function of the momentum and the position operators as in classical mechanics.

We “pass” to quantum mechanics from classical mechanics by considering the classical expression for the Hamiltonian $H(\vec{q}_i, \vec{p}_i)$, which is a function of the generalized coordinates $\vec{q}_i$ and their corresponding conjugate momenta $\vec{p}_i$, as a function of the operators $\hat{\vec{q}}_i$ and its corresponding momentum operator $\hat{\vec{p}}_i$, that is, $\hat{H} \equiv H(\hat{\vec{q}}_i, \hat{\vec{p}}_i)$; these conjugate operators obey the Canonical commutation relations:

$$\left[\hat{\vec{q}}_i, \hat{\vec{p}}_j\right] = i\hbar \delta_{i,j}. \tag{4.17}$$

In the example of the 1D single non-relativistic particle in a potential $V(x)$, we can express the Hamiltonian operator,

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}), \tag{4.18}$$

in the x-labeled basis. The result for the operator $\hat{\mathcal{H}}$ defined as

$$\langle x|\hat{H}|\psi\rangle = \hat{\mathcal{H}}\langle x|\psi\rangle, \tag{4.19}$$

is the following

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x). \tag{4.20}$$

4.4 Problems

Problem 1

Consider the momentum space basis, that is, the states $|k\rangle$ defined in the present chapter. Consider an arbitrary state $|\psi\rangle$ in momentum space, that is,

$$|\psi\rangle = \sum_k \tilde{\psi}(k)|k\rangle, \tag{4.21}$$

where $\tilde{\psi}(k) = \langle k|\psi\rangle$.

Show that the position operator defined by Eq. 4.4 has the following representation in momentum space:

$$\langle k|\hat{x}|\psi\rangle = -i\hbar\frac{\partial}{\partial k}\tilde{\psi}(k). \tag{4.22}$$

Problem 2

Assume that the particle is under the influence of the following potential

$$V(x) = -V_0 \exp(-\frac{x^2}{2\lambda^2}). \tag{4.23}$$

What is the Schrödinger equation in k-space? Namely, what is the differential equation for the amplitude $\tilde{\psi}(k,t) = \langle k|\psi(t)\rangle$?

5

Time evolution and wavepackets

Here we analyze time evolution in quantum mechanics. Examples include the case of a free-particle state which is initially prepared as a wavepacket.

5.1 Time-independent Hamiltonian

Here we discuss the time evolution of the state when the Hamiltonian is time independent. In this case, we can integrate the time-dependent Schrödinger equation:

$$\hat{H}|\psi(t)\rangle = i\hbar\partial_t|\psi(t)\rangle, \tag{5.1}$$

to find the following solution

$$|\psi(t)\rangle = \exp(-\frac{i}{\hbar}\hat{H}t)|\psi(0)\rangle. \tag{5.2}$$

This expression yields the state $|\psi(t)\rangle$ at a latter time t, if we know it at some initial time $t = 0$.

To find the state $|\psi(t)\rangle$ explicitly, it is useful to diagonalize the Hamiltonian operator, that is,

$$\hat{H}|\phi_n\rangle = E_n|\phi_n\rangle, \tag{5.3}$$

and, thus, to determine the eigenstates and eigenvalues. Then, we use the fact that the eigenstates form a complete basis, that is,

$$\sum_n |\phi_n\rangle\langle\phi_n| = \hat{1}, \tag{5.4}$$

to expand the initial state $|\psi(0)\rangle$ in this basis, that is,

$$|\psi(0)\rangle = \sum_n C_n|\phi_n\rangle, \tag{5.5}$$

where the coefficients C_n, given the initial state $|\psi(0)\rangle$, can be computed as overlap integrals, that is,

$$C_n = \langle\phi_n|\psi(0)\rangle, \tag{5.6}$$

of the given initial state $|\psi(0)\rangle$ and each one of the Hamiltonian eigenstates which, as we assumed, we have determined. Therefore, we find that

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$$|\psi(t)\rangle = \sum_n C_n \exp(-\frac{i}{\hbar}E_n t)|\phi_n\rangle. \tag{5.7}$$

Thus, we have succeeded expressing the state at a later time t in terms of known quantities.

5.2 An example of time evolution

Consider a problem spanned by a basis of just two states, such as a spin-1/2 problem, or simply a model which is designed to describe a system in which the full spectrum is truncated and only a pair of states is retained.

In this case, the system is governed by a Hamiltonian which in the basis $|1\rangle$, $|2\rangle$ is a matrix of the following form:

$$H = -\begin{pmatrix} 0 & g \\ g & 0 \end{pmatrix} = -g\hat{\sigma}_x, \tag{5.8}$$

where σ_x is x-component of the Pauli matrix to be defined in chapter 23. As we will see later on in chapter 23, this Hamiltonian corresponds to the Zeeman term for spin-1/2, where the magnetic field is along the x-axis and we used the basis labeled by the spin eigenstates along the z-axis. In such a case, g represents the product of the external magnetic field times the magnetic moment due to spin.

Problem: Now, we wish to solve the following problem: Given that we prepare the system to be in state $|1\rangle$ at time $t = 0$, what is the probability to be found in state $|1\rangle$ if a measurement is carried out at a later time t?

Solution:

If we explicitly determine the state $|\psi(t)\rangle$ of the system at time t, the requested probability is given by

$$P(t) = |\langle 1|\psi(t)\rangle|^2. \tag{5.9}$$

Therefore, the problem reduces to determining $|\psi(t)\rangle$ using the discussion of the previous section.

Step 1: We need to diagonalize the Hamiltonian and determine the energy eigenvalues and corresponding eigenstates. The eigenvalues are $E_\pm = \pm g$, which correspond to the following eigenstates:

$$|\pm\rangle = \frac{1}{\sqrt{2}}\left(|1\rangle \mp |2\rangle\right). \tag{5.10}$$

Step 2: We need to expand the initial state in the basis formed by the above energy eigenstates. Namely, we write

$$|1\rangle = \alpha|+\rangle + \beta|-\rangle, \tag{5.11}$$

and we need to determine the coefficients α and β, which are given as

$$\alpha = \langle +|1\rangle, \qquad \beta = \langle -|1\rangle. \tag{5.12}$$

Substituting the expressions (5.10) for $|\pm\rangle$ above, we explicitly find that

$$\alpha = \beta = \frac{1}{\sqrt{2}}. \tag{5.13}$$

Therefore, we conclude that

$$|1\rangle = \frac{1}{\sqrt{2}}(|+\rangle + |-\rangle). \tag{5.14}$$

This allows us to find the result of the action of the time-evolution operator (5.2) on the above state, that is,

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}(\exp(-\frac{i}{\hbar}gt)|+\rangle + \exp(\frac{i}{\hbar}gt)|-\rangle), \tag{5.15}$$

As a result, we find that

$$P(t) = |\langle 1|\psi(t)\rangle|^2 = \cos^2(gt/\hbar). \tag{5.16}$$

In the next section, we will present the case of the time-evolution of a Gaussian wavepacket, which is another case where the same method is applied.

5.3 Wavepackets

Consider the free particle Hamiltonian in 1D

$$\hat{H} = \frac{\hat{p}^2}{2m}, \tag{5.17}$$

and imagine that we have prepared an initial state to be a Gaussian wavefunction of the form

$$\Psi(x, t = 0) = \frac{1}{(2\pi\sigma^2)^{\frac{1}{4}}} \exp\{-\frac{x^2}{4\sigma^2}\} \exp(ik_0 x). \tag{5.18}$$

We are interested in the time evolution of this initial state under the influence of the free Hamiltonian, which has plane waves as eigenstates. Therefore, following the prescription of how to find the time evolution of the initial state, we expand the initial state in plane waves, and we find

$$\Psi(x, t = 0) = C \int \frac{dk}{2\pi} \exp\{-\sigma^2(k - k_0)^2\} \exp\{ikx\}, \tag{5.19}$$

namely, in momentum space the wavefunction is a superposition of plane waves and the probability amplitude is peaked near some momentum k_0. The constant C is determined by the normalization condition

$$1 = |C|^2 \int \frac{dk}{2\pi} \exp\{-2\sigma^2(k - k_0)^2\}, \tag{5.20}$$

and it is given by

$$C = \sqrt{2}(2\pi\sigma^2)^{\frac{1}{4}}. \tag{5.21}$$

Inversely, and to verify that we have done the calculation correctly so far, we can carry out the integral over k in Eq. 5.19 by completing the square. This calculation should yield the state given by Eq. 5.18.

Now, by applying the time-evolution operator on the state given by Eq. 5.19 we obtain:

$$\Psi(x,t) = C\int \frac{dk}{2\pi}\exp\{-\sigma^2(k-k_0)^2\}\exp\{-i\frac{\hbar k^2 t}{2m}\}e^{ikx}, \tag{5.22}$$

The integral over k in the above equation can be done using the usual trick of completing the square in the sum of the exponents. We obtain

$$\Psi(x,t) = C\frac{1}{2\sqrt{\pi(\sigma^2+\frac{i\hbar t}{2m})}}\exp\Big(\frac{(2\sigma^2 k_0 + ix)^2}{4(\sigma^2+\frac{i\hbar t}{2m})} - \sigma^2 k_0^2\Big). \tag{5.23}$$

By separating the real and imaginary parts of the exponent in the exponential we obtain:

$$\Psi(x,t) = D(t)\exp\Big(-\frac{(x-x_c(t))^2}{4\tilde{\sigma}^2(t)}\Big)e^{i\phi(x,t)}, \tag{5.24}$$

$$x_c(t) = \frac{\hbar k_0 t}{m}, \tag{5.25}$$

$$\tilde{\sigma}^2(t) = \sigma^2\Big(1+\frac{x_c^2(t)}{4k_0^2\sigma^4}\Big), \tag{5.26}$$

$$D(t) \equiv C\frac{1}{2\sqrt{\pi(\sigma^2+\frac{i\hbar t}{2m})}}, \tag{5.27}$$

$$\phi(x,t) = \frac{k_0(x-x_c(t)/2)+\frac{x^2 x_c}{8\sigma^4 k_0}}{\frac{\tilde{\sigma}^2}{\sigma^2}}. \tag{5.28}$$

Notice that $x_c(t)$ is the classical trajectory of a free particle moving with momentum $p_0 = \hbar k_0$.

In Fig. 5.1 the real part of $\Psi(x,t)$ is shown as a function of x for $x_c(t) = 0, 10$, and 20 and for $k_0 = 20$, and in Fig. 5.2 for $k_0 = 1$. Notice that when the wavepacket momentum is large, the shape of the wavepacket is preserved as a function of time and the center of the wavepacket moves with momentum $p_0 = \hbar k_0$ (classical limit), while in the case where the momentum is relatively low the shape of the wavepacket is not preserved during the time evolution. In fact the spread of the wavepacket increases as a function of time.

5.4 Time-dependent Hamiltonian

In this section, we focus our attention on the more general case where the Hamiltonian depends explicitly on time. This section is particularly useful for chapter 22 where we discuss time-dependent perturbation theory.

We are interested in finding the evolution operator, that is, an operator $\hat{U}(t,t_0)$ which yields the state of our system at a later time t starting for the initial state at t_0:

$$|\psi(t)\rangle = \hat{U}(t,t_0)|\psi(t_0)\rangle. \tag{5.29}$$

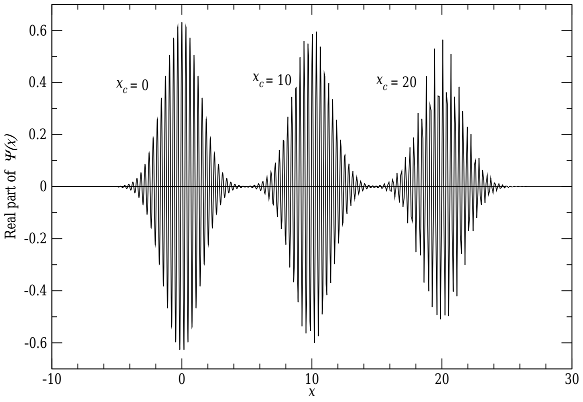

Fig. 5.1

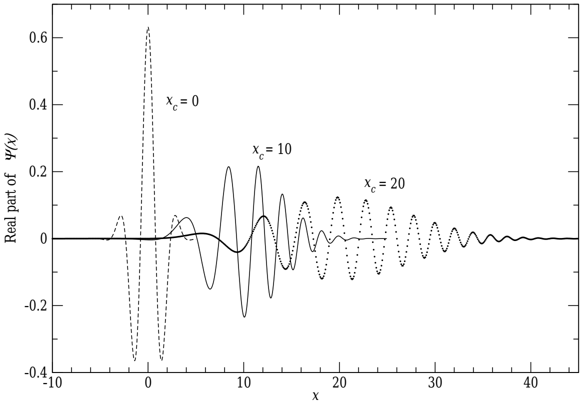

Fig. 5.2

It is straightforward to show that $\hat{U}(t, t_0)$ satisfies the following integral equation:

$$\hat{U}(t, t_0) = 1 + \frac{1}{i\hbar} \int_{t_0}^{t} \hat{H}(t')\hat{U}(t', t_0)dt'. \tag{5.30}$$

In order to show this, we take the time derivative of both sides of the above equation and we find that

$$i\hbar\partial_t \hat{U}(t, t_0) = \hat{H}(t)\hat{U}(t, t_0). \tag{5.31}$$

This is an equation for operators. We apply both sides of this equation to the initial state $|\psi(t_0)\rangle$ and find that

$$\hat{H}(t)|\psi(t)\rangle = i\hbar\partial_t|\psi(t)\rangle, \tag{5.32}$$

where $|\psi(t)\rangle$ is given by Eq. 5.29 and, therefore, we have shown that the state given by by Eq. 5.29 with $\hat{U}(t, t_0)$ satisfying Eq. 5.30, obeys the the time-dependent Schrödinger equation.

The integral Eq. 5.30 can be formally solved iteratively, that is,

$$\begin{aligned}
\hat{U}(t,t_0) &= \sum_{n=0}^{\infty} U^{(n)}(t,t_0), && (5.33)\\
U^{(0)}(t,t_0) &= \hat{1}, && (5.34)\\
U^{(1)}(t,t_0) &= \frac{1}{i\hbar}\int_{t_0}^{t} dt' H(t'), && (5.35)\\
U^{(2)}(t,t_0) &= \frac{1}{(i\hbar)^2}\int_{t_0}^{t} dt' H(t')\int_{t_0}^{t'} dt'' H(t''), && (5.36)\\
&\cdots\\
U^{(n)}(t,t_0) &= \frac{1}{(i\hbar)^n}\int_{t_0}^{t} dt_1 H(t_1)\int_{t_0}^{t_1} dt_2 H(t_2)...\\
&\quad\times\int_{t_0}^{t_{n-1}} dt_n H(t_n). && (5.37)
\end{aligned}$$

Therefore, we can obtain the evolution operator and, hence, the state $|\psi(t)\rangle$ in any order. This equation is also formally equivalent to the following equation:

$$|\psi(t)\rangle = \hat{T}e^{-\frac{i}{\hbar}\int_{t_0}^{t} dt'\hat{H}(t')}|\psi(t_0)\rangle, \tag{5.38}$$

where the operator $\hat{T}$ is called the time-ordering operator and it acts on a product of operators as follows:

$$\hat{T}(\hat{H}(t_1)\hat{H}(t_2)) = \begin{pmatrix} \hat{H}(t_1)\hat{H}(t_2)\ for\ t_1 > t_2 \\ \hat{H}(t_2)\hat{H}(t_1)\ for\ t_2 > t_1 \end{pmatrix}. \tag{5.39}$$

One can easily show by expanding the exponential, that for the nth order term there are $n!$ ways of arranging the operators in order to achieve a time-ordered sequence. This cancels the $1/n!$ prefactor coming from the expansion and, in addition, it gives rise to the same nested integrals as in Eq. 5.37.

5.5 Problems

Problem 1

Consider the two-level system with Hamiltonian given by Eq. 5.8 in the basis

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{5.40}$$

We prepare the system, such as at $t = 0$, it is in the state $|1\rangle$. In this chapter we determined the probability that if we carry out a measurement after the elapse of time t, we find the system in state $|1\rangle$.

a) Imagine that we repeat the measurement periodically in intervals of time extent $\delta\tau$ between measurements. Namely, we prepare the system in state $|1\rangle$ at time $t = 0$. Then, we carry out measurements at times $t = \delta\tau$, $t = 2\delta\tau$, $t = 3\delta\tau$, ..., $t = n\delta\tau$, ... What is the probability that the system remains in state $|1\rangle$ after n such successive measurements?

b) Consider the limit $\delta\tau << T$, where $T = \frac{\pi\hbar}{g}$. Show that in this limit the probability for the system to be continuously observed to be in state $|1\rangle$ decays exponential with the elapsed total time $t = n\delta\tau$. In particular, show that the probability is approximately given by

$$P(t) = e^{-t/\tau}, \tag{5.41}$$

$$t = n\delta\tau, \qquad \tau = \frac{\hbar^2}{g^2\delta\tau}. \tag{5.42}$$

Thus, the characteristic half lifetime goes to infinity in the limit where $\delta\tau \to 0$? Namely, the state becomes stable by continuous observation. This is the so-called *Quantum Zeno effect.*

Problem 2

Consider the Hilbert space spanned by the two possible states $|1\rangle$ and $|2\rangle$ and a Hamiltonian, which in this basis is given by the following 2×2 matrix

$$H = \begin{pmatrix} 0 & i\gamma \\ -i\gamma & 0 \end{pmatrix}, \tag{5.43}$$

where γ is a real and positive number. Imagine that the state at $t = 0$ is given as

$$|\psi(t = 0)\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle). \tag{5.44}$$

Find the probability for the particle to be found in state $|1\rangle$ if an experiment is carried out after time t.

Problem 3

Consider Problem 1 of chapter 1 which is a three-state problem. Imagine that we have initially (at $t = 0$) placed the particle in position 1, that is, in state $|1\rangle$. What is the probability, if we measure the position, to find the particle in state $|1\rangle$ after time t?

Problem 4

a) Carry out the integral over k in Eq. 5.19 by completing the square. This calculation should yield the state given by Eq. 5.18.

b) Carry out the integral over k in Eq. 5.22 using the same trick of completing the square in the sum of the exponents. Show that the result is Eq. 5.23.

Problem 5

Show by expanding the exponential in Eq. 5.38, that for the nth order term there are $n!$ ways of arranging the operators in order to achieve a time-ordered sequence. Show that this cancels the $1/n!$ prefactor coming from the expansion and, in addition, that it gives rise to the same nested integrals as in Eq. 5.37.

Problem 5

Consider the time-dependent Scrödinger equation in 1D for a time-independent interaction potential:

$$i\hbar\partial_t\Psi(x,t) = \hat{H}\Psi(x,t), \tag{5.45}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\partial_x^2 + V(x). \tag{5.46}$$

Consider the transformation to imaginary time $\tau = it$, when it takes the form

$$-\hbar\partial_\tau\Phi(x,\tau) = \hat{H}\Phi(x,\tau). \tag{5.47}$$

a) Show that the formal solution to the above “diffusion”-type equation is of the following form

$$\Phi(x,\tau) = \exp\Big(-\frac{\tau}{\hbar}\hat{H}\Big)\Phi(x,0), \tag{5.48}$$

where $\Phi(x,0)$ is the starting wavefunction at $\tau = 0$.

b) Show that in the long-time limit ($\tau \to \infty$) the normalized wavefunction $\Phi(x,\tau)$ approaches the ground state of the Hamiltonian $\hat{H}$ above, provided that our starting state is not orthogonal to the true ground state of $\hat{H}$.

6
Simultaneous observables

In this chapter, we investigate when two observables, which are represented by operators $\hat{A}$ and $\hat{B}$, can be simultaneously observable. These two observables can be simultaneously known if the operators $\hat{A}$ and $\hat{B}$ which represent them commute with each other. If $[\hat{A}, \hat{B}] \neq 0$ there is an uncertainty relationship which holds between these two observables.

6.1 Uncertainty principle

Consider two operators $\hat{A}$ and $\hat{B}$ which do not commute; we wish to examine their variances, that is,

$$(\Delta A)^2 \equiv \langle\psi|(\hat{A} - \langle\hat{A}\rangle)^2|\psi\rangle, \qquad (\Delta B)^2 \equiv \langle\psi|(\hat{B} - \langle\hat{B}\rangle)^2|\psi\rangle. \tag{6.1}$$

ΔA and ΔB give us a measure of the fluctuations of the possible values of the observables represented by these operators from their expectation values. We will show next that if the system is in any arbitrary but given state $|\psi\rangle$:

$$\Delta A \Delta B \geq \frac{1}{2}|\langle\psi|[\hat{A}, \hat{B}]|\psi\rangle|. \tag{6.2}$$

In order to prove this we will take advantage of the so-called Cauchy–Schwartz inequality:

$$|\langle\chi|\psi\rangle|^2 \leq \langle\chi|\chi\rangle\langle\phi|\phi\rangle. \tag{6.3}$$

Let us apply this inequality using as $|\chi\rangle$ and $|\psi\rangle$ the following,

$$|\chi\rangle = (\hat{A} - \langle\hat{A}\rangle)|\psi\rangle \equiv \hat{\alpha}|\psi\rangle, \tag{6.4}$$

$$|\phi\rangle = (\hat{B} - \langle\hat{B}\rangle)|\psi\rangle \equiv \hat{\beta}|\psi\rangle. \tag{6.5}$$

This leads to the following inequality:

$$\begin{aligned}(\Delta A)^2(\Delta B)^2 &\geq |\langle\psi|\hat{\alpha}\hat{\beta}|\psi\rangle|^2, \\ &= |\frac{1}{2}\langle\psi|(\hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha})|\psi\rangle + \frac{1}{2}\langle\psi|(\hat{\alpha}\hat{\beta} + \hat{\beta}\hat{\alpha})|\psi\rangle|^2 \\ &= \frac{1}{4}|\langle\psi|[\hat{\alpha}, \hat{\beta}]|\psi\rangle|^2 + \frac{1}{4}|\langle\psi|\{\hat{\alpha}, \hat{\beta}\}|\psi\rangle|^2,\end{aligned} \tag{6.6}$$

where

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$$\{\hat{\alpha}, \hat{\beta}\} \equiv \hat{\alpha}\hat{\beta} + \hat{\beta}\hat{\alpha}, \tag{6.7}$$

that is, the so-called "anticommutator." Notice that the cross terms vanish:

$$\frac{1}{4}\Big[\langle\psi|[\hat{\alpha}, \hat{\beta}]|\psi\rangle\langle\psi|\{\hat{\alpha}, \hat{\beta}\}|\psi\rangle^* + \langle\psi|[\hat{\alpha}, \hat{\beta}]|\psi\rangle^*\langle\psi|\{\hat{\alpha}, \hat{\beta}\}|\psi\rangle\Big] = 0, \tag{6.8}$$

due to the following relations:

$$\langle\psi|[\hat{\alpha}, \hat{\beta}]|\psi\rangle^* = \langle\psi|[\hat{\beta}, \hat{\alpha}]|\psi\rangle, \tag{6.9}$$

$$\langle\psi|\{\hat{\alpha}, \hat{\beta}\}|\psi\rangle^* = \langle\psi|\{\hat{\alpha}, \hat{\beta}\}|\psi\rangle. \tag{6.10}$$

Therefore, we find that

$$(\Delta A)^2(\Delta B)^2 \geq \frac{1}{4}|\langle\psi|[\hat{\alpha}, \hat{\beta}]|\psi\rangle|^2. \tag{6.11}$$

This means that we cannot measure both observables with infinite accuracy. For example, if the system is in a state which is an eigenstate of the operator $\hat{A}$, then $(\Delta A)^2 = 0$, which means that we precisely know the observable $\hat{A}$. In this case, the uncertainty associated with the observable $\hat{B}$ must be infinite, because

$$(\Delta B)^2 \geq \frac{1}{4}|\langle\psi|[\hat{\alpha}, \hat{\beta}]|\psi\rangle|^2/(\Delta A)^2. \tag{6.12}$$

As an example, consider the case where $\hat{A} = \hat{x}$ and $\hat{B} = \hat{p}_x$, that is, the x-component of the position and momentum operators. In this case, since

$$\langle\psi|[\hat{x}, \hat{p}]|\psi\rangle = |i\hbar| = \hbar, \tag{6.13}$$

we immediately find that

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}. \tag{6.14}$$

6.2 Commuting operators

Now, let us examine the case where the operators $\hat{A}$ and $\hat{B}$, which represent the two observables, commute with each other:

$$\Big[\hat{A}, \hat{B}\Big] = 0. \tag{6.15}$$

First, we consider the eigenstates of the operator $\hat{A}$:

$$\hat{A}|\alpha, n\rangle = \alpha|\alpha, n\rangle, \qquad n = 1, 2, .., N_\alpha, \tag{6.16}$$

where the index n labels the different eigenstates of $\hat{A}$ which correspond to the same eigenvalue α. Namely, N_α is the degree of degeneracy of the eigenvalue α.

To each and every definite eigenvalue α, there is a corresponding subspace S_α spanned by all the N_α eigenvectors, $|\alpha, 1\rangle$,$|\alpha, 2\rangle$, ..., $|\alpha, N\rangle$. What is characteristic of this subspace is that any vector from this subspace, that is,

$$|\psi_\alpha\rangle = \sum_{n=1}^{N_\alpha} C_n |\alpha, n\rangle, \tag{6.17}$$

is also an eigenstate corresponding to the same eigenvalue α, because

$$\hat{A}|\psi_\alpha\rangle = \sum_{n=1}^{N_a} C_n \hat{A}|\alpha, n\rangle = \alpha \sum_{n=1}^{N_a} C_n |\alpha, n\rangle = \alpha|\psi_\alpha\rangle. \tag{6.18}$$

Conversely, *any state $|\phi_\alpha\rangle$ that we might encounter which turns out to be an eigenstate of $\hat{A}$ with eigenvalue α belongs to S_α*, which means that it is a linear combination of $|\alpha, n\rangle$. Because if it cannot be written as a linear combination of just the other N_α eigenstates, that is, it does not strictly belong to the subspace S_α, then the degree of degeneracy should be higher than the assumed degree of degeneracy N_α.

Now, given an eigenstate $|\psi_\alpha\rangle$ of $\hat{A}$ with corresponding eigenvalue α, the state

$$|\chi_\alpha\rangle = \hat{B}|\psi_\alpha\rangle, \tag{6.19}$$

is also an eigenstate of $\hat{A}$ with corresponding eigenvalue also α. To prove it, let us apply the operator $\hat{A}$ on this state and use the fact that the operators $\hat{A}$ and $\hat{B}$ commute:

$$\hat{A}|\chi_\alpha\rangle = \hat{A}\hat{B}|\psi_\alpha\rangle = \hat{B}\hat{A}|\psi_\alpha\rangle = \alpha\hat{B}|\psi_\alpha\rangle = \alpha|\chi_\alpha\rangle. \tag{6.20}$$

In the above we made use of the fact that $\hat{A}|\psi_\alpha\rangle = \alpha|\psi_\alpha\rangle$. Therefore, the immediate conclusion of the above is that the subspace S_α is invariant under the action of the operator $\hat{B}$. Namely, when $\hat{B}$ acts on any vector

$$|\psi_\alpha\rangle = \sum_{n=1}^{N_\alpha} C_n^{(\alpha} |\alpha, n\rangle, \tag{6.21}$$

which lies inside S_α the result is a vector which lies totally inside S_α:

$$\hat{B}|\psi_\alpha\rangle = \sum_{n=1}^{N_\alpha} C_n |\alpha, n\rangle. \tag{6.22}$$

Since we seek eigenstates of $\hat{B}$, and because of the above, we are allowed to demand that:

$$\hat{B}|\psi_\alpha\rangle = \beta|\psi_\alpha\rangle, \tag{6.23}$$

where β is some eigenvalue of $\hat{B}$ to be determined. Projecting both sides of the above equation on any element $|\alpha, m\rangle$ of the basis vectors which span S_α we find the familiar eigenvalue equation:

$$\sum_{n=1}^{N_\alpha} \langle \alpha, m|\hat{B}|\alpha, n\rangle C_n^\alpha = \beta C_m^\alpha. \tag{6.24}$$

The key point here is that there is no projection of the left-hand-side of Eq. 6.23 outside S_α. This allows us to label the eigenstates of $\hat{B}$ found as solutions to the above equation as $|\alpha, \beta\rangle$ because they are eigenstates of the operator $\hat{B}$ and of the operator $\hat{A}$ because they are inside the subspace S_α. Thus, these two operators can share eigenstates.

6.3 Symmetries of the Hamiltonian

Imagine that the Hamiltonian commutes with an operator $\hat{P}$ due to a symmetry. As an example, consider the case where the Hamiltonian is invariant with respect to the parity transformation, that is, under the transformation $x \to -x$; then the operator $\hat{P}$ defined as

$$\hat{P}\psi(x) = \psi(-x), \tag{6.25}$$

where $\psi(x)$ is any state of our Hilbert space, is the parity transformation operator. In the one-body case, $\hat{P}$ commutes with the Hamiltonian when the external potential, which is felt by the particle, is an even function of x, that is, $\hat{P}V(x) = V(-x) = V(x)$. The reason is that the kinetic energy operator

$$\hat{T}(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}, \tag{6.26}$$

is also invariant under the transformation $x \to -x$, because $\hat{P}\hat{T}(x) = \hat{T}(-x) = \hat{T}(x)$. In this case

$$[\hat{H}, \hat{P}] = 0. \tag{6.27}$$

To prove this, consider an arbitrary state $\psi(x)$ and apply $\hat{P}\hat{H}$ on it, that is,

$$\hat{P}(\hat{H}\psi(x)) = \hat{H}(-x)\psi(-x) = \hat{H}(x)\psi(-x) = \hat{H}\hat{P}\psi(x), \tag{6.28}$$

where by comparing the first and last side of the above equation, we conclude that

$$[\hat{P}, \hat{H}]\psi(x) = 0. \tag{6.29}$$

In the case where the Hamiltonian commutes with such an operator $\hat{P}$, we can simultaneously diagonalize $\hat{H}$ and $\hat{P}$. This means that they can share eigenstates as was shown in the previous section for the most general case. Next, we prove this theorem again for the particular case of the operator $\hat{P}$ and the Hamiltonian operator $\hat{H}$.

Let us consider a particular energy level E and all the eigenstates $|\psi_n(x)\rangle$ with corresponding energy $E_n = E$. These states constitute the subspaces S_E of degeneracy of $\hat{H}$. These subspaces are invariant subspaces under the operation of $\hat{P}$. This means that when $\hat{P}$ operates on any state inside a given subspace S_E, the resulting state is also inside the subspace S_E. To show this, let us consider such a state $|\psi\rangle$ which is inside S_E which implies that

$$\hat{H}|\psi\rangle = E|\psi\rangle. \tag{6.30}$$

Now, the state $|\phi\rangle \equiv \hat{P}|\psi\rangle$ is also an eigenstate of $\hat{H}$ with the same eigenvalue E. To see this let us apply the Hamiltonian on this state:

$$\begin{aligned}\hat{H}|\phi\rangle &= \hat{H}\hat{P}|\psi\rangle = \hat{P}\hat{H}|\psi\rangle = E\hat{P}|\psi\rangle = E|\phi\rangle, \\ \rightarrow \quad & \hat{H}|\phi\rangle = E|\phi\rangle. \end{aligned} \tag{6.31}$$

In the second step of the above equation we have used the fact that $\hat{P}$ and $\hat{H}$ commute. Since the state $\hat{P}|\psi\rangle$ is an eigenstate of $\hat{H}$ with the same eigenvalue E, it belongs to the subspace S_E. Therefore, when $\hat{P}$ acts on any state $|\psi\rangle$ of S_E it produces a state with no component outside of S_E. This means that the operator $\hat{P}$ can be diagonalized in each of the subspaces S_E independently. To see that we can find eigenstates of $\hat{P}$ inside such as subspace, consider as basis the states $|n = 1, 2, ..., \nu\rangle$ where ν is the degree of degeneracy of the level E and the dimensionality of S_E. These states are all eigenstates of H, that is,

$$\hat{H}|n\rangle = E|n\rangle, \qquad \rightarrow \qquad n = 1, 2, ..., \nu. \tag{6.32}$$

The action of $\hat{P}$ on any of these states $|n\rangle$ gives a state inside S_E, thus, it can be written as a linear combination of the same states,

$$\hat{P}|n\rangle = \sum_{k=1}^{\nu} d_{k,n}|k\rangle. \tag{6.33}$$

With these properties at hand, we consider a state $|\psi_p\rangle$ from S_E, that is,

$$|\psi_p\rangle = \sum_{m=1}^{\nu} c_m|m\rangle. \tag{6.34}$$

and we are asking if this state can be an eigenstate of $\hat{P}$, that is,

$$\hat{P}|\psi_p\rangle = p|\psi_p\rangle. \tag{6.35}$$

The left-hand-side of the equation is

$$\hat{P}|\psi_p\rangle = \sum_{m=1}^{\nu} c_m \sum_{k=1}^{\nu} d_{k,m}|k\rangle = \sum_{k=1}^{\nu} e_k|k,\rangle. \tag{6.36}$$

where e_k, $k = 1, 2, ..., \nu$, are the components of a vector $\vec{e}$ obtained by applying the matrix $d_{k,m}$ on the vector $\vec{c}$ with components c_m, $m = 1, 2, ..., \nu$, that is,

$$e_k = \sum_{m=1}^{\nu} d_{k,m}c_m. \tag{6.37}$$

Therefore, the eigenvalue problem (6.35) is equivalent to the following matrix diagonalization problem:

$$\sum_{m=1}^{\nu} d_{k,m}c_m = pc_k, \tag{6.38}$$

where as can be seen from Eq. 6.33 the matrix elements $d_{k,m}$ are the matrix elements of $\hat{P}$ in the basis $|n\rangle$, that is, $d_{k,m} = \langle k|\hat{P}|m\rangle$. Thus, the above equation takes the familiar form

$$\sum_{m=1}^{\nu} \langle k|\hat{P}|m\rangle c_m = pc_k. \tag{6.39}$$

Therefore, we can find eigenstates of $\hat{P}$ inside each of the subspaces S_E independently.

Any such eigenstate of $\hat{P}$, must be labeled as $|\psi_{p,E}\rangle$ because, first, it is an eigenstate of $\hat{P}$:

$$\hat{P}|p,E\rangle = p|p,E\rangle, \tag{6.40}$$

with eigenvalue p, and, in addition, since it is inside S_E, it is an eigenstate of $\hat{H}$ with eigenvalue E.

We can use this theorem in a useful way as follows. Since we know we are allowed to search for common eigenstates of both operators, we first find the eigenstates of $\hat{P}$. This is typically easier than finding the eigenstates of $\hat{H}$. For example, for the case of the parity operator, which we discussed above, the eigenstates $\phi_p(x)$ of $\hat{P}$ can be found as follows. Notice that

$$\begin{aligned} \hat{P}\phi_p(x) &= p\phi_p(x), \quad \rightarrow \quad \hat{P}^2\phi_p(x) = p\hat{P}\phi_p(x), \\ &\rightarrow \quad \hat{P}^2\phi_p(x) = p^2\phi_p(x). \end{aligned} \tag{6.41}$$

However, $\hat{P}^2 = \hat{1}$, because carrying out the transformation $x \rightarrow -x$ twice leads to the identity operation. This implies that

$$p^2 = 1, \qquad \rightarrow \qquad p = \pm 1. \tag{6.42}$$

The corresponding eigenstates are:

$$\hat{P}\phi_+(x) = \phi_+(x), \qquad \rightarrow \qquad \phi_+(-x) = \phi_+(x), \tag{6.43}$$

that is, all the even functions of x and

$$\hat{P}\phi_-(x) = -\phi_-(x), \qquad \rightarrow \qquad \phi_-(-x) = -\phi_-(x), \tag{6.44}$$

that is, all the odd functions of x. Thus, the approach becomes clear. Instead of looking to diagonalize the Hamiltonian inside the full Hilbert space, we split it into subspaces S_p, each characterized by a given value of the eigenvalue of the operator $\hat{P}$. Namely, for any state $|\phi_p\rangle$ from S_p we have

$$\hat{P}|\phi_p\rangle = p|\phi_p\rangle. \tag{6.45}$$

We then diagonalize the Hamiltonian in each of these subspaces because they are invariant subspaces of the Hamiltonian. In the example of the parity operator, this means that we consider the even and odd functions separately.

Now, if we consider all the symmetry operations of the Hamiltonian $\hat{H}$, these commute with $\hat{H}$ and form a group, the symmetry group G of the Hamiltonian. As in the previous example, in this more general case also we need to find the irreducible subspaces of the Hilbert space on which the Hamiltonian operates with respect to the symmetry group G. These irreducible subspaces are invariant subspaces which have no lower dimension invariant subspaces. An invariant subspace is a subspace S which remains invariant under the operation of any element of the group G, namely, when any element $\hat{g}$ of the group G acts on an arbitrary vector $\vec{v}$ of S the result is a vector $\vec{v}'$ which also belongs to S.

The Hilbert subspace spanned by the eigenstates $|n\rangle$ of the Hamiltonian which correspond to the same eigenvalue E, span such an invariant subspace of G. To show that, let us consider any element $\hat{g}$ of G, then the state $|\chi\rangle \equiv \hat{g}|n\rangle$ is also an eigenstate of $\hat{H}$ corresponding to the same eigenvalue, because:

$$\hat{H}|\chi\rangle = \hat{H}\hat{g}|n\rangle = \hat{g}\hat{H}|n\rangle = E\hat{g}|n\rangle = E|\chi\rangle. \tag{6.46}$$

Such an invariant subspace can be broken into irreducible subspaces, where we can find irreducible representations of the group G. An irreducible representation in such an irreducible subspace of dimension l, spanned by the l basis vectors $|l, m\rangle$, is an $l \times l$ matrix $D^{(l)}_{mm'}(g)$ defined as follows:

$$\hat{g}|l, m\rangle = \sum_{m'} D^{(l)}_{mm'}(g)|l, m'\rangle. \tag{6.47}$$

The full study of this more general problem is generally discussed in a group theory course and is beyond the scope of the present lecture notes. However, we will come back to some useful theorems later in this book when we discuss the Wigner–Eckart theorem in Chapter 18.

6.4 Problems

Problem 1

The momentum-space wavefunction of a 1D wavepacket describing a single particle is given by

$$\tilde{\psi}(p) = C \exp(-\frac{p^2}{4\sigma^2}). \tag{6.48}$$

a) Find the normalization constant C.
b) Using the above wavefunction show that the expectation value of p^2 is σ^2.
c) Using the above given form for $\tilde{\psi}(p)$ find the wavefunction $\psi(x)$ in real space.
d) Use the real-space wavefunction $\psi(x)$ to calculate the expectation value of x^2.
e) Use your findings in the above parts a), b), and c) to show that

$$\sqrt{\langle p^2\rangle}\sqrt{\langle x^2\rangle} = \frac{\hbar}{2}. \tag{6.49}$$

Problem 2

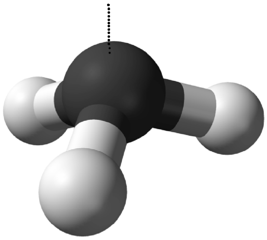

Fig. 6.1

Consider the molecule of ammonia NH_3 (shown in Fig. 6.1) which has a three-fold symmetry rotation axis by 120°, represented in the figure as a vertical dashed-line, which goes through the center of the N atom (represented by the black sphere in the figure) and is perpendicular to the plane defined by the three hydrogen atoms (represented in the figure as white spheres). The Hamiltonian describing the electrons should, therefore, commute with the operator $\hat{R}_{120^\circ}$ which carries out such rotation and with the operator $\hat{R}^2_{120^\circ}$ which carries out rotations by 240°. The C_3 point group is an Abelian group (that is, all its elements commute with each other) which contains the identity $\hat{E}$, $\hat{R}_{120^\circ}$, and $\hat{R}^2_{120^\circ}$. Notice that $\hat{R}^3_{120^\circ} = \hat{E}$, and, thus, the result of any multiplication of these three elements is one of these three operators, thus, it forms a group. Furthermore, the Hamiltonian commutes with all the elements of the C_3 group.

a) Assume that we have diagonalized $\hat{H}$ and we found its eigenstates $|n\rangle$ and its corresponding eigenvalues E_n.

b) Show that for any given eigenstate $|n\rangle$ of $\hat{H}$, and any of the three elements of C_3, say $\hat{g}$, the state $\hat{g}|n\rangle$ is also an eigenstate of $\hat{H}$ with the same eigenvalue E_n.

c) Show that the following three states

$$|\nu\rangle = \frac{1}{\sqrt{3}}\Big(|n\rangle + e^{-i\nu 2\pi/3}\hat{R}_{120^\circ}|n\rangle + e^{-i\nu 4\pi/3}\hat{R}^2_{120^\circ}|n\rangle\Big), \tag{6.50}$$

where ν is an integer and takes the values 0,1,2, are eigenstates of the elements of C_3 and in particular

$$\hat{R}_{120^\circ}|\nu\rangle = e^{i\nu 2\pi/3}|\nu\rangle. \tag{6.51}$$

d) Since the state $|\nu\rangle$ is an eigenstate of $\hat{H}$, we have successfully found common eigenstates between any of the $\hat{g}$ and $\hat{H}$.

7

Continuity equation and wavefunction properties

In this chapter, we discuss the continuity equation and continuity properties of the wavefunction and its spatial derivatives. In addition, we introduce other theorems which are useful for calculations, such as the variational theorem.

7.1 Continuity equation

By imposing that the total probability to find a particle is normalized to unity, that is,

$$\int d^d r |\Psi(\vec{r})|^2 = 1, \tag{7.1}$$

we imply the following conservation law: The particle must be somewhere, it cannot disappear, that is, we imply the particle number conservation.

A conservation law can be expressed mathematically by a continuity equation:

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \vec{J} = 0, \tag{7.2}$$

where ρ is the density of the conserved quantity, which in our case is the probability density, that is,

$$\rho(\vec{r}, t) = |\Psi(\vec{r}, t)|^2, \tag{7.3}$$

and $\vec{J}$ is the conserved quantity density current, which in our case is the probability current density. This is to be determined by our equation of motion: the Schrödinger equation.

The continuity equation in its integrated form is expressed as

$$\frac{\partial P(V)}{\partial t} = -\int_{S(V)} \vec{J} \cdot d\vec{S}, \tag{7.4}$$

$$P(V) = \int_V d^d r |\Psi(\vec{r}, t)|^2, \tag{7.5}$$

namely, $P(V)$ is the total probability inside the volume V (see Fig. 7.1). We have used Gauss's theorem to convert the volume integral over the divergence of the current into

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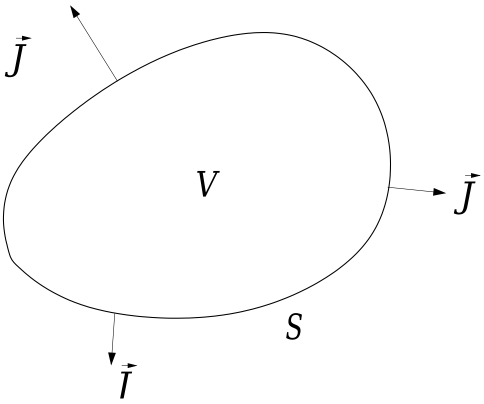

Fig. 7.1

a surface integral over the surface S which binds the volume V. This equation tells us that the rate of change of the total probability to find the particle inside the volume V equals the probability flow out of the volume through its surface.

All of the above are general statements, and in order to make them useful for our case, we need to determine $\vec{J}$. We begin from Schrödinger's equation:

$$\hat{H}\Psi(\vec{r},t) = i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t}, \tag{7.6}$$

and we multiply both sides by $\Psi^*(\vec{r},t)$

$$\Psi^*(\vec{r},t)\hat{H}\Psi(\vec{r},t) = i\hbar\Psi^*(\vec{r},t)\frac{\partial\Psi(\vec{r},t)}{\partial t}. \tag{7.7}$$

Then, we subtract from the above equation its complex conjugate to obtain the following equation:

$$\Psi^*(\vec{r},t)\hat{H}\Psi(\vec{r},t) - \Psi(\vec{r},t)\hat{H}\Psi^*(\vec{r},t) = i\hbar\frac{\partial(\Psi^*(\vec{r},t)\Psi(\vec{r},t))}{\partial t}. \tag{7.8}$$

The left-hand-side, using the familiar non-relativistic form for $\hat{H}$, can be transformed to:

$$\begin{aligned} &\Psi^*(\vec{r},t)\hat{H}\Psi(\vec{r},t) - \Psi(\vec{r},t)\hat{H}\Psi^*(\vec{r},t) \\ &= -\frac{\hbar^2}{2m}\Big(\Psi^*(\vec{r},t)\nabla^2\Psi(\vec{r},t) - \Psi(\vec{r},t)\nabla^2\Psi^*(\vec{r},t)\Big) \\ &= -i\hbar\vec{\nabla}\cdot\vec{J}, \end{aligned} \tag{7.9}$$

with $\vec{J}$ given by

$$\vec{J} = \frac{\hbar}{2mi}\Big(\Psi^*(\vec{r},t)\nabla\Psi(\vec{r},t) - \Psi(\vec{r},t)\nabla\Psi^*(\vec{r},t)\Big). \tag{7.10}$$

Notice then that we have derived the continuity equation, with $\vec{J}$ given by the above expression.

This is the expression for the probability current density $\vec{J}$ of non-relativistic particles. We can multiply both sides of the continuity equation (7.2 by a factor of m (the mass of the particle) and then define the mass density as $\rho_m = m\rho$ and the mass current density as $\vec{J}_m = m\vec{J}$. Then, the continuity equation expresses the conservation of mass.

7.2 Conditions on the wavefunction and its derivative

Imagine that the potential has a discontinuity at a certain point $x = a$ as shown in Fig. 7.2. This is very typical in problems in which a piecewise potential is given to solve. The wavefunction needs to be continuous and single-valued at $x = a$, namely,

$$\Psi(x = a - 0) = \Psi(x = a + 0). \tag{7.11}$$

If a discontinuous wavefunction were to be allowed, we would be in the absurd position where we could not assign a unique probability to that point in space.

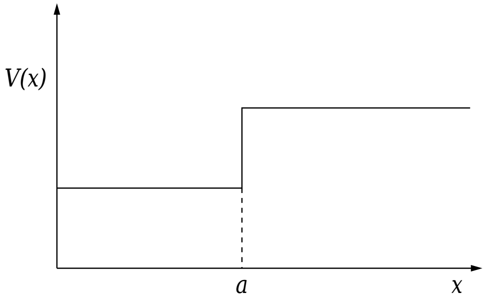

Fig. 7.2

What is the condition on the derivative of the wavefunction? Let us consider the Schrödinger equation in 1D:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x)\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t}, \tag{7.12}$$

and integrate both sides from $a - \epsilon$ to $a + \epsilon$.

$$\begin{aligned}&-\frac{\hbar^2}{2m}\int_{a-\epsilon}^{a+\epsilon} dx\frac{\partial^2\Psi(x,t)}{\partial x^2} + \int_{a-\epsilon}^{a+\epsilon} dxV(x)\Psi(x,t)\\ &= i\hbar\frac{\partial}{\partial t}\int_{a-\epsilon}^{a+\epsilon} dx\Psi(x,t).\end{aligned} \tag{7.13}$$

The first term gives

$$-\frac{\hbar^2}{2m}\Big(\frac{\partial\Psi(a+\epsilon,t)}{\partial x} - \frac{\partial\Psi(a-\epsilon,t)}{\partial x}\Big). \tag{7.14}$$

We want to consider the limit of $\epsilon \to 0$. In this limit, the above term becomes

$$-\frac{\hbar^2}{2m}\Big(\frac{\partial\Psi(a+0,t)}{\partial x} - \frac{\partial\Psi(a-0,t)}{\partial x}\Big), \tag{7.15}$$

namely, the difference between the right and left derivative at $x = a$. However, the integral of any function $f(x)$, which is finite at $x = a$, that is,

$$\lim_{\epsilon\to 0}\int_{a-\epsilon}^{a+\epsilon} dx f(x) = \lim_{\epsilon\to 0} 2\epsilon f(a) = 0. \tag{7.16}$$

This implies that the right-hand-side of the equation (7.13) vanishes. Furthermore, *if the potential* $V(x)$ *is finite* at $x = a$, the second term of Eq. 7.13 vanishes also. This leads to the conclusion that the difference between left and right derivative, that is, the term given by Eq. 7.15 must be zero also:

$$\frac{\partial\Psi(a+0,t)}{\partial x} = \frac{\partial\Psi(a-0,t)}{\partial x}. \tag{7.17}$$

This conclusion, however, is incorrect if the potential $V(x \to a) \to \infty$. For example, let us consider the case where

$$V(x) = \lambda\delta(x-a). \tag{7.18}$$

Then, the second term in the Eq. 7.13 for any finite ϵ becomes

$$\int_{a-\epsilon}^{a+\epsilon} dx V(x)\Psi(x,t) = \lambda\Psi(a,t). \tag{7.19}$$

Therefore, the entire Eq. 7.13 yields

$$\frac{\partial\Psi(a+0,t)}{\partial x} - \frac{\partial\Psi(a-0,t)}{\partial x} = \frac{2m\lambda\Psi(a,t)}{\hbar^2}, \tag{7.20}$$

which means that the derivative of the wavefunction is not continuous at $x = a$ in this case and the above is a cusp condition on the derivative of $\Psi(x,t)$ at $x = a$.

In a different case where the potential is infinite on the right of $x = a$, then, while $\Psi(a+0,t)$ is zero, because otherwise the expectation value of the potential energy would be infinite. In this case, Eq. 7.13 yields no specific condition on the difference between left and right derivative of the wavefunction at $x = a$.

7.3 Non-negative kinetic energy expectation value

For any state $|\Psi\rangle$, suitable to describe a physical system, the expectation value of the kinetic energy operator is non-negative. Namely,

$$\langle\Psi|\frac{\hat{p}^2}{2m}|\Psi\rangle \geq 0, \qquad \text{for any} \quad |\Psi\rangle. \tag{7.21}$$

To prove this statement is straightforward, if we notice that the norm of any $|\Phi\rangle$ is non-negative, that is,

$$\langle\Phi|\Phi\rangle = \int dx|\Phi(x)|^2 \geq 0. \tag{7.22}$$

We can apply this, using for the state $|\Phi\rangle$ the following state

$$|\Phi\rangle = \hat{p}|\Psi\rangle, \tag{7.23}$$

where, $\hat{p}$ is the momentum operator and $|\Psi\rangle$ is the state of the physical system. Therefore, we conclude that

$$\langle\Psi|\hat{p}^2|\Psi\rangle \geq 0. \tag{7.24}$$

This theorem implies that for any state $|\Psi\rangle$ suitable to describe a physical system, the expectation value of the Hamiltonian

$$\langle\Psi|\hat{H}|\Psi\rangle \geq \langle\Psi|\hat{V}|\Psi\rangle, \tag{7.25}$$

where $\hat{V}$ is the potential energy operator. A *weaker statement* which follows from the above inequality, is that *the energy of the system is bounded from below by the lowest value of the potential energy function.*

7.4 Variational theorem

The variational theorem can be stated in the following way:

The energy eigenvalue equation

$$\hat{H}|\Psi\rangle = E|\Psi\rangle, \tag{7.26}$$

is equivalent to the Euler–Lagrange equation of the following variational problem:

Determine the state $|\Psi\rangle$ which yields zero variation of the expectation value of $\hat{H}$ under the constraint: $\langle\Psi|\Psi\rangle = 1$, namely

$$\frac{\delta}{\delta\langle\Psi|}\Big(\langle\Psi|\hat{H}|\Psi\rangle - \lambda(\langle\Psi|\Psi\rangle - 1)\Big) = 0, \tag{7.27}$$

where λ is a Lagrange multiplier, by means of which we take into consideration the normalization constraint.

The above variational problem leads to the following Euler-Lagrange equation:

$$\hat{H}|\Psi\rangle = \lambda|\Psi\rangle. \tag{7.28}$$

Namely, the Lagrange multiplier plays the role of the energy eigenvalues.

For those readers who are not familiar with functional derivatives, we can prove this by putting the Schrödinger equation on the lattice, as was done in chapter 1.

Using as a basis the states $|n\rangle$ labeled by the lattice sites n, we can write the general state as

$$|\Psi\rangle = \sum_{n=1}^{N} \psi_n|n\rangle. \tag{7.29}$$

The Hamiltonian becomes an $N \times N$ matrix and the eigenvalue equation (7.26) above takes a simple matrix-vector multiplication form:

$$\sum_{m=1}^{N} \langle n|\hat{H}|m\rangle \psi_m = E\psi_n \tag{7.30}$$

which is a system of N equations.

Now, consider the function defined as follows:

$$\begin{aligned} f(\psi_1, \psi_2, ..., \psi_N, \psi_1^*, \psi_2^*, ..., \psi_N^*) &\equiv \langle \Psi|\hat{H}|\Psi\rangle - \lambda(\langle \Psi|\Psi\rangle - 1) \\ = \sum_n \sum_m \psi_n^* \langle n|\hat{H}|m\rangle \psi_m - \lambda(\sum_n \psi_n^* \psi_n - 1). \end{aligned} \tag{7.31}$$

We can treat $\psi_n = u_n + iw_n$ and $\psi_n^* = u_n - iw_n$ as $2N$ independent variables. One might think that the real and imaginary parts of these $2N$ variables are related, however, there the following $2N$ independent variables, u_1, u_2, ..., u_N and w_1, w_2, ..., w_N. We can, therefore, think of going to the $2N$ variables $\psi_n, n = 1, 2, .., N$ and $\psi_n^*, n = 1, 2, .., N$ as a transformation which also yields $2N$ independent variables.

Requiring that the above function f is stationary with respect to variation of any of the ψ_n^* variable, that is,

$$\frac{\partial f(\psi_1, \psi_2, ..., \psi_N, \psi_1^*, \psi_2^*, ..., \psi_N^*)}{\partial \psi_n^*} = 0, \tag{7.32}$$

leads to the following set of N equations

$$\sum_m \langle n|\hat{H}|m\rangle \psi_m = \lambda \psi_n, \tag{7.33}$$

which is the same as Eq. 7.30, with the identification of λ with the energy eigenvalue.

If we choose to make f stationary with respect to variations in ψ_n, we will obtain the N equations which correspond to the complex conjugate of the above equations.

7.5 Practical use of the variational theorem

From the previously derived eigenvalue problem it is straightforward to conclude that given an arbitrary trial state $|\Psi_T\rangle$ which depends a number of parameters, say, $\alpha, \beta, ...$, and which is normalized, that is, $\langle \Psi_T|\Psi_T\rangle = 1$, the expectation value of the Hamiltonian, $E_T \equiv \langle \Psi_T|\hat{H}|\Psi_T\rangle$ yields an upper bound to the ground-state energy for all values of these parameters $\alpha, \beta, ...$.

It is useful to obtain a lowest upper bound to the ground-state energy of a system, because this gives us more information about the ground-state energy. For example, suppose that we want to find out if a system of interacting particles is bound; if, using a suitable ansatz for the ground-state wavefunction we find that $E_T < 0$ (and E_T is measured from the energy of the particles at infinite separation from one another), that is, an upper bound to the ground-state energy of the system is negative, this tells us that the system is necessarily bound.

A detailed example of the applicability of the variational theorem is given next. Consider the case of the harmonic oscillator with the Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}, \tag{7.34}$$

$$\hat{T} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}, \qquad \hat{V} = \frac{1}{2}m\omega^2 x^2, \tag{7.35}$$

and let us take as a trial state the following Gaussian wavefunction:

$$\psi_T(x) = Ce^{-\lambda x^2}, \tag{7.36}$$

After normalization the constant C is given in terms of λ as

$$C = \left(\frac{2\lambda}{\pi}\right)^{\frac{1}{4}}. \tag{7.37}$$

Then, we can easily compute the expectation value of the Hamiltonian with this trial state because it involves Gaussian integrals. First, the potential energy expectation value is given as

$$\langle\hat{V}\rangle \equiv \langle\psi_T|\hat{V}|\psi_T\rangle = \frac{1}{2}m\omega^2\langle\psi_T|x^2|\psi_T\rangle, \tag{7.38}$$

$$\langle x^2\rangle \equiv \langle\psi_T|x^2|\psi_T\rangle = |C|^2\int_{-\infty}^{\infty} dx x^2 e^{-2\lambda x^2} = \frac{1}{4\lambda}, \tag{7.39}$$

$$\langle\hat{V}\rangle = \frac{1}{8}\frac{m\omega^2}{\lambda}. \tag{7.40}$$

Similarly, the expectation value of the kinetic energy operator is given as

$$\langle\hat{T}\rangle \equiv \langle\psi_T|\hat{T}|\psi_T\rangle = \frac{1}{2m}\langle\psi_T|\hat{p}^2|\psi_T\rangle, \tag{7.41}$$

$$\begin{aligned}\langle\hat{p}^2\rangle \equiv \langle\psi_T|\hat{p}^2|\psi_T\rangle &= |C|^2\int_{-\infty}^{\infty} dx e^{-\lambda x^2}\left(-\hbar^2\frac{\partial^2}{\partial x^2}e^{-\lambda x^2}\right)\\ &= \hbar^2\lambda,\end{aligned} \tag{7.42}$$

$$\langle\hat{T}\rangle = \frac{\hbar^2\lambda}{2m}. \tag{7.43}$$

Therefore, the expectation value of the Hamiltonian with the trial state which we considered is given by

$$E_T(\lambda) = \frac{\hbar^2\lambda}{2m} + \frac{1}{8}\frac{m\omega^2}{\lambda}. \tag{7.44}$$

If we minimize the above expectation value with respect to λ, we will find the lowest upper bound to the ground-state energy:

$$\begin{aligned}\frac{\partial E_T(\lambda)}{\partial\lambda}\Big|_{\lambda=\lambda_0} = 0, \quad &\rightarrow \quad \frac{\hbar^2}{2m} - \frac{m\omega^2}{8\lambda_0^2} = 0,\\ &\rightarrow \quad \lambda_0 = \frac{m\omega}{2\hbar}.\end{aligned} \tag{7.45}$$

We have discarded the solution $\lambda_0 < 0$ because it leads to an unphysical, non-normalizable wavefunction. Substituting the "optimal" value of the variational parameter $\lambda = \lambda_0$ in the energy expectation value and the trial wavefunction, we find that

$$E_T(\lambda = \lambda_0) = \frac{1}{2}\hbar\omega, \tag{7.46}$$

$$\psi_T(\lambda = \lambda_0) = \left(\frac{m\omega}{2\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2}. \tag{7.47}$$

As we will find out in chapter 11 this is the exact ground-state energy and wavefunction! Therefore, one of the things that this calculation tells us is that if we can guess the form of the ground-state wavefunction we will obtain the exact parameters.

Notice that there are two "opposing" terms: The kinetic energy increases with increasing λ, while the potential energy decreases with decreasing λ. Fig. 7.3 demonstrates that while these two terms have "opposing tastes," the sum of the two is to be optimized and this yields a "compromise" solution, which is the minimum of the total energy. The reason for the "opposing tastes" of these two terms is simply the following. The potential energy is minimized by having the particle localized at the potential minimum allowing for no quantum fluctuations of the position. Because any fluctuation of position from the minimum will raise the potential energy. However, a localized wavefunction, such as a Gaussian peaked at $x = 0$ with zero standard deviation, leads to an infinite kinetic energy because the kinetic energy operator, that is, the second derivative, measures the curvature of the wavefunction, which is infinite at $x = 0$.

This can be shown also by the fact that the expectation value of the kinetic energy is proportional to the variance of the momentum, that is, $(\Delta p)^2 \equiv \langle \hat{p}^2 \rangle - \langle \hat{p} \rangle^2$ (notice that $\langle \hat{p} \rangle = 0$ here, and take a look at Eq. 7.41), while the expectation value of the potential energy is proportional to the variance of position, that is, $(\Delta x)^2$ (notice that $\langle \hat{x} \rangle = 0$ here, and take a look at Eq. 7.38). These two quantities work against each other because of the uncertainty principle which sets limits of the value of their product. In fact using the results found in this calculation, we find that for the case of the Harmonic oscillator potential:

$$(\Delta p)(\Delta x) = \frac{\hbar}{2}. \tag{7.48}$$

Namely, the Harmonic oscillator attains the minimum possible combined uncertainty.

In general we will not be able to guess the exact form of the wavefunction. So, in what way is this variational principle useful? If we can write down the approximate form of the wavefunction in such a way to correctly describe the important features that the true wavefunction should embrace, we will obtain a closer result to the exact one. For example, let us consider the case where the potential is very repulsive in one region; the form of the wavefunction should be such that it is smaller in that region, and a variational parameter which describes the degree of how small the wavefunction is in that region should be introduced which should be allowed to take its optimal value by the variational approach. Furthermore, this lower value of the wavefunction, in the

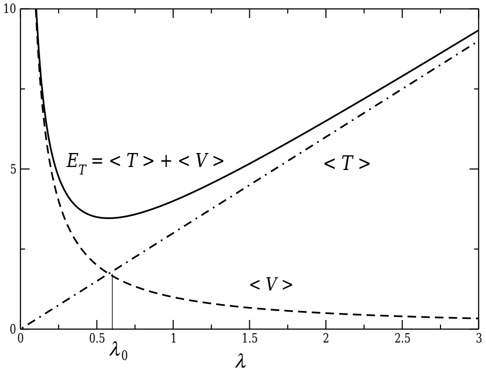

Fig. 7.3

region where the potential is large and positive should not occur two quickly (in space) because the kinetic energy term (which measures the curvature of the wavefunction) is going to grow large. The final best "compromise" is going to be made by the optimizing power of the variational approach.

The variational approach has been used to approximately solve a number of problems in many-body quantum mechanics. It will be used in chapter 26 to derive a mean-field solution to the interacting multi-electron atomic problem, namely the so-called Hartree–Fock approximation.

7.6 Problems

Problem 1

Consider the electron in the hydrogen atom with a Hamiltonian of the form

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r}. \tag{7.49}$$

Consider a trial function of the following form

$$\psi_T(r) = C\exp(-r/\lambda). \tag{7.50}$$

(a) Find the normalization constant in terms of the parameter λ.

(b) Calculate the expectation value of the Hamiltonian using the above trial state.

(c) Minimize the expectation value of the Hamiltonian with respect to λ.

(d) Compare the optimum solution with exact ground-state energy and wavefunction of the hydrogen atom.

Problem 2

Consider the 1D harmonic oscillator with the familiar Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2. \tag{7.51}$$

Now consider the following trial wavefunction for its first excited state.

$$\phi(x) = Ax\exp(-\lambda x^2). \tag{7.52}$$

(a) Find the normalization constant A.

(b) Calculate the expectation value of the kinetic and potential energy.

(c) Minimize the total energy expectation value with respect to the parameter λ.

(d) Compare your answer for the energy and wavefunction to the exact answer of the first excited state of the Harmonic oscillator.

Problem 3

Consider a 1D problem with the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - V_0\delta(x), \tag{7.53}$$

where $V_0 > 0$. We will solve this problem exactly in the following chapter and the ground-state energy is

$$E_0 = -\frac{mV_0^2}{2\hbar^2}, \tag{7.54}$$

with a corresponding wavefunction which can be cast in the form

$$\psi_0(x) = \sqrt{k}\exp(-k|x|), \tag{7.55}$$

$$k = \sqrt{\frac{2m|E_0|}{\hbar^2}}. \tag{7.56}$$

Now, assume that you have not solved the problem exactly and because the potential is attractive at $x = 0$ you want to use a trial wavefunction of the Gaussian form:

$$\psi_T(x) = C\exp(-\lambda x^2), \tag{7.57}$$

which has its peak at $x = 0$.

(a) Determine the constant C for the above to play the role of a trial wavefunction.

(b) Determine the optimum value of λ and the minimum energy.

(c) How does the energy compare with the exact expression above? Is it lower, higher, and why is this so?

8

Bound states in one dimension

In this and in the following chapter, we review an important part of undergraduate material, namely, solving for bound states and for scattering in 1D for the case where the potential is constructed from different constant values in various regions pieced together.

8.1 Square-well potential

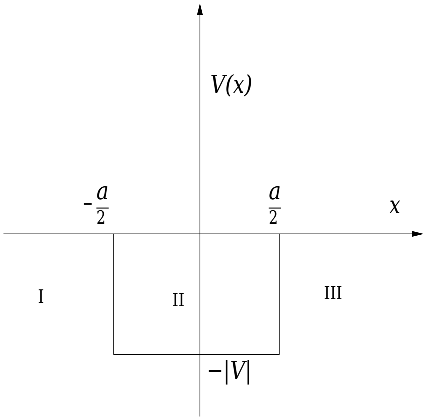

Fig. 8.1

In order to illustrate the general method of solving for bound states in 1D, where the potential is constant in various regions pieced together, we consider the square-well potential shown in Fig. 8.1:

$$V(x) = \left\{ \begin{array}{cc} 0 & x < -\frac{a}{2} \\ -|V| & -\frac{a}{2} \le x \le \frac{a}{2} \\ 0 & x > \frac{a}{2} \end{array} \right\}. \tag{8.1}$$

Since we are considering bound states, that is, states with energy less than the energy of the particle at infinite distance from the potential, we need to take

$$-|V| \le E < 0. \tag{8.2}$$

The lower limit is due to the theorem which we proved in chapter 7 that states that the total energy is greater than the lowest value of the potential.

Practical Quantum Mechanics. First Edition. Efstratios Manousakis.

In this type of problem, we consider each region in which the potential is constant separately. We find the wavefunction in each of these regions, and then we require the wavefunction and its derivative to be continuous at the boundaries (see discussion in chapter 7). In addition, the wavefunction has to behave well at infinity. Namely, it should vanish as $|x| \to \infty$, in order to have a normalizable state.

Region I: The Schrödinger equation in this region is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_I(x)}{dx^2} = E\psi_I(x), \tag{8.3}$$

with general solution

$$\psi_I(x) = A_I e^{kx} + B_I e^{-kx}, \qquad k \equiv \sqrt{\frac{2m|E|}{\hbar^2}}. \tag{8.4}$$

This region includes $-\infty$, therefore the wavefunction $\psi_I(x)$ must vanish as $x \to -\infty$. This requirement forces B_I to be zero, and so the most general wavefunction satisfying this boundary condition is the following:

$$\psi_I(x) = A_I e^{kx}. \tag{8.5}$$

Region II: The Schrödinger equation in this region is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_{II}(x)}{dx^2} = (E + |V|)\psi_{II}(x), \tag{8.6}$$

where, because of the constraint (8.2) on the energy, $E + |V| \geq 0$ and, thus, its general solution can be written as

$$\psi_{II}(x) = A_{II}\cos(k'x) + B_{II}\sin(k'x),\ k' \equiv \sqrt{\frac{2m(E+|V|)}{\hbar^2}}. \tag{8.7}$$

If we take into consideration the symmetry of the Hamiltonian, that under the parity transformation $x \to -x$ the Hamiltonian remains invariant, we can use the technique discussed in chapter 7 of looking for simultaneous eigenstates of the Hamiltonian and the parity operator. In this case we will write the solution in Region II as

$$\psi_{II}(x) = \left\{ \begin{array}{ll} A_e \cos(k'x) & \text{even} \\ A_o \sin(k'x) & \text{odd} \end{array} \right\}.$$

This approach, at the technical level, simplifies our life a little. It does not mean that we have to follow this approach. The problem can be solved (with some additional pain) using the wavefunction given by Eq. 8.7. When there is a symmetry of the Hamiltonian, it is always to our computational advantage to take it into consideration. When I was grading exams and in homework problems, I noticed that students were making the following common mistake. Imagine that we shift the origin such that the potential is not centered at $x = 0$ but we take:

$$V(x) = \left\{ \begin{array}{cc} 0 & x < 0 \\ -|V| & 0 \leq x \leq a \\ 0 & x > a \end{array} \right\}. \tag{8.8}$$

In this case, one does not have the right to separate even and odd states with respect to $x = 0$. Still, there is a "reflection" symmetry of the Hamiltonian, but it is with respect to the new center of the potential, that is, $x_0 = a/2$; namely, the potential remains invariant under the transformation: $x \to a - x$. Therefore, if one wants to take this symmetry into account, one should separate the solutions into $A_e \cos(k'(x - a/2))$ ("even") and $A_o \sin(k'(x - a/2))$ ("odd").

Region III. In this region, the form of the Schrödinger equation is the same as in Region I. Therefore, we write the general solution in Region II as follows:

$$\psi_{III}(x) = A_{III} e^{kx} + B_{III} e^{-kx}, \tag{8.9}$$

where k is the same as in Region I. Now, this region includes $+\infty$, therefore, $A_{III} = 0$, and so the most general wavefunction satisfying this boundary condition is the following:

$$\psi_{III}(x) = B_{III} e^{-kx}. \tag{8.10}$$

Now, since we are considering the even and odd functions separately because of the symmetry of the potential, we must have that

$$\begin{aligned} B_{III} &= A_I, \quad \text{even}, \\ B_{III} &= -A_I, \quad \text{odd}. \end{aligned} \tag{8.11}$$

These relations simplify the algebraic problem significantly. However, remember: if the origin of the potential is shifted, as discussed previously (Eq. 8.8), then one has to keep both terms in Eq. 8.4 and in Eq. 8.9 and then impose the condition that the even should map to each other and the odd should have opposite sign with respect to the transformation $x \to a - x$, such that they can be even or odd with respect to the new center.

Now, we need to apply the boundary conditions for the continuity of the wavefunction and its derivative at $x = -a/2$. For the case of the even functions we find:

$$\psi_I(-\frac{a}{2}) = \psi_{II}(-\frac{a}{2}), \to \ A_I e^{-ka/2} = A_e \cos(k'a/2), \tag{8.12}$$

$$\psi'_I(-\frac{a}{2}) = \psi'_{II}(-\frac{a}{2}), \to \ A_I k e^{-ka/2} = A_e k' \sin(k'a/2). \tag{8.13}$$

Since we have separated the solutions into subspaces of even and odd, the boundary condition at $x = a/2$ does not yield additional information. If we decide to solve the problem without taking this symmetry into account, then we need to start from Eq. 8.7 and without the constraints given by Eqs. 8.11. In this case we have two more unknowns; however, the boundary condition at $x = -a/2$ provides two additional equations.

Now, by dividing Eq. 8.12 and Eq. 8.13 we find that

$$k = k' \tan(k'a/2). \tag{8.14}$$

Similarly for the odd case we obtain:

$$k = -k' \cot(k'a/2). \tag{8.15}$$

These equations can be solved graphically. Let us consider the even case for illustration. It is convenient to change variables and rewrite Eq. 8.14 as follows:

$$\tan(x) = f(x), \qquad f(x) \equiv \sqrt{\left(\frac{x_0}{x}\right)^2 - 1}, \tag{8.16}$$

$$x = \frac{k'a}{2} = \sqrt{\frac{m(E+|V|)a^2}{2\hbar^2}}, \qquad x_0 = \sqrt{\frac{m|V|a^2}{2\hbar^2}}. \tag{8.17}$$

As illustrated in Fig. 8.2, in order for a solution to exist, the two curves, that is, the $\tan(x)$ and the monotonically decreasing function $f(x)$, should intersect at a value of $x < x_0$ because $f(x)$ turns into an imaginary number for $x > x_0$.

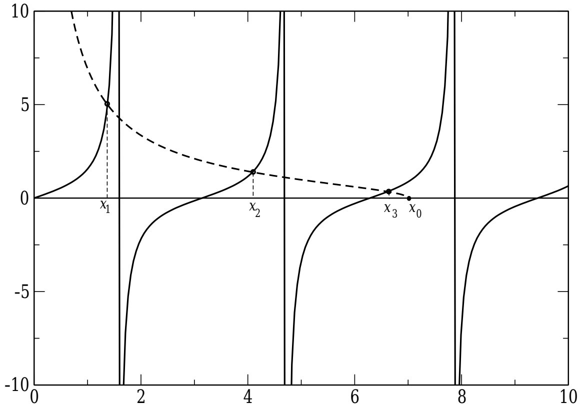

Fig. 8.2 The red lines are some of the infinite number of branches of the $\tan(x)$ function. The blue line is the function $f(x)$. The intersections of these two curves are the solutions to Eq. 8.16. Notice that for the chosen value of $x_0 = 7$, there are three solutions depicted as x_1, x_2, and x_3 in the graph.

Therefore, for a given value of x_0 there is a limited number $n_{max} = [\frac{x_0}{\pi}] + 1$ (here, $[z]$ stands for the integer part of z) of possible solutions and if $x_0 < \pi$, there is just a single bound state. Let us examine what happens in the opposite limit, that is, when $x_0 >> 1$, or when

$$|V| >> \frac{2\hbar^2}{ma^2}. \tag{8.18}$$

When $x_0 >> 1$, there are many solutions for x such that $f(x) \simeq x_0/x$. When $x_0/x \to \infty$ we have that $\tan(x) \to \infty$ and so, $x \to \pi/2$. In this case we can write $x = \pi/2 - \delta$ where $\delta << 1$ and, thus, $\tan(x) \sim \cot(\delta) = 1/\tan\delta \sim 1/\delta$. Therefore, Eq. 8.16 becomes

$$\frac{1}{\delta} \sim \frac{x_0}{x} = \frac{x_0}{\pi/2 - \delta} \quad \to \quad \delta \sim \frac{\pi}{2x_0} \quad \to \quad x \simeq \frac{\pi}{2}(1 - \frac{1}{x_0}). \tag{8.19}$$

Using Eq. 8.17, this leads to the following value of k' and energy eigenvalues:

$$k \simeq \frac{\pi}{a}(1 - \frac{1}{x_0}), \tag{8.20}$$

$$E_n + |V| = \frac{\hbar^2\pi^2}{2ma^2}(1 - \frac{1}{x_0^2}), \tag{8.21}$$

which is the result for the infinite square-well potential plus a correction due to finite $|V|$.

8.2 Delta function potential

Here we consider the case of an attractive delta function potential of the form

$$V(x) = -V_0\delta(x), \tag{8.22}$$

where $V_0 > 0$, as illustrated in Fig. 8.3, and we are interested to find bound states with $E < 0$.

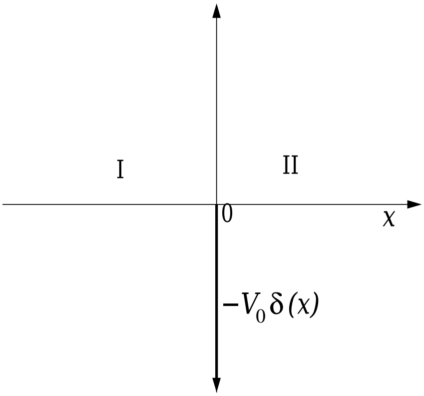

Fig. 8.3

To solve this problem, we also separate the space into Regions I and II as shown in Fig. 8.3.

In Region I where the Schrödinger equation has $V(x) = 0$ and $E < 0$, the wavefunction can be written as

$$\psi_I(x) = A_I e^{kx}, \tag{8.23}$$

$$k = \sqrt{\frac{2m|E|}{\hbar^2}}. \tag{8.24}$$

As in the square-well potential which is our previous problem, we have excluded the term proportional to e^{-kx} because it does not behave well in the $x \to -\infty$ limit.

Similarly in Region II the wavefunction can be written as

$$\psi_{II}(x) = A_{II} e^{-kx}, \tag{8.25}$$

and the k is the same as in Region I.

Boundary conditions at $x = 0$.

a) The wavefunction must be continuous

$$\psi_I(0) = \psi_{II}(0) \qquad \rightarrow \qquad A_I = A_{II}. \tag{8.26}$$

b) The cusp condition on the derivative of the wavefunction. As we discussed in chapter 7, if we integrate both sides of Schrödinger's equation from $-\epsilon$ to ϵ and we let $\epsilon \rightarrow 0$, we find the cusp condition (7.20) on the derivative of the wavefunction which in our case reads:

$$\frac{\partial \psi_{II}(+0)}{\partial x} - \frac{\partial \psi_I(-0)}{\partial x} = -\frac{2mV_0\psi_I(0)}{\hbar^2}. \tag{8.27}$$

On the left-hand-side we need the function at $x = 0$; since we have imposed the continuity condition $\psi_I(0)$ and $\psi_{II}(0)$ are equal and, thus, it does not matter whether we choose $\psi_I(0)$ or $\psi_{II}(0)$ in the above equation.

Combining Eq. 8.26 with Eq. 8.27 we find

$$k = \frac{m|V_0|}{\hbar^2} \qquad \rightarrow \qquad E = -\frac{mV_0^2}{2\hbar^2}. \tag{8.28}$$

Notice that the minus sign was added by hand because the first equation involving k yields only the magnitude of E through Eq. 8.24.

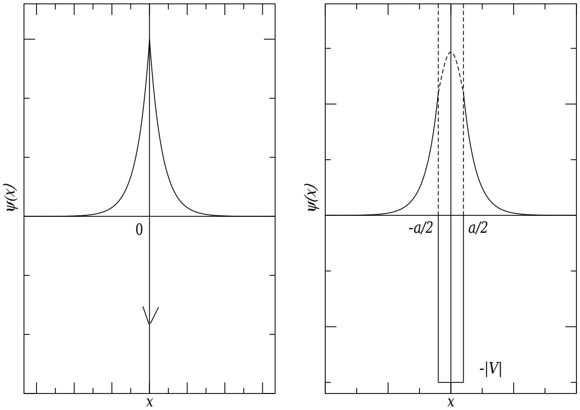

Fig. 8.4

Notice that there is a single bound state. In addition, notice that this is an even function due to the continuity of the wavefunction at $x = 0$ and the fact that $A_I = A_{II} \neq 0$, otherwise the wavefunction would vanish everywhere.

We can compare the results for the square-well potential with the results of the delta function potential in the case where we consider the limit of $a \to 0$. We need to take the limit $a \to 0$ in such a way that we keep the product $|V|a = |V_0|$ a constant. As a result in this limit the square-well potential becomes the delta function potential given by Eq. 8.22.

In this limit the square-well potential ground-state energy is obtained as follows. First in the limit of $a \to 0$, $V = \lim_{a\to 0} V_0/a \to \infty$ and, thus, the equation for k' yields

$$k'a/2 \to \sqrt{\frac{m|V_0|a}{2\hbar^2}}, \tag{8.29}$$

which, by holding V_0 to be a constant, becomes infinitesimal in the limit of $a \to 0$. Thus, $\tan(k'a/2) \to k'a/2$ and the eigenvalue equation for even eigenfunctions reduces to

$$\sqrt{\frac{2m|E|}{\hbar^2}} = \sqrt{\frac{2m|V_0|}{\hbar^2 a}}\sqrt{\frac{m|V_0|a}{2\hbar^2}}, \quad \to \quad |E| = \frac{m|V_0|}{2\hbar^2}. \tag{8.30}$$

which is the same result obtained for the delta function.

From the normalization condition on the wavefunction we find that

$$2|A_{I,II}|^2 \int_0^\infty e^{-2kx}dx = 1 \quad \to \quad A_{I,II} = \sqrt{k}. \tag{8.31}$$

The wavefunction is plotted in Fig. 8.4 along with the ground state of the square-well potential for comparison. On the left, the wavefunction of the delta function potential is schematically drawn. Notice that the wavefunction is a decaying exponential on both sides, positive and negative, of the x-axis with a cusp at $x = 0$. On the right part of Fig. 8.4 the wavefunction of the square-well potential is also schematically plotted. Notice that it is also a decaying exponential outside the region of the attractive potential, while in the region of the attractive potential the ground state is the even function $\cos(k'x)$, with $k'a \to 0$, which matches the decaying functions at the $x = \pm a/2$ boundaries as shown schematically in Fig. 8.4. Thus, for any finite a, there is no discontinuity of the derivative of the wavefunction.

8.3 Problems

Problem 1

Consider a particle in the 1D potential given by

$$V(x) = \left\{ \begin{array}{cc} \infty & x \le 0 \\ 0 & 0 < x < a \\ V & x > a \end{array} \right\}, \tag{8.32}$$

which is illustrated in Fig. 8.5. In the limit of $V \to \infty$ the ground-state wavefunction of this potential is given by

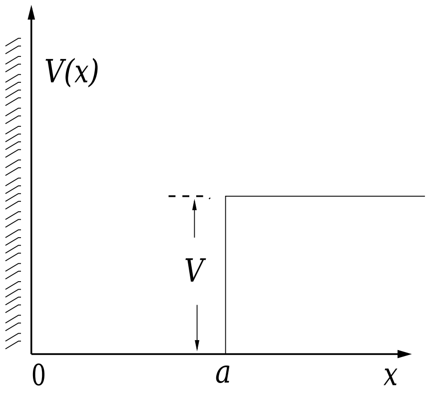

Fig. 8.5

$$\psi_0(x) = \sqrt{\frac{2}{a}}\sin(k_0 x), \tag{8.33}$$

$$k_0 = \frac{\pi}{a}, \tag{8.34}$$

and the ground-state energy is

$$E_0 = \frac{\hbar^2 k_0^2}{2m}. \tag{8.35}$$

a) Find the equation for the energy E of bound states in this potential.

b) Provide a schematic graphical solution for the energy eigenvalues which correspond to bound states.

c) Based on your understanding gained from the above schematic graphical solution, argue that in the limit of very large potential step V, that is, when $E/V \to 0$, the wave-number $k = \sqrt{2mE}/\hbar$ which corresponds to the ground state is close to π/a (the case of $V \to \infty$) and more specifically,

$$ka \simeq \pi - \epsilon, \tag{8.36}$$

and $\epsilon \to 0^+$ as $V \to \infty$. What is the leading term of ϵ in the large V limit?

d) Determine the ground-state wavefunction, inside the classically forbidden region, that is, when $E < V$, including the normalization constants, in the leading order of $\frac{1}{\lambda_0}$, where $\lambda_0 = \sqrt{2mV}a/\hbar$.

Problem 2

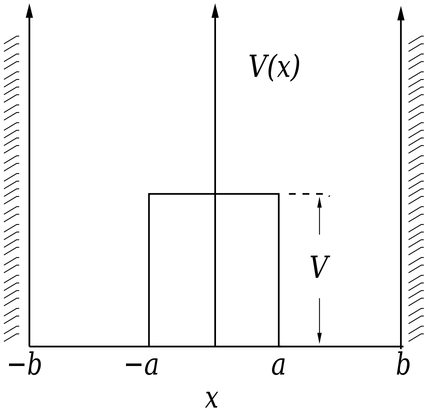

Fig. 8.6

Consider a particle in the 1D potential given as

$$V(x) = \left\{ \begin{array}{ll} \infty & |x| > b \\ V & |x| < a \\ 0 & a < |x| < b \end{array} \right\}, \tag{8.37}$$

which is illustrated in Fig. 8.6. We would like to study the large V limit of this potential. In the infinite V limit, the problem reduces to that of two infinite square-well potentials separated by a distance $2a$. However, for a finite but very large V, (that is, V is much larger than the energy E of the ground state), the tunneling rate between the two zero-potential sides of the well is small and the particle can be thought of as being in one of nearly two degenerate ground states $|1\rangle$ and $|2\rangle$, corresponding to being localized in the left or in the right well, respectively, each with energy $E_0 = \hbar^2 k_0^2/(2m)$ (where $k_0 = \pi/(b-a)$, in this case).

a) When V is finite but large compared to E_0, find the wavefunctions of the two states $|1\rangle$ and $|2\rangle$ in the leading order in E/V, by applying the findings of the previous problem.

b) Having found the two localized states $|1\rangle$ and $|2\rangle$ in leading order in E/V, consider these two states as the only states spanning the space of your problem. In such a case you can write the Hamiltonian $\hat{H}$ of your system

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x), \tag{8.38}$$

in the basis of these two states, as a 2×2 matrix

$$\begin{pmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{pmatrix}, \tag{8.39}$$

where the matrix elements h_{ij} are the matrix elements

$$h_{ij} = \int dx \psi_i^*(x) \hat{H} \psi_j(x), \tag{8.40}$$

between the wavefunction $\psi_i(x)$ corresponding to the states $|1\rangle$ and $|2\rangle$ which you found above.
Calculate the above 2×2 matrix. Make sure that the wavefunctions $\psi_1(x)$ and $\psi_2(x)$ are centered around the correct part of space within the potential well.

c) Diagonalize the above matrix and find the eigenstates and eigenvalues. What is the energy difference between the two energy eigenvalues.

d) Assume that the particle is in state $|1\rangle$ at time $t = 0$. What is the probability for a particle to tunnel from state $|1\rangle$ to state $|2\rangle$ at a later time t?

Problem 3

Now consider the potential shown in Fig. 8.7, that is,

$$V(x) = \begin{Bmatrix} -V \ 0 \leq |x| < b \\ 0 \quad b \leq |x| < a \\ \infty, \quad\ |x| \geq a \end{Bmatrix} \tag{8.41}$$

where $V > 0$.

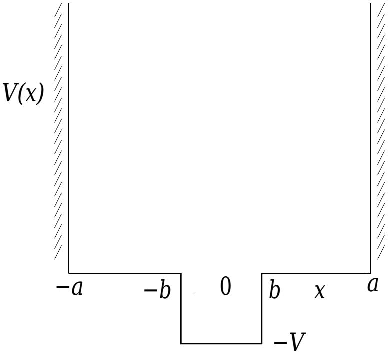

Fig. 8.7

a) Find the equation that determines the negative energy eigenvalues.

b) Provide a graphical solution for the energy eigenvalues.

Problem 4

A particle of mass m is under the influence of a 1D potential of the form

$$V(x) = V\Big(\delta(x-a) + \delta(x+a)\Big), \tag{8.42}$$

where $V < 0$.

a) What is the wavefunction for a bound state with an even parity?
b) Find the expression that determines the bound-state energies for even parity states, and determine graphically how many even parity bound states there are.
c) Solve for the even parity bound state analytically in the case where $m|V|a/\hbar^2 << 1$.
d) Repeat parts (a) and (b) for odd parity. For what values of $|V|$ are there bound states?
e) Find the even and odd parity state binding energies for $a >> \hbar^2/m|V|$. Explain physically why these energies move closer and closer together as $a \to \infty$.

Problem 5

A particle of mass m is under the influence of a 1D potential shown in Fig. 8.8, that is, of the form

$$V(x) = \left\{ \begin{array}{cc} -V\delta(x) & 0 \leq |x| < a \\ \infty, & |x| \geq a \end{array} \right\} \tag{8.43}$$

where $V > 0$. More simply the particle is in an infinite square well with a delta function at the center of the well.

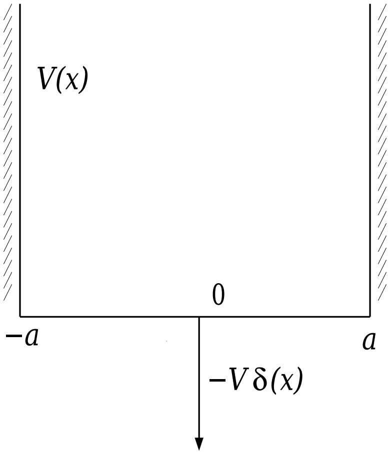

Fig. 8.8

a) Find the equation that determines the negative energy eigenvalues.

b) Provide a graphical solution for the energy eigenvalues.

c) In the large a limit, that is, when $\epsilon = \hbar^2/(mVa) << 1$ show that the ground-state energy is given by

$$E = -\frac{\hbar^2 k_0^2}{2m}, \tag{8.44}$$

where k_0 to first order in ϵ can be approximated by

$$k_0 \simeq \frac{1}{a\epsilon}, \tag{8.45}$$

Namely,

$$E = -\frac{mV^2}{2\hbar^2}. \tag{8.46}$$

Problem 6

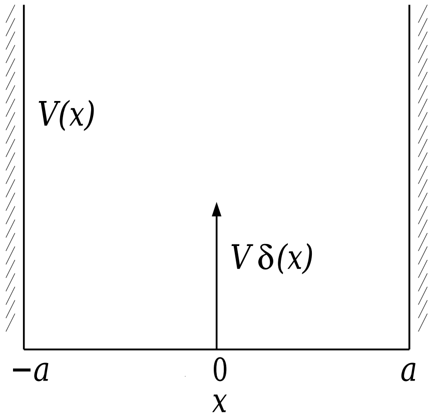

Fig. 8.9

A particle of mass m is under the influence of a 1D potential shown in Fig. 8.9, that is, of the form

$$V(x) = \left\{ \begin{array}{cc} V\delta(x) & 0 \leq |x| < a \\ \infty, & |x| \geq a \end{array} \right\} \tag{8.47}$$

where $V > 0$. More simply the particle is in an infinite square well with a delta function at the center of the well.

a) What should be the sign of the energy eigenvalues in this case where $V > 0$? Find the equation that determines the energy eigenvalues.

b) Provide a graphical solution for the energy eigenvalues.

c) In the limit of a very weak delta function potential, that is, when $\epsilon = 2mVa/(\pi\hbar^2) << 1$ show that the ground-state energy is given by

$$E = \frac{\hbar^2 k_0^2}{2m}, \tag{8.48}$$

where k_0 to first order in ϵ can be approximated by

$$k_0 a \simeq \frac{\pi}{2} + \epsilon. \tag{8.49}$$

d) Provide a schematic drawing of the ground-state wavefunction. Explain how it behaves near $x = 0$.

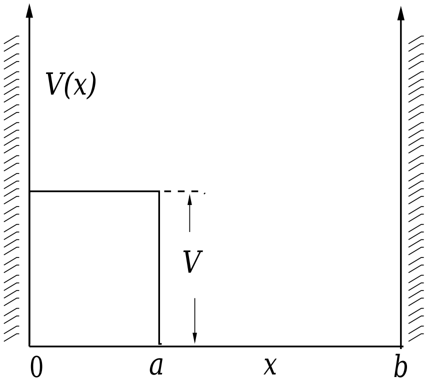

Fig. 8.10

Problem 7

A particle of mass m is under the influence of a 1D potential of the form (see also Fig. 8.10)

$$V(x) = \left\{ \begin{array}{ll} \infty & x < 0 \\ V & 0 \le x < a \\ 0, & a < x < b \\ \infty & x > b \end{array} \right\} \tag{8.50}$$

where $V > 0$.

a) Find the equations that determine the energy eigenvalues for the case where $0 < E < V$.

b) Find the equations that determine the energy eigenvalues for the case where $E > V$.

c) Consider the limit $V \to 0$ in both case a) and case b) above. Which one of the two cases leads to a possible solution which is the same as the solution for the energy eigenvalues as the infinite square-well potential of size b (that is, the same as in Fig. 8.10 with $V = 0$)? Explain why only one of the two leads to the correct limit.

9

Scattering in one dimension

In this chapter we investigate the case of scattering in 1D. First, we consider simple examples; we analyze the case of tunnelling, and the analytic structure of the scattering amplitude. We also discuss the concept of a resonance.

