Exercises in Quantum Mechanics

A Self-Contained Book of Questions and Answers

David ATKINSON
Mahouton Norbert HOUNKONNOU
Porter Wear JOHNSON

Volume 3

Rinton Press

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This book is the third in a series of four volumes. It contains the full solutions of all 100 exercises and problems of Volume 1, *Quantum Mechanics: A Self-Contained Course*. For the convenience of the user, each question is reproduced in this book, followed immediately by the solution. Beside solving the problem, many of the expositions include additional didactic material. Where feasible, algebraic answers are given; but in some places recourse to approximate methods was necessary. Some of the numerical results were obtained by using Mathematica (which is a trademark of Wolfram Research Inc.), but for readers without access to this system, many of our numerical answers can be checked by means of a scientific calculator. It cannot be emphasized too strongly that the temptation for a student to look immediately at the worked-out answers is self-defeating. Look at the answers, certainly, but only after you have engaged in serious battle. Physics cannot be learned just by reading or listening, but only by thinking, writing and worrying.

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ISBN 1-58949-026-6

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Rinton Press, Inc.

Library of Congress Control Number: 2003100658

12 Castleton Road
Princeton, New Jersey 08540
USA
rinton@rintonpress.com
http://www.rintonpress.com

Idea for cover design: Jeanne Peijnenburg

Published by Rinton Press, Inc.

Printed in the United States of America

ISBN 1-58949-026-6

Preface

This book is the third in a series of four volumes devoted respectively to

(1) Nonrelativistic Quantum Mechanics
(2) Relativistic Quantum Field Theory
(3) Exercises and problems, with fully worked out solutions, on the subjects treated in Volume 1.
(4) Exercises and problems, with fully worked out solutions, on the subjects treated in Volume 2.

The first two volumes were self-contained in the sense that the only prerequisites were a knowledge of integral calculus and partial differential equations, as well as Newton's mechanics of point masses and Maxwell's theory of electromagnetism.

Each chapter was complemented by ten problems, and the present volume constitutes the full solution of the hundred exercises contained in Volume 1. For the convenience of the reader, each question is reproduced in this book, followed immediately by the solution. Beside solving the problem, many of the expositions include additional didactic material. Where feasible, algebraic answers are given; but in some places recourse to approximate methods was necessary. Some of the numerical results were obtained by using *Mathematica* (which is a trademark of Wolfram Research Inc.), but for readers without access to this system, many of our numerical answers can be checked by means of a scientific calculator. Since only a few examples are solvable in algebraic closed form, numerical exercises are important for exploring the intricacies of quantum mechanics.

We acknowledge the assistance afforded by perusal of the works listed in the references, in particular Atkins, P.W., (1983b), Gol'dman, I.I. and Krivchenkov, V.D., (1961), Haar, D. ter, (1975) and Kok, L.P. and Visser, J., (1996). These books of solutions to quantum mechanics problems may be rightly seen as our precursors in the art of solving exercises in quantum mechanics; but, if we have sometimes taken over solutions from these authors, we have always added details, in order to enhance the pedagogical quality.

It cannot be emphasized too strongly that the temptation for a student to look immediately at the worked-out answers is self-defeating. Look at the answers, certainly, but only after you have engaged in serious battle. Physics cannot be learned just by reading or listening, but only by thinking, writing and worrying.

Despite the plethora of books of instruction on these subjects, we hope that our work will fill a need, and we believe our approach to be pedagogically sound, given its attention to mathematical detail combined with physics.

The drawings on the covers of the volumes are ambiguous representations.

Volume 1: a duck, or is it a rabbit?
Volume 2: a vase, or are there two faces?
Volume 3: a young, or is it an old woman?
Volume 4: an American Indian, or is it an Eskimo?

The simultaneous existence of two pictures is perhaps the closest metaphor we can find to the fundamental mystery of quantum mechanics, namely the linear superposition of two aspects of reality, each of which separately can be pictured, and whose combination can barely be comprehended by the eye of introspection, but which can be apprehended by the power of mathematical language.

February 2003,

David Atkinson (The Netherlands)
Mahouton Norbert Hounkonnou (République du Bénin).
Porter Wear Johnson (United States of America)

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Chapter 1

Transition from Classical to Quantum Mechanics

1.1 Axioms of Linear Vector Spaces

From the axioms of the theory of linear vector spaces prove:

(1) Any linear operator can be written in the form $A + iB$, where A and B are Hermitian operators.
(2) If A and B are Hermitian operators, so is $i[A, B]$.
(3) For any vector ϕ, $\mathcal{S}(\phi, A^\dagger A\phi) \geq 0$.

Solution
(1) Let C be a linear operator and define

$$A = (C + C^\dagger)/2 \qquad B = -i(C - C^\dagger)/2\,.$$

Then clearly $A = A^\dagger$, $B = B^\dagger$ and $A + iB = C$. In this demonstration, it has been tacitly assumed that $C^\dagger$ exists, i.e., for any ϕ and ψ in the Hilbert space on which C acts as a linear operator, $C\phi$ is a vector in the space, and thus that $\mathcal{S}(\psi, C\phi)$ is finite. This is equivalent to requiring C to be a bounded operator. For an unbounded operator, one can make still make sense of the theorem, on condition that one restricts the space to a subspace of the Hilbert space, namely the intersection of the range and the domain of C, for on this space C and $C^\dagger$ are both bounded.
(2) For any bounded, linear, Hermitian operators, A and B,

$$[i(AB - BA)]^\dagger = -i(BA - AB) = i(AB - BA)\,.$$

(3) For any bounded, linear operator, A,

$$\mathcal{S}(\phi, A^\dagger A\phi) = \mathcal{S}(A\phi, A\phi) = \mathcal{S}(\chi, \chi) \geq 0\,,$$

where $\chi = A\phi$, and the third property of the scalar product has been used. Here we have implicitly used the property $\left(A^\dagger\right)^\dagger = A$. This follows from

$$\begin{aligned} \mathcal{S}(\psi, A\phi) &= \mathcal{S}(A^\dagger\psi, \phi) = \mathcal{S}(\phi, A^\dagger\psi)^* \\ &= \mathcal{S}(\left(A^\dagger\right)^\dagger\phi, \psi)^* = \mathcal{S}(\psi, \left(A^\dagger\right)^\dagger\phi)\,. \end{aligned}$$

Since ϕ and ψ can be any vectors in the space, for example two vectors in a basis, the required result follows.

1.2 Orthonormal Basis of a Hilbert Space

Suppose that $\{e_n\}$ is an orthonormal basis of a Hilbert space, $\mathcal{H}$, and let A be a linear operator on $\mathcal{H}$. The trace of A with respect to the basis is defined by

$$\mathrm{Tr}A = \sum_n \langle e_n|A|e_n\rangle\,.$$

(1) Demonstrate that $\mathrm{Tr}A$ is independent of the choice of the orthonormal basis.

(2) If A and B are linear operators on $\mathcal{H}$, show that

$$\mathcal{S}(A, B) = \mathrm{Tr}\left(A^\dagger B\right)$$

satisfies the axioms of the scalar product.

Solution

(1) Let $\{f_n\}$ be any other orthonormal basis. Then

$$\begin{aligned} \mathrm{Tr}A = \sum_n \langle e_n|A|e_n\rangle &= \sum_n\sum_m \langle e_n|A|f_m\rangle\langle f_m|e_n\rangle \\ &= \sum_m\sum_n \langle f_m|e_n\rangle\langle e_n|A|f_m\rangle = \sum_m \langle f_m|A|f_m\rangle\,, \end{aligned}$$

where use has been made of the fact that both sets of basis vectors, $\{e_n\}$ and $\{f_n\}$, span the space.

(2) Let $\{e_n\}$ be an orthonormal basis. Then the three axioms pertaining to the scalar product are satisfied as follows:

(a) $[S(A,B)]^* = \left\{\mathrm{Tr}(A^\dagger B)\right\}^* = \left\{\sum_n \langle e_n|A^\dagger B|e_n\rangle\right\}^*$.

Insert a unit operator between $A^\dagger$ and B:

$$\begin{aligned} [S(A,B)]^* &= \sum_{m,n} \langle e_n|A^\dagger|e_m\rangle^*\langle e_m|B|e_n\rangle^* \\ &= \sum_{m,n} \langle e_m|A|e_n\rangle\langle e_n|B^\dagger|e_m\rangle = [S(B,A)]\,. \end{aligned}$$

(b) $S(A, cB + dC) = \sum_n \langle e_n|A^\dagger(cB + dC)|e_n\rangle$.

$$= c\sum_n \langle e_n|A^\dagger B|e_n\rangle + d\sum_n \langle e_n|A^\dagger C|e_n\rangle$$
$$= cS(A, B) + dS(A, C) .$$

(c) $S(A, A) = \sum_{m,n} \langle e_n|A^\dagger|e_m\rangle\langle e_m|A|e_n\rangle = \sum_{m,n} |\langle e_m|A|e_n\rangle|^2$. Thus
(i) $S(A, A) > 0$ unless $\langle e_m|A|e_n\rangle = 0$ for all (m, n) i.e., $A = 0$.
(ii) $S(A, A) = 0$ if $A = 0$, for then $\langle e_m|A|e_n\rangle = 0$ for all (m, n).

1.3 Linear Operators on a Hilbert Space

Suppose that A and B are linear operators on a Hilbert space, $\mathcal{H}$, and that $\langle\psi|A|\psi\rangle = \langle\psi|B|\psi\rangle$ for all $\psi \in \mathcal{H}$. Show that necessarily $\langle\phi|A|\psi\rangle = \langle\phi|B|\psi\rangle$ for all $\phi \in \mathcal{H}$ and $\psi \in \mathcal{H}$. Under these conditions, i.e., when all matrix elements of A and B are equal, we write $A = B$ as an identity of two operators on a given Hilbert space.

Solution
Consider the identity,

$$4\langle\phi|A|\psi\rangle = \langle\phi+\psi|A|\phi+\psi\rangle - \langle\phi-\psi|A|\phi-\psi\rangle - i\langle\phi+i\psi|A|\phi+i\psi\rangle + i\langle\phi-i\psi|A|\phi-i\psi\rangle$$

and the corresponding identity obtained by replacing A by B. Since all matrix elements on the right-hand side are diagonal, their values are independent of whether A or B appears in them. Hence the non-diagonal matrix element on the left-hand side must also be independent of whether A or B occurs. This demonstrates the proposition that equality of diagonal matrix elements implies equality of non-diagonal matrix elements.

Note that this proof worked because, while a ket is linear, i.e., $|c\phi\rangle = c|\phi\rangle$, a bra is antilinear, $\langle c\phi| = c^*\langle\phi|$. In terms of the vector space scalar product,

$$S(c\phi, d\psi) = c^* d\, S(\phi, \psi) .$$

Thus the fact that the vector space is defined on the field of complex numbers is essential. On a *real* Hilbert space, the above proof would not work. Notice also that the operator equality, $A = B$, is valid as a statement restricted to the space for which the diagonal matrix elements are equal. This should not be regarded as a shortcoming, since, strictly speaking, *any* operator is fully defined only when one specifies the space on which it acts, or more generally on which it is densely defined.

1.4 Spaces of Functions

Consider the following spaces of functions of all ψ, such that, respectively

$$\mathcal{H} \quad : \quad \int_{-\infty}^{\infty} dx\, |\psi(x)|^2 < \infty$$

$$\Omega \quad : \quad \int_{-\infty}^{\infty} dx\, |\psi(x)|^2 [1 + |x|^n] < \infty\,, \text{ for } n = 0, 1, 2, \ldots .$$

$$\Xi \quad : \quad \left| \int_{-\infty}^{\infty} dx\, \psi^*(x)\phi(x) \right| < \infty\,, \text{ for all } \phi \in \Omega\,.$$

Show that

(1) $\Omega \subset \mathcal{H} \subset \Xi$.
(2) $x \notin \mathcal{H}$.
(3) $\operatorname{sech} x \in \Omega\,, \quad \frac{\sin x}{x} \notin \Omega\,, \quad \frac{\sin x}{x} \in \mathcal{H}$.
(4) $x^2 \cos x \notin \mathcal{H}\,, \quad x^2 \cos x \in \Xi$.
(5) $\mathrm{e}^{-x} \notin \Xi$.

Solution

(1) Clearly, every element of Ω belongs to H. Furthermore, since $\psi(x) = (1 + x^2)^{-\frac{1}{2}}$ is clearly square integrable, but equally clearly does not belong to Ω, it follows that $\Omega \subset \mathcal{H}$. To prove $\mathcal{H} \subset \Xi$, we shall use the Schwarz inequality. This states that, for any ψ_1 and ψ_2 in a vector space equipped with a scalar product $\mathcal{S}$,

$$|\mathcal{S}(\psi_1, \psi_2)|^2 \leq \mathcal{S}(\psi_1, \psi_1)\mathcal{S}(\psi_2, \psi_2)\,. \tag{1.1}$$

To prove this theorem, consider any real or complex number λ. Then

$$\mathcal{S}(\psi_1 + \lambda\psi_2, \psi_1 + \lambda\psi_2) \geq 0\,,$$

and expanding this, we find

$$\mathcal{S}(\psi_1, \psi_1) + |\lambda|^2 \mathcal{S}(\psi_2, \psi_2) + \lambda \mathcal{S}(\psi_1, \psi_2) + \lambda^* \mathcal{S}(\psi_2, \psi_1) \geq 0\,. \tag{1.2}$$

If ψ_2 is not the null vector (when the theorem is trivially true), define

$$\lambda = -\frac{\mathcal{S}(\psi_2, \psi_1)}{\mathcal{S}(\psi_2, \psi_2)}\,.$$

The last three terms in Eq.(1.2) satisfy

$$|\lambda|^2 \mathcal{S}(\psi_2, \psi_2) = -\lambda \mathcal{S}(\psi_1, \psi_2) = -\lambda^* \mathcal{S}(\psi_2, \psi_1) = \frac{|\mathcal{S}(\psi_1, \psi_2)|^2}{\mathcal{S}(\psi_2, \psi_2)}\,.$$

Hence the inequality (1.2) yields

$$\mathcal{S}(\psi_1,\psi_1) \geq \frac{|\mathcal{S}(\psi_1,\psi_2)|^2}{\mathcal{S}(\psi_2,\psi_2)}\,,$$

and this is equivalent to Eq.(1.1). In the case that the scalar product is

$$\mathcal{S}(\psi_1,\psi_2) = \int_{-\infty}^{\infty} dx\, \psi_1^*(x)\psi_2(x)\,,$$

the Schwarz inequality takes on the form

$$\left|\int_{-\infty}^{\infty} dx\, \psi_1^*(x)\psi_2(x)\right|^2 \leq \int_{-\infty}^{\infty} dx\, |\psi_1(x)|^2 \int_{-\infty}^{\infty} dx\, |\psi_2(x)|^2\,.$$

We shall now use this integral form of the Schwarz inequality to investigate the space Ξ. Insert $\psi_1(x) = [1+|x|^n]^{-\frac{1}{2}}\psi(x)$ and $\psi_2(x) = [1+|x|^n]^{\frac{1}{2}}\phi(x)$ into the above inequality, thus yielding

$$\left|\int_{-\infty}^{\infty} dx\, \psi^*(x)\phi(x)\right|^2 \leq \int_{-\infty}^{\infty} dx\, [1+|x|^n]^{-1}\, |\psi(x)|^2 \int_{-\infty}^{\infty} dx\, [1+|x|^n]\, |\phi(x)|^2\,.$$

We are free to choose n as we like; and if $\phi \in \Omega$ then the second integral is finite for any n. If $\psi \in \mathcal{H}$, then the first integral is finite for $n = 0$. This shows that any square integrable function lies also in the space Ξ. On the other hand, there are functions that do not lie in $\mathcal{H}$, but which do lie in Ξ. Take for example $\psi(x) = 1$ and choose $n = 2$. The first integral is in this case $\int_{-\infty}^{\infty} dx\, [1+x^2]^{-1}$, which converges. Hence $\psi(x) = 1$ lies in Ξ, and so $\mathcal{H} \subset \Xi$.
(2) Clearly x does not belong to $\mathcal{H}$, because $\int_{-L}^{L} dx\, x^2 = \frac{2}{3}L^3$, and which diverges as $L \to \infty$.
(3a) Since $\operatorname{sech} x$ tends exponentially to zero as $|x| \to \infty$, it belongs to Ω, since

$$\int_{-\infty}^{\infty} dx\, \operatorname{sech}^2 x\, [1+|x|^n] < \infty\,, \text{ for } n = 0,1,2,\ldots$$

(3b) Clearly $\frac{\sin x}{x} \notin \Omega$, since $\frac{\sin^2 x}{x^2}[1+|x|^n]$ is not integrable for $n = 1,2,3,\ldots$
(3c) On the other hand, $\frac{\sin x}{x} \in \mathcal{H}$, since

$$\int_{-\infty}^{\infty} dx\, \frac{\sin^2 x}{x^2} < 2\int_0^1 dx + 2\int_1^{\infty} \frac{dx}{x^2} = 4\,.$$

(4) It is clear that $x^2\cos x$ is not square integrable, so it does not belong to $\mathcal{H}$. On the other hand, it does belong to Ξ, since

$$\left|\int_{-\infty}^{\infty} dx\, x^2\cos x\, \phi(x)\right|^2 \leq \int_{-\infty}^{\infty} dx\, x^4\cos^2 x\, [1+|x|^n]^{-1} \int_{-\infty}^{\infty} dx\, |\phi(x)|^2[1+|x|^n]\,,$$

for any n, where we have used the Schwarz inequality again. The first integral above is finite if we choose $n = 6$, for example, and the second integral is guaranteed to be finite for any $\phi \in \Omega$.
(5) Consider $\phi(x) = \operatorname{sech} x$, which was shown in solution (3a) to belong to the space Ω. We have $e^{-x}\operatorname{sech} x \to 2$, in the limit $x \to -\infty$, so that $e^{-x}\phi(x)$ is not integrable. Hence e^{-x} does not belong to the space Ξ.

1.5 Representations of Delta Funtion

By introducing a suitable space of test functions, justify the following representations of the Dirac delta distribution:

$$\text{(a)} \qquad \delta(x) = \lim_{\varepsilon \to 0} \frac{1}{\pi} \frac{\varepsilon}{x^2 + \varepsilon^2}$$

$$\text{(b)} \qquad \delta(x) = \lim_{N \to \infty} \frac{1}{\pi} \frac{\sin Nx}{x}$$

Solution
(a) Let $g(x)$ be an infinitely differentiable function of finite support. Then, setting $x = y\varepsilon$, we find

$$\lim_{\varepsilon \to 0} \frac{\varepsilon}{\pi} \int_{-\infty}^{\infty} dx \frac{g(x)}{x^2 + \varepsilon^2} = \frac{1}{\pi} \lim_{\varepsilon \to 0} \int_{-\infty}^{\infty} dy \frac{g(y\varepsilon)}{y^2 + 1} = \frac{2}{\pi} g(0) \int_0^{\infty} \frac{dy}{y^2 + 1} = g(0).$$

The y-integral can be performed by making the substitution $y = \tan\theta$.
(b) With the same space of test functions, and with $z = x/N$,

$$\begin{aligned} \lim_{N \to \infty} \frac{1}{\pi} \int_{-\infty}^{\infty} dx\, g(x) \frac{\sin(Nx)}{x} &= \lim_{N \to \infty} \frac{1}{\pi} \int_{-\infty}^{\infty} dz g(z/N) \frac{\sin z}{z} \\ &= \frac{1}{\pi} g(0) \int_{-\infty}^{\infty} dz \frac{\sin z}{z} = g(0). \end{aligned}$$

The z-integral can be evaluated by writing $\frac{\sin z}{z} = \frac{e^{iz} - e^{-iz}}{2iz}$ and then by closing the integration contour in the upper half z-plane for e^{iz} and in the lower half z-plane for e^{-iz}.

1.6 Schur's Lemma

Let G be the space of complex differentiable test functions, $g(x)$, of finite support, where x is real. It is convenient to extend G slightly to encompass all functions, $\tilde{g}$, such that $\tilde{g}(x) = g(x) + c$, where $g \in G$ and c is any constant. Let us call the

extended space $\tilde{G}$. Let $\mathbf{q}$ and $\mathbf{p}$ be linear operators on $\tilde{G}$ such that

$$\begin{aligned} \mathbf{q}g(x) &= xg(x), \\ \mathbf{p}g(x) &= -i\frac{d}{dx}g(x) = -ig'(x). \end{aligned}$$

Suppose M to be a linear operator on $\tilde{G}$ that commutes with $\mathbf{q}$ and $\mathbf{p}$. Show that

(1) $\mathbf{q}$ and $\mathbf{p}$ are Hermitian on $\tilde{G}$.
(2) M is a constant multiple of the identity operator.

Solution

We shall equip the space $\tilde{G}$ with the scalar product

$$\mathcal{S}(f,g) = \int_{-\infty}^{\infty} dx f^*(x)g(x),$$

for any f and g in $\tilde{G}$. Clearly

$$\mathcal{S}(f,qg) = \int_{-\infty}^{\infty} dx\, xf^*(x)g(x).$$

On the other hand

$$\mathcal{S}(f,q^\dagger g) = \mathcal{S}(qf,g) == \int_{-\infty}^{\infty} dx\, xf^*(x)g(x).$$

since x is real. Hence $\mathcal{S}(f,qg) = \mathcal{S}(f,q^\dagger g)$ for all f and g in G, and thus $q = q^\dagger$.

For the operator p,

$$\mathcal{S}(f,pg) = -i\int_{-\infty}^{\infty} dx\, f^*(x)g'(x),$$

and

$$\begin{aligned} \mathcal{S}(f,p^\dagger g) = \mathcal{S}(pf,g) &= \int_{-\infty}^{\infty} dx\big[-if'(x)\big]^* g(x) \\ &= i\int_{-\infty}^{\infty} dx f'^*(x)g(x). \end{aligned}$$

We perform an integration by parts:

$$\mathcal{S}(f,p^\dagger g) = i\big[f(\infty)g(\infty) - f(-\infty)g(-\infty)\big] - i\int_{-\infty}^{\infty} dx f^*(x)g'(x).$$

Now the integrated term vanishes, since $f(\infty) = f(-\infty)$ and $g(\infty) = g(-\infty)$ for f and g in $\tilde{G}$. Thus indeed $p^\dagger = p$.

Since $[M, q] = 0$, it follows that $[M, q^n] = 0$, $n = 1, 2, 3, \ldots$ and hence that $[M, \mathrm{e}^{itq}] = 0$, Thus any function of the operator, q, that has a Fourier transform,

$$f(q) = \int_{-\infty}^{\infty} dt \tilde{f}(t)\, \mathrm{e}^{itq}\,, \tag{1.3}$$

also commutes with M. For such a function,

$$Mf(q)g(x) = f(q)Mg(x)\,.$$

Since $qg(x) = xg(x)$, $q^n g(x) = x^n g(x)$ and $\mathrm{e}^{itq}g(x) = \mathrm{e}^{itx}g(x)$ and hence any Fourier transformable function, (1.3), satisfies

$$f(q)g(x) = f(x)g(x)\,,$$

and so

$$Mf(x)g(x) = f(q)Mg(x)\,.$$

It follows now that and if we choose $g(x) = 1$ in the above expression, we find

$$Mf(x) = f(q)m(x) = f(x)m(x)\,, \tag{1.4}$$

where $m(x)$ is the function of x that arises by letting the operator M act on the unit function. Certainly the unit function belongs to $\tilde{G}$, and we are sure that the function $m(x)$ lies *in* the space $\tilde{G}$. [N.B. This is the reason we had to extend the space of test functions from G to $\tilde{G}$. In G the above statements are not true!] Since Eq.(1.4) holds for any Fourier transformable function, it certainly holds if we replace $f(x)$ by $g(x)$, or by $g'(x)$:

$$Mg(x) = g(x)m(x) \tag{1.5}$$

$$Mg'(x) = g'(x)m(x)\,. \tag{1.6}$$

Now consider the fact that M commutes with p. This implies

$$pMg(x) = Mpg(x) = -iMg'(x)\,.$$

From Eq.(1.5) we write the left side in the form $pg(x)m(x) = -i\frac{d}{dx}\left[g(x)m(x)\right]$, whereas from Eq.(1.6) we have, for the right side, $-ig'(x)m(x)$. Hence

$$\frac{d}{dx}\left[g(x)m(x)\right] = g'(x)m(x)\,,$$

and this implies $m'(x) = 0$ or $m(x) = \kappa$, a constant. Then Eq.(1.5) reads

$$Mg(x) = \kappa g(x)\,,$$

or in other words, $M = \kappa I$, where I is the unit operator on G.

1.7 Commutators

Given that $[\mathbf{q}, \mathbf{p}] = i\hbar$, show that

(1) $[\mathbf{q}^{-1}, \mathbf{p}] = -i\hbar\mathbf{q}^{-2}$
(2) $[\mathbf{q}^n, \mathbf{p}] = i\hbar n\mathbf{q}^{n-1}$ $\qquad n = \pm1, \pm2, \pm3, \ldots$
(3) $[\exp(it\mathbf{q}), \mathbf{p}] = -\hbar t \exp(it\mathbf{q})$.
(4) $[\mathbf{q}^{-\frac{1}{2}}, \mathbf{p}] = -\frac{1}{2}i\hbar\mathbf{q}^{-\frac{3}{2}}$
(5) $[\mathbf{q}^{\frac{1}{2}}, \mathbf{p}] = \frac{1}{2}i\hbar\mathbf{q}^{-\frac{1}{2}}$

Solution
(1) $\mathbf{q}^{-1}(\mathbf{qp} - \mathbf{pq})\mathbf{q}^{-1} = i\hbar\mathbf{q}^{-2}$ so that $\mathbf{pq}^{-1} - \mathbf{q}^{-1}\mathbf{p} = i\hbar\mathbf{q}^{-2}$,
and hence $[\mathbf{q}^{-1}, \mathbf{p}] = -i\hbar\mathbf{q}^{-2}$.
(2) Suppose that $[\mathbf{q}^n, \mathbf{p}] = i\hbar n\mathbf{q}^{n-1}$ is true for some value of n. Multiplying this by the operator $\mathbf{q}$ from the left, we have $\mathbf{q}^{n+1}\mathbf{p} - \mathbf{qpq}^n = i\hbar n\mathbf{q}^n$.
The left-hand side can be written $[\mathbf{q}^{n+1}, \mathbf{p}] - [\mathbf{q}, \mathbf{p}]\mathbf{q}^n = [\mathbf{q}^{n+1}, \mathbf{p}] - i\hbar\mathbf{q}^n$ so if we transfer the term $-i\hbar\mathbf{q}^n$ to the other side, we find $[\mathbf{q}^{n+1}, \mathbf{p}] = i\hbar(n+1)\mathbf{q}^n$, which has the same form as what we supposed in the first place, excepting only that n has been replaced by $n+1$.
Since we know that $[\mathbf{q}^n, \mathbf{p}] = i\hbar n\mathbf{q}^{n-1}$ is true for $n = 1$, our demonstration establishes its truth for $n = 2$. In turn, this new truth establishes the result for $n = 3$, and so on. The validity of the formula for general n is thus established. The method that has been used is called mathematical induction.
(3) With use of the previous result, we find

$$[\exp(it\mathbf{q}), \mathbf{p}] = \sum_{n=0}^{\infty} \frac{(it)^n}{n!}[\mathbf{q}^n, \mathbf{p}] = i\hbar \sum_{n=1}^{\infty} \frac{(it)^n}{n!} n\mathbf{q}^{n-1} = -\hbar t \sum_{n=0}^{\infty} \frac{(it)^n}{n!}\mathbf{q}^n,$$

where n has been replaced by $n-1$ in the last step. We recognize the last sum as being $\exp(it\mathbf{q})$, so

$$[\exp(it\mathbf{q}), \mathbf{p}] = -\hbar t \exp(it\mathbf{q}).$$

(4) Consider the Fourier integral

$$\mathbf{q}^{-\frac{1}{2}} = \kappa \int_{-\infty}^{\infty} \frac{dt}{\sqrt{t}} \exp(it\mathbf{q}). \tag{1.7}$$

The constant κ can be evaluated by substituting $s = t\mathbf{q}$, yielding

$$\mathbf{q}^{-\frac{1}{2}} = \kappa\, \mathbf{q}^{-\frac{1}{2}} \int_{-\infty}^{\infty} \frac{ds}{\sqrt{s}} e^{is}.$$

Thus we find $\kappa^{-1} = \int_{-\infty}^{\infty} \frac{ds}{\sqrt{s}} \mathrm{e}^{is} = \sqrt{\pi}$. From the result of part (3) above, we can compute

$$\begin{aligned} [\mathbf{q}^{-\frac{1}{2}}, \mathbf{p}] &= \kappa \int_{-\infty}^{\infty} \frac{dt}{\sqrt{t}} [\exp(it\mathbf{q}), \mathbf{p}] \\ &= -\hbar\kappa \int_{-\infty}^{\infty} dt\sqrt{t}\, \exp(it\mathbf{q}) \\ &= -\hbar\kappa \mathbf{q}^{-\frac{3}{2}} \int_{-\infty}^{\infty} ds\sqrt{s}\, \mathrm{e}^{is}\,. \end{aligned} \tag{1.8}$$

By an integration by parts, we see that

$$\int_{-\infty}^{\infty} ds\sqrt{s}\, \mathrm{e}^{is} = \frac{i}{2} \int_{-\infty}^{\infty} \frac{ds}{\sqrt{s}} \mathrm{e}^{is} = \frac{i}{2\kappa}\,,$$

where the above manipulations must be understood in the sense of distributions: as an ordinary function, the integral does not exist, but once it is convoluted with a suitable test function, for example one with infinitely many derivatives and of finite support, the integration by parts is allowed. On combining this last result with Eq.(1.8), we find

$$[\mathbf{q}^{-\frac{1}{2}}, \mathbf{p}] = -\tfrac{1}{2} i\hbar \mathbf{q}^{-\frac{3}{2}}$$

(5) Using the previous result, we have

$$\mathbf{q}^{\frac{1}{2}} [\mathbf{q}^{-\frac{1}{2}}, \mathbf{p}] \mathbf{q}^{\frac{1}{2}} = -\tfrac{1}{2} i\hbar \mathbf{q}^{\frac{1}{2}} \mathbf{q}^{-\frac{3}{2}} \mathbf{q}^{\frac{1}{2}}\,,$$

which gives

$$\mathbf{p}\mathbf{q}^{\frac{1}{2}} - \mathbf{q}^{\frac{1}{2}}\mathbf{p} = -\tfrac{1}{2} i\hbar \mathbf{q}^{-\frac{1}{2}}\,,$$

or in other words, $[\mathbf{q}^{\frac{1}{2}}, \mathbf{p}] = \frac{1}{2} i\hbar \mathbf{q}^{-\frac{1}{2}}$.

1.8 Classical Poisson Bracket

In one space dimension, consider the classical Poisson bracket of the square of the coordinate and the square of the conjugate momentum, $\{q^2, p^2\}$.

(1) Show that the quantum mechanical commutator, $[\mathbf{q}^2, \mathbf{p}^2]$, divided by $i\hbar$, *does not* correspond to that Poisson bracket.
(2) How must one rewrite the classical Poisson bracket so that the commutator does so correspond?

Solution

(1) The classical Poisson bracket is

$$\{q^2, p^2\} = \frac{\partial q^2}{\partial q}\frac{\partial p^2}{\partial p} - \frac{\partial q^2}{\partial p}\frac{\partial p^2}{\partial q} = 4qp\,, \tag{1.9}$$

whereas the quantum mechanical commutator is

$$[\mathbf{q}^2, \mathbf{p}^2] = \mathbf{q}^2\mathbf{p}^2 - \mathbf{p}^2\mathbf{q}^2 = \mathbf{q}[\mathbf{q}, \mathbf{p}^2] + [\mathbf{q}, \mathbf{p}^2]\mathbf{q}\,. \tag{1.10}$$

Now

$$[\mathbf{q}, \mathbf{p}^2] = [\mathbf{q}, \mathbf{p}]\mathbf{p} + \mathbf{p}[\mathbf{q}, \mathbf{p}] = 2i\hbar\mathbf{p}\,, \tag{1.11}$$

so

$$[\mathbf{q}^2, \mathbf{p}^2] = 2i\hbar(\mathbf{qp} + \mathbf{pq})\,, \tag{1.12}$$

and indeed this is not of the same form as $i\hbar$ times the classical Poisson bracket of q^2 and p^2.

(2) One only has to rewrite the classical Poisson bracket in the form

$$\{q^2, p^2\} = 2(qp + pq)\,, \tag{1.13}$$

which is allowed, since the order of writing q and p does not matter classically. This form clearly *does* correspond to the commutator of $\mathbf{q}^2$ and $\mathbf{p}^2$, divided by $i\hbar$. In general, one must always rearrange the right-hand side of any Poisson bracket of observables such that, when quantized, it gives a Hermitian expression. $\mathbf{qp}$ is not Hermitian, since

$$(\mathbf{qp})^\dagger = \mathbf{pq}\,,$$

but $\mathbf{qp} + \mathbf{pq}$ is Hermitian.

1.9 Time-Dependent Schrödinger Equation

Suppose that $\psi(t, \vec{x}\,)$ satisfies the time-dependent Schrödinger equation, with a real, time-independent potential. Define the probability density by

$$P(t, \vec{x}\,) = |\psi(t, \vec{x}\,)|^2\,.$$

(1) Show that

$$\frac{\partial}{\partial t}P(t, \vec{x}\,) + \vec{\nabla} \cdot \vec{\jmath}\,(t, \vec{x}\,) = 0\,,$$

where the probability current is defined by

$$\vec{j}(t,\vec{x}) = -\frac{i\hbar}{2m}\psi^*(t,\vec{x})\overleftrightarrow{\nabla}\psi(t,\vec{x})\,.$$

Discover thereby the meaning of the symbol $\overleftrightarrow{\nabla}$.

(2) Show that, for a square integrable $\psi(t,\vec{x})$,

$$\frac{d}{dt}\int d^3x\, P(t,\vec{x}) = 0\,,$$

the integral being over all space. Give a physical interpretation of this result.

(3) Evaluate next

$$\frac{d}{dt}\int_V d^3x\, P(t,\vec{x})\,,$$

in terms of $\vec{j}(t,\vec{x})$, the integral now being over a finite volume, V. Give a physical interpretation of this result.

Solution

Consider the time-dependent Schrödinger equation, and its complex conjugate:

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\psi(t,\vec{x}) &= -\frac{\hbar^2}{2m}\nabla^2\psi(t,\vec{x}) + V(\vec{x})\psi(t,\vec{x}) \\ -i\hbar\frac{\partial}{\partial t}\psi^*(t,\vec{x}) &= -\frac{\hbar^2}{2m}\nabla^2\psi^*(t,\vec{x}) + V(\vec{x})\psi^*(t,\vec{x})\,, \end{aligned}$$

where the reality of the potential has been used. Multiply the equation for ψ by ψ^* and that for ψ^* by ψ and subtract one result from the other:

$$\begin{aligned} & i\hbar\left\{\psi^*\frac{\partial}{\partial t}\psi(t,\vec{x}) + \psi\frac{\partial}{\partial t}\psi^*(t,\vec{x})\right\} \\ & \qquad = -\frac{\hbar^2}{2m}\left\{\psi^*(t,\vec{x})\nabla^2\psi(t,\vec{x}) - \psi(t,\vec{x})\nabla^2\psi^*(t,\vec{x})\right\}. \end{aligned}$$

This can be rewritten

$$\frac{\partial}{\partial t}\left\{\psi^*(t,\vec{x})\psi(t,\vec{x})\right\} = \frac{i\hbar}{2m}\vec{\nabla}\cdot\left\{\psi^*(t,\vec{x})\vec{\nabla}\psi(t,\vec{x}) - \psi(t,\vec{x})\vec{\nabla}\psi^*(t,\vec{x})\right\},$$

which is equivalent to

$$\frac{\partial}{\partial t}P(t,\vec{x}) + \vec{\nabla}\cdot\vec{j}(t,\vec{x}) = 0\,, \tag{1.14}$$

where the density is $P(t,\vec{x}) = |\psi(t,\vec{x})|^2$, and where the current is

$$\begin{aligned}\vec{\jmath}(t,\vec{x}) &= -\frac{i\hbar}{2m}\Big\{\psi^*(t,\vec{x})\vec{\nabla}\psi(t,\vec{x}) - \psi(t,\vec{x})\vec{\nabla}\psi^*(t,\vec{x})\Big\}, \\ &\stackrel{def}{=} -\frac{i\hbar}{2m}\psi^*(t,\vec{x})\overleftrightarrow{\nabla}\psi(t,\vec{x}).\end{aligned}$$

(2) From Eq.(1.14) we find

$$\frac{d}{dt}\int d^3x\, P(t,\vec{x}) = -\int d^3x\, \vec{\nabla}\cdot\vec{\jmath}(t,\vec{x}),$$

and this vanishes for a square-integrable $\psi(t,\vec{x})$, since for such a solution the probability current, $\vec{\jmath}(t,\vec{x})$, vanishes exponentially at spatial infinity. The left-hand side above is interpreted as the probability that the particle described by the wave function, $\psi(t,\vec{x})$, is found to be somewhere in space at all times. This is sometimes referred to as the conservation of probability, and usually one normalizes this time-invariant integral to unity.
(3) In the case of a finite integration volume,

$$\begin{aligned}\frac{d}{dt}\int_V d^3x\, P(t,\vec{x}) &= -\int_V d^3x\, \vec{\nabla}\cdot\vec{\jmath}(t,\vec{x}) \\ &= -\int_S dS\, \vec{n}\cdot\vec{\jmath}(t,\vec{x}),\end{aligned}$$

where S is the surface of the volume V and $\vec{n}$ is the unit vector normal to the surface. This is an application of the Gauß theorem. The interpretation is that the rate of change of the probabilty of finding the particle in the volume V is equal to minus the current density, integrated across the boundary of the volume. This is clearer if one thinks of an ensemble of particles described by the wave function $\psi(t,\vec{x})$. Then the left-hand side of the above equation is proportional to the rate of increase of the number of particles that are inside V, and the right-hand side is proportional to the rate at which particles enter V through its surface.

1.10 Bell's Theorem with Photons

Two photons fly apart from one another, and are in oppositely oriented circularly polarized states. One strikes a polaroid film with axis parallel to the unit vector $\vec{a}$, the other a polaroid with axis parallel to the unit vector $\vec{b}$. Let $P_{++}(\vec{a},\vec{b})$ be the joint probability that both photons are transmitted through their respective polaroids. Similarly $P_{--}(\vec{a},\vec{b})$ is the probability that both photons are absorbed by the polaroids, $P_{+-}(\vec{a},\vec{b})$ is the probability that the photon at the $\vec{a}$ polaroid is

transmitted, while the other is absorbed, and finally $P_{-+}(\vec{a},\vec{b})$ is the probability that the photon at the $\vec{a}$ polaroid is absorbed, while the other is transmitted.

The classical realist assumption is that these probabilities can be separated:

$$P_{ij}(\vec{a},\vec{b}) = \int d\lambda \rho(\lambda) P_i(\vec{a},\lambda) P_j(\vec{b},\lambda),$$

where i and j take on the values $+$ and $-$, where λ signifies the so-called hidden variables, and where $\rho(\lambda)$ is a weight function.

The correlation coefficient is defined by

$$C(\vec{a},\vec{b}) = P_{++}(\vec{a},\vec{b}) + P_{--}(\vec{a},\vec{b}) - P_{+-}(\vec{a},\vec{b}) - P_{-+}(\vec{a},\vec{b}),$$

and so we can write

$$C(\vec{a},\vec{b}) = \int d\lambda \rho(\lambda) C(\vec{a},\lambda) C(\vec{b},\lambda),$$

where

$$\begin{aligned} C(\vec{a},\lambda) &= P_+(\vec{a},\lambda) - P_-(\vec{a},\lambda), \\ C(\vec{b},\lambda) &= P_+(\vec{b},\lambda) - P_-(\vec{b},\lambda). \end{aligned}$$

It is required that

(a) $\rho(\lambda) \geq 0$

(b) $\int d\lambda \rho(\lambda) = 1$

(c) $-1 \leq C(\vec{a},\lambda) \leq 1$ and $-1 \leq C(\vec{b},\lambda) \leq 1$.

The Bell coefficient,

$$B = C(\vec{a},\vec{b}) + C(\vec{a},\vec{b}') + C(\vec{a}',\vec{b}) - C(\vec{a}',\vec{b}'),$$

combines four different combinations of polaroid directions.

(1) Show that the above classical realist assumptions imply $|B| \leq 2$.

(2) Show that quantum mechanics predicts

$$C(\vec{a},\vec{b}) = 2\left(\vec{a}\cdot\vec{b}\right)^2 - 1.$$

(3) Show that the maximum value of the Bell coefficient is $2\sqrt{2}$, according to quantum mechanics.

(4) Cast the quantum mechanical expression for $C(\vec{a},\vec{b})$ into separable form. Which of the classical requirements, (a), (b) or (c) above is violated?

Solution

(1) With the separability assumption,

$$C(\vec{a},\vec{b}) = \int d\lambda \rho(\lambda) C(\vec{a},\lambda) C(\vec{b},\lambda),$$

it follows that the Bell coefficient can be written in the form

$$\begin{aligned} B &= C(\vec{a},\vec{b}) + C(\vec{a},\vec{b}') + C(\vec{a}',\vec{b}) - C(\vec{a}',\vec{b}') \\ &= \int d\lambda \rho(\lambda) \Big\{ C(\vec{a},\lambda)[C(\vec{b},\lambda) + C(\vec{b}',\lambda)] + C(\vec{a}',\lambda)[C(\vec{b},\lambda) - C(\vec{b}',\lambda)] \Big\}. \end{aligned}$$

Since $|C(\vec{a},\lambda)|$ and $|C(\vec{a}',\lambda)|$ are both not larger than unity, we have

$$|B| \le \int d\lambda \rho(\lambda) \Big\{ |C(\vec{b},\lambda) + C(\vec{b}',\lambda)| + |C(\vec{b},\lambda) - C(\vec{b}',\lambda)| \Big\},$$

where the positivity of the weight function has been used. Suppose that, for a given λ, $C_M(\lambda)$ is the maximum and $C_m(\lambda)$ is the minimum of $C(\vec{b},\lambda)$ and $C(\vec{b}',\lambda)$, so that $C_M(\lambda) \ge C_m(\lambda)$. Then

$$|B| \le \int d\lambda \rho(\lambda) \Big\{ |C_M(\lambda) + C_m(\lambda)| + C_M(\lambda) - C_m(\lambda) \Big\}.$$

Now in the case $C_M(\lambda) \ge 0$, we have $|C_M(\lambda) + C_m(\lambda)| = C_M(\lambda) + C_m(\lambda)$, so

$$\begin{aligned} |B| &\le \int d\lambda \rho(\lambda) \Big\{ C_M(\lambda) + C_m(\lambda) + C_M(\lambda) - C_m(\lambda) \Big\} \\ &= 2 \int d\lambda \rho(\lambda) C_M(\lambda) \\ &\le 2 \int d\lambda \rho(\lambda) = 2, \end{aligned}$$

where the normalization of the weight function has been taken into account. However, if $C_M(\lambda) < 0$, we have $|C_M(\lambda) + C_m(\lambda)| = -C_M(\lambda) - C_m(\lambda)$, so then

$$\begin{aligned} |B| &\le \int d\lambda \rho(\lambda) \Big\{ -C_M(\lambda) - C_m(\lambda) + C_M(\lambda) - C_m(\lambda) \Big\} \\ &= 2 \int d\lambda \rho(\lambda) |C_m(\lambda)| \\ &\le 2 \int d\lambda \rho(\lambda) = 2. \end{aligned}$$

In all cases, then, we have shown that $|B| \le 2$.

(2) A photon, traveling in the y direction, might have right- or left-handed circular polarization. The corresponding quantum states will be written $|R\rangle$ and

$|L\rangle$ respectively. These circular polarization states can be expressed as coherent superpositions of linearly polarized states in the z and the x directions:

$$\begin{aligned} |R\rangle &= (|z\rangle + i|x\rangle)/\sqrt{2} \\ |L\rangle &= (|z\rangle - i|x\rangle)/\sqrt{2}\,. \end{aligned} \tag{1.15}$$

Under a rotation of the coordinate axes by an angle θ about the y direction, $|R\rangle \to \mathrm{e}^{i\theta}|R\rangle$ and $|L\rangle \to \mathrm{e}^{-i\theta}|L\rangle$, or equivalently

$$\begin{pmatrix} |z\rangle \\ |x\rangle \end{pmatrix} \to \begin{pmatrix} |z'\rangle \\ |x'\rangle \end{pmatrix} = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} |z\rangle \\ |x\rangle \end{pmatrix}. \tag{1.16}$$

If each photon is in a state of right-handed circular polarization, we write the corresponding state vector $|R_1\rangle|R_2\rangle$. However, since the photons are moving in opposite directions, one along the positive, and the other along the negative y axis, it follows that the actual directions in which the electric fields rotate, in time, in the vicinity of the two photons, are opposed to one another. The same holds for a state, $|L_1\rangle|L_2\rangle$, corresponding to each photon's being in a state of left-handed circular polarization. The linear combination of these two states,

$$|EPR\rangle = \big(|R_1\rangle|R_2\rangle + |L_1\rangle|L_2\rangle\big)/\sqrt{2}\,, \tag{1.17}$$

corresponds to the more general situation in which the photons are in oppositely oriented states of circular polarization, where the sense of this polarization is not specified. From Eq.(1.15), we see that this *entangled*, or Einstein-Rosen-Podolsky state, can also be written in the form

$$|EPR\rangle = \big(|z_1\rangle|z_2\rangle - |x_1\rangle|x_2\rangle\big)/\sqrt{2}\,, \tag{1.18}$$

which is a superposition of states of linear polarization. A more detailed justification of the Einstein-Rosen-Podolsky form, Eqs.(1.17)-(1.18), will be given in Volume 2, using the second quantization of the electromagnetic field.

Suppose now that a measurement of linear polarization is made on photon 1 in the z direction, and of photon 2 in the z' direction, i.e., the z direction after a rotation of the axes about the y axis. The probability amplitude associated with this measurement on the EPR state is

$$\langle EPR|z_1, z_2'\rangle = \langle z_2|z_2\cos\theta - x_2\sin\theta\rangle/\sqrt{2} = \cos\theta/\sqrt{2}\,,$$

where the first equality is a consequence of the orthonormality of the states $|z_1\rangle$ and $|x_1\rangle$. The probability that photon 1 is found to have linear polarization in the direction z, and photon 2 in the direction z', is

$$P_{++}(\vec{a}\,,\vec{b}\,) = \big|\langle EPR|z_1, z_2'\rangle\big|^2 = \tfrac{1}{2}\cos^2\theta\,,$$

where we suppose $\vec{a}$ to be in the direction z and $\vec{b}$ to be in the direction z'.

Suppose next that the linear polarization of photon 1 were measured in the x direction, and that of photon 2 again in the z' direction. The probability amplitude is

$$\langle EPR|x_1, z_2'\rangle = -\langle x_2|z_2\cos\theta - x_2\sin\theta\rangle/\sqrt{2} = \sin\theta/\sqrt{2}\,.$$

If photon 1 has polarization in the x direction, then it will not be transmitted by a polarizer in the direction z: it will be absorbed. Hence

$$P_{-+}(\vec{a},\vec{b}) = \left|\langle EPR|x_1, z_2'\rangle\right|^2 = \tfrac{1}{2}\sin^2\theta\,.$$

Similarly,

$$\begin{aligned} P_{+-}(\vec{a},\vec{b}) = \left|\langle EPR|z_1, x_2'\rangle\right|^2 &= \tfrac{1}{2}\sin^2\theta \\ P_{--}(\vec{a},\vec{b}) = \left|\langle EPR|x_1, x_2'\rangle\right|^2 &= \tfrac{1}{2}\cos^2\theta\,. \end{aligned}$$

The correlation coefficient is accordingly

$$\begin{aligned} C(\vec{a},\vec{b}) &= P_{++}(\vec{a},\vec{b}) + P_{--}(\vec{a},\vec{b}) - P_{+-}(\vec{a},\vec{b}) - P_{-+}(\vec{a},\vec{b}) \\ &= \cos^2\theta - \sin^2\theta = 2\cos^2\theta - 1 = \cos 2\theta\,. \end{aligned}$$

Since $\vec{a}$ and $\vec{b}$ are unit vectors at an angle θ to one another, it follows that $\vec{a}\cdot\vec{b} = \cos\theta$, and hence

$$C(\vec{a},\vec{b}) = 2\left(\vec{a}\cdot\vec{b}\right)^2 - 1\,.$$

(3) Suppose the angle between the vectors $\vec{a}'$ and $\vec{a}$ is $x/2$, between $\vec{a}$ and $\vec{b}$ is $y/2$, and between $\vec{b}$ and $\vec{b}'$ is $z/2$. Then the angle between $\vec{a}'$ and $\vec{b}'$ is $(x+y+z)/2$; and, according to quantum mechanics, the Bell coefficient has the form

$$B = \cos x + \cos y + \cos z - \cos(x+y+z)\,.$$

This function of x, y, z, has its turning points when

$$\begin{aligned} \frac{\partial B}{\partial x} &= -\sin x + \sin(x+y+z) = 0 \\ \frac{\partial B}{\partial y} &= -\sin y + \sin(x+y+z) = 0 \\ \frac{\partial B}{\partial z} &= -\sin z + \sin(x+y+z) = 0\,. \end{aligned}$$

and therefore

$$\sin x = \sin y = \sin z = \sin(x+y+z)\,,$$

with a solution $x = y = z$ and $3x = \pi - x$, i.e., $x = \frac{1}{4}\pi$. For this turning point,

$$B = 3\cos\frac{\pi}{4} - \cos\frac{3\pi}{4} = \frac{3}{\sqrt{2}} + \frac{1}{\sqrt{2}} = 2\sqrt{2}\,.$$

This is a maximum, for at it,

$$\frac{\partial^2 B}{\partial x^2} = \frac{\partial^2 B}{\partial y^2} = \frac{\partial^2 B}{\partial z^2} = -\cos\pi/4 + \cos 3\pi/4 = -\sqrt{2} < 0\,.$$

(4) Let the vector $\vec{a}$ be at an angle θ_a with respect to some direction in the xz plane, and let $\vec{b}$ be at an angle θ_b with respect to the same direction. Then

$$\begin{aligned} C(\vec{a},\vec{b}) &= \cos 2(\theta_a - \theta_b) \\ &= \cos 2\theta_a \cos 2\theta_b + \sin 2\theta_a \sin 2\theta_b \\ &= \int d\lambda \rho(\lambda) C(\vec{a},\lambda) C(\vec{b},\lambda)\,, \end{aligned}$$

with the assignments

$$\begin{aligned} \rho(\lambda) &= \delta(\lambda+1) + \delta(\lambda-1) \\ C(\vec{a},1) &= \cos 2\theta_a \qquad\qquad C(\vec{a},-1) = \sin 2\theta_a \\ C(\vec{b},1) &= \cos 2\theta_b \qquad\qquad C(\vec{b},-1) = \sin 2\theta_b\,. \end{aligned}$$

We see that (a) $\rho(\lambda) \geq 0$ and (c) $-1 \leq C(\vec{a},\lambda)$ and $-1 \leq C(\vec{b},\lambda)$, for $\lambda = \pm 1$, but $\int d\lambda \rho(\lambda) = 1 + 1 = 2$, so that the normalization condition (b) is violated.

Chapter 2

Three-Dimensional Harmonic Oscillator

2.1 Recurrence Relation for Hermite Polynomial

Prove the recurrence relation for the Hermite polynomial,

$$H_n(x) = 2xH_{n-1}(x) - H'_{n-1}(x)\,,$$

$$H_n(x) = \mathrm{e}^{x^2}\left(-\frac{d}{dx}\right)^n \mathrm{e}^{-x^2}\,.$$

Deduce a second-order differential equation satisfied by the Hermite polynomial. Work out $H_0(x)$, $H_1(x)$, $H_2(x)$, $H_3(x)$ and $H_4(x)$ and sketch them graphically.

Solution

On using the rule for differentiating the product of two terms, we find

$$\begin{aligned} H'_n(x) &= 2x\,\mathrm{e}^{x^2}\left(-\frac{d}{dx}\right)^n \mathrm{e}^{-x^2} - \mathrm{e}^{x^2}\left(-\frac{d}{dx}\right)^{n+1} \mathrm{e}^{-x^2} \\ &= 2xH_n(x) - H_{n+1}(x)\,. \end{aligned} \tag{2.1}$$

After replacing n by $n-1$, and rearranging terms, we obtain the recurrence relation that was to be proved. We can also write Eq.(2.1) in the form

$$H'_n(x) = 2xH_n(x) - 2(-1)^n\,\mathrm{e}^{x^2}\left(\frac{d}{dx}\right)^n (x\,\mathrm{e}^{-x^2})\,, \tag{2.2}$$

where one differential operator, $\frac{d}{dx}$, has been allowed to work on the factor e^{-x^2}. However, by the Leibniz rule for repeated differentiation of a product,

$$\left(\frac{d}{dx}\right)^n (x\,\mathrm{e}^{-x^2}) = x\left(\frac{d}{dx}\right)^n \mathrm{e}^{-x^2} + n\left(\frac{d}{dx}\right)^{n-1} \mathrm{e}^{-x^2}\,, \tag{2.3}$$

and on using this in Eq.(2.2) we find

$$H_n'(x) = 2xH_n(x) - 2xH_n(x) + 2nH_{n-1}(x) = 2nH_{n-1}(x)\,. \tag{2.4}$$

On comparing Eq.(2.1) and Eq.(2.4) we obtain

$$2xH_n(x) - H_{n+1}(x) = H_n'(x) = 2nH_{n-1}(x)\,, \tag{2.5}$$

and so we obtain the three-term recurrence relation

$$H_{n+1}(x) - 2xH_n(x) + 2nH_{n-1}(x) = 0\,. \tag{2.6}$$

This can be easily converted into a differential equation by repeated use of Eq.(2.4). Indeed, $H_n(x) = H_{n+1}'(x)/[2(n+1)]$, while $2nH_{n-1}(x) = H_n'(x)$, and a further application of Eq.(2.4) yields $H_n'(x) = H_{n+1}''(x)/[2(n+1)]$. After replacing n by $n-1$, and rearranging terms, we obtain

$$H_n''(x) - 2xH_n'(x) + 2nH_n(x) = 0\,,$$

which is the required differential equation.

We can evaluate the Hermite polynomials sequentially from the recurrence relation, $H_n(x) = 2xH_{n-1}(x) - H_{n-1}'(x)$, starting with $H_0(z) = 1$. We find $H_1(z) = 2z$, $H_2(z) = 4z^2 - 2$, $H_3(z) = 8z^3 - 12z$, $H_4(z) = 16z^4 - 48z^2 + 12$. In graphical form:

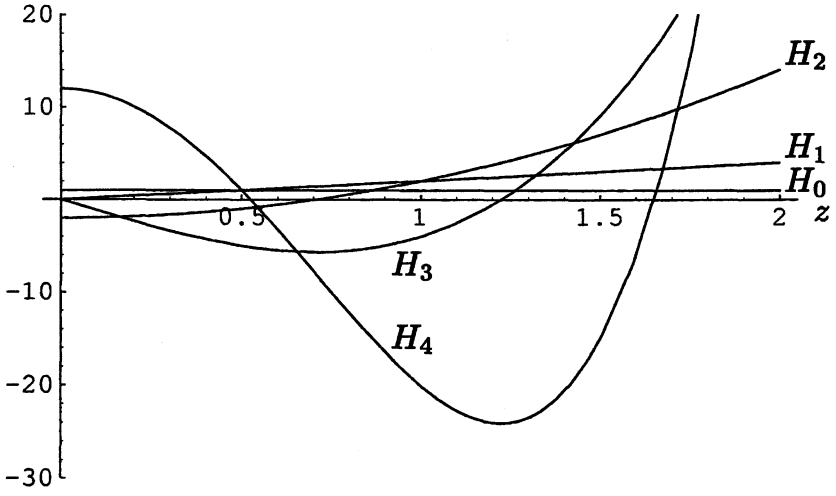

Fig. 2.1 Hermite Polynomials

This graph was generated by the Mathematica command line:

```
Plot [{HermiteH[0,x],HermiteH[1,x],HermiteH[2,x], HermiteH[3,x],
        HermiteH[4,x] },{x,0,2}, PlotRange -> {-30,20}]
```

We may also obtain the Hermite polynomials from a generating function, $\exp(2xt - t^2)$, which is expanded in powers of t to define the polynomials $h_n(x)$:

$$\mathrm{e}^{2xt-t^2} = \sum_{n=0}^{\infty} \frac{t^n}{n!} h_n(x) \,. \tag{2.7}$$

The functions $h_n(x)$ are given by

$$h_n(x) = \frac{\partial^n}{\partial t^n} \mathrm{e}^{2xt-t^2}\bigg|_{t=0} = e^{x^2} \frac{\partial^n}{\partial t^n} \mathrm{e}^{-(x-t)^2}\bigg|_{t=0} .$$

We may use the identity $\partial_t g(x-t) = -\partial_x g(x-t)$ to obtain

$$h_n(x) = (-1)^n \mathrm{e}^{x^2} \frac{\partial^n}{\partial x^n} \mathrm{e}^{-(x-t)^2}\bigg|_{t=0} = (-1)^n \mathrm{e}^{x^2} \frac{\partial^n}{\partial x^n} \mathrm{e}^{-x^2} .$$

The polynomials $h_n(x)$ are thus precisely the Hermite polynomials $H_n(x)$.

This generating function provides a simple way of investigating the orthogonality properties of the Hermite polynomials. Consider the double series

$$\sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{s^m}{m!} \frac{t^n}{n!} H_m(x) H_n(x) = \exp(2sx - s^2 + 2tx - t^2) ,$$

multiply both sides by e^{-x^2}, and integrate:

$$\begin{aligned} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{s^m}{m!} \frac{t^n}{n!} \int_{-\infty}^{\infty} dx \, \mathrm{e}^{-x^2} H_m(x) H_n(x) &= \int_{-\infty}^{\infty} dx \, \mathrm{e}^{2sx-s^2+2tx-t^2-x^2} \\ &= \mathrm{e}^{2st} \int_{-\infty}^{\infty} dx \, \mathrm{e}^{-(x-s-t)^2} \\ &= \sqrt{\pi} \, \mathrm{e}^{2st} . \end{aligned} \tag{2.8}$$

Now the last expression can be written as a series:

$$\sqrt{\pi} \, \mathrm{e}^{2st} = \sqrt{\pi} \sum_{m=0}^{\infty} \frac{(2st)^m}{m!} ,$$

and this shows immediately that the terms with $m \neq n$, on the left-hand side of Eq.(2.8), are zero. For $m = n$, we can read off the value of the integral, obtaining finally

$$\int_{-\infty}^{\infty} dx \, \mathrm{e}^{-x^2} H_m(x) H_n(x) = \sqrt{\pi} 2^m m! \, \delta_{mn} .$$

2.2 One Dimensional Harmonic Oscillator

Two particles, each of mass m, move in a one-dimensional harmonic oscillator well. In addition, there is an interaction, $V(q)$, which depends only on the separation between the particles, $q = q_1 - q_2$.

