

Perturbation Theory

9.1 Perturbation Theory

This chapter discusses the second major quantum-mechanical approximation method, perturbation theory.

Suppose we have a system with a time-independent Hamiltonian operator $\hat{H}$ and we are unable to solve the Schrödinger equation

$$\hat{H}\psi_n = E_n\psi_n \quad (9.1)$$

for the eigenfunctions and eigenvalues of the bound stationary states. Suppose also that the Hamiltonian $\hat{H}$ is only slightly different from the Hamiltonian $\hat{H}^0$ of a system whose Schrödinger equation

$$\hat{H}^0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} \quad (9.2)$$

we can solve. An example is the one-dimensional anharmonic oscillator with

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}kx^2 + cx^3 + dx^4 \quad (9.3)$$

The Hamiltonian (9.3) is closely related to the Hamiltonian

$$\hat{H}^0 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}kx^2 \quad (9.4)$$

of the harmonic oscillator. If the constants c and d in (9.3) are small, we expect the eigenfunctions and eigenvalues of the anharmonic oscillator to be closely related to those of the harmonic oscillator.

We shall call the system with Hamiltonian $\hat{H}^0$ the **unperturbed system**. The system with Hamiltonian $\hat{H}$ is the **perturbed system**. The difference between the two Hamiltonians is the **perturbation** $\hat{H}'$:

$$\hat{H}' \equiv \hat{H} - \hat{H}^0 \quad (9.5)$$

$$\hat{H} = \hat{H}^0 + \hat{H}' \quad (9.6)$$

(The prime does not denote differentiation.) For the anharmonic oscillator with Hamiltonian (9.3), the perturbation on the related harmonic oscillator is $\hat{H}' = cx^3 + dx^4$.

In $\hat{H}^0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$ [Eq. (9.2)], $E_n^{(0)}$ and $\psi_n^{(0)}$ are called the **unperturbed energy** and **unperturbed wave function** of state n . For $\hat{H}^0$ equal to the harmonic-oscillator

Hamiltonian (9.4), $E_n^{(0)}$ is $(n + \frac{1}{2})h\nu$ [Eq. (4.45)], where n is a nonnegative integer. (n is used instead of v for consistency with the perturbation-theory notation.) Note that the superscript (0) does not mean the ground state. Perturbation theory can be applied to any state. The subscript n labels the state we are dealing with. The superscript (0) denotes the unperturbed system.

Our task is to relate the unknown eigenvalues and eigenfunctions of the perturbed system to the known eigenvalues and eigenfunctions of the unperturbed system. To aid in doing so, we shall imagine that the perturbation is applied gradually, giving a continuous change from the unperturbed to the perturbed system. Mathematically, this corresponds to inserting a parameter λ into the Hamiltonian, so that

$$\hat{H} = \hat{H}^0 + \lambda \hat{H}' \quad (9.7)$$

When λ is zero, we have the unperturbed system. As λ increases, the perturbation grows larger, and at $\lambda = 1$ the perturbation is fully “turned on.” We inserted λ to help relate the perturbed and unperturbed eigenfunctions, and ultimately we shall set $\lambda = 1$, thereby eliminating it.

Sections 9.1 to 9.7 deal with time-independent Hamiltonians and stationary states. Section 9.8 deals with time-dependent perturbations.

9.2 Nondegenerate Perturbation Theory

The perturbation treatments of degenerate and nondegenerate energy levels differ. This section examines the effect of a perturbation on a nondegenerate level. If some of the energy levels of the unperturbed system are degenerate while others are nondegenerate, the treatment in this section will apply to the nondegenerate levels only.

Nondegenerate Perturbation Theory

Let $\psi_n^{(0)}$ be the wave function of some particular unperturbed nondegenerate level with energy $E_n^{(0)}$. Let ψ_n be the perturbed wave function into which $\psi_n^{(0)}$ is converted when the perturbation is applied. From (9.1) and (9.7), the Schrödinger equation for the perturbed state is

$$\hat{H}\psi_n = (\hat{H}^0 + \lambda \hat{H}')\psi_n = E_n \psi_n \quad (9.8)$$