9.1 Step barrier potential

Consider an incident particle represented by a plane wave in Region I which scatters against the potential shown in Fig. 9.1. In what follows we are considering the case where $E > 0$. However, we have two separate cases to consider: 1) $E < V$ and 2) $E > V$, where V is the size of the energy barrier.

As in the case of bound states, our strategy starts with separating the regions where the potential remains constant.

a) First, we consider the case where $E < V$.

In Region I, the wavefunction is written as

$$\psi_I(x) = A_I e^{ikx} + B_I e^{-ikx}, \qquad k = \sqrt{\frac{2mE}{\hbar^2}}. \tag{9.1}$$

We keep both coefficients A_I and B_I different from zero and the interpretation of the e^{-ikx} term is that it represents a reflected wave.

In Region II, the Schrödinger equation takes the form

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_{II}(x)}{dx^2} = (E - V)\psi_{II}(x), \qquad E - V < 0, \tag{9.2}$$

which has a solution of the form:

$$\psi_{II}(x) = A_{II} e^{-k'x}, \tag{9.3}$$

$$k' = \sqrt{\frac{2m(V - E)}{\hbar^2}}. \tag{9.4}$$

The other solution $e^{k'x}$ is excluded because it diverges as $x \to +\infty$.

Boundary conditions at $x = 0$: The wavefunction and its derivative must be continuous:

$$\psi_I(0) = \psi_{II}(0) \;\to\; A_I + B_I = A_{II}, \tag{9.5}$$

$$\psi'_I(0) = \psi'_{II}(0) \;\to\; ik(A_I - B_I) = -k'A_{II}. \tag{9.6}$$

Practical Quantum Mechanics. First Edition. Efstratios Manousakis.

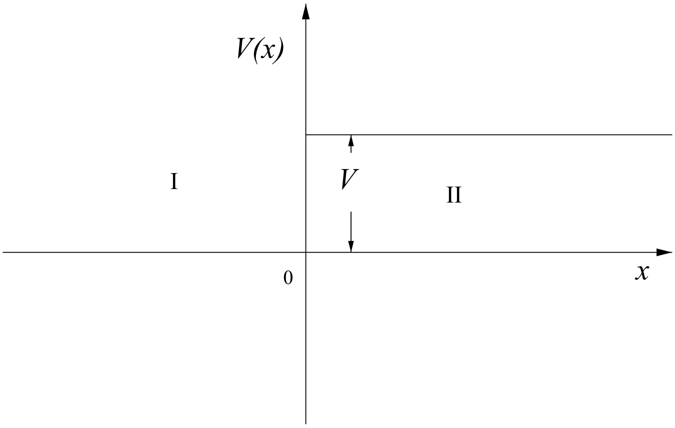

Fig. 9.1

Here, we are only interested in finding the ratio of the coefficients as opposed to the coefficients themselves. From the above two equations we find that

$$\frac{A_{II}}{A_I} = \frac{2ik}{ik - k'}. \tag{9.7}$$

The Barrier penetration probability is given by

$$P = \int_0^\infty dx|\psi_{II}(x)|^2 = |A_{II}|^2 \int_0^\infty e^{-2k'x} = |A_{II}|^2 \frac{1}{2k'}. \tag{9.8}$$

We can measure the total penetration probability relative to the incident flux of particles. The probability current density of the incident particles can be calculated using the expression (7.10) and is given by

$$J_0 = \frac{\hbar k}{m}|A_I|^2. \tag{9.9}$$

Therefore, the penetration probability relative to the incident particle flux is proportional to

$$\frac{P}{J_0} = \frac{m}{2\hbar k k'} \frac{|A_{II}|^2}{|A_I|^2} = \frac{\hbar k}{V} \frac{\hbar}{\sqrt{2m(V-E)}}. \tag{9.10}$$

This is proportional to the scattering cross-section using the analysis discussed in chapter 19. In 1D the reflected wave (scattering angle $\theta = 180^\circ$) and the transmitted (scattering angle $\theta = 0^\circ$) waves are parts of the scattered wave using the scattering geometry which corresponds to the 3D case. Notice that the relative penetration probability diverges as $E \to V^-$.

Now, let us examine the wavefunction in the classically forbidden region. It decays exponentially from the point of entrance in the classically forbidden region ($x = 0$) within a characteristic length λ given by

$$\lambda = \frac{1}{k'} = \frac{\hbar}{\sqrt{2m(V-E)}}. \tag{9.11}$$

Notice again that as $E \to V-$, the penetration depth $\lambda \to \infty$.

Is the conservation of energy violated in this case? How do I reconcile this with the uncertainty principle?

b) Let us now examine the case where $E > V$.

Region I: the wavefunction in this region is the same as in the previous case where $E < V$, that is, it is given by Eq. 9.1.

Region II: In this case the Schrödinger equation is given by Eq. 9.2, with the difference that $E - V > 0$ and thus

$$\psi_{II}(x) = \tilde{A}_{II} e^{i\tilde{k}x} + \tilde{B}_{II} e^{-i\tilde{k}x}, \qquad \tilde{k} = \sqrt{\frac{2m(E-V)}{\hbar^2}}. \tag{9.12}$$

However, we need to set $B_{II} = 0$ because we do not have a wave coming from $+\infty$.

Application of boundary conditions at $x = 0$ yields:

$$A_I + B_I = A_{II}, \tag{9.13}$$

$$ik(A_I - B_I) = i\tilde{k} A_{II}. \tag{9.14}$$

Therefore, in this case we can define the transmission amplitude ratio as:

$$T = \frac{A_{II}}{A_I} = \frac{2k}{k+\tilde{k}}, \tag{9.15}$$

and the reflection amplitude ratio as:

$$R = \frac{B_I}{A_I} = \frac{k-\tilde{k}}{k+\tilde{k}}. \tag{9.16}$$

9.2 Tunneling

Here, we wish to study tunneling of an incident particle, represented by a plane wave, through the square barrier shown in Fig. 9.2. We consider the case where the energy E of the incident particle is less than the height V of the barrier.

In Region I, the solution to the Schrödinger equation is the same as in Region I of the previous problem, which is given by Eq. 9.1.

In Region II, the energy E is less than V, therefore the solution can be written as

$$\psi_{II}(x) = A_{II} e^{-k'x} + B_{II} e^{k'x}, \qquad k' = \sqrt{\frac{2m(V-E)}{\hbar^2}}. \tag{9.17}$$

In this region, in general we keep both solutions because neither $+\infty$ nor $-\infty$ is included in the region.

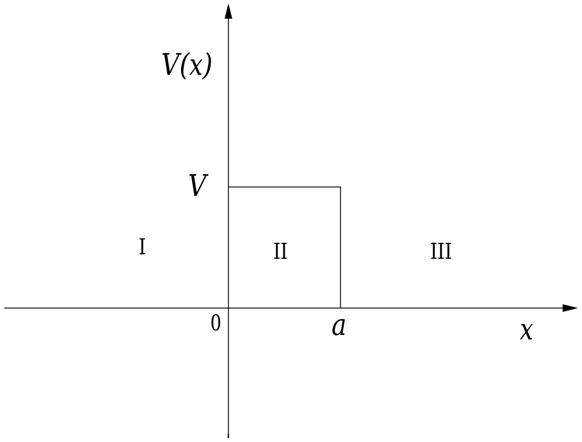

Fig. 9.2

In Region III, the acceptable solution is of the form

$$\psi_{III}(x) = A_{III} e^{ikx}, \tag{9.18}$$

because by our initial condition there is no particle coming from $+\infty$.

Notice that the origin of our axis could be shifted to make this potential symmetric under parity transformation. In this case, however, while parity is a symmetry of the Hamiltonian, our initial conditions are such that it breaks this symmetry of the parity. Namely, the particle comes from $-\infty$ and "part of it" goes through the barrier traveling to the positive direction of our axis. As a result the symmetry of the Hamiltonian under the parity transformation is not useful in this case.

Let us now apply the boundary conditions at $x = 0$:

$$\psi_I(0) = \psi_{II}(0) \to A_I + B_I = A_{II} + B_{II}, \tag{9.19}$$

$$\psi'_I(0) = \psi'_{II}(0) \to ik(A_I - B_I) = k'(-A_{II} + B_{II}). \tag{9.20}$$

Furthermore, application of the boundary conditions at $x = a$ yields:

$$\psi_{II}(a) = \psi_{III}(a) \to A_{II} e^{-k'a} + B_{II} e^{k'a} = A_{III} e^{ika}, \tag{9.21}$$

$$\begin{aligned} \psi'_{II}(a) = \psi'_{III}(a) \to & -k'(A_{II} e^{-k'a} - B_{II} e^{k'a}) \\ & = ikA_{III} e^{ika}. \end{aligned} \tag{9.22}$$

We can solve the system of Eq. 9.21 and Eq. 9.22 for A_{II} and B_{II} in terms of A_{III} to find that

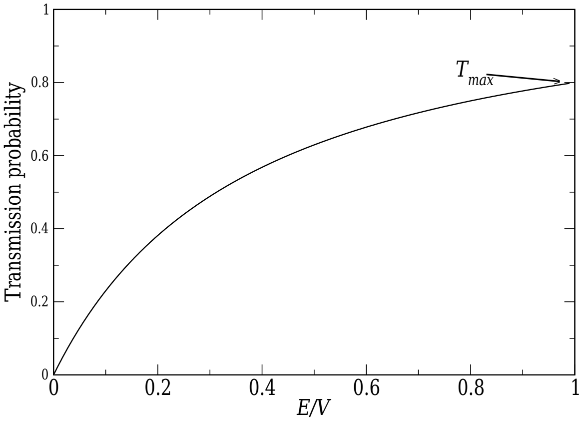

Fig. 9.3

$$A_{II} = \frac{k' - ik}{2k'} e^{(ik+k')a} A_{III}, \tag{9.23}$$

$$B_{II} = \frac{k' + ik}{2k'} e^{(ik-k')a} A_{III}. \tag{9.24}$$

We can solve the system of Eq. 9.19 and Eq. 9.20 for A_I considering A_{II} and B_{II} as knowns to find that

$$A_I = \frac{ik - k'}{2ik} A_{II} + \frac{ik + k'}{2ik} B_{II}. \tag{9.25}$$

Therefore, using the above and Eqs. 9.23 and 9.24 we find that

$$\frac{A_I}{A_{III}} = -ie^{ika}\Big[\frac{k^2 - k'^2}{2kk'}\sinh(k'a) + i\cosh(k'a)\Big]. \tag{9.26}$$

The relative transmission probability is given by

$$T = \Big|\frac{A_{III}}{A_I}\Big|^2 = \frac{1}{1 + \frac{V^2}{4E(V-E)\sinh^2(k'a)}}. \tag{9.27}$$

In Fig. 9.3 $T(E/V)$ is illustrated. Notice that as $E \to V^-$ the transmission probability is finite and given by

$$T(E \to V^-) = T_{max} = \frac{1}{1 + \frac{mVa^2}{2\hbar^2}}. \tag{9.28}$$

9.3 Attractive square-well potential

We consider scattering of a particle with energy $E > 0$ from the potential well shown in Fig. 9.4.

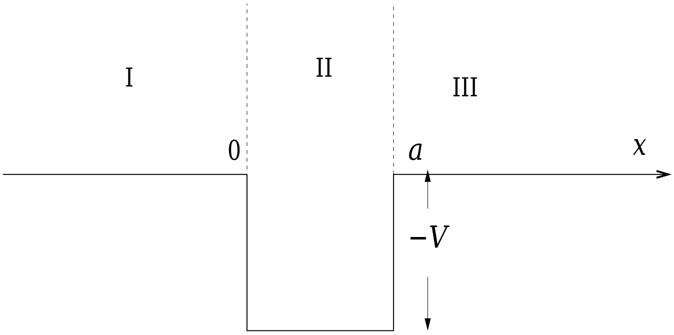

Fig. 9.4

As usual, we separate in regions where the potential is a constant; in the present case we need to consider the three regions indicated in Fig. 9.4 as I, II, and III where the wavefunction is given as follows:

$$\Psi_I(x) = A_I e^{ikx} + B_I e^{-ikx},\, k = \sqrt{\frac{2mE}{\hbar^2}}, \tag{9.29}$$

$$\Psi_{II}(x) = A_{II} e^{ik'x} + B_{II} e^{-ik'x}, \tag{9.30}$$

$$k' = \sqrt{\frac{2m(E+V)}{\hbar^2}}, \tag{9.31}$$

$$\Psi_{III}(x) = A_{III} e^{ikx}. \tag{9.32}$$

Notice that we have not centered the potential at $x = 0$ in order to make it symmetric under the transformation $x \to -x$. The reason is that this symmetry is not useful because the wavefunction of the incident and transmitted wave breaks this symmetry. We have assumed that there is an incident particle from the left of the square well, part of it is reflected back and part of it is transmitted through the well. As part of the statement of the problem, we have assumed that there is no wave coming from the right of the well, thus, our imposed condition on the wavefunction breaks the inversion symmetry which we took advantage of in chapter 8.

Next, we apply the boundary conditions of the continuity of the wavefunction and its derivative at $x = 0$ and $x = a$:

$$\Psi_I(0) = \Psi_{II}(0) \to\ A_I + B_I = A_{II} + B_{II}, \tag{9.33}$$

$$\Psi'_I(0) = \Psi'_{II}(0) \to\ kA_I - kB_I = k'A_{II} - k'B_{II}, \tag{9.34}$$

$$\begin{aligned}\Psi_{II}(a) = \Psi_{III}(a) \to\ & A_{II}e^{ik'a} + B_{II}e^{-ik'a} \\ &= A_{III}e^{ika},\end{aligned} \tag{9.35}$$

$$\begin{aligned}\Psi'_{II}(a) = \Psi'_{III}(a) \to\ & k'A_{II}e^{ik'a} - k'B_{II}e^{-ik'a} \\ &= kA_{III}e^{ika}.\end{aligned} \tag{9.36}$$

The system of the last two equations, that is, Eq. 9.35 and Eq. 9.36, can be solved to find A_{II} and B_{II} in terms of A_{III}:

$$A_{II} = \frac{1}{2}(1 + \frac{k}{k'})e^{i(k-k')a}A_{III}, \tag{9.37}$$

$$B_{II} = \frac{1}{2}(1 - \frac{k}{k'})e^{i(k+k')a}A_{III}. \tag{9.38}$$

Similarly from Eq. 9.33 and Eq. 9.34 we obtain:

$$A_I = \frac{1}{2}(1 + \frac{k'}{k})A_{II} + \frac{1}{2}(1 - \frac{k'}{k})B_{II} \tag{9.39}$$

$$B_I = \frac{1}{2}(1 - \frac{k}{k'})A_{II} + \frac{1}{2}(1 + \frac{k}{k'})B_{II}. \tag{9.40}$$

By substituting the expressions found for A_{II} and B_{II} in the above equations, we obtain:

$$\begin{aligned}\frac{A_I}{A_{III}} &= \frac{1}{4}\Big[(1 + \frac{k'}{k})(1 + \frac{k}{k'})e^{i(k-k')a} \\ &\quad + (1 - \frac{k}{k'})(1 - \frac{k'}{k})e^{i(k+k')a}\Big].\end{aligned} \tag{9.41}$$

The ratio of the amplitudes of the transmitted wave to the incident wave is given by expression

$$S(E) \equiv \frac{A_{III}}{A_I} = \frac{e^{-ika}}{\cos(k'a) - \frac{i}{2}(\frac{k'}{k} + \frac{k}{k'})\sin(k'a)}. \tag{9.42}$$

9.4 Poles of $S(E)$

In several diverse areas of physics we carry out scattering experiments to find out information about the properties of the target, such as in the case of scattering from a static 1D square-well potential, we can find information about the shape and bound states of the potential. The particles which are scattered by the target have positive energy, that is, they are unbound, thus they provide direct information about the scattering cross section for $E > 0$. Bound states in any attractive potential correspond to a state of the particle with negative energy relative to its energy at infinite distance from the potential. Is it possible to use the information obtained from the transmission probability $T(E)$ for $E > 0$ to characterize the region of $E < 0$ where there may be bound states?

It turns out that the analytic structure of $S(E)$ contains a lot of information about the potential of the target. In order to reveal this information, we need to analytically continue this function of E to the entire complex plane of E. First, we show below that the poles of $S(E)$, on the negative real axis of the complex E-plane, are at the bound state energies.

The poles of $S(E)$ are the solutions of the equation:

$$cot(k'a) = \frac{i}{2}\Big(\frac{k}{k'} + \frac{k'}{k}\Big). \tag{9.43}$$

This equation can be transformed using the trigonometric identity

$$\cot(2\theta) = \frac{1}{2}\Big(\frac{1}{\tan\theta} - \tan\theta\Big) \tag{9.44}$$

using for $2\theta = k'a$. This leads to the following equation for the poles:

$$\frac{1}{x} - x = i\Big(\frac{k}{k'} + \frac{k'}{k}\Big) \tag{9.45}$$

$$x \equiv \tan(k'a/2). \tag{9.46}$$

This is a quadratic equation for x with solutions

$$x = -i\frac{k'}{k}, \qquad x = -i\frac{k}{k'}, \tag{9.47}$$

which lead to the equations This is a quadratic equation for x with solutions

$$k\tan(k'a/2) = -ik' \tag{9.48}$$

$$k'\tan(k'a/2) = -ik. \tag{9.49}$$

By analytic continuation to $E < 0$, these equations become the same to those obtained for even and odd parity bound states in the case of the same square-well potential.

Conclusion: When we analytically continue $S(E)$ to the complex E-plane, the poles of $S(E)$ on the negative E-axis are the bound states of the potential.

9.5 Resonances

The relative transmission probability, that is, $T(E) = |S(E)|^2$ is obtained as

$$T(E) = \Big[1 + \frac{sin^2(k'a)}{4E/V(1+E/V)}\Big]^{-1}. \tag{9.50}$$

$T(E)$ can be expressed as a function of the dimensionless quantity

$$\epsilon = \frac{2mEa^2}{\hbar^2}, \tag{9.51}$$

and it is illustrated in Fig. 9.5 as a black solid line in the range of $0 < \epsilon < 200$, for the case where the only other dimensionless variable in the problem

$$\phi = \frac{2mVa^2}{\hbar^2} \tag{9.52}$$

is equal to 100. Notice that the transmission probability becomes unity at specific values of the energy. These are the so-called resonances. The resonances occur when $\sin^2(k'a) = 0$, that is, when

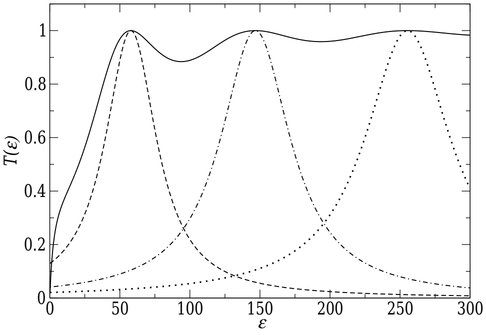

Fig. 9.5 Each of the resonance peaks of the transmission probability for the square-well potential are approximated by a single pole.

$$k'a = n\pi, \tag{9.53}$$

or equivalently, at $\epsilon = \epsilon_n$,, where

$$\epsilon_n = n^2\pi^2 - \phi. \tag{9.54}$$

In order to have a resonance we need to have $\epsilon_n \geq 0$ which implies that the lowest energy resonance for given value of V is

$$n_{min} = \left[\sqrt{\frac{\phi}{\pi^2}}\right] + 1 \tag{9.55}$$

and for the case of the graph in Fig. 9.5 this means that $n_{min} = 4$.

Near a resonance, that is, when the quantity δ defined below, which is a measure of the deviation from resonance, that is,

$$\delta = k'a - n\pi, \tag{9.56}$$

is a small quantity, it is straightforward to show that we can approximate $1/S(E)$ up to linear order in the quantity

$$\delta\epsilon \equiv \epsilon - \epsilon_n \tag{9.57}$$

as follows:

$$\begin{aligned} \frac{1}{S(\epsilon)} &= (-1)^n e^{ika}\Big(1 - \frac{i}{2}(\frac{\sqrt{\epsilon_n}}{\sqrt{\epsilon_n + \phi}} \\ &+ \frac{\sqrt{\epsilon_n + \phi}}{\sqrt{\epsilon_n}})\frac{\partial \tan(\sqrt{\epsilon + \phi})}{\partial \epsilon}|_{\epsilon=\epsilon_n}\delta\epsilon\Big) \end{aligned} \tag{9.58}$$

and to linear order in $\delta\epsilon$, we took

$$\cos(\sqrt{\epsilon+\phi}) = \cos(\sqrt{\epsilon_n+\phi}) = \cos(n\pi) = (-1)^n. \tag{9.59}$$

In the above, we have neglected terms of order $(\delta\epsilon)^2$. As we will see later, this is not going to lead to a good approximation. We do it here because many textbooks do it, but we will show that it is actually incorrect.

If we define

$$\frac{1}{\gamma} \equiv \frac{1}{4}\Big[\big(\frac{\sqrt{\epsilon_n}}{\sqrt{\epsilon_n+\phi}} + \frac{\sqrt{\epsilon_n+\phi}}{\sqrt{\epsilon_n}}\big)\frac{\partial \tan(\sqrt{\epsilon+\phi})}{\partial\epsilon}|_{\epsilon=\epsilon_n}\Big], \tag{9.60}$$

then, $S(\epsilon)$ takes the following form

$$S(\epsilon) = (-1)^n e^{-ika}\frac{i\gamma/2}{\delta\epsilon + i\gamma/2} \tag{9.61}$$

and γ can be calculated to be

$$\gamma = \frac{8n^2\pi^2\sqrt{n^2\pi^2-\phi}}{2n^2\pi^2-\phi} \tag{9.62}$$

and to show the above we have used the relation given by Eq. 9.54.

The transmission probability $T(\epsilon)$ can be calculated using Eq. 9.61, which leads to a Lorentzian approximation for $T(\epsilon)$, that is,

$$T(\epsilon) = \frac{(\gamma/2)^2}{(\delta\epsilon)^2 + (\gamma/2)^2} \tag{9.63}$$

and we have plotted it for values of ϵ near the first and second and third resonance peaks in Fig. 9.5. Notice the disagreement in the width of the peak. What is the reason for the disagreement?

The reasons are the following:

1) First, the expansion which we carried out above, where we only kept up to linear terms in $\delta\epsilon$, is valid as long as $|\delta\epsilon| << 1$. However, using the above solution, we find that near the pole, $\delta\epsilon = i\gamma/2$, and, thus, for the expansion to be valid being near the resonance peak is not sufficient; we need to also have a very sharp resonance, that is, $\gamma/2 << 1$. The expression for γ in Eq. 9.62 indicates that for most values of ϕ, this condition is not satisfied.

2) The approximated form for $1/S(\epsilon)$ leads to the inverse of the Lorentzian expression for $1/T(\epsilon)$. This expression is quadratic in our expansion variable $\delta\epsilon$. However, when we approximated $1/S(\epsilon)$ we only kept terms which were correct only up to linear order in the variable $\delta\epsilon$. If our intention is to ultimately approximate a quantity such as $1/T(\epsilon)$ to order $(\delta\epsilon)^2$ correctly, we need to make sure that we do not leave out any terms in the expansion in powers of $\delta\epsilon$ which, when we take the absolute magnitude of $S(\epsilon)$ to compute $T(\epsilon)$, give contribution to the coefficient of $(\delta\epsilon)^2$. For example, if we expand $\cos(\sqrt{\epsilon+\phi})$ near the resonance, we obtain

$$\cos(\sqrt{\epsilon+\phi}) \simeq \cos(n\pi)\Big(1 - \frac{1}{8(n\pi)^2}(\delta\epsilon)^2\Big), \tag{9.64}$$

and the square of $\cos(\sqrt{\epsilon+\phi})$, needed in the expression for $T(\epsilon)$, will have a term of order $(\delta\epsilon)^2$. On the other hand, we do not need to worry about expanding the

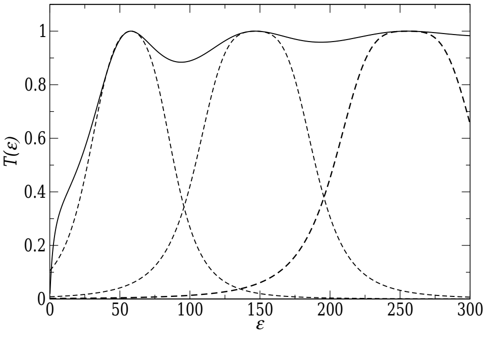

Fig. 9.6 Each of the resonance peaks of the transmission probability for the square-well potential are approximated by a pair of poles, with negative imaginary parts.

imaginary part of the denominator in the expression (9.42) beyond terms linear in $\delta\epsilon$, because in the absolute magnitude of $S(\epsilon)$ any term beyond the linear yields higher than second order.

We combine the two factors, that is,

$$S(\epsilon) = \frac{e^{-ika}}{\cos(n\pi)} \frac{1}{1 - \frac{1}{8(n\pi)^2}(\delta\epsilon)^2} \frac{i\gamma/2}{\delta\epsilon + i\gamma/2} \tag{9.65}$$

which leads to

$$S(\epsilon) = -\frac{1}{\cos(n\pi)} \frac{8(n\pi)^2}{(\delta\epsilon)^2 + i\frac{2(2(n\pi)^2-\phi)}{\sqrt{(n\pi)^2-\phi}}\delta\epsilon - 8(n\pi)^2}. \tag{9.66}$$

Here we have neglected terms of order δ^3. Now, we find the poles of the above expression:

$$\delta_\pm = -i\frac{(2(n\pi)^2 - \phi)}{\sqrt{(n\pi)^2 - \phi}} \pm \sqrt{-\frac{(2(n\pi)^2 - \phi)^2}{(n\pi)^2 - \phi} + 8(n\pi)^2}. \tag{9.67}$$

As a result $S(\epsilon)$ can be written as

$$S(\epsilon) = -\frac{1}{\cos(n\pi)} \frac{8(n\pi)^2}{(\delta\epsilon - \delta_+)(\delta\epsilon - \delta_-)} \tag{9.68}$$

which implies that the correct way to approximate $T(\epsilon)$ near the peak is

$$T(\epsilon) = \frac{64(n\pi)^4}{|\delta\epsilon - \delta_+|^2 |\delta\epsilon - \delta_-|^2}. \tag{9.69}$$

This is shown in Fig. 9.6.

9.6 Analytic structure of $S(E)$

In Fig. 9.7 the analytic structure of $S(E)$ is schematically illustrated. As discussed, if analytically continued to the entire complex E plane, $S(E)$ has poles on the negative real axis, which represent the bound states. It has a branch cut along the positive real axis and this is associated with the multi-valued function: $f(E) = \sqrt{E}$. In addition, there are poles at $E = En - i\gamma/2$ where $E_n > 0$ and $\gamma > 0$, and these poles represent the resonances. The closer these poles are to the real positive axis, the longer lived the resonances are. This is so because in the next section we will show that the lifetime of a resonance is $\tau = \hbar/\gamma$.

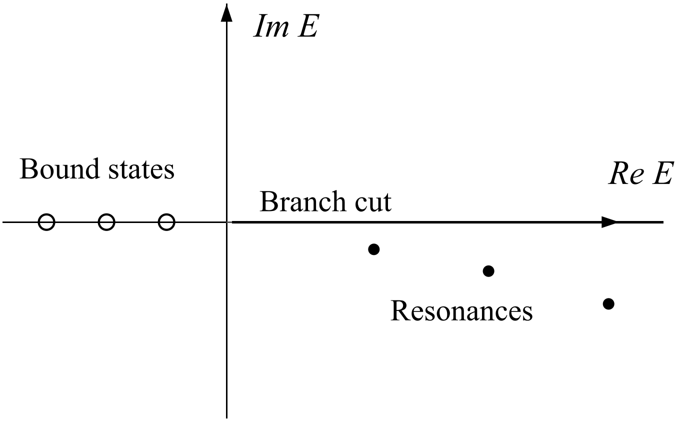

Fig. 9.7

9.7 Meaning of the resonance

In practice an experimentalist prepares the incident wavepacket with a distribution of k near some k_0 as discussed in section 5.3. Thus, the incident wavepacket is of the following form:

$$\Psi_I(x, t=0) = \int \frac{dk}{2\pi} A_I(k) e^{ikx}. \tag{9.70}$$

The transmitted wavepacket is of the following form:

$$\Psi_{III}(x, t) = \int \frac{dk}{2\pi} A_I(k) S(E)\ e^{-\frac{i}{\hbar}E(k)t} e^{ikx}, \tag{9.71}$$

where $E(k) = \hbar^2 k^2/(2m)$. We can change our integration variable from $k \to E$, using the transformation $E = \hbar^2 k^2/(2m)$. We find that:

$$\Psi_{III}(x, t) = \frac{m}{\hbar^2} \int \frac{dE}{2\pi} \frac{A_I(k(E))}{k(E)} S(E) e^{-\frac{i}{\hbar}Et} e^{ik(E)x}, \tag{9.72}$$

where $k(E) = \sqrt{2mE/\hbar^2}$.

Let us assume that we are dealing with a very sharp resonance. In this case we can approximate $S(E)$ by a single pole, that is, using Eq. 9.61 and this may be true in a case of a very sharp resonance. In such a case the integrand is sharply picked near the resonance and the integral above for $\Psi_{III}(x,t)$ can be approximated as

$$\begin{aligned}\Psi_{III}(x,t) = \cos(n\pi)\frac{m}{\hbar^2}\frac{A_I(k(E_n))}{k(E_n)}e^{-\frac{i}{\hbar}E_n t}e^{ik(E_n)(x-a)} \\ \times \int \frac{dE}{2\pi}\frac{i\Gamma/2}{(E-E_n)+i\Gamma/2}e^{-\frac{i}{\hbar}(E-E_n)t}e^{i(k(E)-k(E_n))(x-a)}.\end{aligned} \tag{9.73}$$

and this is so because of the fact that the integrand is sharply peaked near $E = E_n$, we have taken all other slowly varying functions of E outside the integration and we evaluated them at $E = E_n$. Now, we can further simplify this integral by noting that for E near E_n,

$$\begin{aligned}k(E) - k(E_n) &= \frac{dk(E)}{dE}|_{E=E_n}(E-E_n) \\ &= \frac{m}{\hbar^2 k(E_n)}(E-E_n).\end{aligned} \tag{9.74}$$

This approximation allows us to write the integral in Eq. 9.73 in the following form:

$$\int_{-\infty}^{\infty}\frac{dE'}{2\pi}\frac{i\Gamma/2}{E'+i\Gamma/2}e^{\frac{i}{\hbar}E'\xi}. \tag{9.75}$$

$$\xi \equiv \frac{m}{\hbar k(E_n)}(x-a) - t, \tag{9.76}$$

and the new integration variable is $E' = E - E_n$. Because the integrand is only non-zero very near the resonance, the integration limits can be extended to be from $-\infty$ to $+\infty$.

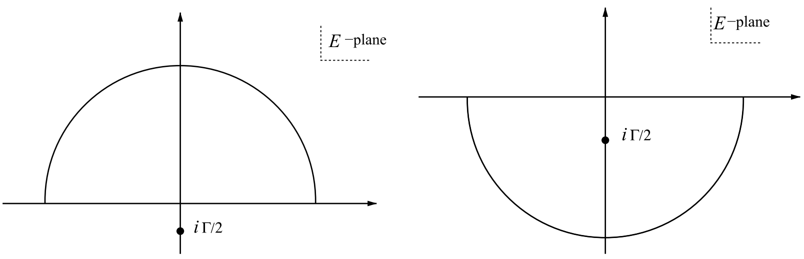

Fig. 9.8 Left: Contour C_1 chosen for the case where $\xi > 0$. Right: Contour C_2 chosen for the case where $\xi < 0$.

Depending on the sign of the real parameter ξ above, the contour of integration can be extended to include the semi-circular path illustrated in Fig. 9.8. If $\xi > 0$, we can choose the integration path illustrated on the left part of Fig. 9.8, the contribution of the added semi-circular arc is zero, because along this path the imaginary part E_i of the integration variable $E' = E_r + iE_i$ is positive and, therefore, the factor $e^{\frac{i}{\hbar}E'\xi} = e^{-\frac{1}{\hbar}E_i\xi}e^{\frac{i}{\hbar}E_r\xi}$ becomes exponentially small and negligible along this part of the integration. Thus, we can write

$$\int_{-\infty}^{\infty} \frac{dE'}{2\pi} \frac{i\Gamma/2}{E' + i\Gamma/2} e^{\frac{i}{\hbar}E'\xi} = \oint_{C_1} \frac{dE'}{2\pi} \frac{i\Gamma/2}{E' + i\Gamma/2} e^{\frac{i}{\hbar}E'\xi}. \tag{9.77}$$

The integration along a closed path is the sum of the residues of the poles of the integrand which are enclosed by the path. However, the integrand has only one pole at $-i\Gamma/2$ and this lies outside the integration contour. Therefore, the integral in the case of $\xi > 0$ vanishes.

On the other hand, in the case where $\xi < 0$, we cannot close the contour as before, because the contribution of the added semi-circular part does not vanish. We can, however, add the semi-circular part shown in the right part of Fig. 9.8. The contribution of this part vanishes for $\xi < 0$. Therefore, the integral of our interest in this case becomes

$$\begin{aligned}\int_{-\infty}^{\infty} \frac{dE'}{2\pi} \frac{i\Gamma/2}{E' + i\Gamma/2} e^{\frac{i}{\hbar}E'\xi} &= \oint_{C_2} \frac{dE'}{2\pi} \frac{i\Gamma/2}{E' + i\Gamma/2} e^{\frac{i}{\hbar}E'\xi} \\ &= -\frac{\Gamma}{2} \exp(\frac{\Gamma\xi}{\hbar}).\end{aligned} \tag{9.78}$$

Therefore, the wavefunction in Region III takes the form:

$$\Psi_{III}(x,t) = \left\{ \begin{array}{cc} 0, & \xi > 0 \\ Ce^{-\frac{i}{\hbar}E_n t} e^{ik(E_n)(x-a)} \exp(-\frac{\Gamma t}{\hbar}), & \xi < 0 \end{array} \right\}. \tag{9.79}$$

The condition $\xi < 0$ means that $v_n t > a$, where $v_n \equiv \hbar k_n/m$, that is, the "classical velocity" of a particle moving with a momentum $\hbar k_n$. Thus, the wavefunction in Region III becomes non-zero after an elapse of a time which is required for the wavepacket to cross the region of the potential well. After this time the wavepacket is approximately a traveling plane wave apart from a decaying envelope with a characteristic decay time of the order of

$$\tau = \frac{\hbar}{\Gamma}. \tag{9.80}$$

This characteristic timescale plays the role of the resonance lifetime.

9.8 Problems

Problem 1

Find a complete set of equations and unknowns which determine the scattering amplitude $S(E)$ for scattering from the following potential:

$$V(x) = \left\{ \begin{array}{cc} 0, & 0 \leq |x| \leq \frac{b}{2} \\ V(>0), & \frac{b}{2} \leq |x| < \frac{a}{2} \\ 0, & |x| \geq \frac{a}{2} \end{array} \right\}. \tag{9.81}$$

Problem 2

Show explicitly all the steps leading to Eq. 9.69 starting from Eq. 9.50 for the transmission probability for scattering from the 1D attractive square-well potential.

Problem 3

Consider scattering of a particle with energy $E > 0$ from the following attractive delta-function potential

$$V(x) = -\lambda\delta(x). \tag{9.82}$$

(a) Find the scattering amplitude and compare the result with that obtained in this chapter for the attractive square-well potential in the limit where $a \to 0$ and $V \to \infty$ in such a way that $Va \to \lambda$.
(b) Find the bound states by analytic continuation to $E < 0$.
(c) Are there resonances?

Problem 4

Consider scattering of a particle with energy $E > 0$ from the following attractive delta functions potential

$$V(x) = -\lambda(\delta(x+a) + \delta(x-a)). \tag{9.83}$$

(a) Find the scattering amplitude $S(E)$.
(b) Study the resonances of $S(E)$ as was done in this chapter for the case of the square-well potential.

10

Periodic potentials

In this chapter, we explore the consequences of the translational symmetry of a periodic potential, namely, we consider a single particle under the influence of the following Hamiltonian:

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x), \qquad V(x+a) = V(x), \tag{10.1}$$

that is, the potential is periodic with a period a.

In addition, we are going to consider periodic boundary conditions, that is, that after N steps of translations by a we go back to the same spatial position, that is, $x+Na \to x$. This means that we have the topology of the circle considered in chapter 1.

10.1 Bloch's theorem

The case discussed above is a particular example of the more general case of a symmetry group of the Hamiltonian. The symmetry group is a group with elements operators which commute with the Hamiltonian. In general this problem requires knowledge of group theory and how to find the so-called irreducible representations of the group. In the present case, the group consists of translations $\hat{T}_a$ by a finite amount a and because the group is essentially the Abelian $U(1)$ group, the problem becomes rather simple and we will do it here.

Let us define the operator $\hat{T}_a$ which carries out translations by a when acting on any arbitrary function $\psi(x)$:

$$\hat{T}_a \psi(x) \equiv \psi(x+a). \tag{10.2}$$

We can easily show that

$$[\hat{T}_a, \hat{H}] = 0. \tag{10.3}$$

This can be shown by operating with $\hat{T}_a \hat{H}$ on any function $\psi(x)$

$$\hat{T}_a(\hat{H}\psi(x)) = \hat{H}\psi(x+a) = \hat{H}\hat{T}_a\psi(x). \tag{10.4}$$

The second step above is obtained by using the facts that $V(x+a) = V(x)$ and that the kinetic energy term is also invariant under such translations because of the following:

$$\frac{d}{d(x+a)} \frac{d}{d(x+a)} = \frac{d}{dx}\frac{d}{dx}. \tag{10.5}$$

Practical Quantum Mechanics. First Edition. Efstratios Manousakis.

The fact that the operators $\hat{H}$ and $\hat{T}_a$ commute means that we have the "green-light" to go ahead to look for shared eigenstates. Following the strategy discussed in chapter 7, we first look for eigenstates of $\hat{T}_a$, that is,

$$\hat{T}_a \phi_\lambda(x) = \lambda \phi_\lambda(x). \tag{10.6}$$

Since we are considering periodic boundary conditions, we must require that after N such steps we must go back to the same spatial location. This means that

$$\hat{T}_a^N \phi_\lambda(x) = \lambda^N \phi_\lambda(x), \qquad \rightarrow \qquad \phi_\lambda(x + Na) = \lambda^N \phi_\lambda(x), \tag{10.7}$$

and, since $\phi_\lambda(x + Na) = \phi_\lambda(x)$, we obtain:

$$\lambda^N = 1, \rightarrow \lambda = e^{ika}; \quad k = \frac{2\pi}{Na} m, m = 0, \pm 1, \pm 2, ... \tag{10.8}$$

Namely, λ is the Nth root of unity and there are exactly N different such roots, or solutions to the above order-N algebraic equation. Therefore, we need to restrict the value of N in the so-called *first Brillouin zone*, a concept which has already been discussed in chapter 1.

Now, let us consider eigenstates of $\hat{H}$:

$$\hat{H} \psi_n(x) = E_n \psi_n(x). \tag{10.9}$$

If $\psi_n(x)$ is an eigenstate of $\hat{H}$ with corresponding energy eigenvalue $E_n = E$, then the state $\chi_n(x) \equiv \hat{T}_a \psi_n(x)$ is also an eigenstate of $\hat{H}$ corresponding to the same energy eigenvalue because

$$\begin{aligned} \hat{H} \chi_n(x) &= \hat{H} \hat{T}_a \psi_n(x) = \hat{T}_a \hat{H} \psi_n(x) \\ &= E \hat{T}_a \psi_n(x) = E \chi_n(x). \end{aligned} \tag{10.10}$$

In fact any power of $\hat{T}_a$ acting on $\psi_n(x)$ yields an eigenstate of $\hat{H}$ with the same eigenvalue $E_n = E$. Namely, the state

$$\chi_n^{(l)}(x) \equiv \hat{T}_a^l \psi_n(x) = \psi_n(x + la), \tag{10.11}$$

is an eigenstate of $\hat{H}$ with the same corresponding eigenvalue $E_n = E$. This means that the energy level with energy E is at least N-fold degenerate.

This means that we can make the following linear combinations:

$$\Psi_k^{(n)}(x) = \sum_{l=0}^{N-1} e^{-ikla} \psi_n(x + la), \tag{10.12}$$

$$k = \frac{2\pi}{Na} m, \qquad -\frac{N}{2} \leq m < \frac{N}{2}. \tag{10.13}$$

These N different states are simultaneous eigenstates of $\hat{H}$ and $\hat{T}_a$. First, they are clearly eigenstates of $\hat{H}$ because each of the N states which participate in the linear combination is an eigenstate of $\hat{H}$ with *the same corresponding eigenvalue E*. This means that if we apply $\hat{H}$ on this linear combination, each state will produce itself and the same factor E which can be factorized from all the other states too.

Why are they eigenstates of the operator $\hat{T}_a$?

$$\begin{aligned}\hat{T}_a \Psi_k^{(n)}(x) &= \sum_{l=0}^{N-1} e^{-ikla} \hat{T}_a \psi_n(x+la) = \sum_{l=0}^{N-1} e^{-ikla} \psi_n(x+la+a) \\ &= \sum_{l'=1}^{N} e^{-ik(l'-1)a} \psi_n(x+l'a) \\ &= e^{ika} \sum_{l'=1}^{N} e^{-ikl'a} \psi_n(x+l'a), \end{aligned} \tag{10.14}$$

where l' is defined as $l' = l+1$. Now, the sum over l' is from 1 to N. However, the Nth term $\psi_n(x+Na) = \psi_n(x)$, that is, it is the same as the 0th due to our periodic boundary conditions. In addition, the factor $e^{-ikNa} = e^{-i2\pi m} = 1$ which is also the same factor when $l' = 0$. Therefore, the states given by Eq. 10.12 are also eigenstates of $\hat{T}_a$ with corresponding eigenvalue e^{ika}:

$$\hat{T}_a \Psi_k^{(n)}(x) = e^{ika} \Psi_k^{(n)}(x). \tag{10.15}$$

Now, we are ready to state *Bloch's theorem*: Common eigenstates of $\hat{H}$ and $\hat{T}_a$ can be written as:

$$\Psi_k^{(n)}(x) = e^{ikx} u_k^{(n)}(x), \tag{10.16}$$

where $u_k^{(n)}(x)$ is a periodic function, that is,

$$u_k^{(n)}(x+a) = u_k^{(n)}(x), \tag{10.17}$$

with period a.

This can be proven immediately by considering the function

$$u_k^{(n)}(x) \equiv e^{-ikx} \Psi_k^{(n)}(x), \tag{10.18}$$

and showing that it is a periodic function with period a. This is obvious by means of the property given by Eq. 10.15.

10.2 The Kronig–Penney model

Consider the periodic potential shown in Fig. 10.1, which has period a, that is,

$$V(x+a) = V(x), \tag{10.19}$$

and within a period $-a+b < x < b$, it is given as

$$V(x) = \left\{ \begin{array}{ll} V_0 \ for & -a+b < x < 0, \\ 0 \ \ for & \quad 0 \leq x < b \end{array} \right\}. \tag{10.20}$$

We are interested to solve this problem for $0 < E < V_0$.

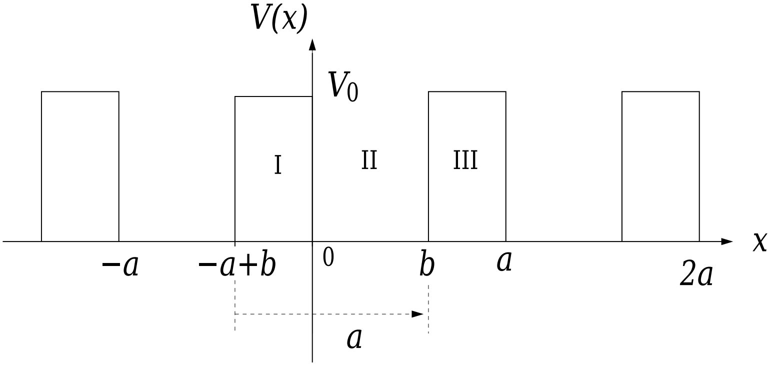

Fig. 10.1

In Region I ($-a + b < x < 0$), where $V(x) = V_0$, the solution to the Schrödinger equation for $E < V_0$ can be written as

$$\psi_I(x) = A_I e^{q'x} + B_{II} e^{-q'x}, \qquad q' = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}. \tag{10.21}$$

In Region II, ($0 \le x < b$) where $V(x) = 0$, the solution to the Schrödinger equation can be written as

$$\psi_{II}(x) = A_{II} e^{iqx} + B_{II} e^{-iqx}, \qquad q = \sqrt{\frac{2mE}{\hbar^2}}. \tag{10.22}$$

The solution in the other regions of this periodic potential are related to the above simply by Bloch's theorem. For example, the wavefunction and its derivative in Region I above are related to the wavefunction in Region III as follows:

$$\psi_{III}(x) = \psi_I(x - a)e^{ika}, \psi'_{III}(x) = \psi'_I(x - a)e^{ika}, \tag{10.23}$$

where k is Bloch's index which is limited inside the first Brillouin zone and it is due to the periodic symmetry of the potential. Using the above expression, we can compute the wavefunction and its derivative at $x = b + \epsilon$ ($\epsilon \to 0$) in terms of the wavefunction in Region I above.

Now, we are able to apply the boundary conditions at $x = 0$ and at $x = b$.

The boundary conditions at $x = 0$ yield:

$$\psi_I(0) = \psi_{II}(0) \;\; \to \;\; A_I + B_I = A_{II} + B_{II}, \tag{10.24}$$

$$\psi'_I(0) = \psi'_{II}(0) \;\; \to \;\; q'(A_I - B_I) = iq(A_{II} - B_{II}). \tag{10.25}$$

The boundary conditions at $x = b$ (with the aid of Eq. 10.23) yield first, the boundary condition on the wavefunction

$$\psi_{II}(b) = \psi_I(b - a)e^{ika} \tag{10.26}$$

leads to

$$A_{II}e^{iqb} + B_{II}e^{-iqb} = (A_I e^{q'(b-a)} + B_I e^{-q'(b-a)}) \\ \times e^{ika}, \tag{10.27}$$

and the condition on its derivative:

$$\psi'_{II}(b) = \psi'_I(b-a)e^{ika} \tag{10.28}$$

leads to

$$iq(A_{II}e^{iqb} - B_{II}e^{-iqb}) = q'(A_I e^{q'(b-a)} - B_I e^{-q'(b-a)})e^{ika}. \tag{10.29}$$

We have a system of four homogeneous linear algebraic equations and four unknowns. Namely, the above four equations can be written as

$$\mathbf{MX} = \mathbf{0}, \tag{10.30}$$

$$\mathbf{X} = \begin{pmatrix} A_I \\ B_I \\ A_{II} \\ B_{II} \end{pmatrix}, \tag{10.31}$$

and the matrix $\mathbf{M}$ of the coefficients is the following matrix

$$\begin{pmatrix} 1 & 1 & -1 & -1 \\ q' & -q' & -iq & iq \\ -e^{-q'(a-b)}e^{ika} & -e^{q'(a-b)}e^{ika} & e^{iqb} & e^{-iqb} \\ -q'e^{-q'(a-b)}e^{ika} & q'e^{q'(a-b)}e^{ika} & iqe^{iqb} & -iqe^{-iqb} \end{pmatrix}. \tag{10.32}$$

The trivial solution ($\mathbf{X} = \mathbf{0}$; that is, $A_I = A_{II} = B_I = B_{II} = 0$) is always there. However, we are seeking a non-trivial solution and in order to guarantee its existence we must require that the determinant of the matrix $\mathbf{M}$ must be zero. After some amount of algebra and factorization we obtain the following expression for the determinant:

$$det(\mathbf{M}) = 8iqq'e^{ika}D, \tag{10.33}$$

$$D = \cos(ka) - \frac{q'^2 - q^2}{2qq'}\sinh[q'(a-b)]\sin(qb) \\ - \cosh[q'(a-b)]\cos(qb). \tag{10.34}$$

Therefore, we obtain the following equation for the energy eigenvalues

$$\cos(ka) = \frac{q'^2 - q^2}{2qq'}\sinh[q'(a-b)]\sin(qb) \\ + \cosh[q'(a-b)]\cos(qb). \tag{10.35}$$

This is a rather general expression and it can be specialized to the case of a periodic array of delta functions in the limit where $a - b \to 0$ and $V_0 \to \infty$ in such a way

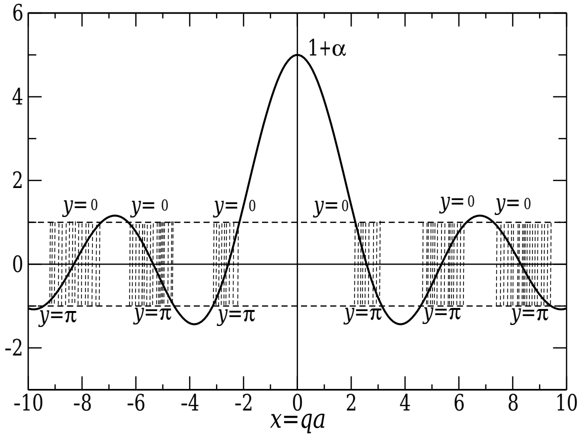

Fig. 10.2

that the product $(a-b)V_0 \to V$ where V is kept constant. This limit represents the periodic potential

$$V(x) = V \sum_{n=-\infty}^{\infty} \delta(x - na). \tag{10.36}$$

In this limit it is straightforward to see that

$$q' \to \sqrt{\frac{2mV_0}{\hbar^2}} \to \infty \tag{10.37}$$

and, so the term

$$\frac{q'^2 - q^2}{2qq'} \sinh[q'(a-b)] \to \frac{q'^2(a-b)}{2q} = \frac{mV}{\hbar^2 q}. \tag{10.38}$$

Thus, Eq. 10.35 becomes

$$\cos(y) = \alpha \frac{\sin(x)}{x} + \cos(x), \tag{10.39}$$

$$y = ka, \qquad x = qa, \qquad \alpha = \frac{mVa}{\hbar^2}. \tag{10.40}$$

This equation is solved graphically in Fig. 10.2. The solid line represents the right-hand-side of the above equation. The horizontal lines represent the bounds of the left-hand-side for which $-1 \le \cos(y) \le 1$, thus, there are only solutions in the red-shaded areas. As can be concluded by examining the graphical solutions, the same value of

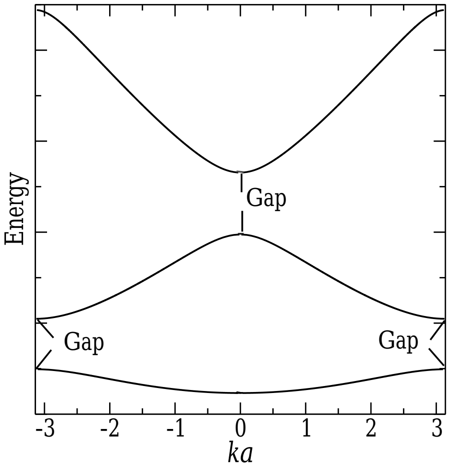

Fig. 10.3

$y = ka$ can yield an infinite number of solutions for $x = qa$. For a given value of k, these different solutions for x, which correspond to different values of q, that is, $q_1(k)$, $q_2(k)$, ..., correspond to different values of the energy, say, $E_1(k)$, $E_2(k)$, ... These solutions form bands, that is, continuous functions of k with k ranging from $-\pi/a$ to π/a (a has been set to unity in the figures), that is, inside the so-called first Brillouin zone. These bands are separated by energy gaps as illustrated in Fig. 10.3. The gaps fall in the regions of $x = qa$, where there are no solutions because the right-hand-side of Eq. 10.40 falls outside the $[-1, 1]$ interval.

10.3 Problems

Problem 1

Solve the problem of an array of delta functions, that is, a periodic potential of the form

$$V(x) = V \sum_{n=-\infty}^{\infty} \delta(x - na). \tag{10.41}$$

and show that the energy eigenvalues for given value of the Bloch index k are given as solutions to Eq. 10.40.

Problem 2

Consider the Kronig–Penney problem as described by the eigenvalue Eq. 10.35. Assume that this describes a 1D solid with non-interacting electrons.

Assume that the electron filling-factor corresponds to one electron per delta function (that is, per unit cell of the periodic potential).

(a) Find the Fermi energy.

(b) Calculate the "Fermi velocity" defined by the following derivative,

$$V_F = \frac{1}{\hbar}\frac{\partial E(k)}{\partial k}, \tag{10.42}$$

when evaluated at the momentum which corresponds to the Fermi energy.

From now on, assume that the electron filling-factor corresponds to two electrons per delta-function (that is, per unit cell of the periodic potential).

(c) What is the energy of the highest occupied state in this case? What is the energy of the lowest unoccupied state? Find the effective mass for electrons near the conduction band edge, that is, near $k = 0$.

(d) Calculate the effective mass for electrons near the conduction band minimum, that is, near $k = 0$.

(e) Calculate the effective mass for holes near the top of the valence band, that is, near $k = 0$.

Hint: The effective mass is defined as:

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2E(k)}{dk^2}. \tag{10.43}$$

11

The harmonic oscillator

In this chapter we discuss the 1D harmonic oscillator. We begin by analyzing the conditions in which the harmonic approximation can be used. We then transform the Hamitlonian of the harmonic oscillator in terms of "ladder" operators and find its eigenvalues and eigenstates.

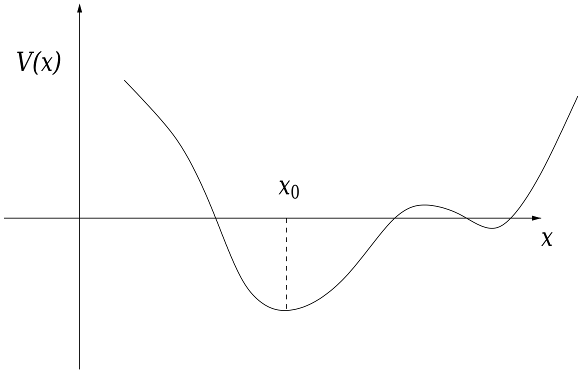

Fig. 11.1

11.1 Why is it useful?

We consider the case of the 1D potential landscape illustrated in Fig. 11.1. Any such potential can be approximated near its minimum $x = x_0$ as follows:

$$V(x) = V(x_0) + V'(x_0)(x - x_0) + \frac{1}{2}V''(x_0)(x - x_0)^2 + ... \tag{11.1}$$

and the linear term vanishes, because x_0 is the minimum of $V(x)$. Therefore, we can rewrite the above expression as

$$V(x) = V(x_0) + \frac{1}{2}m\omega^2(\Delta x)^2 + ... \tag{11.2}$$

$$\omega^2 \equiv \frac{V''(x_0)}{m} \geq 0, \qquad \Delta x = x - x_0. \tag{11.3}$$

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Since, the constant $V(x_0)$ can be absorbed into the definition of the zero in our energy scale, we have obtained the harmonic oscillator Hamiltonian.

This approximation can be used, for example, to describe small oscillations of atoms in a solid near the minimum of their interaction energy landscape. It can also be used to describe small oscillations of atoms in molecular systems, and so on. It can always be used to describe the motion of a particle in any rather complex potential when its mass is rather large which may restrict the zero point motion in such way that the term

$$\frac{1}{2}V''(x_0)\langle (x-x_0)^2\rangle \tag{11.4}$$

is small as compared to the average of the next surviving term of the expansion of $V(x)$ near the minimum. As we will see later in this chapter, for the harmonic oscillator

$$\langle (x-x_0)^2\rangle = \frac{2\hbar}{m\omega}, \tag{11.5}$$

which means that a large mass and/or high curvature of the potential near its minimum limits the fluctuations of the position near its classical minimum.

Since, we can solve the harmonic oscillator problem exactly this can provide useful information and insight in real systems.

11.2 One-dimensional harmonic oscillator

Let us begin from the Hamiltonian of the 1D harmonic oscillator:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2. \tag{11.6}$$

We wish to find the energy eigenvalues and eigenstates:

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle. \tag{11.7}$$

We change variables from $\hat{x}$ and $\hat{p}$ to the dimensionless variables $\hat{X}$ and $\hat{Y}$ respectively to keep the kinetic and potential energy terms looking symmetric:

$$\frac{1}{2}m\omega^2\hat{x}^2 \quad \to \hbar\omega\hat{X}^2, \tag{11.8}$$

$$\frac{\hat{p}^2}{2m} \quad \to \hbar\omega\hat{Y}^2. \tag{11.9}$$

Notice that we have pulled out a prefactor of $\hbar\omega$ because it has dimensions of energy, and this makes both $\hat{X}$ and $\hat{Y}$ dimensionless operators. More precisely, we define the transformation:

$$\hat{X} = \sqrt{\frac{m\omega}{2\hbar}}\hat{x}, \tag{11.10}$$

$$\hat{Y} = \frac{1}{\sqrt{2m\hbar\omega}}\hat{p}. \tag{11.11}$$

This transforms the Hamiltonian to the following form:

$$\hat{H} = \hbar\omega(\hat{X}^2 + \hat{Y}^2). \tag{11.12}$$

Namely, in units of $\hbar\omega$ the Hamiltonian is simply $\hat{X}^2 + \hat{Y}^2$ and if we define the complex operator

$$\hat{a} \equiv \hat{X} + i\hat{Y}, \tag{11.13}$$

and its adjoint

$$\hat{a}^\dagger \equiv \hat{X} - i\hat{Y}, \tag{11.14}$$

because we have that

$$\hat{a}^\dagger\hat{a} = \hat{X}^2 + \hat{Y}^2 + i[\hat{X}, \hat{Y}] = \hat{X}^2 + \hat{Y}^2 - \frac{1}{2}, \tag{11.15}$$

the Hamiltonian is simply

$$\hat{H} = \hbar\omega(\hat{a}^\dagger\hat{a} + \frac{1}{2}). \tag{11.16}$$

We define

$$\hat{N} = \hat{a}^\dagger\hat{a}. \tag{11.17}$$

This will turn out to be the so-called "number operator," but for now, it is just a symbol in terms of which

$$\hat{H} = \hbar\omega(\hat{N} + \frac{1}{2}). \tag{11.18}$$

Let us figure out the properties of these operators and their spectrum. First, we can easily show that the commutation relation

$$[\hat{x}, \hat{p}] = i\hbar, \tag{11.19}$$

leads to

$$[\hat{a}, \hat{a}^\dagger] = 1. \tag{11.20}$$

We denote the eigenvalues and eigenstates of the operator $\hat{N}$ as n and $|n\rangle$ respectively, namely that

$$\hat{N}|n\rangle = n|n\rangle, \tag{11.21}$$

without implying anything about the nature of n. We will show next that n takes integer values. First, it is straightforward to show that $\hat{N}$ is Hermitian. This is so, because

$$\begin{aligned} \hat{N} = \hat{a}^\dagger\hat{a} \quad \rightarrow \quad \hat{N}^\dagger &= (\hat{a}^\dagger\hat{a})^\dagger = \hat{a}^\dagger(\hat{a}^\dagger)^\dagger \\ &= \hat{a}^\dagger\hat{a}. \end{aligned} \tag{11.22}$$

Furthermore,

$$\langle n|\hat{N}|n\rangle \geq 0. \tag{11.23}$$

This identity can be easily shown by considering the state $|\phi\rangle \equiv a|n\rangle$. For any state $|\phi\rangle$ it is true that $\langle\phi|\phi\rangle \geq 0$. By immediate substitution, this leads to the relation (11.23).

Now, the following statement is true: If $|n\rangle$ is an eigenstate of $\hat{N}$ with eigenvalue n, then, a) if $n \neq 0$, the state $|\phi\rangle \equiv \hat{a}|n\rangle$ is an eigenstate of $\hat{N}$ with eigenvalue $n-1$, b) if $n = 0$, then $\hat{a}|n\rangle = 0$.

The proof of this statement is simple. Using the commutation relation between $\hat{a}$ and $\hat{a}^\dagger$ given by Eq. 11.20, we can write:

$$\begin{aligned}\hat{N}(|\phi\rangle) &= \hat{N}(\hat{a}|n\rangle) = \hat{a}^\dagger\hat{a}\hat{a}|n\rangle = (\hat{a}\hat{a}^\dagger - 1)\hat{a}|n\rangle \\ &= \hat{a}\hat{N}|n\rangle - \hat{a}|n\rangle = n\hat{a}|n\rangle - \hat{a}|n\rangle \\ &= (n-1)|\phi\rangle. \end{aligned} \tag{11.24}$$

Thus, we have shown that apart from a normalization constant $|\phi\rangle = \hat{a}|n\rangle$ is an eigenstate of $\hat{N}$ with eigenvalue $n-1$. This allows us to write:

$$\hat{a}|n\rangle = C_n|n-1\rangle, \tag{11.25}$$

where is a normalization constant which can be determined as follows:

$$\langle n|a^\dagger\hat{a}|n\rangle = |C_n|^2\langle n-1|n-1\rangle. \tag{11.26}$$

Now, we demand that $\langle n-1|n-1\rangle = 1$, that is, we have used the symbol $|n\rangle$ to denote normalized eigenstates of $\hat{N}$, for any n. The left-hand-side is simply n because it is $\langle n|\hat{N}|n\rangle$. Therefore, we conclude that $C_n = \sqrt{n}$ and, thus, we arrive at the conclusion:

$$\hat{a}|n\rangle = \sqrt{n}|n-1\rangle. \tag{11.27}$$

This equation also tells us that

$$\hat{a}|0\rangle = 0. \tag{11.28}$$

In a parallel derivation, starting from proving the statement that the state defined as $|\phi\rangle \equiv a^\dagger|n\rangle$ is an eigenstate of $\hat{N}$ with a corresponding eigenvalue $n+1$, we can show that

$$\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle. \tag{11.29}$$

Now, we are equipped to prove next that: *n is an integer.*

Let us see what happens if n is not an integer. It is true that if $|n\rangle$ is an eigenstate of $\hat{N}$ with eigenvalue n, then, $|n-1\rangle$, $|n-2\rangle$, ..., $|n-m\rangle$ are also eigenstates of $\hat{N}$ with corresponding eigenvalues $n-1$,$n-2$, ..., $n-m$ respectively. Let us keep increasing the value of the integer m, starting from $m = 1$ and keeping $m < n$ until its difference from n is less than 1. Then, we write $n = m + \epsilon$ where $m = [n]$ and $0 < \epsilon < 1$. Then, the state $|n-m = \epsilon\rangle$ is an eigenstate of $\hat{N}$ with corresponding eigenvalue ϵ. However, if $\epsilon \neq 0$ the state $|\epsilon - 1$ should also be an eigenstate of $\hat{N}$ with corresponding eigenvalue $\epsilon - 1 < 0$! However, this cannot be true because we have shown that $\langle \epsilon-1|\hat{N}|\epsilon-1\rangle \geq 0$.

What went wrong? Our assumption that $\epsilon \neq 0$, that is, equivalently, that n is not an integer, is not true. How is the problem fixed if $\epsilon = 0$? We can no longer repeat the last argument above which led us to the incorrect conclusion. Namely, in this case, we are not able to reason that if the state $|\epsilon\rangle$ is an eigenstate, the state $|\epsilon - 1\rangle = \hat{a}|0\rangle$ is an eigenstate of $\hat{N}$. The reason is that $\hat{a}|0\rangle$ is not a state, it is the real number 0 (see Eq. 11.28). This can also be shown from the fact that $|0\rangle$ is an eigenstate of $\hat{N}$ with eigenvalue 0, that is,

$$\hat{N}|0\rangle = 0, \qquad \hat{a}^\dagger \hat{a}|0\rangle = 0. \tag{11.30}$$

The only way the last step could be true is if $\hat{a}|0\rangle = 0$.

Since the Hamiltonian is a linear function of $\hat{N}$ (see Eq. 11.18) the eigenstates of $\hat{N}$ are the same as the eigenstates of $\hat{H}$, that is,

$$|\psi_n\rangle = |n\rangle, \tag{11.31}$$

and

$$\hat{H}|n\rangle = \hbar\omega(n + \frac{1}{2})|n\rangle, \quad n = 0, 1, 2, ... \tag{11.32}$$

11.3 Eigenstates

What about the eigenstates of $\hat{H}$ and of $\hat{N}$? In addition, can we determine $\langle x|n\rangle$?

First: $|0\rangle$ is the ground state and the excited states $|n\rangle$ can be produced by acting on the ground state with the operator $\hat{a}^\dagger$, as follows:

$$|1\rangle = \hat{a}^\dagger|0\rangle, \tag{11.33}$$

$$|2\rangle = \frac{\hat{a}^\dagger}{\sqrt{2}}|1\rangle = \frac{(\hat{a}^\dagger)^2}{\sqrt{2}}|0\rangle, \tag{11.34}$$

$$|3\rangle = \frac{\hat{a}^\dagger}{\sqrt{3}}|2\rangle = \frac{(\hat{a}^\dagger)^3}{\sqrt{3!}}|0\rangle, \tag{11.35}$$

$$\ldots \tag{11.36}$$

$$|n\rangle = \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}}|0\rangle. \tag{11.37}$$

In order to determine the eigenstates in the position representation, we consider:

$$\langle x|\hat{a}|0\rangle = \langle x|\sqrt{\frac{m\omega}{2\hbar}}\hat{x} + i\sqrt{\frac{1}{2m\hbar\omega}}\hat{p}|0\rangle. \tag{11.38}$$

However, $\langle x|\hat{a}|0\rangle = 0$, precisely because of the fact that $\hat{a}|0\rangle = 0$. Therefore, a first order differential equation will ultimately arise from the above equation as follows:

$$\begin{aligned} &\sqrt{\frac{m\omega}{2\hbar}}\langle x|\hat{x}|0\rangle + i\sqrt{\frac{1}{2m\hbar\omega}}\langle x|\hat{p}|0\rangle = 0, \quad \to \\ &\sqrt{\frac{m\omega}{2\hbar}}x\langle x|0\rangle + i\sqrt{\frac{1}{2m\hbar\omega}}(-i\hbar\frac{d}{dx}\langle x|0\rangle) = 0. \end{aligned} \tag{11.39}$$

Since $\langle x|0\rangle = \psi_0(x)$ is the ground-state wavefunction, we obtain from the previous equation the following differential equation for $\psi_0(x)$:

$$\frac{d\psi_0(x)}{dx} = -\frac{m\omega}{\hbar} x\psi_0(x). \tag{11.40}$$

which can be integrated for $\psi_0(x)$ and we find that

$$\psi_0(x) = C\exp(-\frac{m\omega}{2\hbar}x^2), \tag{11.41}$$

and by normalizing this state we find that

$$C = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}. \tag{11.42}$$

Now, how do we determine the first and higher excited states? This is simpler than the previous step where we determined the ground-state wavefunction. The first excited state $|1\rangle$ has the following corresponding wavefunction

$$\begin{aligned}\psi_1(x) = \langle x|1\rangle = \langle x|\hat{a}^\dagger|0\rangle &= \langle x|\sqrt{\frac{m\omega}{2\hbar}}\hat{x} - i\frac{1}{\sqrt{2m\hbar\omega}}\hat{p}|0\rangle, \\ &= \sqrt{\frac{m\omega}{2\hbar}}x\langle x|0\rangle - \sqrt{\frac{\hbar}{2m\omega}}\frac{d}{dx}\langle x|0\rangle. \end{aligned} \tag{11.43}$$

However, since $\langle x|0\rangle = \psi_0(x)$, and since we have already determined $\psi_0(x)$, to determine $\psi_1(x)$ requires a simple differentiation. The result is

$$\psi_1(x) = \sqrt{\frac{2m\omega}{\hbar}}x\psi_0(x). \tag{11.44}$$

In general for the nth excited state we find that

$$\langle x|n\rangle = \frac{1}{\sqrt{2^n n!}}H_n(\sqrt{\frac{m\omega}{\hbar}}x)\psi_0(x), \tag{11.45}$$

where $H_n(\xi)$ is the nth order Hermite polynomial.

11.4 Problems

Problem 1

A particle of mass m is under the influence of a 1D harmonic oscillator (HO) potential with a Hamiltonian of the form

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2. \tag{11.46}$$

Assume that the ground-state wavefunction is a Gaussian of the form

$$\psi(x) = A\exp(-\alpha x^2). \tag{11.47}$$

a) Determine the pre-factor A such that the state $\psi(x)$ is normalized.

b) Calculate the expectation value of the HO Hamiltonian with the state given above as a function of the parameter α, that is,

$$E(\alpha) = \langle \psi | \hat{H} | \psi \rangle. \tag{11.48}$$

c) Determine the parameter α by minimizing the expectation value $E(\alpha)$ with respect to α. What is the value α_0 at which the energy has a minimum?

d) Compare the energy and the wavefunction obtained by using the optimum value α_0 found above, with the exact ground-state energy and wavefunction for the HO.

e) Plot the energy expectation value $E(\alpha)$ as a function of α. In a different figure, plot together the potential as a function of x and the wavefunction as a function of x. Use three different values for α, $\alpha = \alpha_0$, $\alpha = \alpha_0/2$, and $\alpha = 2\alpha_0$. The classical lowest energy state is the one in which the particle is at the minimum of the potential, that is, at $x = 0$, which corresponds to a state obtained as a limit of $\alpha \to \infty$. Explain why. What is the expectation value of the Hamiltonian in this limit?

Problem 2

A particle of mass m is under the influence of a 1D potential of the so-called Lennard–Jones form

$$V(x) = -4\epsilon \left(\left(\frac{\sigma}{x} \right)^6 - \left(\frac{\sigma}{x} \right)^{12} \right), \tag{11.49}$$

with a Hamiltonian of the form

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x). \tag{11.50}$$

a) Draw this potential and show that its minimum is at $x_0/\sigma = 2^{1/6}$.

b) Now assume that the amplitude of the zero-point motion of the particle in the ground state is small; this assumption allows you to expand the potential near the minimum $x = x_0$. Show that the leading term is of the form

$$V(x) = V(x_0) + \frac{1}{2} m\omega^2 (x - x_0)^2, \tag{11.51}$$

namely, there is no linear term in $x - x_0$. What is the value of the parameter ω introduced above?

c) What is the ground-state energy of the Hamiltonian using the harmonic approximation (given by Eq. 11.51) for the potential? What is the ground-state wavefunction?

d) Calculate the expectation value

$$(\Delta x)^2 \equiv \langle \psi_0 | (x - x_0)^2 | \psi_0 \rangle, \tag{11.52}$$

in the ground state within the harmonic approximation (11.51).

e) Find a critical value λ_c for the dimensionless combination

$$\lambda = \frac{\hbar^2}{m\sigma^2 \epsilon}, \tag{11.53}$$

such that for $\lambda > \lambda_c$ there is no bound state.

f) What is the value of $\Delta x/\sigma$ as the value of λ becomes the critical λ_c? Do you think that the harmonic approximation could still be valid for $\lambda = \lambda_c$?

Problem 3

A 1D harmonic oscillator with the familiar Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2, \tag{11.54}$$

is prepared in an initial state with a wavefunction of the following form

$$\phi(x) = Ax^2 \exp(-\frac{m\omega}{2\hbar}x^2). \tag{11.55}$$

a) Find the normalization constant A.

b) Write the above initial state as a linear combination of the eigenstates of the harmonic oscillator.

c) Assume that the harmonic oscillator at $t = 0$ is in a state described by the above wavefunction. Find the state of the system $|\psi(t)\rangle$ at a later time t.

d) Show that the expectation value of $\hat{x}$ is zero at all times. Find the expectation value of $\hat{x}^2$, that is, $\langle\psi(t)|\hat{x}^2|\psi(t)\rangle$ as a function of time. Plot the quantity

$$\sigma(t) = \sqrt{\langle\psi(t)|\hat{x}^2|\psi(t)\rangle}, \tag{11.56}$$

as a function of t. Can you interpret your result?

12

WKB approximation

Here we present a simple way to derive the semiclassical approximation of Wenzel, Kramers, and Brillouin (WKB). This approximation is valid in the limit where the external potential varies smoothly over a length-scale much larger than the particle local de Broglie wavelength as illustrated in Fig. 12.1.

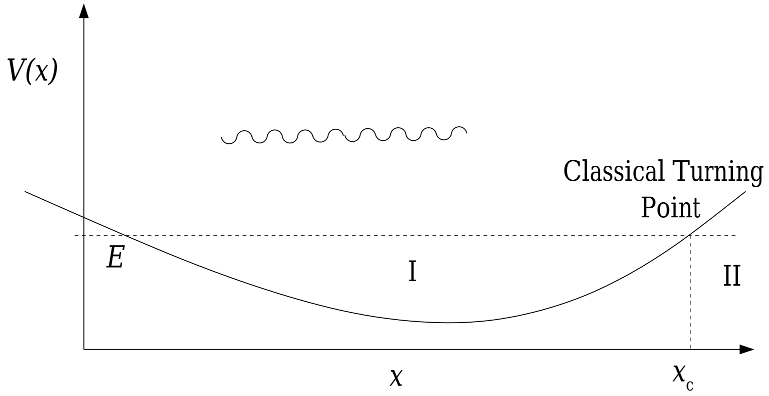

Fig. 12.1 A potential which is slowly varying over a scale much longer than the wavelength of the particle. The wave representing the particle is schematically shown by a wave which varies fast on the scale over which the potential changes. The dashed line is the energy E which we are considering, and the point at x_c is a classical turning point, that is, $V(x_c) = E$, and the region $x > x_c$ is a classically forbidden region.

12.1 The approximation

Let us consider the 1D time-independent Schrödinger equation. A smoothly varying potential introduces smooth variations to the wavelength. The potential should vary over a length-scale much larger than a wavelength. A local "wavelength" may be defined as

$$\lambda(x) = \frac{2\pi\hbar}{p(x)} = \frac{2\pi\hbar}{\sqrt{2m(E - V(x))}}, \tag{12.1}$$

which corresponds to a local "momentum" defined as

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$$p(x) = \sqrt{2m(E - V(x))}. \tag{12.2}$$

In the limit of $\hbar \to 0$, the wavelength $\lambda(x)$ also approaches zero. In such a case any potential appears smooth. So what we need is an asymptotic expansion of the solutions of the Schrodinger equation in $\hbar$. We will find such solutions by writing

$$\psi(x) = e^{\frac{i}{\hbar}S(x)}. \tag{12.3}$$

This is an exact transformation provided that we allow $S(x)$ to be complex. Substituting this expression into the 1D Schrödinger equation yields the following equation for $S(x)$:

$$-S'^2(x) + i\hbar S''(x) + p^2(x) = 0. \tag{12.4}$$

Next, we expand $S(x)$ in powers of $\hbar$, that is,

$$S(x) = S_0(x) + \hbar S_1(x) + \hbar^2 S_2(x) + ... \tag{12.5}$$

and we substitute into the equation for $S(x)$ and obtain an equation of the form

$$a_0(x) + a_1(x)\hbar + ... + a_n(x)\hbar^n + ... = 0. \tag{12.6}$$

Then, by considering $\hbar$ as a variable which takes a continuum of values, all the coefficients $a_n(x)$ for $n = 0, 1, ...$ should independently vanish. This way, we obtain an infinite number of coupled equations, the first two of which (the $a_0(x) = 0$ and $a_1(x) = 0$) are the following:

$$-S_0'^2(x) + p^2(x) = 0, \tag{12.7}$$

$$-2S_0'(x)S_1'(x) + iS_0''(x) = 0. \tag{12.8}$$

If we just keep the zeroth order term above by integrating the first equation we obtain:

$$S_0(x) = S_0(x_0) \pm \int_{x_0}^{x} p(x')dx', \tag{12.9}$$

which implies that the approximate wavefunction can then be written in terms of the phase accumulated from x_0 to x as

$$\psi(x) = \psi(x_0)e^{\pm\frac{i}{\hbar}\int_{x_0}^{x} p(x')dx'}, \tag{12.10}$$

where ± corresponds to the right/left moving wave.

Within the full WKB approximation, we also keep the second equation in Eq. 12.8. After substituting the solution to the first into the second equation and integrating we obtain:

$$S_1(x) = S_1(x_0) + \frac{i}{2}\ln\frac{p(x)}{p(x_0)}. \tag{12.11}$$

Therefore, the WKB wavefunctions are

$$\psi_{\pm}(x) = \psi_{\pm}(x_0)\sqrt{\frac{p(x_0)}{p(x)}}e^{\pm\frac{i}{\hbar}\int_{x_0}^{x} p(x')dx'}. \tag{12.12}$$

Let us discuss an interesting consequence which can be drawn from this resulting WKB expression for the wavefunctions. The probability density $|\psi(x)|^2$ is

$$|\psi(x)|^2 \sim \frac{1}{p(x)}. \tag{12.13}$$

This dependence on the local momentum can be obtained from classical mechanics if we consider a particle confined in some region in space. The probability to find it between x and $x + dx$ is proportional to the time it spends in this interval. This amount of time is given by $mdx/|p(x)|$, which is exactly what the amplitude of the WKB wavefunction yields.

12.2 Region of validity of WKB

In order for the truncation of the infinite series to make sense, which allows us to keep the first few terms in an expansion in powers of $\hbar$, we must require that

$$\left|\frac{S'^2(x)}{\hbar^2}\right| >> \left|\frac{S''(x)}{\hbar}\right| \tag{12.14}$$

which leads to

$$\frac{|p^2(x)|}{\hbar} >> |p'(x)| \qquad \rightarrow \qquad |\frac{d\lambda}{dx}| << 2\pi. \tag{12.15}$$

Clearly, the above conditions are not satisfied for x near the so-called classical turning point x_c which is defined by $V(x = x_c) = E$ (see Fig. 12.1) because the momentum at such a turning point vanishes: $p(x_c) = 0$. The WKB approximation breaks down in the vicinity of such turning points, as is clear from the divergence of the wavefunctions. Exactly how close to the turning point do we need to be so that we can no longer trust the WKB approximation?

In the vicinity of a turning point x_c, we expand the potential $V(x)$ and we keep only linear terms

$$V(x) = V(x_c) + V'(x_c)(x - x_c), \qquad V(x_c) = E. \tag{12.16}$$

The linearized approximation Eq. 12.16 is valid when the second order term is small compared to the first-order term in the expansion (12.16). Namely, it is valid in the region:

$$|x - x_c| << \frac{2|V'(x_c)|}{|V''(x_c)|}. \tag{12.17}$$

In this regime where the linearization is valid we can write

$$p^2(x) = 2m(E - V(x)) \simeq -2mV'(x_c)(x - x_c). \tag{12.18}$$

Using this linearized approximation near x_c, the condition for the validity of WKB, that is, Eq. 12.15 becomes

$$|x - x_c| >> \frac{\hbar^{2/3}}{2(mV'(x_c))^{1/3}}. \tag{12.19}$$

As expected as $\hbar \to 0$, the region where WKB breaks down shrinks.

12.3 Exact solution near a turning point

For x sufficiently close to the turning point x_c the Schrödinger equation becomes

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V'(x_c)(x - x_c)\psi(x) = 0. \tag{12.20}$$

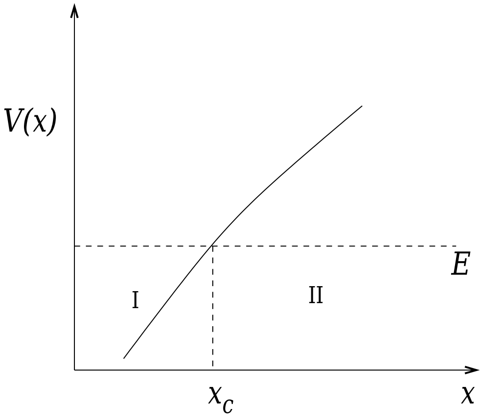

Fig. 12.2

Now consider a turning point as shown in Fig. 12.2 where the slope of the potential at the turning point is positive. Using the following scale transformation

$$\xi = \left(\frac{2mV'(x_c)}{\hbar^2}\right)^{\frac{1}{3}}(x - x_c), \tag{12.21}$$

it is straightforward to show that the Schrödinger equation takes the form

$$\frac{d^2\psi}{d\xi^2} - \xi\psi = 0. \tag{12.22}$$

This is known as the Airy or Stokes equation. Its solutions are the Airy functions $Ai(\xi)$ and $Bi(\xi)$. So, a general solution is of the form

$$\psi(\xi) = \psi_1(\xi) + \psi_2(\xi), \tag{12.23}$$

$$\psi_1(\xi) = aAi(\xi), \qquad \psi_2(\xi) = bBi(\xi). \tag{12.24}$$

What we need from this problem is only the asymptotic behavior of each of the individual solutions given by

$$Ai(\xi \to +\infty) \to \frac{1}{2\sqrt{\pi}\xi^{1/4}} e^{-\frac{2}{3}\xi^{\frac{3}{2}}}, \tag{12.25}$$

$$Bi(\xi \to +\infty) \to \frac{1}{\sqrt{\pi}\xi^{1/4}} e^{\frac{2}{3}\xi^{\frac{3}{2}}}, \tag{12.26}$$

and

$$Ai(\xi \to -\infty) \to \frac{1}{\sqrt{\pi}|\xi|^{1/4}} \sin\Big(\frac{2}{3}|\xi|^{3/2} + \frac{\pi}{4}\Big), \tag{12.27}$$

$$Bi(\xi \to -\infty) \to \frac{1}{\sqrt{\pi}|\xi|^{1/4}} \cos\Big(\frac{2}{3}|\xi|^{3/2} + \frac{\pi}{4}\Big). \tag{12.28}$$

As will become clear, we will need to asymptotically match the WKB solution with the exact solution of the linearized Schrödinger equation in the region where there is overlap of the validity of the two methods.

In this limit, the first part, that is, $aAi(\xi)$ of the general solution to the linearized equation can be written

$$\psi_1(x \to x_c^-) = \frac{F}{\sqrt{p(x)}} \sin\Big[\frac{1}{\hbar}\int_x^{x_c} p(x')dx' + \frac{\pi}{4}\Big], \tag{12.29}$$

$$\psi_1(x \to x_c^+) = \frac{F}{2\sqrt{|p(x)|}} e^{-\frac{1}{\hbar}\int_{x_c}^{x} |p(x')|dx'}. \tag{12.30}$$

One may show, by carrying out the integrals above, that we obtain the asymptotic forms Eq. 12.25 and Eq. 12.27 above.

In addition, it can easily be shown that the second part $bBi(x)$ of the general solution to the linearized equation can be written as:

$$\psi_2(x \to x_c^-) = \frac{G}{\sqrt{p(x)}} \cos\Big[\frac{1}{\hbar}\int_x^{x_c} p(x')dx' + \frac{\pi}{4}\Big], \tag{12.31}$$

$$\psi_2(x \to x_c^+) = \frac{G}{\sqrt{|p(x)|}} e^{\frac{1}{\hbar}\int_{x_c}^{x} |p(x')|dx'}. \tag{12.32}$$

One may show, by carrying out the integrals above, that we obtain the asymptotic forms Eq. 12.26 and Eq. 12.28 above.

Now, we consider the case where the potential has a negative slope as shown in Fig. 12.3. It is straightforward to show that using the following scale transformation

$$\xi = \Big(\frac{-2mV'(x_c)}{\hbar^2}\Big)^{\frac{1}{3}}(x_c - x), \tag{12.33}$$

the Schrödinger equation takes the same form as before, that is, the form of the Airy equation (Eq. 12.22).

In this limit, the first part, that is, $aAi(\xi)$, of the general solution to the linearized equation can be written as

$$\psi_1(x \to x_c^+) = \frac{F'}{\sqrt{p(x)}} \sin\Big[\frac{1}{\hbar}\int_{x_c}^{x} p(x')dx' + \frac{\pi}{4}\Big], \tag{12.34}$$

$$\psi_1(x \to x_c^-) = \frac{F'}{2\sqrt{|p(x)|}} \exp\Big[-\frac{1}{\hbar}\int_{x}^{x_c} |p(x')|dx'\Big]. \tag{12.35}$$

In addition, we can show that the second part $bBi(x)$ of the general solution to the linearized equation can be written as:

$$\psi_2(x \to x_c^+) = \frac{G'}{\sqrt{p(x)}} \cos\Big[\frac{1}{\hbar}\int_{x_c}^{x} p(x')dx' + \frac{\pi}{4}\Big], \tag{12.36}$$

$$\psi_2(x \to x_c^-) = \frac{G'}{\sqrt{|p(x)|}} \exp\Big[\frac{1}{\hbar}\int_{x}^{x_c} |p(x')|dx'\Big]. \tag{12.37}$$

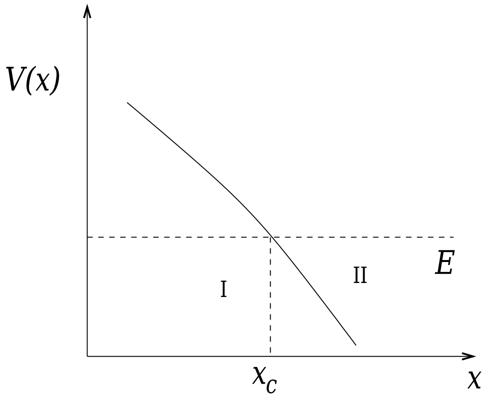

Fig. 12.3

12.4 Matching of WKB and exact solution: right turning point

We will need to asymptotically match the WKB solution with the exact solution of the linearized Schrödinger equation in the region where there is overlap of the validity of the two methods.

First notice that as $\hbar \to 0$ not only the region of invalidity of the WKB approximation near the turning point shrinks, which makes the overlap region with the exact solution of the linearized equation larger, but, in addition, as can be seen from Eq. 12.21, $\lim_{\hbar\to 0} \xi \to \infty$ or $-\infty$ depending on whether we are above or below the turning point respectively if the slope of the potential is positive. Keeping the distance from the turning point $|x - x_c|$ constant and within the validity of WKB (by letting $\hbar \to 0$) we find that as $\hbar \to 0$, $\xi \to \pm\infty$ which allows us to use the asymptotic forms of the Airy functions to match with the WKB solutions.

Now, we can write the WKB solution as follows:

$$\psi_{WKB}(x < x_c) = \frac{A}{\sqrt{p(x)}} \sin\Big[\int_x^{x_c} p(x')\frac{dx'}{\hbar} + \alpha\Big], \tag{12.38}$$

$$\psi_{WKB}(x > x_c) = \frac{B}{\sqrt{|p(x)|}} e^{-\frac{1}{\hbar}\int_x^{x_c} |p(x')| dx'}. \tag{12.39}$$

Forming a general linear combination of the two solutions given by Eq. 12.12 leads to the above expression (12.38) where the two constants A and α are to be determined by boundary conditions: this means by matching it with the exact asymptotic solution to the linearized equation given by Eq. 12.25. In Region II, there are also two WKB solutions, one given by Eq. 12.39 above and another with a positive exponential which is excluded because it goes to infinity as $x \to \infty$. While the constants A, B, and α are unrelated within WKB, using the asymptotic match with the exact solution (Eq. 12.29 and Eq. 12.30) near the turning point, they will be constrained to be:

$$A = F, \qquad B = F/2, \quad \alpha = \frac{\pi}{4}, \tag{12.40}$$

and the WKB solutions become

$$\psi_{WKB}(x < x_c) = \frac{F}{\sqrt{p(x)}} \sin\Big[\int_x^{x_c} p(x')\frac{dx'}{\hbar} + \frac{\pi}{4}\Big], \tag{12.41}$$

$$\psi_{WKB}(x > x_c) = \frac{F}{2\sqrt{|p(x)|}} e^{-\frac{1}{\hbar}\int_x^{x_c} |p(x')| dx'}. \tag{12.42}$$

Now, the wavefunction has only one common undetermined coefficient F which is to be determined by whatever boundary condition exists on the left.

12.5 Two turning points: bound states

Here, we consider the case of the two turning points shown in the case of the potential in Fig. 12.1 and we will call x_1 the left turning point where the slope of the potential is negative and x_2 the right turning point where the slope of the potential is positive.

The WKB solution for turning point x_2 is the one which we have derived in the previous section, that is,

$$\psi_{WKB}(x < x_2) = \frac{F}{\sqrt{p(x)}} \sin\Big[\int_x^{x_2} p(x')\frac{dx'}{\hbar} + \frac{\pi}{4}\Big], \tag{12.43}$$

$$\psi_{WKB}(x > x_2) = \frac{F}{2\sqrt{|p(x)|}} e^{-\frac{1}{\hbar}\int_{x_2}^{x} |p(x')| dx'}. \tag{12.44}$$

For the left turning point x_1 we can do a similar calculation as we did in the previous section for the right turning point. We find that:

$$\psi_{WKB}(x < x_1) = \frac{G}{2\sqrt{|p(x)|}} e^{-\int_x^{x_1} |p(x')| \frac{dx'}{\hbar}}, \tag{12.45}$$

$$\psi_{WKB}(x > x_1) = \frac{G}{\sqrt{p(x)}} \sin\Big[\int_{x_1}^{x} p(x')\frac{dx'}{\hbar} + \frac{\pi}{4}\Big]. \tag{12.46}$$

Now, the solution for $x > x_1$ and the one for $x < x_2$ should match and, therefore, we find that we must require that

$$F \sin\Big[\int_x^{x_2} p(x')\frac{dx'}{\hbar} + \frac{\pi}{4}\Big] = G \sin\Big[\int_{x_1}^{x} p(x')\frac{dx'}{\hbar} + \frac{\pi}{4}\Big]. \tag{12.47}$$

This should be valid for a continuum of x values in the interval $x_1 < x < x_2$. We can satisfy this requirement by rewriting the sin in the right-hand-side of the above equation as follows:

$$\begin{aligned} &\sin\Big[-\frac{1}{\hbar}\int_x^{x_2} p(x')\frac{dx'}{\hbar} + \frac{1}{\hbar}\int_{x_1}^{x_2} p(x')\frac{dx'}{\hbar} + \frac{\pi}{4}\Big] \\ &= -\sin\Big[\int_x^{x_2} p(x')\frac{dx'}{\hbar} - \int_{x_1}^{x_2} p(x')\frac{dx'}{\hbar} - \frac{\pi}{4}\Big], \\ &= -\sin\Big[\int_x^{x_2} p(x')\frac{dx'}{\hbar} + \frac{\pi}{4} - \int_{x_1}^{x_2} p(x')\frac{dx'}{\hbar} - \frac{\pi}{2}\Big]. \end{aligned} \tag{12.48}$$

Now, because $\sin(\phi + m\pi) = (-1)^m \sin(\phi)$ where m can be taken to be a negative integer, it becomes clear that if we require that

$$F = (-1)^{m+1}G, \tag{12.49}$$

$$-\frac{1}{\hbar}\int_{x_1}^{x_2} p(x')dx' - \frac{\pi}{2} = m\pi, \tag{12.50}$$

$$m = -1, -2, -3, ..., \tag{12.51}$$

the left and right solutions match. Finally, we can write the last equation as follows

$$\oint dx' p(x') \equiv 2\int_{x_1}^{x_2} p(x')dx' = 2\pi\hbar(n + \frac{1}{2}), \tag{12.52}$$

where $n = -m - 1 = 0, 1, 2, ...$, which is the old Bohr–Sommerfeld quantization condition.