(1) Show that the Schrödinger equation can be separated into two equations, each of one variable only.
(2) Find the energy eigenvalues in the case that $V(q) = \lambda q^2$.

Solution

(1) Let us write the Hamiltonian in the form

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \mu q_1^2 + \mu q_2^2 + V(q_1 - q_2)\,. \tag{2.9}$$

We now make the canonical transformation from the conjugate pairs (q_1, p_1) and (q_2, p_2) to the pairs (q, p) and (Q, P), defined by

$$\begin{aligned} q &= q_1 - q_2 \\ Q &= \tfrac{1}{2}(q_1 + q_2) \\ p &= \tfrac{1}{2}(p_1 - p_2) \\ P &= p_1 + p_2\,. \end{aligned}$$

The Hamiltonian can be written

$$H = H_1 + H_2\,, \tag{2.10}$$

where

$$H_1 = \frac{P^2}{4m} + 2\mu Q^2 \qquad\qquad H_2 = \frac{p^2}{m} + \frac{\mu}{2} q^2 + V(q)\,. \tag{2.11}$$

In configuration representation, the Schrödinger equation for this system is

$$\left\{ -\frac{\hbar^2}{4m}\nabla_R^2 - \frac{\hbar^2}{m}\nabla_r^2 + 2\mu R^2 + \tfrac{1}{2}\mu r^2 + V(r) \right\} \psi(\vec{R}, \vec{r}) = E\psi(\vec{R}, \vec{r})$$

This partial differential equation is separable: set $\psi(\vec{R}, \vec{r}) = \Phi(\vec{R})\phi(\vec{r})$, so that, after dividing both sides of the above equation by $\psi(\vec{R}, \vec{r})$, we find

$$\frac{\left\{ -\frac{\hbar^2}{4m}\nabla_R^2 + 2\mu R^2 \right\} \Phi(\vec{R})}{\Phi(\vec{R})} + \frac{\left\{ -\frac{\hbar^2}{m}\nabla_r^2 + \frac{1}{2}\mu r^2 + V(r) \right\} \phi(\vec{r})}{\phi(\vec{r})} = E\,.$$

The first term on the left is a function only of $\vec{R}$, while the second term on the left is a function only of $\vec{r}$. Since the sum is a constant, it follows that each must

be constant (the terms separately depend on different independent variables, and thus neither can vary). Let us call these constants E_1 and E_2 respectively. Then $E = E_1 + E_2$ and the equation separates into two Schrödinger equations, one in the variable $\vec{R}$, and the other in the variable $\vec{r}$.

(2) If $V(q) = \lambda q^2$, we have

$$H_2 = \frac{p^2}{m} + \left(\lambda + \frac{\mu}{2}\right) q^2 , \tag{2.12}$$

and we can write the energy eigenvalues as

$$E = E_1 + E_2 = \hbar \left[n_1\omega_1 + n_2\omega_2 + \tfrac{1}{2}(\omega_1 + \omega_2) \right] ,$$

where n_1 and n_2 can take on the values 0, 1, 2, ..., and where

$$\omega_1 = \sqrt{2\mu/m} \qquad \omega_2 = \sqrt{2(2\lambda + \mu)/m} .$$

2.3 Mean and Uncertainty

Let q and p be the Cartesian coordinates of the position and momentum operators of a particle in a quantum mechanical one-dimensional simple harmonic oscillator. Let $|n\rangle$ be the normalized eigenvector of the Hamiltonian belonging to the eigenvalue $(n + \frac{1}{2})\hbar\omega$. The mean, $\bar{q}$, and the uncertainty, Δq, of q in the state $|n\rangle$ are defined by $\bar{q} = \langle n|q|n\rangle$ and $(\Delta q)^2 = \langle n|q^2|n\rangle - \bar{q}^2$, and similarly for p. Calculate $\Delta q \Delta p$ for the nth excited state.

Solution

The relation between the position operator and the ladder operators a and $a^\dagger$ is

$$q = \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger) , \tag{2.13}$$

where $\omega = \sqrt{2\lambda/m}$, and the normalized eigenvectors of the oscillator satisfy

$$\begin{aligned} a|n\rangle &= \sqrt{n}\,|n-1\rangle \\ a^\dagger|n\rangle &= \sqrt{n+1}\,|n+1\rangle . \end{aligned}$$

Since $\langle n_1|n_2\rangle = 0$ if $n_1 \neq n_2$, we see that $\bar{q} = \langle n|q|n\rangle = 0$, and

$$\begin{aligned} (\Delta q)^2 &= \langle n|q^2|n\rangle - \bar{q}^2 = \frac{\hbar}{2m\omega}\langle n|aa^\dagger + a^\dagger a|n\rangle \\ &= \frac{\hbar}{2m\omega}\left\{(n+1)\langle n+1|n+1\rangle + n\langle n-1|n-1\rangle\right\} \\ &= (n + \tfrac{1}{2})\frac{\hbar}{m\omega} . \end{aligned} \tag{2.14}$$

The relation between the momentum operator and the ladder operators is

$$p = -i\sqrt{\frac{m\omega\hbar}{2}}(a - a^\dagger)\,, \tag{2.15}$$

and so also the mean value of the momentum is zero, $\overline{p} = 0$, while

$$\begin{aligned}(\Delta p)^2 &= \langle n|p^2|n\rangle - \overline{p}^2 \\ &= \frac{m\omega\hbar}{2}\langle n|aa^\dagger + a^\dagger a|n\rangle \\ &= (n + \tfrac{1}{2})\hbar m\omega\,. \end{aligned} \tag{2.16}$$

Therefore

$$\Delta q \Delta p = \hbar(n + \tfrac{1}{2})\,,$$

and, in particular, for the ground state, $n = 0$,

$$\Delta q \Delta p = \tfrac{1}{2}\hbar\,,$$

which is the smallest value allowed by the Heisenberg Uncertainty Principle,

$$\Delta q \Delta p \geq \tfrac{1}{2}\hbar\,.$$

2.4 Classically Forbidden Region

Calculate the probability of finding a particle in the ground state of an isotropic harmonic oscillator to be in a classically forbidden region.

Solution

The potential energy is $V(r) = \lambda r^2 = \frac{1}{2}m\omega^2 r^2$, and the ground state energy is $\frac{3}{2}\hbar\omega$. Classically, the total energy can never be less than the potential energy, so the classically forbidden region is defined by $r > a$, where $\frac{1}{2}m\omega^2 a^2 = \frac{3}{2}\hbar\omega$, so $a = \sqrt{\frac{3\hbar}{m\omega}}$. The non-normalized ground state wave function is $\psi_0(r) = \mathrm{e}^{-\frac{1}{2}R^2}$, where R is the scaled radial variable, given by $R = \sqrt{m\omega/\hbar}\,r$. We see therefore that $r = a$ corresponds to $R = \sqrt{3}$. The probability that the particle is outside the classically allowed region is therefore

$$\begin{aligned}\frac{\int_a^\infty dr\, r^2|\psi_0(r)|^2}{\int_0^\infty dr\, r^2|\psi_0(r)|^2} &= \frac{\int_{\sqrt{3}}^\infty dR\, R^2\,\mathrm{e}^{-R^2}}{\int_0^\infty dR\, R^2\,\mathrm{e}^{-R^2}} = \frac{\sqrt{3}\,\mathrm{e}^{-3} + \int_{\sqrt{3}}^\infty dR\,\mathrm{e}^{-R^2}}{\int_0^\infty dR\,\mathrm{e}^{-R^2}} \\ &= 2\sqrt{\frac{3}{\pi}}\,\mathrm{e}^{-3} + \frac{2}{\sqrt{\pi}}\int_{\sqrt{3}}^\infty dR\,\mathrm{e}^{-R^2} \approx 0.1116\,. \end{aligned}$$

This numerical result can be obtained by integrating the last term numerically, or looking up the value of the complementary error function, erfc $(\sqrt{3})$, in statistical tables, or by using Mathematica. The command line

```
2.*Sqrt[3/Pi]*Exp[-3] + Erf[Sqrt[3.], Infinity]
```

returns the value 0.11161. We conclude that the probability that a quantum particle, in the ground state of an isotropic harmonic oscillator potential, lies outside the region that is permitted classically is 11.16%.

2.5 Thomas-Reiche-Kuhn Sum Rule

The Thomas-Reiche-Kuhn sum rule for a particle of mass m in one dimension is

$$\sum_k (E_k - E_n)|\langle k|q|n\rangle|^2 = \frac{\hbar^2}{2m}.$$

Here q is the operator whose eigenvalues give the position of the particle, E_n is the nth energy level, and $|n\rangle$ is the corresponding eigenvector.

(1) Check this sum rule for the simple harmonic oscillator.
(2) Prove it for a general potential.

Solution

(1) Since $E_n = \hbar\omega(n + \frac{1}{2})$, then $E_k - E_n = (k - n)\hbar\omega$.
From $q = \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger)$, it follows that

$$\begin{aligned}
\langle k|q|n\rangle &= \sqrt{\frac{\hbar}{2m\omega}}\langle k|(a + a^\dagger)|n\rangle \\
&= \sqrt{\frac{\hbar}{2m\omega}}\left\{\sqrt{n}\langle k|n-1\rangle + \sqrt{n+1}\langle k|n+1\rangle\right\} \\
&= \sqrt{\frac{\hbar}{2m\omega}}\left\{\sqrt{n}\delta_{k,n-1} + \sqrt{n+1}\delta_{k,n+1}\right\}. \qquad (2.17)
\end{aligned}$$

Thus we find

$$|\langle k|q|n\rangle|^2 = \frac{\hbar}{2m\omega}\left\{n\delta_{k,n-1} + (n+1)\delta_{k,n+1}\right\}, \qquad (2.18)$$

$$\begin{aligned}
\sum_k (E_k - E_n)|\langle k|q|n\rangle|^2 &= \frac{\hbar^2}{2m}\sum_k (k-n)\left\{n\delta_{k,n-1} + (n+1)\delta_{k,n+1}\right\} \\
&= \frac{\hbar^2}{2m}(-n + n + 1) = \frac{\hbar^2}{2m}. \qquad (2.19)
\end{aligned}$$

(2) The canonical momentum of a particle in a conservative potential, in one dimension, is given by

$$p = m\dot{q} = \frac{m}{ih}[q, H]\,, \tag{2.20}$$

where we have used the Hamilton-Poisson-Heisenberg equation of motion for the position operator, q. This relation can also be obtained without explicit use of the equation of motion if one recalls that q commutes with the potential, which is a function only of q. Hence

$$[q, H] = \left[q, \frac{p^2}{2m}\right] = \frac{i\hbar p}{m}\,,$$

which is equivalent to Eq.(2.20). Since $[q, p] = i\hbar$, it follows that

$$[q, [q, H]] = -\frac{\hbar^2}{m}\,. \tag{2.21}$$

We have then the matrix element

$$\langle n|[q, H]q - q[q, H]|n\rangle = \frac{\hbar^2}{m}\,. \tag{2.22}$$

By inserting a complete set of states we see that

$$\begin{aligned}
\langle n|[q, H]q|n\rangle &= \sum_k \langle n|[q, H]|k\rangle\langle k|q|n\rangle \\
&= \sum_k (E_k - E_n)\langle n|q|k\rangle\langle k|q|n\rangle \\
&= \sum_k (E_k - E_n)\,|\langle k|q|n\rangle|^2\,;
\end{aligned} \tag{2.23}$$

here $\sum_k$ is to be understood as a sum over discrete (bound) states, and an integral over continuous (scattering) states. By similar reasoning, we find

$$\langle n|q[q, H]|n\rangle = \sum_k (E_n - E_k)\,|\langle k|q|n\rangle|^2\,. \tag{2.24}$$

On combining Eq.(2.22), Eq.(2.23) and Eq.(2.24), we see that

$$\sum_k (E_k - E_n)\,|\langle k|q|n\rangle|^2 = \frac{\hbar^2}{2m}\,. \tag{2.25}$$

2.6 Half Oscillator

Calculate the energy levels of a 1-D "half" oscillator, defined by the potential $V(x) = \frac{1}{2}m\omega^2 x^2$ for $x \geq 0$, and $V(x) = \infty$ for $x < 0$. Which of the eigenvectors of the 3-D isotropic oscillator correspond to those of the half-oscillator?

Solution

The energy levels of the complete oscillator are $E_n = (n + \frac{1}{2})\hbar\omega$, $n = 0, 1, 2, \ldots$ in one dimension. For even values of n, the eigenvectors of the Hamiltonian are even functions of x, and they do not have a zero at $x = 0$. for it follows by substituting $x = 0$ in the generating function (2.7), that

$$H_{2n}(0) = (-1)^n \frac{(2n)!}{n!} \neq 0 .$$

For odd values of n, on the other hand, the eigenvectors are odd functions of x, and so they do have a zero at $x = 0$. Since the wave functions in this problem must vanish at $x = 0$, it follows that the odd eigenfunctions of the complete oscillator are eigenvectors of the half oscillator Hamiltonian. Accordingly, the energy levels are

$$E_{n'} = (2n' + \tfrac{3}{2})\hbar\omega , \; n' = 0, 1, 2, \ldots$$

The S-wave bound state wave functions of the 3-D isotropic oscillator correspond to the eigenvectors of the half-oscillator, since they satisfy the same differential equation, and also the boundary condition at $r = 0$ (corresponding to $x = 0$ for the half-oscillator). This is not true for the states P, D, and so on, because of the centrifugal term in the radial Schrödinger equation.

2.7 Number Operator

Define $N = a^\dagger a$, where $a^\dagger$ is the Hermitian conjugate of the operator a, and where $aa^\dagger - a^\dagger a = 1$.

(1) Prove that a and $a^\dagger$ have no inverse.
(2) Show that the only analytic functions of a and $a^\dagger$ that commute with N are functions of N.

Solution

(1) If a were to have an inverse, a^{-1}, then we would have $a^{-1}a = 1$ as an operator relation, and this implies that the ground state vector, $|0\rangle$, satisfies

$$a^{-1}a\,|0\rangle = |0\rangle . \tag{2.26}$$

However, $|0\rangle$ is by definition the state of lowest energy, with $a|0\rangle = 0$, where the right-hand side here signifies the null vector. Then Eq.(2.26) implies $|0\rangle = 0$, which in turn implies that the whole ladder of states built on the ground state is trivial (i.e., equal to the null vector).

Therefore, if the ground state is not trivial, a has no inverse. Also, $a^\dagger$ has no inverse; for if it had one, we could write $a^\dagger(a^\dagger)^{-1} = 1$, and the Hermitian conjugate of this is $a^{-1}a = 1$, which we have seen to be impossible under the stated assumption.

Strictly speaking, we have shown that a cannot have a left inverse, a_L^{-1}, such that $a_L^{-1}a = 1$. However, the operator does have a right inverse, a_R^{-1}, such that $aa_R^{-1} = 1$. In particular, we may take a_R^{-1}, applied to a particular oscillator wavefunction $|n\rangle$, to give

$$a_R^{-1}|n\rangle = \sqrt{\frac{1}{n+1}}|n+1\rangle\,.$$

Then

$$aa_R^{-1}|n\rangle = \sqrt{\frac{1}{n+1}}a|n+1\rangle = |n\rangle\,.$$

This right inverse exists if the oscillator wavefunctions form a complete set, but of course it is not a full inverse of the operator a.

How do we know whether the ground state is trivial or not? That depends on the vector space on which the operators a and $a^\dagger$ are taken to act. In a configuration space of differentiable functions, we know the ground state to be non-trivial, for $\langle x|q+ip|0\rangle \propto \langle x|a|0\rangle = 0$, so

$$\left(x + \frac{d}{dx}\right)\psi_0(x) = 0\,, \tag{2.27}$$

where $\psi_0(x) = \langle x|0\rangle$. The differential equation Eq.(2.27) has a nontrivial solution in a space of differentiable functions, namely $\exp(-x^2/2)$.

(2) If $F(a^\dagger, a)$ is analytic, we can write

$$F(a^\dagger, a) = \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} c_{mn}(a^\dagger)^m a^n\,. \tag{2.28}$$

The commutator of N and F can thus be written

$$[N, F] = \sum_m \sum_n c_{mn}\Big\{[N,(a^\dagger)^m]a^n + (a^\dagger)^m[N,a^n]\Big\}\,. \tag{2.29}$$

In Lemma 1 we show that $[N, a^n] = -na^n$, thus $[N, (a^\dagger)^m] = m(a^\dagger)^m$, and so

$$[N, F] = \sum_m \sum_n c_{mn}(m-n)(a^\dagger)^m a^n .$$

If $[N, F] = 0$, then $c_{mn} = 0$ when $m \neq n$. This follows from the fact that the operators $(a^\dagger)^m a^n$ are independent; more precisely, if $\sum_m \sum_n d_{mn}(a^\dagger)^m a^n = 0$, then $d_{mn} = 0$ for all m and n. This is shown in Lemma 2.
Let us write $c_{mn} = c_n \delta_{mn}$, so that Eq.(2.28) becomes

$$F(a^\dagger, a) = \sum_n c_n (a^\dagger)^n a^n .$$

In Lemma 3, we show that $(a^\dagger)^n a^n = N(N-1)\ldots(N-n+1)$, so that

$$F(a^\dagger, a) = \sum_n c_n N(N-1)\ldots(N-n+1) ,$$

which is indeed a function of the operator $N = a^\dagger a$.

In fact the theorem has much more generality than the restriction to analytic functions would suggest. The proof can be easily extended any function with a Fourier transform,

$$F(a^\dagger, a) = \int\int du dv \, f(u, v) \, \mathrm{e}^{i(ua^\dagger + va)} .$$

Lemma 1
The proof of

$$[N, a^n] = -na^n , \tag{2.30}$$

proceeds by induction. For suppose Eq.(2.30) to be true for a given n. Then

$$\begin{aligned} [N, a^{n+1}] &= [a^\dagger, a]a^n + a[a^\dagger, a^n] \\ &= -a^n - na^n = -(n+1)a^n , \end{aligned}$$

which has the same form as Eq.(2.30), except that n has been replaced by $n+1$. Since Eq.(2.30) is certainly true for $n = 1$, the proof works for $n = 2, 3, \ldots$

Lemma 2
If $\sum_{m=0}^{\infty} \sum_{n=0}^{\infty} d_{mn}(a^\dagger)^m a^n = 0$, then for any integers, M, N,

$$\sum_{m=0}^{M} \sum_{n=0}^{N} d_{mn} \langle M | (a^\dagger)^m a^n | N \rangle = 0 .$$

With $M = 0 = N$, we find $d_{00} = 0$. With $M = 0$ and $N = 1$ we then obtain $d_{01} = 0$, and with $M = 0$, $N = 2, 3, 4, \ldots$ we find successively that d_{02}, d_{03}, d_{04}, and so on must vanish. Now we set $M = 1$ and let N be successively $0, 1, 2, \ldots$, which allows us to show that all the coefficients d_{1j}, $j = 0, 1, 2, \ldots$ must be zero. Then we set $M = 2$ and show that d_{2j}, $j = 0, 1, 2, \ldots$ must be zero. The procedure is continued ineluctably, with $M = 3, 4, 5, \ldots$, finally reaching an arbitrary d_{ij}, showing that it, too, must vanish.

Lemma 3
Since $N = a^\dagger a$, it follows that

$$\begin{aligned}
(a^\dagger)^n a^n &= (a^\dagger)^{n-1} N a^{n-1} \\
&= (a^\dagger)^{n-1}[N, a^{n-1}] + (a^\dagger)^{n-1} a^{n-1} N \\
&= -(n-1)(a^\dagger)^{n-1} a^{n-1} + (a^\dagger)^{n-1} a^{n-1} N \\
&= (a^\dagger)^{n-1} a^{n-1}(N - n + 1) \\
&= (a^\dagger)^{n-2} a^{n-2}(N - n + 2)(N - n + 1) \\
&= \ldots \\
&= N(N-1)\ldots(N - n + 2)(N - n + 1)\,,
\end{aligned}$$

by iteration.

2.8 Differential Operator

Let the differential operator $a = (x + d/dx)/\sqrt{2}$ act on the space of infinitely differentiable functions, $g(x)$, of compact support. Use the language of test-function spaces.

(1) Calculate the Hermitian conjugate, $a^\dagger$, of a.
(2) Deduce the commutator of a and $a^\dagger$.
(3) Prove $[a^\dagger a, a^\dagger] = a^\dagger$ and $[a^\dagger a, a] = -a$.

Solution
(1) We define the standard scalar product on the space of infinitely differentiable functions of compact support as

$$S(f, g) = \int dx f^*(x) g(x)\,,$$

and so

$$\begin{aligned} \mathcal{S}(f, ag) &= 2^{-\frac{1}{2}} \int dx f^*(x)\{xg(x) + g'(x)\} \\ &= 2^{-\frac{1}{2}} \int dx g(x)\{xf^*(x) - f^{*\prime}(x)\}, \end{aligned}$$

where an integration by parts has been performed, the integrated terms being zero, because of the properties of the test functions. Hence

$$\mathcal{S}(g, a^\dagger f) = \{\mathcal{S}(f, ag)\}^* = 2^{-\frac{1}{2}} \int dx g^*(x)\{xf(x) - f'(x)\}..$$

Consequently, $a^\dagger = (x - d/dx)/\sqrt{2}$.
(2) We calculate

$$\begin{aligned} aa^\dagger g(x) &= \tfrac{1}{2}\left\{x^2 g(x) + g(x) - g''(x)\right\} \\ a^\dagger a g(x) &= \tfrac{1}{2}\left\{x^2 g(x) - g(x) - g''(x)\right\}, \end{aligned}$$

and so $[a, a^\dagger]\, g(x) = g(x)$, i.e., $[a, a^\dagger] = 1$, as an operator relation.
(3) The following equalities between operators hold:

$$[a^\dagger a, a^\dagger] = a^\dagger a a^\dagger - a^\dagger a^\dagger a = a^\dagger [a, a^\dagger] = a^\dagger .$$

The Hermitian conjugate of this result is $[a, a^\dagger a] = a$, i.e.,

$$[a^\dagger a, a] = -a .$$

2.9 High-T_c Cuprate

An electron of mass m moves in a two dimensional Cu-O plane in a high-T_c superconducting cuprate. The effective potential is an isotropic oscillator.

(1) Express the eigenstates $\psi_{n_1 n_2}$ of this system in terms of the eigenstates $\psi_{n_i}(x_i)$ of the one-dimensional harmonic oscillator and show that the energy eigenvalues are given by $E_{n_1 n_2} = (n_1 + n_2 + 1)\hbar\omega$.
(2) Calculate the degeneracy of the nth excited level, i.e., the one with energy $E_n = (n + 1)\hbar\omega$.
(3) Express the eigenfunctions belonging to the ground state and the first excited state in terms of polar coordinates.

Solution

(1) The eigenvectors of the Hamiltonian in configuration space are

$$\psi_{n_1 n_2}(x_1, x_2) = \psi_{n_1}(x_1)\psi_{n_2}(x_2) = \exp[-\tfrac{1}{2}(X_1^2 + X_2^2)]\, H_{n_1}(X_1)\, H_{n_2}(X_2),$$

where $H_n(X)$ is the Hermite polynomial, and where $X_i = (m\omega/\hbar)^{\frac{1}{2}} x_i$. The energy eigenvalues, with $n = n_1 + n_2$, are

$$E(n_1, n_2) = E_1(n_1) + E_2(n_2) = \hbar\omega(n_1 + n_2 + 1) = \hbar\omega(n+1)\,.$$

(2) For a given $n = n_1 + n_2$, n_1 may have any of the $n+1$ values $0, 1, 2, \ldots, n$, and then n_2 is fixed at the value $n_2 = n - n_1$. Accordingly, the degeneracy of the nth level is $n+1$.
(3) Clearly the ground state wave function is

$$\psi_{00}(x_1, x_2) = \exp[-\tfrac{1}{2}(X_1^2 + X_2^2)] = \exp[-\tfrac{1}{2}R^2]\,,$$

where $R = (m\omega/\hbar)^{\frac{1}{2}} r$. The degenerate states at the first excited level are

$$\begin{aligned} \psi_{10}(x_1, x_2) &= 2X_1 \exp[-\tfrac{1}{2}R^2] = 2R\cos\theta \exp[-\tfrac{1}{2}R^2] \\ \psi_{01}(x_1, x_2) &= 2X_2 \exp[-\tfrac{1}{2}R^2] = 2R\sin\theta \exp[-\tfrac{1}{2}R^2]\,, \end{aligned}$$

and the linear combinations

$$\psi_{10}(x_1, x_2) \pm i\psi_{01}(x_1, x_2) = 2R\, \mathrm{e}^{\pm i\theta}\, \mathrm{e}^{-\frac{1}{2}R^2}\,,$$

are eigenfunctions of the angular operator, $\partial^2/\partial\theta^2$.

2.10 Anisotropic Harmonic Oscillator

In three dimensions, consider a particle of mass m and potential energy

$$V(\vec{r}) = \frac{m\omega^2}{2}[(1-\tau)(x^2 + y^2) + (1+\tau)z^2]$$

where $\omega \geq 0$ and $0 \leq \tau < 1$.

(1) What are the eigenstates of the Hamiltonian and the corresponding energies?
(2) Calculate and discuss, as functions of τ, the variation of energy and the degree of degeneracy of the ground state and the first two excited states.

Solution
(1) The eigenvectors of the Hamiltonian in configuration space are

$$\begin{aligned} \psi_{n_1 n_2 n_3}(X_1, X_2, X_3) &= \prod_{j=1}^{3} \left[X_j - \frac{\partial}{\partial X_j}\right]^{n_j} \exp[-\tfrac{1}{2}X_j^2] \\ &= \prod_{j=1}^{3} \exp[-\tfrac{1}{2}X_j^2]\, H_{n_j}(X_j)\,, \end{aligned} \tag{2.31}$$

where $H_n(X)$ is the Hermite polynomial, and where

$$X_j = \sqrt{\frac{m\omega_j}{\hbar}} x_j \,,$$

with

$$\begin{aligned} \omega_0 &\equiv \omega_1 = \omega_2 = \omega\sqrt{1-\tau} \\ \omega_3 &= \omega\sqrt{1+\tau} \,. \end{aligned}$$

The corresponding energy eigenvalues are

$$E(n_1, n_2, n_3) = \hbar\omega_0(n_1 + n_2 + 1) + \hbar\omega_3(n_3 + \tfrac{1}{2}) \,.$$

(2) For generic values of τ, the degeneracy is the same as that of the two-dimensional oscillator. Indeed, we may write

$$E(n, n_3) \equiv E(n_1, n_2, n_3) = \hbar\omega_0(n - n_3 + 1) + \hbar\omega_3(n_3 + \tfrac{1}{2}) \,,$$

where $n = n_1 + n_2 + n_3$. For a given n and n_3, all the eigenvectors with $n_1 = 0, 1, 2, \ldots, n - n_3$, have the same energy, so the degeneracy is $n - n_3 + 1$. The ground state corresponds to $n = 0 = n_3$, so this state is not degenerate. For $n = 1$ there are two different energy levels,

$$\begin{aligned} E(1,0) &= 2\hbar\omega\sqrt{1-\tau} + \tfrac{1}{2}\hbar\omega\sqrt{1+\tau} \\ E(1,1) &= \hbar\omega\sqrt{1-\tau} + \tfrac{3}{2}\hbar\omega\sqrt{1+\tau} \,. \end{aligned}$$

$E(1,0)$ has degeneracy 2, while $E(1,1)$ is not degenerate. Since

$$E(1,1) - E(1,0) = \hbar\omega(\sqrt{1+\tau} - \sqrt{1-\tau}) > 0 \,,$$

for $\tau > 0$, it follows that

$$E(0,0) < E(1,0) < E(1,1) \,.$$

For special values of τ the degeneracies can be 'accidentally' higher. For example, if $\tau = 0$ we have the isotropic three-dimensional oscillator, and the energy levels depend only on n, and we know that the degeneracy of the nth level is $\frac{1}{2}(n+1)(n+2)$. Then $E(1,1) = E(1,0)$ and this level is triply degenerate. There are other values of τ for which the degeneracies are higher than the generic values. For example, for $\tau = \frac{3}{5}$,

$$\sqrt{1+\tau} = 2\sqrt{1-\tau} \,,$$

and then

$$E(n, n_3) = (n + n_3 + 2)\hbar\omega\sqrt{1-\tau} \,.$$

In this case

$$\begin{aligned} E(0,0) &= 2\hbar\omega\sqrt{1-\tau} \\ E(1,0) &= 3\hbar\omega\sqrt{1-\tau} \\ E(1,1) &= 4\hbar\omega\sqrt{1-\tau}, \end{aligned}$$

so these levels remain separated. However, for $n = 2$ we have the levels

$$\begin{aligned} E(2,0) &= 4\hbar\omega\sqrt{1-\tau} \\ E(2,1) &= 5\hbar\omega\sqrt{1-\tau} \\ E(2,2) &= 6\hbar\omega\sqrt{1-\tau}, \end{aligned}$$

so the three eigenvectors corresponding to $E(2,0)$ are degenerate with the eigenvector corresponding to $E(1,1)$. The energy level is thus quadruply degenerate for this particular value of τ. Evidently, similar 'coincidental' degeneracies will occur whenever τ is such that $\sqrt{1+\tau} = N\sqrt{1-\tau}$, with N a positive integer.

Chapter 3

Orbital Angular Momentum

3.1 Two Components of Angular Momentum

Show that any operator that commutes with two Cartesian components of the angular momentum operator necessarily commutes with the total angular momentum operator.

Solution
Choose the Cartesian axes such that a given operator, Ω, satisfies

$$[\Omega, L_1] = 0 = [\Omega, L_2]\,. \tag{3.1}$$

It follows that

$$\begin{aligned} [\Omega, L_1 L_2] &= [\Omega, L_1]L_2 + L_1[\Omega, L_2] = 0 \\ [\Omega, L_2 L_1] &= [\Omega, L_2]L_1 + L_2[\Omega, L_1] = 0\,, \end{aligned}$$

and hence

$$i\hbar[\Omega, L_3] = [\Omega, L_1 L_2 - L_2 L_1] = 0\,.$$

Thus Ω indeed commutes with the angular momentum operator, $\vec{L}$.

3.2 Momentum and Angular Momentum

The position, the momentum and the angular momentum of a particle are represented respectively by the operators $\vec{q}$, $\vec{p}$ and $\vec{L}$. Show that

(1) $$\vec{L} \cdot \vec{p} = 0 = \vec{L} \cdot \vec{q}$$

(2) $$\vec{L} \wedge \vec{L} = i\hbar\vec{L}$$

Solution

(1) Since p_k and p_i commute with one another,

$$\vec{L} \cdot \vec{p} = L_i p_i = \epsilon_{ijk} q_j p_k p_i = 0 \,,$$

because $\epsilon_{ijk} p_k p_i = \epsilon_{kji} p_i p_k = -\epsilon_{ijk} p_k p_i$. ($\epsilon_{ijk} p_k p_i$ is equal to minus itself, so it must be zero.) Similarly, since also q_k and q_i commute with one another,

$$\vec{L} \cdot \vec{q} = L_i q_i = \epsilon_{ijk} q_j p_k q_i = 0 \,,$$

since $\epsilon_{ijk} q_j q_i = 0$, for the same reason as before. Note also that $\vec{p} \cdot \vec{L} = 0$ and $\vec{q} \cdot \vec{L} = 0$. The fact that q_j and p_k do not commute with one another if $j = k$ does not invalidate the reasoning, for when $j = k$ the factor ϵ_{ijk} vanishes. Thus in fact

$$L_i = \epsilon_{ijk} q_j p_k = \epsilon_{ijk} p_k q_j \,.$$

(2) In classical physics, the vector product of a vector with itself is always zero, but in quantum mechanics this is no longer necessarily the case. We have

$$(\vec{L} \wedge \vec{L})_i = \epsilon_{ijk} L_j L_k \,,$$

but we can also write

$$(\vec{L} \wedge \vec{L})_i = \epsilon_{ikj} L_k L_j = -\epsilon_{ijk} L_k L_j \,.$$

Taking the average of these two expressions, and using the algebra of the angular momentum operators, we find

$$\begin{aligned} (\vec{L} \wedge \vec{L})_i &= \tfrac{1}{2} \epsilon_{ijk} (L_j L_k - L_k L_j) \\ &= \tfrac{1}{2} i\hbar \epsilon_{ijk} \epsilon_{jkm} L_m \\ &= \tfrac{1}{2} i\hbar \epsilon_{ijk} \epsilon_{mjk} L_m \,. \end{aligned}$$

We use the lemma

$$\epsilon_{ijk} \epsilon_{mnk} = \delta_{im} \delta_{jn} - \delta_{in} \delta_{jm} \,,$$

to deduce that

$$\begin{aligned} (\vec{L} \wedge \vec{L})_i &= \tfrac{1}{2} i\hbar (\delta_{im} \delta_{jj} - \delta_{ij} \delta_{jm}) L_m \\ &= \tfrac{1}{2} i\hbar (3\delta_{im} - \delta_{im}) L_m \\ &= i\hbar L_i \,, \end{aligned}$$

which is the desired result.

We will now prove the lemma that was needed. It has many other uses, as we will soon see.

Lemma: Contraction of Levi-Civita symbols

$$\epsilon_{ijk}\epsilon_{mnk} = \delta_{im}\delta_{jn} - \delta_{in}\delta_{jm}\,,$$

where, as usual, there is summation over the repeated index, k.

Proof

This lemma can be demonstrated by assiduously listing left and right sides for all 81 values of the quadruple $\{ijmn\}$, or more astutely by considering the triple vector product,

$$\begin{aligned}[\vec{a}\wedge(\vec{b}\wedge\vec{c})]_1 &= a_2(\vec{b}\wedge\vec{c})_3 - a_3(\vec{b}\wedge\vec{c})_2 \\ &= a_2(b_1c_2 - b_2c_1) - a_3(b_3c_1 - b_1c_3) \\ &= a_2b_1c_2 + a_3b_1c_3 - a_2b_2c_1 - a_3b_3c_1\,.\end{aligned}$$

Now by adding and subtracting $a_1b_1c_1$ we obtain

$$[\vec{a}\wedge(\vec{b}\wedge\vec{c})]_1 = a_jb_1c_j - a_jb_jc_1\,,$$

with summation over j. A similar formula holds for the second and third components of the triple vector product, so we have

$$[\vec{a}\wedge(\vec{b}\wedge\vec{c})]_i = a_jb_ic_j - a_jb_jc_i = (\delta_{im}\delta_{jn} - \delta_{in}\delta_{jm})a_jb_mc_n\,. \tag{3.2}$$

However, we also have

$$[\vec{a}\wedge(\vec{b}\wedge\vec{c})]_i = \epsilon_{ijk}\epsilon_{kmn}a_jb_mc_n = \epsilon_{ijk}\epsilon_{mnk}a_jb_mc_n\,. \tag{3.3}$$

The 27 triples $a_jb_mc_n$ are at our disposal, and so the required result follows by comparing Eq.(3.2) and Eq.(3.3) and equating the coefficients of $a_jb_mc_n$.

END OF LEMMA

3.3 Position and Angular Momentum

Show that

(1) $$\vec{L}\wedge\vec{q} + \vec{q}\wedge\vec{L} = 2i\hbar\vec{q}$$

(2) $$\left[L^2, \vec{q}\right] = -2i\hbar\left(\vec{L}\wedge\vec{q} - i\hbar\vec{q}\right)$$

Solution

(1) By using the antisymmetry of ϵ_{ijk} under interchange of j and k, we find

$$\begin{aligned}(\vec{L}\wedge\vec{q}+\vec{q}\wedge\vec{L})_i &= \epsilon_{ijk}(L_jq_k+q_jL_k)=\epsilon_{ijk}(L_jq_k-q_kL_j)\\ &= \epsilon_{ijk}\epsilon_{jmn}(q_mp_nq_k-q_kq_mp_n)\\ &= (\delta_{km}\delta_{in}-\delta_{kn}\delta_{im})q_m[p_n,q_k]\\ &= -i\hbar(\delta_{km}\delta_{ik}-\delta_{kk}\delta_{im})q_m=2i\hbar q_i\,, \end{aligned}\tag{3.4}$$

since $\delta_{kk}=1+1+1=3$.

(2) With summation over n,

$$\begin{aligned}[L^2,q_i] &= L_n[L_n,q_i]+[L_n,q_i]L_n\\ &= \epsilon_{njk}\{L_n[q_jp_k,q_i]+[q_jp_k,q_i]L_n\}\\ &= \epsilon_{njk}\{L_nq_j[p_k,q_i]+q_j[p_k,q_i]L_n\}\\ &= -i\hbar\epsilon_{nji}(L_nq_j+q_jL_n)\\ &= -i\hbar\epsilon_{inj}(L_nq_j-q_nL_j)\,.\end{aligned}$$

In vector notation, this is

$$[L^2,\vec{q}]=-i\hbar(\vec{L}\wedge\vec{q}-\vec{q}\wedge\vec{L})\,.\tag{3.5}$$

However, from Eq.(3.4) we have

$$\vec{q}\wedge\vec{L}=-\vec{L}\wedge\vec{q}+2i\hbar\vec{q}\,.\tag{3.6}$$

Together with Eq.(3.5), this implies

$$[L^2,\vec{q}]=-2i\hbar(\vec{L}\wedge\vec{q}-i\hbar\vec{q})\,.\tag{3.7}$$

3.4 Commutation of Angular Momentum and Central Potential

Given a Hamiltonian

$$H=\frac{p^2}{2m}+V(q^2)\,,$$

where V depends only on q^2 and is such that it possesses a Fourier transform, show that $[\vec{L}\,,H]=0$.

Solution

The commutator can be divided into a kinetic and a potential contribution:

$$[\vec{L}, H] = \frac{1}{2m}[\vec{L}, p^2] + [\vec{L}, V(q^2)]\,. \tag{3.8}$$

Consider first

$$[L_i, p^2] = \epsilon_{ijk}[q_j p_k, p^2]\,. \tag{3.9}$$

Now $q_j p_k p^2 - p^2 q_j p_k = [q_j, p^2]p_k$, since p^2 and p_k commute, and further

$$[q_j, p^2] = [q_j, p_\ell]p_\ell + p_\ell[q_j, p_\ell] = 2i\hbar p_j\,,$$

since $[q_j, p_\ell] = i\hbar\delta_{j\ell}$. Hence

$$[L_i, p^2] = 2i\hbar\epsilon_{ijk}p_j p_k = 0\,. \tag{3.10}$$

Thus the kinetic contribution to the commutator is zero.

A demonstration analogous to the above serves to show that

$$[\vec{L}, q^2] = 0\,; \tag{3.11}$$

it is not necessary to repeat the above steps, for one only needs to interchange the roles of q and p. It follows immediately that

$$[\vec{L}, q^{2n}] = 0\,, \tag{3.12}$$

since one may write q^{2n} as the product of n factors of q^2, and it follows from Eq.(3.11) that $\vec{L}$ commutes with each of these factors.

Now suppose that the central potential is sufficiently well-behaved that it possesses a Fourier cosine transform:

$$V(q^2) = \int_0^\infty dt\, v(t)\cos tq^2\,. \tag{3.13}$$

If $V(q^2)$ is piecewise continuous this will be the case, according to Fourier theory (finite discontinuities are allowed). Since the cosine has a series expansion with an infinite radius of convergence, we may legally write

$$[\vec{L}, V(q^2)] = \int_0^\infty dt\, v(t)\sum_{n=0}^{\infty}\frac{t^n}{n!}[\vec{L}, q^{2n}] = 0\,, \tag{3.14}$$

where we have used the result of our induction. So the potential contribution to the commutator is also zero, and we conclude that

$$[\vec{L}, H] = \left[\vec{L}, \frac{p^2}{2m} + V(q^2)\right] = 0\,. \tag{3.15}$$

As an important special case, let us consider the Coulomb potential. By transforming to polar coordinates, we see that

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\, \mathrm{e}^{-(x^2+y^2)} = \int_0^{\infty} dr\, r\, \mathrm{e}^{-r^2} \int_0^{2\pi} d\theta = \tfrac{1}{2} \times 2\pi = \pi\,.$$

Since the left-hand side is the square of $\int_{-\infty}^{\infty} dx\, \mathrm{e}^{-x^2}$, it follows that the latter integral is equal to $\sqrt{\pi}$, and half of that is $\int_0^{\infty} dx\, \mathrm{e}^{-x^2} = \sqrt{\pi}/2$. Now rotate the integration contour in the x-plane by an angle ϕ, and set $x = \mathrm{e}^{i\phi}\sqrt{\xi}$:

$$\int_0^{\infty} \frac{d\xi}{\sqrt{\xi}} \exp\left(-\mathrm{e}^{2i\phi}\xi\right) = \sqrt{\pi}\,\mathrm{e}^{-i\phi}\,,$$

with the restriction $|\phi| \leq \frac{1}{4}\pi$. On taking the average of this integral for the two values, $\phi = \frac{1}{4}\pi$ and $\phi = -\frac{1}{4}\pi$, we obtain

$$\int_0^{\infty} d\xi\, \frac{\cos\xi}{\sqrt{\xi}} = \sqrt{\frac{\pi}{2}}\,.$$

Finally, make the substitution $\xi = tq^2$ in this integral to show that, when

$$v(t) = -e^2\sqrt{\frac{2}{\pi t}}\,,$$

is inserted into Eq.(3.13), the Coulomb potential results, namely

$$V(q^2) = \int_0^{\infty} dt\, v(t) \cos tq^2 = -\frac{e^2}{q}\,.$$

Here q is of course shorthand for $q = \sqrt{q^2} = \sqrt{q_i q_i}$.

3.5 Measurement Results

The wave function of a particle has the form $f(r,\theta)\cos\phi$. Give the possible results of a measurement of the z-component of the angular momentum, with the corresponding probabilities.

Solution

The eigenvectors of L_z are $\mathrm{e}^{im\phi}$, with the corresponding eigenvalues $m\hbar$. Since

$$f(r,\theta)\cos\phi = \tfrac{1}{2} f(r,\theta)\left[\mathrm{e}^{i\phi} + \mathrm{e}^{-i\phi}\right]\,,$$

we see that the possible results of a measurement of L_z are $\hbar$ or $-\hbar$, with equal probabilities of $\frac{1}{2}$, since the projections onto the two eigenvectors is the same.

3.6 Mean Values of Angular Momenta

$|\ell, m\rangle$ is an eigenket of L^2 and L_3 with eigenvalues $\ell(\ell+1)\hbar^2$ and $m\hbar$. Show

$$\langle \ell, m|L_1^2|\ell, m\rangle = \langle \ell, m|L_2^2|\ell, m\rangle = \tfrac{1}{2}\hbar^2[\ell(\ell+1) - m^2]$$

Solution
Since $L_\pm = L_1 \pm iL_2$, we find

$$L_1^2 = \tfrac{1}{4}(L_+ + L_-)^2 = \tfrac{1}{4}(L_+^2 + L_+L_- + L_-L_+ + L_-^2)\,.$$

Hence

$$\langle \ell, m|L_1^2|\ell, m\rangle = \tfrac{1}{4}\langle \ell, m|L_+L_- + L_-L_+|\ell, m\rangle\,,$$

since the other terms involve overlaps of orthogonal states. Now

$$\begin{aligned} L_\pm L_\mp &= (L_1 \pm iL_2)(L_1 \mp iL_2) \\ &= L_1^2 + L_2^2 \mp i[L_1, L_2] \\ &= L^2 - L_3^2 \pm \hbar L_3\,, \end{aligned}$$

which is Eq.(3.10) of Volume 1. Therefore

$$L_+L_- + L_-L_+ = 2(L^2 - L_3^2)\,,$$

and so

$$\langle \ell, m|L_1^2|\ell, m\rangle = \tfrac{1}{2}\langle \ell, m|L^2 - L_3^2|\ell, m\rangle = \tfrac{1}{2}\hbar^2[\ell(\ell+1) - m^2]\,.$$

Since

$$L_2^2 = -\tfrac{1}{4}(L_+ - L_-)^2 = \tfrac{1}{4}(-L_+^2 + L_+L_- + L_-L_+ - L_-^2)\,,$$

the demonstration proceeds in the same way for $\langle \ell, m|L_2^2|\ell, m\rangle$.

3.7 Possible Results and Probabilities

A particle in a spherically symmetrical potential is in a state given by the wave function

$$\psi(\vec{r}) = [\alpha x^2 + \beta(y^2 + z^2)]f(r)\,,$$

where α and β are constants.

(1) Take $\alpha = \beta = 1$. What are the possible results of a measurement of L^2? Calculate the corresponding probabilities. What are the possible results and the probabilities associated with measurements of L_x, L_y and L_z?

(2) Take $\alpha = 0$ but $\beta = 1$. Answer the same questions for this case.

Solution

(1) With $\alpha = \beta = 1$, the wave-function is spherically symmetric, i.e., it is a function only of r. Since the components of the angular momentum, L_x, L_y and L_z, are expressed in configuration representation in terms of partial differentials with respect to θ and ϕ, but not r, it follows that

$$L_x\psi(r) = L_y\psi(r) = L_z\psi(r) = 0\,. \tag{3.16}$$

This can also be seen by noting that

$$\begin{aligned} L_x\psi(r) &= -i\hbar\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]\psi(r) \\ &= -i\hbar\left[\frac{yz}{r} - \frac{zy}{r}\right]\psi'(r) = 0\,, \end{aligned}$$

and similarly for the other components. We see from Eq.(3.16) that $\psi(r)$ is an simultaneous eigenvector of L_x, L_y and L_z, belonging to the eigenvalue 0. Hence it is an eigenvector of L^2, also belonging to the eigenvalue 0. Thus the result of measuring any component of the angular momentum, or the total angular momentum squared, in this spherically symmetrical state, is certainly 0; or in other words, the probability of measuring 0 is 1.

(2) With $\alpha = 0$ but $\beta = 1$,

$$\psi(\vec{r}) = (y^2 + z^2)f(r)\,,$$

which has cylindrical symmetry about the x axis only. Thus we expect the x component of the angular momentum to vanish. More formally,

$$\begin{aligned} L_x\psi(r) &= -i\hbar\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right](y^2 + z^2)]f(r) \\ &= -2i\hbar\,[yz - zy]\,f(r) - i\hbar\left[\frac{yz}{r} - \frac{zy}{r}\right](y^2 + z^2)]f'(r) = 0\,, \end{aligned}$$

so the value that is measured for the x component of the angular momentum is 0, with probability 1.

To see what the results of measurements of other components of the angular momentum may be, we observe that

$$y^2 + z^2 = \tfrac{1}{4}r^2\big[-\sin^2\theta(\mathrm{e}^{2i\phi} + \mathrm{e}^{-2i\phi}) + 2 + 2\cos^2\theta\big]\,. \tag{3.17}$$

This is a superposition of $\ell = 0$ and $\ell = 2$ spherical harmonics. The spherical harmonic, $Y_{\ell m}(\theta, \phi)$, is proportional to $P_\ell^m(\cos\theta)\, e^{im\phi}$, where the associated Legendre function of the first kind can be defined by

$$P_\ell^m(\cos\theta) = \frac{(-1)^\ell}{2^\ell \ell!} \sin^m\theta \left(\frac{d}{d\cos\theta}\right)^{\ell+m} \sin^{2\ell}\theta\,,$$

so $P_0^0(\cos\theta) = 1$, $P_2^0(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$ and $P_2^2(\cos\theta) = 3(1-\cos^2\theta)$. Thus

$$\begin{aligned} Y_{00} &= \sqrt{\frac{1}{4\pi}} \\ Y_{20} &= \sqrt{\frac{5}{16\pi}}\,(3\cos^2\theta - 1) \\ Y_{2,\pm 2} &= \sqrt{\frac{15}{32\pi}}\,\sin^2\theta\, e^{\pm 2i\phi}\,, \end{aligned}$$

with the standard normalization. In terms of them, Eq.(3.17) is

$$y^2 + z^2 = \tfrac{4}{3}\sqrt{\pi} r^2 \left[Y_{00}(\theta,\phi) + \sqrt{\tfrac{1}{20}} Y_{20}(\theta,\phi) - \sqrt{\tfrac{3}{40}}\Big(Y_{22}(\theta,\phi) + Y_{2,-2}(\theta,\phi)\Big)\right].$$

As can be seen from this decomposition, the possible values obtained if L^2 is measured are $\ell(\ell+1)\hbar^2$, with $\ell = 0$ or 2. The ratio of the probabilities is

$$\mathsf{Pr}(\ell = 2)/\mathsf{Pr}(\ell = 0) = \tfrac{1}{20} + \tfrac{3}{40} + \tfrac{3}{40} = \tfrac{1}{5}\,,$$

and since $\mathsf{Pr}(\ell = 0) + \mathsf{Pr}(\ell = 2) = 1$, it follows that

$$\mathsf{Pr}(\ell = 0) = \tfrac{5}{6} \qquad \mathsf{Pr}(\ell = 2) = \tfrac{1}{6}\,.$$

If, instead of measuring L^2, L_z is measured, the possible results are $m\hbar$, with the one of the values $m = -2$, 0 or 2. The ratio of the corresponding probabilities is

$$\mathsf{Pr}(m = 2)/\mathsf{Pr}(m = 0) = \mathsf{Pr}(m = -2)/\mathsf{Pr}(m = 0) = \tfrac{3}{40}(1 + \tfrac{1}{20})^{-1} = \tfrac{1}{14}\,.$$

Since $\mathsf{Pr}(m = -2) + \mathsf{Pr}(m = 0) + \mathsf{Pr}(m = 2) = 1$, it follows that

$$\mathsf{Pr}(m = 0) = \tfrac{7}{8} \qquad \mathsf{Pr}(m = 2) = \mathsf{Pr}(m = -2) = \tfrac{1}{16}\,.$$

If L_y is measured instead of L_z, the possible values, and the corresponding probabilities, will be just as they were for L_z, since the wave function is unchanged under a rotation of the coordinate axes through $\frac{\pi}{2}$ about the x axis. This rotation interchanges the y and z axes, so indeed the answers we obtained for measurements on L_z apply unchanged for measurements on L_y.

3.8 Uncertainty Principle

Suppose that the wave function $\psi(\mathbf{r})$ is an eigenfunction of L_x and L_y.

(1) Does this not contradict the uncertainty principle for noncommuting operators?
(2) What are the possible results of a measurement of L_z?
(3) Show that ψ is spherically symmetric.

Solution

Suppose $L_x\psi(\mathbf{r}) = \lambda_x\psi(\mathbf{r})$ and $L_y\psi(\mathbf{r}) = \lambda_y\psi(\mathbf{r})$. Since $[L_x, L_y] = i\hbar L_z$, it follows that $L_z\psi(\mathbf{r}) = 0$; but $[L_y, L_z] = i\hbar L_x$, so $L_x\psi(\mathbf{r}) \propto [L_y, L_z]\psi(\mathbf{r}) = 0$, i.e., $L_x\psi(\mathbf{r}) = 0$, and similarly $L_y\psi(\mathbf{r}) = 0$.

(1) Heisenberg's uncertainty principle gives a lower bound on the product of the standard deviations of the measured values of two noncommuting operators, like q and p, when the commutator is not an operator. However, the commutator of L_x and L_y *is* an operator, since it is proportional to L_z. The mean and standard deviations of both L_x and L_y in the state $\psi(\mathbf{r})$ are zero, as are those of L_z, and, although this does mean that L_x and L_y have a precise value in the state $\psi(\mathbf{r})$, namely zero, this does not contradict the uncertainty principle.

(2) Since $\psi(\mathbf{r})$ is an eigenfunction of L_z corresponding to the eigenvalue 0, it follows that a measurement of L_z, in the state $\psi(\mathbf{r})$, always yields the result 0.

(3) The most general continuous function of $\mathbf{r}$ can be written

$$\psi(\mathbf{r}) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \phi_{\ell m}(r) Y_{\ell m}(\theta, \phi) .$$

Since $L^2 Y_{\ell m}(\theta, \phi) = \ell(\ell+1) Y_{\ell m}(\theta, \phi)$, and we have proved that $L^2\psi(\mathbf{r}) = 0$, it follows that $\phi_{\ell m}(r) = 0$ for all $\ell \geq 1$, since the spherical harmonics constitute a linearly independent set of functions of θ and ϕ. So $\psi(\mathbf{r}) = \phi_{00}(r)/\sqrt{4\pi}$, which means that $\psi(\mathbf{r})$ is spherically symmetric.

3.9 Matrix Representations

Consider the following matrix representations of of the x- and y-components of the angular momentum operator.

$$L_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \qquad L_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}$$

(1) Calculate L_3, using the algebra of angular momentum operators.
(2) What is the corresponding value of ℓ, the angular momentum quantum number?
(3) Calculate $\langle L_1 \rangle$, $\langle L_1^2 \rangle$ and $\Delta L_1 = \langle [L_1 - \langle L_1 \rangle]^2 \rangle^{1/2}$. Here $\langle\ \rangle$ refers to matrix elements taken with respect to a normalized eigenvector of L_3 belonging to the eigenvalue 1.
(4) Consider the state $\langle \phi | = \frac{1}{2}(1, 1, \sqrt{2})$. If L_1^2 is measured in this state and the result $+1$ is obtained, what is the state after the measurement? How probable was this result? If L_1 is now measured, what are the outcomes and their probabilities? Does this second measurement change the state?

Solution

(1) By direct matrix mutiplication, we find

$$L_1 L_2 = \frac{1}{2} \begin{pmatrix} i & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & -i \end{pmatrix} \qquad L_2 L_1 = \frac{1}{2} \begin{pmatrix} -i & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & i \end{pmatrix},$$

and since $[L_1, L_2] = iL_3$, we have

$$L_3 = -i[L_1, L_2] = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

(2) The eigenvalues of L_3 are by inspection -1, 0 and 1. Since the eigenvalues (in units such that $\hbar = 1$) are $-\ell$, $-\ell + 1, \ldots, \ell$, it follows that $\ell = 1$.
(3) The eigenvectors of L_3 belonging to the eigenvalues 1, 0 and -1 are

$$|1, 1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \qquad |1, 0\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \qquad |1, -1\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}.$$

The mean of L_1 in the state $|1, 1\rangle$ is therefore

$$\langle L_1 \rangle = \langle 1, 1 | L_1 | 1, 1 \rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = 0.$$

The square of L_1 is

$$L_1^2 = \frac{1}{2} \begin{pmatrix} 1 & 0 & 1 \\ 0 & 2 & 0 \\ 1 & 0 & 1 \end{pmatrix},$$

and hence the mean of L_1^2 in the state $|1,1\rangle$ is

$$\langle L_1^2\rangle = \langle 1,1|L_1^2|1,1\rangle = \frac{1}{2}\begin{pmatrix}1 & 0 & 0\end{pmatrix}\begin{pmatrix}1 & 0 & 1\\ 0 & 2 & 0\\ 1 & 0 & 1\end{pmatrix}\begin{pmatrix}1\\0\\0\end{pmatrix} = \frac{1}{2}.$$

Finally,

$$\Delta L_1 = \langle [L_1 - \langle L_1\rangle]^2\rangle^{1/2} = \langle L_1^2\rangle^{1/2} = \frac{1}{\sqrt{2}}.$$

(4) The eigenvalues of L_1^2 are 1 and 0. Consider the eigenvectors

$$|\chi(1a)\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\0\\1\end{pmatrix} \quad |\chi(1b)\rangle = \begin{pmatrix}0\\1\\0\end{pmatrix} \quad |\chi(0)\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\0\\-1\end{pmatrix}, \tag{3.18}$$

the first two belonging to the eigenvalue 1, and the last one to the eigenvalue 0. The projection operator onto the eigenspace of L_1^2 belonging to eigenvalue 1 is

$$\mathcal{P}_1 = |\chi(1a)\rangle\langle\chi(1a)| + |\chi(1b)\rangle\langle\chi(1b)| = \frac{1}{2}\begin{pmatrix}1 & 0 & 1\\ 0 & 2 & 0\\ 1 & 0 & 1\end{pmatrix}.$$

If L_1^2 is measured in the state represented by $|\phi\rangle$, with the result 1, the state vector is thereby projected on to

$$\mathcal{P}_1|\phi\rangle = \frac{1}{4}\begin{pmatrix}1 & 0 & 1\\ 0 & 2 & 0\\ 1 & 0 & 1\end{pmatrix}\begin{pmatrix}1\\1\\\sqrt{2}\end{pmatrix} = \frac{1}{4}\begin{pmatrix}1+\sqrt{2}\\2\\1+\sqrt{2}\end{pmatrix}.$$

The probability of this result (i.e., unity for the measured value of L_1^2) is

$$|\langle\chi(1a)|\mathcal{P}_1|\phi\rangle|^2 + |\langle\chi(1b)|\mathcal{P}_1|\phi\rangle|^2 = \langle\phi|\mathcal{P}_1|\phi\rangle = \frac{5+2\sqrt{2}}{8}.$$

In properly normalized form, let us define the projection

$$|\tilde{\phi}\rangle = \frac{\mathcal{P}_1|\phi\rangle}{\sqrt{\langle\phi|\mathcal{P}_1|\phi\rangle}} = \frac{1}{\sqrt{10+4\sqrt{2}}}\begin{pmatrix}1+\sqrt{2}\\2\\1+\sqrt{2}\end{pmatrix}. \tag{3.19}$$

The state (3.19) can be rewritten in terms of the eigenvectors Eq.(3.18) of L_1^2:

$$|\tilde{\phi}\rangle = \frac{1+\sqrt{2}}{\sqrt{5+2\sqrt{2}}}|\chi(1a)\rangle + \frac{\sqrt{2}}{\sqrt{5+2\sqrt{2}}}|\chi(1b)\rangle.$$

It is easy to check that

$$|\tau(\pm 1)\rangle = \frac{1}{\sqrt{2}}\{|\chi(1a)\rangle \pm |\chi(1b)\rangle\}$$

are normalized eigenvectors of L_1 with eigenvalues ± 1. Hence we can also write

$$|\tilde{\phi}\rangle = \frac{1+2\sqrt{2}}{\sqrt{10+4\sqrt{2}}}|\tau(1)\rangle + \frac{1}{\sqrt{10+4\sqrt{2}}}|\tau(-1)\rangle\,.$$

So if L_1 is measured in the state $\tilde{\phi}$, the result can be 1, and the probability of obtaining this value is $\left(9+4\sqrt{2}\right)/\left(10+4\sqrt{2}\right)$, or it can be -1, with probability $1/\left(10+4\sqrt{2}\right)$. Clearly the state $\tilde{\phi}$ will be changed by this measurement, being thrown into the state $\tau(1)$ or the state $\tau(-1)$. The probability of obtaining the result 0 (the remaining eigenvalue of L_1), is zero.

