Chapter 9

Approximation Methods for Stationary States

9.1 Introduction

Most problems encountered in quantum mechanics cannot be solved exactly. *Exact* solutions of the Schrödinger equation exist only for a few *idealized* systems. To solve general problems, one must resort to approximation methods. A variety of such methods have been developed, and each has its own area of applicability. In this chapter we consider approximation methods that deal with *stationary* states corresponding to *time-independent* Hamiltonians. In the following chapter we will deal with approximation methods for explicitly time-dependent Hamiltonians.

To study problems of stationary states, we focus on three approximation methods: *perturbation theory, the variational method*, and *the WKB method*.

Perturbation theory is based on the assumption that the problem we wish to solve is, in some sense, only *slightly* different from a problem that can be solved exactly. In the case where the deviation between the two problems is *small*, perturbation theory is suitable for calculating the contribution associated with this deviation; this contribution is then added as a correction to the energy and the wave function of the exactly solvable Hamiltonian. So perturbation theory builds on the known exact solutions to obtain approximate solutions.

What about those systems whose Hamiltonians cannot be reduced to an exactly solvable part plus a small correction? For these, we may consider the variational method or the WKB approximation. The variational method is particularly useful in estimating the energy eigenvalues of the ground state and the first few excited states of a system for which one has only a qualitative idea about the form of the wave function.

The WKB method is useful for finding the energy eigenvalues and wave functions of systems for which the *classical limit is valid*. Unlike perturbation theory, the variational and WKB methods do not require the existence of a closely related Hamiltonian that can be solved exactly.

The application of the approximation methods to the study of stationary states consists of finding the energy eigenvalues E_n and the eigenfunctions $\mid \psi_n\rangle$ of a time-independent Hamiltonian $\hat{H}$ that does not have exact solutions:

$$\hat{H} \mid \psi_n\rangle = E_n \mid \psi_n\rangle. \tag{9.1}$$

Depending on the structure of $\hat{H}$, we can use any of the three methods mentioned above to find the approximate solutions to this eigenvalue problem.

9.2 Time-Independent Perturbation Theory

This method is most suitable when $\hat{H}$ is very close to a Hamiltonian $\hat{H}_0$ that can be solved exactly. In this case, $\hat{H}$ can be split into two time-independent parts

$$\hat{H} = \hat{H}_0 + \hat{H}_p, \tag{9.2}$$

where $\hat{H}_p$ is very small compared to $\hat{H}_0$ ($\hat{H}_0$ is known as the Hamiltonian of the unperturbed system). As a result, $\hat{H}_p$ is called the perturbation, for its effects on the energy spectrum and eigenfunctions will be small; such perturbation is encountered, for instance, in systems subject to *weak* electric or magnetic fields. We can make this idea more explicit by writing $\hat{H}_p$ in terms of a dimensionless real parameter λ which is very small compared to 1:

$$\hat{H}_p = \lambda \hat{W} \qquad (\lambda \ll 1). \tag{9.3}$$

Thus the eigenvalue problem (9.1) becomes

$$(\hat{H}_0 + \lambda \hat{W}) \mid \psi_n\rangle = E_n \mid \psi_n\rangle. \tag{9.4}$$

In what follows we are going to consider two separate cases depending on whether the exact solutions of $\hat{H}_0$ are nondegenerate or degenerate. Each of these two cases requires its own approximation scheme.

9.2.1 Nondegenerate Perturbation Theory

In this section we limit our study to the case where $\hat{H}_0$ has no degenerate eigenvalues; that is, for every energy $E_n^{(0)}$ there corresponds only one eigenstate $\mid \phi_n\rangle$:

$$\hat{H}_0 \mid \phi_n\rangle = E_n^{(0)} \mid \phi_n\rangle, \tag{9.5}$$

where the exact eigenvalues $E_n^{(0)}$ and exact eigenfunctions $\mid \phi_n\rangle$ are known.

The main idea of perturbation theory consists in assuming that the perturbed eigenvalues and eigenstates can both be expanded in power series in the parameter λ:

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots, \tag{9.6}$$

$$\mid \psi_n\rangle = \mid \phi_n\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \cdots. \tag{9.7}$$

We need to make two remarks. First, one might think that whenever the perturbation is sufficiently weak, the expansions (9.6) and (9.7) always exist. Unfortunately, this is not always the case. There are cases where the perturbation is small, yet E_n and $\mid \psi_n\rangle$ are not expandable in powers of λ. Second, the series (9.6) and (9.7) are frequently not convergent. However, when λ is small, the first few terms do provide a reliable description of the system. So in practice, we keep only one or two terms in these expansions; hence the problem of nonconvergence of these series is avoided (we will deal later with the problem of convergence). Note that when $\lambda = 0$ the expressions (9.6) and (9.7) yield the unperturbed solutions: $E_n = E_n^{(0)}$ and $\mid \psi_n\rangle = \mid \phi_n\rangle$.

The parameters $E_n^{(k)}$ and the kets $\mid \psi_n^{(k)}\rangle$ represent the kth corrections to the eigenenergies and eigenvectors, respectively.

The job of perturbation theory reduces then to the calculation of $E_n^{(1)}$, $E_n^{(2)}$, ... and $|\psi_n^{(1)}\rangle$, $\mid \psi_n^{(2)}\rangle$, ... In this section we shall be concerned only with the determination of $E_n^{(1)}$, $E_n^{(2)}$, and $|\psi_n^{(1)}\rangle$. Assuming that the unperturbed states $\mid \phi_n\rangle$ are nondegenerate, and substituting (9.6) and (9.7) into (9.4), we obtain

$$\begin{aligned}&\left(\hat{H}_0 + \lambda \hat{W}\right)\left(\mid \phi_n\rangle + \lambda \mid \psi_n^{(1)}\rangle + \lambda^2 \mid \psi_n^{(2)}\rangle + \cdots\right)\\ &\quad = \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots\right)\left(\mid \phi_n\rangle + \lambda \mid \psi_n^{(1)}\rangle + \lambda^2 \mid \psi_n^{(2)}\rangle + \cdots\right).\end{aligned} \tag{9.8}$$

The coefficients of successive powers of λ on both sides of this equation must be equal. Equating the coefficients of the first three powers of λ, we obtain these results:

- Zero order in λ:

$$\hat{H}_0 \mid \phi_n\rangle = E_n^{(0)} \mid \phi_n\rangle, \tag{9.9}$$

- First order in λ:

$$\hat{H}_0 \mid \psi_n^{(1)}\rangle + \hat{W} \mid \phi_n\rangle = E_n^{(0)} \mid \psi_n^{(1)}\rangle + E_n^{(1)} \mid \phi_n\rangle, \tag{9.10}$$

- Second order in λ:

$$\hat{H}_0 \mid \psi_n^{(2)}\rangle + \hat{W} \mid \psi_n^{(1)}\rangle = E_n^{(0)} \mid \psi_n^{(2)}\rangle + E_n^{(1)} \mid \psi_n^{(1)}\rangle + E_n^{(2)} \mid \phi_n\rangle. \tag{9.11}$$

We now proceed to determine the eigenvalues $E_n^{(1)}$, $E_n^{(2)}$ and the eigenvector $\mid \psi_n^{(1)}\rangle$ from (9.9) to (9.11). For this, we need to specify how the states $\mid \phi_n\rangle$ and $\mid \psi_n\rangle$ overlap. Since $\mid \psi_n\rangle$ is considered not to be very different from $\mid \phi_n\rangle$, we have $\langle \phi_n \mid \psi_n\rangle \simeq 1$. We can, however, normalize $\mid \psi_n\rangle$ so that its overlap with $\mid \phi_n\rangle$ is exactly equal to one:

$$\langle \phi_n \mid \psi_n\rangle = 1. \tag{9.12}$$

Substituting (9.7) into (9.12) we get

$$\lambda\langle \phi_n \mid \psi_n^{(1)}\rangle + \lambda^2\langle \phi_n \mid \psi_n^{(2)}\rangle + \cdots = 0; \tag{9.13}$$

hence the coefficients of the various powers of λ must vanish separately:

$$\langle \phi_n \mid \psi_n^{(1)}\rangle = \langle \phi_n \mid \psi_n^{(2)}\rangle = \cdots = 0. \tag{9.14}$$

First-order correction

To determine the first-order correction, $E_n^{(1)}$, to E_n we need simply to multiply both sides of (9.10) by $\langle \phi_n \mid$:

$$\boxed{E_n^{(1)} = \langle \phi_n \mid \hat{W} \mid \phi_n\rangle,} \tag{9.15}$$

where we have used the facts that $\langle \phi_n \mid \hat{H}_0 \mid \psi_n^{(1)}\rangle$ and $\langle \phi_n \mid \psi_n^{(1)}\rangle$ are both equal to zero and $\langle \phi_n \mid \phi_n\rangle = 1$. The insertion of (9.15) into (9.6) thus yields the energy to first-order perturbation:

$$\boxed{E_n = E_n^{(0)} + \langle \phi_n \mid \hat{H}_p \mid \phi_n\rangle.} \tag{9.16}$$

Note that for some systems, the first-order correction $E_n^{(1)}$ vanishes exactly. In such cases, one needs to consider higher-order terms.

Let us now determine $| \psi_n^{(1)}\rangle$. Since the set of the unperturbed states $| \phi_n\rangle$ form a complete and orthonormal basis, we can expand $| \psi_n^{(1)}\rangle$ in the $\{| \phi_n\rangle\}$ basis:

$$| \psi_n^{(1)}\rangle = \left(\sum_m | \phi_m\rangle\langle\phi_m |\right) | \psi_n^{(1)}\rangle = \sum_{m\neq n} \langle\phi_m | \psi_n^{(1)}\rangle | \phi_m\rangle; \tag{9.17}$$

the term $m = n$ does not contribute, since $\langle\phi_n | \psi_n^{(1)}\rangle = 0$. The coefficient $\langle\phi_m | \psi_n^{(1)}\rangle$ can be inferred from (9.10) by multiplying both sides by $\langle\phi_m |$:

$$\langle\phi_m | \psi_n^{(1)}\rangle = \frac{\langle\phi_m | \hat{W} | \phi_n\rangle}{E_n^{(0)} - E_m^{(0)}}, \tag{9.18}$$

which, when substituted into (9.17), leads to

$$| \psi_n^{(1)}\rangle = \sum_{m\neq n} \frac{\langle\phi_m | \hat{W} | \phi_n\rangle}{E_n^{(0)} - E_m^{(0)}} | \phi_m\rangle. \tag{9.19}$$

The eigenfunction $| \psi_n\rangle$ of $\hat{H}$ to first order in $\lambda\hat{W}$ can then be obtained by substituting (9.19) into (9.7):

$$\boxed{| \psi_n\rangle = | \phi_n\rangle + \sum_{m\neq n} \frac{\langle\phi_m | \hat{H}_p | \phi_n\rangle}{E_n^{(0)} - E_m^{(0)}} | \phi_m\rangle.} \tag{9.20}$$

Second-order correction

Now, to determine $E_n^{(2)}$ we need to multiply both sides of (9.11) by $\langle\phi_n |$:

$$E_n^{(2)} = \langle\phi_n | \hat{W} | \psi_n^{(1)}\rangle; \tag{9.21}$$

in obtaining this result we have used the facts that $\langle\phi_n | \psi_n^{(1)}\rangle = \langle\phi_n | \psi_n^{(2)}\rangle = 0$ and $\langle\phi_n | \phi_n\rangle = 1$. Inserting (9.19) into (9.21) we end up with

$$\boxed{E_n^{(2)} = \sum_{m\neq n} \frac{\left|\langle\phi_m|\hat{W} | \phi_n\rangle\right|^2}{E_n^{(0)} - E_m^{(0)}}.} \tag{9.22}$$

The eigenenergy to second order in $\hat{H}_p$ is obtained by substituting (9.22) and (9.15) into (9.6):

$$\boxed{E_n = E_n^{(0)} + \langle\phi_n | \hat{H}_p | \phi_n\rangle + \sum_{m\neq n} \frac{\left|\langle\phi_m|\hat{H}_p | \phi_n\rangle\right|^2}{E_n^{(0)} - E_m^{(0)}} + \cdots.} \tag{9.23}$$

In principle one can obtain energy corrections to any order. However, pushing the calculations beyond the second order, besides being mostly intractable, is a futile exercise, since the first two orders are generally sufficiently accurate.

Validity of the time-independent perturbation theory
For perturbation theory to work, the corrections it produces must be small; convergence must be achieved with the first two corrections. Expressions (9.20) and (9.23) show that the expansion parameter is $\langle\phi_m|\hat{H}_p \mid \phi_n\rangle/(E_n^{(0)} - E_m^{(0)})$. Thus, for the perturbation schemes (9.6) and (9.7) to work (i.e., to converge), the expansion parameter must be small:

$$\left|\frac{\langle\phi_m|\hat{H}_p \mid \phi_n\rangle}{E_n^{(0)} - E_m^{(0)}}\right| \ll 1 \qquad (n \neq m). \tag{9.24}$$

If the unperturbed energy levels $E_n^{(0)}$ and $E_m^{(0)}$ were equal (i.e., degenerate) then condition (9.24) would break down. Degenerate energy levels require an approach that is different from the nondegenerate treatment. This question will be taken up in the following section.

Example 9.1 (Charged oscillator in an electric field)
A particle of charge q and mass m, which is moving in a one-dimensional harmonic potential of frequency ω, is subject to a *weak* electric field $\mathcal{E}$ in the x-direction.

(a) Find the exact expression for the energy.

(b) Calculate the energy to first nonzero correction and compare it with the exact result obtained in (a).

Solution
The interaction between the oscillating charge and the external electric field gives rise to a term $\hat{H}_P = q\mathcal{E}\hat{X}$ that needs to be added to the Hamiltonian of the oscillator:

$$\hat{H} = \hat{H}_0 + \hat{H}_p = -\frac{\hbar}{2m}\frac{d^2}{dX^2} + \frac{1}{2}m\omega^2\hat{X}^2 + q\mathcal{E}\hat{X}. \tag{9.25}$$

(a) First, note that the eigenenergies of this Hamiltonian can be obtained exactly without resorting to any perturbative treatment. A variable change $\hat{y} = \hat{X} + q\mathcal{E}/(m\omega^2)$ leads to

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dy^2} + \frac{1}{2}m\omega^2\hat{y}^2 - \frac{q^2\mathcal{E}^2}{2m\omega^2}. \tag{9.26}$$

This is the Hamiltonian of a harmonic oscillator from which a constant, $q^2\mathcal{E}^2\omega^2/(2m)$, is subtracted. The exact eigenenergies can thus be easily inferred:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega - \frac{q^2\mathcal{E}^2}{2m\omega^2}. \tag{9.27}$$

This simple example allows us to compare the exact and approximate eigenenergies.

(b) Let us now turn to finding the approximate eigenvalues of $\hat{H}$ by means of perturbation theory. Since the electric field is weak, we can treat $\hat{H}_p$ as a perturbation.

Note that the first-order correction to the energy, $E_n^{(1)} = a\langle n \mid \hat{X} \mid n\rangle$, is zero (since $\langle n \mid \hat{X} \mid n\rangle = 0$), but the second-order correction is not:

$$E_n^{(2)} = q^2\mathcal{E}^2 \sum_{m\neq n} \frac{\left|\langle m \mid \hat{X} \mid n\rangle\right|^2}{E_n^{(0)} - E_m^{(0)}}. \tag{9.28}$$

Since $E_n^{(0)} = \left(n + \frac{1}{2}\right)\hbar\omega$, and using the relations

$$\langle n+1 \mid \hat{X} \mid n\rangle = \sqrt{n+1}\sqrt{\frac{\hbar}{2m\omega}}, \qquad \langle n-1 \mid \hat{X} \mid n\rangle = \sqrt{n}\sqrt{\frac{\hbar}{2m\omega}}, \tag{9.29}$$

$$E_n^{(0)} - E_{n-1}^{(0)} = \hbar\omega, \qquad E_n^{(0)} - E_{n+1}^{(0)} = -\hbar\omega, \tag{9.30}$$

we can reduce (9.28) to

$$\begin{aligned} E_n^{(2)} &= q^2\mathcal{E}^2\left[\frac{|\langle n+1 \mid \hat{X} \mid n\rangle|^2}{E_n^{(0)} - E_{n+1}^{(0)}} + \frac{|\langle n-1 \mid \hat{X} \mid n\rangle|^2}{E_n^{(0)} - E_{n-1}^{(0)}}\right] \\ &= -\frac{q^2\mathcal{E}^2}{2m\omega^2}; \end{aligned} \tag{9.31}$$

hence the energy is given to second order by

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} = \left(n + \frac{1}{2}\right)\hbar\omega - \frac{q^2\mathcal{E}^2}{2m\omega^2}. \tag{9.32}$$

This agrees fully with the exact energy found in (9.27).

Similarly, using (9.19) along with (9.29) and (9.30), we can easily ascertain that $\mid \psi_n^{(1)}\rangle$ is given by

$$\mid \psi_n^{(1)}\rangle = \frac{q\mathcal{E}}{\hbar\omega}\sqrt{\frac{\hbar}{2m\omega}}\left\{\sqrt{n} \mid n-1\rangle - \sqrt{n+1} \mid n+1\rangle\right\}; \tag{9.33}$$

hence the state $\mid \psi_n\rangle$ is given to first order by

$$\mid \psi_n\rangle = \mid n\rangle + \frac{q\mathcal{E}}{\hbar\omega}\sqrt{\frac{\hbar}{2m\omega}}\left\{\sqrt{n} \mid n-1\rangle - \sqrt{n+1} \mid n+1\rangle\right\}, \tag{9.34}$$

where $\mid n\rangle$ is the exact eigenstate of the nth excited state of a one-dimensional harmonic oscillator.

Example 9.2 (The Stark effect)

(a) Study the effect of an external uniform weak electric field, which is directed along the positive z-axis, $\vec{\mathcal{E}} = \mathcal{E}\vec{k}$, on the ground state of a hydrogen atom; ignore the spin degrees of freedom.

(b) Find an approximate value for the polarizability of the hydrogen atom.

Solution

(a) The effect that an external electric field has on the energy levels of an atom is called the Stark effect. In the absence of an electric field, the (unperturbed) Hamiltonian of the hydrogen atom (in CGS units) is:

$$\hat{H}_0 = \frac{\hat{\vec{p}}^{\,2}}{2\mu} - \frac{e^2}{r}. \tag{9.35}$$

The eigenfunctions of this Hamiltonian, $\psi_{nlm}(\vec{r})$, were obtained in Chapter 6; they are given by

$$\langle r\theta\varphi \mid nlm\rangle = \psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm}(\theta, \varphi). \tag{9.36}$$

When the electric field is turned on, the interaction between the atom and the field generates a term $\hat{H}_p = e\vec{\mathcal{E}} \cdot \vec{r} = e\mathcal{E}\hat{Z}$ that needs to be added to $\hat{H}_0$.

Since the excited states of the hydrogen atom are degenerate while the ground state is not, nondegenerate perturbation theory applies only to the ground state, $\psi_{100}(\vec{r})$. Ignoring the spin degrees of freedom, the energy of this system to second-order perturbation is given as follows (see (9.23)):

$$E_{100} = E_{100}^{(0)} + e\mathcal{E}\langle 100 \mid \hat{Z} \mid 100\rangle + e^2\mathcal{E}^2 \sum_{nlm \neq 100} \frac{\left|\langle nlm \mid \hat{Z} \mid 100\rangle\right|^2}{E_{100}^{(0)} - E_{nlm}^{(0)}}. \tag{9.37}$$

The term

$$\langle 100 \mid \hat{Z} \mid 100\rangle = \int |\psi_{100}(\vec{r})|^2 z \, d^3r \tag{9.38}$$

is zero, since $\hat{Z}$ is odd under parity and $\psi_{100}(\vec{r})$ has a definite parity. This means that there can be no correction term to the energy which is proportional to the electric field and hence there is no linear Stark effect. The underlying physics behind this is that when the hydrogen atom is in its ground state, it has no permanent electric dipole moment. We are left then with only a *quadratic* dependence of the energy (9.37) on the electric field. This is called the quadratic Stark effect. This correction, which is known as the energy shift ΔE, is given by

$$\Delta E = e^2\mathcal{E}^2 \sum_{nlm \neq 100} \frac{\left|\langle nlm \mid \hat{Z} \mid 100\rangle\right|^2}{E_{100}^{(0)} - E_{nlm}^{(0)}}. \tag{9.39}$$

(b) Let us now estimate the value of the polarizability of the hydrogen atom. The *polarizability* α of an atom which is subjected to an electric field $\vec{\mathcal{E}}$ is given in terms of the energy shift ΔE as

$$\alpha = -2\frac{\Delta E}{\mathcal{E}^2}. \tag{9.40}$$

Substituting (9.39) into (9.40), we obtain the polarizability of the hydrogen atom in its ground state:

$$\alpha = -2e^2 \sum_{nlm \neq 100} \frac{\left|\langle nlm \mid \hat{Z} \mid 100\rangle\right|^2}{E_{100}^{(0)} - E_{nlm}^{(0)}}. \tag{9.41}$$

To estimate this sum, let us assume that the denominator is constant. Since $n \geq 2$, we can write

$$E_{100}^{(0)} - E_{nlm}^{(0)} \leq E_{100} - E_{200} = \frac{e^2}{2a_0}\left(-1 + \frac{1}{4}\right) = -\frac{3e^2}{8a_0}; \tag{9.42}$$

hence

$$\alpha \leq \frac{16a_0}{3} \sum_{nlm \neq 100} |\langle nlm \mid \hat{Z} \mid 100\rangle|^2, \tag{9.43}$$

where

$$\begin{aligned} \sum_{nlm \neq 100} |\langle nlm \mid \hat{Z} \mid 100\rangle|^2 &= \sum_{\text{all } nlm} |\langle nlm \mid \hat{Z} \mid 100\rangle|^2 \\ &= \langle 100 \mid \hat{Z}\left(\sum_{\text{all } nlm} \mid nlm\rangle\langle nlm \mid\right)\hat{Z} \mid 100\rangle \\ &= \langle 100 \mid \hat{Z}^2 \mid 100\rangle; \end{aligned} \tag{9.44}$$

in deriving this relation, we have used the facts that $\langle 100 \mid \hat{Z} \mid 100\rangle = 0$ and that the set of states $\mid nlm\rangle$ is complete. Now since $z = r\cos\theta$ and $\langle r\theta\varphi \mid 100\rangle = R_{10}(r)Y_{00}(\theta,\ \varphi) = R_{10}(r)/\sqrt{4\pi}$, we immediately obtain

$$\langle 100 \mid \hat{Z}^2 \mid 100\rangle = \frac{1}{4\pi}\int_0^\infty r^4 R_{10}^2(r)\,dr \int_0^\pi \sin\theta\cos^2\theta\,d\theta \int_0^{2\pi} d\varphi = a_0^2. \tag{9.45}$$

Substituting (9.45) and (9.44) into (9.43), we see that the polarizability for hydrogen has an upper limit

$$\alpha \le \frac{16}{3}a_0^3. \tag{9.46}$$

This limit, which is obtained from perturbation theory, agrees with the exact value $\alpha = \frac{9}{2}a_0^3$.

9.2.2 Degenerate Perturbation Theory

In the discussion above, we have considered only systems with nondegenerate $\hat{H}_0$. We now apply perturbation theory to determine the energy spectrum and the states of a system whose unperturbed Hamiltonian $\hat{H}_0$ is degenerate:

$$\hat{H} \mid \psi_n\rangle = (\hat{H}_0 + \hat{H}_p) \mid \psi_n\rangle = E_n \mid \psi_n\rangle. \tag{9.47}$$

If, for instance, the level of energy $E_n^{(0)}$ is f-fold degenerate (i.e., there exists a set of f different eigenstates $\mid \phi_{n_\alpha}\rangle$, where $\alpha = 1, 2, \ldots, f$, that correspond to the same eigenenergy $E_n^{(0)}$), we have

$$\hat{H}_0 \mid \phi_{n_\alpha}\rangle = E_n^{(0)} \mid \phi_{n_\alpha}\rangle \qquad (\alpha = 1, 2, \ldots, f), \tag{9.48}$$

where α stands for one or more quantum numbers; the energy eigenvalues $E_n^{(0)}$ are independent of α.

In the zeroth-order approximation we can write the eigenfunction $\mid \psi_n\rangle$ as a linear combination in terms of $\mid \phi_{n_\alpha}\rangle$:

$$\mid \psi_n\rangle = \sum_{\alpha=1}^{f} a_\alpha \mid \phi_{n_\alpha}\rangle. \tag{9.49}$$

Considering the states $\mid \phi_{n_\alpha}\rangle$ to be orthonormal with respect to the label α (i.e., $\langle \phi_{n_\alpha} \mid \phi_{n_\beta}\rangle = \delta_{\alpha,\beta}$) and $\mid \psi_n\rangle$ to be normalized, $\langle \psi_n \mid \psi_n\rangle = 1$, we can ascertain that the coefficients a_α obey the relation

$$\langle \psi_n \mid \psi_n\rangle = \sum_{\alpha,\beta} a_\alpha^* a_\beta \delta_{\alpha,\beta} = \sum_{\alpha=1}^{f} |a_\alpha|^2 = 1. \tag{9.50}$$

In what follows we are going to show how to determine these coefficients and the first-order corrections to the energy. For this, let us substitute (9.48) and (9.49) into (9.47):

$$\sum_\alpha \left[E_n^{(0)} \mid \phi_{n_\alpha}\rangle + \hat{H}_p \mid \phi_{n_\alpha}\rangle\right] a_\alpha = E_n \sum_\alpha a_\alpha \mid \phi_{n_\alpha}\rangle. \tag{9.51}$$

The multiplication of both sides of this equation by $\langle \phi_{n_\beta} \mid$ leads to

$$\sum_\alpha a_\alpha \left[E_n^{(0)}\delta_{\alpha,\beta} + \langle \phi_{n_\beta} \mid \hat{H}_p \mid \phi_{n_\alpha}\rangle\right] = E_n \sum_\alpha a_\alpha \delta_{\alpha,\beta} \tag{9.52}$$

or to

$$a_\beta E_n = a_\beta E_n^{(0)} + \sum_{\alpha=1}^{f} a_\alpha \langle \phi_{n_\beta} \mid \hat{H}_p \mid \phi_{n_\alpha} \rangle, \tag{9.53}$$

where we have used $\langle \phi_{n_\beta} \mid \phi_{n_\alpha} \rangle = \delta_{\beta,\,\alpha}$. We can rewrite (9.53) as follows:

$$\sum_{\alpha=1}^{f} \left(\hat{H}_{p_{\beta\alpha}} - E_n^{(1)} \delta_{\alpha,\,\beta} \right) a_\alpha = 0 \qquad (\beta = 1,\ 2,\ \ldots,\ f), \tag{9.54}$$

with $\hat{H}_{p_{\beta\alpha}} = \langle \phi_{n_\beta} \mid \hat{H}_p \mid \phi_{n_\alpha} \rangle$ and $E_n^{(1)} = E_n - E_n^{(0)}$. This is a system of f homogeneous linear equations for the coefficients a_α. These coefficients are nonvanishing only when the determinant $|\hat{H}_{p_{\alpha\beta}} - E_n^{(1)} \delta_{\alpha,\,\beta}|$ is zero:

$$\begin{vmatrix} \hat{H}_{p_{11}} - E_n^{(1)} & \hat{H}_{p_{12}} & \hat{H}_{p_{13}} & \cdots & \hat{H}_{p_{1f}} \\ \hat{H}_{p_{21}} & \hat{H}_{p_{22}} - E_n^{(1)} & \hat{H}_{p_{23}} & \cdots & \hat{H}_{p_{2f}} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \hat{H}_{p_{f1}} & \hat{H}_{p_{f2}} & \hat{H}_{p_{f3}} & \cdots & \hat{H}_{p_{ff}} - E_n^{(1)} \end{vmatrix} = 0. \tag{9.55}$$

This is an fth degree equation in $E_n^{(1)}$ and in general it has f different real roots, $E_{n_\alpha}^{(1)}$. These roots are the first-order correction to the eigenvalues, E_{n_α}, of $\hat{H}$. To find the coefficients a_α, we need simply to substitute these roots into (9.54) and then solve the resulting expression. Knowing these coefficients, we can then determine the eigenfunctions, $|\ \psi_n\rangle$, of $\hat{H}$ in the zeroth approximation from (9.49).

The roots $E_{n_\alpha}^{(1)}$ of (9.55) are in general different. In this case the eigenvalues $\hat{H}$ are not degenerate, hence the f-fold degenerate level $E_n^{(0)}$ of the unperturbed problem is split into f different levels E_{n_α}: $E_{n_\alpha} = E_n^{(0)} + E_{n_\alpha}^{(1)}$, $\alpha = 1,\ 2,\ \ldots,\ f$. In this way, the perturbation lifts the degeneracy. The lifting of the degeneracy may be either total or partial, depending on whether all the roots of (9.55), or only some of them, are different.

In summary, to determine the eigenvalues to first-order and the eigenstates to zeroth order for an f-fold degenerate level from perturbation theory, we proceed as follows:

- First, for each f-fold degenerate level, determine the $f \times f$ matrix of the perturbation $\hat{H}_p$:

$$H_p = \begin{pmatrix} \hat{H}_{p_{11}} & \hat{H}_{p_{12}} & \cdots & \hat{H}_{p_{1f}} \\ \hat{H}_{p_{21}} & \hat{H}_{p_{22}} & \cdots & \hat{H}_{p_{2f}} \\ \vdots & \vdots & \ddots & \vdots \\ \hat{H}_{p_{f1}} & \hat{H}_{p_{f2}} & \cdots & \hat{H}_{p_{ff}} \end{pmatrix}, \tag{9.56}$$

  where $\hat{H}_{p_{\alpha\beta}} = \langle \phi_{n_\alpha} | \hat{H}_p | \phi_{n_\beta} \rangle$.

- Second, diagonalize this matrix and find the f eigenvalues $E_{n_\alpha}^{(1)}$ ($\alpha = 1,\ 2,\ \ldots,\ f$) and their corresponding eigenvectors

$$a_\alpha = \begin{pmatrix} a_{\alpha_1} \\ a_{\alpha_2} \\ \vdots \\ a_{\alpha_f} \end{pmatrix} \qquad (\alpha = 1,\ 2,\ \ldots,\ f). \tag{9.57}$$

- Finally, the energy eigenvalues are given to first order by

$$E_{n_\alpha} = E_n^{(0)} + E_{n_\alpha}^{(1)} \qquad (\alpha = 1,\ 2,\ \ldots,\ f) \tag{9.58}$$

and the corresponding eigenvectors are given to zero order by

$$|\psi_{n_\alpha}\rangle = \sum_{\beta=1}^{f} a_{\alpha\beta}|\phi_{n_\beta}\rangle. \tag{9.59}$$

Example 9.3 (The Stark effect of hydrogen)

Using first-order (degenerate) perturbation theory, calculate the energy levels of the $n = 2$ states of a hydrogen atom placed in an external uniform weak electric field along the positive z-axis.

Solution

In the absence of any external electric field, the first excited state (i.e., $n = 2$) is fourfold degenerate: the states $\mid nlm\rangle = \mid 200\rangle$, $\mid 210\rangle$, $\mid 211\rangle$, and $\mid 21-1\rangle$ have the same energy $E_2 = -R_y/4$, where $R_y = \mu e^4/(2\hbar^2) = 13.6\,\text{eV}$ is the Rydberg constant.

When the external electric field is turned on, some energy levels will split. The energy due to the interaction between the dipole moment of the electron ($\vec{d} = -e\vec{r}$) and the external electric field ($\vec{\mathcal{E}} = \mathcal{E}\vec{k}$) is given by

$$\hat{H}_p = -\vec{d}\cdot\vec{\mathcal{E}} = e\vec{r}\cdot\vec{\mathcal{E}} = e\mathcal{E}\hat{Z}. \tag{9.60}$$

To calculate the eigenenergies, we need to determine and then diagonalize the 4×4 matrix elements of $\hat{H}_p$: $\langle 2l'm' \mid \hat{H}_p \mid 2lm\rangle = e\mathcal{E}\langle 2l'm' \mid \hat{Z} \mid 2lm\rangle$. The matrix elements $\langle 2l'm' \mid \hat{Z} \mid 2lm\rangle$ can be calculated more simply by using the relevant selection rules and symmetries. First, since $\hat{Z}$ does not depend on the azimuthal angle φ, $z = r\cos\theta$, the elements $\langle 2l'm' \mid \hat{Z} \mid 2lm\rangle$ are nonzero only if $m' = m$. Second, as Z is odd, the states $\mid 2l'm'\rangle$ and $\mid 2lm\rangle$ must have opposite parities so that $\langle 2l'm' \mid \hat{Z} \mid 2lm\rangle$ does not vanish. Therefore, the only nonvanishing matrix elements are those that couple the 2s and 2p states (with $m = 0$); that is, between $\mid 200\rangle$ and $\mid 210\rangle$. In this case we have

$$\begin{aligned}\langle 200 \mid \hat{Z} \mid 210\rangle &= \int_0^\infty R_{20}^*(r)R_{21}(r)r^2dr \int Y_{00}^*(\Omega)zY_{10}(\Omega)\,d\Omega \\ &= \sqrt{\frac{4\pi}{3}}\int_0^\infty R_{20}(r)R_{21}(r)r^3dr \int Y_{00}^*(\Omega)Y_{10}^2(\Omega)\,d\Omega \\ &= -3a_0,\end{aligned} \tag{9.61}$$

since $z = r\cos\theta = \sqrt{4\pi/3}rY_{10}(\Omega)$, $\langle\vec{r} \mid 200\rangle = R_{20}(r)Y_{00}(\Omega)$, $\langle\vec{r} \mid 210\rangle = R_{21}(r)Y_{10}(\Omega)$, and $d\Omega = \sin\theta\,d\theta d\varphi$; $a_0 = \hbar^2/(\mu e^2)$ is the Bohr radius. Using the notations $\mid 1\rangle = \mid 200\rangle$, $\mid 2\rangle = \mid 211\rangle$, $\mid 3\rangle = \mid 210\rangle$, and $\mid 4\rangle = \mid 21-1\rangle$, we can write the matrix of H_p as

$$H_p = \begin{pmatrix} \langle 1 \mid \hat{H}_p \mid 1\rangle & \langle 1 \mid \hat{H}_p \mid 2\rangle & \langle 1 \mid \hat{H}_p \mid 3\rangle & \langle 1 \mid \hat{H}_p \mid 4\rangle \\ \langle 2 \mid \hat{H}_p \mid 1\rangle & \langle 2 \mid \hat{H}_p \mid 2\rangle & \langle 2 \mid \hat{H}_p \mid 3\rangle & \langle 2 \mid \hat{H}_p \mid 4\rangle \\ \langle 3 \mid \hat{H}_p \mid 1\rangle & \langle 3 \mid \hat{H}_p \mid 2\rangle & \langle 3 \mid \hat{H}_p \mid 3\rangle & \langle 3 \mid \hat{H}_p \mid 4\rangle \\ \langle 4 \mid \hat{H}_p \mid 1\rangle & \langle 4 \mid \hat{H}_p \mid 2\rangle & \langle 4 \mid \hat{H}_p \mid 3\rangle & \langle 4 \mid \hat{H}_p \mid 4\rangle \end{pmatrix} \tag{9.62}$$

or as

$$H_p = -3e\mathcal{E}a_0 \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \tag{9.63}$$

The diagonalization of this matrix leads to the following eigenvalues:

$$E^{(1)}_{2\ 1} = -3e\mathcal{E}a_0, \qquad E^{(1)}_{2\ 2} = E^{(1)}_{2\ 3} = 0, \qquad E^{(1)}_{2\ 4} = 3e\mathcal{E}a_0. \tag{9.64}$$

Thus, the energy levels of the $n = 2$ states are given to first order by

$$E_{2_1} = -\frac{R_y}{4} - 3e\mathcal{E}a_0, \quad E_{2_2} = E_{2_3} = -\frac{R_y}{4}, \quad E_{2_4} = -\frac{R_y}{4} + 3e\mathcal{E}a_0. \tag{9.65}$$

The corresponding eigenvectors to zeroth order are

$$\mid \psi_2\rangle_1 \;=\; \frac{1}{\sqrt{2}}\left(\mid 200\rangle + \mid 210\rangle\right), \qquad \mid \psi_2\rangle_2 = \mid 211\rangle, \tag{9.66}$$

$$\mid \psi_2\rangle_3 \;=\; \mid 21-1\rangle, \qquad \mid \psi_2\rangle_4 = \frac{1}{\sqrt{2}}\left(\mid 200\rangle - \mid 210\rangle\right). \tag{9.67}$$

This perturbation has only partially removed the degeneracy of the $n = 2$ level; the states $\mid 211\rangle$ and $\mid 21-1\rangle$ still have the same energy $E_3 = E_4 = -R_y/4$.