12.6 Tunneling within the WKB approximation

Consider the problem of tunneling through a barrier as illustrated in Fig. 12.4 within the WKB approximation.

In Region I, we can write the WKB wavefunction as a linear combination of an incident and a reflected wave, that is,

$$\psi_I(x) = \frac{A_I}{\sqrt{p(x)}} e^{\frac{i}{\hbar}\int_{x_1}^{x} dx' p(x')} + \frac{B_I}{\sqrt{p(x)}} e^{-\frac{i}{\hbar}\int_{x_1}^{x} dx' p(x')}. \tag{12.53}$$

In Region II, which is the classically forbidden region, because $E < V(x)$ for $x_1 < x < x_2$, we write the wavefunction as a sum of two exponentials

$$\psi_{II}(x) = \frac{A_{II}}{\sqrt{|p(x)|}} e^{-\frac{1}{\hbar}\int_{x_1}^{x} dx' |p(x')|} + \frac{B_{II}}{\sqrt{p(x)}} e^{\frac{1}{\hbar}\int_{x_1}^{x} dx' |p(x')|}. \tag{12.54}$$

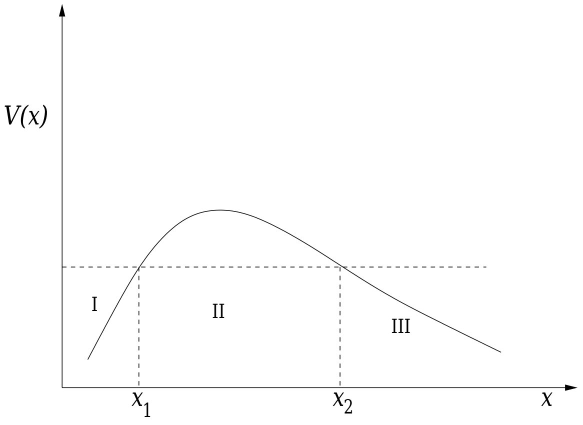

Fig. 12.4

In Region III, because we have no other wave coming from $+\infty$, we write the wavefunction as

$$\psi_{III}(x) = \frac{A_{III}}{\sqrt{p(x)}} e^{\frac{i}{\hbar}\int_{x_2}^{x} dx' p(x')}. \tag{12.55}$$

We need to relate these coefficients. However, boundary conditions at $x = x_1$ and $x = x_2$ are not applicable because these WKB wavefunctions become less and less valid as we approach these turning points.

We will use the approach established in the previous two sections, where by asymptotically matching the solutions with the exact solutions in the vicinity of each turning point, we end up relating the coefficients of the above WKB wavefunctions.

We can rewrite the above wavefunctions in each region so that they acquire the same form with the exact solutions found in the previous problem. In Region I, we rewrite the WKB solution to have the following form:

$$\begin{aligned}\psi_I(x) = {} & \frac{a_I}{\sqrt{p(x)}} \cos\Big(\frac{1}{\hbar}\int_x^{x_1} dx' p(x') + \alpha_I\Big), \\ & + \frac{b_I}{\sqrt{p(x)}} \sin\Big(-\frac{1}{\hbar}\int_x^{x_1} dx' p(x') + \beta_I\Big). \end{aligned} \tag{12.56}$$

where the real quantities: a_I, α_I, b_I, β_I are related to the coefficients A_I and B_I as follows:

$$A_I = \frac{1}{2}\Big(i a_I e^{-i\alpha_I} + b_I e^{-i\beta_I}\Big), \tag{12.57}$$

$$B_I = \frac{1}{2}\Big(-i a_I e^{i\alpha_I} + b_I e^{-i\beta_I}\Big). \tag{12.58}$$

Next, we apply asymptotic matching in the vicinity of $x = x_1$ with the exact solutions of the linearized equation. We use the forms introduced in Section 12.3, allowing for a linear combination of an $Ai(\xi)$ and $Bi(\xi)$ for the general solution. This determines the phases and relates the coefficients of the solutions in Regions I and II. We find that

$$\alpha_I = \frac{\pi}{4}, \qquad \beta_I = \frac{\pi}{4}, \tag{12.59}$$

$$a_I = 2A_{II}, \qquad b_I = B_{II}. \tag{12.60}$$

We need to express the wavefunction in Region II using the turning point x_2 as reference, that is, as follows

$$\psi_{II}(x) = \frac{A'_{II}}{\sqrt{|p(x)|}} e^{-\frac{1}{\hbar}\int_x^{x_2} dx' |p(x')|} + \frac{B'_{II}}{\sqrt{p(x)}} e^{\frac{1}{\hbar}\int_x^{x_2} dx' |p(x')|}. \tag{12.61}$$

In order for the two different forms of the same wavefunction, that is, Eq. 12.54 and Eq. 12.61, to be consistent, the coefficients A'_{II} and B'_{II} should be related to the coefficients A_{II} and B_{II} in the following way:

$$B_{II} = \lambda A'_{II}, \qquad A_{II} = B'_{II}/\lambda, \tag{12.62}$$

$$\lambda \equiv e^{-\frac{1}{\hbar}\int_{x_1}^{x_2} |p(x')| dx'}. \tag{12.63}$$

Now, we rewrite the wavefunction in region III as

$$\begin{aligned}\Psi_{III}(x) = \frac{|A_{III}|}{\sqrt{p(x)}} \Big(&\cos(\frac{1}{\hbar}\int_{x_2}^{x} p(x')dx' + \alpha_{III}) \\ &+ i\sin(\frac{1}{\hbar}\int_{x_2}^{x} p(x')dx' + \alpha_{III}) \Big).\end{aligned} \tag{12.64}$$

The purpose of doing this is in order to match these WKB solutions for Regions II and III with the exact solution at the turning point x_2. Using forms introduced in Section 12.3 for a left turning point, we find that

$$\alpha_{III} = \frac{\pi}{4}, \tag{12.65}$$

$$|A_{III}| = B'_{II}, \tag{12.66}$$

$$i|A_{III}| = 2A'_{II}. \tag{12.67}$$

Our plan is to calculate the relative transmission probability through the barrier, defined in the usual way as

$$P_{trans} = \frac{|A_{III}|^2}{|A_I|^2}. \tag{12.68}$$

In order to calculate this we need to express both $|A_{III}|$ and $|A_I|$ in terms of the same variable and take the ratio. We choose this variable to be B'_{II}. For $|A_{III}|$, this is achieved through Eq. 12.66 and for A_I this is achieved using Eq. 12.57 and Eqs 12.60. We find that

$$A_I = \frac{1}{2}\Big(2iA_{II} + B_{II}\Big)e^{-i\pi/4}. \tag{12.69}$$

Then, by combining Eq. 12.66 and Eq. 12.67 we find that $iB'_{II} = 2A'_{II}$. Using this relation and Eq. 12.62 we find that

$$A_I = i(\frac{1}{\lambda} + \frac{\lambda}{4})B'_{II}e^{-i\pi/4}. \tag{12.70}$$

Therefore,

$$P_{trans} = \frac{4}{|\frac{2}{\lambda} + \frac{\lambda}{2}|^2}. \tag{12.71}$$

In the limit where $\lambda << 1$, we find that

$$P_{trans} \simeq \lambda = e^{-\frac{1}{\hbar}\int_{x_1}^{x_2}|p(x')|dx'}. \tag{12.72}$$

This is the well-known WKB result for the probability for tunneling through a potential barrier.

12.7 Problems

Problem 1

Show by carrying out the integrals in Eq. 12.29 and Eq. 12.30 that you obtain the asymptotic forms Eq. 12.25 and Eq. 12.27 above. Show that $F = D(2m\hbar V'(x_c)/\sqrt{\pi})^{1/6}$.

Problem 2

Show by carrying out the integrals in Eq. 12.31 and Eq. 12.32 that you obtain the asymptotic forms Eq. 12.26 and Eq. 12.28 above. What is the common constant G which you obtain?

Problem 3

Consider the WKB approximation for a particle in a symmetric double-well potential. Assume that the energy of the particle is below the top of the barrier.

Show that the condition which determines the energy eigenvalues is the following

$$\tan(\frac{1}{\hbar}\int_{x_1}^{x_2} p(x)dx + \alpha) = \pm 2\exp(\int_{x_1}^{x_2} |p(x)|dx), \tag{12.73}$$

where x_1 and x_2 are the classical turning points in one of the separate wells and α is a constant which depends on the boundary conditions.

13

Quantum mechanics and path integrals

In this chapter we discuss the Feymann path-integral approach to quantum mechanics. First we derive a path-integral expression for the evolution operator. While we work in 1D, the approach can be straightforwardly generalized to any number of dimensions. Next we show that the classical equations of motion, that is, those obtained from the least-action principle, are obtained from the path-integral formulation in the limit where the variation in the action of the problem at hand is small compared to $\hbar$. Last, we discuss how the WKB approximation is derived from the path-integral formulation.

13.1 Derivation of the path integral in 1D

Consider a particle in 1D which is described by a time-independent Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}) = \hat{T} + V(\hat{x}). \tag{13.1}$$

We are interested in finding the probability amplitude $K(x, t; x_0, 0)$ for the particle to be in position x at time t given that at $t = 0$ the particle was in position x_0. Under the influence of the time-independent Hamiltonian for elapsed time t, the particle is in the state

$$|\psi\rangle = e^{-\frac{i}{\hbar}\hat{H}t}|x_0\rangle. \tag{13.2}$$

Therefore, the probability amplitude $K(x, t; x_0, 0)$ is given as follows:

$$K(x, t; x_0, 0) = \langle x|\psi\rangle = \langle x|e^{-\frac{i}{\hbar}\hat{H}t}|x_0\rangle. \tag{13.3}$$

How do I calculate this matrix element? Let us consider the free case ($H = \hat{T}$) first, where:

$$\begin{aligned} K_0(x, t; x_0, 0) &= \langle x|\exp(-\frac{i}{\hbar}\frac{\hat{p}^2}{2m}t)|x_0\rangle \\ &= \int \frac{dp}{2\pi\hbar}\langle x|\exp(-\frac{i}{\hbar}\frac{\hat{p}^2}{2m}t)|p\rangle\langle p|x_0\rangle \\ &= \int \frac{dp}{2\pi\hbar}\exp(-\frac{i}{\hbar}\frac{p^2}{2m}t)\langle x|p\rangle\langle p|x_0\rangle, \end{aligned} \tag{13.4}$$

Practical Quantum Mechanics. First Edition. Efstratios Manousakis.

where I have inserted the unit operator $\int \frac{dp}{2\pi\hbar}|p\rangle\langle p|$, where $|p\rangle$ are the momentum operator eigenstates. We recall that $\langle x|p\rangle = e^{\frac{i}{\hbar}px}$ and we write:

$$K_0(x,t;x_0,0) = \int \frac{dp}{2\pi\hbar} e^{-\frac{it}{2m\hbar}\left(p^2 - \frac{2m}{t}(x-x_0)p\right)}. \tag{13.5}$$

Once again we are facing a Gaussian integral; we can do it by completing the square in the exponential by adding and subtracting the square of the constant $c = m(x-x_0)/t$. The final result is

$$K_0(x,t;x_0,0) = \sqrt{\frac{m}{2\pi\hbar ti}} \exp\Big[\frac{i}{\hbar}\frac{m(x-x_0)^2}{2t}\Big]. \tag{13.6}$$

Notice that if we were working in imaginary time, we would obtain

$$K_0(x,\tau;x_0,0) = \sqrt{\frac{m}{2\pi\hbar\tau}} \exp\Big[-\frac{1}{\hbar}\frac{m(x-x_0)^2}{2t}\Big], \tag{13.7}$$

which describes diffusion of the particle.

Now, how do we proceed if $V(x) \neq 0$? One straightforward approach is to assume that we have solved the eigenvalue problem of $\hat{H}$, that is, we found the eigenstates $|\psi_n\rangle$ and corresponding eigenvalues E_n of the Hamiltonian operator and using the completeness relation

$$\sum_n |\psi_n\rangle\langle\psi_n| = \hat{1} \tag{13.8}$$

we can write

$$\begin{aligned} K(x,t;x_0,0) &= \sum_n \langle x|e^{-\frac{i}{\hbar}\hat{H}t}|\psi_n\rangle\langle\psi_n|x_0\rangle \\ &= \sum_n e^{\frac{-i}{\hbar}E_n t}\psi_n^*(x_0)\psi_n(x). \end{aligned} \tag{13.9}$$

This expression, however, requires the full diagonalization of the Hamiltonian and to carry out the sum in the above equation which in general has infinite terms.

Here, we are going to follow Feynmann's approach. We can break the exponential operator in Eq. 13.3 in a product of M terms, such that $M\Delta t = t$, as follows:

$$\exp\Big(-\frac{i}{\hbar}\hat{H}t\Big) = \exp\Big(-\frac{i}{\hbar}\hat{H}\Delta t\Big)\exp\Big(-\frac{i}{\hbar}\hat{H}\Delta t\Big)...\exp\Big(-\frac{i}{\hbar}\hat{H}\Delta t\Big). \tag{13.10}$$

Then, we insert the identity $\int dx'|x'\rangle\langle x'| = \hat{1}$ $M-1$ times between every two successive factors above and so the expression given by Eq. 13.3 takes the following form:

$$\begin{aligned} &K(x,t;x_0,0) = \langle x|\exp\Big(-\frac{i}{\hbar}\hat{H}t\Big)|x_0\rangle = \\ &\int dx_1 dx_2...dx_{M-1}\langle x|e^{-\frac{i}{\hbar}\hat{H}\Delta t}|x_{M-1}\rangle \\ &\times \langle x_{M-1}|e^{-\frac{i}{\hbar}\hat{H}\Delta t}|x_{M-2}\rangle...\langle x_1|e^{-\frac{i}{\hbar}\hat{H}\Delta t}|x_0\rangle. \end{aligned} \tag{13.11}$$

Thus, we need to figure out how to calculate the quantity

$$K(x_{x+1}, \Delta t; x_n, 0) = \langle x_{n+1}| \exp\Big(-\frac{i}{\hbar}\hat{H}\Delta t\Big)|x_n\rangle, \tag{13.12}$$

for small Δt. Since Δt is infinitesimally small, we are going to use the so-called Trotter approximation or breakup:

$$\exp\Big(-\frac{i}{\hbar}(\hat{T}+\hat{V})\Delta t\Big) \simeq \exp\Big(-\frac{i}{\hbar}\hat{T}\Delta t\Big)\exp\Big(-\frac{i}{\hbar}\hat{V}\Delta t\Big), \tag{13.13}$$

and the correction is of the order of $O((\Delta t)^2)$. For our purposes this approximation, which is correct only to linear order in Δt, as we will see in a few steps, is going to be good enough. Therefore, we obtain

$$\begin{aligned}\langle x_{n+1}| \exp\Big(-\frac{i}{\hbar}(\hat{T}+\hat{V})\Delta t\Big)|x_n\rangle \simeq{}& \langle x_{n+1}|e^{-\frac{i}{\hbar}\hat{T}\Delta t}|x_n\rangle \\ &\times e^{-\frac{i}{\hbar}\hat{V}(x_n)\Delta t},\end{aligned} \tag{13.14}$$

and in order to obtain the above expression we have used the fact that $|x_n\rangle$ is an eigenstate of any function $f(\hat{x})$ of the operator $\hat{x}$ with eigenvalue $f(x_n)$. Therefore, we conclude that

$$K(x_{x+1}, \Delta t; x_n, 0) \simeq K_0(x_{x+1}, \Delta t; x_n, 0)e^{-\frac{i}{\hbar}\hat{V}(x_n)\Delta t}, \tag{13.15}$$

where we have already computed the free propagator and so the final expression is given by

$$K(x_{x+1}, \Delta t; x_n, 0) \simeq c e^{\frac{i}{\hbar}\left[\frac{m(x_{n+1}-x_n)^2}{2\Delta t} - \hat{V}(x_n)\Delta t\right]}, \tag{13.16}$$

and as discussed before, we have neglected terms of order $O((\Delta t)^2)$.

Therefore, the original integral (Eq. 13.11) takes the following compact form:

$$K(x, t; x_0, 0) \simeq C\int\prod_{n=1}^{M-1} dx_n e^{\frac{i}{\hbar}S}, \tag{13.17}$$

$$S \equiv \sum_{n=1}^{M-1}\Big[\frac{1}{2}m(\frac{x_{n+1}-x_n}{\Delta t})^2 - \hat{V}(x_n)\Big]\Delta t, \tag{13.18}$$

$$C = \Big[\frac{m}{2\pi\hbar\delta t i}\Big]^{M-1}. \tag{13.19}$$

In the limit of $\Delta t \to 0$ and $M \to \infty$, while keeping the product $M\delta t$ constant and equal to the elapsed time t, we can formally write:

$$K(x,t;x_0,0) = C\int \mathcal{D}[x(t)]e^{\frac{i}{\hbar}S}, \tag{13.20}$$

$$S \equiv \int_0^t \Big[\frac{1}{2}m(\frac{dx}{dt'})^2 - \hat{V}(x(t'))\Big]dt', \tag{13.21}$$

$$\mathcal{D}[x(t)] \equiv \lim_{M\to\infty}\prod_{n=1}^{M-1} dx_n, \tag{13.22}$$

$$C = \lim_{M\to\infty}\Big[\frac{mt}{2\pi\hbar M i}\Big]^{M-1}. \tag{13.23}$$

Notice that, now, we have replaced the $\simeq$ sign by the equal sign because the terms of order $O((\Delta t)^2)$ make no contribution since Δt is infinitesimal, only the linear terms in Δt survive in the exponent and lead to the integral over dt. In practice, however, in order to calculate the above integral, which is a functional integral, an integral over paths, one would need to go back to a the discrete number of integrals and then take the limit of $\Delta t \to 0$. In this process one needs to make sure that the corrections of order $(\Delta t)^2$ are removed in a controlled way.

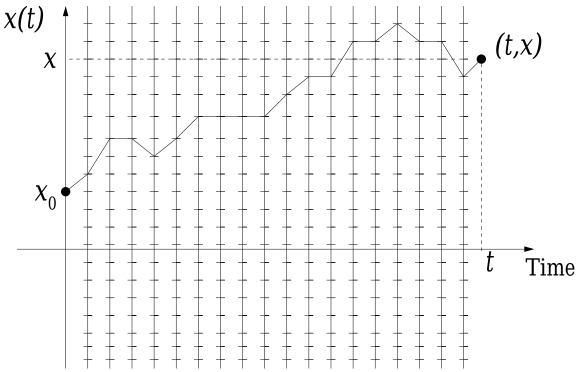

Fig. 13.1

In Fig. 13.1 we illustrate the meaning of this functional integration. First, there are $M-1$ integrations over x_1, x_2, ..., x_{M-1}. These are shown by the $M-1$ vertical lines which are placed at $t_1 = \Delta t$, $t_2 = 2\Delta t$, ..., $t_{M-1} = M\Delta t$. There is nothing peculiar or special about where we placed these x-integration axes, we just placed them at different times to remind us that they come due to our introducing the completeness associated with this particular x variable in this particular "time slice." In addition, the "time derivative" of x used in the above expression given by Eq. 13.23 is meant in this sense, namely that in order to define $dx/dt = \lim_{\Delta\to 0}(x_{n+1}-x_n)/\Delta t$ the values of x_{n+1} and of x_n should be close to each other, but they may not be. Now, the product of the $M-1$ integrals, if we also discretize each spatial integral, becomes a product of $M-1$ sums. This product can be written as a sum over all possible products of terms. An example of such terms is shown in Fig. 13.1. In this sense we are thinking of the above infinite product of integrals as a path integral. This is illustrated in Fig. 13.2

where the integration variable is an entire path with fixed end points, that is, the integration is over paths which start at x_0 at $t = 0$ and end at x at time t.

As a result we can formally write the integral as follows

$$K(x, t; x_0, 0) = C \int_{x(0)=x_0}^{x(t)=x} \mathcal{D}[x(t)] e^{\frac{i}{\hbar} S(\{x(t)\})}, \tag{13.24}$$

$$S(\{x(t)\}) \equiv \int_0^t L(x(t'), \dot{x}(t'))dt', \tag{13.25}$$

$$L(x(t), \dot{x}(t)) = \frac{1}{2} m\dot{x}^2(t) - \hat{V}(x(t)). \tag{13.26}$$

Namely, the path integral is over all possible paths connecting the initial and final position at time t. Each path contributes the same magnitude but with a different phase. The phase is just $S/\hbar$, where S is the action of this path. Schematically,

$$K(x, t; x_0, 0) = C \sum_{paths: x(0)=x_0}^{x(t)=x} \exp\Big(\frac{i}{\hbar} S(path)\Big). \tag{13.27}$$

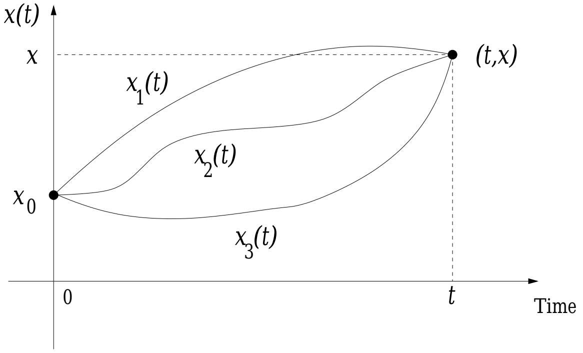

Fig. 13.2

In simulations, the fractal dimension of the path contributing to the integral is 2, reminding us of the fact that in quantum mechanics the velocity is not defined and if you zoom in on any path you will find that there is more and more structure to it at any length scale.

13.2 Classical mechanics as limit of quantum mechanics

Here we would like to take the limit of $\hbar \to 0$. This means the limit where $\hbar$ is small as compared to any other action in the problem, such as the integral of the kinetic energy of the particle. So, what types of paths, subject to the constraints $x(0) = x_0$, $x(t) = x$, contribute the most to the integral in this limit?

To make the question clearer, let us consider the contribution of two such paths $x_1(t)$ and $x_2(t)$ to the path integral, that is,

$$e^{\frac{i}{\hbar}S(x_1)} + e^{\frac{i}{\hbar}S(x_2)} = e^{\frac{i}{\hbar}S(x_1)}(1 + e^{\frac{i}{\hbar}(S(x_2)-S(x_1))}). \tag{13.28}$$

Clearly, the combined contribution of two paths which differ in action significantly, such that $\delta S/\hbar \sim \pi$, is zero. However, in the limit with $\hbar \to 0$, the phases of paths with even close action wildly differ and their combined contribution will vanish. Only paths near the extrema of S (extrema with respect to variations in $x(t)$) will contribute because the linear deviations from such paths give no contribution of δS. Thus, only paths which make S stationary will contribute in the limit of $\hbar \to 0$, namely:

$$\frac{\delta S(\{x(t)\})}{\delta x(t)} = 0. \tag{13.29}$$

This variation under the constraints that $x(0) = x_0$ and $x(t) = x$ leads to the Lagrange equations of classical mechanics:

$$\frac{d}{dt}\frac{\partial L(x,\dot{x})}{\partial \dot{x}} = \frac{\partial L(x,\dot{x})}{\partial x}, \tag{13.30}$$

which leads to Newton's equation of motion for the single particle problem described by the Hamiltonian (13.1) under consideration here:

$$m\ddot{x} = -\frac{dV(x)}{dx}, \qquad x(0) = x_0, \qquad x(t) = x, \tag{13.31}$$

where its solution is the classical path $x(t) = x_c(t)$ connecting the positions x_0 and x at $t = 0$ and at time t respectively.

The fact that the least action condition leads to the Lagrange equation of classical mechanics can be obtained as follows. We consider small deviations in a given path and the change this causes in the action is obtained as

$$\delta S = \int_0^t dt' \Big(\delta x(t')\frac{\partial L}{\partial x} + \delta\dot{x}(t')\frac{\partial L}{\partial \dot{x}}\Big). \tag{13.32}$$

We can rewrite the second terms as follows:

$$\begin{aligned}\delta S = &\int_0^t dt' \delta x(t')\Big(\frac{\partial L}{\partial x} - \frac{d}{dt'}\frac{\partial L}{\partial \dot{x}}\Big)\\ &+ \int_0^t dt' \frac{d}{dt'}\Big(\delta x(t')\frac{\partial L}{\partial \dot{x}}\Big).\end{aligned} \tag{13.33}$$

Notice that the second term is the total time derivative so it is equal to the function $\delta x(t)\frac{\partial L}{\partial \dot{x}}$ evaluated at the limits of integration. At the limits $t = 0$ and t of the integration $\delta x(t)$ vanishes because all paths are subject to the initial and final condition. Therefore, the conclusion is that the first term vanishes for all independent path variations, which leads to the Lagrange equation (13.30).

13.3 WKB from path integrals

First, the following equation holds between the wavefunction at $t = 0$ and the wavefunction at t:

$$\psi(x,t) = \int dx' K(x,t;x',0)\psi(x',0), \tag{13.34}$$

and this follows in a straightforward manner from the evolution of the state vector

$$|\psi(t)\rangle = \exp\Big(\frac{i}{\hbar}\hat{H}t\Big)|\psi(0)\rangle. \tag{13.35}$$

Because of the facts that the wavefunction is given by $\psi(x,t) = \langle x|\psi(t)\rangle$ and $K(x,t,;x',0)$ is given by Eq. 13.3, Eq. 13.34 follows as a direct consequence of these facts.

Suppose that the system is prepared at some initial state given by the Gaussian wavefunction

$$\psi(x,0) = \frac{1}{(2\pi\sigma^2)^{1/4}}\exp(-\frac{(x-x_0)^2}{4\sigma^2}). \tag{13.36}$$

Notice that we have chosen the constants such that

$$\int dx|\psi(x,0)|^2 = 1, \tag{13.37}$$

and we shall consider the limit of $\sigma \to 0$, when the particle can be said to be localized at $x = x_0$. Starting from this initial wavefunction, the wavefunction at a later time t and for small σ is obtained from Eq. 13.34 as

$$\psi(x,t) = c_0 K(x,t;x_0,0), \tag{13.38}$$

where $c_0 = (2\sqrt{2\pi}\sigma)^{1/2}$ is a constant. We have shown that in the limit where $\hbar \to 0$ only the classical path contributes to the path integral expression of K and, thus,

$$\psi(x,t) \sim \exp\Big(\frac{i}{\hbar}S(x_c(t))\Big), \tag{13.39}$$

$$\begin{aligned} S(x_c(t)) &= \int_0^t dt' L = \int_0^t dt'(p\frac{dx}{dt'} - H) \\ &= \int_{x_0}^x pdx - \int_0^t dt' H. \end{aligned} \tag{13.40}$$

Since the Hamiltonian is time independent, the integral of H along the classical path is simply the energy E times the time interval. Thus, we find that

$$\psi(x,t) \sim \exp\Big(\frac{i}{\hbar}\int_{x_0}^x pdx - E(t-t_0)\Big), \tag{13.41}$$

where p is the momentum along the classical path, that is, $p = \sqrt{2m(E-V(x))}$. Therefore, we find the same phase of the wavefunction as in the WKB approximation.

Furthermore, it can be shown (see B. R. Holstein and A. R. Swift, Am. J. Phys. **50**, 929 (1982)), by integrating out the quadratic fluctuations of paths near the classical path, that the amplitude prefactor is the same as the one found in the WKB approximation.

13.4 Further reading

For further reading about the path integral formulation of quantum mechanics, the reader is referred to the classic book by Feynmann and Hibbs:

R.P. Feynmann and A. R. Hibbs, *Quantum Mechanics and Path Integrals*, McGraw-Hill, New York (1965).

In addition, the book contains problems for the student to practice and applications of path integrals.

14

Applications of path integrals

In this chapter we discuss some applications of path integrals. First, we illustrate how their qualitative use can yield insight. As an example, we apply it to the so-called Bohm–Aharonov effect. Then we discuss the generalization of the path-integral formalism for the so-called many-body problem. We only treat distinguishable particles (what we call Boltzmannons) in this chapter. We will discuss indistinguishable particles in chapter 25. We will also discuss the formulation of quantum statistical mechanics of Boltzmannons.

14.1 Bohm–Aharonov effect

Consider a particle under the influence of a magnetic field. In this case the Hamiltonian is obtained from the non-interacting free-particle Hamiltonian by replacing the momentum $\vec{p}$ with $\vec{p} - e/c\vec{A}$, where $\vec{A}$ is the vector potential, and the Hamiltonian takes the form:

$$H = \frac{1}{2m}(\vec{p} - \frac{e}{c}\vec{A})^2. \tag{14.1}$$

For the path integral we will need the Lagrangian in order to calculate the action. It is straightforward to find the Lagrangian corresponding to the above Hamiltonian:

$$L = \vec{p} \cdot \dot{\vec{q}} - H, \tag{14.2}$$

where $\vec{q}$ is the generalized coordinate which is conjugate to the canonical momentum $\vec{p}$, that is,

$$\dot{\vec{q}} = \frac{\partial H}{\partial \vec{p}}. \tag{14.3}$$

However, since the Lagrangian is a function of $\vec{q}$ and $\dot{\vec{q}}$ only we need to use the above expression to eliminate the variable $\vec{p}$. From the above equation we find that

$$\vec{p} = m\dot{\vec{q}} + \frac{e}{c}\vec{A}, \tag{14.4}$$

and by mere substitution of this expression for $\vec{p}$ in the expression (14.2) for L we obtain

$$L = \frac{1}{2}m|\dot{\vec{q}}|^2 + \frac{e}{c}\dot{\vec{q}} \cdot \vec{A}. \tag{14.5}$$

Practical Quantum Mechanics. First Edition. Efstratios Manousakis.

Therefore, we are ready to compute the action

$$S = \frac{1}{2}m\int_0^t dt'\frac{d\vec{q}}{dt'}\cdot\frac{d\vec{q}}{dt'} + \frac{e}{c}\int_0^t dt'\frac{d\vec{q}}{dt'}\cdot\vec{A}$$
$$= \frac{1}{2}m\int_{path} d\vec{q}\cdot\frac{d\vec{q}}{dt'} + \frac{e}{c}\int_{path} d\vec{q}\cdot\vec{A}. \tag{14.6}$$

Now, imagine that we have a "perfect" conductor shown in Fig. 14.1 which is wrapped around a solenoid that produces a magnetic field through the conducting wire restricted only to the circle shown in the figure.

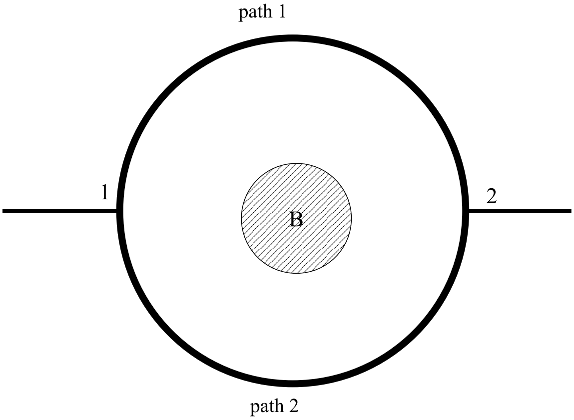

Fig. 14.1

Imagine that the current enters the loop through wire at point 1 and it is extracted at point 2. Following the discussion in the previous chapter, the total amplitude for an electron which enters the circular wire at point 1 at time $t = 0$ to be observed at point 2 at some later time is proportional to the following sum:

$$e^{\frac{i}{\hbar}S(path1)} + e^{\frac{i}{\hbar}S(path2)} = e^{\frac{i}{\hbar}S(path1)}\left(1 + e^{\frac{i}{\hbar}\Delta S}\right),$$
$$\Delta S = S(path2) - S(path1), \tag{14.7}$$

where $S(pathn)$ is the action along either path 1 or 2. Now, we can rewrite this difference of action as follows:

$$\Delta S = S(path2) - S(path1) = \frac{e}{c}\left[\int_{path2}\vec{A}\cdot d\vec{q} - \int_{path1}\vec{A}\cdot d\vec{q}\right]$$
$$= -\frac{e}{c}\oint\vec{A}\cdot d\vec{q}. \tag{14.8}$$

Notice that the kinetic energy contributions from the two paths are equal due to symmetry and cancel. The last step above was obtained by noticing that in the line integral along path 2 the path can be reversed which gives rise to only a minus sign difference. Using Stoke's theorem we can convert the last line integral over the closed path to a surface integral of the curl of $\vec{A}$ integrated over the area of the circular conductor, that is,

$$\Delta S = -\frac{e}{c}\int \nabla \times \vec{A}\cdot d\vec{S} \tag{14.9}$$

$$= \frac{e}{c}\int \vec{B}\cdot d\vec{S} = \frac{e}{c}\Phi, \tag{14.10}$$

where $\vec{B} = \nabla \times A$ is the magnetic field and Φ is the magnetic flux through the area of the closed conducting loop.

Therefore, apart from a multiplicative factor (of absolute magnitude 1) the probability amplitude K for the electron to be observed at point 2 is proportional to

$$K \sim 1 + e^{\frac{ie}{\hbar c}\Phi}, \tag{14.11}$$

and the probability is proportional to $|K|^2$. This means that constructive interference occurs at well-defined values of the magnetic flux, that is, when the phase in the second term becomes a integer multiple of 2π, which implies that

$$\Phi = n\phi_0, \tag{14.12}$$

$$\phi_0 = \frac{hc}{e}. \tag{14.13}$$

Namely, at these discrete values of the flux the electrical current will be maximum. This was observed experimentally by Chambers in 1960 (R.G. Chambers, "Shift of an electron interference pattern by enclosed magnetic flux," *Phys. Rev. Lett.* **5**, 3(1960)) and can provide an accurate measurement of the combination of the fundamental constants, Planck's constant h, the speed of light c, and the electron charge e, $hc/e = 4.135 \times 10^{-7} gauss \times$ cm^2. The effect was discussed by Aharonov and Bohm in a paper published in *Physical Review*: Y. Aharonov and D. Bohm, "Significance of electromagnetic potentials in quantum theory." *Phys. Rev.* **115** 485 (1959).

14.2 The harmonic oscillator and path integrals

In the case of the harmonic oscillator we can calculate the path integral for the Feynmann propagator exactly. Let us begin from the path-integral expression for $K(x,t;x_0,0)$, namely:

$$K(x,t;x_0,0) = \int_{x(0)=x_0}^{x(t)=x} \mathcal{D}x(t') e^{\frac{i}{\hbar}S[x(t')]}, \tag{14.14}$$

$$S[x(t')] = \int_0^t dt' \Big[\frac{1}{2}m\dot{x}^2 - \frac{1}{2}m\omega^2 x^2\Big]. \tag{14.15}$$

In order to calculate the path integral we shift the path variable as:

$$x(t') = x_c(t') + y(t'), \tag{14.16}$$

where $x_c(t')$ is the classical path which minimizes the action under the constraints

$$x_c(0) = x_0, \qquad x_c(t) = x \tag{14.17}$$

and, thus, satisfies the Euler–Lagrange equation which yields the classical equation of motion:

$$\ddot{x}_c(t') + \omega^2 x_c(t') = 0. \tag{14.18}$$

The constraints on the new variable $y(t')$ are

$$y(0) = y(t) = 0. \tag{14.19}$$

We substitute Eq. 14.16 in the action given by Eq. 14.16 and we find that

$$\begin{aligned} S[x(t')] &= \frac{1}{2}m \int_0^t dt' \Big[(\dot{x}_c(t') + \dot{y}(t'))^2 - \omega^2 (x_c(t') + y(t'))^2\Big] \\ . &= \frac{1}{2}m \int_0^t dt' \Big[\dot{x}_c^2(t') + \dot{y}(t')^2 + 2\dot{x}_c(t')\dot{y}(t')) \\ &- \omega^2 (x_c^2(t') + y^2(t') + 2x_c(t')y(t'))\Big]. \end{aligned} \tag{14.20}$$

The first cross term can be integrated by parts as follows:

$$\int_0^t dt' 2\dot{x}_c(t')\dot{y}(t') = 2\dot{x}_c(t')y(t')|_{t'=0}^{t'=t} - \int_0^t dr' 2\ddot{x}_c(t')y(t'). \tag{14.21}$$

Now, the boundary term vanishes because of our Eq. 14.19. The two cross terms together yield:

$$-m \int_0^t dt' \Big(\ddot{x}_c(t') + \omega^2 x_c(t')\Big) y(t') = 0, \tag{14.22}$$

because the term in the parenthesis is the equation of motion (Eq. 14.18). Thus, the action takes the following form:

$$\begin{aligned} S[x(t')] &= \frac{1}{2}m \int_0^t dt' \Big[\dot{x}_c^2(t') - \omega^2 x_c^2(t')\Big] \\ &+ \frac{1}{2}m \int_0^t dt' \Big[\dot{y}^2(t') - \omega^2 y^2(t')\Big]. \end{aligned} \tag{14.23}$$

This leads to the following simplified form of the path integral:

$$K(x, t; x_0, 0) = K(0, t; 0, 0) e^{\frac{i}{\hbar} S[x_c(t')]}, \tag{14.24}$$

where

$$S[x_c(t')] = \int_0^t dt' \Big[\frac{1}{2} m \dot{x}_c(t')^2 - \frac{1}{2} m \omega^2 x_c(t')^2\Big], \tag{14.25}$$

and

$$K(0,t;0,0) = \int_{y(0)=0}^{y(t)=0} \mathcal{D}y(t') e^{\frac{i}{\hbar}S[y(t')]}, \tag{14.26}$$

where

$$S[y(t')] = \int_0^t dt' \Big[\frac{1}{2}m\dot{y}(t')^2 - \frac{1}{2}m\omega^2 y(t')^2\Big]. \tag{14.27}$$

Notice that $K(0,t;0,0)$ does not depend on x_0 or x. For our application which follows next this is very important, and we do not need the explicit form of $K(0,t;0,0)$. A rather cumbersome calculation yields:

$$K(0,t;0,0) = \sqrt{\frac{m\omega}{2\pi i\hbar \sin(\omega t)}}. \tag{14.28}$$

The calculation of the action of the classical path $S[x_c(t)]$ which is needed is straightforward. The most general solution to the harmonic oscillator equation of motion (Eq. 14.18) can be written as

$$x_c(t') = A\cos(\omega t') + B\sin(\omega t'), \tag{14.29}$$

where by applying the initial and final condition given by Eq. 14.17 we find that

$$A = x_0, \qquad B = \frac{x - x_0\cos(\omega t)}{\sin(\omega t)}. \tag{14.30}$$

By substituting the expression given by Eq. 14.29 in the action given by Eq. 14.25 for the classical path, and doing a straightforward integration over t', we find that

$$S[x_c(t')] = \frac{m\omega}{2\sin(\omega t)}\Big[(x^2 + x_0^2)\cos(\omega t) - 2xx_0\Big]. \tag{14.31}$$

Therefore, the final expression for the Feynmann propagator is

$$K(x,t;x_0,0) = \sqrt{\frac{m\omega}{2\pi i\hbar \sin(\omega t)}}\exp\Big[\frac{i}{\hbar}S[x_c(t)]\Big]. \tag{14.32}$$

14.3 Projection of the ground state

Next, we are going to apply a computational method which projects the ground-state wavefunction from an initial trial wavefunction for the case of the harmonic oscillator. We will make use of our result of the previous section for the Feynmann propagator of the harmonic oscillator.

In a problem assigned in chapter 1, we discussed the following theorem. Given an initial ansatz $|\Phi_0\rangle$ which has a non-zero overlap with the true ground-state $|\Psi_0\rangle$ of a Hamiltonian H, we can project the exact ground state from the state $|\Phi_0\rangle$ as follows:

$$|\Psi_0\rangle = C \lim_{\beta\to\infty} e^{-\beta\hat{H}}|\Phi_0\rangle. \tag{14.33}$$

To prove this theorem, we just need to expand the initial state $|\Phi_0\rangle$ in the complete set $|\Psi_n\rangle$ of the eigenstates of the Hamiltonian:

$$|\Phi_0\rangle = \sum_n c_n |\Psi_n\rangle, \tag{14.34}$$

and subsequently apply the operator $e^{-\beta \hat{H}}$ on this state:

$$e^{-\beta \hat{H}}|\Phi_0\rangle = c_0 e^{-\beta E_0}\Big(|\Psi_0\rangle + \frac{c_1}{c_0} e^{-\beta(E_1 - E_0)}|\Psi_1\rangle + ...\Big). \tag{14.35}$$

Notice that in the limit of $\beta \to \infty$, provided that there is an energy gap between the ground state and the first excited state, all the terms with $n > 0$ in the parenthesis are negligible as compared to the first term. Therefore, this operator projects the exact ground-state wavefunction. Eq. 14.33 in the position representation is written as

$$\begin{aligned}
\langle x|\Psi_0\rangle &= C \lim_{\beta\to\infty} \langle x|e^{-\beta\hat{H}}|\Phi_0\rangle \\
&= C \lim_{\beta\to\infty} \int dx' \langle x|e^{-\beta\hat{H}}|x'\rangle\langle x'|\Phi_0\rangle. \qquad \to \\
\Psi_0(x) &= \lim_{\beta\to\infty} \int dx' \langle x|e^{-\beta\hat{H}}|x'\rangle \Phi_0(x').
\end{aligned} \tag{14.36}$$

This theorem is the basis of a many-body computational technique which is based on Monte Carlo simulation to obtain the ground-state wavefunction. The method is called Green's function Monte Carlo. (For further reading of the GFMC method, the reader is referred to the second reference at the end of this chapter.) According to this method one begins with a population of walkers distributed according to $\langle x|\phi_0\rangle$ and then these walkers move in configuration space according to the transition probability

$$G(x', x, \beta) \equiv \langle x|e^{-\beta\hat{H}}|x'\rangle = K(x, t = -i\hbar\beta; x', 0). \tag{14.37}$$

At the end of a sufficiently long iterative scheme, the distribution of the positions of walkers is proportional to the true ground-state $\Psi_0(x)$.

Notice that since we have calculated $K(x, t; x_0, 0)$ for the case of the harmonic oscillator, the expression for $G(x' \to x, \beta)$ can be obtained by simply making the analytic continuation to imaginary (Euclidean) time, that is, $t = -i\hbar\beta$. This is straightforward. Using Eq. 14.32 and Eq. 14.31 we obtain

$$G(x', x, \beta) \sim \exp\Big[\frac{m\omega\Big((x^2 + x'^2)\cosh(\beta\hbar\omega) - 2xx'\Big)}{2\hbar\sinh(\beta\hbar\omega)}\Big], \tag{14.38}$$

where the proportionality constant is a function of β, ω, and m; we did not calculate it in the previous section, because it does not depend on x or x'. In the limit of $\beta\hbar\omega >> 1$, we obtain

$$G(x', x, \beta) \sim \exp\Big[\frac{m\omega}{2\hbar}(x^2 + x'^2)\Big]. \tag{14.39}$$

Inserting this expression in Eq. 14.36 we obtain

$$\Psi_0(x) = De^{-\frac{m\omega}{2\hbar}x^2}, \tag{14.40}$$

where

$$D \sim \int dx' e^{-\frac{m\omega}{2\hbar}x'^2} \Phi_0(x'), \tag{14.41}$$

namely, an integral independent of x, which is the overlap $\langle \Psi_0 | \Phi_0 \rangle$. Thus, apart from an unknown normalization constant, we have obtained the exact ground-state wavefunction.

14.4 Application to many-body physics

Let us consider N interacting non-relativistic particles described by the Hamiltonian

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + \sum_{i<j} V(r_{ij}), \tag{14.42}$$

where $V(r_{ij})$ is a pairwise interaction which depends only on the distance r_{ij} between particles i and j. Here, we will assume that while these particles have the same mass and the interact in the same way, we are dealing with *distinguishable particles*. In such a case the positions basis is defined as

$$|\{\vec{r}_i\}\rangle \equiv |\vec{r}_1, \vec{r}_2, ..., \vec{r}_N\rangle \equiv |\vec{r}_1\rangle_1 |\vec{r}_2\rangle_2 ... |\vec{r}_N\rangle_N, \tag{14.43}$$

where the state $|\vec{r}\rangle_i$ spans the Hilbert space of a the ith particle and, when in this state, the ith particle is in position $\vec{r}$.

The probability amplitude such that, given that the particles were at positions $\vec{r}_1^{(0)}$, $\vec{r}_2^{(0)}$, ..., $\vec{r}_N^{(0)}$, at time $t = 0$ to be found at positions $\vec{r}_1$, $\vec{r}_2$, ..., $\vec{r}_N$ at a later time t, is given by

$$K(\{\vec{r}_i\}, t; \{\vec{r}_i^{(0)}\}, 0) = \langle \{\vec{r}_i\} | e^{-\frac{i}{\hbar}\hat{H}t} | \{\vec{r}_i^{(0)}\} \rangle. \tag{14.44}$$

In the very same way which we used in chapter 13 to derive the expression for the path integral of a single particle in one dimension, we can show that the above amplitude can be expressed as follows:

$$K(\{\vec{r}_i\}, t; \{\vec{r}_i^{(0)}\}, 0) = C \int_{\vec{r}_i^{(0)}}^{\vec{r}_i} \prod_{i=1}^{N} \mathcal{D}\vec{r}_i(t) e^{\frac{i}{\hbar} S(\{\vec{r}_i(t)\})}, \tag{14.45}$$

where the action S is given in terms of the Lagrangian as follows:

$$S(\{\vec{r}_i(t)\}) = \int_0^t L(\{\vec{r}_i(t)\}, \{\dot{\vec{r}}_i(t)\}) dt, \tag{14.46}$$

$$L(\{\vec{r}_i(t)\}, \{\dot{\vec{r}}_i(t)\}) = \frac{1}{2} m \sum_{i=1}^{N} \dot{\vec{r}}_i^2 - \sum_{i<j} V(r_{ij}). \tag{14.47}$$

This is a very useful expression in quantum many-body physics and its analytic continuation to imaginary time will be used in the following section.

14.5 Quantum statistical mechanics

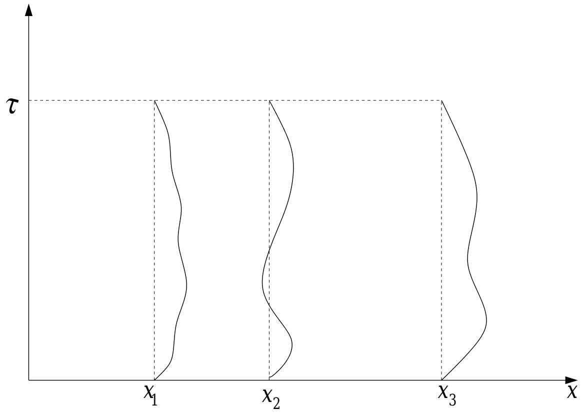

Fig. 14.2

Within the canonical ensemble, equilibrium properties in statistical mechanics are obtained by calculating the partition function:

$$Z = \sum_n e^{-\beta E_n}, \tag{14.48}$$

where the summation is over all microscopic eigenstates of the interacting Hamiltonian and E_n is their corresponding eigenvalues. Namely, this is the trace of the following operator

$$Z = Tre^{-\beta \hat{H}}. \tag{14.49}$$

Since the trace is independent of the choice of the basis, we can change the basis to the many-body basis given by Eq. 14.43 and compute the trace in a different way, that is,

$$Z = \int d\vec{r}_1 d\vec{r}_2 ... d\vec{r}_N \langle \{\vec{r}_i\} | e^{-\beta \hat{H}} | \{\vec{r}_i\} \rangle. \tag{14.50}$$

Now, compare the integrand with the kernel K calculated using path integrals. We notice that the integrand can be obtained by simply going to imaginary time (also called Euclidean time), that is, taking for time $t = -i\tau$ where $\tau = \hbar\beta$ and by taking the initial and final positions to be the same and equal to $\{\vec{r}_i\}$. As a result, by making the above transformation of variables, we can express Z as follows

$$Z = C \int_{\vec{r}_i(0)=\vec{r}_i(\hbar\beta)} \prod_{i=1}^{N} \mathcal{D}\vec{r}_i(\tau) e^{-S_E(\{\vec{r}_i\})}, \tag{14.51}$$

$$S_E\{\vec{r}_i\}) = \int_0^{\hbar\beta} d\tau \Big[\frac{1}{2} m \sum_{i=1}^{N} |\dot{\vec{r}}_i|^2 + \sum_{i<j} V(r_{ij} \Big]. \tag{14.52}$$

Now, we are thinking of the particle trajectories $\vec{r}_i(\tau)$ as occurring in the variable τ (the imaginary time variable), which takes real values from 0 to $\hbar\beta$ and has dimensions of time. Notice that the exponent of the integrand is the so-called Euclidean action S_E; S_E is no longer the integral of the Lagrangian but rather the integral of a function of $\{\vec{r}_i\}$ and $\{\dot{\vec{r}}_i\}$, and it is equal to the total energy of the system. In addition, notice that the particles end up at the same position as their starting position; namely, this is a path integral over all many-body paths which start and finish at the same positions over which we also integrate. Fig. 14.2 illustrates these many-body paths in one spatial dimension for three particles. Therefore, we have periodic boundary conditions in imaginary time.

When we discuss identical particles we will see that the paths which contribute are all the paths considered here but, in addition, paths in which two or more particles exchange their positions at the end of their trajectory in Euclidean time.

The above expression (14.52) for the quantum many-body partition function has become the basis for Monte Carlo simulations in quantum statistical mechanics. The reason is that the integrand contains only real (not imaginary) quantities which can be interpreted as sampling probabilities in a stochastic integration approach. A stochastic integration becomes overwhelmingly more advantageous as compared to any numerical integration method when the number of integration variables is very large. For further reading on this, the reader is referred to the first reference at the end of this chapter.

14.6 Further reading

For further reading about path-integral Monte Carlo techniques and Green's function Monte Carlo method, the reader is referred to the following review papers:

1. D. M. Ceperley, "Path integrals in the theory of condensed helium," *Rev. Mod. Phys.* **67**, 279 (1995).

2. E. Manousakis, "The spin-1/2 quantum Heisenberg antiferromagnet on a square lattice and its applications to the cuprous oxides," *Rev. Mod. Phys.* **61**, 1 (1991).

15

Angular momentum

In this chapter we discuss the algebra, the eigenvalues, and the eigenstates of angular momentum operators.

15.1 Angular momentum operators

As in classical mechanics and using the correspondence principle the angular momentum operator is defined as

$$\hat{\vec{L}} = \hat{\vec{r}} \times \hat{\vec{p}} = \begin{pmatrix} \hat{L}_x \\ \hat{L}_y \\ \hat{L}_z \end{pmatrix} = \begin{pmatrix} \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \\ \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \\ \hat{x}\hat{p}_y - \hat{y}\hat{p}_z \end{pmatrix}. \tag{15.1}$$

Using this definition and the commutation relations between position and momentum operators, the commutation relations between the angular momentum operators and the position and momentum operators are obtained as follows:

$$\left[\hat{L}_i, \hat{r}_j\right] = i\hbar\epsilon_{ijk}\hat{r}_k. \tag{15.2}$$

Here, we are following a short-hand notation where i, j, or k, each, independently, take the values $1, 2, 3$ and correspond to the x-, y-, and z- component respectively. Thus, $\hat{r}_1 = \hat{x}$, $\hat{r}_2 = \hat{y}$, and $\hat{r}_3 = \hat{z}$. Similarly $\hat{L}_1, \hat{L}_2$, and $\hat{L}_3$ stand for the x-, y-, and z-components of $\vec{L}$. Here, ϵ_{ijk} is the totally antisymmetric tensor. These commutation relations follow directly from the more basic commutation relations:

$$[\hat{r}_i, \hat{p}_j] = i\hbar\delta_{ij}. \tag{15.3}$$

Similarly, using the above commutation relations, it is straightforward to show the following two families of commutation relations:

$$\left[\hat{L}_i, \hat{p}_j\right] = i\hbar\epsilon_{ijk}\hat{p}_k, \tag{15.4}$$

$$\left[\hat{L}_i, \hat{L}_j\right] = i\hbar\epsilon_{ijk}\hat{L}_k. \tag{15.5}$$

In Fig. 15.1 the spherical coordinate system is illustrated. The gradient operator can be written in spherical coordinates as

$$\vec{\nabla} = \hat{r}\frac{\partial}{\partial r} + \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial\theta}, \tag{15.6}$$

where $\hat{r}$ is the unit vector along the direction of $\vec{r}$; in addition, $\hat{\phi}$ is the unit vector along a direction perpendicular to the plane defined by the z-direction and the vector

Practical Quantum Mechanics. First Edition. Efstratios Manousakis.

$\vec{r}$ and the unit vector $\hat{\theta}$ is on this plane and in addition it is perpendicular to the vector $\vec{r}$. In terms of the Cartesian unit vectors i, j, and k they are given as follows

$$\hat{r} = \sin\theta\cos\phi\ \hat{\imath} + \sin\theta\sin\phi\ \hat{\jmath} + \cos\theta\ \hat{k}, \tag{15.7}$$

$$\hat{\phi} = -\sin\phi\ \hat{\imath} + \cos\phi\ \hat{\jmath}, \tag{15.8}$$

$$\hat{\theta} = \cos\theta\cos\phi\ \hat{\imath} + \cos\theta\sin\phi\ \hat{\jmath} - \sin\theta\ \hat{k}. \tag{15.9}$$

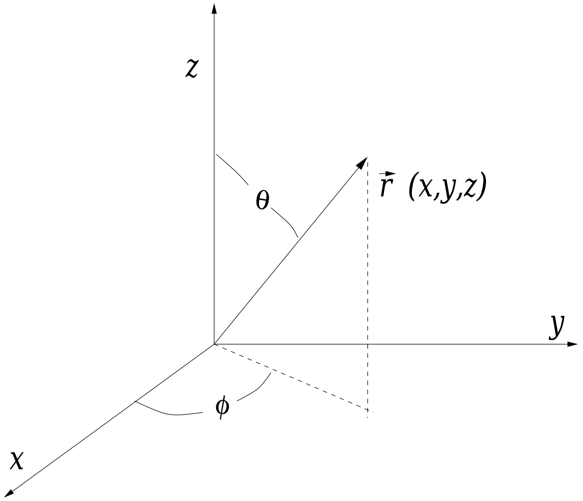

Fig. 15.1

In the representation in which the position operator is diagonal, the angular momentum operator is given as

$$\langle\vec{r}|\hat{\vec{L}}|\phi\rangle \equiv \hat{\vec{\mathcal{L}}}\langle\vec{r}|\psi\rangle = -i\hbar\vec{r}\times\nabla\langle\vec{r}|\psi\rangle, \tag{15.10}$$

$$\vec{\mathcal{L}} = -i\hbar\Big(\hat{\phi}\frac{\partial}{\partial\theta} - \hat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}.\Big). \tag{15.11}$$

The last equation is obtained by simply substituting for $\vec{\nabla}$ its expression given by Eq. 15.6 in spherical coordinates and by calculating the cross product between the vector $\hat{r}$ and $\vec{\nabla}$.

Now, using the expressions given by Eq. 15.9 for $\hat{\phi}$ and $\hat{\theta}$ in terms of $\hat{\imath}$, $\hat{\jmath}$, and $\hat{k}$ we find that

$$\hat{\mathcal{L}}_x = i\hbar\Big(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\Big), \tag{15.12}$$

$$\hat{\mathcal{L}}_y = -i\hbar\Big(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\Big), \tag{15.13}$$

$$\hat{\mathcal{L}}_z = -i\hbar\frac{\partial}{\partial\phi}, \tag{15.14}$$

$$\hat{\mathcal{L}}^2 = -\hbar^2\Big[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial}{\partial\theta}\Big)\Big]. \tag{15.15}$$

15.2 The spectrum of angular momentum operators

Each of the angular momentum operators $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ commutes with $\hat{L}^2$; however, they do not mutually commute. Therefore, for the maximum set of commuting angular momentum operators, we can choose L^2 and only one of the three projections, say the $\hat{L}_z$. We are allowed to search for common eigenstates of $\hat{L}^2$ and $\hat{L}_z$. Let these common eigenstates be labeled as $|l, m\rangle$ and let

$$\hat{L}^2|l, m\rangle = \hbar^2 l(l+1)|lm\rangle, \tag{15.16}$$

$$\hat{L}_z|l, m\rangle = \hbar m|l, m\rangle. \tag{15.17}$$

Here, we have simply expressed the eigenstates of $\hat{L}^2$ and $\hat{L}_z$, which have units of $\hbar^2$ and $\hbar$ respectively, by means of some yet unknown dimensionless real numbers l and m. We imply nothing further about the specific nature of these numbers, and we will investigate this next.

First, we notice that the expectation value of the operator $\hat{L}^2$ with any physical state $|\psi\rangle$ is non-negative,

$$\langle\psi|\hat{L}^2|\psi\rangle \geq 0. \tag{15.18}$$

If we consider the state $|\phi\rangle \equiv \vec{L}|\psi\rangle$, because of the Hermitian nature of the operator $\vec{L}$ we have that $\langle\psi|\hat{L}^2|\psi\rangle = \langle\phi|\phi\rangle \geq 0$. If we use for $|\psi\rangle = |l, m\rangle$ we conclude that the combination of $l(l+1) \geq 0$. Given a value of λ which is the actual, that is, the measurable eigenvalue of $\hat{L}^2$, this value can be obtained by two different values of l:

$$l_+ = \sqrt{\frac{1}{4} + \lambda} - \frac{1}{2} \geq 0, \tag{15.19}$$

$$l_- = -\sqrt{\frac{1}{4} + \lambda} - \frac{1}{2} < 0. \tag{15.20}$$

We can remove this double valueness of the parameter l by choosing the non-negative value. As discussed before, l is just a parameter which parametrizes the physically observable quantity λ which is non-negative. There are two choices for l both of which lead to the same non-negative value for the actual observable, we just choose the non-negative.

Therefore, in the following we are allowed to take $l \geq 0$ and any allowed non-negative value of the eigenvalue λ of $\hat{L}^2$ can be constructed as $\lambda = l_+(l_+ + 1)$ using the non-negative value of l given above.

Next, we define the so-called angular momentum raising and lowering operators as follows:

$$\hat{L}_\pm \equiv \hat{L}_x \pm i\hat{L}_y, \tag{15.21}$$

and the justification of their name will become clear below. First, it can be easily shown that

$$\left[\hat{L}_z, \hat{L}_\pm\right] = \pm\hbar\hat{L}_\pm, \tag{15.22}$$

$$\hat{L}_+\hat{L}_- = \hat{L}^2 - \hat{L}_z^2 + \hbar\hat{L}_z, \tag{15.23}$$

$$\hat{L}_-\hat{L}_+ = \hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z, \tag{15.24}$$

$$\left[\hat{L}_+, \hat{L}_-\right] = 2\hbar\hat{L}_z. \tag{15.25}$$

Because of the fact that the state $|lm\rangle$ is an eigenstate of $\hat{L}_z$ with corresponding eigenvalue $\hbar m$, the state $|\kappa\rangle \equiv \hat{L}_-|lm\rangle$ is also an eigenstate of $\hat{L}_z$ with corresponding eigenvalue $\hbar(m-1)$. This can be shown easily by taking into account the commutation relation $\left[\hat{L}_-, \hat{L}_z\right]$, as follows

$$\begin{aligned}\hat{L}_z|\kappa\rangle = \hat{L}_z\hat{L}_-|l,m\rangle &= (\hat{L}_-\hat{L}_z - \hbar\hat{L}_-)|l,m\rangle \\ &= \hbar(m-1)|\kappa\rangle.\end{aligned} \tag{15.26}$$

Therefore, the above equation means that the state $|\kappa\rangle$ apart from a normalization constant is an eigenstate of $\hat{L}_z$ with eigenvalue $\hbar(m-1)$. Since within our notation we defined the state $|l, m-1\rangle$ to be the normalized eigenstate of $\hat{L}_z$ with corresponding eigenvalue $\hbar(m-1)$, we have found that

$$\hat{L}_-|l,m\rangle = C|l,m-1\rangle, \tag{15.27}$$

$$|c|^2 = \langle l,m|\hat{L}_+\hat{L}_-|l,m\rangle. \tag{15.28}$$

Carrying out a simple calculation using Eq. 15.23 we obtain:

$$\hat{L}_-|l,m\rangle = \hbar\sqrt{l(l+1) - m(m-1)}|l,m-1\rangle. \tag{15.29}$$

Using a very similar argument and very similar calculation we can find that

$$\hat{L}_+|l,m\rangle = \hbar\sqrt{l(l+1) - m(m+1)}|l,m+1\rangle. \tag{15.30}$$

The above two equations justify the use of the term *raising* and *lowering* operators for $\hat{L}_+$ and $\hat{L}_-$ respectively.

Then, we can easily show that

$$\langle l,m|\hat{L}_+\hat{L}_-|l,m\rangle \geq 0. \tag{15.31}$$

This follows directly from the observation that if we define a state $|\phi\rangle = \hat{L}_-|l,m\rangle$, then the above expectation value becomes

$$\langle l,m|\hat{L}_+\hat{L}_-|l,m\rangle = \langle\phi|\phi\rangle, \tag{15.32}$$

because $(\hat{L}_-)^\dagger = \hat{L}_+$. The inequality (15.31) follows from the fact that $\langle\phi|\phi\rangle \geq 0$.

By means of substitution of Eq. 15.23 in Eq. 15.31 we obtain

$$l(l+1) - m^2 + m \geq 0, \tag{15.33}$$

which implies that

$$-l \leq m \leq l+1. \tag{15.34}$$

In a very similar way we can show that

$$\langle l, m|\hat{L}_-\hat{L}_+|l, m\rangle \geq 0, \tag{15.35}$$

which together with Eq. 15.24 lead to the inequality:

$$l(l+1) - m^2 - m \geq 0, \tag{15.36}$$

which implies that

$$-(l+1) \leq m \leq l. \tag{15.37}$$

Since the two inequalities, given by the relations (15.34) and (15.37), should be simultaneously valid, we obtain that

$$-l \leq m \leq l. \tag{15.38}$$

Now, using these bounds on the possible values of m, we can show that both $m - l$ and $m + l$ are integers. The argument is very similar in spirit to the one we used in the harmonic oscillator case to show that n is an integer. It goes as follows: Let us consider an eigenstate $|lm\rangle$ of $\hat{L}_z$ where $-l \leq m \leq l$ according to Eq. 15.38. The states $|l, m-1\rangle$, $|l, m-2\rangle$, ..., $|l, m-m'\rangle$ are eigenstates of $\hat{L}_z$ according to Eq. 15.26. However, if $l + m$ is not an integer then we can write

$$l + m = [l+m] + \xi, \tag{15.39}$$

$$0 < \xi < 1, \tag{15.40}$$

where $[l+m]$ denotes the integer part of $l+m$. Then, we can consider the case where the integer m' used above takes the value $m' = [l+m]$; in this case we obtain the state $|l, m - [l+m]\rangle = |l, -l+\xi\rangle$. As a result, according to Eq. 15.29, we find that

$$\begin{aligned}\hat{L}_-|l, -l+\xi\rangle = {} & \hbar\sqrt{l(l+1) - (l-\xi)(l-\xi+1)} \\ & \times |l, -l-1+\xi\rangle,\end{aligned} \tag{15.41}$$

and, as shown, this should be an eigenstate of $\hat{L}_z$ with corresponding eigenvalue $M = -l - 1 + \xi$ which is less than $-l$ because $0 < \xi < 1$. This contradicts the bounds given by Eq. 15.38. Therefore, our assumption that $l + m$ is not an integer is not valid.

How is this contradiction resolved if $l + m$ is an integer? In this case $\xi = 0$ and Eq. 15.41 reduces to

$$\hat{L}_-|l, -l\rangle = 0, \tag{15.42}$$

and this ends the ladder process and there is no contradiction about this.

Similarly we can show that $l-m$ is an integer by starting from the state $|l,m\rangle$ and applying the raising operator $\hat{L}_+$.

We have, therefore, reached the conclusion that $l+m$ and $l-m$ are integers. By adding or subtracting two integers we obtain an integer, therefore, $2l$ and $2m$ are integers. *Conclusion:* l and m can be either both integers or both half-integers.

In the next section, we will see that for orbital angular momentum the case of half-integer l and m should be excluded. It is interesting, however, that the angular momentum algebra by itself allows half-integer values for the total angular momentum and its projection. We will see later that spin-operators obey the same algebra as the orbital angular momentum operators. In this case half-integer spins are allowed.

15.3 Eigenstates of angular momentum

Now we wish to find the common eigenstates of $\hat{L}^2$ and $\hat{L}_z$, that is, $|l,m\rangle$ in the position representation. First, we consider the $\hat{L}_z$:

$$\hat{\mathcal{L}}_z\langle r,\theta,\phi|l,m\rangle = \hbar m\langle r,\theta,\phi|l,m\rangle, \tag{15.43}$$

$$-i\hbar\frac{\partial}{\partial\phi}\langle r,\theta,\phi|l,m\rangle = \hbar m\langle r,\theta,\phi|l,m\rangle. \tag{15.44}$$

This is a simple first-order differential equation to solve for the azimuthal angle ϕ. The solution is

$$\langle r,\theta,\phi|l,m\rangle = e^{im\phi}\langle r,\theta,0|l,m\rangle. \tag{15.45}$$

Notice that the eigenfunction has to be single valued when we make the transformation $\phi \to \phi + 2\pi$ because we return to the very same spatial position. This requirement forces the value of m to be an integer. Thus, the facts that a) m must be an integer together with b) the constraint given by Eq. 15.38, imply that there are only $2l+1$ possible values of m, the following $-l, -l+1, -l+2, ..., 0, ..., l-1, l$.

Using the expressions (15.15) for the angular momentum components in position space representation we find that

$$\hat{\mathcal{L}}_+ = \hat{\mathcal{L}}_x + i\hat{\mathcal{L}}_y = -i\hbar e^{i\phi}\Big(i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\phi}\Big), \tag{15.46}$$

$$\hat{\mathcal{L}}_- = \hat{\mathcal{L}}_x - i\hat{\mathcal{L}}_y = i\hbar e^{-i\phi}\Big(i\frac{\partial}{\partial\theta} + \cot\theta\frac{\partial}{\partial\phi}\Big). \tag{15.47}$$

Let us apply the operator $\hat{\mathcal{L}}_+$ on the state $\langle r,\theta,\phi|l,l\rangle$ knowing that

$$\hat{\mathcal{L}}_+\langle r,\theta,\phi|l,l\rangle = \langle r,\theta,\phi|\hat{L}_+|l,l\rangle = 0, \tag{15.48}$$

which implies that

$$\Big(i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\phi}\Big)\langle r,\theta,\phi|l,l\rangle = 0. \tag{15.49}$$

Using Eq. 15.45 which gives the ϕ-dependence of $\langle r,\theta,\phi|l,l\rangle$ we obtain:

$$\Big(i\frac{\partial}{\partial\theta} - l\cot\theta\Big)\langle r,\theta,\phi|l,l\rangle = 0. \tag{15.50}$$

This differential equation can be solved by separation of the variables r, θ, and ϕ as

$$\langle r,\theta,\phi|l,l\rangle = f(r)\Theta(\theta)\Phi(\phi), \tag{15.51}$$

$$\Phi(\phi) = e^{il\phi}, \tag{15.52}$$

and $f(r)$ is any (spherically symmetric) function of r. The differential equation which is satisfied by the function $\Theta(\theta)$ is the following:

$$\Big(\frac{d}{d\theta} - l\cot\theta\Big)\Theta(\theta) = 0, \tag{15.53}$$

which can be integrated as follows:

$$\begin{aligned}\frac{d\Theta}{d\theta} &= l\cot\theta\Theta \rightarrow \frac{d\Theta}{\Theta} = l\cot\theta d\theta\\ &\rightarrow \ln\Big(\frac{\Theta}{\Theta_0}\Big) = l\ln\Big(\frac{\sin\theta}{\sin\theta_0}\Big).\end{aligned} \tag{15.54}$$

The last equation leads to the solution

$$\Theta(\theta) = C(\sin\theta)^l, \tag{15.55}$$

where C is an integration constant $C = \Theta_0/(\sin\theta_0)^l$. Therefore, we found that

$$\langle r,\theta,\phi|l,l\rangle = f(r)Y_{l,l}(\theta,\phi), \tag{15.56}$$

$$Y_{l,l}(\theta,\phi) \equiv Ce^{il\phi}(\sin\theta)^l, \tag{15.57}$$

where C is treated as a normalization constant. The function $Y_{l,l}(\theta,\phi)$ is a member of a family of functions $Y_{l,m}(\theta,\phi)$ called spherical harmonics which will be found next by finding the eigenstates $\langle r,\theta,\phi|l,m\rangle$ for all $2l+1$ possible values of m. We will impose the following orthonormalization condition on these functions:

$$\int d\Omega Y^*_{l,m}(\theta,\phi)Y_{l',m'}(\theta,\phi) = \delta_{l,l'}\delta_{m,m'}. \tag{15.58}$$

For the special case where $l = l' = m = m'$, that is, for the case given by Eq. 15.57, the normalization constant C is determined from the condition:

$$|C|^2\int_0^{2\pi} d\phi \int_0^{\pi} d\theta\sin\theta(\sin\theta)^{2l} = 1. \tag{15.59}$$

Therefore,

$$|C|^2 = \frac{1}{2\pi I_{2l+1}}, \tag{15.60}$$

$$I_{2l+1} = \int_0^{\pi} d\theta(\sin\theta)^{2l+1}. \tag{15.61}$$

In Appendix B, we calculate the integral I_{2l+1} above. Using this calculation, the normalization constant C above is given by

$$C = \frac{(-1)^l}{2^l l!}\sqrt{\frac{(2l+1)!}{4\pi}}, \tag{15.62}$$

where we have added by hand the phase factor $(-1)^l$ following the traditional convention.

In order to find the other spherical harmonics we use the lowering operator $\hat{\mathcal{L}}_-$ (Eq. 15.47) as follows

$$\begin{aligned} Y_{l,l-1}(\theta,\phi) = \langle\theta,\phi|l,l-1\rangle &= \frac{1}{\hbar\sqrt{l(l+1)-l(l-1)}}\hat{\mathcal{L}}_-\langle\theta,\phi|l,l\rangle \\ &= -C\sqrt{2l}e^{i(l-1)\phi}\cos\theta(\sin\theta)^{l-1}. \end{aligned} \tag{15.63}$$

Therefore, we can find the spherical harmonic $Y_{l,m}(\theta,\phi)$ by applying the operator $\hat{\mathcal{L}}_-$ $(l-m)$ times on the spherical harmonic $Y_{l,l}(\theta,\phi)$.

Using this technique we can determine the first few spherical harmonics as follows:

$$Y_{00} = \frac{1}{\sqrt{4\pi}} \tag{15.64}$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta, \qquad Y_{1\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}, \tag{15.65}$$

$$Y_{20} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1), \tag{15.66}$$

$$Y_{2\pm1} = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\phi}, \tag{15.67}$$

$$Y_{2\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm 2i\phi}. \tag{15.68}$$

15.4 Legendre polynomials and spherical harmonics

Since $\langle r,\theta,\phi|l,m\rangle$ are common eigenstates of $\hat{\mathcal{L}}^2$ and $\hat{\mathcal{L}}_z$, apart from a multiplicative function of r, we may write them as

$$\langle r,\theta,\phi|l,m\rangle = f(r)Y_{l,m}(\theta,\phi), \tag{15.69}$$

$$Y_{l,m}(\theta,\phi) = \Theta(\theta)e^{im\phi}. \tag{15.70}$$

The eigenvalue equation for $\hat{\mathcal{L}}^2$, that is, Eq. 15.16 using the expression for $\hat{\mathcal{L}}^2$ given by Eq. 15.15, takes the following form:

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) - \frac{m^2}{\sin^2\theta}\Theta + l(l+1)\Theta = 0. \tag{15.71}$$

If we change variables to $s = \cos\theta$, the above equation is transformed to

$$\frac{d}{ds}\left[(1-s^2)\frac{df}{ds}\right]-\frac{m^2}{1-s^2}f+l(l+1)f=0, \tag{15.72}$$

where $f(s)=\Theta(\theta)$. In the case where $m=0$ the above equation takes the form of the Legendre equation:

$$\frac{d}{ds}\left[(1-s^2)\frac{dP_l(s)}{ds}\right]+l(l+1)P_l(s)=0. \tag{15.73}$$

The solutions to this equation are the Legendre polynomials which can be generated as follows

$$P_l(s)=\frac{1}{2^l l!}\frac{d^l}{ds^l}(s^2-1)^l. \tag{15.74}$$

In Appendix C, it is shown that the above expression generates solutions to the Legendre equation, that is, the Legendre polynomials.

The prefactor of the Legendre polynomials are determined via the condition $P_l(0)=1$. Therefore, their orthonormalization is as follows:

$$\int_{-1}^{1} dsP_l(s)P_{l'}(s)=\frac{2}{2l+1}\delta_{l,l'}. \tag{15.75}$$

Since, we have found that for $m=0$ the equation which determines the spherical harmonics is the Legendre equation, we conclude that

$$Y_{l,0}(\theta,\phi)=\sqrt{\frac{2l+1}{4\pi}}P_l(\cos\theta). \tag{15.76}$$

15.5 Problems

Problem 1

(a) Explicitly construct the 3×3 matrices that represent the operators $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ in the space of $l=1$, that is,

$$\begin{aligned}(\hat{L}_i)_{m,m'}=\langle l=1,m|\hat{L}_i|l=1,m'\rangle=\int d\Omega Y^*_{1,m}(\theta,\phi)\\ \times\hat{L}_iY_{1,m'}(\theta,\phi),\end{aligned} \tag{15.77}$$

where $i=x,y,z$.

(b) Show by explicit calculation that these three matrices obey the commutation relations of angular momentum.

(c) Find the matrices that represent the “ladder” operators, $\hat{L}_+$, $\hat{L}_-$, and also $\hat{L}^2$.

Problem 2

A quantum system is described by the following Hamiltonian

$$\hat{H} = \lambda \hat{L}_z^2 - B\hat{L}_x, \tag{15.78}$$

where $\hat{L}_x$ and $\hat{L}_z$ are the x and z components of the angular momentum operator. Here, λ and B are parameters. Consider the $l = 1$ subspace of the total angular momentum.

(a) Find the eigenvalues of the above Hamiltonian.

(b) Find the eigenstates of the Hamiltonian.

(c) Imagine that we prepare the system in the initial state

$$|\psi(t = 0)\rangle = |l = 1, m = 1\rangle, \tag{15.79}$$

namely, with projection of the angular momentum along the z-axis characterized by $m = 1$ at time $t = 0$. Find the probability for the system to be observed in state $|l = 1, m = -1\rangle$ at time $t > 0$.

Problem 3

Given the fact that the spherical harmonics $Y_{l,m}(\theta, \phi)$ form a complete basis for the angular part of any function of the spherical coordinates r, θ, ϕ expand the following functions

$$f_1 = x, \qquad f_2 = y, \qquad f_3 = z, \tag{15.80}$$

$$f_4 = x^2 - y^2, \qquad f_5 = z^2, \qquad f_6 = xy, \tag{15.81}$$

as a linear combination of the spherical harmonics, that is,

$$f_i = \phi_i(r) \sum_{l,m} c(l, m) Y_{l,m}(\theta, \phi), \tag{15.82}$$

where $\phi_i(r)$ are specific functions of r only. Find the coefficients $c(l, m)$.

Problem 4

Consider the 2D harmonic oscillator, with

$$V(r) = \frac{1}{2} m\omega^2 r^2. \tag{15.83}$$

$$r^2 = x^2 + y^2. \tag{15.84}$$

(a) Find the energy and wavefunctions by working in Cartesian coordinates. What are the wavefunctions of the ground state and each of the first excited states? What is the degree of degeneracy of the ground and first excited energy level?

(b) Use polar coordinates and find wavefunctions for the ground state and the excited states which correspond to the ground-state energy and the first excited energy level.

(c) How are the approaches a) and b) related?
Hint: Use the states which you found in part (a) to span the space of degeneracy of the first excited energy level. Show that you can make linear combinations of these states to construct eigenstates of the only angular momentum operator in 2D. Does the corresponding energy eigenvalue change when you make linear combinations of states which span the space of degeneracy? Show that these states satisfy the Schrödinger equation in polar coordinates.

Problem 5

(a) Reproduce the derivation that the Legendre polynomials generated as follows:

$$P_l(x) = \frac{1}{2^l l}\frac{d^l}{dx^l}(x^2-1)^l, \tag{15.85}$$

satisfy the Legendre equation:

$$\frac{d}{dx}\Big[(1-x^2)\frac{dP_l(x)}{dx} + l(l+1)P_l(x) = 0. \tag{15.86}$$

(b) Show that the Legendre polynomials defined in part a) obey the following orthonormalization:

$$\int_{-1}^{+1} dx P_l(x)P_{l'}(x) = \frac{2}{2l+1}\delta_{l,l'}. \tag{15.87}$$

Problem 6

(a) Show that the following expansion is valid

$$\frac{1}{\sqrt{1-2xs+s^2}} = \sum_{l=0}^{\infty} P_l(x)s^l. \tag{15.88}$$

(b) Show that the following relationship exists between the spherical harmonics and the Legendre polynomials

$$Y_{l,0}(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}}P_l(cos\theta). \tag{15.89}$$

Problem 7

Consider a particle in 3D with a wavefunction given by

$$\Psi(r,\theta,\phi) = W(r,\theta)A\sin^2\phi, \tag{15.90}$$

where the W part of the wavefunction is a known function and it is normalized as follows:

$$\int_0^{\infty} dr r^2 \int_0^{\pi} d\theta \sin\theta |W(r,\theta)|^2 = 1. \tag{15.91}$$

(a) Determine the coefficient A.

(b) Find the probability of measuring different values of the z-component of the angular momentum $\hat{L}_z$.

(c) What is the expectation value of $\hat{L}_z$ and $\hat{L}_z^2$?

16

Bound states in spherically symmetric potentials

In this chapter we will deal with bound states in the case where the potential is spherically symmetric.

In the previous chapter we found that the ∇ operator in spherical coordinates is given by Eq. 15.6. Using this expression and the expressions (15.9) of the unit vectors $\hat{r}$, $\hat{\theta}$, and $\hat{\phi}$, we can find the expression for ∇^2:

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Big(\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \cot\theta\frac{\partial}{\partial\theta}\Big). \tag{16.1}$$

In order to derive this, we need to make sure that we take into account the contributions arising from the angular dependence of the unit vectors, specifically that

$$\hat{\phi}\cdot\frac{\partial\hat{r}}{\partial\phi} = \sin\theta, \tag{16.2}$$

$$\hat{\phi}\cdot\frac{\partial\hat{\theta}}{\partial\phi} = \cos\theta, \tag{16.3}$$

$$\hat{\theta}\cdot\frac{\partial\hat{r}}{\partial\theta} = 1. \tag{16.4}$$

Using the expression for $\hat{\mathcal{L}}^2$ given by Eq. 15.15, the above Eq. 16.1 can be conveniently written as

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\Big(r^2\frac{\partial}{\partial r}\Big) - \frac{\hat{\mathcal{L}}^2}{\hbar^2 r^2}. \tag{16.5}$$

Using this expression, the Hamiltonian for the case of a particle in a spherically symmetric potential can be written as

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\Big(r^2\frac{\partial}{\partial r}\Big) + \frac{\hat{\mathcal{L}}^2}{2mr^2}. \tag{16.6}$$

Notice that the Hamiltonian commutes with both $\hat{\mathcal{L}}^2$ and $\hat{\mathcal{L}}_z$. This allows us to look for eigenstates which are shared by $\hat{H}$, $\hat{\mathcal{L}}^2$, and $\hat{\mathcal{L}}_z$. In addition, in order to diagonalize the Hamiltonian we are justified to seek eigenstates of the form:

$$\Psi(r,\theta,\phi) = R_l(r)Y_{l,m}(\theta,\phi), \tag{16.7}$$

Practical Quantum Mechanics. First Edition. Efstratios Manousakis.

where $Y_{l,m}$ are the spherical harmonics which are eigenstates of $\hat{\mathcal{L}}^2$. Using the expression (16.7) the Schrödinger equation, $\hat{H}\Psi = E\Psi$ takes the following form:

$$\begin{aligned}-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\Big(r^2\frac{\partial R_l(r)}{\partial r}\Big) + \Big[\frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\Big]R_l(r) \\ = ER_l(r).\end{aligned} \tag{16.8}$$

The reason why we have assigned the angular momentum label to $R_l(r)$ is now obvious.

Next, if we make the transformation

$$R_l(r) = \frac{u_l(r)}{r}, \tag{16.9}$$

the radial part of the Schrödinger equation (i.e., Eq. 16.8) is transformed to

$$-\frac{\hbar^2}{2m}\frac{\partial^2 u_l}{\partial r^2} + \Big[\frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\Big]u_l = Eu_l(r). \tag{16.10}$$

This is exactly like a 1D problem with an effective potential of the form:

$$V_{eff}(r) \equiv V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}. \tag{16.11}$$

The last term is the centrifugal potential which acts as a repulsive potential. Furthermore, notice that for $l = 0$, this term is absent and the problem reduces to a 1D problem.

16.1 Spherical Bessel functions

First, we deal with the case of a $V(r)$ which as a function of the distance r consists of various regions in which the potential remains constant, an example of which is shown in Fig. 16.1.

In any one particular region in which the potential is a constant, say V, the radial equation (16.8) may be written as follows:

$$-\frac{1}{r^2}\frac{\partial}{\partial r}\Big(r^2\frac{\partial R_l(R)}{\partial r}\Big) + \frac{l(l+1)}{r^2}R_l(R) = k^2 R_l(r), \tag{16.12}$$

$$k \equiv \sqrt{\frac{2m(E-V)}{\hbar^2}}. \tag{16.13}$$

Using the variable $\rho = kr$, this equation is transformed to the so-called spherical Bessel equation:

$$\rho^2\frac{d^2\mathcal{R}_l}{d\rho^2} + 2\rho\frac{d\mathcal{R}_l}{d\rho} + \Big(\rho^2 - l(l+1)\Big)\mathcal{R}_l = 0, \tag{16.14}$$

where $\mathcal{R}_l(\rho) = R_l(r)$.

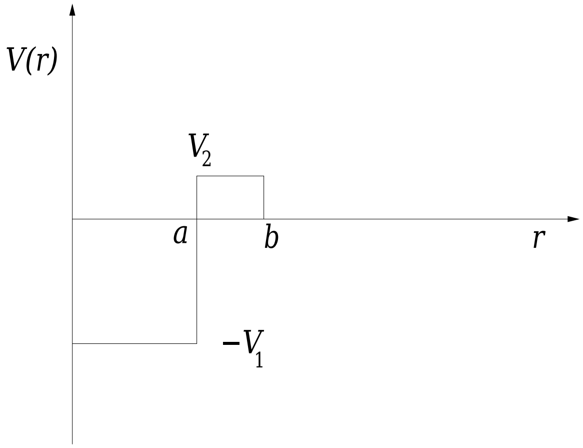

Fig. 16.1 This potential is constant in the three regions of r. It is $-V_1$ for $0 \leq r \leq a$, it is V_2 for $a < r < b$, and it is zero for $r > b$.

By making the same transformation as (16.9), that is,

$$\mathcal{R}_l(\rho) = \frac{\tilde{u}_l(\rho)}{\rho}, \tag{16.15}$$

the spherical Bessel equation becomes

$$\Big(-\frac{d^2}{d\rho^2} + \frac{l(l+1)}{\rho^2}\Big)\tilde{u}_l(\rho) = \tilde{u}_l(\rho). \tag{16.16}$$

Let us define the following two operators

$$a_l^+ \equiv \frac{d}{d\rho} + \frac{l+1}{\rho}, \tag{16.17}$$

$$a_l \equiv -\frac{d}{d\rho} + \frac{l+1}{\rho}. \tag{16.18}$$

The transformed Bessel equation (16.16) now reads

$$(a_l^+ a_l)\tilde{u}_l(\rho) = \tilde{u}_l(\rho). \tag{16.19}$$

Now, by multiplying both sides of this equation by a_l we find that

$$(a_l a_l^+)\tilde{w}_l(\rho) = \tilde{w}_l(\rho), \tag{16.20}$$

$$\tilde{w}_l(\rho) \equiv a_l \tilde{u}_l(\rho). \tag{16.21}$$

However, using the definitions given by Eq. 16.18, it is straightforward to show that

$$a_l a_l^+ = a_{l+1}^+ a_{l+1}, \tag{16.22}$$

which leads to the conclusion

$$(a^{+}_{l+1}a_{l+1})\tilde{w}_l(\rho) = \tilde{w}_l(\rho). \tag{16.23}$$

Taking into consideration our notation that Eq. 16.19 defines the state $\tilde{u}_l(\rho)$ as the eigenstate of the operator $a^{+}_{l}a_l$ with eigenvalue 1, the above equation (16.23) means that apart from a normalization constant the state $\tilde{w}_l(\rho)$ is nothing but $\tilde{u}_{l+1}(\rho)$. This simply implies that

$$a_l\tilde{u}_l(\rho) = c_l\tilde{u}_{l+1}(\rho), \tag{16.24}$$

where we have explicitly substituted the definition of $\tilde{w}_l(\rho)$ from Eq. 16.21. Here, c_l is a normalization constant which we will set equal to 1, and we will remember that the solutions are normalized in this way.

The above equation implies that we can find all the solutions to the spherical Bessel equation recursively starting from $\tilde{u}_0(\rho)$ and using

$$\tilde{u}_{l+1}(\rho) = \Big(-\frac{d}{d\rho} + \frac{l+1}{\rho}\Big)\tilde{u}_l(\rho). \tag{16.25}$$

In the case of $l = 0$, however, Eq. 16.16 takes the form

$$\frac{d^2\tilde{u}_0(\rho)}{d\rho^2} + \tilde{u}_0(\rho) = 0, \tag{16.26}$$

for which we can choose the linearly independent solutions to be

$$\tilde{u}_0(\rho) = \sin\rho, \tag{16.27}$$

$$\tilde{u}_0(\rho) = -\cos(\rho). \tag{16.28}$$

Let us reformulate the recursion relation (16.25) for the solution $\mathcal{R}_l(\rho)$ to the spherical Bessel equation. The manipulations are straightforward:

$$\begin{aligned}
\rho\tilde{R}_{l+1}(\rho) &= \Big(-\frac{d}{d\rho} + \frac{l+1}{\rho}\Big)\rho\tilde{R}_l(\rho), \quad \rightarrow\\
\tilde{R}_{l+1}(\rho) &= \Big(-\frac{d}{d\rho} + \frac{l}{\rho}\Big)\tilde{R}_l(\rho), \qquad \rightarrow\\
\tilde{R}_{l+1}(\rho) &= \rho^l\Big(-\frac{d}{d\rho}\Big)\frac{\tilde{R}_l(\rho)}{\rho^l}, \qquad \rightarrow\\
\frac{\tilde{R}_{l+1}(\rho)}{\rho^{l+1}} &= \Big(-\frac{1}{\rho}\frac{d}{d\rho}\Big)\frac{\tilde{R}_l(\rho)}{\rho^l}.
\end{aligned} \tag{16.29}$$

We can iterate this recursion relation to find that:

$$\tilde{R}_l(\rho) = (-\rho)^l\Big(-\frac{1}{\rho}\frac{d}{d\rho}\Big)^l\tilde{R}_0(\rho). \tag{16.30}$$

This is the so-called Rayleigh formula. Therefore, as expected for a second-order differential equation, there are two families of solutions. First, there are the so-called spherical Bessel functions which correspond to starting from

$$\mathcal{R}_0(\rho) = j_0(\rho) = \frac{\sin\rho}{\rho}, \tag{16.31}$$

which are obtained when we use the solution $\tilde{u}_0(\rho) = \sin\rho$. The second family of solutions are the so-called Neumann functions, which are obtained from the $l = 0$ solutions for $\tilde{u}_0(\rho) = -\cos\rho$, that is, using as zeroth order the following function:

$$\mathcal{R}_0(\rho) = n_0(\rho) = -\frac{\cos\rho}{\rho}. \tag{16.32}$$

Using the Rayleigh formula we can calculate the first few spherical Bessel functions and we can plot them:

$$j_1(\rho) = -\frac{\cos\rho}{\rho} + \frac{\sin\rho}{\rho^2}, \tag{16.33}$$

$$j_2(\rho) = \Big(\frac{3}{\rho^3} - \frac{1}{\rho}\Big)\sin\rho - \frac{3}{\rho^2}\cos\rho, \tag{16.34}$$

$$n_1(\rho) = -\frac{\sin\rho}{\rho} - \frac{\cos\rho}{\rho^2}, \tag{16.35}$$

$$n_2(\rho) = -\Big(\frac{3}{\rho^3} - \frac{1}{\rho}\Big)\cos\rho - \frac{3}{\rho^2}\sin\rho. \tag{16.36}$$

The asymptotic small ρ and large ρ limits of the spherical Bessel and Neumann function can be obtained from the Rayleigh formulas. In the case of $j_l(\rho)$ we may expand $j_0(\rho)$ in an infinite series as

$$j_0(\rho) = \sum_{k=0}^{\infty} \frac{(-1)^k}{(2k+1)!}\rho^{2k}, \tag{16.37}$$

and then, following Eq. 16.30, we apply the operator

$$\hat{O}(\rho) \equiv \frac{1}{\rho}\frac{d}{d\rho} \tag{16.38}$$

l times. Notice that the first time we apply it we eliminate the constant. The second time we eliminate the $k = 1$ term, and so on. Thus the leading term after l applications comes from the term $k = l$. This term gives,

$$j_l(\rho << l) \sim \frac{2^l l!}{(2l+1)!}\rho^l. \tag{16.39}$$

The case of the spherical Neumann function is simpler. We are looking for the most singular term and this comes by simply differentiating the leading term of the expansion of $n_0(\rho)$, that is, from $-1/\rho$. First we find that

$$[\frac{1}{\rho}\frac{d}{d\rho}]^l\frac{1}{\rho} = (-1)(-3)(-5)...[-(2l-1)]\rho^{-(2l+1)}. \tag{16.40}$$

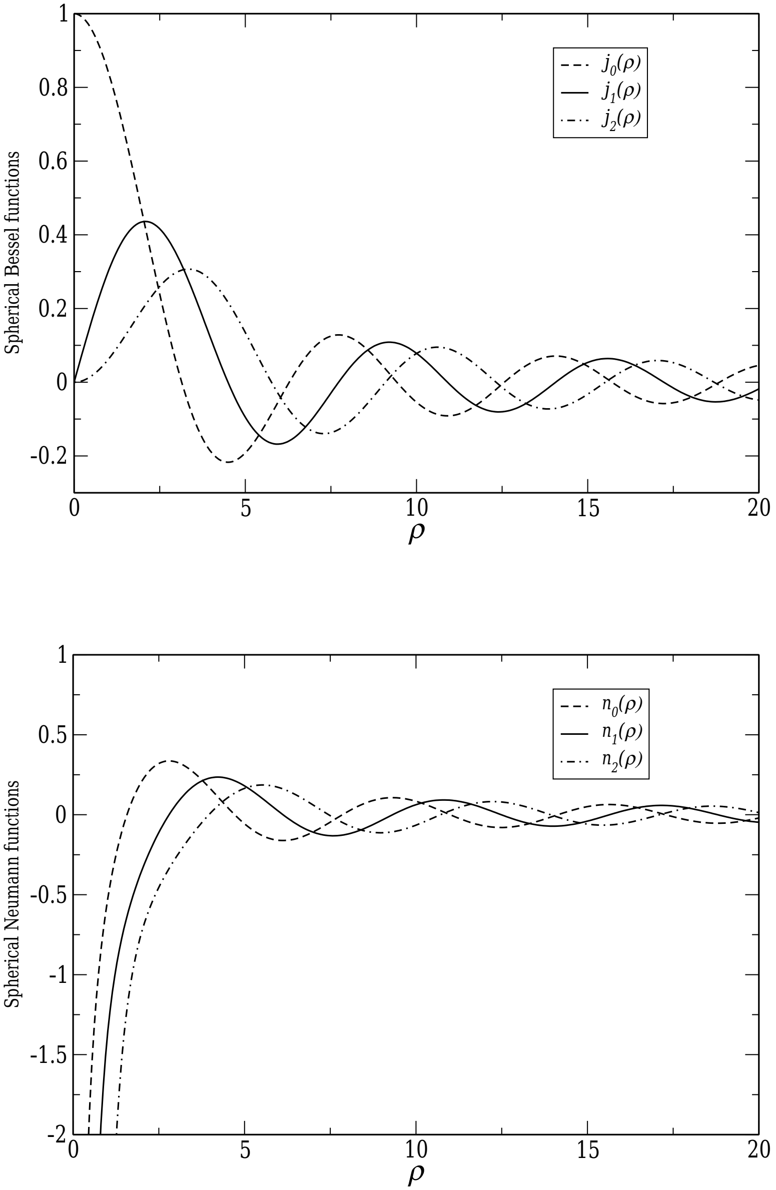

Fig. 16.2 The spherical Bessel (top) and Neumann (bottom) functions for $l = 0, 1, 2$.