3.10 Four Euclidean Dimensions

The generalization of angular momentum in configuration space from 3 to 4 Euclidean dimensions involves the differential operators

$$L_{jk} = -i(x_j\partial_k - x_k\partial_j)\,,$$

where j and k take on the values $1, 2, 3, 4$, with $\hbar = 1$. Introduce

$$\left(J_1, J_2, J_3\right) = \left(L_{23}, L_{31}, L_{12}\right) \qquad \left(K_1, K_2, K_3\right) = \left(L_{14}, L_{24}, L_{34}\right).$$

(1) Discover the commutation relations between $\vec{J}$ and $\vec{K}$.

(2) Show that the operators

$$\vec{J}^{\pm} = \tfrac{1}{2}(\vec{J} \pm \vec{K})$$

each obey the standard commutation relations for an angular momentum, and that they commute with one another.

Solution

(1) L_{jk} is construed as an operator on a space of differentiable functions, ϕ:

$$\begin{aligned}[L_{ij}, L_{k\ell}]\phi &= -[x_i\partial_j - x_j\partial_i, x_k\partial_\ell - x_\ell\partial_k]\phi \\ &= -\mathcal{D}_{ijk\ell} - \mathcal{D}_{ji\ell k} + \mathcal{D}_{ij\ell k} + \mathcal{D}_{jik\ell}\,, \end{aligned} \tag{3.20}$$

$$\begin{aligned}\mathcal{D}_{ijk\ell} &= [x_i\partial_j, x_k\partial_\ell]\phi = x_i\partial_j x_k\partial_\ell\phi - x_k\partial_\ell\phi x_i\partial_j\phi \\ &= x_i(\delta_{jk}\partial_\ell\phi + x_k\partial_j\partial_\ell\phi) - x_k(\delta_{i\ell}\partial_j\phi + x_i\partial_\ell\partial_j\phi) \\ &= (\delta_{jk}x_i\partial_\ell - \delta_{i\ell}x_k\partial_j)\phi\,. \end{aligned} \tag{3.21}$$

Hence Eq.(3.20) becomes

$$\begin{aligned}[L_{ij}, L_{k\ell}]\phi &= \delta_{ik}(x_j\partial_\ell - x_\ell\partial_j)\phi + \delta_{j\ell}(x_i\partial_k - x_k\partial_i)\phi \\ &\quad -\delta_{i\ell}(x_j\partial_k - x_k\partial_j)\phi - \delta_{jk}(x_i\partial_\ell - x_\ell\partial_i)\phi\,. \end{aligned} \tag{3.22}$$

Evidently we have the operator relation

$$[L_{ij}, L_{k\ell}] = i\delta_{ik}L_{j\ell} + i\delta_{j\ell}L_{ik} - i\delta_{i\ell}L_{jk} - i\delta_{jk}L_{i\ell}\,. \tag{3.23}$$

Consider in succession the substitution of $ijk\ell$ by 2331, 1424, 2324 and 1431. This yields the following four commutators:

$$\begin{aligned}[J_1, J_2] &= [L_{23}, L_{31}] = iL_{12} = iJ_3 \\ [K_1, K_2] &= [L_{14}, L_{24}] = iL_{12} = iJ_3 \\ [J_1, K_2] &= [L_{23}, L_{24}] = iL_{34} = iK_3 \\ [K_2, J_1] &= [L_{14}, L_{31}] = -iL_{43} = iL_{34} = iK_3\,, \end{aligned}$$

where the definitions of J_i and K_i have been used.
(2) Evidently the linear combinations, $J_i^{\pm}$, satisfy

$$\begin{aligned}[J_1^{\pm}, J_2^{\pm}] &= \tfrac{1}{4}[J_1, J_2] + \tfrac{1}{4}[K_1, K_2] \pm \tfrac{1}{4}[J_1, K_2] \pm \tfrac{1}{4}[K_1, J_2] \\ &= \tfrac{i}{2}(J_3 \pm K_3) = iJ_3^{\pm}\,, \end{aligned}$$

whereas

$$\begin{aligned}[J_1^{\pm}, J_2^{\mp}] &= \tfrac{1}{4}[J_1, J_2] - \tfrac{1}{4}[K_1, K_2] \pm \tfrac{1}{4}[J_1, K_2] \mp \tfrac{1}{4}[K_1, J_2] \\ &= \tfrac{i}{4}(J_3 - J_3 \pm K_3 \mp K_3) = 0\,. \end{aligned}$$

By cyclic and anticyclic permutation of the indices 123, it is clear that

$$\begin{aligned}[J_i^{\pm}, J_j^{\pm}] &= i\epsilon_{ijk}J_k^{\pm} \\ [J_i^{\pm}, J_j^{\mp}] &= 0\,. \end{aligned}$$

This concludes the proof that $\vec{J}^{\pm}$ are independent angular momentum operators.

Chapter 4

Central Potential

4.1 Spherical Bessel and Neumann Functions

The spherical Bessel and Neumann functions are respectively

$$j_\ell(\rho) = (-\rho)^\ell \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^\ell \frac{\sin\rho}{\rho}$$

$$n_\ell(\rho) = -(-\rho)^\ell \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^\ell \frac{\cos\rho}{\rho}\,.$$

(1) Prove the recurrence relation

$$j_{\ell+1}(\rho) = -j'_\ell(\rho) + \frac{\ell}{\rho} j_\ell(\rho)\,.$$

(2) Prove the recurrence relation

$$n_{\ell+1}(\rho) = -n'_\ell(\rho) + \frac{\ell}{\rho} n_\ell(\rho)\,.$$

(3) Work out $j_\ell(\rho)$ and $n_\ell(\rho)$ for $\ell = 0, 1, 2, 3$, and sketch them graphically.

Solution

The most efficient way to prove the recurrence relations is to use the Hankel function of the first kind,

$$h_\ell^{(1)}(\rho) = j_\ell(\rho) + i n_\ell(\rho)\,,$$

for which we find

$$h_\ell^{(1)}(\rho) = -i(-\rho)^\ell \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^\ell \frac{e^{i\rho}}{\rho}\,.$$

It follows that

$$h^{(1)}_{\ell+1}(\rho) = i(-\rho)^{\ell}\frac{d}{d\rho}\left[i(-\rho)^{-\ell}h^{(1)}_{\ell}(\rho)\right] = -h^{(1)'}_{\ell}(\rho) + \frac{\ell}{\rho}h^{(1)}_{\ell}(\rho)\,. \tag{4.1}$$

(1) From the real part of Eq.(4.1), we immediately deduce the recurrence relation for the spherical Bessel functions.
(2) From the imaginary part of Eq.(4.1), we obtain the recurrence relation for the spherical Neumann functions.
(3) We can evaluate the spherical Bessel and Neumann functions sequentially from from Eq.(4.1), obtaining

$$\begin{aligned}
j_0(\rho) &= \frac{\sin\rho}{\rho} & n_0(\rho) &= -\frac{\cos\rho}{\rho}\\
j_1(\rho) &= \frac{\sin\rho}{\rho^2} - \frac{\cos\rho}{\rho} & n_1(\rho) &= -\frac{\cos\rho}{\rho^2} - \frac{\sin\rho}{\rho}\\
j_2(\rho) &= 3\frac{\sin\rho}{\rho^3} - 3\frac{\cos\rho}{\rho^2} - \frac{\sin\rho}{\rho}\\
n_2(\rho) &= -3\frac{\cos\rho}{\rho^3} - 3\frac{\sin\rho}{\rho^2} + \frac{\cos\rho}{\rho}\\
j_3(\rho) &= 15\frac{\sin\rho}{\rho^4} - 15\frac{\cos\rho}{\rho^3} - 6\frac{\sin\rho}{\rho^2} + \frac{\cos\rho}{\rho}\\
n_3(\rho) &= -15\frac{\cos\rho}{\rho^4} - 15\frac{\sin\rho}{\rho^3} + 6\frac{\cos\rho}{\rho^2} + \frac{\sin\rho}{\rho}
\end{aligned}$$

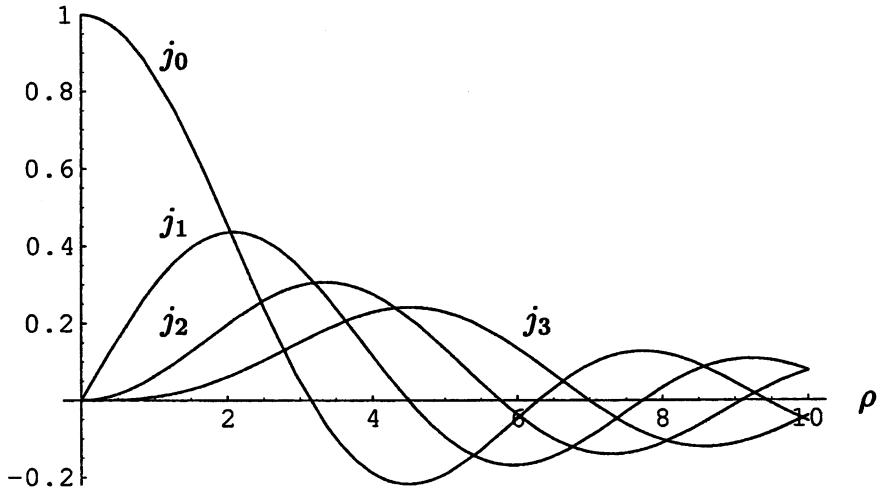

Fig. 4.1 Spherical Bessel Functions

These functions are displayed in Figures 4.1 and 4.2.

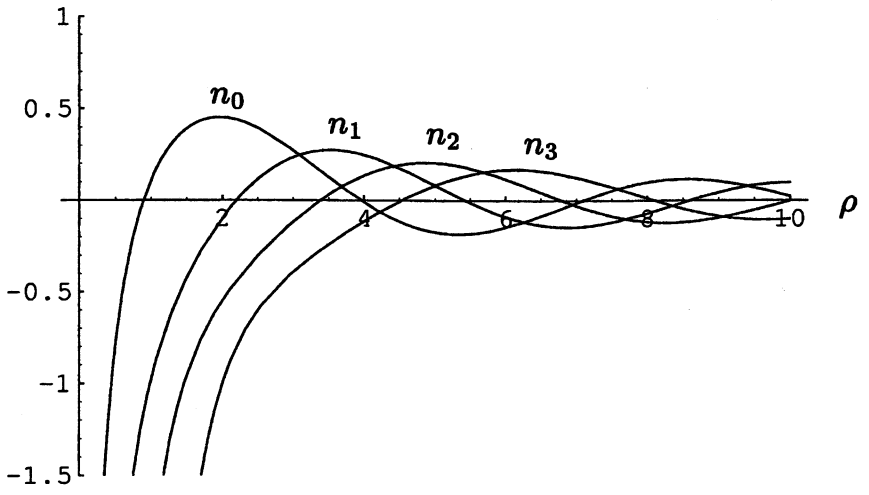

Fig. 4.2 Spherical Neumann Functions

4.2 Function of Bound State Energy

Let $\psi(\vec{r}) = u_0(r)/r$ be an S-wave solution of the Schrödinger equation for a potential that has bound states, and which is strictly zero for $r \geq a$. Define the following function of the total energy:

$$f(E) = \frac{u_0'(a)}{u_0(a)}.$$

Let E_B be a bound-state energy. Evaluate $f(E_B)$.

Solution

Since there is no potential energy for $r \geq a$, the wave function must be a solution of the free Schrödinger equation in this region. For a negative energy, E, the general solution is

$$u_0(r) = A\,\mathrm{e}^{-\kappa r} + B\,\mathrm{e}^{\kappa r},$$

where $\kappa = \sqrt{-2mE}/\hbar$. At a bound-state energy, $E = E_B$, the coefficient B is zero. In this case, $u_0'(r)/u_0(r) = -\kappa$, and so

$$f(E_B) = \frac{u_0'(a)}{u_0(a)} = -\kappa = -\frac{\sqrt{-2ME_B}}{\hbar}.$$

4.3 Infinite Square Well

Solve the bound state problem for a particle of mass m in the following potential:

$$\begin{aligned} V(r) &= 0 \qquad 0 < r < a \\ &= \infty \qquad r > a\,, \end{aligned}$$

where $a = \hbar/\sqrt{2m}$.

(1) List all the energy levels for which $n \leq 3$ and $\ell \leq 3$.
(2) Show that energy levels of the same n are ordered by their ℓ values.
(3) Show that energy levels of the same ℓ are ordered by their n values.

Solution

The regular solution of the free radial Schrödinger equation for $0 < r < a$ is

$$u_\ell(r) = Arj_\ell(kr)\,,$$

where $k = \sqrt{2mE}/\hbar$, E being the energy. This wave function must vanish at $r = a$, so E must satisfy $j_\ell(\sqrt{E}) = 0$. For a given ℓ, there is an infinite number of solutions of this equation, which we will label $E(n, \ell)$, with $n = 1, 2, 3, \ldots$ The first few zeros of the spherical Bessel functions can be read off from Figure 4.1. The following Mathematica program was used to obtain accurate values:

```
sphb[k_,z_]:=Sqrt[Pi/(2*z)]*BesselJ[k+1/2,z];
root[k_,z0_,zn_,zx_]:=FindRoot[sphb[k,z]==0,{z,z0,zn,zx}];
energy[k_,z0_,zn_,zx_]:=(root[k,z0,zn,zx][[1,2]])^2;
```

(1) This yields the following values for $E(n, \ell)$:

ℓ	0	1	2	3
$n = 1$	9.870	20.191	33.218	48.831
$n = 2$	39.478	59.680	82.719	187.636
$n = 3$	88.826	118.900	151.855	286.409

Bound-state Energies of Infinite Square Well

(2) By observation from the table, we see that $E(n, \ell+1) > E(n, \ell)$ for the values of n and ℓ that are listed. To prove the inequality for any n or ℓ, we employ the recurrence relation that was obtained in the solution to Problem **4.1**:

$$j_{\ell+1}(\rho) = -j_\ell{}'(\rho) + \frac{\ell}{\rho} j_\ell(\rho)\,. \tag{4.2}$$

Multiply this equation by ρ and rewrite it

$$[\rho j_\ell(\rho)]' = \rho j_\ell'(\rho) + j_\ell(\rho) = (\ell+1) j_\ell(\rho) - \rho j_{\ell+1}(\rho)\,.$$

On differentiating this again,

$$[\rho j_\ell(\rho)]'' = (\ell+1) j_\ell'(\rho) - \rho j_{\ell+1}'(\rho) - j_{\ell+1}(\rho)\,,$$

and using the Schrödinger equation,

$$\left[-\frac{d^2}{d\rho^2} + \frac{\ell(\ell+1)}{\rho^2} - 1\right][\rho j_\ell(\rho)] = 0\,,$$

we obtain

$$j_\ell(\rho) = j_{\ell+1}'(\rho) + \frac{\ell+2}{\rho} j_{\ell+1}(\rho)\,. \tag{4.3}$$

The recurrence relations (4.2)-(4.3) can be rewritten

$$\begin{aligned} \frac{d}{d\rho}\left[\rho^{-\ell} j_\ell(\rho)\right] &= -\rho^{-\ell} j_{\ell+1}(\rho) \\ \frac{d}{d\rho}\left[\rho^{\ell+2} j_{\ell+1}(\rho)\right] &= -\rho^{\ell+2} j_\ell(\rho)\,. \end{aligned} \tag{4.4}$$

Consider two successive zeros of $j_\ell(\rho)$, hence of $\rho^{-\ell} j_\ell(\rho)$ (apart from $\rho = 0$, which is not interesting). There must be at least one point between these zeros where the derivative of $\rho^{-\ell} j_\ell(\rho)$ is zero, since it is continuous, and so it must have at least one turning point between the two successive zeros. The first of the equations (4.4) shows that $\rho^{-\ell} j_{\ell+1}(\rho)$, and therefore $j_{\ell+1}(\rho)$ itself, must have at least one zero between the above two zeros. From the second of the two equations (4.4), we can use similar reasoning to show that, between any two consecutive zeros of $j_{\ell+1}(\rho)$, there must be at least one zero of $j_\ell(\rho)$. On combining these results together, we see that there is precisely one zero of $j_\ell(\rho)$ between any two consecutive zeros of $j_{\ell+1}(\rho)$, and vice versa.

We see from Figure 4.1, and from the table, that the first zero of $j_0(\rho)$ is at a lower energy than the first positive zero of $j_1(\rho)$. Then, from the theorem that we have just proved, the first zero of $j_2(\rho)$ lies between the first and second zeros of $j_1(\rho)$, and so on, showing thus that the first zero ($n = 0$) of each wave lies at a higher energy than that of the wave just before it. The same ordering applies to the second zero, and to the third, and so on, and this observation completes the proof.

(3) From the table, we see that $E(n+1,\ell) > E(n,\ell)$ for $n = 1, 2$. In fact there is nothing to prove here, since the zeros of $j_\ell(\rho)$, for a given ℓ, are simply labeled $n = 1, 2, 3, \ldots$, in order of increasing energy.

4.4 *P* Wave Bound State

Given a central potential, $V(r) = -V_0$ for $r < a$ and $V(r) = 0$ otherwise, find the minimum value of a^2V_0 such that there is a P wave bound state.

Solution

The regular solution of the P-wave radial equation, aside from a normalization constant, is

$$u_1(r) = rj_1(\bar{k}r)\,, \tag{4.5}$$

for $r < a$, where $\bar{k} = \sqrt{2m(V_0 + E)}/\hbar$. A bound state occurs if this solution goes over into

$$u_1(r) = rh_1^{(1)}(i\kappa r)\,, \tag{4.6}$$

for $r > a$, where $\kappa = \sqrt{-2mE}/\hbar$. The continuity condition can be written

$$\frac{u_1'(a-\epsilon)}{u_1(a-\epsilon)} = \frac{u_1'(a+\epsilon)}{u_1(a+\epsilon)}\,,$$

in the limit $\epsilon \to 0$, which is equivalent to

$$\frac{d}{da}\log[a\bar{k}^2 u_1(a-\epsilon)] = \frac{d}{da}\log[a\kappa^2 u_1(a+\epsilon)]\,,$$

where the extra factors, $a\bar{k}^2$ and $a\kappa^2$, which do not contribute to the derivatives, have been included for convenience. Insert the expressions (4.5) and (4.6):

$$\bar{k}a\left[\frac{d}{d\rho}\log[\rho^2 j_1(\rho)]|\right]_{\rho=\bar{k}a} = i\kappa a\left[\frac{d}{d\rho}\log[\rho^2 h_1^{(1)}(\rho)|\right]_{\rho=i\kappa a}\,,$$

Now we see from the solution to Problem **4.1** that

$$\begin{aligned}\log\rho^2 j_1(\rho) &= \log(1-\rho\cot\rho) + \log\sin\rho \\ \log\rho^2 h_1^{(1)}(\rho) &= i\pi + \log(i+\rho) + i\rho\,.\end{aligned}$$

The continuity condition can now be cast in the form

$$\frac{\bar{k}^2a^2}{1-\bar{k}a\cot\bar{k}a} = -\frac{\kappa^2a^2}{1+\kappa a}\,. \tag{4.7}$$

Now $\bar{k}$ and κ are related by

$$\bar{k}^2 + \kappa^2 = \frac{2m}{\hbar^2}V_0\,, \tag{4.8}$$

and this equation has to be solved, together with Eq.(4.7).

To effect a numerical solution of this nonlinear problem, we first invert both sides of Eq.(4.7) and define

$$\alpha = -\frac{1}{\kappa^2 a^2} - \frac{1}{\kappa a}, \tag{4.9}$$

the inverse of the right-hand side of Eq.(4.7). Evidently, we require

$$\alpha = \frac{1}{\bar{k}^2 a^2} - \frac{1}{\bar{k}a}\cot \bar{k}a, \tag{4.10}$$

the inverse of the left-hand side of Eq.(4.7). We shall first solve the quadratic equation for κa that arises by rationalizing Eq.(4.9), namely

$$\alpha\kappa^2 a^2 + \kappa a + 1 = 0,$$

with the physically relevant solution

$$\kappa a = -\frac{\sqrt{1-4\alpha}+1}{2\alpha}. \tag{4.11}$$

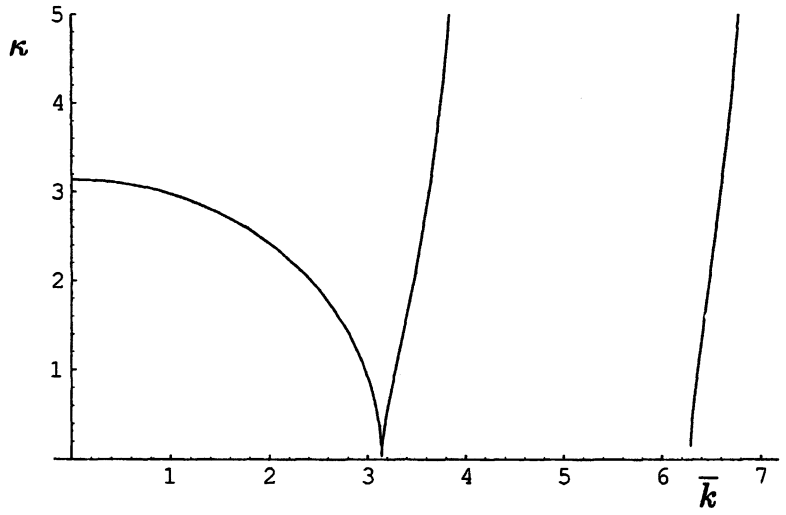

Fig. 4.3 *P*-Wave Bound State

In Figure 4.3, we plot κ against $\bar{k}$ (for $a = 1$). The curves show κ, as a function of $\bar{k}$, defined by Eqs.(4.10)-(4.11), while the quarter circle is given by Eq.(4.8). The circle corresponds to the smallest radius for which it intersects the curve. This occurs for

$$\kappa = 0 \qquad \text{and} \qquad \bar{k}a = \pi = \frac{\sqrt{2mV_0}}{\hbar}a^2.$$

For this value of $\bar{k}a$, we find $\alpha = \infty$, which indeed corresponds to $\kappa = 0$, as can be seen from Eq.(4.11). The minimum potential for a P-wave bound state is

$$a^2 V_0 = \frac{\pi^2 \hbar^2}{2m},$$

which is four times that required for an S-wave bound state.

The graph was produced by the following Mathematica program:

```
kappa[a_] := (-Sqrt[1 - 4*a] - 1)/(2*a);
alpha[k_] := (1 - k/Tan[k])/k^2;
circ[k_] := Sqrt[Pi^2 - k^2];
Plot[{kappa[alpha[k]], circ[k]}, {k, 0, 7}, PlotRange -> {0, 5}]
```

4.5 Two Step Square Well Potential

Suppose that the spherically symmetric potential, $V(r)$, is equal to the positive constant V_0 for $r < a$, is zero for $a < r < b$, and is infinite for $r > b$. Calculate the energies of the ground state and the first excited state, and obtain an approximate expression for the energy splitting of these levels if V_0 is very large compared to these energy levels.

Solution

Let us first consider the S wave. With $E < V_0$, the regular solution of the radial Schrödinger equation in the region $r < a$ is $u_0(r) = A \sinh \kappa r$, where $V_0 - E = \hbar^2 \kappa^2/(2m)$. Thus

$$\frac{u_0'(r)}{u_0(r)} = \kappa \coth \kappa r \qquad\qquad r < a\,.$$

In the region $a < r < b$, the solution $u_0(r) = B \sin k(r - b)$ vanishes at $r = b$, where $E = \hbar^2 k^2/(2m)$, so here

$$\frac{u_0'(r)}{u_0(r)} = k \cot k(r - b) \qquad\qquad a < r < b\,.$$

The condition of continuity at $r = a$ is

$$\kappa a \coth \kappa a = ka \cot k(a - b) = -ka \cot k(b - a)\,. \tag{4.12}$$

The left-hand side is a positive number between 1 and ∞. The right-hand side is negative for $k(b - a) < \pi/2$ and tends to $+\infty$ as $k(b - a) \to \pi$ from below. If E is negligible compared with V_0, $\kappa \approx \sqrt{2mV_0}/\hbar$, and if $\kappa a >> 1$, the left-hand side is large, in fact approximately κa. Under these conditions, the first solution

is given approximately by $k(b-a) = \pi$, the second by $k(b-a) = 2\pi$. The ground state energy is then approximately

$$E_0 = \frac{\pi^2 \hbar^2}{2m(b-a)^2} \cdot$$

To verify this behavior, we iterate the equation (4.12):

$$\kappa_0 = -k \cot k(b-1) \tag{4.13}$$

$$\kappa_{n+1} = -k \cot k(b-1) \tanh \kappa_n \,, \tag{4.14}$$

where we have set $a = 1$, and we will choose $b = 5$.

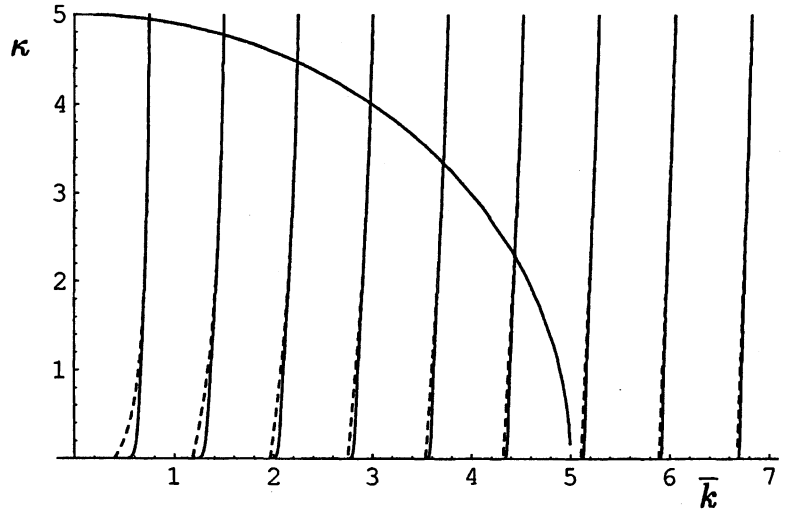

Fig. 4.4 *P*-Wave Bound State

The dotted curve in Figure 4.4 shows the zeroth approximation (4.13), while the solid curve is the result of four iterations of the system (4.14). The quarter circle is given by Eq.(4.8), the same relation as in the previous problem. The graph was produced by the following Mathematica program:

```
b = 5;
kappa[0, k_] := -k*Cot[k*(b - 1)];
kappa[n_, k_] := -k*Cot[k*(b - 1)]*Tanh[kappa[n - 1, k]];
kappac[n_, k_] := If[0 < kappa[n, k] < 10, kappa[n, k], I];
Plot[{Sqrt[25 - k^2], kappac[0, k], kappac[4, k]}, {k, 0, 7},
  PlotRange -> {0, 5}, PlotStyle -> {{}, {Dashing[{0.01}]}, {}}]
```

The second S-wave state occurs at about four times the energy of the first one (i.e. twice the $\overline{k}$-value), as can be checked from the graph; but we do not expect

this to be the first excited state of the system. That is expected to be the lowest bound state of the P wave, to which we now turn.

For $r < a$, the regular solution of the P wave equation is $Arj_1(i\kappa r)$, and for $a < r < b$ the solution that vanishes at $r = b$ is

$$Br\left\{\frac{j_1(kr)}{j_1(kb)} - \frac{n_1(kr)}{n_1(kb)}\right\}.$$

The equation of continuity at $r = a$ is

$$i\kappa a\,\frac{j_1'(i\kappa a)}{j_1(i\kappa a)} = ka\,\frac{j_1'(ka)n_1(kb) - n_1'(ka)j_1(kb)}{j_1(ka)n_1(kb) - n_1(ka)j_1(kb)}. \tag{4.15}$$

Now the left side of this is

$$i\kappa a\,\frac{j_1'(i\kappa a)}{j_1(i\kappa a)} = -2 + \frac{\kappa^2 a^2 \tanh \kappa a}{\kappa a - \tanh \kappa a},$$

which behaves like κa for large κ. The right side of Eq.(4.15) becomes large close to a zero of the denominator, and this denominator is $1/(a^2b^2k^4)$ times

$$[1 + k^2ab]\sin k(b-a) - k(b-a)\cos k(b-a).$$

This is zero when

$$\tan k(b-a) = \frac{k(b-a)}{1+k^2ab} \approx k(b-a),$$

if $k^2ab << 1$. The lowest nontrivial solution of the equation $\tan x = x$ is $x = 4.4934 \approx 1.430\pi$, and so the value of k^2 for the lowest P wave state is approximately $2.046\pi^2/(b-a)^2$. The splitting between the P and S levels, under the conditions stipulated, is roughly

$$E_1 - E_0 = \frac{1.046\pi^2\hbar^2}{2m(b-a)^2}.$$

4.6 No More Than One Bound State

Show that there cannot be more than one linearly independent bound state wave function for a given E and ℓ, i.e., with the same energy and angular momentum.

Solution

Suppose that there are two solutions of the radial Schrödinger equation, $u_\ell(r)$ and $v_\ell(r)$, with the same energy, E, and the same angular momentum quantum number, ℓ. Then by mutiplying the equation for $u_\ell(r)$ by $v_\ell(r)$, and the equation for $v_\ell(r)$ by $u_\ell(r)$, and subtracting one equation from the other, we

find $v_\ell(r)u''_\ell(r) - u_\ell(r)v''_\ell(r) = 0$. The left-hand side of this equation is however $\left[v_\ell(r)u'_\ell(r) - u_\ell(r)v'_\ell(r)\right]'$, and thus $v_\ell(r)u'_\ell(r) - u_\ell(r)v'_\ell(r) = C$, where C is an integration constant. Divide this by $u_\ell^2(r)$ and observe that

$$\frac{d}{dr}\left[\frac{v_\ell(r)}{u_\ell(r)}\right] = -\frac{v_\ell(r)u'_\ell(r) - u_\ell(r)v'_\ell(r)}{u_\ell^2(r)}\,.$$

On integrating this, we find

$$v_\ell(r) = -Cu_\ell(r)\int_D^r \frac{ds}{u_\ell^2(s)}\,, \tag{4.16}$$

where D is the second integration constant. This is the general solution of the second-order differential equation; but we must now consider the question of physical boundary conditions. We are interested in the case that the energy is negative (a bound state), so as usual we set $\kappa^2 = -\frac{2mE}{\hbar^2}$, and the bound-state wave function has the asymptotic behavior, $u_\ell(r) \sim \mathrm{e}^{-\kappa r}$ as $r \to \infty$. From Eq.(4.16) this means that

$$v_\ell(r) \sim \mathrm{e}^{-\kappa r}\int_D^r ds\,\mathrm{e}^{2\kappa s} \sim \mathrm{e}^{\kappa s}\,,$$

i.e., the most general second solution is not square integrable, so indeed there is at most one square-integrable solution (up to normalization); in other words, for a given E and ℓ there can be at most one bound state.

Actually one can say more. Since the physical solution of the radial Schrödinger equation has the threshold behavior $r^{\ell+1}$ as $r \to 0$, it follows that, at threshold,

$$v_\ell(r) \sim r^{\ell+1}\int_D^r ds s^{-2\ell-2} \sim r^{-\ell}\,,$$

i.e., the the most general second solution has the irregular threshold behavior, and is thus not eligible on physical grounds. The conclusion is that for *any* E, positive or negative, there is at most one physical solution for a given ℓ.

4.7 Vibrational and Rotational States

Given the radial potential energy for a diatomic molecule,

$$V(r) = V(r_0) + \tfrac{1}{2}m\omega^2(r - r_0)^2 + \frac{\hbar^2}{2mr^2}\ell(\ell+1)\,,$$

find the radius, r_ℓ, at which this potential energy is minimum. Evaluate A and B in the expansion

$$V(r_\ell) = V(r_0) + A\ell(\ell+1) + B\ell^2(\ell+1)^2 + \ldots\,.$$

Solution

The first derivative of the potential is

$$V'(r) = m\omega^2(r - r_0) - \frac{\hbar^2}{mr^3}\ell(\ell+1)\,,$$

and this vanishes if $r = r_\ell$, where r_ℓ satisfies equation,

$$r_\ell = r_0 + \frac{\hbar^2\ell(\ell+1)}{m^2\omega^2 r_\ell^3}\,.$$

This quartic equation can be solved numerically, but instead of doing that, we make a power series expansion in the quantity

$$\gamma = \frac{\hbar^2}{m^2\omega^2 r_0^4}\,,$$

obtaining

$$r_\ell = r_0\,[\,1 + \gamma\ell(\ell+1)] + O(\gamma^2)\,.$$

Evaluated at this turning point, the potential is

$$\begin{aligned} V(r_\ell) &= V(r_0) + \tfrac{1}{2}m\omega^2(r_\ell - r_0)^2 + \frac{\hbar^2}{2mr_\ell^2}\ell(\ell+1) \\ &= V(r_0) + \tfrac{1}{2}m\omega^2 r_0^2\gamma\ell(\ell+1)[1 - \gamma\ell(\ell+1)] + O(\gamma^3)\,. \end{aligned}$$

Thus, with $V(r_\ell) = V(r_0) + A\ell(\ell+1) + B\ell^2(\ell+1)^2 + \ldots$, we have

$$\begin{aligned} A &= \tfrac{1}{2}m\omega^2 r_0^2\gamma = \frac{\hbar^2}{2mr_0^2}\,, \\ B &= -\tfrac{1}{2}m\omega^2 r_0^2\gamma^2 = -\frac{\hbar^4}{2m^3\omega^2 r_0^6}\,. \end{aligned}$$

4.8 Cylindrical Potential

A particle is in a cylindrical potential in three dimensions, defined by $V(\rho) = 0$ if $\rho = \sqrt{x_1^2 + x_2^2} < a$, and $V(\rho) = \infty$ elsewhere.

(1) Determine the three lowest eigenvalues for states that have $p_3 = 0$ and $L_3 = 0$.

(2) Determine the three lowest eigenvalues for states that have $p_3 = 0$.

Solution

We separate the x_3-dependence of the wave function by introducing the Ansatz

$$\psi(\vec{r}) = \omega(x_1, x_2)\zeta(x_3)\,.$$

The Schrödinger equation for ψ, divided by ψ, may be be written

$$-\frac{\hbar^2}{2m}\frac{\nabla^2\omega}{\omega} - \frac{\hbar^2}{2m}\frac{\zeta''(x_3)}{\zeta(x_3)} + V(x_1, x_2) = E\,, \tag{4.17}$$

where ∇^2 is the Laplacian in two dimensions. Since

$$-\frac{\hbar^2}{2m}\frac{\zeta''(x_3)}{\zeta(x_3)}$$

is the only term in Eq.(4.17) that could depend on x_3, it must in fact be a constant:

$$-\frac{\hbar^2}{2m}\zeta''(x_3) = E_3\,\zeta(x_3) = \frac{p_3^2}{2m}\,\zeta(x_3)\,.$$

Eq.(4.17) becomes

$$-\frac{\hbar^2}{2m}\nabla^2\omega + V(x_1, x_2)\omega = \left[E - \frac{p_3^2}{2m}\right]\omega\,,$$

which is the Schrödinger equation in two dimensions. The two-dimensional Laplacian can be written

$$\nabla^2 = \frac{1}{h_1 h_2}\left\{\frac{\partial}{\partial u_1}\left[\frac{h_2}{h_1}\frac{\partial}{\partial u_1}\right] + \frac{\partial}{\partial u_2}\left[\frac{h_1}{h_2}\frac{\partial}{\partial u_2}\right]\right\}\,,$$

where $(d\rho)^2 + (\rho d\phi)^2 = (h_1 du_1)^2 + (h_2 du_2)^2$, i.e., $u_1 = \rho$, $h_1 = 1$, $u_2 = \phi$ and $h_2 = \rho$. Note that ρ and ϕ take the place of the more usual r and θ in discussions of two-dimensional polar coordinates. Hence

$$-\frac{\hbar^2}{2m}\left[\frac{1}{\rho}\frac{\partial}{\partial\rho}\rho\frac{\partial\omega}{\partial\rho} + \frac{1}{\rho^2}\frac{\partial^2\omega}{\partial\phi^2}\right] + V(\rho)\,\omega = \left[E - \frac{p_3^2}{2m}\right]\omega\,. \tag{4.18}$$

Since the potential depends only on the radial variable, ρ, we can separate again:

$$\omega(x_1, x_2) = R(\rho)\Phi(\phi)\,.$$

On multiplying Eq.(4.18) by ρ^2/ω, we see that $\frac{\partial^2\Phi}{\partial\phi^2}/\Phi$ must be a constant, with the solution $\Phi(\phi) = \mathrm{e}^{in\phi}$, where n must be an integer, in order that Φ be one-valued. The angular momentum operator is

$$L_3 = -i\hbar\left[x_1\frac{\partial}{\partial x_2} - x_2\frac{\partial}{\partial x_1}\right] = -i\hbar\frac{\partial}{\partial\phi}\,,$$

and $\Phi(\phi)$ is an eigenfunction, belonging to eigenvalue $n\hbar$. Eq.(4.18) becomes

$$-\frac{\hbar^2}{2m}\left[\frac{1}{\rho}\frac{d}{d\rho}\rho\frac{d}{d\rho}-\frac{n^2}{\rho^2}\right]R(\rho)+V(\rho)R(\rho)=\left[E-\frac{p_3^2}{2m}\right]R(\rho)\,. \tag{4.19}$$

Since $V(\rho)=0$ for $\rho<a$, in this region we may write

$$\rho^2R''+\rho R'+(\rho^2k^2-n^2)R=0\,,$$

where $k^2=(2mE-p_3^2)/\hbar^2$. This is called the Bessel equation (for the function $k\rho$, with the index n); and the regular solution is called the Bessel function,

$$R(\rho)=J_n(k\rho)\,.$$

Since the potential is infinite for $\rho\geq 0$, we need to choose k in such a way that $J_n(ka)=0$. If x_0 is a zero of the Bessel function, then we have $k=x_0/a$. With $p_3=0$ this entails

$$E=\frac{\hbar^2x_0^2}{2ma^2}.$$

In Figure 4.5 we display the first three Bessel functions, from which the zeros of the Bessel functions can be estimated.

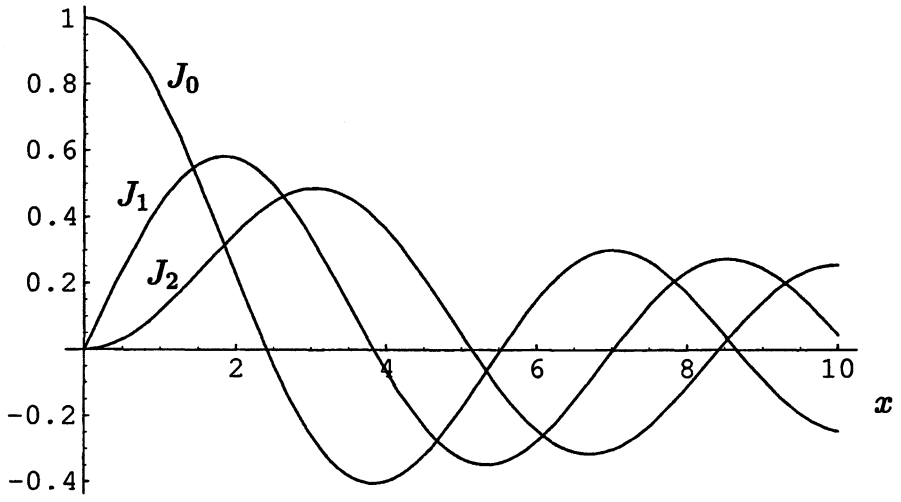

Fig. 4.5 Bessel Functions

To get better accuracy the following Mathematica command line was used:

```
FindRoot[BesselJ[n,x]==0,{\{}x,z\} ]
```

Here n must be set equal to 0, 1 or 2, and z to an approximate zero position, as read off from the graph.

(1) We find the first three zeros of $J_0(x)$ to lie at 2.4048, 5.5201, 8.6537. These zeros correspond to the three lowest energy eigenvalues for which $p_3 = 0$ and $L_3 = 0$. The energies are then $\hbar^2/(2ma^2)$ times 5.7831, 30.4715, 74.8865.
(2) The first zero of $J_1(x)$ is at 3.8317, and the first zero of $J_2(x)$ is at 5.1356, and we see that these values lie below the second zero of $J_0(x)$, which, as we saw, is at 5.5201. Thus the three lowest energy eigenvalues, for which $p_3 = 0$ but the value of L_3 is unrestricted, are $\hbar^2/(2ma^2)$ times 5.7831, 14.6819, 26.3744.

4.9 Relative Probabilities

A particle in a spherically symmetric potential is described by a wave packet $\psi = (x_1x_2 + x_2x_3 + x_3x_1)\,\mathrm{e}^{-ar^2}$ What is the probability that a measurement of the square of the angular momentum yields zero? What is the probability that it yields $6\hbar^2$? If the angular momentum is 2, what are the relative probabilities for $m = -2, -1, 0, 1, 2$?

Solution
The configuration representation of the Cartesian components of the angular momentum operator is

$$L_i = -i\hbar\epsilon_{ijk}x_j\partial_k\,,$$

and so

$$\begin{aligned} L_3\,r^2 &= -i\hbar[x_1\partial_2 - x_2\partial_1][x_1^2 + x_2^2 + x_3^2] \\ &= -2i\hbar[x_1x_2 - x_2x_1] = 0\,. \end{aligned}$$

Thus the differential operator, L_3, working on any function of r^2, gives zero. When L_3 works on ψ, we can thus ignore the function e^{-ar^2}, and we find

$$\begin{aligned} L_3\psi &= -i\hbar[x_1\partial_2 - x_2\partial_1](x_1x_2 + x_2x_3 + x_3x_1)\,\mathrm{e}^{-ar^2} \\ &= i\hbar(x_2^2 - x_1^2 + x_2x_3 - x_3x_1)\,\mathrm{e}^{-ar^2}\,, \end{aligned}$$

and

$$\begin{aligned} L_3^2\psi &= \hbar^2[x_1\partial_2 - x_2\partial_1](x_2^2 - x_1^2 + x_2x_3 - x_3x_1)\,\mathrm{e}^{-ar^2} \\ &= \hbar^2(x_3x_1 + x_2x_3 + 4x_1x_2)\,\mathrm{e}^{-ar^2}\,. \end{aligned}$$

By symmetry,

$$L^2\psi = (L_1^2 + L_2^2 + L_3^2)\psi = 6\hbar^2(x_1x_2 + x_2x_3 + x_3x_1)\,\mathrm{e}^{-ar^2} = 6\hbar^2\psi\,.$$

Hence ψ is an eigenvector of L^2 belonging to the eigenvalue $\ell(\ell+1)\hbar^2$, with $\ell = 2$. Thus the probability that a measurement of the square of the angular momentum yields $6\hbar^2$ is 1, i.e., it is certain. The probability that such a measurement yields zero is 0, i.e., it never happens.

The angular momentum is certainly 2, and so the only allowed values for the azimuthal quantum number are $m = -2, -1, 0, 1, 2$. To calculate the various probabilities, we express ψ in spherical polar coordinates:

$$\begin{aligned}\psi &= r^2\{\sin^2\theta\sin\phi\cos\phi + \sin\theta\cos\theta\sin\phi + \sin\theta\cos\theta\cos\phi\}\,\mathrm{e}^{-ar^2} \\ &= -\tfrac{1}{4}ir^2\{\sin^2\theta(\mathrm{e}^{2i\phi} - \mathrm{e}^{-2i\phi}) + 2\sin\theta\cos\theta[(1+i)\,\mathrm{e}^{i\phi} - (1-i)\,\mathrm{e}^{-i\phi}]\}\,\mathrm{e}^{-ar^2}\,.\end{aligned}$$

The eigenvector of L_3 belonging to eigenvalue $m\hbar$ is $\mathrm{e}^{im\phi}$, and we see that there is no constant term, i.e., the value $m = 0$ is missing. Moreover, since the probabilities associated with the remaining values are proportional to the square moduli of the coefficients of the corresponding eigenvectors, it follows that

$$\mathsf{Pr}(m=2) = \mathsf{Pr}(m=-2) \qquad \mathsf{Pr}(m=1) = \mathsf{Pr}(m=-1)\,,$$

and also that

$$\frac{\mathsf{Pr}(m=1)}{\mathsf{Pr}(m=2)} = \frac{8\int_{-1}^{1} dz\, z^2(1-z^2)}{\int_{-1}^{1} dz\,(1-z^2)^2} = 2\,,$$

Since the sum of all four probabilities must be 1,

$$\mathsf{Pr}(m=2) + \mathsf{Pr}(m=1) = \tfrac{1}{2}\,,$$

and so

$$\mathsf{Pr}(m=2) = \mathsf{Pr}(m=-2) = \tfrac{1}{6} \qquad \mathsf{Pr}(m=1) = \mathsf{Pr}(m=-1) = \tfrac{1}{3}\,.$$

4.10 Hidden Symmetry of Isotropic Harmonic Oscillator

With $\hbar = m = \omega = 1$, consider the isotropic harmonic oscillator Hamiltonian in three dimensions,

$$H = \tfrac{1}{2}(p^2 + q^2)\,,$$

and the operator

$$U = (q_1 + iq_2)^2 + (p_1 + ip_2)^2\,.$$

Suppose that $H|n\ell m\rangle = E_{n\ell m}|n\ell m\rangle$.

(1) Show that $[H, U] = 0$,

(2) Show that $\langle \vec{x}|U|n\ell\ell\rangle \propto \langle \vec{x}|n, \ell+2, \ell+2\rangle$. Under what restrictions on n and ℓ is this true?

(3) Deduce from (1) and (2) that $E_{n\ell\ell} = E_{n,\ell+2,\ell+2}$, and hence that $E_{n\ell m}$ is independent of ℓ and m.

(4) The isotropic oscillator Hamiltonian is symmetric under orthogonal rotations of the coordinate axes. By expressing H and U in terms of creation and annihilation operators, discover the larger symmetry of the Hamiltonian that is responsible for the ℓ-degeneracy.

Solution

(1) Since q_3^2 and p_3^2 commute trivially with U, we may write

$$\begin{aligned}
[H, U] &= \tfrac{1}{2}[q_1^2 + q_2^2 + p_1^2 + p_2^2, q_1^2 - q_2^2 + 2iq_1q_2 + p_1^2 - p_2^2 + 2ip_1p_2] \\
&= ip_2[q_1^2, p_1] + ip_1[q_2^2, p_2] + iq_2[p_1^2, q_1] + iq_1[p_2^2, q_2] \\
&= -2(q_1p_2 + q_2p_1 - q_2p_1 - q_1p_2) = 0\,.
\end{aligned}$$

(2) From the lemma below, we may write the eigenfunction of the isotropic oscillator corresponding to quantum numbers n, ℓ and m, as

$$\begin{aligned}
\psi_{n\ell m}(\vec{x}) &= \langle \vec{x}|n\ell m\rangle \\
&= \mathrm{e}^{-\frac{r^2}{2}} L^{\frac{2\ell+1}{2}}_{\frac{n+\ell+1}{2}}(r^2) r^\ell P_\ell^m(\cos\theta)\,\mathrm{e}^{im\phi}\,, \qquad (4.20)
\end{aligned}$$

where $L^{\frac{2\ell+1}{2}}_{\frac{n+\ell+1}{2}}(\rho)$ is a Laguerre polynomial. Note that $\psi_{n\ell m}(\vec{x})$ is not normalized. Now consider $m = \ell$, which is the maximum value allowed for the azimuthal quantum number. From Eq.(3.67) of Volume 1, we easily obtain

$$r^\ell P_\ell^\ell(\cos\theta)\,\mathrm{e}^{i\ell\phi} = \frac{(2\ell)!}{2^\ell \ell!}\left(r\sin\theta\cos\phi + ir\sin\theta\sin\phi\right)^\ell = \frac{(2\ell)!\,(x_1 + ix_2)^\ell}{2^\ell \ell!}\,.$$

Hence we may write $\psi_{n\ell\ell}(\vec{x}) = f_{n\ell}(r^2)(x_1 + ix_2)^\ell$, where

$$f_{n\ell}(r^2) = \frac{(2\ell)!}{2^\ell \ell!}\,\mathrm{e}^{-\frac{r^2}{2}} L^{\frac{2\ell+1}{2}}_{\frac{n+\ell+1}{2}}(r^2)\,. \qquad (4.21)$$

Next consider the matrix element

$$\langle \vec{x}|U|n\ell m\rangle = [(x_1 + ix_2)^2 - (\partial_1 + i\partial_2)^2] f_{n\ell}(r^2)(x_1 + ix_2)^\ell\,.$$

Now $(\partial_1 + i\partial_2)(x_1 + ix_2) = (1 - 1) = 0$, and so

$$\begin{aligned}
(\partial_1 + i\partial_2)^2 (x_1 + ix_2)^\ell &= 0 \\
(\partial_1 + i\partial_2) f_{n\ell}(r^2) &= 2f'_{n\ell}(r^2)(x_1 + ix_2) \\
(\partial_1 + i\partial_2)^2 f_{n\ell}(r^2) &= 4f''_{n\ell}(r^2)(x_1 + ix_2)^2\,,
\end{aligned}$$

where the primes mean differentiation with respect to r^2. Hence

$$\langle \vec{x}|U|n\ell\ell\rangle = [f_{n\ell}(r^2) - 4f''_{n\ell}(r^2)](x_1 + ix_2)^{\ell+2}$$

In the lemma we show that

$$f_{n\ell}(r^2) - 4f''_{n\ell}(r^2) \propto f_{n,\ell+2}(r^2)\,,$$

and this means that

$$\langle \vec{x}|U|n\ell\ell\rangle \propto \psi_{n,\ell+2,\ell+2}(\vec{x}\,) = \langle \vec{x}|n,\ell+2,\ell+2\rangle\,,$$

on condition that $\ell = n-2, n-4, \ldots$

(3) Let $E_{n\ell m}$ be the eigenvalue of the Hamiltonian corresponding to the quantum numbers n, ℓ and m. Then on the one hand we see that

$$UH|n\ell\ell\rangle = E_{n\ell\ell}\,U|n\ell\ell\rangle\,,$$

but on the other hand, from the results (1) and (2), we have

$$UH|n\ell\ell\rangle = HU|n\ell\ell\rangle = E_{n,\ell+2,\ell+2}\,U|n\ell\ell\rangle\,,$$

and so $E_{n,\ell+2,\ell+2} = E_{n\ell\ell}$, for $\ell = n-2, n-4, \cdots$. However, since we already know from the spherical symmetry of the Hamiltonian that $E_{n\ell m} = E_{n,\ell,m+1}$, for $m = -\ell, -\ell+1, \cdots \ell-1$, it follows that $E_{n\ell m}$ is independent of ℓ and m.

(4) The Hamiltonian can be written $H = \vec{a}^{\,\dagger}\cdot\vec{a} + \frac{3}{2}$, where $\vec{a} = (\vec{q} + i\vec{p})/\sqrt{2}$. Clearly this Hamiltonian is not only invariant under the group $O(3)$ (orthogonal transformations in 3 real dimensions, i.e., rotations in ordinary space), but it is also invariant under the group $U(3)$ (complex, unitary transformations in 3 dimensions). That is, the Hamiltonian is invariant under the transformation

$$a'_i = \sum_{j=1}^{3} U_{ij}a_j\,,$$

for any 3-dimensional, unitary matrix, U. This is the extra symmetry that lies at the heart of the ℓ-independence of the energy levels of the isotropic harmonic oscillator.

Lemma

With $\hbar = m = \omega = 1$, we see from Section **4.3** of Volume 1 that

$$\psi_{n\ell m}(\vec{x}\,) = \exp\left[-\tfrac{1}{2}r^2\right] v_{n\ell}(r^2) r^\ell P_\ell^m(\cos\theta)\,\mathrm{e}^{im\phi}\,, \qquad (4.22)$$

(not normalized). Here $v_{n\ell}(\rho)$ satisfies the equation,

$$\rho v''_{n\ell}(\rho) + (\ell + \tfrac{3}{2} - \rho)v'_{n\ell}(\rho) + \tfrac{1}{2}(n-\ell)v_{n\ell}(\rho) = 0\,. \tag{4.23}$$

Setting $v_{n\ell}(\rho) = L_t^s(r^2)$, with $t = \frac{1}{2}(n+\ell+1)$ and $s = \ell + \frac{1}{2}$, we obtain the differential equation for the associated Laguerre function,

$$\rho L_t^{s\prime\prime}(\rho) + (1+s-\rho)L_t^{s\prime}(\rho) + (t-s)L_t^s(\rho) = 0\,. \tag{4.24}$$

We write a series expansion

$$L_t^s(\rho) = \sum_{m=0}^{\infty} a_m \rho^m\,,$$

and obtain, from the differential equation Eq.(4.24), the recurrence relation

$$a_m = \frac{m+s-t-1}{m(m+s)}\,a_{m-1} = (-1)^m \frac{(t-s)_m}{m!\,(m+s)_m}\,a_0\,,$$

with the definition $(a)_m = a(a-1)(a-2)\ldots(a-m+1)$. We have

$$L_t^s(\rho) = a_0 \sum_{m=0}^{\infty} \frac{(t-s)_m}{(m+s)_m}\,\frac{(-\rho)^m}{m!}\,, \tag{4.25}$$

and the series terminates only if $t - s \equiv N$ is an integer, in which case

$$L_t^s(\rho) = a_0 \sum_{m=0}^{N} \frac{(N)_m}{(m+s)_m}\,\frac{(-\rho)^m}{m!}\,, \tag{4.26}$$

is a polynomial of order N. On differentiating this polynomial we find, after a shift of summation variable from m to $m-1$,

$$L_t^{s\prime}(\rho) = a_0 \sum_{m=0}^{N} \frac{(N-m)(N)_m}{(m+s+1)_{(m+1)}}\,\frac{(-\rho)^m}{m!}\,, \tag{4.27}$$

where we have used the identities $(m+s+1)(m+s)_m = (m+s+1)_{(m+1)}$ and $(N)_{m+1} = (N-m)(N)_m$. Hence

$$L_t^s(\rho) - L_t^{s\prime}(\rho) = a_0(N+s+1) \sum_{m=0}^{N} \frac{(N)_m}{(m+s+1)_{(m+1)}}\,\frac{(-\rho)^m}{m!}\,.$$

On differentiating this and shifting m again, we find

$$\left\{L_t^s(\rho) - L_t^{s\prime}(\rho)\right\}' = -a_0(N+s+1) \sum_{m=0}^{N-1} \frac{(N)_{(m+1)}}{(m+s+2)_{(m+2)}}\,\frac{(-\rho)^m}{m!}\,. \tag{4.28}$$

Consider now

$$\begin{aligned} L_{t+1}^{s+2}(\rho) &= a_0 \sum_{m=0}^{N-1} \frac{(N-1)_m}{(m+s+2)_m} \frac{(-\rho)^m}{m!} \\ &= a_0 \frac{(s+1)(s+2)}{N} \sum_{m=0}^{N-1} \frac{(N)_{(m+1)}}{(m+s+2)_{(m+2)}} \frac{(-\rho)^m}{m!} . \end{aligned} \tag{4.29}$$

With the definition Eq.(4.21), we have

$$f_{n\ell}(\rho) - 4f''_{n\ell}(\rho) = 4 \frac{(2\ell)!}{2^\ell \ell!} \mathrm{e}^{-\rho/2} \left\{ L_t^s(\rho) - L_t^{s\prime}(\rho) \right\}' ,$$

so that Eqs.(4.28)-(4.29) yield

$$f_{n\ell}(\rho) - 4f''_{n\ell}(\rho) = \gamma_{n\ell} f_{n,\ell+2}(\rho) , \tag{4.30}$$

where

$$\gamma_{n\ell} = -4 \frac{(n+\ell+3)(n+\ell+5)}{(2\ell+3)(2\ell+5)} \frac{(2\ell)!}{2^\ell \ell!} \frac{a_{t,0}^s}{a_{t+1,0}^{s+2}} .$$

Here the possibility has been left open that the constant term in the polynomial, a_0, can be chosen to depend on n and ℓ, or equivalently s and t. Just how the normalization is chosen will however be of no concern to us; it is enough to have shown that $f_{n\ell}(\rho) - 4f''_{n\ell}(\rho)$ and $f_{n,\ell+2}(\rho)$ are the same function of ρ, up to a ρ-independent factor that is not zero.

Chapter 5

Hydrogen Atom

5.1 Laguerre Polynomials

The associated Laguerre polynomial is defined by

$$L_t^s(\rho) = \left(\frac{d}{d\rho}\right)^s e^\rho \left(\frac{d}{d\rho}\right)^t \rho^t e^{-\rho}\,.$$

(1) Prove the recurrence relation

$$L_{t+1}^s(\rho) = \rho L_t^{s+1}(\rho) + (s+t+1-\rho)L_t^s(\rho) - sL_t^{s-1}(\rho)\,.$$

(2) Work out $L_t^s(\rho)$ for $t = 0, 1, 2, 3$ and all integral values of s and sketch them graphically.

Solution

(1) Eq.(5.15) of Volume 1, namely

$$L_{t+1}(\rho) = \rho L_t'(\rho) + (t+1-\rho)L_t(\rho)\,, \tag{5.1}$$

can be differentiated s times to yield

$$\frac{d^s}{d\rho^s}L_{t+1}(\rho) = \rho\frac{d^{s+1}}{d\rho^{s+1}}L_t(\rho) + s\frac{d^s}{d\rho^s}L_t(\rho) + (t+1-\rho)\frac{d^s}{d\rho^s}L_t(\rho) - s\frac{d^{s-1}}{d\rho^{s-1}}L_t(\rho)\,.$$

On gathering the second and third terms together, and using the definition of the associated Laguerre function, we obtain the required recurrence relation.

(2) From the the recurrence relation, we find

$$\begin{aligned}
L_0^0(\rho) &= 1 \qquad L_1^1(\rho) = -1 \qquad L_2^2(\rho) = 2 \qquad L_3^3(\rho) = -6\\
L_1^0(\rho) &= 1-\rho \qquad L_2^1(\rho) = -4+2\rho \qquad L_3^2(\rho) = 18-6\rho\\
L_2^0(\rho) &= 2-4\rho+\rho^2 \qquad L_3^1(\rho) = -18+18\rho-3\rho^2\\
L_3^0(\rho) &= 6-18\rho+9\rho^2-\rho^3
\end{aligned}$$

These are all the nonzero associated Laguerre polynomials, $L_t^s(\rho)$, for $t \leq 3$. We suppress the constants L_0^0, L_1^1, L_2^2, L_3^3 in the following graph:

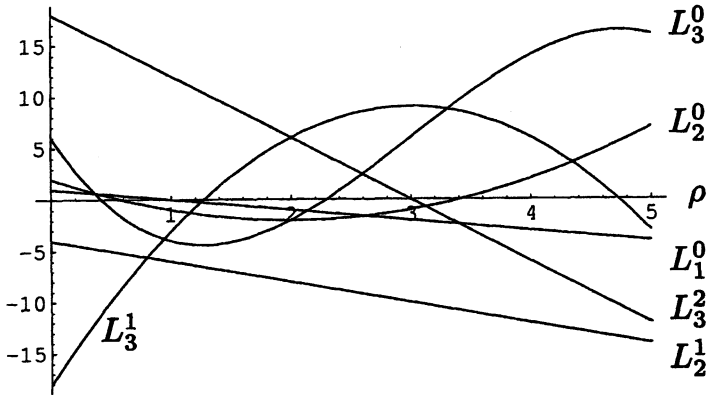

Fig. 5.1 Laguerre Polynomials

5.2 Orbitals

Is the electron in a hydrogen atom on the average further away from the proton when it is in the 2P orbital than when it is in the 2S orbital?