9.2.3 Fine Structure and the Anomalous Zeeman Effect

One of the most useful applications of perturbation theory is to calculate the energy corrections for the hydrogen atom, notably the corrections due to the fine structure and the Zeeman effect. The fine structure is in turn due to two effects: spin–orbit coupling and the relativistic correction. Let us look at these corrections separately.

9.2.3.1 Spin–Orbit Coupling

The spin–orbit coupling in hydrogen arises from the interaction between the electron's spin magnetic moment, $\vec{\mu}_S = -e\vec{S}/(m_e c)$, and the proton's orbital magnetic field $\vec{B}$.

The origin of the magnetic field experienced by the electron moving at $\vec{v}$ in a circular orbit around the proton can be explained classically as follows. The electron, within its rest frame, sees the proton moving at $-\vec{v}$ in a circular orbit around it (Figure 9.1). From classical electrodynamics, the magnetic field experienced by the electron is

$$\vec{B} = -\frac{1}{c}\vec{v} \times \vec{E} = -\frac{1}{m_e c}\vec{p} \times \vec{E} = \frac{1}{m_e c}\vec{E} \times \vec{p}, \tag{9.68}$$

where $\vec{p} = m_e\vec{v}$ is the linear momentum of the electron and $\vec{E}$ is the electric field generated by the proton's Coulomb's field: $\vec{E}(\vec{r}) = (e/r^2)(\vec{r}/r) = e\vec{r}/r^3$. For a more general problem of hydrogen-like atoms—atoms with one valence electron outside a closed shell—where an electron moves in the (central) Coulomb potential of a nucleus $V(r) = -e\phi(r)$, the electric field is

$$\vec{E}(\vec{r}) = -\vec{\nabla}\phi(r) = \frac{1}{e}\vec{\nabla}V(r) = \frac{1}{e}\frac{\vec{r}}{r}\frac{dV}{dr}. \tag{9.69}$$

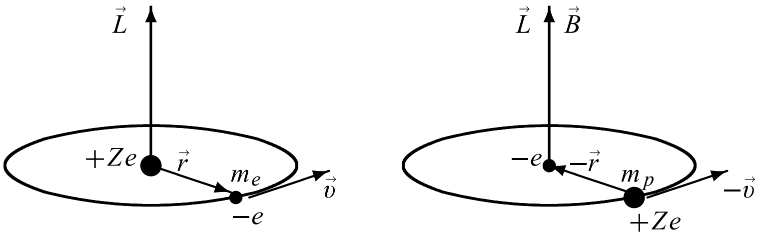

Figure 9.1 (Left) An electron moving in a circular orbit as seen by the nucleus. (Right) The same motion as seen by the electron within its rest frame; the electron sees the nucleus moving in a circular orbit around it.

So the magnetic field of the nucleus calculated in the rest frame of the electron is obtained by inserting (9.69) into (9.68):

$$\vec{B} = \frac{1}{m_e c}\vec{E} \times \vec{p} = \frac{1}{em_e c}\frac{1}{r}\frac{dV}{dr}\vec{r} \times \vec{p} = \frac{1}{em_e c}\frac{1}{r}\frac{dV}{dr}\vec{L}, \tag{9.70}$$

where $\vec{L} = \vec{r} \times \vec{p}$ is the orbital angular momentum of the electron.

The interaction of the electron's spin dipole moment $\vec{\mu}_S$ with the orbital magnetic field $\vec{B}$ of the nucleus gives rise to the following interaction energy:

$$\hat{H}_{SO} = -\vec{\mu}_S \cdot \vec{B} = \frac{e}{m_e c}\vec{S} \cdot \vec{B} = \frac{1}{m_e^2 c^2}\frac{1}{r}\frac{dV}{dr}\vec{S} \cdot \vec{L}. \tag{9.71}$$

This energy turns out to be twice the observed spin–orbit interaction. This is due to the fact that (9.71) was calculated within the rest frame of the electron. This frame is not inertial, for the electron accelerates while moving in a circular orbit around the nucleus. For a correct treatment, we must transform to the rest frame of the nucleus (i.e., the lab frame). This transformation, which involves a relativistic transformation of velocities, gives rise to an additional motion resulting from the precession of $\vec{\mu}_S$; this is known as the *Thomas precession*. The precession of the electron's spin moment is a relativistic effect which occurs even in the absence of an external magnetic field. The transformation back to the rest frame of the nucleus leads to a reduction of the interaction energy (9.71) by a factor of 2:

$$\hat{H}_{SO} = \frac{1}{2m_e^2 c^2}\frac{1}{r}\frac{dV}{dr}\vec{S} \cdot \vec{L}. \tag{9.72}$$

As this relation was derived from a classical treatment, we can now obtain the corresponding quantum mechanical expression by replacing the dynamical variables with the corresponding operators:

$$\boxed{\hat{H}_{SO} = \frac{1}{2m_e^2 c^2}\frac{1}{r}\frac{d\hat{V}}{dr}\hat{\vec{S}} \cdot \hat{\vec{L}}.} \tag{9.73}$$

This is the *spin–orbit* energy. For a hydrogen's electron, $V(r) = -e^2/r$ and $dV/dr = e^2/r^2$, equation (9.73) reduces to

$$\hat{H}_{SO} = \frac{e^2}{2m_e^2 c^2}\frac{1}{r^3}\hat{\vec{S}} \cdot \hat{\vec{L}}. \tag{9.74}$$

We can now use perturbation theory to calculate the contribution of the spin–orbit interaction in a hydrogen atom:

$$\hat{H} = \frac{\hat{\vec{p}}^{\,2}}{2m_e} - \frac{e^2}{r} + \frac{e^2}{2m_e^2c^2r^3}\hat{\vec{S}}\cdot\hat{\vec{L}} = \hat{H}_0 + \hat{H}_{SO}, \tag{9.75}$$

where $\hat{H}_0$ is the unperturbed Hamiltonian and $\hat{H}_{SO}$ is the perturbation. To apply perturbation theory, we need to specify the unperturbed states—the eigenstates of $\hat{H}_0$. Since the spin of the hydrogen's electron is taken into account, the total wave function of $\hat{H}_0$ consists of a direct product of two parts: a spatial part and a spin part. To specify the eigenstates of $\hat{H}_0$, we have two choices: first, the joint eigenstates $\mid nlm_lm_s\rangle$ of $\hat{L}^2$, $\hat{S}^2$, $\hat{L}_z$, and $\hat{S}_z$ and, second, the joint eigenstates $\mid nljm\rangle$ of $\hat{L}^2$, $\hat{S}^2$, $\hat{J}^2$, and $\hat{J}_z$. While $\hat{H}_0$ is diagonal in both of these representations, $\hat{H}_{SO}$ is diagonal in the second but not in the first, because $\hat{H}_{SO}$ (or $\hat{\vec{S}}\cdot\hat{\vec{L}}$ to be precise) commutes with neither $\hat{L}_z$ nor with $\hat{S}_z$ (Chapter 7). Thus, if $\hat{H}_{SO}$ were included, the first choice would be a bad one, since we would be forced to diagonalize the matrix of $\hat{H}_{SO}$ within the states $\mid nlm_lm_s\rangle$; this exercise is nothing less than tedious and cumbersome. The second choice, however, is ideal for our problem, since the first-order energy correction is given simply by the expectation value of the perturbation, because $\hat{H}_{SO}$ is already diagonal in this representation. We have shown in Chapter 7 that the states $\mid nljm\rangle$,

$$\Psi_{n,l,j=l\pm\frac{1}{2},m} = R_{nl}(r)\left[\sqrt{\frac{l\mp m+\frac{1}{2}}{2l+1}}\,Y_{l,m+\frac{1}{2}}\left|\frac{1}{2},-\frac{1}{2}\right\rangle \pm \sqrt{\frac{l\pm m+\frac{1}{2}}{2l+1}}\,Y_{l,m-\frac{1}{2}}\left|\frac{1}{2},\frac{1}{2}\right\rangle\right], \tag{9.76}$$

are eigenstates of $\hat{\vec{S}}\cdot\hat{\vec{L}}$ and that the corresponding eigenvalues are given by

$$\langle nljm \mid \hat{\vec{L}}\cdot\hat{\vec{S}} \mid nljm\rangle = \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right], \tag{9.77}$$

since $\hat{\vec{S}}\cdot\hat{\vec{L}} = \frac{1}{2}\left[\hat{J}^{\,2} - \hat{L}^{\,2} - \hat{S}^{\,2}\right]$.

The eigenvalues of (9.75) are then given to first-order correction by

$$E_{nlj} = E_n^{(0)} + \langle nljm_j \mid \hat{H}_{SO} \mid nljm_j\rangle = -\frac{e^2}{2a_0}\frac{1}{n^2} + E_{SO}^{(1)}, \tag{9.78}$$

where $E_n^{(0)} = -e^2/(2a_0n^2) = -(13.6/n^2)$ eV are the energy levels of hydrogen and $E_{SO}^{(1)}$ is the energy due to spin–orbit interaction:

$$E_{SO}^{(1)} = \langle nljm_j \mid \hat{H}_{SO} \mid nljm_j\rangle = \frac{e^2\hbar^2}{4m_e^2c^2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right]\left\langle nl\left|\frac{1}{r^3}\right|nl\right\rangle. \tag{9.79}$$

Using the value of $\left\langle nl\left|r^{-3}\right|nl\right\rangle$ calculated in Chapter 6,

$$\left\langle nl\left|\frac{1}{r^3}\right|nl\right\rangle = \frac{2}{n^3l(l+1)(2l+1)a_0^3}, \tag{9.80}$$

we can rewrite (9.79) as

$$E_{SO}^{(1)} = \frac{e^2\hbar^2}{2m_e^2c^2}\left[\frac{j(j+1) - l(l+1) - \frac{3}{4}}{n^3l(l+1)(2l+1)a_0^3}\right]$$

$$= \left(\frac{e^2}{2a_0}\frac{1}{n^2}\right)\left(\frac{\hbar}{m_e c a_0}\right)^2 \frac{1}{n}\left[\frac{j(j+1) - l(l+1) - \frac{3}{4}}{l(l+1)(2l+1)}\right] \tag{9.81}$$

or

$$\boxed{E_{SO}^{(1)} = \frac{|E_n^{(0)}|\alpha^2}{n}\left[\frac{j(j+1) - l(l+1) - \frac{3}{4}}{l(l+1)(2l+1)}\right],} \tag{9.82}$$

where α is a dimensionless constant called the *fine structure constant*:

$$\alpha = \frac{\hbar}{m_e c a_0} = \frac{e^2}{\hbar c} \simeq \frac{1}{137}. \tag{9.83}$$

Since $a_0 = \hbar^2/(m_e e^2)$ and hence $E_n^{(0)} = -e^2/(2a_0 n^2) = -\alpha^2 m_e c^2/(2n^2)$, we can express (9.82) in terms of α as

$$\boxed{E_{SO}^{(1)} = \frac{\alpha^4 m_e c^2}{2n^3}\left[\frac{j(j+1) - l(l+1) - \frac{3}{4}}{l(l+1)(2l+1)}\right].} \tag{9.84}$$

9.2.3.2 Relativistic Correction

Although the relativistic effect in hydrogen due to the motion of the electron is small, it can still be detected by spectroscopic techniques. The relativistic kinetic energy of the electron is given by $\hat{T} = \sqrt{\hat{p}^2 c^2 + m_e^2 c^4} - m_e c^2$, where $m_e c^2$ is the rest mass energy of the electron; an expansion of this relation to $\hat{p}^4$ yields

$$\sqrt{\hat{p}^2 c^2 + m_e^2 c^4} - m_e c^2 \simeq \frac{\hat{p}^2}{2m_e} - \frac{\hat{p}^4}{8m_e^3 c^2} + \cdots. \tag{9.85}$$

When this term is included, the hydrogen's Hamiltonian becomes

$$\hat{H} = \frac{\hat{p}^2}{2m_e} - \frac{e^2}{r} - \frac{\hat{p}^4}{8m_e^3 c^2} = \hat{H}_0 + \hat{H}_R, \tag{9.86}$$

where $\hat{H}_0 = \hat{p}^2/(2m_e) - e^2/r$ is the unperturbed Hamiltonian and $\hat{H}_R = -\hat{p}^4/(8m_e^3 c^2)$ is the relativistic mass correction which can be treated by first-order perturbation theory:

$$E_R^{(1)} = \langle nljm_j \mid \hat{H}_R \mid nljm_j\rangle = -\frac{1}{8m_e^3 c^2}\left\langle nljm_j \left|\hat{p}^4\right| nljm_j\right\rangle. \tag{9.87}$$

The value of $\left\langle nljm_j \left|\hat{p}^4\right| nljm_j\right\rangle$ was calculated in the last solved problem of Chapter 6 (see equation (6.331)):

$$\left\langle nljm_j \left|\hat{p}^4\right| nljm_j\right\rangle = \frac{m_e^4 e^8}{\hbar^4 n^4}\left(\frac{8n}{2l+1} - 3\right) = \frac{\alpha^4 m_e^4 c^4}{n^4}\left(\frac{8n}{2l+1} - 3\right). \tag{9.88}$$

An insertion of this value in (9.87) leads to

$$\boxed{E_R^{(1)} = -\frac{\alpha^4 m_e c^2}{8n^4}\left(\frac{8n}{2l+1} - 3\right) = -\frac{\alpha^2 |E_n^{(0)}|}{4n^2}\left(\frac{8n}{2l+1} - 3\right).} \tag{9.89}$$

Note that the spin–orbit and relativistic corrections (9.84) and (9.89) have the same order of magnitude, 10^{-3} eV, since $\alpha^2|E_n^{(0)}| \simeq 10^{-3}$ eV.

Remark

For a hydrogenlike atom having Z electrons, and if we neglect the spin–orbit interaction, we may use (9.89) to infer the atom's ground state energy:

$$\boxed{E_n = Z^2\left(E_n^{(0)} + E_R^{(1)}\right) = Z^2 E_n^{(0)}\left[1 + \frac{\alpha^2}{n}\left(\frac{2}{2l+1} - \frac{3}{4n}\right)\right],} \tag{9.90}$$

where $E_n^{(0)} = -e^4 m_e/(2\hbar^2 n^2) = -\alpha^2 m_e c^2/(2n^2) = -13.6\ \text{eV}/n^2$ is the Bohr energy.

9.2.3.3 The Fine Structure of Hydrogen

The fine structure correction is obtained by adding the expressions for the spin–orbit and relativistic corrections (9.84) and (9.89):

$$E_{FS}^{(1)} = E_{SO}^{(1)} + E_R^{(1)} = \frac{\alpha^4 m_e c^2}{2n^3}\left[\frac{j(j+1) - l(l+1) - \frac{3}{4}}{l(l+1)(2l+1)}\right] - \frac{\alpha^4 m_e c^2}{8n^4}\left[\frac{8n}{2l+1} - 3\right], \tag{9.91}$$

where $j = l \pm \frac{1}{2}$. If $j = l + \frac{1}{2}$ a substitution of $l = j - \frac{1}{2}$ into (9.91) leads to

$$\begin{aligned}
E_{FS}^{(1)} &= \frac{\alpha^4 m_e c^2}{8n^4}\left[\frac{4nj(j+1) - 4n\left(j-\frac{1}{2}\right)\left(j+\frac{1}{2}\right) - 3n}{\left(j-\frac{1}{2}\right)\left(j+\frac{1}{2}\right)(2j-1+1)} - \frac{8n}{2j-1+1} + 3\right] \\
&= \frac{\alpha^4 m_e c^2}{8n^4}\left[\frac{4nj - 2n}{2j\left(j-\frac{1}{2}\right)\left(j+\frac{1}{2}\right)} - \frac{4n}{j} + 3\right] = \frac{\alpha^4 m_e c^2}{8n^4}\left[\frac{2n}{j\left(j+\frac{1}{2}\right)} - \frac{4n}{j} + 3\right] \\
&= \frac{\alpha^4 m_e c^2}{8n^4}\left[3 - \frac{4n}{j+\frac{1}{2}}\right].
\end{aligned} \tag{9.92}$$

Similarly, if $j = l - \frac{1}{2}$, and hence $l = j + \frac{1}{2}$, we can reduce (9.91) to

$$\begin{aligned}
E_{FS}^{(1)} &= \frac{\alpha^4 m_e c^2}{8n^4}\left[\frac{4nj(j+1) - 4n\left(j+\frac{1}{2}\right)\left(j+\frac{3}{2}\right) - 3n}{\left(j+\frac{1}{2}\right)\left(j+\frac{3}{2}\right)(2j+1+1)} - \frac{8n}{2j+1+1} + 3\right] \\
&= \frac{\alpha^4 m_e c^2}{8n^4}\left[\frac{-4nj - 6n}{2\left(j+\frac{1}{2}\right)\left(j+\frac{3}{2}\right)(j+1)} - \frac{4n}{j+1} + 3\right] \\
&= \frac{\alpha^4 m_e c^2}{8n^4}\left[\frac{-2n}{\left(j+\frac{1}{2}\right)(j+1)} - \frac{4n}{j+1} + 3\right] \\
&= \frac{\alpha^4 m_e c^2}{8n^4}\left[3 - \frac{4n}{j+\frac{1}{2}}\right].
\end{aligned} \tag{9.93}$$

As equations (9.92) and (9.93) show, the expressions for the fine structure correction corresponding to $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$ are the same:

$$\boxed{E_{FS}^{(1)} = E_{SO}^{(1)} + E_{R}^{(1)} = \frac{\alpha^4 m_e c^2}{8n^4}\left(3 - \frac{4n}{j+\frac{1}{2}}\right) = \frac{\alpha^2 E_n^{(0)}}{4n^2}\left(\frac{4n}{j+\frac{1}{2}} - 3\right),} \tag{9.94}$$

where $E_n^{(0)} = -\alpha^2 m_e c^2/(2n^2)$ and $j = l \pm \frac{1}{2}$.

Since the bracket-terms in (9.82), (9.89), and (9.94) are of the order of unity, the ratios of the spin–orbit, relativistic, and fine structure corrections to the energy of the hydrogen atom are of the order of α^2:

$$\frac{E_{SO}^{(1)}}{|E_n^{(0)}|} \simeq \alpha^2, \qquad \left|\frac{E_{R}^{(1)}}{E_n^{(0)}}\right| \simeq \alpha^2, \qquad \frac{E_{FS}^{(1)}}{|E_n^{(0)}|} \simeq \alpha^2. \tag{9.95}$$

All these terms are of the order of 10^{-4} since $\alpha^2 = (1/137)^2 \simeq 10^{-4}$.

In sum, the hydrogen's Hamiltonian, when including the fine structure, is given by

$$\hat{H} = \hat{H}_0 + \hat{H}_{FS} = \hat{H}_0 + \left(\hat{H}_{SO} + \hat{H}_R\right) = \frac{\hat{p}^2}{2m_e} - \frac{e^2}{r} + \left(\frac{e^2}{2m_e^2c^2r^3}\hat{\vec{S}} \cdot \hat{\vec{L}} - \frac{\hat{p}^4}{8m_e^3c^2}\right). \tag{9.96}$$

A first-order perturbation calculation of the energy levels of hydrogen, when including the fine structure, yields

$$\boxed{E_{nj} = E_n^{(0)} + E_{FS}^{(1)} = E_n^{(0)}\left[1 + \frac{\alpha^2}{4n^2}\left(\frac{4n}{j+\frac{1}{2}} - 3\right)\right],} \tag{9.97}$$

where $E_n^{(0)} = -13.6\,\mathrm{eV}/n^2$. Unlike $E_n^{(0)}$, which is degenerate in l, each energy level E_{nj} is split into two levels $E_{n\ (l\pm\frac{1}{2})}$, since for a given value of l there are two values of j: $j = l \pm \frac{1}{2}$.

In addition to the fine structure, there is still another (smaller) effect which is known as the *hyperfine structure*. The hydrogen's hyperfine structure results from the interaction of the spin of the electron with the spin of the nucleus. When the hyperfine corrections are included, they would split each of the fine structure levels into a series of hyperfine levels. For instance, when the hyperfine coupling is taken into account in the ground state of hydrogen, it would split the $1S_{1/2}$ level into two hyperfine levels separated by an energy of 5.89×10^{-6} eV. This corresponds, when the atom makes a spontaneous transition from the higher hyperfine level to the lower one, to a radiation of 1.42×10^9 Hz frequency and 21 cm wavelength. We should note that most of the information we possess about interstellar hydrogen clouds had its origin in the radioastronomy study of this 21 cm line.

9.2.3.4 The Anomalous Zeeman Effect

We now consider a hydrogen atom that is placed in an external uniform magnetic field $\vec{B}$. The effect of an external magnetic field on the atom is to cause a shift of its energy levels; this is called the *Zeeman effect*. In Chapter 6 we studied the Zeeman effect, but with one major omission: we ignored the spin of the electron. In this section we are going to take it into account. The interaction of the magnetic field with the electron's orbital and spin magnetic dipole moments, $\vec{\mu}_L$ and $\vec{\mu}_S$, gives rise to two energy terms, $-\vec{\mu}_L \cdot \vec{B}$ and $-\vec{\mu}_S \cdot \vec{B}$, whose sum we call the Zeeman energy:

$$\hat{H}_Z = -\vec{\mu}_L \cdot \vec{B} - \vec{\mu}_S \cdot \vec{B} = \frac{e}{2m_e c}\vec{L} \cdot \vec{B} + \frac{e}{m_e c}\vec{S} \cdot \vec{B} = \frac{e}{2m_e c}\left(\vec{L} + 2\vec{S}\right) \cdot \vec{B} = \frac{eB}{2m_e c}\left(\hat{L}_z + 2\hat{S}_z\right), \tag{9.98}$$

with $\vec{\mu}_L = -e\vec{L}/(2m_e c)$ and $\vec{\mu}_S = -\vec{S}/(m_e c)$; for simplicity, we have taken $\vec{B}$ along the z-axis: $\vec{B} = B\hat{z}$.

When a hydrogen atom is placed in an external magnetic field, its Hamiltonian is given by

$$\hat{H} = \hat{H}_0 + \hat{H}_{FS} + \hat{H}_Z. \tag{9.99}$$

Like $\hat{H}_{FS}$, the correction due to $\hat{H}_Z$ of (9.99) is expected to be small compared to $\hat{H}_0$; hence it can be treated perturbatively. We may now consider separately the cases where the magnetic field $\vec{B}$ is strong or weak. Strong or weak compared to what? Since $\hat{H}_{SO}$ and $\hat{H}_Z$ can be written as $\hat{H}_{SO} = W\vec{L} \cdot \vec{S}$ (9.74) and since $\hat{H}_Z = B\mu_B(\hat{L}_z + 2\hat{S}_z)/\hbar$, we have $\hat{H}_Z/\hat{H}_{SO} \sim B\mu_B/W$, where μ_B is the Bohr magneton, $\mu_B = e\hbar/(2m_e c)$. Thus, the cases $B \ll W/\mu_B$ and $B \gg W/\mu_B$ would correspond to the weak and strong magnetic fields, respectively.

The strong-field Zeeman effect

The effect of a strong external magnetic field on the hydrogen atom is called the *Paschen–Back effect*. If $\vec{B}$ is strong, $B \gg W/\mu_B$, the term $eB(\hat{L}_z + 2\hat{S}_z)/(2m_e c)$ will be much greater than the fine structure. Neglecting $\hat{H}_{FS}$, we can reduce (9.99) to

$$\hat{H} = \hat{H}_0 + \hat{H}_Z = \hat{H}_0 + \frac{eB}{2m_e c}\left(\hat{L}_z + 2\hat{S}_z\right). \tag{9.100}$$

Since $\hat{H}$ commutes with $\hat{H}_0$ (because $\hat{H}_0$ commutes with $\hat{L}_z$ and $\hat{S}_z$), they can be diagonalized by a common set of states, $\mid nlm_l m_s\rangle$:

$$\hat{H} \mid nlm_l m_s\rangle = \left[\hat{H}_0 + \frac{eB}{2m_e c}\left(\hat{L}_z + 2\hat{S}_z\right)\right] \mid nlm_l m_s\rangle = E_{nlm_l m_s} \mid nlm_l m_s\rangle, \tag{9.101}$$

where

$$E_{nlm_l m_s} = E_n^{(0)} + \frac{eB\hbar}{2m_e c}(m_l + 2m_s) = -\frac{e^2}{2a_0 n^2} + \frac{eB\hbar}{2m_e c}(m_l + 2m_s). \tag{9.102}$$

The energy levels $E_n^{(0)}$ are thus shifted by an amount equal to $\Delta E = B\mu_B(m_l + 2m_s)$ with $\mu_B = e\hbar/(2m_e c)$, known as the Paschen–Back shift (Figure 9.2). When $\vec{B} = 0$ the degeneracy of each level of hydrogen is given by $g_n = 2\sum_{l=0}^{n-1}(2l+1) = 2n^2$; when $\vec{B} \neq 0$ states with the same value of $(m_l + 2m_s)$ are still degenerate.

The weak-field Zeeman effect

If $\vec{B}$ is weak, $B \ll W/\mu_B$, we need to consider all the terms in the Hamiltonian (9.99); the fine structure term $\hat{H}_{FS}$ will be the dominant perturbation. In the case where the Hamiltonian contains several perturbations at once, we should treat them individually starting with the most dominant, then the next, and so on. In this case the eigenstate should be selected to be one that diagonalizes the unperturbed Hamiltonian and the dominant perturbation[1]. In the weak-field

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[1] When the various perturbations are of approximately equal size, a state that is a joint eigenstate of $\hat{H}_0$ and any perturbation would be an acceptable choice.

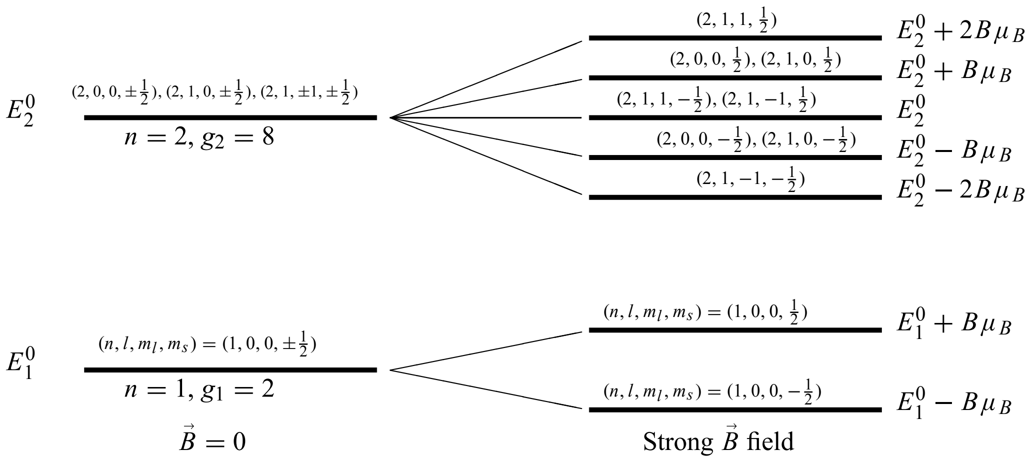

Figure 9.2 Splittings of the energy levels $n = 1$ and $n = 2$ of a hydrogen atom when placed in a *strong* external magnetic field; $\mu_B = e\hbar/(2m_e c)$.

Zeeman effect, since $\hat{H}_{FS}$ is the dominant perturbation, the best eigenstates to use are $\mid nljm_j\rangle$, for they simultaneously diagonalize $\hat{H}_0$ and $\hat{H}_{FS}$. Writing $\hat{L}_z + 2\hat{S}_z$ as $\hat{J}_z + \hat{S}_z$, where $\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$ represents the total angular momentum of the electron, we may rewrite (9.99) as

$$\hat{H} = \hat{H}_0 + \hat{H}_{FS} + \hat{H}_Z = \hat{H}_0 + \hat{H}_{FS} + \frac{eB}{2m_e c}\left(\hat{J}_z + \hat{S}_z\right). \tag{9.103}$$

In a first-order perturbation calculation, the contribution of $\hat{H}_Z$ is given by

$$E_Z^{(1)} = \langle nljm_j \mid \hat{H}_Z \mid nljm_j\rangle = \frac{eB}{2m_e c}\langle nljm_j \mid \hat{J}_z + \hat{S}_z \mid nljm_j\rangle. \tag{9.104}$$

Since $\langle nljm_j \mid \hat{J}_z \mid nljm_j\rangle = \hbar m_j$ and using the expression of $\langle nljm_j \mid \hat{S}_z \mid nljm_j\rangle$ that was calculated in Chapter 7,

$$\begin{aligned}\langle nljm_j \mid \hat{S}_z \mid nljm_j\rangle &= \frac{\langle nljm_j \mid \hat{\vec{J}}\cdot\hat{\vec{S}} \mid nljm_j\rangle}{\hbar^2 j(j+1)}\langle nljm_j \mid \hat{J}_z \mid nljm_j\rangle \\ &= \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}\hbar m_j,\end{aligned} \tag{9.105}$$

we can reduce (9.104) to

$$\boxed{E_Z^{(1)} = \frac{eB\hbar}{2m_e c}\left[1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}\right]m_j = \frac{eB\hbar}{2m_e c}g_j m_j = B\mu_B m_j g_j,} \tag{9.106}$$

where $\mu_B = e\hbar/(2m_e c)$ is the Bohr magneton for the electron and g_j is the Landé factor or the gyromagnetic ratio:

$$g_j = 1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}. \tag{9.107}$$

This shows that when $l = 0$ and $j = s$ we have $g_s = 2$ and when $s = 0$ and $j = l$ we have $g_l = 1$. For instance, for an atomic state[2] such as ${}^2\mathrm{P}_{3/2}$, (9.107) shows that its factor is given by $g_{j=3/2} = \frac{4}{3}$, since $j = l + s = 1 + \frac{1}{2} = \frac{3}{2}$; this is how we infer the factor of any state:

$$\begin{array}{cccccccc} \text{State} & {}^2\mathrm{S}_{1/2} & {}^2\mathrm{P}_{1/2} & {}^2\mathrm{P}_{3/2} & {}^2\mathrm{D}_{3/2} & {}^2\mathrm{D}_{5/2} & {}^2\mathrm{F}_{5/2} & {}^2\mathrm{F}_{7/2} \\ g_j & 2 & \frac{2}{3} & \frac{4}{3} & \frac{4}{5} & \frac{6}{5} & \frac{6}{7} & \frac{8}{7} \end{array} \tag{9.108}$$

From (9.107), we see that the Landé factors corresponding to the same l but different values of j (due to spin) are not equal, since for $s = \frac{1}{2}$ and $j = l \pm \frac{1}{2}$ we have

$$g_{j=l\pm\frac{1}{2}} = 1 \pm \frac{1}{2l+1} = \begin{cases} \frac{2l+2}{2l+1} & \text{for} \quad j = l + \frac{1}{2}, \\ \frac{2l}{2l+1} & \text{for} \quad j = l - \frac{1}{2}. \end{cases} \tag{9.109}$$

Combining (9.97), (9.103), and (9.106), we can write the energy of a hydrogen atom in a weak external magnetic field as follows:

$$\boxed{E_{nj} = E_n^{(0)} + E_{FS}^{(1)} + E_Z^{(1)} = E_n^{(0)} + \frac{\alpha^2 E_n^{(0)}}{4n^2}\left(\frac{4n}{j+\frac{1}{2}} - 3\right) + \frac{eB\hbar}{2m_e c} m_j g_j.} \tag{9.110}$$

The effect of the magnetic field on the atom is thus to split the energy levels with a spacing $\Delta E = B\mu_B m_j g_j$. Unlike the energy levels obtained in Chapter 6, where we ignored the electron's spin, the energy levels (9.110) are not degenerate in l. Each energy level j is split into an *even number* of $(2j + 1)$ sublevels corresponding to the $(2j + 1)$ values of m_j: $m_j = -j, -j + 1, \ldots, j - 1, j$. As displayed in Figure 9.3, the splittings between the sublevels corresponding to the same j are constant: the spacings between the sublevels corresponding to $j = l - 1/2$ are all equal to $\Delta\epsilon_1 = B\mu_B(2l)/(2l+1)$, and the spacings between the $j = l + 1/2$ sublevels are equal to $\Delta\epsilon_2 = B\mu_B(2l + 2)/(2l + 1)$. In contrast to the normal Zeeman effect, however, the spacings between the split levels of the same l (and different values of j) are no longer constant, $\Delta\epsilon_1 \neq \Delta\epsilon_2$, since they depend on the Landé factor g_j; for a given value of j, there are two different values of g_j corresponding to $l = j \pm \frac{1}{2}$: $g_{j=l+1/2} = (2l + 2)/(2l + 1)$ and $g_{j=l-1/2} = (2l)/(2l + 1)$; see (9.109). This *unequal* spacing between the split levels is called the *anomalous* Zeeman effect.