The prefactor can be conveniently written as $(2l)!/(2^l l!)$ and, thus, we obtain:

$$n_l(\rho << l) \sim -\frac{(2l)!}{2^l l!}\frac{1}{\rho^{l+1}}. \tag{16.41}$$

In the limit of large ρ, that is, $\rho >> l$, the most important term (the one with the lowest power of $1/\rho$) is the one which is obtained by differentiating the $\sin\rho$ in the case of $j_l(\rho)$ or the $\cos(\rho)$ in the case of $n_l(\rho)$. This way we obtain that

$$j_l(\rho >> l) \sim \frac{1}{\rho}\sin(\rho - l\frac{\pi}{2}), \tag{16.42}$$

$$n_l(\rho >> l) \sim -\frac{1}{\rho}\cos(\rho - l\frac{\pi}{2}). \tag{16.43}$$

Note that for any given value of l after taking the derivative l times we will end up with either a $\sin(\rho)$ or a $\cos\rho$ depending on whether the value of l is even or odd. Adding a multiple of $\pi/2$ inside the argument of the sin or cos results in either itself or the other depending on whether or not l is even or odd. This also automatically takes the case of the overall sign.

In Fig. 16.2 the spherical Bessel (top) and Neumann (bottom) functions for $l = 0, 1, 2$ are illustrated. Notice that the j_l start as ρ^l for small ρ, while the n_l diverge as $1/\rho^{l+1}$. Also, notice that the places where the zeros of these functions occur move up by approximately $\pi/2$ as we increase l by one.

It may be convenient to use instead of the spherical Bessel and Neumann functions, the so-called Hankel functions of first and second kind defined as the linear combinations:

$$h_l(\rho) = j_l(\rho) + i n_l(\rho), \tag{16.44}$$

$$h_l^*(\rho) = j_l(\rho) - i n_l(\rho). \tag{16.45}$$

They are both singular at small ρ and they diverge in the same way as the spherical Neumann functions. For large ρ their asymptotic form is the following

$$h_l(\rho >> l) \sim (-1)^{l+1}\frac{e^{i\rho}}{\rho}, \tag{16.46}$$

$$h_l^*(\rho >> l) \sim (-1)^{l+1}\frac{e^{-i\rho}}{\rho}. \tag{16.47}$$

16.2 Relation to ordinary Bessel equation

The spherical Bessel equation (16.14) maps to the ordinary Bessel equation:

$$\rho^2\frac{d^2y}{d\rho^2} + \rho\frac{dy}{d\rho} + (\rho^2 - \alpha^2)y = 0, \tag{16.48}$$

when we use the transformation:

$$\mathcal{R}_l(\rho) = \frac{y(\rho)}{\sqrt{\rho}}. \tag{16.49}$$

Then, the spherical Bessel equation (16.14) becomes the ordinary Bessel equation with

$$\alpha = l + \frac{1}{2}. \tag{16.50}$$

The ordinary Bessel equation has, as solutions, the ordinary Bessel functions of first kind given by the following infinite series:

$$J_\alpha(\rho) = \sum_{m=0}^{\infty} \frac{(-1)^m}{m!\Gamma(m+\alpha+1)} (\frac{\rho}{2})^{2m+\alpha}. \tag{16.51}$$

This solution is finite at $\rho = 0$. Since, when $\alpha \to -\alpha$ the equation remains the same, the $J_{-\alpha}(\rho)$ is also a solution. The Bessel function of second kind is defined as

$$Y_\alpha(\rho) = \frac{J_\alpha(\rho)\cos(\alpha\pi) - J_{-\alpha}(\rho)}{\sin(\alpha\pi)}. \tag{16.52}$$

When α is an integer say n, $J_{-n}(\rho) = (-1)^n J_n(\rho)$, and, thus, in this case, J_n and J_{-n} are linearly dependent. In this case, as a second solution one considers the above expression (16.52) by considering α to be non-integer and by taking the limit $\alpha \to n$.

The mapping of the spherical Bessel equation to the ordinary Bessel equation by means of the transformation given by Eq. (16.49) and (16.50) relates the solutions to these two equations as follows:

$$j_l(\rho) = \sqrt{\frac{\pi}{2\rho}} J_{l+1/2}(\rho), \tag{16.53}$$

$$n_l(\rho) = \sqrt{\frac{\pi}{2\rho}} Y_{l+1/2}(\rho). \tag{16.54}$$

Here, a constant prefactor $\sqrt{\pi/2}$ has been inserted.

16.3 Spherical Bessel functions and Legendre polynomials

The spherical Bessel function $j_l(\rho)$ can also be written as an integral, as follows:

$$j_l(\rho) = \frac{\rho^l}{2^{l+1} l!} \int_{-1}^{1} e^{i\rho s}(1-s^2)^l ds. \tag{16.55}$$

It is rather straightforward to show (see Appendix D if you have cannot show it by yourself) that this expression satisfies the spherical Bessel equation.

Next, we can transform this integral to the following:

$$j_l(\rho) = \frac{1}{2i^l} \int_{-1}^{1} e^{i\rho s} P_l(s) ds, \tag{16.56}$$

where $P_l(s)$ are the Legendre polynomials. The above expression can be shown by utilizing the expression (15.74) for the Legendre and by integrating by parts l times.

16.4 Bound states in a spherical well

Next, we will seek bound-state solutions ($E < 0$) in the case of the spherical-well potential shown in Fig. 16.3 and given as

$$V(r) = \left\{ \begin{array}{cl} -V_0 & \text{for } r < a \\ 0 & \text{for } r \geq a \end{array} \right\}. \tag{16.57}$$

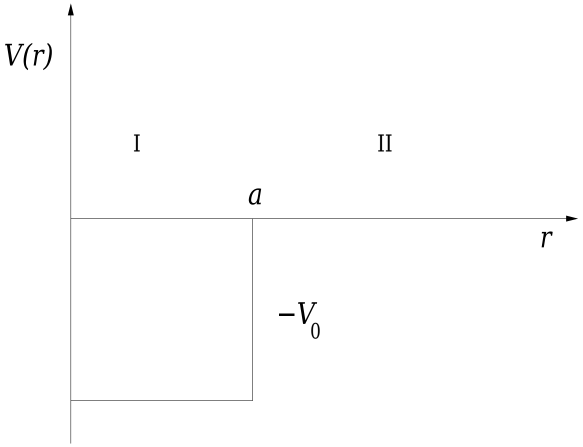

Fig. 16.3 The spherical-well potential.

In this case there are two regions:

Region I: $r < a$. In this region, the radial part of the wavefunction satisfies the spherical Bessel equation (16.14) with

$$k' = \sqrt{\frac{2m(V_0 + E)}{\hbar^2}}, \tag{16.58}$$

and this k' is a real number. Therefore, the general solution

$$R_l^{(I)}(r) = A_l^{(I)} j_l(k'r) + B_l^{(I)} n_l(k'r). \tag{16.59}$$

However, we need to take $B_l^{(I)} = 0$ because the Neumann functions are not well-behaved at $r = 0$ which is included as part of Region I.

Region II: In this region the radial part of the wavefunction also satisfies the spherical Bessel equation (16.14) with an imaginary value of k, and it is given by

$$k^2 = -\frac{2m|E|}{\hbar^2}, \tag{16.60}$$

$$k = i\mu, \qquad \mu = \sqrt{\frac{2m|E|}{\hbar^2}}. \tag{16.61}$$

Since the value of k in the argument of the spherical Bessel function turned out to be imaginary in this region, we will use the Hankel function to write down the solution as

$$R_l^{(II)}(r) = A_l^{(II)} h_l(i\mu r) + B_l^{(II)} h_l^*(i\mu r). \tag{16.62}$$

Here, we need to deal with the boundary condition at $r \to \infty$. If we keep both contributions, for large r we obtain:

$$R_l^{(II)}(r \to \infty) = \frac{(-1)^{l+1}}{\rho}(A_l^{(II)} e^{-\mu r} + B_l^{(II)} e^{\mu r}). \tag{16.63}$$

Therefore, we need to set $B_l^{(II)} = 0$.

Now, we need to match the two solutions and their derivatives at $r = a$. Namely,

$$A_l^{(I)} j_l(k'a) = A_l^{(II)} h_l(i\mu a), \tag{16.64}$$

$$A_l^{(I)} j_l'(k'a) = A_l^{(II)} h_l'(i\mu a). \tag{16.65}$$

where $j_l'(k'r)$ and $h_k'(i\mu r)$ denotes the derivatives of $j_l(k'r)$ and $h_k(i\mu r)$ with respect to r and not the full argument. Taking the ratio of these two equations we obtain an equation which determines the energy eigenvalues for bound states to occur.

$$\frac{j_l'(k'a)}{j_l(k'a)} = \frac{h_l'(i\mu a)}{h_l(i\mu a)}. \tag{16.66}$$

This is the equation which determines the energy eigenvalues and can be solved numerically or graphically.

16.5 Expansion of a plane wave

The application of spherical Bessel functions and Legendre polynomials, which we are about to discuss, is going to be very useful in our discussion of three-dimensional scattering in chapter 19.

We consider a plane wave in three dimensions characterized by a wavevector $\vec{k}$, and let the z-axis defining the vector $\vec{r}$ be taken along the direction of $\vec{k}$. Then,

$$e^{i\vec{k}\cdot\vec{r}} = e^{ikr\cos\theta}, \tag{16.67}$$

where θ is the polar angle in spherical coordinates. Utilizing the completeness of the Legendre polynomials, we can expand this function of $\cos\theta$ using Legendre polynomials as follows:

$$e^{ikr\cos\theta} = \sum_{l=0}^{\infty} C_l(r) P_l(\cos\theta). \tag{16.68}$$

The coefficient $c_l(r)$ which is a function of r can be determined by multiplying both sides of the above equation by $P_{l'}(\cos\theta)$ and integrating over the angle θ as follows:

$$\int_{-1}^{i} d\cos\theta P_{l'}(\cos\theta) e^{ikr\cos\theta} = \sum_{l=0}^{\infty} C_l(r) \int_{-1}^{1} d\cos\theta P_l(\cos\theta) \times P_{l'}(\cos\theta). \tag{16.69}$$

Using the orthogonalization properties of the Legendre polynomials (Eq. 15.75) we obtain

$$\int_{-1}^{i} d\cos\theta P_{l'}(\cos\theta) e^{ikr\cos\theta} = \sum_{l=0}^{\infty} C_l(r) \frac{2}{2l'+1} \delta_{l,l'}. \tag{16.70}$$

which leads to

$$C_l(r) = \frac{2l+1}{2} \int_{-1}^{1} ds e^{ikrs} P_l(s). \tag{16.71}$$

Comparing this expression with Eq. 16.56 we conclude that

$$C_l(r) = (2l+1) i^l j_l(kr). \tag{16.72}$$

As a result we found that

$$e^{i\vec{k}\cdot\vec{r}} = \sum_{l=0}^{\infty} i^l (2l+1) j_l(kr) P_l(\cos\theta). \tag{16.73}$$

16.6 Problems

Problem 1

Consider a particle enclosed in a sphere of radius R. Namely, the potential is zero for $0 \le r < R$ and infinite for $r \ge R$.

(a) What is the general form of the wavefunction if the radial part is a function of r, which you consider known at the moment.

(b) What is the equation that the abovementioned radial part of the wavefunction obeys?

(c) Provide the general form of the wavefunction. Write it as a linear combination of the spherical Bessel and Neumann functions. Show that for $l > 0$ the normalization condition cannot be satisfied unless the coefficient of the Neumann function in the above linear combination is zero. For the $l = 0$ part consider the expectation value of the energy with the above linear combination and show that the Neumann term makes the energy diverge.

(d) Apply the boundary condition at $r = R$ and find the equations which determine the energy eigenvalues.

(e) Determine the energy levels for $l = 0$. Graphically find the energy levels for $l = 1$. What is the order of energy level (that is, is it the ground state, is it the first second, third, ... , excited state?) of the lowest energy state for $l = 1$?

(f) Draw the wavefunction of the second excited state for $l = 0$ and the wavefunction of the lowest energy state for $l = 1$.

Problem 2

Consider a particle in a 3D square-well potential of finite depth, namely

$$V(r) = \begin{Bmatrix} -V_0 & r < R \\ 0 & r > R \end{Bmatrix}, \tag{16.74}$$

which is shown in Fig. 16.4.

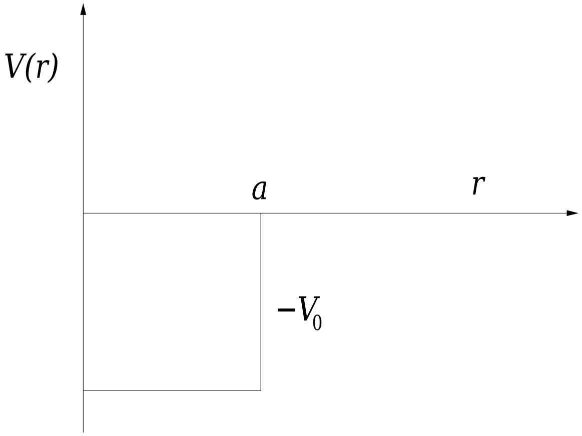

Fig. 16.4

(a) Give the equations which determine the eigenvalues of bound states in the above potential for angular momentum $l = 0, 1,$ and 2.

(b) Solve these equations graphically for the case where

$$\frac{2mV_0R^2}{\hbar^2} = 100. \tag{16.75}$$

Problem 3

Consider a 2D isotropic harmonic oscillator in polar coordinates. The energy eigenfunctions, which are simultaneously eigenstates of the only angular momentum operator in 2D, can be written as

$$\Psi(\rho, \phi) = u(\rho)e^{iM\phi}, \tag{16.76}$$

where $M = 0, \pm 1, \pm 2, ...$ Show that $u(\rho)$ satisfies the following radial equation

$$(u'' + \frac{1}{\rho}u' - \frac{M^2}{\rho^2}u) + (k^2 - \lambda^2\rho^2)u = 0, \tag{16.77}$$

where $k = \sqrt{2mE}/\hbar$ and $\lambda = m\omega/\hbar$. Putting

$$u = \rho^{|M|}e^{-\lambda\rho^2/2}P(\rho), \tag{16.78}$$

show that $P(\rho)$ satisfies the following differential equation

$$P'' + \Big(\frac{2|M|+1}{\rho} - 2\lambda\rho\Big)P' - \Big(2\lambda(|M|+1) - k^2\Big)P \\ = 0. \tag{16.79}$$

Now use the transformation of variables to $t = \lambda\rho^2$ and show that P satisfies the following equation:

$$t\frac{d^2P}{dt^2} + ((|M|+1) - t)\frac{dP}{dt} - \frac{1}{2}((|M|+1) - \frac{k^2}{2\lambda})P \\ = 0. \tag{16.80}$$

By writing the solution for P as a series in powers of t, that is,

$$P(t) = P_0 + P_1t + P_2t^2 + ...P_nt^n + ..., \tag{16.81}$$

show that in order for the solution to exist (not-diverge) the function $P(t)$ must be a polynomial of order n_r ($n_r = 0, 1, 2, ...$, an integer) and, thus, the energy of the 2D harmonic oscillator is given by

$$E = \hbar\omega(|M| + 1 + 2n_r). \tag{16.82}$$

Problem 4

Consider bound states ($E < 0$) of a particle which moves in a 3D centrally symmetric potential of the following form:

$$V(r) = \left\{ \begin{array}{cl} 0 & \text{for } 0 \leq r < a \\ -V_0 & \text{for } a \leq r < b \\ 0 & \text{for } \quad r \geq b \end{array} \right\} \tag{16.83}$$

where $V_0 > 0$. This potential is illustrated in Fig. 16.5.

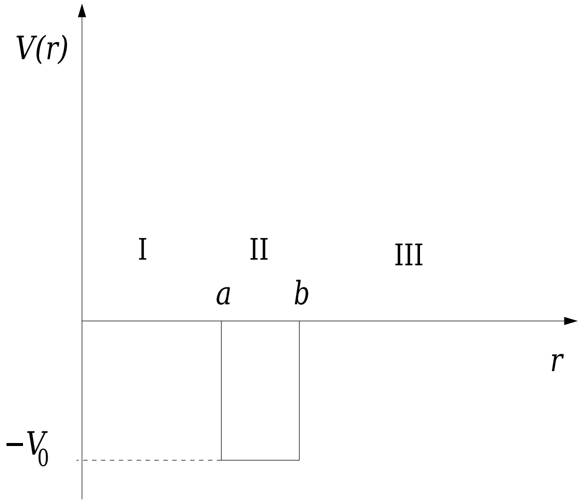

Fig. 16.5

(a) Write down the wavefunction for given angular momentum l which is a solution to the Schrödinger equation in each of the regions where the potential remains the same. Make sure that you keep only the special functions which behave well at $r = 0$ and infinity.

(b) Apply the boundary conditions.

(c) Explain how many equations and how many unknowns you have. You are interested in finding the bound-state energy eigenvalues. Without actually doing all the algebra from this point on, explain in detail what needs to be done to find the energy eigenvalues.

17
The hydrogen-like atom

In this chapter we solve the problem of two particles interacting via a $1/r$ type of interaction, just like in the case of the hydrogen atom. We find the eigenstates and the energy eigenvalues of this system. This requires a discussion of the Laguerre polynomials.

17.1 The general two-body problem

Here we will solve the problem of two particles interacting via the Coulomb interaction, that is,

$$V(r) = -\frac{Ze^2}{r}. \tag{17.1}$$

This problem finds applications in the case of the hydrogen atom, the positronium atom, an exciton in a semiconductor, and so on. It also has applications in the multi-electron atom, within some "mean-field" approximation.

The Hamiltonian for this problem has the following general form:

$$\hat{H} = \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + V(r_{12}), \tag{17.2}$$

$$\hat{\vec{p}}_1 = -i\hbar\nabla_{\vec{r}_1}, \qquad \hat{\vec{p}}_2 = -i\hbar\nabla_{\vec{r}_2}, \qquad r_{12} = |\vec{r}_1 - \vec{r}_2|. \tag{17.3}$$

Let us transform the Hamiltonian into the center of mass and relative position coordinate system. Namely, we transform our coordinates from $\vec{r}_1$ and $\vec{r}_2$ to the following:

$$\vec{r} = \vec{r}_2 - \vec{r}_1, \qquad \vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}. \tag{17.4}$$

Now, the corresponding conjugate momenta are given by:

$$\hat{\vec{p}} = -i\hbar\nabla_{\vec{r}}, \qquad \vec{P} = -i\hbar\nabla_{\vec{R}}, \tag{17.5}$$

because with these definitions, they satisfy the canonical commutation relatons

$$[\hat{r}_i, \hat{p}_j] = i\hbar\delta_{ij}, \qquad [\hat{R}_i, \hat{P}_j] = i\hbar\delta_{ij}. \tag{17.6}$$

How are these new momenta related to the old ones? We need these relationships in order to transform the Hamiltonian in terms of the new variables. In order to find

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them, we just need to use the transformation $\vec{r}_1 = (x_1, y_1, z_1), \vec{r}_2 = (x_2, y_2, z_2)$ to $\vec{r} = (x, y, z), \vec{R} = (X, Y, Z)$ and the derivative-chain rule:

$$\frac{\partial}{\partial x_1} = \frac{\partial x}{\partial x_1}\frac{\partial}{\partial x} + \frac{\partial X}{\partial x_1}\frac{\partial}{\partial X}, \tag{17.7}$$

which simply leads to

$$\frac{\partial}{\partial x_1} = -\frac{\partial}{\partial x} + \frac{m_1}{m_1 + m_2}\frac{\partial}{\partial X}, \tag{17.8}$$

and consequently to

$$\nabla_{\vec{r}_1} = -\nabla_{\vec{r}} + \frac{m_1}{m_1 + m_2}\nabla_{\vec{R}}, \tag{17.9}$$

which implies that

$$\hat{\vec{p}}_1 = -\hat{\vec{p}} + \frac{m_1}{m_1 + m_2}\hat{\vec{P}}. \tag{17.10}$$

In a similar way we obtain:

$$\hat{\vec{p}}_2 = \hat{\vec{p}} + \frac{m_2}{m_1 + m_2}\hat{\vec{P}}. \tag{17.11}$$

These relations can be easily inverted to find

$$\hat{\vec{P}} = \hat{\vec{p}}_1 + \hat{\vec{p}}_2, \tag{17.12}$$

$$\hat{\vec{p}} = \frac{m_1\hat{\vec{p}}_2 - m_2\hat{\vec{p}}_1}{m_1 + m_2}. \tag{17.13}$$

Substituting $\hat{\vec{p}}_1$ and $\hat{\vec{p}}_2$ in terms of $\hat{\vec{p}}$ and $\hat{\vec{P}}$ in the expression for $\hat{H}$, we find that

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \frac{\hat{P}^2}{M} + V(r), \tag{17.14}$$

$$M = m_1 + m_2, \qquad \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}. \tag{17.15}$$

This can be found by treating the problem as one of classical mechanics. The eigenvalue problem for the above Hamiltonian becomes

$$\Big[-\frac{\hbar^2}{2M}\nabla^2_{\vec{R}} - \frac{\hbar^2}{2\mu}\nabla^2_{\vec{r}} + V(r)\Big]\Phi(\vec{r}, \vec{R}) = E_T\Phi(\vec{r}, \vec{R}), \tag{17.16}$$

where E_T denotes the total energy, that is, the center of mass energy E_c plus the energy E of the system on the center of mass frame. By means of separation of variables, that is, by writing:

$$\Phi(\vec{r}, \vec{R}) = \Psi_c(\vec{R})\psi(\vec{r}), \tag{17.17}$$

we obtain

$$-\frac{\hbar^2}{2M}\nabla^2_{\vec{R}}\Psi_c(\vec{R}) = E_c\Psi_c(\vec{R}), \tag{17.18}$$

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2_{\vec{r}} + V(r)\right]\psi(\vec{r}) = E\psi(\vec{r}), \tag{17.19}$$

$$E_T = E + E_c. \tag{17.20}$$

Thus, as expected, the center of mass moves as a free particle with mass M and, therefore,

$$\Psi_c(\vec{R}) = Ce^{\frac{i}{\hbar}\vec{P}_c\cdot\vec{R}}, \tag{17.21}$$

$$E_c = \frac{{P_c}^2}{2M}. \tag{17.22}$$

The equation (17.19) which describes the relative motion is discussed in the next section.

17.2 The relative motion

The relative coordinate part looks like a one-body problem in a central potential. Therefore, we may write

$$\psi(\vec{r}) = R_l(r)Y_{l,m}(\theta,\phi), \tag{17.23}$$

and by substitution in Eq. 17.19 we find that the radial part satisfies the already familiar radial equation

$$-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R_l(r)}{\partial r}\right) + \left[\frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r)\right]R_l(r) = ER_l(r) \tag{17.24}$$

with the reduced mass μ. Once again, if we use the transformation (16.9) we obtain

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2 u_l}{\partial r^2} + \left[\frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r)\right]u_l = Eu_l(r). \tag{17.25}$$

Next, we are going to find the behavior of $u_l(r)$ as $r \to 0$ and as $r \to \infty$.

First, in the limit $r \to 0$, Eq. 17.25 takes the simple form:

$$-\frac{d^2u_l(r)}{dr^2} + \frac{l(l+1)}{r^2}u_l(r) = 0, \tag{17.26}$$

because among the terms, $l(l+1)/r^2$, $V(r)$, and E, we kept just the first term, because in the limit of $r \to 0$ it dominates over the second, which only diverges as $1/r$, and over the third, which is only a constant.

The most general solution to the above equation is of the form

$$u_l(r) = Ar^{l+1} + Br^{-l}, \tag{17.27}$$

however, because, in general, the second term does not behave well in the limit of small r, we need to take $B = 0$.

Conclusion:

$$u_l(r \to 0) = Ar^{l+1}. \tag{17.28}$$

In the limit of large r, Eq. 17.25 takes the simple form:

$$-\frac{d^2u_l(r)}{dr^2} = \frac{2\mu E}{\hbar^2}u_l(r), \tag{17.29}$$

and, because we are interested in finding bound states where $E < 0$, we conclude that

$$u_l(r \to \infty) = Be^{-kr}, \tag{17.30}$$

$$k = \sqrt{\frac{2\mu|E|}{\hbar^2}}. \tag{17.31}$$

Therefore, by taking into account the above found asymptotic limits, that is, the $r \to 0$ and $r \to \infty$ limit of $u_l(r)$, we consider the following ansatz

$$u_l(r) = \rho^{l+1}e^{-\rho}\chi(\rho), \tag{17.32}$$

where $\rho = kr$. This ansatz satisfies both asymptotic limits and the constants have been hidden in the function $\chi(\rho)$ which needs to be determined next.

First, the radial equation for the function $\tilde{u}_l(\rho) = u_l(r)$ is the following:

$$\frac{\partial^2\tilde{u}_l}{\partial r^2} - \left[\frac{l(l+1)}{r^2} - \frac{\lambda}{r} + 1\right]\tilde{u}_l = 0, \tag{17.33}$$

$$\lambda = \frac{2Ze^2\mu}{k\hbar^2}. \tag{17.34}$$

Next, we substitute the ansatz (17.32) in the above equation and we find the following differential equation for $\chi_l(\rho)$:

$$\rho\chi_l'' + 2(l+1-\rho)\chi_l' - \Big(2(l+1) - \lambda\Big)\chi_l = 0, \tag{17.35}$$

$$\alpha = 2(l+1) - \lambda. \tag{17.36}$$

Now, let us expand the function $\chi_l(\rho)$ as a power series, that is,

$$\chi_l(\rho) = \sum_{\nu=0}^{\infty} b_\nu\rho^\nu, \tag{17.37}$$

$$\chi_l'(\rho) = \sum_{\nu=0}^{\infty} b_\nu\rho^{\nu-1}, \tag{17.38}$$

$$\chi_l''(\rho) = \sum_{\nu=0}^{\infty} \nu(\nu-1)b_\nu\rho^{\nu-2}, \tag{17.39}$$

and we simply substitute in the differential equation for $\chi_l(\rho)$ to find that:

$$\sum_{\nu=0}^{\infty}\Big[\nu(\nu-1)b_\nu\rho^{\nu-1}+2(l+1)\nu b_\nu\rho^{\nu-1}-2\nu b_\nu\rho^\nu \\ -\Big(2(l+1)-\lambda\Big)b_\nu\rho^\nu\Big]=0. \tag{17.40}$$

For this to be valid for a continuum of values of ρ, the coefficient of the ρ^ν should vanish, that is,

$$(\nu+1)\nu b_{\nu+1}+2(l+1)(\nu+1)b_{\nu+1}-2\nu b_\nu-\Big(2(l+1)-\lambda\Big)b_\nu \\ =0. \tag{17.41}$$

First, the equation for $\nu=-1$ leads to the conclusion that $b_{-1}=0$. From this and the above equation, we conclude that all other coefficients b_ν for $\nu<0$ also vanish. Thus, the wavefunction starts from a constant b_0. Furthermore, this equation leads to the following recursion relation of the coefficients

$$\frac{b_{\nu+1}}{b_\nu}=\frac{2(\nu+l+1)-\lambda}{(\nu+1)\Big[\nu+2(l+1)\Big]}. \tag{17.42}$$

Assuming that the series does not terminate for a given maximum value of ν, for large values of ν we obtain:

$$\lim_{\nu\to\infty}\frac{b_{\nu+1}}{b_\nu}=\frac{2}{\nu+1}. \tag{17.43}$$

This implies, that asymptotically

$$\chi(\rho\to\infty)\simeq\sum_{\nu=0}^{\infty}\frac{1}{\nu!}(2\rho)^\nu=e^{2p}. \tag{17.44}$$

Therefore, this leads to the conclusion that

$$u_l(r\to\infty)\sim e^\rho\to\infty, \tag{17.45}$$

which is non-normalizable. Hence, the series must terminate at some maximum value of ν. In order for this to happen, it is necessary and sufficient that $\lambda=2n$, n is an integer. In this case, there is a maximum value of $\nu=N$ defined by the equation

$$2(N+l+1)-2n=0, \qquad \to \qquad N=n-l-1, \tag{17.46}$$

such that, for $\nu>N$, the coefficients $b_\nu=0$ (see Eq. 17.42). As a result, the function $\chi(\rho)$ is a polynomial of degree N and $u_l(\rho)$ at very large ρ behaves as $e^{-\rho}$ as can be inferred from Eq. 17.32. Therefore, we conclude that in order to have a normalizable solution

$$\frac{\lambda}{2}=n=\text{integer}, \tag{17.47}$$

in which case $u_l(\rho)$ is given by Eq. 17.32, where $\chi_l(\rho)$ is a polynomial of degree $N = n-l-1$. Furthermore, using the expression (17.34) for λ we conclude that the energy must be quantized and given by the following expression:

$$E_n = -\frac{Z^2e^4\mu}{2\hbar^2}\frac{1}{n^2}, \qquad n = 1, 2, ... \tag{17.48}$$

Given a value of l, the possible values of the integer n start from $l+1$ and higher, that is, $n \geq l+1$.

In addition, any given energy level which corresponds to a given integer value of n is the same for all possible values of $l = 0, 1, 2, ..., n-1$. For a given value of n and a given value of l, there $2l+1$ possible states for different values of the quantum number m. Therefore, excluding spin, the total number of states for a given value of n is

$$\begin{aligned}\text{Degeneracy} &= \sum_{l=0}^{n-1}(2l+1) = 2\sum_{l=0}^{n-1} l + \sum_{l=0}^{n-1} 1 \\ &= n(n-1) + n = n^2. \end{aligned} \tag{17.49}$$

17.3 Wavefunctions

Using our findings about the energy spectrum, the parameter $k = \sqrt{2\mu|E_n|/\hbar^2}$ can be written as

$$k = k_n = \frac{1}{na_0}, \qquad a_0 \equiv \frac{\hbar^2}{Ze^2\mu}, \tag{17.50}$$

that is, a_0 is the Bohr radius. Therefore, the total wavefunction has the following form:

$$\psi_{nlm}(r,\theta,\phi) = C\rho^l e^{-\rho}\chi_l^{(n)}(\rho)Y_{l,m}(\theta,\phi), \tag{17.51}$$

$$\rho = \frac{r}{na_0}, \tag{17.52}$$

where C is an overall normalization constant. Notice that the function $\chi_l^{(n)}(\rho)$ is the same as the function $\chi(\rho)$ considered in our previous discussion. Now we have just added explicitly its dependence on the values of the principal quantum number n and the angular momentum value l.

Given the values of the principal quantum number n and of the angular momentum l, we can compute the polynomial, the so-called associated Laguerre polynomial, which gives the radial part of the wavefunction directly, by computing the coefficients b_ν of the polynomial of order $N = n-l-1$ given by the relation

$$\frac{b_{\nu+1}}{b_\nu} = \frac{2(\nu - N)}{(\nu+1)\Big[\nu + 2(l+1)\Big]}, \quad \nu = 0, 1, ..., N. \tag{17.53}$$

$$N = n - l - 1. \tag{17.54}$$

Next, we would like to determine a few examples for the ground state and a few excited states of the hydrogen atom, using the above approach.

1) The ground state of the hydrogen atom corresponds to $n = 1$ and, thus, $l = 0$. In this case $N = 0$ and, thus, the corresponding polynomial is just a constant. Using the form given by Eq. 17.51 the total wavefunction for this case is given as

$$\psi_{100}(r) = Ce^{-r/a_0}, \tag{17.55}$$

and in order to normalize the wavefunction

$$C = \frac{1}{\sqrt{\pi a_0^3}}. \tag{17.56}$$

2) First excited state $n = 2$, $l = 0$. This means that the polynomial is of order $N = 1$ and using Eq. 17.54 we obtain the relation of the two coefficients:

$$\frac{b_1}{b_0} = -1, \tag{17.57}$$

which means that

$$\psi_{200}(r, \theta, \phi) = C(1 - \frac{r}{2a_0})e^{-r/(2a_0)}, \tag{17.58}$$

and by normalizing the wavefunction we find that

$$C = \frac{1}{2\sqrt{2\pi a_0^3}}. \tag{17.59}$$

3) $n = 2$ $l = 1$. We find that $N = 0$, thus, the polynomial is just a constant. Thus,

$$\psi_{21m}(r, \theta, \phi) = C\frac{r}{2a_0}e^{-r/(2a_0)}Y_{1,m}(\theta, \phi), \tag{17.60}$$

and by normalizing we find that

$$C = \frac{1}{\sqrt{6a_0^3}}. \tag{17.61}$$

17.4 Associated Laguerre polynomials

It is customary to link the solution $\chi_l^n(\rho)$ with the associated Laguerre polynomials as follows. By substituting for $\lambda = 2(N + j + 1)$ the equation for $\chi_l(\rho)$ takes the form

$$\frac{\rho}{2}\frac{d^2\chi_l^{(n)}}{d\rho^2} + (l + 1 - \rho)\frac{d\chi_l^{(n)}}{d\rho} + N\chi_l^{(n)} = 0. \tag{17.62}$$

Using the change of variable ρ to $x = 2\rho$, this equation maps to the following equation

$$x\frac{d^2y}{dx^2} + (\alpha + 1 - x)\frac{dy}{dx} + Ny = 0, \tag{17.63}$$

where $y(x) = \chi_l^{(n)}(\rho)$ with

$$\alpha = 2l + 1, \qquad N = n - l - 1. \tag{17.64}$$

This equation has as solutions the associated Laguerre polynomials. These polynomials are generated by the following expression:

$$L_N^{(\alpha)}(x) = \frac{x^{-\alpha}}{N!}e^x\frac{d^N}{dx^N}\Big(e^{-x}x^{N+\alpha}\Big). \tag{17.65}$$

17.5 Problems

Problem 1

Consider the hydrogen atom in an external static and constant electric field E with direction along the z-axis. The interaction Hamiltonian of the atomic electron with the external field is given by

$$H_{int} = -eEz. \tag{17.66}$$

Show that the matrix elements $\langle 100|H_{int}|nlm\rangle$ of this interaction Hamiltonian between the hydrogen atom ground state $|100\rangle$ and one of its excited states $|nlm\rangle$ are only non-zero when $l = 1$ and $m = 0$.

Problem 2

(a) Calculate the average $\langle nlm|r^2|nlm\rangle$ for $n = 1$ and $n = 2$.

(b) Does this expectation value depend on the values of l or m? Explain your answer.

Problem 3

Assume that the nucleus in a hydrogen-like atom is a sphere of radius a and $a/a_0 \sim 10^{-5}$, where a_0 is the Bohr radius.

(a) Calculate the probability that the electron when it is in the atomic ground state will find itself "inside" the nucleus.

(b) Since a/a_0 is much smaller than 1, calculate the above probability to leading order in a/a_0.

Problem 4

Use the approach applied in Section 17.3 to determine the hydrogen atom wavefunction for $n = 3$ and $l = 1$, and for $n = 3$ and $l = 2$.

18

Angular momentum and spherical symmetry

In this chapter we present orbital angular momentum as the generator or rotations in space. The operators which carry out rotations in space form a group G, which is a symmetry group of the Hamiltonian when the interaction is spherically symmetric. In such a case, there are certain useful statements which we can make about the role of invariant and irreducible subspaces of the Hilbert space under the group operations and how to calculate matrix elements of tensor operators within such spaces.

18.1 Generators of infinitesimal rotations

Under an infinitesimal rotation by an angle $\delta\phi$ around an axis along the direction of a unit vector $\hat{u}$, the vector $\vec{r}$ transforms to the following vector:

$$\vec{r}' = \vec{r} + \delta\phi \hat{u} \times \vec{r}. \tag{18.1}$$

This can be easily shown by considering the z-axis along the direction of $\hat{u}$. In this case, the rotation by the angle $\delta\phi$ occurs in the x-y plane as shown in Fig. 18.1.

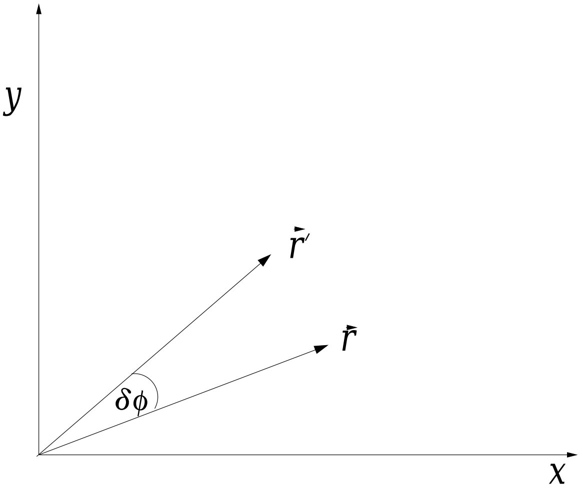

Fig. 18.1

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In this case we see that

$$\vec{r}' = \begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos\delta\phi & -\sin\delta\phi \\ \sin\delta\phi & \cos\delta\phi \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}. \tag{18.2}$$

and for infinitesimal $\delta\phi$ we may write $\cos\delta\phi = 1+O((\delta\phi)^2)$, and $\sin\delta\phi \simeq \delta\phi$. Therefore, we find that

$$x' = x - y\delta\phi, \tag{18.3}$$

$$y' = y + x\delta\phi, \tag{18.4}$$

which can be written as

$$\vec{r}' = \vec{r} + \delta\phi\hat{z} \times \vec{r}, \tag{18.5}$$

where $\hat{z}$ is the unit vector along the z-axis. Since we have taken $\hat{z} = \hat{u}$, we conclude that Eq. 18.1 is true.

Now, consider the change caused by this infinitesimal rotation to a function of $\vec{r}$, namely,

$$f(\vec{r}) \to f(\vec{r}') = f(\vec{r}) + \nabla f(\vec{r}) \cdot (\vec{r}' - \vec{r}). \tag{18.6}$$

Therefore, using the above, we may write the change in the function f caused by the rotation as

$$\delta f = \delta\phi\hat{u} \times \vec{r} \cdot \nabla f = \delta\phi\hat{u} \cdot (\vec{r} \times \nabla f) = \frac{i}{\hbar}\delta\vec{\phi} \cdot \vec{\mathcal{L}} f, \tag{18.7}$$

where we have used the notation $\delta\vec{\phi} \equiv \delta\phi\hat{u}$. Namely, the direction of this vector specifies the axis of rotation and its magnitude the angle of rotation. From the last equation, we may say that the angular momentum operator is *the generator of rotations*.

If we integrate this equation over a finite rotation, we find that

$$f(\vec{r}') = \exp\Big(\frac{i}{\hbar}\vec{\phi} \cdot \vec{\mathcal{L}}\Big) f(\vec{r}). \tag{18.8}$$

This a useful relation which tells us how a function of $\vec{r}$ transforms under a rotation in space.

18.2 Invariant subspaces and tensor operators

First, we would like to define the term *invariant subspaces* to show a statement that follows from the definition.

Invariant subspaces: A subspace S is invariant with respect to rotations, if an arbitrary rotation operation $\hat{R}$ acting on an arbitrary vector $|x\rangle$ from within S ($|x\rangle \in S$) leads to a vector $|y\rangle = \hat{R}|x\rangle$ which is also inside S ($|y\rangle \in S$).

Statement: The subspace $S^{(j)}$ spanned by the $2j+1$ vectors $|j,m\rangle$, that is, the common eigenstates of the total angular momentum $\hat{j}^2$ and its projection $\hat{j}_z$ along the z-axis, is invariant under rotations.

This means that when we take an arbitrary vector from this subspace and we apply an arbitrary rotation operation to it, the resultant vector belongs entirely to this subspace, that is, it has no component outside this subspace. Namely,

$$\hat{R}|j,m\rangle = \sum_{m'=-j}^{j} R^{(j)}_{m'm}|j,m'\rangle. \tag{18.9}$$

Proof: In order to prove the above statement, we notice that an arbitrary rotation is carried out by the following operator:

$$\hat{R}(\alpha,\beta,\gamma) = e^{\frac{i}{\hbar}\alpha\hat{j}_z} e^{\frac{i}{\hbar}\beta\hat{j}_y} e^{\frac{i}{\hbar}\gamma\hat{j}_z}, \tag{18.10}$$

where, (α,β,γ) are the so-called Euler angles. This is so because the generators of rotations around the x-, y-, and z-axes are, respectively, $\hat{j}_x$, $\hat{j}_y$, and $\hat{j}_z$ (see Eq. 18.8).

Now, when $\hat{j}_z$ acts on $|j,m\rangle$, it does not change the state. This means that the result of the first operator $\exp(\frac{i}{\hbar}\gamma\hat{j}_z)$ on the state $|j,m\rangle$ multiplies the state by a phase factor $\exp(i\gamma m)$. The second operator $\exp(\frac{i}{\hbar}\beta\hat{j}_y)$ is a function of the operator $\hat{j}_y = (j^+ - j^-)/(2i)$, and when either $\hat{j}^+$ or $\hat{j}^-$ acts on $|j,m\rangle$ it does not change the value of j, that is, this action yields a linear combination of states $|j,m'\rangle$ which all share the same value of j. Furthermore, the third factor $\exp(\frac{i}{\hbar}\alpha\hat{j}_z)$, does not change the value of j when acting on any linear combination of states with given value of j. Therefore, we conclude that Eq. 18.9 is valid.

Next, we would like to define the term *irreducible subspaces* to show a statement that follows from the definition.

Irreducible subspace: An invariant subspace S is irreducible with respect to rotations when there is no subspace of S, different from S itself, which is invariant under rotations.

Statement: The subspace $S^{(j)}$ spanned by the $2j+1$ vectors $|j,m\rangle$ is an irreducible subspace with respect to rotations.

It is easy to see why this maybe true by using the form given by Eq. 18.10 for a general rotation. When the operator

$$\exp(\frac{i}{\hbar}\beta\hat{j}_y) = \sum_{n=0}^{\infty}\frac{1}{n!}(\frac{\beta}{2\hbar})^n(\hat{j}^+ - \hat{j}^-)^n, \tag{18.11}$$

acts on a state $|j,m\rangle$, in general it leads to a linear combination of all possible $2j+1$ states $|j,m\rangle$. If for a particular value of β this is not the case, that is, some states from this set of $2j+1$ states maybe missing in the linear combination, it is not a problem. The same states need to be missing for all possible values of β.

Next, we would like to define the *irreducible tensor operators*.

Irreducible tensor operators: Tensor operators are irreducible tensor operators if the space in which they are defined is irreducible with respect to rotations.

Statement: We will say that the $2k+1$ operators

$$\hat{\mathrm{T}}^{(k)}_q, \qquad q = -k, -k+1, ..., k-1, k, \tag{18.12}$$

stand for the components of an irreducible so-called kth order tensor operator $\hat{\mathbb{T}}^{(k)}$, if they transform under rotation as follows:

$$\hat{R}\hat{\mathrm{T}}_q^{(k)}\hat{R}^{(-1)} = \sum_{q'=-k}^{k} R_{q'q}^{(k)}\hat{\mathrm{T}}_{q'}^{(k)}. \tag{18.13}$$

Namely, they transform just like the $2k+1$ vectors $|k,q\rangle$, $q=-k,-k+1,...,k-1,k$ of a k angular momentum multiplet transform under rotation.

18.3 Wigner–Eckart theorem for scalar operators

Here, we will discuss the Wigner–Eckart theorem for the case of scalar operators. This case is simpler and its generalization to any tensor operator becomes easier to understand. Let $\hat{O}_s$ be a scalar operator, such as the Hamiltonian $\hat{H}$ of the system. Let us consider, in addition, the operators $\hat{j}^2, \hat{j}_z$ and let us assume that

$$[\hat{\vec{j}}, \hat{O}_s] = 0, \tag{18.14}$$

which implies that

$$[\hat{j}_z, \hat{O}_s] = 0, \qquad [\hat{j}_\pm, \hat{O}_s] = 0. \tag{18.15}$$

Let us consider a complete set of states $|n,j,m\rangle$ which are also eigenstates of $\hat{j}^2$ and $\hat{j}_z$ with corresponding eigenvalues j and m. In this case the following is true:

$$\langle n,j,m|\hat{O}_s|n',j',m'\rangle = O_{nn'}^{(j)}\delta_{jj'}\delta_{m,m'}, \tag{18.16}$$

where $O_{nn'}^{(j)}$ is what we can call a "reduced matrix element," that is, it does not depend on m, m'.

Before we show this statement, let us briefly discuss why this is useful. This statement implies that not only the matrix defined by the operator $\hat{O}_s$ is diagonal both in j and m, but, in addition, we only need to calculate the left-hand-side for any given value of m, because it is the same for all values of m.

Proof: First, we show that the matrix element

$$\langle n,j,m|\hat{O}_s|n',j',m'\rangle = 0, \quad \text{if} \quad j \neq j' \quad \text{or} \quad m \neq m'. \tag{18.17}$$

For this purpose, consider the matrix element

$$\langle n,j,m|\hat{O}_s\hat{j}_z|n',j',m'\rangle = \langle n,j,m|\hat{j}_z\hat{O}_s|n',j',m'\rangle, \tag{18.18}$$

because of Eq. 18.15, and, thus, this leads to

$$\hbar m'\langle n,j,m|\hat{O}_s|n',j',m'\rangle = \hbar m\langle n,j,m|\hat{O}_s|n',j',m'\rangle, \tag{18.19}$$

which means that either $m'=m$ or $\langle n,j,m|\hat{O}_s|n',j',m'\rangle = 0$ for all $m \neq m'$.

Similarly, because of Eq. 18.15,

$$\langle n,j,m|\hat{O}_s\hat{j}^2|n',j',m'\rangle = \langle n,j,m|\hat{j}^2\hat{O}_s|n',j',m'\rangle, \tag{18.20}$$

which means that

$$\begin{aligned} j'(j'+1)\langle n,j,m|\ \hat{O}_s\ |n',j',m'\rangle &= j(j+1) \\ &\times\ \langle n,j,m|\hat{O}_s|n',j',m'\rangle, \end{aligned} \tag{18.21}$$

and this implies that $j'=j$ or that $\langle n,j,m|\hat{O}_s|n',j',m'\rangle = 0$ for all $j \neq j'$.

Now, consider the case where $j'=j$ and $m'=m$. We can write:

$$\begin{aligned} \langle n,j,m|\ \hat{O}_s\ |n',j,m\rangle &= \frac{\langle n,j,m|\hat{O}_s\hat{j}^+|n',j,m-1\rangle}{\hbar\sqrt{j(j+1)-m(m-1)}} \\ &= \frac{\langle n,j,m|\hat{j}^+\hat{O}_s|n',j,m-1\rangle}{\hbar\sqrt{j(j+1)-m(m-1)}} \\ &= \langle n,j,m-1|\hat{O}_s|n',j,m-1\rangle. \end{aligned} \tag{18.22}$$

Which implies that the matrix element $\langle n,j,m|\hat{O}_s|n',j',m'\rangle$ is independent of m and m' and, thus, we can use the symbol $O^{(j)}_{nn'}$ for it.

18.4 Wigner–Eckart theorem: general case

This section assumes that the reader is familiar with Clebsch–Gordan coefficients which are discussed in chapter 24. If not, the reader should come back here after studying chapter 24.

Next, we state without proof the generalization of the Wigner–Eckart theorem for the case of any kth-order tensor operator $\hat{\mathbb{T}}^{(k)}$ with components $\hat{\mathrm{T}}^{(k)}_q$ $(q=-k,-k+1,...,k-1,k)$. The dependence of the matrix elements $\langle njm|\hat{\mathrm{T}}^{(k)}_q|n'j'm'\rangle$ of these components on m, m', and q comes through the Clebsch–Gordan coefficient $\langle j'km'q|jm\rangle$, namely,

$$\langle njm|\hat{\mathrm{T}}^{(k)}_q|n'j'm'\rangle = \frac{\langle nj||\hat{\mathbb{T}}^{(k)}||n'j'\rangle}{\sqrt{2j+1}}\langle j'km'q|jm\rangle, \tag{18.23}$$

where $\langle nj||\hat{\mathbb{T}}^{(k)}||n'j'\rangle$ is the so-called "reduced matrix element" of the tensor $\hat{\mathbb{T}}^{(k)}$. This is a complex number independent of m, m' and q.

What is its use?

If you need to calculate $\langle njm|\hat{\mathrm{T}}^{(k)}_q|n'j'm'\rangle$ for given values of j,j', and k and for various values of m, q, m', all you have to do is to calculate it for given values of $m=m_0$, $m'=m'_0$, and $q=q_0$ and then the rest of these matrix elements are given as

$$\langle njm|\hat{\mathrm{T}}^{(k)}_q|n'j'm'\rangle = \langle njm_0|\hat{\mathrm{T}}^{(k)}_{q_0}|n'j'm'_0\rangle\frac{\langle j'km'q|jm\rangle}{\langle j'km'_0q_0|jm_0\rangle}. \tag{18.24}$$

Namely, all other matrix elements for other values of m, m', and q can be calculated using the already calculated matrix element $\langle njm_0|\hat{\mathrm{T}}^{(k)}_{q_0}|n'j'm'_0\rangle$ and the ration of the

Clebsch–Gordan coefficients which are easier to calculate and do not depend on the details of the operator $\hat{\mathrm{T}}^{(k)}_q$.

We will discuss applications of the Wigner–Eckart theorem when we discuss atomic physics in chapter 26 and spin–orbit coupling.

18.5 Problems

Problem 1

Show that the trace of an irreducible tensor operator is zero unless it is a scalar operator.

Problem 2

Consider the electric multi-dipole moments of a charge distribution. The interaction energy of an electron in an atom described by the wavefunction $\psi(\vec{r})$ with an electric field $\vec{E} = -\nabla\phi$ is given by

$$E_{int} = \int \rho(\vec{r})\phi(\vec{r})d^3r, \tag{18.25}$$

$$\rho(\vec{r}) = -e|\psi(\vec{r})|^2. \tag{18.26}$$

(a) Explain why the interaction energy is given by the above expression.

(b) Show that, when the charges which give rise to the electric potential $\phi(\vec{r})$ are far away, ϕ can be written as

$$\phi(\vec{r}) = \sum_{l=0}^{\infty}\sum_{m=-l}^{+l} C_l^{(m)} r^l Y_{lm}(\theta,\phi). \tag{18.27}$$

What is the expression of the $C_l^{(m)}$ in terms of ϕ and Y_{lm}? Explain why the interaction energy is given by

$$E_{int} = \sum_{l=0}^{\infty}\sum_{m=-l}^{+l} C_l^m \langle\psi|r^l Y_{lm}|\psi\rangle, \tag{18.28}$$

$$\langle\psi|r^l Y_{lm}|\psi\rangle = \int \psi^*(\vec{r}) r^l Y_{lm}(\theta,\phi)\psi(\vec{r})d^3r. \tag{18.29}$$

The operator $r^l Y_{lm}$ is the electric 2^l-pole moment operator.

(c) Use the Wigner–Eckart theorem to show that the expectation value of the quadrupole moment ($l = 2$) operator of a charge distribution is zero for any state with zero angular momentum.

19

Scattering in three dimensions

In this chapter we discuss scattering in three spatial dimensions. We introduce the concepts of the scattering amplitude and cross section. We analyze the Born approximation and how to systematically go beyond this approximation. We also discuss the concepts of phase shifts and partial-wave expansion.

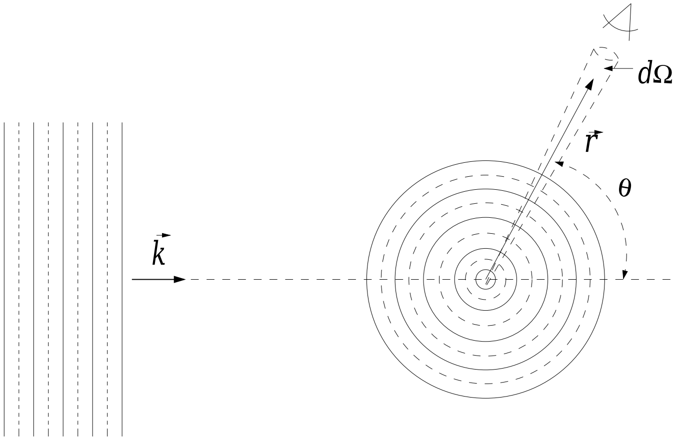

Fig. 19.1 Geometry of scattering.

19.1 Scattering cross section

In Fig. 19.1 we depict the simplest conception of scattering. An incident beam of particles, represented by a incident plane wave characterized by a wavevector $\vec{k}$, scatters from a spherically symmetric potential at the origin of the coordinate system. The scattered wave is a spherical wave traveling outward from the point target. An observing apparatus is placed at a vectorial distance $\vec{r}$ from the target and observes the scattered particles through an area dA which corresponds to a solid angle $d\Omega$ as seen from the target point. The scattering angle between the incident vector $\vec{k}$ and the vector $\vec{r}$ is θ. In practice the incident beam of particles is collimated such that at the detector position only scattered particles are collected.

We will only discuss scattering by a potential V which is of microscopic range, namely, the range of the interaction of the incident particles with the target is negligibly

Practical Quantum Mechanics. First Edition. Efstratios Manousakis.

small as compared to the detector–target distance.

We are interested in calculating the differential scattering cross section $d\sigma/d\Omega$. Let the total incoming particle current density be $\vec{J}_0$ (and this should be along the direction of $\vec{k}$) and let the current density of the scattered particles be $\vec{J}_{sc}$. The elementary cross section $d\sigma$ due to particles arriving at the detector is given by

$$d\sigma = \frac{\vec{J}_{sc} \cdot \hat{r} dA}{|\vec{J}_0|}, \tag{19.1}$$

where $\hat{r}$ is the unit vector along the direction of $\vec{r}$ (the target–detector direction). Namely, the total particle current (number of particles per unit time) through the area of the detector divided by the total incident current density. Notice that this quantity has dimensions of area as it should.

Using the relation between the element of area dA and the solid-angle element $d\Omega$ which corresponds to this area, that is, $dA = r^2 d\Omega$, we find that the differential cross section is given by

$$\frac{d\sigma}{d\Omega} = \frac{\vec{J}_{sc} \cdot \hat{r}}{|\vec{J}_0|} r^2. \tag{19.2}$$

Notice that this quantity should be a constant independent of the distance from the target. The factor of r^2 should get canceled by another factor of $1/r^2$ coming from the ratio of the current density going through the small detector area dA to the total current density going through the entire sphere of radius r. (The so-called $1/r^2$ law.)

Therefore, given the scattering potential $V(r)$, and taking as an initial condition a plane wave incident from a position very far away from the target, we need to calculate the wavefunction of the scattered wave; from that we need to calculate the incident and scattered current densities.

19.2 Quantum mechanical scattering

Consider the time-independent Schrödinger equation for the case of 3D scattering from a spherically symmetric potential $V(r)$:

$$\Big(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\Big)\Psi = E\Psi. \tag{19.3}$$

This equation can be rewritten as follows:

$$(\nabla^2 + k^2)\Psi_{\vec{k}}(\vec{r}) = U(r)\Psi_{\vec{k}}(\vec{r}), \tag{19.4}$$

$$k = \sqrt{\frac{2mE}{\hbar^2}}, \qquad U(r) = \frac{2mV(r)}{\hbar^2}. \tag{19.5}$$

We can show that the following equation gives the solution:

$$\Psi_{\vec{k}}(\vec{r}) = \phi_{\vec{k}}(\vec{r}) + \int G(\vec{r} - \vec{r}')U(r')\Psi_{\vec{k}}(\vec{r}')d^3r', \tag{19.6}$$

where $G(\vec{r}-\vec{r'})$ is Green's function, which is obtained as the solution of the following equation:

$$(\nabla^2_{\vec{r}} + k^2)G(\vec{r}-\vec{r'}) = \delta(\vec{r}-\vec{r'}), \tag{19.7}$$

and $\phi_{\vec{k}}(\vec{r})$ is a solution to the following Schrödinger equation which describes a free particle:

$$(\nabla^2 + k^2)\phi_{\vec{k}}(\vec{r}) = 0. \tag{19.8}$$

To see that the expression (19.6) solves the Schrödinger equation, we just apply to both sides of this equation the operator $\nabla^2 + k^2$ and we use the definition of G, that is, Eq. 19.7.

Now, in order to proceed we need to determine Green's function for our scattering geometry and boundary conditions. First, we go to Fourier space:

$$G(\vec{r}-\vec{r'}) = \int \frac{d^3k'}{(2\pi)^3} e^{i\vec{k'}\cdot(\vec{r}-\vec{r'})}\tilde{G}(\vec{k'}), \tag{19.9}$$

$$\tilde{G}(\vec{k'}) = \int d^3x e^{-i\vec{k'}\cdot\vec{x}} G(\vec{x}), \tag{19.10}$$

$$\delta(\vec{r}-\vec{r'}) = \int \frac{d^3k'}{(2\pi)^3} e^{i\vec{k'}\cdot(\vec{r}-\vec{r'})}. \tag{19.11}$$

We substitute these expressions in Eq. 19.7 and we find that:

$$(-k'^2 + k^2)\tilde{G}(\vec{k'}) = 1, \quad \rightarrow \quad \tilde{G}(\vec{k'}) = \frac{1}{-k'^2 + k^2}, \tag{19.12}$$

which leads to

$$G(\vec{R}) = -\int \frac{d^3k'}{(2\pi)^3} e^{i\vec{k'}\cdot\vec{R}} \frac{1}{k'^2 - k^2}. \tag{19.13}$$

We can carry out the ϕ and θ integration in the above 3D integral by choosing the z-axis along the direction of the vector $\vec{R}$:

$$G(\vec{r}) = -2\pi \int_0^\infty \frac{dk'}{(2\pi)^3} \frac{k'^2}{k'^2 - k^2} \int_{-1}^{1} d\cos\theta e^{ik'R\cos\theta}, \tag{19.14}$$

and we obtain:

$$G(\vec{r}) = -\frac{1}{2\pi^2 R} \int_0^\infty dk' \frac{k' \sin(k'R)}{k'^2 - k^2}. \tag{19.15}$$

The last expression can also be written as an integral from $-\infty$ to ∞ by realizing that $\sin(k'R) = (e^{ik'R} - e^{-ik'R})/(2i)$,

$$G(\vec{r}) = -\frac{1}{4i\pi^2 R} \int_{-\infty}^{\infty} dk' \frac{k' e^{ik'R}}{k'^2 - k^2}. \tag{19.16}$$

All of these manipulations are very nice; however, this integral does not exist! There are poles on the real axis at $k' = \pm k$. We need to redefine the integral. We have at least the following two ways to redefine it. First we can use the definition:

$$G_+(\vec{r}) = -\frac{1}{4i\pi^2 R}\lim_{\eta\to 0}\int_{-\infty}^{\infty} dk' \frac{k' e^{ik'R}}{k'^2 - (k^2 + i\eta)}. \tag{19.17}$$

Another definition is the following:

$$G_-(\vec{r}) = -\frac{1}{4i\pi^2 R}\lim_{\eta\to 0}\int_{-\infty}^{\infty} dk' \frac{k' e^{ik'R}}{k'^2 - (k^2 - i\eta)}. \tag{19.18}$$

In the first case we have shifted the two poles at

$$k' \simeq \pm\Big(k + i\eta/(2k)\Big), \tag{19.19}$$

and we have neglected terms of the order of η^2 and higher because we need the limit of $\eta \to 0$ and these terms as irrelevant in this limit. This redefinition shifts the poles as shown in Fig. 19.2.

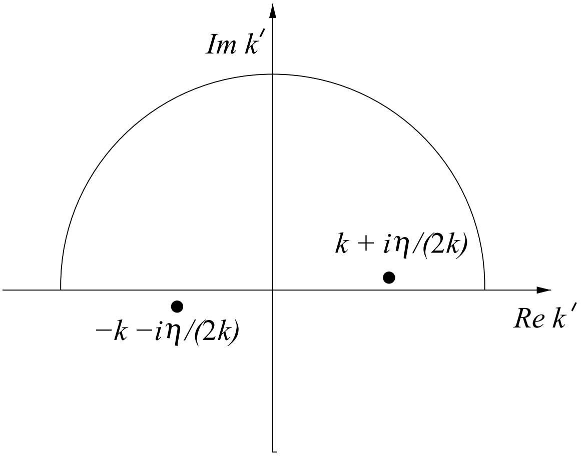

Fig. 19.2

In order to use Cauchy's theorem we add to the integration contour the semi-circular part shown in Fig. 19.2 with infinite radius. This part makes no contribution to the integral because the factor $e^{ik'R}$ becomes $e^{i(Rek')R}e^{-(Imk')R}$ and the $Imk' \to +\infty$ along this semi-circle.

Now we have an integral on the complex plane over a closed contour, which allows us to use Cauchy's theorem. Calculating the residue of the only pole inside the contour, that is, at $k' = k + i\eta/(2k)$ and taking the limit $\eta \to 0$, yields:

$$G_+(R) = -\frac{e^{ikR}}{4\pi R}. \tag{19.20}$$

If we were to use the other definition, that is, the one defined by Eq. 19.18, we would find:

$$G_-(R) = -\frac{e^{-ikR}}{4\pi R}. \tag{19.21}$$

Using G_+ our scattered wavefunction (19.6) takes the form:

$$\Psi^{(+)}_{\vec{k}}(\vec{r}) = \phi_{\vec{K}}(\vec{r}) - \frac{1}{4\pi}\int \frac{e^{ik'|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|}U(r')\Psi_{\vec{k}}(\vec{r}')d^3r', \tag{19.22}$$

and far away from the target that is, at the detector, which is at a distance from the target much greater than the range of the interaction $U(r')$, the distance factor can be approximated as follows:

$$|\vec{r}-\vec{r}'| \simeq r - \hat{r}\cdot\vec{r}' + ... \tag{19.23}$$

Therefore, we can write:

$$\Psi^{(+)}_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} + f_k(\theta)\frac{e^{ikr}}{r}, \tag{19.24}$$

$$f(\theta) = -\frac{1}{4\pi}\int e^{i\vec{k}'\cdot\vec{r}'}U(r')\Psi_{\vec{k}}(\vec{r}')d^3r', \tag{19.25}$$

where we have defined as $\vec{k}' \equiv k\hat{r}$.

This equation describes an incident plane wave which, upon scattering from the point target, produces a spherical wave going outward from the target characterized by a *scattering amplitude* $f(\theta)$. If we to choose the redefinition $G_-(R)$ instead, we would obtain a solution which contains a spherical wave going inward to the target which we eliminate as inapplicable in this case.

A convenient way to write the scattering amplitude is as follows:

$$f(\theta) = -\frac{1}{4\pi}\langle\phi_{\vec{k}'}|U|\Psi_{\vec{k}}\rangle, \tag{19.26}$$

$$\phi_{\vec{k}'} = e^{i\vec{k}'\cdot\vec{r}}. \tag{19.27}$$

19.3 Scattering amplitude and differential cross section

Now that we have found the wavefunction of the scattered wave in terms of the scattering amplitude $f_k(\theta)$, we are in a position to relate $f_k(\theta)$ to the differential cross section $d\sigma/d\Omega$. Towards this end, we will use Eq. 19.2, which requires us to compute the current density $\vec{J}_{sc}$ of the scattered wave. First, we are going to be less rigorous because we want to stay simple. At the end we will discuss how one can make the argument more precise.

The wavefunction of the incident wave (well before it comes near the influence of the potential) is

$$\Psi^{(0)}_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}. \tag{19.28}$$

Using this wavefunction and the expression for the current given by Eq. 7.10, we find that the current density of the incident wave is

$$\vec{J}_0 = \frac{\hbar\vec{k}}{m}. \tag{19.29}$$

Now we will take the wavefunction of the scattered wave to be the part of the wavefunction (19.24) without the incident wave, that is, only the second part:

$$\Psi_{sc}(r,\theta) = f_k(\theta)\frac{e^{ikr}}{r}. \tag{19.30}$$

The general expression for the current given by Eq. 7.10 can be used to find the scattered wave current density along the direction $\hat{r}$ defined by the target–detector line:

$$\hat{r}\cdot\vec{J}_{sc} = \frac{\hbar}{2mi}\Big[\Psi^*_{sc}\frac{\partial\Psi_{sc}}{\partial r} - \Psi_{sc}\frac{\partial\Psi^*_{sc}}{\partial r}\Big]. \tag{19.31}$$

Using this expression and the wavefunction for the scattered wave given by Eq. 19.30 above we can calculate $\hat{r}\cdot\vec{J}_{sc}$ and we find that:

$$\hat{r}\cdot\vec{J}_{sc} = \frac{\hbar k}{m}\frac{|f_k(\theta)|^2}{r^2} + O(1/r^3). \tag{19.32}$$

Thus, the main term is of order of $1/r^2$ and we have dropped terms of the order of $1/r^3$. Using this expression and the expression given by Eq. 19.2, we find that

$$\frac{d\sigma}{d\Omega} = |f_k(\theta)|^2. \tag{19.33}$$

Conclusion: The differential scattering cross section is equal to the square of the magnitude of the scattering amplitude.

The way we separated only the second term from the total wavefunction and identified it as the wavefunction of the scattered wave might sound a bit artificial. This is related to what the experiment measures and we call it the "cross section." In practice, we do not want to measure contributions from the incident wave, that is, to measure something which carries no information about the target. As a result, the beam has to be collimated in such a way that all the incident particles come within a narrow cylinder. This is done by modifying the incident wave and forming a wavepacket which, within the time of flight, acquires a spread which is much smaller than the target–detector distance. As a result, in the absence of a target, no particles come to the detector. Therefore, one needs to repeat the calculation with this modified incident wavefunction, by expanding it onto plane waves of a definite $\vec{k}$ and, then, by calculating the superposition of the wavefunctions of the scattered waves for each $\vec{k}$. If we follow such a recipe, it turns out that the final answer is the same, namely Eq. 19.33. However, this more rigorous calculation is a lot more tedious and the point that we are trying to convey is illustrated much more clearly with the above less rigorous approach.

19.4 Born series expansion

The general solution given by Eq. 19.6 can be iterated as follows:

In zeroth order in U:

$$\Psi^{(0)}_{\vec{k}}(\vec{r}) = \phi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}. \tag{19.34}$$

In first order in U, we use the zeroth-order approximation of $\Psi_{\vec{k}}$ inside the integral of the right-hand-side of Eq. 19.6 and we find that:

$$\Psi^{(1)}_{\vec{k}}(\vec{r}) = \phi_{\vec{k}}(\vec{r}) + \int d^3r' G(\vec{r}-\vec{r}')U(\vec{r}')\phi_{\vec{k}}(\vec{r}'). \tag{19.35}$$

In second order in U, we use the above first-order approximation of $\Psi_{\vec{k}}$ inside the integral of the right-hand-side of Eq. 19.6 and we find that:

$$\begin{aligned}\Psi^{(2)}_{\vec{k}}(\vec{r}) &= \phi_{\vec{k}}(\vec{r}) + \int d^3r' G(\vec{r}-\vec{r}')U(\vec{r}')\phi_{\vec{k}}(\vec{r}') \\ &+ \int d^3r' \int d^3r'' G(\vec{r}-\vec{r}')U(\vec{r}')G(\vec{r}'-\vec{r}'')U(\vec{r}'') \\ &\times \phi_{\vec{k}}(\vec{r}'').\end{aligned} \tag{19.36}$$

And after an infinite number of such iterations the general solution can also be cast in the following way

$$\begin{aligned}|\Psi_{\vec{k}}\rangle &= |\phi_{\vec{k}}\rangle + \hat{G}\hat{U}|\phi_{\vec{k}}\rangle + \hat{G}\hat{U}\hat{G}\hat{U}|\phi_{\vec{k}}\rangle + ... \\ &= \sum_{n=0}^{\infty}(\hat{G}\hat{U})^n|\phi_{\vec{k}}\rangle,\end{aligned} \tag{19.37}$$

where we have introduced a short-hand notation that $\hat{G}$ is an operator with matrix elements in the position basis defined as follows:

$$\langle\vec{r}|\hat{G}|\vec{r}'\rangle \equiv G(\vec{r}-\vec{r}'), \tag{19.38}$$

and, of course, the matrix elements of $\hat{U}$ are

$$\langle\vec{r}|\hat{U}|\vec{r}'\rangle = U(r)\delta(\vec{r}-\vec{r}'). \tag{19.39}$$

In addition, as usual,

$$\Psi_{\vec{k}}(\vec{r}) = \langle\vec{r}|\Psi_{\vec{k}}\rangle, \tag{19.40}$$

$$\phi_{\vec{k}}(\vec{r}) = \langle\vec{r}|\phi_{\vec{k}}\rangle. \tag{19.41}$$

Therefore, using Eq. 19.27 for the scattering amplitude, we obtain:

$$\begin{aligned}f(\theta) &= -\frac{1}{4\pi}\langle\phi_{\vec{k}'}|U|\Psi_{\vec{k}}\rangle, \\ f(\theta) &= -\frac{1}{4\pi}\langle\phi_{\vec{k}'}|U + \hat{G}\hat{U} + \hat{G}\hat{U}\hat{G}\hat{U}|\phi_{\vec{k}}\rangle + ... \\ &= -\frac{1}{4\pi}\sum_{n=0}^{\infty}\langle\phi_{\vec{k}'}|U(\hat{G}\hat{U})^n|\phi_{\vec{k}}\rangle.\end{aligned} \tag{19.42}$$

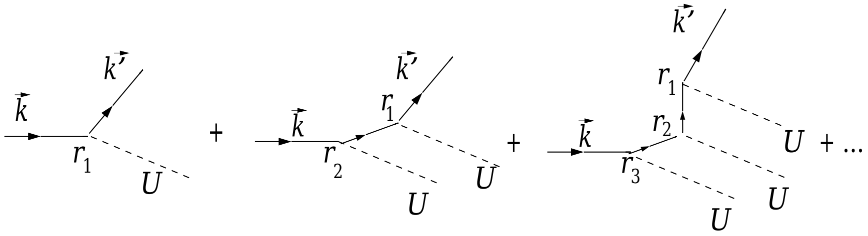

Fig. 19.3 Diagrammatic illustration of the terms in the series given by the Eq. 19.42.

In Fig. 19.3 this infinite series is represented graphically by a set of diagrams. The notation may be obvious. For example, the second-order term in U is given as

$$-\frac{1}{4\pi}\int d^3r d^3r' d^3r''\ \phi_{\vec{k}'}(\vec{r})\ G(\vec{r}-\vec{r}')U(\vec{r}')G(\vec{r}'-\vec{r}'')U(\vec{r}'') \times \ \phi_{\vec{k}}(\vec{r}''). \tag{19.43}$$

Therefore, the sum in Eq. 19.42 represents a series of multiple scattering "events."

The leading-order approximation for the scattering amplitude

$$f(\theta) = -\frac{1}{4\pi}\langle\phi_{\vec{k}'}|U|\phi_{\vec{k}}\rangle, \tag{19.44}$$

is known as the Born approximation. Now, this can be calculated as follows. First, notice that:

$$f(\theta) = -\frac{1}{4\pi}\int d^3r' e^{i\vec{q}\cdot\vec{r}'}U(\vec{r}'), \tag{19.45}$$

$$\vec{q} = \vec{k}-\vec{k}', \qquad q = 2k\sin(\theta/2), \tag{19.46}$$

where the last equation is obtained by using that $|\vec{k}'| = |\vec{k}|$. The quantity $\hbar\vec{q} = \hbar k - \hbar k'$ is called *momentum transfer*. The above expression means that, apart from a constant and a minus sign, the scattering amplitude, within the Born approximation, is the $\vec{q}$ amplitude of the Fourier transform of the interaction potential. The angular part of the integration can be calculated in the familiar way to obtain:

$$f(\theta) = -\int_0^\infty dr' r' \frac{\sin(qr')}{q}U(r'). \tag{19.47}$$

19.5 Partial wave expansion

In the previous section we treated the problem of scattering using Green's functions. Here, we will treat it as a far-field solution of the Schrödinger equation for a spherically symmetric potential $V(r)$.

First, we consider the Schrödinger Eq. 19.3 with the initial condition that

$$\Psi^{(0)}_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} = \sum_{l=0}^{\infty} i^l(2l+1)P_l(\cos\theta)j_l(kr). \tag{19.48}$$

The second part of the above equation is the expansion (16.73) which we have already shown.

Consider scattering from a spherically symmetric potential $V(r)$ such that $r^2V(r) \to 0$ as $r \to \infty$. We have already shown that in this case the wavefunction is simply modified, as in Eq. 19.24, by an additional term which represents a spherical scattered wave due to the presence of a spherically symmetrical target-potential at the origin. Notice that in both the initial plane wave and in the scattered wavefunction, there is no ϕ-dependence. This is because the problem is cylindrically symmetric, with the axis of the cylindrical symmetry the line connecting the origin of the incoming particles and the target. This observation of a lack of ϕ-dependence allows us to expand the wavefunction in angular momentum eigenstates as

$$\Psi_{\vec{k}}(\vec{r}) = \sum_{l=0}^{\infty} i^l(2l+1)P_l(\cos\theta)R_l(r), \tag{19.49}$$

and use only Legendre polynomials as opposed to full spherical harmonics. We have pulled the constant factor of $i^l(2l+1)$ out of the radial function $R_l(r)$.

As we have already discussed in the previous chapter, the radial functions $R_l(r)$ satisfy the following equation

$$\begin{aligned}-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\Big(r^2\frac{\partial R_l(r)}{\partial r}\Big) + \Big[\frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\Big]R_l(r)& \\ = ER_l(r).&\end{aligned} \tag{19.50}$$

The detector is at a macroscopic distance r from the target, which acts on the incident particle by means of a potential of a microscopic range. Therefore, at the detector distance R_l satisfies the spherical Bessel equation

$$\rho^2\frac{d^2\mathcal{R}_l}{d\rho^2} + 2\rho\frac{d\mathcal{R}_l}{d\rho} + \Big(\rho^2 - l(l+1)\Big)\mathcal{R}_l = 0, \tag{19.51}$$

where $\mathcal{R}_l(\rho) = R_l(r)$ and

$$\rho = kr, \qquad k = \sqrt{\frac{2mE}{\hbar^2}}. \tag{19.52}$$

The general solution to this equation can be expressed in terms of the Hankel functions as

$$R_l(r) = a_l h_l(kr) + b_l h_l^*(kr), \tag{19.53}$$

which can be rewritten as

$$R_l(r) = b_l(h_l^*(kr) + S_l h_j(kr)), \qquad S_l \equiv \frac{a_l}{b_l}. \tag{19.54}$$

The radial current density is given by

$$\begin{aligned} J_r(r,\theta,\phi) = \hat{r}\cdot\vec{J} = \frac{\hbar}{2mi}\left[R_l^*(r)\frac{\partial R_l(r)}{\partial r} - R_l(r)\frac{\partial R_l^*(r)}{\partial r}\right] \\ \times\, |Y_{l,m}(\theta,\phi)|^2, \end{aligned} \tag{19.55}$$

and if we integrate it over all solid angles, the average radial current density that goes through a spherical surface at distance r from the target is given by

$$\bar{J}_r(r) = \frac{\hbar}{2mi}\left[R_l^*(r)\frac{\partial R_l(r)}{\partial r} - R_l(r)\frac{\partial R_l^*(r)}{\partial r}\right], \tag{19.56}$$

and using the expression (19.54) for $R_l(r)$ we obtain:

$$\bar{J}_r(r) = \frac{\hbar}{8mi}\left[h_l h_l^{*'} - h_l^* h_l'\right](1-|s_l|^2), \tag{19.57}$$

where $h_l' = \partial h_l(kr)/\partial r$. At this point, we need to guarantee particle conservation, namely the target is neither a sink nor a source of particles; therefore, we must require that

$$\bar{J}_r(r) = 0, \qquad \rightarrow \qquad |s_l|^2 = 1, \qquad \rightarrow \qquad s_l = e^{i2\delta_l}. \tag{19.58}$$

The angle δ_l is the so-called phase shift of the partial wave l.

Using the expression Eq. 19.48, in which we substitute $j_l(kr)$ with its equivalent expression $1/2(h_l(kr) + h_l^*(kr))$, and by comparing the result with Eq. 19.49 where the above expression Eq. 19.54 is used for R_l, we conclude that in the absence of interaction with the target

$$b_l = \frac{1}{2}, \qquad s_l = 1. \tag{19.59}$$

Let us take into account a) the asymptotic form of the Hankel functions (Eq. 16.47), and combine it with b) the form of the scattered wavefunction (Eq. 19.24). We conclude that the presence of the spherically symmetric target-potential modifies only the phase of the coefficient of the $h_l(kr)$, therefore,

$$b_l = \frac{1}{2}, \tag{19.60}$$

even in the presence of a non-zero, short-ranged, spherically symmetric target-potential.

Therefore, putting all the pieces of the above conclusions together, we find that

$$\Psi_{\vec{k}}(\vec{r}) = \frac{1}{2}\sum_{l=0}^{\infty} i^l(2l+1)P_l(\cos\theta)\Big[h_l^*(kr) + e^{2i\delta_l}h_l(kr)\Big]. \tag{19.61}$$

Now, we can use the expression given by Eq. 19.48 to rewrite the above expression as follows:

$$\Psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} + \frac{1}{2}\sum_{l=0}^{\infty} i^l(2l+1)P_l(\cos\theta)[e^{2i\delta_l} - 1]h_l(kr). \tag{19.62}$$

Since the expression is correct at distances far away from the target, we can use the asymptotic form of the Hankel function Eq. 16.47 to cast the above form into the form given by Eq. 19.24 with the following explicit form of the scattering amplitude:

$$f_k(\theta) = \sum_{l=0}^{\infty}(2l+1)P_l(\cos\theta)d_l(k), \tag{19.63}$$

$$d_l(k) = \frac{1}{2ik}(e^{2i\delta_l} - 1) = \frac{e^{i\delta_l}}{k}\sin\delta_l. \tag{19.64}$$

Next, we can use the above finding and the relationship between the differential scattering cross section and the scattering amplitude, that is, Eq. 19.33, to find the total scattering cross section σ as follows:

$$\begin{aligned}\sigma = \int d\Omega|f_k(\theta)|^2 &= \sum_{l=0}^{\infty}\sum_{l'=0}^{\infty}(2l+1)(2l'+1)d_l^*(k)d_{l'}(k) \\ &\times \int d\Omega P_l(\cos\theta)P_{l'}(\cos\theta).\end{aligned} \tag{19.65}$$

Using the orthogonality of the Legendre polynomials (Eq. 15.75) we find that the total scattering cross section is given by

$$\sigma = \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2\delta_l. \tag{19.66}$$

We can relate this expression to the imaginary part of the scattering amplitude $f_k(\theta)$ for $\theta = 0$ (forward scattering) using the expression Eq. 19.63 as follows:

$$\sigma = \frac{4\pi}{k}Imf_k(\theta). \tag{19.67}$$

This expression is the *optical theorem.*

19.6 Examples: phase shift calculation

19.6.1 Scattering from a hard sphere

Let us consider the case of a hard sphere as in Fig. 19.4, that is,

$$V(r) = \left\{\begin{array}{c}\infty \ for\ r \le a, \\ 0 \ \ for\ \ r > a\end{array}\right\}. \tag{19.68}$$

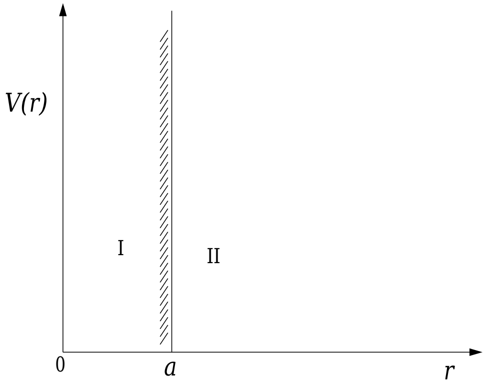

Fig. 19.4 Scattering from a hard sphere.

In Region I ($r \leq a$) the wavefunction should be zero. In Region II ($r \geq a$) the radial part of the wavefunction satisfies the radial equation represented by Eq. 19.51 with a general solution which can be expressed as a linear combination of the spherical Hankel functions:

$$R_l(r) = a_l h_l(kr) + b_l h_l^*(kr), \tag{19.69}$$

or equivalently as a linear combination of the spherical Bessel or Neumann functions

$$R_l(r) = A_l j_l(kr) + B_l n_l(kr). \tag{19.70}$$

In Section 19.5 we expressed the far-field solution as a linear combination of spherical Hankel functions, namely as in Eq. 19.69, and the phase shifts were defined as

$$e^{2i\delta_l} = \frac{a_l}{b_l}. \tag{19.71}$$

In some problems, it might more convenient to write the wavefunction as in Eq. 19.70 because the spherical Bessel and Neumann functions are real. We would like to find an expression to compute δ_l in such a case.

The coefficients A_l and B_l are related to a_l and b_l by the following expression:

$$A_l = a_l + b_l, \qquad B_l = i(a_l - b_l). \tag{19.72}$$

Now, let us consider the ratio B_l/A_l, which, using the definition (19.71) of the phase-shifts, can be written as follows

$$\frac{B_l}{A_l} = i\frac{a_l - b_l}{a_l + b_l} = i\frac{\frac{a_l}{b_l} - 1}{\frac{a_l}{b_l} + 1} = i\frac{e^{2i\delta_l} - 1}{e^{2i\delta_l} + 1} = i\frac{e^{i\delta_l} - e^{-i\delta_l}}{e^{i\delta_l} + e^{i\delta_l}}. \tag{19.73}$$

Therefore, we conclude that the phase shift can be also calculated as

$$\tan\delta_l = -\frac{B_l}{A_l}. \tag{19.74}$$

For Region II ($r \geq a$) it is convenient to write the wavefunction as in Eq. 19.70. The boundary condition at $r = a$ means that

$$A_l j_l(ka) + B_l n_l(ka) = 0. \tag{19.75}$$

Therefore, we obtain that

$$\tan\delta_l = \frac{j_l(ka)}{n_l(ka)}. \tag{19.76}$$

For $l = 0$ we have

$$\tan\delta_0 = \frac{j_0(ka)}{n_0(ka)} = -\tan(ka), \tag{19.77}$$

therefore,

$$\delta_0 = -ka. \tag{19.78}$$

Conclusion: The s-wave phase-shift is negative: The wave is pushed out of the origin by the repulsive interaction.

In the long-wavelength limit $ka << 1$, we can compute the approximate form of the spherical Bessel and Neumann functions using the expressions given by Eq. 16.39 and Eq. 16.41. We find that

$$\delta_l \simeq -\frac{(ka)^{2l+1}}{2l+1} \tag{19.79}$$

which is also negative. In addition, notice that as l increases the the phase shift decreases.

Therefore, in the limit of $ka \to 0$ only the $l = 0$ (s-wave) contributes to the scattering amplitude $f_k(\theta)$ and we find that

$$\lim_{k\to 0} f_k(\theta) \simeq \frac{1}{k} e^{-ika} \sin(ka) P_0(\cos\theta) \simeq a, \tag{19.80}$$

$$\frac{d\sigma}{d\Omega} \simeq a^2. \tag{19.81}$$

Therefore, the differential is isotropic in all θ directions. The total cross section is given by

$$\sigma = \int d\Omega \frac{d\sigma}{d\Omega} \simeq 4\pi a^2. \tag{19.82}$$

The differential scattering cross section can be calculated numerically for finite values of ka and is illustrated in Fig. 19.5 for $ka = 0.1, 1.0$, and π. Notice that while at $k = 0.1$ is almost isotropic and mainly of s-wave type, as we increase the value of ka we see that it becomes more and more elongated in the forward scattering direction.

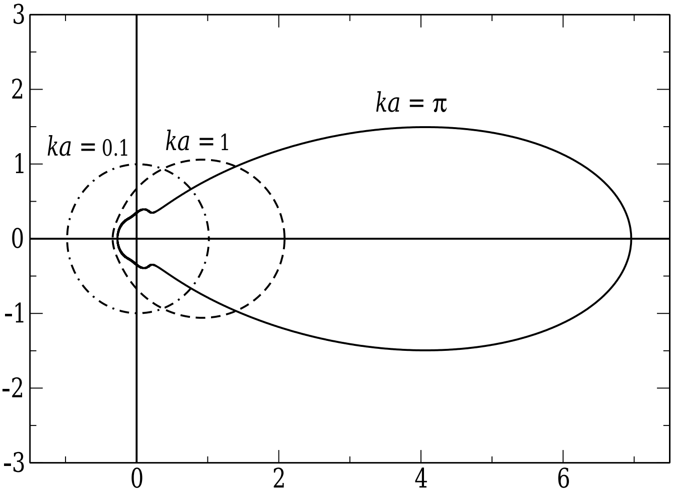

Fig. 19.5 Polar graphs of $f(\theta)$ for scattering from a hard sphere.

19.6.2 Scattering from a spherical well

We consider the same potential as in Fig. 16.3 which we studied in chapter 16 when we were discussing bound states in spherically symmetric potentials. Here, we will investigate the scattering phase shifts and cross sections.

We consider the same form of wavefunctions as for case of the bound states; however, now the nature of the arguments about the special functions are different. In Region I ($r < a$), we have

$$R_l^{(I)}(r) = A_l^{(I)} j_l(k'r), \qquad k' = \sqrt{\frac{2m(V_0 + E)}{\hbar^2}}. \tag{19.83}$$

For the reason discussed in the previous example, namely that the calculation of the phase shift becomes easier, in Region II ($r > a$) we will write the solution as

$$R_l^{(II)}(r) = A_l^{(II)} j_l(kr) + B_l^{(II)} n_l(kr), \quad k = \sqrt{\frac{2mE}{\hbar^2}}. \tag{19.84}$$

At $r = a$ we will need to match the wavefunctions and their derivatives for the two regions, that is,

$$A_l^{(I)} j_l(k'a) = A_l^{(II)} j_l(ka) + B_l^{(II)} n_l(ka), \tag{19.85}$$

$$k' A_l^{(I)} j_l'(k'a) = k\Big(A_l^{(II)} j_l'(ka) + B_l^{(II)} n_l'(ka)\Big), \tag{19.86}$$

where the derivatives are considered with respect to the entire argument of $j_l(\rho)$ and $n_l(\rho)$. By taking the ratio of these two equations we obtain:

$$\frac{j_l'(k'a)}{j_l(k'a)} = \frac{k}{k'} \frac{A_l^{(II)} j_l'(ka) + B_l^{(II)} n_l'(ka)}{A_l^{(II)} j_l(ka) + B_l^{(II)} n_l(ka)}. \tag{19.87}$$

By dividing by $A_l^{(II)}$ both the numerator and denominator, this equation can be expressed in terms of the phase shifts, that is, using Eq. 19.74:

$$\frac{j_l'(k'a)}{j_l(k'a)} = \frac{k}{k'} \frac{j_l'(ka) - \tan(\delta_l) n_l'(ka)}{j_l(ka) - \tan(\delta_l) n_l(ka)}. \tag{19.88}$$

It is straightforward to solve this equation for $\tan(\delta_l)$ and obtain the following expression:

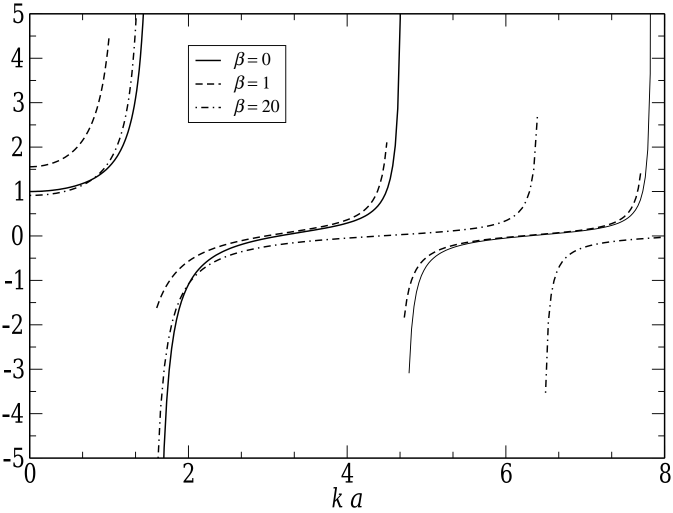

Fig. 19.6 Graphical solution to Eq. 19.92. The solid curve is $\frac{\tan\sqrt{x^2+\beta}}{\sqrt{x^2+\beta}}$ for $\beta = 0$, the red curve for $\beta = 1$, the dashed curve for $\beta = 1$ and the dash-dotted curve for $\beta = 20$.

$$\tan(\delta_l) = \frac{k j_l'(ka) j_l(k'a) - k' j_l'(k'a) j_l(ka)}{k n_k'(ka) j_l(k'a) - k' j_l'(k'a) n_l(ka)}. \tag{19.89}$$

For the case of $l = 0$, we find that

$$\tan(\delta_0) = \frac{x \tan(x') - x' \tan(x)}{x \tan(x) \tan(x') + x'}, \tag{19.90}$$

$$x = ka, \quad x' = \sqrt{x^2 + \beta}, \quad \beta = \frac{2mV_0 a^2}{\hbar^2}. \tag{19.91}$$

Therefore, for certain values of the well-depth V_0, there are values of x where $\tan\delta_0 = 0$, that is, when

$$\frac{\tan\sqrt{x^2+\beta}}{\sqrt{x^2+\beta}} = \frac{\tan x}{x}. \tag{19.92}$$

As can be seen from the graphical solution illustrated in Fig. 19.6, for the three different values of β used we find solutions for $\beta = 20$.