Solution
The mean distance of the electron from the proton is

$$\langle n\ell m|r|n\ell m\rangle = \tfrac{1}{2}[3n^2 - \ell(\ell+1)]\,, \tag{5.2}$$

in units of the Bohr radius, see the solution to Problem **5.6**, Eq.(5.2). The mean distance for the 2S and 2P orbitals are thus

$$\langle 200|r|200\rangle = 6 \qquad \langle 21m|r|21m\rangle = 5\,,$$

so the electron is on average closer to the nucleus in the P than in the S orbital. In fact, one can see more generally that, for a given n, the mean distance is a decreasing function of ℓ, attaining its minimum value of $n(n+\frac{1}{2})$ for $\ell = n-1$.

5.3 Deuterium

Calculate the wavelength of the $2P \to 1S$ transitions in deuterium. Use these masses for the deuteron and the electron:
$m_d c^2 = 1875.6$ MeV, $m_e c^2 = 0.51100$ MeV, $\alpha = e^2/(\hbar c) = 1/137.036$.

Solution

The energy difference between energy levels $n = 2$ and $n = 1$ is

$$E_2 - E_1 = \tfrac{1}{2}mc^2\alpha^2\,(1 - \tfrac{1}{4})\,,$$

and so the wavelength in question is

$$\lambda = \frac{2\pi\hbar c}{E_2 - E_1} = \frac{16\pi\hbar c}{3mc^2\alpha^2}\,. \tag{5.3}$$

The reduced rest energy of the electron is

$$mc^2 = \frac{m_e c^2}{1 + m_e/m_d} = 0.51086 \text{ MeV}\,,$$

and, with $\hbar c = 197.33 \times 10^{-15}$ MeV-m, we find from formula (5.3) the value 1.21537×10^{-7} m, i.e., about 121.5 nm or 1215 Å, which is in the ultraviolet part of the spectrum.

5.4 Complete Set?

Do the bound-state eigenfunctions corresponding to the following potentials form a complete set? Motivate your answers.

(1) Attractive Coulomb: $V(r) = -e^2/r$
(2) Attractive Coulomb plus harmonic oscillator: $V(r) = \lambda r^2 - e^2/r$

Solution

(1) The bound state eigenfunctions, corresponding to the discrete eigenvectors $|n\ell m\rangle$, do not form a complete set. To span the whole Hilbert space for the attractive Coulomb problem, one must add to them the scattering, continuous states, $|r\ell m\rangle$. The orthogonormality conditions read

$$\begin{aligned}
\langle n\ell m|n'\ell'm'\rangle &= \delta_{nn'}\delta_{\ell\ell'}\delta_{mm'} \\
\langle r\ell m|r'\ell'm'\rangle &= \delta(r - r')\delta_{\ell\ell'}\delta_{mm'} \\
\langle r\ell m|n\ell'm'\rangle &= 0\,,
\end{aligned}$$

and the condition of completeness is

$$\sum_{n=1}^{\infty}\sum_{\ell=0}^{n-1}\sum_{m=-\ell}^{\ell} |n\ell m\rangle\langle n\ell m| + \int_0^{\infty} dr \sum_{\ell=0}^{n-1}\sum_{m=-\ell}^{\ell} |r\ell m\rangle\langle r\ell m| = 1\,.$$

Here $\delta(r - r')$ is the Dirac delta distribution, and 1 means the unit operator on the Hilbert space.

(2) In this case there are no continuum states, since the potential tends to infinity as $r \to \infty$, so the bound-state eigenfunctions form a complete set.

5.5 Nonvanishing Matrix Elements

Calculate all the nonvanishing matrix elements

$$\langle 100|x|2\ell m\rangle\,,$$

where $|n\ell m\rangle$ is the normalized hydrogen atom stationary state corresponding to principal quantum number n, angular momentum quantum number ℓ, and magnetic quantum number m, while $x = r\sin\theta\cos\phi$ is the x-coordinate, reckoned from the center-of-mass of the proton and the electron.

Solution

We shall express all distances in terms of the Bohr radius $a = \hbar^2/(me^2)$. Since $|100\rangle$, $|200\rangle$ and $|210\rangle$ are independent of ϕ, and

$$\int_0^{2\pi} d\phi\, x = r\sin\theta \int_0^{2\pi} d\phi\cos\phi = 0\,,$$

it follows that

$$\langle 100|x|200\rangle = \langle 100|x|210\rangle = 0\,.$$

The normalized eigenfunctions for the $|2,1,\pm1\rangle$ states are

$$-\frac{1}{8\sqrt{\pi}} r\,\mathrm{e}^{-r/2}\sin\theta\,\mathrm{e}^{\pm i\phi}\,,$$

and so the overlap with the normalized ground state eigenfunction,

$$\langle\vec{r}|100\rangle = \frac{\mathrm{e}^{-r}}{\sqrt{\pi}}$$

is, written out fully,

$$\langle 100|x|2,1,\pm1\rangle = -\frac{1}{8\pi}\int_0^\infty dr\, r^4\,\mathrm{e}^{-3r/2}\int_0^\pi d\theta\sin^3\theta\int_0^{2\pi} d\phi\cos\phi\,\mathrm{e}^{\pm i\phi}\,.$$

The imaginary part of this integral vanishes, and so we obtain

$$-\frac{1}{16\pi}\left(\frac{2}{3}\right)^5\int_0^\infty d\rho\,\rho^4\,\mathrm{e}^{-\rho}\int_{-1}^1 dz\,(1-z^2)\int_0^{2\pi} d\phi(1+\cos 2\phi) = -\frac{2^7}{3^5} = -\frac{128}{243}\,.$$

5.6 Kramers' Relation

Let $\langle r^s \rangle$ stand for the mean value of r^s in the $(n\ell m)$ state of the H atom.

(1) With $a_0 = 1$, derive the recurrence relation

$$\frac{s+1}{n^2}\langle r^s \rangle - (2s+1)\langle r^{s-1} \rangle + \tfrac{1}{4}s[(2\ell+1)^2 - s^2]\langle r^{s-2} \rangle = 0\,.$$

(2) Calculate the mean distance of the electron from the proton, and its standard deviation, $\sqrt{\langle r^2 \rangle - \langle r \rangle^2}$. For a given n, for which values of ℓ do the mean and the standard deviation have extremal values?

Solution

(1) The radial equation for the hydrogen atom can be written

$$-\frac{\hbar^2}{2m}u_\ell'' + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}u_\ell - \frac{e^2}{r}u_\ell = -\frac{me^4}{2n^2\hbar^2}u_\ell\,,$$

where the energy eigenvalue has been inserted. For convenience, we set the Bohr radius, $\hbar^2/(me^2)$, equal to unity. The equation now reads

$$u_\ell'' + \left[\frac{2}{r} - \frac{\ell(\ell+1)}{r^2} - \frac{1}{n^2}\right]u_\ell = 0\,. \tag{5.4}$$

Multiply this equation by $r^s u_\ell(r)$ and integrate from zero to infinity:

$$\int_0^\infty dr\, r^s u_\ell(r) u_\ell''(r) = \int_0^\infty dr\, r^s \left[\frac{1}{n^2} + \frac{\ell(\ell+1)}{r^2} - \frac{2}{r}\right][u_\ell(r)]^2\,. \tag{5.5}$$

Two partial integrations suffice to show that the left-hand side here is equal to

$$\tfrac{1}{2}s(s-1)\int_0^\infty dr\, r^{s-2}[u_\ell(r)]^2 - \int_0^\infty dr\, r^s [u_\ell'(r)]^2\,,$$

and after rearrangement we find

$$\int_0^\infty dr\, r^s [u_\ell'(r)]^2 = \left[\tfrac{1}{2}s(s-1) - \ell(\ell+1)\right]\langle r^{s-2} \rangle - \frac{1}{n^2}\langle r^s \rangle + 2\langle r^{s-1} \rangle\,. \tag{5.6}$$

A second evaluation of this integral can be made by multiplying the Schrödinger equation (5.4) by $r^{s+1}u_\ell'(r)$ and integrating from zero to infinity:

$$\int_0^\infty dr\, r^{s+1} u_\ell'(r) u_\ell''(r) = \int_0^\infty dr\, r^{s+1}\left[\frac{1}{n^2} + \frac{\ell(\ell+1)}{r^2} - \frac{2}{r}\right]u_\ell'(r)u_\ell(r)\,. \tag{5.7}$$

Perfom an integration by parts on both sides of this equation, using the facts that $u'_\ell(r)u_\ell(r) = \frac{1}{2}\frac{d}{dr}u_\ell^2(r)$ and $u'_\ell(r)u''_\ell(r) = \frac{1}{2}\frac{d}{dr}u'^2_\ell(r)$. This gives

$$\int_0^\infty dr\, r^s[u'_\ell(r)]^2 = \frac{s+1}{n^2}\langle r^s\rangle + (s-1)\ell(\ell+1)\langle r^{s-2}\rangle - 2s\langle r^{s-1}\rangle\,. \tag{5.8}$$

On equating the right-hand sides of Eq.(5.6) and Eq.(5.8), and gathering like terms together, we obtain the required relation.

Note that the above partial integrations are valid, so long as $s + 2\ell + 1 > 0$, since this condition ensures that the contributions of the iterated terms vanish as $r \to 0$. In the limit $r \to \infty$ their vanishing is guaranteed by the fact that bound-state wave functions decrease exponentially. We conclude that, for all $\ell = 0, 1, 2, \ldots$, we may freely take $s = 0, 1, 2, \ldots$.

(2) If we set $s = 0$ in Kramers' relation, we obtain

$$\frac{1}{n^2}\langle r^0\rangle - \langle r^{-1}\rangle = 0\,,$$

and since $\langle r^0\rangle = 1$ for a normalized state, we find that $\langle r^{-1}\rangle = \frac{1}{n^2}$. Next, with $s = 1$, we find

$$\frac{2}{n^2}\langle r\rangle - 3 + \tfrac{1}{4}[(2\ell+1)^2 - 1]\langle r^{-1}\rangle = 0\,,$$

and the mean distance of the electron from the proton is therefore

$$\langle r\rangle = \tfrac{1}{2}[3n^2 - \ell(\ell+1)]\,. \tag{5.9}$$

Finally, set $s = 2$ to obtain the mean square of the distance,

$$\frac{3}{n^2}\langle r^2\rangle - 5\langle r\rangle + \tfrac{1}{2}[(2\ell+1)^2 - 4] = 0\,,$$

which yields

$$\langle r^2\rangle = \tfrac{1}{2}n^2[5n^2 - 3\ell(\ell+1) + 1]\,. \tag{5.10}$$

The standard deviation of the distance of the electron from the proton is

$$\sigma = \tfrac{1}{2}\sqrt{n^4 + 2n^2 - [\ell(\ell+1)]^2}\,.$$

The mean distance and its standard deviation both take on their largest values for $\ell = 0$, and their smallest values for $\ell = n - 1$.

5.7 Tritium

An electron is in the ground state of tritium (H^3). A nuclear reaction changes the nucleus to that of He^3.

(1) Calculate the probability that the electron remains in the ground state of He^3.

(2) What is the probability that the electron becomes free?

Solution

(1) The ground state of a hydrogen-like atom or ion is $\psi = Z^{\frac{3}{2}}\pi^{-\frac{1}{2}}\,\mathrm{e}^{-Zr}$, where we have set the Bohr radius equal to unity, and where Z is 1 for the initial and 2 for the final state. The probability amplitude in question is

$$\langle 100; H^3 | 100; He^3 \rangle = \frac{2\sqrt{2}}{\pi} \int d^3r\, \mathrm{e}^{-3r} = 8\sqrt{2} \int_0^\infty dr\, r^2\, \mathrm{e}^{-3r} = \frac{16\sqrt{2}}{27}\,.$$

The probability that the electron remains in the ground state is

$$P_1 = \left|\langle 100; H^3 | 100; He^3 \rangle\right|^2 = \frac{2^9}{3^6} \approx 0.70233\,.$$

(2) The probability that the final state is *not* the ground state of the He^3 ion is $1 - 0.70233 = 0.29767$. This final state could be that of totally stripped He^3, in which the electron is in the positive energy continuum, or it could be one of the excited S states of the He^3 ion. Angular momentum conservation ensures that only $\ell = 0$ states are possible; and indeed the overlap integrals for the initial state and an $\ell \neq 0$ final state is automatically zero. The probability that the electron is in the continuum is accordingly

$$P_c = 1 - \sum_{n=1}^{\infty} P_n\,, \tag{5.11}$$

where $P_n = \left|\langle 100; H^3 | n00; He^3 \rangle\right|^2$. The wave function can be written, in terms of the associated Laguerre function, in the non-normalized form

$$\psi_{n00}(r) = \mathrm{e}^{-Zr/n} L_n^1\left(\frac{2Zr}{n}\right)\,.$$

The required Laguerre function (compare Eq.(4.26)) is

$$L_n^1(x) = {}_1F_1(1-n, 2; x) = \sum_{p=0}^{n-1} \frac{(1-n)(2-n)\ldots(p-n)}{p!(p+1)!} x^p\,,$$

where ${}_1F_1$ is the confluent hypergeometric function, which is used in the following Mathematica program for P_c:

```
psi[n_,z_,r_]:=r*Exp[-z*r/n]*Hypergeometric1F1[1-n,2,2z*r/n];
mu[n_]:=N[(Integrate[psi[1,1,r]*psi[n,2,r],{r,0,Infinity}])^2/
          (Integrate[(psi[1,1,r])^2,{r,0,Infinity}]*
           Integrate[(psi[n,2,r])^2,{r,0,Infinity}])];
psubc[n_]:=1-Sum[mu[p],{p,1,n}];
```

This produces the answer $P_c = 0.0263$ with $n = 40$ or more.

5.8 Coulomb and Oscillator Potentials

Consider the transformation

$$\tau = \sqrt{r} \qquad \sqrt{\tau} v_\ell(\tau) = u_\ell(r)\,,$$

where $u_\ell(r)$ satifies the radial equation for the hydrogen atom. Show that $v_\ell(\tau)$ satisfies the radial equation for the isotropic harmonic oscillator. Discuss the relation between the solutions of the Schrödinger equation for the Coulomb and for the oscillator potentials.

Solution
The radial Schrödinger equation for the hydrogen atom is

$$\frac{\hbar^2}{2m}\left[-\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2}\right] u_\ell(r) - \frac{e^2}{r} u_\ell(r) = E u_\ell(r)\,. \tag{5.12}$$

We have $r = \tau^2$, so

$$\frac{d}{dr} = \frac{1}{2\tau}\frac{d}{d\tau}\,,$$

and $u_\ell(r) = \sqrt{\tau} v_\ell(\tau)$, which leads to

$$\frac{d^2 u_\ell(r)}{dr^2} = \tfrac{1}{4}\tau^{-\frac{3}{2}} v_\ell''(\tau) - \tfrac{3}{16}\tau^{-\frac{7}{2}} v_\ell(\tau)\,,$$

the two first-order derivative terms having cancelled. Eq.(5.12) becomes

$$\frac{\hbar^2}{2m}\left[-\frac{d^2}{d\tau^2} + \frac{4\ell(\ell+1)+\frac{3}{4}}{\tau^2}\right] v_\ell(\tau) - 4E\tau^2 v_\ell(\tau) = 4e^2 v_\ell(\tau)\,. \tag{5.13}$$

This equation has indeed the form of the radial Schrödinger equation for the isotropic harmonic oscillator in three dimensions. To make this explicit, set

$$\bar{\ell} = 2\ell + \tfrac{1}{2} \qquad \lambda = -4E > 0 \qquad \bar{E} = 4e^2 \qquad \bar{v}_{\bar{\ell}}(\tau) = v_\ell(\tau) = r^{-\frac{1}{4}} u_\ell(r)\,.$$

In terms of these variables, Eq.(5.13) can be written

$$\frac{\hbar^2}{2m}\left[-\frac{d^2}{d\tau^2}+\frac{\bar{\ell}(\bar{\ell}+1)}{\tau^2}\right]\bar{v}_{\bar{\ell}}(\tau)+\lambda\tau^2\bar{v}_{\bar{\ell}}(\tau)=\bar{E}\,\bar{v}_{\bar{\ell}}(\tau)\,. \tag{5.14}$$

The energy levels of the hydrogen atom,

$$E=-\frac{e^4m}{2\hbar^2}\frac{1}{n^2}\,,$$

where $n=k+\ell+1$, with $k=0,1,2,\ldots$, transform into

$$\bar{E}=\hbar\omega(\bar{n}+\tfrac{3}{2})\,,$$

where $\lambda=\frac{1}{2}m\omega^2$ and $\bar{n}=2k+\bar{\ell}$. These are indeed the energy levels of the isotropic harmonic oscillator.

The bound state wave functions respect the mapping also. The radial wave function for the hydrogen atom is

$$u_\ell(r)=r^{\ell+1}\exp\left(-\frac{me^2r}{n\hbar^2}\right)L_{n+\ell}^{2\ell+1}\left(\frac{2me^2r}{n\hbar^2}\right)\,.$$

Under the substitutions $\ell\to\frac{1}{4}(2\bar{\ell}-1)$, $n=k+\ell+1\to\frac{1}{2}(2k+\bar{\ell}+\frac{3}{2})=\frac{1}{2}(\bar{n}+\frac{3}{2})$, $e^2\to\frac{1}{4}\bar{E}=\frac{1}{4}(\bar{n}+\frac{3}{2})\hbar\omega$, $r\to\tau^2$ and $u_\ell(r)\to\sqrt{\tau}\bar{v}_{\bar{\ell}}(\tau)$, we find

$$\bar{v}_{\bar{\ell}}(\tau)=\tau^{\bar{\ell}+1}\exp\left(-\frac{m\tau^2\omega}{2\hbar}\right)L_{\frac{\bar{n}+\bar{\ell}+1}{2}}^{\frac{2\bar{\ell}+1}{2}}\left(\frac{m\tau^2\omega}{\hbar}\right)\,,$$

which is indeed the radial wave function for the isotropic harmonic ascillator in three dimensions.

5.9 Alkali Atoms

The alkali atoms have an electronic structure which resembles that of hydrogen. In particular, the spectral lines and chemical properties are largely determined by one electron. A model for the potential in which this electron moves is

$$V(r)=-\frac{e^2}{r}\left(1+\frac{b}{r}\right)$$

Calculate the energy levels.

Solution

The radial Schrödinger equation for the alkali atom is

$$\frac{\hbar^2}{2m}\left[-\frac{d^2}{dr^2}+\frac{\ell(\ell+1)}{r^2}\right]u_\ell(r)-\frac{e^2}{r}u_\ell(r)-\frac{e^2b}{r^2}u_\ell(r)=Eu_\ell(r)\,, \tag{5.15}$$

which can be rewritten

$$\frac{\hbar^2}{2m}\left[-\frac{d^2}{dr^2}+\frac{\bar{\ell}(\bar{\ell}+1)}{r^2}\right]u_\ell(r)-\frac{e^2}{r}u_\ell(r)=Eu_\ell(r)\,, \tag{5.16}$$

where

$$\bar{\ell}(\bar{\ell}+1)=\ell(\ell+1)-be^2\,;$$

or

$$\bar{\ell}=-\tfrac{1}{2}+\sqrt{\ell(\ell+1)-\ be^2+\tfrac{1}{4}}\,.$$

The quadratically integrable solution of Eq.(5.16) is proportional to

$$r^{\ell+1}\exp\left(-\frac{r}{a_0(k+\bar{\ell}+1)}\right)L^{2\bar{\ell}+1}_{k+2\bar{\ell}+1}\left(\frac{2r}{a_0(k+\bar{\ell}+1)}\right)\,,$$

where $a_0=\hbar^2/(me^2)$, the Bohr radius, and where $k=0,1,2,\ldots$ (see the Lemma of Solution **4.10** for a definition of the Laguerre polynomial when $\bar{\ell}$ is not an integer). The hydrogen atom energy levels are

$$E_n=-\frac{e^4m}{2\hbar^2}\frac{1}{n^2}\,,$$

where $n=k+\ell+1$. We only have to change ℓ into $\bar{\ell}$ to obtain the alkali atom energy levels:

$$E=-\frac{e^4m}{2\hbar^2}\frac{1}{(k+\bar{\ell}+1)^2}\,.$$

We now define $n=k+\ell+1$, as before (*not* $n=k+\bar{\ell}+1$, which would not be integral), and we write the alkali energy levels as

$$E_{n\ell}=-\frac{e^4m}{2\hbar^2}\frac{1}{\left(n+\sqrt{(\ell+\frac{1}{2})^2-\ be^2+\frac{1}{4}}-\ell-\frac{1}{2}\right)^2}\,.$$

Note that the energy levels depend on the angular momentum quantum number, ℓ, as well as the principal quantum number, n. We need to restrict the parameter b by the requirement $be^2\leq\frac{1}{4}$, to ensure that all these energy levels are real. The 'accidental' degeneracy of the hydrogen atom Hamiltonian (see next exercise) has been lifted.

5.10 Runge-Lenz vector

Let $\vec{q}$ and $\vec{p}$ be the position and momentum operators of the electron in a hydrogen atom. The Runge-Lenz vector is defined by

$$\vec{N} = \frac{1}{2m}(\vec{p} \wedge \vec{L} - \vec{L} \wedge \vec{p}) - \frac{e^2}{q}\vec{q}\,,$$

where $\vec{L} = \vec{q} \wedge \vec{p}$ is the angular momentum operator, where $q = [\vec{q} \cdot \vec{q}]^{\frac{1}{2}}$, and where H is the Hamiltonian.

(1) Show that $[\vec{L}, H] = 0 = [\vec{N}, H]$, so that both $\vec{L}$ and $\vec{N}$ are conserved.
(2) Show that the Hamiltonian has a larger symmetry than that of rotations in three dimensions. Identify this larger symmetry.
(3) Show that the energy eigenvalues depend on only one quantum number.

Solution

The hydrogen atom Hamiltonian is

$$H = \frac{p^2}{2m} - \frac{e^2}{q}\,.$$

We shall adopt units in which $\hbar = 1$.

(1) A proof that the angular momentum commutes with the hydrogen atom Hamiltonian, $[\vec{L}, H] = 0$, may be found in the solution of Problem **3.4**, so here we only consider the commutator of the Runge-Lenz vector with the Hamiltonian. Much as in the solution of Problem **3.3**(1), we find

$$\begin{aligned}(\vec{L} \wedge \vec{p} + \vec{p} \wedge \vec{L})_i &= \epsilon_{ijk}(L_j p_k + p_j L_k) = \epsilon_{ijk}(L_j p_k - p_k L_j) \\ &= \epsilon_{ijk}\epsilon_{jmn}(q_m p_n p_k - p_k q_m p_n) \\ &= (\delta_{km}\delta_{in} - \delta_{kn}\delta_{im})[q_m, p_k]p_n \\ &= i(\delta_{kk}\delta_{in} - \delta_{kn}\delta_{ik})p_n = 2ip_i\,. \end{aligned} \tag{5.17}$$

Thus we may write

$$\vec{N} = \frac{\vec{n}}{m} - e^2\vec{u}\,, \tag{5.18}$$

where

$$\vec{n} = \tfrac{1}{2}(\vec{p} \wedge \vec{L} - \vec{L} \wedge \vec{p}) = \vec{p} \wedge \vec{L} - i\vec{p}\,, \tag{5.19}$$

and $\vec{u}$ is the unit vector

$$\vec{u} = \vec{q}q^{-1}\,. \tag{5.20}$$

Accordingly,

$$[\vec{N}\,,H] = \frac{1}{m}\left\{[\vec{p}\wedge\vec{L}\,,H] + ie^2[\vec{p}\,,q^{-1}] - \tfrac{1}{2}e^2[\vec{u}\,,p^2]\right\}, \tag{5.21}$$

so we must calculate three commutators. The second commutator is given by $[p_j, q^{-1}] = iq^{-3}q_j$, see Lemma 1 below. The first commutator can be written

$$[(\vec{p}\wedge\vec{L})_i, H] = \epsilon_{ijk}[p_j, H]\, L_k\,,$$

where we have used the fact that L_k commutes with H. Thus

$$\begin{aligned}[(\vec{p}\wedge\vec{L})_i, H] &= -ie^2\epsilon_{ijk}\epsilon_{kmn}q^{-3}q_jq_mp_n \\ &= -ie^2(\delta_{im}\delta_{jn} - \delta_{in}\delta_{jm})q^{-3}q_jq_mp_n \\ &= ie^2(q^{-1}p_i - q^{-3}q_iq_jp_j)\,, \end{aligned} \tag{5.22}$$

from Lemma 1 again. The third commutator is

$$[u_i, p^2] = 2(iq^{-1}p_i - iq^{-3}q_iq_jp_j - q^{-3}q_i)\,, \tag{5.23}$$

see Lemma 2(b) below. On using these results, we find

$$[N_i, H] = \frac{e^2}{m}\Big\{i(q^{-1}p_i - q^{-3}q_iq_jp_j) - q^{-3}q_j - (iq^{-1}p_i - iq^{-3}q_iq_jp_j - q^{-3}q_i)\Big\} = 0\,.$$

Thus $[\vec{N}\,,H] = 0$, and so $\dot{\vec{N}} = 0$, i.e., the Runge-Lenz vector, as well as the angular momentum vector, are conserved in time. It is this extra symmetry that lies at the root of the ℓ-degeneracy.

(2) The following commutation relations are proved in Lemmata 3, 4 and 5:

$$[L_i, L_j] = i\epsilon_{ijk}L_k$$

$$[L_i, N_j] = i\epsilon_{ijk}N_k$$

$$[N_i, N_j] = -\frac{2i}{m}\epsilon_{ijk}L_kH$$

Suppose that $|\psi\rangle$ is an eigenvector of the Hamiltonian corresponding to a bound-state energy, i.e.,

$$H|\psi\rangle = E|\psi\rangle\,,$$

where $E < 0$. Define then

$$\vec{M} = \sqrt{-\frac{m}{2E}}\,\vec{N}\,. \tag{5.24}$$

We now have

$$[L_i, L_j]\,|\psi\rangle = i\epsilon_{ijk}L_k|\psi\rangle$$

$$[L_i, M_j]\,|\psi\rangle = i\epsilon_{ijk}M_k|\psi\rangle$$

$$[M_i, M_j]\,|\psi\rangle = i\epsilon_{ijk}L_k|\psi\rangle\,.$$

In terms of the combinations

$$\vec{J}^{\pm} = \tfrac{1}{2}(\vec{L} \pm \vec{M})\,,$$

the commutation relations decouple, in the sense that

$$\begin{aligned}[J_i^{\pm}, J_j^{\pm}]|\psi\rangle &= \tfrac{1}{4}\big\{[L_i, L_j] + [M_i, M_j] \pm [L_i, M_j] \pm [M_i, L_j]\big\}|\psi\rangle \\ &= \tfrac{1}{4}i\epsilon_{ijk}\big\{L_k + L_k \pm M_k \pm M_k\big\}|\psi\rangle = i\epsilon_{ijk}J_k^{\pm}|\psi\rangle\end{aligned}$$

$$\begin{aligned}[J_i^{\pm}, J_j^{\mp}]|\psi\rangle &= \tfrac{1}{4}\big\{[L_i, L_j] - [M_i, M_j] \pm [L_i, M_j] \mp [M_i, L_j]\big\}|\psi\rangle \\ &= \tfrac{1}{4}i\epsilon_{ijk}\big\{L_k - L_k \pm M_k \mp M_k\big\}|\psi\rangle = 0\,.\end{aligned}$$

Thus the symmetry of the Hamiltonian, limited to a subspace corresponding to a given energy eigenvalue, is $SO(3) \times SO(3)$, that is, the product of two independent rotations in 3-dimensional Euclidean space.

(3) It is proved in Lemma 6 that

$$N^2 = \frac{2}{m}(L^2 + 1)H + e^2\,.$$

Allow both sides to operate on $|\psi\rangle$ and use Eq.(5.24):

$$N^2|\psi\rangle = -\frac{2E}{m}M^2|\psi\rangle = \left\{\frac{2E}{m}\left(L^2 + 1\right) + e^2\right\}|\psi\rangle\,,$$

or equivalently

$$\left(L^2 + M^2 + 1\right)|\psi\rangle = -\frac{me^2}{2E}|\psi\rangle\,. \tag{5.25}$$

From Lemma 7 we have

$$\vec{L}\cdot\vec{M} = 0 = \vec{M}\cdot\vec{L}\,,$$

so that

$$(J^{\pm})^2 = \tfrac{1}{4}(L^2 \pm \vec{L}\cdot\vec{M} \pm \vec{M}\cdot\vec{L} + M^2) = \tfrac{1}{4}(L^2 + M^2)\,. \tag{5.26}$$

So $(J^+)^2$ and $(J^-)^2$ are equal to one another. Choosing $(J^+)^2$ for definiteness, we see from Eq.(5.25) and Eq.(5.26) that

$$\left\{4(J^+)^2+1\right\}|\psi\rangle = -\frac{me^2}{2E}|\psi\rangle\,.$$

Since L^2 and M^2, and therefore also $(J^+)^2$, commute with the Hamiltonian, we can choose $|\psi\rangle$ to be a simultaneous eigenvector of $(J^+)^2$ and of the Hamiltonian:

$$(J^+)^2|\psi\rangle = j(j+1)|\psi\rangle\,,$$

where we know from the work of Volume 1, Chapter 3, that the allowed values of j are $0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$. Hence

$$[4j(j+1)+1]|\psi\rangle = (2j+1)^2|\psi\rangle = -\frac{me^2}{2E}|\psi\rangle\,,$$

and so finally

$$E = -\frac{me^2}{2\hbar^2}\frac{1}{n^2}\,,$$

where

$$n = 2j+1\,.$$

Consequently, n has the allowed values $1, 2, 3, \ldots$. The energy eigenvalues indeed depend on just one quantum number. Two comments are in order:

(a) The four operators, $(J^+)^2$, $(J^-)^2$, J_3^+ and J_3^- commute with the Hamiltonian, and so at first sight all of their eigenvalues might be expected to label the eigenvectors of the Hamiltonian. However, since $\vec{J}^{\pm}$ commutes with the Hamiltonian, we know that the energy must be independent of m_3^+ and m_3^-, and since $(J^+)^2 = (J^-)^2$, that leaves only one eigenvalue of relevance, namely $j(j+1)$. Moreover, the fact that the principal quantum number, n, is equal to $2j+1$, requires that we employ the half-odd integral values of j, as well as the integral ones. The degeneracy of eigenvalues for a given j is $(2j+1)^2 = n^2$, and the complete, simultaneous eigenstates of $(J^+)^2, (J^-)^2, J_3^+, J_3^-$, and H may be labeled by j, m_3^+, m_3^-.

(b) This method of finding the eigenvalues of the Hamiltonian of the hydrogen atom was first employed by Pauli (Pauli, W., (1926) Zeitschrift für Physik, Vol. 36, page 336), independently of the method of Schrödinger, in which use was made of the wave equation that had just been invented (Schrödinger, E., (1926) Annalen der Physik, Vol. 79, page 361).

LEMMATA

Lemma 1: $[p_j, q^{-1}] = iq^{-3}q_j$.

Proof

In configuration space, q_i is represented by x_i, and p_j by $-i\partial_j = -i\frac{\partial}{\partial x_j}$, so

$$-i[\partial_j, r^{-1}]\phi = -i(\partial_j r^{-1})\phi = \frac{i}{r^2}\frac{\partial r}{\partial x_j}\phi = i\frac{x_j}{r^3}\phi\,,$$

which corresponds to the abstract operator relation that was to be proved. Although this proof refers specifically to the configuration representation, the result is valid generally. For let $g(\vec{x})$ be a suitable test function. Then

$$\begin{aligned}
\int d^3x\, g(\vec{x})\langle\vec{x}\,|[p_j, q^{-1}]|\vec{y}\rangle &= -i\int d^3x\, g(\vec{x})\left(\frac{1}{y}-\frac{1}{x}\right)\frac{\partial}{\partial x_j}\delta^3(\vec{x}-\vec{y}) \\
&= i\int d^3x\,\delta^3(\vec{x}-\vec{y})\frac{\partial}{\partial x_j}\left\{\left(\frac{1}{y}-\frac{1}{x}\right)g(\vec{x})\right\} \\
&= i\int d^3x\,\delta^3(\vec{x}-\vec{y})\left\{\frac{x_j}{x^3}g(\vec{x}) + \frac{x-y}{xy}\,\frac{\partial g(\vec{x})}{\partial x_j}\right\} \\
&= i\frac{y_j}{y^3}g(\vec{y})\,.
\end{aligned}$$

It is also the case that

$$\begin{aligned}
\int d^3x g(\vec{x})\langle\vec{x}\,|iq^{-3}q_j|\vec{y}\rangle &= i\int d^3x\, g(\vec{x})x^{-3}x_j\delta^3(\vec{x}-\vec{y}) \\
&= i\frac{y_j}{y^3}g(\vec{y})\,.
\end{aligned}$$

Hence the following integral vanishes:

$$\int d^3x g(\vec{x})\langle\vec{x}\,|[p_j, q^{-1}] - iq^{-3}q_j|\vec{y}\rangle = 0\,,$$

which means that, as a distribution,

$$\langle\vec{x}\,|[p_j, q^{-1}] - iq^{-3}q_j|\vec{y}\rangle = 0\,.$$

Since the kets $|\vec{x}\rangle$ span the Hilbert space, it follows that

$$[p_j, q^{-1}] - iq^{-3}q_j = 0\,,$$

as an operator relation.

Lemma 2: (a) $[q_i q^{-1}, p_j] = i(\delta_{ij} q^{-1} - q^{-3} q_i q_j)$
(b) $[q_i q^{-1}, p^2] = 2i(q^{-1} p_i - q^{-3} q_i q_j p_j + i q^{-3} q_i)$

Proof
In configuration space, p^2 is represented by $-\nabla^2 = -\partial_j \partial_j$ and so

$$[q_i q^{-1}, p^2]\phi = \partial_j \partial_j \left(\frac{x_i}{r}\phi\right) - \frac{x_i}{r}\partial_j \partial_j \phi = \left(\partial_j \partial_j \frac{x_i}{r}\right)\phi + 2\left(\partial_j \frac{x_i}{r}\right)\partial_j \phi\,.$$

Now

$$\begin{aligned} \partial_j \frac{x_i}{r} &= \frac{\delta_{ij}}{r} - \frac{x_i x_j}{r^3}\,, \\ \partial_j \partial_j \frac{x_i}{r} &= -\delta_{ij}\frac{x_j}{r^3} + 3\frac{x_i x_j x_j}{r^5} - \frac{\delta_{ij} x_j + \delta_{jj} x_i}{r^3} = -\frac{2x_i}{r^3}\,. \end{aligned}$$

From the last three equations, we obtain

$$\begin{aligned} \text{(a)}\quad [q_i q^{-1}, p_j]\phi &= i(\delta_{ij} r^{-1} - r^{-3} x_i x_j)\phi \\ &= (i\delta_{ij} q^{-1} - i q^{-3} q_i q_j)\phi \\ \text{(b)}\quad [q_i q^{-1}, p^2]\phi &= 2\left(r^{-1}\partial_i - r^{-3} x_i x_j \partial_j - r^{-3} x_i\right)\phi \\ &= 2i(q^{-1} p_i - q^{-3} q_i q_j p_j + i q^{-3} q_i)\phi\,, \end{aligned}$$

As in Lemma 1, one can show that this proof, worked out in configuration representation, is actually valid as an operator identity.

Lemma 3: $[L_i, L_j] = i\epsilon_{ijk} L_k$

Proof
The algebra of the components of the angular momentum operator was worked out in Chapter 3 of Volume 1 by calculating $[L_1, L_2]$ and then generalizing the result. We give here an alternative proof that uses the lemma that was demonstrated in the solution of Problem **3.2**.

$$\begin{aligned} [L_i, L_j] &= i\epsilon_{ik\ell}\epsilon_{jmn}\left(q_k [p_\ell, q_m] p_n - q_m [p_n, q_k] p_\ell\right) \\ &= i\epsilon_{ik\ell}\epsilon_{jmk} q_m p_\ell - i\epsilon_{ik\ell}\epsilon_{j\ell n} q_k p_n \\ &= i(\delta_{\ell j}\delta_{im} - \delta_{\ell m}\delta_{ij}) q_m p_\ell - i(\delta_{in}\delta_{kj} - \delta_{ij}\delta_{kn}) q_k p_n \\ &= i(q_i p_j - q_\ell p_\ell \delta_{ij}) - i(q_j p_i - q_k p_\ell \delta_{ij}) = i(q_i p_j - q_j p_i)\,. \end{aligned}$$

On the other hand,

$$\begin{aligned} \epsilon_{ijk} L_k &= i\epsilon_{ijk}\epsilon_{kmn} q_m p_n \\ &= (\delta_{im}\delta_{jn} - \delta_{in}\delta_{jm}) q_m p_n = (q_i p_j - q_j p_i)\,, \end{aligned} \tag{5.27}$$

and the required result follows on comparing the last two equations.

Lemma 4: $[L_i, N_j] = i\epsilon_{ijk}N_k$

Proof

We can write this commutator in the form

$$[L_i, N_j] = \frac{1}{m}[L_i, n_j] - e^2[L_i, u_j]\,. \tag{5.28}$$

From Eq.(5.19), we see that

$$\begin{aligned}[L_i, n_j] &= \epsilon_{jnk}[L_i, p_n L_k] - i[L_i, p_j] \\ &= \epsilon_{jnk}\left\{[L_i, p_n]L_k + p_n[L_i, L_k]\right\} - i[L_i, p_j]\,.\end{aligned}$$

The commutator of L_i and L_k was given in Lemma 3, and moreover

$$[L_i, p_j] = \epsilon_{imk}[q_m p_k, p_j] = \epsilon_{imk}[q_m, p_j]p_k = i\epsilon_{ijk}p_k\,.$$

These commutators yield

$$\begin{aligned}[L_i, n_j] &= i\epsilon_{jnk}\left\{\epsilon_{inm}p_m L_k + \epsilon_{ikm}p_n L_m\right\} + \epsilon_{ijk}p_k \\ &= i(\delta_{ij}\delta_{km} - \delta_{ik}\delta_{jm})p_m L_k + i(\delta_{in}\delta_{jm} - \delta_{ij}\delta_{mn})p_n L_m + \epsilon_{ijk}p_k \\ &= i(p_i L_j - p_j L_i) + \epsilon_{ijk}p_k\,.\end{aligned}$$

On the other hand,

$$\begin{aligned}i\epsilon_{ijk}n_k &= i\epsilon_{ijk}\left(\epsilon_{kmn}p_m L_n - ip_k\right) \\ &= i(\delta_{im}\delta_{jn} - \delta_{in}\delta_{jm})p_m L_n + \epsilon_{ijk}p_k = i(p_i L_j - p_j L_i) + \epsilon_{ijk}p_k\,,\end{aligned}$$

from which it follows that

$$[L_i, n_j] = i\epsilon_{ijk}n_k\,. \tag{5.29}$$

Next we use Lemma 2(a) to calculate

$$\begin{aligned}[L_i, u_j] &= \epsilon_{imn}[q_m p_n, u_j] \\ &= \epsilon_{imn}q_m[p_n, u_j] \\ &= -i\epsilon_{imn}q_m[\delta_{jn}q^{-1} - q^{-3}q_j q_n] \\ &= -i\epsilon_{imj}u_m + i\epsilon_{imn}u_m u_j u_n\,.\end{aligned}$$

The last term vanishes here, because of the antisymmetry of ϵ_{imn} under interchange of m and n, and the fact that u_m and u_n commute. Hence

$$[L_i, u_j] = i\epsilon_{ijk}u_k\,. \tag{5.30}$$

From Eqs.(5.28)-(5.30) we obtain $[L_i, N_j] = i\epsilon_{ijk}N_k$.

Lemma 5: $[N_i, N_j] = -\frac{2i}{m}\epsilon_{ijk}L_k H$

Proof

From Eqs.(5.18)and (5.20), we have

$$\begin{aligned}[N_i, N_j] &= \left[\frac{n_i}{m} - e^2 u_i, \frac{n_j}{m} - e^2 u_j\right] \\ &= \frac{1}{m^2}[n_i, n_j] - \frac{e^2}{m}\Big\{[n_i, u_j] - [n_j, u_i]\Big\}, \end{aligned} \tag{5.31}$$

so we have to calculate two different commutators. Now

$$[n_i, n_j] = [(\vec{p}\wedge\vec{L})_i, (\vec{p}\wedge\vec{L})_j] - i[p_i, (\vec{p}\wedge\vec{L})_j] + i[p_j, (\vec{p}\wedge\vec{L})_i]\,.$$

However,

$$[p_i, (\vec{p}\wedge\vec{L})_j] = \epsilon_{jmn}p_m[p_i, L_n] = i\epsilon_{jmn}\epsilon_{ink}p_m p_k = i(p_i p_j - p^2\delta_{ij})\,,$$

and that is symmetric under interchange of i and j, so

$$-\Big[p_i, (\vec{p}\wedge\vec{L})_j\Big] + \Big[p_j, (\vec{p}\wedge\vec{L})_i\Big] = 0\,.$$

We see then that

$$\begin{aligned}[n_i, n_j] &= \epsilon_{ik\ell}\epsilon_{jmn}\big[p_k L_\ell, p_m L_n\big] \\ &= \epsilon_{ik\ell}\epsilon_{jmn}\left\{p_k\big[L_\ell, p_m\big]L_n - p_m\big[L_n, p_k\big]L_\ell + p_k p_m\big[L_\ell, L_n\big]\right\} \\ &= i\epsilon_{ik\ell}\epsilon_{jmn}\left\{\epsilon_{\ell mq}p_k p_q L_n - \epsilon_{nkq}p_m p_q L_\ell + \epsilon_{\ell nq}p_k p_m L_q\right\} \\ = i\epsilon_{ik\ell}&\left\{p_k p_q L_q\delta_{j\ell} - p_j p_k L_\ell + p_j p_k L_\ell - p^2 L_\ell\delta_{jk} + p_k p_\ell L_j - p_k p_q L_q\delta_{j\ell}\right\} \\ &= -i\epsilon_{ij\ell}\,p^2 L_\ell\,. \end{aligned} \tag{5.32}$$

The second commutator we have to calculate is $[n_i, u_j]$, and in fact we need only $[n_i, u_j] - [n_j, u_i]$, so we may throw away all terms that are symmetric under the interchange $i \leftrightarrow j$. With use of Lemma 2 and Eq.(5.27), we have

$$\begin{aligned}[n_i, u_j] &= \epsilon_{ik\ell}[p_k L_\ell, u_j] - i[p_i, u_j] \\ &= \big[p_k(q_i p_k - q_k p_i), u_j\big] + q^{-1}\big(q_i q_j - \delta_{ij}\big) \\ &= p_k q_i p_k u_j - u_j p_k q_i p_k + u_j p_k q_k p_i - p_k q_k p_i u_j + \mathcal{E}\,. \end{aligned} \tag{5.33}$$

where $\mathcal{E}$ refers to terms that are symmetric under the interchange $i \leftrightarrow j$, and which will be discarded. The first two terms in Eq.(5.33) are

$$\begin{aligned} p_k q_i p_k u_j - u_j p_k q_i p_k &= \big\{q_i p_k - i\delta ik\big\}p_k u_j - u_j\big\{q_i p_k - i\delta ik\big\}p_k \\ &= q_i\big[p^2, u_j\big] - i\big[p_i, u_j\big] \\ &= -2iu_i p_j + \mathcal{E}\,, \end{aligned}$$

where we have used Lemma 2 again. The third and fourth terms in Eq.(5.33) yield a term that is symmetric under interchange $i \leftrightarrow j$, and so may be discarded:

$$\begin{aligned} u_j p_k q_k p_i - p_k q_k p_i u_j &= p_k u_j q_k p_i - i u_j u_k u_k p_i + i u_j p_i - p_k q_k p_i u_j \\ &= -i p_k u_k \big(u_i u_j - i\delta_{ij}\big) + \mathcal{E} = \mathcal{E}\,. \end{aligned}$$

Hence

$$[n_i, u_j] - [n_j, u_i] = -2iq^{-1}\big(q_i p_j - q_j p_i\big)\,. \tag{5.34}$$

Eqs.(5.31)-(5.34) yield the result

$$[N_i, N_j] = -\frac{2i}{m} H(q_i p_j - q_j p_i)$$

Now from Eq.(5.27) we know that $q_i p_j - q_j p_i = \epsilon_{ijk} L_k$, and this completes the proof of the Lemma, since we also know that the Hamiltonian commutes with the angular momentum, so that H may be placed on the extreme right.

Lemma 6: $\quad N^2 = 2(L^2+1)H/m + e^4$

Proof

We may write N^2 as the sum of the three terms

$$N^2 = \big(n_i/m - e^2 u_i\big)^2 = n^2/m^2 - e^2(n_i u_i + u_i n_i)/m + e^4\,. \tag{5.35}$$

The first term may be evaluated as follows:

$$\begin{aligned} n^2 &= \big(p^2 q_i - p_j q_j p_i\big)^2 \\ &= p^2 q_i p_j (p_j q_i - q_j p_i) + p_j q_j p_i p_k (q_k p_i - p_k q_i)\,. \end{aligned}$$

Now $q_i p_j (p_j q_i - q_j p_i) = q_i p_j (q_i p_j - q_j p_i - i\delta_{ij}) = L^2 - i q_j p_j$, since

$$L^2 = \epsilon_{ijk} q_i p_j \epsilon_{mnk} q_m p_n = \big(\delta_{im}\delta_{jn} - \delta_{in}\delta_{jm}\big) q_i p_j q_m p_n = q_i p_j \big(q_i p_j - q_j p_i\big)\,.$$

Also, $p_i p_k (q_k p_i - p_k q_i) = p_i p_k (q_k p_i - p_i q_k) = i p^2$, whereas $p_j q_j = -3i + q_j p_j$, and so

$$n^2 = p^2 L^2 + 3p^2 + i\left[q_j p_j, p^2\right]\,.$$

Since $\left[q_i p_i, p^2\right] = [q_i, p^2] p_i = 2i p_i p_i = 2i p^2$, we have finally

$$n^2 = p^2\big(L^2 + 1\big)\,. \tag{5.36}$$

As to the second term in Eq.(5.35), we have on the one hand

$$\begin{aligned} u_i n_i &= q^{-1} q_i \{\epsilon_{ijk} p_j L_k - i p_i\} \\ &= q^{-1} q_i p_j \{q_i p_j - q_j p_i\} - i q^{-1} q_j p_j \\ &= q^{-1} L^2 - i q^{-1} q_j p_j \,, \end{aligned}$$

and on the other hand

$$\begin{aligned} n_i u_i &= \{ -\epsilon_{ijk} L_j p_k + i p_i \} q_i q^{-1} \\ &= -\{q_k p_i - q_i p_k\} q_i p_k q^{-1} + i p_i q_i q^{-1} \\ &= L^2 q^{-1} + i p_i q_i q^{-1} \,. \end{aligned}$$

Now we know that L^2 commutes with any function of q^2, and thus in particular with q^{-1}. Also $p_j q_j = q_j p_j - i\delta_{jj} = q_j p_j - 3i$, so

$$u_i n_i + n_i u_i = 2q^{-1} L^2 + 3q^{-1} + i \left[q_i p_i, q^{-1} \right] .$$

Now $[q_j p_j, q^{-1}] = [p_j, q^{-1}] q_j = i q^{-3} q_j q_j = i q^{-1}$ and so

$$u_i n_i + n_i u_i = 2q^{-1} \left(L^2 + 1 \right) . \tag{5.37}$$

On combining Eqs.(5.35), (5.36) and (5.37), we find

$$N^2 = \frac{2}{m} \left(\frac{p^2}{2m} - e^2 q^{-1} \right) \left(L^2 + 1 \right) + e^4 .$$

Since the Hamiltonian commutes with L^2, this is equivalent to that which was to be proved.

Lemma 7: $\vec{L} \cdot \vec{N} = 0 = \vec{N} \cdot \vec{L}$

Proof

From Eqs.(5.17)-(5.20), $\vec{N} = (i\vec{p} - \vec{L} \wedge \vec{p})/m - e^2 \vec{q} q^{-1}$, and we know that $\vec{L} \cdot \vec{q} = 0$ and $\vec{L} \cdot \vec{p} = 0$. Moreover,

$$\vec{L} \cdot (\vec{L} \wedge \vec{p}) = (\vec{L} \wedge \vec{L}) \cdot \vec{p} = i\hbar \vec{L} \cdot \vec{p} = 0 .$$

Hence $\vec{L} \cdot \vec{N} = 0$; and similar reasoning establishes $\vec{N} \cdot \vec{L} = 0$ also.

Chapter 6

Spin and Addition of Angular Momenta

6.1 Clebsch-Gordan Coefficients

Work out the Clebsch-Gordan coefficients for the combination $\frac{3}{2} \otimes \frac{1}{2}$.

Solution
We know that $\frac{3}{2} \otimes \frac{1}{2} = 1 \oplus 2$, and there is only one possibility for the state with $j = 2$ and $m = 2$, namely

$$|2,2\rangle = |\tfrac{3}{2},\tfrac{3}{2}\rangle^a |\tfrac{1}{2},\tfrac{1}{2}\rangle^b .$$

From the general formula for ladder operators [Condon-Shortley phase convention],

$$J_\pm |j,m\rangle = \sqrt{j(j+1) - m(m\pm 1)}\,|j,m\pm 1\rangle ,$$

with $\hbar = 1$ for convenience, we have

$$\begin{aligned} 2|2,1\rangle = J_-|2,2\rangle &= (J_-^a + J_-^b)|\tfrac{3}{2},\tfrac{3}{2}\rangle^a |\tfrac{1}{2},\tfrac{1}{2}\rangle^b \\ &= \sqrt{3}|\tfrac{3}{2},\tfrac{1}{2}\rangle^a |\tfrac{1}{2},\tfrac{1}{2}\rangle^b + |\tfrac{3}{2},\tfrac{3}{2}\rangle^a |\tfrac{1}{2}\,\tfrac{-1}{2}\rangle^b . \end{aligned}$$

Applying the lowering operator again, we find

$$\begin{aligned} 2\sqrt{6}|2,0\rangle = (J_-)^2|2,2\rangle &= (J_-^a + J_-^b)^2 |\tfrac{3}{2},\tfrac{3}{2}\rangle^a |\tfrac{1}{2},\tfrac{1}{2}\rangle^b \\ &= 2\sqrt{3}|\tfrac{3}{2},\tfrac{-1}{2}\rangle^a |\tfrac{1}{2},\tfrac{1}{2}\rangle^b + 2\sqrt{3}|\tfrac{3}{2},\tfrac{1}{2}\rangle^a |\tfrac{1}{2},\tfrac{-1}{2}\rangle^b . \end{aligned}$$

The state with $j = 2$ and $m = -1$ could be obtained by applying J_- again, but it is easier to apply J_+ to the state $|2,-2\rangle$, which yields

$$\begin{aligned} 2|2,-1\rangle = J_+|2,-2\rangle &= (J_+^a + J_+^b)|\tfrac{3}{2},\tfrac{-3}{2}\rangle^a |\tfrac{1}{2},\tfrac{-1}{2}\rangle^b \\ &= \sqrt{3}|\tfrac{3}{2},\tfrac{-1}{2}\rangle^a |\tfrac{1}{2},\tfrac{-1}{2}\rangle^b + |\tfrac{3}{2},\tfrac{-3}{2}\rangle^a |\tfrac{1}{2},\tfrac{1}{2}\rangle^b . \end{aligned}$$

The states corresponding to spin $\frac{1}{2}$ now follow by orthonormalization:

$$\begin{aligned} 2|1,1\rangle &= \sqrt{3}|\tfrac{3}{2},\tfrac{3}{2}\rangle^a|\tfrac{1}{2},\tfrac{-1}{2}\rangle^b - |\tfrac{3}{2},\tfrac{1}{2}\rangle^a|\tfrac{1}{2},\tfrac{1}{2}\rangle^b \\ \sqrt{2}|1,0\rangle &= |\tfrac{3}{2},\tfrac{1}{2}\rangle^a|\tfrac{1}{2},\tfrac{-1}{2}\rangle^b - |\tfrac{3}{2},\tfrac{-1}{2}\rangle^a|\tfrac{1}{2},\tfrac{1}{2}\rangle^b \\ 2|1,-1\rangle &= -\sqrt{3}|\tfrac{3}{2},\tfrac{-3}{2}\rangle^a|\tfrac{1}{2},\tfrac{1}{2}\rangle^b + |\tfrac{3}{2},\tfrac{-1}{2}\rangle^a|\tfrac{1}{2},\tfrac{-1}{2}\rangle^b . \end{aligned}$$

In the contracted notation of Chapter 6 of Volume 1, we have

	$\|\frac{3}{2}\rangle^a\|\frac{1}{2}\rangle^b$	$\|\frac{3}{2}\rangle^a\|\frac{-1}{2}\rangle^b$	$\|\frac{1}{2}\rangle^a\|\frac{1}{2}\rangle^b$	$\|\frac{1}{2}\rangle^a\|\frac{-1}{2}\rangle^b$	S/A
$\|2,2\rangle$	1	0	0	0	
$\|2,1\rangle$	0	$\frac{1}{2}$	$\frac{\sqrt{3}}{2}$	0	
$\|2,0\rangle$	0	0	0	$\frac{1}{\sqrt{2}}$	S
$\|2,-1\rangle$	0	0	0	0	
$\|2,-2\rangle$	0	0	0	0	
$\|1,1\rangle$	0	$\frac{\sqrt{3}}{2}$	$-\frac{1}{2}$	0	
$\|1,0\rangle$	0	0	0	$\frac{1}{\sqrt{2}}$	A
$\|1,-1\rangle$	0	0	0	0	

Clebsch-Gordan coefficients for $\frac{3}{2} \otimes \frac{1}{2}$

6.2 Pauli Matrices

Show that

(1) an arbitrary matrix in two dimensions can be written as a linear superposition of the three Pauli matrices and the unit matrix.
(2) no two-dimensional matrix anticommutes with all of the Pauli matrices.

Solution

(1) Consider the following combinations of the unit and the Pauli matrices:

$$\tfrac{1}{2}(1+\sigma_3) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}; \qquad \tfrac{1}{2}(1-\sigma_3) = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix};$$

$$\tfrac{1}{2}(\sigma_1+i\sigma_2) = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}; \qquad \tfrac{1}{2}(\sigma_1-i\sigma_2) = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}.$$

Hence an arbitrary matrix in two dimensions can be written as follows:

$$\begin{aligned} m = \begin{pmatrix} a & b \\ c & d \end{pmatrix} &= \tfrac{1}{2}a(1+\sigma_3) + \tfrac{1}{2}d(1-\sigma_3) + \tfrac{1}{2}b(\sigma_1+i\sigma_2) + \tfrac{1}{2}c(\sigma_1-i\sigma_2) \\ &= \tfrac{1}{2}(a+d) + \tfrac{1}{2}(a-d)\sigma_3 + \tfrac{1}{2}(b+c)\sigma_1 + \tfrac{i}{2}(b-c)\sigma_2 . \end{aligned}$$

(2) Since $\{\sigma_i, \sigma_j\} = 2\delta_{ij}$, if m anticommutes with the Pauli matrices,

$$\begin{aligned} \{\sigma_1, m\} &= (a+d)\sigma_1 + (b+c) = 0 \\ \{\sigma_2, m\} &= (a+d)\sigma_2 + i(b-c) = 0 \\ \{\sigma_3, m\} &= (a+d)\sigma_3 + (a-d) = 0\,. \end{aligned}$$

These equations imply

$$a = d \qquad a = -d \qquad b = c \qquad b = -c,$$

which is possible only if $a = b = c = d = 0$.

6.3 Manipulations with Pauli Matrices

Demonstrate

(1) $\mathrm{Tr}\sigma_i = 0$, $\mathrm{Tr}\sigma_i\sigma_j = 2\delta_{ij}$, $\mathrm{Tr}\sigma_i\sigma_j\sigma_k = 2i\epsilon_{ijk}$.
(2) If $A = a + \vec{b}\cdot\vec{\sigma}$, then $\mathrm{Tr}A = 2a$ and $\mathrm{Tr}\vec{\sigma}\,A = 2\vec{b}$.
(3) By using these formulas, show that

$$(\vec{b}\cdot\vec{\sigma})(\vec{c}\cdot\vec{\sigma}) = \vec{b}\cdot\vec{c} + i(\vec{b}\wedge\vec{c})\cdot\vec{\sigma}$$

(4) Write the following explicitly as 2×2 matrices: (i) e^{σ_1}, (ii) $\mathrm{e}^{i\sigma_1}$, where σ_1 is the first Pauli matrix.
(5) Show that, if $\vec{n}$ is a unit vector,

$$\exp[i\theta\,\vec{n}\cdot\vec{\sigma}] = \cos\theta + i\sin\theta\,\vec{n}\cdot\vec{\sigma}$$

Solution

(1) By inspection, $\mathrm{Tr}\sigma_1 = \mathrm{Tr}\sigma_2 = \mathrm{Tr}\sigma_3 = 0$. Further, for any two matrices,

$$\mathrm{Tr}(ab) = \sum_i\sum_j a_{ij}b_{ji} = \sum_j\sum_i b_{ji}a_{ij} = \mathrm{Tr}(ba)\,.$$

Hence $\mathrm{Tr}\sigma_i\sigma_j = \mathrm{Tr}\frac{1}{2}\{\sigma_i, \sigma_j\} = \delta_{ij}\mathrm{Tr}\,1 = 2\delta_{ij}$, since $\mathrm{Tr}1 = 2$. Now

$$\begin{aligned} \sigma_i\sigma_j - \sigma_j\sigma_i &= 2i\epsilon_{ijk}\sigma_k \\ \sigma_i\sigma_j + \sigma_j\sigma_i &= 2\delta_{ij}\,, \end{aligned}$$

so we find on adding and dividing by two that

$$\sigma_i\sigma_j = \delta_{ij} + i\epsilon_{ij\ell}\sigma_\ell\,, \tag{6.1}$$

thus $\sigma_i\sigma_j\sigma_k = \delta_{ij}\sigma_k + i\epsilon_{ij\ell}\sigma_\ell\sigma_k$, and so $\mathrm{Tr}\sigma_i\sigma_j\sigma_k = 2i\epsilon_{ij\ell}\delta_{\ell k} = 2i\epsilon_{ijk}$.