9.3 The Variational Method

There exist systems whose Hamiltonians are known, but they cannot be solved exactly or by a perturbative treatment. That is, there is no closely related Hamiltonian that can be solved exactly or approximately by perturbation theory because the first order is not sufficiently accurate. One of the approximation methods that is suitable for solving such problems is the *variational method*, which is also called the Rayleigh–Ritz method. This method does not require knowledge of simpler Hamiltonians that can be solved exactly. The variational method is useful for determining upper bound values for the eigenenergies of a system whose Hamiltonian is known

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[2] We use here the spectroscopic notation where ${}^{(2s+1)}\mathrm{L}_j$ designates an atomic state whose spin is s, its total angular momentum is j, and whose orbital angular momentum is L where the values $L = 0, 1, 2, 3, 4, 5, \ldots$ are designated, respectively, by the capital letters S, P, D, F, G, H, … (see Chapter 8).

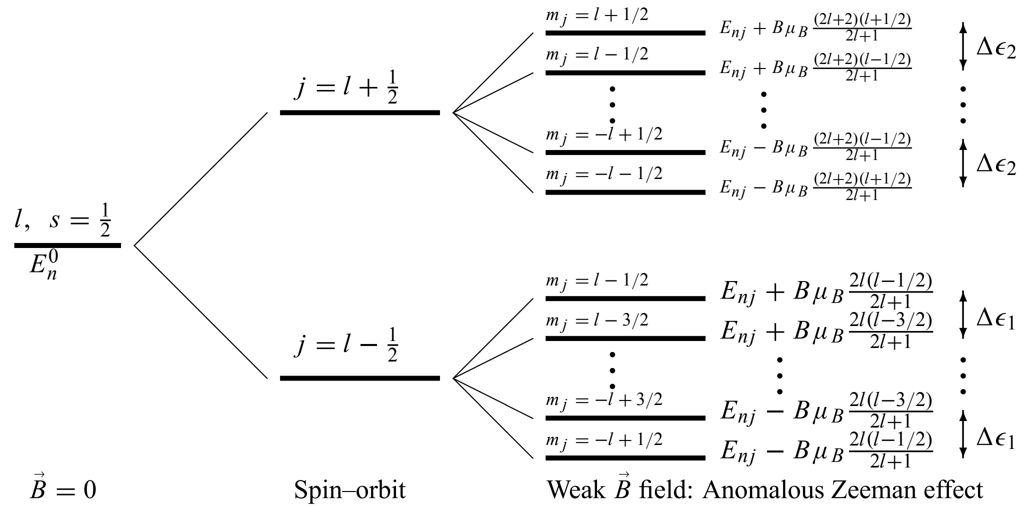

Figure 9.3 Splittings of a level l due to the spin–orbit interaction and to a weak external magnetic field, with $E_{nj} = E_n^0 + E_{SO}^{(1)}$. All the lower sublevels are equally spaced, $\Delta\epsilon_1 = B\mu_B(2l)/(2l+1)$, and so are the upper sublevels, $\Delta\epsilon_2 = B\mu_B(2l+2)/(2l+1)$, with $\mu_B = e\hbar/(2m_e c)$.

whereas its eigenvalues and eigenstates are not known. It is particularly useful for determining the ground state. It becomes quite cumbersome to determine the energy levels of the excited states.

In the context of the variational method, one does not attempt to solve the eigenvalue problem

$$\hat{H} \mid \psi\rangle = E \mid \psi\rangle, \tag{9.111}$$

but rather one uses a variational scheme to find the approximate eigenenergies and eigenfunctions from the variational equation

$$\delta E(\psi) = 0, \tag{9.112}$$

where $E(\psi)$ is the expectation value of the energy in the state $\mid \psi\rangle$:

$$E(\psi) = \frac{\langle\psi \mid \hat{H} \mid \psi\rangle}{\langle\psi \mid \psi\rangle}. \tag{9.113}$$

If $\mid \psi\rangle$ depends on a parameter α, $E(\psi)$ will also depend on α. The variational ansatz (9.112) enables us to vary α so as to minimize $E(\psi)$. The minimum value of $E(\psi)$ provides an upper limit approximation for the true energy of the system.

The variational method is particularly useful for determining the ground state energy and its eigenstate without explicitly solving the Schrödinger equation. Note that for any (arbitrary) trial function $\mid \psi\rangle$ we choose, the energy E as given by (9.113) is always larger than the exact energy E_0:

$$E = \frac{\langle\psi \mid H|\psi\rangle}{\langle\psi \mid \psi\rangle} \geq E_0; \tag{9.114}$$

the equality condition occurs only when $| \psi\rangle$ is proportional to the true ground state $|\psi_0\rangle$. To prove this, we simply expand the trial function $| \psi\rangle$ in terms of the exact eigenstates of $\hat{H}$:

$$| \psi\rangle = \sum_n a_n \mid \phi_n\rangle, \tag{9.115}$$

with

$$H \mid \phi_n\rangle = E_n \mid \phi_n\rangle, \tag{9.116}$$

and since $E_0 \geq E_n$ for nondegenerate one-dimensional bound systems, we have

$$E = \frac{\langle\psi \mid H|\psi\rangle}{\langle\psi \mid \psi\rangle} = \frac{\sum_n |a_n|^2 E_n}{\sum_n |a_n|^2} \geq \frac{E_0 \sum_n |a_n|^2}{\sum_n |a_n|^2} = E_0, \tag{9.117}$$

which proves (9.114).

To calculate the ground state energy, we need to carry out the following four steps:

- First, based on physical intuition, make an educated guess of a trial function that takes into account all the physical properties of the ground state (symmetries, number of nodes, smoothness, behavior at infinity, etc.). For the properties you are not sure about, include in the trial function *adjustable parameters* $\alpha_1, \alpha_2, \ldots$ (i.e., $| \psi_0\rangle = |\psi_0(\alpha_1, \alpha_2, \ldots)\rangle$) which will account for the various possibilities of these unknown properties.

- Second, using (9.113), calculate the energy; this yields an expression which depends on the parameters $\alpha_1, \alpha_2, \ldots$:

$$E_0(\alpha_1, \alpha_2, \ldots) = \frac{\langle\psi_0(\alpha_1, \alpha_2, \ldots)|\hat{H}|\psi_0(\alpha_1, \alpha_2, \ldots)\rangle}{\langle\psi_0(\alpha_1, \alpha_2, \ldots)|\psi_0(\alpha_1, \alpha_2, \ldots)\rangle}. \tag{9.118}$$

  In most cases $|\psi_0(\alpha_1, \alpha_2, \ldots)\rangle$ will be assumed to be normalized; hence the denominator of this expression is equal to 1.

- Third, using (9.118) search for the minimum of $E_0(\alpha_1, \alpha_2, \ldots)$ by varying the adjustable parameters α_i until E_0 is minimized. That is, *minimize* $E(\alpha_1, \alpha_2, \ldots)$ with respect to $\alpha_1, \alpha_2, \ldots$:

$$\frac{\partial E_0(\alpha_1, \alpha_2, \ldots)}{\partial \alpha_i} = \frac{\partial}{\partial \alpha_i} \frac{\langle\psi_0(\alpha_1, \alpha_2, \ldots)|\hat{H}|\psi_0(\alpha_1, \alpha_2, \ldots)\rangle}{\langle\psi_0(\alpha_1, \alpha_2, \ldots)|\psi_0(\alpha_1, \alpha_2, \ldots)\rangle} = 0, \tag{9.119}$$

  with $i = 1, 2, \ldots$. This gives the values of $(\alpha_{1_0}, \alpha_{2_0}, \ldots)$ that minimize E_0.

- Fourth, substitute these values of $(\alpha_{1_0}, \alpha_{2_0}, \ldots)$ into (9.118) to obtain the approximate value of the energy. The value $E_0(\alpha_{1_0}, \alpha_{2_0}, \ldots)$ thus obtained provides an upper bound for the exact ground state energy E_0. The exact ground state eigenstate $| \phi_0\rangle$ will then be approximated by the state $|\psi_0(\alpha_{1_0}, \alpha_{2_0}, \ldots)\rangle$.

What about the energies of the excited states? The variational method can also be used to find the approximate values for the energies of the first few excited states. For instance, to find the energy and eigenstate of the first excited state that will approximate E_1 and $| \phi_1\rangle$, we need to choose a trial function $| \psi_1\rangle$ that must be orthogonal to $| \psi_0\rangle$:

$$\langle\psi_1 \mid \phi_0\rangle = 0. \tag{9.120}$$

Then proceed as we did in the case of the ground state. That is, solve the variational equation (9.112) for $|\ \psi_1\rangle$:

$$\frac{\partial}{\partial \alpha_i} \frac{\langle \psi_1(\alpha_1, \alpha_2, \ldots) | \hat{H} | \psi_1(\alpha_1, \alpha_2, \ldots)\rangle}{\langle \psi_1(\alpha_1, \alpha_2, \ldots) | \psi_1(\alpha_1, \alpha_2, \ldots)\rangle} = 0 \qquad (i = 1,\ 2,\ \ldots). \tag{9.121}$$

Similarly, to evaluate the second excited state, we solve (9.112) for $|\ \psi_2\rangle$ and take into account the following two conditions:

$$\langle \psi_2 \mid \psi_0\rangle = 0, \qquad \langle \psi_2 \mid \psi_1\rangle = 0. \tag{9.122}$$

These conditions can be included in the variational problem by means of *Lagrange multipliers*, that is, by means of a constrained variational principle.

In this way, we can in principle evaluate any other excited state. However, the variational procedure becomes increasingly complicated as we deal with higher excited states. As a result, the method is mainly used to determine the ground state.

Remark

In those problems where the first derivative of the wave function is discontinuous at a given value of x, one has to be careful when using the expression

$$-\left\langle \psi \left| \frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right| \psi \right\rangle = -\frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} \psi^*(x) \frac{d^2\psi(x)}{dx^2}\, dx. \tag{9.123}$$

A straightforward, careless use of this expression sometimes leads to a negative kinetic energy term (Problem 9.6 on page 541). One might instead consider using the following form:

$$\boxed{-\left\langle \psi \left| \frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right| \psi \right\rangle = \frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} \left| \frac{d\psi(x)}{dx} \right|^2 dx.} \tag{9.124}$$

Note that (9.123) and (9.124) are identical; an integration by parts leads to

$$\int_{-\infty}^{+\infty} \left| \frac{d\psi(x)}{dx} \right|^2 dx = \psi^*(x) \frac{d\psi(x)}{dx} \bigg|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \psi^*(x) \frac{d^2\psi(x)}{dx^2} dx = -\int_{-\infty}^{+\infty} \psi^*(x) \frac{d^2\psi(x)}{dx^2} dx, \tag{9.125}$$

since $\psi^*(x) d\psi(x)/dx$ goes to zero as $x \longrightarrow \pm\infty$ (this is the case whenever $\psi(x)$ is a bound state, but not so when $\psi(x)$ is a plane wave).

What about the calculation of $\langle \psi\ | -(\hbar^2/(2m))\Delta |\ \psi\rangle$ in three dimensions? We might consider generalizing (9.124). For this, we need simply to invoke Gauss's theorem[3] to show that

$$\int \left(\vec{\nabla}\psi^*(\vec{r})\right) \cdot \left(\vec{\nabla}\psi(\vec{r})\right)\, d^3r = -\int \psi^*(\vec{r}) \Delta \psi(\vec{r})\, d^3r. \tag{9.126}$$

To see this, an integration by parts leads to the following relation:

$$\int_S \psi^*(\vec{r}) \vec{\nabla}\psi(\vec{r}) \cdot d\vec{A} = \int_V \left[\left(\vec{\nabla}\psi^*(\vec{r})\right) \cdot \left(\vec{\nabla}\psi(\vec{r})\right) + \psi^*(\vec{r}) \Delta \psi(\vec{r}) \right] d^3r, \tag{9.127}$$

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[3] Gauss's theorem states that the surface integral of a vector $\vec{B}$ over a closed surface S is equal to the volume integral of the divergence of that vector integrated over the volume V enclosed by the surface S: $\int_S \vec{B} \cdot d\vec{S} = \int_V \vec{\nabla} \cdot \vec{B}\, dV$.

and since, as $S \longrightarrow \infty$, the surface integral $\int_S \psi^*(\vec{r})\vec{\nabla}\psi(\vec{r}) \cdot d\vec{S}$ vanishes if $\psi(\vec{r})$ is a bound state, we recover (9.126). So the kinetic energy term (9.124) is given in three dimensions by

$$\boxed{-\left\langle \psi \left| \frac{\hbar^2}{2m}\Delta \right| \psi \right\rangle = \frac{\hbar^2}{2m}\int \left(\vec{\nabla}\psi^*(\vec{r})\right) \cdot \left(\vec{\nabla}\psi(\vec{r})\right) d^3r.} \tag{9.128}$$

Example 9.4

Show that (9.112) is equivalent to the Schrödinger equation (9.111) .

Solution

Using (9.113), we can rewrite (9.112) as

$$\delta\left(\langle \psi \mid \hat{H} - E \mid \psi\rangle\right) = 0. \tag{9.129}$$

Since $\mid \psi\rangle$ is a complex function, we can view $\mid \psi\rangle$ and $\langle \psi \mid$ as two independent functions; hence we can carry out the variations over $|\delta\psi\rangle$ and $\langle\delta\psi|$ independently. Varying first over $\langle\delta\psi|$, equation (9.129) yields

$$\langle\delta\psi|\hat{H} - E \mid \psi\rangle = 0. \tag{9.130}$$

Since $\mid \psi\rangle$ is arbitrary, then (9.130) is equivalent to $\hat{H} \mid \psi\rangle = E \mid \psi\rangle$. The variation over $|\delta\psi\rangle$ leads to the same result. Namely, varying (9.129) over $|\delta\psi\rangle$, we get

$$\langle\psi|\hat{H} - E|\delta\psi\rangle = 0, \tag{9.131}$$

from which we obtain the complex conjugate equation $\langle \psi \mid \hat{H} = E\langle \psi \mid$, since $\hat{H}$ is Hermitian.

Example 9.5

Consider a one-dimensional harmonic oscillator. Use the variational method to estimate the energies of (a) the ground state, (b) the first excited state, and (c) the second excited state.

Solution

This simple problem enables us to illustrate the various aspects of the variational method within a predictable setting, because the exact solutions are known: $E_0 = \hbar\omega/2$, $E_1 = 3\hbar\omega/2$, $E_2 = 5\hbar\omega/2$.

(a) The trial function we choose for the ground state has to be even and smooth everywhere, it must vanish as $x \to \pm\infty$, and it must have no nodes. A Gaussian function satisfies these requirements. But what we are not sure about is its width. To account for this, we include in the trial function an adjustable scale parameter α:

$$\psi_0(x, \alpha) = Ae^{-\alpha x^2}; \tag{9.132}$$

A is a normalization constant. Using $\int_{-\infty}^{+\infty} x^{2n}e^{-ax^2}dx = \sqrt{\pi/a}\, 1 \cdot 3 \cdot 5 \cdots (2n-1)/(2a)^n$, we can show that A is given by $A = (2\alpha/\pi)^{1/4}$. The expression for $E_0(\alpha)$ is thus given by

$$\langle\psi_0|H|\psi_0\rangle = A^2\int_{-\infty}^{+\infty} e^{-\alpha x^2}\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2\right)e^{-\alpha x^2}dx$$

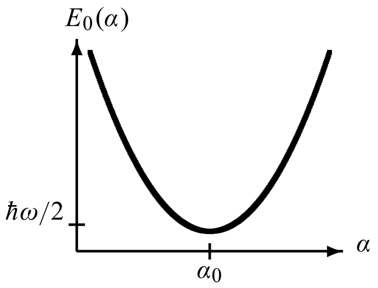

Figure 9.4 Shape of $E_0(\alpha) = \hbar^2\alpha/(2m) + m\omega^2/(8\alpha)$.

$$= A^2\frac{\hbar^2\alpha}{m}\int_{-\infty}^{+\infty} e^{-2\alpha x^2}dx + A^2\left(\frac{1}{2}m\omega^2 - \frac{2\hbar^2\alpha^2}{m}\right)\int_{-\infty}^{+\infty} x^2e^{-2\alpha x^2}dx$$

$$= \frac{\hbar^2\alpha}{m} + \frac{1}{4\alpha}\left(\frac{1}{2}m\omega^2 - \frac{2\hbar^2\alpha^2}{m}\right) = \frac{\hbar^2}{2m}\alpha + \frac{m\omega^2}{8\alpha} \tag{9.133}$$

or

$$E_0(\alpha) = \frac{\hbar^2}{2m}\alpha + \frac{m\omega^2}{8\alpha}. \tag{9.134}$$

Its shape is displayed in Figure 9.4. The value of α_0, corresponding to the lowest point of the curve, can be obtained from the minimization of $E(\alpha)$ with respect to α,

$$\frac{\partial E_0(\alpha)}{\partial\alpha} = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha^2} = 0, \tag{9.135}$$

yields $\alpha_0 = m\omega/(2\hbar)$ which, when inserted into (9.134) and (9.132), leads to

$$E_0(\alpha_0) = \frac{\hbar\omega}{2} \qquad \text{and} \qquad \psi_0(x,\alpha_0) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar}. \tag{9.136}$$

The ground state energy and wave function obtained by the variational method are identical to their exact counterparts.

(b) Let us now find the approximate energy E_1 for the first excited state. The trial function $\psi_1(x,\alpha)$ we need to select must be odd, it must vanish as $x \to \pm\infty$, it must have only one node, and it must be orthogonal to $\psi_0(x,\alpha_0)$ of (9.136). A candidate that satisfies these requirements is

$$\psi_1(x,\alpha) = Bxe^{-\alpha x^2}; \tag{9.137}$$

B is the normalization constant. We can show that $B = (32\alpha^3/\pi)^{1/4}$. Note that $\langle\psi_0 \mid \psi_1\rangle$ is zero,

$$\langle\psi_0 \mid \psi_1\rangle = B\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\int_{-\infty}^{+\infty} xe^{-\alpha x^2}e^{-m\omega x^2/2\hbar}dx = 0, \tag{9.138}$$

since the symmetric integration of an odd function is zero; $\psi_0(x)$ is even and $\psi_1(x)$ is odd.

Proceeding as we did for $E_0(\alpha)$, and since $\psi_1(x,\alpha)$ is normalized, we can show that

$$E_1(\alpha) = \langle\psi_1(\alpha)|H|\psi_1(\alpha)\rangle = B^2\int_{-\infty}^{+\infty} xe^{-\alpha x^2}\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2\right]xe^{-\alpha x^2}dx$$

$$= \frac{3\hbar^2}{2m}\alpha + \frac{3m\omega^2}{8\alpha}. \tag{9.139}$$

The minimization of $E_1(\alpha)$ with respect to α (i.e., $\partial E_1(\alpha)/\partial\alpha = 0$) leads to $\alpha_0 = m\omega/2\hbar$. Hence the energy and the state of the first excited state are given by

$$E_1(\alpha_0) = \frac{3\hbar\omega}{2}, \qquad \psi_1(x,\alpha_0) = \left(\frac{4m^3\omega^3}{\pi\hbar^3}\right)^{1/4} x e^{-m\omega x^2/2\hbar}. \tag{9.140}$$

They are in full agreement with the exact expressions.

(c) The trial function

$$\psi_2(x,\alpha,\beta) = C(\beta x^2 - 1)e^{-\alpha x^2}, \tag{9.141}$$

which includes two adjustable parameters α and β, satisfies all the properties of the second excited state: even under parity, it vanishes as $x \to \pm\infty$ and has two nodes. The term $(\beta x^2 - 1)$ ensures that $\psi_2(x,\alpha,\beta)$ has two nodes $x = \pm 1/\sqrt{\beta}$ and the normalization constant C is given by

$$C = \left(\frac{2\alpha}{\pi}\right)^{1/4} \left[\frac{3\beta^2}{16\alpha^2} - \frac{\beta}{2\alpha} + 1\right]^{-1/2}. \tag{9.142}$$

The trial function $\psi_2(x,\alpha,\beta)$ must be orthogonal to both $\psi_0(x)$ and $\psi_1(x)$. First, notice that it is indeed orthogonal to $\psi_1(x)$, since $\psi_2(x,\alpha,\beta)$ is even while $\psi_1(x)$ is odd:

$$\langle\psi_1 \mid \psi_2\rangle = C\left(\frac{4m^3\omega^3}{\pi\hbar^3}\right)^{1/4} \int_{-\infty}^{+\infty} x(\beta x^2 - 1)e^{-\alpha x^2} e^{-m\omega x^2/2\hbar} dx = 0. \tag{9.143}$$

As for the orthogonality condition of $\psi_2(x)$ with $\psi_0(x)$, it can be written as

$$\begin{aligned}\langle\psi_0 \mid \psi_2\rangle &= \int_{-\infty}^{+\infty} \psi_0(x)\psi_2(x,\alpha,\beta)\,dx = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} C \int_{-\infty}^{+\infty} (\beta x^2 - 1)e^{-(m\omega/2\hbar+\alpha)x^2} dx \\ &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} C\left[\frac{\beta}{2\,(m\omega/2\hbar+\alpha)} - 1\right]\sqrt{\frac{\pi}{m\omega/2\hbar+\alpha}} = 0. \end{aligned} \tag{9.144}$$

This leads to a useful condition between β and α:

$$\beta = \frac{m\omega}{\hbar} + 2\alpha. \tag{9.145}$$

Now let us focus on determining the energy $E_2(\alpha,\beta) = \langle\psi_2|\hat{H} \mid \psi_2\rangle$:

$$E_2(\alpha,\beta) = C^2 \int_{-\infty}^{+\infty} (\beta x^2 - 1)e^{-\alpha x^2}\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2\right](\beta x^2 - 1)e^{-\alpha x^2} dx. \tag{9.146}$$

After lengthy but straightforward calculations, we obtain

$$-\frac{\hbar^2}{2m}\left\langle\psi_2\left|\frac{d^2}{dx^2}\right|\psi_2\right\rangle = \frac{\hbar^2}{2m}\left(\alpha + \frac{\beta}{2} + \frac{7\beta^2}{16\alpha}\right)C^2\sqrt{\frac{\pi}{2\alpha}}, \tag{9.147}$$

$$\frac{1}{2}m\omega^2\langle\psi_2|x^2 \mid \psi_2\rangle = m\omega^2\left(\frac{15\beta^2}{128\alpha^3} - \frac{3\beta}{16\alpha^2} + \frac{1}{8\alpha}\right)C^2\sqrt{\frac{\pi}{2\alpha}}; \tag{9.148}$$

hence

$$E_2(\alpha,\beta) = C^2\sqrt{\frac{\pi}{2\alpha}}\left(\frac{\hbar^2\alpha}{2m} + \frac{\hbar^2\beta}{4m} + \frac{7\hbar^2\beta^2}{32m\alpha} + \frac{15m\beta^2\omega^2}{128\alpha^3} - \frac{3m\beta\omega^2}{16\alpha^2} + \frac{m\omega^2}{8\alpha}\right). \tag{9.149}$$

To extract the approximate value of E_2, we need to minimize $E_2(\alpha, \beta)$ with respect to α and to β: $\partial E_2(\alpha, \beta)/\partial\alpha = 0$ and $\partial E_2(\alpha, \beta)/\partial\beta = 0$. The two expressions we obtain will enable us to extract (by solving a system of two linear equations with two unknowns) the values of α_0 and β_0 that minimize $E_2(\alpha, \beta)$. This method is lengthy and quite cumbersome; α_0 and β_0 have to satisfy the condition (9.145). We can, however, exploit this condition to come up with a much shorter approach: it consists of replacing the value of β as displayed in (9.145) into the energy relation (9.149), thereby yielding an expression that depends on a single parameter α:

$$E_2(\alpha) = \left(\frac{15\hbar^2\alpha}{18m} + \frac{9\hbar\omega}{8} + \frac{7m\omega^2}{16\alpha} + \frac{15m^3\omega^4}{128\hbar^2\alpha^3} + \frac{9m^2\omega^3}{32\hbar\alpha^2}\right)\left(\frac{3m^2\omega^2}{16\hbar^2\alpha^2} + \frac{m\omega}{4\hbar\alpha} + \frac{3}{4}\right)^{-1}; \tag{9.150}$$

in deriving this relation, we have substituted (9.145) into the expression for C as given by (9.142), which in turn is inserted into (9.149). In this way, we need to minimize E_2 with respect to one parameter only, α. This yields $\alpha_0 = m\omega/(2\hbar)$ which, when inserted into (9.145) leads to $\beta_0 = 2m\omega/\hbar$. Thus, the energy and wave function are given by

$$E_2(\alpha_0,\ \beta_0) = \frac{5}{2}\hbar\omega, \qquad \psi_2(x,\ \alpha_0,\ \beta_0) = \left(\frac{m\omega}{4\pi\hbar}\right)^{1/4}\left(\frac{2m\omega}{\hbar}x^2 - 1\right)e^{-\frac{m\omega}{2\hbar}x^2}. \tag{9.151}$$

These are identical with the exact expressions for the energy and the wave function.

Example 9.6

Use the variational method to estimate the ground state energy of the hydrogen atom.

Solution

The ground state wave function has no nodes and vanishes at infinity. Let us try

$$\psi(r, \theta, \phi) = e^{-r/\alpha}, \tag{9.152}$$

where α is a scale parameter; there is no angular dependence of $\psi(r)$ since the ground state function is spherically symmetric. The energy is given by

$$E(\alpha) = \frac{\langle\psi \mid \hat{H} \mid \psi\rangle}{\langle\psi \mid \psi\rangle} = -\frac{\left\langle\psi\left|(\hbar^2/2m)\nabla^2 + e^2/r\right|\psi\right\rangle}{\langle\psi \mid \psi\rangle}, \tag{9.153}$$

where

$$\langle\psi \mid \psi\rangle = \int_0^{+\infty} r^2 e^{-2r/\alpha}dr \int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi = \pi\alpha^3 \tag{9.154}$$

and

$$-\left\langle\psi\left|\frac{e^2}{r}\right|\psi\right\rangle = -4\pi e^2\int_0^{+\infty} re^{-2r/\alpha}dr = -\pi e^2\alpha^2. \tag{9.155}$$

To calculate the kinetic energy term, we may use (9.128)

$$-\left\langle\psi\left|\frac{\hbar^2}{2m}\nabla^2\right|\psi\right\rangle = \frac{\hbar^2}{2m}\int\left(\vec{\nabla}\psi^*(r)\right)\cdot\left(\vec{\nabla}\psi(r)\right)d^3r, \tag{9.156}$$

where

$$\vec{\nabla}\psi^*(r) = \vec{\nabla}\psi(r) = \frac{d\psi(r)}{dr}\hat{r} = -\frac{1}{\alpha}e^{-r/\alpha}\hat{r}; \tag{9.157}$$

hence

$$-\left\langle \psi \left| \frac{\hbar^2}{2m}\nabla^2 \right| \psi \right\rangle = \frac{4\pi}{\alpha^2}\frac{\hbar^2}{2m}\int_0^{+\infty} r^2 e^{-2r/\alpha}\, dr = \frac{\hbar^2\pi}{2m}\alpha. \tag{9.158}$$

Inserting (9.154), (9.155), and (9.158) into (9.153), we obtain

$$E(\alpha) = \frac{\hbar^2}{2m\alpha^2} - \frac{e^2}{\alpha}. \tag{9.159}$$

Minimizing this relation with respect to α, $dE(\alpha)/d\alpha = -\hbar^2/(m\alpha_0^3) + e^2/\alpha_0^2 = 0$, we obtain $\alpha_0 = \hbar^2/(me^2)$ which, when inserted into (9.159), leads to the ground state energy

$$E(\alpha_0) = -\frac{me^4}{2\hbar^2}. \tag{9.160}$$

This is the correct ground state energy for the hydrogen atom. The variational method has given back the correct energy because the trial function (9.152) happens to be identical with the exact ground state wave function. Note that the scale parameter $\alpha_0 = \hbar^2/(me^2)$ has the dimensions of length; it is equal to the Bohr radius.

9.4 The Wentzel–Kramers–Brillouin Method

The Wentzel–Kramers–Brillouin (WKB) method is useful for approximate treatments of systems with *slowly* varying potentials; that is, potentials which remain almost *constant* over a region of the order of the de Broglie wavelength. In the case of classical systems, this property is always satisfied since the wavelength of a classical system approaches zero. The WKB method can thus be viewed as a *semiclassical* approximation.

9.4.1 General Formalism

Consider the motion of a particle in a time-independent potential $V(\vec{r})$; the Schrödinger equation for the corresponding stationary state is

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r}) \tag{9.161}$$

or

$$\nabla^2\psi(\vec{r}) + \frac{1}{\hbar^2}p^2(\vec{r})\psi(\vec{r}) = 0, \tag{9.162}$$

where $p(\vec{r})$ is the classical momentum at $\vec{r}$: $p(\vec{r}) = \sqrt{2m(E - V(\vec{r}))}$. If the particle is moving in a region where $V(\vec{r})$ is constant, the solution of (9.162) is of the form $\psi(\vec{r}) = Ae^{\pm i\vec{p}\cdot\vec{r}/\hbar}$. But how does one deal with those cases where $V(\vec{r})$ is not constant? The WKB method provides an approximate treatment for systems whose potentials, while not constant, are *slowly* varying functions of $\vec{r}$. That is, $V(\vec{r})$ is almost constant in a region which extends over several de Broglie wavelengths; we may recall that the de Broglie wavelength of a particle of mass m and energy E that is moving in a potential $V(\vec{r})$ is given by $\lambda = h/p = h/\sqrt{2m(E - V(\vec{r}))}$.

In essence, the WKB method consists of trying a solution to (9.162) in the following form:

$$\psi(\vec{r}) = A(\vec{r})e^{iS(\vec{r})/\hbar}, \tag{9.163}$$

where the amplitude $A(\vec{r})$ and the phase $S(\vec{r})$, which are real functions, are yet to be determined. Substituting (9.163) into (9.162) we obtain

$$A\left[\frac{\hbar^2}{A}\nabla^2 A - (\vec{\nabla}S)^2 + p^2(\vec{r})\right] + i\hbar\left[2(\vec{\nabla}A)\cdot(\vec{\nabla}S) + A\nabla^2 S\right] = 0. \tag{9.164}$$

The real and imaginary parts of this equation must vanish separately:

$$(\vec{\nabla}S)^2 = p^2(\vec{r}) = 2m(E - V(\vec{r})), \tag{9.165}$$

$$2(\vec{\nabla}A)\cdot(\vec{\nabla}S) + A\nabla^2 S = 0. \tag{9.166}$$

In deriving (9.165) we have neglected the term that contains $\hbar$ (i.e., $(\hbar^2/A)\nabla^2 A$), since it is small compared to $(\vec{\nabla}S)^2$ and to $p^2(\vec{r})$; $\hbar$ is considered to be very small for classical systems.

To illustrate the various aspects of the WKB method, let us consider the simple case of the *one-dimensional* motion of a single particle. We can thus reduce (9.165) and (9.166), respectively, to

$$\frac{dS}{dx} = \pm\sqrt{2m\,(E - V)} = \pm p(x), \tag{9.167}$$

$$2\left(\frac{d}{dx}\ln A\right)p(x) + \frac{d}{dx}p(x) = 0. \tag{9.168}$$

Let us find the solutions of (9.167) and (9.168). Integration of (9.167) yields

$$S(x) = \pm\int dx\sqrt{2m\,(E - V(x))} = \pm\int p(x)\,dx. \tag{9.169}$$

We can reduce (9.168) to

$$\frac{d}{dx}\left[2\ln A + \ln p(x)\right] = 0, \tag{9.170}$$

which in turn leads to

$$A(x) = \frac{C}{\sqrt{|p(x)|}}, \tag{9.171}$$

where C is an arbitrary constant. So (9.169) and (9.171) give, respectively, the phase $S(x)$ and amplitude $A(x)$ of the WKB wave function (9.163).

Inserting (9.171) and (9.169) into (9.163), we obtain two approximate solutions to equation (9.162):

$$\psi_\pm(x) = \frac{C_\pm}{\sqrt{|p(x)|}}\exp\left[\pm\frac{i}{\hbar}\int^x p(x')dx'\right]. \tag{9.172}$$

The amplitude of this wave function is proportional to $1/\sqrt{p(x)}$; hence the probability of finding the particle between x and $x + dx$ is proportional to $1/p(x)$. This is what we expect for a "classical" particle because the time it will take to travel a distance dx is proportional to the inverse of its speed (or its momentum).

We can now examine two separate cases corresponding to $E > V(x)$ and $E < V(x)$. First, let us consider the case $E > V(x)$, which is called the *classically allowed* region. Here $p(x)$ is a real function; the most general solution of (9.162) is a combination of $\psi_+(x)$ and $\psi_-(x)$:

$$\psi(x) = \frac{C_+}{\sqrt{p(x)}} \exp\left[\frac{i}{\hbar}\int^x p(x')dx'\right] + \frac{C_-}{\sqrt{p(x)}} \exp\left[-\frac{i}{\hbar}\int^x p(x')dx'\right]. \tag{9.173}$$

Second, in the case where $E < V(x)$, which is known as the *classically forbidden* region, the momentum $p(x)$ is imaginary and the exponents of (9.172) become real:

$$\psi(x) = \frac{C'_-}{\sqrt{|p(x)|}} \exp\left[-\frac{1}{\hbar}\int_x |p(x')|dx'\right] + \frac{C'_+}{\sqrt{|p(x)|}} \exp\left[\frac{1}{\hbar}\int^x |p(x')|dx'\right]. \tag{9.174}$$

Equations (9.173) and (9.174) give the system's wave function in the allowed and forbidden regions, respectively. But what about the structure of the wave function near the regions $E \simeq V(x)$? At the points x_i, we have $E = V(x_i)$; hence the momentum (9.167) vanishes, $p(x_i) = 0$. These points are called the *classical turning points*, because classically the particle stops at x_i and then turns back to resume its motion in the opposite direction. At these points the wave function (9.172) becomes infinite since $p(x_i) = 0$. One then needs to examine how to find the wave function at the turning points. Before looking into that, let us first study the condition of validity for the WKB approximation.