19.7 Problems

Problem 1

Start from the Born approximation for the scattering amplitude

$$f_{\mathbf{k}}(\hat{r}) = -\frac{m}{2\pi\hbar^2}\int d^3r' e^{-i\mathbf{k}'\cdot\mathbf{r}'}V(r')e^{i\mathbf{k}\cdot\mathbf{r}'} \tag{19.93}$$

where $\mathbf{k}' = |\mathbf{k}|\hat{r}$ and show that when the phase shift δ_l is small, it is approximately given by

$$\delta_l \simeq -\frac{2mk}{\hbar^2}\int_0^\infty |j_l(kr)|^2 V(r) r^2 dr. \tag{19.94}$$

Problem 2

Consider scattering from the following 3D potential

$$V(r) = \left\{ \begin{array}{cc} V_0(>0), & r \le R \\ 0, & r > R \end{array} \right\}. \tag{19.95}$$

(a) Use the Schrödinger equation to determine the exact phase shift δ_0 for $l = 0$ as a function of the energy E of the incident particles.

(b) Find the cross section σ_0 and the corresponding scattering length a_0.

(c) Calculate the approximate phase shift δ_0 within the Born approximation. Compare graphically your answer with the exact solution as a function of kR where $k = \sqrt{2mE/\hbar^2}$.

(d) Find the phase shift δ_0 and scattering cross section σ_0 for the case of a hard sphere where $V_0 \to \infty$.

Problem 3

Consider scattering from a spherical cavity of radius R which is bounded by a thin wall of the form

$$V(r) = \frac{\hbar^2}{2m}\frac{\Omega}{R}\delta(r-R), \tag{19.96}$$

where Ω is a measure of the opacity of the spherical wall.

(a) Use the Schrödinger equation to find the equation which determines the exact phase shift δ_0 for $l = 0$ as a function of the energy E of the incident particles.

(b) Choose $\Omega = 4$ and plot δ_0 as a function of kR.

(c) Show that the phase shift δ_0 for the hard sphere limit agrees with the result of Problem 1 for the hard sphere. Plot δ_0 as a function of kR in the same graph as in case (b).

Problem 4

Consider scattering from the attractive Yukawa potential of the form

$$V(r) = -V_0\frac{e^{-r/\lambda}}{r}. \tag{19.97}$$

Use the Born approximation to find:

(a) the scattering amplitude,

(b) the phase shift, scattering cross section and scattering length for $l \leq 2$.

Problem 5

Consider scattering from an exponential potential of the form

$$V(r) = -V_0 e^{-r/\lambda}. \tag{19.98}$$

Use the Born approximation to find:

(a) the scattering amplitude,

(b) the total scattering cross section.

20

Time-independent perturbation expansion

In this chapter we discuss time-indendent perturbation theory. We analyze the non-degenerate case first, and then the case of application of perturbation theory for the case in which the state is degenerate. We further investigate how to treat the case of quasi-degeneracy.

20.1 Statement of the problem

As discussed many times most realistic problems are not exactly soluble. Perturbation theory is a Taylor expansion of the full problem near the solution of a different problem, which is considered closely related which we know how to solve. The full problem is described by a Hamiltonian which can be cast into the following general form

$$\hat{H} = \hat{H}_0 + \epsilon \hat{V} \tag{20.1}$$

where $\hat{H}_0$ is the Hamiltonian of a problem which we know how to solve, that is, it can be diagonalized as

$$\hat{H}_0 |n\rangle_0 = E_n^{(0)} |n\rangle_0, \tag{20.2}$$

and we explicitly know all eigenvalues $E_n^{(0)}$ and all corresponding eigenstates $|n\rangle_0$. Here ϵ is a dimensionless small parameter ($\epsilon << 1$) and $\hat{V}$ is considered as the perturbation.

The energy eigenvalues and eigenstates of $\hat{H}$, that is,

$$\hat{H}|n\rangle = E_n|n\rangle, \tag{20.3}$$

which is what we are interested in, can be written as an infinite series expansion in powers of ϵ as follows:

$$E_n = E_n^{(0)} + \epsilon E_n^{(1)} + \epsilon^2 E_n^{(2)} + ..., \tag{20.4}$$

$$|n\rangle = |n\rangle_0 + \epsilon |n\rangle_1 + \epsilon^2 |n\rangle_2 + ..., \tag{20.5}$$

where we need to determine the prefactors

$$E_n^{(1)}, E_n^{(2)}, ... \tag{20.6}$$

and the contributions

Practical Quantum Mechanics. First Edition. Efstratios Manousakis.

$$|n\rangle_1, |n\rangle_2, ..., \tag{20.7}$$

to the state vectors. Notice that the zeroth-order in both the expansion of energy and eigenvectors are taken to be those of $\hat{H}_0$, because of the fact that in the limit $\epsilon \to 0$, $E_n \to E_n^{(0)}$ and $|n\rangle \to |n\rangle_0$.

This calculation can be carried out to a finite order n and this provides a systematic order-by-order estimate to the full problem. This expansion assumes that the function $E_n(\epsilon)$ and the state $|n\rangle$ as a function of ϵ is an analytic function of ϵ and the expansion is done within its radius of convergence.

20.2 Non-degenerate case

The answer to the above problem is straightforward: Substitute Eq. 20.1, Eq. 20.4, and Eq. 20.5 into Eq. 20.3 to find the following equation:

$$\begin{aligned}&(H_0 + \epsilon\hat{V})(|n\rangle_0 + \epsilon|n\rangle_1 + \epsilon^2|n\rangle_2 + ...)\\ &= (E_n^{(0)} + \epsilon E_n^{(1)} + \epsilon^2 E_n^{(2)} + ...)(|n\rangle_0 + \epsilon|n\rangle_1\\ &+ \epsilon^2|n\rangle_2 + ...),\end{aligned} \tag{20.8}$$

and equate the terms of the same order in ϵ on both sides of the resulting equation. Namely, we obtain the following hierarchy of equations

$$\text{0th order} \Rightarrow \hat{H}_0|n\rangle_0 = E_n^{(0)}|n\rangle_0, \tag{20.9}$$

$$\text{1st order} \Rightarrow (\hat{H}_0 - E_n^{(0)})|n\rangle_1 = (E_n^{(1)} - \hat{V})|n\rangle_0, \tag{20.10}$$

$$\begin{aligned}\text{2nd order} \Rightarrow (\hat{H}_0 - E_n^{(0)})|n\rangle_2 &= (E_n^{(1)} - \hat{V})|n\rangle_1\\ &+ E_n^{(2)}|n\rangle_0,\end{aligned} \tag{20.11}$$

and, this can go on to higher and higher order. The equation for the nth order requires the solution of all the previous $n-1$ equations. For example, in order to solve the first-order we need to have solved the zeroth-order. As discussed in the previous section, we will assume that we know all energy eigenstates and eigenvalues of $\hat{H}_0$.

20.2.1 First-order correction

Here, we will solve Eq. 20.10 to determine both the first-order correction to the energy and corresponding eigenstate. Since the eigenstates $|n\rangle_0$ of H_0 form a complete set we expand the correction $|n\rangle_1$ as follows

$$|n\rangle_1 = \sum_m C_m^{(1)}|m\rangle_0, \tag{20.12}$$

and we need to determine the coefficients $C_m^{(1)}$. We substitute this into the first-order Eq. 20.10 and we find that

$$\sum_m C_m^{(1)}[E_m^{(0)} - E_n^{(0)}]|m\rangle_0 = (E_n^{(1)} - \hat{V})|n\rangle_0. \tag{20.13}$$

In order to determine the first-order correction to the energy, that is, $E_n^{(1)}$, we project both sides of the above equation onto $|n\rangle_0$. The resulting equation is

$$C_n^{(1)}[E_n^{(0)} - E_n^{(0)}] = {}_0\langle n|E_n^{(1)} - V|n\rangle_0, \tag{20.14}$$

which leads directly to the determination of $E_n^{(1)}$ as

$$E_n^{(1)} = {}_0\langle n|\hat{V}|n\rangle_0. \tag{20.15}$$

Now, in order to determine the coefficient $C_m^{(1)}$ of the wavefunction, we project both sides of Eq. 20.13 onto the state $|k\rangle_0$ with $k \neq n$:

$$C_k^{(1)}[E_k^{(0)} - E_n^{(0)}] = {}_0\langle k|E_n^{(1)} - \hat{V}|n\rangle_0, \tag{20.16}$$

which yields

$$C_k^{(1)} = \frac{{}_0\langle k|\hat{V}|n\rangle_0}{E_n^{(0)} - E_k^{(0)}}, \quad k \neq n. \tag{20.17}$$

Notice that we have not been able to determine $C_n^{(1)}$. The reason is that it cannot be determined from Eq. 20.10. Namely any such coefficient provides a solution to Eq. 20.10 which we try to solve. This is an inhomogeneous algebraic equation with general solution of the form

$$|n\rangle_1 = C_n^{(1)}|n\rangle_0 + \epsilon \sum_{m\neq n} \frac{{}_0\langle m|\hat{V}|n\rangle_0}{E_n^{(0)} - E_m^{(0)}}|m\rangle_0, \tag{20.18}$$

where $C_n^{(1)}$ is any coefficient. When the operator $(\hat{H}_0 - E_n^{(0)})$ (that is, the left-hand-side of Eq. 20.10) operates on the first part of the above expression, it gives zero. Since the second part of the above expression is a particular solution to the inhomogeneous Eq. 20.10, by adding another part proportional to $|n\rangle_0$ it will still be a solution.

Therefore, the wavefunction to first-order in ϵ is given by

$$|n\rangle = C_n|n\rangle_0 + \epsilon \sum_{m\neq n} \frac{{}_0\langle m|\hat{V}|n\rangle_0}{E_n^{(0)} - E_m^{(0)}}|m\rangle_0, \tag{20.19}$$

$$C_n = 1 + \epsilon C_n^{(1)}, \tag{20.20}$$

where C_n is an arbitrary coefficient. If we are going to stop our calculation in first-order in ϵ namely, we neglect the corrections of order ϵ^2 as negligible, then we can write the above expression as

$$|n\rangle = C_n\Big(|n\rangle_0 + \epsilon \sum_{m\neq n} \frac{{}_0\langle m|\hat{V}|n\rangle_0}{E_n^{(0)} - E_m^{(0)}}|m\rangle_0\Big). \tag{20.21}$$

The error introduced by writing the above is of order ϵ^2. Again, by limiting ourselves to be correct to first-order in ϵ, we require that the first-order corrected state $|n\rangle$ be normalized up to order ϵ, that is, that

$$\langle n|n\rangle = 1 + O(\epsilon^2), \tag{20.22}$$

namely, the corrections to the normalization are of an order higher than the order to which our calculation is correct. This determines the coefficient C_n:

$$C_n = 1. \tag{20.23}$$

Notice that we have chosen the phase of C_n to be zero because it is an overall phase factor.

20.2.2 Second-order correction

Having determined the first-order correction to the energy given by Eq. 20.15 and the first-order correction to the wavefunction given by Eq. 20.18, we will solve Eq. 20.11 to determine both the second-order correction to the energy and corresponding eigenstate. We expand the correction $|n\rangle_2$ as follows

$$|n\rangle_{2} = \sum_m C_m^{(2)} |m\rangle_{0}, \tag{20.24}$$

and using Eq. 20.12, Eq. 20.11 takes the following form:

$$\begin{aligned}\sum_m C_m^{(2)} [E_m^{(0)} - E_n^{(0)}] |m\rangle_{0} = {} & \sum_m C_m^{(1)} (E_n^{(1)} - \hat{V}) |m\rangle_{0} \\ & + E_n^{(2)} |n\rangle_{0}.\end{aligned} \tag{20.25}$$

To determine $E_n^{(2)}$, we project both sides of Eq. 20.25 to $|n\rangle_{0}$:

$$0 = \sum_m C_m^{(1)} {}_{0}\langle n| E_n^{(1)} - \hat{V} |m\rangle_{0} + E_n^{(2)}. \tag{20.26}$$

First, notice that if we use Eq. 20.15 the $m = n$ term of the sum vanishes. Using the expression (20.17)for $C_m^{(1)}$ we obtain

$$E_n^{(2)} = \sum_{m \neq n} \frac{|{}_{0}\langle n|\hat{V}|m\rangle_{0}|^2}{E_n^{(0)} - E_m^{(0)}}. \tag{20.27}$$

In order to find the coefficient of the second-order correction to the eigenstate, we project both sides of Eq. 20.25 to the state $|k\rangle_{0}$ for a fixed and given value of $k \neq n$. This yields

$$C_k^{(2)} [E_k^{(0)} - E_n^{(0)}] = \sum_m C_m^{(1)} {}_{0}\langle k| E_n^{(1)} - \hat{V} |m\rangle_{0}. \tag{20.28}$$

The coefficient $C_k^{(2)}$ for $k \neq n$ is obtained as

$$\begin{aligned}C_k^{(2)} = {} & C_n^{(1)} \frac{{}_{0}\langle k|\hat{V}|n\rangle_{0}}{E_n^{(0)} - E_k^{(0)}} - \frac{{}_{0}\langle k|\hat{V}|n\rangle_{0} (E_n^{(1)} - E_k^{(1)})}{(E_n^{(0)} - E_k^{(0)})^2} \\ & + \frac{1}{E_n^{(0)} - E_k^{(0)}} \sum_{m \neq n,k} \frac{{}_{0}\langle k|\hat{V}|m\rangle_{0}{}_{0}\langle m|\hat{V}|n\rangle n_{0}}{E_n^{(0)} - E_m^{(0)}}.\end{aligned} \tag{20.29}$$

The $m = n$ term of the right-hand-side involves the constant $C_n^{(1)}$. This constant is arbitrary because we are keeping all the terms up to second-order and, thus, we do not apply the constraint given by Eq. 20.22. As a result the $m = n$ term adds just a term proportional to $|n\rangle_0$ to the second-order contribution to the energy eigenstate with an arbitrary coefficient. This can be absorbed to the overall coefficient of $|n\rangle_0$ in the total eigenstate.

Therefore, the state $|n\rangle$ correct up to second-order is given by

$$|n\rangle = C_n|n\rangle_0 + C_n\epsilon \sum_{m\neq n} C_m^{(1)}|m\rangle_0 + \epsilon^2 \sum_{k\neq n} \tilde{C}_k^{(2)}|k\rangle_0, \tag{20.30}$$

$$\begin{aligned} \tilde{C}_k^{(2)} &= -\frac{{}_0\langle k|\hat{V}|n\rangle_0 (E_n^{(1)} - E_k^{(1)})}{(E_n^{(0)} - E_k^{(0)})^2} + \frac{1}{E_n^{(0)} - E_k^{(0)}} \\ &\quad \times \sum_{m\neq n,k} \frac{{}_0\langle k|\hat{V}|m\rangle_0 {}_0\langle m|\hat{V}|n\rangle n_0}{E_n^{(0)} - E_m^{(0)}}, \qquad k \neq n, \quad (20.31) \\ C_n &= 1 + \epsilon C_n^{(1)} + \epsilon^2 C_n^{(2)}. \quad (20.32) \end{aligned}$$

Here, the coefficient C_n which appears as a coefficient in the second term is actually of the form given by Eq. 20.20, that is, first-order in ϵ. The first term (the factor 1) came as a first-order correction and the second term is due to the first term in Eq. 20.29. However, using the above form (20.32), which has a third term of order ϵ^2, it is still correct to order ϵ^2. The additional term adds to $|n\rangle$ a term of order ϵ^3.

The coefficient C_n is determined by requiring that the eigenstate $|n\rangle$ is normalized as follows:

$$\langle n|n\rangle = 1 + O(\epsilon^3), \tag{20.33}$$

which, by keeping terms up to ϵ^2, yields that

$$C_n = 1 - \frac{1}{2}\epsilon^2 \sum_{m\neq n} |C_m^{(1)}|^2. \tag{20.34}$$

Notice again that we have chosen the phase of the coefficient C_n to be zero.

20.3 Degenerate perturbation theory

Why are we treating the problem of degeneracy in a separate fashion from the previously discussed treatment of the non-degenerate case? Examine, for example, the first-order corrections to the eigenstates given by the expression (20.18), where we see that the amplitude of contribution of any state $|m \neq n\rangle_0$ to the perturbed eigenstate $|n\rangle$ is given by the coefficient $\epsilon C_m^{(1)}$ (Eq. 20.17). Therefore, this coefficient becomes very large anytime the unperturbed energy of a state $|m\rangle_0$ gets too close to the energy of the unperturbed state $|n\rangle_0$. In such a case the perturbation expansion cannot be justified. This is the case of degenerate perturbation theory, discussed here, and the case of what we term quasi-degenerate perturbation theory, which we discuss in the next section.

For simplicity, let us consider, first, the case of two-fold degeneracy. Namely, we are interested in calculating the perturbative corrections to two states $|n_1\rangle_0$ and $|n_2\rangle_0$ which share the same energy eigenvalue:

$$E^{(0)}_{n_1} = E^{(0)}_{n_2} = E^{(0)}_Q. \tag{20.35}$$

First, notice that any linear combination of $|n_1\rangle_0$ and $|n_2\rangle_0$ is also an eigenstate of $\hat{H}_0$ with the same eigenvalue. Therefore, any vector from the subspace Q spanned by the degenerate eigenvectors is characterized by the same eigenvalue $E^{(0)}_Q$. Thus, $E^{(0)}_Q$ characterizes the entire subspace Q. This implies that we can transform the basis vectors of this subspace by a unitary transformation to any other set of our choice. Let us choose the basis to be the two vectors which are the eigenvectors of the perturbation term $\hat{V}$ in this subspace. Namely, we write $\hat{V}$ in this subspace:

$$\hat{V} \Rightarrow \begin{pmatrix} {}_0\langle n_1|\hat{V}|n_1\rangle_0 & {}_0\langle n_1|\hat{V}|n_2\rangle_0 \\ {}_0\langle n_2|\hat{V}|n_1\rangle_0 & {}_0\langle n_2|\hat{V}|n_2\rangle_0 \end{pmatrix} \equiv \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix}, \tag{20.36}$$

and we find its eigenvectors of the form

$$\begin{pmatrix} \alpha \\ \beta \end{pmatrix} \Rightarrow \alpha|n_1\rangle_0 + \beta|n_2\rangle_2, \tag{20.37}$$

and the corresponding eigenvalues. The latter are given by

$$\lambda_\pm = \frac{V_{11}+V_{22}}{2} \pm \sqrt{(\frac{V_{11}-V_{22}}{2})^2 + |V_{12}|^2}, \tag{20.38}$$

and the corresponding normalized eigenvectors are given as

$$\begin{pmatrix} \alpha_\pm \\ \beta_\pm \end{pmatrix} \Rightarrow |\pm\rangle_0 = \alpha_\pm|n_1\rangle_0 + \beta_\pm|n_2\rangle_2, \tag{20.39}$$

where

$$\alpha_\pm = \frac{V_{12}}{\sqrt{|V_{12}|^2 + (\lambda_\pm - V_{11})^2}}, \tag{20.40}$$

$$\beta_\pm = \frac{\lambda_\pm - V_{11}}{V_{12}}\alpha_\pm. \tag{20.41}$$

We change the eigenstates of the unperturbed Hamiltonian to $|+\rangle_0$, $|-\rangle_0$ (instead of $|n_1\rangle_0$ and $|n_2\rangle_0$), and all others states $|n\rangle_0$ with $n \neq n_1, n_2$ we keep the same. We still have

$$\hat{H}_0|\pm\rangle_0 = E^{(0)}_Q|\pm\rangle_0, \tag{20.42}$$

because $|\pm\rangle_0$ is just a linear combination of $|n_1\rangle_0$ and $|n_2\rangle_0$.

Notice that because $\hat{V}$ is diagonal in the subspace Q, in the new basis there are no matrix elements between the state $|+\rangle_0$ and $|-\rangle_0$, that is,

$$ {}_0\langle +|\hat{V}|-\rangle_0 = {}_0\langle -|\hat{V}|+\rangle_0 = 0. \tag{20.43}$$

This means that the first-order correction to the energy eigenstates is given by

$$|\pm\rangle = |\pm\rangle_0 + \sum_{m\neq\pm} \frac{{}_0\langle m|\hat{V}|\pm\rangle_0}{E_Q^{(0)} - E_m^{(0)}}|m\rangle_0, \tag{20.44}$$

and the sum is only over all states m outside the subspace Q because there are no matrix elements connecting states inside Q.

One might still be puzzled because, while the matrix element between the states inside Q after the diagonalization is zero, the states are still degenerate and the coefficient of their contribution is of the form 0/0 which is undetermined. Indeed if we go back to the beginning, we will still derive an equation like Eq. 20.13 for both $|+\rangle_0$ and $|-\rangle_0$ instead of $|n_1\rangle_0$ and $|n_2\rangle_0$. However, we will find that the coefficient $C_-^{(1)}$ of the state $|+\rangle_1$, or the coefficient $C_+^{(1)}$ of the state $|-\rangle_1$, cannot be determined, that is, they are arbitrary. All other coefficients are given by the previously derived first-order formula. Thus, we can add a term of the form

$$|\pm\rangle = |\pm\rangle_0 + \epsilon C_\mp^{(1)}|\mp\rangle_0 + \epsilon \sum_{m\neq\pm} \frac{{}_0\langle m|\hat{V}|\pm\rangle_0}{E_Q^{(0)} - E_m^{(0)}}|m\rangle_0, \tag{20.45}$$

to the state. However, by requiring that the state $|+\rangle$ and the state $|-\rangle$ should be orthogonal to each other we find that

$$C_+^{(1)} = -C_-^{(1)}. \tag{20.46}$$

This mixes the zeroth-order contribution of states inside Q. The energy to first-order in ϵ is given as

$$E_\pm = E_Q^{(0)} + \epsilon\lambda_\pm. \tag{20.47}$$

This first-order approach can be generalized to the case where the degree of degeneracy is d. Then, the subspace of degeneracy Q is spanned by d states, $|n_1\rangle_0$, $|n_2\rangle_0$, ..., $|n_d\rangle_0$ and $E_{n_1}^{(0)} = E_{n_2}^{(0)} =\ldots = E_{n_d}^{(0)} = E_Q^{(0)}$. Again, we need to diagonalize $\hat{V}$ inside this subspace and let its eigenvalues be denoted by λ_i and the corresponding eigenvectors by $|\lambda_i\rangle_0$. The energy to first-order in ϵ is given by

$$E_i = E_Q^{(0)} + \epsilon\lambda_i, \tag{20.48}$$

and the first-order correction to the wavefunction outside of Q is given by

$$|\lambda_i\rangle_1 = \epsilon \sum_{m\neq Q} \frac{{}_0\langle m|\hat{V}|\lambda_i\rangle_0}{E_Q^{(0)} - E_m^{(0)}}|m\rangle_0. \tag{20.49}$$

20.4 Quasi-degenerate perturbation theory

As already discussed, for the perturbative expansion to be valid we need to make sure that for all states $m \neq n$:

$$\epsilon \Big| \frac{{}_0\langle m|\hat{V}|n\rangle_0}{E_n^{(0)} - E_m^{(0)}} \Big| << 1. \tag{20.50}$$

When two or more energy levels correspond to unperturbed energy eigenvalues which are very close, in the sense that for these level the above expression is comparable to unity or larger, the perturbation expansion cannot be justified.

Let us consider the subspace Q formed by the set of states which are quasi-degenerate in the above sense. For simplicity and to demonstrate this method, let us consider the case of two such states $|n_1\rangle_0$ and $|n_2\rangle_0$.

The interaction $\hat{V}$ can be written as:

$$\hat{V} = \sum_m \sum_n |m\rangle_{0\,0}\langle m|\hat{V}|n\rangle_{0\,0}\langle n|. \tag{20.51}$$

We split the interaction $\hat{V}$ as follows:

$$\begin{aligned}
\hat{V} &= \hat{V}_Q + V', &(20.52)\\
\hat{V}_Q &\equiv V_{11}|n_1\rangle_{0\,0}\langle n_1| + V_{12}|n_1\rangle_{0\,0}\langle n_2| + V_{21}|n_2\rangle_{0\,0}\langle n_1| \\
&\quad + V_{22}|n_2\rangle_{0\,0}\langle n_2|, &(20.53)\\
V_{ij} &= {}_0\langle n_i|\hat{V}|n_j\rangle_0, &(20.54)\\
\hat{V}' &= \hat{V} - \hat{V}_Q. &(20.55)
\end{aligned}$$

Namely, $\hat{V}_Q$ is the part of $\hat{V}$ which couples only states inside the subspace Q, and $\hat{V}'$ is the rest which couples Q with the rest of the Hilbert space and couples the states outside Q. Now, we rewrite the full Hamiltonian as follows:

$$\begin{aligned}
\hat{H} &= \hat{H}'_0 + \epsilon\hat{V}', &(20.56)\\
\hat{H}'_0 &= \hat{H}_0 + \epsilon\hat{V}_Q, &(20.57)
\end{aligned}$$

and we are going to treat $\hat{H}'_0$ as unperturbed part and $\epsilon\hat{V}'$ as perturbation.

(a) First, notice that $\hat{H}'_0$ and H are the same matrices inside Q:

$$\begin{aligned}
\hat{H} &\Rightarrow \begin{pmatrix} {}_0\langle n_1|\hat{H}|n_1\rangle_0 & {}_0\langle n_1|\hat{H}|n_2\rangle_0 \\ {}_0\langle n_2|\hat{H}|n_1\rangle_0 & {}_0\langle n_2|\hat{H}|n_2\rangle_0 \end{pmatrix} \\
&= \begin{pmatrix} E_{n_1}^{(0)} + V_{11} & V_{12} \\ V_{21} & E_{n_2}^{(0)} + V_{22} \end{pmatrix}.
\end{aligned} \tag{20.58}$$

(b) In addition, notice that

$${}_0\langle n_i|\hat{V}'|n_j\rangle_0 = 0, \qquad i,j = 1,2. \tag{20.59}$$

This implies that the new perturbation does not couple any state in the subspace Q. This means that if we diagonalize H_0' (or H) inside the subspace Q and we find its eigenstates $|\pm\rangle_0$ and eigenvalues $\lambda_\pm$ as follows:

$$\begin{aligned}
\lambda_\pm &= \frac{H_{11}+H_{22}}{2} \pm \sqrt{(\frac{H_{11}-H_{22}}{2})^2 + |V_{12}|^2}, && (20.60)\\
H_{11} &= E^{(0)}_{n_1} + V_{11}, \qquad H_{22} = E^{(0)}_{n_2} + V_{11}, && (20.61)\\
|\pm\rangle_{_0} &= \alpha_\pm |n_1\rangle_{_0} + \beta_\pm |n_2\rangle_{_0}, && (20.62)\\
\alpha_\pm &= \frac{V_{12}}{\sqrt{|V_{12}|^2 + (\lambda_\pm - H_{11})^2}}, && (20.63)\\
\beta_\pm &= \frac{\lambda_\pm - H_{11}}{V_{12}} \alpha_\pm, && (20.64)
\end{aligned}$$

the interaction $\epsilon \hat{V}'$ does not couple the new eigenstates:

$$_{_0}\langle + |\hat{V}'| - \rangle_{_0} = {_{_0}\langle - |\hat{V}'| + \rangle_{_0}} = 0. \tag{20.65}$$

Therefore, the first-order correction to the energy is given by

$$|\pm\rangle = |\pm\rangle_{_0} + \epsilon \sum_{m \neq \pm} \frac{_{_0}\langle m|\hat{V}'|\pm\rangle_{_0}}{E^{(1)}_\pm - E^{(0)}_m} |m\rangle_{_0}, \tag{20.66}$$

Notice that the sum extends outside the subspace Q.

In addition, the energy to second-order can be calculated as

$$E_\pm = E^{(1)}_\pm + \epsilon^2 \sum_{m \neq Q} \frac{|_{_0}\langle m|\hat{V}|\pm\rangle_{_0}|^2}{E^{(1)}_\pm - E^{(0)}_m}. \tag{20.67}$$

This approach can be used to determine the effective low-energy properties of an interacting system, by integrating out all high-energy states and finding an effective Hamiltonian which operates only inside a subspace Q where the energy levels are very close to each other.

20.5 Problems

Problem 1

Show that the error introduced by writing Eq. 20.21 is of order ϵ^2.

Problem 2

Show that the wavefunction given by Eq. 20.30, where the coefficients are given by Eq. 20.32, is correct to second-order in ϵ.

Problem 3

Consider the following Hamiltonian

$$\hat{H} = \hat{H}_0 + \lambda x^2, \tag{20.68}$$

where $\hat{H}_0$ is the simple 1D harmonic oscillator

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 x^2. \tag{20.69}$$

(a) Consider the term proportional to λ as perturbation and calculate the energy of the nth level using non-degenerate perturbation theory up to second-order.

(b) Now you can consider the full Hamiltonian $\hat{H}$ as a single harmonic oscillator with a modified frequency. What is the modified frequency?

(c) What is the exact energy of the nth level above? Expand this expression in powers of λ and keep terms up to λ^2. Compare this expression for the energy with that which obtained in part (a) above.

Problem 4

Consider a particle of mass m and charge e under the influence of a potential of the form

$$V(x) = \frac{1}{2} m\omega^2 x^2, \tag{20.70}$$

that is, the familiar 1D harmonic oscillator. Now the particle is perturbed by an external electric field of strength E along the positive x direction.

(a) Calculate the change in each energy level to second-order in perturbation, and calculate the induced dipole moment.

(b) Show that this problem can be solved exactly.

(c) Compare the results with second-order perturbation theory.

Problem 5

A 1D harmonic oscillator is perturbed by an extra potential energy term of the form λx^3. Calculate the change in each energy level to second-order in perturbation theory.

Problem 6

Consider a three-state problem, in which the Hilbert space is spanned by states $|1\rangle$, $|2\rangle$, and $|3\rangle$, with the Hamiltonian matrix in this basis given by the following:

$$\hat{H} = \begin{pmatrix} e_1 & \lambda & \epsilon \\ \lambda & e_2 & \epsilon \\ \epsilon & \epsilon & e_3 \end{pmatrix}. \tag{20.71}$$

Let us assume that $e_1 < e_2 < e_3$ and that the energy difference $|e_1 - e_2|$ is much smaller than the energy differences $|e_1 - e_3|$ and $|e_2 - e_3|$, and, in addition, that the ratios $|\epsilon|/|e_1 - e_3|$, $|\epsilon|/|e_2 - e_3|$ are both much smaller than 1.

(a) Explain why it makes sense to split the above Hamiltonian as follows:

$$\hat{H} = \hat{H}_0 + \epsilon\hat{V}, \tag{20.72}$$

$$\hat{H}_0 = \begin{pmatrix} e_1 & \lambda & 0 \\ \lambda & e_2 & 0 \\ 0 & 0 & e_3 \end{pmatrix}, \qquad \hat{V} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}, \tag{20.73}$$

and to treat the $\epsilon\hat{V}$ part using the quasi-degenerate perturbation theory discussed in this chapter.

(b) Calculate up to second-order in ϵ the perturbatively corrected energy levels e_1 and e_2.

21

Applications of perturbation theory

In this chapter we apply the technique of perturbation expansion to well-known physics problems. Such applications are: the Stark effect, the origin of the van der Waals interaction, and the case of electrons in a weak periodic potential.

21.1 Stark effect

We consider the hydrogen atom in an external static electric $\vec{E}$. The electron in the atom experiences an additional term in the Hamiltonian and the total Hamiltonian takes the form:

$$\hat{H} = \hat{H}_0 + e\vec{E} \cdot \vec{r}, \tag{21.1}$$

where $\hat{H}_0$ is the hydrogen atom Hamiltonian. If we choose our z-axis along the direction of the external electric field, this term becomes eEz. For laboratory electric fields of magnitudes as high as 100,000 V/m the electric field term has a much smaller contribution than the first term. While the expectation value of z is zero in the unperturbed atom, the electric field causes the expectation value of z to be non-zero and a very small fraction of the Bohr radius a_0. However, to get an idea of an upper bound of the relative size of this term in $\hat{H}$, if we take $\langle z \rangle \sim 1$ Å and a rather high value for the electric field $E = 100,000$ V/m, we find that $\langle eEz \rangle \sim 10^{-5}$ eV. This is much smaller than the energy difference between successive energy levels in the hydrogen spectrum. In actuality, the contribution is even smaller than that because $\langle z \rangle$, caused by such a field, is also much smaller than the size of the Bohr radius a_0. This justifies our plan to treat the effects of this added term in the Hamiltonian by perturbation theory.

First, we consider the ground state $|nlm\rangle = |100\rangle$ of the hydrogen atom, which is non-degenerate. The first-order correction is the ground-state expectation value of the perturbation, that is, $\langle 100|eEz|100\rangle$, which vanishes because the ground state is spherically symmetric.

The second-order correction to the energy is given as

$$E^{(2)}_{1s} = -e^2E^2 \sum_{nlm \neq 100} \frac{|z_{100\to nlm}|^2}{E_n - E_1}, \tag{21.2}$$

$$z_{100\to nlm} \equiv \langle nlm|z|100\rangle, \tag{21.3}$$

and E_n denotes the hydrogen atom energy spectrum which depends only on the principal quantum number n.

Practical Quantum Mechanics. First Edition. Efstratios Manousakis.

The electric dipole moment of the atom in its ground state is given by the expectation value

$$\vec{d} = -e \int d^3r |\psi_0(\vec{r})|^2 \vec{r}, \tag{21.4}$$

where ψ_0 is the ground-state wavefunction. Clearly for the hydrogen atom ground state, this expectation value is zero. However, in the presence of an external electric field the wavefunction changes and in first-order it is given by Eq. 20.18. Using this first-order corrected wavefunction and keeping only terms up to first-order we find that

$$\vec{d} = \overleftrightarrow{\alpha} \vec{E}, \tag{21.5}$$

$$\alpha_{ij} = e^2 \sum_{nlm \neq 100} \frac{\langle 100|x_i|nlm\rangle\langle nlm|x_j|100\rangle + c.c}{E_n - E_1}, \tag{21.6}$$

and we have used the abbreviation x_i to denote the x, y, z component of the vector $\vec{r}$ for $i = 1, 2, 3$ respectively and *c.c* stands for "complex conjugate." This procedure defines a 3×3 tensor, $\overleftrightarrow{\alpha}$, which is the atomic polarizability tensor. This is a response function of the atom and characterizes the atom alone and it is independent of the size of the perturbation. This is one example of the more general case of the so-called *linear response theory.*

Now, as an application of degenerate perturbation expansion, we consider the case where the atom is placed in an external electric field giving rise to the Hamiltonian (21.1) but we measure its effect on the spectrum of the excited states. As an example, we consider the case of $n = 2$, which is four-fold degenerate: the states $|200\rangle$, $|210\rangle$, $|21-1\rangle$, and $|211\rangle$ all have the same energy which corresponds to a value of the principal quantum number $n = 2$. Therefore, the first-order correction is obtained by diagonalizing the interaction in the above 4D subspace of the degeneracy. If we form the 4×4 matrix of eEz using the above four states, we will notice that the only non-zero matrix elements are between states $|200\rangle$ and $|210\rangle$. One of the reasons for this is that the interaction is cylindrically symmetric with the axis of cylindrical symmetry along the direction of the electric field. As a result $m = m'$. In addition, there are no diagonal matrix elements because the interaction is proportional to $\cos\theta$. Therefore, the only two states which will be affected by this perturbation are $|200\rangle$ and $|210\rangle$ which, by diagonalizing the matrix

$$\begin{pmatrix} 0 & T \\ T & 0 \end{pmatrix}, \qquad T \equiv eE\langle 210|z|200\rangle, \tag{21.7}$$

are split and their corresponding wavefunctions are as follows

$$E_2 - T \Rightarrow \frac{1}{\sqrt{2}}\Big(|200\rangle + |210\rangle\Big), \tag{21.8}$$

$$E_2 + T \Rightarrow \frac{1}{\sqrt{2}}\Big(|200\rangle - |210\rangle\Big). \tag{21.9}$$

21.2 Origin of the Van der Walls interaction

Consider two hydrogen atoms in which their nuclei are at distance R from each other, which is kept fixed as illustrated in Fig. 21.1. We assume that the distance R is much larger that the Bohr radius a_0, so that each atom is only weakly disturbed by the presence of the other. We would like to calculate the total energy of the system using perturbation theory.

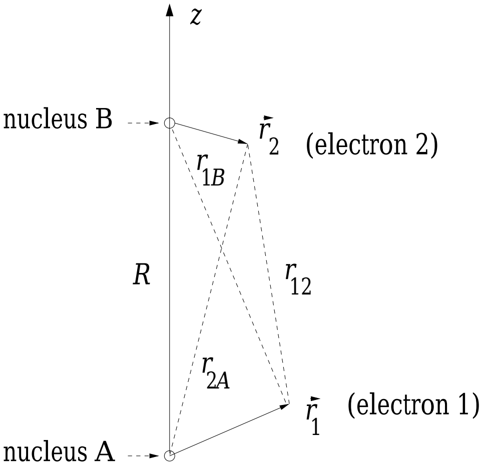

Fig. 21.1

21.2.1 Dipole–dipole interaction

The full Hamiltonian of the system in this case may be written as

$$\hat{H} = \hat{H}_0 + \hat{V}, \tag{21.10}$$

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{r_2}, \tag{21.11}$$

$$\hat{V} = \frac{e^2}{R} + \frac{e^2}{|\vec{R} + \vec{r}_2 - \vec{r}_1|} - \frac{e^2}{|\vec{R} - \vec{r}_1|} - \frac{e^2}{|\vec{R} + \vec{r}_2|}. \tag{21.12}$$

The unperturbed Hamiltonian H_0 is taken to be the sum of the Hamiltonian of the two atoms as if they were at infinite distance from each other. The perturbation part $\hat{V}$ is taken to be the following remaining four terms which are all weaker if $R >> a_0$: the repulsion between the two nuclei, the electron–electron repulsion (determined by the distance between the electrons $r_{12} = \vec{R} + \vec{r}_2 - \vec{r}_1|$), the attractive interaction between nucleus B and the electron of the first atom (determined by the distance between the electrons $r_{1B} = \vec{R} - \vec{r}_1$), and, lastly, the attractive interaction between nucleus A and the electron of the second atom (determined by the distance between the electrons $r_{2A} = \vec{R} + \vec{r}_2$).

By taking our z-axis along the direction of $\vec{R}$, the term $\hat{V}$ can be rewritten as follows:

$$\hat{V} = \frac{e^2}{R}\Big(1 + u_{12} - u_{1B} - u_{2A}\Big), \tag{21.13}$$

$$u_{12} = \bigg[1 + \frac{2(z_2 - z_1)}{R} + \frac{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}{R^2}\bigg]^{-1/2}, \tag{21.14}$$

$$u_{1B} = \bigg[1 - \frac{2z_1}{R} + \frac{x_1^2 + y_1^2 + z_1^2}{R^2}\bigg]^{-1/2}, \tag{21.15}$$

$$u_{2A} = \bigg[1 + \frac{2z_2}{R} + \frac{x_2^2 + y_2^2 + z_2^2}{R^2}\bigg]^{-1/2}. \tag{21.16}$$

We expand the terms u_{12}, u_{1B} and u_{2A} in powers of $1/R$ (actually, in powers of the dimensionless ratio a_0/R, which can be explicitly recovered by dividing $x_{1,2}, y_{1,2}, z_{1,2}$, and R by a_0 everywhere in the above expression) and we keep terms up to $(1/R)^2$. The constants (that is, all the 1's) and the linear term cancel and the second-order term which is the first surviving term is

$$\hat{V} = \frac{e^2}{R^3}(x_1x_2 + y_1y_2 - 2z_1z_2). \tag{21.17}$$

The same result can be obtained using the familiar expression for the electric dipole–dipole interaction:

$$V_{d-d} = \frac{\vec{d}_1 \cdot \vec{d}_2 - 3(\hat{R} \cdot d_1)(\hat{R} \cdot \vec{d}_2)}{R^3}, \tag{21.18}$$

where $\hat{R}$ is the unit vector along the direction of the line connecting the dipoles, using for dipole moments of each of the atoms the following expressions:

$$\vec{d}_1 = -e\vec{r}_1, \qquad \vec{d}_2 = -e\vec{r}_2. \tag{21.19}$$

Therefore, the higher orders in powers of $1/R$ which we omitted are the higher-order multiple-moment expansions of the two neutral charge distributions around the two atoms.

21.2.2 Perturbation theory

In zeroth-order perturbation theory, $\hat{H}_0$ consists of two independent hydrogen atoms; therefore, we already know the eigenstates: electrons as

$$|nlm; n'l'm'\rangle = |nlm\rangle_1 |n'l'm'\rangle_2. \tag{21.20}$$

Namely, we have written the eigenstates of the two independent electrons as the direct product between the eigenstates of the electron labeled as 1 and the eigenstates of the electron labeled 2. The unperturbed Hamiltonian acting on each of these states yields:

$$\hat{H}_0|nlm;n'l'm'\rangle = (E_{n_1} + E_{n_2})|nlm;n'l'm'\rangle, \tag{21.21}$$

$$E_n = -\frac{e^2}{2a_0}\frac{1}{n^2}. \tag{21.22}$$

In general the Hilbert space $\mathcal{H}_2$ of two *distinguishable* particles is the so-called direct product of the single particle Hilbert space times itself, symbolically:

$$\mathcal{H}_2 = \mathcal{H}_1 \otimes \mathcal{H}_1. \tag{21.23}$$

What this means is simply that a complete basis of $\mathcal{H}_2$ for distinguishable particles can be constructed out of the basis elements of $\mathcal{H}_1$ as follows:

$$|\gamma_1, \gamma_2\rangle = |\gamma_1\rangle_1 \otimes |\gamma_2\rangle_2 \tag{21.24}$$

where $|\gamma\rangle_i$ for fixed i (here γ labels the different basis states) is a complete basis of $\mathcal{H}_1$ and i is the particular particle identity index.

In our particular case of the two different spatially separated atoms, we consider the two electrons as distinguishable. Because the two atoms are far away from one another, the probability for electron exchange between the two atoms is exponentially small with the distance R between the atoms. This fact leads to the spontaneous breaking of the permutation symmetry between electron identities. What needs to be done in general in order to treat the problem of identical particles is discussed in chapter 25.

We are interested in the case where the two atoms are in their own ground state. In this case the first-order correction is given as the expectation value of the perturbation, that is,

$${}_1\langle 100|{}_2\langle 100|\hat{V}|100\rangle_1|1,0,0\rangle_2 \tag{21.25}$$

and using the expression given by Eq. 21.17 we may write the above expectation value as

$$\langle\hat{V}\rangle = -\frac{e^2}{R^3}\Big[\langle x_1\rangle_1\langle x_2\rangle_2 + \langle y_1\rangle_1\langle y_2\rangle_2 - 2_1\langle z_1\rangle_1\langle z_2\rangle_2\Big], \tag{21.26}$$

where

$$\langle x_i\rangle_i = {}_i\langle 100|x_i|100\rangle_i, \tag{21.27}$$

and similarly for $\langle y_i\rangle_i$ and $\langle z_i\rangle_i$. These expectation values, however, all vanish due to the fact that each hydrogen atom in its ground state (the 1s state) is spherically symmetric. Therefore, the direct–dipole interaction term vanishes because there is no permanent electric dipole in the ground state of the hydrogen atom:

$$\langle\vec{d_1}\rangle = \langle\vec{d_2}\rangle = 0. \tag{21.28}$$

The second-order perturbation correction to the energy is given as:

$$E^{(2)}(R) = \sum_{nlm\neq 100, n'l'm'\neq 100} \frac{|\langle nlm, n'l'm'|\hat{V}|100,100\rangle|^2}{2E_1 - E_n - E_{n'}} \tag{21.29}$$

which can be written as

$$E^{(2)}(R) = -\frac{C}{R^6}, \qquad C \geq 0, \tag{21.30}$$

where the non-negative coefficient C can be computed as:

$$e^4 \sum \frac{|\langle nlm, n'l'm'|(x_1x_2 + y_1y_2 - 2z_1z_2)|100, 100\rangle|^2}{(E_n - E_1) + (E_{n'} - E_1)}, \tag{21.31}$$

where the summation is over all values of $nlm \neq 100$, and $n'l'm' \neq 100$. Notice that this leads to an *effective interaction* between the two atoms which is always attractive. There are two items which need to be discussed. First, we call this term "effective interaction" for the following reason. The atomic nuclei are much more massive compared to the electrons. This means that between two not-too-different configurations of the nuclei, the electrons have enough time to "travel" around the two atoms numerous times and to sample their entire wavefunction. This means that there are two different timescales involved and two different energy scales. One scale controlling the electronic problem and one energy scale that controls the motion of the atoms due to their mutual "effective interaction." This allows us to solve the electronic problem, as we did for a fixed relative distance between the nuclei, and then to consider the following "effective Hamiltonian" to describe the atom–atom interaction:

$$\hat{H}_a = \frac{P_A^2}{2M} + \frac{P_B^2}{2M} + V(R). \tag{21.32}$$

Where $V(R)$ is the total energy of the electrons for a fixed relative position between the nuclei. Here, $\vec{P}_{A,B}$ denote the momenta of the two nuclei and M is their mass. Now, in a correct calculation, one has to determine $V(R)$ even for short distances. Here, we only determined it for $R >> a_0$. This separation of the electronic from the nuclear motion, is called the "Born–Oppenheimer" approximation.

The second item which we wish to discuss is the following question: What is the interpretation of this Van der Waals interaction and why is it attractive at long distances as we found?

The two hydrogen atoms in their ground states have no permanent dipole moments as their ground state is spherically symmetric. However, as the second atom approaches closer to the first atom, due to quantum fluctuations produced by their mutual interactions (namely, when the two nuclei are at a finite distance from each other, the electrons are, with some small weight, also virtually in excited states of the unperturbed atom), each of the two atoms has a fluctuating dipole moment; at a given instant this fluctuating dipole moment polarizes and induces a dipole moment on the other atoms. This effect fluctuates in time; however, it always leads to an effective attractive interaction between the two atoms at large distances. It is of order $1/R^6$ because the induced dipole moment on one atom is of order of $1/R^3$ and, then, this leads to an interaction with the neutral charge distribution of the other atom yielding an additional $1/R^3$ factor.

21.3 Electrons in a weak periodic potential

Let us consider an electron moving under the influence of an external weak periodic potential. This can approximate the situation of conduction-band electrons in a metal. These electrons are not bound to any particular atom and they almost freely move inside the crystal under the influence of a weak periodic potential. Let us consider the simpler case of 1D and write:

$$\hat{H} = H_0 + V(x), \tag{21.33}$$

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}, \tag{21.34}$$

$$V(x+a) = V(x). \tag{21.35}$$

We also apply periodic boundary conditions, that is,

$$\psi(x+Na) = \psi(x), \tag{21.36}$$

namely, our system size is $L = Na$ where N is a large integer. We also assume that the contribution of $V(x)$ as compared to the contribution of the free particle part of the Hamiltonian $\hat{H}_0$ is small. This allows us to use the perturbation approach. An exact treatment of the special case where the potential is different constants at different regions of space pieced together was carried out in chapter 10. The present perturbative approach provides only an approximate treatment, but it is applicable to any periodic form that $V(x)$ may have.

Before we start our approximate treatment based on the perturbation expansion, let us recall the exact theorem, called Bloch's theorem, discussed in chapter 10, which is a simple consequence of the periodic potential. Since the Hamiltonian commutes with the operator of translations by a, we can choose its eigenstates to be of the following form:

$$\psi_k(x) = e^{ikx}u_k(x),\ u_k(x+a) = u_k(x), \tag{21.37}$$

$$k = \frac{2\pi}{Na}n,\ n = 0, \pm 1, \pm 2, ..., \quad -\frac{\pi}{a} \leq k < \frac{\pi}{a}, \tag{21.38}$$

namely, k is restricted inside the so-called first Brillouin zone.

On the other hand, we know that the unperturbed Hamiltonian is the free-particle Hamiltonian with eigenvalues and eigenstates given as:

$$\hat{H}_0\psi_q^{(0)}(x) = E_q^{(0)}\psi_q^{(0)}, \tag{21.39}$$

$$\psi_q(x) = \frac{1}{\sqrt{Na}}e^{iqx}, \qquad E_q^{(0)} = \frac{\hbar^2 q^2}{2m}, \tag{21.40}$$

$$q = \frac{2\pi}{Na}n', \qquad n' = 0, \pm 1, \pm 2, ..., \tag{21.41}$$

and while Bloch's wavevector k is restricted inside the first Brillouin zone, the wavevector q characterizing the free-particle wavefunction is not restricted.

In order to proceed, we will need to reconcile the free-particle state with the requirement of Bloch's theorem. This is simple once we realize that we can reduce any such vector q inside the first BZ by subtracting a multiple of $G_0 = 2\pi/a$, which is the size of the first BZ. Namely, we can always write:

$$q = k + G, \tag{21.42}$$

$$G = \frac{2\pi}{a}m, \qquad m = 0, \pm 1, \pm 2, ..., \tag{21.43}$$

$$-\frac{\pi}{a} \leq k < \frac{\pi}{a}. \tag{21.44}$$

Namely, for any given q, there is always a unique k and a unique G which allows us to write q as $k + G$. With the above separation, the free-particle wavefunction can be written as

$$\psi_q^{(0)}(x) = \frac{1}{\sqrt{Na}} e^{i(k+G)x} = e^{ikx} u(x); \quad u(x) = \frac{1}{\sqrt{Na}} e^{iGx}, \tag{21.45}$$

and, in fact, as shown next, the function $u(x)$ is a periodic function with period a as required by Bloch's theorem:

$$u(x + a) = e^{iGa} u(x) = u(x). \tag{21.46}$$

Now, the free-particle energy eigenvalues can be written as

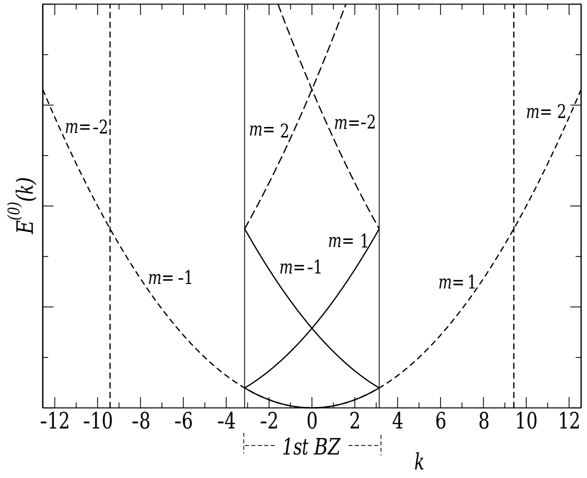

Fig. 21.2

$$E^{(0)}(q) = E_G^{(0)}(k) = \frac{\hbar^2 (k + G)^2}{2m}, \tag{21.47}$$

with k restricted inside the 1BZ. In this way we have taken all the pieces of the original free-particle energy dispersion relation which were in the mth BZ and move them inside the 1BZ as shown in Fig. 21.2. Therefore, now the energy dispersion has an infinite number of branches for different values of G, which is the result of folding all higher BZs inside the 1BZ. Notice that under the influence of an infinitesimal periodic potential with period a these correspond to the many bands which one finds with the approaches discussed in chapter 10.

Let us assume that the periodic potential is weak so that we can proceed with perturbation expansion. First, let us clarify that only states with the same value of k and different value of G couple through the periodic potential. Namely, if $V(x)$ is periodic:

$$\langle\psi_k|V(x)|\psi_{k'}\rangle = 0, \quad for \quad k - k' \neq G. \tag{21.48}$$

This can be shown by taking into account explicitly the periodicity of $V(x)$ as follows:

$$\begin{aligned}\langle\psi_k|V(x)|\psi_{k'}\rangle &= \frac{1}{Na}\int_0^{Na} dxV(x)e^{i(k'-k)x} \\ &= \frac{1}{Na}\int_0^{Na} dxV(x+a)e^{i(k'-k)x},\end{aligned} \tag{21.49}$$

and by changing the integration variable from x to $x' = x + a$ we can see that

$$\begin{aligned}\langle\psi_k|\ V(x)\ |\psi_{k'}\rangle &= \frac{1}{Na}\int_a^{Na+a} dx'V(x')e^{i(k'-k)(x'-a)}, \\ &= \ e^{-i(k'-k)a}\frac{1}{Na}\int_a^{Na+a} dx'V(x')e^{i(k'-k)x'}.\end{aligned} \tag{21.50}$$

Therefore, we conclude that

$$\langle\psi_k|V(x)|\psi_{k'}\rangle = e^{-i(k'-k)a}\langle\psi_k|V(x)|\psi_{k'}\rangle. \tag{21.51}$$

The last step is obtained by changing the integration limits from $[a, Na+a]$ to $[0, Na]$ because of our periodic boundary conditions. This equation can only be valid either if $(k'-k) = 2\pi m$, that is, if $k' = k + G$ or if $\langle\psi_k|V(x)|\psi_{k'}\rangle = 0$. This means that in carrying out perturbation theory to find corrections to states of given k, we only need to consider states which have the same Bloch index k but different values of G.

Notice that near the 1BZ boundaries, that is, near $k = \pm\pi/a$, the two branches for $G = 0$ and for $G = m2\pi/a$ with $m \mp 1$ approach each other, requiring the treatment discussed for quasi-degenerate perturbation theory. In particular, when $k = \pm\pi/a$ there are two states with the same energy:

$$\frac{\hbar^2(k+G)^2}{2m} = \frac{\hbar^2k^2}{2m}, \quad \text{for} \quad k = \pm\frac{\pi}{a} \quad \text{and} \quad G = \mp\frac{2\pi}{a}. \tag{21.52}$$

Since the treatment of the degenerate perturbation theory is a particular case of the more general approach to the quasi-degenerate perturbation treatment, we follow the latter to also treat the values of k near the zone boundaries. Thus, we need to diagonalize the Hamiltonian in the subspace spanned by the states $|\psi_k\rangle$ and $|\psi_{k+G}\rangle$, that is, the following matrix:

$$\begin{pmatrix} \langle\psi_k|\hat{H}_0+\hat{V}|\psi_k\rangle & \langle\psi_k|\hat{H}_0+\hat{V}|\psi_{k+G}\rangle \\ \langle\psi_{k+G}|\hat{H}_0+\hat{V}|\psi_k\rangle & \langle\psi_{k+G}|\hat{H}_0+\hat{V}|\psi_{k+G}\rangle \end{pmatrix}. \tag{21.53}$$

$\hat{H}_0$ is diagonal with diagonal matrix elements

$$\langle\psi_k|\hat{H}_0|\psi_k\rangle = E_0^{(0)}(k) = \frac{\hbar^2k^2}{2m}, \tag{21.54}$$

$$\langle\psi_{k+G}|\hat{H}_0|\psi_{k+G}\rangle = E_G^{(0)}(k) = \frac{\hbar^2(k+G)^2}{2m}. \tag{21.55}$$

We also need the matrix elements of the periodic potential, which can be simply reduced to an integral inside the first unit cell, that is, $0 < x < a$, as follows:

$$\begin{aligned}\langle\psi_k|\hat{V}|\psi_{k+G}\rangle &= \frac{1}{Na}\int_0^{Na} dx e^{ikx}V(x)e^{-i(k+G)x}, \\ &= \frac{1}{Na}\int_0^{Na} dx V(x)e^{-iGx} \\ &= \frac{1}{a}\int_0^{a} dx V(x)e^{-iGx} \equiv \tilde{V}_G.\end{aligned} \tag{21.56}$$

In the last step we have reduced the integration inside one unit cell because of the periodicity of both $V(x)$ and e^{-iGx}. Similarly, we find that

$$\langle\psi_{k+G}|\hat{V}|\psi_k\rangle = \tilde{V}_G^*. \tag{21.57}$$

Furthermore,

$$\langle\psi_k|\hat{V}|\psi_k\rangle = \langle\psi_{k+G}|\hat{V}|\psi_{k+G}\rangle = \frac{1}{a}\int_0^a dx V(x) \equiv \tilde{V}_0. \tag{21.58}$$

At this point, we have all the matrix elements of the Hamiltonian matrix to carry out the diagonalization in the subspace spanned by $|\psi_k\rangle$ and $|\psi_{k+G}\rangle$. We obtain the following energy eigenvalues:

$$\begin{aligned}\lambda_\pm &= \frac{E_0(k)+E_G(k)}{2} \\ &\quad \pm\sqrt{\left(\frac{E_0(k)-E_G(k)}{2}\right)^2 + |\tilde{V}_G|^2},\end{aligned} \tag{21.59}$$

$$E_G(k) = E_G^{(0)}(k) + \tilde{V}_0. \tag{21.60}$$

This expression is plotted in Fig. 21.3 by taking $\tilde{V}_0 = 0$. Notice that at the BZ boundaries an energy gap opens up which is given by:

$$\Delta = 2|\tilde{V}_G|. \tag{21.61}$$

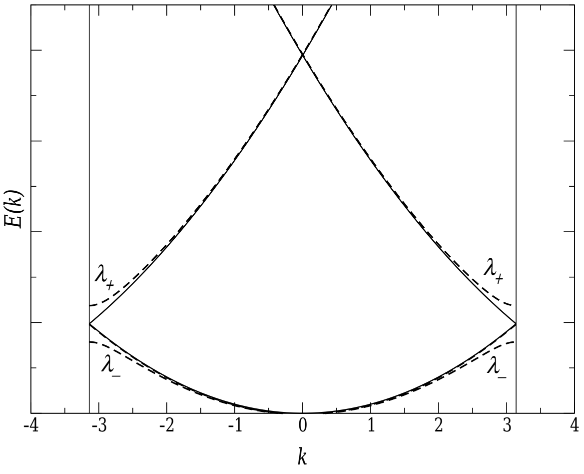

Fig. 21.3

21.4 Problems

Problem 1

The Van der Waals interaction between two hydrogen atoms in the ground state and separated by a large distance R is given by

$$V(R) = -\frac{C}{R^6}, \tag{21.62}$$

where

$$C = e^4 \sum_{\nu_1 \neq 0, \nu_2 \neq 0} \frac{|\langle 0,0|(x_1x_2 + y_1y_2 - 2z_1z_2)|\nu_1,\nu_2\rangle|^2}{\epsilon_{\nu_1} + \epsilon_{\nu_2} - 2\epsilon_0}, \tag{21.63}$$

where $|\nu_1\rangle$ and $|\nu_2\rangle$ denote excited states of the hydrogen atom with corresponding energies ϵ_{ν_1} and ϵ_{ν_2}.

Calculate the above coefficient C of the Van der Waals interaction explicitly by limiting the number of states ν_1 and ν_2 in the sum to states $|\nu_1\rangle = |n_1, l_1, m_1\rangle$ and $|\nu_2\rangle = |n_2, l_2, m_2\rangle$ with $n_1 \leq 2$ and $n_2 \leq 2$.

Problem 2

Consider the following two cases of a 1D crystal, that is, a periodic array of atoms. Use the finding of the perturbation approach in this chapter to:

(a) explain that when there is an even number of electrons per atom the crystal will be an insulator,

(b) explain that when there is an odd number of electrons per atom the crystal will be a metal.

To answer these questions, think classically about the response of the electrons to an external constant electric field. In addition, assume that a typical energy scale for the gap Δ is 1 eV. Show that a laboratory made electric field is way too small for the energy scale eEx (by taking a typical value for $x \sim 1$ Å), supplied by the external field to each electron, to be comparable to Δ to enable the electron to overcome the energy gap.

22
Time-dependent Hamiltonian

This chapter discusses how to treat the case of a perturbation which depends on time. We also discuss the case of the so-called real-time evolution and the adiabatic process which has received more recent attention because of experiments on quantum dynamics in trapped cold atoms.

22.1 Time-dependent perturbation theory

Here, our Hamiltonian is conveniently written as:

$$\hat{H}(t) = \hat{H}_0 + \epsilon \hat{V}(t), \tag{22.1}$$

and we are interested in solving the time-dependent Schrödinger equation,

$$H(t)|\psi(t)\rangle = i\partial_t|\psi(t)\rangle, \tag{22.2}$$

under the initial condition

$$|\psi(t = t_0)\rangle = |\psi_0\rangle, \tag{22.3}$$

where the state $|\psi_0\rangle$ is a state known to us, that is, we know all of its projections to a known complete set of states, for example, the eigenstates of $\hat{H}_0$:

$$\hat{H}_0|n\rangle_0 = E_n^{(0)}|n\rangle_0, \tag{22.4}$$

which, along with their corresponding eigenvalues, are also known to us.

In order to find a series expansion solution to Eq. 22.2 we expand $|\psi(t)\rangle$ using the complete set of unperturbed eigenstates $|n\rangle_0$ of $\hat{H}_0$:

$$|\psi(t)\rangle = \sum_k C_k(t) e^{-\frac{i}{\hbar}E_k^{(0)}t}|k\rangle_0, \tag{22.5}$$

where the coefficients $C_k(t)$ are to be determined. We also expand the initial state:

$$|\psi_0\rangle = \sum_k C_k(t_0)|k\rangle_0, \tag{22.6}$$

where clearly the coefficients associated with the state $|n\rangle_0$ are the same as the coefficients in Eq. 22.5 for $t = t_0$. Since the state $|\psi_0\rangle$ is known, the projections

$$C_k(t_0) = {}_0\langle k|\psi_0\rangle, \tag{22.7}$$

are also known.

Practical Quantum Mechanics. First Edition. Efstratios Manousakis.

By substituting expression (22.5) in Eq. 22.2 we find

$$\begin{aligned}
&\sum_k C_k(t) e^{-\frac{i}{\hbar}E_k^{(0)}t}(E_k^{(0)} + \epsilon \hat{V}(t))|k\rangle_0 \\
&= \sum_k [i\hbar \dot{C}_k(t) + E_k^{(0)} C_k(t)] e^{-\frac{i}{\hbar}E_k^{(0)}t}|k\rangle_0. \qquad (22.8)
\end{aligned}$$

Notice that the first term of the left-hand-side (the unperturbed part) appears on both sides and cancels out. Next, by projecting both sides onto $|m\rangle_0$ for given m, we obtain:

$$\dot{C}_m(t) = \epsilon \frac{1}{i\hbar} \sum_k C_k(t) e^{-\frac{i}{\hbar}(E_k^{(0)} - E_m^{(0)})t} {}_0\langle m|\hat{V}(t))|k\rangle_0. \qquad (22.9)$$

Next, we expand $C_k(t)$ in powers of ϵ (defined in Eq. 22.1) as follows:

$$C_k(t) = C_k^{(0)}(t) + \epsilon C_k^{(1)}(t) + \epsilon^2 C_k^{(2)} + ... \qquad (22.10)$$

and we substitute in Eq. 22.9, that is,

$$\begin{aligned}
\dot{C}_m^{(0)}(t) + \epsilon \dot{C}_m^{(1)}(t) + \epsilon^2 \dot{C}_m^{(2)} + ... &= \epsilon \frac{1}{i\hbar} \sum_k [C_k^{(0)}(t) + \epsilon C_k^{(1)}(t) \\
&+ \epsilon^2 C_k^{(2)} + ...] e^{-\frac{i}{\hbar}(E_k^{(0)} - E_m^{(0)})t} {}_0\langle m|\hat{V}(t))|k\rangle_0. \qquad (22.11)
\end{aligned}$$

By equating the same order of ϵ on both sides of the above equation, we find the following hierarchy of equations:

$$\begin{aligned}
\dot{C}_m^{(0)}(t) &= 0, \qquad (22.12) \\
\dot{C}_m^{(1)}(t) &= \frac{1}{i\hbar} \sum_k C_k^{(0)}(t) e^{-\frac{i}{\hbar}(E_k^{(0)} - E_m^{(0)})t} \\
&\quad \times {}_0\langle m|\hat{V}(t))|k\rangle_0, \qquad (22.13) \\
&..., \\
&..., \\
&..., \\
\dot{C}_m^{(l)}(t) &= \frac{1}{i\hbar} \sum_k C_k^{(l-1)}(t) e^{-\frac{i}{\hbar}(E_k^{(0)} - E_m^{(0)})t} \\
&\quad \times {}_0\langle m|\hat{V}(t))|k\rangle_0. \qquad (22.14)
\end{aligned}$$

These equations can be solved successively, that is, the zeroth-order first, then using the solution for $C_m^{(0)}(t)$ we substitute it in the first-order equation to solve for $C_m^{(1)}(t)$, and so on.

The zeroth-order equation has a simple solution, that is,

$$C_m^{(0)}(t) = C_m^{(0)}(t_0), \qquad (22.15)$$

that is, it is time independent. If we are going to stop at zeroth-order, then $C_m^{(0)}$ is given by Eq. 22.7.

22.1.1 First-order perturbation

The first-order equation (22.13) can be integrated in time to obtain:

$$\begin{aligned} C_m^{(1)}(t) = C_m^{(1)}(t_0) + \frac{1}{i\hbar}\sum_k \int_{t_0}^{t} dt' e^{-\frac{i}{\hbar}(E_k^{(0)}-E_m^{(0)})t'} \\ \times {}_0\langle m|\hat{V}(t')|k\rangle_0, \end{aligned} \tag{22.16}$$

where $C_m^{(1)}(t_0)$ is time independent. If we are going to stop at first-order, then

$$C_m^{(0)}(t_0) + \epsilon C_m^{(1)}(t_0) = C_m(t_0), \tag{22.17}$$

which is given by the initial condition. The situation becomes simplified when the initial time t_0 is chosen to be the instant when the time-dependent perturbation begins to act, that is, such that $V(t \le t_0) = 0$. In this particular case,

$$C_m^{(n\neq 0)}(t_0) = 0, \tag{22.18}$$

that is, for all orders except for the zeroth-order. In the following part of this subsection we consider an example in which we restrict ourselves to the case where

$$\hat{V}(t) = \hat{V}_0\Theta(t), \tag{22.19}$$

where $\Theta(t)$ is the Heavyside step function (that is, $\Theta(t \ge 0) = 1$ and $\Theta(t < 0) = 0$), and we will take as an initial condition at $t_0 = 0$ that the state of the system before the perturbation begins to act was such that

$$C_m(t = t_0) = \delta_{m,m_0}, \tag{22.20}$$

namely, the system was in the m_0 eigenstate of the unperturbed Hamiltonian. We want to find the probability for the system to decay in different eigenstate m at a later time t, which to first-order is given as

$$P_{m_0\to m}(t) = |C_m^{(1)}(t)|^2. \tag{22.21}$$

Under these specialized conditions, the expression given by Eq. 22.16 becomes,

$$\begin{aligned} C_{m_0\to m}^{(1)}(t) &= \frac{1}{i\hbar}{}_0\langle m|\hat{V}_0|m_0\rangle_0 \int_0^t dt' \exp(-i\omega_{m_0m}t') \\ &= \frac{1}{\hbar}{}_0\langle m|\hat{V}_0|m_0\rangle_0 \frac{\exp(-i\omega_{m_0m}t)-1}{\omega_{m_0m}}, \end{aligned} \tag{22.22}$$

$$\omega_{m_0m} \equiv \frac{E_k^{(0)} - E_m^{(0)}}{\hbar}. \tag{22.23}$$

Therefore, the probability for a transition $m_0 \to m$ is given by

$$P_{m_0 \to m}(t) = |C_m^{(1)}(t)|^2 = \frac{2\pi}{\hbar^2}\chi(x,t)t \times |{}_0\langle m|\hat{V}_0|m_0\rangle_0|^2, \tag{22.24}$$

$$\chi(\omega_{m_0,m},t) \equiv \frac{1}{2\pi}\frac{\sin^2(x)}{x^2}t, \tag{22.25}$$

$$x \equiv \frac{\omega_{m_0 m}t}{2}. \tag{22.26}$$

The function $\chi(\omega,t)$ is shown in Fig. 22.1 as a function of ω for two values of $t = 1, 2$. Notice that at $\chi(\omega = 0, t)$ grows linearly with t because of the fact that $\lim_{x\to 0}\sin(x)/x =$ 1. In addition, the integral under the curve is a constant, that is,

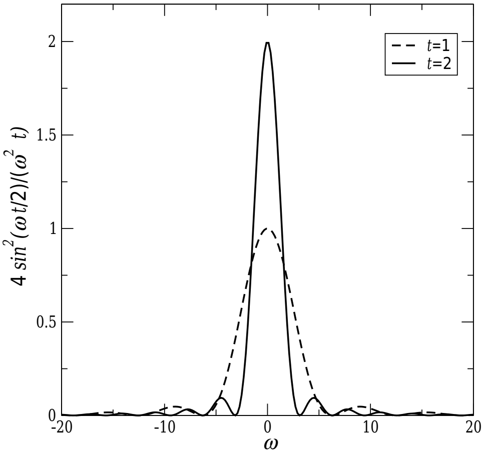

Fig. 22.1

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}\chi(\omega,t) = 1, \tag{22.27}$$

because of the fact that

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}dx\frac{\sin^2(x)}{x^2} = 1. \tag{22.28}$$

As a result, when t increases the width of $\chi(\omega,t)$ becomes narrower and narrower. In fact, in the limit where $t \to \infty$ we have that

$$\lim_{t\to\infty}\chi(\omega,t) = \delta(\omega). \tag{22.29}$$

Therefore, we can write that the transition rate $\Gamma_{m_0,m}$ becomes

$$\Gamma_{m_0,m} = \lim_{t\to\infty} \frac{P_{m_0,m}(t)}{t} = \frac{2\pi}{\hbar} |_0\langle m|\hat{V}_0|m_0\rangle_0|^2 \times \delta(E^{(0)}_{m_0} - E^{(0)}_{m}). \tag{22.30}$$

If we view this as an experiment to measure the energy of the system by applying a perturbation, this equation tells us that if the interaction time t with the system for carrying out the measurement is infinitely long, the energy should be conserved. If the interaction time is finite, then there is a finite width of the states allowed for transition. This width is approximately given by finding the first zero of $\chi(x,t)$ which occurs at $x_0 = \pi$; therefore, which implies that the width in ω is $\delta\omega t \sim 2\pi$ or

$$\Delta E \quad t \sim h. \tag{22.31}$$

Therefore, this can be understood simply by means of the uncertainly principle.

Now, let us consider that there is a continuum of states near the initial state m_0 described by a function $\rho(E)$ which is the density of states, namely $\rho(E)dE$ gives the number of states in the energy range $(E, E+dE)$. In this case we are interested in finding the probability for transition to any state m. This implies that we need to compute the following sum:

$$\Gamma_{m_0} = \sum_m \lim_{t\to\infty} \frac{P_{m_0m}(t)}{t} = \frac{2\pi}{\hbar^2} \sum_m |_0\langle m|\hat{V}_0|m_0\rangle_0|^2 \times \chi(\omega_{m_0m}, t). \tag{22.32}$$

Using the density of states this sum can be transformed into an integral over energy as follows:

$$\Gamma_{m_0} = \frac{2\pi}{\hbar} \int dE \rho(E) |_0\langle m|\hat{V}_0|m_0\rangle_0|^2 \chi(\omega_{m_0m}, t). \tag{22.33}$$

Since the function $\chi(\omega,t)$ is strongly peaked near $\omega = 0$, assuming that the functions $\rho(E)$ and the matrix element do not vary wildly near $\omega = 0$, we can write the above expression as

$$\Gamma_{m_0} = \frac{2\pi}{\hbar^2} |_0\langle m|\hat{V}_0|m_0\rangle_0|^2 \rho(E_{m_0}) \int dE \quad \chi(\omega_{m_0m}, t). \tag{22.34}$$

Using the identity (22.27) we find that

$$\Gamma_{m_0} = \frac{2\pi}{\hbar} |_0\langle m|\hat{V}_0|m_0\rangle_0|^2 \rho(E^{(0)}_{m_0}). \tag{22.35}$$

The last expression is sometimes called Fermi's golden rule.

22.1.2 Harmonic perturbation

Consider a perturbation which turns on at $t = 0$ and varies as $\sin(\omega t)$ or $\cos(\omega t)$, for example:

$$\hat{V}(t) = \hat{V}_0 \Theta(t) \sin(\omega t). \tag{22.36}$$

In addition, we assume that the system before the perturbation was in state $|m_0\rangle_0$, that is, we assume that Eq. 22.20 is valid. Using Eq. 22.16 we obtain:

$$\begin{aligned} C_{m_0 \to m} &= \frac{e^{i\omega_{m_0 m} t}}{2\hbar} {}_0\langle m|\hat{V}_0|m_0\rangle_0 \\ &\times \int_0^t dt' \Big(e^{i(\omega_{m_0 m} - \omega)t'} - e^{i(\omega_{m_0 m} + \omega)t'} \Big), \end{aligned} \tag{22.37}$$

and by doing the integrals we find that

$$\begin{aligned} C_{m_0 \to m} &= \frac{e^{i\omega_{m_0 m} t}}{2i\hbar} {}_0\langle m|\hat{V}_0|m_0\rangle_0 \\ &\times \Big(\frac{e^{i(\omega_{m_0 m} - \omega)t} - 1}{\omega_{m_0 m} - \omega} - \frac{e^{i(\omega_{m_0 m} + \omega)t} - 1}{\omega_{m_0 m} + \omega} \Big). \end{aligned} \tag{22.38}$$

Therefore, the transition probability is

$$\begin{aligned} P_{m_0,m}(t) &= |C_{m_0,m}(t)|^2 = \frac{\pi}{2\hbar^2} |{}_0\langle m|\hat{V}_0|m_0\rangle_0|^2 \\ &\times f(\omega, t)t, \end{aligned} \tag{22.39}$$

$$\begin{aligned} f(\omega, t) &= \chi(\omega - \omega_{m_0 m}, t) + \chi(\omega - \omega_{m_0 m}, t) \\ &+ \xi(\omega, t), \end{aligned} \tag{22.40}$$

$$\xi(\omega, t) = \frac{e^{i(\omega_{m_0 m} - \omega)t} - 1}{\omega_{m_0 m} - \omega} \frac{e^{i(\omega_{m_0 m} + \omega)t} - 1}{\omega_{m_0 m} + \omega} + c.c.. \tag{22.41}$$

and $\chi(\omega, t)$ is given by Eq. 22.25. When the energy difference between the initial and final states, that is, $\omega_{m_0 m}$ is large, the interference term $\xi(t)$ is small, because the first term contributing to the product above is significant near $\omega \sim \omega_{m_0 m}$ (absorption) and the other near $\omega \sim -\omega_{m_0 m}$ (emission). In the limit of $t \to \infty$ we have that

$$P_{m_0,m}(t) = \Gamma_{m_0 m} t, \tag{22.42}$$

$$\begin{aligned} \Gamma_{m_0 m} &= \frac{\pi}{2\hbar^2} |{}_0\langle m|\hat{V}_0|m_0\rangle_0|^2 \\ &\times \Big(\delta(\omega + \omega_{m_0 m}) + \delta(\omega - \omega_{m_0 m} \Big). \end{aligned} \tag{22.43}$$

22.1.3 Higher-order terms

It is straightforward to see that the coefficient of the nth order contribution to the coefficient $C_{m_0 m}(t)$ is given by

$$C^{(n)}_{m_0 m}(t) = \frac{1}{(i\hbar)^n} \sum_{k_1}\sum_{k_2} \;...\; \sum_{k_{n-1}} \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_2} dt_3$$
$$... \int_{t_0}^{t_{n-1}} dt_n e^{i\omega_{m_0 k_1} t_1} e^{i\omega_{k_1 k_2} t_2} \;...\; e^{i\omega_{k_{n-1} m} t_n}$$
$$\times\, {}_0\langle m|V(t_1)|k_1\rangle_0 {}_0\langle k_1|V(t_2)|k_2\rangle_0 \;...$$
$$\times\, {}_0\langle k_n|V(t_n)|m\rangle_0. \tag{22.44}$$

In order to obtain this expression, we have made use of Eq. 22.20 for the zeroth-order contribution.

The zeroth, first, and second-order are depicted in Fig. 22.2 as diagrams where the straight line with an arrow labeled by k, which begins at time instant t_1 and ends at time instant t_2, denotes the free propagator, that is,

$$g_0(E_k^{(0)}, t_2 - t_1) = e^{-\frac{i}{\hbar}E_k^{(0)}(t_2 - t_1)} \tag{22.45}$$

For an nth-order diagram there is a factor of $(i\hbar)^{-n}$ and n integration time variables, t_1, t_2, ..., t_n, that is, with nested integration time limits: (t_0, t), (t_0, t_1), ..., (t_0, t_{n-1}) respectively. There should be $n-1$ intermediate states k_1,k_2, ..., k_{n-1}, which we need to sum over. Lastly, at every introduced time instant t_i between intermediate states k_{i-1} and k_i, there is an interaction matrix element (illustrated as red dashed-line in Fig. 22.2).

$${}_0\langle k_{i-1}|\hat{V}(t_i)|k_i\rangle_0. \tag{22.46}$$

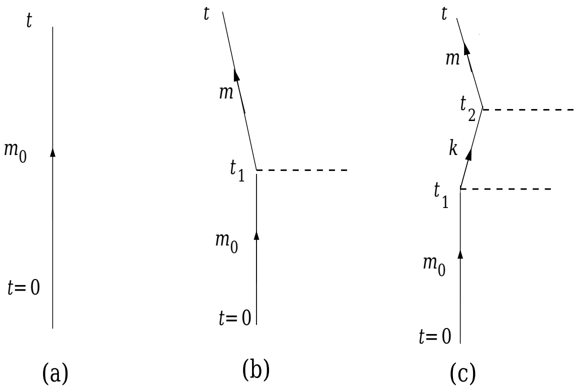

Fig. 22.2

22.1.4 Calculation of second-order correction

The second-order correction to the coefficient $C_{m_0m}(t)$ is given by

$$C^{(2)}_{m_0m}(t) = \frac{1}{(i\hbar)^2}\sum_k \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 e^{i\omega_{mk}t_1} e^{i\omega_{km_0}t_2} \times {}_0\langle m|\hat{V}(t_1)|k\rangle_{0\,0}\langle k|\hat{V}(t_2)|m_0\rangle_0. \tag{22.47}$$

Again, we consider the case of a perturbation which was suddenly turned on at $t = 0$, that is, using the following expression

$$\hat{V}(t) = \Theta(t)\hat{V}_0, \tag{22.48}$$

we obtain

$$C^{(2)}_{m_0m}(t) = \frac{1}{(i\hbar)^2}\sum_k {}_0\langle m|\hat{V}_0|k\rangle_{0\,0}\langle k|\hat{V}_0|m_0\rangle_0 \times \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 e^{i\omega_{mk}t_1} e^{i\omega_{km_0}t_2}. \tag{22.49}$$

After carrying out both integrations successively, we find that

$$C^{(2)}_{m_0m}(t) = \frac{1}{\hbar^2}\sum_k {}_0\frac{\langle m|\hat{V}_0|k\rangle_{0\,0}\langle k|\hat{V}_0|m_0\rangle_0}{\omega_{km_0}} \times \left[\frac{e^{i\omega_{mm_0}t}-1}{\omega_{mm_0}} - \frac{e^{i\omega_{mk}t}-1}{\omega_{mk}}\right]. \tag{22.50}$$

22.2 Adiabatic processes

We consider a time-dependent Hamiltonian of the form

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t), \tag{22.51}$$

where the time dependence of the interaction comes from the time dependence of the coupling constants $f_i(t)$, that is, the interaction potential is written as

$$\hat{V} = f_1(t)\hat{V}_1 + f_2(t)\hat{V}_2 + ... + f_M(t)\hat{V}_M. \tag{22.52}$$

The functions $f_i(t)$ are slowly changing functions of time as illustrated in Fig. 22.3. Namely, all characteristic timescales T_1, T_2, ..., T_M are longer than the inverse of all of the frequencies $\omega_{km}(t) = (E_k(t) - E_m(t))/\hbar$ associated with any pair of energy levels of the instantaneous Hamiltonian $\hat{H}(t)$, that is,

$$|\omega_{km}(t)|T_i >> 1, \text{ for any } k, m, i. \tag{22.53}$$

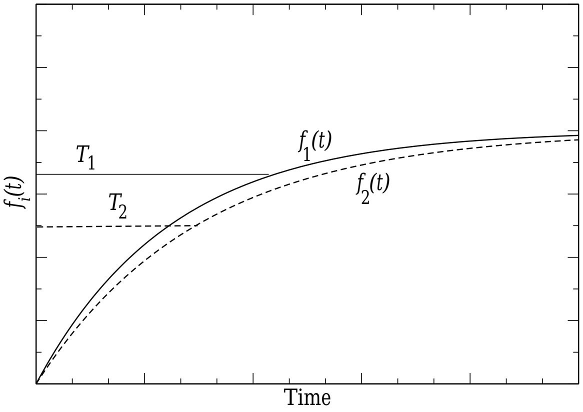

Fig. 22.3

Now we consider the following two problems which are, in general, two different problems:

1. We are interested in the instantaneous eigenstates of the above time-dependent Hamiltonian, that is,

$$\hat{H}(t)|n\rangle_t = E_n(t)|n\rangle_t. \tag{22.54}$$

2. We are interested in the solution of the time-dependent Schrödinger equation for the above time-dependent Hamiltonian:

$$\hat{H}(t)|\psi(t)\rangle = i\partial_t|\psi(t)\rangle, \tag{22.55}$$

under the initial condition that

$$|\psi(t=0)\rangle = |n\rangle_0, \tag{22.56}$$

and this is one of the $t = 0$ eigenstates of the Hamiltonian.

The adiabatic theorem states that:

i) If the energy levels of the unperturbed system are discrete and all characteristic timescales T_i are infinitely large (this will be defined better by the proof of the theorem provided next) and

ii) if during the evolution process there is no level crossing, that is, $E_k(t) \neq E_m(t)$ for all k and m and for all t,

then asymptotically

$$|\psi(t \to \infty)\rangle = |n\rangle_t, \tag{22.57}$$

within an overall phase factor to be discussed next.

22.2.1 Proof of the adiabatic theorem

In order to prove and understand the problem at a deeper level, let us expand the instantaneous solution $|\psi(t)\rangle$ to the time-dependent Schrödinger Eq. 22.55 in the basis set formed by the instantaneous eigenstates obtained by solving the eigenvalue problem of the instantaneous Hamiltonian, that is, Eq. 22.54:

$$|\psi(t)\rangle = \sum_{n'} C_{n'}(t) e^{-i\phi_{n'}(t)} |n'\rangle_t, \tag{22.58}$$

$$\phi_{n'}(t) \equiv \frac{1}{\hbar}\int_0^t dt' En'(t'), \tag{22.59}$$

$$C_{n'}(0) = \delta_{n',n}. \tag{22.60}$$

By substituting this in the time-dependent Schrödinger Eq. 22.55 we obtain:

$$\sum_{n'} \dot{C}_{n'}(t) e^{-i\phi_{n'}(t)} |n'\rangle_t - \sum_{n'} C_{n'}(t) e^{-i\phi_{n'}(t)} \partial_t |n'\rangle_t = 0. \tag{22.61}$$

Notice that the left-hand-side of the Schrödinger Eq. 22.55, that is, $\hat{H}(t)|\psi(t)\rangle$ is canceled by the term which arises from taking the time derivative of the phase $\phi_{n'}(t)$. So, both terms of the above equation come from the right-hand-side of Eq. 22.55.

Now, we project both sides of Eq. 22.61 onto state $|m\rangle_t$ and we find that:

$$\dot{C}_m(t) = -\sum_{n'} C_{n'}(t) e^{-i(\phi_{n'}(t)-\phi_m(t))} {}_t\langle m|\partial_t|n'\rangle_t. \tag{22.62}$$

Let us first consider the case where $m = n$, that is, the initial state:

$$\begin{aligned}\dot{C}_n(t) = {} & -C_n(t)\, {}_t\langle n|\partial_t|n\rangle_t - \sum_{n' \neq n} C_{n'}(t) e^{-i(\phi_{n'}(t)-\phi_n(t))} \\ & \times {}_t\langle n|\partial_t|n'\rangle_t.\end{aligned} \tag{22.63}$$

Before we proceed we need to find ${}_t\langle n|\partial_t|n'\rangle_t$ for $n' \neq n$. For this purpose we take the time derivative of both sides of Eq. 22.54 which yields that:

$$\dot{H}(t)|n'\rangle_t + H(t)\partial_t|n'\rangle_t = \dot{E}_{n'}(t)|n'\rangle_t + E_{n'}(t)\partial_t|n'\rangle_t. \tag{22.64}$$

In order to construct the matrix element ${}_t\langle n|\partial_t|n'\rangle_t$, which is what we are looking for, we project both sides of the above equation onto $|n\rangle_t$. Using the facts that ${}_t\langle n|n'\rangle_t = 0$ (for $n' \neq n$) and ${}_t\langle n|\hat{H}(t)\partial_t|n'\rangle_t = E_n(t)\, {}_t\langle n|\partial_t|n'\rangle_t$ (by having $\hat{H}(t)$ act on the bra), we obtain a linear algebraic equation for ${}_t\langle n|\partial_t|n'\rangle_t$, which yields the following solution:

$${}_t\langle n|\partial_t|n'\rangle_t = \frac{{}_t\langle n|\dot{H}(t)|n\rangle_t}{E_{n'}(t) - E_n(t)}. \tag{22.65}$$

Now for a process to qualify for the so-called adiabatic character, the above quantity should give negligible contribution to the expression (22.63). If we approximate the functions $f_i(t)$ as exponentials with a characteristic timescale T_i in the exponents, that is, if we write

$$\frac{df_i(t)}{dt} = \frac{1}{T_i} f_i(t), \tag{22.66}$$

then an estimate for the expression for ${}_t\langle n|\partial_t|n'\rangle_t$ above is given as

$${}_t\langle n|\partial_t|n'\rangle_t = \frac{1}{\hbar} \sum_{i=1}^{M} \frac{f_i(t)_t\langle n|\hat{V}_i(t)|n\rangle_t}{T_i \omega_{n'n}(t)}. \tag{22.67}$$

The numerators of the above expression have dimensions of energy and they are of order of unity in units of the energy scale governing the particular physical problem. The denominators, however, are the dimensionless quantities which we have assumed to be much larger than unity for an adiabatic process. Therefore, this term is negligible for adiabatic processes.

Thus, an adiabatic process is synonymous with neglecting the second term in Eq. 22.63, that is, we have

$$\dot{C}_n(t) = -C_n(t)_t\langle n|\partial_t|n\rangle_t. \tag{22.68}$$

We will now focus on finding the nature of ${}_t\langle n|\partial_t|n\rangle_t$. Let us consider the normalization condition of the instantaneous eigenstates, that is, ${}_t\langle n|n\rangle_t = 1$ and take time derivatives of both sides:

$$(\partial_{t\,t}\langle n|)|n\rangle_t + {}_t\langle n|\partial_t|n\rangle_t = 0, \tag{22.69}$$

This implies that ${}_t\langle n|n\rangle_t$ has no real part, that is, it can be written as a pure imaginary number:

$${}_t\langle n|\partial_t|n\rangle_t = i\alpha(t), \tag{22.70}$$

where $\alpha(t)$ is a real function of t. Therefore, we can now go back to the adiabatic Eq. 22.68, which can be integrated to yield

$$\dot{C}_n(t) = -i\alpha(t)C_n(t) \quad \Rightarrow \quad C_n(t) = C_n(0)e^{-i\int_0^t dt'\alpha(t')}, \tag{22.71}$$

which means that the coefficient $C_n(t)$ is the same as the one at $t = 0$ apart from a phase factor.

What about the contribution to $|\psi(t)\rangle$ of states other than $|n\rangle_t$? They should not be there; first of all, because of the fact that the state $|\psi(t)\rangle$ should remain normalized at all times and since $C_n(0) = 1$ we conclude from the above derivation that $|C_n(t)| = 1$, there is no room for contribution from any other state different than $|n\rangle_t$. The same conclusion is reached by examining the coefficient $C_m(t)$ using Eq. 22.62 for $m \neq n$. Within the adiabatic condition, we find that $\dot{C}_m(t) = 0$. And since $C_{m\neq n}(0) = 0$ we come to the conclusion that $C_{m\neq n}(t) = 0$ at all times.

Now, one piece of further information: If the process is adiabatic and at the same cyclic, that is, $|n\rangle_t = |n\rangle_0$ the accumulated phase factor in Eq. 22.71 is called the "Berry phase."

22.3 Problems

Problem 1

Consider the following Hamiltonian

$$\hat{H} = \hat{H}_0 + e^{\eta t}\hat{V}_0, \tag{22.72}$$

where $\eta > 0$ and $t \leq 0$ where $\hat{H}_0$ is the unperturbed Hamiltonian for which you know the eigenvalues and eigenstates:

$$\hat{H}_0|n\rangle_0 = E_n^{(0)}|n\rangle_0. \tag{22.73}$$

Show that the first-order coefficient of the wavefunction in doing time-dependent perturbation theory is given by

$$C_{k\to m}^{(1)}(t) = \frac{1}{i\hbar}\frac{e^{(\eta+i\omega_{mk})t}}{i\omega_{mk}+\eta}\,{}_0\langle m|\hat{V}_0|k\rangle_0, \tag{22.74}$$

$$\omega_{mk} \equiv \frac{E_m^{(0)} - E_k^{(0)}}{\hbar}. \tag{22.75}$$

Calculate the rate of change (derivative) of the transition probability and show that it is given by

$$\frac{dP_{k\to m}}{dt} = \frac{1}{\hbar^2}e^{2\eta t}\frac{2\eta}{\omega_{mk}^2+\eta^2}|{}_0\langle m|\hat{V}_0|k\rangle_0|^2. \tag{22.76}$$

Now consider the limit of very slow turning on of the interaction, that is, $\eta \to 0+$. Show that in this limit the rate of change $\Gamma_{k\to m}$ of the transition probability for decay to the state $|m\rangle_0$ given that the initial state is $|k\rangle_0$ is given by

$$\Gamma_{k\to m} \equiv \frac{dP_{k\to m}}{dt} = \frac{2\pi}{\hbar}|{}_0\langle m|\hat{V}_0|k\rangle_0|^2\delta(E_k^{(0)} - E_m^{(0)}). \tag{22.77}$$

Problem 2

A hydrogen atom in its ground state is placed in an time-dependent uniform external electric field given by

$$E(t) = \left\{ \begin{array}{cc} 0, & t \leq 0 \\ E_0 e^{-t/\tau}, & t > 0 \end{array} \right\}, \tag{22.78}$$

namely, a sudden electric field pulse is applied which lasts roughly for a timescale of order τ.

(a) Find the first-order probability for the electron to be in the $2s$ state of the atom after a long time.

(b) Find the first-order probability for the electron to be in each one of the $2p$ states of the atom after a long time.