(2) $\mathrm{Tr}A = a\mathrm{Tr}1 + \mathrm{Tr}\,(\vec{b}\cdot\vec{\sigma}\,) = 2a$
$\mathrm{Tr}(\sigma_i A) = \mathrm{Tr}(a\sigma_i + b_j\sigma_i\sigma_j) = 2\delta_{ij}b_j = 2b_i.$

(3) With use of Eq.(6.1) we find

$$\begin{aligned}(\vec{b}\cdot\vec{\sigma}\,)(\vec{c}\cdot\vec{\sigma}\,) &= b_i c_j \sigma_i\sigma_j \\ &= b_i c_j(\delta_{ij} + i\epsilon_{ij\ell}\sigma_\ell) \\ &= \vec{b}\cdot\vec{c} + i(\vec{b}\wedge\vec{c})\cdot\vec{\sigma}\,.\end{aligned}$$

(4)
(i) $\mathrm{e}^{\sigma_1} = \sum_n \frac{\sigma_1^n}{n!} = \sum_m \frac{\sigma^{2m}}{(2m)!} + \sum_m \frac{\sigma^{2m+1}}{(2m+1)!} = \sum_m \frac{1}{(2m)!} + \sigma_1 \sum_m \frac{1}{(2m+1)!}$
Now $\cosh x = \sum_n \frac{x^n+(-x)^n}{n!} = \sum_m \frac{x^{2m}}{(2m)!}$
and $\sinh x = \sum_n \frac{x^n-(-x)^n}{n!} = \sum_m \frac{x^{2m+1}}{(2m+1)!}$,
and thus we conclude that $\mathrm{e}^{\sigma_1} = \cosh 1 + \sigma_1 \sinh 1 = \begin{pmatrix} \cosh 1 & \sinh 1 \\ \sinh 1 & \cosh 1 \end{pmatrix}$.
(ii) $\mathrm{e}^{i\sigma_1} = \sum_n \frac{(i\sigma_1)^n}{n!} = \sum_m \frac{(-1)^m}{(2m)!} + i\sigma_1 \sum_m \frac{(-1)^m}{(2m+1)!}$,
and here we conclude that $\mathrm{e}^{i\sigma_1} = \cos 1 + i\sigma_1 \sin 1 = \begin{pmatrix} \cos 1 & i\sin 1 \\ i\sin 1 & \cos 1 \end{pmatrix}$.

(5) $\exp[i\theta\,\vec{n}\cdot\vec{\sigma}\,] = \sum_n \frac{(i\theta\,\vec{n}\cdot\vec{\sigma}\,)^n}{n!} = \sum_m \frac{(-\theta^2)^m}{(2m)!} + i\theta\vec{n}\cdot\vec{\sigma}\sum_m \frac{(-\theta^2)^m}{(2m+1)!}$,
where we have used the fact that
$(\vec{n}\cdot\vec{\sigma}\,)^2 = n_i n_j \sigma_i\sigma_j = \frac{1}{2}n_i, n_j\{\sigma_i,\sigma_j\} = n^2 = 1$. Moreover, since
$\cos\theta = \sum_m \frac{(-1)^m\theta^{2m}}{(2m)!}$, and $\sin\theta = \sum_m \frac{(-1)^m\theta^{2m+1}}{(2m+1)!}$, the proof is complete.

6.4 Fermion Operators

Define $N = b^\dagger b$, $b^\dagger$ being the Hermitian conjugate of the operator b, where $bb^\dagger + b^\dagger b = 1$, and $b^2 = 0$.

(1) Is b Hermitian?
(2) Is N Hermitian?
(3) Show that $N^2 = N$ and find the eigenvalues of N.
(4) Find a representation for b in terms of the Pauli matrices.

Solution
(1) If b were Hermitian, i.e., $b = b^\dagger$, one would have $b^2 = \frac{1}{2}$, which is inconsistent with $b^2 = 0$, therefore b is not Hermitian.
(2) On the other hand, N is Hermitian, since

$$N^\dagger = \left(b^\dagger b\right)^\dagger = b^\dagger b = N\,.$$

(3) Since $bb^\dagger = 1 - b^\dagger b$ and $b^2 = 0$, we have

$$N^2 = b^\dagger bb^\dagger b = b^\dagger(1 - b^\dagger b)b = b^\dagger b = N\,.$$

If $|n\rangle$ is an eigenvector of N belonging to the eigenvalue n, we find that $n|n\rangle = N|n\rangle = N^2|n\rangle = n^2|n\rangle$, so that $n(n-1) = 0$. The eigenvalues are therefore 0 and 1.

(4) Any expression of the form

$$b = \tfrac{1}{2}(\sigma_j + i\sigma_k)\,,$$

where j and k are different, is a valid representation:

(a) $b^2 = \frac{1}{4}\left(\sigma_j^2 - \sigma_k^2 + i\{\sigma_j, \sigma_k\}\right) = 0\,.$

(b) However, since $b^\dagger = \frac{1}{2}(\sigma_j - i\sigma_k)$, it follows that $bb^\dagger = \frac{1}{4}(\sigma_j^2 + \sigma_k^2 - i[\sigma_j, \sigma_k])$, and $b^\dagger b = \frac{1}{4}(\sigma_j^2 + \sigma_k^2 + i[\sigma_j, \sigma_k])\,.$

Thus $\{b, b^\dagger\} = \frac{1}{2}(\sigma_j^2 + \sigma_k^2) = 1\,.$

A specific example is

$$b = \tfrac{1}{2}(\sigma_1 + i\sigma_2) = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}.$$

The most general representation of b, in terms of a 2×2 matrix, is

$$b = a_1\sigma_1 + a_2\sigma_2 + a_3\sigma_3\,,$$

with the following constraints on the complex numbers (a_1, a_2, a_3):

$$\begin{aligned} a_1^2 + a_2^2 + a_3^2 &= 0 \\ |a_1|^2 + |a_2|^2 + |a_3|^2 &= \tfrac{1}{2}\,. \end{aligned}$$

6.5 Positronium

The spin interaction energy of an electron and a positron in a positronium bound state is proportional to $\sigma_1 \cdot \sigma_2$, the spin matrices corresponding to the two particles.

(1) Evaluate the interaction energies in the singlet state, $|0,0\rangle$, and in the triplet state, $|1,m\rangle$, $m = -1, 0, 1$.

(2) Suppose now that a weak, uniform magnetic field is applied to this system. Show that the the triplet states $|1,1\rangle$ and $|1,-1\rangle$ are still eigenstates of the Hamiltonian, but that $|1,0\rangle$ and $|0,0\rangle$ are not.

(3) Obtain the energies of the three levels.

Solution

(1) The total spin of the positronium system, consisting of an electron and a positron, is $\vec{S} = \vec{s_1} + \vec{s_2}$, and so $S^2 = s_1^2 + 2\vec{s_1} \cdot \vec{s_2} + s_2^2$. The eigenvalues of

$$\sigma_1 \cdot \sigma_2 = \frac{4}{\hbar^2}\vec{s_1} \cdot \vec{s_2} = \frac{2}{\hbar^2}\left[S^2 - s_1^2 - s_2^2\right]$$

are $2\left[S(S+1) - \frac{1}{2}(\frac{1}{2}+1) - \frac{1}{2}(\frac{1}{2}+1)\right] = 2S(S+1) - 3$, where $S = 0$ for the singlet and $S = 1$ for the triplet. The Hamiltonian, $H = H_0 + \lambda\sigma_1 \cdot \sigma_2$, gives

$$H|0,0\rangle = (E_0 - 3\lambda)|0,0\rangle \qquad H|1,m\rangle = (E_0 + \lambda)|1,m\rangle\,, \tag{6.2}$$

so the interaction energies are -3λ for the singlet and λ for the triplet.

(2) Let us write

$$H(\mu) = H_0 + \lambda\sigma_1 \cdot \sigma_2 + \mu(\sigma_{1z} - \sigma_{2z})\,.$$

Since

$$(\sigma_{1z} - \sigma_{2z})|\tfrac{1}{2}\rangle_1|\tfrac{1}{2}\rangle_2 = 0 \qquad (\sigma_{1z} - \sigma_{2z})|\tfrac{-1}{2}\rangle_1|\tfrac{-1}{2}\rangle_2 = 0\,,$$

where we have suppressed the quantum number, $s = \frac{1}{2}$, showing only the value of the eigenvalue of s_z, as in the Clebsch-Gordan tables. It follows then that the energies of the states $|1,1\rangle$ and $|1,-1\rangle$ remain unchanged at $E_0 + \lambda$. However,

$$(\sigma_{1z} - \sigma_{2z})|\tfrac{1}{2}\rangle_1|\tfrac{-1}{2}\rangle_2 = 2|\tfrac{1}{2}\rangle_1|\tfrac{-1}{2}\rangle_2 \qquad (\sigma_{1z} - \sigma_{2z})|\tfrac{-1}{2}\rangle_1|\tfrac{1}{2}\rangle_2 = -2|\tfrac{-1}{2}\rangle_1|\tfrac{1}{2}\rangle_2\,.$$

We see from the $\frac{1}{2} \otimes \frac{1}{2}$ Clebsch-Gordan table that consequently

$$(\sigma_{1z} - \sigma_{2z})|1,0\rangle = 2|0,0\rangle \qquad (\sigma_{1z} - \sigma_{2z}|0,0\rangle = 2|1,0\rangle\,.$$

Hence $|0,0\rangle$ and $|1,0\rangle$ are not eigenstates of the Hamiltonian.

(3) Suppose that $\alpha|1,0\rangle + \beta|0,0\rangle$ is an eigenstate of $H(\mu)$. Then

$$H(\mu)\left[\alpha|1,0\rangle + \beta|0,0\rangle\right] = E(\mu)\left[\alpha|1,0\rangle + \beta|0,0\rangle\right]$$

and this leads to

$$\alpha(E_0+\lambda)|1,0\rangle+2\alpha\mu|0,0\rangle+\beta(E_0-3\lambda)|0,0\rangle+2\beta\mu|1,0\rangle = \alpha E(\mu)|1,0\rangle+\beta E(\mu)|0,0\rangle\,.$$

Let us separate the coefficients of the orthogonal states $|0,0\rangle$ and $|1,0\rangle$,

$$\begin{aligned} \alpha(E_0 + \lambda) + 2\beta\mu &= \alpha E(\mu) \\ 2\alpha\mu + \beta(E_0 - 3\lambda) &= \beta E(\mu)\,. \end{aligned}$$

The condition of solubility of this homogeneous system is the quadratic equation

$$[E_0 + \lambda - E(\mu)][E_0 - 3\lambda - E(\mu)] - 4\mu^2 = 0\,,$$

with solutions

$$E(\mu) = E_0 - \lambda \pm 2\sqrt{\lambda^2 + \mu^2}\,,$$

which are the new, μ-dependent energy levels. Notice that, in the limit $\mu \to 0$, these levels tend to $E_0 + \lambda$ and $E_0 - 3\lambda$, as should be the case.

6.6 Two Deuterons

What are the spin and total angular momentum states of two deuterons in an arbitrary orbital angular momentum state, L?

Solution

The possible spin values are 0, 1 and 2: $1 \otimes 1 = 0 \oplus 1 \oplus 2$. Let $|S, S_3\rangle$ signify the spin state of the two deuteron system with quantum numbers S for the total spin and S_3 for the third component of this spin. Let $|s, s_3\rangle^a$ and $|s, s_3\rangle^b$ signify the spin states of deuteron a and deuteron b. Then, with the Condon-Shortley phase convention,

$$\begin{aligned}
|2,2\rangle &= |1,1\rangle^a|1,1\rangle^b \\
|2,1\rangle &= \{|1,1\rangle^a|1,0\rangle^b + |1,0\rangle^a|1,1\rangle^b\}/\sqrt{2} \\
|2,0\rangle &= \{|1,1\rangle^a|1,-1\rangle^b + 2|1,0\rangle^a|1,0\rangle^b + |1,-1\rangle^a|1,1\rangle^b\}/\sqrt{6} \\
|2,-1\rangle &= \{|1,0\rangle^a|1,-1\rangle^b + |1,-1\rangle^a|1,0\rangle^b\}/\sqrt{2} \\
|2,-2\rangle &= |1,-1\rangle^a|1,-1\rangle^b \\
|1,1\rangle &= \{|1,1\rangle^a|1,0\rangle^b - |1,0\rangle^a|1,1\rangle^b\}/\sqrt{2} \\
|1,0\rangle &= \{|1,1\rangle^a|1,-1\rangle^b - |1,-1\rangle^a|1,1\rangle^b\}/\sqrt{2} \\
|1,-1\rangle &= \{|1,0\rangle^a|1,-1\rangle^b - |1,-1\rangle^a|1,0\rangle^b\}/\sqrt{2} \\
|0,0\rangle &= \{|1,1\rangle^a|1,-1\rangle^b - |1,0\rangle^a|1,0\rangle^b + |1,-1\rangle^a|1,1\rangle^b\}/\sqrt{3}\,.
\end{aligned}$$

The deuteron has spin 1, and so it is a boson, i.e., it satisfies Bose-Einstein statistics. This means that a two-deuteron system must be symmetric under interchange of the deuterons. Thus $L + S$ must be even. Classifying the allowed states by the value of the orbital angular momentum, we construct the following table:

L	S	J
0	0	0
0	2	2
1	1	0 or 1 or 2
2	0	2
2	2	0 or 1 or 2 or 3 or 4
3	1	2 or 3 or 4
4	0	4
4	2	2 or 3 or 4 or 5 or 6

and so on.

6.7 Particle of Spin One

A particle is known to have spin one. Measurements of the state of the particle yield $\langle S_1 \rangle = 0 = \langle S_2 \rangle$ and $\langle S_3 \rangle = a$, where $0 \leq a \leq 1$. What is the most general possibility for the state?

Solution
We consider first the case of a pure state, which can be written

$$|\psi\rangle = \begin{pmatrix} x \\ y \\ z \end{pmatrix} = x \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + y \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} + z \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$
$$= x|1,1\rangle + y|1,0\rangle + z|1,-1\rangle ,$$

where $|1,m\rangle$ is the normalized eigenvector of S_3 belonging to the eigenvalue m (with $\hbar = 1$). Since the matrix elements of S_1 and S_2 vanish, so too do those of $S_\pm = S_1 \pm iS_2$, and since

$$S_+|1,1\rangle = 0 \qquad S_+|1,0\rangle = \sqrt{2}|1,1\rangle \qquad S_+|1,-1\rangle = \sqrt{2}|1,0\rangle$$

it follows that

$$\langle \psi | S_+ | \psi \rangle = \sqrt{2}(x^* y + y^* z) = 0 \tag{6.3}$$

We see then that

$$x^* y = -y^* z , \tag{6.4}$$

and the equation $\langle \psi | S_- | \psi \rangle = 0$ yields nothing new, since it is just the Hermitian

conjugate of Eq.(6.3). The normalization of ψ gives

$$|x|^2 + |y|^2 + |z|^2 = a\,, \tag{6.5}$$

and Eq.(6.4) implies $|x|\,|y| = |z|\,|y|$, and thus that

$$\big(|x|^2 - |z|^2\big)|y|^2 = 0\,. \tag{6.6}$$

The matrix element of S_3 is given by

$$\langle\psi|S_3|\psi\rangle = |x|^2 - |z|^2 = a\,. \tag{6.7}$$

Combining the last two equations, we find $a|y|^2 = 0$, and so if $a \neq 0$, necessarily $|y| = 0$. We will treat this case first, returning to $a = 0$ at the end. From Eq.(6.5) and Eq.(6.7), with $|y| = 0$, we find $|x|^2 = (1+a)/2$ and $|z|^2 = (1-a)/2$. Since the overall phase of ψ is of no significance, we make x real and write

$$|\psi\rangle = \begin{pmatrix} \sqrt{\frac{1+a}{2}} \\ 0 \\ \sqrt{\frac{1-a}{2}}\,\mathrm{e}^{i\phi} \end{pmatrix},$$

with just one free parameter, the phase ϕ. In the special subcase $a = 1$, this reduces to the unique solution $|1,1\rangle$.

The case $a = 0$ requires special treatment. Now $|y|$ need not vanish, and we see from Eq.(6.6) that in general $|x| = |z| = \alpha$, say. If we fix the overall phase by requiring y to be real, then Eq.(6.4) implies that $z = -x^*$; and the normalization condition Eq.(6.5) yields $y = \sqrt{1-2\alpha^2}$. The general solution is

$$|\psi\rangle = \begin{pmatrix} \alpha\,\mathrm{e}^{i\phi} \\ \sqrt{1-2\alpha^2} \\ -\alpha\,\mathrm{e}^{-i\phi} \end{pmatrix},$$

which depends on two parameters, α and ϕ.

The above considerations apply to pure states. More generally, a state can be expressed by an operator of the form

$$\rho = \sum_{i=-1}^{1}\sum_{j=-1}^{1} \rho_{ij}|1,i\rangle\langle 1,j|\,,$$

where $\rho_{ij} = \rho_{ji}^*$, i.e., the operator ρ is Hermitian. Thus there are 3 real diagonal elements, but of these only two are independent, because of the normalization condition, $\mathrm{Tr}\rho = 1$. There are 3 complex elements above the diagonal, thus 6 real numbers that determine the nondiagonal elements above and below the diagonal. The conditions $\langle S_1\rangle = 0 = \langle S_2\rangle$ and $\langle S_3\rangle = a$ yield 3 real constraints

on these 8 real numbers, thus leaving 5 real parameters for the general solution, say $c_1 \ldots c_5$.

$$\rho = \begin{pmatrix} c_1 & c_2 + ic_3 & c_4 + ic_5 \\ c_2 - ic_3 & 1 + a - 2c_1 & -c_2 - ic_3 \\ c_4 - ic_5 & -c_2 + ic_3 & c_1 - a \end{pmatrix}.$$

We see therefore that there is much more freedom for a general state than for a pure state.

6.8 Spin of a Neutron

The spin of a neutron is aligned with the z-axis. What is the probability that

(1) a spin measurement along an axis at angle θ to z will yield $\frac{1}{2}\hbar$?
(2) a subsequent measurement (i.e., after a successful measurement as above) along the z-axis will yield a result $-\frac{1}{2}\hbar$?
(3) Suppose now instead that after the successful measurement (a) above, the measurement (b) is made but not recorded. What is now the probability that a subsequent measurement of spin along an axis at angle θ to z will yield the result $\frac{1}{2}\hbar$?

Solution
Define the unit vector, $\vec{n} = (\sin\theta, 0, \cos\theta)$, which is at an angle θ to the z-axis. The eigenvalues of $\vec{\sigma} \cdot \vec{n}$ are ± 1, and with

$$\vec{\sigma} \cdot \vec{n} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \pm \begin{pmatrix} a_1 \\ a_2 \end{pmatrix},$$

we find $a_1(\pm 1 - \cos\theta) = a_2 \sin\theta$. This yields the normalized eigenvectors

$$\begin{pmatrix} \cos\frac{1}{2}\theta \\ \sin\frac{1}{2}\theta \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} \sin\frac{1}{2}\theta \\ -\cos\frac{1}{2}\theta \end{pmatrix}, \tag{6.8}$$

belonging to the eigenvalues 1 and -1, respectively.
(1) The probability amplitude corresponding to a spin measurement of $\frac{1}{2}\hbar$ in the direction of $\vec{n}$ is the matrix product of $(1, 0)$ with the first of the eigenvectors in Eq.(6.8), i.e., $\cos\frac{1}{2}\theta$, so the probability is the square of that, $\cos^2\frac{1}{2}\theta$.
(2) After a successful measurement of spin $\frac{1}{2}\hbar$ in the direction of $\vec{n}$, the state of the neutron is represented by the eigenvector of $\vec{\sigma} \cdot \vec{n}$ belonging to eigenvalue $+1$. A subsequent spin measurement in the original z-direction amounts again to a projection at an angle θ, with probability amplitudes $\cos\frac{1}{2}\theta$ for the result $\frac{1}{2}\hbar$, and

$\sin\frac{1}{2}\theta$ for the result $-\frac{1}{2}\hbar$. Accordingly, the probability that the measurement yields $-\frac{1}{2}\hbar$ is $\sin^2\frac{1}{2}\theta$.
(3) Since a measurement of the type (2) has been made, the state vector has been projected on to either spin up or spin down, with respect to the direction of $\vec{n}$. If this measurement *had yielded* $\frac{1}{2}\hbar$, and this fact were known, then the probability that a subsequent measurement in the z-direction would yield $\frac{1}{2}\hbar$ is $\cos^2\frac{1}{2}\theta$. However, the probability that the measurement of the type (2) yields $\frac{1}{2}\hbar$ is itself $\cos^2\frac{1}{2}\theta$, so the contribution to the probability of an outcome $\frac{1}{2}\hbar$ is $\cos^4\frac{1}{2}\theta$. This is not the end of the story, for if the measurement of the type (2) had yielded $-\frac{1}{2}\hbar$ rather than $\frac{1}{2}\hbar$, and had this been known, then the probability that a subsequent measurement in the z-direction would yield $\frac{1}{2}\hbar$ is $\sin^2\frac{1}{2}\theta$. The probability that the measurement of the type (2) yields $\frac{1}{2}\hbar$, given that the measurement of the type (2) yields $-\frac{1}{2}\hbar$, is itself $\sin^2\frac{1}{2}\theta$, so the contribution to the probability of an outcome $\frac{1}{2}\hbar$ is $\sin^4\frac{1}{2}\theta$. Accordingly, the final result for the probability in question is

$$P(\theta) = \cos^4\tfrac{1}{2}\theta + \sin^4\tfrac{1}{2}\theta = \tfrac{1}{2}(1+\cos^2\theta)\,.$$

Note that $P(\theta)$ attains its maximum (1) for $\theta = 0$ or π, and its minimum $(\frac{1}{2})$ for $\theta = \pi/2$.

The probabilities in (1) and (2) may be termed objective, while that in (3) is subjective, since it depends on the ignorance of the experimenter as to the result of the measurement (2). More technically, one speaks in the first case of ontological probabilities (referring to actual *propensities* of the world, according to quantum mechanics); and in the second case of epistemological probabilities (relating to states of ignorance, or incomplete knowledge).

6.9 Bell's Theorem with Neutrons

Suppose that two neutrons are created in the singlet state. They fly apart; the spin of one particle is measured in the direction a, the other in the direction b.

(1) Calculate the relative frequencies of the coincidences R(up,up), R(up,down), R(down,up) and R(down, down), as a function of θ, the angle between a and b.
(2) Calculate the correlation coefficient

$$C(a,b) = \mathrm{R(up,up)} - \mathrm{R(up,down)} - \mathrm{R(down,up)} + \mathrm{R(down,down)}\,.$$

(3) Given two possible directions, a and a', for one measurement, and two possible directions, b and b', for the other, deduce the maximum possible value for the Bell coefficient, defined by

$$B = C(a,b) + C(a',b) + C(a',b') - C(a,b') .$$

(4) Show that this prediction of quantum mechanics is inconsistent with classical local realism.

Solution

(1) Let $|z^{\pm}(\theta)\rangle$ be states corresponding to spin up (down), with respect to a direction at an angle θ to the z-axis. According Eq.(6.8) of the solution to the previous problem, we can write

$$\begin{aligned} |z^{+}(\theta)\rangle = \begin{pmatrix} \cos\frac{1}{2}\theta \\ \sin\frac{1}{2}\theta \end{pmatrix} &= \cos\tfrac{1}{2}\theta \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \sin\tfrac{1}{2}\theta \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ &= \cos\tfrac{1}{2}\theta|z^{+}\rangle + \sin\tfrac{1}{2}\theta|z^{-}\rangle , \end{aligned}$$

where $|z^{\pm}\rangle$ means $|z^{\pm}(0)\rangle$. Similarly,

$$|z^{-}(\theta)\rangle = \begin{pmatrix} \sin\frac{1}{2}\theta \\ -\cos\frac{1}{2}\theta \end{pmatrix} = \sin\tfrac{1}{2}\theta|z^{+}\rangle - \cos\tfrac{1}{2}\theta|z^{-}\rangle .$$

The singlet state can be written

$$|EPR\rangle = \frac{1}{\sqrt{2}}\left\{|z^{+}\rangle^{a}|z^{-}\rangle^{b} - |z^{-}\rangle^{a}|z^{+}\rangle^{b}\right\} ,$$

so the probability amplitude associated with a measurement of spin up along the z-axis at a, and (i) a measurement of of spin up at b along a direction at an angle θ to the z-axis, is

$$\begin{aligned} \langle EPR|z^{+}\rangle^{a}|z^{+}(\theta)\rangle^{b} &= \langle EPR|z^{+}\rangle^{a}\left\{\cos\tfrac{1}{2}\theta|z^{+}\rangle^{b} + \sin\tfrac{1}{2}\theta|z^{-}\rangle^{b}\right\} \\ &= \frac{1}{\sqrt{2}}\,{}^{b}\langle z^{-}|\cos\tfrac{1}{2}\theta\, z^{+} + \sin\tfrac{1}{2}\theta\, z^{-}\rangle^{b} \\ &= \frac{1}{\sqrt{2}}\sin\tfrac{1}{2}\theta , \end{aligned}$$

or (ii) a measurement of spin down at b at an angle θ to the z-axis is

$$\begin{aligned} \langle EPR|z^{+}\rangle^{a}|z^{-}(\theta)\rangle^{b} &= \langle EPR|z^{+}\rangle^{a}\left\{\sin\tfrac{1}{2}\theta|z^{+}\rangle^{b} - \cos\tfrac{1}{2}\theta|z^{-}\rangle^{b}\right\} \\ &= \frac{1}{\sqrt{2}}\,{}^{b}\langle z^{-}|\sin\tfrac{1}{2}\theta z^{+} - \cos\tfrac{1}{2}\theta z^{-}\rangle^{b} \\ &= -\frac{1}{\sqrt{2}}\cos\tfrac{1}{2}\theta . \end{aligned}$$

So quantum mechanics predicts for the relative frequencies of the coincidences R(up,up)= $\frac{1}{2}\sin^2\frac{1}{2}\theta$, and R(up,down)= $\frac{1}{2}\cos^2\frac{1}{2}\theta$. By similar reasoning, we find R(down,down)= $\frac{1}{2}\sin^2\frac{1}{2}\theta$, and R(down,up)= $\frac{1}{2}\cos^2\frac{1}{2}\theta$.

(2) The correlation coefficient is therefore

$$C(a,b) = \tfrac{1}{2}\sin^2\tfrac{1}{2}\theta - \tfrac{1}{2}\cos^2\tfrac{1}{2}\theta - \tfrac{1}{2}\cos^2\tfrac{1}{2}\theta + \tfrac{1}{2}\sin^2\tfrac{1}{2}\theta = -\cos\theta\,.$$

(3) Let us call the angles between a and b, b and a', and a' and b' respectively $\pi - x$, $\pi - y$ and $\pi - z$, the angle between a and b' being $3\pi - x - y - z$. Then we find

$$B = \cos x + \cos y + \cos z - \cos(x + y + z)\,,$$

and we can use the method of part (3) of the solution to problem (1.10) to show that the maximum value that B can attain is $\sqrt{2}$.

(4) This prediction of quantum mechanics is inconsistent with classical local realism, as can be seen by the method of part (1) of the solution to problem (1.10). Just as in the case for an entangled state of photons, here also the assumption of the existence of local hidden variables, and of separability of the joint conditional probabilities, leads to the Bell inequality, $|B| \leq 2$, which is violated by the quantum mechanical prediction for the angles $x = y = z = \pi/4$.

6.10 Greenberger-Horne-Zeilinger State

The Greenberger-Horne-Zeilinger (GHZ) state of three identical spin-$\frac{1}{2}$ particles is defined by

$$|GHZ\rangle = \frac{1}{\sqrt{2}}\left[z_a^+ z_b^+ z_c^+ - z_a^- z_b^- z_c^-\right]\,,$$

where z_a^+ is the eigenket of the z-component of the spin operator of particle a belonging to eigenvalue $\frac{1}{2}\hbar$ (z-spin up), z_a^- is the eigenket belonging to eigenvalue $-\frac{1}{2}\hbar$ (z-spin down), and similarly for the particles b and c. Show that, if spin measurements are made on the three particles in the x- or y-directions,

(1) the product of three spins in the x-direction is always $-\frac{1}{8}\hbar^3$,
(2) the product of two spins in the y-direction and one spin in the x-direction is always $\frac{1}{8}\hbar^3$.
(3) Consider a prize game for a team of three players, A, B, and C. The players are told that they will be separated from one another and that each will be asked one of two questions, say X or Y, to which each must

give one of two allowed answers, namely $+1$ or -1. Moreover, *either*

(a) all players will be asked the same question X,
or
(b) one of the three players will be asked X and the other two Y.

After having been asked X or Y, no player may communicate with the others until after all three players have given their answers, 1 or -1. To win the game, the players must give answers such that, in case (a) the product of the three answers is -1, whereas in case (b) the product of the three answers is $+1$.

(a) Show that no classical strategy gives certainty of a win for the team.
(b) Show that a quantum strategy, in which each player may take one of the GHZ particles with her, exists for which a win is certain.

Solution

The spin operator, $\vec{S}$, of an electron can be represented by $\frac{1}{2}\hbar\vec{\sigma}$, where the Cartesian components of $\vec{\sigma}$ are the Pauli matrices. Normalized eigenvectors of the matrices σ_x, σ_y and σ_z, belonging to the eigenvalues $+1$ and -1, are respectively

$$x^+ = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad x^- = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \qquad \sigma_x x^\pm = \pm x^\pm$$

$$y^+ = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix} \qquad y^- = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix} \qquad \sigma_y y^\pm = \pm y^\pm$$

$$z^+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad z^- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \qquad \sigma_z z^\pm = \pm z^\pm$$

We find the following relations between these eigenvectors:

$$z^+ = \left(x^+ + x^-\right)/\sqrt{2} = \left(y^+ + y^-\right)/\sqrt{2}$$

$$z^- = \left(x^+ - x^-\right)/\sqrt{2} = -i\left(y^+ - y^-\right)/\sqrt{2}$$

Hence the GHZ vector can be written in the following five ways

$$
\begin{aligned}
|GHZ\rangle &= \left[z_a^+ z_b^+ z_c^+ - z_a^- z_b^- z_c^-\right]/\sqrt{2} \\
&= \tfrac{1}{2}\left[x_a^+ x_b^+ x_c^- + x_a^- x_b^+ x_c^+ + x_a^+ x_b^- x_c^+ + x_a^- x_b^- x_c^-\right] \\
&= \tfrac{1}{2}\left[x_a^+ y_b^- y_c^- + x_a^- y_b^+ y_c^- + x_a^- y_b^- y_c^+ + x_a^+ y_b^+ y_c^+\right] \\
&= \tfrac{1}{2}\left[y_a^+ x_b^- y_c^- + y_a^- x_b^+ y_c^- + y_a^- x_b^- y_c^+ + y_a^+ x_b^+ y_c^+\right] \\
&= \tfrac{1}{2}\left[y_a^+ y_b^- x_c^- + y_a^- y_b^+ x_c^- + y_a^- y_b^- x_c^+ + y_a^+ y_b^+ x_c^+\right]
\end{aligned}
$$

It follows then that

$$
\begin{aligned}
|GHZ\rangle &= -\sigma_x^a \sigma_x^b \sigma_x^c |GHZ\rangle \\
&= \sigma_x^a \sigma_y^b \sigma_y^c |GHZ\rangle = \sigma_y^a \sigma_x^b \sigma_y^c |GHZ\rangle = \sigma_y^a \sigma_y^b \sigma_x^c |GHZ\rangle \qquad (6.9)
\end{aligned}
$$

(1) From the first line of Eq.(6.9), we see that the GHZ state is an eigenvector of the product of the three Pauli matrices, σ_x, belonging to eigenvalue -1. Since the $x-$component of spin is represented by $\frac{1}{2}\hbar\sigma_x$, it follows that a measurement of the product of three spins in the x-direction is certainly $-\frac{1}{8}\hbar^3$.

(2) From the second line of Eq.(6.9), we see that the GHZ state is an eigenvector of the product of one Pauli matrix, σ_x, and two Pauli matrices, σ_y, belonging to eigenvalue $+1$. It follows that a measurement of two spins in the y-direction and one spin in the x-direction is certainly $\frac{1}{8}\hbar^3$.

(3a) What is the best strategy upon which the players might agree? Let $A(X)$ be the agreed answer that A will give if asked the X question, and $A(Y)$ the agreed answer if she is instead asked the Y question. $B(X)$, $B(Y)$, $C(X)$ and $C(Y)$ are similarly defined, and note that we do not restrict our proof of impossibility to the symmetric situation in which A, B and C necessarily give the same answers as each other in the case that they are asked the same question. In order to guarantee success when all players are asked the X question, we need

$$A(X)B(X)C(X) = -1\,. \qquad (6.10)$$

If, however, A is asked X, but B and C are asked Y, then we need

$$A(X)B(Y)C(Y) = +1\,. \qquad (6.11)$$

In the same way, if B is asked X but A and C are asked Y, we need

$$A(Y)B(X)C(Y) = +1\,, \qquad (6.12)$$

and finally if A and B are asked Y but C is asked X, then we need

$$A(Y)B(Y)C(X) = +1\,. \qquad (6.13)$$

In order to be sure of winning, the team needs all of the above equations (6.10)-(6.13) to hold, so that a winning combination of answers is given, no matter which permutation of questions is asked. To see that these equations are not mutually consistent, multiply all the left-hand sides together and equate the answer to the product of all the right-hand sides, which latter is clearly -1. However, the product of all the left-hand sides contains *each* of the assignments, $A(X)$, $A(Y)$, $B(X)$, $B(Y)$, $C(X)$, $C(Y)$, *twice*, i.e. every possible assignment occurs as its square. Since each assignment is $+1$ or -1, the square is in all cases $+1$, and so the product of all the left-hand sides is $+1$, contradicting the fact that the product of the right-hand sides is -1.

(3b) The quantum strategy consists in *not* deciding in advance on the various assignments, $A(X)$, $A(Y)$, $B(X)$, $B(Y)$, $C(X)$, $C(Y)$, but rather in agreeing on a measurement procedure, the precise nature of which depends on whether the X or the Y question is asked. On being separated, each player takes with her one of the three electrons that have been prepared in the GHZ state. They all know what the x, y and z directions are, and each player has an apparatus that can measure whether the spin of the electron is 'up' or 'down' with respect to any of these directions. If a player is asked the X question, she orients her apparatus in the x direction, and makes a spin measurement. If she finds that the x component of spin is 'up', then she gives the answer $+1$, and if it is 'down', she says -1. However, if she is asked the Y question, then she orients her apparatus in the y direction before making her spin measurement. In this case her answer, $+1$ or -1, is conditioned by the result of the y spin measurement. The classical impossibility proof has been evaded by the expedient of allowing the answers to depend on the results of three measurements, results that are individually indeterminate, but which are correlated in such a way that the game can certainly be won on every playing (100% probability of success).

Chapter 7

Perturbation Theory

7.1 First-Order Perturbation with Spins

Let $\vec{s}_1$ and $\vec{s}_2$ be the spin operators of two spin $\frac{1}{2}$ particles. Then

$$\vec{S} = \vec{s}_1 + \vec{s}_2$$

is the spin operator for this two-particle system.

(1) Consider the Hamiltonian $H_0 = (S_x^2 + S_y^2 - S_z^2)/\hbar^2$. Determine the eigenvalues and eigenvectors of this Hamiltonian.

(2) Consider the perturbation $H_1 = s_{1x} - s_{2x}$. Calculate the eigenvalues of $H_0 + \lambda H_1$ in first-order perturbation theory.

Solution

(1) We can write $H_0 = (S^2 - 2S_z^2)/\hbar^2$, where S^2 is the square of the total spin operator. The eigenvectors of H_0 can be labeled $|s, m\rangle$, where s is the total spin quantum number, which can be 0 or 1, and m is the quantum number of the z component of the spin. We find $H_0|s, m\rangle = [s(s+1) - 2m^2]|s, m\rangle$, so

$$\begin{aligned} H_0|0,0\rangle &= H_0|1,1\rangle = H_0|1,-1\rangle = 0 \\ H_0|1,0\rangle &= 2|1,0\rangle\,. \end{aligned}$$

There are thus two eigenvalues of H_0, namely 0, which is triply degenerate, and 2, which is simple. The eigenvectors are

$$\begin{aligned} |1,1\rangle &= |\tfrac{1}{2}\rangle^1 |\tfrac{1}{2}\rangle^2 \\ |1,0\rangle &= \tfrac{1}{\sqrt{2}}\Big(|\tfrac{1}{2}\rangle^1 |-\tfrac{1}{2}\rangle^2 + |-\tfrac{1}{2}\rangle^1 |\tfrac{1}{2}\rangle^2 \Big) \\ |1,-1\rangle &= |-\tfrac{1}{2}\rangle^1 |-\tfrac{1}{2}\rangle^2 \\ |0,0\rangle &= \tfrac{1}{\sqrt{2}}\Big(|\tfrac{1}{2}\rangle^1 |-\tfrac{1}{2}\rangle^2 - |-\tfrac{1}{2}\rangle^1 |\tfrac{1}{2}\rangle^2 \Big)\,. \end{aligned}$$

(2) Since

$$s_x|\tfrac{1}{2}\rangle = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2}|-\tfrac{1}{2}\rangle$$

and similarly $s_x|-\frac{1}{2}\rangle = \frac{\hbar}{2}|\frac{1}{2}\rangle$, it follows that

$$\begin{aligned} H_1|1,1\rangle &= \tfrac{1}{2}\hbar\Big(-|\tfrac{1}{2}\rangle^1|-\tfrac{1}{2}\rangle^2 + |-\tfrac{1}{2}\rangle^1|\tfrac{1}{2}\rangle^2\Big) = -\tfrac{\hbar}{\sqrt{2}}|0,0\rangle \\ H_1|1,0\rangle &= \tfrac{1}{2}\hbar\Big(|\tfrac{1}{2}\rangle^1|\tfrac{1}{2}\rangle^2 + |-\tfrac{1}{2}\rangle^1|-\tfrac{1}{2}\rangle^2 - |\tfrac{1}{2}\rangle^1|\tfrac{1}{2}\rangle^2 - |-\tfrac{1}{2}\rangle^1|-\tfrac{1}{2}\rangle^2\Big) = 0 \\ H_1|1,-1\rangle &= \tfrac{1}{2}\hbar\Big(|\tfrac{1}{2}\rangle^1|-\tfrac{1}{2}\rangle^2 - |-\tfrac{1}{2}\rangle^1|\tfrac{1}{2}\rangle^2\Big) = \tfrac{\hbar}{\sqrt{2}}|0,0\rangle\,. \end{aligned}$$

Hence $\langle 1,0|H_1|1,0\rangle = 0$, which means that the eigenvector, $|1,0\rangle$, of energy 2, is not shifted by the perturbation, to first order. Among the matrix elements involving the degenerate eigenvectors, the only nonzero ones are

$$\langle 0,0|H_1|1,-1\rangle = \tfrac{\hbar}{\sqrt{2}} = -\langle 0,0|H_1|1,1\rangle\,,$$

and their Hermitian conjugates. Accordingly, the perturbed energy levels are given by the zeros of the determinant

$$\begin{Vmatrix} E(\lambda) & -\frac{\lambda\hbar}{\sqrt{2}} & 0 \\ -\frac{\lambda\hbar}{\sqrt{2}} & E(\lambda) & \frac{\lambda\hbar}{\sqrt{2}} \\ 0 & \frac{\lambda\hbar}{\sqrt{2}} & E(\lambda) \end{Vmatrix},$$

which reduces to $E(\lambda)\Big(E^2(\lambda) - \lambda^2\hbar^2\Big) = 0$. Thus the degenerate levels are split into three simple levels, $E(\lambda) = 0$ and $E(\lambda) = \pm\lambda\hbar$.

7.2 Second-Order Perturbation with Spins

Two spin-half particles, 1 and 2, have the unperturbed Hamiltonian

$$H_0 = -A(s_{1z} + s_{2z}).$$

A perturbing Hamiltonian is brought to bear of the form

$$H_1 = B(s_{1x}s_{2x} - s_{1y}s_{2y})\,.$$

(1) Calculate the eigenvalues and the eigenfunctions of H_0.
(2) Calculate the exact eigenvalues of $H_0 + H_1$.
(3) By means of perturbation theory, calculate the first- and the second-order shifts of the ground state energy of H_0, as a consequence of the perturbation H_1. Compare these results with those of (2).

Solution

(1) The state in which both spins are 'up' corresponds to the eigenvalue $-2A$, that in which both spins are 'down' to the eigenvalue $2A$, while the two states in which one spin is 'up' and one is 'down' correspond to the eigenvalue 0.

(2) In terms of $\sigma_\pm = \sigma_x \pm i\sigma_y$, we can write $H_1 = \frac{1}{2}B[\sigma_{1+}\sigma_{2+} + \sigma_{1-}\sigma_{2-}]$, so

$$\begin{aligned} H_1|\mathsf{up},\mathsf{up}\rangle &= 2B\,|\mathsf{down},\mathsf{down}\rangle \\ H_1|\mathsf{down},\mathsf{down}\rangle &= 2B\,|\mathsf{up},\mathsf{up}\rangle \\ H_1|\mathsf{up},\mathsf{down}\rangle &= 0 \\ H_1|\mathsf{down},\mathsf{up}\rangle &= 0\,. \end{aligned} \tag{7.1}$$

The latter two states are eigenvectors of the complete Hamiltonian, $H_0 + H_1$, corresponding to the eigenvalue 0, and of course one may replace them by any orthonormal combination, for example the symmetric and antisymmetric states, $[|\mathsf{up},\mathsf{down}\rangle \pm |\mathsf{down},\mathsf{up}\rangle]/\sqrt{2}$. To obtain the other eigenvectors, consider

$$(H_0+H_1)[\cos\theta|\mathsf{up},\mathsf{up}\rangle+\sin\theta|\mathsf{down},\mathsf{down}\rangle] = \lambda[\cos\theta|\mathsf{up},\mathsf{up}\rangle+\sin\theta|\mathsf{down},\mathsf{down}\rangle]\,.$$

On using the above results, and equating coefficients of the two orthogonal states, $|\mathsf{up},\mathsf{up}\rangle$ and $|\mathsf{down},\mathsf{down}\rangle$, we find

$$\begin{aligned} (2A+\lambda)\cos\theta &= 2B\sin\theta \\ (2A-\lambda)\sin\theta &= 2B\cos\theta\,, \end{aligned}$$

and hence

$$\lambda = \pm 2\sqrt{A^2+B^2}\,.$$

For $\lambda = -2\sqrt{A^2+B^2}$, we obtain

$$\tan\theta = \frac{A}{B} - \sqrt{1+\frac{A^2}{B^2}}\,,$$

and on inserting this value into

$$\cos\theta|\mathsf{up},\mathsf{up}\rangle + \sin\theta|\mathsf{down},\mathsf{down}\rangle$$

we get the ground state eigenvector. For $\lambda = 2\sqrt{A^2+B^2}$, we obtain

$$\tan\theta = \frac{A}{B} + \sqrt{1+\frac{A^2}{B^2}}\,,$$

and on using this we get the eigenvector corresponding to the highest energy.

(3) From Eq.(7.1) we find $\langle H_1 \rangle = 0$ for all of the four independent vectors, so the first order perturbation of the eigenvalues of H_0 by H_1 is zero. To second order, the only contribution to the ground state energy, $-2A$ (we suppose $A > 0$), comes from the matrix element

$$\langle \text{down, down}|H_1|\text{up, up}\rangle = 2B\,,$$

and so, to second order in B, the ground state energy is

$$-2A + \frac{\left|\langle \text{down, down}|H_1|\text{up, up}\rangle\right|^2}{(-2A) - (2A)} = -2A - \frac{B^2}{A}\,,$$

which agrees with the exact result, $-2\sqrt{A^2 + B^2}$, to order B^2.

7.3 Zeeman and Stark Effects

Suppose that a hydrogen atom is exposed to a uniform electric field, $\vec{\mathcal{E}}$, and a parallel, uniform magnetic induction, $\vec{B}$. Consider the first excited energy level, corresponding to $n = 2$, which is quadruply degenerate if $\vec{\mathcal{E}} = 0 = \vec{B}$.

(1) Show that in general the level is split into four nondegenerate energy levels.
(2) For what values of $\vec{\mathcal{E}}$ and $\vec{B}$ are there instead only three levels, and what are the degeneracies of these levels?
(3) For what values of $\vec{\mathcal{E}}$ and $\vec{B}$ are there only two levels, and what are the degeneracies of these levels?

In the answers, assume that the fields are strong compared with the fine structure effects, and ignore the complications caused by the electron spin.

Solution

Let $\{|\psi_n^i\rangle\}$, $j = 1, 2, \ldots, N$, be a set of degenerate eigenvectors belonging to the energy eigenvalue $E_n^{(0)}$ of the Hamiltonian H_0. If E_n is an eigenvalue of the perturbed Hamiltonian, $H_0 + H_1$, where H_1 is small, we have

$$\det\left\{[E_n^{(0)} - E_n]\,\delta_{ij} + \langle\psi_n^i|H_1|\psi_n^j\rangle\right\} = 0\,, \tag{7.2}$$

according to first-order perturbation theory for degenerate states. In our case, the set of eigenvectors belonging to the energy eigenvalue $E_2^{(0)} = -me^4/(8\hbar^2)$ is $\{|2,0,0\rangle, |2,1,1\rangle, |2,1,0\rangle, |2,1,-1\rangle\}$, and the perturbation is

$$H_1 = e\mathcal{E}r\cos\theta - \frac{eB}{2mc}L_3\,,$$

(see Sections 3.3 and 7.4 of Volume 1). The only nonvanishing matrix elements of H_1 are

$$\begin{aligned}\langle 2,1,0|H_1|2,0,0\rangle = \langle 2,0,0|H_1|2,1,0\rangle &= -3e\mathcal{E} \\ \langle 2,1,1|H_1|2,1,1\rangle = -\langle 2,1,-1|H_1|21,-1\rangle &= -\frac{eB}{2mc}.\end{aligned}$$

The determinant condition Eq.(7.2) is in our case

$$\begin{Vmatrix} \Delta & 0 & -3e\mathcal{E} & 0 \\ 0 & \Delta - \frac{eB}{2mc} & 0 & 0 \\ -3e\mathcal{E} & 0 & \Delta & 0 \\ 0 & 0 & 0 & \Delta + \frac{eB}{2mc} \end{Vmatrix} = 0, \tag{7.3}$$

where $\Delta = E_n - E_n^{(0)}$. This reduces to $\left(\Delta^2 - \frac{e^2B^2}{4m^2c^2}\right)\left(\Delta^2 - 9e^2\mathcal{E}^2\right) = 0$.

(1) There are four solutions of Eq.(7.3), namely

$$E_n = E_n^{(0)} \pm \frac{eB}{2mc} \tag{7.4}$$

$$E_n = E_n^{(0)} \pm 3e\mathcal{E}, \tag{7.5}$$

which are in general distinct. Thus the fourfold degeneracy of the $n = 2$ energy level has been completely lifted: the four perturbed energy levels are simple (i.e., nondegenerate).

(2) If $\mathcal{E} = 0$, while $B \neq 0$, only the $m = 1$ and $m = -1$ are shifted, the two $m = 0$ states remaining degenerate at the unperturbed energy value. If, on the other hand, $\mathcal{E} \neq 0$, while $B = 0$, the $m = 1$ and $m = -1$ now are not shifted, remaining degenerate at the unperturbed energy value, while the two $m = 0$ states are shifted, resulting in two simple states. So in either of the two cases,

$$\mathcal{E} = 0 \text{ and } B \neq 0, \text{ or } \mathcal{E} \neq 0 \text{ and } B = 0,$$

we have three energy levels, the outer two being simple and the central one being doubly degenerate.

(3) If $B = 6mc\mathcal{E}$ or $B = -6mc\mathcal{E}$, i.e, the electric field and the magnetic inductions have strengths that are in a special relation to one another, then there are only two levels, each doubly degenerate. This is clear, since in this case the energies in Eq.(7.4) and Eq.(7.5) coincide.

7.4 Coulomb Potential and 3D Oscillator

An electron is in a superposition of the Coulomb and the 3D oscillator potential:

$$V(r) = -\frac{e^2}{r} + \lambda r^2 .$$

(1) What is the shift of the ground state energy to first order in λ?
(2) How large must λ be in order that the ground state have zero energy?
(3) What are the first-order shifts of the $n = 2$ energies?

Solution

(1) The normalized ground-state wave function of the hydrogen atom is

$$\psi_{100}(r) = \left(\pi a_0^3\right)^{-\frac{1}{2}} e^{-r/a_0},$$

with $a_0 = \hbar^2/(me^2)$, the Bohr radius. The energy of the ground state, to first order in λ, is $E_1 + \Delta E_1$, where $E_1 = -me^4/(2\hbar^2)$, and

$$\Delta E_1 = \frac{\lambda}{\pi a_0^3} \int d^3r\, r^2 \exp(-2r/a_0) = \frac{3\lambda\hbar^4}{m^2e^4} .$$

(2) Setting $\lambda = \frac{1}{2}m\omega^2$ for convenience, we find

$$E_1 + \Delta E_1 = -\frac{me^4}{2\hbar^2} + \frac{3\hbar^4\omega^2}{2me^4},$$

and this vanishes if

$$\omega = \frac{me^4}{\sqrt{3}h^3} .$$

This condition may be rewritten $E_0 = -\sqrt{3}E_1 \approx -1.7321\, E_1$, where $E_0 = \frac{3}{2}\hbar\omega$, the ground-state energy of the isotropic oscillator in three dimensions.

One may reasonably question the accuracy of this result, given that the perturbation is not small (indeed, a potential r^2 is large compared to r^{-1}, for large values of r). Let us then turn the calculation around by treating the Coulomb term as a perturbation of the oscillator potential. The normalized ground-state wave function of the isotropic oscillator is

$$\phi_0(r) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{3}{4}} \exp\left[-\frac{m\omega r^2}{2\hbar}\right],$$

and so the energy of the perturbed state, to first order in e^2, is $E_0 + \Delta E_0$, where

$$\Delta E_0 = -e^2 \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{3}{2}} \int d^3r\, r^{-1} \exp\left[-\frac{m\omega r^2}{\hbar}\right] = -2e^2 \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}} .$$

The condition $E_0 + \Delta E_0 = 0$ can be written $\omega = 16me^4/(9\pi h^3)$, or in other words $E_0 = 16E_1/(3\pi) \approx -1.6977\,E_1$, which agrees within a couple of percent with the previous estimate. One may show by direct integration that the zero energy bound state occurs when $E_0 = -1.7862E_1$.

(3) The four degenerate states of the hydrogen atom, $\psi_{2\ell m}$, corresponding to energy $E_2 = -me^4/(8\hbar^2)$, yield the following expectation values:

$$\begin{aligned}
\langle\psi_{200}|r^2|\psi_{200}\rangle &= \frac{1}{8}\int_0^\infty dr\, r^4(2-r)^2\,\mathrm{e}^{-r} = 42 \\
\langle\psi_{210}|r^2|\psi_{210}\rangle &= \frac{1}{16}\int_0^\infty dr\, r^4\,\mathrm{e}^{-r}\int_{-1}^{1} dz\, z^2 = 1 \\
\langle\psi_{211}|r^2|\psi_{211}\rangle = \langle\psi_{21,-1}|r^2|\psi_{21,-1}\rangle &= \frac{1}{32}\int_0^\infty dr\, r^4\,\mathrm{e}^{-r}\int_{-1}^{1} dz\,(1-z^2) = 1\,.
\end{aligned}$$

Since all nondiagonal terms vanish, we find two shifts, of magnitudes 42λ and λ. The S wave has energy $E_{20} = E_2 + 42\lambda$ and this state is nondegenerate; but the P wave is triply degenerate, with energy $E_{21} = E_2 + \lambda$. Note that, since the potential is spherically symmetric, the energies may not depend on the magnetic quantum number, m, but they may depend on ℓ. It is interesting to see that indeed the ℓ-degeneracy, which the energy eigenvalues of *both* the Coulomb and the oscillator potentials possess when they act alone, is broken when they act together. The reason is that, in the combined potential, the 'hidden symmetries' have been broken [$U(3)$ for the oscillator and $SO(3) \times SO(3)$ for the Coulomb, see the solutions to problems 4.10 and 5.10].

7.5 Two Dimensional Oscillator

Consider the two-dimensional oscillator Hamiltonian,

$$H_0 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2\,,$$

with the perturbation

$$H_1 = \lambda q_1 q_2\,.$$

(1) Calculate the energy shift of the ground state in first- and second-order perturbation theory.
(2) Calculate the energy shift of the first excited state in first-order perturbation theory.
(3) Calculate the first two energy levels exactly.

Solution

(1) In terms of creation and annihilation operators, the perturbation is

$$H_1 = \frac{\lambda\hbar}{2m\omega}\left(a_1 + a_1^\dagger\right)\left(a_2 + a_2^\dagger\right),$$

and since

$$H_1|0,0\rangle = \lambda\hbar/(2m\omega)|1,1\rangle,$$

it follows that the first order perturbation of the ground state energy is zero. To second order, the ground state energy reduces to

$$E(\lambda) = \hbar\omega + \frac{\left|\langle 1,1|H_1|0,0\rangle\right|^2}{E_0(0,0) - E_0(1,1)} = \hbar\omega + \frac{\lambda^2\hbar}{8m^2\omega^3}.$$

(2) The energy of the first two (degenerate) excited states of H_0, namely $|1,0\rangle$ and $|0,1\rangle$, is $2\hbar\omega$. We find

$$\begin{aligned} H_1|1,0\rangle &= \lambda\hbar/(2m\omega)\left[\,|0,1\rangle + \sqrt{2}|2,1\rangle\right] \\ H_1|0,1\rangle &= \lambda\hbar/(2m\omega)\left[\,|1,0\rangle + \sqrt{2}|1,2\rangle\right], \end{aligned}$$

and in terms of the symmetric and antisymmetric combinations,

$$|\psi_\pm\rangle = \left[\,|1,0\rangle \pm |0,1\rangle\right]/\sqrt{2},$$

we have

$$\langle\psi_\pm|H_1|\psi_\pm\rangle = \pm\lambda\hbar/(2m\omega).$$

In first order perturbation, the first excited level is split into

$$E_\pm(\lambda) = 2\hbar\omega \pm \frac{\lambda\hbar}{2m\omega},$$

of which $E_-(\lambda)$ is the lower, if $\lambda > 0$, while $E_+(\lambda)$ is the lower, if $\lambda < 0$.

(3) To calculate the energy levels exactly, transform from $\{(q_1,p_1),(q_2,p_2)\}$ to

$$\begin{aligned} \bar{q}_1 &= [q_1 + q_2]/\sqrt{2} \qquad & \bar{p}_1 &= [p_1 + p_2]/\sqrt{2} \\ \bar{q}_2 &= [q_1 - q_2]/\sqrt{2} \qquad & \bar{p}_2 &= [p_1 - p_2]/\sqrt{2}. \end{aligned}$$

Note that $q_1q_2 = \frac{1}{2}[\bar{q}_1^2 - \bar{q}_1^2]$. Hence

$$H_0 + H_1 = \frac{\bar{p}^2}{2m} + \tfrac{1}{2}(m\omega^2 + \lambda)\bar{q}_1^2 + \tfrac{1}{2}(m\omega^2 - \lambda)\bar{q}_2^2,$$

and so the energy levels are

$$E(n_1,n_2) = \hbar(n_1 + \tfrac{1}{2})\sqrt{\omega^2 + \lambda/m} + \hbar(n_2 + \tfrac{1}{2})\sqrt{\omega^2 - \lambda/m}.$$

Thus the ground state energy is

$$\frac{\hbar}{2}\left[\sqrt{\omega^2+\lambda/m}+\sqrt{\omega^2-\lambda/m}\right],$$

and the next two energies are

$$\frac{\hbar}{2}\left[\sqrt{\omega^2+\lambda/m}+3\sqrt{\omega^2-\lambda/m}\right],$$
$$\frac{\hbar}{2}\left[3\sqrt{\omega^2+\lambda/m}+\sqrt{\omega^2-\lambda/m}\right].$$

If $\lambda > 0$, the first of these is the first excited state, otherwise it is the second. Note that in any case, $|\lambda|$ must not be greater than $m\omega^2$. If it *were* greater, the Hamiltonian would not be bounded from below. The perturbative results agree with the above exact expressions, to order λ^2 for the ground state, and to order λ for the excited states.

7.6 Is There Always a Bound State?

Show that a function $\psi(x)$ exists, such that, if $V(x) < 0$ for all $-\infty < x < \infty$,

$$\int_{-\infty}^{\infty} dx\psi^*(x)\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi(x) < 0.$$

Use this result to prove that an attractive potential in one dimension always has a bound state. What can be said in 2 and 3 dimensions?

Solution

Since $V(x) < 0$ for all x, we can find numbers a, b and W_0, such that a square well potential of the form

$$\begin{aligned} W(x) &= -W_0 < 0 \qquad \text{for} \quad a < x < b \\ &= 0 \qquad\quad\;\; \text{for} \quad x < a \quad \text{or} \quad x > b, \end{aligned} \tag{7.6}$$

majorizes the given potential, in the sense that

$$W(x) \geq V(x) \qquad \text{for all} \quad -\infty < x < \infty. \tag{7.7}$$

As we show in Lemma 1, $W(x)$ always gives rise to a bound state, no matter how small W_0 and $b-a$ are. Let the normalized ground state of the Hamiltonian containing $W(x)$ instead of $V(x)$ be $\omega(x)$ (a square-integrable wave function), and the corresponding bound state energy be E_W. Then

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+W(x)\right]\omega(x) = E_W\omega(x).$$

Hence, by adding and subtracting $W(x)$, we find

$$\begin{aligned}\int_{-\infty}^{\infty} dx\omega^*(x)\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\omega(x) &= E_W - \int_{-\infty}^{\infty} dx\,[W(x)-V(x)]\,|\omega(x)|^2 \\ &< E_W < 0, \end{aligned} \tag{7.8}$$

thanks to Eq.(7.7), and the fact that E_W, being a bound state energy, is negative. Evidently $\omega(x)$ satisfies the requirements of the function $\psi(x)$ in the first part of the question. By the variational method, we know that the ground state energy of the Hamiltonian containing $V(x)$ is less than the left hand side of Eq.(7.8), which we have shown to be negative. Hence this ground state energy is itself negative, i.e., $V(x)$ has a bound state.