Since the Hamiltonian in (9.8) depends on the parameter λ , both the eigenfunction ψ_n and the eigenvalue E_n depend on λ :

$$\psi_n = \psi_n(\lambda, q) \quad \text{and} \quad E_n = E_n(\lambda)$$

where q denotes the system's coordinates. We now expand ψ_n and E_n as Taylor series (Prob. 4.1) in powers of λ :

$$\psi_n = \psi_n|_{\lambda=0} + \left. \frac{\partial \psi_n}{\partial \lambda} \right|_{\lambda=0} \lambda + \left. \frac{\partial^2 \psi_n}{\partial \lambda^2} \right|_{\lambda=0} \frac{\lambda^2}{2!} + \cdots \quad (9.9)$$

$$E_n = E_n|_{\lambda=0} + \left. \frac{dE_n}{d\lambda} \right|_{\lambda=0} \lambda + \left. \frac{d^2 E_n}{d\lambda^2} \right|_{\lambda=0} \frac{\lambda^2}{2!} + \cdots \quad (9.10)$$

By hypothesis, when λ goes to zero, ψ_n and E_n go to $\psi_n^{(0)}$ and $E_n^{(0)}$:

$$\psi_n|_{\lambda=0} = \psi_n^{(0)} \quad \text{and} \quad E_n|_{\lambda=0} = E_n^{(0)} \quad (9.11)$$

We introduce the following abbreviations:

$$\psi_n^{(k)} \equiv \left. \frac{1}{k!} \frac{\partial^k \psi_n}{\partial \lambda^k} \right|_{\lambda=0}, \quad E_n^{(k)} \equiv \left. \frac{1}{k!} \frac{d^k E_n}{d\lambda^k} \right|_{\lambda=0}, \quad k = 1, 2, \dots \quad (9.12)$$

Equations (9.9) and (9.10) become

$$\psi_n = \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots + \lambda^k\psi_n^{(k)} + \cdots \quad (9.13)$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots + \lambda^k E_n^{(k)} + \cdots \quad (9.14)$$

For $k = 1, 2, 3, \dots$, we call $\psi_n^{(k)}$ and $E_n^{(k)}$ the **k th-order corrections** to the wave function and energy. We shall assume that the series (9.13) and (9.14) converge for $\lambda = 1$, and we hope that for a small perturbation, taking just the first few terms of the series will give a good approximation to the true energy and wave function. (Quite often, perturbation-theory series do not converge, but even so, the first few terms of a nonconvergent series can often give a useful approximation.)

We shall take $\psi_n^{(0)}$ to be normalized: $\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = 1$. Instead of taking ψ_n as normalized, we shall require that ψ_n satisfy

$$\langle \psi_n^{(0)} | \psi_n \rangle = 1 \quad (9.15)$$

If ψ_n does not satisfy this equation, then multiplication of ψ_n by the constant $1 / \langle \psi_n^{(0)} | \psi_n \rangle$ gives a perturbed wave function with the desired property. The condition (9.15), called **intermediate normalization**, simplifies the derivation. Note that multiplication of ψ_n by a constant does not change the energy in the Schrödinger equation $\hat{H}\psi_n = E_n\psi_n$, so use of intermediate normalization does not affect the results for the energy corrections. If desired, at the end of the calculation, the intermediate-normalized ψ_n can be multiplied by a constant to normalize it in the usual sense.

Substitution of (9.13) into $1 = \langle \psi_n^{(0)} | \psi_n \rangle$ [Eq. (9.15)] gives

$$1 = \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle + \lambda \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + \lambda^2 \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle + \cdots$$

Since this equation is true for all values of λ in the range 0 to 1, the coefficients of like powers of λ on each side of the equation must be equal, as proved after Eq. (4.11). Equating the λ^0 coefficients, we have $1 = \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle$, which is satisfied since $\psi_n^{(0)}$ is normalized. Equating the coefficients of λ^1 , of λ^2 , and so on, we have

$$\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0, \quad \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle = 0, \quad \text{etc.} \quad (9.16)$$

The corrections to the wave function are orthogonal to $\psi_n^{(0)}$ when intermediate normalization is used.

Substituting (9.13) and (9.14) into the Schrödinger equation (9.8), we have

$$\begin{aligned} (\hat{H}^0 + \lambda\hat{H}')(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots) \\ = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots)(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots) \end{aligned}$$

Collecting like powers of λ , we have

$$\begin{aligned} \hat{H}^0\psi_n^{(0)} + \lambda(\hat{H}'\psi_n^{(0)} + \hat{H}^0\psi_n^{(1)}) + \lambda^2(\hat{H}'\psi_n^{(1)} + \hat{H}^0\psi_n^{(2)}) + \cdots \\ = E_n^{(0)}\psi_n^{(0)} + \lambda(E_n^{(1)}\psi_n^{(0)} + E_n^{(0)}\psi_n^{(1)}) + \lambda^2(E_n^{(2)}\psi_n^{(0)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(0)}\psi_n^{(2)}) + \cdots \end{aligned} \quad (9.17)$$

Now (assuming suitable convergence) for the two series on each side of (9.17) to be equal to each other for all values of λ , the coefficients of like powers of λ in the two series must be equal.