Problem 3

Consider an electron in the ground state of a three-dimensional square-well potential of depth V_0 and radius a, that is,

$$V(r) = \left\{ \begin{array}{c} -V_0,\; r \leq a \\ 0, \quad r > a \end{array} \right\}. \tag{22.79}$$

A uniform electric field, $E = E_0 \cos(\omega t)$, is applied to the electron along the z-axis. Calculate the rate of ionization of the electron as a function of the frequency ω.

Problem 4

A harmonic oscillator in its ground state is exposed to a constant force which at $t = 0$ is suddenly removed. Calculate the transition probabilities to the first and second excited states of the oscillator.

Problem 5

Consider a charge q in a 1D harmonic oscillator potential with a Hamiltonian of the following form:

$$H_0 = -\frac{\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2, \tag{22.80}$$

in its ground state. It is exposed to the following perturbation

$$\hat{H}_1(x,t) = \hat{V}(x)\cos(\Omega t)e^{\eta t}, \tag{22.81}$$

$$\hat{V}(x) = -qE_0 x. \tag{22.82}$$

Namely, an external electric field $E_0 \cos(\Omega t)e^{\eta t}$ is applied at $t_0 = -\infty$ very slowly, that is, $\eta \to 0$. Notice that the frequency of the oscillating field Ω and the frequency of the harmonic oscillator ω are, in general, different.

(a) To what excited states of the harmonic oscillator is there a non-zero transition probability from the ground state?

(b) Calculate the transition probability rate to the first excited state of the oscillator.

23

Spin angular momentum

In this chapter we discuss the case of spin as an internal angular-momentum-like degree of freedom. We consider and analyze the case of spin-1/2 explicitly. We also discuss the coupling of spin to an externally applied magnetic field. Lastly we discuss rotations in the spin space.

23.1 Spin and orbital angular momentum

In chapter 15 we showed that simply starting from the commutation relations of the angular momentum operators, we can find the spectrum of the eigenvalues of the total angular momentum and its projection on a given fixed axis. Let us summarize our main findings and approach. Making use of just the following angular momentum commutation relations

$$\left[\hat{L}_i, \hat{L}_j\right] = i\hbar\epsilon_{ijk}\hat{L}_k, \tag{23.1}$$

the following definitions and facts follow strictly from the above. In the eigenvalues of the operators $\hat{L}^2$ and $\hat{L}_z$ and in the shared eigenstates labeled as $|l, m\rangle$, namely,

$$\hat{L}^2|l, m\rangle = \hbar^2 l(l+1)|l, m\rangle, \tag{23.2}$$

$$\hat{L}_z|l, m\rangle = \hbar m|l, m\rangle, \tag{23.3}$$

either, the labels
i) l and m are both integers, or
ii) l and m are both half-integers
and m takes only the $2l + 1$ values in the interval

$$-l \leq m \leq l. \tag{23.4}$$

The half-integer values (case ii) were excluded when we specialized to the specific form of the *orbital* angular momentum, that is, $\vec{L} = \vec{r} \times \vec{p}$, which allows us to find the eigenfunctions of the above operators. In this case, we required that the eigenfunctions of $\hat{L}_z$, that is, $e^{im\phi}$, be single-valued under rotations with respect to the z-axis by an angle $\phi = 2\pi$.

However, there is no reason to exclude the case of half-integer values when we want to represent some internal degree of freedom which is of angular-momentum-like character, the so-called *spin angular momentum.* These half-integer cases correspond

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to the even representations of the group formed by the generators of a generalized rotation operation. For this case of spin vector operators $\hat{S}_{x,y,z}$, we keep the same algebra as the orbital angular momentum, that is,

$$\left[\hat{S}_i, \hat{S}_j\right] = i\hbar\epsilon_{ijk}\hat{S}_k. \tag{23.5}$$

From just this algebra alone, it straightforwardly follows that

$$\hat{S}^2 \equiv \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2, \tag{23.6}$$

$$\left[\hat{S}^2, \hat{S}_z\right] = 0, \tag{23.7}$$

$$\hat{S}^2|S, m_s\rangle = \hbar^2 S(S+1)|S, m_s\rangle, \tag{23.8}$$

$$\hat{S}_z|S, m_s\rangle = \hbar m_s|S, m_s\rangle, \tag{23.9}$$

and with the aid of the following auxiliary operators and their properties

$$\hat{S}_\pm \equiv \hat{S}_x \pm i\hat{S}_y, \tag{23.10}$$

$$\begin{aligned}\hat{S}_-|S, m_s\rangle &= \hbar\sqrt{S(S+1) - m_s(m_s-1)} \\ &\quad \times |S, m_s - 1\rangle,\end{aligned} \tag{23.11}$$

$$\begin{aligned}\hat{S}_+|S, m_s\rangle &= \hbar\sqrt{S(S+1) - m_s(m_s+1)} \\ &\quad \times |l, m_s + 1\rangle,\end{aligned} \tag{23.12}$$

it follows (exactly as shown in chapter 15) that either

i) S and m_S are both integers, or

ii) S and m_S are both half-integers

and m takes only the $2S+1$ values in the interval

$$-S \leq m_S \leq S. \tag{23.13}$$

However, if these angular-momentum-like operators are meant to describe internal degrees of freedom of a particle, we have no reason to exclude either of these two possibilities. As a matter of fact, in chapter 31, when we study the Dirac equation, we will find that the orbital angular momentum is not conserved for a free electron. It is the total angular momentum, with the inclusion of spin, which is converged.

Since we do not have the restricting relationship of the angular momentum with the position and momentum operators, the other two families of commutation relation valid for orbital angular momentum, that is, Eq. 15.2, Eq. 15.4, and Eq. 15.5 are replaced by

$$\left[\hat{S}_i, \hat{r}_j\right] = 0, \tag{23.14}$$

$$\left[\hat{S}_i, \hat{p}_j\right] = 0, \tag{23.15}$$

$$\left[\hat{S}_i, \hat{L}_j\right] = 0, \tag{23.16}$$

which quantify the statement that the spin variables operate in an unrelated internal space.

23.2 Spin-1/2

In chapter 31 we will discuss that Dirac's equation describes the case of the relativistic electron which is a spin-1/2 particle. The spin-1/2, as an internal quantum number which corresponds to operators which behave like angular-momentum operators, emerges naturally from an attempt to find a *first-order* differential equation to describe relativistic particles quantum mechanically. Here, we will work out the example of spin-1/2 explicitly, just using the algebra above for spin angular momentum operators. In the case of $S = 1/2$, the internal space of spin is spanned by the following two states:

$$|+\rangle \equiv |S = \frac{1}{2}, m_S = \frac{1}{2}\rangle, \tag{23.17}$$

$$|-\rangle \equiv |S = \frac{1}{2}, m_S = -\frac{1}{2}\rangle, \tag{23.18}$$

where

$$\hat{S}^2|\pm\rangle = \hbar^2\frac{1}{2}(\frac{1}{2}+1)|\pm\rangle, \tag{23.19}$$

$$\hat{S}_z|\pm\rangle = \pm\frac{1}{2}\hbar|\pm\rangle. \tag{23.20}$$

In this basis the spin operators have the following 2 × 2 representation:

$$\hat{S}^2 \quad \Rightarrow \quad \begin{pmatrix} \langle +|\hat{S}^2|+\rangle & \langle +|\hat{S}^2|-\rangle \\ \langle -|\hat{S}^2|+\rangle & \langle -|\hat{S}^2|-\rangle \end{pmatrix} = \frac{3\hbar^2}{4}\hat{1}, \tag{23.21}$$

$$\hat{S}_z \quad \Rightarrow \quad \begin{pmatrix} \langle +|\hat{S}_z|+\rangle & \langle +|\hat{S}_z|-\rangle \\ \langle -|\hat{S}_z|+\rangle & \langle -|\hat{S}_z|-\rangle \end{pmatrix} = \frac{\hbar}{2}\hat{\sigma}_z, \tag{23.22}$$

$$\begin{aligned}\hat{S}_x \quad &\Rightarrow \quad \begin{pmatrix} \langle +|\frac{\hat{S}_+ + \hat{S}_-}{2}|+\rangle & \langle +|\frac{\hat{S}_+ + \hat{S}_-}{2}|-\rangle \\ \langle -|\frac{\hat{S}_+ + \hat{S}_-}{2}|+\rangle & \langle -|\frac{\hat{S}_+ + \hat{S}_-}{2}|-\rangle \end{pmatrix} \\ &= \frac{\hbar}{2}\hat{\sigma}_x,\end{aligned} \tag{23.23}$$

$$\begin{aligned}\hat{S}_y \quad &\Rightarrow \quad \begin{pmatrix} \langle +|\frac{\hat{S}_+ - \hat{S}_-}{2i}|+\rangle & \langle +|\frac{\hat{S}_+ - \hat{S}_-}{2i}|-\rangle \\ \langle -|\frac{\hat{S}_+ - \hat{S}_-}{2i}|+\rangle & \langle -|\frac{\hat{S}_+ - \hat{S}_-}{2i}|-\rangle \end{pmatrix} \\ &= \frac{\hbar}{2}\hat{\sigma}_y,\end{aligned} \tag{23.24}$$

where $\hat{1}$ is the 2 × 2 unit matrix and the matrices $\hat{\sigma}_{x,y,z}$ are the Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \tag{23.25}$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \tag{23.26}$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{23.27}$$

with the following properties:

$$\sigma_i \sigma_j + \sigma_j \sigma_i = 0, \qquad i \neq j, \tag{23.28}$$

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1. \tag{23.29}$$

23.3 Coupling of spin to a uniform magnetic field

First, if we ignore spin, a particle of charge q couples to an external uniform magnetic field $\vec{B}$ which is generated by a vector potential $\vec{A}$ which can be written as

$$\vec{A} = \frac{1}{2}\vec{B} \times \vec{r}, \tag{23.30}$$

by the familiar minimal substitution, $\vec{p} \to \vec{p} - q/c\vec{A}$, that is,

$$\hat{H} = \frac{p^2}{2m} \Rightarrow \frac{(\vec{p} - \frac{q}{c}\vec{A})^2}{2m}, \tag{23.31}$$

and the linear term in $\vec{A}$ can be transformed to take the following form:

$$H_L = -\vec{\mu}_L \cdot \vec{B}, \tag{23.32}$$

where the magnetic moment $\vec{\mu}_L$ due to the orbital angular momentum is given by

$$\vec{\mu}_L \equiv \frac{q}{2mc}\vec{L}, \tag{23.33}$$

where $\vec{L} = \vec{r} \times \vec{p}$ is the angular momentum.

For the case of spin angular momentum, its coupling to an external magnetic field $\vec{B}$ is also given by

$$H_S = -\vec{\mu}_S \cdot \vec{B}, \tag{23.34}$$

where the magnetic moment due to spin is given as

$$\vec{\mu}_S = g\frac{q}{2mc}\vec{S}, \tag{23.35}$$

where the prefactor g is called the Landé g-factor. This expression will be derived from the Dirac equation in the non-relativistic limit and we will find that for an electron $g = 2$ in this case. The actual value of the g-factor is approximately $g = 2.0023$ and the small correction is due to the leading vertex correction contribution in a perturbative treatment of Quantum Electrodynamics (QED). The first diagram in Fig. 23.1 denotes the scattering of an electron from an electromagnetic field as it comes from the Dirac equation. The second term denotes vertex correction to this scattering process due to a virtual photon. This contribution is of order of $\alpha = e^2/(\hbar c) \sim 1/137$ the coupling constant of QED which is small.

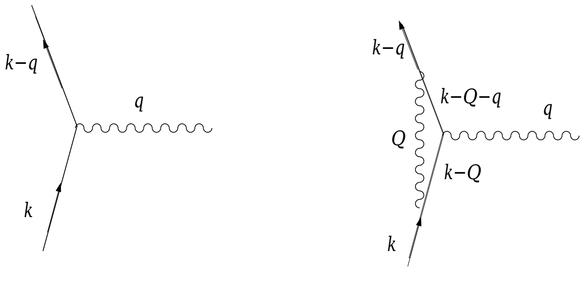

Fig. 23.1

23.4 Rotations in spin space

23.4.1 Rotations in ordinary space

We have discussed in chapter 15 that the generator of infinitesimal rotations in space by angle $\delta\phi$ around an axis along the unit vector $\hat{u}$, is the orbital angular momentum operator $\vec{L}$, in the sense that any function $f(\vec{r})$ changes due to the rotation by an amount δf given by

$$\delta f = \frac{i}{\hbar}\delta\vec{\phi}\cdot\vec{L}f, \tag{23.36}$$

$$\delta\vec{\phi} \equiv \delta\phi\hat{u}. \tag{23.37}$$

When the rotation is for a finite angle $\vec{\phi} = \phi\hat{u}$, by integrating this equation we found that f is transformed to

$$f' = \exp(\frac{i}{\hbar}\vec{\phi}\cdot\vec{L})f. \tag{23.38}$$

In the same way, the states are transformed under rotations as follows:

$$|f'\rangle = \exp(\frac{i}{\hbar}\vec{\phi}\cdot\vec{L})|f\rangle. \tag{23.39}$$

23.4.2 Rotations in spin space

If we want to carry out a rotation by an angle $\delta\phi$ around an axis defined by the unit vector $\hat{u}$ in spin space, then a state $|\chi\rangle$ in spin space, that is, for spin-S,

$$|\chi\rangle = \sum_{m_S=-S}^{S} C(m_S)|S, m_S\rangle, \tag{23.40}$$

the change of the state $\delta|\chi\rangle$ due to the infinitesimal rotation is given by

$$\delta|\chi\rangle = \frac{i}{\hbar}\delta\vec{\phi}\cdot\vec{S}|\chi\rangle. \tag{23.41}$$

Therefore, we may say that the spin operator is the generator of infinitesimal rotations in spin space.

Rotations by a finite angle $\vec{\phi} = \phi\hat{u}$ transform the state $|\chi\rangle$ to $|\chi'\rangle$ as follows:

$$|\chi'\rangle = \exp(\frac{i}{\hbar}\vec{\phi}\cdot\vec{S})|\chi\rangle. \tag{23.42}$$

23.4.3 Example

Let us consider the case of spin-1/2. Let us start from the state $|+\rangle$ which corresponds to a spin along the positive direction of the z-axis. We will carry out a rotation around the y-axis by a angle of $\pi/2$. This is represented by

$$|\chi\rangle = \hat{R}_y(\pi/2)|+\rangle, \tag{23.43}$$

$$\hat{R}_y(\pi/2) = \exp(i\frac{\pi}{4}\sigma_y). \tag{23.44}$$

Now, it is straightforward to show that the operator $\hat{R}_y(\pi/2)$ can be written as

$$\hat{R}_y(\pi/2) = \cos(\pi/4)\hat{1} + i\sin(\pi/4)\sigma_y. \tag{23.45}$$

This is so because of the fact that $\sigma_y^2 = \hat{1}$ and, thus, all even powers of σ_y are equal to $\hat{1}$ and all its odd powers are equal to σ_y. Using this identity we find that after the rotation the state $|+\rangle$ becomes

$$|\chi\rangle = \frac{1}{\sqrt{2}}(|+\rangle + |-\rangle). \tag{23.46}$$

Now we are in a position to show that this state is an eigenstate of the operator $\hat{S}_x$ with corresponding eigenvalue $+\hbar/2$:

$$\hat{S}_x|\chi\rangle = \frac{\hat{S}_+ + \hat{S}_-}{2}|\chi\rangle = \frac{\hbar}{2}|\chi\rangle. \tag{23.47}$$

Therefore, this represents a rotation of the original state by $\pi/2$ along the y-axis which makes the state an eigenstate of the rotated spin operator.

23.5 Problems

Problem 1

Rotations by a finite angle $\vec{\phi} = \phi\hat{u}$ define the unitary operator

$$\hat{U}(\vec{\phi}) = \exp(\frac{i}{\hbar}\vec{\phi}\cdot\vec{S}). \tag{23.48}$$

(a) Show that

$$\hat{U}(\vec{\phi}) = \hat{1}\cos(\phi/2) - i\hat{u}\cdot\vec{\sigma}\sin(\phi/2). \tag{23.49}$$

(b) Show that

$$\hat{U}^\dagger(\vec{\phi})\vec{\sigma}\hat{U}(\vec{\phi}) = \hat{u}(\hat{u}\cdot\vec{\sigma}) - \hat{u}\times(\hat{u}\times\vec{\sigma})\cos(\phi) + \hat{u}\times\vec{\sigma}\sin(\phi). \tag{23.50}$$

Problem 2

Consider two spin-1/2 quantum spins interacting according to the following Hamiltonian

$$\mathcal{H} = -K\vec{s}_1\cdot\vec{s}_2 - BS_z, \tag{23.51}$$

$$S_z = s_{1z} + s_{2z}. \tag{23.52}$$

(a) What are the “good” quantum numbers?
(b) Find the energy eigenvalues and eigenstates.

24

Adding angular momenta

In this chapter we discuss how to add angular momenta. This means that we investigate how to build eigenstates of the total angular momentum and its projection to a given axis, from eigenstates of the individual angular momenta and their projections to the same axis. We analyze and discuss how to calculate the Glebsh-Gordan coefficients.

24.1 Coupling between angular momenta

We have already discussed that if a charged particle has an angular momentum $\vec{J}$, it couples to an external magnetic field $\vec{B}$ through the Zeeman interaction,

$$\mathcal{H}_Z = -\vec{\mu} \cdot \vec{B}, \tag{24.1}$$

and, thus, it behaves as a dipole moment $\vec{\mu}$ given by the relationship

$$\vec{\mu} = g\frac{q}{2mc}\vec{J}, \tag{24.2}$$

where q is the charge of the particle and $g = 1$ if $\vec{J}$ is orbital angular momentum and $g \sim 2$ in the case where $\vec{J}$ is a spin angular momentum.

Classically, if a charged particle has an angular momentum $\vec{J}$, it generates a magnetic field $\vec{B}$ which is proportional to $\vec{J}$. This means that two particles with angular momenta $\vec{J}_1$ and $\vec{J}_2$ interact as follows

$$\mathcal{H}_{12} = K\vec{J}_1 \cdot \vec{J}_2, \tag{24.3}$$

where K is a coupling parameter which depends on the distance between the particles.

Similarly, two particles with spin angular momentum interact in the following way:

$$\mathcal{H}_{12} = J(r_{12})\vec{S}_1 \cdot \vec{S}_2, \tag{24.4}$$

where $\vec{S}_{1,2}$ are spin operators. In most condensed matter systems, this term due to the direct dipole–dipole interaction is orders of magnitude smaller than a term of similar form emerging as an effective spin–spin interaction. The origin of such a term in condensed matter is due to a combination of causes including:

- The Pauli exclusion principle.
- The fact that electronic kinetic energy is lowered by electrons hopping from one atom to another nearby.
- Possible strong Coulomb repulsion between electrons in configurations in which two electrons are on the same atom.
- Electron–electron correlations.

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24.2 Spin–orbit coupling

As we will see when we discuss the Dirac equation another form of coupling between angular momenta is the coupling between the spin $\vec{S}$ of an electron with its own orbital angular momentum $\vec{L}$, the so-called spin–orbit coupling:

$$\mathcal{H}_{s.o} = J(r)\vec{S}\cdot\vec{L}, \tag{24.5}$$

This term can be also argued semi-classically. There are two contributions. First, there is the term which is due to the fact that the electron in the atom in its co-moving frame sees a magnetic field due to central potential from the nucleus and the static electric field produced from the effective contribution of the other electrons. This magnetic field interacts with the spin of the electron. This contribution is obtained by considering a general Lorentz transformation from the frame of the nucleus to the frame of the moving electron (which moves with relative velocity $\vec{V}$).

Under a general Lorentz transformation (see J.D. Jackson *Classical Electrodynamics*, 1998) the electric and magnetic fields $\vec{E}$ and $\vec{B}$ in a frame moving with velocity $\vec{v}$, transform to $\vec{E}'$ and $\vec{B}'$ respectively:

$$\vec{E}' = \gamma(\vec{E} + \vec{\beta}\times\vec{B}) - \frac{\gamma^2}{\gamma+1}\vec{\beta}(\vec{\beta}\cdot\vec{E}), \tag{24.6}$$

$$\vec{B}' = \gamma(\vec{B} - \vec{\beta}\times\vec{E}) - \frac{\gamma^2}{\gamma+1}\vec{\beta}(\vec{\beta}\cdot\vec{B}), \tag{24.7}$$

where $\vec{\beta} \equiv \vec{v}/c$ and $\gamma = 1/\sqrt{1-\beta^2}$. In the rest frame of the electron, moving under the influence of a static electric field $\vec{E}$ produced by the nucleus and all the other electrons, "sees" a magnetic field $\vec{B}$ which to leading order in $\vec{v}/c$ is given by

$$\vec{B}' = -\frac{\vec{v}\times E}{c}. \tag{24.8}$$

Thus, the spin angular momentum should interact with this magnetic field according to:

$$\mathcal{H}_1 = -\frac{g_s}{2mc}\vec{S}\cdot\vec{B}. \tag{24.9}$$

Using the expression for the magnetic field (24.8) and the fact that the electric field $\vec{E}$ due to the electrostatic interaction energy $U(r)$ (due to the nucleus and the average mean interaction due to the other electrons) acts as a central potential, that is,

$$\vec{E} = -\frac{1}{e}\nabla U = +\frac{1}{|e|}\frac{\vec{r}}{r}\frac{dU}{dr}, \tag{24.10}$$

we find that

$$\mathcal{H}_1 = \frac{1}{m^2c^2}\frac{1}{r}\frac{dU}{dr}\vec{L}\cdot\vec{S}, \tag{24.11}$$

where we have used the fact that $\vec{L} = m\vec{r} \times \vec{v}$. This expression is incorrect by a factor of 2; namely, as we will find out in chapter 31, Dirac's equation yields

$$\mathcal{H}_{so} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dU}{dr}\vec{L}\cdot\vec{S}. \tag{24.12}$$

In 1927 Thomas showed that in order to obtain the above correct result, one should include the following term:

$$\mathcal{H}_T = \vec{\omega}_T \cdot \vec{S}, \tag{24.13}$$

$$\omega_T = \frac{\gamma^2}{\gamma^2+1}\frac{\vec{a}\times\vec{v}}{c^2}, \tag{24.14}$$

where $\vec{a}$ is the acceleration due to the total electric potential $U(r)$, that is,

$$\vec{a} = \frac{e\vec{E}}{m} = -\frac{\vec{r}}{r}\frac{dU}{dr}, \tag{24.15}$$

which in the limit $v/c << 1$ yields,

$$\mathcal{H}_T = -\frac{1}{2m^2c^2}\frac{1}{r}\frac{dU}{dr}\vec{L}\cdot\vec{S}, \tag{24.16}$$

therefore, by including both contributions $\mathcal{H}_1$ and $\mathcal{H}_T$ we find the same expression as Eq. 24.12.

24.3 The angular momentum coupling

We learned from the previous sections of this chapter that there is coupling between angular momentum operators and between spin and angular momentum. This leads to a natural need for adding angular momenta and adding angular momentum and spin angular momentum.

Consider the Hamiltonian

$$\hat{\mathcal{H}} = K\vec{j}_1\cdot\vec{j}_2 + \mathcal{H}_0(\hat{j}_1^2, \hat{j}_2^2), \tag{24.17}$$

where $\mathcal{H}_0$ is any function of j_1^2 and j_2^2. Here, $\vec{j}_{1,2}$ can be either orbital or spin angular momentum or a combination of these two.

First of all, let us consider the eigenstates of each of the pairs of operators $\hat{j}_1^2, \hat{j}_{1z}$ and $\hat{j}_2^2, \hat{j}_{2z}$, which we may write symbolically as $|j_1, m_1\rangle$ and $|j_2, m_2\rangle$ respectively, and

$$\hat{j}_{1,2}^2|j_{1,2}, m_{1,2}\rangle = \hbar^2 j_{1,2}(j_{1,2}+1)|j_{1,2}, m_{1,2}\rangle, \tag{24.18}$$

$$\hat{j}_{1z,2z}|j_{1,2}, m_{1,2}\rangle = \hbar m_{1,2}|j_{1,2}, m_{1,2}\rangle. \tag{24.19}$$

The above Hamiltonian involves two angular momentum operators and, therefore, the Hilbert space on which it operates is spanned by the $(2j_1+1)(2j_2+1)$ states which are obtained by the following direct product

$$|j_1, m_1, j_2, m_2\rangle = |j_1, m_1\rangle|j_2, m_2\rangle. \tag{24.20}$$

These states are not eigenstates of the above Hamiltonian because of the term which couples $\vec{j}_1$ and $\vec{j}_2$. Its eigenstates will be a linear combination of such states.

This Hamiltonian is also invariant under rotations in spin space which rotate both spins along a global axis. Such rotations do not change the dot product between $\vec{j}_1$ and $\vec{j}_2$. They also do not affect the magnitude of any vectors, such as $\hat{j}_1^2$ and j_2^2. The generator of such rotations is the total angular momentum $\vec{J} = \vec{j}_1 + \vec{j}_2$. This can also be verified by using the well-known commutation relations

$$\left[\vec{j}_1, \hat{j}_1^2\right] = 0, \qquad \left[\vec{j}_2, \hat{j}_2^2\right] = 0, \tag{24.21}$$

$$\left[\vec{j}_1, \vec{j}_2\right] = 0, \tag{24.22}$$

and by verifying the validity of the following commutation relations:

$$\left[\vec{j}_1 \cdot \vec{j}_2, \hat{j}_1^2\right] = 0, \qquad \left[\vec{j}_1 \cdot \vec{j}_2, \hat{j}_2^2\right] = 0, \tag{24.23}$$

$$\left[\hat{\mathcal{H}}, \hat{J}^2\right] = 0, \qquad \left[\hat{\mathcal{H}}, \hat{J}_z\right] = 0, \tag{24.24}$$

$$\left[\hat{\mathcal{H}}, \hat{j}_1^2\right] = 0, \qquad \left[\hat{\mathcal{H}}, \hat{j}_2^2\right] = 0, \tag{24.25}$$

$$\left[\hat{J}^2, \hat{J}_z\right] = 0, \qquad \left[\hat{J}^2, \hat{j}_1^2\right] = \left[\hat{J}^2, \hat{j}_2^2\right] = 0, \tag{24.26}$$

$$\left[\hat{J}_z, \hat{j}_1^2\right] = \left[\hat{J}_z, \hat{j}_2^2\right] = 0, \tag{24.27}$$

where $\hat{J}_z = j_{1z} + j_{2z}$. These commutation relations imply that there can be simultaneous eigenstates of J^2, J_z, j_1^2, j_2^2, and $\mathcal{H}$ which are denoted as $|J, M, j_1, j_2\rangle$ or for brevity as $|J, M\rangle$ because a given $2J + 1$ multiplet is constructed for a certain fixed pair of values of j_1, j_2. Thus, we have:

$$\hat{J}^2 |J, M\rangle = \hbar^2 J(J+1) |J, M\rangle, \tag{24.28}$$

$$\hat{J}_z |J, M\rangle = \hbar M |J, M\rangle, \tag{24.29}$$

$$\hat{j}_{1,2}^2 |J, M\rangle = \hbar^2 j_{1,2}(j_{1,2} + 1) |J, M\rangle. \tag{24.30}$$

Furthermore, we can now use the identity:

$$\vec{j}_1 \cdot \vec{j}_2 = \frac{1}{2}[\hat{J}^2 - j_1^2 - j_2^2], \tag{24.31}$$

to write the above Hamiltonian as

$$\mathcal{H} = \frac{K}{2}(\hat{J}^2 - j_1^2 - \hat{j}_1^2 - \hat{j}_2^2) + \mathcal{H}_0(\hat{j}_1^2, \hat{j}_2^2). \tag{24.32}$$

Thus, it is now clear that the states $|J, M\rangle$ are also eigenstates of the Hamiltonian with eigenvalues:

$$\hat{\mathcal{H}} |J, M\rangle = E(J, M) |J, M\rangle, \tag{24.33}$$

$$\begin{aligned} E(J, M) = {} & \frac{K}{2}\hbar^2 \Big(J(J+1) - j_1(j_1+1) - j_2(j_2+1) \Big) \\ & + \mathcal{H}_0(\hbar^2 j_1(j_1+1), \hbar^2 j_2(j_2+1)). \end{aligned} \tag{24.34}$$

There are two questions which immediately arise:

- Given the values of j_1 and j_2, how can we change the basis formed by the $(2j_1+1)(2j_2+1)$ states $|j_1, m_1, j_2, m_2\rangle$ to construct the states $|J, M\rangle$ as a linear combination of $|j_1, m_1, j_2, m_2\rangle$?
- Since we are talking about a mere change of basis we must have the same number of states of the form $|J, M\rangle$. We know that given the value of J there are $2J+1$ possible values of M, that is, $M = -J, -J+1, ..., J-1, J$. However, given the values of j_1 and j_2, what are the possible values of J?

We will answer the second question first. The following inequality, known as the triangular rule, applies to the magnitude J of the resultant vector $\vec{J}$ obtained by adding two vectors $\vec{j}_1$ and $\vec{j}_2$:

$$|j_1 - j_2| \leq J \leq j_1 + j_2, \tag{24.35}$$

where j_1 and j_2 are the magnitudes of $\vec{j}_1$ and $\vec{j}_2$. This is demonstrated in Fig. 24.1.

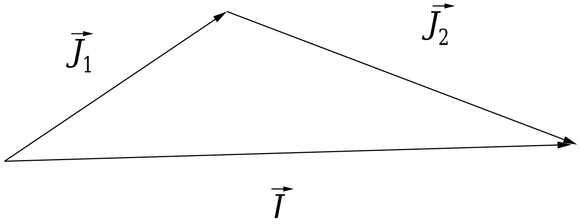

Fig. 24.1

This shows that the quantum numbers which characterize the total angular momentum eigenvalues behave in the same way that the magnitude of the result of adding two *classical* vectors $\vec{j}_1$ and $\vec{j}_2$ would behave. Because in this case

$$J^2 = |\vec{j}_1 + \vec{j}_2|^2 = j_1^2 + j_2^2 + 2j_1 j_2 \cos\theta, \tag{24.36}$$

and because $-1 \leq \cos\theta \leq 1$, the above inequality holds. This explains the origin of the name for the above inequality, it does not explain why J and j_1, j_2 which label the eigenvalues of the corresponding vector operators obey a similar inequality. This requires a proof; however, we refer the reader to any other quantum mechanics book for the proof.

The inequality (24.35) implies that the total number of states which correspond to the same fixed and given values of j_1 and j_2 are given by carrying out the following summation:

$$\sum_{J=|j_1-j_2|}^{J=j_1+j_2} (2J+1). \tag{24.37}$$

It is straightforward to carry out this summation over integer increments starting from $|j_1 - j_2|$ and ending at $j_1 + j_2$. The final result is $(2j_1+1)(2j_2+1)$. Therefore,

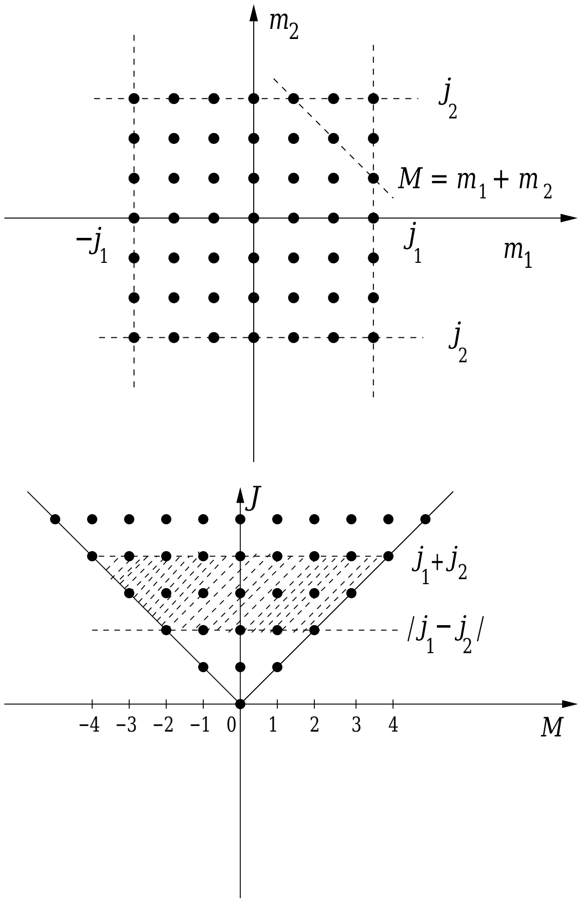

Fig. 24.2

by changing the basis of the two-body (two angular momenta) Hilbert space, from the direct product of single angular momentum eigenstates to eigenstates of the total angular momentum, the number of basis states is preserved. This is also illustrated in Fig. 24.2. At the top of Fig. 24.2 the space spanned by the basis $|j_1, m_1\rangle |j_2, m_2\rangle$ with $m_1 = -j_1, -j_1 + 1, ..., j_1$, $m_2 = -j_2, -j_2 + 1, ..., j_2$ is illustrated. Notice that only the states on the line $m_2 = M - m_1$ with $-45°$ slope correspond to a given fixed value of total $M = m_1 + m_2$. These states correspond to the various values of total J which have this given value of M as a possible projection. At the bottom of Fig. 24.2 all possible two-body states of the form $|J, M\rangle$, where the total angular momentum and its projection is specified, are illustrated. Notice that the entire allowed space for given values of j_1 and j_2 is the shaded trapezoid which includes a total of $(2j_1 + 1)(2j_2 + 1)$ states (including its edge states). The same number of states are also included in the parallelogram (including its edge states) of the m_1 versus m_2 space (top of Fig. 24.2). Therefore, the total number of states in each of the two bases (top and bottom of

Fig. 24.2) is the same.

24.3.1 Calculation of Clebsch–Gordan coefficients

As can be also seen from Fig. 24.2, the space of the two-body states for any given values of j_1 and j_2 can be spanned by either the set of states $|j_1, m_1\rangle|j_2, m_2\rangle$ or the set $|J, M\rangle$ and both sets contain a total of $(2j_1 + 1)(2j_2 + 1)$ states. The question which arises now is: Can we find the transformation of one of the two bases to the other? We can formally write:

$$|J, M\rangle = \sum_{m_1+m_2=M} C(J, M, j_1, j_2, m_1, m_2) \times |m_1\rangle|m_2\rangle, \tag{24.38}$$

$$|m_1\rangle \equiv |j_1, m_1\rangle \qquad |m_2\rangle \equiv |j_2, m_2\rangle, \tag{24.39}$$

where the so-called Clebsch–Gordan coefficient C is defined as follows:

$$C(J, M, j_1, j_2, m_1, m_2) \equiv \langle m_1, m_2|J, M\rangle, \tag{24.40}$$

$$|m_1, m_2\rangle \equiv |j_1, m_1\rangle|j_2, m_2\rangle. \tag{24.41}$$

We will present an algorithm on how to calculate the Clebsch–Gordan coefficients. In order to make the presentation of the algorithm clear, we will discuss a particular example, the case of two spin-1/2 angular momenta. The presentation of the steps will be given for the general case of any two pairs of angular momentum.

We take the case of $j_1 = j_2 = 1/2$. The non-interacting basis $|m_1, m_2\rangle$ consists of the following four $((2j_1 + 1)(2j_2 + 1) = 4)$ elements:

$$|\uparrow,\uparrow\rangle, \qquad |\uparrow,\downarrow\rangle, \qquad |\downarrow,\uparrow\rangle, \qquad |\downarrow,\downarrow\rangle, \tag{24.42}$$

where we have used the short-hand notation $|\uparrow\rangle = |1/2, 1/2\rangle$ and $|\downarrow\rangle = |1/2, -1/2\rangle$. The possible values of the total angular momentum J are (using the triangular inequality 24.35) $J = 0, 1$ and thus, the total number of states forming the $|J, M\rangle$ basis is four, that is, one for $J = 0$ (singlet) and three states (triplet) for $J = 1$.

Rule 1: Begin from the largest possible value of $J = J_{max} = j_1 + j_2$ and of $M = j_1 + j_2$. This state consists of just one $|j_1, m_1\rangle|j_2, m_2\rangle$ state, that is, the state $|j_1, m_1 = j_1\rangle|j_2 m_2 = j_2\rangle$. Then you can find all other $2J_{max} + 1$ states of this J_{max}-multiplet, by applying the lowering operator $J^- = \hat{J}_x - i\hat{J}_y = \hat{j}_1^- + \hat{j}_2^-$. For our example, we obtain:

$$|J = 1, M = 1\rangle = |\uparrow\rangle_1|\uparrow\rangle_2, \tag{24.43}$$

$$\hat{J}^-|J = 1, M = 1\rangle = (\hat{j}_1^-|\uparrow\rangle_1)|\uparrow\rangle_2 + |\uparrow\rangle_1(\hat{j}_2^-|\uparrow\rangle_2), \tag{24.44}$$

and using the properties (15.29, and 23.11) of the lowering operators on both sides of the above equations, that is, using the fact that

$$\hat{J}^-|1, 1\rangle = \hbar\sqrt{2}|J = 1, M = 0\rangle, \tag{24.45}$$

$$\hat{j}_{1,2}^-|\uparrow\rangle_{1,2} = \hbar|\downarrow\rangle_{1,2}, \tag{24.46}$$

we conclude that

$$|J=1,M=0\rangle = \frac{1}{\sqrt{2}}\Big(|\downarrow,\uparrow\rangle + |\uparrow,\downarrow\rangle\Big). \tag{24.47}$$

By acting one more time by $\hat{J}^-$ we obtain that (or simply by realizing in this particular case that)

$$|J=1,M=-1\rangle = |\downarrow,\downarrow\rangle. \tag{24.48}$$

Rule 2: For any other value of $J \neq J_{max}$, we consider the maximum value of $M = J$ for this given value of J. First, we determine this state $|J, M = J\rangle$ by writing it as a general linear combination of all possible $|m_1\rangle_1|m_2\rangle_2$ with $m_1 + m_2 = J$, and, then, the condition:

$$\hat{J}^+|J,J\rangle = 0, \tag{24.49}$$

and the normalization condition, lead to exactly the required number of equations to determine the Clebsch–Gordan coefficients. Application to our example for $J = 0$ and $M = 0$, is done as follows. We write

$$|J=0,M=0\rangle = C_1|\uparrow\rangle_1|\downarrow\rangle_2 + C_2|\downarrow\rangle_1|\uparrow\rangle_2. \tag{24.50}$$

The condition

$$\hat{J}^+|J=0,M=0\rangle = 0, \tag{24.51}$$

leads to

$$\begin{aligned} &C_1\Big((\hat{j}_1^+|\uparrow\rangle_1)|\downarrow\rangle_2 + |\uparrow\rangle_1(\hat{j}_2^+|\downarrow\rangle_2)\Big) + \\ &C_2\Big((\hat{j}_1^+|\downarrow\rangle_1)|\uparrow\rangle_2 + |\downarrow\rangle_1(\hat{j}_2^+|\uparrow\rangle_2)\Big) = 0 \end{aligned} \tag{24.52}$$

which yields the following result:

$$\hbar C_1|\uparrow\rangle_1|\uparrow\rangle_2 + \hbar C_2|\uparrow\rangle_1|\uparrow\rangle_2 = 0, \tag{24.53}$$

and to the conclusion that

$$C_2 = -C_1. \tag{24.54}$$

Using the normalization and by choosing the overall phase, we find that

$$C_1 = 1/\sqrt{2}, \qquad C_2 = -1/\sqrt{2}. \tag{24.55}$$

Thus,

$$|J=0,M=0\rangle = \frac{1}{\sqrt{2}}\Big(|\downarrow\rangle_1|\uparrow\rangle_2 - |\uparrow\rangle_1|\downarrow\rangle_2\Big). \tag{24.56}$$

Rule 3: Having determined the state $|J, M = J\rangle$, we can determined all $2J + 1$ states one by one of the j-multiplet by repetitive application of $\hat{J}^-$ on both sides of the equation which yields the state $|J, M = J\rangle$. For the case of our example with $J = 0$ there is only one state, which we have already determined.

24.4 Problems

Problem 1

Consider two quantum spins interacting according to the following Hamiltonian

$$H = -K\vec{S}_1 \cdot \vec{S}_2 \tag{24.57}$$

and both $\vec{S}_1 = (\hat{S}_{1x}, \hat{S}_{1y}, \hat{S}_{1z})$ and $\vec{S}_2 = (\hat{S}_{2x}, \hat{S}_{2y}, \hat{S}_{2z})$ are spin-1 operators, and

$$\hat{S}_1|S_1 = 1, m_1\rangle = \hbar m_1|S_1 = 1, m_1\rangle, \tag{24.58}$$

$$\hat{S}_1^2|S_1 = 1, m_1\rangle = \hbar S_1(S_1 + 1)|S_1 = 1, m_1\rangle, \tag{24.59}$$

$$\hat{S}_2|S_2 = 1, m_2\rangle = \hbar m_2|S_2 = 1, m_2\rangle, \tag{24.60}$$

$$\hat{S}_2^2|S_2 = 1, m_2\rangle = \hbar S_2(S_2 + 1)|S_2 = 1, m_2\rangle, \tag{24.61}$$

that is, the states $|S_i, m_i\rangle$ describe the Hilbert space for each of the two spins $i = 1, 2$.

Find all eigenvalues of the above Hamiltonian and the corresponding eigenstates as a linear combination of the nine states $|1, m_1\rangle|1, m_2\rangle$.

Problem 2

Consider a spin-1/2 particle in a state of orbital angular momentum $L = 1$ (p-wave) and the spin–orbit coupling

$$H = -K\vec{S} \cdot \vec{L}, \tag{24.62}$$

where $\vec{S} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)$ is a spin-1/2 operator and $\vec{L} = (\hat{L}_x, \hat{L}_y, \hat{L}_z)$ is a spin-1 operator, namely,

$$\hat{S}^2|S = 1/2, m_S\rangle = \hbar^2 S(S + 1)|S = 1/2, m_S\rangle, \tag{24.63}$$

$$\hat{S}_z|S = 1/2, m_S\rangle = \hbar m_S|S = 1/2, m_S\rangle, \tag{24.64}$$

$$\hat{L}^2|L = 1, m_L\rangle = \hbar^2 L(L + 1)|L = 1, m_L\rangle, \tag{24.65}$$

$$\hat{L}_z|L = 1, m_L\rangle = \hbar m_L|L = 1, m_L\rangle, \tag{24.66}$$

where $m_s = -1/2, 1/2$ and $m_L = -1, 0, 1$. Now, because of the spin–orbit coupling neither the spin projection nor the orbital angular momentum projection are good quantum numbers. However, the eigenvalues of $\hat{J}_z$ and of $\hat{J}^2$ associated with the total angular momentum $\vec{J} = \vec{L} + \vec{S}$ are conserved (that is, they are "good" quantum numbers).

(a) Find the possible values of the eigenvalues of the total angular momentum J.

(b) What are the eigenvalues of the above Hamiltonian?

(c) For the two cases, $|J = 3/2, M = 1/2\rangle$, and $|J = 1/2, M = 1/2\rangle$, determine the (Clebsch–Gordan) coefficients $C(m_L, m_S)$ associated with the states of the form $|L, m_L\rangle|S, m_S\rangle$ in the linear combination

$$|J, M\rangle = \sum_{m_L, m_S} C(m_L, m_S)|L, m_L\rangle|S, m_S\rangle, \tag{24.67}$$

where $|J, M\rangle$ denotes the eigenstates of the total angular momentum $\hat{J}^2$ and its projection $\hat{J}_z$ along the z-axis.

25

Identical particles

In this chapter we discuss the case of a many-body system of identical particles. We consider the consequencies of the symmetry of the Hamiltonian under particle permutations. We investigate how to build many-body Boson and Fermion states. We then introduce the formalism of so-called second quantization, a useful tool in the case of identical particles. We also express the many-body Hamiltonian in terms of creation and annihilation operators.

25.1 Symmetry under particle permutations

When we deal with a system of identical particles in quantum mechanics, we need to worry about the fact that the Hamiltonian of the system is characterized by the following symmetry: The Hamiltonian is invariant under any particle label permutation. This means that there is an observable which is conserved and, in addition, it is wise to construct eigenstates of the Hamiltonian which respect the fact that the particles are indistinguishable. Namely, if we are dealing with two identical particles, we cannot distinguish the case where the particle labeled 1 is in a state $|\psi_1\rangle$ and the particle labeled 2 is in the state $|\psi_2\rangle$ from the case where particle 1 is the state $|\psi_2\rangle$ and particle 2 is in the state $|\psi_1\rangle$. As a result the true quantum mechanical state of the system of the two particles will be a superposition of the states $|\psi_1\rangle_1|\psi_2\rangle_2$ and $|\psi_2\rangle_1|\psi_1\rangle_2$ where in our notation $\psi_i\rangle_j$ means that the particle j is in the state $|\psi_i\rangle$. Let us assume that we have succeeded solving the N-particle Schrödinger equation

$$\mathcal{H}|\Psi_n(1,2,...,N)\rangle = E_n|\Psi_n(1,2,...,N)\rangle, \tag{25.1}$$

and Ψ_n is an eigenstate of the system corresponding to energy eigenvalue E_n and 1,2,...,N, denote the particle labels.

Let us also define the pair-permutation operator $\hat{P}_{ij}$ as

$$\hat{P}_{ij}\Psi(1,...,i,...,j,...,N) = \Psi(1,...,j,...,i,...,N), \tag{25.2}$$

where $\Psi(1,...,N)$ is an arbitrary function of variables which are labeled by particle labels. We can construct any permutation where several particles are involved in the permutation by using products of two-particle permutation operators P_{ij}. For example, the cyclic permutation $P_{123}(123) = (312)$ can be obtained from the product $P_{12}P_{13}$, namely $P_{13}P_{12}(123) = P_{13}(213) = (312)$. In fact there are $N!$ such permutations.

Given the fact that the state $|\Psi_n(1,2,...,N)\rangle$ is an eigenstate of $\mathcal{H}$ all $N!$ states obtained by applying all possible permutations on this state are also eigenstates with

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the same eigenvalue due to the fact that the Hamiltonian is symmetric under particle exchange and

$$[\hat{\mathcal{H}}, \hat{P}] = 0. \tag{25.3}$$

This means that energy eigenstates can be characterized by the eigenvalues of the permutation operators also. Let us consider the eigenvalues and eigenstates of the two-particle permutation operator $\hat{P}_{ij}$

$$\hat{P}_{ij}|\Psi^{(\lambda)}(1, ..., i, ..., j, ..., N)\rangle = \lambda|\Psi^{(\lambda)}(1, ..., i, ..., j, ..., N)\rangle. \tag{25.4}$$

This equation can be rewritten as

$$|\Psi^{(\lambda)}(1, ..., j, ..., i, ..., N)\rangle = \lambda|\Psi^{(\lambda)}(1, ..., i, ..., j, ..., N)\rangle, \tag{25.5}$$

and applying again the operator $\hat{P}_{ij}$ on both sides of the above equation we obtain:

$$|\Psi^{(\lambda)}(1, ..., i, ..., j, ..., N)\rangle = \lambda\hat{P}_{ij}|\Psi^{(\lambda)}(1, ..., i, ..., j, ..., N)\rangle, \tag{25.6}$$

and using Eq. (25.4) for the right-hand-side of the previous equation we obtain that

$$\lambda^2 = 1. \tag{25.7}$$

Thus, there are only two possible eigenvalues $\lambda = \pm 1$ and two corresponding eigenstates of a two-particle permutation operator. We can easily construct simultaneous eigenstates of any pair-permutation operator and the Hamiltonian operator. Consider the following linear combination of the eigenstates Ψ_E of the Hamiltonian operator:

$$|\Psi_n^{(\pm)}(1, 2, ..., N)\rangle = \frac{1}{\sqrt{N!}} \sum_P (\pm)^{[P]} \hat{P} \Psi_n(1, 2, ..., N), \tag{25.8}$$

where the sum is over all possible many-particle $N!$ possible permutations $\hat{P}$ and the exponent $[P]$ is the so-called order of the permutation, namely the number of pair permutation operators we need in order to construct the action of the operator $\hat{P}$ in terms of two-particle operators. As an example let us consider a two-particle problem. Then

$$|\Psi_n^{(\pm)}(1, 2)\rangle = \frac{1}{\sqrt{2}}\Big(|\Psi_n(1, 2)\rangle \pm |\Psi_n(2, 1)\rangle\Big). \tag{25.9}$$

It is straightforward to verify that $|\Psi_n^{(\pm)}\rangle$ (given by Eq. 25.8 or by Eq. 25.9) are eigenstates of any pair permutation operator with eigenvalues ±1. The +1 (−1) eigenvalue corresponds to symmetric (antisymmetric) eigenstates under pair exchange.

As already discussed, there is no way of identifying identical particles in quantum mechanics unless we interact with the system in such a way that we effectively "attach identification labels" to the particles. For that to happen, the way of interacting with the system must be such that the Hamiltonian treats differently the different particles. If this is not the case, the only meaningful question we can raise is whether the system of these identical particles is in a symmetric or an antisymmetric state. Such systems of identical particles can be in a simultaneous eigenstate of the pair permutation operator and the Hamiltonian operator. It cannot be in a simultaneous eigenstate of the Hamiltonian operator and the particle index identifying operator.

Therefore, there can be only two families of particles. The so-called Bosons which are those that correspond to the symmetric eigenstates of the permutation operator, and the so-called Fermions, which are those corresponding to the antisymmetric eigenstates. It is an experimental fact that there is an intimate connection between the spin and the fact that the particles may be Fermions or Bosons; particles with integer (half-integer) spin are Bosons (Fermions), namely the wavefunction for two or more is symmetric (or antisymmetric) under pair exchange operations.

In the case of non-interacting identical particles an eigenstate of the many-body Hamiltonian

$$\hat{\mathcal{H}} = \sum_{i=1}^{N} \hat{h}(\hat{\vec{p}}_i, \vec{\gamma}_i), \tag{25.10}$$

where $\hat{h}$ are single particle Hamiltonians referring to the ith particle and for all i's they have identical forms. The eigenstates of this Hamiltonian are

$$\Psi_n(\vec{\gamma}_1, \vec{\gamma}_2, ..., \vec{\gamma}_N) = \prod_{i=1}^{N} u_i(\vec{\gamma}_i), \tag{25.11}$$

where $u_i(\vec{\gamma}_i)$ are normalized single-particle wavefunctions characterized by energy eigenvalue e_i namely

$$\hat{h}(\hat{\vec{p}}, \vec{\gamma})u_i(\vec{\gamma}) = e_i u_i(\vec{\gamma}), \tag{25.12}$$

and

$$E = \sum_{i=1}^{N} e_i. \tag{25.13}$$

A properly symmetrized (antisymmetrized) wavefunction can be obtained as

$$\Psi_E^{(\pm)}(\vec{\gamma}_1, \vec{\gamma}_2, ..., \vec{\gamma}_N) = \frac{1}{\sqrt{N!}} \sum_P (\pm)^{[P]} \hat{P} u_1(\vec{\gamma}_1) u_2(\vec{\gamma}_2) ... u_N(\vec{\gamma}_N), \tag{25.14}$$

where the permutation operator permutes particles or states. The Fermion state in this case corresponds to a determinant of $d_{ij} = u_i(\vec{\gamma}_j)$.

25.2 Second quantization

Here, we will present the formalism of second quantization. There is no additional quantization, the quantization procedure is the only one. The name "second quantization" originates in the history of the problem and the name itself gives no information on what it is, and might even be confusing. A more appropriate name is "formulation of operators in terms of creation and annihilation operators." This is exactly what we plan on doing. The idea is simply the following. Operators in quantum mechanics act on states and change them: In this equation $\hat{O}|\psi\rangle = |\psi'\rangle$, the operator $\hat{O}$ acted on state $|\psi\rangle$ and changed it to $|\psi'\rangle$. Any change can be viewed as a destruction and a creation at the same time. Namely, the operator $\hat{O}$ contains a destructive part and a creative part, the destructive part "annihilates" $|\psi\rangle$ and the creative part "creates" $|\psi'\rangle$.

Consider that the particle number is not definite. The reason for that is that we plan to facilitate the formulation of the above mentioned creation and annihilation processes, in which a particle may be "annihilated" from a given state and "created" on a different state.

25.3 Hilbert space for identical particles

Let us start by considering the Hilbert space $\mathcal{H}$ which has no definite number of particles symbolically:

$$\mathcal{H} = \mathcal{H}_0 \oplus \mathcal{H}_1 \oplus \mathcal{H}_2 \oplus ... \mathcal{H}_N \oplus ... \tag{25.15}$$

Namely, it is thought of as the direct sum of the Hilbert subspaces $\mathcal{H}_n$ with a well-defined number of particles n.

Now a complete basis of the $\mathcal{H}_N$ for distinguishable particles can be constructed out of the basis elements of $\mathcal{H}_1$ as follows:

$$|\gamma_1, \gamma_2, ..., \gamma_N\rangle = |\gamma_1\rangle_1 \otimes |\gamma_2\rangle_2 \otimes ... |\gamma_N\rangle_N, \tag{25.16}$$

where $|\gamma\rangle_i$ for fixed i (here γ labels the different basis states) is a complete basis of $\mathcal{H}_1$ and i is the particular particle identity index. This is the same as saying that

$$\mathcal{H}_N = \mathcal{H}_1 \otimes^N, \tag{25.17}$$

where the direct product of $\mathcal{H}_1$ with itself is taken N times.

For indistinguishable particles the situation is different. In such cases one needs to project out only the symmetric or antisymmetric part of the Hilbert space as discussed in the previous section. In the case of Bosons or Fermions, a basis in the $\mathcal{H}_N$ is constructed as follows:

$$|\gamma_1, \gamma_2, ..., \gamma_N)_\pm = \hat{P}_\pm\big(|\gamma_1\rangle_1 |\gamma_2\rangle_2 ... |\gamma_N\rangle_N\big), \tag{25.18}$$

where $\hat{P}_\pm$ is a symmetrization (+) or antisymmetrization (-) operator defined as

$$\hat{P}_\pm\big(|\gamma_1\rangle_1 |\gamma_2 ... |\gamma_N\rangle_N\big) = \frac{1}{\sqrt{N!}} \sum_P (\pm 1)^{[P]} |\gamma_1\rangle_{P1} |\gamma_2\rangle_{P2} ... |\gamma_N\rangle_{PN}. \tag{25.19}$$

and the notation regarding the summation is the same as that used in the previous section. In particular Pi is the mapping of the label of particle i after the permutation P. Here, we have chosen to permute the particle indices; however, the same can be done by choosing to permute the indices of the single-particle states. Notice that in the case of Fermions the above antisymmetrized state is an $N \times N$ determinant, where the column index is the particle index and the row index is the state index. This determinant which represents N non-interacting fermions is called the *Slater determinant*. The larger Hilbert space $\mathcal{H}$ can be projected to two (dimensionally smaller) spaces each one separately transforming according to the representations of the pair permutations. Symbolically,

$$\mathcal{H}^{\pm} = \hat{P}_{\pm}\mathcal{H}. \tag{25.20}$$

Next we shall examine the normalization of the states. Let us consider the overlap of two states. It is immediately clear that the states are orthogonal if they are states corresponding to different particle numbers. Thus, we consider states having the same particle number

$$\begin{aligned}(\gamma_1, \gamma_2, ...\gamma_N|\gamma_1', \gamma_2', ..., \gamma_N')_{\pm} &= \frac{1}{N!}\sum_{P,P'}(\pm 1)^{([P]+[P'])} \\ &\langle \gamma_{P1}|\gamma_{P'1}'\rangle_1\langle \gamma_{P2}|\gamma_{P'2}'\rangle_2 ... \langle \gamma_{PN}|\gamma_{P'N}'\rangle \\ &= \frac{1}{N!}\sum_P\sum_Q(\pm 1)^{[Q]}\langle \gamma_{P1}|\gamma_{QP1}'\rangle_1\langle \gamma_{P2}|\gamma_{QP2}'\rangle_2 \\ &... \ \langle \gamma_{PN}|\gamma_{QP}'\rangle. \end{aligned} \tag{25.21}$$

Here, for convenience we have permuted the state indices. The second part of the equation is obtained by realizing that we can write $P' = QP$ where Q another permutation and change the summation variables from P and P' to P and Q. The overall sign is determined by the sign of the relative permutation Q. Then the sum over Q is independent of P which can be regarded as the reference permutation. Thus, one find that

$$\begin{aligned}(\gamma_1, \gamma_2, ...\gamma_N|\gamma_1', \gamma_2', ..., \gamma_N')_{\pm} = \sum_Q(\pm 1)^{[Q]}\langle \gamma_1|\gamma_{Q1}'\rangle_1\langle \gamma_2|\gamma_{Q2}'\rangle_2 \\ ... \ \langle \gamma_N|\gamma_{QN}'\rangle. \end{aligned} \tag{25.22}$$

Now, it is clear that, unless the set of states $\{\gamma_1, \gamma_2, ...\gamma_N\}$ is the same as the set $\{\gamma_1', \gamma_2', ...\gamma_N'\}$ the overlap is zero. Therefore they can be different by only a permutation P_0 in which case the overlap is the same as the one with itself multiplied by the factor $(\pm 1)^{[P_0]}$ which is required to create the same permutation. Therefore, let us consider

$$\begin{aligned}(\gamma_1, \gamma_2, ...\gamma_N \ | \ \gamma_1, \gamma_2, ..., \gamma_N)_{\pm} = \sum_Q(\pm 1)^{[Q]}\langle \gamma_1|\gamma_{Q1}\rangle_1\langle \gamma_2|\gamma_{Q2}\rangle_2 \\ ... \ \langle \gamma_N|\gamma_{QN}\rangle. \end{aligned} \tag{25.23}$$

Let us say that we have ordered the single-particle basis states according to our choice so that they are in one to one correspondence with the natural numbers $1, 2, 3, ..., k, ...$. Then, let the set n_i, $i = 1, 2, ..., k, ..., \infty$ give the number of particles occupying each one of these single-particle states using the same state ordering. The numbers n_i are called occupation numbers. Therefore given a state characterized by the set of single particle states $\gamma_1, \gamma_2, ..., \gamma_N$, there is a corresponding set of occupation numbers n_i with at most N non-zero elements and $\sum_{i=1}^{\infty} n_i = N$. It is clear that for Fermions each n_i can only take two possible values $n_i = 0, 1$, otherwise the state collapses to zero because the determinant vanishes when two columns or rows are identical. Coming back to the above Eq. 25.23, in the case of Fermions all single-particle states in both N-particle states (bra and ket) are different, thus only the identity permutation gives non-zero contribution. Thus for fermions, the states defined by Eq. (25.18) are normalized. For the case of bosons, however, there can be $n_i > 1$, then there are $\prod_{i=1}^{\infty} n_i!$ permutations corresponding to the same state. Thus for both Fermions (for Fermions always $n_i! = 1$) and Bosons one can write:

$$(\gamma_1, \gamma_2, ... \gamma_N | \gamma_1, \gamma_2, ..., \gamma_N)_\pm = \prod_{i=1}^{\infty} n_i!. \tag{25.24}$$

Thus, an orthonormal set of states can be defined as

$$|\gamma_1, \gamma_2, ... \gamma_N\rangle_\pm = \frac{1}{\sqrt{\prod_{i=1}^{\infty} n_i!}} |\gamma_1, \gamma_2, ..., \gamma_N)_\pm. \tag{25.25}$$

With the convention that $0! = 1$, there is no ambiguity in the case of Fermion states. However, in the case of Bosons in order to guarantee normalization of the state when $n_i \neq 0, 1$, we need to divide by a normalization factor, which is the square root of the number of ways by which one is able to re-arrange n_1 states, n_2 states, and so on.

Once such a complete set of orthonormal states is constructed, then the completeness relationship in each of the spaces $\mathcal{H}^\pm$ is automatic

$$|0\rangle\langle 0| + \sum_{N=1}^{\infty} \sum_{\{\gamma_i\}} |\gamma_1, \gamma_2, ..., \gamma_N\rangle\langle\gamma_1, \gamma_2, ..., \gamma_N| = 1. \tag{25.26}$$

For simplicity in the notation, we have omitted the label ± of the state which stands for its symmetrization or antisymmetrization. Here $|0\rangle$ stands for the no-particle state. Here, we need to worry about the meaning of the summation. We should sum over all different states. Any permutation of the states $\gamma_1, \gamma_2, ..., \gamma_N$ does not produce any different state because of the symmetrization (or antisymmetrization). Thus, the summation is over all different sets $\{\gamma_i\}$. Two sets with the same elements but differing by a permutation are still the same sets.

25.4 Operators

An operator $\hat{O}$ which does not change the particle number can be expressed in this orthonormal basis as

$$\hat{O} = \sum_N \sum_{\{\gamma\},\{\gamma'\}} |\gamma_1, ..., \gamma_N\rangle\langle\gamma_1, ..., \gamma_N|\hat{O}|\gamma'_1, ..., \gamma'_N\rangle\langle\gamma'_1, ..., \gamma'_N|. \tag{25.27}$$

Here, again, we have omitted the antisymmetrization (and symmetrization) label for simplicity.

Let us first consider a one-body operator such as an external field acting on each one of the particles or the kinetic energy operator. In the standard notation:

$$\hat{O}^{(1)} = \sum_{i=1}^{N} \hat{o}_i^{(1)}. \tag{25.28}$$

In this case, it is straightforward for one to carry out the evaluation of the matrix elements which enter in (25.27) and show that

$$\hat{O}^{(1)} = \sum_N \sum_{m=1}^{N} \sum_{\{\gamma\},\gamma'_m} |\gamma_1, ..., \gamma_m, ..., \gamma_N\rangle \langle \gamma_m|\hat{o}^{(1)}|\gamma'_m\rangle \\ \times \langle \gamma_1, ..., \gamma'_m, ..., \gamma_N|. \tag{25.29}$$

Namely, the one-body operator can only change one state at a time and so the bra and the ket differ by only one single-particle state.

In the case of two-body operators such as the usual pair interaction

$$\hat{O}^{(2)} = \frac{1}{2} \sum_{i=1,j=1}^{N} \hat{o}^{(2)}_{ij}. \tag{25.30}$$

we find

$$\hat{O}^{(2)} = \frac{1}{2} \sum_N \sum_{m=1,n=1}^{N} \sum_{\{\gamma\},\gamma'_m,\gamma'_n} |\gamma_1, ..., \gamma_m, ..., \gamma_n, ..., \gamma_N\rangle \\ \langle \gamma_m, \gamma_n|\hat{o}^{(2)}|\gamma'_m, \gamma'_n\rangle \langle \gamma_1, ..., \gamma'_m, ..., \gamma'_n, ..., \gamma_N|. \tag{25.31}$$

Notice that the two-body operator can only change two single-particle states at a time and so the bra and the ket differ by only two single-particle states.

In the same way one can define other many-particle operators. We are only going to be concerned with problems involving at the most two-particle operators.

25.5 Creation and annihilation operators

We now wish to define the following operators

$$\hat{a}^\dagger_\gamma |\gamma_1, \gamma_2, ..., \gamma_N)_\pm \equiv |\gamma, \gamma_1, \gamma_2, ..., \gamma_N)_\pm. \tag{25.32}$$

For the case of Fermions, this operator adds a column and a row to the $N \times N$ determinant and creates an $(N+1) \times (N+1)$ Slater determinant. Notice that the definition is at the level of the unnormalized states (25.18). Its application on the orthonormal set of states (25.25) gives

$$\hat{a}^\dagger_\gamma |\gamma_1, \gamma_2, ..., \gamma_N\rangle_\pm = \sqrt{n_i + 1} |\gamma, \gamma_1, \gamma_2, ..., \gamma_N\rangle_\pm. \tag{25.33}$$

The operator itself increases the occupation number of that particular state by one. Thus, the state on the left-hand-side is an N particle state while the state produced on the right-hand-side is an $N+1$ state with the same symmetry (symmetric or antisymmetric). It is clear that for the case of Fermions the factor $\sqrt{n_i + 1}$ will never play any role because if $n_i = 0$ then this factor is 1, while if $n_i \geq 1$ we cannot produce a Fermion state with $n_i + 1 \geq 2$ fermions in the same single-particle state, thus the state in the right-hand-side will be zero.

Let us consider the adjoint operator of $\hat{a}_i^\dagger$, namely $\hat{a}_i \equiv (\hat{a}_i^\dagger)^\dagger$. We wish to find what is the result of the action of $\hat{a}_i$ on a state $|\gamma_1, \gamma_2, ..., \gamma_N\rangle_\pm$ as defined by Eq. (25.18). We obtain:

$$\hat{a}_i|\gamma_1, \gamma_2, ..., \gamma_N)_\pm = \langle 0|\hat{a}_i|\gamma_1, \gamma_2, ..., \gamma_N\rangle_\pm|0\rangle +$$

$$\sum_{n=1}^{\infty}\sum_{\{\gamma_i'\}}\langle\gamma_1', \gamma_2', ..., \gamma_n'|\hat{a}_\gamma|\gamma_1, \gamma_2, ..., \gamma_N)_\pm|\gamma_1', \gamma_2', ..., \gamma_n')_\pm$$

$$= \sum_{m=1}^{N}(\pm 1)^{m-1}\delta_{\gamma,\gamma_m}|\gamma_1, \gamma_2, ..., \check{\gamma}_m, \gamma_N)_\pm, \tag{25.34}$$

where the notation $\check{\gamma}_{P1}$ means that the state γ_{P1} is missing, thus, the state $|\check{\gamma}_{P1}, \gamma_{P2}, ..., \gamma_{PN}\rangle_\pm$ is an $N-1$ particle state. The last equation is obtained by noticing that

$$\begin{aligned}&\langle\gamma_1', \gamma_2', ..., \gamma_n'|\hat{a}_\gamma|\gamma_1, \gamma_2, ..., \gamma_N)_\pm\\ &= \langle\gamma_1, \gamma_2, ..., \gamma_N|\hat{a}_\gamma^\dagger|\gamma_1', \gamma_2', ..., \gamma_n')_\pm^*\\ &= \langle\gamma_1, \gamma_2, ..., \gamma_N|\gamma, \gamma_1', \gamma_2', ..., \gamma_n')_\pm^*.\end{aligned} \tag{25.35}$$

The last part is non-zero only when $n = N-1$ and the set of single-particle states $\{\gamma, \gamma_1', \gamma_2', ..., \gamma_{N-1}'\}$ is the same as the set $\{\gamma_1, \gamma_2, ..., \gamma_N\}$. Therefore, there are N different possibilities such that this can happen which are: $\gamma = \gamma_m$, and the set $\gamma_1', \gamma_2', ..., \gamma_{N-1}'$ is the same as the set $\gamma_1, ..., \check{\gamma_m}, ..., \gamma_N$.

Therefore we have been able to show the following:

$$\hat{a}_\gamma|\gamma_1, \gamma_2, ..., \gamma_N\rangle_\pm = \sqrt{n_\gamma}|\check{\gamma}, \gamma_1, \gamma_2, ..., \gamma_N\rangle_\pm, \hat{a}_i|\{n_i\}\rangle = \sqrt{n_i}|\{n_i\}\rangle. \tag{25.36}$$

One can easily show that the following commutation or anticommutation relations are valid respectively for the Boson or the Fermion creation and annihilation operators.

$$[a_\gamma, a_{\gamma'}]_\mp = 0, \tag{25.37}$$

$$\left[a_\gamma^\dagger, a_{\gamma'}^\dagger\right]_\mp = 0, \tag{25.38}$$

$$\left[a_\gamma, a_{\gamma'}^\dagger\right]_\mp = \delta_{\gamma,\gamma'}, \tag{25.39}$$

where the meaning of the above symbol is $[a, b]_\mp = ab \mp ba$, and the commutator $[a, b]_-$ is used for the case of Bosons and the anticommutator $[a, b]_+$ for Fermions. These relations can be easily shown by straightforward application of this commutator/anticommutator operator to an N-particle state, and by using Eq. 25.32 and Eq. 25.34.

Since for identical particles there is no meaning to asking which particle occupies which state, the many-particle state is specified by giving the occupation numbers of all states, namely in the state $|n_1, n_2, ..., n_k, ..., \rangle_\pm$ the integers n_i with $i = 1, 2, ...$ give how many particles occupy the ith state.

It can be easily shown that the one-body operator which has been expressed as (25.29) can be written in terms of creation and annihilation operators as:

$$\hat{O}^{(1)} = \sum_{\gamma,\gamma'} \langle\gamma|\hat{o}^{(1)}|\gamma'\rangle a^\dagger_\gamma a_{\gamma'}. \tag{25.40}$$

Also using the expression (25.31) for the two-body operator we can show that

$$\hat{O}^{(2)} = \frac{1}{2} \sum_{\gamma_1,\gamma_2,\gamma_1',\gamma_2'} \langle\gamma_1,\gamma_2|\hat{o}^{(2)}|\gamma_1',\gamma_2'\rangle a^\dagger_{\gamma_1} a^\dagger_{\gamma_2} a_{\gamma_2'} a_{\gamma_1'}. \tag{25.41}$$

As an example of this we consider the case of a uniform system of interacting non-relativistic particles such as the Hamiltonian

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{N} \nabla_i^2 + \frac{1}{2}\sum_{i\neq j} u(r_{ij}), \tag{25.42}$$

for a uniform fluid or electron gas. In the non-interacting plane wave basis this Hamiltonian takes the form

$$H = \sum_{\vec{p}\sigma} e(p) a^\dagger_{\vec{p}\sigma} a_{\vec{p}\sigma}$$

$$+\frac{1}{2} \sum_{\vec{p}_1,\vec{p}_2,\vec{p}_1',\vec{p}_2',\sigma_1,\sigma_2} \langle\vec{p}_1',\vec{p}_2'|u|\vec{p}_1,\vec{p}_2\rangle a^\dagger_{\vec{p}_1'\sigma_1} a^\dagger_{\vec{p}_2'\sigma_2} a_{\vec{p}_2\sigma_2} a_{\vec{p}_1\sigma_1}, \tag{25.43}$$

where the creation operator $a^\dagger_{\vec{p}\sigma}$ adds a particle in an eigenstate of the momentum and spin:

$$a^\dagger_{\vec{p}\sigma}|0\rangle = |\vec{p}\rangle|\sigma\rangle, \tag{25.44}$$

where

$$\langle\vec{r}|\vec{p}\rangle = \frac{1}{\sqrt{V}} e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}, \tag{25.45}$$

and $|\sigma\rangle$ is the spin state with spin projection along the z-axis σ. The matrix element can be easily evaluated

$$\langle\vec{p}_1',\vec{p}_2'|u|\vec{p}_1,\vec{p}_2\rangle = \frac{1}{V}\tilde{u}(\vec{q})\delta_{\vec{p}_1+\vec{p}_2,\vec{p}_1'+\vec{p}_2'}, \tag{25.46}$$

where the Kronecker δ expresses the momentum conservation and $\tilde{u}(\vec{q})$ is the Fourier transform of $u(r)$

$$\tilde{u}(\vec{q}) = \int d^3r u(r) e^{\frac{i}{\hbar}\vec{q}\cdot\vec{r}}, \tag{25.47}$$

and $\vec{q} = \vec{p}_1 - \vec{p}_1' = \vec{p}_2 - \vec{p}_2'$ is the momentum transfer. The same Hamiltonian can be expressed in terms of creation and annihilation operators $\hat{\psi}^\dagger(\vec{r},\sigma)$ which add particles in eigenstates of the position operator:

$$H = -\frac{\hbar^2}{2m}\sum_\sigma \int d^3x \hat{\psi}^\dagger(\vec{r},\sigma)\nabla^2\hat{\psi}(\vec{r},\sigma) + \frac{1}{2}\sum_{\sigma_1,\sigma_2}\int d^3x d^3y$$

$$\times\, u(|\vec{x}-\vec{y}|)\hat{\psi}^\dagger(\vec{x},\sigma_1)\hat{\psi}^\dagger(\vec{y},\sigma_2)\hat{\psi}(\vec{y},\sigma_2)\hat{\psi}(\vec{x},\sigma_1). \tag{25.48}$$

25.6 Problems

Problem 1

Show that the adjoint of the creation operator $a_\gamma^\dagger$ acts as an annihilation operator.

Problem 2

Show that the expressions given by Eq. 25.29 and Eq. 25.31 represent one-body and two-body operators.

Problem 3

Show that the expressions given by Eq. 25.40 and Eq. 25.41 represent one-body and two-body operators.

26

Elementary atomic physics

In this chapter, we apply quantum mechanics and its approximations to some elementary atomic physics questions. We will also apply the so-called Hartree–Fock approximation and discuss how one can go beyond it. We also discuss spin–orbit coupling and how to fully characterize the atomic states.

26.1 Helium atom

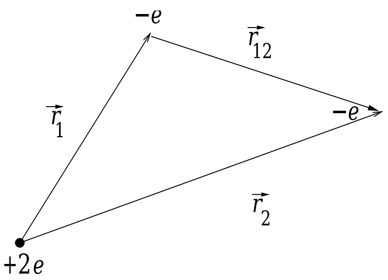

Fig. 26.1

We start with the simplest atom with more than one electron, that is, the helium atom, where the electron–electron interaction should be taken into account.

The Hamiltonian of the two electrons of the helium atom, assuming that the nucleus is massive as compared to the electrons and therefore its kinetic energy maybe neglected, is given as follows

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - 2\frac{e^2}{r_1} - 2\frac{e^2}{r_2} + \frac{e^2}{r_{12}}, \tag{26.1}$$

see also Fig. 26.1 where the coordinates of the two electrons are indicated as $\vec{r}_1$ and $\vec{r}_2$. If the Coulomb repulsion were not present, the spatial part of the ground-state wavefunction would be:

$$\psi(\vec{r}_1, \vec{r}_2) = \frac{Z^3}{\pi a_0^3} \exp(-Z\frac{r_1}{a_0}) \exp(-Z\frac{r_2}{a_0}), \tag{26.2}$$

Practical Quantum Mechanics. First Edition. Efstratios Manousakis.

with $Z = 2$. Namely, we would have two independent hydrogen-like electrons, one with spin-up and another with spin-down. The state becomes antisymmetric with respect to electron exchange by including the spin-part which is a spin-singlet state, which is antisymmetric (see example in chapter 24). Now, we can use the above as a trial wavefunction with Z treated as a variational parameter. What is the idea behind such a variational treatment? Each of the two electrons "sees" a reduced nuclear charge due to screening due to the presence of the other electron. Namely, we treat the two electrons as independent particles. The role of the other electron is simply to reduce the effective charge of the nucleus as "seen" from the other electron. This is a mean-field like approximation and, as we will see in this chapter, this can be generalized to the Hartree–Fock approximation.

It is straightforward to calculate the expectation value of the kinetic energy term for both electrons; the result is:

$$\langle\psi| - \frac{\hbar^2}{2m}\Big(\nabla_1^2 + \nabla_2^2\Big)|\psi\rangle = \frac{e^2 Z^2}{a_0}, \tag{26.3}$$

where we have used the fact that $a_0 = \hbar^2/(me^2)$. It is also straightforward to calculate the expectation value of the interaction of each of the electrons with the nucleus. The result is:

$$-Ze^2\langle\psi|\frac{1}{r_1} + \frac{1}{r_2}|\psi\rangle = -4\frac{e^2 Z^2}{a_0}. \tag{26.4}$$

Now, we also need to compute the expectation value of the Coulomb repulsion term between the two electrons. Namely,

$$e^2\langle\psi|\frac{1}{r_{12}}|\psi\rangle = e^2\frac{Z^3}{\pi {a_0}^3}\int d^3r_1 d^3r_2 e^{-2Z\frac{r_1}{a_0}} e^{-2Z\frac{r_2}{a_0}} \frac{1}{r_{12}}. \tag{26.5}$$

In the above two-body integral, when we carry, first, the integration over $\vec{r}_2$ we

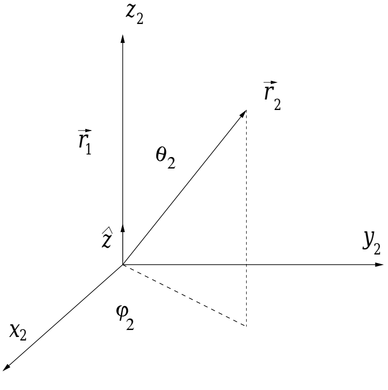

Fig. 26.2

regard the vector $\vec{r}_1$ as fixed, and, thus, we choose the direction of the z-axis for the $\vec{r}_2$

integration, to be along the direction of the vector $\vec{r_1}$ (see Fig. 26.2). With this choice, we can write

$$r_{12}^2 = r_1^2 + r_2^2 + 2r_1 r_2 \cos\theta_2, \tag{26.6}$$

and the integration over $\vec{r_2}$ can be expressed as follows:

$$e^2 \frac{Z^3}{\pi a_0^3} \int d^3 r_1 e^{-2Z\frac{r_1}{a_0}} \int dr_2 r_2^2 e^{-2Z\frac{r_2}{a_0}} \int_0^{2\pi} d\phi_2 \int_{-1}^{1} d\cos\theta_2 \frac{1}{r_{12}}. \tag{26.7}$$

The integration over ϕ_2 can be done to yield a 2π factor, because r_{12} does not depend on ϕ_2. The integration over $\cos\theta_2$ can be transformed to an integration over r_{12} using Eq. 26.6 to yield:

$$\langle \frac{e^2}{r_{12}} \rangle = \frac{2e^2 Z^3}{a_0^3} \int d^3 r_1 \frac{1}{r_1} e^{-2Z\frac{r_1}{a_0}} \int dr_2 r_2 e^{-2Z\frac{r_2}{a_0}} \int_{|r_1-r_2|}^{r_1+r_2} dr_{12}. \tag{26.8}$$

The integration over r_{12} yields $r_1 + r_2 - |r_1 - r_2|$ which equals to $2r_1$ when $r_2 > r_1$, while it is equal to $2r_2$ when $r_2 < r_1$. This requires us to split the integration over r_2 into two regions, that is,

$$\begin{aligned} \langle \frac{e^2}{r_{12}} \rangle = \frac{8\pi e^2 Z^3}{a_0^3} \Big(& \int_0^\infty dr_1 r_1^2 e^{-2Z\frac{r_1}{a_0}} \int_0^{r_1} dr_2 r_2 e^{-2Z\frac{r_2}{a_0}} \\ & + \int_0^\infty dr_1 r_1 e^{-2Z\frac{r_1}{a_0}} \int_{r_1}^\infty dr_2 r_2^2 e^{-2Z\frac{r_2}{a_0}} \Big). \end{aligned} \tag{26.9}$$

After carrying out straightforward integrations over r_2 first and, then, over r_1, we obtain:

$$\langle \frac{e^2}{r_{12}} \rangle = \frac{5e^2 Z}{8a_0}. \tag{26.10}$$

Putting together the result of every term contributing to the expectation value of $\hat{H}$ we obtain:

$$\frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = E(Z) = \frac{e^2}{a_0}\Big(Z^2 - \frac{27}{8}Z\Big). \tag{26.11}$$

The function $E(Z)$ has a minimum at $Z = Z_0 = 27/16$ and an optimum energy $E_0 = E(Z_0) = -(27/16)^2 e^2/a_0 \simeq -2.85 e^2/a_0$. The experimental value is $-2.90 e^2/a_0$. Therefore, we found that the effective charge seen by each electron is $Z_0 \sim 1.69$ instead of the base charge which is 2.

If instead of doing this variational calculation we did a perturbation theory calculation, treating the electron–electron interaction to first order, the result would be obtained by using the state given by Eq. 26.2 with $Z = 2$ as the zeroth-order wavefunction and calculate $\langle\psi|H|\psi\rangle$ for $Z = 2$. We would obtain:

$$\langle\psi|H|\psi\rangle = \frac{e^2}{a_0}\Big(Z^2 - \frac{27}{8}Z\Big)|_{Z=2} \sim -2.75\frac{e^2}{a_0}, \tag{26.12}$$

which is in worse agreement with the experiment.

26.2 Hartree and Hartree–Fock approximation

Let us begin from the full Hamiltonian which describes a N-electron atom, that is,

$$\mathcal{H} = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\frac{Ze^2}{r_i} + \frac{1}{2}\sum_{i,j,i\neq j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|}, \tag{26.13}$$

In a similar spirit with the mean-field/variational treatment of the helium atom, we take as a variational wavefunction the most general determinant

$$\Psi(1,2,...,N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_1(1) & \psi_1(2) & ... & \psi_1(N) \\ \psi_2(1) & \psi_2(2) & ... & \psi_2(N) \\ . & . & ... & . \\ . & . & ... & . \\ . & . & ... & . \\ \psi_N(1) & \psi_N(2) & ... & \psi_N(N) \end{vmatrix}. \tag{26.14}$$

Here the arguments of these functions, abbreviated for convenience as $1, 2, ..., N$, denote the positions as well as the spin projections of all the particles. The ith single particle state $\psi_i(j)$ for the jth particle corresponds to

$$\psi_i(j) \to \phi_i(\vec{r}_j)\chi_i(\sigma_j), \tag{26.15}$$

where ϕ_i is the spatial part of the state i and χ_i is the spin part of the state i. Here $\vec{r}_j$ and σ_j are the position and spin projection of the particle labeled as j:

$$\phi_i(\vec{r}) = \langle\vec{r}|\phi_i\rangle, \tag{26.16}$$

$$\chi_i(\sigma) = \langle\sigma|\chi_i\rangle, \tag{26.17}$$

where $|\sigma\rangle$ are spin-space basis vectors.

As we discussed in chapter 25, such a determinant is a sum of terms of the form

$$\pm\psi_{p1}(1)\psi_{p2}(2)...\psi_{pN}(N), \tag{26.18}$$

where $p1, p2, ..., pN$ stands for a particular permutation of the state indices $1, 2, 3..., N$. For example, in the particular case that the permutation is $1 \to 2$, $2 \to 1$, and all the other particles map to themselves, that is, $3 \to 3$, ..., $N \to N$, we have: $p1 = 2$, $p2 = 1$, $p3 = 3$, ..., $pN = N$. When such a permutation is odd there is a minus sign associated with this term, and when the permutation is even the sign is positive. Every permutation can be built as a product of pair-exchanges. A particular permutation is odd or even depending on whether the number of pair-exchanges is odd or even respectively.

First we can show that the expectation value of the above Hamiltonian with a general wavefunction of the above form, that is, $\langle\Psi|\mathcal{H}|\Psi\rangle$, is given by

$$\sum_P(-1)^{[P]}\langle\psi_1(1),\psi_2(2),...\psi_N(N)|\mathcal{H}|\psi_{p1}(1),\psi_{p2}(2),...,\psi_{pN}\rangle. \tag{26.19}$$

The "bra" state above is just a single product of single-particle states and corresponds to the identity permutation. The "ket" state above includes any product of states, that is, any state which is obtained from the simple product of single-particle states and applying any permutation P under which the indices which label the single-particle states are permuted as $1 \to p1$, $2 \to p2$, ..., $N \to pN$. The sign of each term is $(-1)^{[P]}$ where $[P]$ stands for the order of the permutation. This simply means that if the permutation is odd the sign is -, otherwise the sign is +. In order to prove this, one simply needs to realize that by combining all possible permutations in the state $|\Psi\rangle$ both in the "bra" and in the "ket" of the expectation value above we still get only $N!$ different terms, which can be also produced by the above sum in which only the "ket" is antisymmetrized.

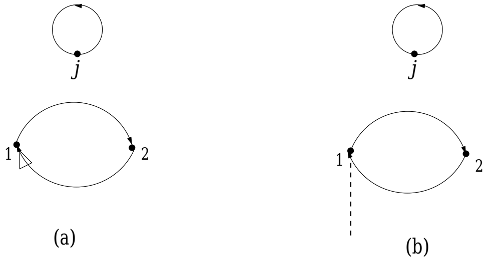

Fig. 26.3

Using the above simplification, one can subsequently show that the expectation value of the one-body terms, that is, the kinetic energy term and the electron–nucleus interaction, may be written as follows:

$$\langle\Psi|\mathcal{H}_1|\Psi\rangle = \sum_{i=1}^{N}\sum_{\sigma}\int d^3r\psi_i^*(\vec{r},\sigma)\Big(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}\Big)\psi_i(\vec{r},\sigma). \tag{26.20}$$

In order to show this we need to realize that, because of the orthogonality of the single-particle states, only the identity permutation contributes. Let us consider one of the single-particle terms in the Hamiltonian, say the term which corresponds to particle 1, such as $-\frac{\hbar^2}{2m}\nabla_1^2$, then, the permutation $1 \to 2$ and $2 \to 1$ and for all other state indices $pj \to j$. Then, in this case we are dealing with the N-body integral

$$-\frac{\hbar^2}{2m}\sum_{\{\sigma_i\}}\int d^3r_1d^3r_2...d^3r_N\psi_1^*(\vec{r}_1,\sigma_1)\psi_2^*(\vec{r}_2,\sigma_2)$$
$$\times\Big(\nabla_1^2\psi_2(\vec{r}_1,\sigma_1)\Big)\psi_1(\vec{r}_2,\sigma_2)\prod_{j=3}^{N}|\psi_j(\vec{r}_j,\sigma_j)|^2. \tag{26.21}$$

In this case it becomes clear that the tracing (that is, integration over spatial variables and summation over spin variables) over each of the $\vec{r}_j, \sigma_j$, $j = 3, ..., N$, gives 1, due to the fact that the single-particle states are normalized. However, the tracing over $\vec{r}_2, \sigma_2$ is zero because of the orthogonality of the states ψ_1 and ψ_2. In order to obtain a visualization of this term to help us with the computation, we use its illustration in Fig. 26.3. This is a diagrammatic representation of terms occurring in calculating the expectation value of the Hamiltonian. These diagrams should not be confused with the Feynman diagrams representing terms obtained in time-dependent perturbation theory. For example, Fig. 26.3(a), a directed line, starting from point 1 and ending in point 2, denotes that the particle labeled 1 is in state 1 in the "bra" and in the "ket," it is in the same state in which particle labeled as 2 is in the "bra." Similarly a directed line starting from 2 and going to 1, depicts that a particle labeled 2 is in state 2 in the "bra" and in the "ket" it is in the same state in which particle labeled as 1 is in the "bra." A simple loop like the circle of a directed line starting at j and ending at j denotes that a particle labeled j is in state j both in the "bra" and in the "ket." The triangle directed at point 1 represents the kinetic energy operator $-\hbar^2/(2m)\nabla_1^2$ acting on the single-particle state $\psi_2(\vec{r}_1\sigma_1)$ of the particle labeled 1. A tracing over all the spin and space coordinates of all particle labels, which are represented by solid points, is implied. In the example, of Eq. 26.21 and in Fig. 26.3(a), because the tracing over the spin and space coordinates of particles j with labels 3,4,...,N gives 1, the loops can be omitted. However, tracing over the coordinates of particle 2 yields zero because of the orthogonality of the two states meeting at point 2. The same conclusion cannot be drawn by tracing over 1, because the kinetic energy operator changes the state ψ_2 and the resulting function is no longer necessarily orthogonal to ψ_1. The same is true in the term of Fig 26.3(b) where the dashed line represents the external one-body Coulomb interaction of particle labeled 1 with the nucleus, that is, the term $-Ze^2/r_1$. The integral $-Ze^2 \int d^3r_1 \psi_1^*(\vec{r}_1, \sigma_1)\psi_2(\vec{r}_2, \sigma_2)(1/r_1)$ does not vanish, even though the states ψ_1 and ψ_2 are orthogonal.

As might have become clear from the previous discussion, the only terms involving the kinetic energy operator or the one-body potential are those depicted in Fig. 26.4 and the result is given by the Eq. 26.20.

When the two-body interaction term is "sandwiched" between the same Slater determinant, then the presence of the two-body interaction between, say, particle labeled 1 and particle labeled 2 allows the states which are occupied by these two particles in the "bra" and the "ket" to be the same or different. All other particles should occupy the same single-particle states in both "bra" and "ket," otherwise the term should vanish due to the orthogonality of single-particle states. This leads to the two diagrams depicted in Fig. 26.5. The top diagram is the so-called *Hartree* term, that is,

$$\frac{1}{2}\sum_{i,j,i\neq j}\int d^3r d^3r' |\phi_i(\vec{r})|^2 |\phi_j(\vec{r}')|^2 \frac{e^2}{|\vec{r}-\vec{r}'|}, \tag{26.22}$$

and the bottom diagram of Fig. 26.5 is the *exchange* or *Fock* term:

$$-\frac{1}{2}\sum_{i,j,i\neq j}\delta_{\sigma_i,\sigma_j}\int d^3r d^3r' \phi_i^*(\vec{r})\phi_j^*(\vec{r}')\phi_i(\vec{r}')\phi_j(\vec{r})\frac{e^2}{|\vec{r}-\vec{r}'|}. \tag{26.23}$$

The summations in the above expressions extend over all N values of the state indices i and j.

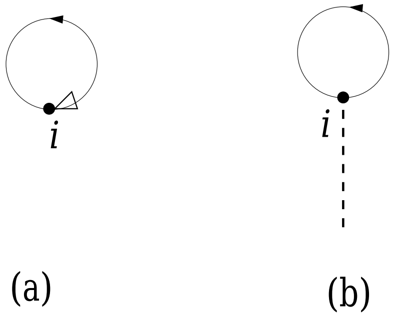

Fig. 26.4

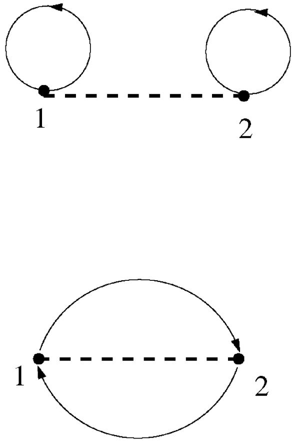

Fig. 26.5

The approximation in which the wavefunction is written as an antisymmetrized product of single-particle wavefunctions is called the *Hartree–Fock* approximation.

Now, we need to find a set of differential equations which have as solution the "best" set of normalized single-particle states ϕ_1,ϕ_2,..., ϕ_N. By "best" we mean the set of single-particle states which minimize the expectation value of the Hamiltonian (Eq. 26.13) under the constraint that these states are normalized. This means that we need to consider the functional

$$F(\{\phi_i(\vec{r})\}) = \langle\Psi|\mathcal{H}|\Psi\rangle - \sum_{i=1}^{N}\lambda_i\Big(\int d^3r|\phi_i(\vec{r})|^2 - 1\Big), \tag{26.24}$$

and to minimize it with respect to variations in $\phi_i^*(\vec{r})$.

We need to calculate functional derivatives with respect to $\phi_i^*(\vec{r})$. In doing so, the following identity is used

$$\frac{\delta\phi_k^*(\vec{x})}{\delta\phi_l^*(\vec{y})} = \delta_{k,l}\delta(\vec{x}-\vec{y}). \tag{26.25}$$

In this approach the functional variables $\phi_i(\vec{r}) = \phi_i^R(\vec{r}) + i\phi^I(\vec{r})$ (where $\psi_i^R(\vec{r})$ and $\psi_i^I(\vec{r})$ are the real and imaginary parts of $\phi_i(\vec{r})$) and $\phi_i^*(\vec{r}) = \phi_i^R(\vec{r}) - i\phi^I(\vec{r})$ are independent variables. This is so in the same sense where in the familiar differentiation with ordinary independent variables x and y, when one makes the transformation to new variables $w = x + iy$ and $w^* = x - iy$, w and w^* are independent variables.