In three dimensions, we know from Volume 1, Section **4.4**, that there exist square well potentials that are too shallow to carry a bound state. The existence of these shallow potentials demonstrates that it is not true in three dimensions that all negative potentials have bound states. The precise reason for the difference between the one-dimensional and three-dimensional cases in this respect is further explained in Lemma 1.

In Lemma 2, it is shown that the square well potential in two dimensions always has a bound state, as in the one-dimensional case. We can then find a two-dimensional square well potential, $W(\vec{r})$, that majorizes the given negative potential, $V(\vec{r})$, i.e., for which $W(\vec{r}) \geq V(\vec{r})$ for all $\vec{r}$. As in the one-dimensional case, we let $\omega(\vec{r})$ be the ground-state wave function corresponding to the square well potential. Then

$$\begin{aligned}\int d^2r\omega^*(\vec{r})\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right]\omega(\vec{r}) &= E_W - \int d^2r\,[W(\vec{r})-V(\vec{r})]\,|\omega(\vec{r})|^2 \\ &< E_W < 0, \end{aligned} \tag{7.9}$$

just as in the one-dimensional case. The variational principle assures the existence of a bound state, since the lowest energy eigenvalue of the Hamiltonian containing $V(\vec{r})$ is negative.

Lemma 1. One and three dimensions.
We shall consider first the bound states of the square well in one dimension. For convenience we shift the origin, so that the well extends from $-d$ to d, instead of a to b. Thus $V(x) = -V_0 < 0$ for $|x| < d$ and $V(x) = 0$ for $|x| > d$. Define

$$\bar{k} = \frac{\sqrt{2m(E+V_0)}}{\hbar} \qquad \kappa = \frac{\sqrt{-2mE}}{\hbar}, \tag{7.10}$$

with $E < 0$ and $E + V_0 > 0$. Clearly

$$\kappa^2 + \bar{k}^2 = \frac{2m}{\hbar^2} V_0 \,, \tag{7.11}$$

which shows that $\bar{k}$ and κ are constrained to lie on a circle of radius $\sqrt{2mV_0}/\hbar$ in a graph of κ plotted against $\bar{k}$.

The most general square integrable real solutions of the Schrödinger equation for $E < 0$, are

$$\begin{aligned} \psi(x) &= C\,\mathrm{e}^{-\kappa x} && \text{for} && x > d \\ \psi(x) &= A\sin \bar{k}x + B\cos \bar{k}x && \text{for} && |x| < d \\ \psi(x) &= D\,\mathrm{e}^{\kappa x} && \text{for} && x < -d\,. \end{aligned} \tag{7.12}$$

Continuity of this wave function at $x = \pm d$ implies

$$\begin{aligned} A\sin \bar{k}d + B\cos \bar{k}d &= C\,\mathrm{e}^{-\kappa d} \\ -A\sin \bar{k}d + B\cos \bar{k}d &= D\,\mathrm{e}^{-\kappa d}\,, \end{aligned}$$

or equivalently

$$\begin{aligned} 2A\sin \bar{k}d &= (C - D)\,\mathrm{e}^{-\kappa d} \\ 2B\cos \bar{k}d &= (C + D)\,\mathrm{e}^{-\kappa d}\,. \end{aligned} \tag{7.13}$$

The derivative of Eq.(7.12) is

$$\begin{aligned} \psi'(x) &= -C\kappa\,\mathrm{e}^{-\kappa x} && \text{for} && x > d \\ \psi'(x) &= \bar{k}(A\cos \bar{k}x - B\sin \bar{k}x) && \text{for} && |x| < d \\ \psi'(x) &= D\kappa\,\mathrm{e}^{\kappa x} && \text{for} && x < -d\,. \end{aligned} \tag{7.14}$$

Continuity of the derivative of the wave function at $x = \pm a$ implies

$$\begin{aligned} \bar{k}(A\cos \bar{k}d - B\sin \bar{k}d) &= -C\kappa\,\mathrm{e}^{-\kappa d} \\ \bar{k}(A\cos \bar{k}d + B\sin \bar{k}d) &= D\kappa\,\mathrm{e}^{-\kappa d}\,, \end{aligned}$$

or equivalently

$$\begin{aligned} 2A\bar{k}\cos \bar{k}d &= -(C - D)\,\mathrm{e}^{-\kappa d} \\ 2B\bar{k}\sin \bar{k}d &= (C + D)\,\mathrm{e}^{-\kappa d}\,. \end{aligned} \tag{7.15}$$

From Eq.(7.13) and Eq.(7.15) we deduce

$$\begin{aligned} A(\kappa\sin \bar{k}d + \bar{k}\cos \bar{k}d) &= 0 \\ B(\kappa\cos \bar{k}d - \bar{k}\sin \bar{k}d) &= 0\,. \end{aligned} \tag{7.16}$$

We have therefore

$$\begin{aligned} \bar{k}\cot\bar{k}d &= -\kappa \qquad \text{if} \qquad A \neq 0 \\ \bar{k}\tan\bar{k}d &= \kappa \qquad \text{if} \qquad B \neq 0\,. \end{aligned} \tag{7.17}$$

Evidently it is impossible to have $A \neq 0$ *and* $B \neq 0$, for that would lead to the requirement $\cot\bar{k}d = -\tan\bar{k}d$, i.e., $\tan^2\bar{k}d = -1$, which has no solution for real $\bar{k}d$. Thus $A = 0$ and

$$\bar{k}\tan\bar{k}d = \kappa\,, \tag{7.18}$$

which leads to even solutions, or $B = 0$ and

$$\bar{k}\cot\bar{k}d = -\kappa\,, \tag{7.19}$$

which leads to odd solutions.

For very small V_0, Eq.(7.11) shows that $\bar{k}$ and κ must also be very small. This is consistent with Eq.(7.18), but it is inconsistent with Eq.(7.19). We conclude that there is always an even solution, no matter how small V_0 is, but there is no odd solution if V_0 is too small.

With a spherically symmetric potential, the radial Schrödinger equation in three dimensions for the S wave function, $u_0(r)$, has precisely the form of the one dimensional Schrödinger equation. However, the requirement of regularity at the origin, $u_0(r) = 0$, means that the even solutions that lead to Eq.(7.18) are excluded. Only the odd solutions satisfy the regularity condition, and these lead to Eq.(7.19). As we have seen, for small V_0, there is no solution.

Lemma 2. Two dimensions.
To find an S wave solution of the Schrödinger equation, with a central potential in two dimensions, consider

$$\begin{aligned} \frac{\partial}{\partial x_j}\psi(r) &= \psi'(r)\frac{\partial r}{\partial x_j} = \frac{x_i}{r}\psi'(r)\,, \\ \frac{\partial}{\partial x_j}\frac{\partial}{\partial x_j}\psi(r) &= \frac{x_i}{r}\frac{x_i}{r}\psi''(r) + \frac{\delta_{ii}}{r}\psi'(r) - \frac{x_i}{r^2}\frac{x_i}{r}\psi'(r)\,, \end{aligned}$$

with summation over $i = 1, 2$. Now in two dimensions, $\delta_{ii} = 2$, $x_i x_i = r^2$, so

$$\nabla^2\psi(r) = \psi''(r) + \frac{1}{r}\psi'(r)\,,$$

and the S wave equation is

$$-\frac{\hbar^2}{2m}\left[\frac{d^2}{dr^2} + \frac{1}{r}\frac{d}{dr}\right]\psi(r) = [E - V(r)]\psi(r)\,.$$

Suppose $V(r) = -V_0$ for $r < a$. We define $\bar{k}$ as in Eq.(7.10), and so we can write the S wave equation in the form

$$\psi''(r) + \frac{1}{r}\psi'(r) = \left[\frac{d}{dr} + \frac{1}{r}\right]\frac{d}{dr}\psi(r) = -\bar{k}^2\psi(r)\,. \tag{7.20}$$

A solution of this equation can be found as a series in powers in r^2,

$$\psi(r) = \sum_{n=0}^{\infty} a_n r^{2n}\,.$$

On inserting this series into Eq.(7.20), we obtain

$$\sum_{n=1}^{\infty} 4n^2 a_n r^{2n-2} = -\bar{k}^2 \sum_{n=0}^{\infty} a_n r^{2n} = -\bar{k}^2 \sum_{n=1}^{\infty} a_{n-1} r^{2n-2}\,.$$

We obtain then the recurrence relation

$$a_n = -\frac{\bar{k}^2}{4n^2}\,a_{n-1} = \left(-\frac{\bar{k}^2}{4}\right)^n \frac{1}{(n!)^2}\,a_0\,,$$

and so the (everywhere convergent) series solution is

$$\psi(r) = a_0 \sum_{n=0}^{\infty} \left(-\frac{\bar{k}^2 r^2}{4}\right)^n \frac{1}{(n!)^2} = a_0\, J_0(\bar{k}r)\,, \tag{7.21}$$

where $J_0(x)$ is the so-called Bessel function of zero order. For small x,

$$J_0(x) \sim 1 - \tfrac{1}{4}x^2\,. \tag{7.22}$$

Eq.(7.21) yields the regular solution of the Schrödinger equation, the one that is finite in a neighborhood of the origin. For $r = a - \epsilon$, and for $\bar{k} \to 0$,

$$\frac{d}{da}\log\psi(a-\epsilon) \sim -\tfrac{1}{2}a\bar{k}^2\,. \tag{7.23}$$

Consider next $r > a$, where the square well potential is zero. Here we define κ as in Eq.(7.10), and one solution of the equation

$$\psi''(r) + \frac{1}{r}\psi'(r) = \kappa^2\psi(r)\,, \tag{7.24}$$

in this region is

$$J_0(i\kappa r) = \sum_{n=0}^{\infty} \left(\frac{\kappa^2 r^2}{4}\right)^n \frac{1}{(n!)^2}\,, \tag{7.25}$$

which clearly tends to infinity faster than any power of r, as $r \to \infty$. To obtain a more general solution, ψ, of Eq.(7.24), note that $J_0(i\kappa r)$ satisfies

$$J_0''(i\kappa r) + \frac{1}{r} J_0'(i\kappa r) = \kappa^2 J_0(i\kappa r)\,. \tag{7.26}$$

Multiply Eq.(7.24) by $J_0(i\kappa r)$ and Eq.(7.25) by $\psi(r)$ and subtract the two equations, yielding

$$W'(r) + \frac{W(r)}{r} = 0\,,$$

where $W(r) = J_0(i\kappa r)\frac{d}{dr}\psi(r) - \psi(r)\frac{d}{dr}J_0(i\kappa r)$, which is called the Wronskian of ψ and J_0. The general solution is $W(r) = A/r$, and so we can write

$$\left[\frac{\psi(r)}{J_0(i\kappa r)}\right]' = \frac{W(r)}{[J_0(i\kappa r)]^2} = \frac{A}{r[J_0(i\kappa r)]^2}\,. \tag{7.27}$$

We obtain the general solution of Eq.(7.24) by integrating Eq.(7.27), obtaining

$$\psi(r) = -AJ_0(i\kappa r)\int_r^B \frac{ds}{s[J_0(i\kappa s)]^2}\,. \tag{7.28}$$

where B is the second integration constant.

We see from Eq.(7.25) that $J_0(i\kappa r)$ is a positive, monotonic increasing function of r. Accordingly, the only way to make the solution (7.28) tend to zero as $r \to \infty$ is to set $B = \infty$. This is then the solution that corresponds to a bound state of the square well. Note that, since $J_0(i\kappa r) \sim 1$ as $r \to 0$, it follows that the solution (7.28) has a logarithmic singularity at the origin, $\psi(r) \sim A \log \kappa r$, and also $\psi'(r) \sim A/r$. Hence, for $r = a + \epsilon$, and for $\kappa \to 0$,

$$\frac{d}{da}\log\psi(a+\epsilon) \sim \frac{1}{a\log\kappa a}\,. \tag{7.29}$$

The matching condition at $r = a$ can be written

$$\frac{d}{da}\log\psi(a-\epsilon) = \frac{d}{da}\log\psi(a+\epsilon)\,,$$

and when Eq.(7.23) and Eq.(7.29) are inserted, we find, after rearrangement,

$$\kappa a = \exp\left[-\frac{2}{\bar{k}^2 a^2}\right]\,, \tag{7.30}$$

which shows that $\kappa \to 0$ as $\bar{k} \to 0$. We recall from Eq.(7.11) that κ and $\bar{k}$ are constrained to lie on a circle of radius $\sqrt{2mV_0}/\hbar$, and so, no matter how small V_0 is, the graph of κ against $\bar{k}$, as given by Eq.(7.30), will always intersect the

circle. In other words, a square well potential in two dimensions always has a bound state.

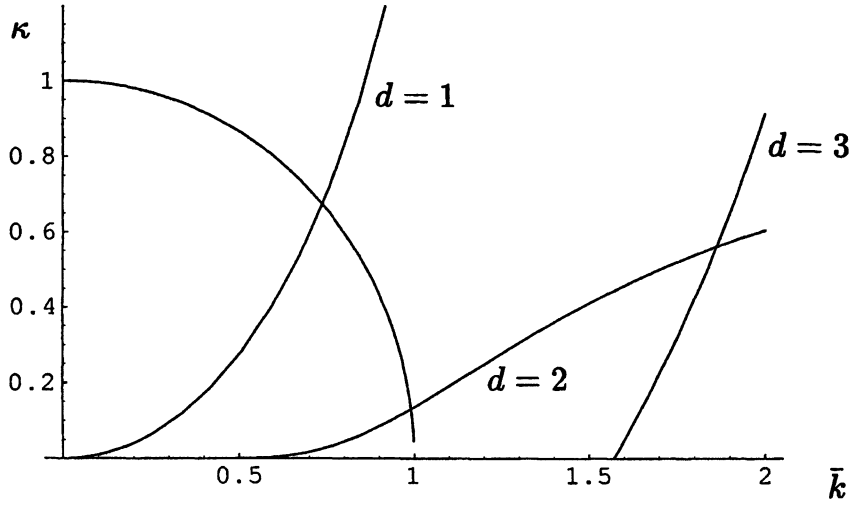

Fig. 7.1 Bound State Conditions

In Figure 7.1 we plot κ against $\bar{k}$, for $a = 1$. The curve labeled $d = 1$ is Eq.(7.18), corresponding to the ground state in one dimension. The curve labeled $d = 2$ is Eq.(7.30), the S wave equation in two dimensions that we have just derived. The curve labeled $d = 3$ is Eq.(7.19), corresponding to the lowest odd state in one dimension, which is also the ground state in three dimensions. Finally, the quarter circle comes from the constraint equation (7.11), for a small value of V_0, the potential strength. It can clearly be seen that the curves 1 and 2 must cut the circle, whereas the curve 3 does not do so for small V_0.

7.7 Ground States for Different Angular Momenta

Given a central potential with bound states, use the variational method to show

$$\min(E_\ell) < \min(E_{\ell+1}),$$

where $\min(E_\ell)$ is the smallest energy eigenvalue for angular momentum ℓ.

Solution

The Hamiltonian in the radial Schrödinger equation is

$$H_\ell = \frac{p^2}{2m} + V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$$

$$H_{\ell+1} = \frac{p^2}{2m} + V(r) + \frac{\hbar^2}{2m}\frac{(\ell+1)(\ell+2)}{r^2},$$

so it it follows that

$$H_{\ell+1} - H_\ell = \frac{(\ell+1)\hbar^2}{mr^2}.$$

Hence for any radial state-function, $u(r)$,

$$\langle u|H_{\ell+1} - H_\ell|u\rangle = \frac{(\ell+1)\hbar^2}{mr^2}\langle u|u\rangle > 0.$$

thus we see that

$$\langle u|H_{\ell+1}|u\rangle > \langle u|H_\ell|u\rangle. \tag{7.31}$$

Set $E^1_\ell = \min(E_\ell)$, the minimum energy eigenvalue for angular momentum ℓ, and let u^1_ℓ be the corresponding eigenvector of the Hamiltonian, H_ℓ. Then from Eq.(7.31) we see that

$$\begin{aligned} E^1_{\ell+1} &= \langle u^1_{\ell+1}|H_{\ell+1}|u^1_{\ell+1}\rangle \\ &> \langle u^1_{\ell+1}|H_\ell|u^1_{\ell+1}\rangle \\ &= \sum_n \langle u^1_{\ell+1}|H_\ell|u^n_\ell\rangle\langle u^n_\ell|u^1_{\ell+1}\rangle, \end{aligned}$$

the sum being over the complete set of eigenvectors of H_ℓ (including the continuum states). Note that H_ℓ is Hermitian on a space of functions of r, with $0 < r < \infty$, that are bounded, twice differentiable and that vanish at $r = 0$. Since $H_\ell|u^n_\ell\rangle = E^n_\ell|u^n_\ell\rangle$, it follows that

$$\begin{aligned} E^1_{\ell+1} &> \sum_n E^n_\ell \left|\langle u^1_{\ell+1}|u^n_\ell\rangle\right|^2 \\ &> E^1_\ell \sum_n \langle u^1_{\ell+1}|u^n_\ell\rangle\langle u^n_\ell|u^1_{\ell+1}\rangle \\ &= E^1_\ell \langle u^1_{\ell+1}|u^1_{\ell+1}\rangle \\ &= E^1_\ell, \end{aligned}$$

where we explicitly used the fact that $E^n_\ell > E^1_\ell$ for all n.

7.8 Screened Coulomb Potential

Estimate by means of the variational method the ground-state energy of an electron in a screened Coulomb potential,

$$V(r) = -\frac{e^2}{r}\,\mathrm{e}^{-\alpha r}\,.$$

Take e^{-br} as test function, and if possible use a computer to find the minima. Make a table of the numerical results, showing $E(\alpha)/E(0)$ as a function of α.

Solution

With the Bohr radius set equal to unity, the variational estimate of the ground state energy is

$$E(\alpha) = \frac{\int d^3r\ \mathrm{e}^{-br}(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r}\,\mathrm{e}^{-\alpha r})\,\mathrm{e}^{-br}}{\int d^3r\ \mathrm{e}^{-2br}} = E(0)\left[\frac{8b^3}{(\alpha+2b)^2} - b^2\right], \quad (7.32)$$

where $E(0) = -\frac{e^2}{2}$, and where b must be chosen to minimize the right hand side. The condition for minimization is

$$\frac{\partial E(\alpha)}{\partial b} = e^2 x\left[\alpha - \frac{4x(3+2x)}{(1+2x)^3}\right] = 0\,, \quad (7.33)$$

where $x = b/\alpha$. To produce a table of ground state energies against the screening parameter, α, choose a positive value of x, and then calculate

$$\alpha = \frac{4x(3+2x)}{(1+2x)^3}\,,$$

which guarantees satisfaction of Eq.(7.33). With this value for α, one can then obtain $b = x\alpha$ and thence $E(\alpha)/E(0)$ from Eq.(7.32). Repeating the procedure for many values of x, one can produce a table.

On the other hand, Eq.(7.33) can be solved for x as a function of α, which only involves the solution of a cubic equation. Then

$$\frac{E(\alpha)}{E(0)} = \alpha x^2\left[\frac{8x}{(1+2x)^2} - \alpha\right].$$

This method is implemented in the following Mathematica program:

```
f[a_]:=Solve[4*x*(3+2*x)/((1+2*x)^3)==a,x];
x[a_]:=f[a][[3]][[1,2]];
e[a_]:=N[a*x[a]^2*(8*x[a]/((1+2*x[a])^2)-a)];
```

where the function e[α] is $E(\alpha)/E(0)$. This was used to produce the following table:

α	b	$E(\alpha)/E(0)$
0.1	0.99333	0.81410
0.2	0.97568	0.65346
0.3	0.94922	0.51465
0.4	0.91502	0.39515
0.5	0.87349	0.29302
0.6	0.82444	0.20671
0.7	0.76697	0.13500
0.8	0.69903	0.07694
0.9	0.61564	0.03194
1.0	0.50000	0

Screened Coulomb Potential

For comparision with the exact results, the Yukawa potential with $\alpha = 1.19065$ has a zero energy bound state, to be compared with $\alpha = 1$ in this approximation.

7.9 Stark Effect to Second Order

Calculate the Stark shift of the ground-state energy of the hydrogen atom, to second order in $e\mathcal{E}$, where

$$H = H_0 + e\,\mathcal{E} r\cos\theta\,,$$

H_0 being the hydrogen atom Hamiltonian. Prove first that, in configuration space, $[\Omega, H_0]\,\mathrm{e}^{-r} = -e^2 r\cos\theta\,\mathrm{e}^{-r}$, where $\Omega = (1+\frac{1}{2}r)r\cos\theta$. The Bohr radius has been set to unity.

Solution

The Hamiltonian of the hydrogen atom in configuration space is

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} = -\frac{e^2}{2}\left(\nabla^2 + \frac{2}{r}\right), \tag{7.34}$$

with $a_0 = \hbar^2/(me^2) = 1$, the Bohr radius. The Stark perturbation is

$$H_1 = er\cos\theta\,, \tag{7.35}$$

so that $H = H_0 + \mathcal{E}H_1$. We have

$$[\Omega, H_0]\,\mathrm{e}^{-r} = -\frac{e^2}{2}[(1+\tfrac{1}{2}r)r\cos\theta, \nabla^2]\,\mathrm{e}^{-r}\,. \tag{7.36}$$

Now for any twice-differentiable functions,

$$[\nabla^2, f]\,g = (\nabla^2 f)g + 2(\vec{\nabla} f)\cdot(\vec{\nabla} g)\,,$$

so from Eq.(7.36) we have

$$[\Omega, H_0]\,\mathrm{e}^{-r} = \frac{e^2}{2}\left\{\left[\nabla^2\Big((1+\tfrac{1}{2}r)r\cos\theta\Big)\right]\mathrm{e}^{-r} + 2\left[\vec{\nabla}\Big((1+\tfrac{1}{2}r)r\cos\theta\Big)\right]\cdot\left[\vec{\nabla}\,\mathrm{e}^{-r}\right]\right\}.$$

Now

$$\begin{aligned}
\nabla^2(1+\tfrac{1}{2}r)r\cos\theta &= \left\{\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right\}(r+\tfrac{1}{2}r^2)\cos\theta \\
&= \frac{1}{r}\frac{\partial^2}{\partial r^2}(r^2+\tfrac{1}{2}r^3)\cos\theta + \left(\frac{1}{2}+\frac{1}{r}\right)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\cos\theta \\
&= 2\cos\theta\,.
\end{aligned}$$

Moreover,

$$\begin{aligned}
\Big(\vec{\nabla}(1+\tfrac{1}{2}r)r\cos\theta\Big)\cdot\Big(\vec{\nabla}\,\mathrm{e}^{-r}\Big) &= \left(\frac{\partial}{\partial r}(r+\tfrac{1}{2}r^2)\cos\theta\right)\left(\frac{\partial}{\partial r}\,\mathrm{e}^{-r}\right) \\
&= -(1+r)\cos\theta\,\mathrm{e}^{-r}\,.
\end{aligned}$$

From the last three equations we find

$$[\Omega, H_0]\,\mathrm{e}^{-r} = -e^2 r\cos\theta\,\mathrm{e}^{-r}\,. \tag{7.37}$$

In terms of the perturbation, H_1, this result can be written

$$[\Omega, H_0]\phi_1(r) = -eH_1\phi_1(r)\,, \tag{7.38}$$

where the ground state of hydrogen corresponds to the normalized eigenvector $\phi_1(r) = \pi^{-\frac{1}{2}}\,\mathrm{e}^{-r}$. The perturbation series for the ground state energy, E_1, is

$$\begin{aligned}
E_1 &= E_1^{(0)} + \mathcal{E}\langle\phi_1|H_1|\phi_1\rangle + \mathcal{E}^2\sum_{k\neq 1}\frac{|\langle\phi_1|H_1|\phi_k\rangle|^2}{E_1^{(0)} - E_k^{(0)}} + O(\mathcal{E}^3) \\
&= E_1^{(0)} + \mathcal{E}\langle\phi_1|H_1|\phi_1\rangle - \frac{\mathcal{E}^2}{e}\sum_{k\neq 1}\frac{\langle\phi_1|H_1|\phi_k\rangle\langle\phi_k|\Omega H_0 - H_0\Omega|\phi_1\rangle}{E_1^{(0)} - E_k^{(0)}} + O(\mathcal{E}^3) \\
&= E_1^{(0)} + \mathcal{E}\langle\phi_1|H_1|\phi_1\rangle - \frac{\mathcal{E}^2}{e}\sum_{k\neq 1}\langle\phi_1|H_1|\phi_k\rangle\langle\phi_k|\Omega|\phi_1\rangle + O(\mathcal{E}^3)\,,
\end{aligned} \tag{7.39}$$

where $E_1^{(0)} = -\frac{1}{2}e^2$ is the ground-state energy. The first-order term vanishes:

$$\langle\phi_1|H_1|\phi_1\rangle = \frac{e}{\pi}\int d^3r\, r\cos\theta\, \mathrm{e}^{-2r} = 2e\int_0^\infty dr r^3\, \mathrm{e}^{-2r}\int_{-1}^{1} dz\, z = 0\,.$$

This means that

$$\begin{aligned} E_1 &= E_1^{(0)} - \frac{\mathcal{E}^2}{e}\sum_k \langle\phi_1|H_1|\phi_k\rangle\langle\phi_k|\Omega|\phi_1\rangle + O(\mathcal{E}^3) \\ &= E_1^{(0)} - \frac{\mathcal{E}^2}{e}\langle\phi_1|H_1\Omega|\phi_1\rangle + O(\mathcal{E}^3) \\ &= E_1^{(0)} - \frac{\mathcal{E}^2}{\pi}\int d^3r\, r^2(1+\tfrac{1}{2}r)\cos^2\theta\, \mathrm{e}^{-2r} + O(\mathcal{E}^3) \\ &= E_1^{(0)} - 2\mathcal{E}^2\int_0^\infty dr(r^4+\tfrac{1}{2}r^5)\,\mathrm{e}^{-2r}\int_{-1}^{1} dz\, z^2 + O(\mathcal{E}^3) \\ &= -\tfrac{1}{2}e^2 - \tfrac{9}{4}\mathcal{E}^2 + O(\mathcal{E}^3)\,. \end{aligned} \tag{7.40}$$

7.10 Anharmonic Oscillator

Consider the anharmonic oscillator in one dimension defined by the Hamiltonian

$$H(\lambda) = \frac{p^2}{2m} + q^2 + \lambda q^4$$

and set $m = \hbar^2/2$, so that the ground state energy of the oscillator in the absence of the quartic perturbation is unity, i.e., $E_0(0) = 1$.

(1) Calculate the ground state energy of the oscillator to second order in perturbation theory,

$$E_0(\lambda) = 1 + a_1\lambda + a_2\lambda^2 + \ldots\,,$$

giving explicit expressions for the coefficients a_1 and a_2.

(2) From this second-order perturbative result, calculate the $[1,1]$ Padé approximant, $E_0^{[1,1]}$. The $[M,N]$ Padé approximant to a function that has a power series expansion,

$$f(\lambda) = \sum_{n=0}^{\infty} a_n\lambda^n$$

is given by the relation

$$f^{[N,M]}(\lambda) = \frac{\sum_{n=0}^{M} b_n \lambda^n}{1 + \sum_{n=1}^{N} c_n \lambda^n} = \sum_{n=0}^{M+N} a_n \lambda^n + O(\lambda^{M+N+1}),$$

which defines the coefficients b_n and c_n uniquely in terms of the first $M + N + 1$ coefficients a_n.

(3) Make a table of $E_0^{[0,1]}(\lambda)$, $E_0^{[0,2]}(\lambda)$ and $E_0^{[1,1]}(\lambda)$, giving 6 significant figures, for each of the cases $\lambda = 0.1$, 0.2, 1.0, and, if you have computer facilities, write a program to calculate $E_0(\lambda)$ to sufficient accuracy to guarantee the correctness of 7 significant figures.

Solution

(1) We have $E_0(0) = \frac{1}{2}\hbar\omega = 1$, so $\hbar\omega = 2$, and

$$\begin{aligned} a_1 &= \langle 0|q^4|0\rangle \\ a_2 &= \sum_{k\neq 0} \frac{|\langle 0|q^4|k\rangle|^2}{(\frac{1}{2} - k - \frac{1}{2})\hbar\omega} \\ &= -\tfrac{1}{4}|\langle 0|q^4|2\rangle|^2 - \tfrac{1}{8}|\langle 0|q^4|4\rangle|^2 . \end{aligned}$$

No more terms contribute to the last sum, since $q = (a + a^\dagger)/\sqrt{2}$ and so

$$q^4 = \tfrac{1}{4}(a + a^\dagger)^4 ,$$

which means that the most destructive term in the expansion of the quartic, namely $\frac{1}{4}a^4$, could not serve to render $\langle 0|q^4|6\rangle$ non-zero. As it is, this is the only term that contributes to

$$\langle 0|q^4|4\rangle = \tfrac{1}{4}\langle 0|a^4|4\rangle .$$

Now we know that $a|k\rangle = \sqrt{k}\,|k-1\rangle$ so

$$\langle 0|q^4|4\rangle = \tfrac{1}{4}\sqrt{4.3.2}\langle 0|0\rangle = \sqrt{3/2} .$$

For the term corresponding to $k = 2$ in the sum, we need only retain the terms involving one creation and three annihilation operators:

$$\langle 0|q^4|2\rangle = \tfrac{1}{4}\langle 0|a^3a^\dagger + a^2a^\dagger a + aa^\dagger a^2|2\rangle ,$$

where $a^\dagger a^3$ has been left out, since it clearly contributes nothing. With use of $a^\dagger|k\rangle = \sqrt{k+1}\,|k+1\rangle$, we find

$$\begin{aligned}\langle 0|q^4|2\rangle &= \tfrac{1}{4}\left[\sqrt{6}\sqrt{3}\langle 3|3\rangle + \sqrt{2}\sqrt{2}\langle 2|a^\dagger|1\rangle + \sqrt{2}\langle 1|a^\dagger|0\rangle\right] \\ &= \tfrac{1}{4}\left[3\sqrt{2} + 2\sqrt{2} + \sqrt{2}\right] = 3/\sqrt{2}\,.\end{aligned}$$

Finally,

$$\begin{aligned}\langle 0|q^4|0\rangle &= \tfrac{1}{4}\langle 0|a^2(a^\dagger)^2 + aa^\dagger aa^\dagger|0\rangle \\ &= \tfrac{1}{4}\left[2\langle 2|2\rangle + \langle 0|0\rangle\right] = \tfrac{3}{4}\,.\end{aligned}$$

We find then

$$a_1 = \tfrac{3}{4} \qquad a_2 = -\tfrac{1}{4}\times\tfrac{9}{2} - \tfrac{1}{8}\times\tfrac{3}{2} = -\tfrac{21}{16}\,,$$

so the perturbation series is

$$E^{[2]}(\lambda) = 1 + \tfrac{3}{4}\lambda - \tfrac{21}{16}\lambda^2 + O(\lambda^3)\,. \tag{7.41}$$

(2) The [1, 1] Padé approximant of the ground state energy is defined by

$$E^{[1,1]}(\lambda) = \frac{1 + b_1\lambda}{1 + c_1\lambda} = 1 + a_1\lambda + a_2\lambda^2 + O(\lambda^3)\,,$$

which means that

$$1 + b_1\lambda = (1 + c_1\lambda)(1 + a_1\lambda + a_2\lambda^2) + O(\lambda^3)\,.$$

Hence

$$b_1 = a_1 + c_1 \qquad a_1c_1 + a_2 = 0\,,$$

$$c_1 = -a_2/a_1 \qquad b_1 = a_1 + c_1\,.$$

With the values of a_1 and a_2 that we calculated, this yields

$$c_1 = \tfrac{21}{16}/\tfrac{3}{4} = \tfrac{7}{4} \qquad b_1 = \tfrac{3}{4} + \tfrac{7}{4} = \tfrac{5}{2}\,.$$

The [1, 1] Padé approximant is then

$$E^{[1,1]}(\lambda) = \frac{1 + \frac{5}{2}\lambda}{1 + \frac{7}{4}\lambda}\,,$$

and this may be compared with the perturbation series to second order, Eq.(7.41).

(3) The results are given in the following table:

λ	$E^{[1]}$	$E^{[2]}$	$E^{[1,1]}$	$E^{[20,20]}$	Runge-Kutta
0.1	1.075	1.062	1.06383	1.065286	1.065286
0.2	1.150	1.098	1.11111	1.118293	1.118293
1.0	1.750	0.438	1.27273	1.392337	1.392353

Ground-state energy of the anharmonic oscillator

The second and third columns give the results to first and second order in the perturbation series, and the $[1,1]$ diagonal Padé approximant is shown in the fourth column. The fifth column gives the result of a calculation of the $[20,20]$ diagonal Padé approximant, as given in the paper, "Padé Approximants and the Anharmonic oscillator", by J.J. Loeffel, A. Martin, B. Simon and A.S. Wightman, Physics Letters, vol. 30B (1969) p. 656-658. In this paper, it was shown that the diagonal Padé approximants converge to the correct answer (see also M. Reed and B. Simon, "Methods of Mathematical Physics. IV Analysis of Operators", Academic Press (1969) pages 63-64). Even at the large value $\lambda = 1$, the $[1,1]$ Padé gives a reasonable, if not very accurate answer. At this value of λ, the perturbation series diverges so strongly that the calculation to second-order is hopelessly bad. In contrast, the variational result is better than the $[1,1]$ Padé, being less than one per cent wrong (see page 119 of Volume 1).

The energy eigenvalue was also calculated with a fourth-order Runge-Kutta integration routine applied directly to the Schrödinger equation,

$$\psi''(x) = \big(x^2 + \lambda x^4 - E\big)\psi(x)\,.$$

The method involves first writing the second-order differential equation as two simultaneous first-order differential equations for $f(x) = \psi(x)$ and $g(x) = \psi'(x)$:

$$\begin{aligned} f'(x) &= g(x) \\ g'(x) &= \big(x^2 + \lambda x^4 - E\big)f(x)\,. \end{aligned}$$

The derivatives of $f(x)$ and $g(x)$ are calculated from the differential equations, and then $f(x+\Delta x)$ and $g(x+\Delta x)$ are estimated. If E is close to the eigenvalue, a graph of the solution shows a curve that decreases to very small values at moderate values of x, but then shoots up to very large values. By tuning the value of E with care, one can find the critical value such that a change of one unit in the last decimal results in a change from negative to positive divergence for large x. The method is sensitive, if a trifle laborious. The calculation was performed and the graph generated by the following Mathematica program:

```
e=1.392351642;
lam=1. ;
xmax=4;

sol:=NDSolve[{f'[x]==g[x], g'[x]==(x^2+lam*x^4-e)*f[x],
f[0]==1, g[0]==0}, {f,g},{x,0,xmax},
WorkingPrecision -> 25,MaxSteps->10000 ];
fq[x_]:=f[x]/. sol[[1]];
kkk=sol;

Plot[fq[x],{x,0,xmax}]
```

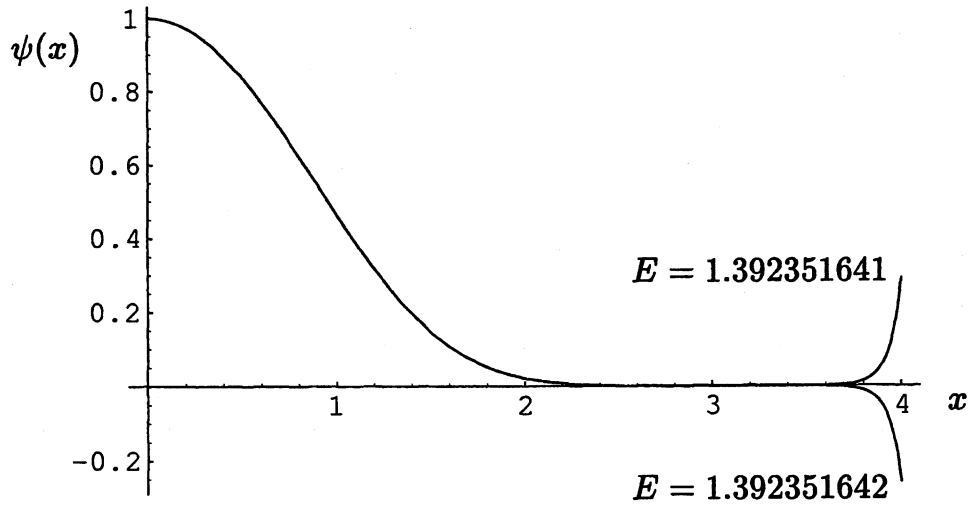

Fig. 7.2 Ground State Function with $\lambda = 1$

The results are shown in the sixth column of the table. It will be noted that they agree with the [20, 20] diagonal Padé approximant results for $\lambda = 0.1$ and $\lambda = 0.2$, but there is disagreement in the fifth decimal place for $\lambda = 1$. To examine this case more closely, we experimented with the working precision of the Mathematica calculation, and with the maximum number of permitted Runge-Kutta steps, and we determined the energy eigenvalue to nine significant figures. The result is shown in Figure (7.2). The wave function, $\psi(x)$, is shown for the values $E = 1.392351641$ and $E = 1.392351642$. They are indistinguishable to the eye below about $x = 3.5$, but above that value one curve explodes towards $+\infty$, the other to $-\infty$. We conclude that the eigenvalue is $E = 1.39235164$ to nine significant figures, and this indicates that the published [20, 20] diagonal Padé approximant is only good to five significant figures.

Chapter 8

Scattering Theory

8.1 Legendre Polynomials

The Legendre polynomial is defined by the Rodrigues formula

$$P_\ell(z) \equiv P_\ell^0(z) = \frac{1}{2^\ell \ell!}\left(\frac{d}{dz}\right)^\ell (z^2-1)^\ell . \tag{8.1}$$

Prove the following recursion relations:

(1) $P_{\ell+1}(z) = zP_\ell(z) + \frac{z^2-1}{\ell+1}P'_\ell(z)$,

(2) $(\ell+1)P_{\ell+1}(z) - (2\ell+1)zP_\ell(z) + \ell P_{\ell-1}(z) = 0$.

(3) Work out $P_\ell(z)$ for $\ell = 0, 1, 2, 3$, and sketch them graphically.

Solution

Replace ℓ by $\ell+1$ in the Rodrigues formula, Eq.(8.1), and differentiate once:

$$P'_{\ell+1}(z) = \frac{1}{2^{\ell+1}(\ell+1)!}\left(\frac{d}{dz}\right)^{\ell+2} (z^2-1)^{\ell+1} . \tag{8.2}$$

Allow one of the differentiations to work through on $(z^2-1)^{\ell+1}$, giving

$$P'_{\ell+1}(z) = \frac{1}{2^\ell \ell!}\left(\frac{d}{dz}\right)^{\ell+1} \{z(z^2-1)^\ell\} . \tag{8.3}$$

Now use the Leibniz rule of differentiation, according to which

$$\left(\frac{d}{dz}\right)^{\ell+1} \{z(z^2-1)^\ell\} = z\left(\frac{d}{dz}\right)^{\ell+1} (z^2-1)^\ell + (\ell+1)\left(\frac{d}{dz}\right)^\ell (z^2-1)^\ell .$$

From Eq.(8.3) we obtain

$$\begin{aligned} P'_{\ell+1}(z) &= \frac{1}{2^\ell \ell!}\left\{ z\left(\frac{d}{dz}\right)^{\ell+1}(z^2-1)^\ell + (\ell+1)\left(\frac{d}{dz}\right)^{\ell}(z^2-1)^\ell \right\} \\ &= zP'_\ell(z) + (\ell+1)P_\ell(z)\,. \end{aligned} \tag{8.4}$$

Now go back to Eq.(8.3) again, but this time allow just one of the differentiations to work on $\{z(z^2-1)^\ell\}$, giving

$$\begin{aligned} P'_{\ell+1}(z) &= \frac{1}{2^\ell \ell!}\left(\frac{d}{dz}\right)^{\ell}\{(z^2-1)^\ell + 2\ell z^2(z^2-1)^{\ell-1}\} \\ &= \frac{1}{2^\ell \ell!}\left(\frac{d}{dz}\right)^{\ell}\{(2\ell+1)(z^2-1)^\ell + 2\ell(z^2-1)^{\ell-1}\} \\ &= (2\ell+1)P_\ell(z) + P'_{\ell-1}(z)\,. \end{aligned} \tag{8.5}$$

These recurrence relations will be used to derive the relations (1) and (2).
(1) From Eq.(8.4) and Eq.(8.5),

$$\begin{aligned} (2\ell+1)P_\ell(z) &= P'_{\ell+1}(z) - P'_{\ell-1}(z) \\ &= zP'_\ell(z) + (\ell+1)P_\ell(z) - P'_{\ell-1}(z)\,. \end{aligned} \tag{8.6}$$

Bring the $(\ell+1)P_\ell(z)$ term from the right to the left, and then use Eq.(8.4) again, but with $\ell-1$ in place of ℓ:

$$\begin{aligned} \ell P_\ell(z) &= zP'_\ell(z) - P'_{\ell-1}(z) \\ &= z\left\{zP'_{\ell-1}(z) + \ell P_{\ell-1}(z)\right\} - P'_{\ell-1}(z) \\ &= (z^2-1)P'_{\ell-1}(z) + \ell z P_{\ell-1}(z)\,, \end{aligned} \tag{8.7}$$

and this is equivalent to the recurrence relation that was to be proved.

(2) By elimination of $P_\ell(z)$ from Eq.(8.4) and Eq.(8.5), and rearrangement of terms, we find the following relation:

$$\ell P'_{\ell+1}(z) - (2\ell+1)zP'_\ell(z) + (\ell+1)P'_{\ell-1}(z) = 0\,. \tag{8.8}$$

Now consider

$$\begin{aligned} &\frac{d}{dx}\{(\ell+1)P_{\ell+1}(z) - (2\ell+1)zP_\ell(z) + \ell P_{\ell-1}(z)\} \\ &\quad= (\ell+1)P'_{\ell+1}(z) - (2\ell+1)zP'_\ell(z) + \ell P'_{\ell-1}(z) - (2\ell+1)P_\ell(z) \\ &\quad= \left\{\ell P'_{\ell+1}(z) - (2\ell+1)zP'_\ell(z) + (\ell+1)P'_{\ell-1}(z)\right\} \\ &\qquad\quad + \left\{P'_{\ell+1}(z) - (2\ell+1)P_\ell(z) - P'_{\ell-1}(z)\right\} = 0\,, \end{aligned} \tag{8.9}$$

since both parenthetical expressions vanish (Eq.(8.5) and Eq.(8.8)). Hence

$$(\ell+1)P_{\ell+1}(z) - (2\ell+1)zP_\ell(z) + \ell P_{\ell-1}(z) = \kappa\,, . \tag{8.10}$$

where κ is independent of z. Now from Eq.(8.7) we see that

$$P_\ell(1) = P_{\ell-1}(1)\,,$$

and since $P_0(z) = P_0(1) = 1$, it follows that $P_\ell(1) = 1$ for all ℓ. On evaluating Eq.(8.10) at $z = 1$, we find $\kappa = 0$. This concludes the demonstration.

(3) We can evaluate the Legendre polynomials sequentially from (1), starting with $P_0(z) = 1$. We find $P_1(z) = z$, $P_2(z) = \frac{1}{2}(3z^2 - 1)$, $P_3(z) = \frac{1}{2}(5z^3 - 3z)$. In graphical form:

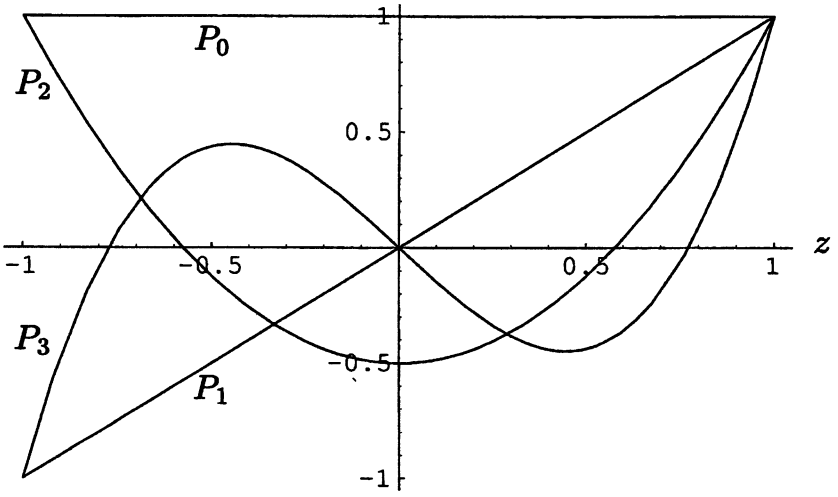

Fig. 8.1 Legendre Polynomials

This graph was generated by the Mathematica command line:

Plot [{LegendreP[0,x],LegendreP[1,x],LegendreP[2,x], LegendreP[3,x]},{x,-1,1}]

One can see that the Legendre polynomial of order n has n zeros, all of which lie in the interval $[-1, 1]$.

One final comment is in order. The recurrence relations, that have been proved for the Legendre polynomials by means of the Rodrigues formulae, are actually also valid when ℓ is not an integer. The proofs must then be generalized, and this can be done via the formula of Schläfli, namely

$$P_\ell(z) = \frac{2^{-\ell}}{2\pi i}\oint d\zeta\,\frac{(\zeta^2-1)^\ell}{(\zeta - z)^{\ell+1}}\,,$$

where the contour in the ζ-plane encircles the points z and 1, but not -1.

8.2 Hard Core Potential

Calculate the phase shifts, $\delta_\ell(k)$, for the hard core potential,

$$\begin{aligned} V(r) &= \infty\,, \; r < a \\ &= 0\,, \; r > a\,. \end{aligned}$$

(1) Simplify the result for the S-wave.
(2) Calculate the total cross-section in the limit $k \to 0$.
(3) Calculate the total cross-section in the limit $k \to \infty$.

Solution

In the region $r > a$, the Schrödinger equation is free, so the most general solution of the radial equation is

$$u_\ell(r) = kr\left[A_\ell j_\ell(kr) + B_\ell n_\ell(kr)\right]\,, \tag{8.11}$$

and the condition for this to vanish at $r = a$ is

$$A_\ell j_\ell(ka) + B_\ell n_\ell(ka) = 0\,.$$

Now $\tan\delta_\ell = -B_\ell/A_\ell$, see Eq.(8.45) of Volume 1. Hence

$$\tan\delta_\ell(k) = \frac{j_\ell(ka)}{n_\ell(ka)}\,. \tag{8.12}$$

(1) For the S-wave, this reduces to $\tan\delta_0 = -\tan ka$, and that implies

$$\delta_0 = -ka\,,$$

on condition that we require the phase shift to start at the value zero and to be a continuous function of k.

(2) From Eqs.(4.54)-(4.57) of Volume 1, and Eq.(8.12), we see that, in the limit $k \to 0$, $\tan\delta_\ell(k) \sim (ka)^{2\ell+1}$. The imaginary part of the forward amplitude is

$$\mathrm{Im}\, f_k(0) = \frac{1}{k}\sum_{\ell=0}^{\infty}(2\ell+1)\sin^2\delta_\ell(k) \sim \frac{[\delta_0(k)]^2}{k} \sim ka^2\,. \tag{8.13}$$

Using solution (1) above, and the optical theorem below (Problem 3), we have

$$\sigma_T = \frac{4\pi}{k}\mathrm{Im} f_k(0) \sim 4\pi a^2\,.$$

(3) For any energy, we have

$$\begin{aligned}\sigma_T &= \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\sin^2\delta_\ell(k) \\ &= \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\,\frac{j_\ell^2(ka)}{j_\ell^2(ka)+n_\ell^2(ka)}\,. \end{aligned} \tag{8.14}$$

We wish to give an estimate for this in the limit of large k. Let us divide the sum into the terms with $\ell \leq ka$ and the rest, the tail of very large ℓ values, whose contribution to the sum will prove to be negligible. For large k, we use the asymptotic expressions for the spherical Bessel and Neumann functions given in Eqs. (4.61)-(4.62) of Volume 1 to yield

$$\begin{aligned}\sigma_T &\sim \frac{4\pi}{k^2}\sum_{\ell=0}^{[ka]}(2\ell+1)\,\sin^2(ka-\tfrac{1}{2}\pi\ell) \\ &= \frac{2\pi}{k^2}\sum_{\ell=0}^{[ka]}(2\ell+1)\,[1-(-1)^\ell\cos 2ka]\,,\end{aligned}$$

where $[ka]$ means the integral part of ka. These sums can be performed explicitly, the result being

$$\sigma_T \sim \frac{2\pi}{k^2}\left\{([ka]+1)^2 \pm ([ka]+1)\cos 2ka\right\}\,,$$

the minus sign being appropriate when $[ka]$ is even, the plus sign when it is odd. In either case, the leading behavior comes from the first term, and we find

$$\sigma_T \sim \frac{2\pi}{k^2}[ka]^2 \sim 2\pi a^2\,.$$

It remains to show that indeed the tail of the infinite sum is negligible.

The function $f_\ell(\rho) = \rho j_\ell(\rho)$ or $\rho n_\ell(\rho)$ satisfies the Schrödinger equation,

$$f_\ell''(\rho) = \left\{\frac{\ell(\ell+1)}{\rho^2} - 1\right\} f_\ell(\rho)\,, \tag{8.15}$$

[see Eq.(4.49) of Volume 1]. We can investigate the behavior of solutions of this equation in the vicinity of the classical turning point, $\rho^2 = \ell(\ell+1)$, by means of the WKB approach, defining an effective attenuation coefficient $\kappa(\rho)$:

$$\kappa^2(\rho) = \left\{\frac{\ell(\ell+1)}{\rho^2} - 1\right\}\,.$$

In the classically forbidden region, $\rho^2 < \ell(\ell+1)$, the WKB approximation yields non-oscillating solutions [for details see Vol 1, Sec 5.3.] In this region, the spherical functions display the known asymptotes

$$j_\ell(\rho) \sim \frac{\ell!}{(2\ell+1)!}(2\rho)^\ell \qquad n_\ell(\rho) \sim -\frac{(2\ell)!}{\ell!}(-\rho)^{-\ell-1}, \tag{8.16}$$

see Eqs.(4.55)-(4.57) of Volume 1. These asymptotic expressions were regarded as being "threshold behaviors", i.e., expressions valid for small ρ only, but in fact they are good approximations for the whole of the classically forbidden region, in particular for large ρ, on condition that ℓ is even larger, $\rho^2 < \ell(\ell+1)$. For large ℓ, we use Stirling's approximation, $\ell! \sim \sqrt{2\pi\ell}\,\ell^\ell\,\mathrm{e}^{-\ell}$, in Eq.(8.16) to yield the asymptote

$$|j_\ell(\rho)/n_\ell(\rho)| \sim \frac{1}{4}\left(\frac{\mathrm{e}}{4}\right)^{2\ell}\left(\frac{\rho}{\ell}\right)^{2\ell+1},$$

which goes exponentially to zero as $\ell \to \infty$. Hence those terms in the series (8.14), for which $\ell(\ell+1) > k^2a^2$ is true, satisfy

$$(2\ell+1)\,\frac{j_\ell^2(ka)}{j_\ell^2(ka)+n_\ell^2(ka)} \sim \frac{\ell}{8}\left(\frac{\mathrm{e}}{4}\right)^{4\ell}\left(\frac{ka}{\ell}\right)^{4\ell+2},$$

which motivates the truncation of the series at the point $\ell \approx ka$.

The preceding considerations are only suggestive, and perhaps not wholly convincing, so we now compute the sum Eq.(8.14) numerically, with a sufficent number of terms to ensure a preassigned accuracy:

$\rho^{2/3}$	$ka = \rho$	$\sigma_T/2\pi a^2 - 1.0$
10	32	0.096103
30	164	0.032811
100	1000	0.009926
300	5196	0.003317
1 000	31623	0.000996
3 000	164317	0.000332
10 000	1 000 000	0.000100
30 000	5 196 150	0.000033
100 000	31 622 800	0.000010

Cross Section for Hard Core Potential

These results were obtained with the help of the following Mathematica program:

```
(* Computation of Hard Core High Energy Limit of Cross Section  *)

$MinPrecision = 50;
sphbess[n_, z_] := Sqrt[Pi/(2*z)]*BesselJ[n + 1/2, z];
sphneum[n_, z_] := Sqrt[Pi/(2*z)]*BesselY[n + 1/2, z];

y = 3000.; x = y^1.5;
ja = sphbess[0, x]; na = sphneum[0, x];
jb = sphbess[1, x]; nb = sphneum[1, x];
s = 1./(1 + (na/ja)^2) + 3./(1 + (nb/jb)^2);
ds = s; j = 1;

While[ds/s > 10^(-17), j = j + 1;
  jc = jb*(2*j - 1)/x - ja; nc = nb*(2*j - 1)/x - na;
  ds = (2*j + 1)/(1 + (nc/jc)^2); s = s + ds;
  ja = jb; jb = jc; na = nb; nb = nc]

ans = (2*s)/x^2 - 1;
Print[{y,x,ans,ds/s}]
```

In this program, in which a calculating precision of 50 significant figures is specified, the spherical Bessel and Neumann functions are constructed by iteration, from the lowest two, by means of the recurrence relation

$$j_\ell(\rho) = \frac{(2\ell - 1)}{\rho} j_{\ell-1}(\rho) - j_{\ell-2}(\rho)\,, \tag{8.17}$$

and a similar one for the spherical Neumann function. This relation can proved by starting with Eq.(4.50) of Volume 1, namely

$$f_\ell(\rho) = -f'_{\ell-1}(\rho) + \frac{\ell}{\rho} f_{\ell-1}(\rho)\,, \tag{8.18}$$

where $f_\ell(\rho) = \rho j_\ell(\rho)$ or $f_\ell(\rho) = \rho n_\ell(\rho)$. Differentiate Eq.(8.18), eliminate the second-order derivative by means of the Schrödinger equation (8.15), and the first-order derivatives by using Eq.(8.18) again, obtaining

$$f_{\ell-1}(\rho) + f_{\ell+1}(\rho) = \frac{(2\ell + 1)}{\rho} f_\ell(\rho)\,,$$

which is equivalent to the required recurrence relation.

As can be seen from the table, the cross-section may be well represented by the approximate formula

$$\sigma_T \approx 2\pi a^2[1 + (ka)^{-2/3}].$$

The first term in this asymptotic scattering cross section corresponds to the geometrical profile, πa^2, and the shadow, which also contributes πa^2. The second term arises because of the sharp discontinuity at the surface of the hard sphere. Thus the total cross section has the asymptotic value $\sigma_T = 4\pi a^2$ as $k \to 0$, and it decreases monotically to the high energy limit, $\sigma_T = 2\pi a^2$. This can be contrasted with the classical total cross section, equal to the geometrical profile, πa^2, at all energies.

8.3 Optical Theorem

Problem 4

Prove the optical theorem for elastic scattering, that is

$$\sigma_T \equiv \int d\Omega \frac{d\sigma}{d\Omega} = \frac{4\pi}{k} \mathrm{Im} f_k(0) .$$

Solution

The partial wave expansion of an elastic scattering amplitude is

$$f_k(\theta) = \frac{1}{k} \sum_{\ell=0}^{\infty} (2\ell + 1)\, \mathrm{e}^{i\delta_\ell} \sin\delta_\ell \, P_\ell(\cos\theta) , \tag{8.19}$$

where δ_ℓ is real, see Eq.(8.42) of Volume 1. The total cross-section is

$$\begin{aligned} \sigma &= \int d\Omega \, |f_k(\theta)|^2 \qquad (8.20) \\ &= \frac{2\pi}{k^2} \int_{-1}^{1} dz \sum_k \sum_\ell (2k+1)(2\ell+1)\, \mathrm{e}^{i(\delta_k - \delta_\ell)} \sin\delta_k \sin\delta_\ell \, P_k(z) P_\ell(z) . \end{aligned}$$

The orthogonality relation for the Legendre polynomials leads to

$$\sigma = \frac{4\pi}{k^2} \sum_\ell (2\ell + 1) \sin^2 \delta_\ell . \tag{8.21}$$

Since $P_\ell(1) = 1$ for all ℓ, the imaginary part of Eq.(8.19) yields

$$\mathrm{Im}\, f_k(0) = \frac{1}{k} \sum_{\ell=0}^{\infty} (2\ell + 1) \sin^2 \delta_\ell ,$$

from which the required result follows immediately.

8.4 Generalized Optical Theorem

When there is inelasticity, the partial wave scattering function, $S_\ell(k)$, can be written $\eta_\ell \exp(2i\delta_\ell)$, where $0 < \eta_\ell(k) < 1$. Show that the optical theorem is still true, where now σ_T is the sum of the integrated elastic and inelastic cross-sections.

Solution

According to Section 8.2 of Volume 1, the number of particles scattered through a small area $\Delta\mathcal{A}$, per second, is

$$-\frac{i\hbar N}{2m}\Delta\mathcal{A}\left[\psi_k^* \overleftrightarrow{\nabla} \psi_k\right]_{\mathcal{N}} = \frac{\hbar N}{m}\Delta\mathcal{A}\left[\vec{k} + \frac{\vec{k}'}{r^2}|f_k(\theta)|^2\right]_{\mathcal{N}} . \tag{8.22}$$

Here N is the number of particles per unit area per unit time that fall upon a scattering center. The incoming particles (in a plane-wave beam) are described by the term $\vec{k}$. The incident flux is $\frac{\hbar N k}{m}$, whereas the outgoing flux in direction $\vec{r}$ is $\frac{\hbar N k}{m}|f_k(\theta)|^2/r^2$, as explained in the above section. The elastic differential cross-section is the ratio of these two fluxes,

$$\frac{d\sigma_{\text{el}}}{d\Omega} = |f_k(\theta)|^2 . \tag{8.23}$$

We have added the suffix 'el', because this refers to the elastic cross section, i.e., the effective scattering area that accounts for the outward flow of scattered particles, per unit area, in the direction $\vec{r}$.

We obtain the integrated elastic cross-section by integrating Eq.(8.23):

$$\sigma_{\text{el}} = \int d\Omega \frac{d\sigma_{\text{el}}}{d\Omega} = 4\pi \sum_{\ell=0}^{\infty}(2\ell+1)|f_\ell(k)|^2 , \tag{8.24}$$

where the orthogonality of the Legendre polynomials has been used, as in Eqs.(8.20)-(8.21). The partial-wave amplitude is related to the scattering matrix by

$$S_\ell(k) \equiv 1 + 2ikf_\ell(k) = \eta_\ell \, e^{2i\delta_\ell(k)} , \tag{8.25}$$

where η_ℓ is generally less than unity. Thus

$$f_\ell(k) = \frac{\eta_\ell \sin 2\delta_\ell + i(1 - \eta_\ell \cos 2\delta_\ell)}{2k} , \tag{8.26}$$

and so

$$\sigma_{\text{el}} = \frac{\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\left(1 + \eta_\ell^2 - 2\eta_\ell \cos 2\delta_\ell\right) . \tag{8.27}$$

To calculate the inelastic cross-section, we write the wave-function

$$\psi_k(\vec{r}) = \frac{1}{2ikr}\sum_{\ell=0}^{\infty}(2\ell+1)\left\{S_\ell(k)\,\mathrm{e}^{ikr} - (-1)^\ell\,\mathrm{e}^{-ikr}\right\}P_\ell(\cos\theta)\,, \tag{8.28}$$

cf., Eq.(8.36) and Eq.(8.38) of Volume 1. Since the term in e^{-ikr} is an incoming spherical wave in the ℓth partial wave, and the term in e^{ikr} an outgoing spherical wave (representing the scattering), we can obtain the inelasticity by calculating the difference between the integrated contributions from the incoming and the outgoing waves.