Validity of the WKB approximation

To obtain the condition of validity for the WKB method, let us examine the size of the various terms in (9.164), notably $A(\vec{\nabla}S)^2$ and $i\hbar A\nabla^2 S$. Since quantities of the order of $\hbar$ are too small in the classical limit, the quasi-classical region is expected to be given by the condition[4]

$$\left|\hbar\nabla^2 S\right| \ll (\vec{\nabla}S)^2, \tag{9.175}$$

which can be written in one dimension as

$$\hbar\left|\frac{S''}{S'^2}\right| \ll 1 \tag{9.176}$$

or

$$\left|\frac{d}{dx}\left(\frac{\hbar}{S'}\right)\right| \ll 1, \tag{9.177}$$

since $\nabla^2 S = d^2S/dx^2 = S''$ and $|\vec{\nabla}S| = dS(x)/dx = S'$. In what follows we are going to verify that this relation yields the condition of validity for the WKB approximation.

Since $S' = \pm p(x)$ (see (9.167)), we can reduce (9.177) to

$$\left|\frac{d\bar{\lambda}(x)}{dx}\right| \ll 1, \tag{9.178}$$

where $\bar{\lambda}(x) = \lambda(x)/(2\pi)$ and $\lambda(x)$ is the de Broglie wavelength of the particle:

$$\bar{\lambda}(x) = \frac{\hbar}{p(x)} = \frac{\hbar}{\sqrt{2m\,(E - V(x))}}. \tag{9.179}$$

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[4] The condition (9.175) can be found as follows. Substituting $\psi(\vec{r}) = e^{iS(\vec{r})/\hbar}$ into (9.162) and multiplying by $\hbar^2$, we get $i\hbar\nabla^2 S(\vec{r}) - (\vec{\nabla}S)^2 + p^2(\vec{r}) = 0$. In the classical limit, the term containing $\hbar$, $|i\hbar\nabla^2 S(\vec{r})|$, must be small compared to the terms that do not, $(\vec{\nabla}S)^2$; i.e., $|\hbar\nabla^2 S(\vec{r})| \ll (\vec{\nabla}S)^2$.

The condition (9.178) means that the rate of change of the de Broglie wavelength is small (i.e., the wavelength of the particle must vary only slightly over distances of the order of its size). But this condition is always satisfied for classical systems. So the condition of validity for the WKB method is given by

$$\left|\frac{d\bar{\lambda}(x)}{dx}\right| = \left|\frac{d}{dx}\left(\frac{\hbar}{p(x)}\right)\right| \ll 1. \tag{9.180}$$

This condition clearly breaks down at the classical turning points, $E = V(x_i)$, since $p(x_i) = 0$; classically, the particle stops at $x = x_i$ and then moves in the opposite direction. As $p(x)$ becomes small, the wavelength (9.179) becomes large and hence violates the requirement that it remains small and varies only slightly; when $p(x)$ is too small, the condition (9.180) breaks down. So the WKB approximation is valid in both the allowed and forbidden regions but not at the classical turning points.

How does one specify the particle's wave function at $x = x_i$? Or how does one connect the allowed states (9.173) with their forbidden counterparts (9.174)? As we go through the classical turning point, from the allowed to the forbidden region and vice versa, we need to examine how to determine the particle's wave function everywhere and notably at the turning points. This is the most difficult issue of the WKB method, for it breaks down at the turning points. In the following section we are going to deal with this issue by solving the Schrödinger equation near and at $x = x_i$. We will do so by resorting to an approximation: we consider the potential to be given, near the turning points, by a straight line whose slope is equal to that of the potential at the turning point.

In what follows, we want to apply the WKB approximation to find the energy levels and the wave function of a particle moving in a potential well. We are going to show that the formulas giving the energy levels depend on whether or not the potential well has rigid walls. In fact, it even depends on the number of rigid walls the potential has. For this, we are going to consider three separate cases pertaining to the potential well with: no rigid walls, a single rigid wall, and two rigid walls.

9.4.2 Bound States for Potential Wells with No Rigid Walls

Consider a potential well that has no rigid walls as displayed in Figure 9.5. Here the classically forbidden regions are specified by $x < x_1$ and $x > x_2$, the classically allowed region by $x_1 < x < x_2$; x_1 and x_2 are the classical turning points. This is a suitable and simple example to illustrate the various aspects of the WKB method, notably how to determine the particle's wave function at the turning points. We will see how this method yields the Bohr–Sommerfeld quantization rule from which the bound state energies are to be extracted.

The WKB method applies everywhere in the three regions (1), (2), and (3), except near the two turning points $x = x_1$ and $x = x_2$ at which $E = V(x_1) = V(x_2)$. The WKB approximation to the wave function in regions (1) and (3) can be inferred from (9.174) and the approximation in region (2) from (9.173): the wave function must decay exponentially in regions (1) and (3) as $x \to -\infty$ and $x \to +\infty$, respectively, but must be oscillatory in region (2):

$$\psi_{1_{WKB}}(x) = \frac{C_1}{\sqrt{|p(x)|}} \exp\left[-\frac{1}{\hbar}\int_x^{x_1} |p(x')|\, dx'\right], \qquad x < x_1, \tag{9.181}$$

$$\psi_{2_{WKB}}(x) = \frac{C_2'}{\sqrt{p(x)}} \exp\left[\frac{i}{\hbar}\int_x p(x')dx'\right] + \frac{C_2''}{\sqrt{p(x)}} \exp\left[-\frac{i}{\hbar}\int_x p(x')dx'\right], \quad x_1 < x < x_2, \tag{9.182}$$

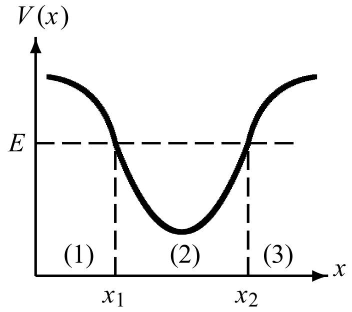

Figure 9.5 Potential with no rigid walls: regions (1) and (3) are classically forbidden, while (2) is classically allowed.

$$\psi_{3_{WKB}}(x)=\frac{C_3}{\sqrt{|p(x)|}}\exp\left[-\frac{1}{\hbar}\int_{x_2}^{x}\left|p(x')\right|dx'\right], \qquad x > x_2; \tag{9.183}$$

the coefficients C_1, C_2', C_2'', and C_3 have yet to be determined. For this, we must *connect* the solutions $\psi_1(x)$, $\psi_2(x)$, and $\psi_3(x)$ when passing from one region into another through the turning points $x = x_1$ and $x = x_2$ where the quasi-classical approximation ceases to be valid. That is, we need to connect $\psi_3(x)$ to $\psi_2(x)$ as we go from region (3) to (2), and then connect $\psi_1(x)$ to $\psi_2(x)$ as we go from (1) to (2). Since the WKB approximation breaks down at x_1 and x_2, we need to look for the exact solutions of the Schrödinger equation near x_1 and x_2.

9.4.2.1 Connection of $\psi_{3_{WKB}}(x)$ to $\psi_{2_{WKB}}(x)$

The WKB approximation to the wave function in region (2) can be inferred from (9.182):

$$\psi_{2_{WKB}}(x)=\frac{C_2'}{\sqrt{p(x)}}\exp\left[\frac{i}{\hbar}\int_{x}^{x_2}p(x')dx'\right]+\frac{C_2''}{\sqrt{p(x)}}\exp\left[-\frac{i}{\hbar}\int_{x}^{x_2}p(x')dx'\right], \quad x_1 < x < x_2; \tag{9.184}$$

this can be written as

$$\psi_{2_{WKB}}(x) = \frac{C_2}{\sqrt{p(x)}}\sin\left(\frac{1}{\hbar}\int_{x}^{x_2}p(x')dx'+\alpha\right), \qquad x_1 < x < x_2, \tag{9.185}$$

where α is a phase to be determined. Since the WKB approximation breaks down near the turning point x_2 (i.e., on both sides of $x = x_2$), we need to find a scheme for determining the wave function near x_2.

For this, let us now look for the exact solution of the Schrödinger equation near $x = x_2$. As mentioned above, if $|x - x_2|$ is small enough, within the region $|x - x_2|$, we can approximately represent the potential by a straight line whose slope is equal to that of the potential at the classical turning point $x = x_2$. That is, expanding $V(x)$ to first order around $x = x_2$, we obtain

$$V(x) \simeq V(x_2) + (x - x_2)\left.\frac{dV(x)}{dx}\right|_{x=x_2} = E + (x - x_2)F_0, \tag{9.186}$$

where we have used the fact that $V(x_2) = E$ and where F_0 is given by $F_0 = \left.\frac{dV(x)}{dx}\right|_{x=x_2}$. Equation (9.186) means that $V(x)$ is approximated by a straight line $(x - x_2)F_0$, where F_0 is the slope of $V(x)$ at $x = x_2$. The Schrödinger equation for the potential (9.186) can be written as

$$\frac{d^2\psi(x)}{dx^2} - \frac{2mF_0}{\hbar^2}(x - x_2)\psi(x) = 0. \tag{9.187}$$

Using the change of variable

$$y = \left(\frac{2mF_0}{\hbar^2}\right)^{1/3}(x - x_2), \tag{9.188}$$

we can transform (9.187) into

$$\left(\frac{2mF_0}{\hbar^2}\right)^{2/3}\left[\frac{d^2\psi(y)}{dy^2} - y\psi(y)\right] = 0 \tag{9.189}$$

or

$$\frac{d^2\psi(y)}{dy^2} - y\psi(y) = 0. \tag{9.190}$$

This is a well-known differential equation whose solutions are usually expressed in terms of the Airy functions[5] $\mathrm{Ai}(y)$:

$$\psi(y) = A'\mathrm{Ai}(y) = \frac{A'}{\pi}\int_0^\infty \cos\left(\frac{z^3}{3} + yz\right)dz, \tag{9.191}$$

where A' is a normalization constant.

From the properties of the Airy function $\mathrm{Ai}(y) = 1/\pi \int_0^\infty \cos(z^3/3+yz)dz$, the asymptotic behavior of $\mathrm{Ai}(y)$ is given for large positive and large negative values of y by

$$\mathrm{Ai}(y) \sim \begin{cases} \frac{1}{\sqrt{\pi}|y|^{1/4}}\sin\left[\frac{2}{3}(-y)^{3/2} + \frac{\pi}{4}\right], & y \ll 0, \\ \frac{1}{2\sqrt{\pi}y^{1/4}}\exp\left[-\frac{2}{3}y^{3/2}\right], & y \gg 0. \end{cases} \tag{9.192}$$

The asymptotic expression of (9.191) is therefore given for large positive and large negative values of y by

$$\psi(y) = \begin{cases} \frac{A'}{\sqrt{\pi}|y|^{1/4}}\sin\left[\frac{2}{3}(-y)^{3/2} + \frac{\pi}{4}\right], & y \ll 0, \\ \frac{A'}{2\sqrt{\pi}y^{1/4}}\exp\left[-\frac{2}{3}y^{3/2}\right], & y \gg 0. \end{cases} \tag{9.193}$$

Since $F_0 > 0$ equation (9.188) implies that the cases $y \ll 0$ and $y \gg 0$ correspond to $x \ll x_2$ and $x \gg x_2$, respectively.

Now near the turning point $x = x_2$, (9.186) shows that $E - V(x) = -(x - x_2)F_0$; hence the square of the classical momentum $p^2(x)$ is given by

$$p^2(x) = 2m\left(E - V(x)\right) = -2m(x - x_2)F_0, \tag{9.194}$$

which is negative for $x > x_2$ and positive for $x < x_2$. Combining equations (9.188) and (9.194), we obtain

$$p^2(x) = -\left(2m\hbar F_0\right)^{2/3} y. \tag{9.195}$$

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[5] The solution to the differential equation $d^2\phi(y)/dy = y\phi(y)$ is given by the Airy function $\phi(y) = \mathrm{Ai}(y) = \frac{1}{\pi}\int_0^\infty \cos(z^3/3 + yz)dz$.

Now since $dx = (\hbar^2/(2mF_0))^{1/3}dy$ (see (9.188)), we use (9.195) to infer the following expression:

$$\frac{1}{\hbar}\int_x^{x_2} p(x')\,dx' = \frac{1}{\hbar}\,(2m\hbar F_0)^{1/3}\left(\frac{\hbar^2}{2mF_0}\right)^{1/3}\int_y^0 \sqrt{-y'}\,dy' = \int_y^0 \sqrt{-y'}\,dy' = \frac{2}{3}(-y)^{3/2}. \tag{9.196}$$

Inserting this into (9.193), we obtain

$$\psi(x) = \begin{cases} \frac{A}{\sqrt{p(x)}}\sin\left(\frac{1}{\hbar}\int_x^{x_2} p(x')dx' + \frac{\pi}{4}\right), & x \ll x_2, \\ \frac{A}{2\sqrt{|p(x)|}}\exp\left[-\frac{1}{\hbar}\int_x^{x_2}\left|p(x')\right|dx'\right], & x \gg x_2, \end{cases} \tag{9.197}$$

where $A = (2m\hbar F_0)^{1/6}A'/\sqrt{\pi}$. A comparison of (9.197a) with (9.185) and (9.197b) with (9.183) reveals that

$$A = 2C_3, \qquad C_2 = A, \qquad \alpha = \frac{\pi}{4}; \tag{9.198}$$

these expressions are known as the *connection formulas*, for they connect the WKB solutions at either side of a turning point. Since $\alpha = \pi/4$, $\psi_{2_{WKB}}(x)$ of (9.185) becomes

$$\psi_{2_{WKB}}(x) = \frac{C_2}{\sqrt{p(x)}}\sin\left(\frac{1}{\hbar}\int_x^{x_2} p(x')\,dx' + \frac{\pi}{4}\right). \tag{9.199}$$

9.4.2.2 Connection of $\psi_{1_{WKB}}(x)$ to $\psi_{2_{WKB}}(x)$

The WKB wave function for $x < x_1$ is given by (9.181); the WKB solution for $x > x_1$ can be inferred from (9.182):

$$\psi_{2_{WKB}}(x) = \frac{C_2'}{\sqrt{p(x)}}\exp\left[\frac{i}{\hbar}\int_{x_1}^{x} p(x')dx'\right] + \frac{C_2''}{\sqrt{p(x)}}\exp\left[-\frac{i}{\hbar}\int_x^{x_1} p(x')dx'\right], \quad x_1 < x < x_2, \tag{9.200}$$

which can be written as

$$\psi_{2_{WKB}}(x) = \frac{D}{\sqrt{p}}\sin\left(\frac{1}{\hbar}\int_{x_1}^{x} p(x')\,dx' + \beta\right). \tag{9.201}$$

Recall that near $x = x_1$ the WKB approximation breaks down.

The shape of the wave function near $x = x_1$ can, however, be found from an exact solution of the Schrödinger equation. For this, we proceed as we did for $x = x_2$. That is, we look for the exact solution of the Schrödinger equation for small values of $|x - x_1|$. Expanding $V(x)$ near $x = x_1$, we obtain a Schrödinger equation similar to (9.190). Its solutions for $x < x_1$ and $x > x_1$ are given by expressions that are similar to (9.197b) and (9.197a) respectively:

$$\psi(x) = \begin{cases} \frac{E}{2\sqrt{|p(x)|}}\exp\left[\frac{1}{\hbar}\int_{x_1}^{x}\left|p(x')\right|dx'\right], & x \ll x_1, \\ \frac{E}{\sqrt{p(x)}}\sin\left(\frac{1}{\hbar}\int_{x_1}^{x} p(x')\,dx' + \frac{\pi}{4}\right), & x \gg x_1. \end{cases} \tag{9.202}$$

Again, comparing (9.202a) with (9.181) and (9.202b) with (9.201), we obtain the other set of connection formulas:

$$E = 2C_1, \qquad E = D, \qquad \beta = \frac{\pi}{4}; \tag{9.203}$$

hence $\psi_2(x)$ of (9.201) becomes

$$\psi_{2_{WKB}}(x) = \frac{D}{\sqrt{p(x)}} \sin\left(\frac{1}{\hbar}\int_{x_1}^{x} p(x')\,dx' + \frac{\pi}{4}\right). \tag{9.204}$$

9.4.2.3 Quantization of the Energy Levels of the Bound States

Since the two solutions (9.199) and (9.204) represent the same wave function in the same region, they must be equal:

$$\psi_{2_{WKB}}(x) = \frac{D}{\sqrt{p(x)}} \sin\left(\frac{1}{\hbar}\int_{x_1}^{x} p(x')\,dx' + \frac{\pi}{4}\right) = \frac{C_2}{\sqrt{p(x)}} \sin\left(\frac{1}{\hbar}\int_{x}^{x_2} p(x')\,dx' + \frac{\pi}{4}\right). \tag{9.205}$$

This is an equation of the form $D\sin\theta_1 = C_2\sin\theta_2$. Its solutions must satisfy the following two relations. The first is $\theta_1 + \theta_2 = (n+1)\pi$, i.e.,

$$\left(\frac{1}{\hbar}\int_{x_1}^{x} p(x')\,dx' + \frac{\pi}{4}\right) + \left(\frac{1}{\hbar}\int_{x}^{x_2} p(x')\,dx' + \frac{\pi}{4}\right) = (n+1)\pi \tag{9.206}$$

or

$$\frac{1}{\hbar}\int_{x_1}^{x_2} p(x)\,dx = \left(n+\frac{1}{2}\right)\pi, \qquad n = 0,\ 1,\ 2,\ 3,\ \ldots; \tag{9.207}$$

and the second is

$$D = (-1)^n C_2. \tag{9.208}$$

Since the integral between the turning points $\int_{x_1}^{x_2} p(x)\,dx$ is equal to half the integral over a complete period of the quasi-classical motion of the particle, i.e., $\int_{x_1}^{x_2} p(x)\,dx = \frac{1}{2}\oint p(x)\,dx$, we can reduce (9.207) to

$$\oint p(x)\,dx = 2\int_{x_1}^{x_2} p(x)\,dx = \left(n+\frac{1}{2}\right)h, \qquad n = 0,\ 1,\ 2,\ 3,\ \ldots. \tag{9.209}$$

This relation determines the *quantized* (WKB) energy levels E_n of the bound states of a semiclassical system. It is similar to the *Bohr–Sommerfeld quantization rule*, which in turn is known to represent an improved version of the Wilson–Sommerfeld rule $\oint p(x)\,dx = nh$, because the Wilson–Sommerfeld rule does not include the zero-point energy term $h/2$ (in the case of large values of n, where the classical approximation becomes reliable, we have $n + 1/2 \simeq n$; hence (9.209) reduces to $\oint p(x)\,dx = nh$). We can interpret this relation as follows: since the integral $\oint p(x)\,dx$ gives the area enclosed by the closed trajectory of the particle in the xp phase space, the condition (9.209) provides the mechanism for selecting, from the continuum of energy values of the semiclassical system, only those energies E_n for which the areas of the contours $p(x, E_n) = \sqrt{2m\,(E_n - V(x))}$ are equal to $(n+\frac{1}{2})h$:

$$\boxed{\oint p(x, E_n)\,dx = 2\int_{x_1}^{x_2} \sqrt{2m(E_n - V(x))}\,dx = \left(n+\frac{1}{2}\right)h,} \tag{9.210}$$

with $n = 0, 1, 2, 3, \ldots$. So in the xp phase space, the area between two successive bound states is equal to h: $\oint p(x, E_{n+1})\,dx - \oint p(x, E_n)\,dx = h$. Each single state therefore corresponds to an area h in the phase space. Note that the number n present in this relation is equal to the number of bound states; that is, the number of nodes of the wave function $\psi(x)$.

In summary, for a particle moving in a potential well like the one shown in Figure 9.5, the bound state energies can be extracted from the quantization rule (9.210) and the wave function is given in regions (1) and (3) by (9.181) and (9.183), respectively, and in region (2) either by (9.199) or (9.204). Combining the *connection relations* (9.198), (9.203), and (9.208) with the wave functions (9.181), (9.183), (9.199), and (9.204), we get the WKB approximation to the wave function:

$$\psi_{WKB}(x) = \begin{cases} \psi 1_{WKB}(x) = \frac{(-1)^n C_3}{\sqrt{|p(x)|}} \exp\left[-\frac{1}{\hbar}\int_x^{x_1} \left|p(x')\right| dx'\right], & x < x_1, \\ \psi 3_{WKB}(x) = \frac{C_3}{\sqrt{|p(x)|}} \exp\left[-\frac{1}{\hbar}\int_{x_2}^{x} \left|p(x')\right| dx'\right], & x > x_2. \end{cases} \tag{9.211}$$

In the region $x_1 < x < x_2$, $\psi 2_{WKB}(x)$ is given either by (9.199) or by (9.204)

$$\psi 2_{WKB}(x) = \begin{cases} \frac{2(-1)^n C_3}{\sqrt{p(x)}} \sin\left(\frac{1}{\hbar}\int_{x_1}^{x} p(x')dx' + \frac{\pi}{4}\right), & x_1 < x < x_2, \\ \frac{2C_3}{\sqrt{p(x)}} \sin\left(\frac{1}{\hbar}\int_{x}^{x_2} p(x')dx' + \frac{\pi}{4}\right), & x_1 < x < x_2. \end{cases} \tag{9.212}$$

The coefficient C_3 has yet to be found from the normalization of $\psi_{WKB}(x)$. This is the wave function of the nth bound state.

Remark

An important application of the WKB method consists of using the quantization rule (9.210) to calculate the energy levels of central potentials. The energy of a particle of mass m bound in a central potential $V(r)$ is given by

$$E = \frac{p_r^2}{2m} + V_{eff}(r) = \frac{p_r^2}{2m} + V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}. \tag{9.213}$$

The particle is bound to move between the turning points r_1 and r_2 whose values are given by $E = V_{eff}(r_1) = V_{eff}(r_2)$ and its bound state energy levels can be obtained from

$$\int_{r_1}^{r_2} dr\, p_r(E, r) = \int_{r_1}^{r_2} dr \sqrt{2m\left(E - V(r) - \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right)} = \left(n + \frac{1}{2}\right)\pi\hbar, \tag{9.214}$$

where $n = 0, 1, 2, 3, \ldots$.

Example 9.7

Use the WKB method to estimate the energy levels of a one-dimensional harmonic oscillator.

Solution

The classical energy of a harmonic oscillator

$$E(x, p) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \tag{9.215}$$

leads to $p(E, x) = \pm\sqrt{2mE - m^2\omega^2 x^2}$. At the turning points, x_{min} and x_{max}, the energy is given by $E = V(x) = \frac{1}{2}m\omega^2 x^2$ where $x_{min} = -a$ and $x_{max} = a$ with $a = \sqrt{2E/(m\omega^2)}$. To

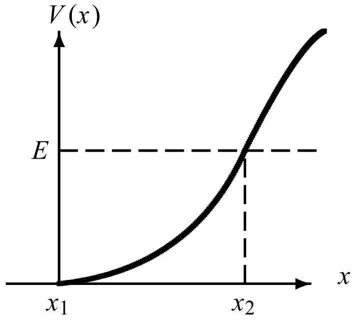

Figure 9.6 Potential well with one rigid wall located at $x = x_1$.

obtain the quantized energy expression of the harmonic oscillator, we need to use the Bohr–Sommerfeld quantization rule (9.210):

$$\oint p\,dx = 2\int_{-a}^{a} \sqrt{2mE - m^2\omega^2 x^2}dx = 4m\omega \int_0^a \sqrt{a^2 - x^2}dx. \tag{9.216}$$

Using the change of variable $x = a\sin\theta$, we have

$$\int_0^a \sqrt{a^2 - x^2}dx = a^2 \int_0^{\pi/2} \cos^2\theta\, d\theta = \frac{a^2}{2}\int_0^{\pi/2}(1+\cos 2\theta)d\theta = \frac{\pi a^2}{4} = \frac{\pi E}{2m\omega^2}; \tag{9.217}$$

hence

$$\oint p\,dx = \frac{2\pi E}{\omega}. \tag{9.218}$$

Since $\oint p\,dq = \left(n + \frac{1}{2}\right)h$ or $2\pi E/\omega = (n + 1/2)h$, we obtain

$$E_n^{WKB} = \left(n + \frac{1}{2}\right)\hbar\omega. \tag{9.219}$$

This expression is identical with the *exact* energy of the harmonic oscillator.

9.4.3 Bound States for Potential Wells with One Rigid Wall

Consider a particle moving in a potential well that has a rigid wall at $x = x_1$ (Figure 9.6); it is given by $V(x) = +\infty$ for $x < x_1$ and by a certain function $V(x)$ for $x > x_1$. The classically allowed region is specified by $x_1 < x < x_2$; x_1 and x_2 are the turning points.

To obtain the quantization rule which gives the bound state energy levels for this potential, we proceed as we did in obtaining (9.210). The WKB wave function in region $x_1 < x < x_2$ has an oscillatory form; it can be inferred from (9.201):

$$\psi_{WKB}(x) = \frac{A}{\sqrt{p(x)}}\sin\left(\frac{1}{\hbar}\int p(x')\,dx' + \alpha\right), \qquad x_1 \le x \le x_2, \tag{9.220}$$

where α is a phase factor that needs to be specified. For this, we need to find the WKB wave function near the two turning points x_1 and x_2.

First, near x_2 (i.e., for $x \leq x_2$) we can determine the value of α as we did in obtaining (9.199). That is, expand $V(x)$ around $(x - x_2)$ and then match the WKB solutions at $x = x_2$; this leads to a phase factor $\alpha = \pi/4$ and hence

$$\psi_{WKB}(x) = \frac{B}{\sqrt{p(x)}} \sin\left(\frac{1}{\hbar}\int_x^{x_2} p(x')dx' + \frac{\pi}{4}\right), \qquad x_1 \leq x \leq x_2. \tag{9.221}$$

Second, since the wave function has to vanish at the rigid wall, $\psi_{WKB}(x_1) = 0$, the phase factor α must be zero; then (9.220) yields

$$\psi_{WKB}(x) = \frac{A}{\sqrt{p(x)}} \sin\left(\frac{1}{\hbar}\int_{x_1}^{x} p(x')\,dx'\right), \qquad x_1 \leq x \leq x_2. \tag{9.222}$$

Now, since (9.221) and (9.222) represent the same wave function in the same region, the sum of their arguments must be equal to $(n+1)\pi$ and $A = (-1)^n B$ (see Eq. (9.208)):

$$\left(\frac{1}{\hbar}\int_{x_1}^{x} p(x')\,dx'\right) + \left(\frac{1}{\hbar}\int_x^{x_2} p(x')\,dx' + \frac{\pi}{4}\right) = (n+1)\pi. \tag{9.223}$$

Thus, the quantization rule which gives the bound state energy levels for potential wells with one single rigid wall is given by

$$\boxed{\int_{x_1}^{x_2} p(x)\,dx = \left(n + \frac{3}{4}\right)\pi\hbar, \qquad n = 0, 1, 2, 3, lcdots.} \tag{9.224}$$

Remark

From the study carried out above, we may state that the phase factor α of the WKB solution (9.220) is in general equal to

- zero for turning points located at the rigid walls
- $\pi/4$ for turning points that are not located at the rigid walls.

9.4.4 Bound States for Potential Wells with Two Rigid Walls

Consider a potential well that has two rigid walls at $x = x_1$ and $x = x_2$. That is, as shown in Figure 9.7, $V(x)$ is infinite for $x \leq x_1$ and $x \geq x_2$ and given by a certain function $V(x)$ for $x_1 < x < x_2$. The wave function of a particle that is confined to move between the two rigid walls must vanish at the walls: $\psi(x_1) = \psi(x_2) = 0$.

To obtain the quantization rule which gives the bound state energy levels for this potential, we proceed as we did in obtaining (9.224). The WKB wave function has an oscillatory form in $x_1 < x < x_2$ and vanishes at both x_1 and x_2; the phase factor is zero at x_1 and x_2. By analogy with the procedure that led to (9.222), we can show that the WKB wave function in the vicinity of x_1 (i.e., in the region $x > x_1$) is given by

$$\psi_{WKB}(x) = \frac{A}{\sqrt{p(x)}} \sin\left(\frac{1}{\hbar}\int_{x_1}^{x} p(x')\,dx'\right), \qquad x_1 < x < x_2, \tag{9.225}$$

and in the vicinity of x_2 (i.e., in the region $x < x_2$) it is given by

$$\psi_{WKB}(x) = \frac{B}{\sqrt{p(x)}} \sin\left(\frac{1}{\hbar}\int_x^{x_2} p(x')dx'\right), \qquad x_1 < x < x_2. \tag{9.226}$$

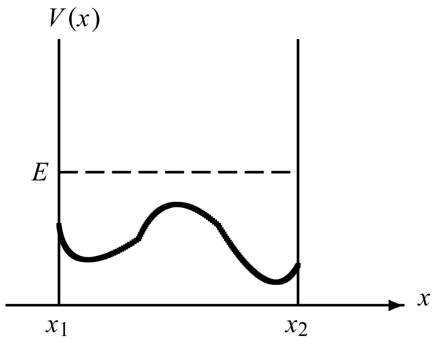

Figure 9.7 Potential well with two rigid walls located at x_1 and x_2.

Note that the last two wave functions satisfy the correct boundary conditions at x_1 and x_2: $\psi_{WKB}(x_1) = \psi_{WKB}(x_2) = 0$.

Since equations (9.225) and (9.226) represent the same wave function in the same region, the sum of the arguments must then be equal to $(n+1)\pi$ and $A = (-1)^n B$ (see Eq. (9.208)):

$$\left(\frac{1}{\hbar}\int_{x_1}^{x} p(x')\,dx'\right) + \left(\frac{1}{\hbar}\int_{x}^{x_2} p(x')\,dx'\right) = (n+1)\pi; \tag{9.227}$$

hence the quantization rule for potential wells with two rigid walls is given by

$$\int_{x_1}^{x_2} p(x')\,dx' = (n+1)\,\pi\hbar, \qquad n = 0,\ 1,\ 2,\ 3,\ \ldots, \tag{9.228}$$

or by

$$\boxed{\int_{x_1}^{x_2} p(x)dx = n\pi\hbar, \qquad n = 1,\ 2,\ 3,\ \ldots.} \tag{9.229}$$

The only difference between (9.228) and (9.229) is in the minimum value of the quantum number n: the lowest value of n is $n = 0$ in (9.228) and $n = 1$ in (9.229).

Remark

In this section we have derived three quantization rules (9.210), (9.224), and (9.229); they provide the proper prescriptions for specifying the energy levels for potential wells with zero, one, and two rigid walls, respectively. These rules differ only in the numbers $\frac{1}{2}$, $\frac{3}{4}$, and 0 that are added to n. In the cases where n is large, which correspond to the semiclassical domain, these three quantization rules become identical; the semiclassical approximation is most accurate for large values of n.

Example 9.8

Use the WKB approximation to calculate the energy levels of a spinless particle of mass m moving in a one-dimensional box with walls at $x = 0$ and $x = L$.

Solution

This potential has two rigid walls, one at $x = 0$ and the other at $x = L$. To find the energy levels, we make use of the quantization rule (9.229). Since the momentum is constant within the well $p(E, x) = \sqrt{2mE}$, we can easily infer the WKB energy expression of the particle within the well. The integral is quite simple to calculate:

$$\int_0^L p\,dx = \sqrt{2mE}\int_0^L dx = L\sqrt{2mE}. \tag{9.230}$$

Now since $\int_0^L p\,dx = n\pi\hbar$ we obtain

$$L\sqrt{2mE_n^{WKB}} = n\pi\hbar; \tag{9.231}$$

hence

$$E_n^{WKB} = \frac{\pi^2\hbar^2}{2mL^2}n^2. \tag{9.232}$$

This is the exact value of the energy of a particle in an infinite well.

Example 9.9 (WKB method for the Coulomb potential)

Use the WKB approximation to calculate the energy levels of the s states of an electron that is bound to a Ze nucleus.

Solution

The electron moves in the Coulomb field of the Ze nucleus: $V(r) = -Ze^2/r$. Since the electron is bound to the nucleus, it can be viewed as moving between two rigid walls $0 \le r \le a$ with $E = V(a)$, $a = -Ze^2/E$; the energy of the electron is negative, $E < 0$.

The energy levels of the s states (i.e., $l = 0$) can thus be obtained from (9.229):

$$\int_0^a \sqrt{2m\left(E + \frac{Ze^2}{r}\right)}\,dr = n\pi\hbar. \tag{9.233}$$

Using the change of variable $x = a/r$, we have

$$\begin{aligned}\int_0^a \sqrt{2m\left(E + \frac{Ze^2}{r}\right)}\,dr &= \sqrt{-2mE}\int_0^a \sqrt{\frac{a}{r} - 1}\,dr = a\sqrt{-2mE}\int_0^1 \sqrt{\frac{1}{x} - 1}dx \\ &= \frac{\pi}{2}a\sqrt{-2mE} = -\pi Ze^2\sqrt{-\frac{m}{2E}}.\end{aligned} \tag{9.234}$$

In deriving this relation, we have used the integral $\int_0^1 \sqrt{1/x - 1}\,dx = \pi/2$; this can be easily obtained by the application of the residue theorem. Combining (9.233) and (9.234) we end up with

$$E_n = -\frac{mZ^2e^4}{2\hbar^2}\frac{1}{n^2} = -\frac{Z^2e^2}{2a_0}\frac{1}{n^2}, \tag{9.235}$$

where $a_0 = \hbar^2/(me^2)$ is the Bohr radius. This is the correct (Bohr) expression for the energy levels.

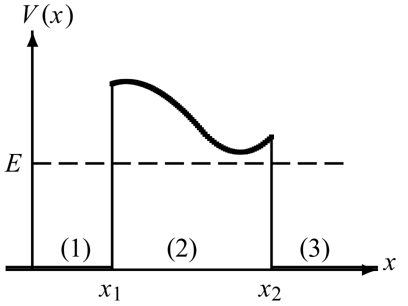

Figure 9.8 A potential barrier whose classically allowed regions are specified by $x < x_1$ and $x > x_2$ and the forbidden region by $x_1 < x < x_2$.

9.4.5 Tunneling through a Potential Barrier

Consider the motion of a particle of momentum $p_0 = \sqrt{2mE}$ incident from left onto a potential barrier $V(x)$, shown in Figure 9.8, with an energy E that is smaller than the potential's maximum value V_{max}.

Classically, the particle can in no way penetrate inside the barrier; hence it will get reflected backwards. Quantum mechanically, however, the probability corresponding to the particle's tunneling through the barrier and "emerging" to the right of the barrier is not zero. In what follows we want to use the WKB approximation to estimate the particle's probability of passing through the barrier.

In regions (1) and (3) of Figure 9.8 the particle is free:

$$\psi_1(x) = \psi_{incident}(x) + \psi_{reflected}(x) = Ae^{ip_0x/\hbar} + Be^{-ip_0x/\hbar}, \tag{9.236}$$

$$\psi_3(x) = \psi_{transmitted}(x) = Ee^{ip_0x/\hbar}, \tag{9.237}$$

where A, B, and E are the amplitudes of the incident, reflected, and transmitted waves, respectively; in region (3) we have outgoing waves only.