By carrying out this functional differentiation we find the following N coupled differential equations:

$$\Big(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} + \sum_{j\neq i}\int d^3r'\frac{e^2}{|\vec{r}-\vec{r'}|}|\phi_j(\vec{r'})|^2\Big)\phi_i(\vec{r}) -$$

$$\sum_{j\neq i}\delta_{\sigma_j,\sigma_i}\int d^3r'\frac{e^2}{|\vec{r}-\vec{r'}|}\phi_i(\vec{r'})\phi_j^*(\vec{r'})\phi_j(\vec{r}) = \lambda_i\phi_i(\vec{r}). \tag{26.26}$$

The 3rd term above is the Hartree term, which can be also rewritten as

$$V_H(r) = e\int d^3r'\frac{\rho(\vec{r'})}{|\vec{r}-\vec{r'}|}, \tag{26.27}$$

$$\rho(\vec{r}) = e\sum_{j\neq i}|\phi_j(\vec{r})|^2, \tag{26.28}$$

where $\rho(\vec{r'})$ is the density of the electrons, and the sum is over all states j which are occupied by the other $N-1$ electrons. Notice that the Hartree term represents the average electrostatic potential energy produced by all other electrons. This term could have been written down thinking in a semiclassical way. Notice that this term is local *centrally symmetric* because it is an average potential over all other occupied single-particle states.

26.3 Hartree equations

If we ignore the Fock (exchange) term, the above equation takes a simpler form which is known as the Hartree equation:

$$\Big(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} + V_H(r)\Big)\phi_i(\vec{r}) = \lambda_i\phi_i(\vec{r}). \tag{26.29}$$

Notice that the above equation could be interpreted as the familiar single-particle Schrödinger equation for an electron in a local central potential which is composed of the interaction of this electron with the nucleus and the average electrostatic interaction with all other electrons. This equation should be solved self-consistently as follows. Imagine that we first set $\rho(r) = 0$ or, better, we use an initial guess for $\rho(r)$ and we solve the above equation to determine the single-particle states. We then use these single-particle states to calculate a different $\rho(r)$ by selecting N states from this set in order of increasing energy starting from the lowest single-particle level. Next, we use this $\rho(r)$ to determine a different $V_H(r)$ which, subsequently, is used in order to solve the new Hartree equation to determine an improved set of single-particle wavefunctions. We keep iterating this procedure until the results of the nth iteration and the previous iteration agree within a desired degree of approximation. Notice, however, that these equations are *non-linear* in the unknown functions $\phi_i(\vec{r})$, thus care should be taken.

Since the net potential seen by a single electron is centrally symmetric; as usual, that is, following the approach of chapter 16, we write the wavefunction $\phi_i(\vec{r})$ as follows

$$\phi_i(\vec{r}) = R_l^{(n)}(r) Y_{lm}(\theta, \phi), \tag{26.30}$$

where $R_l^{(n)}(r)$ obeys the usual differential equation for the radial part of the wavefunction:

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\Big(r^2 \frac{\partial R_l^{(n)}(r)}{\partial r}\Big) + V_{eff}(r) R_l^{(n)}(r) = E_{nl} R_l^{(n)}(r), \\ V_{eff}(r) = -\frac{Ze^2}{r} + V_H(r) + \frac{\hbar^2 l(l+1)}{2mr^2}, \end{aligned} \tag{26.31}$$

where the index n labels the various physically acceptable solutions to the above equation for a given value of l. While these solutions do not depend on m as in the case of the hydrogen atom, here, because the potential is not simply the Coulomb potential, they depend on l. Namely, for a given value of $l = 0, 1, 2, ...$ we need to solve the above equations to find the energy eigenvalues which are, then, enumerated in order of increasing energy by the label $n = 1, 2, ...$ Thus, the single electron orbitals depend on n and l but they do not depend on m. In general for a given value of n, the energy increases with increasing value of l, that is,

$$E_{n,0} < E_{n,1} < E_{n,2} .... \tag{26.32}$$

Given an initial electron density profile $\rho(r)$ we solve the above equations to find the eigenstates and eigenvalues. Then, using Eq. 26.28 we recalculate the new electron density by selecting the N lowest energy states including the states which have the same energy (that is, all values of m) including the spin part of the wavefunction. From that, using Eq. 26.27, we calculate the Hartree potential $V_H(r)$ to be used in Eq. 26.31 and then to solve again the Hartree equations to determine the new $R_l^{(n)}$. This is repeated until we reach self-consistency.

26.4 Hartree–Fock and non-locality

The Fock term in the Hartree–Fock equation is of the following form:

$$-\sum_{j\neq i}\delta_{\sigma_j,\sigma_i}\int d^3r'\frac{e^2}{|\vec{r}-\vec{r}'|}\phi_i(\vec{r}')\phi_j^*(\vec{r}')\phi_j(\vec{r}), \tag{26.33}$$

which can be written as follows:

$$\int d^3r' U_F(\vec{r},\vec{r}')\phi_i(\vec{r}'), \tag{26.34}$$

where

$$U_F(\vec{r},\vec{r}') = -e^2\sum_{j\neq i}\delta_{\sigma_j,\sigma_i}\int d^3r'\frac{\phi_j^*(\vec{r}')\phi_j(\vec{r})}{|\vec{r}-\vec{r}'|}. \tag{26.35}$$

Namely, it acts as a "non-local" potential on the wavefunction $\phi_i(\vec{r}')$ at all spatial points $\vec{r}'$, that is, it is a non-local kernel. Again, in order to compute it, when we try to solve the problem using an iterative scheme, we need all the states ϕ_i found in the previous iteration.

An example of the application of the Hartree–Fock approximation is the helium atom problem in its ortho excited state. The helium atom is in its ground state where the spins are anti-parallel, the Fock term is zero. There are the following two excited states: (a) the state with total spin $S = 0$ (the para-helium) and (b) the state with $S = 1$ (the ortho-helium). Again, in the case of the para-helium the two spins must be anti-parallel and, thus, the Fock term is not present. In the case of the $S = 1$, the Fock term is operative and this distinguishes the energy of these two states within this mean-field-like approximation. The result is,

$$E_{S=0}(\text{para}) = -2.146\frac{e^2}{a_0}, \tag{26.36}$$

$$E_{S=1}(\text{ortho}) = -2.175\frac{e^2}{a_0}. \tag{26.37}$$

Notice that while in the case of $S = 1$ one of the electrons should occupy an orbital with a much higher energy (at the single particle level the energy difference between $1s$ and $2s$ is $3/8e^2/a_0$), the actual energy difference between the ortho- and para-helium is much smaller due to the presence of the exchange term in the former case, which lowers the energy significantly.

26.5 Beyond mean-field theory

The Hartree–Fock approximation misses the correlations between electrons in the atomic state of a multi-electron atom. There are several approaches on how to correct for this problem; here, we will restrict ourselves to briefly discussing just two such methods in order to give the reader a feeling of what is really missing in the Hartree–Fock approximation.

The position correlations can be partially taken into account by using a variational wavefunction of the following form:

$$|\Psi_J\rangle = \prod_{i<j} f(r_{ij})|\Psi_{HF}\rangle, \tag{26.38}$$

where $|\Psi_{HF}\rangle$ is the Slater determinant obtained in the Hartree–Fock approximation. The product is over all $N(N-1)/2$ electron pairs. The factor $f(r)$ is schematically plotted in Fig. 26.6 along with the Coulomb repulsion between two electrons. This factor is called the Jastrow factor and takes into account pair correlations. Namely, there is no information in any Hartree–Fock wavefunction on how two electrons should avoid getting close to each other in order to avoid the Coulomb repulsion. This can be done by the Jastrow factor which goes to zero as the inter-particle distance goes to zero. One can specify a particular form of $f(r)$ which allows for the general behavior near the origin and as $f(r \to \infty) \to 1$ and determine the variational parameters which may be introduced in this variational wavefunction (that is, in $f(r)$) by calculating the ground-state energy and finding its minimum numerically. The integration over many particle can be handled by means of Monte Carlo integration.

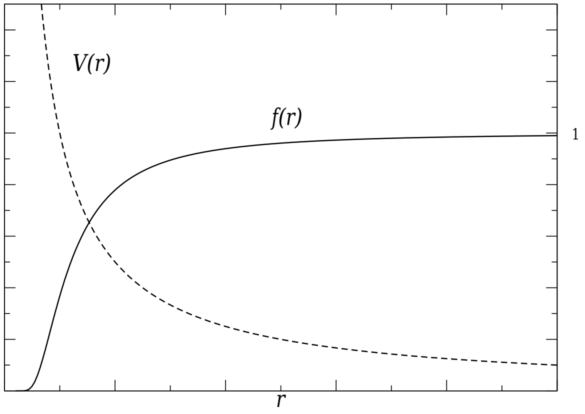

Fig. 26.6

Another way to go beyond the simple Hartree–Fock approximation is by means of the so-called Configuration-Interaction (CI) approximation. Within this approximation one mixes various Hartree-Fock configurations. Namely, after determining the Hartree–Fock "orbitals," that is, the single-particle states ϕ_i, which determine the ground state, by placing the N electrons to occupy the lowest N such orbitals, we can form Hartree-Fock configurations, that is, one-particle-one-hole ($1p$-$1h$), two-particle-two-hole ($2p$-$2h$), ..., or n-particle-n-hole (np-nh) excitations by promoting one, two, ..., or n electrons from the occupied to the unoccupied orbitals. These states span the multi-electron Hilbert space. Then, due to the presence of correlations, the true ground-state wavefunction is a linear combination of such multi-particle-multi-hole excitations. In the CI approximation, we can truncate the basis of such HF configurations and include only up to $2p$-$2h$ states; then, we write down the Hamiltonian matrix in this subspace and carry out a diagonalization to find the correlated ground-state wavefunction and energy.

26.6 Characterization of atomic states

The first element needed to characterize an atomic state is the electronic configuration, which, as is well-known, is given by the sequence of occupied orbitals with their electron occupation given as superscript. For example, Carbon's electronic configuration is $1s^2$ $2s^2$ $2p^2$.

However, the electronic configuration alone does not specify the state of an atom completely. Consider for example, C, where the last two electrons can be in any of the following possible states: $p_x^\uparrow p_x^\downarrow$, $p_x^\uparrow p_y^\downarrow$, ... The fact is that these states have a small (in units of Rd) energy difference due to:

1. electron–electron interaction.
2. spin–orbit interaction.

In smaller atoms the former is dominant, while the spin-orbit interaction becomes larger as the atomic number grows. Furthermore, as we discussed in Section 26.5, a single atomic configuration ignores the effects of electron correlations.

Let us ask the following question: What are the good quantum numbers?

1. If we neglect the spin–orbit coupling:
   The z component of the operator of the total spin, $\hat{S}_z = \sum_{i=1}^N \hat{s}_i^z$ and its magnitude squared $\hat{S}^2$ commute with the atomic Hamiltonian $\hat{H}$.
   The z component of the operator of the total orbital angular momentum, $\hat{L}_z = \sum_{i=1}^N \hat{l}_i^z$ and its magnitude squared $\hat{L}^2$ also commute with $\hat{H}$.
   The first follows directly from the fact that the total $\hat{S}_z$ is the generator of rotations in spin-space and $\hat{S}^2$ and $\hat{H}$ are scalar operators (see chapter 18). The second is a consequence of the fact that the total $\hat{L}_z$ is the generator of rotations and $\hat{L}^2$ and $\hat{H}$ are scalar operators.
2. If we include spin–orbit coupling:
   The z component of the operator of the total angular momentum, $\hat{J}_z = \hat{L}_z + \hat{S}_z$ commutes with $\hat{H}$.
   The magnitude squared of the total angular momentum $\hat{J}^2$, that of the total spin $\hat{S}^2$, and of the orbital angular momentum $\hat{L}^2$ commute with $\hat{H}$.
   Now, we will show in Section 26.7, by means of the Wigner–Eckart theorem, that the spin–orbit coupling term takes the form: $\hat{\vec{S}} \cdot \hat{\vec{L}}$, where $\hat{\vec{S}}$ and $\hat{\vec{L}}$ are the total spin and angular momentum vector operators. This term, because it is a dot product between two vectors in the space of the total (spin+orbital) angular momentum, remains invariant under rotations carried out by the generator $\hat{J}_z$ in this space. Another way to see this, is by writing

$$\hat{\vec{S}} \cdot \hat{\vec{L}} = \frac{1}{2}\left(\hat{J}^2 - \hat{S}^2 - \hat{L}^2\right). \tag{26.39}$$

An atomic energy level is completely specified by giving the electronic configuration and the values of the quantum numbers of the total orbital angular momentum L, of the total spin S, and of the total angular momentum J. The notation ${}^{2S+1}L_J$ is used in order to denote the values of these three quantum numbers with L standing for the capital letters S, P, D, ... when $L = 0, 1, 2, \ldots$. For example, when $S = 1$ and $L = 1$, an atom can be in one of the following three states, ${}^3P_0$, ${}^3P_1$, and ${}^3P_2$ for $J = 0, 1$, and 2 respectively.

In Table 26.1 is a list of energy levels of helium. First, closed shells have always $L = S = J = 0$. Thus, the ground state of helium, which corresponds to the configuration $1s^2$, has $S = L = J = 0$, and can be written as ${}^1S_0$. The configuration $1s^1 2s^1$ corresponds to the four states $1s^{\uparrow}2s^{\downarrow}$, $1s^{\downarrow}2s^{\uparrow}$, $1s^{\uparrow}2s^{\uparrow}$, $1s^{\downarrow}2s^{\downarrow}$. These states cannot be eigenstates of the atomic Hamiltonian, because they are not eigenstates of $\hat{L}^2$, $\hat{S}^2$, and $\hat{J}^2$. Linear combinations of these four states lead to the four states which are labeled as ${}^3S$ and ${}^1S$. The triplet is the first excited state where the value of J is uniquely determined to be 1, that is, the state is ${}^3S_1$. The singlet is the second excited level with $J = 0$, that is, ${}^1S_0$. Notice that the configuration $1s^1 2p^1$ corresponds to 12 states which become ${}^3P_2$, ${}^3P_1$, ${}^3P_0$, ${}^1P_1$. If we ignore the spin–orbit couplings the first three states, which form an $L - S$ multiplet with $S = 1$ and $L = 1$, would be degenerate. Therefore, the small energy difference (of the order of 0.001 eV in this case) for different values of J is due to the spin–orbit interaction. Also notice that, and this is generally true, the energy difference between energy levels (originating from the same atomic configuration) which differ by the values of L or S, that is, between LS multiplets, is of the order of a few tens of one eV. The energy difference between states belonging to the same LS multiplet with different J values is much smaller than that.

As can be concluded by examining Table 26.2, the situation is similar for the case of the Li atom. The states shown in this table correspond to a completed $1s$ shell, so that these electrons do not contribute to the values of L, S, and J. The ground state of Li which corresponds to the configuration $1s^2 2s^1$ is ${}^2S_{1/2}$.

26.6.1 Hund's rules

Hund's rules aim at answering the following question: Which one of the JLS multiplets corresponds to the atomic ground state?
Hund's rules state the following:

1. The LS multiplet with the largest value of S has the lowest energy. The reason for this is that when S is largest, the state is spin symmetric and, thus, spatially antisymmetric which means that the wavefunction has nodes and the electrons stay away from each other, thus avoiding the mutual Coulomb repulsion.
2. If the largest value of S is associated with several values of L, the lowest energy state among these corresponds to the one with the largest value of L which is allowed keeping a totally antisymmetric wavefunction. In a state with the largest allowed angular momentum, the electrons tend to stay away from each other, thus avoiding the Coulomb repulsion.
3. For a single partially filled shell: If the shell is less than half-filled the value of $J = |L - S|$ corresponds to the lowest energy.

Table 26.1 Energy levels of a helium atom

Configuration	^{2S+1}L	J	Energy (eV)
$1s^2$	^1S	0	0
$1s2s$	^3S	1	19.818943
$1s2s$	^1S	0	20.615078
$1s2p$	^3P	2	20.963377
$1s2p$		1	20.963388
$1s2p$		0	20.963511
$1s2p$	^1P	1	21.217304
$1s3s$	^3S	1	22.717699
$1s3s$	^1S	0	22.919542
$1s3p$	^3P	2	23.006294
$1s3p$	^3P	1	23.006298
$1s3p$	^3P	0	23.006332
$1s3d$	^3D	3	23.072870
$1s3d$		2	23.072870
$1s3d$		1	23.072876
$1s3d$	^1D	2	23.073296
$1s3p$	^1P	1	23.086237
$1s4p$	^1P	1	23.741268

If the shell is more than half-filled the value of $J = L + S$ corresponds to the lowest energy.

Next, we apply Hund's rules to a few examples.

Beryllium: The ground state of Beryllium is in the configuration $1s^2 2s^2 2p^1$. The outer unpaired electron is in the $2p$ state, thus the total orbital angular momentum of the atom is $L = 1$. Furthermore the total spin is $S = 1/2$ for the same reason. Thus, the possible values of J are $J = 1/2, 3/2$. The $n = 2$ shell is 1/6-filled, thus, applying Hund's third rule above leads to the value of $J = |L-S| = 1/2$. Therefore, the ground state of Beryllium is $^2P_{1/2}$.

Carbon: The ground state of carbon is in the configuration $1s^2 2s^2 2p^2$. Therefore, the value of total spin should be $S = 1$, because this corresponds to its maximum value for the system of the two electrons in the p-shell. The possible values of L are 2, 1, and 0. If we select $L = 2$ as the largest value the total wavefunction will not be antisymmetric because the spin part with $S = 1$ is symmetric and the spatial part with $L = 2$ would also be symmetric. Thus, we need to select the next largest value, that is, $L = 1$. Since the shell is less that half-filled, we need to take $J = 0$, which leads to the ground state, $^3P_0$.

Oxygen: The electronic configuration of the ground state of O is $1s^2 2s^2 2p^4$. Here, we will follow a somewhat different approach. The p-shell is missing two electrons in order to be completely filled. It is easier to consider it as a filled shell plus two holes, because we know that the filled shell has $S = L = J = 0$. The possible values of total

Table 26.2 Energy levels of a lithium atom

Configuration	${}^{2S+1}L$	J	Energy (eV)
$1s^2 2s$	${}^2S$	1/2	0
$1s^2 2p$	${}^2P$	1/2	1.847751
$1s^2 2p$		3/2	1.847793
$1s^2 3s$	${}^2S$	1/2	3.373008
$1s^2 3p$	${}^2P$	1/2	3.834146
$1s^2 3p$		3/2	3.834158
$1s^2 3d$	${}^2D$	3/2	3.878469
$1s^2 3d$		5/2	3.878473
$1s^2 4p$	${}^2P$	1/2	4.521515
$1s^2 4p$		3/2	4.521520
$1s^2 4d$	${}^2D$	3/2	4.540556
$1s^2 4d$		5/2	4.540558

spin of the two-hole system is $S = 0, 1$ and the possible values of the orbital angular momentum for two such holes in the p-shell are $L = 0, 1, 2$. We need to select the maximum value of S which is 1 and leads to a symmetric wavefunction in spin space. This means that its spatial part should be antisymmetric and because a state with $L = 2$ is symmetric, we need to select the next largest which is $L = 1$. The shell is more than half-filled, thus, $J = L + S = 2$. Therefore, the ground state of oxygen is ${}^3P_2$.

26.7 Spin–orbit interaction in multi-electron atoms

We have discussed the spin–orbit coupling for the case of a single electron under the influence of a central potential $U(r)$ in chapter 24 and we derived Eq. 24.12. The same expression will be obtained in chapter 31 in the non-relativistic limit of the Dirac equation. Imagine that we have an atom with N electrons in various orbitals, then we can write the total spin–orbit coupling term as follows:

$$\hat{H}_{s.o} = \sum_{i=1}^{N} \mathcal{J}(r_i)\hat{\vec{l}}_i \cdot \hat{\vec{s}}_i, \tag{26.40}$$

$$\mathcal{J}(r) = \frac{1}{2mc^2}\frac{1}{r}\frac{dU(r)}{dr}. \tag{26.41}$$

where $U(r)$ is the self-consistently obtained electrostatic potential energy due to the nucleus and all other electrons. Here $\hat{\vec{l}}_i$ and $\hat{\vec{s}}_i$ are the angular momentum and spin operators of the individual electron.

As we noted in section 26.6 of this chapter, for light atoms, the effect of spin–orbit coupling is very small. This allows us to treat this term using perturbation theory.

Let L, S, M_L, M_S stand for the eigenvalues characterizing the total angular momentum and spin and their projections. In the absence of spin–orbit coupling the above are good quantum numbers. When the spin–orbit coupling term is introduced as perturbation, L and S remain good quantum numbers; therefore, for given values of these two, we need to diagonalize the perturbation in the subspace spanned by the various values of M_L and M_s. For that we need the matrix elements:

$$\langle nLSM_LM_S|\hat{H}_{s.o}|nLSM'_LM'_S\rangle, \tag{26.42}$$

where the state $|nLSM_LM_S\rangle$ can be expressed as follows:

$$|nLSM_LM_S\rangle = \sum_{\alpha,\beta} C_{\alpha,\beta}|nLM_L,\alpha\rangle|SM_S,\beta\rangle, \tag{26.43}$$

where β enumerates a set of states within the spin space of the N electron system which share the same total spin eigenvalue and its projection M_s along some z-axis. Namely, the N electron spin space has a dimension of 2^N and there are many linearly independent states which can be formed in this space sharing the same values of S and M_S. For example, take three spin-1/2 electrons. There four states characterized by $S = 1/2$, not just two, that is, there two each with $M_s = 1/2$ and two each having $M_s = -1/2$. Adding the spin of two of these electrons we find the possible values of their total spin $S_{12} = 0, 1$ and then there two ways to obtain $S = 1/2$, one by adding $0 + 1/2$ and a second by adding $1 + 1/2$.

The index β enumerates the states which correspond to the same value of L and M_L.

The matrix element of $\hat{H}_{s.o}$ can be written as:

$$\sum_{i=1}^{N} \sum_{\alpha\beta,\alpha'\beta'} C^*_{\alpha\beta}C_{\alpha'\beta'}\langle \alpha nLM_L|\mathcal{J}_i\hat{\vec{l}}_i|\alpha' nLM'_L\rangle \cdot \langle \beta SM_S|\hat{\vec{s}}_i|\beta' SM'_S\rangle. \tag{26.44}$$

The Winger–Eckart theorem implies the following

$$\langle \alpha nLM_L|\hat{\vec{l}}_i|\alpha' nLM'_L\rangle = D(n,L,\alpha,\alpha')\langle LM_L|\hat{\vec{L}}|LM'_L\rangle, \tag{26.45}$$

namely, the proportionality constant does not depend on M_L nor M'_L. It is easy to show this statement and we do so next.

The vector operator $\hat{\vec{l}}_i$ is a tensor operator of rank $k = 1$; therefore, using the Wigner–Eckart theorem, we can write it as

$$\langle \alpha nLM_L|\hat{\vec{l}}_i|\alpha' nLM'_L\rangle = O_1(n,L,\alpha,\alpha')\langle LM_L|LM'_Lk = 1, q\rangle, \tag{26.46}$$

where q stands for any of the components of the vector $\hat{\vec{l}}_i$, and $\langle LM_L|LM'_Lk = 1, q\rangle$ is the Glebsch–Gordan coefficient. Similarly, using the Wigner–Eckart theorem we can write

$$\langle LM_L|\hat{\vec{L}}|LM'_L\rangle = O_2(L)\langle LM_L|LM'_L1, q\rangle. \tag{26.47}$$

By dividing both sides of the above two equations, we derive Eq. 26.45, where

$$D(n, L, \alpha, \alpha') \equiv \frac{O_1(n, L, \alpha, \alpha')}{O_2(L)}. \tag{26.48}$$

In a very similar way we can also show that

$$\langle \beta S M_S | \hat{\vec{s}}_i | \beta' S M'_S \rangle = E(\beta, \beta', S) \langle S M_S | \hat{\vec{S}} | S M_S \rangle. \tag{26.49}$$

Therefore, summing over i and α and β we obtain

$$\begin{aligned} &\langle nLSM_L M_S | \hat{H}_{s.o} | nLSM'_L M'_S \rangle = \\ &\zeta(nLS) \langle L, M_L | \hat{\vec{L}} | L, M'_L \rangle \cdot \langle S M_S | \hat{\vec{S}} | S M'_S \rangle, \end{aligned} \tag{26.50}$$

where

$$\zeta(nLS) \equiv \sum_{i=1}^{N} \mathcal{J}_i \sum_{\alpha\beta, \alpha'\beta'} C^*_{\alpha\beta} C_{\alpha'\beta'} D(n, L, \alpha, \alpha') E(\beta, \beta', S). \tag{26.51}$$

Equation 26.50 can be also expressed as follows:

$$\begin{aligned} &\langle nLSM_L M_S | \hat{H}_{s.o} | nLSM'_L M'_S \rangle = \zeta(nLS) \\ &\times \langle nLSM_L M_S | \hat{\vec{L}} \cdot \hat{\vec{S}} | nLSM'_L M'_S \rangle, \end{aligned} \tag{26.52}$$

which means that we need to diagonalize the effective Hamiltonian:

$$\hat{\mathcal{H}}_{s.o} = \zeta(nLS) \hat{\vec{L}} \cdot \hat{\vec{S}}, \tag{26.53}$$

in the subspace of fixed values of n, L, S.

Now, this Hamiltonian can be diagonalized by rewriting it using the identity given by Eq. 26.39. Therefore, its eigenstates can be written as $|nLSJM_J\rangle$ with corresponding eigenvalues $E_{nLS}(J)$ given as

$$\hat{H}_{s.o} | nLSJM_J \rangle = E_{nLS}(J) | nLSJM_J \rangle, \tag{26.54}$$

where

$$E_{nLS}(J) = \frac{\hbar^2}{2} \zeta(nLS) \Big(J(J+1) - L(L+1) - S(S+1) \Big). \tag{26.55}$$

From the above equation for the eigenvalues, Lande's rule follows:

$$E_{nLS}(J) - E_{nLS}(J-1) = \hbar^2 \zeta(nLS) J, \tag{26.56}$$

that the difference in energy in successive J-values within the same LS multiplet increases linearly with the value of J.

26.8 Problems

Problem 1

Consider the helium atom in the presence of a hypothetically very large magnetic field such that the spins of the two electrons in the atom are parallel.

(a) What is the Hamiltonian which describes the two electrons in the atom?

(b) Write down the most general wavefunction of the two electrons in the atom *within* the Hartree–Fock approximation.

(c) Calculate the expectation value of the Hamiltonian using the Hartree–Fock wavefunction. Namely, express it as a function of one-body and two-body integrals. Indicate which term is the so-called Hartree and which term is the Fock term.

(d) Minimize the expectation value of the Hamiltonian with respect to variations in the spatial part of the single-particle wavefunctions, under the constraint that they are normalized. Namely, derive the so-called Hartree–Fock equations for the specific case of the two electrons in the helium atom.

Problem 2

Use the Wigner–Eckart theorem to show the following:

(a) The matrix elements of a scalar tensor operator $\hat{O}_s$ (rank $k = 0$) obey the following relation

$$\langle n, j, m|\hat{O}_s|n', j', m'\rangle = \mathcal{O}_j^{n,n'}\delta_{j,j'}\delta_{m,m'}, \tag{26.57}$$

where $\mathcal{O}_j^{n,n'} = \langle nj||\hat{O}_s||n', j\rangle$ is the so-called reduced matrix element of $\hat{O}_s$ which is independent of m and m'.

(b) For an $L - S$ multiplet of atomic states and for the spin angular momentum operators $\vec{s}_i$ of an individual electron and $\vec{S}$ of all the electrons, the following is true

$$\langle n, S, M_S|\vec{s}_i|n', S', M'_S\rangle = C(n, n', S, S')\langle n, S, M_S|\hat{\vec{S}}|n', S, M'_S\rangle, \tag{26.58}$$

where the coefficient $C(n, n', L)$ does not depend on M and M'.

Problem 3

Use Hund's rules to determine the ground states of B, C, and N, using the notation ${}^{2S+1}L_J$.

Problem 4

Consider the so-called *Jellium model* of the metallic state of matter. In this model the positive ions in a metallic solid are smashed to make a uniform inert background of positive uniform charge of charge density $\rho_+ = N|e|/V$ exactly opposite to the average electronic charge density $\rho_e = -N|e|/V$. For convenience we consider N electrons and N ions in a volume V with *periodic boundary conditions.*

(a) Extend the considerations of the previous atomic physics problem to the problem of interacting electrons in a uniform solid, as conceptualized by the Jellium model. Explain why the following

$$\mathcal{H} = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 - |e|\sum_{i=1}^{N}\int d^3R\frac{\rho_+(\vec{R})}{|\vec{R}-\vec{r}_i|} + \frac{1}{2}\sum_{i,j,i\neq j}\frac{e^2}{|\vec{r}_i-\vec{r}_j|}$$
$$+\frac{1}{2}\int d^3Rd^3R'\frac{\rho_+(\vec{R})\rho_+(\vec{R}')}{|\vec{R}-\vec{R}'|}, \tag{26.59}$$

is the Hamiltonian of N electrons and N ions in this case. Here, $\vec{r}_i$ are the electron positions. Namely, we have taken the ionic charge distribution to be given by a general function $\rho_+(\vec{R})$, which is, in fact, the constant discussed above. Notice, that we have ignored the ionic kinetic energy because the ionic masses M are much larger than the electron mass m and therefore the terms $P^2/(2M)$ are much smaller than the electronic kinetic energy terms by a factor of m/M. This is the so-called Born–Oppenheimer approximation. Therefore, there are no active ionic degrees of freedom.

(b) Use the experience you gained from the previous problem to write down the Hartree–Fock equations for the N-electron system in this case.

(c) Show that the non-interacting single electron states

$$\phi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}}e^{i\vec{k}\cdot\vec{r}}, \tag{26.60}$$

are solutions to the Hartree–Fock equations. For our case with periodic boundary conditions, what are the possible values of $\vec{k}$ and why?

(d) What is the ground-state wavefunction of this system of N electrons. Namely, determine the wavevector k_F and energy E_F of the highest occupied (or lowest unoccupied) state as a function of the electron density $\rho = N/V$. Namely, determine the so-called Fermi momentum and Fermi energy respectively. For convenience consider the thermodynamic limit; namely, while $N \to \infty$ and $V \to \infty$ the ratio N/V is kept constant and equal to the average electronic density ρ.

(e) What is the total kinetic energy contribution to the total energy? Express your answer in terms of k_F (or E_F).

(f) Show that the Hartree term is a constant and together with the ion–ion interaction term get canceled by the electron–ion interaction in the uniform Jellium model case. These terms are infinite but they exactly cancel each other out.

(e) What is the exchange (Fock) contribution to the total energy? Give your answer as a function of k_F or E_F.

27

Molecules

In this chapter, we discuss some elementary molecular physics. When possible, we generalize our conclusions and discussion to the case of a solid. Our goal is to understand the reason why neutral atoms form aggregates, that is, molecules, solids, and the matter which we see around us. The answer that it is simply because of the dipole–dipole attraction is not correct. In the case of the hydrogen molecule, for example, the size of its binding energy is orders of magnitude larger than the size of the dipole–dipole attraction between two isolated hydrogen atoms. In fact, in the hydrogen molecule, the two electrons are shared by both nuclei, so the integrity of each atom is completely lost in the molecule. Just like in the case of atoms, quantum mechanics is crucial to answer this question correctly. That is why we try it here.

27.1 H_2^+ and the Born–Oppenheimer approximation

The H_2^+ ion is illustrated in Fig. 27.1 where the positions of the two protons are $\vec{R}_1$ and $\vec{R}_2$, respectively, and the position of the single electron in this problem is denoted by $\vec{r}$. The Hamiltonian describing the H_2^+ ion is given by

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla_1^2 - \frac{\hbar^2}{2M}\nabla_2^2 - \frac{\hbar^2}{2M}\nabla_{\vec{r}}^2 - \frac{e^2}{|\vec{r}-\vec{R}_1|} - \frac{e^2}{|\vec{r}-\vec{R}_2|} + \frac{e^2}{|\vec{R}_2-\vec{R}_1|}. \tag{27.1}$$

The Born–Oppenheimer approximation is based on the fact that the protons are moving on a much different timescale than the electrons because they are heavier; namely, for the electronic problem the first two terms could be initially neglected, because of the prefactor of the ∇^2 in each of these terms. This means that: a) As a first step, we freeze the proton at a given relative distance $\vec{R} = \vec{R}_2 - \vec{R}_1$. b) We solve the electronic problem for any such fixed positions of the ions and determine the total energy of the electronic problem, that is, $E_e(R)$ as a function of R. c) Lastly, we allow the atoms to move obeying the effective Hamiltonian:

$$\hat{H}_{eff} = -\frac{\hbar^2}{2M}\nabla_1^2 - \frac{\hbar^2}{2M}\nabla_2^2 + V_{eff}(R), \tag{27.2}$$

$$V_{eff}(R) = E_e(R) + \frac{e^2}{R}, \tag{27.3}$$

and we treat this two-body effective Hamiltonian quantum mechanically to find the ground state, the vibrational and rotational excitations of the ion.

Practical Quantum Mechanics. First Edition. Efstratios Manousakis.

Therefore, the Born–Oppenheimer approximation assumes that the electron responds to any given protonic configuration "instantly" (or on a much smaller timescale than the protons) producing an effective proton–proton interaction, which includes the direct Coulomb repulsion e^2/R as well as electronic energy cost $E_e(R)$ as a result of responding to a particular proton separation R. In all of the following regarding molecules we will be working within the Born–Oppenheimer approximation.

In order to describe the electron in the H_2^+ ion, we will use the following variational wavefunction,

$$\psi(\vec{r}) = a\psi_1(\vec{r}) + b\psi_2(\vec{r}), \tag{27.4}$$

which is a linear combination of the atomic orbitals (LCAO)

$$\psi_{1,2}(\vec{r}) = \frac{1}{\sqrt{\pi a_0}} \exp(-\frac{|\vec{r} - \vec{R}_{1,2}|}{a_0}), \tag{27.5}$$

where a_0 is the Bohr radius. These atomic orbitals describe states in which the electron forms virtually an "isolated" hydrogen atom with the proton at position $\vec{R}_1$ or with the proton at position $\vec{R}_2$. Namely, this describes an electron in a state which neither forms an atom 1 nor an atom 2 but sort-of does both, and the electron tunnels through interatomic space (where the potential is higher than near any one particular proton), such that it can increase its uncertainty in its position and, thus, decrease its uncertainty in momentum and lower its kinetic energy. Therefore, by sacrificing some of its average potential energy, it minimizes its total energy by lowering its kinetic energy more than the loss in potential energy. In the general case this optimum situation is reached by treating a (because b is related to a through the normalization condition) as a variational parameter. In this case, however, because the two nuclei are identical, there is a symmetry which forces the value of the magnitude of a to be the same as the magnitude of b. Therefore, there is no variational freedom in this problem and, apart from an overall phase factor which does not have any significance, there are the following possible solutions: a) the even parity solution $a = b$ and, b) the odd parity solution $a = -b$. Therefore, using the normalization condition $\int d^3r|\psi(\vec{r})|^2 = 1$, we find that the solutions are

$$\psi_\pm(\vec{r}) = a_\pm\Big(\psi_1(\vec{r}) \pm \psi_2(\vec{r})\Big), \tag{27.6}$$

$$a_\pm = \frac{1}{\sqrt{2(1 \pm T(R))}}, \tag{27.7}$$

$$T(R) \equiv \int d^r \psi_1(\vec{r})\psi_2(\vec{r}) = \Big(1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2}\Big)e^{-R/a_0}, \tag{27.8}$$

where $R = |\vec{R}_1 - \vec{R}_2|$.

The expectation value of the Hamiltonian with the exclusion of the protonic kinetic energy is

$$E^{(\pm)}(R) = \langle\psi_\pm|\hat{H}|\psi_\pm\rangle = \frac{\langle\psi_1|\hat{H}|\psi_1\rangle + \langle\psi_2|\hat{H}|\psi_2\rangle \pm 2\langle\psi_1|\hat{H}_e|\psi_2\rangle}{2 \pm 2T(R)}, \tag{27.9}$$

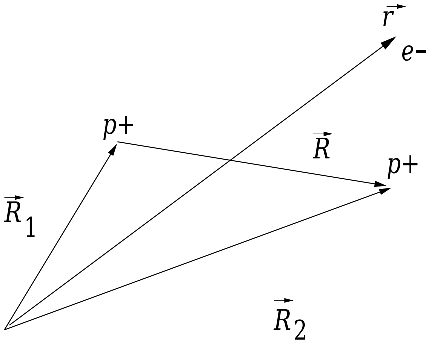

Fig. 27.1

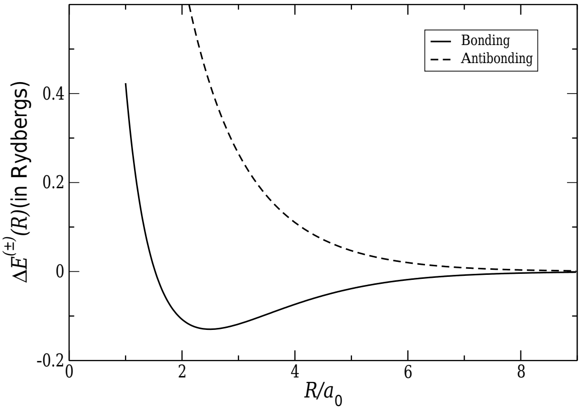

Fig. 27.2

where

$$\langle\psi_1|\hat{H}|\psi_1\rangle = \langle\psi_2|\hat{H}|\psi_2\rangle = -\frac{e^2}{2a_0} + \frac{e^2}{R} - \int d^3r|\psi_1|^2\frac{1}{|\vec{r}-\vec{R}_2|}. \tag{27.10}$$

The integral can be calculated with the same technique applied in chapter 26 to calculate the two-electron integral for the helium atom. In the present case we need to choose the origin of coordinate system for the integration at $\vec{R}_1$ (that is, change variables from $\vec{r}$ to $\vec{r}' = \vec{r} - \vec{R}_1$), that is,

$$-\frac{e^2}{\pi a_0^3}\int d^3r' e^{-2r'/a_0}\frac{1}{|\vec{r}' - \vec{R}|}, \tag{27.11}$$

and then choose the z-axis along the vector $\vec{R} = \vec{R}_1 - \vec{R}_2$. This way the integral becomes

$$-\frac{2e^2}{a_0^3}\int dr' r' e^{-2r'/a_0}\int_{|r'-R|}^{r'+R} dx = -\frac{4e^2}{a_0^3}\Big(\frac{1}{R}\int_0^R dr' r'^2 e^{-2r'/a_0}$$

$$+\int_R^\infty dr' r' e^{-2r'/a_0}\Big) = -\frac{e^2}{R} + \frac{e^2}{R}(1+\frac{R}{a_0})e^{-2R/a_0}. \tag{27.12}$$

To conclude this part of the calculation we write:

$$\langle\psi_1|\hat{H}|\psi_1\rangle = -\frac{e^2}{2a_0} + \frac{e^2}{R}(1+\frac{R}{a_0})e^{-2R/a_0}. \tag{27.13}$$

Furthermore, we have:

$$\langle\psi_1|\hat{H}|\psi_2\rangle = \Big(-\frac{e^2}{2a_0} + \frac{e^2}{R}\Big)T(R) - \int d^3r\psi_1(\vec{r})\psi_2(\vec{r})\frac{e^2}{|\vec{r}-\vec{R}_2|}, \tag{27.14}$$

in which the integral can be calculated in a similar way as above to yield:

$$\langle\psi_1|\hat{H}|\psi_2\rangle = \Big(-\frac{e^2}{2a_0} + \frac{e^2}{R}\Big)T(R) - \frac{e^2}{a_0}(1+\frac{R}{a_0})e^{-R/a_0}. \tag{27.15}$$

Putting the results together, we obtain for $V_{eff}(R)$ the energy functions $\Delta E^{(\pm)}(R) \equiv E^{(\pm)}(R) + e^2/(2a_0)$ (where the energy of the isolated hydrogen ground state has been subtracted) shown in Fig. 27.2 for bonding (+) and antibonding (-) states. Notice that the bonding state has a negative energy (relative with the energy of fully separated hydrogen atom for the proton).

27.2 Hybridization

When atoms form molecules or crystalline solids, they lose their spherical symmetry, therefore, the pure Y_{lm} are no longer part of the electronic wavefunctions. However, these states can be used as a complete basis to express these wavefunctions. For example, imagine the carbon atom in a graphene sheet shown in Fig. 27.3. In this example, the full rotational symmetry is reduced to only rotations by 120° around an axis which goes through each C atom nucleus and is perpendicular to the graphene plane (for the following discussion we will take the z-axis along this axis). The C atom $2s$ and $2p$ states are very close in energy, and in this geometry in order to begin thinking about the formation of the molecular bond it is a better approximation to consider the transformation of the $2s$ and three $2p$ to the following four states instead. The $2s$ and p_x and p_y states "hybridize," that is, form three linearly independent combinations, the so-called sp^2 hybridization, that is,

$$|sp^2\rangle_\nu = \alpha|2s\rangle + \beta_\nu|2p_x\rangle + \gamma_\nu|2p_y\rangle, \qquad \nu = 1,2,3 \tag{27.16}$$

and they are related to one another by a 120° rotation, that is,

$$|sp^2\rangle_{\nu+1} = e^{\frac{i}{\hbar}2\pi/3\hat{J}_z}|sp^2\rangle_\nu, \tag{27.17}$$

and we have taken cyclic boundary conditions, that is, $|sp^2\rangle_4 = |sp^2\rangle_1$. The fourth orbital, that is, $2p_z$, remains unchanged. The three sp^2 orbitals shown schematically in Fig. 27.4 and the coefficients α β_1 and γ_1 are chosen such that a) the state $|sp^2\rangle$ is normalized, and b) the bonded molecular state formed between the two sp^2 orbitals of the two neighboring C atoms minimizes the total electronic energy. Once these coefficients are fixed the other four, that is, $\beta_{2,3}$ and $\gamma_{2,3}$ are related by a 120° rotation through Eq. 27.17.

Each carbon atom has four electrons on the $n = 2$ shell. In the example discussed above, three of these four electrons will occupy the three bonded molecular states formed with the three neighboring carbon atoms. The antibonding states are much higher in energy and remain unoccupied. The fourth electron in each C atom will occupy two bands formed from the $2p_z$ orbitals of each C atom. This part can be treated with the so-called tight-binding approximation (TBA) but application of this method to the problem of graphene is beyond the scope of these notes. The TBA is discussed next and it is applied to a simpler problem, that of a benzene molecule.

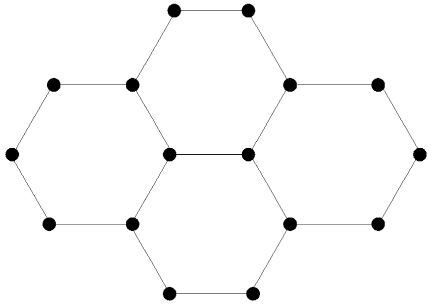

Fig. 27.3

27.3 Tight-binding approximation

Let us consider the molecule of benzene shown in Fig. 27.5. We can describe the molecule of benzene by considering the four valence states $2s$ and $2p_x$, $2p_y$ and $2p_z$ of carbon. The $1s$ state lies too deep and, thus, it does not participate directly in the formation of the molecular bond. Let us use a rectangular coordinate system in which the z-axis for each atom is perpendicular to the plane of benzene and the x and y axes are both on the benzene plane. The $2s$ state and the p_x and p_y states hybridize to form three sp^2 planar orbitals (shown in red in Fig. 27.5) which allow each carbon atom to bond with its two neighbor C atoms at 120°. Each pair of the carbon sp^2 bonds form one (σ) bonding and one antibonding state. A pair of electrons (one from each C atom) occupies completely the (σ) bonding state. The antibonding (σ) state lies at a much higher energy and remains unoccupied. A third polar bond is formed between the other sp^2 electron of C and the hydrogen atom $1s$ electron as shown in Fig. 27.5 and the antibonding state also remains empty because it is of high energy. Now, the fourth electron of each carbon atom will go on the p_z orbital (shown with a

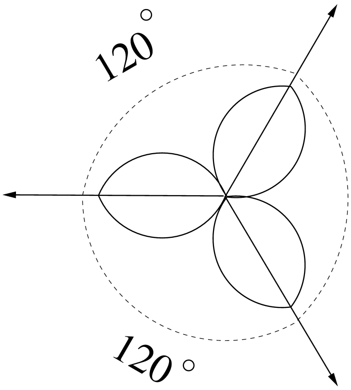

Fig. 27.4

dashed line in Fig. 27.5). These p_z orbitals of each pair of nearest neighboring (n.n.) atoms overlap and form six molecular orbitals.

Now, let us restrict ourselves in the case of these six electrons occupying the six p_z orbitals located on each of the six carbon atoms, namely, the orbitals $|p_z(i)\rangle$, where $i = 1, 2, 3, 4, 5, 6$. If we consider as our basis the above six states $|p_z(i)\rangle$ we can consider the overlap integrals between nearest neighboring atoms

$$\langle p_z(i)|\hat{H}|p_z(i+1)\rangle = -t_p, \tag{27.18}$$

and we can neglect the overlap between the further away neighbors. The atomic orbitals decay exponentially with distance from the atomic nucleus. As a result the overlap and the matrix elements of the Hamiltonian with atoms which are far away are very small. We also need to consider the on-site energies, that is,

$$\langle p_z(i)|\hat{H}|p_z(i)\rangle = E_0. \tag{27.19}$$

Notice that because the atoms are the same, these energies and overlap integrals are the same for all atoms and n.n. pairs of atoms. In this way we have managed to form a 6×6 Hamiltonian matrix in the above basis, which can be diagonalized to provide a band of six states and the corresponding energy eigenvalues. Let us neglect the overlap integrals between n.n. orbitals and take the six states to be orthonormal. This overlap integral is treated more accurately in the following section. Because of the symmetry of this Hamiltonian under 60° rotations, this problem can be solved exactly (it is like the Bloch problem in chapter 10), with the following six eigenstates:

$$|\nu\rangle = \frac{1}{\sqrt{6}} \sum_{n=1}^{6} e^{i2\pi n\nu/6} |p_z(n)\rangle, \qquad \nu = 1, 2, 3, 4, 5, 6 \tag{27.20}$$

with corresponding eigenvalues $E_\nu = E_p - 2t_p cos(2\pi\nu/6)$. The available six electrons will occupy just three of these six molecular orbitals. This approximation is called the *tight-binding approximation.*

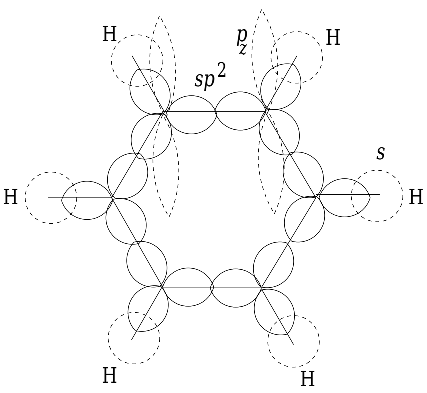

Fig. 27.5

27.3.1 A tight-binding model of polyacetylene

In Fig. 27.6 a schematic drawing of the polyacetylene macromolecule is shown. For the reasons discussed in the previous section, the sp^2 hybridized orbitals form occupied bonding states with nearest neighboring C atoms and the hydrogen atoms. Thus, three of the four C electrons from the $2s$ and $2p$ states fully occupy these bonding states. The fourth electron from every C atom will occupy the p_z orbital (shown in Fig. 27.6), just like in the case of Benzene discussed in the previous section. Therefore, the highest occupied orbitals of polyacetylene are these p_z orbitals, and there is one per C atoms and one electron per C atom available for such orbitals. In order to solve this problem of N atomic p_z orbitals and N electrons we will imagine that, because N is very large, we will consider the limit $N \to \infty$. In this limit we will choose periodic boundary conditions for simplicity, which means the necklace geometry shown in Fig. 27.7.

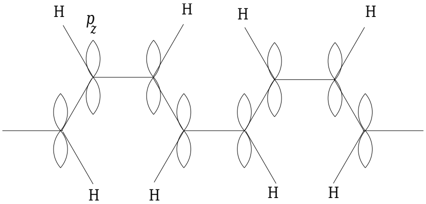

Fig. 27.6

In this case the atomic energy of each electron on the p_z orbital will be denoted by ϵ_0 and the p_z of the nth C atom will be denoted as $|n\rangle$. In this case also, the electron lowers its energy by hopping from atom (site) to atom. In the above problem we have that $|n+N\rangle = |n\rangle$, that is, we have periodic (Born von Karman) boundary conditions.

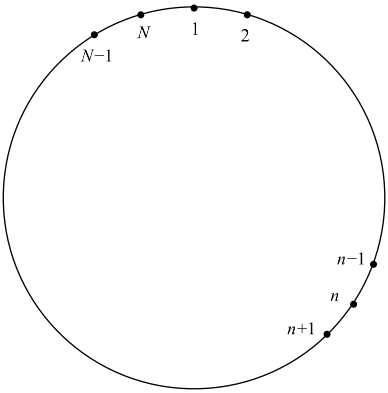

Fig. 27.7

However, because these atoms are close enough together, the electron is not entirely "committed" to a particular atom as it can lower its energy by "hopping" from one atomic potential minimum to a nearest neighboring atomic potential minimum. We consider, therefore, the states formed from all the N atomic wavefunctions $|n\rangle$, $n = 1, 2, ..., N$ as a basis set of functions to carry out an approximate calculation.

The states $|n\rangle$ are normalized; however, they are not orthogonal to each other. Namely,

$$\langle n|n\rangle = 1, \tag{27.21}$$

$$\langle n|n+1\rangle = \langle n-1|n\rangle = \gamma, \tag{27.22}$$

and let us assume that $\langle n|m\rangle = 0$, if the atoms m and n are not nearest neighbors. This assumption makes sense because, since the states $|n\rangle$ represent bound states at the atom n, the wavefunctions are expected to fall off exponentially as we move away from the location of the atom. In the above notation, when $n = N$, then $n + 1 \to 1$ and when $n = 1$, then $n - 1 \to N$ due to the cyclical boundary conditions. For the same reason, only the following matrix elements of the Hamiltonian are significantly different from zero for any atom n:

$$\langle n|\hat{H}|n\rangle = \epsilon_0, \tag{27.23}$$

$$\langle n|\hat{H}|n+1\rangle = -\beta, \tag{27.24}$$

$$\langle n-1|\hat{H}|n\rangle = -\beta, \tag{27.25}$$

and also, here, when $n = N$, then $n + 1 \to 1$ and when $n = 1$, then $n - 1 \to N$ due to the cyclical boundary conditions. Therefore, the electron when it is in any given atom n can "hop" to only its two nearest neighboring atoms.

Now, we wish to diagonalize the Hamiltonian matrix in this basis. The problem, however, is that the Hamiltonian is an $N \times N$ matrix. Let us utilize the symmetry of the problem, namely, that the Hamiltonian commutes with the operator $\hat{T}_a$ which translates by one spacing a (we work in units in which $a = 1$), that is,

$$\hat{T}_a|n\rangle = |n + 1\rangle. \tag{27.26}$$

It is straightforward to show (see also chapter 10) that the following state

$$|k\rangle = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{ikn}|n\rangle, \tag{27.27}$$

when $k = 2\pi/Nm$ where m is an integer, is an eigenstate of this translation operator and of the Hamiltonian.

Next, let us consider a given state $|\psi\rangle$ and let us suppose that we know this state, therefore, we can compute the overlap integrals with the also known basis states $|n\rangle$:

$$\lambda_n = \langle n|\psi\rangle. \tag{27.28}$$

Now, we wish to write $|\psi\rangle$ as a linear combination of the basis states $|n\rangle$ as follows:

$$|\psi\rangle = \sum_{n=1}^{N} c_n|n\rangle, \tag{27.29}$$

and, thus, we need to determine the coefficients c_n. By projecting both sides of the above equation to a given state $|m\rangle$, it is straightforward to show that these N coefficients satisfy the following N algebraic equations:

$$c_m + \gamma(c_{m+1} + c_{m-1}) = \lambda_m, \tag{27.30}$$

and as already discussed $c_{N+1} = c_1$ and $c_0 = c_N$. In order to approximately solve the system of the N equations above we will assume that $\gamma << 1$, because γ is the overlap integral between two normalized wavefunctions which are displaced by distance a. Clearly, when we take $\gamma = 0$ the solution to these equations is trivial: $c_n = \lambda_n$. Now, we write $c_n = \lambda_n + \delta_n$ and we can easily determine the small correction δ_n to first order in γ by using the above Eq. 27.30 and expanding in powers of δ_n. We find that

$$c_n = \lambda_n + (\lambda_{n+1} + \lambda_{n-1})\gamma. \tag{27.31}$$

Now we are ready to apply the previous findings to our problem. To first order in γ we can easily show that the state given by Eq. 27.27 is an eigenstate of the

Hamiltonian. To do that we proceed as follows: We apply the Hamiltonian operator explicitly on the state given by Eq. 27.27. This will yield a state

$$|\psi\rangle = \hat{H}|k\rangle. \tag{27.32}$$

Then, we expand this known state $|\psi\rangle$ in the basis $|n\rangle$ as in Eq. 27.29 where the coefficients c_n to first order in γ are given by Eq. 27.31 where

$$\lambda_n = \langle n|\hat{H}|k\rangle. \tag{27.33}$$

The right-hand-side of the above equation can be easily calculated to be given as

$$\lambda_n = \frac{1}{\sqrt{N}}(\epsilon_0 - 2\beta\cos(k))e^{ikn}. \tag{27.34}$$

Therefore, using this equation and Eq. 27.31 we find that

$$c_n = \epsilon(k)\frac{1}{\sqrt{N}}e^{ikn}, \tag{27.35}$$

$$\epsilon(k) = (\epsilon_0 - 2\beta\cos(k))(1 + 2\gamma\cos(k)). \tag{27.36}$$

Which implies that

$$\hat{H}|k\rangle = |\psi\rangle = \epsilon(k)|k\rangle. \tag{27.37}$$

Therefore we have determined both the wavefunction and the energy eigenvalues. The energy eigenvalues can be plotted in the first Brillouin zone, that is, for $\pi/a < k \leq \pi/a$, to give an energy band.

27.4 The hydrogen molecule

27.4.1 Uncorrelated electrons

Let us consider the hydrogen molecule schematically shown in Fig. 27.8. Two hydrogen nuclei are at distance $\vec{R}$ from each other. We imagine the Coulomb potentials which the electron experiences from each proton (one located at the origin and the other at $\vec{R}$), and the ground-state wavefunctions $\phi_{1s}(r)$ and $\phi_{1s}(|\vec{r} - \vec{R}|)$ due to the $1s$ levels around each atom. For simplicity of notation let us simplify the names of the two states as

$$\phi_1(\vec{r}) = \phi_{1s}(r), \tag{27.38}$$

$$\phi_2(\vec{r}) = \phi_{1s}(|\vec{r} - \vec{R}|)). \tag{27.39}$$

Borrowing from the treatment of the H_2^+ ion (see Section 27.1), an approximation to the wavefunction of each electron is the following

$$\psi_\pm(\vec{r}) = \frac{1}{\sqrt{2}}(\phi_1(\vec{r}) \pm \phi_2(\vec{r})). \tag{27.40}$$

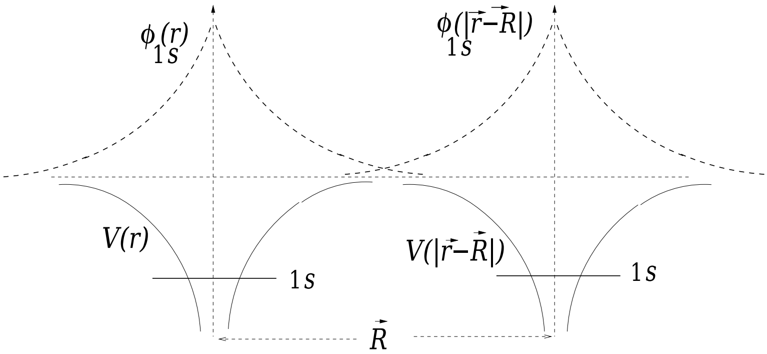

Fig. 27.8

A non-interacting wavefunction for the two electrons in the total spin $S = 0$ (singlet) maybe the following

$$\Psi^{(0)}(1,2) = \psi_+(\vec{r}_1)\psi_+(\vec{r}_2)\chi_{12}^{(0)}, \tag{27.41}$$

where $\chi_{12}^{(0)}$ is the spin-singlet part:

$$\chi_{12}^{(0)} = \frac{1}{\sqrt{2}}(|\uparrow\rangle_1|\downarrow\rangle_2 - |\downarrow\rangle_1|\uparrow\rangle_2), \tag{27.42}$$

which is antisymmetric, and so the total wavefunction (27.41) is antisymmetric. The same wavefunction (27.41) can also be obtained from a single Slater determinant formed from the two single-particle states $\psi_+(\vec{r})|\uparrow\rangle$ and $\psi_+(\vec{r})|\downarrow\rangle$.

Similarly, the spin-triplet ($S = 1$) state is obtained as follows

$$\Psi^{(1)}(1,2) = \frac{1}{\sqrt{2}}(\psi_+(\vec{r}_1)\psi_-(\vec{r}_2) - \psi_+(\vec{r}_2)\psi_-(\vec{r}_1))\chi_{12}^{(1)}, \tag{27.43}$$

where $\chi_{12}^{(1)}$ is one of the following three states (spin triplet):

$$\chi_{12}^{(1)} = \left\{ \begin{matrix} \frac{1}{\sqrt{2}}(|\uparrow\rangle_1|\downarrow\rangle_2 + |\downarrow\rangle_1|\uparrow\rangle_2, \\ |\uparrow\rangle_1|\uparrow\rangle_2 \\ |\downarrow\rangle_1|\downarrow\rangle_2 \end{matrix} \right\}, \tag{27.44}$$

which are symmetric and, thus, the states (27.43) are totally antisymmetric because of their spatial part.

Now, let us consider the Hamiltonian:

$$\hat{H} = H_1 + H_2 + V_{12}, \tag{27.45}$$

where $\hat{H}_1$ and $\hat{H}_2$ contain the parts for each electron in an H_2^+ ion (see Section 27.1) and V_{12} is the electron–electron Coulomb repulsion.

The energy of the two electron system in the spin-singlet state is approximately given by

$$E_S \simeq 2E_+ + \frac{U}{2}, \tag{27.46}$$

$$U \equiv \int d^3r_1 d^3r_2 |\phi_1(r_1)|^2 |\phi_2(r_2)|^2, \tag{27.47}$$

and we have neglected Coulomb interaction terms in which one electron is in one atom and the other is in the other atom. The reason is that we have assumed that the Coulomb interaction is much stronger when the two electrons are on the same atom. Here, $E_\pm$ is the energy of one electron in the H_2^+ state which, within the TBA by neglecting the overlaps $\langle\phi_1|\phi_2\rangle$, can be approximated by

$$E_\pm \simeq E_{1s} \mp t_s, \tag{27.48}$$

where t_s is the hopping matrix element

$$t_s = -\langle\phi_1|H_1|\phi_2\rangle, \tag{27.49}$$

which causes tunneling of the electron from one atomic state around one proton to the other.

On the other hand, the energy expectation value of the Hamiltonian in the triplet state does not include such an on-site interaction term:

$$E_t = E_+ + E_- \simeq 2E_{1s}. \tag{27.50}$$

The reason is the Pauli exclusion principle which prevents the two electrons of the same spin to be on the same atom.

Therefore, we conclude that within this independent particle approximation, when $U > 4t_s$, the lowest energy state is the spin–triplet ($S = 1$). This happens, within our approximation, because the electrons, when they are in the $S = 1$ state, avoid the configuration in which they are on the same atomic state; this configuration, when U is large, costs a lot of energy.

27.4.2 Correlated electrons: The Hubbard model

The independent particle approximation in the previous subsection ignores the fact that the electrons in the singlet state, when they are allowed to visit the same atom, can move in a correlated fashion. Namely, in the pair wavefunction, the amplitude for such a configuration could be optimized in such a way that the electrons could be allowed to hop from one atom to the other, avoiding the Coulomb repulsion in an optimal fashion.

The subspace of the spin-singlet space ($S = 0$) is spanned by the following symmetric two-electron configurations:

$$\Phi_0(1,2) = \frac{1}{\sqrt{2}}\Big(\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) + \phi_2(\vec{r}_1)\phi_1(\vec{r}_2)\Big), \tag{27.51}$$

$$\Phi_1(1,2) = \phi_1(\vec{r}_1)\phi_1(\vec{r}_2), \tag{27.52}$$

$$\Phi_2(1,2) = \phi_2(\vec{r}_1)\phi_2(\vec{r}_2). \tag{27.53}$$

The two-electron Hamiltonian (27.45) can be expressed in the above subspace and becomes the following 3×3 matrix,

$$\begin{pmatrix} 3E_{1s} & -\sqrt{2}t_s & -\sqrt{2}t_s \\ -\sqrt{2}t_s & 2E_{1s}+U & 0 \\ -\sqrt{2}t_s & 0 & 2E_{1s}+U \end{pmatrix}. \tag{27.54}$$

It is straightforward to diagonalize this matrix to find the following energy eigenvalues:

$$E_0 = 2E_{1s} + \frac{U}{2} - \sqrt{\left(\frac{U}{2}\right)^2 + 4t_s^2}, \tag{27.55}$$

$$E_1 = 2E_{1s} + \frac{U}{2} + \sqrt{\left(\frac{U}{2}\right)^2 + 4t_s^2}, \tag{27.56}$$

$$E_2 = 2E_{1s} + U, \tag{27.57}$$

with corresponding eigenstates:

$$\Psi_0 = C\left(\frac{1}{\sqrt{2}}\Phi_0 + \left(\sqrt{1+\left(\frac{U}{4t_s}\right)^2} - \frac{U}{4t_s}\right)\frac{\Phi_1+\Phi_2}{2}\right), \tag{27.58}$$

$$\Psi_1 = C\left(\frac{1}{\sqrt{2}}\Phi_0 + \left(\sqrt{1+\left(\frac{U}{4t_s}\right)^2} + \frac{U}{4t_s}\right)\frac{\Phi_1+\Phi_2}{2}\right), \tag{27.59}$$

$$\Psi_2 = \frac{1}{\sqrt{2}}(\Phi_1 - \Phi_2), \tag{27.60}$$

For the case of the subspace which is spatially antisymmetric, which can combine with the spin-triplet space, it is spanned by only the following state

$$\Psi_t(1,2) = \frac{1}{\sqrt{2}}(\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) - \phi_2(\vec{r}_1)\phi_1(\vec{r}_2)). \tag{27.61}$$

Thus, the energy of the triplet state has no further corrections within this limited subspace and is given by Eq. 27.50.

Notice, that now, since,

$$\frac{U}{2} - \sqrt{\left(\frac{U}{2}\right)^2 + 4t_s^2} < 0, \tag{27.62}$$

for any value of U, the ground state of the spin-singlet configuration is always lower than the spin-triplet state, independently of the value of the Coulomb repulsion U.

As can be realized by the treatments of this problem, the nature of magnetism of the ground state of molecules and of solids in general, namely, whether or not the spin configuration is one in which the spins are aligned (ferromagnetism) or anti-aligned (antiferromagnetism), is a matter of solving the electronic problem correctly. It has nothing to do with the direct bare spin–spin interaction between the electrons. The latter effect is negligible. To gain some further understanding about this issue, we recommend Problem 2.

27.5 Problems

Problem 1

Use the idea of linear combination of atomic orbitals (LCAO) to write the wavefunction of the electron in the H_2^+ ion as

$$\psi(\vec{r}) = a\psi_1(\vec{r}) + b\psi_2(\vec{r}), \tag{27.63}$$

where

$$\psi_1(\vec{r}) = \frac{1}{\sqrt{\pi a_0^3}} \exp(-|\vec{r} - \vec{R}_1|/a_0), \tag{27.64}$$

$$\psi_2(\vec{r}) = \frac{1}{\sqrt{\pi a_0^3}} \exp(-|\vec{r} - \vec{R}_2|/a_0). \tag{27.65}$$

(a) Use the integration method to show that the results of the integrals below are given by

$$T(R) \equiv \int d^3r \psi_1(\vec{r})\psi_2(\vec{r}) = \Big(1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2}\Big)e^{-R/a_0}, \tag{27.66}$$

$$\int d^3r |\psi_A(\vec{r})|^2 \frac{e^2}{|\vec{r} - \vec{R}|} = \frac{e^2}{R}(1 - e^{-2R/a_0}) - \frac{e^2}{a_0}e^{-2R/a_0}, \tag{27.67}$$

$$\int d^3r \psi_1(\vec{r})\psi_2(\vec{r}) \frac{e^2}{|\vec{r} - \vec{R}|} = \frac{e^2}{a_0}(1 + \frac{R}{a_0})e^{-R/a_0}. \tag{27.68}$$

(b) Plot the even (bonding) wavefunction $\psi_+(r)$ and the odd (antibonding) wavefunction $\psi_-(r)$ for the H_2^+ ion as a function of r/a_0 for $R/a_0 = 2$ and $R/a_0 = 4$. In addition, compare $|\psi_+(r)|^2$ with $|\psi_-(r)|^2$ for $R/a_0 = 2$ and $R/a_0 = 4$. By examining these plots of the wavefunctions and by using a simple argument, can you explain why the even wavefunction gives lower energy than the odd wavefunction?

Problem 2

Consider the solution of the Hubbard model as was applied to the hydrogen molecule for the spin-singlet and spin-triplet state. Assume that the following quantum spin-1/2 Heisenberg model:

$$H = J\hat{\vec{s}}_1 \cdot \hat{\vec{s}}_2 + C, \tag{27.69}$$

where $\hat{\vec{s}}_{1,2}$ are spin-1/2 operators, describes the effective spin–spin interaction of the two electrons in the hydrogen molecule. This is an effective phenomenological Hamiltonian to describe the low-lying spin excitations and the nature of the ground state of the spin sector of the hydrogen molecule.

(a) Show that the above Hamiltonian can share the same energy splitting between the triplet and singlet states of the hydrogen atom. What should the value of J be in order for the two spectra to agree? Notice that we can always add an overall constant to the Hamiltonian, which does not affect the physics of the problem.

(b) What is the value of J in the limit of large U/t_s, the so-called strong correlation limit of the Hubbard model?

28

The elasticity field

In this chapter, we treat a monoatomic and a diatomic chain of atoms interacting with harmonic springs. First, we find the classical normal modes and then we quantize them. This part is also useful in order to draw an analogy with the problem of quantization of the electromagnetic field which is investigated in the next chapter.

28.1 Monoatomic chain

Let us consider the 1D monoatomic chain as a first example to illustrate how one introduces the phonon modes and their quantization. We shall follow the Hamiltonian formalism for both the classical and quantum treatment of the problem for uniformity and for pedagogical purposes. Thus, we shall consider the 1D chain of N atoms and periodic boundary conditions as illustrated in Fig. 28.1.

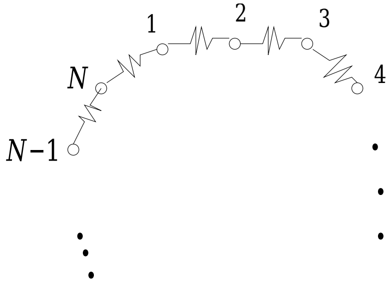

Fig. 28.1 Monoatomic chain of atoms interacting with harmonic springs.

Let the atomic displacement of the nth atom be denoted by u_n and the corresponding momentum by P_n. The Hamiltonian of this problem in the harmonic approximation can be expressed as:

$$H = \sum_{n=1}^{N} \left(\frac{P_n^2}{2M} + \frac{1}{2} G (u_{n+1} - u_n)^2 \right). \tag{28.1}$$

The coupling constant G is the second derivative of the interaction between nearest neighbor atoms with respect to the displacement from the equilibrium location $R = na$ on the 1D Bravais lattice with lattice spacing a.

Practical Quantum Mechanics. First Edition. Efstratios Manousakis.

28.1.1 Classical treatment

First we shall solve the problem at the classical level. The classical equations of motion for the coordinates u_n of the nth atom are the following

$$M\frac{\partial^2 u_n}{\partial t^2} = -G(2u_n - u_{n+1} - u_{n-1}). \tag{28.2}$$

A partial solution of the above equation is of the form

$$u_n(t) = u_k(\omega)e^{i(kna-\omega t)}. \tag{28.3}$$

Substituting the above form in Eq. (28.2) we find that the following condition between ω and k must be satisfied in order for this form to be a solution:

$$\omega = \omega_k \equiv 2\sqrt{\frac{G}{M}}|sin\frac{ka}{2}|. \tag{28.4}$$

In addition, we need to impose that our solution (28.3) should satisfy the periodic boundary conditions, namely $u_{n+N}(t) = u_n(t)$ which implies that k should take N discrete values given by

$$k = \frac{2\pi}{Na}m, \qquad m = 0, \pm 1, \pm 2, ..., \tag{28.5}$$

$$\frac{-N}{2} \leq m < \frac{N}{2}, \tag{28.6}$$

and thus k must be inside the first Brillouin Zone (1BZ). (The meaning of the 1BZ has been discussed in chapter 3 and in chapter 10 and elsewhere.) Thus, as expected, there are N independent modes given by Eq. (28.3) which are obtained for N different wavevectors k and are characterized by frequencies $\omega = \omega_k$. Notice that in the long-wavelength ω_k is linear with k, namely $\lim_{ka\to 0}\omega_k = ck$ where $c = \sqrt{G/M}a$ is the velocity of elastic waves (sound velocity) in the 1D crystal.

We can look at the classical problem from a slightly different point of view. Let us transform the set of the degrees of freedom u_n where $n = 1, 2, ..., N$ to the following set

$$\tilde{u}_k \equiv \frac{1}{\sqrt{N}}\sum_n u_n e^{ikna}. \tag{28.7}$$

The new label k takes the above mentioned N different values from inside the first Brillouin zone. Therefore this transformation transforms the original N degrees of freedom to a new set of also N collective degrees of freedom. Now, if we define the following momentum variables as

$$\tilde{P}_k \equiv \frac{1}{\sqrt{N}}\sum_n P_n e^{-ikna}, \tag{28.8}$$

we can easily show that the following is true for the classical Poisson brackets:

$$\left[\tilde{u}_k, \tilde{P}_{k'}\right]_{P.B} = \delta_{k,k'}. \tag{28.9}$$

This implies that the variables $\tilde{P}_k$ as defined above are the canonically conjugate momenta to the collective position variables $\tilde{u}_k$.

The inverse transformation is given by

$$u_n \equiv \frac{1}{\sqrt{N}} \sum_k \tilde{u}_k e^{-ikna}, \tag{28.10}$$

$$P_n \equiv \frac{1}{\sqrt{N}} \sum_k \tilde{P}_k e^{ikna}. \tag{28.11}$$

Again the summation is over the N different values of k inside the first Brillouin zone. A straightforward substitution of the above expressions for u_n and P_n in Eq. 28.1 gives

$$H = \sum_k H_k, \tag{28.12}$$

$$H_k = \frac{|\tilde{P}_k|^2}{2M} + \frac{1}{2} M\omega_k^2 |\tilde{u}_k|^2, \tag{28.13}$$

where ω_k is the same function as (28.4). Thus, the new Hamiltonian describes a set N of non-interacting degrees of freedom of a collective nature $\tilde{u}_k$ with conjugate momenta $\tilde{P}_k$. Each of these non-interacting degrees of freedom is a harmonic oscillator with a frequency that depends on k.

28.1.2 Quantization of the phonon field

We have been able to perform a unitary transformation and cast the Hamiltonian in a form that describes a set of non-interacting harmonic modes with a band of frequencies $\omega = \omega_k$. A very analogous procedure can be followed for the quantum mechanical version of the problem. We will follow the procedure introduced in chapter 11 for the solution to the harmonic oscillator problem using the formalism of creation and annihilation operators.

Following the canonical quantization procedure, we define the atomic displacement and momentum operators $\hat{u}_n$ and $\hat{P}_n$ and we keep the form of the Hamiltonian (28.1) and we replace u_n and P_n by their corresponding operators. These operators should obey the standard commutation relations

$$[\hat{u}_n, \hat{P}_{n'}] = i\hbar\delta_{n,n'}, \tag{28.14}$$

$$[\hat{u}_n, \hat{u}_{n'}] = [\hat{P}_n, \hat{P}_{n'}] = 0. \tag{28.15}$$

We then perform a transformation identical to the one given by Eqs. 28.7–28.8 to new operators $\hat{\tilde{u}}_k$ and $\hat{\tilde{P}}_k$ and the Hamiltonian operator takes the same form given by Eqs. 28.12–28.13 as in the classical treatment with $\tilde{u}_k$ and $\tilde{P}_k$ replaced by $\hat{\tilde{u}}_k$ and $\hat{\tilde{P}}_k$ respectively. The difference in the algebraic manipulations between the classical and quantum treatment is that the operators do not commute; however, neither the transformation nor the two terms of the Hamiltonian mix these non-commuting operators.

It is straightforward to show that the new operators follow the standard canonical commutation relations:

$$[\hat{\tilde{u}}_k, \hat{\tilde{P}}_{k'}] = i\hbar\delta_{k,k'}, \tag{28.16}$$

$$[\hat{\tilde{u}}_k, \hat{\tilde{u}}_{k'}] = [\hat{\tilde{P}}_k, \hat{\tilde{P}}_{k'}] = 0. \tag{28.17}$$

Following the approach of solving the problem of a single harmonic oscillator, we define the following operators:

$$a_k \equiv \sqrt{\frac{M\omega_k}{2\hbar}}\hat{\tilde{u}}_k + i\sqrt{\frac{1}{2\hbar M\omega_k}}\hat{\tilde{P}}_{-k}, \tag{28.18}$$

$$a^{\dagger}_{-k} \equiv \sqrt{\frac{M\omega_k}{2\hbar}}\hat{\tilde{u}}_k - i\sqrt{\frac{1}{2\hbar M\omega_k}}\hat{\tilde{P}}_{-k}. \tag{28.19}$$

Using the commutations relations given by Eq. 28.17, we can easily show that these operators satisfy the commutation relations obeyed by Boson creation and annihilation operators, that is,

$$[a_k, a^{\dagger}_{k'}] = \delta_{k,k'}, \tag{28.20}$$

$$[a_k, a_{k'}] = [a^{\dagger}_k, a^{\dagger}_{k'}] = 0. \tag{28.21}$$

Eqs. 28.18–28.19 can be solved for $\hat{\tilde{u}}_k$ and $\hat{\tilde{P}}_k$ in terms of a_k and $a^{\dagger}_k$ and by straightforward substitution, the Hamiltonian can be expressed in terms of the above creation and annihilation operators as follows:

$$\hat{H} = \sum_k \hbar\omega_k(a^{\dagger}_k a_k + \frac{1}{2}). \tag{28.22}$$

Therefore, the Hamiltonian is a sum of N independent harmonic oscillator with characteristic frequencies given by ω_k. The ground state of the system of the N oscillators is a state that is annihilated by all the a_k operators:

$$a_k|\Psi_0\rangle = 0. \tag{28.23}$$

As in the case of a single harmonic oscillator, the eigenstates of the Hamiltonian are shared with the number operator $\hat{n}_k = a^{\dagger}_k a_k$. Thus, the energy eigenstates are all the states obtained as follows

$$|\{n_k\}\rangle = \prod_k \frac{1}{\sqrt{n_k!}}(a^{\dagger}_k)^{n_k}|\Psi_0\rangle. \tag{28.24}$$

Namely, the above state is characterized by the number n_k of quanta of the harmonic oscillator of type k present. An elementary excitation where the mode k is populated by only one quantum is called one-phonon of frequency ω_k. The reason for this quasi-particle (that is, phonon) interpretation of the excitation spectrum of these modes is the following. First, the energy excitation spectrum for any given mode is evenly spaced. This allows us to think that the first excitation corresponds to creation of one such quasi-particle, the second excitation corresponds to the creation of two such quasi-particles, and so on. Furthermore, we found that the operators which create these emerging quasi-particles obey Boson commutation relations. Thus, it is natural to give the interpretation that these phonons behave like particles which obey Bose statistics.

The ground state is a direct product over all N independent decoupled harmonic oscillators where each one is in its ground state characterized by no phonons. This state could be called: *the vacuum of the phonon field*, namely, the no-phonon state, that is, vacuum in the sense that is empty of these quasi-particles. At this point, it may be worth studying the ground-state wavefunction a bit further. The ground state of the system of these N decoupled harmonic oscillators is given by

$$\Psi_0(\{u_n\}) = \langle \{u_n\}|\Psi_0\rangle = \prod_k (\frac{M\omega_k}{\pi\hbar})^{\frac{1}{4}} exp(-M\omega_k|\tilde{u}_k|^2/2\hbar). \tag{28.25}$$

Using the expression (28.7) for $\tilde{u}_k$ we obtain

$$\Psi_0(\{u_n\}) = Cexp(-\sum_{n,m} f_{n-m}u_n u_m), \tag{28.26}$$

where C is a normalization constant and

$$f_{n-m} = \frac{M}{2\hbar N}\sum_k \omega_k e^{ik(n-m)a}. \tag{28.27}$$

Notice that the ground-state wavefunction represents a system of degrees of freedom $u_1, u_2, ...u_N$ which are correlated at a long distance from one another. The first exercise of the problem set of this section deals with the precise form of correlation factor f_{n-m} for the 1D monoatomic chain. If one takes the limit of an infinite chain, then when $n-m$ is even $f_{n-m} = 0$, while for odd values of $n-m$ $f_{n-m} = \frac{8\sqrt{GM}}{\pi\hbar}\frac{1}{2(n-m)+1}$

28.2 Diatomic chain

Now, we shall add some complication to the problem by considering a diatomic 1D chain as illustrated in Fig. 28.2 where the lattice spacing of the corresponding Bravais lattice is a (i.e, the distance between adjacent unit cells, each containing a pair of atoms) and there are two different spring constants G_1 and G_2 and N unit cells ($2N$ atoms). In this more complicated problem, we will find out that for any given value of the wavevector k there are two different modes because there are two different degrees of freedom in each unit cell. This is analogous to the modes of the electromagnetic field where for each wavevector there are two modes which correspond to the two transverse directions of polarization. If we consider a 3D lattice of atoms, we will

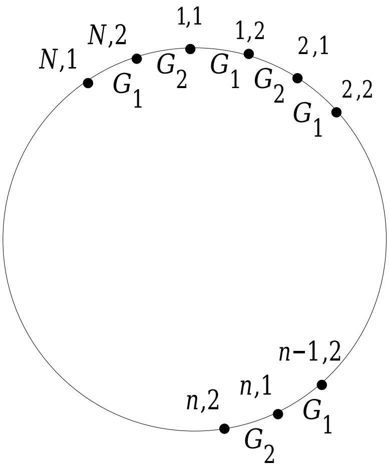

Fig. 28.2 Diatomic chain of atoms interacting with harmonic springs.

find three different directions of polarization for phonons, that is, two transverse and one longitudinal polarization. As we will see, there is no longitudinal polarization for photons due to the gauge invariance.

We need to introduce two different displacements $u_{1,n}$ and $u_{2,n}$ of the two atoms in the nth unit cell and their corresponding momenta denoted by $P_{1,n}$ and $P_{2,n}$ respectively. The Hamiltonian of this problem in the harmonic approximation can be expressed as:

$$\begin{aligned} H = \sum_{n=1}^{N} \bigg(& \frac{P_{1,n}^2}{2M} + \frac{P_{2,n}^2}{2M} \\ & + \frac{1}{2} G_1 (u_{1,n} - u_{2,n})^2 + \frac{1}{2} G_2 (u_{1,n} - u_{2,n-1})^2 \bigg). \end{aligned} \tag{28.28}$$

28.2.1 Classical treatment

The classical equations of motion for this problem are the following

$$M \frac{\partial^2 u_{1,n}}{\partial t^2} = -G_1 (u_{1,n} - u_{2,n}) - G_2 (u_{1,n} - u_{2,n-1}), \tag{28.29}$$

$$M \frac{\partial^2 u_{2,n}}{\partial t^2} = -G_1 (u_{2,n} - u_{1,n}) - G_2 (u_{2,n} - u_{1,n+1}). \tag{28.30}$$

A partial solution of the above equation is of the form

$$u_{1,n}(t) = \epsilon_1 e^{i(kna - \omega t)}, \tag{28.31}$$

$$u_{2,n}(t) = \epsilon_2 e^{i(kna - \omega t)}. \tag{28.32}$$

Substituting the above form in Eqs. 28.29–28.30 we find a system of two equations which can be cast in the following matrix form:

$$\begin{pmatrix} G_1+G_2 & -(G_1+G_2e^{-ika}) \\ -(G_1+G_2e^{ika}) & G_1+G_2 \end{pmatrix} \begin{pmatrix} \epsilon_1 \\ \epsilon_2 \end{pmatrix} = M\omega^2 \begin{pmatrix} \epsilon_1 \\ \epsilon_2 \end{pmatrix}.$$

The above matrix equation has the form of an eigenvalue problem and it is of the form $D(k)\epsilon_k = \lambda_k\epsilon_k$ where $D(k)$ is a 2×2 matrix which depends only on k and is independent of ω. Thus, the eigenvalues and eigenvectors depend on k and thus, ω depends on k. Diagonalizing the matrix $D(k)$, which is called the "dynamical matrix," we find the following two eigenvalues:

$$\omega_k^{(\pm)2} = \frac{1}{M}\left(G_1+G_2 \pm \sqrt{G_1^2+G_2^2+2G_1G_2coska}\right), \tag{28.33}$$

with corresponding eigenvectors:

$$\frac{\epsilon_{1,k}^{\pm}}{\epsilon_{2,k}^{\pm}} = \mp\frac{G_1+G_2e^{-ika}}{|G_1+G_2e^{-ika}|}. \tag{28.34}$$

If we normalize these eigenvectors, we obtain,

$$\epsilon_{1,k}^{\pm} = \mp\frac{1}{\sqrt{2}}\frac{G_1+G_2e^{-ika}}{|G_1+G_2e^{-ika}|}. \tag{28.35}$$

$$\epsilon_{2,k}^{\pm} = \frac{1}{\sqrt{2}}. \tag{28.36}$$

As in the monoatomic chain, there are only N different values of k, obtained by applying periodic boundary conditions on the $u_{i,n}$, and they are identical to those given by Eq. (28.6) with a, now, the unit-cell to unit-cell distance. Notice that the number of degrees of freedom is conserved before and after the solution to the problem, that is, we have $2N$ atomic displacements $(u_{1,1}, u_{2,1}, u_{1,2}, u_{2,2}, ..., u_{1,N}, u_{2,N})$ and at the end of the calculation we end up with $2N$ different modes, that is, N different k-values in the first Brillouin zone and two branches shown in Fig. 28.3.

The lower branch which is linear in the long wavelength limit ($ka << 1$) is the so-called *acoustic* branch, while the upper corresponds to the so-called *optical* phonons. Eq. 28.34 suggests that in the long wavelength limit, for acoustic modes $\epsilon_1^- = \epsilon_2^-$, while for optical phonons $\epsilon_1^+ = -\epsilon_2^+$. Thus, in the case of acoustic phonons the two atoms in the unit cell move towards the same direction in the long wavelength limit, while optical phonons move in opposite directions. In the case of ionic crystals in which the two atoms may have different charges in the case of optical modes, the atomic oscillations in opposite directions give rise to an electric dipole moment, which couples to the light and these modes can be optically activated.

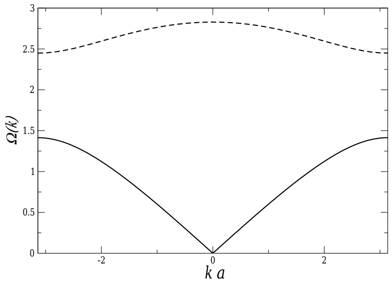

Fig. 28.3 Frequency-wavevector dispersion of the phonon modes of a diatomic chain.

28.2.2 Quantum mechanical treatment

Following the canonical quantization procedure, we substitute the momenta $P_{i,n}$ and the atomic displacements $u_{i,n}$ in the Hamiltonian (28.28) by the corresponding operators which follow the standard commutation relations. As in the case of the monoatomic chain, we take advantage of the translational invariance by introducing new operators $\hat{\hat{P}}_{i,k}$ and $\hat{\hat{u}}_{i,k}$ ($i = 1, 2$ for each atom) as follows:

$$\hat{\hat{u}}_{i,k} \equiv \frac{1}{\sqrt{N}} \sum_n \hat{u}_{i,n} e^{ikna}, \tag{28.37}$$

$$\hat{\hat{P}}_{i,k} \equiv \frac{1}{\sqrt{N}} \sum_n \hat{P}_{i,n} e^{-ikna}. \tag{28.38}$$

The new label k takes N different values from inside the first Brillouin zone. The inverse transformation is easily obtained as

$$\hat{u}_{i,n} \equiv \frac{1}{\sqrt{N}} \sum_k \hat{\hat{u}}_{i,k} e^{-ikna}, \tag{28.39}$$

$$\hat{P}_{i,n} \equiv \frac{1}{\sqrt{N}} \sum_k \hat{\hat{P}}_{i,k} e^{ikna}. \tag{28.40}$$

In terms of the new operators, which also obey canonical commutation rules (the reader is encouraged to show this), the Hamiltonian takes the following form:

$$H = \sum_k \left(\frac{\hat{\hat{P}}^2_{1,k}}{2M} + \frac{\hat{\hat{P}}^2_{2,k}}{2M} + \frac{1}{2} \hat{u}^*_{i,k} D_{ij}(k) \hat{u}_{j,k} \right), \tag{28.41}$$

where the $D_{ij}(k)$ is the dynamical matrix defined earlier, and a summation over the i and j indices is implied. Notice that, as far as the k-variable is concerned, the above

Hamiltonian is diagonal; however, the labels of the atoms in the unit cell do couple in the second term. This Hamiltonian can be also diagonalized within the unit cell by performing the same transformation which diagonalizes the dynamical matrix in the classical treatment. Namely, if we define the transformation

$$U = \begin{pmatrix} \epsilon_1^+ & \epsilon_2^+ \\ \epsilon_1^- & \epsilon_2^- \end{pmatrix},$$

the matrix $L = U^\dagger D U$ is diagonal. Here we have dropped the k-dependence of the eigenvectors and of the matrix for simplification of the notation. The second term of the Hamiltonian (28.41), which is of the form $\tilde{\mathbf{u}} D \tilde{\mathbf{u}}$ (where $\tilde{\mathbf{u}} = \begin{pmatrix} \tilde{u}_1 \\ \tilde{u}_2 \end{pmatrix}$), can be rewritten as $\tilde{\mathbf{u}} U^\dagger U D U^\dagger U \tilde{\mathbf{u}} = \Upsilon^* L \Upsilon$, where the new vector $\boldsymbol{\Upsilon} = U\tilde{\mathbf{u}}$. Thus, the second term can be written as $\tilde{\mathbf{u}} D \tilde{\mathbf{u}} = \lambda^+ |\Upsilon^+|^2 + \lambda^- |\Upsilon^-|^2$ where $\Upsilon^\pm$ are the two components of the vector Υ and $\lambda^\pm = M\omega^{\pm 2}$, that is, the two eigenvalues of D. This is the standard procedure of diagonalizing the quadratic part of a Hamiltonian. Now, let us turn our attention to the kinetic energy term of the Hamiltonian. So far we have defined

$$\hat{\Upsilon}_k^{(\lambda)} = \epsilon_{1,k}^{(\lambda)*} \hat{\tilde{u}}_{1,k} + \epsilon_{2,k}^{(\lambda)*} \hat{\tilde{u}}_{2,k}, \tag{28.42}$$

where the superscript $\lambda = \pm$ stands for the two different eigenvectors found by diagonalizing D_k. It can be easily shown that the canonical momentum $\hat{\Pi}_k^{(\lambda)}$ conjugate to $\hat{\Upsilon}_k^{(\lambda)}$ (that is, $\hat{\Pi}_k^{(\lambda)} = -i\hbar \frac{\partial}{\partial \Upsilon_k^{(\lambda)}}$) is also given by

$$\hat{\Pi}_k^{(\lambda)} = \sum_i \epsilon_{i,k}^{(\lambda)} \hat{\tilde{P}}_{i,k}. \tag{28.43}$$

The transformation is unitary and thus it can be inverted very easily to yield:

$$\hat{\tilde{P}}_{i,k} = \sum_\lambda \epsilon_{i,k}^{(\lambda)*} \hat{\Pi}_k^{(\lambda)}, \tag{28.44}$$

where in our case $i = 1, 2$. By straightforward substitution the kinetic energy term takes a diagonal form and the Hamiltonian becomes:

$$H = \sum_{k,\lambda} \left(\frac{|\hat{\Pi}_k^{(\lambda)}|^2}{2M} + \frac{1}{2} M (\omega_k^{(\lambda)})^2 |\Upsilon_k^{(\lambda)}|^2 \right). \tag{28.45}$$

Thus, we have shown that the Hamiltonian operator can be transformed to a form which is a sum over $2N$ harmonic oscillators with frequencies given by Eq. 28.33. The steps from now on are identical to those followed in the monoatomic case. The phonon creation operators carry an additional index λ which specifies the branch and the Hamiltonian takes the form

$$H = \sum_{k,\lambda} \hbar \omega_k^{(\lambda)} (a_{\lambda,k}^\dagger a_{\lambda,k} + \frac{1}{2}), \tag{28.46}$$

and the operator $a_{\lambda,k}$ is given by Eq. 28.18 where the operators $\tilde{u}_k$ and $\tilde{P}_k$ should be replaced by $\Upsilon_k^{(\lambda)}$ and $\Pi_k^{(\lambda)}$ and ω_k by $\omega_k^{(\lambda)}$.

28.3 Problems

Problem 1

Consider a 1D monoatomic chain as shown in Fig. 28.4. Namely, a similar problem to that considered in the present chapter, but this time each atom is coupled through a spring of constant g to a fixed external point, the center of the circle. Namely consider a periodic arrangement of atoms on a circle of radius R and perimeter $L = 2\pi R$. When the atoms do not move (in the classical case) their distance is a and they have the same mass m. Let us consider a periodic array of N atoms, such that the atoms can only move along the perimeter of the circle, and let the displacement along the perimeter from the equilibrium position of the nth atom be $u_n(t)$. Each pair of atoms couple with spring-like interactions, with spring constant G. In addition, each atom in the chain is coupled to the center of the circle with a spring-like interaction of spring constant g. This means that due to this spring, the interaction energy of the nth atom with the center due to the spring is $1/2gu_n^2$.