For a spherical wave, we can replace $\left[\psi_k^* \overleftrightarrow{\nabla} \psi_k\right]_{\mathcal{N}}$ by $\psi_k^* \overleftrightarrow{\frac{\partial}{\partial r}} \psi_k$, and, to leading order in r, we have

$$\frac{\partial}{\partial r}\psi_k(\vec{r}) = \frac{1}{2r}\sum_{\ell=0}^{\infty}(2\ell+1)\left\{S_\ell(k)\,\mathrm{e}^{ikr} + (-1)^\ell\,\mathrm{e}^{-ikr}\right\}P_\ell(\cos\theta)\,. \tag{8.29}$$

If we now integrate Eq.(8.22) over a spherical shell of radius r, this will yield, as the net particle loss,

$$-\frac{i\hbar N}{2m}r^2\int d\Omega\left[\psi_k^* \overleftrightarrow{\nabla} \psi_k\right]_{\mathcal{N}} = \frac{\pi\hbar N}{2mk}\sum_{\ell=0}^{\infty}(2\ell+1)\tau_\ell(r,k)\,, \tag{8.30}$$

where

$$\begin{aligned}\tau_\ell(r,k) &= -[S_\ell^*(k)\,\mathrm{e}^{-ikr} - (-1)^\ell\,\mathrm{e}^{ikr}][S_\ell(k)\,\mathrm{e}^{ikr} + (-1)^\ell\,\mathrm{e}^{-ikr}] \\ &\quad -[S_\ell^*(k)\,\mathrm{e}^{-ikr} + (-1)^\ell\,\mathrm{e}^{ikr}][S_\ell(k)\,\mathrm{e}^{ikr} - (-1)^\ell\,\mathrm{e}^{-ikr}] \\ &= -2[\,|S_\ell(k)|^2 - 1] = 2[1-\eta_\ell^2]\,.\end{aligned}$$

Since the incident flux is $\frac{\hbar Nk}{m}$, we obtain the inelastic integrated cross-section by dividing Eq.(8.30) by this quantity, yielding

$$\sigma_{\mathrm{inel}} = \frac{\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)(1-\eta_\ell^2)\,. \tag{8.31}$$

Finally, on adding Eq.(8.27) and Eq.(8.31), we obtain, for the total cross-section,

$$\sigma_T = \sigma_{\mathrm{el}} + \sigma_{\mathrm{inel}} = \frac{2\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\,(1-\eta_\ell\cos 2\delta_\ell)\,. \tag{8.32}$$

On the other hand, we see from Eq.(8.26) that

$$\mathrm{Im}f_\ell(k) = \frac{1-\eta_\ell\cos 2\delta_\ell}{2k}\,, \tag{8.33}$$

so that

$$f_k(0) = \frac{1}{2k}\sum_{\ell=0}^{\infty}(2\ell+1)\,(1-\eta_\ell\cos 2\delta_\ell)\ .$$

From the last two equations we see that

$$\sigma_T = \frac{4\pi}{k}\mathrm{Im}f_k(0)\,,$$

which is precisely the same expression as the one that holds for elastic scattering.

8.5 Born Approximation

Calculate the scattering amplitude in Born approximation with the following spherically symmetric potentials, $V(r)$:

(1) (a) $-g\theta(a-r)$. (b) $-\frac{g}{r^2+a^2}$.
(2) (a) $-\frac{g\hbar^2}{2m}\exp(-\frac{r}{a})$. (b) $-\frac{g\hbar^2}{2m}\exp(-\frac{r^2}{a^2})$.

Solution
The scattering amplitude in this approximation is given by

$$f_k(\theta) = -\frac{2m}{\hbar^2 q}\int_0^\infty r dr V(r)\sin(qr)\,. \tag{8.34}$$

Where $q = 2k\sin\frac{\theta}{2}$.
(1a) The scattering amplitude for the step function, in Born approximation, is

$$\begin{aligned} f_k(\theta) &= \frac{2mg}{\hbar^2 q}\int_0^a dr\, r\sin(qr) \\ &= \frac{2mg}{\hbar^2 q}\left\{\left[-\frac{r\cos qr}{q}\right]_0^a + \int_0^a dr\frac{\cos qr}{q}\right\} \\ &= \frac{2mg}{\hbar^2}\left\{\frac{\sin qa}{q^3} - \frac{a\cos qa}{q^2}\right\}. \end{aligned}$$

(1b) Here we write the sine in terms of complex exponentials,

$$\begin{aligned} f_k(\theta) &= \frac{mg}{i\hbar^2 q}\int_0^\infty r dr\frac{e^{iqr}-e^{-iqr}}{r^2+a^2} \\ &= \frac{mg}{2i\hbar^2 q}\int_{-\infty}^{\infty} dr\, e^{iqr}\left\{\frac{1}{r-ia}+\frac{1}{r+ia}\right\} = \frac{\pi mg}{\hbar^2 q}e^{-aq}\,. \end{aligned}$$

To obtain the second line from the first, set $r \to -r$ in the second term, and also make a partial fraction decomposition. To get the third line, close the contour

in the upper half of the complex r plane and pick up the residue of the pole at $r = ia$.

(2a) Here we write

$$\begin{aligned} f_k(\theta) &= \frac{g}{q}\,\mathrm{Im}\int_0^\infty r dr\, \mathrm{e}^{iqr}\,\mathrm{e}^{-r/a} \\ &= \mathrm{Im}\,\frac{g}{q(iq-1/a)}\int_0^\infty dr\,\exp(-r(iq-1/a) \\ &= \mathrm{Im}\,\frac{g}{q(iq-1/a)^2} \\ &= \mathrm{Im}\,\frac{g(iq-1/a)^2}{q(q^2+1/a^2)^2} = -\frac{2a^3 g}{(a^2q^2+1)^2}\,. \end{aligned}$$

(2b) Lastly

$$\begin{aligned} f_k(\theta) &= \frac{g}{2iq}\int_0^\infty r dr(\,\mathrm{e}^{iqr} - \mathrm{e}^{-iqr})\,\mathrm{e}^{-r^2/a^2} \\ &= \frac{g}{2iq}\int_{-\infty}^\infty r dr\,\mathrm{e}^{-r^2/a^2}\,\mathrm{e}^{iqr} \\ &= \frac{g}{2iq}\int_{-\infty}^\infty dr\,\left\{r - \tfrac{i}{2}qa^2 + \tfrac{i}{2}qa^2\right\}\exp\left[-\frac{(r-\frac{i}{2}qa^2)^2}{a^2}\right]\exp\left[-\frac{q^2a^2}{4}\right] \\ &= \frac{ga^3\sqrt{\pi}}{4}\exp\left[-\frac{q^2a^2}{4}\right]. \end{aligned}$$

8.6 Yukawa in Born Approximation

Calculate the differential scattering cross-section in Born approximation for the scattering of two identical particles that move under a Yukawa interaction:

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{g}{|\vec{r}_1 - \vec{r}_2|}\,\mathrm{e}^{-\mu|\vec{r}_1-\vec{r}_2|/\hbar},$$

Solution

The center-of-mass and total system coordinates are

$$\begin{aligned} \vec{r} &= \vec{r}_1 - \vec{r}_2 \\ \vec{p} &= \tfrac{1}{2}(\vec{p}_1 - \vec{p}_2) \\ \vec{R} &= \tfrac{1}{2}(\vec{r}_1 + \vec{r}_2) \\ \vec{P} &= \vec{p}_1 + \vec{p}_2\,. \end{aligned}$$

In terms of these new canonical variables,

$$H = \frac{P^2}{2m_R} + \frac{p^2}{2m_r} + \frac{g}{r}\,\mathrm{e}^{-\mu r/\hbar}\,, \tag{8.35}$$

where $m_R = 2m$ is the total mass of the system, and $m_r = \frac{1}{2}m$ is the reduced mass (cf. Eq.(4.35) in Volume 1). The Born approximation to the amplitude for the potential $g\,\mathrm{e}^{-\mu r/\hbar}/r$ is

$$\begin{aligned} f_k(\theta) &= -\frac{2gm_r}{\hbar^2 q}\,\mathrm{Im}\int_0^\infty dr\,\mathrm{e}^{iqr}\,\mathrm{e}^{-\mu r/\hbar} \\ &= -\mathrm{Im}\,\frac{gm}{\hbar^2 q(\mu/\hbar - iq)} = -\frac{gm}{\mu^2 + \hbar^2 q^2}\,. \end{aligned}$$

8.7 Two Different Spin Half Particles

Consider two different particles of spin $\frac{1}{2}$. The interaction potential is

$$V(r) = W(r)\vec{s}_1 \cdot \vec{s}_2\,,$$

where $\vec{s}_j = \frac{1}{2}\hbar\vec{\sigma}_j$ and $W(r)$ is a continuous, scalar function. Calculate in Born approximation the ratio of the probabilities that, after the scattering process, one finds $s_{1z} = \frac{1}{2}\hbar$ or $s_{1z} = -\frac{1}{2}\hbar$, given that, before scattering, $s_{1z} = \frac{1}{2}\hbar = -s_{2z}$.

Solution

The spatial parts of the probabilities cancel out of the ratio, and we are left with the spin-dependent parts:

$$\frac{P(+)}{P(-)} = \frac{\sum_{s=\pm}|\langle +,s|\vec{s}_1\cdot\vec{s}_2|+,-\rangle|^2}{\sum_{s=\pm}|\langle -,s|\vec{s}_1\cdot\vec{s}_2|+,-\rangle|^2}\,. \tag{8.36}$$

In terms of the spin raising and lowering operators, $s_{1\pm}$ and $s_{2\pm}$,

$$s_{1+}s_{2-} + s_{1-}s_{2+} = 2(s_{1x}s_{2x} + s_{1y}s_{2y})\,,$$

and so the scalar product of the spin operators can be written

$$\vec{s}_1 \cdot \vec{s}_2 = \tfrac{1}{2}(s_{1+}s_{2-} + s_{1-}s_{2+}) + s_{1z}s_{2z}\,,$$

from which it follows that

$$\vec{s}_1 \cdot \vec{s}_2|+,-\rangle = \tfrac{1}{2}\hbar^2|-,+\rangle + \tfrac{1}{4}\hbar^2|+,-\rangle\,.$$

Hence $\sum_{s=\pm}|\langle +,s|\vec{s}_1\cdot\vec{s}_2|+,-\rangle|^2 = \langle +,-|\vec{s}_1\cdot\vec{s}_2|+,-\rangle|^2 = \frac{1}{16}\hbar^4$, and similarly $\sum_{s=\pm}|\langle -,s|\vec{s}_1\cdot\vec{s}_2|+,-\rangle|^2 = \langle -,+|\vec{s}_1\cdot\vec{s}_2|+,-\rangle|^2 = \frac{1}{4}\hbar^4$. Inserting these results into Eq.(8.36), we find $P(+)/P(-) = \frac{1}{4}$.

8.8 Perturbation Theory for Scattering

Let $\delta_\ell(k)$ and $\overline{\delta}_\ell(k)$ be the ℓ-wave phase shifts corresponding to the central potentials $V(r)$ and $\overline{V}(r)$, respectively. Prove that

$$\sin(\overline{\delta}_\ell - \delta_\ell) = -\frac{2m}{\hbar^2 k}\int_0^\infty dr\,[\overline{V}(r) - V(r)]u_\ell(r)\overline{u}_\ell(r)\,,$$

where $u_\ell(r)$ and $\overline{u}_\ell(r)$ are the radial wave functions. If $\overline{V}(r) = V(r) + \lambda W(r)$, where $W(r)$ is suitably well-behaved, sketch a perturbation method to be used for small λ.

Solution

Let $u_\ell(r)$ and $\overline{u}_\ell(r)$ be regular solutions of the radial Schrödinger equations,

$$\begin{aligned} u_\ell''(r) + \left\{k^2 - \frac{2m}{\hbar^2}V(r) - \frac{\ell(\ell+1)}{r^2}\right\}u_\ell(r) &= 0 \\ \overline{u}_\ell''(r) + \left\{k^2 - \frac{2m}{\hbar^2}\overline{V}(r) - \frac{\ell(\ell+1)}{r^2}\right\}\overline{u}_\ell(r) &= 0\,, \end{aligned} \tag{8.37}$$

where $k^2 = 2mE/\hbar^2$. Multiply the first equation by $\overline{u}_\ell(r)$, the second by $u_\ell(r)$, and subtract one equation from the other:

$$[\overline{u}_\ell(r)u_\ell'(r) - u_\ell(r)\overline{u}_\ell'(r)]' = -\frac{2m}{\hbar^2}[\overline{V}(r) - V(r)]\overline{u}_\ell(r)u_\ell(r)\,.$$

The left-hand side of this equation vanishes at $r = 0$, because the solutions are regular, and so we may integrate to get

$$\overline{u}_\ell(r)u_\ell'(r) - u_\ell(r)\overline{u}_\ell'(r) = -\frac{2m}{\hbar^2}\int_0^r [\overline{V}(r) - V(r)]\overline{u}_\ell(r)u_\ell(r)\,. \tag{8.38}$$

Normalize the solutions so that, in the limit $r \to \infty$,

$$\begin{aligned} u_\ell(r) &\sim \sin(kr + \delta_\ell - \ell\pi/2) \\ u_\ell'(r) &\sim k\cos(kr + \delta_\ell - \ell\pi/2)\,, \end{aligned}$$

and similarly for $\overline{u}_\ell(r)$ and $\overline{u}_\ell'(r)$. Setting $r = \infty$ in Eq.(8.38) and using the asymptotic expressions for the radial wave functions, we obtain the required expression for $\sin(\overline{\delta}_\ell - \delta_\ell)$, which may be rewritten

$$\sin(\overline{\delta}_\ell - \delta_\ell) = -\frac{2m\lambda}{\hbar^2 k}\int_0^\infty dr\,W(r)u_\ell^2(r)\,,$$

where $\overline{u}_\ell(r)$ has been approximated, to zeroth order in λ, by $u_\ell(r)$. This amounts to first-order perturbation theory. In particular, if we set $V(r) = 0$, so that $\delta_\ell = 0$

and $u_\ell(r) = krj_\ell(kr)$, then $\overline{V}(r) = \lambda W(r)$ and

$$\sin\overline{\delta}_\ell = -\frac{2mk}{\hbar^2}\int_0^\infty dr\, r^2\, \overline{V}(r) j_\ell^2(kr)\,.$$

This is an approximate expression for the phase shift for a weak, well-behaved potential.

8.9 Solitonic Potential

By considering the differential operators

$$\mathcal{L}_\pm = \tanh r \pm \frac{d}{dr}\,,$$

solve the S-wave Schrödinger equation for the spherically symmetric potential

$$V(r) = -\frac{\hbar^2}{m}\cosh^{-2} r\,.$$

Calculate the S-wave phase shift. Are there any resonances and/or bound states?

Solution

For any twice differentiable function, $w(r)$,

$$\begin{aligned}\mathcal{L}_+\mathcal{L}_- w(r) &= \left(\tanh r + \frac{d}{dr}\right)\left(\tanh r - \frac{d}{dr}\right) w(r) \\ &= \left(\tanh^2 r - \tanh r\frac{d}{dr} + \tanh r\frac{d}{dr} + \operatorname{sech}^2 r - \frac{d^2}{dr^2}\right) w(r)\,.\end{aligned}$$

Since $\tanh^2 r = 1 - \operatorname{sech}^2 r$, it follows that

$$\mathcal{L}_+\mathcal{L}_- w(r) = w(r) - w''(r)\,. \tag{8.39}$$

On the other hand, for a twice differentiable function, $u(r)$,

$$\begin{aligned}\mathcal{L}_-\mathcal{L}_+ u(r) &= \left(\tanh r - \frac{d}{dr}\right)\left(\tanh r + \frac{d}{dr}\right) u(r) \\ &= \left(\tanh^2 r + \tanh r\frac{d}{dr} - \tanh r\frac{d}{dr} - \operatorname{sech}^2 r - \frac{d^2}{dr^2}\right) u(r)\,,\end{aligned}$$

so in this case we find

$$\mathcal{L}_-\mathcal{L}_+ u(r) = (1 - 2\operatorname{sech}^2 r)u(r) - u''(r)\,. \tag{8.40}$$

Now suppose that $w(r)$ is such that

$$(1+k^2)w(r) = \mathcal{L}_+\mathcal{L}_-w(r) = w(r) - w''(r)\,, \tag{8.41}$$

i.e., $w''(r) = -k^2 w(r)$, for which the general solution is

$$w(r) = A\,\mathrm{e}^{ikr} + B\,\mathrm{e}^{-ikr}\,. \tag{8.42}$$

Define $u(r)$ by

$$\begin{aligned} u(r) &= \mathcal{L}_-w(r) = \left(\tanh r - \frac{d}{dr}\right)(A\,\mathrm{e}^{ikr} + B\,\mathrm{e}^{-ikr}) \\ &= A\,(\tanh r - ik)\;\mathrm{e}^{ikr} + B\,(\tanh r + ik)\;\mathrm{e}^{-ikr}\,. \end{aligned} \tag{8.43}$$

Multiply Eq.(8.41) by $\mathcal{L}_-$,

$$(1+k^2)\mathcal{L}_-w(r) = \mathcal{L}_-\mathcal{L}_+\mathcal{L}_-w(r)\,,$$

and use the definition, $u = \mathcal{L}_-w$, giving

$$(1+k^2)u(r) = \mathcal{L}_-\mathcal{L}_+u(r) = (1 - 2\mathrm{sech}^2\, r)u(r) - u''(r)\,.$$

This can be cast into the form of the radial Schrödinger equation,

$$-\frac{\hbar^2}{2m}u''(r) + V(r)u(r) = \frac{\hbar^2k^2}{2m}u(r)\,, \tag{8.44}$$

where the potential is

$$V(r) = -\frac{\hbar^2}{m}\cosh^{-2} r\,.$$

The general solution of this equation was given in Eq.(8.43), but the S-wave must behave like r as $r \to 0$ (the regularity condition). That implies $A = B$, so we obtain, as the physical solution of Eq.(8.44),

$$u(r) = A(\tanh r + ik)\left(\mathrm{e}^{-ikr} + \frac{\tanh r - ik}{\tanh r + ik}\,\mathrm{e}^{ikr}\right)\,. \tag{8.45}$$

As $r \to \infty$, we find

$$u(r) \sim -A(1+ik)\left(\frac{k+i}{k-i}\,\mathrm{e}^{ikr} - \mathrm{e}^{-ikr}\right)\,.$$

Hence the S-wave scattering matrix and phase shift are given by

$$S_0(k) = \mathrm{e}^{2i\delta_0} = \frac{k+i}{k-i} = \frac{(k+i)^2}{k^2+1}\,,$$

and so

$$e^{i\delta_0} = \frac{k+i}{\sqrt{k^2+1}} \qquad \text{or} \qquad \delta_0 = \cot^{-1} k\,.$$

There are no resonances, since the phase shift does not rise through an odd multiple of $\frac{\pi}{2}$. In fact, it begins at the threshold value $\frac{\pi}{2}$ and tends to 0 at infinite energies (modulo π).

To find out if there are any bound states, we set $k = i\kappa$, and write the solution Eq.(8.45) as

$$u(r) = A\left\{(\tanh r + \kappa)\, e^{-\kappa r} + (\tanh r - \kappa)\, e^{\kappa r}\right\}\,. \tag{8.46}$$

The only value of κ for which the exponentially increasing term, $e^{\kappa r}$, vanishes asymptotically is $\kappa = 1$. At first sight, one might think that this signals a bound state, but with $\kappa = 1$ we find

$$u(r) = A\,\mathrm{sech} r\,\left\{(\sinh r + \cosh r)\, e^{-r} + (\sinh r - \cosh r)\, e^{r}\right\} = 0\,.$$

So the putative bound state is extinct. There are no bound states nor resonances in the classic sense of those terms. However, the fact that the phase shift is not 0, modulo π, at threshold, indicates that this potential is a transitional case. With a potential $V(r) = -\alpha\frac{\hbar^2}{2m}\cosh^{-2} r$, there is a bound state if $\alpha > 2$ and a resonance if $\alpha < 2$. The case $\alpha = 2$ corresponds to what is sometimes called a zero-energy bound state.

This is a special case of Levinson's Theorem, which relates the number of bound states in a given partial wave, n_B, to the difference between the phase shift between zero and infinite energies; $\delta(0) - \delta(\infty) = n_B\pi$. The zero energy bound state counts as "half" in this relation. For details see [Newton, R.G. (1982)].

8.10 Crichton Ambiguity

A nuclear physicist measures a scattering process, and finds on analyzing his data that the following phase shifts (in radians) describe his data well: $\delta_0 = 0.88779$, $\delta_1 = -0.56640$, $\delta_2 = 0.23447$, and $\delta_\ell = 0$ for $\ell \geq 3$.

(1) Draw a graph of the differential cross-section against $\cos\theta$.

(2) A research student of the nuclear physicist analyses the same experimental results but she arrives at the following phase shifts: $\delta_0 = 0.10930$, $\delta_1 = -0.76993$, $\delta_2 = 0.23447$, again with all the higher phase shifts vanishing. Draw a graph of the differential cross-section against $\cos\theta$.

Has the research student, or the nuclear physicist made a mistake, or are they both correct? Explain.

(3) If there is an infinite number of non-zero phase shifts, are they uniquely determined by the differential cross-section?

Solution

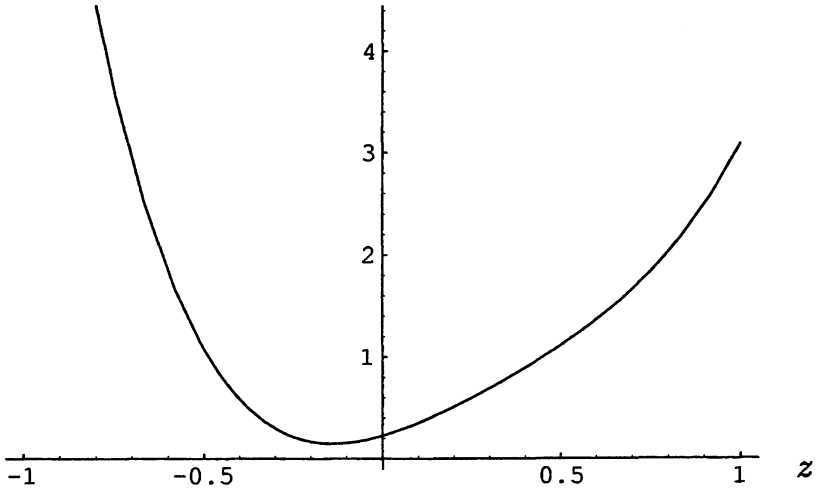

Fig. 8.2 Crichton Cross Section

(1) A scattering amplitude containing only S, P and D waves can be written

$$f_k(\theta) = f_0(k) + 3z f_1(k) + \tfrac{5}{2}(3z^2 - 1) f_2(k)\,,$$

where $z = \cos\theta$ and the partial wave amplitudes satisfy

$$f_\ell(k) = \frac{1}{k}\, \mathrm{e}^{i\delta_\ell(k)} \sin\delta_\ell(k)\,.$$

The scattering differential cross-section is $|f_k(\theta)|^2$, and in Figure 8.2 we plot

$$\begin{aligned} k^2 \frac{d\sigma}{d\Omega} &= \left| f_0(k) + 3z f_1(k) + \tfrac{5}{2}(3z^2 - 1) f_2(k) \right|^2 \qquad (8.47) \\ &= \sin^2\delta_0 + 6z \sin\delta_0 \sin\delta_1 \cos(\delta_0 - \delta_1) + \\ &\quad 9z^2 \sin^2\delta_1 + 15z(3z^2 - 1) \sin\delta_1 \sin\delta_2 \cos(\delta_1 - \delta_2) + \\ &\quad \tfrac{25}{4}(3z^2 - 1)^2 \sin^2\delta_2 + +5(3z^2 - 1) \sin\delta_0 \sin\delta_2 \cos(\delta_0 - \delta_2)\,, \end{aligned}$$

with the phase shifts given in the first part of the exercise.

(2) Exactly the same curve is obtained with the alternative set of phase shifts given in the second part, so we will not plot it again. Evidently the scatter-

ing differential cross-section does not uniquely determine the phase shifts. To examine the general situation when only S, P and D waves are nonzero, we set

$$k^2|f_k(\theta)|^2 = k^2|f'_k(\theta)|^2\,, \tag{8.48}$$

where $f'_k(\theta)$ has a partial-wave expansion like that of $f_k(\theta)$, excepting only that the phase shifts, δ_ℓ, are replaced by δ'_ℓ. Following Crichton, we shall show that nontrivial solutions of this problem exist. For Eq.(8.48) to be true, it must be so that the fourth-order polynomial equation holds that is formed by setting the right side of Eq.(8.47) equal to the corresponding expression with δ'_ℓ in place of δ_ℓ. Since the fourth-order polynomials on either side of the equation must be equal for all values of z, we may equate the coefficients of the various powers of z. To ensure equality of the power z^4, we require

$$\sin^2\delta_2 = \sin^2\delta'_2\,,$$

and so $\delta_2 = \pm\delta'_2$ (the phase-shifts are in general only defined modulo π, and the only solutions of the above equation in the interval $-\pi/2 \le \delta_2 \le \pi/2$ are as given, i.e., only the sign is undetermined). However, if one changes the sign of every phase shift, the cross-section does not change, and this is referred to as the *trivial* ambiguity in the determination of the phase shifts by the data. Accordingly, we can say that $\delta_2 = \delta'_2$, aside from the trivial ambiguity, which we do not count as an interesting alternative solution, since it is always possible.

To determine the four phase shifts, δ_0, δ'_0, δ_1 and δ'_1, in terms of δ_2, we have four nonlinear equations, namely the equality of the coefficients of the powers z^3, z^2, z and 1. Equating coefficients of z^3, we find

$$\sin\delta_1\cos(\delta_1-\delta_2) = \sin\delta'_1\cos(\delta'_1-\delta_2)\,,$$

where a common factor $\sin\delta_2$ has already been canceled. From this we find

$$\sin 2\delta_1\cos\delta_2 - \cos 2\delta_1\sin\delta_2 = \sin 2\delta'_1\cos\delta_2 - \cos 2\delta'_1\sin\delta_2\,.$$

Set now $\alpha_1 = \delta_1 + \delta'_1$ and $\epsilon_1 = \delta_1 - \delta'_1$. Straightforward manipulations yield

$$\cos\alpha_1\sin\epsilon_1\cos\delta_2 + \sin\alpha_1\sin\epsilon_1\sin\delta_2 = 0\,.$$

A common factor $\sin\epsilon_1$ can be canceled, on condition that it is not zero, and we find $\tan\alpha_1 = -\cot\delta_2 = \tan(\delta_2 - \frac{\pi}{2})$, with the solution

$$\alpha_1 = \delta_2 - \frac{\pi}{2}\,. \tag{8.49}$$

Next, on equating coefficients of z^0, we have

$$\sin^2\delta_0 - 5\sin\delta_0\sin\delta_2\cos(\delta_0-\delta_2) = \sin^2\delta'_0 - 5\sin\delta'_0\sin\delta_2\cos(\delta'_0-\delta_2)\,, \tag{8.50}$$

and, on equating coefficients of z^2,

$$3\sin^2\delta_1 + 5\sin\delta_0\sin\delta_2\cos(\delta_0-\delta_2) = 3\sin^2\delta_1' + 5\sin\delta_0'\sin\delta_2\cos(\delta_0'-\delta_2)\,.$$

The sum of the last two equations is

$$\sin^2\delta_0 + 3\sin^2\delta_1 = \sin^2\delta_0' + 3\sin^2\delta_1'\,, \tag{8.51}$$

which in fact could also have been deduced from the optical theorem. After a little work, Eq.(8.50) can be cast into the form

$$\sin 2\delta_2\{\sin 2\delta_0 - \sin 2\delta_0'\} + \{\cos 2\delta_2 - \tfrac{3}{5}\}\{\cos 2\delta_0 - \cos 2\delta_0'\} = 0\,,$$

which, in terms of $\alpha_0 = \delta_0 + \delta_0'$ and $\epsilon_0 = \delta_0 - \delta_0'$, reads

$$\sin 2\delta_2\cos\alpha_0\sin\epsilon_0 + \{\cos 2\delta_2 - \tfrac{3}{5}\}\sin\alpha_0\sin\epsilon_0 = 0\,.$$

A common factor $\sin\epsilon_0$ can be canceled, on condition that it is not zero, and so

$$\tan\alpha_0 = \frac{\sin 2\delta_2}{\cos 2\delta_2 - \frac{3}{5}}\,. \tag{8.52}$$

Finally, on equating coefficients of z, we have

$$\begin{aligned} \sin\delta_0\sin\delta_1\cos(\delta_0-\delta_1) &= \sin\delta_0'\sin\delta_1'\cos(\delta_0'-\delta_1') \\ \sin(\alpha_0-\alpha_1)\sin(\epsilon_0-\epsilon_1) &= \sin\alpha_0\sin\epsilon_0 + \sin\alpha_1\sin\epsilon_1\,. \end{aligned} \tag{8.53}$$

It is relatively easy to cast Eq.(8.51) in the form

$$\sin\alpha_0\sin\epsilon_0 + 3\sin\alpha_1\sin\epsilon_1 = 0\,, \tag{8.54}$$

and we have to solve the last two equations for ϵ_0 and ϵ_1. They can be rewritten

$$\begin{aligned} \sin\epsilon_0 &= \kappa\sin\epsilon_1 \qquad & \sin(\epsilon_0-\epsilon_1) &= \Delta\sin\epsilon_1\,, \\ \text{with} \qquad \kappa &= -3\frac{\sin\alpha_1}{\sin\alpha_0} \qquad & \Delta &= -2\frac{\sin\alpha_1}{\sin(\alpha_0-\alpha_1)}\,. \end{aligned}$$

Clearly these equations together imply

$$\kappa\sin\epsilon_1\cos\epsilon_1 - \cos\epsilon_0\sin\epsilon_1 = \Delta\sin\epsilon_1\,,$$

from which a factor $\sin\epsilon_1$ may be canceled. Hence

$$\begin{aligned} \cos\epsilon_0 &= \kappa\cos\epsilon_1 - \Delta \\ 1 = \cos^2\epsilon_0 + \sin^2\epsilon_0 &= \kappa^2[\sin^2\epsilon_1 + \cos^2\epsilon_1] - 2\Delta\kappa\cos\epsilon_1 + \delta^2\,. \end{aligned}$$

This leads directly to

$$\cos\epsilon_0 = \frac{\kappa^2 - \Delta^2 - 1}{2\Delta} \qquad \cos\epsilon_1 = \frac{\kappa^2 + \Delta^2 - 1}{2\kappa\Delta}.$$

With $\delta_2 = 0.23447$, the above solutions yield $\alpha_0 = 0.99709$, $\alpha_1 = 1.80527$, $\epsilon_0 = \pm 0.77850$ and $\epsilon_1 = \pm 2.93807$. The signs of ϵ_0 and ϵ_1 are not determined by the inverse cosines, so we need to check the four possibilities against Eq.(8.54). With plus signs, we find $\sin\alpha_0 \sin\epsilon_0 = 0.589782$ and also $3\sin\alpha_1 \sin\epsilon_1 = 0.589782$, so it is clear from Eq.(8.54) that we need to choose the signs of ϵ_0 and ϵ_1 to be opposite. With $\epsilon_0 = 0.77850$ and $\epsilon_1 = -2.93807$, we find $\delta_0 = 0.88779$ and $\delta_1 = -0.56640$, in agreement with the phase-shift analysis of the nuclear physicist. With the same value of δ_2, we find the alternative S and P wave phase shifts to be $\delta_0' = 0.10930$ and $\delta_1' = 2.37167$, in agreement (modulo π) with the analysis of the research student, since $2.37167 - \pi = -0.76993$.

(3) To investigate the case in which there is an infinite number of non-vanishing phase shifts, consider an amplitude that has the expansion

$$f_k(\theta) = \frac{1}{2i}\frac{z - z_1}{1 - z_1}\left\{\gamma - 1 - 3z - \sum_{\ell=2}^{\infty}(2\ell+1)\epsilon_\ell P_\ell(z)\right\},, \tag{8.55}$$

where z_1 and γ are complex but the ϵ_ℓ are real. An alternative amplitude, $f_k'(\theta)$, is defined by the same expression, except that z_1 is replaced by z_1^*, its complex conjugate. Since

$$\left|\frac{z - z_1^*}{1 - z_1^*}\right| = \left|\frac{z - z_1}{1 - z_1}\right|$$

for real z, it is clear that $|f_k(\theta)|^2 = |f_k'(\theta)|^2$ so both amplitudes correspond to the same cross section. The S and P partial-wave amplitudes can be read off from Eq.(8.55):

$$\begin{aligned} f_0 &= -\frac{1}{2i}\frac{1 + z_1(\gamma - 1)}{1 - z_1} \\ f_1 &= \frac{1}{6i}\frac{\gamma - 1 + 3z_1 - 2\epsilon_2}{1 - z_1}, \end{aligned}$$

and this leads to

$$\begin{aligned} S_0 = 1 + 2if_0 &= -\frac{z_1\gamma}{1 - z_1} \\ S_1 = 1 + 2if_1 &= \frac{2 + \gamma - 2\epsilon_2}{3(1 - z_1)}. \end{aligned}$$

The unitarity requirements $|S_0|^2 = 1 = |S_1|^2$ are satisfied if γ is determined by

$$\begin{aligned} |\gamma|^2 &= \left|\frac{1-z_1}{z_1}\right|^2 \\ \mathrm{Re}\,\gamma &= \frac{9|1-z_1|^2 - |\gamma|^2 - 4(1-\epsilon_2)^2}{4(1-\epsilon_2)}\,. \end{aligned}$$

For $\ell \geq 2$, we find

$$S_\ell = 1 + \frac{\eta_\ell - z_1\epsilon_\ell}{1-z_1}\,,$$

where

$$\eta_\ell = \frac{(\ell+1)\epsilon_{\ell+1} + \ell\epsilon_{\ell-1}}{2\ell+1}\,, \tag{8.56}$$

with the understanding that $\epsilon_1 = 1$. The unitarity condition $|S_\ell|^2 = 1$ yields

$$\eta_\ell^2 - 2\eta_\ell + 2\mathrm{Re}\,z_1\left(\eta_\ell + \epsilon_\ell - \eta_\ell\epsilon_\ell\right) + |z_1|^2\left(\epsilon_\ell^2 - 2\epsilon_\ell\right) = 0\,. \tag{8.57}$$

In the case that $\epsilon_3 << 1$, we have from Eq.(8.56) that

$$\eta_2 = \frac{3\epsilon_3 + 2\epsilon_1}{5} \approx \frac{2}{5}\,,$$

and, on inserting this into Eq.(8.57), we find

$$\epsilon_2 \approx \frac{2(4 - 5\mathrm{Re}\,z_1)}{5(3\mathrm{Re}\,z_1 - 5|z_1|^2)}\,,$$

on condition that $\epsilon_2 << 1$. Evidently this condition is satisfied if $\mathrm{Re}\,z_1$ is approximately equal to $\frac{4}{5}$. With $\mathrm{Re}\,z_1 = \frac{4}{5}$ exactly, $\epsilon_2 = 0$ exactly, and all the higher partial wave amplitudes vanish too. The second order polynomial that remains is precisely the case examined in part (2) above. With $\mathrm{Re}\,z_1 = \frac{4}{5} + \zeta$, where $\zeta << 1$, we have an amplitude with an infinite number of partial waves, which corresponds however to a cross section that differs very little from the pure SPD case, and for which there exists an ambiguous set of scattering phase shifts. This suffices to answer the third part of the question negatively: even when there are infinitely many nonvanishing partial waves, a measurement of the differential cross-section does not necessarily determine the phase shifts uniquely. There can exist a twofold, nontrivial ambiguity of the Crichton type.

Further details of the above method and results, as well as references to the original paper of Crichton, may be found in this paper:

D. Atkinson, L.P. Kok and M. de Roo, 'Crichton Ambiguities with Infinitely Many Partial Waves', Phys. Rev. vol. D17 (1978) pages 2492-2502.

Chapter 9

Atomic Physics

9.1 Terms and Levels

Consider the following terms: ^1S, ^2P, ^3P, ^3D, ^2D, ^1D, ^4D.

(1) What levels may arise from these terms (i.e., which values of spin, orbital angular momentum, and total angular momentum can occur)? Express your findings in the standard form, $^{2S+1}L_J$.

(2) Arrange in order of increasing energy the levels that may arise from the following configurations: $1s2p$, $2p3p$, $3p3d$.

Solution

(1) The values of S, L and J are as follows:

$S = 0,\ L = 0,\ J = \underline{0} \times \underline{0} = \underline{0} \longrightarrow {}^1S_0.$

$S = \frac{1}{2},\ L = 1,\ J = \underline{\frac{1}{2}} \times \underline{1} = \underline{\frac{1}{2}} + \underline{\frac{3}{2}} \longrightarrow {}^2P_{\frac{1}{2}} + {}^2P_{\frac{3}{2}}.$

$S = 1,\ L = 1,\ J = \underline{1} \times \underline{1} = \underline{0} + \underline{1} + \underline{2} \longrightarrow {}^3P_0 + {}^3P_1 + {}^3P_2.$

$S = 1,\ L = 2,\ J = \underline{1} \times \underline{2} = \underline{1} + \underline{2} + \underline{3} \longrightarrow {}^3D_1 + {}^3D_2 + {}^3D_3.$

$S = \frac{1}{2},\ L = 2,\ J = \underline{\frac{1}{2}} \times \underline{2} = \underline{\frac{3}{2}} + \underline{\frac{5}{2}} \longrightarrow {}^2D_{\frac{3}{2}} + {}^2D_{\frac{5}{2}}.$

$S = 0,\ L = 2,\ J = \underline{0} \times \underline{2} = \underline{2} \longrightarrow {}^1D_2.$

$S = \frac{3}{2},\ L = 2,\ J = \underline{\frac{3}{2}} \times \underline{2} = \underline{\frac{1}{2}} + \underline{\frac{3}{2}} + \underline{\frac{5}{2}} + \underline{\frac{7}{2}} \longrightarrow {}^4D_{\frac{1}{2}} + {}^4D_{\frac{3}{2}} + {}^4D_{\frac{5}{2}} + {}^4D_{\frac{7}{2}}.$

(2) The spins may combine to give a singlet, $S = 0$, or a triplet, $S = 1$.

$1s2p$: Here the combined orbital angular momentum is $\underline{0} \times \underline{1} = \underline{1}$ and so
$J = \underline{0} \times \underline{1} = \underline{1} \longrightarrow {}^1P_1$, or
$J = \underline{1} \times \underline{1} = \underline{0} + \underline{1} + \underline{2} \longrightarrow {}^3P_0 + {}^3P_1 + {}^3P_2.$
By the Hund rules, we expect the following ordering of the energy levels:
$^3P_0 < {}^3P_1 < {}^3P_2 < {}^1P_1$.

$2p3p$: Here $\underline{1} \times \underline{1} = \underline{0} + \underline{1} + \underline{2}$ and so,
for combined orbital angular momentum 0
$J = \underline{0} \times \underline{0} = \underline{0} \longrightarrow {}^1S_0$, or
$J = \underline{1} \times \underline{0} = \underline{1} \longrightarrow {}^3S_1$.
For combined orbital angular momentum 1
$J = \underline{0} \times \underline{1} = \underline{1} \longrightarrow {}^1P_1$, or
$J = \underline{1} \times \underline{1} = \underline{0} + \underline{1} + \underline{2} \longrightarrow {}^3P_0, {}^3P_1, {}^3P_2$.
For combined orbital angular momentum 2
$J = \underline{0} \times \underline{2} = \underline{2} \longrightarrow {}^1D_1$, or
$J = \underline{1} \times \underline{2} = \underline{0} + \underline{1} + \underline{2} \longrightarrow {}^3D_0, {}^3D_1, {}^3D_2$.
By the Hund rules, we expect the following ordering of the energy levels:
${}^3D_1 < {}^3D_2 < {}^3D_3 < {}^3P_0 < {}^3P_1 < {}^3P_2 < {}^3S_1 < {}^1D_2 < {}^1P_1 < {}^1S_0$.

$3p3d$: Here $\underline{1} \times \underline{2} = \underline{1} + \underline{2} + \underline{3}$ and so,
for combined orbital angular momentum 1
$J = \underline{0} \times \underline{1} = \underline{1} \longrightarrow {}^1P_1$, or
$J = \underline{1} \times \underline{1} = \underline{0} + \underline{1} + \underline{2} \longrightarrow {}^3P_0, {}^3P_1, {}^3P_2$.
For combined orbital angular momentum 2
$J = \underline{0} \times \underline{2} = \underline{2} \longrightarrow {}^1D_1$, or
$J = \underline{1} \times \underline{2} = \underline{1} + \underline{2} + \underline{3} \longrightarrow {}^3D_1, {}^3D_2, {}^3D_3$.
For combined orbital angular momentum 3
$J = \underline{0} \times \underline{3} = \underline{3} \longrightarrow {}^1F_1$, or
$J = \underline{1} \times \underline{3} = \underline{2} + \underline{3} + \underline{4} \longrightarrow {}^3F_2, {}^3F_3, {}^3F_4$.
By the Hund rules, we expect the following ordering of the energy levels:
${}^3F_2 < {}^3F_3 < {}^3F_4 < {}^3D_1 < {}^3D_2 < {}^3D_3 < {}^3P_0 < {}^3P_1 < {}^3P_2 < {}^3S_1 <$
${}^1F_3 < {}^1D_2 < {}^1P_1$.

9.2 Probability Density in H_2^+ Molecular Ion

Calculate the probability density, $\rho(\vec{r}) = |\psi_+(\vec{R}, \vec{r})|^2$, for the electron in the H_2^+ molecular ion, and plot it on the line joining the two protons. Evaluate

(1) $\rho(\vec{R})/\rho(\frac{1}{2}\vec{R})$,
(2) $\rho(0)/\rho(\frac{1}{2}\vec{R})$.

Solution

The variational calculation for the hydrogenic molecular ion was performed in Section **9.5** of Volume 1. In units of the Bohr radius of the hydrogen atom, the

trial wave function is

$$\psi(\vec{R},\vec{r}) = C_+ \left\{ \exp[-|\vec{r} - \tfrac{1}{2}\vec{R}|] + \exp[-|\vec{r} + \tfrac{1}{2}\vec{R}|] \right\},$$

where C_+ is a normalization constant. The two protons are at positions $\pm\frac{1}{2}\vec{R}$, and the electron is at position $\vec{r}$. After evaluating C_+, we find

$$\rho(\vec{r}) = |\psi_+(\vec{R},\vec{r})|^2 = \frac{\left[\exp\left(-|\vec{r} - \tfrac{1}{2}\vec{R}|\right) + \exp\left(-|\vec{r} + \tfrac{1}{2}\vec{R}|\right)\right]^2}{2\pi(1 + R + \frac{1}{3}R^2)\,\mathrm{e}^{-R}},$$

where the variational method showed that the optimal value of $R = |\vec{R}|$ is 2.5.

When $\vec{r}$ is parallel to $\vec{R}$, i.e., the electron is on the line drawn between the two protons, when $r > \frac{1}{2}R$ or $r < -\frac{1}{2}R$ we have

$$\rho(\vec{r}) = \frac{2\exp[2(R - |r|)]}{\pi(1 + R + \frac{1}{3}R^2)} \cosh^2\frac{R}{2},$$

whereas in the case that $-\frac{1}{2}R < r < \frac{1}{2}R$ we find

$$\rho(\vec{r}) = \frac{2\,\mathrm{e}^R}{\pi(1 + R + \frac{1}{3}R^2)} \cosh^2 r\,.$$

In graphical form, this is as follows:

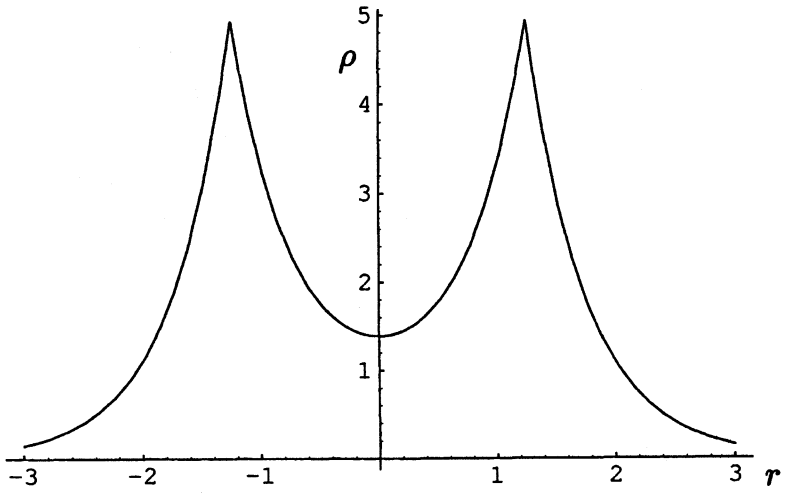

Fig. 9.1 Electron Probability Density

(1) We evaluate the two ratios

$$\frac{\rho(\vec{R})}{\rho(\frac{1}{2}\vec{R})} = \left[\frac{e^{-R/2} - \exp[-3R/2]}{1 - e^{-R}}\right]^2 = e^{-R} \approx 0.082$$

(2) and

$$\frac{\rho(0)}{\rho(\frac{1}{2}\vec{R})} = \left[\frac{2\,e^{-R/2}}{1 - e^{-R}}\right]^2 = \frac{1}{\cosh^2 \frac{1}{2}R} \approx 0.280\,.$$

9.3 Ionization Energies for Helium

Calculate the first and second ionization energies for helium (i.e., the energy required to strip first one, and then the other of the electrons from the atom). Compare your results with the experimental values of 24.85 eV and 54.40 eV.

Solution

Let us define the energy of two free protons, and two free electrons, all infinitely far apart, to be zero, and then calculate the energy required to bring
(a) one electron and the protons together to form an ion, He^+, or
(b) both electrons and the protons together to form an atom, He.
The energy required in step (a) is just the binding energy of a hydrogen-like atom with $Z = 2$ in its ground state, which is

$$E_B = \frac{me^4Z^2}{2\hbar^2} = 4 \times 13.60\,\text{eV} = 54.40\,\text{eV}\,,$$

where we used the value 13.60 eV, the binding energy of the hydrogen atom in its ground state. This is the second ionization energy, and it agrees very well with the experimental measurement. For step (b), we refer to the variational calculation of the ground state energy of the neutral helium atom that was given in Section **9.1** of Volume 1. The result, using a one-term trial function,

$$\tilde{\psi}(\vec{r}_1, \vec{r}_2) = \exp\left[-\tilde{Z}\,\frac{r_1 + r_2}{a_0}\right],$$

was found to be 77.5 eV. The first ionization energy is the difference between the binding energy of the atom and that of the ion, $77.5 - 54.4 = 23.1$ eV, which is about 7% too low, as compared with the experimental value. The 13-term variational calculation result, 79.0 eV, was also given in the above section, and this yields 24.6 eV for the first ionization energy, with an error of 1%.

For additional details see [Bethe, H.A. and Salpeter,E.E., (1957) pp 150 ff.]

9.4 S Terms of Helium

The first few S terms of helium have the following energies, relative to $1s^2\,{}^1S$, the ground state: $1s2s\,{}^1S$: 20.89436; $1s2s\,{}^3S$: 20.08735; $1s3s\,{}^1S$: 23.23007; $1s3s\,{}^3S$: 23.02549 (all in units of the electron-volt) . Calculate the contributions to the energy coming from the overlap integrals in the $1s2s$ and the $1s3s$ configurations.

Solution

According to the analysis of Section **9.2**, the energy of a helium atom, in which the principal states n_1 and n_2 are occupied, is

$$E(n_1, n_2, S) = E_{n_1} + E_{n_2} + \mathcal{D} \pm \mathcal{E}\,.$$

Here E_{n_1} and E_{n_2} are the contributions from the two states without the electron-electron repulsion term, $\mathcal{D}$ is the direct term and $\mathcal{E}$ is the exchange term coming from this electron-electron repulsion term. The plus sign corresponds to a singlet state, in which the total spin of the two electrons is $S = 0$, so that the spin part of the wave function is antisymmetric, the space part symmetric. The minus sign corresponds to a triplet state, in which the total spin of the electrons is $S = 1$, so that the spin part of the wave function is symmetric, the space part antisymmetric.

For fixed values of the principal quantum numbers, n_1 and n_2, the difference between the singlet and the triplet energy levels is twice the exchange term. Hence

$$\mathcal{E} = \tfrac{1}{2}[E(n_1, n_2, 0) - E(n_1, n_2, 1)]\,.$$

For the $1s2sS$ levels, this yields

$$\mathcal{E} = \tfrac{1}{2}(20.89436 - 20.08735) = 0.40351\ \text{eV}\,,$$

and for the $1s3sS$ levels,

$$\mathcal{E} = \tfrac{1}{2}(23.23007 - 23.02549) = 0.10229\ \text{eV}\,.$$

9.5 Lithium

Calculate the energy of the ground state of the lithium atom. With the Bohr radius set equal to unity, use the trial functions $2Z_1^{3/2}\exp(-Z_1 r)$ for the 1s electrons, and $cZ_2^{3/2}\exp(-Z_2 r/2)(1 - dZ_2 r)$ for the 2s electron. Here Z_1 and Z_2 are variational parameters, while c and d are determined by considerations of normalization and of orthogonality.

Solution

Let the three electrons in a lithium atom be at positions $\vec{r}_i$, $i = 1, 2, 3$, with respect to the nucleus. In configuration representation, the Hamiltonian is

$$H = H_1 + H_2 + H_3 + V_{12} + V_{23} + V_{31}\,, \tag{9.1}$$

where

$$H_i = -\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{r_i} \qquad V_{ij} = \frac{e^2}{|\vec{r}_i - \vec{r}_j|}\,,$$

with $Z = 3$, the atomic number of lithium.

In the ground state, there are two electrons in the (100) state, and one in the (200) state. The wave function is given by the Slater determinant,

$$\Phi = \frac{1}{\sqrt{3!}}\begin{Vmatrix} \phi_1(r_1) & \phi_2(r_1) & \phi_3(r_1) \\ \phi_1(r_2) & \phi_2(r_2) & \phi_3(r_2) \\ \phi_1(r_3) & \phi_2(r_3) & \phi_3(r_3) \end{Vmatrix}\,,$$

where

$$\begin{aligned} \phi_1(r_i) &= \psi_{100}(r_i)\chi_+^i \\ \phi_2(r_i) &= \psi_{100}(r_i)\chi_-^i \\ \phi_3(r_i) &= \psi_{200}(r_i)\chi_+^i\,. \end{aligned}$$

Written out in full,

$$\begin{aligned} \Phi = \frac{1}{\sqrt{6}}\{&\psi_{200}(r_1)\psi_{100}(r_2)\psi_{100}(r_3)\chi_+^1(\chi_+^2\chi_-^3 - \chi_-^2\chi_+^3) \\ &+\psi_{200}(r_2)\psi_{100}(r_1)\psi_{100}(r_3)\chi_+^2(\chi_+^3\chi_-^1 - \chi_-^3\chi_+^1) \\ &+\psi_{200}(r_3)\psi_{100}(r_1)\psi_{100}(r_2)\chi_+^3(\chi_+^1\chi_-^2 - \chi_-^1\chi_+^2)\}\,. \end{aligned} \tag{9.2}$$

The expectation value of the Hamiltonian, $\langle\Phi|H|\Phi\rangle$, involves nine terms, each with six factors of ψ. One of the diagonal, or direct integrals is

$$\mathcal{D} = \int d^3r_1 \int d^3r_2 \int d^3r_3 \psi_{200}(r_1)\psi_{100}(r_2)\psi_{100}(r_3) H \psi_{200}(r_1)\psi_{100}(r_2)\psi_{100}(r_3)\,.$$

The spin vectors yield a factor $\chi_+^{1\dagger}(\chi_+^{2\dagger}\chi_-^{3\dagger} - \chi_-^{2\dagger}\chi_+^{3\dagger})\chi_+^1(\chi_+^2\chi_-^3 - \chi_-^2\chi_+^3) = 2$, since the Hamiltonian does not depend on spin, and therefore cannot affect the spin terms. There are two other direct integrals, which however are equal to $\mathcal{D}$, since they are obtained from the above by the substitutions $\{1,2,3\} \to \{2,3,1\}$ and $\{1,2,3\} \to \{3,1,2\}$, and the Hamiltonian is symmetric under these changes. Thus the total direct term is $\mathcal{D}$, since there are three identical terms,

each carrying a spin factor 2, and this just cancels the normalization factor, $(3!)^{-1} = \frac{1}{6}$. One of the six crossed, or exchange integrals is

$$\mathcal{E} = \int d^3r_1 \int d^3r_2 \int d^3r_3 \psi_{200}(r_1)\psi_{100}(r_2)\psi_{100}(r_3) H \psi_{200}(r_2)\psi_{100}(r_1)\psi_{100}(r_3)\,,$$

the spin factor in this case being

$$\chi_+^{1\dagger}(\chi_+^{2\dagger}\chi_-^{3\dagger} - \chi_-^{2\dagger}\chi_+^{3\dagger})\chi_+^2(\chi_+^3\chi_-^1 - \chi_-^3\chi_+^1) = -\chi_+^{1\dagger}\chi_+^{2\dagger}\chi_-^{3\dagger}\chi_+^2\chi_-^3\chi_+^1 = -1\,.$$

Another crossed term is

$$\mathcal{E} = \int d^3r_1 \int d^3r_2 \int d^3r_3 \psi_{200}(r_1)\psi_{100}(r_2)\psi_{100}(r_3) H \psi_{200}(r_3)\psi_{100}(r_1)\psi_{100}(r_2)\,,$$

and the spin factor here is

$$\chi_+^{1\dagger}(\chi_+^{2\dagger}\chi_-^{3\dagger} - \chi_-^{2\dagger}\chi_+^{3\dagger})\chi_+^3(\chi_+^1\chi_-^2 - \chi_-^1\chi_+^2) = -\chi_+^{1\dagger}\chi_-^{2\dagger}\chi_+^{3\dagger}\chi_+^3\chi_+^1\chi_-^2 = -1\,.$$

The above two expressions for $\mathcal{E}$ are indeed equal to one another, as can be seen by the substitution $\vec{r}_2 \leftrightarrow \vec{r}_3$, and the spin factors are in both cases -1. The remaining 4 crossed integrals are all equal to $\mathcal{E}$, as can be seen from the symmetry of H. The six equivalent terms serve to cancel the normalization factor, $\frac{1}{6}$, and so the final tally for the expectation value is

$$\langle\Phi|H|\Phi\rangle = \mathcal{D} - \mathcal{E}\,.$$

We turn to the evaluation of these direct and exchange terms. The contribution of H_1 to $\mathcal{D}$ is

$$E_1 \equiv \langle\Phi|H_1|\Phi\rangle = \int d^3r_1 \psi_{200}(r_1) H_1 \psi_{200}(r_1)\,, \tag{9.3}$$

since H_1 is a function of r_1 only. The contribution of H_2 to $\mathcal{D}$ is

$$E_2 \equiv \langle\Phi|H_2|\Phi\rangle = \int d^3r_2 \psi_{100}(r_2) H_2 \psi_{100}(r_2)\,, \tag{9.4}$$

since H_2 is a function of r_2 only. The contribution of H_3 to $\mathcal{D}$ is clearly equal to E_2, since it amounts simply to the substitution of r_3 for r_2. From the electron-electron repulsion, we have firstly

$$v_{12} \equiv \langle\Phi|V_{12}|\Phi\rangle = e^2 \int d^3r_1 \int d^3r_2 \psi_{200}^2(r_1)\psi_{100}^2(r_2)|\vec{r}_1 - \vec{r}_2|^{-1}\,, \tag{9.5}$$

and secondly

$$v_{11} \equiv \langle\Phi|V_{12}|\Phi\rangle = e^2 \int d^3r_2 \int d^3r_3 \psi_{100}^2(r_2)\psi_{100}^2(r_3)|\vec{r}_2 - \vec{r}_3|^{-1}\,. \tag{9.6}$$

The expectation value of V_{31} is v_{12}, as can be seen from symmetry. Hence

$$\mathcal{D} = E_1 + 2E_2 + 2v_{12} + v_{11}\,.$$

So far as the exchange term is concerned, there is no contribution from the terms H_1, H_2 and H_3. This is because they depend on only one variable. For example, the exchange integral involving H_1 is

$$\int d^3r_1 \psi_{200}(r_1) H_1 \psi_{100}(r_1) \int d^3r_2 \psi_{100}(r_2)\psi_{200}(r_2)\,,$$

and the second integral here is $\langle\psi_{100}|\psi_{200}\rangle$, which vanishes, since the $n = 1$ and $n = 2$ states are orthogonal. On the other hand, the term V_{12} does contribute:

$$\mathcal{E} = e^2 \int d^3r_1 \int d^3r_2 \psi_{200}(r_1)\psi_{100}(r_1)\psi_{100}(r_2)\psi_{200}(r_2)|\vec{r}_1 - \vec{r}_2|^{-1}\,. \tag{9.7}$$

This is the only non-zero term, for V_{23} gives

$$\int d^3r_1 \psi_{200}(r_1)\psi_{100}(r_1) \int d^3r_2 \int d^3r_3 \psi_{100}(r_2)\psi_{200}(r_2)\psi_{100}(r_3)\psi_{100}(r_3)|\vec{r}_2 - \vec{r}_3|^{-1}\,,$$

and here it is the r_1 integral that vanishes, because of orthogonality. Similarly V_{31} does not contribute. Finally,

$$\langle\Phi|H|\Phi\rangle = E_1 + 2E_2 + 2v_{12} + v_{11} - \mathcal{E}\,. \tag{9.8}$$

where the integral expressions for the five terms are given in Eqs.(9.3)-(9.7).