What about the wave function in the classically forbidden region (2)? The WKB method provides the answer. Since the particle energy is smaller than V_{max}, i.e., $E < V_{max}$, and if the potential $V(x)$ is a slowly varying function of x, the wave function in region (2) is given by the WKB approximation (see (9.174))

$$\psi_2(x) = \frac{C}{\sqrt{|p(x)|}} \exp\left[-\frac{1}{\hbar}\int_{x_1}^{x} |p(x')|dx'\right] + \frac{D}{\sqrt{|p(x)|}} \exp\left[\frac{1}{\hbar}\int_{x_1}^{x} |p(x')|dx'\right], \tag{9.238}$$

where $p(x) = i\sqrt{2m(V(x) - E)}$. The term $D/\sqrt{|p(x)|}\exp\left\{1/\hbar\int_{x_1}^{x} |p(x')|dx'\right\}$ increases exponentially when the barrier is very wide and is therefore unphysical. We shall be considering the case where the barrier is wide enough so that the approximation $D \simeq 0$ is valid; hence $\psi_2(x)$ becomes

$$\psi_2(x) = \frac{C}{\sqrt{|p(x)|}} \exp\left[-\frac{1}{\hbar}\int_{x_1}^{x} |p(x')|dx'\right]. \tag{9.239}$$

The probability corresponding to the particle's passage through the barrier is given by the transmission coefficient

$$T = \frac{v_{trans}}{v_{inc}} \frac{|\psi_{trans}(x)|^2}{|\psi_{inc}(x)|^2} = \frac{|E|^2}{|A|^2}, \tag{9.240}$$

since $v_{trans} = v_{inc}$ (the speeds of the incident and transmitted particles are equal). In what follows we are going to calculate the coefficient E in terms of A. For this, we need to use the continuity of the wave function and its derivative at x_1 and x_2. First, using (9.236) and (9.239), the continuity relations $\psi_1(x_1) = \psi_2(x_1)$ and $\psi_1'(x_1) = \psi_2'(x_1)$ lead, respectively, to

$$Ae^{ip_0x_1/\hbar} + Be^{-ip_0x_1/\hbar} = \frac{C}{\sqrt{a_1}}, \tag{9.241}$$

$$\frac{i}{\hbar}p_0(Ae^{ip_0x_1/\hbar} - Be^{-ip_0x_1/\hbar}) = -\frac{a_1}{\hbar\sqrt{a_1}}C, \tag{9.242}$$

where $a_1 = i\sqrt{2m(V(x_1) - E)}$. The continuity of the wave function and its derivative at x_2, $\psi_2(x_2) = \psi_3(x_2)$, and $\psi_2'(x_2) = \psi_3'(x_2)$ lead to

$$\frac{C}{\sqrt{a_2}} \exp\left[-\frac{1}{\hbar}\int_{x_1}^{x_2} |p(x)|dx\right] = Ee^{ip_0x_2/\hbar} \tag{9.243}$$

$$-\frac{a_2}{\hbar\sqrt{a_2}}C \exp\left[-\frac{1}{\hbar}\int_{x_1}^{x_2} |p(x)|dx\right] = \frac{ip_0}{\hbar}Ee^{ip_0x_2/\hbar}, \tag{9.244}$$

where $a_2 = i\sqrt{2m(V(x_2) - E)}$.

Adding (9.241) and (9.242) we get $C = 2A\sqrt{a_1}e^{ip_0x_1/\hbar}/(1-a_1/ip_0)$ which, when inserted into (9.243), yields

$$\frac{E}{A} = \frac{2}{1 - a_1/ip_0}\sqrt{\frac{a_1}{a_2}}e^{ip_0(x_1-x_2)/\hbar} \exp\left[-\frac{1}{\hbar}\int_{x_1}^{x_2} |p(x)|dx\right], \tag{9.245}$$

which in turn leads to

$$\frac{|E|^2}{|A|^2} = \frac{4}{a_2/a_1 + a_1a_2/p_0^2} \exp\left[-\frac{2}{\hbar}\int_{x_1}^{x_2} |p(x)|dx\right]. \tag{9.246}$$

The substitution of this expression into (9.240) finally yields an approximate value for the transmission coefficient through a potential barrier $V(x)$:

$$\boxed{T \sim e^{-2\gamma}, \qquad \gamma = \frac{1}{\hbar}\int_{x_1}^{x_2} \sqrt{2m(V(x) - E)}dx.} \tag{9.247}$$

Tunneling phenomena are common at the microscopic scale; they occur within nuclei, within atoms, and within solids. In nuclear physics, for instance, there are nuclei that decay into an α-particle (helium nucleus with $Z = 2$) and a daughter nucleus. This process can be viewed as the tunneling of an α-particle through the potential (Coulomb) barrier between the α-particle and the daughter nucleus; once formed inside the nucleus, the α-particle cannot escape unless it tunnels through (penetrates) the Coulomb barrier surrounding it. Tunneling also occurs within metals; when a metal is subject to an external electric field, electrons can be emitted from the metal. This is known as *cold emission*; we will study it in Example 9.10.

Example 9.10

Use the WKB approximation to estimate the transmission coefficient of a particle of mass m and energy E moving in the following potential barrier:

$$V(x) = \begin{cases} 0, & x < 0, \\ V_0 - \lambda, x & x > 0. \end{cases}$$

Solution

The transmission coefficient is given by (9.247), where $x_1 = 0$ and the value of x_2, which can be obtained from the relation $V_0 - \lambda x_2 = E$, is given by $x_2 = (V_0 - E)/\lambda$. Setting the values of x_1 and x_2 into (9.247), and since $V(x) - E = (V_0 - E) - \lambda x$, we get

$$\begin{aligned} \gamma &= \frac{1}{\hbar}\int_{x_1}^{x_2} \sqrt{2m(V(x) - E)}\,dx = \frac{\sqrt{2m}}{\hbar}\int_0^{(V_0-E)/\lambda} \sqrt{V_0 - E - \lambda x}\,dx \\ &= \frac{2\sqrt{2m}}{3\hbar\lambda}(V_0 - E)^{3/2}. \end{aligned} \tag{9.248}$$

The transmission coefficient is thus given by

$$T \sim e^{-2\gamma} = \exp\left\{-\frac{4\sqrt{2m}}{3\hbar\lambda}(V_0 - E)^{3/2}\right\}. \tag{9.249}$$

This problem is useful for the study of *cold emission* of electrons from metals. In the absence of any external electric field, the electrons are bound by a potential of the type $V(x) = V_0$ for $x > 0$, known as the work function of the metal. When we turn on an external electric field $\mathcal{E}$, the potential seen by the electron is no longer V_0 but $V(x) = V_0 - e\mathcal{E}x$. This potential barrier has a width through which the electrons can escape: every electron of energy $E \geq e\mathcal{E}x$ can escape. The quantity $e\mathcal{E}x_2$, where $x_2 = (V_0 - E)/\lambda$, is known as the work function of the metal; the width of the potential barrier of the metal is given by $0 < x < x_2$.

9.5 Concluding Remarks

In this chapter we have studied three approximation methods that apply to stationary Hamiltonians. As we saw, approximation methods offer efficient, short ways for obtaining energy levels that are, at times, identical with the exact results. For instance, in the calculation of the energy levels of the harmonic oscillator and the hydrogen atom, we have seen in a number of solved examples how the variational method and the WKB method lead to the correct energies *without* resorting to solve the Schrödinger equation; the approximation methods deal merely with the solution of a few simple integrals. In Chapters 4 and 7, however, we have seen that, to solve the Schrödinger equation for the harmonic oscillator and for the hydrogen atom, one has to carry out lengthy, laborious calculations.

Approximation methods offer, in general, powerful economical prescriptions for determining reliable results for systems that cannot be solved exactly. In the next chapter we are going to study approximation methods that apply to time-dependent processes such as atomic transitions, decays, and so on.

9.6 Solved Problems

The topic of approximation methods touches on almost all areas of quantum mechanics, ranging from one- to three-dimensional problems, as well as on the various aspects of the formalism of quantum mechanics.

Problem 9.1

Using first-order perturbation theory, calculate the energy of the nth excited state for a spinless particle of mass m moving in an infinite potential well of length $2L$, with walls at $x = 0$ and $x = 2L$:

$$V(x) = \begin{cases} 0, & 0 \le x \le 2L, \\ \infty, & \text{otherwise,} \end{cases}$$

which is modified at the bottom by the following two perturbations:

(a) $V_p(x) = \lambda V_0 \sin(\pi x/2L)$; (b) $V_p(x) = \lambda V_0 \delta(x - L)$, where $\lambda \ll 1$.

Solution

The exact expressions of the energy levels and of the wave functions for this potential are given by

$$E_n = \frac{\hbar^2\pi^2}{8mL^2}n^2, \qquad \psi_n(x) = \frac{1}{\sqrt{L}}\sin\left(\frac{n\pi x}{2L}\right). \tag{9.250}$$

According to perturbation theory, the energy of the nth state is given to first order by

$$E_n = \frac{\hbar^2\pi^2}{8mL^2}n^2 + E_n^{(1)}, \tag{9.251}$$

where

$$E_n^{(1)} = \langle \psi_n | V_p(x) \mid \psi_n \rangle = \frac{1}{L}\int_0^{2L} \sin^2\left(\frac{n\pi x}{2L}\right) V_p(x)\, dx. \tag{9.252}$$

(a) Using the relation

$$\int \cos nx \sin mx dx = -\frac{\cos(m-n)x}{2(m-n)} - \frac{\cos(m+n)x}{2(m+n)}, \qquad m \neq \pm n, \tag{9.253}$$

along with (9.252), we can calculate $E_n^{(1)}$ for $V_p(x) = \lambda V_0 \sin(\pi x/2L)$ as follows:

$$\begin{aligned} E_n^{(1)} &= \frac{\lambda V_0}{L}\int_0^{2L} \sin^2\left(\frac{n\pi x}{2L}\right)\sin\left(\frac{\pi x}{2L}\right) dx \\ &= \frac{\lambda V_0}{2L}\int_0^{2L} \left[1 - \cos\left(\frac{n\pi x}{L}\right)\right]\sin\left(\frac{\pi x}{2L}\right) dx \\ &= \frac{\lambda V_0}{\pi}\left\{-\cos\left(\frac{\pi x}{2L}\right) + \frac{\cos[(1-2n)\pi x/(2L)]}{2(1-2n)} + \frac{\cos[(1+2n)\pi x/(2L)]}{2(1+2n)}\right\}\Bigg|_0^{2L} \\ &= \frac{2\lambda V_0}{\pi}\frac{4n^2}{4n^2-1}. \end{aligned} \tag{9.254}$$

Thus, the energy (9.251) would become

$$E_n = \frac{\hbar^2\pi^2}{8mL^2}n^2 + \frac{2\lambda V_0}{\pi}\frac{4n^2}{4n^2-1}. \tag{9.255}$$

(b) In the case of $V_p(x) = \lambda V_0 \delta(x - L)$, (9.252) leads to

$$E_n^{(1)} = \frac{\lambda V_0}{L} \int_0^{2L} \sin^2\left(\frac{n\pi x}{2L}\right) \delta(x - L) dx = \frac{\lambda V_0}{L} \sin^2\left(\frac{n\pi}{2}\right); \tag{9.256}$$

hence, depending on whether the quantum number n is even or odd, we have

$$E_n = \frac{\hbar^2 \pi^2}{8mL^2} n^2 + \begin{cases} 0 & \text{if } n \text{ is even,} \\ \lambda V_0/L, & \text{if } n \text{ is odd.} \end{cases} \tag{9.257}$$

Problem 9.2

Consider a system whose Hamiltonian is given by $\hat{H} = E_0 \begin{pmatrix} 1+\lambda & 0 & 0 & 0 \\ 0 & 8 & 0 & 0 \\ 0 & 0 & 3 & -2\lambda \\ 0 & 0 & -2\lambda & 7 \end{pmatrix}$, where $\lambda \ll 1$.

(a) By decomposing this Hamiltonian into $\hat{H} = \hat{H}_0 + \hat{H}_p$, find the eigenvalues and eigenstates of the unperturbed Hamiltonian $\hat{H}_0$.

(b) Diagonalize $\hat{H}$ to find the exact eigenvalues of $\hat{H}$; expand each eigenvalue to the second power of λ.

(c) Using first- and second-order nondegenerate perturbation theory, find the approximate eigenergies of $\hat{H}$ and the eigenstates to first order. Compare these with the exact values obtained in (b).

Solution

(a) The matrix of $\hat{H}$ can be separated as follows:

$$H = \hat{H}_0 + \hat{H}_p = E_0 \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 8 & 0 & 0 \\ 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 7 \end{pmatrix} + E_0 \begin{pmatrix} \lambda & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2\lambda \\ 0 & 0 & -2\lambda & 0 \end{pmatrix}. \tag{9.258}$$

Notice that $\hat{H}_0$ is already diagonal; hence its eigenvalues are given by

$$E_1^{(0)} = E_0, \quad E_2^{(0)} = 8E_0, \quad E_3^{(0)} = 3E_0, \quad E_4^{(0)} = 7E_0, \tag{9.259}$$

and its eigenstates by

$$\mid \phi_1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad \mid \phi_2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad \mid \phi_3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad \mid \phi_4\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}. \tag{9.260}$$

(b) The diagonalization of $\hat{H}$ leads to the following secular equation:

$$\begin{vmatrix} (1+\lambda)E_0 - E & 0 & 0 & 0 \\ 0 & 8E_0 - E & 0 & 0 \\ 0 & 0 & 3E_0 - E & -2\lambda E_0 \\ 0 & 0 & -2\lambda E_0 & 7E_0 - E \end{vmatrix} = 0 \tag{9.261}$$

or

$$(E_0 + \lambda E_0 - E)(8E_0 - E)\left[(3E_0 - E)(7E_0 - E) - 4\lambda^2 E_0^2\right] = 0, \tag{9.262}$$

which in turn leads to the following *exact* eigenenergies:

$$E_1 = (1+\lambda)E_0, \quad E_2 = 8E_0, \quad E_3 = (5 - 2\sqrt{1+\lambda^2})E_0, \quad E_4 = (5 + 2\sqrt{1+\lambda^2})E_0. \tag{9.263}$$

Since $\lambda \ll 1$ we can expand $\sqrt{1+\lambda^2}$ to second order in λ: $\sqrt{1+\lambda^2} \simeq 1 + \lambda^2/2$. Hence E_3 and E_4 are given to second order in λ by

$$E_3 \simeq (3 - \lambda^2)E_0, \qquad E_4 \simeq (7 + \lambda^2)E_0. \tag{9.264}$$

(c) From nondegenerate perturbation theory, we can write the first-order corrections to the energies as follows:

$$E_1^{(1)} = \langle \phi_1 \mid \hat{H}_p \mid \phi_1 \rangle = E_0(1\ 0\ 0\ 0)\begin{pmatrix} \lambda & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2\lambda \\ 0 & 0 & -2\lambda & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} = \lambda E_0. \tag{9.265}$$

Similarly, we can verify that the second, third, and fourth eigenvalues have no first-order corrections:

$$E_2^{(1)} = \langle \phi_2 \mid \hat{H}_p \mid \phi_2 \rangle = 0, \quad E_3^{(1)} = \langle \phi_3 \mid \hat{H}_p \mid \phi_3 \rangle = 0, \quad E_4^{(1)} = \langle \phi_4 \mid \hat{H}_p \mid \phi_4 \rangle = 0. \tag{9.266}$$

Let us now consider the second-order corrections to the energy. From nondegenerate perturbation theory, we have

$$E_1^{(2)} = \sum_{m=2,3,4} \frac{\left|\langle \phi_m | \hat{H}_p \mid \phi_1 \rangle\right|^2}{E_1^{(0)} - E_m^{(0)}} = 0, \tag{9.267}$$

since $\langle \phi_2 \mid \hat{H}_p \mid \phi_1 \rangle = \langle \phi_3 \mid \hat{H}_p \mid \phi_1 \rangle = \langle \phi_4 \mid \hat{H}_p \mid \phi_1 \rangle = 0$. Similarly, we can verify that

$$E_2^{(2)} = \sum_{m=1,3,4} \frac{\left|\langle \phi_m | \hat{H}_p \mid \phi_2 \rangle\right|^2}{E_2^{(0)} - E_m^{(0)}} = 0 \tag{9.268}$$

and

$$E_3^{(2)} = \sum_{m=1,2,4} \frac{\left|\langle \phi_m | \hat{H}_p \mid \phi_3 \rangle\right|^2}{E_3^{(0)} - E_m^{(0)}} = \frac{\left|\langle \phi_4 \mid \hat{H}_p \mid \phi_3 \rangle\right|^2}{E_3^{(0)} - E_4^{(0)}} = \frac{(-2\lambda E_0)^2}{(3-7)E_0} = -\lambda^2 E_0, \tag{9.269}$$

because

$$\langle \phi_4 \mid \hat{H}_p \mid \phi_3 \rangle = E_0(0\ 0\ 0\ 1)\begin{pmatrix} \lambda & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2\lambda \\ 0 & 0 & -2\lambda & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} = -2\lambda E_0. \tag{9.270}$$

Similarly, since

$$\langle \phi_3 \mid \hat{H}_p \mid \phi_4 \rangle = E_0 (0\;0\;1\;0) \begin{pmatrix} \lambda & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2\lambda \\ 0 & 0 & -2\lambda & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} = -2\lambda E_0, \tag{9.271}$$

we can ascertain that

$$E_4^{(2)} = \sum_{m=1,2,3} \frac{\left| \langle \phi_m | \hat{H}_p \mid \phi_4 \rangle \right|^2}{E_4^{(0)} - E_m^{(0)}} = \frac{\left| \langle \phi_3 \mid \hat{H}_p \mid \phi_4 \rangle \right|^2}{E_4^{(0)} - E_3^{(0)}} = \frac{(-2\lambda E_0)^2}{(7-3)E_0} = \lambda^2 E_0. \tag{9.272}$$

Now, combining (9.265)-(9.272), we infer that the values of the energies to second-order nondegenerate perturbation theory are given by

$$E_1 = E_1^{(0)} + E_1^{(1)} + E_1^{(2)} = (1+\lambda)E_0, \tag{9.273}$$

$$E_2 = E_2^{(0)} + E_2^{(1)} + E_2^{(2)} = 8E_0, \tag{9.274}$$

$$E_3 = E_3^{(0)} + E_3^{(1)} + E_3^{(2)} = (3-\lambda^2)E_0, \tag{9.275}$$

$$E_4 = E_4^{(0)} + E_4^{(1)} + E_4^{(2)} = (7+\lambda^2)E_0. \tag{9.276}$$

All these values are identical with their corresponding exact expressions (9.263) and (9.264).

Finally, the first-order corrections to the eigenstates are given by

$$\mid \psi_n^{(1)} \rangle = \sum_{m \neq n} \frac{\langle \phi_m | \hat{H}_p \mid \phi_n \rangle}{E_m^{(0)} - E_n^{(0)}} \mid \phi_m \rangle, \tag{9.277}$$

and hence

$$\mid \psi_1^{(1)} \rangle = \sum_{m=2,3,4} \frac{\langle \phi_m | \hat{H}_p \mid \phi_1 \rangle}{E_m^{(0)} - E_1^{(0)}} \mid \phi_m \rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}. \tag{9.278}$$

Similarly, we can show that $\mid \psi_2^{(1)} \rangle$ is also given by a zero column matrix, but $\mid \psi_3^{(1)} \rangle$ and $\mid \psi_4^{(1)} \rangle$ are not:

$$\mid \psi_3^{(1)} \rangle = \sum_{m=1,2,4} \frac{\langle \phi_m | \hat{H}_p \mid \phi_3 \rangle}{E_m^{(0)} - E_3^{(0)}} \mid \phi_m \rangle = \frac{\langle \phi_4 \mid \hat{H}_p \mid \phi_3 \rangle}{E_4^{(0)} - E_3^{(0)}} \mid \phi_4 \rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ -\lambda/2 \end{pmatrix}, \tag{9.279}$$

$$\mid \psi_4^{(1)} \rangle = \sum_{m=1,2,3} \frac{\langle \phi_m | \hat{H}_p \mid \phi_4 \rangle}{E_m^{(0)} - E_4^{(0)}} \mid \phi_m \rangle = \frac{\langle \phi_3 \mid \hat{H}_p \mid \phi_4 \rangle}{E_3^{(0)} - E_4^{(0)}} \mid \phi_3 \rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ \lambda/2 \end{pmatrix}. \tag{9.280}$$

Finally, the states are given to first order by $\mid \psi_n \rangle = \mid \phi_n \rangle + \mid \psi_n^{(1)} \rangle$:

$$\mid \psi_1 \rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad \mid \psi_2 \rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad \mid \psi_3 \rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ -\lambda/2 \end{pmatrix}, \quad \mid \psi_4 \rangle = \begin{pmatrix} 0 \\ 0 \\ \lambda/2 \\ 1 \end{pmatrix}. \tag{9.281}$$

Problem 9.3

(a) Find the exact energies and wave functions of the ground and first excited states and specify their degeneracies for the infinite cubic potential well

$$V(x, y, z) = \begin{cases} 0 & \text{if } 0 < x < L, 0 < y < L, 0 < z < L, \\ \infty & \text{otherwise.} \end{cases}$$

Now add the following perturbation to the infinite cubic well:

$$\hat{H}_p = V_0 L^3 \delta\left(x - \frac{L}{4}\right) \delta\left(y - \frac{3L}{4}\right) \delta\left(z - \frac{L}{4}\right).$$

(b) Using first-order perturbation theory, calculate the energy of the ground state.

(c) Using first-order (degenerate) perturbation theory, calculate the energy of the first excited state.

Solution

The energy and wave function for an infinite, cubic potential well of size L are given by

$$E^{exact}_{n_x,n_y,n_z} = \frac{\pi^2\hbar^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right), \tag{9.282}$$

$$\phi_{n_x,n_y,n_z}(x, y, z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{\pi n_x}{L}x\right) \sin\left(\frac{\pi n_y}{L}y\right) \sin\left(\frac{\pi n_z}{L}z\right). \tag{9.283}$$

(a) The ground state is not degenerate; its exact energy and wave function are

$$E^{exact}_{111} = \frac{3\pi^2\hbar^2}{2mL^2}, \qquad \phi_{111}(x, y, z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{\pi}{L}x\right) \sin\left(\frac{\pi}{L}y\right) \sin\left(\frac{\pi}{L}z\right). \tag{9.284}$$

The first excited state is threefold degenerate: $\phi_{112}(x, y, z)$, $\phi_{121}(x, y, z)$, and $\phi_{211}(x, y, z)$ correspond to the same energy, $E^{exact}_{112} = E^{exact}_{121} = E^{exact}_{211} = 3\pi^2\hbar^2/(mL^2)$.

(b) The first-order correction to the ground state energy is given by

$$\begin{aligned} E_1^{(1)} &= \langle \phi_{111} \mid \hat{H}_p \mid \phi_{111} \rangle \\ &= 8V_0 \int_0^L \delta\left(x - \frac{L}{4}\right) \sin^2\left(\frac{\pi}{L}x\right) dx \int_0^L \delta\left(y - \frac{3L}{4}\right) \sin^2\left(\frac{\pi}{L}y\right) dy \\ &\quad \times \int_0^L \delta\left(z - \frac{L}{4}\right) \sin^2\left(\frac{\pi}{L}z\right) dz = 8V_0 \sin^2\left(\frac{\pi}{4}\right) \sin^2\left(\frac{3\pi}{4}\right) \sin^2\left(\frac{\pi}{4}\right) \\ &= V_0. \end{aligned} \tag{9.285}$$

Thus, the ground state energy is given to first-order perturbation by

$$E_0 = \frac{3\pi^2\hbar^2}{2mL^2} + V_0. \tag{9.286}$$

(c) To calculate the energy of the first excited state to first order, we need to use degenerate perturbation theory. The values of this energy are equal to $3\pi^2\hbar^2/(mL^2)$ plus the eigenvalues of the matrix

$$\begin{pmatrix} V_{11} & V_{12} & V_{13} \\ V_{21} & V_{22} & V_{23} \\ V_{31} & V_{32} & V_{33} \end{pmatrix}, \tag{9.287}$$

with $V_{nm} = \langle n \mid \hat{H}_p \mid m \rangle$, and where the following notations are used:

$$\mid 1\rangle = \phi_{211}(x,y,z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{2\pi}{L}x\right) \sin\left(\frac{\pi}{L}y\right) \sin\left(\frac{\pi}{L}z\right), \tag{9.288}$$

$$\mid 2\rangle = \phi_{121}(x,y,z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{\pi}{L}x\right) \sin\left(\frac{2\pi}{L}y\right) \sin\left(\frac{\pi}{L}z\right), \tag{9.289}$$

$$\mid 3\rangle = \phi_{112}(x,y,z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{\pi}{L}x\right) \sin\left(\frac{\pi}{L}y\right) \sin\left(\frac{2\pi}{L}z\right). \tag{9.290}$$

The calculations of the terms V_{nm} are lengthy but straightforward. Let us show how to calculate two such terms. First, V_{11} can be calculated in analogy to (9.285):

$$\begin{aligned} V_{11} &= 8V_0 \int_0^L \delta\left(x - \frac{L}{4}\right) \sin^2\left(\frac{2\pi}{L}x\right) dx \int_0^L \delta\left(y - \frac{3L}{4}\right) \sin^2\left(\frac{\pi}{L}y\right) dy \\ &\quad \times \int_0^L \delta\left(z - \frac{L}{4}\right) \sin^2\left(\frac{\pi}{L}z\right) dz = 8V_0 \sin^2\left(\frac{\pi}{2}\right) \sin^2\left(\frac{3\pi}{4}\right) \sin^2\left(\frac{\pi}{4}\right) \\ &= 2V_0; \end{aligned} \tag{9.291}$$

V_{12} and V_{13} are given by

$$\begin{aligned} V_{12} &= 8V_0 \int_0^L \delta\left(x - \frac{L}{4}\right) \sin\left(\frac{2\pi}{L}x\right) \sin\left(\frac{\pi}{L}x\right) dx \int_0^L \delta\left(y - \frac{3L}{4}\right) \sin\left(\frac{\pi}{L}y\right) \\ &\quad \times \sin\left(\frac{2\pi}{L}y\right) dy \int_0^L \delta\left(z - \frac{L}{4}\right) \sin^2\left(\frac{\pi}{L}z\right) dz = -2V_0, \end{aligned} \tag{9.292}$$

$$\begin{aligned} V_{13} &= 8V_0 \int_0^L \delta\left(x - \frac{L}{4}\right) \sin\left(\frac{2\pi}{L}x\right) \sin\left(\frac{\pi}{L}x\right) dx \int_0^L \delta\left(y - \frac{3L}{4}\right) \sin^2\left(\frac{\pi}{L}y\right) dy \\ &\quad \times \int_0^L \delta\left(z - \frac{L}{4}\right) \sin\left(\frac{\pi}{L}z\right) \sin\left(\frac{2\pi}{L}z\right) dz = 2V_0. \end{aligned} \tag{9.293}$$

Following this procedure, we can obtain the remaining terms:

$$V = 2V_0 \begin{pmatrix} 1 & -1 & 1 \\ -1 & 1 & -1 \\ 1 & -1 & 1 \end{pmatrix}. \tag{9.294}$$

The diagonalization of this matrix yields a doubly degenerate eigenvalue and a nondegenerate eigenvalue,

$$E_1^{(1)} = E_2^{(1)} = 0, \qquad E_3^{(1)} = 6V_0, \tag{9.295}$$

which lead to the energies of the first excited state:

$$E_1 = E_2 = \frac{3\pi^2\hbar^2}{mL^2}, \qquad E_3 = \frac{3\pi^2\hbar^2}{mL^2} + 6V_0. \tag{9.296}$$

So the perturbation has only partially lifted the degeneracy of the first excited state.

Problem 9.4
Consider a hydrogen atom which is subject to two *weak* static fields: an electric field in the xy planes $\vec{\mathcal{E}} = \mathcal{E}(\vec{i} + \vec{j})$ and a magnetic field along the z-axis $\vec{B} = B\vec{k}$, where $\mathcal{E}$ and B are constant. Neglecting the spin–orbit interaction, calculate the energy levels of the $n = 2$ states to first-order perturbation.

Solution
In the absence of any external field, and neglecting spin–orbit interactions, the energy of the $n = 2$ state is fourfold degenerate: four different states $\mid nlm\rangle = \mid 200\rangle$, $\mid 211\rangle$, $\mid 210\rangle$, and $\mid 21-1\rangle$ correspond to the same energy $E_2 = -\mathcal{R}/4$, where $\mathcal{R} = m_e e^4/(2\hbar^2) = 13.6\,\text{eV}$ is the Rydberg constant.

When the atom is placed in an external electric field $\vec{\mathcal{E}} = \mathcal{E}(\vec{i} + \vec{j})$, the energy of interaction between the electron's dipole moment ($\vec{d} = -e\vec{r}$) and $\vec{\mathcal{E}}$ is given by $-\vec{d} \cdot \vec{\mathcal{E}} = e\mathcal{E}(x + y) = e\mathcal{E}r \sin\theta(\cos\phi + \sin\phi)$. On the other hand, when subjecting the atom to an external magnetic field $\vec{B} = B\vec{k}$, the linear momentum of the electron becomes $\vec{p} \longrightarrow (\vec{p} - e\vec{A}/c)$, where $\vec{A}$ is the vector potential corresponding to $\vec{B}$. So when subjecting a hydrogen atom to both $\vec{\mathcal{E}}$ and $\vec{B}$, its Hamiltonian is given by

$$\begin{aligned}\hat{H} &= \frac{1}{2\mu}\left(\vec{p} - \frac{e}{c}\vec{A}\right)^2 - \frac{e^2}{r} + e\mathcal{E}r \sin\theta(\cos\phi + \sin\phi) \\ &= \frac{\vec{p}^2}{2\mu} - \frac{e^2}{r} - \frac{e}{2\mu c}\vec{B} \cdot \vec{L} + \frac{e}{2\mu c}A^2 + e\mathcal{E}r \sin\theta(\cos\phi + \sin\phi).\end{aligned} \tag{9.297}$$

Since the magnetic field is weak, we can ignore the term $eA^2/(2\mu c)$; hence we can write $\hat{H}$ as $\hat{H} = \hat{H}_0 + \hat{H}_p$, where $\hat{H}_0$ is the Hamiltonian of an unperturbed hydrogen atom, while $\hat{H}_p$ can be treated as a perturbation:

$$\hat{H}_0 = \frac{\vec{p}^2}{2\mu} - \frac{e^2}{r}, \qquad \hat{H}_p = -\frac{eB}{2\mu c}\hat{L}_z + e\mathcal{E}r \sin\theta(\cos\phi + \sin\phi). \tag{9.298}$$

To calculate the energy levels of the $n = 2$ state, we need to use degenerate perturbation theory, since the $n = 2$ state is fourfold degenerate; for this, we need to diagonalize the matrix

$$\begin{pmatrix} \langle 1 \mid \hat{H}_p \mid 1\rangle & \langle 1 \mid \hat{H}_p \mid 2\rangle & \langle 1 \mid \hat{H}_p \mid 3\rangle & \langle 1 \mid \hat{H}_p \mid 4\rangle \\ \langle 2 \mid \hat{H}_p \mid 1\rangle & \langle 2 \mid \hat{H}_p \mid 2\rangle & \langle 2 \mid \hat{H}_p \mid 3\rangle & \langle 2 \mid \hat{H}_p \mid 4\rangle \\ \langle 3 \mid \hat{H}_p \mid 1\rangle & \langle 3 \mid \hat{H}_p \mid 2\rangle & \langle 3 \mid \hat{H}_p \mid 3\rangle & \langle 3 \mid \hat{H}_p \mid 4\rangle \\ \langle 4 \mid \hat{H}_p \mid 1\rangle & \langle 4 \mid \hat{H}_p \mid 2\rangle & \langle 4 \mid \hat{H}_p \mid 3\rangle & \langle 4 \mid \hat{H}_p \mid 4\rangle \end{pmatrix}, \tag{9.299}$$

where $\mid 1\rangle = \mid 200\rangle$, $\mid 2\rangle = \mid 211\rangle$, $\mid 3\rangle = \mid 210\rangle$, and $\mid 4\rangle = \mid 21-1\rangle$. We therefore need to calculate the term

$$\langle 2l'm'|\hat{H}_p \mid 2lm\rangle = -\frac{eB}{2\mu c}m\hbar\delta_{l',l}\delta_{m',m} + e\mathcal{E}\langle 2l'm'|r \sin\theta(\cos\phi + \sin\phi) \mid 2lm\rangle. \tag{9.300}$$

Since $x = r\sin\theta\cos\phi$ and $y = r\sin\theta\sin\phi$ are both odd, the only terms that survive among $\langle 2l'm'|x \mid 2lm\rangle$ and $\langle 2l'm'|y \mid 2lm\rangle$ are $\langle 200 \mid x \mid 21\pm1\rangle$, $\langle 200 \mid y \mid 21\pm1\rangle$, and their complex conjugates. That is, x and y can couple only states of different parities ($l' - l = \pm1$) and whose azimuthal quantum numbers satisfy this condition: $m' - m = \pm 1$. So we need to calculate only

$$\langle 200 \mid x \mid 21 \pm 1\rangle = \int_0^{+\infty} R^*_{20}(r)R_{21}(r)r^3 dr \int Y^*_{00}(\Omega)\sin\theta\cos\phi Y_{1\pm1}(\Omega)d\Omega, \tag{9.301}$$

$$\langle 200 \mid y \mid 21 \pm 1\rangle = \int_0^{+\infty} R^*_{20}(r)R_{21}(r)r^3 dr \int Y^*_{00}(\Omega)\sin\theta\sin\phi Y_{1\pm1}(\Omega)d\Omega, \tag{9.302}$$

where

$$\int_0^{+\infty} R^*_{20}(r)R_{21}(r)r^3 dr = -3\sqrt{3}a_0; \tag{9.303}$$

a_0 is the Bohr radius, $a_0 = \hbar^2/(m_e e^2)$. Using the relations

$$\sin\theta\cos\phi = \sqrt{\frac{2\pi}{3}}\left[Y_{1-1}(\Omega) - Y_{11}(\Omega)\right], \qquad \sin\theta\sin\phi = i\sqrt{\frac{2\pi}{3}}\left[Y_{1-1}(\Omega) + Y_{11}(\Omega)\right], \tag{9.304}$$

along with

$$\int Y^*_{l'm'}(\Omega)Y_{lm}(\Omega)d\Omega = \delta_{l',l}\delta_{m',m}, \tag{9.305}$$

we obtain

$$\int Y^*_{00}(\Omega)\sin\theta\cos\phi Y_{11}(\Omega)d\Omega = \frac{1}{\sqrt{4\pi}}\int \sin\theta\cos\phi Y_{11}(\Omega)d\Omega = \frac{1}{\sqrt{6}}\int Y_{1-1}(\Omega)Y_{11}(\Omega)d\Omega$$
$$= -\frac{1}{\sqrt{6}}, \tag{9.306}$$

$$\int Y^*_{00}(\Omega)\sin\theta\sin\phi Y_{11}(\Omega)d\Omega = \frac{i}{\sqrt{6}}\int Y_{1-1}(\Omega)Y_{11}(\Omega)d\Omega = -\frac{i}{\sqrt{6}}. \tag{9.307}$$

Similarly, we have

$$\int Y^*_{00}(\Omega)\sin\theta\cos\phi Y_{1-1}(\Omega)d\Omega = \frac{1}{\sqrt{6}}. \tag{9.308}$$

$$\int Y^*_{00}(\Omega)\sin\theta\sin\phi Y_{1-1}(\Omega)d\Omega = -\frac{i}{\sqrt{6}}. \tag{9.309}$$

Now, substituting (9.303), (9.306), and (9.308) into (9.301), we end up with

$$\langle 200 \mid x \mid 21 \pm 1\rangle = \pm\frac{3}{\sqrt{2}}a_0, \qquad \langle 200 \mid y \mid 21 \pm 1\rangle = \frac{3i}{\sqrt{2}}a_0; \tag{9.310}$$

hence

$$\langle 21 \pm 1|x \mid 200\rangle = \pm\frac{3}{\sqrt{2}}a_0, \qquad \langle 21 \pm 1|y \mid 200\rangle = -\frac{3i}{\sqrt{2}}a_0. \tag{9.311}$$

The matrix (9.299) thus becomes

$$\begin{pmatrix} 0 & \alpha + i\alpha & 0 & -\alpha + i\alpha \\ \alpha - i\alpha & -\beta & 0 & 0 \\ 0 & 0 & 0 & 0 \\ -\alpha - i\alpha & 0 & 0 & \beta \end{pmatrix}, \tag{9.312}$$

where α and β stand for $\alpha = 3e\mathcal{E}a_0/\sqrt{2}$ and $\beta = e\hbar B/(2\mu c)$.