Equating the coefficients of the λ^0 terms, we have $\hat{H}^0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$, which is the Schrödinger equation for the unperturbed problem, Eq. (9.2), and gives us no new information.

Equating the coefficients of the λ^1 terms, we have

$$\begin{aligned} \hat{H}'\psi_n^{(0)} + \hat{H}^0\psi_n^{(1)} &= E_n^{(1)}\psi_n^{(0)} + E_n^{(0)}\psi_n^{(1)} \\ \hat{H}^0\psi_n^{(1)} - E_n^{(0)}\psi_n^{(1)} &= E_n^{(1)}\psi_n^{(0)} - \hat{H}'\psi_n^{(0)} \end{aligned} \quad (9.18)$$

The First-Order Energy Correction

To find $E_n^{(1)}$ we multiply (9.18) by $\psi_m^{(0)*}$ and integrate over all space, which gives

$$\langle \psi_m^{(0)} | \hat{H}^0 | \psi_n^{(1)} \rangle - E_n^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = E_n^{(1)} \langle \psi_m^{(0)} | \psi_n^{(0)} \rangle - \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle \quad (9.19)$$

where bracket notation [Eqs. (7.1) and (7.3)] is used. $\hat{H}^0$ is Hermitian, and use of the Hermitian property (7.12) gives for the first term on the left side of (9.19)

$$\begin{aligned} \langle \psi_m^{(0)} | \hat{H}^0 | \psi_n^{(1)} \rangle &= \langle \psi_n^{(1)} | \hat{H}^0 | \psi_m^{(0)} \rangle^* = \langle \psi_n^{(1)} | \hat{H}^0 \psi_m^{(0)} \rangle^* \\ &= \langle \psi_n^{(1)} | E_m^{(0)} \psi_m^{(0)} \rangle^* = E_m^{(0)*} \langle \psi_n^{(1)} | \psi_m^{(0)} \rangle^* = E_m^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle \end{aligned} \quad (9.20)$$

where we used the unperturbed Schrödinger equation $\hat{H}^0 \psi_m^{(0)} = E_m^{(0)} \psi_m^{(0)}$, the fact that $E_m^{(0)}$ is real, and (7.4). Substitution of (9.20) into (9.19) and use of the orthonormality equation $\langle \psi_m^{(0)} | \psi_n^{(0)} \rangle = \delta_{mn}$ for the unperturbed eigenfunctions gives

$$(E_m^{(0)} - E_n^{(0)}) \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = E_n^{(1)} \delta_{mn} - \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle \quad (9.21)$$

If $m = n$, the left side of (9.21) equals zero, and (9.21) becomes

$$E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle = \int \psi_n^{(0)*} \hat{H}' \psi_n^{(0)} d\tau \quad (9.22)$$

The first-order correction to the energy is found by averaging the perturbation $\hat{H}'$ over the appropriate unperturbed wave function.

Setting $\lambda = 1$ in (9.14), we have

$$E_n \approx E_n^{(0)} + E_n^{(1)} = E_n^{(0)} + \int \psi_n^{(0)*} \hat{H}' \psi_n^{(0)} d\tau \quad (9.23)$$

EXAMPLE

For the anharmonic oscillator with Hamiltonian (9.3), evaluate $E^{(1)}$ for the ground state if the unperturbed system is taken as the harmonic oscillator.