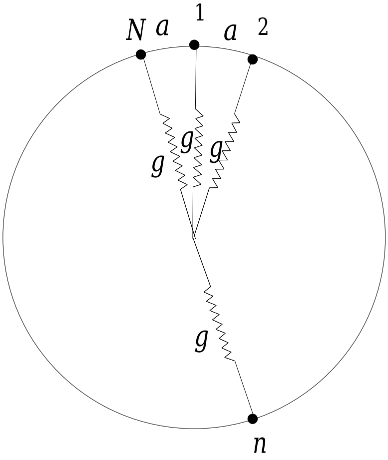

Fig. 28.4

i) Explain why the Hamiltonian of the system is

$$H = \sum_{n=1}^{N} \Big(\frac{p_n^2}{2m} + \frac{1}{2} g u_n^2 + \frac{1}{2} G (u_n - u_{n+1})^2 \Big), \tag{28.47}$$

where, p_n are the conjugate momenta to the displacements u_n. Explain why in this Hamiltonian each nearest-neighbor (n.n) interaction bond (pair of atoms) has been added only once. Have we have included all n.n interactions?

ii) What are the equations of motion for each atom in the chain?

iii) Consider the following ansatz for the time dependence of the displacements of the atom of the nth unit cell,

$$u_n(t) = \tilde{u}_k e^{i(kna-\omega t)}. \tag{28.48}$$

What are the possible values of k for periodic boundary conditions and for this circular system of N unit cells and total length $L = Na$?

Show that this ansatz satisfies the equations of motion and for a non-trivial solution it is given by

$$\omega = \omega_k = \sqrt{\frac{g + 4Gsin^2(ka/2)}{m}}. \tag{28.49}$$

How many physically acceptable solutions are there?

iv) Carry out the quantization of the problem of this monoatomic chain. Explain why the following expression

$$H = \sum_{n=1}^{N} \Big(\frac{\hat{p}_n^2}{2m} + \frac{1}{2} g \hat{u}_n^2 + \frac{1}{2} G(\hat{u}_n - \hat{u}_{n+1})^2 \Big), \tag{28.50}$$

is the Hamiltonian of the system, where $\hat{u}_n$ and $\hat{p}_n$ are the nth atom displacement and its corresponding momentum operators, and explain why these operators should obey the standard commutation relations

$$\begin{aligned} [\hat{u}_n, \hat{p}_{n'}] &= i\hbar\delta_{n,n'}, \\ [\hat{u}_n, \hat{u}_{n'}] &= [\hat{p}_n, \hat{p}_{n'}] = 0. \end{aligned} \tag{28.51}$$

v) Consider the following transformation

$$\tilde{u}_k = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{ikna} \hat{u}_n, \quad \tilde{p}_k = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{-ikna} \hat{p}_n. \tag{28.52}$$

Show that $k = (2\pi/L)m$, where $m = 0, \pm 1, \pm 2, ...$ How many values of k exist which lead to different $\tilde{u}_k$, $\tilde{p}_k$? Select an interval in k-space which contains exactly that number (the so-called Brillouin zone).

vi) Show that the inverse transformation is

$$\hat{u}_n = \frac{1}{\sqrt{N}} \sum_k e^{-ikna} \tilde{u}_k, \quad \hat{p}_n = \frac{1}{\sqrt{N}} \sum_k e^{ikna} \tilde{p}_k. \tag{28.53}$$

What values of k is the sum over?

Hint: In order to show this you may need to use the following identity, first:

$$\lim_{N\to\infty} \frac{1}{N} \sum_{m=0}^{N-1} e^{i(2\pi/N)mn} = \delta_{n,0}, \tag{28.54}$$

where $\delta_{k,0}$ is the Kronecker δ.

vii) Show that the new operators follow the standard canonical commutation relations:

$$[\tilde{u}_k, \tilde{p}_{k'}] = i\hbar\delta_{k,k'}, \tag{28.55}$$

$$[\tilde{u}_k, \tilde{u}_{k'}] = [\tilde{p}_k, \tilde{p}_{k'}] = 0. \tag{28.56}$$

Show that in terms of these new operators the Hamiltonian takes the form

$$\hat{H} = \sum_k \Big(\frac{|\tilde{p}_k|^2}{2m} + \frac{1}{2} m\omega_k^2 |\tilde{u}_k|^2 \Big), \tag{28.57}$$

where we have used the fact that $(\tilde{p}_k)^\dagger = \tilde{p}_{-k}$ and $(\tilde{u}_k)^\dagger = \tilde{u}_{-k}$ (show that this true) and ω_k is defined as

$$\omega_k = \sqrt{\frac{g + 4Gsin^2(ka/2)}{m}}. \tag{28.58}$$

29

Quantization of the free electromagnetic field

In this chapter, in a manner very analogous to that used to quantize the 1D chain of atoms coupled via spring-like constants to its neighboring atoms (see chapter 28), we will quantize the electromagnetic field in a space of volume V with periodic boundary conditions and free of sources (no static charges nor currents).

29.1 Classical treatment

First, we will use the scalar and vector potentials $\phi(\vec{x},t)$ and $\vec{A}(\vec{x},t)$ respectively, in terms of which the electric and magnetic field are given as follows:

$$\vec{E}(\vec{x},t) = -\nabla\phi(\vec{x},t) - \frac{1}{c}\partial_t\vec{A}(\vec{x},t), \tag{29.1}$$

$$\vec{B}(\vec{x},t) = \nabla\times\vec{A}(\vec{x},t). \tag{29.2}$$

If we consider free space without any sources, then we can take $\phi(\vec{x},t)$ to be constant and, therefore,

$$\vec{E}(\vec{x},t) = -\frac{1}{c}\partial_t\vec{A}(\vec{x},t), \tag{29.3}$$

$$\vec{B}(\vec{x},t) = \nabla\times\vec{A}(\vec{x},t), \tag{29.4}$$

namely, they are expressed in terms of the vector potential only. From the four Maxwell's equations only the following (in the absence of sources)

$$\nabla\times\vec{B}(\vec{x},t) = \frac{1}{c}\partial_t\vec{E}(\vec{x},t), \tag{29.5}$$

adds independent information, because the other three have already been implicitly assumed by the forms given by Eq. 29.3 and Eq. 29.4. Straightforward substitution in this equation of the expressions given by Eqs. 29.4 above, gives

$$\nabla^2\vec{A}(\vec{x},t) - \frac{1}{c^2}\frac{\partial^2\vec{A}(\vec{x},t)}{\partial t^2} - \nabla(\nabla\cdot\vec{A}(\vec{x},t)) = 0. \tag{29.6}$$

If we choose to work in the Coulomb gauge, that is,

$$\nabla\cdot\vec{A}(\vec{x},t) = 0, \tag{29.7}$$

Practical Quantum Mechanics. First Edition. Efstratios Manousakis.

the above equation takes the simpler form

$$\nabla^2 \vec{A}(\vec{x},t) - \frac{1}{c^2}\frac{\partial^2 \vec{A}(\vec{x},t)}{\partial t^2} = 0. \tag{29.8}$$

Notice that this is the familiar 3D wave equation where the vector potential is the degree of freedom which oscillates at every point in our volume V. Compare this equation with the classical equation of motion of the coupled harmonic oscillators (the monoatomic or the diatomic chain) problem when we took the continuum limit. Notice that the term $\nabla^2 \vec{A}(\vec{x},t)$ corresponds to the term $\frac{\partial^2 u(x)}{dx^2}$ in the monoatomic chain case. This last term came from the term which coupled neighboring atoms, that is, from the term $G(u_{i+1} + u_{i-1} - 2u_i)$ which gives the force to the atom in position i from the atoms at positions $i-1$ and $i+1$. We will see next that the term $\nabla^2 \vec{A}$ can also be thought of as coming from a similar interaction term between neighboring lattice sites if we put our space on a 3D finite (discrete) grid (lattice).

The energy of the free electromagnetic field is given by

$$\mathcal{E} = \frac{1}{8\pi}\int d^3x\Big(|\vec{E}(\vec{x},t)|^2 + |\vec{B}(\vec{x},t)|^2\Big). \tag{29.9}$$

Using the expressions given by Eqs. 29.4 we obtain

$$\mathcal{E} = \frac{1}{8\pi}\int d^3x\Big(\frac{1}{c^2}|\partial_t \vec{A}(\vec{x},t)|^2 + |\nabla \times \vec{A}(\vec{x},t)|^2\Big). \tag{29.10}$$

Let us compare this expression with the energy of the monoatomic chain, that is,

$$\mathcal{E}_C = \sum_i \Big(\frac{1}{2}m|\partial_t u_i(t)|^2 + \frac{1}{2}G|u_{i+1}(t) - u_i(t)|^2\Big). \tag{29.11}$$

Notice that in the continuum limit where the spacing a between the atoms in the chain goes to zero by keeping the product $Ga^2 = mc_s^2$ finite (this corresponds to a finite compressibility), where c_s is the sound velocity in the chain (see chapter 28), we obtain

$$\mathcal{E}_C = \frac{1}{2a}mc_s^2\int dx\Big(\frac{1}{c_s^2}|\partial_t u(x,t)|^2 + |\frac{\partial u(x,t)}{dx}|^2\Big). \tag{29.12}$$

Notice the similarity of the two problems. Namely, apart from a constant $C = 1/(2a)mc_s^2$ (which is the energy of an atom moving with the speed of sound in the chain divided by the length per atom), the two expressions are qualitatively similar. The differences come from a) the fact that the monoatomic chain is 1D, while the problem of the electromagnetic field is in 3D, and b) in the case of the electromagnetic field energy, the second term is the curl of the corresponding degree of freedom while for the monoatomic chain problem we simply have a derivative.

Inversely, if we put the electromagnetic field on a discrete lattice, we will obtain an expression with degrees of freedom $\vec{A}_i$ on every lattice point with an energy expression given by an expression containing the same "kinetic-energy" term

$$T = \frac{1}{8\pi c^2}\int d^3x|\partial_t \vec{A}(\vec{x},t)|^2, \tag{29.13}$$

involving the "velocity" $\partial_t A_i$ of the local degree of freedom and a "potential-energy"-like term coupling the degree of freedom at lattice point i to its neighbors, which has the continuum limit form

$$V = \frac{1}{8\pi}\int d^3x|\nabla \times \vec{A}(\vec{x},t)|^2, \tag{29.14}$$

such that the total energy is given by $\mathcal{E} = T + V$.

With the above observations and analogies in mind, we can write down the Lagrangian of the electromagnetic field, $L = T - V$, as follows:

$$L = \frac{1}{8\pi}\int d^3x\Big(\frac{1}{c^2}|\partial_t \vec{A}(\vec{x},t)|^2 - |\nabla \times \vec{A}(\vec{x},t)|^2\Big). \tag{29.15}$$

This is the correct form of the Lagrangian which is a function of the degrees of freedom and their time derivatives. Now, we are in a position to find the Hamiltonian of the system, that is, a function of the variables $A_i(\vec{x},t)$ and their corresponding conjugate "momenta" $\Pi_i(\vec{x},t)$. Namely, using the Lagrangian formulation where the canonical momentum is obtained as

$$\Pi_i(\vec{x},t) = \frac{\delta L}{\delta \dot{A}_i(\vec{x},t)}, \tag{29.16}$$

where $\dot{A}_i(\vec{x},t)$ stands for the time derivative of $A_i(\vec{x},t)$, we find that

$$\Pi_i(\vec{x},t) = \frac{1}{4\pi c^2}\dot{A}_i(\vec{x},t). \tag{29.17}$$

Therefore, we can find the Hamiltonian of the problem, as follows:

$$H = \int d^3x \dot{\vec{A}}(\vec{x},t)\cdot\vec{\Pi}(\vec{x},t) - L. \tag{29.18}$$

Using the result given by Eq. 29.17 we can eliminate $\dot{\vec{A}}(\vec{x},t)$ from the expression for H, because the Hamiltonian is only a function of the degrees of freedom $A_i(\vec{x},t)$ and its corresponding momenta $\Pi_i(\vec{x},t)$. We find,

$$H = \int d^3x\Big(2\pi c^2|\vec{\Pi}(\vec{x},t)|^2 + \frac{1}{8\pi}|\nabla \times \vec{A}(\vec{x},t)|^2\Big). \tag{29.19}$$

Therefore, we have been able to obtain the Hamiltonian in terms of the field degrees of freedom and its conjugate momenta. Thus, we are ready to apply the familiar Hamiltonian based quantization procedure.

29.2 Quantization

We begin with the form of the classical Hamiltonian and we make the replacements

$$A_i(\vec{x},t) \rightarrow \hat{A}_i(\vec{x}), \tag{29.20}$$
$$\Pi_i(\vec{x},t) \rightarrow \hat{\Pi}_i(\vec{x}), \tag{29.21}$$

where these are now operators which obey the following commutation relations

$$\left[\hat{A}_i(\vec{x}), \hat{A}_j(\vec{x}')\right] = 0, \tag{29.22}$$
$$\left[\hat{\Pi}_i(\vec{x}), \hat{\Pi}_j(\vec{x}')\right] = 0, \tag{29.23}$$
$$\left[\hat{A}_i(\vec{x}), \hat{\Pi}_j(\vec{x}')\right] = i\hbar\delta_{i,j}\delta(\vec{x}-\vec{x}'). \tag{29.24}$$

With this substitution, the Hamiltonian operator can be diagonalized by means of the following transformation

$$\tilde{A}_{\vec{k},\lambda} = \frac{1}{\sqrt{V}}\int d^3x \vec{\epsilon}_\lambda(\vec{k})\cdot\vec{A}(\vec{x})e^{i\vec{k}\cdot\vec{x}}, \tag{29.25}$$
$$\tilde{\Pi}_{\vec{k},\lambda} = \frac{1}{\sqrt{V}}\int d^3x \vec{\epsilon}_\lambda(\vec{k})\cdot\vec{\Pi}(\vec{x})e^{i\vec{k}\cdot\vec{x}}. \tag{29.26}$$

This is a Fourier transformation of the vector operators $\vec{A}(\vec{x})$ and $\vec{\Pi}(\vec{x})$ and, in addition, we have taken their projection onto the polarization direction $\vec{\epsilon}_\lambda(\vec{k})$. Because of gauge invariance which allows us to work within the Coulomb gauge there are only the two transverse polarization directions; namely, Eq. 29.7 has to be imposed on the operator $\hat{\vec{A}}(\vec{x})$, that is,

$$\nabla\cdot\hat{\vec{A}}(\vec{x}) = 0, \tag{29.27}$$

which also leads to:

$$\vec{k}\cdot\vec{\epsilon}_\lambda(\vec{k}) = 0. \tag{29.28}$$

Thus, we can choose two unit vectors $\vec{\epsilon}_\lambda(\vec{k})$, that is, $\lambda = 1, 2$, which satisfy the following conditions

$$\vec{\epsilon}_1(\vec{k}).\vec{\epsilon}_2(\vec{k}) = 0, \tag{29.29}$$
$$\vec{\epsilon}_\lambda(\vec{k}).\vec{\epsilon}_\lambda(\vec{k}) = 1. \tag{29.30}$$

The inverse transformation is given by

$$\hat{\vec{A}}(\vec{x}) = \frac{1}{\sqrt{V}}\sum_{\vec{k}}\sum_{\lambda}\vec{\epsilon}_\lambda(\vec{k})\tilde{A}_{\vec{k},\lambda}e^{-i\vec{k}\cdot\vec{x}}, \tag{29.31}$$
$$\hat{\vec{\Pi}}(\vec{x}) = \frac{1}{\sqrt{V}}\sum_{\vec{k}}\sum_{\lambda}\vec{\epsilon}_\lambda(\vec{k})\tilde{\Pi}_{\vec{k},\lambda}e^{-i\vec{k}\cdot\vec{x}}. \tag{29.32}$$

It is straightforward to show that these transformed operators obey the commutation relations

$$\left[\tilde{A}_{\vec{k},\lambda}, \tilde{A}_{\vec{k}',\lambda'}\right] = 0, \tag{29.33}$$

$$\left[\tilde{\Pi}_{\vec{k},\lambda}, \tilde{\Pi}_{\vec{k}',\lambda'}\right] = 0, \tag{29.34}$$

$$\left[\tilde{A}_{\vec{k},\lambda}, \tilde{\Pi}_{\vec{k}',\lambda'}\right] = i\hbar\delta_{\lambda,\lambda'}\delta(\vec{k} - \vec{k}'). \tag{29.35}$$

After substitution in Eq. 29.19, and carrying out the integration over $\vec{x}$, we obtain

$$\hat{H} = \sum_{\vec{k}} \sum_{\lambda} \hat{h}_{\vec{k},\lambda}, \tag{29.36}$$

$$\hat{h}_{\vec{k},\lambda} = 2\pi c^2 |\tilde{\hat{\Pi}}_{\vec{k},\lambda}|^2 + \frac{1}{8\pi} k^2 |\tilde{\vec{A}}_{\vec{k},\lambda}|^2. \tag{29.37}$$

This means that the problem is solved, because we were able to transform the Hamiltonian into a sum of decoupled Hamiltonians each of which represents a familiar harmonic oscillator. The "mass" of each such harmonic oscillator and their corresponding frequency is obtained by setting

$$m^* \equiv \frac{1}{4\pi c^2}, \tag{29.38}$$

and the frequency $\omega(k)$ is defined by the requirement

$$\frac{1}{2} m^* \omega(k)^2 \equiv \frac{1}{8\pi} k^2, \tag{29.39}$$

which leads to

$$\omega(k) = ck, \tag{29.40}$$

and the Hamiltonian takes the form

$$\hat{H} = \sum_{\vec{k}} \sum_{\lambda} \hat{h}_{\vec{k},\lambda}, \tag{29.41}$$

$$\hat{h}_{\vec{k},\lambda} = \frac{|\tilde{\hat{\Pi}}_{\vec{k},\lambda}|^2}{2m^*} + \frac{1}{2} m^* \omega(k)^2 |\tilde{\vec{A}}_{\vec{k},\lambda}|^2. \tag{29.42}$$

This situation is very similar to the case of the monoatomic chain. Each harmonic term can be diagonalized by means of the familiar transformation:

$$a_{\vec{k},\lambda} = \sqrt{\frac{m^*\omega(k)}{2\hbar}} \tilde{A}_{\vec{k},\lambda} + i\sqrt{\frac{1}{2\hbar m^* \omega(k)}} \tilde{\Pi}_{-\vec{k},\lambda}, \tag{29.43}$$

$$a^\dagger_{-\vec{k},\lambda} = \sqrt{\frac{m^*\omega(k)}{2\hbar}} \tilde{A}_{\vec{k},\lambda} - i\sqrt{\frac{1}{2\hbar m^* \omega(k)}} \tilde{\Pi}_{-\vec{k},\lambda}, \tag{29.44}$$

obeying the commutation relations

$$\left[a_{\vec{k},\lambda}, a_{\vec{k}',\lambda'}\right] = \left[a^\dagger_{\vec{k},\lambda}, a^\dagger_{\vec{k}',\lambda'}\right] = 0, \tag{29.45}$$

$$\left[a_{\vec{k},\lambda}, a^\dagger_{\vec{k}',\lambda'}\right] = \delta_{\vec{k},\vec{k}'}\delta_{\lambda,\lambda'}, \tag{29.46}$$

in terms of which the Hamiltonian takes the familiar form

$$\hat{H} = \sum_{\vec{k}}\sum_{\lambda} \hbar\omega(k)\Big(a^\dagger_{\vec{k},\lambda}a_{\vec{k},\lambda} + \frac{1}{2}\Big), \tag{29.47}$$

$$\omega(k) = ck. \tag{29.48}$$

The spectrum of each mode specified by the wavevector $\vec{k}$ and the polarization direction λ, is given by

$$E_{\vec{k},\lambda} = \hbar\omega(k)(n_{\vec{k},\lambda} + \frac{1}{2}), \tag{29.49}$$

where $n_{\vec{k},\lambda} = 0, 1, 2, ...$ is an integer giving the number of quanta, the number of photons, which occupy this mode. Namely, the nth excited state of this harmonic oscillator can also be interpreted as a state occupied by n Bosons, since the energy spectrum is equally spaced, and the commutation relation for the corresponding creation operators (Eqs. 29.45, 29.46) is that of Bosons. These Bosons, the photons, are created by the operator $a^\dagger_{\vec{k},\lambda}$ acting on the ground state of the electromagnetic field which is the state with $n_{\vec{k},\lambda} = 0$ for all modes, that is, all wavevectors $\vec{k}$ and all polarization vectors λ. The ground state of the electromagnetic field is the no-photon state.

29.3 Problems

Problem 1

(a) Show that using the Lagrangian given by Eq. 29.15 the Hamiltonian of the electromagnetic field is given by

$$H = \int d^3x\Big(2\pi c^2|\vec{\Pi}(\vec{x},t)|^2 + \frac{1}{8\pi}|\nabla \times \vec{A}(\vec{x},t)|^2\Big). \tag{29.50}$$

(b) Begin with this form of the classical Hamiltonian and make the replacements

$$A_i(\vec{x},t) \to \hat{A}_i(\vec{x}) \tag{29.51}$$

$$\Pi_i(\vec{x},t) \to \hat{\Pi}_i(\vec{x}), \tag{29.52}$$

where these are now *operators* which are taken to obey the canonical commutation relations (canonical quantization).

(c) Show all the steps described in section 29.2 leading to Eqs. 29.41, 29.42.

Problem 2

(a) Show that following the steps outlined in section 29.2 the Hamiltonian can be transformed to the familiar form

$$\hat{H} = \sum_{\vec{k}} \sum_{\lambda} \hbar\omega(k)\left(a^{\dagger}_{\vec{k},\lambda} a_{\vec{k},\lambda} + \frac{1}{2}\right)$$
$$\omega = ck. \tag{29.53}$$

(b) Explain why the spectrum of each mode specified by the wavevector $\vec{k}$ and the polarization direction λ, is given by

$$e_{\vec{k},\lambda} = \hbar\omega(k)(n_{\vec{k},\lambda} + 1/2), \tag{29.54}$$

where $n_{\vec{k},\lambda} = 0, 1, 2, ...$ is an integer giving the number of quanta, the number of photons, which occupy this mode.

Problem 3

(a) Use the creation and annihilation operators to write down the excited state of the electromagnetic field which corresponds to the following occupation numbers: $n_{\vec{k}_0\lambda_0} = 2$, $n_{-\vec{k}_0\lambda_0} = 2$, where $(\vec{k}_0, \lambda_0)$ is a particular wavevector $\vec{k}$ and polarization λ, and for all other values of $(\vec{k}, \lambda)$ the occupation numbers are zero, that is, $n_{\vec{k}\lambda} = 0$.

(b) Which normal modes are excited and how many and what type of photons are present in the state which is discussed in part (a)?

(c) Write down the wavefunction of the ground state (that is, the vacuum or no-photon state) of the electromagnetic field, that is, the probability amplitude for a given field configuration defined by $\tilde{A}_{\vec{k},\lambda}$ specified by all possible values of $(\vec{k}, \lambda)$.

30

Interaction of radiation with charged particles

In this chapter we treat fully quantum mechanically the interaction of charged particles with a fluctuating electromagnetic field using time-dependent pertutbation theory. We discuss absorption, spontaneous emission and stimulated emission in atomic physcs.

30.1 The total Hamiltonian

In order to obtain the form of the Hamiltonian of the electromagnetic field interacting with charged particles we need to make the minimal substitution

$$\vec{p} \to \vec{p} - \frac{e}{c}\vec{A}. \tag{30.1}$$

The total Hamiltonian, which includes the electromagnetic field part, the matter part, and the interaction of the EM field with matter, is the following:

$$\begin{aligned}\hat{H} &= \sum_{\vec{k}}\sum_{\lambda} \hbar\omega(k)\Big(a^{\dagger}_{\vec{k},\lambda}a_{\vec{k},\lambda} + \frac{1}{2}\Big) \\ &+ \frac{1}{2m}\int \psi^{\dagger}(\vec{r})\Big(-i\hbar\nabla - \frac{e}{c}\vec{A}\Big)^2 \psi(\vec{r})d^3r \\ &- e\int d^3r\phi(\vec{r})\psi^{\dagger}(\vec{r})\psi(\vec{r}) + \hat{V}.\end{aligned} \tag{30.2}$$

Let us explain each term separately. The first term is the Hamiltonian of the electromagnetic field as derived in the previous chapter, where the operator $a^{\dagger}_{\vec{k}\lambda}$ increases the occupation of photons with momentum $\vec{k}$ and polarization λ by one and, as was shown, it is given in terms of the vector potential and its corresponding conjugate momenta by the expressions given by Eq. 29.43 and Eq. 29.44 which obey the familiar Boson commutation relations given by Eq. 29.45 and Eq. 29.46.

The second term is obtained as follows. First, as was shown with regard to second quantization, any one-body operator of the form

$$\hat{O}^{(1)} = \sum_{i=1}^{N} o_i^{(1)}, \tag{30.3}$$

can be written as follows using second quantization formalism:

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$$\hat{O}^{(1)} = \sum_{\alpha} \sum_{\beta} \langle \beta | o^{(1)} | \alpha \rangle c^{\dagger}_{\alpha} c_{\beta}, \tag{30.4}$$

where we have chosen as a basis the single-particle states denoted as $|\alpha\rangle$, which are created by a general creation operator $c^{\dagger}_{\alpha}$. Now we choose to work in position representation, that is, to use the basis $|\vec{r}\rangle$ (here we have ignored spin), and the corresponding creation and annihilation operators are denoted as $\hat{\psi}^{\dagger}(\vec{r})$ and $\hat{\psi}(\vec{r})$, which add or remove a particle at position $\vec{r}$, namely

$$\psi^{\dagger}(\vec{r})|\vec{r}_1, \vec{r}_2, ..., \vec{r}_N\rangle_{\pm} = |\vec{r}, \vec{r}_1, \vec{r}_2, ..., \vec{r}_N\rangle_{\pm}, \tag{30.5}$$

and the state $|\vec{r}_1, \vec{r}_2, ..., \vec{r}_N\rangle_{\pm}$ is a properly symmetrized or antisymmetrized N particle state. In this basis the one-body operator (see chapter on second quantization) above is expressed as

$$\hat{O}^{(1)} = \int d^r d^3 r' \langle \vec{r} | o^{(1)}_1 | \vec{r}' \rangle \psi^{\dagger}(\vec{r}) \psi(\vec{r}'), \tag{30.6}$$

and in the special case of the kinetic energy operator, this leads to

$$\hat{T} = \frac{1}{2m} \int d^3 r \psi^{\dagger}(\vec{r}) (-i\hbar\nabla)^2 \psi(\vec{r}). \tag{30.7}$$

When we use the minimal substitution, that is, Eq. 30.1, we find

$$\hat{T} \rightarrow \frac{1}{2m} \int d^3 r \psi^{\dagger}(\vec{r}) (-i\hbar\nabla - \frac{e}{c}\vec{A}(\vec{r}))^2 \psi(\vec{r}). \tag{30.8}$$

This explains the presence of the second term in the expression given by Eq. 30.2 for the total Hamiltonian. The third term comes from the coupling of the charged particles to the scalar potential, that is, $-e\sum_{i=1}^{N} \phi(\vec{r}_i)$ which, being a one-body operator diagonal in position representation, in second quantization takes the form given by the third term in Eq. 30.2.

The last term in Eq. 30.2 stands for any interaction term between the charges themselves, such as the pairwise Coulomb interaction, or the interaction of the atomic electrons with the atomic nucleus, or if we are describing the case of the electrons in a solid, the interaction with the ions.

The total Hamiltonian can be separated into the following two terms

$$\hat{H} = \hat{H}_0 + \hat{H}_{int}, \tag{30.9}$$

$$\begin{aligned} H_0 = & \sum_{\vec{k}} \sum_{\lambda} \hbar\omega(k) \Big(a^{\dagger}_{\vec{k},\lambda} a_{\vec{k},\lambda} + \frac{1}{2} \Big) \\ & - \frac{\hbar^2}{2m} \int \psi^{\dagger}(\vec{r}) \nabla^2 \psi(\vec{r}) d^3 r + \hat{V}, \end{aligned} \tag{30.10}$$

$$\begin{aligned} H_{int} = & -\frac{e\hbar i}{mc} \int \psi^{\dagger}(\vec{r}) \vec{A} \cdot \nabla \psi d^3 r \\ & + \frac{q^2}{2mc^2} \int |\vec{A}|^2 \psi^{\dagger}(\vec{r}) \psi(\vec{r}) d^3 r. \end{aligned} \tag{30.11}$$

We have considered the case where the static field ϕ is a constant which can be taken to be zero. In general a similar one-body term has been included in the term $\hat{V}$

above. Notice that we considered the pure electromagnetic term and the pure matter term as the unperturbed part of the Hamiltonian, and we regarded the interaction of the charges and the external electromagnetic field as the interaction terms in a perturbation theory approach which we are ready to employ.

30.2 Absorption and emission processes

We are going to apply leading order time-dependent perturbation theory because, as it turns out, when calculating transition rates or even corrections to energy, leading non-zero terms would be proportional to the dimensionless quantity $\alpha \equiv e^2/(\hbar c)$ (we are working in cgs units), which is a dimensionless number less than 0.01. We will apply Fermi's golden rule to describe the absorption and emission of photons by an electron in an atom by neglecting spin degrees of freedom. In addition, we will only consider the effects of the first term in H_{int} as it is linear in $\vec{A}$ while the second is quadratic.

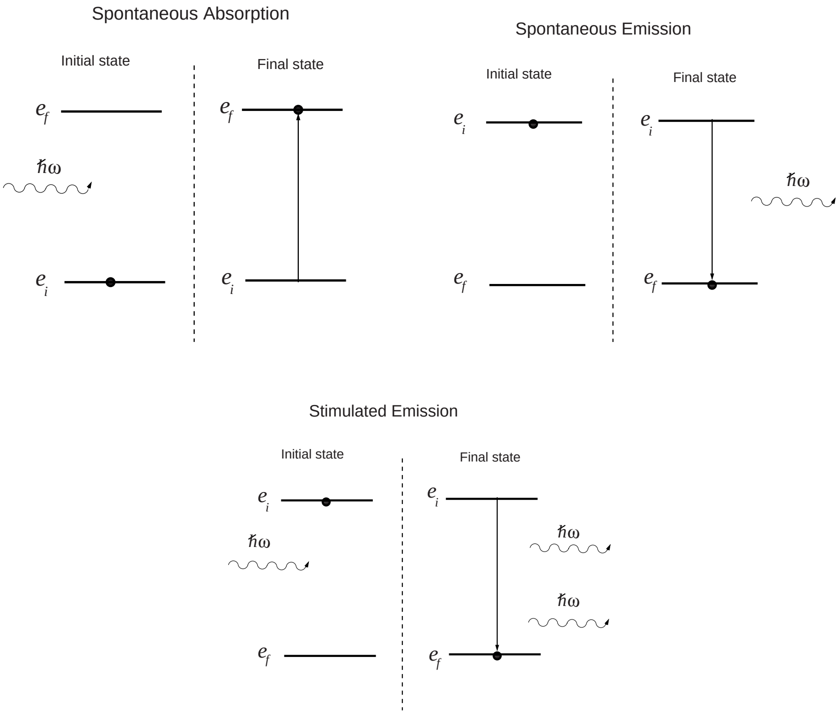

Fig. 30.1

Fermi's golden rule for transition from an initial state $|\Psi_i\rangle$ of the system (the atom plus the electromagnetic field) to a final state $|\Psi_f\rangle$ gives us the rate of transition as

$$\Gamma_{\vec{k}\lambda} = \frac{2\pi}{\hbar} |\langle \Psi_f | \hat{H}_{int} | \Psi_i \rangle|^2 \delta(E_i - E_f). \tag{30.12}$$

By simple inspection of the nature of the interaction term (first term in H_{int}, and we neglect the second term) which, using the fact that using Eqs. 29.43, 29.44, $\vec{A}$ can be expressed as

$$\hat{\vec{A}}(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{k},\lambda} \vec{\epsilon}_\lambda \tilde{A}_{\vec{k},\lambda}(\vec{k}) e^{i\vec{k}\cdot\vec{r}}, \tag{30.13}$$

$$\tilde{A}_{\vec{k},\lambda} = \sqrt{\frac{2\pi\hbar c^2}{\omega(k)}} (a_{\vec{k},\lambda} + a^\dagger_{-\vec{k},\lambda}), \tag{30.14}$$

we realize that in order to have a non-zero matrix element the initial and the final states can differ by only one photon. Namely, we write

$$|\Psi_i\rangle = |\phi_i\rangle |..., n_i(\vec{k},\lambda)...\rangle, \tag{30.15}$$

where $|\phi_i\rangle$ is the initial state of the electron which can be written as

$$|\phi_i\rangle = \int d^3r \phi_i(\vec{r}) \psi^\dagger(\vec{r}) |0\rangle_e, \tag{30.16}$$

where $|0\rangle_e$ is the no-electron state and $\psi^\dagger(\vec{r})$ creates an electron at position $\vec{r}$ when acting on the vacuum, that is,

$$\psi^\dagger(\vec{r})|0\rangle_e = |\vec{r}\rangle, \tag{30.17}$$

and $\phi_i(\vec{r})$ is the electron wavefunction, that is,

$$|\phi_i\rangle = \int d^3r \phi_i(\vec{r}) |\vec{r}\rangle. \tag{30.18}$$

The state $|...n_i(\vec{k},\lambda)...\rangle$ denotes the wavefunction of the photon field, using the occupation number representation. We only explicitly show the initial occupation of the mode specified by $\vec{k},\lambda$. Similarly the final state wavefunction is written as

$$|\Psi_f\rangle = |\phi_f\rangle |..., n_f(\vec{k},\lambda)...\rangle. \tag{30.19}$$

where $n_f(\vec{k},\lambda) = n_i(\vec{k},\lambda) \pm 1$. The matrix element needed in the expression for Fermi's golden rule can be calculated in a straightforward manner and we obtain

$$\begin{aligned}\langle\Psi_f|\hat{H}_{int}|\Psi_i\rangle = -\frac{ie\hbar}{mc}\sqrt{\frac{2\pi c^2}{\omega(k)}} f \frac{1}{\sqrt{V}} \int d^3r \phi^*_f(\vec{r}) \vec{\epsilon}_\lambda(\vec{k})& \\ \cdot\ \nabla\phi_i(\vec{r}) e^{i\vec{k}\cdot r},&\end{aligned} \tag{30.20}$$

where the factor f is either $\sqrt{n_i(\vec{k},\lambda)}$ or $\sqrt{n_i(\vec{k},\lambda)+1}$ depending on whether there is absorption or emission of a photon.

Now, let us denote the energy of the initial and final state of the electron by e_i and e_f. Then, in the case of photon absorption, the energy of the initial state of the system (electromagnetic field plus the atomic electron) is $E_i = e_i$ and the energy of the final state is $E_f = e_f + \hbar\omega(k)$. These quantities enter in the energy conserving δ function in Eq. 30.12 which gives the rate. In the case of emission, $E_i = e_i + \hbar\omega(k)$ and $E_f = e_f$. In Fig. 30.1 the processes of spontaneous emission, absorption, and induced or stimulated emission are schematically illustrated.

In practice, under many circumstances, the state of the electromagnetic field corresponds to a macroscopic occupation of the same mode $\vec{k}, \lambda$ by a large average number of photons $n_i(\vec{k}, \lambda)$, which is proportional to the field energy content of this particular mode. We are interested in calculating the sum over all modes $\vec{k}$ for a given polarization λ, to find the rate

$$\Gamma = \sum_{\vec{k}} \Gamma_{\vec{k},\lambda} = \frac{2\pi}{\hbar} \sum_{\vec{k}} \delta(\hbar\omega(k) - E) |\langle \Psi_f | \hat{H}_{int} | \Psi_i \rangle|^2, \tag{30.21}$$

when $E = e_f - e_i$ for photon absorption and $E = e_i - e_f$ for photon emission is a given definite energy difference. This summation can be written as

$$\begin{aligned} \Gamma &= \frac{2\pi}{\hbar} \int d\Omega \frac{d\rho(E)}{d\Omega} |\langle \Psi_f | \hat{H}_{int} | \Psi_i \rangle|^2, \\ \frac{d\rho(E)}{d\Omega} &= \frac{E^2 V}{8\pi^3 (\hbar c)^3}, \end{aligned} \tag{30.22}$$

where $\frac{d\rho(E)}{d\Omega}$ is the photon density of states per unit solid angle. Therefore, the rate per unit solid angle is given by

$$d\Gamma = \frac{\alpha}{2\pi c^2} \omega(k) f^2 |M|^2 d\Omega, \tag{30.23}$$

$$M = \int d^3 r \phi_f^*(\vec{r}) \vec{\epsilon}_\lambda(\vec{k}) \cdot \frac{\hat{\vec{p}}}{m} \phi_i(\vec{r}) e^{i\vec{k}\cdot\vec{r}}. \tag{30.24}$$

This equation describes both photon absorption, induced (or stimulated emission), and, in addition, spontaneous emission. Notice that

$$\Gamma_{i\to f}^{absorption} = \Gamma_{f\to i}^{Ind.Emission}. \tag{30.25}$$

Spontaneous emission (see Fig. 30.1) occurs when $n_i(\vec{k}, \lambda) = 0$, and the electron is excited at a given excited state of the atom. In this case $f = 1$ and if the transition is of the so-called electric dipole type $e^{i\vec{k}\cdot\vec{r}} \sim 1$. Furthermore, we can replace the electron momentum operator in the matrix element M above by the following commutator

$$\frac{\hat{\vec{p}}}{m} = \frac{i}{\hbar} \left[\hat{H}_e, \vec{r} \right], \tag{30.26}$$

where

$$\hat{H}_e = \frac{p^2}{2m} + V(r), \tag{30.27}$$

is the Hamiltonian of the electron in a hydrogen-like atom. Here, we have neglected electron–electron interaction if we are dealing with a multi-electronic atom. Using these approximations and relations, the matrix element M takes the following form

$$M = \frac{i}{\hbar}\int d^3r\phi_f^*(\vec{r})\vec{\epsilon}_\lambda(\vec{k})\cdot\left[\hat{H}_e,\vec{r}\right]\phi_i(\vec{r}), \tag{30.28}$$

$$= \frac{i}{\hbar}(e_f - e_i)\int d^3r\phi_f^*(\vec{r})\vec{\epsilon}_\lambda(\vec{k})\cdot\vec{r}\phi_i(\vec{r}), \tag{30.29}$$

$$= i\omega(k)\int d^3r\phi_f^*(\vec{r})\vec{\epsilon}_\lambda(\vec{k})\cdot\vec{r}\phi_i(\vec{r}). \tag{30.30}$$

Using these approximations, we may write

$$\Gamma = \frac{\alpha}{2\pi c^2}\omega^3|\vec{D}\cdot\vec{\epsilon}_\lambda(\vec{k})|^2, \tag{30.31}$$

$$\vec{D} = \int d^3r\phi_f^*(\vec{r})\vec{r}\phi_i(\vec{r}), \tag{30.32}$$

and by integrating over the solid angle and summing over both photon polarizations, we obtain for the last part of the above expression

$$\sum_\lambda\int d\Omega|\vec{D}\cdot\vec{\epsilon}(\vec{k})|^2 = \frac{8\pi}{3}|\vec{D}|^2, \tag{30.33}$$

thus, the final expression, for spontaneous emission, is

$$\Gamma = \frac{4\alpha}{3c^2}\omega^3|\vec{D}|^2. \tag{30.34}$$

Therefore, the rate of spontaneous emission in free space increases with ω^3. This approximation breaks down in the case of inner shell electrons in high-Z atoms.

30.3 Problems

Problem 1

Show that using the minimal substitution

$$\vec{p} \to \vec{p} - \frac{e}{c}\vec{A}, \tag{30.35}$$

and the formulation of second quantization, the total Hamiltonian which includes the electromagnetic field part, the matter part, and its direct interaction, and the interaction of the EM field with matter takes the form given by Eq. 30.2 where the operator $\psi^\dagger(\vec{r})$ is defined as follows:

$$\psi^\dagger(\vec{r})|\vec{r}_1,\vec{r}_2,...,\vec{r}_N\rangle_\pm = |\vec{r},\vec{r}_1,\vec{r}_2,...,\vec{r}_N\rangle_\pm \tag{30.36}$$

and the state $|\vec{r}_1,\vec{r}_2,...,\vec{r}_N\rangle_\pm$ is a properly symmetrized or antisymmetrized N particle state. Here, $|\vec{r}\rangle$ is the single-particle position eigenstate.

Problem 2

Derive all the steps leading to formula (30.34) starting from Fermi's golden rule, that is, from formula (30.12).

Problem 3

(a) What is the condition on the hydrogen atom excited state $|nlm\rangle$ such that through a single photon emission it undergoes a transition to the ground state $|100\rangle$?

(b) Calculate the rate of the spontaneous emission through the transition $|210\rangle \to |100\rangle$.

31

Elementary relativistic quantum mechanics

In this chapter we are seeking relativistic wave equations, which are invariant under Lorentz transformations, in an attempt to obtain a quantum mechanical description of relativistic particles. First, we start with the Klein–Gordon equation and then we discuss the Dirac equation. We also take the non-relativistic limit of the Dirac equation to derive the Schrödinger equation with two additional terms, the Zeeman term and the spin–orbit coupling term. These two terms emerge naturally from the Dirac equation, and thus the spin, as an internal quantum number which behaves like angular momentum, is clearly identified. Finally, the existence of antimatter is clearly supported by the nature of the solutions to the Dirac equation.

31.1 Klein–Gordon equation

In this section, we seek an equation to describe the evolution of a relativistic quantum mechanical spin-less particle. In non-relativistic quantum mechanics, we can obtain the Schrödinger equation by considering the energy-momentum dispersion

$$E = \frac{p^2}{2m}. \tag{31.1}$$

We first consider operators corresponding to energy and momentum as follows

$$\begin{aligned} \hat{E} &\to i\hbar\partial_t, \\ \vec{p} &\to -i\hbar\nabla, \end{aligned} \tag{31.2}$$

and then we construct an equation obtained by the corresponding operators acting on wavefunctions representing the state of the particle, that is,

$$\hat{E}\psi(\vec{r},t) = \frac{\hat{p}^2}{2m}\psi(\vec{r},t). \tag{31.3}$$

If we use the expressions given by Eq. 31.2, the above equation is the Schrödinger equation for a free particle.

In the present case we seek an equation which remains invariant under Lorentz transformations. Clearly the Schrödinger equation is not Lorentz invariant because time and space are treated differently. It is invariant under Galilean transformations

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because it provides a non-relativistic description. If we try to apply directly the previous approach by taking the relativistic energy-momentum dispersion

$$E = c\sqrt{p^2 + m^2c^2}, \tag{31.4}$$

and we substitute E and p by the operators specified by Eq. 31.2, we will obtain the following equation

$$i\hbar\partial_t\psi(\vec{r},t) = c\sqrt{\hat{p}^2 + m^2c^2}\psi(\vec{r},t), \tag{31.5}$$

which is plagued with a number of problems and inconsistencies. First, it is not an analytic function as $|\vec{p}| \to 0$ in the zero mass case. Second, it is non-local in space.

A simple differential equation which describes a relativistic particle can be obtained by considering the square of the four-vector $p_\mu \to (E/c, \vec{p})$ where the time-like component p_0 is the energy divided by the speed of light, E/c and the three space-like components p_μ are the three components of the momentum vector $\vec{p}$. Namely, $p_\mu p^\mu$ remains invariant, and it equals m^2c^2, under a Lorentz transformation. This implies the following well-known equation

$$m^2c^2 - p_\mu p^\mu = m^2c^2 - (\frac{E}{c})^2 + \vec{p}^2 = 0. \tag{31.6}$$

If we treat $\vec{p}$ and E as operators given by Eq. 31.2 and we substitute their expressions in Eq. 31.6, we will obtain the following operator

$$\hat{O} = m^2c^2 + \frac{\hbar^2}{c^2}\partial_t^2 - \hbar^2\nabla^2, \tag{31.7}$$

which when acting on a function representing the state of a relativistic particle should give zero at all reference frames, that is,

$$\Big(\frac{1}{c^2}\partial_t^2 - \nabla^2 + (\frac{mc}{\hbar})^2\Big)\psi(\vec{r},t) = 0. \tag{31.8}$$

This is the well-known *Klein–Gordon* equation. Notice that it is like a classical wave equation with an additional constant "mass" term.

If the particle is charged and there is an electromagnetic field present we need to couple it via the substitution

$$E \to E - e\phi, \tag{31.9}$$

$$\vec{p} \to \vec{p} - \frac{e}{c}\vec{A}, \tag{31.10}$$

where ϕ is the electric potential and $\vec{A}$ the vector potential. Therefore, the Klein–Gordon equation in this case takes the form

$$\Big(-\frac{1}{c^2}(i\hbar\partial_t - e\phi)^2 + (-i\hbar\nabla - \frac{e}{c}A)^2 + (mc)^2\Big)\psi(\vec{r},t) = 0. \tag{31.11}$$

31.2 Continuity equation

It is straightforward to derive a continuity equation as in the non-relativistic case. We begin from the Klein–Gordon equation (Eq. 31.8) and we multiply both sides by $\psi^*(\vec{r},t)$; then, we take the complex-conjugate of Eq. 31.8, and after multiplying both sides by $\psi(\vec{r},t)$ we subtract them. We can transform the resulting equation to bring it to the following form

$$\partial_t \rho(\vec{r},t) + \nabla \cdot \vec{J}(\vec{r},t) = 0, \tag{31.12}$$

where the current has the same form as that for the non-relativistic case, that is,

$$\vec{J}(\vec{r},t) = \frac{\hbar}{2mi}\Big(\psi^* \nabla \psi - \psi \nabla \psi^*\Big). \tag{31.13}$$

The quantity $\rho(\vec{r},t)$ which we interpret as density is given by

$$\rho(\vec{r},t) = \frac{i\hbar}{2mc^2}\Big(\psi^* \partial_t \psi - \psi \partial_t \psi^*\Big). \tag{31.14}$$

Notice that this is fundamentally different from the non-relativistic case, where the probability density to find a particle at position $\vec{r}$ at time t is the square of the wave-function. The integral of this quantity over all space does not change in time. This is obtained by integrating the continuity equation and using Gauss's theorem and the boundary condition that the current at infinity is zero. We will see, however, that this quantity $\rho(\vec{r},t)$ above cannot be interpreted as a probability density, but rather as a charge density probability distribution. The reason is that ρ is not positive definite for all types of solutions of the Klein–Gordon equation.

31.3 Solutions of Klein–Gordon equation

Due to the fact that the Klein–Gordon equation is a second-order differential equation in time, we must specify the initial values of $\psi(\vec{r},t)$ and of $\partial_t \psi(\vec{r},t)$. This implies that, as compared to the non-relativistic case, here we must provide more information in order to specify the initial state of the relativistic particle. We will see that this is so because we describe the particle and its corresponding antiparticle together.

Another peculiar property of this equation is the following. In the absence of an external potential it has a solution of the form

$$\psi = A e^{\frac{i}{\hbar}(\vec{p}\cdot r - E_p t)}, \tag{31.15}$$

and the equation is satisfied by the above function provided that

$$E_p = E_p^{\pm} = \pm c\sqrt{p^2 + m^2c^2}, \tag{31.16}$$

and both cases of sign (positive and negative) correspond to different solutions with positive and negative energy, which are solutions which describe a particle and an antiparticle respectively.

In a frame where the free particle rests ($p = 0$) we have

$$\psi_{\pm} = Ae^{\pm \frac{imc^2}{\hbar}}. \tag{31.17}$$

Notice that under a Lorenz transformation to a frame moving with momentum $\vec{p}$, the exponent is transformed to the following

$$mc^2 t = E_p t - \vec{p} \cdot \vec{r}, \tag{31.18}$$

and the wavefunction given by Eq. 31.17 transforms to that given by Eq. 31.15.

Now, using the definitions of $\rho(\vec{r}, t)$ (Eq. 31.14) and $\vec{J}(\vec{r}, t)$ (Eq. 31.13) arising from the continuity equation, we find that

$$\begin{aligned} \rho_{\pm}(\vec{r}, t) &= \frac{E_p^{\pm}}{mc^2}, \\ \vec{J}_{\pm}(\vec{r}, t) &= \frac{\vec{p}}{m}, \end{aligned} \tag{31.19}$$

and the current can be rewritten as

$$\begin{aligned} \vec{J}_{\pm} &= \rho_{\pm}(\vec{r}, t)\vec{v}_{\pm}, \\ \vec{v}_{\pm} &= \frac{\vec{p}c^2}{E_p^{\pm}}, \end{aligned} \tag{31.20}$$

where $\vec{v}_{\pm}$ is the relativistic velocity for particles and antiparticles.

Let us consider the case of the particle rest frame. In this case we obtain that

$$\begin{aligned} \rho_{\pm} &= \pm 1, \\ \vec{J}_{\pm} &= 0, \end{aligned} \tag{31.21}$$

namely, the density ρ for particles is positive and negative for antiparticles.

31.4 First-order Klein–Gordon equation

The Klein–Gordon equation, while it is second order in time-derivative, can be easily cast into a first-order Schródinger-like equation using a two-component vector for the state.

It is straightforward to show the following Schrödinger-like equation

$$i\hbar \partial_t \Psi(\vec{r}, t) = \mathcal{H}\Psi(\vec{r}, t), \tag{31.22}$$

where the state Ψ represents a two-component vector

$$\Psi(\vec{r}, t) = \begin{pmatrix} \psi_+(\vec{r}, t) \\ \psi_-(\vec{r}, t) \end{pmatrix}, \tag{31.23}$$

and

$$\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2(\tau_3 + i\tau_2) + mc^2\tau_3, \tag{31.24}$$

where τ_i are the Pauli matrices

$$\tau_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \ \tau_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \ \tau_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{31.25}$$

This equation is entirely equivalent to the Klein–Gordon equation. This can be verified by simple substitution of the two component vector given by Eq. 31.23 into the Schrödinger-like equation (Eq. 31.22) using the Hamiltonian given by Eq. 31.24. This substitution produces two differential equations from which, by subtracting and adding them, we can produce two equations from which one can show that the combination $\psi = \psi_+ + \psi_-$ satisfies the Klein–Gordon equation.

In this formalism one can derive a continuity equation in which the conserved density and the current are given by

$$\rho(\vec{r}, t) = |\psi_+|^2 - |\psi_-|^2 = \Psi^\dagger \tau_3 \Psi, \tag{31.26}$$

$$\vec{J} = \frac{\hbar}{2mi}\Big[\psi^*\nabla\psi - \psi\nabla\psi^*\Big], \tag{31.27}$$

where $\psi = \psi_+ + \psi_-$. Therefore, because the conserved quantity is $\Psi^\dagger\tau_3\Psi$ the normalization condition should be imposed as follows:

$$\int d^3r\rho(\vec{r}, t) = \int d^3r\Psi^\dagger\tau_3\Psi = \pm 1, \tag{31.28}$$

and the sign depends on the nature of the solution (particle or antiparticle).

As a result the scalar product between two such wavefunctions is defined as

$$\langle\Psi|\Psi'\rangle = \int d^3r\Psi^\dagger\tau_3\Psi'. \tag{31.29}$$

Since an operator is Hermitian when its matrix elements fulfill the property

$$\langle\Psi|\hat{H}|\Psi'\rangle = [\langle\Psi'|H|\Psi\rangle]^*. \tag{31.30}$$

As a consequence of the definition of the scalar product by means of Eq. 31.29, an operator is Hermitian if it satisfies the following identity

$$H = \tau_3 H^\dagger \tau_3. \tag{31.31}$$

The student should show that the Hamiltonian given by Eq. 31.24 satisfies this identity.

31.5 The Dirac equation

We discussed that the Klein–Gordon equation is second order in time. Dirac was trying to find a differential equation first order in time to describe relativistic particles. Namely, the square of the four vector p_μ, that is, $p_\mu p^\mu$ is invariant under Lorentz transformations, however this is not linear. We also discussed that taking the brute force square root of such an operator leads to a non-local operator.

However, let us assume that an intrinsic property of the particle, such as the spin, breaks the rotational invariance of the problem, because the spin polarization axis introduces a direction. Then, we can seek solutions to the following equation

$$\hat{\mathcal{H}}^2 = \hat{\vec{p}}^{\,2} c^2 + m^2 c^4, \tag{31.32}$$

$$\hat{\vec{p}} = -i\hbar\nabla, \tag{31.33}$$

with $\hat{\mathcal{H}}$ being the unknown operator. Furthermore, we can restrict our search for a solution by restricting it to the form

$$\hat{\mathcal{H}} = c\vec{\alpha}\cdot\hat{\vec{p}} + mc^2\hat{\beta}, \tag{31.34}$$

where $\vec{\alpha} = (\hat{\alpha}_1, \hat{\alpha}_2, \hat{\alpha}_3)$ and $\hat{\beta}$ are four Hermitian operators acting on the spin variables alone. In order for the above ansatz, given by Eq. 31.34, to satisfy Eq. 31.32, the squares of these matrices should be unity and their components should anticommute, that is,

$$\hat{\alpha}_i^2 = 1, \qquad \hat{\beta}^2 = 1, \tag{31.35}$$

$$\hat{\alpha}_i\hat{\alpha}_j + \hat{\alpha}_j\hat{\alpha}_i = 0, \qquad \hat{\alpha}_i\hat{\beta} + \hat{\beta}\hat{\alpha}_i = 0. \tag{31.36}$$

The student is strongly encouraged to show that the substitution discussed above along with the properties of these matrices (Eqs. 31.36) leads to Eq. 31.32. Now, our problem, therefore, is to find a solution to the above equations (Eq. 31.36) for $\hat{\alpha}_i$ and $\hat{\beta}$ which should be Hermitian matrices. Using these equations one can show that these are at least 4×4 matrices. Pauli has shown that all matrix solutions are related to one another by unitary transformation and the following particular solution is sufficient.

$$\hat{\alpha}_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix}, \qquad \hat{\beta} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}, \tag{31.37}$$

and σ_i are the three Pauli matrices. This is also called the standard representation.

Therefore, the equation representing the relativistic spin-1/2 particle is given by

$$\begin{aligned} i\hbar\partial_t\Psi &= \hat{\mathcal{H}}\Psi, \\ \hat{\mathcal{H}} &= c\vec{\alpha}\cdot\hat{\vec{p}} + mc^2\hat{\beta}, \end{aligned} \tag{31.38}$$

which is the *Dirac equation.* The state vector $\Psi(\vec{r}, t)$ is a four-component spinor because the matrices $\hat{\alpha}_i$ and β are 4×4 matrices.

In the presence of an electromagnetic field we need to make the minimal substitution given by Eq. 31.10 and we obtain

$$i\hbar\partial_t\Psi = \Big(c\vec{\alpha}\cdot(\hat{\vec{p}} - \frac{q}{c}\vec{A}) + mc^2\hat{\beta} + q\phi\Big)\Psi. \tag{31.39}$$

31.6 Rotational invariance

Consider the case where the particle is free ($\vec{A} = 0$ and $\phi = 0$). The equation of motion for the orbital angular momentum $\vec{L} = \vec{r} \times \vec{p}$ is given by:

$$i\hbar \frac{d\hat{L}_x}{dt} = \hat{L}_x \hat{\mathcal{H}} - \hat{\mathcal{H}} \hat{L}_x, \tag{31.40}$$

$$\hat{\mathcal{H}} = c\vec{\alpha} \cdot \hat{\vec{p}} + mc^2 \hat{\beta}. \tag{31.41}$$

After evaluating the commutator, the result is

$$i\hbar \frac{d\hat{L}_x}{dt} = -i\hbar c(\hat{\alpha}_z \hat{p}_y - \hat{\alpha}_y \hat{p}_z). \tag{31.42}$$

Therefore, the angular momentum is not a constant of motion. The reason for this is that the rotational invariance is broken because of the internal quantum number of spin. Namely, there is the vector $\vec{\alpha}$ associated with the particle which breaks the rotational invariance.

Now, if we consider the time evolution of the vector

$$\vec{\Sigma} = \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{pmatrix}, \tag{31.43}$$

for example its x-component, we find

$$i\hbar \frac{d\hat{\Sigma}_x}{dt} = 2i\hbar c(\hat{\alpha}_z \hat{p}_y - \hat{\alpha}_y \hat{p}_z). \tag{31.44}$$

Therefore, we consider the quantity

$$\vec{J} = \vec{L} + \frac{1}{2}\hbar\vec{\Sigma}, \tag{31.45}$$

is a constant of motion. As a consequence we refer to the quantity $\vec{J} = \vec{L} + \vec{S}$, with $\vec{S} = 1/2\hbar\vec{\Sigma}$, as the total angular momentum and $\vec{S}$ as the spin operator.

31.7 Free-particle solution of the Dirac equation

We would like to investigate the interpretation of the four component spinor which describes the state of the relativistic particles quantum mechanically.

Towards this goal let us construct free particle solutions to the Dirac equation, at first with a particle at rest. In this case the solution of the Dirac equation is of the form

$$\Psi(\vec{r}, t) = e^{-\frac{i}{\hbar}Et}\mathbf{u}, \tag{31.46}$$

and by substitution, the Dirac Eq. 31.38 becomes

$$E\mathbf{u} = mc^2\hat{\beta}\mathbf{u}, \tag{31.47}$$

that is, the spinor $\mathbf{u}$ satisfies an eigenvalue equation. The eigenvalues of the matrix $\hat{\beta}$ are ± 1 which correspond to energy eigenvalues $E = \pm mc^2$ with corresponding eigenvectors $u_\sigma^\pm$ given as follows

$$u_\uparrow^+ = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, u_\downarrow^+ = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \tag{31.48}$$

$$u_\uparrow^- = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, u_\downarrow^- = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}. \tag{31.49}$$

The interpretation of these four solutions is that those positive energy solutions correspond to a particle (e.g., the electron) with spin projection σ, and the negative energy solutions correspond to an antiparticle (e.g., positrons) with spin projection σ. Namely, the two states u_σ^+ corresponding to positive energy eigenvalue are eigenstates of σ_z with eigenvalue σ and they vary in time as $e^{-i/\hbar mc^2 t}$. The same holds true for the two states u_σ^- which correspond to negative energy eigenstates which vary as $e^{i/\hbar mc^2 t}$.

Now, let us consider the case where the particle is not at rest. The simplest case is when the momentum vector is along the positive z-axis (same as the spin quantization axis). In this case the state can be written as

$$\Psi_p(\vec{r}, t) = e^{-\frac{i}{\hbar}(Et - pz)}\mathbf{u}, \tag{31.50}$$

and by substituting this expression into the Dirac equation we find that $\mathbf{u}$ satisfies the equation below

$$\begin{pmatrix} mc^2 & 0 & cp & 0 \\ 0 & mc^2 & 0 & -cp \\ cp & 0 & -mc^2 & 0 \\ 0 & -cp & 0 & -mc^2 \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{pmatrix} = E \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{pmatrix}. \tag{31.51}$$

There are two eigenstates corresponding to the same positive energy eigenvalue

$$E = E_p^+ = E_P = \sqrt{p^2c^2 + m^2c^4}, \tag{31.52}$$

which can be chosen to be the following

$$u^{(R)} = A \begin{pmatrix} 1 \\ 0 \\ \frac{cp}{E_p + mc^2} \\ 0 \end{pmatrix}, \qquad u^{(L)} = B \begin{pmatrix} 0 \\ 1 \\ 0 \\ \frac{-cp}{E_p + mc^2} \end{pmatrix} \tag{31.53}$$

where A and B are determined by appropriate normalization. In addition, there are two eigenstates corresponding to the same negative energy eigenvalue

$$E = E_p^- = -E_p = -\sqrt{p^2c^2 + m^2c^4}, \tag{31.54}$$

which can be chosen to be the following

$$v^{(R)} = C \begin{pmatrix} \frac{-cp}{E_p+mc^2} \\ 0 \\ 1 \\ 0 \end{pmatrix}, \qquad v^{(L)} = D \begin{pmatrix} 0 \\ \frac{cp}{E_p+mc^2} \\ 0 \\ 1 \end{pmatrix}. \tag{31.55}$$

The reason for labeling the states with the L and R index is because we can choose common eigenstates between the Dirac Hamiltonian and the *helicity* operator $\vec{\Sigma} \cdot \vec{p}$ where the operator $\vec{\Sigma}$ is defined by Eq. 31.43. Therefore, the energy eigenstates can be characterized by a definite value of the helicity operator. Namely, the eigenstates labeled R are eigenstates of the helicity operator with eigenvalue $+p$ and the eigenstates labeled L correspond to helicity -p. Helicity corresponds to spin projection along the direction of momentum.

31.8 Non-relativistic limit

We can write the state of the Dirac particle as

$$\Psi(\vec{r}, t) = \begin{pmatrix} \mathbf{u}_1 \\ \mathbf{u}_2 \end{pmatrix}, \tag{31.56}$$

and in terms of $\mathbf{u}_1$ and $\mathbf{u}_2$, the Dirac equation (Eq. 31.39) splits into the following two equations

$$i\hbar\partial_t \mathbf{u}_1 = c(-i\hbar\nabla - \frac{q}{c}\vec{A}) \cdot \vec{\sigma}\mathbf{u}_2 + (q\phi + mc^2)\mathbf{u}_1, \tag{31.57}$$

$$i\hbar\partial_t \mathbf{u}_2 = c(-i\hbar\nabla - \frac{q}{c}\vec{A}) \cdot \vec{\sigma}\mathbf{u}_1 + (q\phi - mc^2)\mathbf{u}_2. \tag{31.58}$$

Now, the time-independent Dirac equation is obtained by realizing that the following time dependence is a solution to its time-dependent version

$$\begin{pmatrix} \mathbf{u}_1 \\ \mathbf{u}_2 \end{pmatrix} = \begin{pmatrix} \tilde{\mathbf{u}}_1 \\ \tilde{\mathbf{u}}_2 \end{pmatrix} e^{-\frac{i}{\hbar}Et}, \tag{31.59}$$

which yields the following equations:

$$E\tilde{\mathbf{u}}_1 = c(-i\hbar\nabla - \frac{q}{c}\vec{A}) \cdot \vec{\sigma}\tilde{\mathbf{u}}_2 + (q\phi + mc^2)\tilde{\mathbf{u}}_1, \tag{31.60}$$

$$E\tilde{\mathbf{u}}_2 = c(-i\hbar\nabla - \frac{q}{c}\vec{A}) \cdot \vec{\sigma}\tilde{\mathbf{u}}_1 + (q\phi - mc^2)\tilde{\mathbf{u}}_2. \tag{31.61}$$

If we define the quantity ϵ as follows

$$E = mc^2 + \epsilon, \tag{31.62}$$

the above second equation can be written as

$$\tilde{\mathbf{u}}_2 = \frac{c}{2mc^2 + \epsilon - q\phi}(-i\hbar\nabla - \frac{q}{c}\vec{A}) \cdot \vec{\sigma}\tilde{\mathbf{u}}_1. \tag{31.63}$$

In the non-relativistic limit where

$$\epsilon \simeq \frac{p^2}{2m}, \tag{31.64}$$

$\epsilon << mc^2$. In addition, by non-relativistic limit we imply that mc^2 is also much larger than $q\phi$, which leads to the following approximation

$$\mathbf{u}_2 = \frac{1}{2mc}(-i\hbar\nabla - \frac{q}{c}\vec{A}) \cdot \vec{\sigma}\mathbf{u}_1. \tag{31.65}$$

Therefore, $\mathbf{u}_2$ is smaller than the upper component $\mathbf{u}_1$ by a factor v/c in the non-relativistic limit. Substituting this approximation for $\mathbf{u}_2$ back into Eq. 31.57 we obtain

$$i\hbar\partial_t\mathbf{u}_1 = \frac{1}{2m}\Big((-i\hbar\nabla - \frac{q}{c}\vec{A}) \cdot \vec{\sigma}\Big)^2\mathbf{u}_1 + (q\phi + mc^2)\mathbf{u}_1. \tag{31.66}$$

Using the following properties of the Pauli matrices,

$$(\vec{a} \cdot \vec{\sigma})(\vec{b} \cdot \vec{\sigma}) = (\vec{a} \cdot \vec{b}) + i\vec{\sigma} \cdot (\vec{a} \times \vec{b}), \tag{31.67}$$

we can transform the first term in the right-hand-side of Eq. 31.66 as

$$\begin{aligned}\Big((-i\hbar\nabla - \frac{q}{c}\vec{A}) \cdot \vec{\sigma}\Big)^2\mathbf{u}_1 &= (-i\hbar\nabla - \frac{q}{c}\vec{A})^2\mathbf{u}_1 \\ - \frac{q\hbar}{c}\vec{\sigma} \cdot (\nabla \times \vec{A} + \vec{A} \times \nabla)\mathbf{u}_1,\end{aligned} \tag{31.68}$$

and using the fact that the magnetic field is given by $\vec{H} = \nabla \times \vec{A}$, we obtain

$$i\hbar\partial_t\mathbf{u}_1 = \Big[\frac{1}{2m}(-i\hbar\nabla - \frac{q}{c}\vec{A})^2 - \frac{q\hbar}{2mc}\vec{\sigma} \cdot \vec{H} + (q\phi + mc^2)\Big]\mathbf{u}_1. \tag{31.69}$$

Namely, we have obtained the Schrödinger equation. In addition, notice that we have derived the expression for the Zeeman interaction of the spin–dipole moment with an external magnetic field. The electron dipole moment due to its spin has a g-factor which takes the value $g = 2$.

31.9 Spin–orbit coupling

Let us consider the Dirac equation for a particle in a central potential $V(r)$, such as the case of the electron under the influence of a very heavy nucleus:

$$i\hbar\partial_t\Psi = (c\vec{\alpha} \cdot \vec{p} + mc^2\hat{\beta} + V(r))\Psi. \tag{31.70}$$

Again we express the energy eigenvalue in terms of the parameter ϵ as in Eq. 31.62 and we will work in the non-relativistic limit where $\epsilon << mc^2$. Unlike in the previous section, where we kept the leading order in the non-relativistic limit $v/c << 1$, in this case we will keep terms up to the next to the leading order. As in the previous section, we write

$$\Psi(\vec{r},t) = \begin{pmatrix} \mathbf{u}_1 \\ \mathbf{u}_2 \end{pmatrix}, \tag{31.71}$$

and the equations for $\mathbf{u}_1$ and $\mathbf{u}_2$ are given as

$$(\epsilon - V)\mathbf{u}_1 - c\vec{\sigma} \cdot \vec{p}\mathbf{u}_2 = 0, \tag{31.72}$$

$$(\epsilon + 2mc^2 - V)\mathbf{u}_2 - c\vec{\sigma} \cdot \vec{p}\mathbf{u}_1 = 0. \tag{31.73}$$

Again, it follows from the above two equations that $\mathbf{u}_2$ is of order u/c times $\mathbf{u}_1$. From the second equation we obtain

$$\mathbf{u}_2 = \frac{1}{\epsilon + 2mc^2 - V} c\vec{\sigma} \cdot \vec{p}\mathbf{u}_1. \tag{31.74}$$

Using this expression, the first equation above becomes:

$$\epsilon\mathbf{u}_1 = \frac{1}{2m}(\vec{\sigma} \cdot \vec{p}) \frac{1}{1 + \frac{\epsilon - V}{2mc^2}} (\vec{\sigma} \cdot \vec{p})\mathbf{u}_1 + V\mathbf{u}_1. \tag{31.75}$$

We will use the expansion:

$$\frac{1}{1 + \frac{\epsilon - V}{2mc^2}} = 1 - \frac{\epsilon - V}{2mc^2} + ... \tag{31.76}$$

and the identities:

$$\hat{\vec{p}}(V\Psi) = V\hat{\vec{p}}\Psi - i\hbar(\nabla V)\Psi, \tag{31.77}$$

$$(\vec{\sigma} \cdot \nabla V)(\vec{\sigma} \cdot \hat{\vec{p}}) = (\nabla V) \cdot \hat{\vec{p}} + i\vec{\sigma} \cdot [(\nabla V) \times \hat{\vec{p}}], \tag{31.78}$$

where $\hat{\vec{p}} = -i\hbar\nabla$, to obtain

$$\begin{aligned} \epsilon\mathbf{u}_1 = {} & \Big[\big(1 - \frac{\epsilon - V}{2mc^2}\big)\frac{p^2}{2m} + V\Big]\mathbf{u}_1 - \frac{\hbar^2}{4m^2c^2}(\nabla V) \cdot (\nabla \mathbf{u}_1) \\ & + \frac{\hbar^2}{4m^2c^2}\vec{\sigma} \cdot [(\nabla V) \times \hat{\vec{p}}\mathbf{u}_1]. \end{aligned} \tag{31.79}$$

For a central potential we have that

$$\nabla V = \frac{1}{r}\frac{dV}{dr}\vec{r}, \tag{31.80}$$

$$(\nabla V) \cdot \nabla = \frac{dV}{dr}\frac{\partial}{\partial r}. \tag{31.81}$$

Approximating the term $(1 - \frac{\epsilon - V}{2mc^2})p^2/2m$ simply by $p^2/2m - O(p^4)$ we see that we have recovered the Schrödinger equation with some additional higher order terms. In particular we see that there is the following term:

$$\frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\vec{S}\cdot\vec{L}, \tag{31.82}$$

$$\vec{L} = \vec{r}\times\vec{p}, \qquad \vec{S} = \frac{\hbar}{2}\vec{\sigma} \tag{31.83}$$

which is the spin–orbit coupling term already discussed in previous chapters. While the other terms which we do not discuss are of the same order in the expansion, we focus on this term because it depends on spin and angular momentum; namely, its existence is much more clearly demonstrated in experimental atomic physics because the observed energy levels need to be classified according to their total angular momentum which includes spin.

31.10 Covariant form

The Dirac equation can be cast in a more compact and covariant form using the so-called γ-matrices. Namely,

$$\gamma^0 \equiv \hat{\beta}, \qquad \gamma^1 \equiv \hat{\beta}\hat{\alpha}_x, \qquad \gamma^2 \equiv \hat{\beta}\hat{\alpha}_y, \qquad \gamma^3 \equiv \hat{\beta}\hat{\alpha}_z, \tag{31.84}$$

for which we can easily show that

$$\gamma^\mu\gamma^\nu + \gamma^\nu\gamma^\mu = 2g^{\mu\nu}\mathbf{1}, \tag{31.85}$$

where $\mathbf{1}$ is the unit 4×4 matrix. We now multiply both sides of Eq. 31.38 by $\hat{\beta}$ and then by moving every term to the left-hand-side we obtain

$$-i\hbar\gamma^\mu\frac{\partial\Psi}{\partial x^\mu} + mc\Psi = 0, \tag{31.86}$$

where as usual this means a summation over the four values of the four-vectors and $x^\mu = (ct, x, y, z)$, that is,

$$\gamma^\mu\frac{\partial}{\partial x^\mu} = \hat{\beta}\frac{1}{c}\frac{\partial}{\partial_t} + \hat{\beta}\vec{\hat{\alpha}}\cdot\nabla. \tag{31.87}$$

The Dirac equation can be written even more compactly as follows

$$(\gamma^\mu\hat{p}_\mu - mc)\Psi = 0, \tag{31.88}$$

where

$$\hat{p}^\mu = (\hat{E}/c, \vec{\hat{p}}) = i\hbar\frac{\partial}{\partial x_\mu} = (\frac{i\hbar}{c}\frac{\partial}{\partial t}, -i\hbar\nabla). \tag{31.89}$$

It is customary to use the following short-hand notation

$$\not{p} = \gamma^\mu\hat{p}_\mu, \tag{31.90}$$

by means of which the Dirac equation takes the following more compact form

$$(\not{p} - mc)\Psi = 0. \tag{31.91}$$

31.11 Coupling to external electromagnetic fields

When an external electromagnetic field is present, the Hamiltonian is obtained by making the minimal substitution

$$\hat{p}^{\mu} \to p^{\mu} - \frac{q}{c}A^{\mu}, \tag{31.92}$$

where $A^{\mu} = (\phi, \vec{A})$ and $q = -e$ for electrons. In this case the Dirac equation takes the form

$$\left[\gamma^{\mu}(\hat{p}_{\mu} - \frac{q}{c}A_{\mu}) - mc\right]\Psi = 0. \tag{31.93}$$

In more compact notation, it can be written as follows:

$$\left[(\not{p} - \frac{q}{c}\not{A}) - mc\right]\Psi = 0. \tag{31.94}$$

31.12 Continuity equation

The continuity equation is obtained following very similar steps as in the non-relativistic case or in the case of the Klein–Gordon equation. We take the Hermitian conjugate of the Dirac equation (Eq. 31.93)

$$(-i\hbar\partial_{\mu} - \frac{q}{c}A_{\mu})\Psi^{\dagger}(\gamma^{\mu})^{\dagger} - mc\Psi^{\dagger} = 0. \tag{31.95}$$

Using the fact that

$$(\gamma^{\mu})^{\dagger} = \gamma^{0}\gamma^{\mu}\gamma^{0}, \tag{31.96}$$

we obtain

$$(-i\hbar\partial_{\mu} - \frac{q}{c}A_{\mu})\bar{\Psi}\gamma^{\mu}\gamma^{0} - mc\Psi^{\dagger} = 0, \tag{31.97}$$

where

$$\bar{\Psi} = \Psi^{\dagger}\gamma^{0}. \tag{31.98}$$

By right-multiplying the above equation by $\gamma^{0}\Psi$ we obtain:

$$(-i\hbar\partial_{\mu} - \frac{q}{c}A_{\mu})\bar{\Psi}\gamma^{\mu}\Psi - mc\bar{\Psi}\Psi = 0. \tag{31.99}$$

By multiplying the Dirac equation from the left by $\bar{\Psi}$ we obtain:

$$\bar{\Psi}\gamma^{\mu}(i\hbar\partial_{\mu} - \frac{q}{c}A_{\mu})\Psi - mc\bar{\Psi}\Psi = 0. \tag{31.100}$$

We subtract the above two equations and we obtain:

$$i\partial_\mu(\bar{\Psi}\gamma^\mu\Psi) = 0. \tag{31.101}$$

This is the continuity equation. In a covariant form for the current density of the four-vector of the electron–positron system it is

$$j^\mu = \bar{\Psi}\gamma^\mu\Psi, \tag{31.102}$$

and the continuity equation is

$$\partial_\mu j^\mu = 0, \tag{31.103}$$

or it can be written in the more familiar form as

$$\partial_t\rho + \nabla\cdot\vec{j} = 0. \tag{31.104}$$

where the probability density ρ is given as

$$j^0 = \bar{\psi}\gamma^0\psi = \psi^\dagger\psi. \tag{31.105}$$

Therefore, as in the Schrödinger's case, the conserved quantity is the norm of the wavefunction.

31.13 Interpretation of the Dirac equation

The negative energy solutions which we found introduce the following problem. An electron placed in positive energy states, when coupled to the electromagnetic field, should decay to lower (negative) energy states. Electrons, however, do not behave this way.

Dirac introduced the so-called hole theory. According to this theory the vacuum should be regarded as the many-body quantum state in which all negative energy states are occupied. This state dressed with quantum fluctuations due to the coupling of the electrons with the electromagnetic field is called the “sea” of electrons or Dirac sea. This is in analogy with the filled Fermi sea of electrons in the ground state of electrons in a metal. The Pauli exclusion principle prohibits electrons from occupying the same state. Thus, an additional electron has to occupy a positive energy eigenstate. In addition, a positive energy electron cannot decay into a negative energy state because they are all occupied.

Now, when a negative energy eigenstate is not filled, that is, when there is a hole at momentum $\vec{p}$ and of definite spin, this would behave as a positively charged particle of positive energy. The energy is positive because energy is required to create an electron–hole pair from the vacuum. Such a hole can be regarded as the positron state. Therefore, when an electron–positron pair is created out of the vacuum, we think of this process as follows: An electron occupying a particular negative energy state in the vacuum is promoted to a positive energy state, thus creating a hole (positron) and an electron state with positive energy above the vacuum.

This theory, however, is not adequate to be used as a straightforward interpretation, because the electrons in the vacuum interact. A better theory should emerge by treating this problem of the interacting vacuum using the tools of quantum field theory.

31.14 Problems

Problem 1

(a) Show that the following continuity equation follows from the Klein–Gordon equation

$$\partial_t \rho(\vec{r}, t) + \nabla \cdot \vec{J}(\vec{r}, t) = 0, \tag{31.106}$$

where the current has the same form as that for the non-relativistic case, that is,

$$\vec{J}(\vec{r}, t) = \frac{\hbar}{2mi}\Big(\psi^* \nabla \psi - \psi \nabla \psi^*\Big). \tag{31.107}$$

The quantity $\rho(\vec{r}, t)$ which we interpret as charge density is given by

$$\rho(\vec{r}, t) = \frac{i\hbar}{2mc^2}\Big(\psi^* \partial_t \psi - \psi \partial_t \psi^*\Big). \tag{31.108}$$

(b) Show that the following Schrödinger-like equation

$$i\hbar \partial_t \Psi(\vec{r}, t) = \mathcal{H}\Psi(\vec{r}, t), \tag{31.109}$$

where the state Ψ represents a two-component vector

$$\Psi(\vec{r}, t) = \begin{pmatrix} \psi_+(\vec{r}, t) \\ \psi_-(\vec{r}, t) \end{pmatrix}, \tag{31.110}$$

and

$$\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2(\tau_3 + i\tau_2) + mc^2\tau_3, \tag{31.111}$$

where τ_i are the Pauli matrices

$$\tau_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \tau_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \tau_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{31.112}$$

is entirely equivalent to the Klein–Gordon equation. This can be verified by simple substitution of the two component vector given by Eq. 31.110 into the Schrödinger-like equation (Eq. 31.109) using the Hamiltonian given by Eq. 31.111. This substitution produces two differential equations from which, by subtracting and adding them, we can produce two equations from which one can show that the combination $\psi = \psi_+ + \psi_-$ satisfies the Klein–Gordon equation.

(c) Using the above first-order equation derive a continuity equation. Show that the conserved density and the current are given by

$$\rho(\vec{r}, t) = |\psi_+|^2 - |\psi_-|^2 = \Psi^\dagger \tau_3 \Psi, \tag{31.113}$$

$$\vec{J} = \frac{\hbar}{2mi}\Big[\psi^* \nabla \psi - \psi \nabla \psi^*\Big], \tag{31.114}$$

where $\psi = \psi_+ + \psi_-$.

(d) Therefore, because the conserved quantity is $\Psi^\dagger \tau_3 \Psi$ the normalization condition should be imposed as follows:

$$\int d^3r\rho(\vec{r},t) = \int d^3r\Psi^\dagger\tau_3\Psi = \pm 1, \tag{31.115}$$

and the sign depends on the nature of the solution (particle or antiparticle).

As a result the scalar product between two such wavefunctions is defined as

$$\langle\Psi|\Psi'\rangle = \int d^3r\Psi^\dagger\tau_3\Psi'. \tag{31.116}$$

As a consequence of this, since an operator is Hermitian when its matrix elements fulfill the property

$$\langle\Psi|\hat{H}|\Psi'\rangle = [\langle\Psi'|H|\Psi\rangle]^*, \tag{31.117}$$

an operator is Hermitian if it satisfies the following identity

$$H = \tau_3 H^\dagger \tau_3. \tag{31.118}$$

Verify that the Hamiltonian given by Eq. 31.111 satisfies this identity.

Problem 2

Show that in the non-relativistic limit the conserved density of the Klein–Gordon equation becomes the square of the magnitude of the wavefunction, as in the Schrödinger case.

Hint: Use the approximation that in the non-relativistic limit we can write

$$\psi(\vec{r},t) = e^{-imc^2t/\hbar}\psi'(\vec{r},t), \tag{31.119}$$

where $\psi'(\vec{r},t)$ varies much less rapidly in time than the factor $e^{-imc^2t/\hbar}$.

Problem 3

Let us consider solutions to the Dirac equation in the case where the momentum vector is along the positive z-axis (same as the spin quantization axis).

(a) Show that, in this case, the state

$$\Psi_p(\vec{r},t) = e^{-\frac{i}{\hbar}(Et-pz)}\mathbf{u}, \tag{31.120}$$

can be a solution of the Dirac equation provided that $\mathbf{u}$ satisfies the equation below

$$\begin{pmatrix} mc^2 & 0 & cp & 0 \\ 0 & mc^2 & 0 & -cp \\ cp & 0 & -mc^2 & 0 \\ 0 & -cp & 0 & -mc^2 \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{pmatrix} = E \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{pmatrix}. \tag{31.121}$$

(b) Show that there are two eigenstates corresponding to the same positive energy eigenvalue

$$E = E_p^+ = E_P = \sqrt{p^2c^2 + m^2c^4}, \tag{31.122}$$

which can be chosen to be the following

$$u^{(R)} = A \begin{pmatrix} 1 \\ 0 \\ \frac{cp}{E_p+mc^2} \\ 0 \end{pmatrix}, \quad u^{(L)} = B \begin{pmatrix} 0 \\ 1 \\ 0 \\ \frac{-cp}{E_p+mc^2} \end{pmatrix} \tag{31.123}$$

where A and B are determined by appropriate normalization.

(c) In addition, show that there are two eigenstates corresponding to the same negative energy eigenvalue

$$E = E_p^- = -E_p = -\sqrt{p^2c^2 + m^2c^4}, \tag{31.124}$$

which can be chosen to be the following

$$v^{(R)} = C \begin{pmatrix} \frac{-cp}{E_p+mc^2} \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad v^{(L)} = D \begin{pmatrix} 0 \\ \frac{cp}{E_p+mc^2} \\ 0 \\ 1 \end{pmatrix}. \tag{31.125}$$

(d) Show that the states labeled with L and R index are also eigenstates of the *helicity* operator $\vec{\Sigma} \cdot \vec{p}$ where $\vec{\Sigma}$ is defined as

$$\vec{\Sigma} = \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{pmatrix}. \tag{31.126}$$

Appendix A
Review of the Dirac delta function

The delta function is defined as

$$\int_{-\infty}^{\infty} \delta(x-x')f(x') \;=\; f(x), \tag{A.1}$$

$$\delta(x-x') \;=\; 0, \qquad \forall \qquad x \neq x', \tag{A.2}$$

$$\delta(x-x') \to \infty, \qquad \text{when} \qquad x' \to x. \tag{A.3}$$

Where, the function $f(x)$ is an arbitrary continuous function. From the definition, the following simple properties follow immediately:

$$\int_{-\infty}^{\infty} \delta(x-x') = 1, \tag{A.4}$$

$$\delta(x-x') = \delta(x'-x), \tag{A.5}$$

$$\delta(ax) = \frac{1}{|a|}\delta(x). \tag{A.6}$$

The delta function is obtained as a limit of functions. Below, we list three well-known examples. First, the step:

$$\delta_\epsilon(x) = \left\{ \begin{array}{l} \frac{1}{\epsilon}, \qquad \text{when} \qquad -\epsilon/2 < x < \epsilon/2 \\ \\ 0, \text{ otherwise.} \end{array} \right\} \tag{A.7}$$

The Dirac delta function is obtained by taking the $\epsilon \to 0$ at the end of the integration.

The Gaussian representation:

$$\delta_\epsilon(x) = \frac{1}{\sqrt{2\pi}\epsilon} \exp(-\frac{x^2}{2\epsilon^2}). \tag{A.8}$$

The Lorentzian representation:

$$\delta_\epsilon(x) = \frac{1}{\pi}\frac{\epsilon}{x^2+\epsilon^2}. \tag{A.9}$$

Another representation of the delta function is the following integral:

$$\delta_{\lambda\to 0+}(x) = \int_{-\infty}^{\infty} d\xi e^{i2\pi\xi x} e^{-\lambda|\xi|}. \tag{A.10}$$

To prove this we write:

$$\begin{aligned}\int_{-\infty}^{\infty} d\xi e^{i2\pi\xi x} e^{-\lambda|\xi|} &= \int_{-\infty}^{0} d\xi e^{i2\pi\xi x} e^{\lambda\xi} + \int_{0}^{\infty} d\xi e^{i2\pi\xi x} e^{-\lambda\xi} \\ &= \frac{1}{2\pi i x + \lambda} + \frac{1}{-2\pi i x + \lambda} \\ &= \frac{2\lambda}{\lambda^2 + (2\pi x)^2}, \end{aligned} \tag{A.11}$$

which is the Lorentzian representation of the delta function with $\epsilon = \lambda/(2\pi)$.

Notice that the integral and the $\lambda \to 0+$ limit do not commute. Namely, the integral with $\lambda = 0$ is undefined.

A.1 Problems

Problem 1

Show that the Gaussian

$$\delta_\epsilon(x) = \frac{1}{\sqrt{2\pi}\epsilon} \exp(-\frac{x^2}{2\epsilon^2}) \tag{A.12}$$

and the Lorentzian

$$\delta_\epsilon(x) = \frac{1}{\pi} \frac{\epsilon}{x^2 + \epsilon^2} \tag{A.13}$$

in the limit of $\epsilon \to 0$ satisfy all the properties of the Dirac delta function.

Appendix B

Normalization integral of spherical harmonics

In this section of the appendix we calculate the normalization integral I_{2l+1} for spherical harmonics defined by Eq. 15.61.

First, by integration by parts we find a recursion relation between such integrals:

$$I_{2l+1} = \int_0^\pi d\theta (\sin\theta)^{2l+1} = -\int_0^\pi d\theta \frac{d\cos\theta}{d\theta} (\sin\theta)^{2l}$$

$$= 2l \int_0^\pi d\theta (\cos\theta)^2 (\sin\theta)^{2l-1} = 2lI_{2l-1} - 2lI_{2l+1}. \tag{B.1}$$

To derive the last step we have used the identity $\cos^2\theta = 1 - \sin^2\theta$. Therefore, we find that

$$(2l+1)I_{2l+1} = 2lI_{2l-1}. \tag{B.2}$$

Applying this relationship for $l \to l-1$ we find that

$$(2l-1)I_{2l-1} = 2(l-1)I_{2l-3}. \tag{B.3}$$

Now, we apply the above equation for $l \to l-2$

$$(2l-3)I_{2l-3} = 2(l-2)I_{2l-5}. \tag{B.4}$$

and so on until we reach $l \to l-(l-1)$

$$3I_3 = 2I_1. \tag{B.5}$$

Now we multiply these l equations together to find (after the cancellation)

$$(2l+1)(2l-1)(2l-3)....3I_{2l+1} = [2l][2(l-1)]...2I_1, \tag{B.6}$$

which implies that

$$I_{2l+1} = \frac{[2^l l!]^2 I_1}{(2l+1)!}, \tag{B.7}$$

where

$$I_1 = \int_0^\pi d\theta \sin\theta = 2. \tag{B.8}$$

Putting the various pieces that we found together, we conclude that the normalization constant C is given by

$$C = \frac{(-1)^l}{2^l l!}\sqrt{\frac{(2l+1)!}{4\pi}}, \tag{B.9}$$

where we have added by hand the phase factor $(-1)^l$ following the traditional convention.

Appendix C
Legendre equation

In this appendix we prove that the polynomials obtained by Eq. 15.74 are indeed solutions to the Legendre equation (15.73).

Consider the identity:

$$(s^2-1)\frac{d}{ds}(s^2-1)^l = 2lx(x^2-1)^l. \tag{C.1}$$

First we calculate the derivative of both sides of the above equation l times and reorganize the terms. We obtain

- after acting once:

$$(s^2-1)\frac{d^2}{ds^2}(s^2-1)^l = 2l(s^2-1)^l + 2(l-1)s\frac{d}{ds}(s^2-1)^l. \tag{C.2}$$

- After acting again we find that

$$\begin{aligned}(s^2-1)\frac{d^3}{ds^3}(s^2-1)^l &= [2l+2(l-1)]\frac{d}{ds}(s^2-1)^l \\ &\quad + 2(l-2)s\frac{d^2}{ds^2}(s^2-1)^l.\end{aligned} \tag{C.3}$$

- After acting for a 3rd time we obtain

$$\begin{aligned}(s^2-1)\frac{d^4}{ds^4}(s^2-1)^l &= [2l+2(l-1)+2(l-2)] \\ \times \frac{d^2}{ds^2}(s^2-1)^l &+ 2(l-3)s\frac{d^3}{ds^3}(s^2-1)^l.\end{aligned} \tag{C.4}$$

- After acting for a lth time we obtain

$$\begin{aligned}&(s^2-1)\frac{d^{l+1}}{ds^{l+1}}(s^2-1)^l \\ &= [2l+2(l-1)+2(l-2)+\ldots+1] \\ &\times \frac{d^{l-1}}{ds^{l-1}}(s^2-1)^l + 2(l-l)s\frac{d^l}{ds^l}(s^2-1)^l,\end{aligned} \tag{C.5}$$

  namely

$$(s^2-1)\frac{d^{l+1}}{ds^{l+1}}(s^2-1)^l = l(l+1)\frac{d^{l-1}}{ds^{l-1}}(s^2-1)^l. \tag{C.6}$$

- Now we act again as follows

$$\frac{d}{ds}\left[(s^2-1)\frac{d^{l+1}}{ds^{l+1}}(s^2-1)^l\right] = l(l+1)\frac{d^l}{ds^l}(s^2-1)^l. \tag{C.7}$$

Therefore, the expression given by Eq. 15.74 satisfies the Legendre equation (15.73).

Appendix D

Expression for the spherical Bessel function

Here, we show that the expression (16.55) satisfies the equation (16.14) for the spherical Bessel function.

First we need to calculate the first and second derivative of $j_l(\rho)$ using the expression (16.55) and substitute in the left-hand-side of the spherical Bessel equation (16.14). We find that the term $l(l+1)j_l(\rho)$ is exactly canceled by a term arising from the derivatives, and after factoring the left-hand-side of Eq. 16.14 it takes the form:

$$i\frac{2(l+1)\rho^{l+1}}{2^{l+1}l!}\int_{-1}^{1} se^{i\rho s}(1-s^2)^l ds$$
$$-\frac{\rho^{l+2}}{2^{l+1}l!}\int_{-1}^{1} s^2 e^{i\rho s}(1-s^2)^l ds + \rho^2 j_l(\rho). \tag{D.1}$$

We rewrite the combination of factors $2(l+1)s(1-s^2)^l$ in the first integral as $-d(1-s^2)^{l+1}/ds$ and we integrate by parts. The first term becomes:

$$-\frac{\rho^{l+2}}{2^{l+1}l!}\int_{-1}^{1} e^{i\rho s}(1-s^2)^{l+1} ds. \tag{D.2}$$

By combining this resulting term and the second term above we find

$$-\frac{\rho^{l+2}}{2^{l+1}l!}\int_{-1}^{1} e^{i\rho s}(1-s^2)^{l} ds, \tag{D.3}$$

which is equal to $-\rho^2 j_l(\rho)$. Thus, the left-hand-side of the Eq. 16.14 is zero.

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