The diagonalization of (9.312) yields the following eigenvalues:

$$\lambda_1 = -\sqrt{\frac{e^2\hbar^2 B^2}{4\mu^2 c^2} + 18e^2\mathcal{E}^2 a_0^2}, \quad \lambda_2 = \lambda_3 = 0, \quad \lambda_4 = \sqrt{\frac{e^2\hbar^2 B^2}{4\mu^2 c^2} + 18e^2\mathcal{E}^2 a_0^2}. \tag{9.313}$$

Finally, the energy levels of the $n = 2$ states are given to first-order approximation by

$$E_{2_1}^{(1)} = -\frac{\mathcal{R}}{4} - \sqrt{\frac{e^2\hbar^2 B^2}{4\mu^2 c^2} + 18e^2\mathcal{E}^2 a_0^2}, \qquad E_{2_2}^{(1)} = -\frac{\mathcal{R}}{4}, \tag{9.314}$$

$$E_{2_3}^{(1)} = -\frac{\mathcal{R}}{4}, \qquad E_{2_4}^{(1)} = -\frac{\mathcal{R}}{4} + \sqrt{\frac{e^2\hbar^2 B^2}{4\mu^2 c^2} + 18e^2\mathcal{E}^2 a_0^2}. \tag{9.315}$$

So the external electric and magnetic fields have lifted the degeneracy of the $n = 2$ level only partially.

Problem 9.5

A system, with an unperturbed Hamiltonian $\hat{H}_0$, is subject to a perturbation $\hat{H}_1$ with

$$\hat{H}_0 = E_0 \begin{pmatrix} 15 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 \\ 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 3 \end{pmatrix}, \qquad \hat{H}_1 = \frac{E_0}{100} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}.$$

(a) Find the eigenstates of the unperturbed Hamiltonian $\hat{H}_0$ as well as the exact eigenvalues of the total Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_p$.

(b) Find the eigenenergies of $\hat{H}$ to first-order perturbation. Compare them with the exact values obtained in (a).

Solution

(a) First, a diagonalization of $\hat{H}_0$ yields the eigenstates

$$\mid \phi_1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad \mid \phi_2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad \mid \phi_3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad \mid \phi_4\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}. \tag{9.316}$$

The values of the unperturbed energies are given by a nondegenerate value $E_1^{(0)} = 15E_0$ and a *threefold degenerate* value $E_2^{(0)} = E_3^{(0)} = E_4^{(0)} = 3E_0$.

The *exact* eigenvalues of $\hat{H}$ can be obtained by diagonalizing $\hat{H}$. Adopting the notation $\lambda = 1/100$, we can write the secular equation as

$$\begin{vmatrix} 15E_0 - E & 0 & 0 & 0 \\ 0 & 3E_0 - E & \lambda E_0 & 0 \\ 0 & \lambda E_0 & 3E_0 - E & 0 \\ 0 & 0 & 0 & 3E_0 - E \end{vmatrix} = 0 \tag{9.317}$$

or

$$(15E_0 - E)(3E_0 - E)\left[(3E_0 - E)^2 - \lambda^2 E_0^2\right] = 0, \tag{9.318}$$

which in turn leads to the *exact* values of the eigenenergies:

$$E_1 = 15E_0, \quad E_2 = 3E_0, \quad E_3 = (3-\lambda)E_0, \quad E_4 = (3+\lambda)E_0. \tag{9.319}$$

(b) To calculate the energy eigenvalues of $\hat{H}$ to first-order degenerate perturbation, and since $\hat{H}_0$ has one nondegenerate eigenvalue, $15E_0$, and a threefold degenerate eigenvalue, $3E_0$, we need to make use of both nondegenerate and degenerate perturbative treatments. First, let us focus on the nondegenerate state; its energy is given by

$$\begin{aligned} E_1 &= 15E_0 + \langle \phi_1 \mid \hat{H}_1 \mid \phi_1 \rangle \\ &= 15E_0 + \frac{E_0}{100}(1\ 0\ 0\ 0)\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & \lambda E_0 & 0 \\ 0 & \lambda E_0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \\ &= 15E_0. \end{aligned} \tag{9.320}$$

This is identical with the *exact* eigenvalue (9.319) obtained in (a).

Second, to find the degenerate states, we need to diagonalize the matrix

$$V = \begin{pmatrix} V_{11} & V_{12} & V_{13} \\ V_{21} & V_{22} & V_{23} \\ V_{31} & V_{32} & V_{33} \end{pmatrix}, \tag{9.321}$$

where

$$V_{11} = \langle \phi_2 \mid \hat{H}_p \mid \phi_2 \rangle = (0\ 1\ 0\ 0)\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & \lambda E_0 & 0 \\ 0 & \lambda E_0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} = 0, \tag{9.322}$$

$$V_{12} = \langle \phi_2 \mid \hat{H}_p \mid \phi_3 \rangle = (0\ 1\ 0\ 0)\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & \lambda E_0 & 0 \\ 0 & \lambda E_0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} = \lambda E_0, \tag{9.323}$$

$$V_{13} = \langle \phi_2 \mid \hat{H}_p \mid \phi_4 \rangle = (0\ 1\ 0\ 0)\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & \lambda E_0 & 0 \\ 0 & \lambda E_0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} = 0. \tag{9.324}$$

Similarly, we can show that

$$V_{21} = \langle \phi_3 \mid \hat{H}_p \mid \phi_2 \rangle = \lambda E_0, \quad V_{22} = \langle \phi_3 \mid \hat{H}_p \mid \phi_3 \rangle = 0, \quad V_{23} = \langle \phi_3 \mid \hat{H}_p \mid \phi_4 \rangle = 0, \tag{9.325}$$

$$V_{31} = \langle \phi_4 \mid \hat{H}_p \mid \phi_2 \rangle = 0, \quad V_{32} = \langle \phi_4 \mid \hat{H}_p \mid \phi_3 \rangle = 0, \quad V_{33} = \langle \phi_4 \mid \hat{H}_p \mid \phi_4 \rangle = 0. \tag{9.326}$$

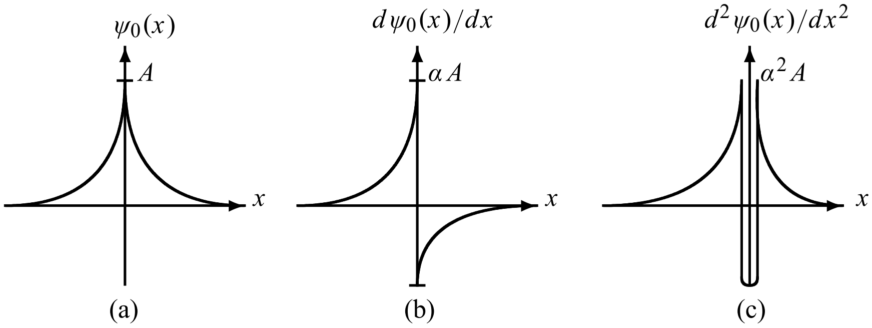

Figure 9.9 Shapes of $\psi_0(x) = Ae^{-\alpha|x|}$, $d\psi_0(x)/dx$, and $d^2\psi_0(x)/dx^2$.

So the diagonalization of

$$V = \begin{pmatrix} 0 & \lambda E_0 & 0 \\ \lambda E_0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{9.327}$$

leads to the corrections $E_2^{(1)} = 0$, $E_3^{(1)} = \lambda E_0$, and $E_4^{(1)} = -\lambda E_0$. Thus, the energy eigenvalues to first-order degenerate perturbation are

$$E_2 = E_2^{(0)} + E_2^{(1)} = 3E_0, \qquad E_3 = E_3^{(0)} + E_3^{(1)} = (3 - \lambda)E_0, \tag{9.328}$$

$$E_4 = E_4^{(0)} + E_4^{(1)} = (3 + \lambda)E_0. \tag{9.329}$$

These are indeed identical with the *exact* eigenenergies (9.319) obtained in (a).

Problem 9.6
Use the variational method to estimate the energy of the ground state of a one-dimensional harmonic oscillator by making use of the following two trial functions:
(a) $\psi_0(x, \alpha) = Ae^{-\alpha|x|}$, (b) $\psi_0(x, \alpha) = A/(x^2 + \alpha)$,
where α is a positive real number and where A is the normalization constant.

Solution
(a) This wave function, whose shape is displayed in Figure 9.9a, is quite different from a Gaussian: it has a cusp at $x = 0$; hence its first derivative is discontinuous at $x = 0$.

The normalization constant A can be calculated at once:

$$\langle \psi_0 \mid \psi_0 \rangle = A^2 \int_{-\infty}^{0} e^{2\alpha x} dx + A^2 \int_0^{\infty} e^{-2\alpha x} dx = 2A^2 \int_0^{\infty} e^{-2\alpha x} dx = \frac{A^2}{\alpha}; \tag{9.330}$$

hence $A = \sqrt{\alpha}$. To find $E_0(\alpha)$ we need to calculate the potential and the kinetic terms. Using the integral $\int_0^{+\infty} x^n e^{-ax} dx = n!/a^{n+1}$ we can easily calculate the potential term:

$$\langle \psi_0 | V(x) \mid \psi_0 \rangle = \frac{1}{2} m\omega^2 A^2 \int_{-\infty}^{+\infty} x^2 e^{-2\alpha|x|} dx = m\omega^2 A^2 \int_0^{+\infty} x^2 e^{-2\alpha x} dx = \frac{m\omega^2}{4\alpha^2}. \tag{9.331}$$

But the kinetic energy term $-(\hbar^2/2m)\langle\psi_0|d^2/dx^2|\psi_0\rangle$ is quite tricky to calculate. Since the first derivative of $\psi_0(x)$ is discontinuous at $x = 0$, a careless, straightforward calculation of $\langle\psi_0|d^2/dx^2|\psi_0\rangle$, which makes use of (9.123), leads to a negative kinetic energy:

$$\begin{aligned}
-\frac{\hbar^2}{2m}\left\langle\psi_0\left|\frac{d^2}{dx^2}\right|\psi_0\right\rangle &= -\frac{\hbar^2}{2m}A^2\int_{-\infty}^{+\infty} e^{-\alpha|x|}\frac{d^2e^{-\alpha|x|}}{dx^2}dx \\
&= -\frac{\hbar^2}{m}A^2\int_0^{+\infty} e^{-\alpha x}\frac{d^2e^{-\alpha x}}{dx^2}dx \\
&= -\frac{\hbar^2\alpha^2}{m}A^2\int_0^{+\infty} e^{-2\alpha x}dx = -\frac{\hbar^2\alpha^2}{2m}. \qquad (9.332)
\end{aligned}$$

So when the first derivative of the wave function is discontinuous, the correct way to calculate the kinetic energy term is by using (9.124):

$$\begin{aligned}
-\frac{\hbar^2}{2m}\left\langle\psi_0\left|\frac{d^2}{dx^2}\right|\psi_0\right\rangle &= \frac{\hbar^2}{2m}A^2\int_{-\infty}^{+\infty}\left|\frac{de^{-\alpha|x|}}{dx}\right|^2 dx = \frac{\hbar^2\alpha^2}{2m}A^2\int_{-\infty}^{+\infty} e^{-2\alpha|x|}dx \\
&= \frac{\hbar^2\alpha^2}{2m}, \qquad (9.333)
\end{aligned}$$

because $A^2\int_{-\infty}^{+\infty} e^{-2\alpha|x|}dx = 1$.

Why do expressions (9.332) and (9.333) yield different results? The reason is that the correct expression of $d^2e^{-\alpha|x|}/dx^2$ must involve a delta function (Figures 9.9a and 9.9b). That is, the correct form of $d\psi(x)/dx$ is given by

$$\frac{d\psi_0(x)}{dx} = A\frac{de^{-\alpha|x|}}{dx} = -\alpha\psi_0(x)\frac{d|x|}{dx} = -\alpha\psi_0(x)\begin{cases} -1, & x < 0, \\ 1, & x > 0. \end{cases} \qquad (9.334)$$

or

$$\frac{d\psi_0(x)}{dx} = -\alpha\left[\Theta(x) - \Theta(-x)\right]\psi_0(x), \qquad (9.335)$$

where $\Theta(x)$ is the Heaviside function

$$\Theta(x) = \begin{cases} 0, & x < 0, \\ 1, & x > 0. \end{cases}. \qquad (9.336)$$

The second derivative of $\psi_0(x)$ therefore contains a delta function:

$$\frac{d^2\psi_0(x)}{dx^2} = \frac{d}{dx}\left\{-\alpha\left[\Theta(x) - \Theta(-x)\right]\psi_0(x)\right\}, \qquad (9.337)$$

and since

$$\frac{d\Theta(x)}{dx} = \delta(x), \qquad \left[\Theta(x) - \Theta(-x)\right]^2 = 1, \qquad (9.338)$$

and since $\delta(x) = \delta(-x)$, we have

$$\begin{aligned}
\frac{d^2\psi_0(x)}{dx^2} &= \alpha^2\left[\Theta(x) - \Theta(-x)\right]^2\psi_0(x) - \alpha\left[\delta(x) + \delta(-x)\right]\psi_0(x) \\
&= \alpha^2\psi_0(x) - 2\alpha\psi_0(x)\delta(x). \qquad (9.339)
\end{aligned}$$

So the substitution of (9.339) into (9.332) leads to the same (correct) expression as (9.333):

$$\begin{aligned}
-\frac{\hbar^2}{2m}\left\langle \psi_0 \left| \frac{d^2}{dx^2} \right| \psi_0 \right\rangle &= -\frac{\hbar^2}{2m}\int_{-\infty}^{+\infty} \psi_0^*(x)\frac{d^2\psi_0(x)}{dx^2}dx \\
&= -\frac{\hbar^2}{2m}\int_{-\infty}^{+\infty} \psi_0^*(x)\left[\alpha^2\psi_0(x) - 2\alpha\,\psi_0(x)\delta(x)\right]dx \\
&= -\frac{\hbar^2}{2m}\alpha^2 + \frac{\hbar^2}{m}\alpha\,|\psi_0(0)|^2 = -\frac{\hbar^2}{2m}\alpha^2 + \frac{\hbar^2}{m}\alpha^2 \\
&= \frac{\hbar^2}{2m}\alpha^2. \qquad (9.340)
\end{aligned}$$

Now, adding (9.331) and (9.340), we get

$$E_0(\alpha) = \frac{\hbar^2}{2m}\alpha^2 + \frac{m\omega^2}{4\alpha^2}. \qquad (9.341)$$

The minimization of $E_0(\alpha)$,

$$0 = \frac{\partial E_0(\alpha)}{\partial\alpha} = \frac{\hbar^2}{m}\alpha_0 - \frac{m\omega^2}{2\alpha_0^3}, \qquad (9.342)$$

leads to $\alpha_0^2 = m\omega/(\sqrt{2}\hbar)$ which, when inserted into (9.341), leads to

$$E_0(\alpha_0) = \frac{\hbar^2}{2m}\frac{m\omega}{\sqrt{2}\hbar} + \frac{m\omega^2}{4}\frac{\sqrt{2}\hbar}{m\omega} = \frac{\hbar\omega}{\sqrt{2}} = 0.707\hbar\omega. \qquad (9.343)$$

This inaccurate result was expected; it is due to the cusp at $x = 0$.

(b) We can show that the normalization constant A is given by $A = (4\alpha^3/\pi^2)^{1/4}$. Unlike $Ae^{-\alpha|x|}$, the first derivative of the trial $A/(1 + x^2)$ is continuous; hence we can use (9.123) to calculate the kinetic energy term. The ground state energy is given by

$$\begin{aligned}
E_0(\alpha) &= \left\langle \psi_0(\alpha)|\hat{H}|\psi_0(\alpha)\right\rangle \\
&= A^2\int_{-\infty}^{+\infty} \frac{1}{x^2+\alpha}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2\right)\frac{1}{x^2+\alpha}dx \\
&= -\frac{A^2\hbar^2}{2m}\int_{-\infty}^{+\infty} \frac{6x^2-2\alpha}{(x^2+\alpha)^4}dx + \frac{1}{2}m\omega^2A^2\int_{-\infty}^{+\infty}\frac{x^2}{(x^2+\alpha)^2}dx \\
&= \frac{\hbar^2}{4m\alpha} + \frac{1}{2}m\omega^2\alpha. \qquad (9.344)
\end{aligned}$$

The minimization of $E_0(\alpha)$ with respect to α (i.e., $\partial E(\alpha)/\partial\alpha = 0$) yields $\alpha_0 = \hbar/(\sqrt{2}m\omega)$ which, when inserted into (9.344), leads to

$$E_0(\alpha_0) = \frac{\hbar\omega}{\sqrt{2}}. \qquad (9.345)$$

This energy, which is larger than the exact value $\hbar\omega/2$ by a factor of $\sqrt{2}$, is similar to that of part (a); this is a pure coincidence. The size of this error is due to the fact that the trial function $A/(x^2+\alpha)$ is not a good approximation to the exact wave function, which has a Gaussian form.

Problem 9.7

For a particle of mass m moving in a one-dimensional box with walls at $x = 0$ and $x = L$, use the variational method to estimate

(a) its ground state energy and

(b) its first excited state energy.

Solution

The exact solutions of this problem are known: $E_n^{exact} = \pi^2\hbar^2 n^2/(2mL^2)$.

(a) The trial function for the ground state must vanish at the walls, it must have no nodes, and must be symmetric (i.e., even) with respect to $x = L/2$. These three requirements can be satisfied by the following parabolic trial function:

$$\psi_0(x) = x(L - x); \tag{9.346}$$

no scale parameter is needed here. Since no parameter is involved, we can calculate the energy directly (no variation is required): $E_0 = \langle\psi_0|\hat{H} \mid \psi_0\rangle/\langle\psi_0 \mid \psi_0\rangle$, where

$$\langle\psi_0 \mid \psi_0\rangle = \int_0^L \psi_0^2(x)\, dx = \int_0^L x^2(L^2 - 2Lx + x^2)\, dx = \frac{1}{30}L^5, \tag{9.347}$$

and

$$\langle\psi_0|\hat{H} \mid \psi_0\rangle = \frac{\hbar^2}{2m}\int_0^L \left(\frac{d\psi_0(x)}{dx}\right)^2 dx = \frac{\hbar^2}{2m}\int_0^L (L^2 - 4Lx + 4x^2)\, dx = \frac{\hbar^2 L^3}{6m}. \tag{9.348}$$

Thus, the ground state energy is given by

$$E_0^{VM} = \frac{\langle\psi_0|\hat{H} \mid \psi_0\rangle}{\langle\psi_0 \mid \psi_0\rangle} = 10\frac{\hbar^2}{2mL^2}. \tag{9.349}$$

This is a very accurate result, for it is higher than the exact result by a mere 1%:

$$E_0^{VM} = \frac{10}{\pi^2}E^{exact}. \tag{9.350}$$

(b) The properties of the exact wave function of the first excited state are known: it has one node at $x = L/2$ and must be odd with respect to $x = L/2$; this last property makes it orthogonal to the ground state which is even about $L/2$. Let us try a polynomial function. Since the wave function vanishes at $x = 0$, $L/2$, and L, the trial function must be at least cubic. The following polynomial function satisfies all these conditions:

$$\psi_1(x) = x\left(x - \frac{L}{2}\right)(x - L). \tag{9.351}$$

Again, no scale parameter is needed.

To calculate E_1^{VM}, we need to find

$$\langle\psi_1 \mid \psi_1\rangle = \int_0^L \psi_1^2(x)dx = \int_0^L x^2\left(x - \frac{L}{2}\right)^2(x - L)^2 dx = \frac{1}{840}L^7 \tag{9.352}$$

and

$$\begin{aligned}\langle\psi_1|\hat{H}\mid\psi_1\rangle &= \frac{\hbar^2}{2m}\int_0^L\left(\frac{d\psi_1(x)}{dx}\right)^2 dx = \frac{\hbar^2}{2m}\int_0^L\left(3x^2-3Lx+\frac{L^2}{2}\right)^2 dx \\ &= \frac{\hbar^2L^5}{40m}. \end{aligned} \tag{9.353}$$

Dividing the previous two expressions, we obtain the energy of the first excited state:

$$E_1^{VM} = \frac{\langle\psi_1|\hat{H}\mid\psi_1\rangle}{\langle\psi_1\mid\psi_1\rangle} = 42\frac{\hbar^2}{2mL^2}. \tag{9.354}$$

This too is a very accurate result; since $E_1^{exact} = (2\pi)^2\hbar^2/(2mL^2)$ we can write E_1^{VM} as $E_1^{VM} = 42E_1^{exact}/(2\pi)^2$; hence E_1^{VM} is higher than E_1^{exact} by 6%.

Problem 9.8
Consider an infinite, one-dimensional potential well of length L, with walls at $x=0$ and $x=L$, that is modified at the bottom by a perturbation $V_p(x)$:

$$V(x) = \begin{cases} 0, & 0<x<L, \\ \infty, & \text{elsewhere,} \end{cases} \qquad V_p(x) = \begin{cases} V_0, & 0\le x\le L/2, \\ 0, & \text{elsewhere,} \end{cases}$$

where $V_0 \ll 1$.

(a) Using first-order perturbation theory, calculate the energy E_n.

(b) Calculate the energy E_n in the WKB approximation. Compare this energy with the expression obtained in (a).

Solution
The exact energy E_n^{exact} and wave function $\phi_n(x)$ for a potential well are given by

$$E_n^{exact} = \frac{\pi^2\hbar^2}{2mL^2}n^2, \qquad \phi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right).$$

(a) Since the first-order correction to the energy caused by the perturbation $V_p(x)$ is given by

$$\begin{aligned} E_n^{(1)} = \langle\phi_n\mid V_p\mid\phi_n\rangle &= \frac{2}{L}V_0\int_0^{L/2}\sin^2\left(\frac{n\pi x}{L}\right)dx \\ &= \frac{1}{L}V_0\int_0^{L/2}\left[1-\cos\left(\frac{2n\pi x}{L}\right)\right]dx = \frac{V_0}{2}; \end{aligned} \tag{9.355}$$

hence the energy is given to first-order perturbation by

$$E_n^{PT} = \frac{\pi^2\hbar^2}{2mL^2}n^2 + \frac{V_0}{2}. \tag{9.356}$$

(b) Since this potential has two rigid walls, the energy within the WKB approximation needs to be extracted from the quantization condition $\int_0^L p(E_n,x)\,dx = n\pi\hbar$, where

$$\begin{aligned}\int_0^L p(E_n,\, x)\,dx &= \sqrt{2m(E_n-V_0)}\int_0^{L/2}dx + \sqrt{2mE_n}\int_{L/2}^L dx \\ &= \frac{L}{2}\sqrt{2m}\left(\sqrt{E_n-V_0}+\sqrt{E_n}\right); \end{aligned} \tag{9.357}$$

hence $L\sqrt{2m}\left(\sqrt{E_n - V_0} + \sqrt{E_n}\right) = 2n\pi\hbar$ or

$$\sqrt{E_n - V_0} + \sqrt{E_n} = \frac{2n\pi\hbar}{L\sqrt{2m}}. \tag{9.358}$$

Squaring both sides of this equation and using the notation $\alpha_n = 2n^2\pi^2\hbar^2/(mL^2)$, we have

$$2\sqrt{E_n(E_n - V_0)} = \alpha_n - 2E_n + V_0. \tag{9.359}$$

Squaring both sides of this equation, we obtain

$$4E_n^2 - 4E_nV_0 = \alpha_n^2 + 4E_n^2 + V_0^2 - 4\alpha_n E_n + 2\alpha_n V_0 - 4E_nV_0, \tag{9.360}$$

which, solving for E_n, leads to

$$E_n = \frac{\alpha_n}{4} + \frac{V_0}{2} + \frac{V_0^2}{4\alpha_n} \tag{9.361}$$

or

$$E_n^{WKB} = \frac{\pi^2\hbar^2}{2mL^2}n^2 + \frac{V_0}{2} + \frac{mL^2V_0^2}{8\pi^2\hbar^2}\frac{1}{n^2}. \tag{9.362}$$

When $n \gg 1$, and since V_0 is very small, the WKB energy relation (9.362) gives back the expression (9.356) that was derived from a first-order perturbative treatment:

$$E_n^{WKB} \simeq E_n^{PT} = \frac{\pi^2\hbar^2}{2mL^2}n^2 + \frac{V_0}{2}.$$

Problem 9.9

Consider a particle of mass m that is bouncing vertically and elastically on a reflecting hard floor where $V(z) = \begin{cases} mgz, & z > 0, \\ +\infty, & z \le 0, \end{cases}$ and g is the gravitational constant.

(a) Use the variational method to estimate the ground state energy of this particle.

(b) Use the WKB method to estimate the ground state energy of this particle.

(c) Compare the results of (a) and (b) with the exact ground state energy.

Solution

(a) The ground state wave function of this particle has no nodes and must vanish at $z = 0$ and be finite as $z \to +\infty$. The following trial function satisfies these conditions:

$$\psi_0(z,\ \alpha) = Aze^{-\alpha z}, \tag{9.363}$$

where α is a parameter and A is the normalization constant. We can show that $A = 2\alpha^{3/2}$ and hence

$$\psi_0(z,\ \alpha) = 2\sqrt{\alpha^3}ze^{-\alpha z}. \tag{9.364}$$

The energy is given by

$$\begin{aligned} E_0^{VM}(\alpha) &= 4\alpha^3\int_0^{+\infty} ze^{-\alpha z}\left[-\frac{\hbar^2}{2m}\frac{d^2}{dz^2} + mgz\right]ze^{-\alpha z}\,dz \\ &= 4\alpha^3\frac{\hbar^2}{2m}\int_0^{+\infty}\left(2\alpha z - \alpha^2z^2\right)e^{-2\alpha z}\,dz + 4\alpha^3 mg\int_0^{+\infty} z^3e^{-2\alpha z}\,dz \\ &= 2\alpha^3\frac{\hbar^2}{m}\left(\frac{1}{2\alpha} - \frac{1}{4\alpha}\right) + 4mg\alpha^3\frac{3}{8\alpha^4}, \end{aligned} \tag{9.365}$$

or

$$E_0^{VM}(\alpha) = \frac{\hbar^2}{2m}\alpha^2 + \frac{3}{2\alpha}mg. \tag{9.366}$$

The minimization of $E_0(\alpha)$ yields $\alpha_0 = (3m^2g/2\hbar^2)^{1/3}$ and hence

$$E_0^{VM}(\alpha_0) = \frac{3}{2}\left(\frac{9}{2}\right)^{1/3}\left(\frac{1}{2}mg^2\hbar^2\right)^{1/3}. \tag{9.367}$$

(b) Since this potential has one rigid wall at $x = 0$, the correct quantization rule is given by (9.224): $\int_0^{E/mg} p\,dz = (n + \frac{3}{4})\pi\hbar$; the turning point occurs at $E = mgz$ and hence $z = E/mg$. Now, since $E = p^2/2m + mgz$ we have $p(E, z) = \sqrt{2mE}\sqrt{1 - mgz/E}$, and therefore

$$\int_0^{E/mg} p(E_n, z)\,dz = \sqrt{2mE}\int_0^{E/mg}\sqrt{1 - \frac{mg}{E}z}\,dz = \sqrt{2mE}\frac{2E}{3mg} = \sqrt{\frac{8E^3}{9mg^2}}. \tag{9.368}$$

Inserting this relation into the quantization condition $\int_0^{E/mg} p\,dz = (n + \frac{3}{4})\pi\hbar$ gives

$$\sqrt{\frac{8E^3}{9mg^2}} = \left(n + \frac{3}{4}\right)\pi\hbar, \tag{9.369}$$

and we obtain the WKB approximation for the energy:

$$E_n^{WKB} = \left[\frac{9\pi^2}{8}mg^2\pi^2\hbar^2\left(n + \frac{3}{4}\right)^2\right]^{1/3}. \tag{9.370}$$

Hence the ground state energy is given by

$$E_0^{WKB} = \frac{3}{4}\left(3\pi^2\right)^{1/3}\left(\frac{1}{2}mg^2\hbar^2\right)^{1/3}. \tag{9.371}$$

(c) Recall that the *exact* ground state energy, calculated in Problem 4.18, page 275, for a particle of mass m moving in the potential $V(z) = mgz$ is given by

$$E_0^{exact} = 2.338\left(\frac{1}{2}mg^2\hbar^2\right)^{1/3}. \tag{9.372}$$

Combining this relation with (9.367) and (9.371), we see that the variational method overestimates the energy by a 5.9% error, while the WKB method underestimates it by a 0.8% error:

$$E_0^{VM} = \frac{3}{2}\left(\frac{9}{2}\right)^{1/3}\frac{E_0^{exact}}{2.338} \simeq 1.059E_0^{exact}, \tag{9.373}$$

$$E_0^{WKB} = \frac{3}{4}\left(3\pi^2\right)^{1/3}\frac{E_0^{exact}}{2.338} \simeq 0.992E_0^{exact}. \tag{9.374}$$

The variational method has given a reasonably accurate result because we succeeded quite well in selecting the trial function. As for the WKB method, it has given a very accurate result because we have used the correct quantization rule (9.224). Had we used the quantization rule (9.210), which contains a factor of $\frac{1}{2}$ instead of $\frac{1}{4}$ in (9.224), the WKB method would have given a very inaccurate result with a 24.3% error, i.e., $E_0^{WKB} \simeq 0.757E_0^{exact}$.

Problem 9.10

Using first-order perturbation theory, and ignoring the spin of the electron, calculate the energy of the 2p level of a hydrogen atom when placed in a *weak* quadrupole field whose principal axes are along the xyz axes: $\hat{H}_p = \sum_{\mu=-2}^{\mu=2} Q_\mu r^2 Y_{2\mu}(\Omega)$, where Q_μ are real numbers, with $Q_{-1} = Q_1 = 0$ and $Q_{-2} = Q_2$, and $Y_{2\mu}(\Omega)$ are spherical harmonics.

Solution

In the absence of the field, the energy levels of the $\mid 2,\ 1,\ m\rangle$ states are threefold degenerate: $\mid 2,\ 1,\ -1\rangle$, $\mid 2,\ 1,\ 0\rangle$, and $\mid 2,\ 1,\ 1\rangle$, and hence correspond to the same energy $E_2 = -\mathcal{R}/4$, where $\mathcal{R} = 13.6\,\text{eV}$ is the Rydberg constant.