The perturbation is given by Eqs. (9.3) to (9.5) as

$$\hat{H}' = \hat{H} - \hat{H}^0 = cx^3 + dx^4$$

and the first-order energy correction for the state with quantum number v is given by (9.22) as $E_v^{(1)} = \langle \psi_v^{(0)} | cx^3 + dx^4 | \psi_v^{(0)} \rangle$, where $\psi_v^{(0)}$ is the harmonic-oscillator wave function for state v . For the $v = 0$ ground state, use of $\psi_0^{(0)} = (\alpha/\pi)^{1/4} e^{-\alpha x^2/2}$ [Eq. (4.53)] gives

$$E_0^{(1)} = \langle \psi_0^{(0)} | cx^3 + dx^4 | \psi_0^{(0)} \rangle = \left(\frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2} (cx^3 + dx^4) dx$$

The integral from $-\infty$ to ∞ of the odd function $cx^3 e^{-\alpha x^2}$ is zero. Use of the Appendix integral (A.10) with $n = 2$ and (4.31) for α gives

$$E_0^{(1)} = 2d \left(\frac{\alpha}{\pi} \right)^{1/2} \int_0^{\infty} e^{-\alpha x^2} x^4 dx = \frac{3d}{4\alpha^2} = \frac{3dh^2}{64\pi^4 v^2 m^2}$$

The unperturbed ground-state energy is $E_0^{(0)} = \frac{1}{2}h\nu$ and $E_0^{(0)} + E_0^{(1)} = \frac{1}{2}h\nu + 3dh^2/64\pi^4 v^2 m^2$.

EXERCISE Consider a one-particle, one-dimensional system with $V = \infty$ for $x < 0$ and for $x > l$, and $V = cx$ for $0 \leq x \leq l$, where c is a constant. (a) Sketch V for $c > 0$. (b) Treat the system as a perturbed particle in a box and find $E^{(1)}$ for the state with quantum number n . Then use Eq. (3.88) to state why the answer you got is to be expected. (Partial Answer: (b) $\frac{1}{2}cl$.)

The First-Order Wave-Function Correction

For $m \neq n$, Eq. (9.21) is

$$(E_m^{(0)} - E_n^{(0)}) \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = -\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle, \quad m \neq n \quad (9.24)$$

To find $\psi_n^{(1)}$, we expand it in terms of the complete, orthonormal set of unperturbed eigenfunctions $\psi_m^{(0)}$ of the Hermitian operator $\hat{H}^0$:

$$\psi_n^{(1)} = \sum_m a_m \psi_m^{(0)}, \quad \text{where } a_m = \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle \quad (9.25)$$

where Eq. (7.41) was used for the expansion coefficients a_m . Use of $a_m = \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle$ in (9.24) gives

$$(E_m^{(0)} - E_n^{(0)}) a_m = -\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle, \quad m \neq n$$

By hypothesis, the level $E_n^{(0)}$ is nondegenerate. Therefore $E_m^{(0)} \neq E_n^{(0)}$ for $m \neq n$, and we may divide by $(E_m^{(0)} - E_n^{(0)})$ to get

$$a_m = \frac{\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}, \quad m \neq n \quad (9.26)$$

The coefficients a_m in the expansion (9.25) of $\psi_n^{(1)}$ are given by (9.26) except for a_n , the coefficient of $\psi_n^{(0)}$. From the second equation in (9.25), $a_n = \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle$. Recall that the choice of intermediate normalization for ψ_n makes $\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0$ [Eq. (9.16)]. Hence $a_n = \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0$, and Eqs. (9.25) and (9.26) give the first-order correction to the wave function as

$$\psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)} \quad (9.27)$$

The symbol $\sum_{m \neq n}$ means we sum over all the unperturbed states except state n .

Setting $\lambda = 1$ in (9.13) and using just the first-order wave-function correction, we have as the approximation to the perturbed wave function

$$\psi_n \approx \psi_n^{(0)} + \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)} \quad (9.28)$$

For $\psi_n^{(2)}$ and the normalization of ψ , see *Kemble*, Chapter XI.

The Second-Order Energy Correction

Equating the coefficients of the λ^2 terms in (9.17), we get

$$\hat{H}^0 \psi_n^{(2)} - E_n^{(0)} \psi_n^{(2)} = E_n^{(2)} \psi_n^{(0)} + E_n^{(1)} \psi_n^{(1)} - \hat{H}' \psi_n^{(1)} \quad (9.29)$$

Multiplication by $\psi_m^{(0)*}$ followed by integration over all space gives

$$\begin{aligned} \langle \psi_m^{(0)} | \hat{H}^0 | \psi_n^{(2)} \rangle - E_n^{(0)} \langle \psi_m^{(0)} | \psi_n^{(2)} \rangle \\ = E_n^{(2)} \langle \psi_m^{(0)} | \psi_n^{(0)} \rangle + E_n^{(1)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle - \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(1)} \rangle \end{aligned} \quad (9.30)$$