We now turn to the evaluation of these integrals, and to do that we must specify the wave functions. If there were no electron-electron repulsion, the $n = 1$ and $n = 2$ wave functions would be

$$\begin{aligned}
\psi_{100}(r) &= \frac{1}{\sqrt{\pi}} Z^{\frac{3}{2}}\, \mathrm{e}^{-Zr} \\
\psi_{200}(r) &= \frac{1}{2\sqrt{2\pi}} Z^{\frac{3}{2}} (1 - \tfrac{1}{2}Zr)\, \mathrm{e}^{-Zr/2}\,,
\end{aligned}$$

where $Z = 3$ and the Bohr radius has been set equal to unity. As trial functions for an application of the variational method, we take, instead of the above,

$$\begin{aligned}
\psi_{100}(r) &= \frac{1}{\sqrt{\pi}} Z_1^{\frac{3}{2}}\, \mathrm{e}^{-Z_1 r} \\
\psi_{200}(r) &= \frac{c}{2\sqrt{2\pi}} Z_2^{\frac{3}{2}} (1 - \tfrac{1}{2}dZ_2 r)\, \mathrm{e}^{-Z_2 r/2}\,.
\end{aligned} \tag{9.9}$$

This allows for screening, where we expect the effective nuclear charges, Z_1 and Z_2, to be different for the $n = 1$ and $n = 2$ electrons. The parameters c and d are

not independent: they are determined by the requirements of normalization and of orthogonality between ψ_{100} and ψ_{200}. Orthogonality is achieved by requiring

$$d = \frac{x\sqrt{3}}{\sqrt{1-x+x^2}},$$

where $x = Z_2/(2Z_1)$; and normalization leads to

$$c = (1 - 3d + 3d^2)^{-\frac{1}{2}}.$$

Consider first the calculation of E_2, Eq.(9.4). The kinetic part is

$$-\frac{Z_1^3\hbar^2}{2\pi m}\int d^3r\, \mathrm{e}^{-Z_1 r}\nabla^2\, \mathrm{e}^{-Z_1 r} = \frac{Z_1^3 e^2}{2\pi}\int d^3r \left(\vec{\nabla}\, \mathrm{e}^{-Z_1 r}\right)\cdot\left(\vec{\nabla}\, \mathrm{e}^{-Z_1 r}\right),$$

where we performed an integration by parts, and also replaced $\hbar^2/m$ by e^2, since we are using units in which the Bohr radius, $a_0 = \frac{\hbar^2}{me^2}$, is unity. Now

$$\left(\vec{\nabla}\, \mathrm{e}^{-Z_1 r}\right)\cdot\left(\vec{\nabla}\, \mathrm{e}^{-Z_1 r}\right) = \left(\frac{\partial}{\partial r}\, \mathrm{e}^{-Z_1 r}\right)^2 = Z_1^2\, \mathrm{e}^{-2Z_1 r},$$

and so the kinetic part of E_2 is

$$2Z_1^5 e^2 \int_0^\infty dr\, r^2\, \mathrm{e}^{-2Z_1 r} = \tfrac{1}{2}e^2 Z_1^2,$$

where we used the standard integral,

$$\int_0^\infty dr r^n\, \mathrm{e}^{-ar} = n!\, a^{-n-1}.$$

The potential part of E_2 is

$$-2Z_1^3 Z e^2 \int_0^\infty dr\, r\, \mathrm{e}^{-2Z_1 r} = -e^2 Z_1 Z = -3e^2 Z_1.$$

Thus we find

$$E_2 = \tfrac{1}{2}e^2 Z_1^2 - e^2 Z_1 Z = \tfrac{1}{2}e^2 Z_1(Z_1 - 6).$$

The calculation of E_1 proceeds analogously, but it is a little more complicated. The kinetic part is now

$$\frac{e^2}{2}\int d^3r \left[\frac{\partial\psi_{200}(r)}{\partial r}\right]^2.$$

and we find

$$\frac{\partial\psi_{200}(r)}{\partial r} = \frac{cdZ_2^{\frac{5}{2}}}{2\sqrt{2\pi}}(\tfrac{1}{4}Z_2 r - 1)\, \mathrm{e}^{-Z_2 r/2}.$$

So we calculate, for the kinetic part of E_1,

$$\frac{c^2d^2e^2Z_2^5}{4}\int_0^\infty dr\,(r^2-\tfrac{1}{2}Z_2r^3+\tfrac{1}{16}Z_2^2r^4)\,\mathrm{e}^{-Z_2r}=\tfrac{1}{8}e^2c^2d^2Z_2^2=\tfrac{1}{2}e^2c^2d^2Z_1^2x^2\,.$$

The potential part of E_1 is

$$-\tfrac{1}{2}e^2ZZ_2^3c^2\int_0^\infty dr\,r(1-\tfrac{1}{2}dZ_2r)^2\,\mathrm{e}^{-Z_2r}=-\tfrac{1}{2}e^2c^2ZZ_2(1-2d+\tfrac{3}{2}d^2)\,.$$

Thus we find

$$E_1=\tfrac{1}{2}e^2c^2d^2Z_1^2x^2-3e^2c^2Z_1x(1-2d+\tfrac{3}{2}d^2)\,.$$

To calculate the contributions of the electron-electron repulsion terms, we define first the angular integral

$$\int_0^\pi d\theta_{12}\,\sin\theta_{12}\,|\vec{r}_1-\vec{r}_2|^{-1}=\int_{-1}^1 dz_{12}\,[r_1^2+r_2^2-2r_1r_2z_{12}]^{-\frac{1}{2}}=\frac{2}{\mathsf{max}(r_1,r_2)}\,,$$

as in Section **9.1** of Volume 1. We find then

$$\begin{aligned}
v_{11} &= 16\pi^2e^2\int_0^\infty dr_1\,r_1^2\int_0^\infty dr_2\,r_2^2\frac{\psi_{100}^2(r_1)\psi_{100}^2(r_2)}{\mathsf{max}(r_1,r_2)}\\
v_{12} &= 16\pi^2e^2\int_0^\infty dr_1\,r_1^2\int_0^\infty dr_2\,r_2^2\frac{\psi_{200}^2(r_1)\psi_{100}^2(r_2)}{\mathsf{max}(r_1,r_2)}\\
\mathcal{E} &= 16\pi^2e^2\int_0^\infty dr_1\,r_1^2\int_0^\infty dr_2\,r_2^2\frac{\psi_{100}(r_1)\psi_{200}(r_1)\psi_{100}(r_2)\psi_{200}(r_2)}{\mathsf{max}(r_1,r_2)}\,.
\end{aligned}$$

For the first two integrals, we need first

$$\int_0^\infty dr_2\,r_2^2\,\frac{\psi_{100}^2(r_2)}{\mathsf{max}(r_1,r_2)}=\frac{4}{\pi r_1}\left[1-\mathrm{e}^{-2Z_1r_1}(1+\tfrac{5}{2}Z_1r_1+3Z_1^2r_1^2)\right]\,.$$

We find then

$$v_{11}=\tfrac{5}{8}e^2Z_1\,,$$

in agreement with the findings of the above-mentioned section, and also

$$v_{12}=e^2Z_1\left\{1-\frac{1}{(1+x)^2}-\frac{x(3+x)}{1-x+x^2}\right\}\,,$$

$$\mathcal{E}=\frac{4e^2Z_1x^5}{(1+x)^5(1-x+x^2)}\,.$$

On inserting the results of all these computations into Eq.(9.8), we find

$$\langle\Phi|H|\Phi\rangle=Z_1^2f(x)+Z_1g(x)\,,$$

where

$$
\begin{aligned}
f(x) &= 1+\frac{x^2}{6}+\frac{x^4}{1-x+x^2} \\
g(x) &= -\frac{27}{8}-\frac{3x}{2}-\frac{2}{(1+x)^2}+\frac{3x^2(1-2x)}{2(1-x+x^2)} \\
&\quad -\frac{x(3+x)}{(1+x)^3(1-x+x^2)}-\frac{4x^5}{(1+x)^5(1-x+x^2)}\,.
\end{aligned}
$$

To obtain the variational estimate of the ground state energy, we must minimize this expression with respect to Z_1 and $x = Z_2/(2Z_1)$:

$$
\begin{aligned}
\frac{\partial}{\partial Z_1}\langle\Phi|H|\Phi\rangle = 2Z_1 f(x)+g(x) &= 0 \\
\frac{\partial}{\partial x}\langle\Phi|H|\Phi\rangle = Z_1^2 f'(x)+Z_1 g'(x) &= 0\,.
\end{aligned}
$$

Hence

$$
\frac{f'(x)}{f(x)}-2\frac{g'(x)}{g(x)}=0\,, \tag{9.10}
$$

which is a complicated expression that determines x. We expect a root of this equation to lie somewhere between 0 and $\frac{1}{2}$, since $Z_2 < Z_1$, reflecting the fact that the $n = 2$ electron is better shielded from the nuclear charge than are the $n = 1$ electrons. When we run the following Mathematica program,

```
a[x_]:=1/(1-x+x*x);
b[x_]:=1/(1+x);
f[x_]:=1+x*x/6+a[x]*x^4;
g[x_]:=-27/8-3*x/2-2*b[x]^2+a[x]*(3*x*x*(1-2*x)/2-
            x*(3+x)*b[x]^3-4*(x*b[x])^5);
FindRoot[f'[x]/f[x]==2*g'[x]/g[x],{x,0.3}]

Plot[f'[x]/f[x]-2*g'[x]/g[x], {x,0,1}]
```

the root $\{x \text{->} 0.284616\}$ is returned; and the graph depicted as Figure 9.2 is produced. In the absence of computer facilities, one could check a few points of this graph, near the root, by using a scientific calculator. With this root, $x_0 = 0.284616$, we find

$$
\begin{aligned}
Z_1 &= -\frac{g(x_0)}{2f(x_0)} = 2.69372 \\
Z_2 &= 2x_0 Z_1 = 1.53335\,.
\end{aligned}
$$

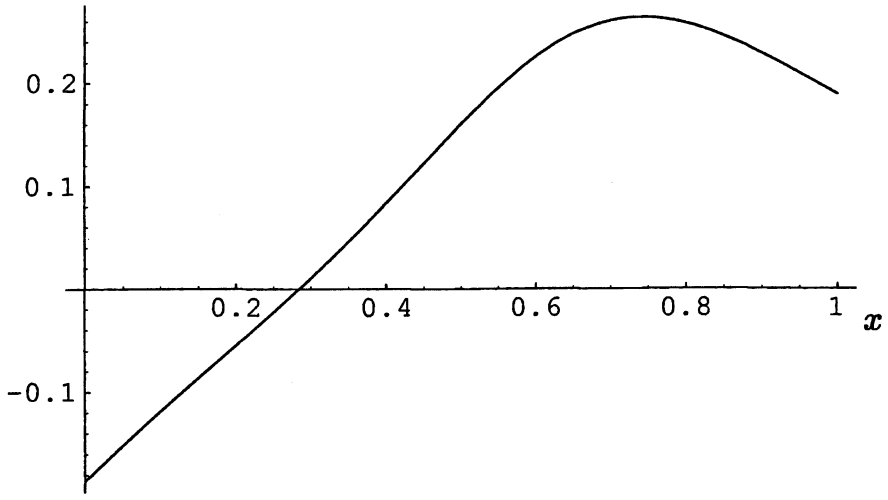

Fig. 9.2 Root of Eq.(9.10)

So we find that the inner electrons see most of the nuclear charge, but the outer one is influenced by about half of the charge, $3|e|$, of the lithium nucleus. The variational estimate of the ground state energy is

$$E_0 = [Z_1^2 f(x_0) + Z_1 g(x_0)]e^2 = -7.41385e^2 .$$

To confront this estimate with experiment, we recall that the ground state energy of the hydrogen atom, -13.6 eV, is given in units of the Bohr radius as $-\frac{1}{2}e^2$, so it follows that $e^2 = 27.2$ eV, and therefore that $E_0 = -201.6$ eV, which compares well with the experimental measurement, namely -202.54 eV.

9.6 Beryllium

Consider the beryllium atom.

(1) Write down the Slater determinant for the ground term of this atom, and find an expression for its energy in terms of Coulomb and exchange integrals;
(2) Find expressions for the energy in terms of the Hartree-Fock expression for the configuration $1s^2 2s^2$;
(3) Evaluate the expectation value $< \Psi \mid H \mid \Psi >$.

Solution

(1) In the ground state of the beryllium atom, there are two electrons in the (100) state, and two in the (200) state. The Slater determinant for this four-electron

system is

$$\Psi = \frac{1}{\sqrt{4!}} \left\| \begin{array}{cccc} \phi_1(r_1) & \phi_2(r_1) & \phi_3(r_1) & \phi_4(r_1) \\ \phi_1(r_2) & \phi_2(r_2) & \phi_3(r_2) & \phi_4(r_2) \\ \phi_1(r_3) & \phi_2(r_3) & \phi_3(r_3) & \phi_4(r_3) \\ \phi_1(r_4) & \phi_2(r_4) & \phi_3(r_4) & \phi_4(r_4) \end{array} \right\| ,$$

where (with the Bohr radius equal to one)

$$\begin{aligned} \phi_1(r_i) &= \psi_{100}(r_i)\chi_+^i = \frac{8}{\sqrt{\pi}} \mathrm{e}^{-4r_i} \begin{pmatrix} 1 \\ 0 \end{pmatrix}^i \\ \phi_2(r_i) &= \psi_{100}(r_i)\chi_-^i = \frac{8}{\sqrt{\pi}} \mathrm{e}^{-4r_i} \begin{pmatrix} 0 \\ 1 \end{pmatrix}^i \\ \phi_3(r_i) &= \psi_{200}(r_i)\chi_+^i = \frac{4}{\sqrt{2\pi}}(1-2r_i) \mathrm{e}^{-2r_i} \begin{pmatrix} 1 \\ 0 \end{pmatrix}^i \\ \phi_4(r_i) &= \psi_{200}(r_i)\chi_-^i = \frac{4}{\sqrt{2\pi}}(1-2r_i) \mathrm{e}^{-2r_i} \begin{pmatrix} 0 \\ 1 \end{pmatrix}^i . \end{aligned}$$

The expectation value of the Hamiltonian in this state is

$$\langle \Psi | H | \Psi \rangle = 2E_1 + 2E_2 + V_{1111} + V_{2222} + 4V_{1122} - 2V_{1212} .$$

Here $E_1 = -8e^2$, $E_2 = -2e^2$ and

$$V_{ijk\ell} = e^2 \int d^3r_1 \int d^3r_2 |\vec{r}_1 - \vec{r}_2|^{-1} \psi_{i00}(r_1)\psi_{j00}(r_1)\psi_{k00}(r_2)\psi_{\ell 00}(r_2) .$$

The terms V_{1111}, V_{2222} and V_{1122} are Coulomb repulsion terms, while V_{1212} is the exchange term.

9.7 Nitrogen

Write down the part of the ground-state wave function that represents the p-state electrons in the atom of nitrogen in terms of their wave functions, ψ_{21m}, where $m = -1, 0, 1$. Assume that the Hund rules apply.

Solution

Nitrogen has atomic number 7, so the ground state has two electrons in the state $\{n = 1, \ell = 0\}$, two in the state $\{n = 2, \ell = 0\}$, and the remaining three in the state $\{n = 2, \ell = 1\}$. These latter are the p-state electrons that are addressed in the exercise. The first of the Hund rules states:

a: Other things being equal, the state of highest spin has the lowest energy.

Hence we expect the total spin of the three p-state electrons in the ground state to be $\frac{3}{2}$, the maximum that can be obtained with three electrons.

We show first that the spin $\frac{3}{2}$ states are formed from symmetric combinations of the spin eigenvectors corresponding to the three p-state electrons, say a, b and c. For the states with $S_3 = \pm\frac{3}{2}$, the situation is clear:

$$\begin{aligned} |\tfrac{3}{2},\tfrac{3}{2}\rangle &= |\tfrac{1}{2},\tfrac{1}{2}\rangle^a|\tfrac{1}{2},\tfrac{1}{2}\rangle^b|\tfrac{1}{2},\tfrac{1}{2}\rangle^c \\ |\tfrac{3}{2},-\tfrac{3}{2}\rangle &= |\tfrac{1}{2},-\tfrac{1}{2}\rangle^a|\tfrac{1}{2},-\tfrac{1}{2}\rangle^b|\tfrac{1}{2},-\tfrac{1}{2}\rangle^c . \end{aligned} \tag{9.11}$$

To obtain the remaining two states, we observe that

$$S_\mp|\tfrac{3}{2},\pm\tfrac{3}{2}\rangle = (S^a_\mp + S^b_\mp + S^c_\mp)|\tfrac{1}{2},\pm\tfrac{1}{2}\rangle^a|\tfrac{1}{2},\pm\tfrac{1}{2}\rangle^b|\tfrac{1}{2},\pm\tfrac{1}{2}\rangle^c ,$$

and so, from the general formula for ladder operators,

$$J_\pm|j,m\rangle = \hbar\sqrt{j(j+1) - m(m\pm 1)}|j,m\pm 1\rangle ,$$

we see that

$$\begin{aligned} |\tfrac{3}{2},\tfrac{1}{2}\rangle &= \tfrac{1}{\sqrt{3}}\left[|\tfrac{1}{2},-\tfrac{1}{2}\rangle^a|\tfrac{1}{2},\tfrac{1}{2}\rangle^b|\tfrac{1}{2},\tfrac{1}{2}\rangle^c + (a\leftrightarrow b) + (a\leftrightarrow c)\right] \\ |\tfrac{3}{2},-\tfrac{1}{2}\rangle &= \tfrac{1}{\sqrt{3}}\left[|\tfrac{1}{2},\tfrac{1}{2}\rangle^a| - \tfrac{1}{2},\tfrac{1}{2}\rangle^b| - \tfrac{1}{2},\tfrac{1}{2}\rangle^c + (a\leftrightarrow b) + (a\leftrightarrow c)\right] . \end{aligned} \tag{9.12}$$

Hence the spin $\frac{3}{2}$ states are indeed formed from symmetric combinations of the spin eigenvectors corresponding to the three p-state electrons. It follows then from the Pauli principle that the spatial part of the wave function of the three p-state electrons must be totally antisymmetric. However, the only way to form an antisymmetric combination of the three p states, $\psi_{2,1,m}$, with $m = -1, 0, 1$, is the determinant

$$\psi = \frac{1}{\sqrt{6}}\begin{vmatrix} \psi^a_{2,1,-1} & \psi^a_{2,1,0} & \psi^a_{2,1,1} \\ \psi^b_{2,1,-1} & \psi^b_{2,1,0} & \psi^b_{2,1,1} \\ \psi^c_{2,1,-1} & \psi^c_{2,1,0} & \psi^c_{2,1,1} \end{vmatrix} . \tag{9.13}$$

9.8 Crystal Lattice

Consider a $3-d$ electron in an atom that is in a crystal lattice. The energy level of this electron is fivefold degenerate. The corresponding wave-functions are

$$\begin{aligned} \langle\vec{r}|1\rangle = xzf(r) \qquad \langle\vec{r}|2\rangle = yzf(r) \qquad \langle\vec{r}|3\rangle = xyf(r) \\ \langle\vec{r}|4\rangle = (x^2-y^2)f(r) \qquad \langle\vec{r}|5\rangle = (3z^2-r^2)f(r) . \end{aligned}$$

(1) Show that these are indeed $3d$ wave-functions.

The influence of the crystal environment on the electron is described by the perturbing (rhombic) potential

$$V(\vec{r}) = Ax^2 + By^2 + Cz^2 .$$

(2) Calculate the energy shifts induced by V in first order perturbation theory.
(3) What are these shifts for a tetragonal field ($A = B$)?
(4) Show that the expectation value of the z-component of the angular momentum always vanishes in the presence of this field (in first order).
(5) Is the same true for the x- and y-components?

Solution

(1) In terms of spherical polar coordinates,

$$\begin{aligned}
\langle\vec{r}|1\rangle &= \tfrac{1}{2}r^2 f(r)\sin\theta\cos\theta[\mathrm{e}^{i\phi} + \mathrm{e}^{-i\phi}] \propto Y_{21}(\theta,\phi) + Y_{2,-1}(\theta,\phi) \\
\langle\vec{r}|2\rangle &= -\tfrac{1}{2}ir^2 f(r)\sin\theta\cos\theta[\mathrm{e}^{i\phi} - \mathrm{e}^{-i\phi}] \propto Y_{21}(\theta,\phi) - Y_{2,-1}(\theta,\phi) \\
\langle\vec{r}|3\rangle &= -\tfrac{1}{4}ir^2 f(r)\sin^2\theta[\mathrm{e}^{2i\phi} - \mathrm{e}^{-2i\phi}] \propto Y_{22}(\theta,\phi) - Y_{2,-2}(\theta,\phi) \\
\langle\vec{r}|4\rangle &= \tfrac{1}{2}r^2 f(r)\sin^2\theta[\mathrm{e}^{2i\phi} + \mathrm{e}^{-2i\phi}] \propto Y_{22}(\theta,\phi) + Y_{2,-2}(\theta,\phi) \\
\langle\vec{r}|5\rangle &= r^2 f(r)[3\cos^2\theta - 1] \propto Y_{20}(\theta,\phi) .
\end{aligned}$$

Hence these five states all correspond to $\ell = 2$, i.e., to d states.

(2) Let us define the integrals

$$R_{ijk} = \int d^3r\, x^{2i} y^{2j} z^{2k} |f(r)|^2 ,$$

for which $R_{ijk} = R_{jik} = R_{ikj} = R_{kji}$. We find for the diagonal matrix elements

$$\begin{aligned}
\langle 1|V|1\rangle &= \int d^3r\, x^2 z^2 g(\vec{r}) = (A + C)R_{210} + BR_{111} \\
\langle 2|V|2\rangle &= \int d^3r\, y^2 z^2 g(\vec{r}) = (B + C)R_{210} + AR_{111} \\
\langle 3|V|3\rangle &= \int d^3r\, x^2 y^2 g(\vec{r}) = (A + B)R_{210} + CR_{111} \\
\langle 4|V|4\rangle &= \int d^3r\, (x^2 - y^2)^2 g(\vec{r}) = (A + B)[R_{300} - R_{210}] + 2C[R_{210} - R_{111}] \\
\langle 5|V|5\rangle &= \int d^3r\, (3z^2 - r^2)^2 g(\vec{r}) = (A + B)[R_{300} + 3R_{210} - 4R_{111}] \\
&\qquad + 2C[2R_{300} - 3R_{210} + R_{111}] ,
\end{aligned}$$

where $g(\vec{r}) = |f(r)|^2[Ax^2 + By^2 + Cz^2]$. All the non-diagonal matrix elements vanish, except $\langle 4|V|5\rangle = \langle 5|V|4\rangle$. This is because all the others involve x, y

and/or z, raised to an odd power, so the integral is zero. For example,

$$\langle 1|V|2\rangle = \int d^3r\, xyz^2 g(\vec{r}) = 0\,.$$

On the other hand,

$$\langle 4|V|5\rangle = \int d^3r\, (x^2-y^2)(2z^2-x^2-y^2)g(\vec{r}) = (A-B)[3R_{210}-2R_{111}-R_{300}]\,.$$

The angular integrals can be worked out. We find

$$\begin{aligned}
R_{111} &= \int d^3r\, x^2y^2z^2|f(r)|^2 = \frac{4\pi}{105}\int_r^\infty dr\, r^8|f(r)|^2 \\
R_{210} &= \int d^3r\, x^4y^2|f(r)|^2 = \frac{4\pi}{35}\int_r^\infty dr\, r^8|f(r)|^2 = 3R_{111} \\
R_{300} &= \int d^3r\, x^6|f(r)|^2 = \frac{4\pi}{7}\int_r^\infty dr\, r^8|f(r)|^2 = 15R_{111}\,.
\end{aligned}$$

The first-order shifts arising from the states $|1\rangle$, $|2\rangle$ and $|3\rangle$ are simply

$$\begin{aligned}
\delta_1 E &= [3(A+C)+B]R_{111} \\
\delta_2 E &= [3(B+C)+A]R_{111} \\
\delta_3 E &= [3(A+B)+C]R_{111}\,,
\end{aligned}$$

but $|4\rangle$ and $|5\rangle$ are not eigenvectors of the Hamiltonian: the eigenvectors are superpositions of these states. The eigenvalue equation is

$$\left[\delta E - \langle 4|V|4\rangle\right]\left[\delta E - \langle 5|V|5\rangle\right] = \left[\langle 4|V|5\rangle\right]^2,$$

and this leads to the following two shifts:

$$\begin{aligned}
\delta E_\pm &= \tfrac{1}{2}\Big\{\langle 4|V|4\rangle + \langle 5|V|5\rangle \pm \sqrt{[\langle 4|V|4\rangle - \langle 5|V|5\rangle)]^2 + 4[\langle 4|V|5\rangle]^2}\Big\} \\
&= 4R_{111}\Big\{4A+4B-5C \pm \sqrt{5A^2+5B^2+36C^2-6AB-12AC-12BC}\Big\}\,.
\end{aligned}$$

(3) If $A = B$, we have $\langle 4|V|5\rangle = 0$, and so

$$\begin{aligned}
\delta_1 E &= [4A+3C]R_{111} = \delta_2 E \\
\delta_3 E &= [6A+C]R_{111} \\
\delta_4 E &= 4[6A+C]R_{111} \\
\delta_5 E &= 4[10A+11C]R_{111}\,.
\end{aligned}$$

(4) From the expression of the eigenvectors of the unperturbed Hamiltonian in terms of spherical harmonics that we gave, we find

$$\begin{aligned} L_z|1\rangle &= \hbar|2\rangle \qquad & L_z|2\rangle &= \hbar|1\rangle \\ L_z|3\rangle &= 2\hbar|4\rangle \qquad & L_z|4\rangle &= 2\hbar|3\rangle \\ L_z|5\rangle &= 0\,. \end{aligned}$$

We know that $|1\rangle$, $|2\rangle$ and $|3\rangle$ are also eigenvectors of the perturbed Hamiltonian, to first order in the perturbation. Now $\langle 1|L_z|1\rangle = \hbar\langle 1|2\rangle = 0$, and similarly for $|2\rangle$ and $|3\rangle$. The other eigenvectors are $\cos\chi|4\rangle + \sin\chi|5\rangle$, for some χ. But

$$\{\cos\chi\langle 4| + \sin\chi\langle 5|\}L_z\{\cos\chi|4\rangle + \sin\chi|5\rangle\} = 2\hbar\cos^2\chi\langle 4|3\rangle = 0\,.$$

Thus the expectation value of the z-component of the angular momentum vanishes in the presence of this perturbation, to first order.
(5) The expectation values of the x- and y-components of the angular momentum must also vanish, to first order, since the x- and y-axes can be brought into the old z direction by a suitable rotation. The Hamiltonian remains the same only if we simultaneously make a suitable permutation of A, B and C, but since the vanishing of the matrix elements in question does not depend on the numerical values of these constants, this does not spoil the demonstration.

9.9 Carbon Dioxide

Carbon dioxide is a linear molecule (OCO) that can combine with an electron to form an ion. Suppose that the electron has energy E_0 when it is attached either to one of the oxygen atoms or to the carbon atom. The state of the molecule when the electron is attached to the carbon atom is $|C\rangle$, while the states corresponding to its being attached to one or other of the oxygen atoms are respectively $|O_1\rangle$ and $|O_2\rangle$. These three states are not eigenvectors of the hamiltonian, because there is a small transition probability that the electron jumps from the central carbon atom to one of the oxygen atoms, or vice versa. The probability that a direct transition takes place between one oxygen atom and the other is very small, and may be neglected.

(1) Write down a Hamiltonian for this ion.
(2) Determine its energy levels and its eigenfunctions.
(3) An external electric field is applied, so that the electron's energy when it is attached to one oxygen atom is $E_0+\delta$, and when attached to the other is $E_0 - \delta$, while the energy of attachment to the carbon atom remains unchanged. Determine the energy shifts to second order in δ.

Solution

(1) We shall write the three states as follows:

$$|O_1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \qquad |C\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \qquad |O_2\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}.$$

The Hamiltonian can then be represented by the matrix

$$H = \begin{pmatrix} E_0 & \alpha & 0 \\ \alpha & E_0 & \alpha \\ 0 & \alpha & E_0 \end{pmatrix}.$$

(2) The eigenvalues, $E(\alpha)$, and the eigenvectors, $|k\rangle, k = 1, 2, 3$, are given by the equation $H|k\rangle = E(\alpha)|k\rangle$, i.e.,

$$\begin{pmatrix} E_0 & \alpha & 0 \\ \alpha & E_0 & \alpha \\ 0 & \alpha & E_0 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = E(\alpha) \begin{pmatrix} a \\ b \\ c \end{pmatrix}.$$

These homogeneous equations have solutions only if

$$\begin{Vmatrix} E_0 - E(\alpha) & \alpha & 0 \\ \alpha & E_0 - E(\alpha) & \alpha \\ 0 & \alpha & E_0 - E(\alpha) \end{Vmatrix} = 0,$$

which reduces to $[E_0 - E(\alpha)][(E_0 - E(\alpha))^2 - 2\alpha^2] = 0$. The energy levels, i.e., the eigenvalues of the Hamiltonian, are therefore E_0 and $E_0 \pm \alpha\sqrt{2}$. With the eigenvalue E_0, we have $aE_0 + b\alpha = aE_0$ and $a\alpha + bE_0 + c\alpha = bE_0$, so $b = 0$ and $a = -c$. Thus the normalized eigenvector belonging to E_0 is

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} = \frac{1}{\sqrt{2}} \big(|O_1\rangle - |O_2\rangle \big).$$

With the eigenvalues $E_0 \pm \alpha\sqrt{2}$, we have the equalities $aE_0 + b\alpha = a(E_0 \pm \alpha\sqrt{2})$ and $a\alpha + bE_0 + c\alpha = b(E_0 \pm \alpha\sqrt{2})$, so $a = c$ and $b = \pm a\sqrt{2}$. The normalized eigenvectors belonging to $E_0 \pm \alpha\sqrt{2}$ are therefore

$$\frac{1}{2} \begin{pmatrix} 1 \\ \pm\sqrt{2} \\ 1 \end{pmatrix} = \frac{1}{2} \big(|O_1\rangle \pm \sqrt{2}|C\rangle + |O_2\rangle \big).$$

(3)Under the influence of the external field, the eigenvalue condition becomes

$$\begin{Vmatrix} E_0+\delta-E(\alpha) & \alpha & 0 \\ \alpha & E_0-E(\alpha) & \alpha \\ 0 & \alpha & E_0-\delta-E(\alpha) \end{Vmatrix} = 0\,,$$

which reduces to $[E_0 - E(\alpha)][(E_0 - E(\alpha))^2 - 2\alpha^2 - \delta^2] = 0$. The energy levels are therefore E_0 and $E_0 \pm \sqrt{\delta^2 + 2\alpha^2}$.

9.10 Six Identical Atoms

Six identical atoms are in a stationary state, with an atom at each of the vertices of a regular hexagon. One electron is added to the molecule. Let $|j\rangle$, $j = 1, 2, 3, 4, 5, 6$, be orthonormal states corresponding to the electron's being attached to atom j. Transition from state $|j\rangle$ is only possible to a neighboring state, i.e., to state $|k\rangle$ if $k = j \pm 1$ (modulo 6). Let H be the Hamiltonian of the system, and set $\langle j|H|j\rangle = E_0$, and $\langle j|H|k\rangle = \alpha\,\mathrm{e}^{i\theta}$ if $k = j + 1$ (modulo 6).

(1) Calculate the energy levels of this system in terms of E_0, α and θ.
(2) Make a sketch of the energy levels when $0 < \theta << \alpha << E_0$.
(3) What are the eigenstates and the eigenvalues (with their degeneracies) in the case $\theta = 0$?

Solution

(1) Expand an eigenvector of H in the basis $\{|k\rangle\}$,

$$|\phi\rangle = \sum_k a_k |k\rangle\,.$$

Suppose the corresponding eigenvalue of H is E. Then

$$\begin{aligned} 0 = (H-E)|\phi\rangle &= \sum_j \sum_k |j\rangle\langle j|H-E|k\rangle a_k \\ &= \sum_j \sum_k |j\rangle \left[(E_0-E)\delta_{jk} + \alpha\,\mathrm{e}^{i\theta}\delta_{j+1,k} + \alpha\,\mathrm{e}^{-i\theta}\delta_{j-1,k}\right] a_k \\ &= \sum_j \left[(E_0-E)a_j + \alpha\,\mathrm{e}^{i\theta}a_{j+1} + \alpha\,\mathrm{e}^{-i\theta}a_{j-1}\right]|j\rangle\,. \end{aligned}$$

Hence the coefficients must satisfy

$$(E_0-E)a_j + \alpha\,\mathrm{e}^{i\theta}a_{j+1} + \alpha\,\mathrm{e}^{-i\theta}a_{j-1} = 0\,,$$

and a solution can be found by trying the Ansatz $a_j = \mathrm{e}^{ij\delta}$, which works if

$$(E_0 - E)\,\mathrm{e}^{ij\delta} + \alpha\,\mathrm{e}^{i\theta}\,\mathrm{e}^{i(j+1)\delta} + \alpha\,\mathrm{e}^{-i\theta}e^{i(j-1)\delta} = 0\,.$$

Hence the eigenvalues have the form

$$E = E_0 + 2\alpha\cos(\theta + \delta)\,.$$

Since the system has periodicity 6, i.e., $a_0 = a_6$, we must impose $\mathrm{e}^{6i\delta} = 1$, and so there are six roots, $\delta = \frac{k\pi}{3}$, with $k = 1, 2, 3, 4, 5, 6$. We may accordingly label the six eigenvalues by the index, k,

$$E_k = E_0 + 2\alpha\cos(\theta + k\pi/3)\,.$$

(2) The six eigenvalues are as follows:

$$\begin{aligned}
E_1 &= E_0 + \alpha\cos\theta + \sqrt{3}\sin\theta \\
E_2 &= E_0 - \alpha\cos\theta + \sqrt{3}\sin\theta \\
E_3 &= E_0 - 2\alpha\cos\theta \\
E_4 &= E_0 - \alpha\cos\theta - \sqrt{3}\sin\theta \\
E_5 &= E_0 + \alpha\cos\theta - \sqrt{3}\sin\theta \\
E_6 &= E_0 + 2\alpha\cos\theta\,.
\end{aligned}$$

If θ is much smaller than α, then E_2 and E_4 are close together, and E_1 and E_5 are close together. The level scheme is shown in Figure 9.1.

Figure 9.1

(3) If $\theta = 0$, the levels are

$$\begin{aligned}
E_1 &= E_5 = E_0 + \alpha \\
E_2 &= E_4 = E_0 - \alpha \\
E_3 &= E_0 - 2\alpha \\
E_6 &= E_0 + 2\alpha\,.
\end{aligned}$$

The levels $E_0 \pm \alpha$ are both doubly degenerate, while the levels $E_0 \pm 2\alpha$ are both simple.

Appendix A

Completeness of Eigenfunctions

In this appendix, whenever the word 'matrix' or 'operator' is used, this means a square matrix of fixed, finite dimension.

A.1 Inverse

Prove that the matrix $(1 - iA)$ has an inverse if A is Hermitian.

Solution

Since A is Hermitian, there exists a unitary matrix, u, such that $uAu^\dagger$ is diagonal, the diagonal elements being the eigenvalues, say λ_i. Thus $u(1 - iA)u^\dagger$ is also diagonal, and its nonzero elements are $(1 - i\lambda_1), (1 - i\lambda_2), \ldots, (1 - i\lambda_n)$, where the λ_i, being the eigenvalues of a Hermitian matrix, are real. The determinant of this diagonal matrix is simply

$$\det[u(1 - iA)u^\dagger] = \prod_{j=1}^{n}(1 - i\lambda_j)\,, \tag{A.1}$$

where n is the dimension of the matrix. However, we know that, for any matrices C and D,

$$\det(CD) = \det(DC)\,,$$

so with $C = u$ and $D = (1 - iA)u^\dagger$, we have

$$\det[u(1 - iA)u^\dagger] = \det[(1 - iA)u^\dagger u] = \det[1 - iA]\,, \tag{A.2}$$

since $u^\dagger u = 1$. From Eq.(A.1) and Eq.(A.2) we see that

$$\Big|\det[1 - iA]\Big| = \left|\prod_{j=1}^{n}(1 - i\lambda_j)\right| = \prod_{j=1}^{n}\sqrt{1 + \lambda_j^2} \geq 1\,,$$

where we have used the fact that the eigenvalues are real. Thus we know that $\det(1 - iA) \neq 0$, and this is the necessary and sufficient condition that the matrix $(1 - iA)$ have an inverse. One may construct that inverse by calculating the inverse to the diagonal matrix $B_d = u(1 - iA)u^\dagger$. That inverse, namely B_d^{-1}, is a diagonal matrix in which the j-th diagonal element is $(1 + i\lambda_j)/(1 + \lambda_j^2)$. Thus $(1 - iA)^{-1} = u^\dagger B_d^{-1} u$.

A.2 Trace of Matrix

Let I be the unit matrix and A an arbitrary square matrix. Show

(1) $\det[I + \epsilon A] = 1 + \epsilon \mathrm{Tr}(A) + O(\epsilon^2)$, where the trace of the matrix is the sum of the matrix elements on the diagonal, i.e., $\mathrm{Tr}(A) = \sum_j A_{jj}$,
(2) $\det[\exp(A)] = \exp[\mathrm{Tr}(A)]$.

Solution
(1) It is intuitively rather clear that $\det[I + \epsilon A]$ is given correctly to order ϵ as the product of diagonal terms, since each non-diagonal term is of order ϵ, and since in the expansion of the determinant as a sum of products of matrix elements, there are no terms containing only one non-diagonal element. We shall now establish this intuitive point through induction.

Let M_{1,i_1} be the cofactor of the matrix $I + \epsilon A$ with respect to the element $\delta_{1,i_1} + \epsilon A_{1,i_1}$. Then we have

$$I + \epsilon A = \sum_{i_1} [\delta_{1,i_1} + \epsilon A_{1,i_1}] M_{1,i_1} . \tag{A.3}$$

We show in the Lemma that, if $i_1 \neq 1$, then $M_{1,i_1} = O(\epsilon)$. However, if $i_1 \neq 1$ it is clear that $\delta_{1,i_1} + \epsilon A_{1,i_1} = \epsilon A_{1,i_1}$, is also of order ϵ. Hence

$$I + \epsilon A = [1 + \epsilon A_{11}] M_{11} + \epsilon \sum_{i_1 \neq 1} A_{1,i_1} M_{1,i_1} \tag{A.4}$$

$$= [1 + \epsilon A_{11}] M_{11} + O(\epsilon^2) , \tag{A.5}$$

and so, taking the determinant of this matrix, we find

$$\det[I + \epsilon A] = [1 + \epsilon A_{11}] \det M_{11} + O(\epsilon^2) . \tag{A.6}$$

M_{11} is the cofactor of the 11 element of the matrix $I + \epsilon A$, i.e., it is the result of deleting the first row and column of $I + \epsilon A$. We can repeat the argument on the matrix M_{11}, and this will result in splitting off the next factor, $[1 + \epsilon A_{22}]$,

to order ϵ^2 . The procedure can be iterated, and finally we obtain

$$\det[I+\epsilon A] = \prod_{j=1}^{n}[1+\epsilon A_{jj}] + O(\epsilon^2) \tag{A.7}$$

$$= 1+\epsilon\sum_{j=1}^{n} A_{jj} + O(\epsilon^2) \tag{A.8}$$

$$= 1+\epsilon \mathrm{Tr}\,(A) + O(\epsilon^2)\,. \tag{A.9}$$

Lemma: The cofactor, M_{1,i_1}, of $I+\epsilon A$, is $O(\epsilon)$ if $i_1 \neq 1$.
Proof
The matrix $I+\epsilon A$ has the form

$$\begin{pmatrix} 1+\epsilon A_{11} & \epsilon A_{12} & \epsilon A_{13} & \dots & \epsilon A_{1N} \\ \epsilon A_{21} & 1+\epsilon A_{22} & \epsilon A_{23} & \dots & \epsilon A_{2N} \\ \epsilon A_{31} & \epsilon A_{32} & 1+\epsilon A_{33} & \dots & \epsilon A_{3N} \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \epsilon A_{N1} & \epsilon A_{N2} & \epsilon A_{N3} & \dots & 1+\epsilon A_{NN} \end{pmatrix}$$

the cofactor M_{12} is

$$\begin{pmatrix} \epsilon A_{21} & \epsilon A_{23} & \dots & \epsilon A_{2N} \\ \epsilon A_{31} & 1+\epsilon A_{33} & \dots & \epsilon A_{3N} \\ \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot \\ \epsilon A_{N1} & \epsilon A_{N3} & \dots & 1+\epsilon A_{NN} \end{pmatrix} =$$

$$\epsilon \begin{pmatrix} A_{21} & \epsilon A_{23} & \dots & \epsilon A_{2N} \\ A_{31} & 1+\epsilon A_{33} & \dots & \epsilon A_{3N} \\ \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot \\ A_{N1} & \epsilon A_{N3} & \dots & 1+\epsilon A_{NN} \end{pmatrix}$$

from which we see explicitly that it is of order ϵ. Similarly all the cofactors M_{1,i_1}, are of order ϵ when $i_1 \neq 1$.

(2) From the representation

$$\exp A = \lim_{n\to\infty}(1+A/n)^n\,,$$

and from the fact that the determinant of the nth power of a matrix is equal to the nth power of the determinant of the matrix, we have

$$\det[\exp A] = \lim_{n\to\infty}\{\det(1 + A/n)\}^n ,$$

Using the result just proved in (1), we have

$$\begin{aligned}\det[\exp A] &= \lim_{n\to\infty}\{1 + \mathrm{Tr}A/n + O(n^{-2})\}^n \\ &= \lim_{n\to\infty}\{(1 + \mathrm{Tr}A/n)\}^n \\ &= \exp[\mathrm{Tr}A] .\end{aligned}$$

A.3 Projection Operator I

A Hermitian operator P is called a projection operator if

$$P^2 = P.$$

(1) Prove that the only projection operator with an inverse is the identity operator.
(2) Let P_1 and P_2 be projection operators. Prove that if $P_1 + P_2$ is a projection operator, then $P_1P_2 = P_2P_1 = 0$. Operators satisfying this condition are called orthogonal projection operators.

Solution
(1) If P has an inverse, $PP^{-1} = 1$, and since $P^2 = P$, it follows that

$$P^2P^{-1} = PP^{-1} = 1 , \tag{A.10}$$

but the left-hand side can be written

$$P(PP^{-1}) = P . \tag{A.11}$$

Comparison of Eq.(A.10) and Eq.(A.11) leads to $P = 1$.
(2) Since P_1 and P_2 are projection operators,

$$(P_1 + P_2)^2 = P_1^2 + P_1P_2 + P_2P_1 + P_2^2 = P_1 + P_2 + P_1P_2 + P_2P_1 .$$

So $P_1 + P_2$ is a projection operator if and only if

$$P_1P_2 + P_2P_1 = 0 . \tag{A.12}$$

Multiply on the left by P_1 to get

$$P_1^2P_2 + P_1P_2P_1 = 0 \Longrightarrow P_1P_2 + P_1P_2P_1 = 0 ,$$

and on the right by P_1 to get

$$P_1P_2P_1 + P_2P_1^2 = 0 \Longrightarrow P_1P_2P_1 + P_2P_1 = 0\,.$$

These last two equations yield

$$P_1P_2 - P_2P_1 = 0\,. \tag{A.13}$$

By adding and subtracting Eq.(A.12) and Eq.(A.13) we find

$$P_1P_2 = 0 = P_2P_1\,.$$

A.4 Projection Operator II

Consider three orthonormal vectors, $\{|\, e_i >\}_{i=1}^{3}$, given by

$$|\, e_1 >= \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix};\quad |\, e_2 >= \frac{1}{\sqrt{6}}\begin{pmatrix} 1 \\ -1 \\ 2 \end{pmatrix};\quad |\, e_3 >= \frac{1}{\sqrt{3}}\begin{pmatrix} -1 \\ 1 \\ 1 \end{pmatrix}.$$

(1) Find the projection operators P_i associated with each of these vectors.
(2) Prove that P_i projects onto the line along $|\, e_i >$.
(3) Verify that $\sum_{i=1}^{3} P_i = I_3$.

Solution

(1) The projection operators P_i associated with $|\, e_i >$ are

$$P_1 =|\, e_1 >< e_1 \,|= \frac{1}{2}\begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}(1\ \ 1\ \ 0) = \frac{1}{2}\begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix};$$

$$P_2 =|\, e_2 >< e_2 \,|= \frac{1}{6}\begin{pmatrix} 1 \\ -1 \\ 2 \end{pmatrix}(1,\ -1,\ 2) = \frac{1}{6}\begin{pmatrix} 1 & -1 & 2 \\ -1 & 1 & -2 \\ 2 & -2 & 4 \end{pmatrix};$$

$$P_3 =|\, e_3 >< e_3 \,|= \frac{1}{3}\begin{pmatrix} -1 \\ 1 \\ 1 \end{pmatrix}(-1,\ 1,\ 1) = \frac{1}{3}\begin{pmatrix} 1 & -1 & -1 \\ -1 & 1 & 1 \\ -1 & 1 & 1 \end{pmatrix}.$$

(2) Let us prove that P_i projects onto the line parallel to $|\, e_i >$. Let P_1 act on the arbitrary column vector, with components x, y, z:

$$P_1 \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$= \frac{1}{2} \begin{pmatrix} x+y \\ x+y \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}}(x+y) \mid e_1 >,$$

which is proportional, i.e., parallel to $\mid e_1 >$. Next

$$P_2 \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \frac{1}{6} \begin{pmatrix} 1 & -1 & 2 \\ -1 & 1 & -2 \\ 2 & -2 & 4 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$= \frac{1}{6} \begin{pmatrix} x-y+2z \\ -x+y-2z \\ 2x-2y+4z \end{pmatrix} = \frac{1}{\sqrt{6}}(x-y+2z) \mid e_2 >,$$

which is along $\mid e_2 >$. Finally,

$$P_3 \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \frac{1}{3} \begin{pmatrix} 1 & -1 & -1 \\ -1 & 1 & 1 \\ -1 & 1 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$= \frac{1}{3} \begin{pmatrix} x-y-z \\ -x+y+z \\ -x+y+z \end{pmatrix} = \frac{1}{\sqrt{3}}(-x+y+z) \mid e_3 >,$$

which is along $\mid e_3 >$.
(3) The sum $P_1 + P_2 + P_3$ is

$$\frac{1}{2} \begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} + \frac{1}{6} \begin{pmatrix} 1 & -1 & 2 \\ -1 & 1 & -2 \\ 2 & -2 & 4 \end{pmatrix} + \frac{1}{3} \begin{pmatrix} 1 & -1 & -1 \\ -1 & 1 & 1 \\ -1 & 1 & 1 \end{pmatrix}$$

which yields the unit matrix.

A.5 Symmetrizing Operator

Show that the symmetrizing operator, S, defined such that, for any matrix, $V(s)$, depending on a variable, s, $SV(s) = \frac{1}{2}[V(s) + V(-s)]$, and the antisymmetrizing operator, A, defined such that $AV(s) = \frac{1}{2}[V(s) - V(-s)]$, are projection operators.

Solution

The square of the symmetrizing operator gives

$$\begin{aligned} S^2V(s) &= \tfrac{1}{2}S[V(s)+V(-s)] \\ &= \tfrac{1}{4}[V(s)+V(-s)+V(-s)+V(s)] \\ &= \tfrac{1}{2}[V(s)+V(-s)] = SV(s)\,, \end{aligned}$$

so $S^2 = S$. The square of the antisymmetrizing operator gives

$$\begin{aligned} A^2V(s) &= \tfrac{1}{2}A[V(s)-V(-s)] \\ &= \tfrac{1}{4}[V(s)-V(-s)-V(-s)+V(s)] \\ &= \tfrac{1}{2}[V(s)-V(-s)] = AV(s)\,, \end{aligned}$$

so $A^2 = A$. Moreover,

$$SAV(s) = \tfrac{1}{2}S[V(s)-V(-s)] = \tfrac{1}{4}[V(s)+V(-s)-V(-s)-V(s)] = 0\,,$$

so $SA = 0$, and

$$ASV(s) = \tfrac{1}{2}A[V(s)+V(-s)] = \tfrac{1}{4}[V(s)-V(-s)+V(-s)-V(s)] = 0\,,$$

so $AS = 0$. Moreover, since

$$(S+A)V(s) = V(s)\,,$$

it follows that $S + A = 1$, as an operator relation. This concludes the demonstration that S and A are projection operators.

A.6 Complete Orthonormal Set of Eigenvectors

Prove that two Hermitian matrices, B and C, commute if there exists a complete orthonormal set of common eigenvectors.

Solution

Let the complete set be $\{|j\rangle\}$, with $B|j\rangle = b_j|j\rangle$ and $C|j\rangle = c_j|j\rangle$. Then

$$\begin{aligned} BC &= \sum_j B|j\rangle\langle j|C = \sum_j b_j c_j |j\rangle\langle j| \\ CB &= \sum_j C|j\rangle\langle j|B = \sum_j b_j c_j |j\rangle\langle j|\,, \end{aligned}$$

so $BC = CB$.

A.7 Matrix Commutators I

Let s be a complex variable and A a constant square matrix of finite dimension. Define $V(s) = \exp(sA)$. Show

(1) $\frac{dV(s)}{ds} = AV = VA$
(2) $\frac{d}{ds}\{V(s)V(-s)\} = 0$ and hence that the inverse of the matrix $V(s)$ is given by $V^{-1}(s) = V(-s)$
(3) Using the above results, show that if A is a hermitian matrix, then e^{iA} is a unitary matrix.

Solution
We write $V(s)$ as a power series expansion:

$$V(s) = \sum_{n=0}^{\infty} \frac{s^n}{n!} A^n \tag{A.14}$$

(1) Term by term differentiation is allowed in this absolutely convergent series:

$$\begin{aligned} \frac{dV(s)}{ds} &= \sum_{n=1}^{\infty} \frac{s^{n-1}}{(n-1)!} A^n \\ &= A \sum_{n=0}^{\infty} \frac{s^n}{n!} A^n = \sum_{n=0}^{\infty} \frac{s^n}{n!} A^n A = AV = VA \end{aligned} \tag{A.15}$$

(2) With use of the previous result,

$$\begin{aligned} \frac{d}{ds}\{V(s)V(-s)\} &= \frac{dV(s)}{ds} V(-s) + V(s) \frac{dV(-s)}{ds} \\ &= V(s)AV(-s) - V(s)AV(-s) = 0\,. \end{aligned} \tag{A.16}$$

So $V(s)V(-s)$ is independent of s, and hence

$$V(s)V(-s) = V(0)V(0) = 1\,, \tag{A.17}$$

which proves that $V(-s)$ is the right-inverse of $V(s)$. To prove that $V(-s)$ is also the left-inverse of $V(s)$, we could repeat the above demonstration, replacing $V(s)V(-s)$ by $V(-s)V(s)$, but this is not really necessary, since for a matrix of finite dimension, N, it is the case that a right-inverse is always a true inverse, since Eq.(A.17) implies that

$$\det V(s) \det V(-s) = \det 1 = N\,,$$

which means that $\det V(s)$ cannot vanish, and this implies the existence of a true inverse.

(3) Set $s = i$, and use the previous result:

$$V^{-1}(i) = V(-i) = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} A^n ,$$

$$V^{\dagger}(i) = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} A^n = V^{-1}(i) ,$$

where the Hermiticity of A has been used. Thus $V(i)V^{\dagger}(i) = 1 = V^{\dagger}(i)V(i)$, i.e., e^{iA} is indeed a unitary matrix.

A.8 Matrix Commutators II

If A and B are square matrices and A commutes with $[A, B]$, show that, for any $n = 1, 2, \ldots$

(1) $[A^n, [A, B]] = 0$
(2) $[A^n, B] = nA^{n-1}[A, B]]$
(3) $[\mathrm{e}^A, B] = \mathrm{e}^A[A, B]$

Solution
(1) We shall use the method of mathematical induction, which works as follows. We are given that

$$[A, [A, B]] = 0 , \tag{A.18}$$

and if it *were* the case that

$$[A^n, [A, B]] = 0 \tag{A.19}$$

for some given n, *any* n, then it would follow, on multiplying this from the left by A, that

$$AA^n[A, B] - A[A, B]A^n = 0 , \tag{A.20}$$

which is equivalent to

$$[A^{n+1}, [A, B]] - [A, [A, B]]A^n = 0. \tag{A.21}$$

On using Eq.(A.18), we see that

$$[A^{n+1}, [A, B]] = 0 . \tag{A.22}$$

This completes the proof by induction, for Eq.(A.19) *is true* for $n = 1$, by virtue of Eq.(A.18), and so the implication Eq.(A.19) $\longrightarrow$ Eq.(A.22) entails

Eq.(A.19) for $n = 2$, which entails Eq.(A.19) for $n = 3, 4, 5 \ldots$, by repeated use of the proven implication, *ad infinitum*. This has the general form of a proof by induction: if a proposition $P(n)$ is known to be true for $n = 1$, and if it can be proved that $P(n) \longrightarrow P(n+1)$, then we say that the induction is complete: for any finite n, $P(n)$ follows from the known $P(1)$ in just $n - 1$ steps of proof, which however need not be spelled out for each value of the argument of $P(.)$, since the general case has been handled.
(2) Again we use induction. We see that

$$[A^n, B] = nA^{n-1}[A, B] \tag{A.23}$$

is an identity for $n = 1$. Suppose now that Eq.(A.23) is true an arbitrary, given n. Then, on multiplying this from the left by A, we find

$$A^{n+1}B - ABA^n = nA^n[A, B]\,. \tag{A.24}$$

The left side can be written in the form $A^{n+1}B - [A, B]A^n - BA^{n+1}$, and, using the solution to part (1) of this problem, we can write $[A^{n+1}, B] - A^n[A, B]$. The second term here can be transferred to the right side of Eq.(A.24), giving

$$[A^{n+1}, B] = (n+1)A^n[A, B]\,, \tag{A.25}$$

and this completes the induction, since Eq.(A.25) has the form of Eq.(A.23), with the substitution $n \to n + 1$.
(3) In terms of the power series expansion of the exponential,

$$\begin{aligned}
[\mathrm{e}^A, B] &= \sum_{n=1}^{\infty} \frac{1}{n!}[A^n, B] \\
&= \sum_{n=1}^{\infty} \frac{1}{(n-1)!} A^{n-1}[A, B] \\
&= \sum_{n=0}^{\infty} \frac{1}{n!} A^n[A, B] \\
&= \mathrm{e}^A[A, B]\,,
\end{aligned} \tag{A.26}$$

where use has been made of the solution to part (2) of this problem.

A.9 Matrix Commutators III

Let t be a complex variable, and define

$$f(t) = \mathrm{e}^{tA}.\mathrm{e}^{tB}.\mathrm{e}^{-t(A+B)}$$

where A and B are square matrices that both commute with $[A, B]$. Show

(1) $f'(t) = 2tf(t)[A, B]$
(2) $f(t) = \exp\{t^2[A, B]\}$
(3) $\mathrm{e}^A . \mathrm{e}^B = \exp\{A + B + [A, B]\}$

Solution
From the solution to part (3) of Problem **A.9**, with the substitutions $B \to A$ and $A \to tB$, we know that

$$[A, \mathrm{e}^{tB}] = \mathrm{e}^{tB}[A, tB] = t[A, B]\,\mathrm{e}^{tB}\,. \tag{A.27}$$

(1) Hence

$$\begin{aligned} f'(t) &= \mathrm{e}^{tA}(A + B)\,\mathrm{e}^{tB}e^{-t(A+B)} - \mathrm{e}^{tA}\,\mathrm{e}^{tB}(A + B)e^{-t(A+B)} \\ &= \mathrm{e}^{tA}[A, \mathrm{e}^{tB}]e^{-t(A+B)} \\ &= t[A, B]\,\mathrm{e}^{tA}\,\mathrm{e}^{tB}e^{-t(A+B)} \\ &= t[A, B]f(t)\,. \end{aligned} \tag{A.28}$$

(2) From its definition, the initial value of the function f is $f(0) = 1$, and so

$$f(t) = \exp\{t^2[A, B]/2\}$$

since this function clearly satisfies Eq.(A.28), and it also satisfies the initial condition at $t = 0$.
(3) With use of Solution 2(b), we find

$$\begin{aligned} \mathrm{e}^{tA}\,\mathrm{e}^{tB} = f(t)e^{t(A+B)} &= \exp\{t^2[A, B]/2\}\exp\{t(A + B)\} \\ &= \exp\{t(A + B) + t^2[A, B]/2\}\,. \end{aligned}$$

The required result follows on setting $t = 1$. To justify the last step, note

$$\begin{aligned} &\exp\{t^2[A, B]/2\}\exp\{t(A + B)\} \\ &\qquad = \lim_{n\to\infty}\{1 + t^2[A, B]/(2n)\}^n \lim_{n\to\infty}\{1 + t(A + B)/n\}^n \\ &\qquad = \lim_{n\to\infty}\{(1 + t(A + B)/n)(1 + t^2[A, B]/(2n))\}^n \\ &\qquad = \lim_{n\to\infty}\{1 + t(A + B)/n + t^2[A, B]/(2n)\}^n \end{aligned}$$

The transition from the first to the second equality is justified by the fact that both A and B commute with $[A, B]$.

A.10 Matrix Commutators IV

Let t be a complex variable, and define

$$g(t) = \mathrm{e}^{tA} B \, \mathrm{e}^{-tA}$$

where A and B are square matrices that do not commute with $[A, B]$. Show

(1) $g'(t) = [A, g(t)]$
(2) $g(t) = \exp[t\Omega_A]B$, where Ω_A is the linear operator, called the commutator operator, that is defined by $\Omega_A C = [A, C]$, where C is any square matrix.
(3) $\mathrm{e}^{A} B \, \mathrm{e}^{-A} = B + [A, B] + \frac{1}{2}[A, [A, B]] + \frac{1}{6}[A, [A, [A, B]]] + \ldots$
Here the $(n+1)$th term has a factor $(n!)^{-1}$ and contains n nested commutators.

Solution

(1) By using the solution of Problem **A.7**(1), we find

$$g'(t) = A \, \mathrm{e}^{tA} B \, \mathrm{e}^{-tA} - \mathrm{e}^{tA} B \, \mathrm{e}^{-tA} A = [A, g(t)] \, . \tag{A.29}$$

(2) From the definition of the commutator operator, it follows that

$$g'(t) = \Omega_A g(t) \, , \tag{A.30}$$

and the formal solution of this first-order differential equation that satisfies the initial condition $g(0) = B$ is

$$\begin{aligned} g(t) &= \exp[t\Omega_A]B \\ &= B + t[A, B] + \frac{t^2}{2!}[A, [A, B]] + \frac{t^3}{3!}[A, [A, [A, B]]] + \ldots \end{aligned} \tag{A.31}$$

and term by term differentiation of this series serves to check that it truly does satisfy Eq.(A.30).

(3) It suffices to set $t = 1$ in Eq.(A.31) to obtain the required result.

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