When the quadrupole field is turned on, and since Q_{-2}, Q_0, and Q_2 are small, we can treat the quadrupole interaction $\hat{H}_p = Q_{-2}r^2Y_{2-2}(\Omega) + Q_0r^2Y_{20}(\Omega) + Q_2r^2Y_{22}(\Omega)$ as a perturbation. To calculate the p split, we need to use degenerate perturbation theory, which, in a first step, requires calculating the matrix

$$\begin{pmatrix} \langle 2,\ 1,\ -1|\hat{H}_p \mid 2,\ 1,\ -1\rangle & \langle 2,\ 1,\ -1|\hat{H}_p \mid 2,\ 1,\ 0\rangle & \langle 2,\ 1,\ -1|\hat{H}_p \mid 2,\ 1,\ 1\rangle \\ \langle 2,\ 1,\ 0|\hat{H}_p \mid 2,\ 1,\ -1\rangle & \langle 2,\ 1,\ 0|\hat{H}_p \mid 2,\ 1,\ 0\rangle & \langle 2,\ 1,\ 0|\hat{H}_p \mid 2,\ 1,\ 1\rangle \\ \langle 2,\ 1,\ 1|\hat{H}_p \mid 2,\ 1,\ -1\rangle & \langle 2,\ 1,\ 1|\hat{H}_p \mid 2,\ 1,\ 0\rangle & \langle 2,\ 1,\ 1|\hat{H}_p \mid 2,\ 1,\ 1\rangle \end{pmatrix}, \tag{9.375}$$

where

$$\langle 2,\ 1,\ m'|\hat{H}_p \mid 2,\ 1,\ m\rangle = \langle 2,\ 1|r^2|2,\ 1\rangle\langle 1,\ m'|Q_{-2}Y_{2-2} + Q_0Y_{20} + Q_2Y_{22}|1,\ m\rangle. \tag{9.376}$$

The radial part is easy to obtain (Chapter 6):

$$\langle n,\ l|r^2|n,\ l\rangle = \int_0^{+\infty} r^4\,|R_{nl}|^2\,dr = \frac{1}{2}n^2\left[5n^2 + 1 - 3l(l+1)\right]a_0^2; \tag{9.377}$$

hence

$$\langle 2,\ 1|r^2|2,\ 1\rangle = 30a_0^2. \tag{9.378}$$

As for the angular part, it can be inferred from the Wigner–Eckart theorem:

$$\langle l',\ m'|Y_{2\mu}|1,\ m\rangle = \langle l, 2;\ m, \mu|l',\ m'\rangle\langle l' \parallel Y_2 \parallel 1\rangle; \tag{9.379}$$

the reduced matrix element $\langle l' \parallel Y_2 \parallel 1\rangle$ was calculated in Chapter 7: $\langle l' \parallel Y_2 \parallel 1\rangle = \sqrt{5/4\pi}\sqrt{(2l+1)/(2l'+1)}\langle l, 2;\ 0, 0|l',\ 0\rangle$ and hence

$$\langle l',\ m'|Y_{2\mu}|1,\ m\rangle = \sqrt{\frac{5}{4\pi}}\sqrt{\frac{2l+1}{2l'+1}}\langle l, 2;\ 0, 0|l',\ 0\rangle\langle l, 2;\ m, \mu|l',\ m'\rangle. \tag{9.380}$$

Using the coefficients $\langle l, 2;\ m, 0|l,\ m\rangle = [3m^2 - l(l+1)]/\sqrt{l(2l-1)(l+1)(2l+3)}$ and $\langle l, 2;\ m, \mp 2,\ \pm 2|l,\ m\rangle = \sqrt{\frac{3(l\pm m-1)(l\pm m)(l\mp m+1)(l\mp m+2)}{2l(2l-1)(l+1)(2l+3)}}$, we have

$$\langle 1,\ -1 \mid Y_{2-2} \mid 1,\ 1\rangle = \langle 1,\ 1 \mid Y_{22} \mid 1,\ -1\rangle = -\sqrt{\frac{3}{10\pi}}, \tag{9.381}$$

$$\langle 1,\ -1 \mid Y_{20} \mid 1,\ -1\rangle = \langle 1,\ 1 \mid Y_{20} \mid 1,\ 1\rangle = -\frac{1}{\sqrt{20\pi}}, \tag{9.382}$$

$$\langle 1,\ 0 \mid Y_{20} \mid 1,\ 0\rangle = \frac{1}{\sqrt{5\pi}}. \tag{9.383}$$

These expressions can also be obtained from the following relations:

$$\int Y_{lm}^*(\Omega) Y_{20}(\Omega) Y_{lm}(\Omega)\, d\Omega = \sqrt{\frac{5}{4\pi}} \frac{l(l+1) - 3m^2}{(2l-1)(2l+3)}, \tag{9.384}$$

$$\begin{aligned}\int Y_{lm+2}^*(\Omega) Y_{22}(\Omega) Y_{lm}(\Omega) d\Omega &= \int Y_{lm}^*(\Omega) Y_{2-2}(\Omega) Y_{lm+2}(\Omega) d\Omega \\ &= \sqrt{\frac{15}{8\pi}} \frac{\sqrt{(l-m-1)(l-m)(l+m+1)(l+m+2)}}{(2l-1)(2l+3)}.\end{aligned} \tag{9.385}$$

Combining (9.376) to (9.383) we can write the matrix (9.375) as

$$30a_0^2 \begin{pmatrix} -\frac{Q_0}{\sqrt{20\pi}} & 0 & -Q_2\sqrt{\frac{3}{10\pi}} \\ 0 & \frac{Q_0}{\sqrt{5\pi}} & 0 \\ -Q_2\sqrt{\frac{3}{10\pi}} & 0 & -\frac{Q_0}{\sqrt{20\pi}} \end{pmatrix}. \tag{9.386}$$

The diagonalization of this matrix leads to the following eigenvalues:

$$E_1^{(1)} = -30\frac{a_0^2}{\sqrt{10\pi}} \left(\frac{Q_0}{\sqrt{2}} + Q_2\sqrt{3}\right), \tag{9.387}$$

$$E_2^{(1)} = 30\frac{Q_0 a_0^2}{\sqrt{5\pi}}, \tag{9.388}$$

$$E_3^{(1)} = 30\frac{a_0^2}{\sqrt{10\pi}} \left(-\frac{Q_0}{\sqrt{2}} + Q_2\sqrt{3}\right). \tag{9.389}$$

Thus, to first-order perturbation theory, the energies of the p level are given by

$$E_{21} = -\frac{\mathcal{R}}{4} - 30\frac{a_0^2}{\sqrt{10\pi}} \left(\frac{Q_0}{\sqrt{2}} + Q_2\sqrt{3}\right), \tag{9.390}$$

$$E_{22} = -\frac{\mathcal{R}}{4} + 30\frac{Q_0 a_0^2}{\sqrt{5\pi}}, \tag{9.391}$$

$$E_{23} = -\frac{\mathcal{R}}{4} + 30\frac{a_0^2}{\sqrt{10\pi}} \left(-\frac{Q_0}{\sqrt{2}} + Q_2\sqrt{3}\right). \tag{9.392}$$

So the quadrupole interaction has lifted all the degeneracies of the p level.

Problem 9.11
Two protons, located on the z-axis and separated by a distance d (i.e., $\vec{r} = d\vec{k}$), are subject to a z-oriented magnetic field $\vec{B} = B\vec{k}$.

(a) Ignoring all interactions between the two protons, find the energy levels and stationary states of this system.

(b) Treating the dipole–dipole magnetic interaction energy between the protons,

$$\hat{H}_p = \frac{1}{r^3}\left[\vec{\mu}_1 \cdot \vec{\mu}_2 - 3\frac{(\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r})}{r^2}\right],$$

as a perturbation, calculate the energy using first-order perturbation theory.

Solution

(a) Since the magnetic moments of the protons are $\vec{\mu}_1 = 2\mu_0\vec{S}_1/\hbar$ and $\vec{\mu}_2 = 2\mu_0\vec{S}_2/\hbar$ where $\mu_0 = \hbar e/(2M_pc)$ is the proton magnetic moment, the Hamiltonian of the two-proton system, ignoring all the interactions between the two protons, is due to the interaction of the magnetic moments of the protons with the external magnetic field:

$$\hat{H}_0 = -(\vec{\mu}_1 + \vec{\mu}_2)\cdot\vec{B} = -\frac{2\mu_0}{\hbar}(\vec{S}_1 + \vec{S}_2)\cdot\vec{B} = -\frac{2\mu_0 B}{\hbar}\hat{S}_z. \tag{9.393}$$

As shown in Chapter 7, the eigenstates of a system consisting of two spin$-\frac{1}{2}$ particles are a triplet state and singlet state; the stationary eigenstates of $\hat{H}_0$ are therefore given by

$$\mid\chi_1\rangle = \mid 1,\ 1\rangle = \left|\frac{1}{2},\frac{1}{2};\ \frac{1}{2},\frac{1}{2}\right\rangle, \tag{9.394}$$

$$\mid\chi_2\rangle = |1,\ -1\rangle = \left|\frac{1}{2},\frac{1}{2};\ -\frac{1}{2},\ -\frac{1}{2}\right\rangle, \tag{9.395}$$

$$\mid\chi_3\rangle = |1,\ 0\rangle = \frac{1}{\sqrt{2}}\left[\left|\frac{1}{2},\frac{1}{2};\ \frac{1}{2},-\frac{1}{2}\right\rangle + \left|\frac{1}{2},\frac{1}{2};\ -\frac{1}{2},\frac{1}{2}\right\rangle\right], \tag{9.396}$$

$$\mid\chi_4\rangle = |0,\ 0\rangle = \frac{1}{\sqrt{2}}\left[\left|\frac{1}{2},\frac{1}{2};\ \frac{1}{2},-\frac{1}{2}\right\rangle - \left|\frac{1}{2},\frac{1}{2};\ -\frac{1}{2},\frac{1}{2}\right\rangle\right]. \tag{9.397}$$

The eigenenergies of $\mid\chi_1\rangle$, $\mid\chi_2\rangle$, $\mid\chi_3\rangle$, and $\mid\chi_4\rangle$ are respectively

$$E_1^{(0)} = -2\mu_0 B, \qquad E_2^{(0)} = 2\mu_0 B, \qquad E_3^{(0)} = E_4^{(0)} = 0. \tag{9.398}$$

So $\mid\chi_3\rangle$ and $\mid\chi_4\rangle$ are (doubly) degenerate, whereas $\mid\chi_1\rangle$ and $\mid\chi_2\rangle$ are not.

(b) To calculate the energy to first order, we need to calculate the matrix elements of $\hat{H}_p$: $\hat{H}_{P_{ij}} = \langle\chi_i|\hat{H}_p|\chi_j\rangle$, with $i,\ j = 1,\ 2,\ 3,\ 4$. For this, since $\vec{r} = d\vec{k}$, we have $\vec{\mu}_1\cdot\vec{r} = 2\mu_0 d\hat{S}_{1_z}/\hbar$ and $\vec{\mu}_2\cdot\vec{r} = 2\mu_0 d\hat{S}_{2_z}/\hbar$. Thus, we can write $\hat{H}_p$ as

$$\hat{H}_p = \frac{1}{r^3}\left[\vec{\mu}_1\cdot\vec{\mu}_2 - 3\frac{(\vec{\mu}_1\cdot\vec{r})(\vec{\mu}_2\cdot\vec{r})}{r^2}\right] = \frac{4\mu_0^2}{d^3\hbar^2}\left[\hat{\vec{S}}_1\cdot\hat{\vec{S}}_2 - 3\hat{S}_{1_z}\hat{S}_{2_z}\right]. \tag{9.399}$$

Using the relations

$$\begin{aligned} 2\vec{S}_1\cdot\vec{S}_2 \mid S,\ S_z\rangle &= \left[\left(\vec{S}_1 + \vec{S}_2\right)^2 - \vec{S}_1^2 - \vec{S}_1^2\right] \mid S,\ S_z\rangle \\ &= \hbar^2\left[S(S+1) - S_1(S_1+1) - S_2(S_2+1)\right] \mid S,\ S_z\rangle \\ &= \hbar^2\left[S(S+1) - \frac{3}{2}\right] \mid S,\ S_z\rangle, \end{aligned} \tag{9.400}$$

$$2\hat{S}_{1_z}\hat{S}_{2_z} \mid S,\ S_z\rangle = \left[\hat{S}_z{}^2 - \hat{S}_{1_z}{}^2\hat{S}_{2_z}{}^2\right] \mid S,\ S_z\rangle = \hbar^2\left(S_z^2 - \frac{1}{2}\right) \mid S,\ S_z\rangle, \tag{9.401}$$

along with (9.399), we can rewrite

$$\begin{aligned} \hat{H}_p \mid S,\ S_z\rangle &= \frac{2\mu_0^2}{d^3}\left[S(S+1) - \frac{3}{2} - 3\left(S_z^2 - \frac{1}{2}\right)\right] \mid S,\ S_z\rangle \\ &= \frac{2\mu_0^2}{d^3}\left[S(S+1) - 3S_z^2\right] \mid S,\ S_z\rangle. \end{aligned} \tag{9.402}$$

Since the values of S and S_z are given for the triplet state by $S = 1$, $S_z = -1, 0, 1$, and by $S = 0$, $S_z = 0$ for the singlet, the matrix elements of $\hat{H}_p$ are

$$E_1^{(1)} = \langle \chi_1 \mid \hat{H}_p \mid \chi_1 \rangle = -\frac{2\mu_0^2}{d^3}, \qquad E_2^{(1)} = \langle \chi_2 \mid \hat{H}_p \mid \chi_2 \rangle = -\frac{2\mu_0^2}{d^3}, \tag{9.403}$$

$$E_3^{(1)} = \langle \chi_3 \mid \hat{H}_p \mid \chi_3 \rangle = \frac{4\mu_0^2}{d^3}, \qquad E_4^{(1)} = \langle \chi_4 \mid \hat{H}_p \mid \chi_4 \rangle = 0. \tag{9.404}$$

All the other matrix elements of $\hat{H}_p$ are zero: $\langle \chi_i | \hat{H}_p | \chi_j \rangle = 0$ for $i \neq j$.

Finally, the energy levels of the two-proton system can be obtained at once from (9.398) along with (9.403) and (9.404):

$$E_1 = E_1^{(0)} + E_1^{(1)} = -2\mu_0 B - \frac{2\mu_0^2}{d^3}, \tag{9.405}$$

$$E_2 = E_2^{(0)} + E_2^{(1)} = 2\mu_0 B - \frac{2\mu_0^2}{d^3}, \tag{9.406}$$

$$E_3 = E_3^{(0)} + E_3^{(1)} = \frac{4\mu_0^2}{d^3}, \tag{9.407}$$

$$E_4 = E_4^{(0)} + E_4^{(1)} = 0. \tag{9.408}$$

So the dipole–dipole magnetic interaction has lifted the degeneracy of the energy levels in the two-proton system.

Problem 9.12

A spin $\frac{1}{2}$ particle of mass m, which is moving in an infinite, symmetric potential well $V(x)$ of length $2L$, is placed in an external *weak* magnetic field $\vec{B}$ with

$$V(x) = \begin{cases} 0, & -L \le x \le L, \\ \infty, & \text{otherwise,} \end{cases} \qquad \vec{B} = \begin{cases} -B\hat{z}, & -L \le x \le 0, \\ -B\hat{x}, & 0 \le x \le L. \end{cases}$$

Using first-order perturbation theory, calculate the energy of the nth excited state of this particle.

Solution

First, let us discuss the physics of this particle before placing it in a magnetic field. As seen in Chapter 4, the energy and wave function of a *spinless* particle of mass m moving in a symmetric potential well of length $2L$ are

$$E_n = \frac{\hbar^2 \pi^2}{8mL^2} n^2, \qquad \psi_n(x) = \frac{1}{\sqrt{L}} \begin{cases} \cos\left(\frac{n\pi x}{2L}\right), & n = 1, 3, 5, \ldots, \\ \sin\left(\frac{n\pi x}{2L}\right), & n = 2, 4, 6, \ldots. \end{cases} \tag{9.409}$$

When the spin of the particle is considered, its wave function is the product of a spacial part $\psi_n(x)$ and a spin part $|\chi_\pm\rangle$:

$$\psi_n^\pm(x) = |\chi_\pm\rangle \psi_n(x) = |\chi_\pm\rangle \begin{cases} \frac{1}{\sqrt{L}} \cos\left(\frac{n\pi x}{2L}\right), & n = 1, 3, 5, \ldots, \\ \frac{1}{\sqrt{L}} \sin\left(\frac{n\pi x}{2L}\right), & n = 2, 4, 6, \ldots, \end{cases} \tag{9.410}$$

where $|\chi_\pm\rangle$ represent the spinor fields corresponding to the spin-up and spin-down states, respectively:

$$|\chi_+\rangle = \left|\frac{1}{2},\frac{1}{2}\right\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad |\chi_-\rangle = \left|\frac{1}{2},-\frac{1}{2}\right\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{9.411}$$

Each energy level, $E_n = \hbar^2\pi^2 n^2/(8mL^2)$, of this particle is doubly degenerate, for it corresponds to two different states.

Let us now consider the case where the particle is placed in the magnetic field $\vec{B}$. The interaction between the external magnetic field and the particle's magnetic moment $\vec{\mu}$ is given by

$$\hat{H}_p = -\vec{\mu}\cdot\vec{B} = B\mu_0 \begin{cases} \sigma_z, & -L \le x \le 0, \\ \sigma_x, & 0 \le x \le L, \end{cases} \tag{9.412}$$

where we have made use of $\vec{\mu} = 2\mu_0\vec{S}/\hbar = \mu_0\vec{\sigma}$; recall that the matrices of σ_x and σ_z are

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{9.413}$$

To estimate the energy of this particle by means of the degenerate perturbation theory, we need to calculate first the matrix

$$\begin{pmatrix} \langle\psi_n^-|\hat{H}_p|\psi_n^-\rangle & \langle\psi_n^-|\hat{H}_p|\psi_n^+\rangle \\ \langle\psi_n^+|\hat{H}_p|\psi_n^-\rangle & \langle\psi_n^+|\hat{H}_p|\psi_n^+\rangle \end{pmatrix}, \tag{9.414}$$

where

$$\begin{aligned} \langle\psi_n^-|\hat{H}_p|\psi_n^-\rangle &= \int_{-L}^{0} |\psi_n(x)|^2 \langle\chi_-|\hat{H}_p|\chi_-\rangle\, dx + \int_0^L |\psi_n(x)|^2 \langle\chi_-|\hat{H}_p|\chi_-\rangle\, dx \\ &= \mu_0 B\left[\langle\chi_-|\sigma_z|\chi_-\rangle \int_{-L}^{0} |\psi_n(x)|^2\, dx + \langle\chi_-|\sigma_x|\chi_-\rangle \int_0^L |\psi_n(x)|^2\, dx\right]. \end{aligned} \tag{9.415}$$

Using $\int_{-L}^{0} |\psi_n(x)|^2\, dx = \int_0^L |\psi_n(x)|^2\, dx = \frac{1}{2}$ and since

$$\begin{aligned} \langle\chi_-|\sigma_z|\chi_-\rangle &= (0\ 1)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = -1, \\ \langle\chi_-|\sigma_x|\chi_-\rangle &= (0\ 1)\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0, \end{aligned} \tag{9.416}$$

we have

$$\langle\psi_n^-|\hat{H}_p|\psi_n^-\rangle = -\frac{\mu_0 B}{2}. \tag{9.417}$$

Following this procedure, we can obtain the remaining matrix elements of (9.414):

$$\frac{\mu_0 B}{2}\begin{pmatrix} -1 & 1 \\ 1 & 1 \end{pmatrix}. \tag{9.418}$$

The diagonalization of this matrix leads to

$$\left(-\frac{\mu_0 B}{2} - E^{(1)}\right)\left(\frac{\mu_0 B}{2} - E^{(1)}\right) - \left(\frac{\mu_0 B}{2}\right)^2 = 0, \tag{9.419}$$

or $E^{(1)} = \pm\mu_0 B/\sqrt{2}$. Thus, the energy of the *n*th excited state to first-order degenerate perturbation theory is given by

$$E_n = \frac{\hbar^2\pi^2}{8mL^2}n^2 \pm \frac{\mu_0 B}{\sqrt{2}}. \tag{9.420}$$

The magnetic field has completely removed the degeneracy of the energy spectrum of this particle.

Problem 9.13

Consider a particle of mass m moving in the potential $V(x) = \begin{cases} +\infty, & x \leq 0, \\ \frac{1}{2}m\omega^2x^2, & x > 0. \end{cases}$
Estimate the ground state energy of this particle using

(a) the variational method and (b) the WKB method.

Solution

(a) As seen in Problem 4.9, page 266, the ground state wave function of this potential must be selected from the harmonic oscillator wave functions that vanish at $x = 0$. Only the *odd* wave functions vanish at $x = 0$. So a trial function that, besides being zero at $x = 0$, is finite as $x \longrightarrow +\infty$ is given by

$$\psi_0(x,\ \alpha) = xe^{-\alpha x^2}. \tag{9.421}$$

Using the results

$$\langle\psi_0 \mid \psi_0\rangle = \int_0^{+\infty} x^2 e^{-2\alpha x^2}\,dx = \frac{1}{8\alpha}\sqrt{\frac{\pi}{2\alpha}}, \tag{9.422}$$

$$\left\langle\psi_0\left|\frac{1}{2}m\omega^2x^2\right|\psi_0\right\rangle = \frac{1}{2}m\omega^2\int_0^{+\infty} x^4 e^{-2\alpha x^2}\,dx = \frac{3m\omega^2}{64\alpha^2}\sqrt{\frac{\pi}{2\alpha}}, \tag{9.423}$$

$$\left\langle\psi_0\left|-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right|\psi_0\right\rangle = \frac{\hbar^2}{2m}\int_0^{+\infty}\left(3\alpha x^2 - 2\alpha^2x^4\right)e^{-2\alpha x^2}\,dx = \frac{3\hbar^2}{16m}\sqrt{\frac{\pi}{2\alpha}}, \tag{9.424}$$

we obtain the ground state energy

$$E_0(\alpha) = \frac{\langle\psi_0(\alpha)|\hat{H}|\psi_0(\alpha)\rangle}{\langle\psi_0 \mid \psi_0\rangle} = \frac{3\hbar^2}{2m}\alpha + \frac{3m\omega^2}{8\alpha}. \tag{9.425}$$

The minimization of $E_0(\alpha)$ with respect to α yields $\alpha_0 = m\omega/(2\hbar)$ and hence $E_0(\alpha_0) = \frac{3}{2}\hbar\omega$. This energy is identical to the exact value obtained in Chapter 4.

(b) This potential contains a single rigid wall at $x = 0$. Thus the proper quantization rule for this potential is given by (9.224): $\int_0^a p\,dx = (n + \frac{3}{4})\pi\hbar$; the turning point occurs at $x = a$ with $E = \frac{1}{2}m\omega^2a^2$ and hence $a = \sqrt{2E/(m\omega^2)}$.

The calculation of $\int_0^a p\,dx$ goes as follows:

$$\int_0^a p\,dx = \int_0^a \sqrt{2mE - m^2\omega^2x^2}dx = m\omega\int_0^a \sqrt{a^2 - x^2}dx. \tag{9.426}$$

The change of variable $x = a\sin\theta$ leads to

$$\int_0^a \sqrt{a^2 - x^2}\,dx = a^2\int_0^{\pi/2}\cos^2\theta\,d\theta = \frac{a^2}{2}\int_0^{\pi/2}(1 + \cos 2\theta)d\theta = \frac{\pi a^2}{4}; \tag{9.427}$$

hence

$$\int_0^a p\,dx = m\omega\frac{\pi a^2}{4} = \frac{\pi E}{2\omega}. \tag{9.428}$$

Since $\int_0^a p\,dx = (n+\frac{3}{4})\pi\hbar$, that is, $\pi E/(2\omega) = (n+\frac{3}{4})\pi\hbar$, we obtain

$$E_n^{WKB} = \left(2n + \frac{3}{2}\right)\hbar\omega, \qquad n = 0,\ 1,\ 2,\ 3,\ \ldots. \tag{9.429}$$

This relation is identical with the *exact* expression obtained in Chapter 4. The WKB ground state energy is thus given by $E_0^{WKB} = \frac{3}{2}\hbar\omega$.

Problem 9.14

Consider an H_2 molecule where the protons are separated by a wide distance R and both are located on the z-axis. Ignoring the spin degrees of freedom and treating the dipole–dipole interaction as a perturbation, use perturbation theory to estimate an upper limit for the ground state energy of this molecule.

Solution

Assuming the protons are fixed in space and separated by a distance R, we can write the Hamiltonian of this molecule as follows:

$$\hat{H} = \hat{H}_0 + \hat{H}_p = \hat{H}_0^A + \hat{H}_0^B + \hat{H}_p, \tag{9.430}$$

where $\hat{H}_0^A$ and $\hat{H}_0^B$ are the unperturbed Hamiltonians of atoms A and B, and $\hat{H}_p$ is

$$\hat{H}_p = \frac{e^2}{R} + \frac{e^2}{|\vec{R} + \vec{r}_A - \vec{r}_B|} - \frac{e^2}{|\vec{R} + \vec{r}_A|} - \frac{e^2}{|\vec{R} - \vec{r}_B|}, \tag{9.431}$$

where $\vec{r}_A$ and $\vec{r}_B$ are the position vectors of the electrons of atoms A and B as measured from the protons. If $R \gg a_0$, where $a_0 = \hbar^2/(\mu e^2)$ is the Bohr radius, an expansion of (9.431) in powers of $\vec{r}_A/R$ and $\vec{r}_B/R$ yields, to first nonvanishing terms, an expression of the order of $1/R^3$:

$$\hat{H}_p = \frac{e^2}{R^3}\left[\vec{r}_A \cdot \vec{r}_B - 3\frac{(\vec{r}_A \cdot \vec{R})(\vec{r}_B \cdot \vec{R})}{R^2}\right]. \tag{9.432}$$

This is the dipole–dipole interaction energy between the dipole moments of the two atoms.

Since $\vec{R} = R\hat{z}$ we can write (9.432) as

$$\hat{H}_p = \frac{e^2}{R^3}\left(\hat{X}_A\hat{X}_B + \hat{Y}_A\hat{Y}_B - 2\hat{Z}_A\hat{Z}_B\right). \tag{9.433}$$

The ground state energy and wave function of the (unperturbed) molecule are

$$E_0 = E_0^A + E_0^B = 2E_{100} = -\frac{e^2}{a_0}, \qquad |\phi_0\rangle = |\phi_0^A\rangle|\phi_0^B\rangle = |\ 100\rangle_A\ |\ 100\rangle_B. \tag{9.434}$$

The first-order correction to the molecule's energy, $E^{(1)} = \langle\phi_0|\hat{H}_p|\phi_0\rangle$, is given by

$$\begin{aligned} E^{(1)} &= \frac{e^2}{R^3}\Big(\langle\phi_0^A|\hat{X}_A|\phi_0^A\rangle\langle\phi_0^B|\hat{X}_B|\phi_0^B\rangle + \langle\phi_0^A|\hat{Y}_A|\phi_0^A\rangle\langle\phi_0^B|\hat{Y}_B|\phi_0^B\rangle \\ &\quad - 2\langle\phi_0^A|\hat{Z}_A|\phi_0^A\rangle\langle\phi_0^B|\hat{Z}_B|\phi_0^B\rangle\Big). \end{aligned} \tag{9.435}$$

Since the operators $\hat{X}$, $\hat{Y}$, and $\hat{Z}$ are odd and the states $|\phi_0^A\rangle$ and $|\phi_0^B\rangle$ are spherically symmetric, then all the terms in (9.435) are zero; hence $E^{(1)} = 0$.

Let us now calculate the second-order correction:

$$E^{(2)} = \sum_{n,l,m;n',l',m' \neq 1,0,0} \frac{\left| \langle n, l, m; n', l', m' | \hat{H}_p | \phi_0 \rangle \right|^2}{2E_{100} - E_n - E_{n'}}, \tag{9.436}$$

where

$$\begin{aligned}\langle n, l, m; n', l', m' | \hat{H}_p | \phi_0 \rangle = \frac{e^2}{R^3} \Big(& \langle n, l, m | X_A | 1, 0, 0 \rangle_A \langle n', l', m' | X_B | 1, 0, 0 \rangle_B \\ & + \langle n, l, m | Y_A | 1, 0, 0 \rangle_A \langle n', l', m' | Y_B | 1, 0, 0 \rangle_B \\ & + -2 \langle n, l, m | Z_A | 1, 0, 0 \rangle_A \langle n', l', m' | Z_B | 1, 0, 0 \rangle_B \Big).\end{aligned} \tag{9.437}$$

The terms of this expression are nonzero only if $l = l' = 1$, since the $\hat{X}$, $\hat{Y}$, and $\hat{Z}$ operators are proportional to Y_{1m}. We can evaluate $E^{(2)}$ using a crude approximation where we assume the denominator of (9.436) is constant and we take $E_n \simeq E_{n'}$. Note that, for $n \geq 2$, we have $E_{nlm} \geq E_{200}$. In this case we can rewrite (9.436) as

$$E^{(2)} \leq \frac{1}{2(E_{100} - E_{200})} \sum_{n,l,m;n',l',m' \neq 1,0,0} \left| \langle n, l, m; n', l', m' | \hat{H}_p | \phi_0 \rangle \right|^2; \tag{9.438}$$

since the diagonal term is zero (i.e., $\langle 1, 0, 0; 1, 0, 0 | \hat{H}_p | 1, 0, 0; 1, 0, 0 \rangle = 0$), we have

$$\begin{aligned}\sum_{n,l,m;n',l',m'} & \left| \langle n, l, m; n', l', m' | \hat{H}_p | \phi_0 \rangle \right|^2 \\ & = \sum_{n,l,m;n',l',m'} \langle 1, 0, 0; 1, 0, 0 | \hat{H}_p | n, l, m; n', l', m' \rangle \langle n, l, m; n', l', m' | \hat{H}_p | 1, 0, 0; 1, 0, 0 \rangle \\ & = \langle 1, 0, 0; 1, 0, 0 | (\hat{H}_p)^2 | 1, 0, 0; 1, 0, 0 \rangle \\ & = \frac{e^4}{R^6} \langle 1, 0, 0; 1, 0, 0 | \left(X_A X_B + Y_A Y_B - 2 Z_A Z_B \right)^2 | 1, 0, 0; 1, 0, 0 \rangle.\end{aligned} \tag{9.439}$$

The calculation of $\langle 1, 0, 0; 1, 0, 0 | \left(X_A X_B + Y_A Y_B - 2 Z_A Z_B \right)^2 | 1, 0, 0; 1, 0, 0 \rangle$ can be made easier by the use of symmetry. Due to spherical symmetry, the cross terms are zero:

$$\langle X_A Y_A \rangle_A = \langle X_A Z_A \rangle_A = \langle Y_A Z_A \rangle_A = \langle X_B Y_B \rangle_B = \cdots = \langle Y_B Z_B \rangle_B = 0, \tag{9.440}$$

while the others are given as follows (see (9.45)):

$$\langle X_A^2 \rangle_A = \langle Y_A^2 \rangle_A = \langle Z_A^2 \rangle_A = \langle X_B^2 \rangle_B = \langle Y_B^2 \rangle_B = \langle Z_B^2 \rangle_B = a_0^2, \tag{9.441}$$

where $\langle C \rangle_A = \langle \phi_0^A | C | \phi_0^A \rangle$ and $\langle D \rangle_B = \langle \phi_0^B | D | \phi_0^B \rangle$. We can thus obtain

$$\langle 1, 0, 0; 1, 0, 0 | \left(X_A X_B + Y_A Y_B - 2 Z_A Z_B \right)^2 | 1, 0, 0; 1, 0, 0 \rangle = 6 a_0^4. \tag{9.442}$$

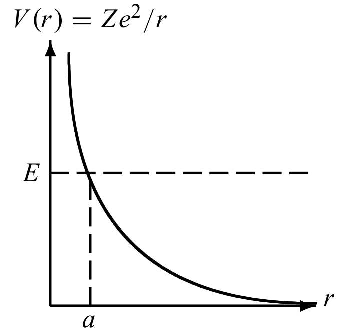

Figure 9.10 Coulomb barrier, $V(r) = Ze^2/r$, seen by a proton of energy E while approaching from the right a nucleus of charge Ze located at the origin.

Inserting (9.442) into (9.439) and then the resultant expression into (9.438), we get

$$E^{(2)} \leq \frac{\langle 1,0,0;1,0,0|(\hat{H}_p)^2|1,0,0;1,0,0\rangle}{2(E_{100}-E_{200})} = \frac{3e^4a_0^4}{R^6}\frac{1}{E_{100}-E_{200}}, \tag{9.443}$$

or

$$E^{(2)} \leq -\frac{8e^2a_0^5}{R^6}, \tag{9.444}$$

because $E_{100} = -e^2/2a_0$ and $E_{200} = -e^2/8a_0$. Finally, the upper limit for the ground state energy of this molecule to second-order perturbation theory is given by

$$E_2 \leq 2E_{100} - \frac{8e^2a_0^5}{R^6} \qquad \Longrightarrow \qquad E_2 \leq -\frac{e^2}{a_0}\left(1 + 8\frac{a_0^6}{R^6}\right). \tag{9.445}$$

Problem 9.15
A proton of energy E is incident from the right on a nucleus of charge Ze. Estimate the transmission coefficient associated with the penetration of the proton inside the nucleus.

Solution
To penetrate inside the nucleus (i.e., to the left of the turning point $r = a$ as shown in Figure 9.10), the proton has to overcome the repulsive Coulomb force of the nucleus. That is, it has to tunnel through the Coulomb barrier $V(r) = Ze^2/r$. The transmission coefficient is given in the WKB approximation by (9.247), where $x_1 = a$ and $x_2 = 0$:

$$T = e^{-2\gamma}, \qquad \gamma = \frac{1}{\hbar}\int_a^0 \sqrt{2m(V(r)-E)}\,dr, \tag{9.446}$$

where a is given by $E = V(a)$: $a = Ze^2/E$. Since $V(r) = Ze^2/r$ we get

$$\gamma = \frac{1}{\hbar}\int_a^0 \sqrt{2m\left(\frac{Ze^2}{r} - E\right)}\,dr = \frac{\sqrt{2mE}}{\hbar}\int_{Ze^2/E}^0 \sqrt{\frac{Ze^2}{Er} - 1}\,dr. \tag{9.447}$$

The change of variable $x = Er/(Ze^2)$ gives

$$\gamma = \frac{Ze^2}{\hbar}\sqrt{\frac{2m}{E}}\int_0^1 \sqrt{\frac{1}{x} - 1}\, dx = \frac{Ze^2\pi}{\hbar}\sqrt{\frac{m}{2E}}; \tag{9.448}$$

in deriving this relation, we have used the integral $\int_0^1 \sqrt{1/x - 1} dx = \pi/2$.

The transmission coefficient is thus given by

$$T = e^{-2\gamma} = \exp\left\{-\frac{Ze^2\pi}{\hbar}\sqrt{\frac{2m}{E}}\right\}. \tag{9.449}$$

The value of this coefficient describes how difficult it is for a positively charged particle, such as a proton, to approach a nucleus.

Problem 9.16

Two identical particles of spin $\frac{1}{2}$ are enclosed in a one-dimensional box potential of length L with walls at $x = 0$ and $x = L$.

(a) Find the energies of the three lowest states.

(b) Then, subjecting the particles to a perturbation

$$\hat{H}_p(x_1,\, x_2) = -V_0 L^2 \delta\left(x_1 - \frac{L}{2}\right)\delta\left(x_2 - \frac{L}{3}\right),$$

calculate its ground state energy using first-order time-independent perturbation theory.

Solution

Since the two particles have the *same* spin, the spin wave function of the system, $\chi_s(s_1, s_2)$, must be *symmetric*, so χ_s is any one of the triplet states:

$$\chi_s = \begin{cases} \mid 1,\, 1\rangle &= \left|\frac{1}{2},\, \frac{1}{2}\right\rangle_1 \left|\frac{1}{2},\, \frac{1}{2}\right\rangle_2, \\ \mid 1,\, 0\rangle &= \frac{1}{\sqrt{2}}\left[\, \left|\frac{1}{2},\, \frac{1}{2}\right\rangle_1 \left|\frac{1}{2},\, -\frac{1}{2}\right\rangle_2 + \left|\frac{1}{2},\, -\frac{1}{2}\right\rangle_1 \left|\frac{1}{2},\, \frac{1}{2}\right\rangle_2\right], \\ \mid 1,\, -1\rangle &= \left|\frac{1}{2},\, -\frac{1}{2}\right\rangle_1 \left|\frac{1}{2},\, -\frac{1}{2}\right\rangle_2. \end{cases} \tag{9.450}$$

In addition, since this two-particle system is a system of *identical fermions*, its wave function must be *antisymmetric*. Since the spin part is symmetric, the spatial part of the wave function has to be antisymmetric:

$$\Psi(x_1, x_2) = \psi_A(x_1, x_2)\chi_s(s_1, s_2); \tag{9.451}$$

that is,

$$\begin{aligned} \psi_A(x_1, x_2) &= \frac{1}{\sqrt{2}}\left[\phi_{n_1}(x_1)\phi_{n_2}(x_2) - \phi_{n_2}(x_1)\phi_{n_1}(x_2)\right] \\ &= \frac{1}{L}\left[\sin\left(\frac{n_1\pi x_1}{L}\right)\sin\left(\frac{n_2\pi x_2}{L}\right) - \sin\left(\frac{n_2\hbar x_1}{L}\right)\sin\left(\frac{n_1\pi x_2}{L}\right)\right]. \end{aligned} \tag{9.452}$$

The energy levels of this two-particle system are

$$E = \frac{\pi^2\hbar^2}{2mL^2}(n_1^2 + n_2^2) = E_0(n_1^2 + n_2^2), \tag{9.453}$$

where $E_0 = \pi^2\hbar^2/(2mL^2)$. Note that these energy levels are threefold degenerate because of the spin part of the wave function; that is, there are three different spin states that correspond to the same energy level $\pi^2\hbar^2(n_1^2+n_2^2)/(2mL^2)$.

(a) Having written the general expressions for the energies and the wave functions, it is now easy to infer the energy levels and wave functions of the three lowest states. First, we should note that the ground state cannot correspond to $n_1 = n_2 = 1$, for the spatial wave function would be *zero*. The ground state corresponds then to $n_1 = 1$, $n_2 = 2$; its energy follows from (9.453),

$$E^{(0)} = E_0(1^2+2^2) = 5E_0 = \frac{5\pi^2\hbar^2}{2mL^2}, \tag{9.454}$$

and the wave function $\psi_0(x_1, x_2)$ follows from (9.452).

The first excited state corresponds to $n_1 = 1$, $n_2 = 3$. So the wave function $\psi_1(x_1,\ x_2)$ can be inferred from (9.452) and the energy from (9.453):

$$E^{(1)} = E_0(1^2+3^2) = 10E_0 = \frac{5\pi^2\hbar^2}{mL^2}. \tag{9.455}$$

The second excited state corresponds to $n_1 = 2$, $n_2 = 3$; hence the energy is given by

$$E^{(2)} = 13E_0 = \frac{13\pi^2\hbar^2}{2mL^2}. \tag{9.456}$$

(b) Introducing the perturbation $\hat{H}_p = -V_0L^2\delta(x_1 - L/2)\delta(x_2 - L/3)$, and since $\hat{H}_p$ is diagonal in the spin space, the ground state energy to first-order perturbation theory is given by

$$E = \frac{5\pi^2\hbar^2}{2mL^2} + \langle\, \psi_0|\hat{H}_p|\psi_0\rangle \tag{9.457}$$

where

$$\langle\psi_0|\hat{H}_p \mid \psi_0\rangle = \int_0^L dx_1 \int_0^L dx_2\psi_0^*(x_1,x_2)\hat{H}_p(x_1,x_2)\psi_0(x_1,x_2). \tag{9.458}$$

Since

$$\psi_0^*(x_1,x_2) = \psi_0(x_1,x_2) = \frac{1}{L}\left[\sin\left(\frac{\pi x_1}{L}\right)\sin\left(\frac{2\pi x_2}{L}\right) - \sin\left(\frac{2\pi x_1}{L}\right)\sin\left(\frac{\pi x_2}{L}\right)\right], \tag{9.459}$$

we have

$$\begin{aligned}\langle\psi_0|\hat{H}_p \mid \psi_0\rangle &= -\frac{V_0L^2}{L^2}\int_0^L dx_1\delta\left(x_1-\frac{L}{2}\right)\int_0^L dx_2\delta\left(x_2-\frac{L}{3}\right)\\ &\quad\times\left[\sin\left(\frac{\pi x_1}{L}\right)\sin\left(\frac{2\pi x_2}{L}\right) - \sin\left(\frac{2\pi x_1}{L}\right)\sin\left(\frac{\pi x_2}{L}\right)\right]^2\\ &= -V_0\left[\sin\left(\frac{\pi}{2}\right)\sin\left(\frac{2\pi}{3}\right) - \sin(\pi)\sin\left(\frac{\pi}{3}\right)\right]^2\\ &= -\frac{3}{4}V_0;\end{aligned} \tag{9.460}$$

hence

$$E = \frac{5\pi^2\hbar^2}{2mL^2} - \frac{3}{4}V_0. \tag{9.461}$$

Problem 9.17

Neglecting the spin–orbit interaction, find the ground state energy of a two-electron atom in these two ways:

(a) Use a first-order perturbation calculation; treat the Coulomb interaction between the two electrons as a perturbation.

(b) Use the variational method.

Compare the results and discuss the merits of the two approximation methods.

Solution

Examples of such a system are the helium atom ($Z = 2$), the singly ionized Li^+ ion ($Z = 3$), the doubly ionized Be^{2+} ion ($Z = 4$), and so on. Each electron of these systems feels the effects of two Coulomb fields: one from the Ze nucleus, $V(r) = -Ze^2/r$, and the other from the other electron, $V_{12} = e^2/r_{12} = e^2/|\vec{r}_1 - \vec{r}_2|$; here we consider the nucleus to be located at the origin and the electrons at $\vec{r}_1$ and $\vec{r}_2$. Neglecting the spin–orbit interaction, we can write the Hamiltonian of the two-electron system as

$$\hat{H} = \hat{H}_0 + \hat{V}_{12} = \hat{H}_0 + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}, \tag{9.462}$$

where

$$\hat{H}_0 = -\frac{\hbar^2}{2\mu}\left(\nabla_1^2 + \nabla_2^2\right) - Ze^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{9.463}$$

is the Hamiltonian of the atom when the interaction between the two electrons is neglected.

We have seen in Chapter 8 that, when the interaction between the two electrons is neglected, the ground state energy and wave function are given by

$$E_0 = -2\frac{Z^2e^2}{2a} = -27.2Z^2\,\text{eV}, \tag{9.464}$$

$$\Psi_0(\vec{r}_1, \vec{S}_1;\ \vec{r}_2, \vec{S}_2) = \psi_0(\vec{r}_1, \vec{r}_2)\chi_{singlet}(\vec{S}_1, \vec{S}_2), \tag{9.465}$$

where the spin part is antisymmetric,

$$\chi_{singlet}(\vec{S}_1, \vec{S}_2) = \frac{1}{\sqrt{2}}\left(\left|\frac{1}{2}, \frac{1}{2}\right\rangle_1 \left|\frac{1}{2}, -\frac{1}{2}\right\rangle_2 - \left|\frac{1}{2}, -\frac{1}{2}\right\rangle_1 \left|\frac{1}{2}, \frac{1}{2}\right\rangle_2\right), \tag{9.466}$$

and the spatial part is symmetric, $\psi_0(\vec{r}_1, \vec{r}_2) = \phi_{100}(\vec{r}_1)\phi_{100}(\vec{r}_2)$, with

$$\phi_{100}(\vec{r}) = R_{10}(r)Y_{00}(\Omega) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2} e^{-Zr_1/a}, \tag{9.467}$$

that is,

$$\psi_0(\vec{r}_1, \vec{r}_2) = \frac{1}{\pi}\left(\frac{Z}{a}\right)^3 e^{-Z(r_1+r_2)/a}. \tag{9.468}$$

(a) To calculate the ground state energy using first-order perturbation theory, we have to treat $\hat{V}_{12}$ as a perturbation. A first-order treatment yields

$$E = E_0 + \langle \psi_0 | \hat{V}_{12} \mid \psi_0 \rangle = -2\frac{Z^2e^2}{2a} + \langle \psi_0 | \hat{V}_{12} \mid \psi_0 \rangle, \tag{9.469}$$

where

$$\begin{aligned} \langle \psi_0 | \hat{V}_{12} \mid \psi_0 \rangle &= \int d^3r_1 \int d^3r_2 \, \psi_0^*(\vec{r}_1, \vec{r}_2) \hat{V}_{12} \psi_0(\vec{r}_1, \vec{r}_2) \\ &= \int d^3r_1 \int d^3r_2 \, |\phi_{100}(\vec{r}_1)|^2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} |\phi_{100}(\vec{r}_2)|^2 . \end{aligned} \tag{9.470}$$

The calculation of this integral is quite involved (I left it as an exercise); the result is

$$\langle \psi_0 | \hat{V}_{12} \mid \psi_0 \rangle = \frac{5}{8} \frac{Ze^2}{a}, \tag{9.471}$$

which, when combined with (9.469), leads to

$$E = -\frac{Ze^2}{a} \left(Z - \frac{5}{8} \right). \tag{9.472}$$

In the case of helium, $Z = 2$, we have

$$E = -108.8\,\text{eV} + 34\,\text{eV} = -74.8\,\text{eV}; \tag{9.473}$$

this result disagrees with the experimental value, $E_{exp} = -78.975\,\text{eV}$, by 4 eV or by a 5.3% relative error. Physically, this may be attributed to the fact that, in our calculation, we have not taken into account the "screening" effect: the presence of one electron tends to decrease the net charge "seen" by the other electron. Suppose electron 1 is "between" the nucleus and electron 2; then electron 2 will not "see" Z protons but $(Z - 1)$ protons (i.e., electron 2 feels an effective charge $(Z - 1)e$ coming from the nucleus).

(b) By analogy with the exact form of the ground state function (9.468), we can choose a trial function that takes into account the screening effect. For this, we need simply to replace Z in (9.468) by a variational parameter α:

$$\psi_0(r_1, r_2) = Ae^{-\alpha(r_1+r_2)/a}, \tag{9.474}$$

where A is a normalization. Using the integral $\int_0^\infty x^n e^{-bx} dx = n!/b^{n+1}$, we can show that $A = (\alpha/a)^3/\pi$; hence

$$\psi_\alpha(r_1, r_2) = \frac{1}{\pi} \left(\frac{\alpha}{a} \right)^3 e^{-\alpha(r_1+r_2)/a}. \tag{9.475}$$

A combination of this relation with (9.471) leads to

$$E(\alpha) = \langle \psi_\alpha | \hat{H}_0 | \psi_\alpha \rangle + \langle \psi_\alpha | \hat{V}_{12} | \psi_\alpha \rangle = \langle \psi_\alpha | \hat{H}_0 | \psi_\alpha \rangle + \frac{5}{8} \frac{\alpha e^2}{a}. \tag{9.476}$$

The calculation of $\langle\psi_\alpha|\hat{H}_0|\psi_\alpha\rangle$ can be simplified by writing it as

$$\begin{aligned}\langle\psi_\alpha|\hat{H}_0|\psi_\alpha\rangle &= -\frac{\hbar^2}{2\mu}\langle\psi_\alpha|\nabla_1^2+\nabla_2^2|\psi_\alpha\rangle - Ze^2\langle\psi_\alpha|\frac{1}{r_1}+\frac{1}{r_2}|\psi_\alpha\rangle \\ &= -\frac{\hbar^2}{2\mu}\langle\psi_\alpha|\nabla_1^2+\nabla_2^2|\psi_\alpha\rangle - \alpha e^2\langle\psi_\alpha|\frac{1}{r_1}+\frac{1}{r_2}|\psi_\alpha\rangle \\ &\quad - (Z-\alpha)e^2\langle\psi_\alpha|\frac{1}{r_1}+\frac{1}{r_2}|\psi_\alpha\rangle. \end{aligned} \tag{9.477}$$

This form is quite suggestive; since $-\hbar^2\langle\psi_0|\vec{\nabla}\mid\psi_0\rangle/(2\mu)-Ze^2\langle\psi_0|1/r\mid\psi_0\rangle=-Z^2e^2/(2a)$ we can write

$$-\frac{\hbar^2}{2\mu}\langle\psi_\alpha|\nabla_1^2+\nabla_2^2|\psi_\alpha\rangle - \alpha e^2\langle\psi_\alpha|\frac{1}{r_1}+\frac{1}{r_2}|\psi_\alpha\rangle = -2\frac{\alpha^2e^2}{2a}. \tag{9.478}$$

Now since

$$\langle\psi_\alpha|\frac{1}{r_1}|\psi_\alpha\rangle = \langle\psi_\alpha|\frac{1}{r_2}|\psi_\alpha\rangle = 4\left(\frac{\alpha}{a}\right)^3\int_0^\infty re^{-2\alpha r/a}dr = \frac{\alpha}{a}, \tag{9.479}$$

we can reduce (9.477) to

$$\langle\psi_\alpha|\hat{H}_0|\psi_\alpha\rangle = -2\frac{\alpha^2e^2}{2a} - 2(Z-\alpha)e^2\frac{\alpha}{a}, \tag{9.480}$$

which, when combined with (9.476), leads to

$$E(\alpha) = -2\frac{\alpha^2e^2}{2a} - 2(Z-\alpha)e^2\frac{\alpha}{a} + \frac{5}{8}\frac{\alpha e^2}{a} = \left[\alpha^2 - 2\left(Z-\frac{5}{16}\right)\alpha\right]\frac{e^2}{a}. \tag{9.481}$$

The minimization of $E(\alpha)$, $dE(\alpha)/d\alpha = 0$, yields

$$\alpha_0 = Z - \frac{5}{16}; \tag{9.482}$$

hence the ground state energy is

$$E(\alpha_0) = -\left[1-\frac{5}{8Z}+\left(\frac{5}{16Z}\right)^2\right]\frac{Z^2e^2}{a} \tag{9.483}$$

and

$$\psi(r_1, r_2) = \frac{1}{\pi}\left(\frac{Z}{a}-\frac{5}{16a}\right)^3\exp\left[-\left(\frac{Z}{a}-\frac{5}{16a}\right)(r_1+r_2)\right]. \tag{9.484}$$

As a numerical illustration, the ground state energy of a helium atom is obtained by substituting $Z = 2$ into (9.483). This yields $E_0 = -77.456$ eV, in excellent agreement with the experimental value $E_{exp} = -78.975$ eV. The variational method, which overestimates the correct result by a mere 1.9%, is significantly more accurate than first-order perturbation theory. The reason is quite obvious; while the perturbation treatment does not account for the screening effect, the variational method includes it quite accurately. The wave function (9.484) shows that the second electron does not see a charge Ze, but a lower charge $(Z - 5/16)e$.

9.7 Exercises

Exercise 9.1

Calculate the energy of the nth excited state to first-order perturbation for a one-dimensional box potential of length $2L$, with walls at $x = -L$ and $x = L$, which is modified at the bottom by the following perturbations with $V_0 \ll 1$:

$$\text{(a) } V_p(x) = \begin{cases} -V_0, & -L \le x \le L, \\ 0, & \text{elsewhere;} \end{cases},$$

$$\text{(b) } V_p(x) = \begin{cases} -V_0, & -L/2 \le x \le L/2, \\ 0, & \text{elsewhere.} \end{cases},$$

Exercise 9.2

Calculate the energy of the nth excited state to first-order perturbation for a one-dimensional box potential of length $2L$, with walls at $x = -L$ and $x = L$, which is modified at the bottom by the following perturbations with $V_0 \ll 1$:

$$\text{(a) } V_p(x) = \begin{cases} -V_0, & -L/2 \le x \le 0, \\ 0, & \text{elsewhere;} \end{cases}$$

$$\text{(b) } V_p(x) = \begin{cases} V_0, & 0 \le x \le L/2, \\ 0, & \text{elsewhere;} \end{cases}$$

$$\text{(c) } V_p(x) = \begin{cases} -V_0, & -L/2 \le x \le 0; \\ V_0, & 0 \le x \le L/2, \\ 0, & \text{elsewhere.} \end{cases}$$

Exercise 9.3

Calculate the energy of the nth excited state to second-order perturbation and the wave function to first-order perturbation for a one-dimensional box potential of length $2L$, with walls at $x = -L$ and $x = L$, which is modified at the bottom by the following perturbations with $V_0 \ll 1$:

$$\text{(a) } V_p(x) = \begin{cases} 0, & -L \le x \le 0, \\ V_0, & 0 \le x \le L; \end{cases} \qquad \text{(b) } V_p(x) = \begin{cases} -V_0(1 - x^2/L^2), & |x| < L, \\ 0, & \text{elsewhere.} \end{cases}$$

Exercise 9.4

Consider a system whose Hamiltonian is given by $\hat{H} = E_0 \begin{pmatrix} 3 & 2\lambda & 0 & 0 \\ 2\lambda & -3 & 0 & 0 \\ 0 & 0 & -7 & \sqrt{2}\lambda \\ 0 & 0 & \sqrt{2}\lambda & 7 \end{pmatrix}$, where $\lambda \ll 1$.

(a) Calculate the *exact* eigenvalues of $\hat{H}$; expand each of these eigenvalues to the second power of λ.

(b) Calculate the energy eigenvalues to second-order perturbation theory and compare them with the exact results obtained in (a).

(c) Calculate the eigenstates of $\hat{H}$ up to the first-order correction.

Exercise 9.5

Consider a particle of mass m that moves in a three-dimensional potential $V(r) = kr$, where k is a constant having the dimensions of a force. Use the variational method to estimate its ground state energy; you may take $R(r) = e^{-r^2/2\alpha^2}$ as the trial radial function where α is an adjustable parameter.

Exercise 9.6
Use the WKB method to estimate the ground state energy of a particle of mass m that moves in a three-dimensional potential $V(r) = kr$, where k is a constant having the dimensions of a force.

Exercise 9.7
Consider a two-dimensional harmonic oscillator Hamiltonian:

$$\hat{H} = \frac{1}{2m}(\hat{P}_x^2 + \hat{P}_y^2) + \frac{1}{2}m\omega^2(\hat{X}^2 + \hat{Y}^2)(1 + \lambda\hat{X}\hat{Y}),$$

where $\lambda \ll 1$.

(a) Give the wave functions for the three lowest energy levels when $\lambda = 0$.

(b) Using perturbation theory, evaluate the first-order corrections of these energy levels when $\lambda \neq 0$.

Exercise 9.8
Consider a particle that has the Hamiltonian $\hat{H} = \hat{H}_0 + \lambda\hbar\omega(\hat{a}^2 + \hat{a}^{\dagger^2})$, where $\hat{H}_0$ is the Hamiltonian of a simple one-dimensional harmonic oscillator, and where $\hat{a}$ and $\hat{a}^\dagger$ are the usual annihilation and creation operators which obey $[\hat{a},\ \hat{a}^\dagger] = 1$; λ is a very small real number.

(a) Calculate the ground state energy to second order in λ.

(b) Find the energy of the nth excited state, E_n, to second order in λ and the corresponding eigenstate $\mid \psi_n\rangle$ to first order in λ.

Exercise 9.9
Consider two identical particles of spin $\frac{1}{2}$ that are confined in an isotropic three-dimensional harmonic oscillator potential of frequency ω.

(a) Find the ground state energy and the corresponding wave function of this system when the two particles do not interact.

(b) Consider now that there exists a weakly attractive spin-dependent potential between the two particles, $V(r_1, r_2) = -kr_1r_2 - \lambda\hat{S}_{1z}\hat{S}_{2z}$, where k and λ are two small positive real numbers. Find the ground state to first-order time-independent perturbation theory.

(c) Use the variational method to estimate the ground state energy of this system of two noninteracting spin $\frac{1}{2}$ particles confined to an isotropic three-dimensional harmonic oscillator. How does your result compare with that obtained in (a).

Exercise 9.10
Two identical spin $\frac{1}{2}$ particles are confined to a one-dimensional box potential of size L with walls at $x = 0$ and $x = L$.

(a) Find the ground state energy and the first excited state energy and their respective wave functions for this system when the two particles do not interact.

(b) Consider now that there exists a *weakly* attractive potential between the two particles:

$$V_p(x) = \begin{cases} -V_0, & 0 \leq x \leq L/2, \\ 0, & L/2 < x \leq L. \end{cases}$$

Find the ground state and first excited state energies to first-order perturbation theory.

(c) Find numerical values for the ground state and first excited state energies calculated in (a) in the case where $L = 10^{-10}$ m, $V_0 = 2$ eV, and the mass of each individual particle is to be taken equal to the electron mass. Compare the sizes of the first order energy corrections with the ground state energy and the first excited state energy (you may simply calculate the ratios between the first-order corrections with the ground state and first excited state energies).

Exercise 9.11
Consider an isotropic three-dimensional harmonic oscillator.

(a) Find the energy of the first excited state and the different states corresponding to this energy.

(b) If we now subject this oscillator to a perturbation $\hat{V}_p(x, y) = -\lambda\hat{x}\hat{y}$, where λ is a small real number, find the energy of the first excited state to first-order degenerate time-independent perturbation theory. *Hint:* You may use $\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}_x + \hat{a}_x^\dagger)$, $\hat{y} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}_y + \hat{a}_y^\dagger)$, $\hat{z} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}_z + \hat{a}_z^\dagger)$, with $\hat{a}_x|n_x\rangle = \sqrt{n_x}|n_x - 1\rangle$, and $\hat{a}_x^\dagger|n_x\rangle = \sqrt{n_x + 1}|n_x + 1\rangle$.

Exercise 9.12
Use the variational method to estimate the ground state energy of the spherical harmonic oscillator by means of the following radial trial functions:

(a) $R(r) = Ae^{-\alpha r^2}$ and

(b) $R(r) = Ae^{-\alpha r}$, where A is a normalization constant that needs to be found in each case and α is an adjustable parameter.

(c) Using the fact that the exact ground state energy is $E_0^{exact} = 3\hbar\omega/2$, find the relative errors corresponding to the energies derived in (a) and (b).

Exercise 9.13
Consider a particle of mass m that is bouncing vertically and elastically on a smooth reflecting floor in the Earth's gravitational field

$$V(z) = \begin{cases} mgz, & z > 0, \\ +\infty, & z \leq 0, \end{cases}$$

where g is a constant (the acceleration due to gravity). Use the variational method to estimate the ground state energy of this particle by means of the trial wave function, $\psi(z) = z\exp(-\alpha z^4)$, where α is an adjustable parameter that needs to be determined. Compare your result with the exact value $E_0^{exact} = 2.338\left(\frac{1}{2}mg^2\hbar^2\right)^{1/3}$ by calculating the relative error.

Exercise 9.14
Calculate the energy of the ground state to first-order perturbation for a particle which is moving in a one-dimensional box potential of length L, with walls at $x = 0$ and $x = L$, when a weak potential $\hat{H}_p = \lambda x^2$ is added, where $\lambda \ll 1$.

Exercise 9.15
Consider a semiclassical system whose energy is given by

$$E = a^2 + \frac{1}{2}\left(\frac{b^2}{4} - a^2\right)p^2 + \frac{1}{2}\left(\frac{4a^2}{b^2/4 - a^2}\right)q^2,$$

where a and b are positive, real constants. Use the Bohr–Sommerfeld quantization rule to extract the expression of the bound state energy E_n for the nth excited state in terms of a.

Exercise 9.16
Use the variational method to estimate the ground state energy of a particle of mass m that is moving in a one-dimensional potential $V(x) = V_0 x^4$; you may use the trial function $\psi_0(x, \alpha) = Ae^{-\alpha x^2/2}$, where A is the normalization constant and α is an adjustable parameter that needs to be determined.

Exercise 9.17
Consider a particle of mass m which is moving in a one-dimensional potential $V(x) = V_0 x^4$. Estimate the ground state energy of this particle by means of the WKB method.

Exercise 9.18
Using $\phi_{100}(\vec{r}) = (1/\sqrt{\pi})(Z/a)^{3/2} e^{-Zr/a}$, show that

$$\int \phi_{100}^2(\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \phi_{100}^2(\vec{r}_2) d^3r_1 d^3r_2 = \frac{5Z}{8a}.$$

Exercise 9.19
Calculate the ground state energy of the doubly ionized beryllium atom Be^{2+} by means of the following two methods and then compare the two results:

(a) a first-order perturbation theory treatment,

(b) the variational method with a trial function $\psi(r_1, r_2) = A\exp[-\alpha(r_1 + r_2)/a]$, where A is the normalization constant, α is an adjusted parameter, and a is the Bohr radius.

Exercise 9.20
Use the variational method to estimate the energy of the second excited state of a particle of mass m moving in a one-dimensional infinite well with walls at $x = 0$ and $x = L$. Calculate the relative error between your result and the exact value (recall that the energy of the second excited state is given by $E_3^{exact} = 9\pi^2\hbar^2/(2mL^2)$).

Exercise 9.21
Consider a spinless particle of orbital angular momentum $l = 1$ whose Hamiltonian is

$$\hat{H}_0 = \frac{\mathcal{E}}{\hbar^2}(\hat{L}_x^2 - \hat{L}_y^2),$$

where $\mathcal{E}$ is a constant having the dimensions of energy.

(a) Calculate the exact energy levels and the corresponding eigenstates of this particle.

(b) We now add a perturbation $\hat{H}_p = \alpha \hat{L}_z/\hbar$, where α is a small constant (small compared to $\mathcal{E}$) having the dimensions of energy. Calculate the energy levels of this particle to second-order perturbation theory.

(c) Diagonalize the matrix of $\hat{H} = \hat{H}_0 + \hat{H}_p$ and find the exact energy eigenvalues. Then expand each eigenvalue to second power in α and compare them with the results derived from perturbation theory in (b).

Exercise 9.22
Consider a system whose Hamiltonian is given by $\hat{H} = E_0 \begin{pmatrix} -5 & 3\lambda & 0 & 0 \\ 3\lambda & 5 & 0 & 0 \\ 0 & 0 & 8 & -\lambda \\ 0 & 0 & -\lambda & -8 \end{pmatrix}$, where $\lambda \ll 1$.

(a) By decomposing this Hamiltonian into $\hat{H} = \hat{H}_0 + \hat{H}_p$, find the eigenvalues and eigenstates of the unperturbed Hamiltonian $\hat{H}_0$.

(b) Diagonalize $\hat{H}$ to find the exact eigenvalues of $\hat{H}$; expand each eigenvalue to the second power of λ.

(c) Using first- and second-order nondegenerate perturbation theory, find the approximate eigenergies of $\hat{H}$. Compare these with the exact values obtained in (b).

Exercise 9.23

Estimate the ground state energy of the hydrogen atom by means of the variational method using the following two trial functions, find the relative errors, compare the two results, and discuss the merit of each trial function.

(a) $\phi_\alpha(r) = \begin{cases} 1 - r/\alpha, & r \leq \alpha, \\ 0, & r > \alpha, \end{cases}$

where α is an adjustable parameter. Find a relation between α_{min} and the Bohr radius.

(b) $\phi_\alpha(r) = Ae^{-\alpha r^2}$.

Exercise 9.24

(a) Calculate to first-order perturbation theory the energy of the nth excited state of a one-dimensional harmonic oscillator which is subject to the following small perturbation: $\hat{H}_p = \lambda(V_0\hat{x}^3 + V_1\hat{x}^4)$, where V_0, V_1, and a are constants and $\lambda \ll 1$.

(b) Use the relation derived in (a) to find the energies of the three lowest states (i.e., $n = 0,\ 1,\ 2$) to first-order perturbation theory.

Exercise 9.25

Use the trial function $\psi_0(x,\ \alpha) = \begin{cases} A(\alpha^2 - x^2)^2, & |x| \leq \alpha, \\ 0, & |x| \geq \alpha, \end{cases}$

to estimate the ground state energy of a one-dimensional harmonic oscillator by means of the variational method; α is an adjustable parameter and A is the normalization constant. Calculate the relative error and assess the accuracy of the result.

Exercise 9.26

Use the WKB approximation to estimate the transmission coefficient of a particle of mass m and energy E moving in the following potential barrier:

$$V(x) = \begin{cases} V_0(x/a + 1), & -a < x < 0, \\ V_0(1 - x/a), & 0 < x < a, \\ 0, & \text{elsewhere}, \end{cases}$$

with $0 < E < V_0$; sketch this potential.

Exercise 9.27

Use the variational method to estimate the energy of the ground state of a one-dimensional harmonic oscillator taking the following trial function:

$$\psi_0(x, \alpha) = A\,(1 + \alpha|x|)\,e^{-\alpha|x|},$$

where α is an adjustable parameter and A is the normalization constant.

Exercise 9.28
Use the WKB approximation to estimate the transmission coefficient of a particle of mass m and energy E moving in the following potential barrier:

$$V(x) = \begin{cases} V_0(1 - x^2/a^2) & |x| < a \\ 0 & |x| > a, \end{cases}$$

where $0 < E \leq V_0$.

Exercise 9.29
Use the WKB approximation to find the energy levels of a particle of mass m moving in the following potential:

$$V(x) = \begin{cases} V_0(x^2/a^2 - 1), & |x| < a, \\ 0, & |x| > a. \end{cases}$$

Exercise 9.30
A particle of mass m is moving in a one-dimensional harmonic oscillator potential, $V(x) = m\omega^2 x^2/2$. Calculate

(a) the ground state energy, and
(b) the first excited state energy

to first-order perturbation theory when a small perturbation $\hat{H}_p = \lambda\delta(x)$ is added to the potential, with $\lambda \ll 1$.

Exercise 9.31
A particle of mass m is moving in a one-dimensional harmonic oscillator potential, $V(x) = m\omega^2 x^2/2$. Calculate

(a) the ground state energy and
(b) the first excited state energy

to first-order perturbation theory when a small perturbation $\hat{H}_p = \lambda x^6$ is added to the potential, with $\lambda \ll 1$.

Exercise 9.32
A particle of mass m is moving in a three-dimensional harmonic oscillator potential, $V(x) = m\omega^2(x^2 + y^2 + z^2)/2$. Calculate the energy of the nth excited state to first-order perturbation theory when a small perturbation $\hat{H}_p = \lambda\hat{X}^2\hat{Y}^4\hat{Z}^2$ is added to the potential, with $\lambda \ll 1$.

Exercise 9.33
Use the following two trial functions:

$$\text{(a) } Ae^{-\alpha|x|}, \qquad \text{(b) } A(1 + \alpha|x|)e^{-\alpha|x|},$$

to estimate, by means of the variational method, the ground state energy of a particle of mass m moving in a one-dimensional potential $V(x) = \lambda|x|$; α is a scale parameter, λ is a constant, and A is the normalization constant. Compare the results obtained.

Exercise 9.34
Three distinguishable particles of equal mass m are enclosed in a one-dimensional box potential with rigid walls at $x = 0$ and $x = L$. If the three particles are subject to a weak, short-range attractive potential

$$\hat{H}_p = -V_0\left[\delta(x_1 - x_2) + \delta(x_2 - x_3) + \delta(x_3 - x_1)\right],$$

use first-order perturbation theory to calculate the system's energy levels of

(a) the ground state, and

(b) the first excited state.

Exercise 9.35

Three distinguishable particles of equal mass m are in a one-dimensional harmonic oscillator potential $\hat{H}_0 = \sum_{i=1}^{3}(p_i^2/2m + \frac{1}{2}m\omega^2 x_i^2)$. If the three particles are subject to a weak, short-range attractive potential

$$\hat{H}_p = -V_0\left[\delta(x_1 - x_2) + \delta(x_2 - x_3) + \delta(x_3 - x_1)\right],$$

use first-order perturbation theory to calculate the system's energy levels of

(a) the ground state and

(b) the first-excited state.

Exercise 9.36

Consider a positronium which is subject to a *weak* static magnetic field in the xz-plane, $\vec{B} = B(\vec{i} + \vec{k})$, where B is a small constant. Neglecting the spin–orbit interaction, calculate the energy levels of the $n = 2$ states to first-order perturbation.

Exercise 9.37

Consider a spherically symmetric top with principal moments of inertia I.

(a) Find the energy levels of the top.

(b) Assuming that the top is in the $l = 1$ angular momentum state, find its energy to first-order perturbation theory when a weak perturbation, $\hat{H}_p = \frac{\mathcal{E}}{I}(\hat{L}_x^2 - \hat{L}_y^2)$, is added where $\mathcal{E} \ll 1$.

Exercise 9.38

Estimate the approximate values of the ground state energy of a particle of mass m moving in the potential $V(x) = V_0|x|$, where $V_0 > 0$, by means of: (a) the variational method and (b) the WKB approximation. Compare the two results.

Exercise 9.39

Calculate to first-order perturbation theory the relativistic correction to the ground state of a spinless particle of mass m moving in a one-dimensional harmonic oscillator potential. *Hint:* You need first to show that the Hamiltonian can be written as $\hat{H} = \hat{H}_0 + \hat{H}_p$, where $\hat{H}_0 = \hat{P}^2/(2m) + m\omega^2\hat{X}^2/2$ and $\hat{H}_p = -\hat{P}^4/(8m^3c^2)$ is the leading relativistic correction term which can be treated as a perturbation.

Exercise 9.40

Consider a hydrogen atom which is subject to a small perturbation $\hat{H}_p = \lambda r^2$. Use a first-order perturbation theory to calculate the energy corrections to

(a) the ground state and

(b) the 2p state.

Exercise 9.41

(a) Calculate to first-order perturbation theory the contribution due to the spin–orbit interaction for the nth excited state for a positronium atom.

(b) Use the result of part (a) to obtain numerical values for the spin–orbit correction terms for the 2p level and compare them to the energy of $n = 2$.

Exercise 9.42
Ignoring the spin of the electron, calculate to first-order perturbation theory the energy of the $n = 2$ level of a hydrogen atom when subject to a *weak* quadrupole field $\hat{H}_p = iQ(y^2 - x^2)$, where Q is a small, real number $Q \ll 1$.

Exercise 9.43
Calculate the energy levels of the $n = 2$ states of positronium in a weak external electrical field $\vec{\mathcal{E}}$ along the z-axis: $\vec{\mathcal{E}} = \mathcal{E}\vec{k}$; positronium consists of an electron and a positron bound by the electric interaction.

Exercise 9.44
(a) Calculate to first-order perturbation theory the contributions due to the spin–orbit interaction for a hydrogen-like ion having Z protons.

(b) Use the result of part (a) to find the spin-orbit correction for the 2p state of a C^{5+} carbon ion and compare it with the energy of the $n = 2$ level.

Exercise 9.45
Two identical particles of spin $\frac{1}{2}$ are enclosed in a cubical box of side L.

(a) Calculate to first-order perturbation theory the ground state energy when the two particles are subject to *weak* short-range, attractive interaction:

$$\hat{V}(\vec{r}_1 - \vec{r}_2) = -\frac{4}{3}\pi a^3 V_0 \delta(\vec{r}_1 - \vec{r}_2).$$

(b) Find a numerical value for the energy derived in (a) for $L = 10^{-10}$ m, $a = 10^{-12}$ m, $V_0 = 10^{-3}$ eV, and the mass of each individual particle is to be taken to be the mass of the electron.