The integral $\langle \psi_m^{(0)} | \hat{H}^0 | \psi_n^{(2)} \rangle$ in this equation is the same as the integral in (9.20), except that $\psi_n^{(1)}$ is replaced by $\psi_n^{(2)}$. Replacement of $\psi_n^{(1)}$ by $\psi_n^{(2)}$ in (9.20) gives

$$\langle \psi_m^{(0)} | \hat{H}^0 | \psi_n^{(2)} \rangle = E_m^{(0)} \langle \psi_m^{(0)} | \psi_n^{(2)} \rangle \quad (9.31)$$

Use of (9.31) and orthonormality of the unperturbed functions in (9.30) gives

$$(E_m^{(0)} - E_n^{(0)}) \langle \psi_m^{(0)} | \psi_n^{(2)} \rangle = E_n^{(2)} \delta_{mn} + E_n^{(1)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle - \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(1)} \rangle \quad (9.32)$$

For $m = n$, the left side of (9.32) is zero and we get

$$\begin{aligned} E_n^{(2)} &= -E_n^{(1)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(1)} \rangle \\ E_n^{(2)} &= \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(1)} \rangle \end{aligned} \quad (9.33)$$

since $\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0$ [Eq. (9.16)]. Note from (9.33) that to find the *second-order* correction to the energy, we have to know only the *first-order* correction to the wave function. In fact, it can be shown that knowledge of $\psi_n^{(1)}$ suffices to determine $E_n^{(3)}$ also.

In general, it can be shown that *if we know the corrections to the wave function through order k , then we can compute the corrections to the energy through order $2k + 1$* (see Bates, Vol. I, p. 184).

Substitution of (9.27) for $\psi_n^{(1)}$ into (9.33) gives

$$E_n^{(2)} = \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \langle \psi_n^{(0)} | \hat{H}' | \psi_m^{(0)} \rangle \quad (9.34)$$

since the expansion coefficients a_m [Eq. (9.26)] are constants that can be taken outside the integral. Since $\hat{H}'$ is Hermitian, we have

$$\begin{aligned} \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle \langle \psi_n^{(0)} | \hat{H}' | \psi_m^{(0)} \rangle &= \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle^* \\ &= |\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle|^2 \end{aligned}$$

and (9.34) becomes

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} \quad (9.35)$$

which is the desired expression for $E_n^{(2)}$ in terms of the unperturbed wave functions and energies.

Inclusion of $E_n^{(2)}$ in (9.14) with $\lambda = 1$ gives the approximate energy of the perturbed state as

$$E_n \approx E_n^{(0)} + H'_{nn} + \sum_{m \neq n} \frac{|H'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}} \quad (9.36)$$

where the integrals are over the unperturbed normalized wave functions.

For formulas for higher-order energy corrections, see Bates, Volume I, pages 181–185. The form of perturbation theory developed in this section is called *Rayleigh–Schrödinger perturbation theory*; other approaches exist.

Discussion

Equation (9.28) shows that the effect of the perturbation on the wave function $\psi_n^{(0)}$ is to “mix in” contributions from other states $\psi_m^{(0)}$, $m \neq n$. Because of the factor $1/(E_n^{(0)} - E_m^{(0)})$, the most important contributions (aside from $\psi_n^{(0)}$) to the perturbed wave function come from states nearest in energy to state n .

To evaluate the first-order correction to the energy, we must evaluate only the single integral H'_{nn} , whereas to evaluate the second-order energy correction, we must evaluate the matrix elements of $\hat{H}'$ between the n th state and all other states m , and then perform the infinite sum in (9.35). In many cases the second-order energy correction cannot be evaluated exactly. It is even harder to deal with third-order and higher-order energy corrections.

The sums in (9.28) and (9.36) are sums over different states rather than sums over different energy values. If some of the energy levels (other than the n th) are degenerate, we must include a term in the sums for each linearly independent wave function corresponding to the degenerate levels.

We have a sum over states in (9.28) and (9.36) because we require a complete set of functions for the expansion (9.25), and therefore we must include all linearly independent wave functions in the sum. If the unperturbed problem has continuum wave functions (for example, the hydrogen atom), we must also include an integration over the continuum functions, if we are to have a complete set. If $\psi_E^{(0)}$ denotes an unperturbed continuum wave function of energy $E^{(0)}$, then (9.27) and (9.35) become

$$\begin{aligned}\psi_n^{(1)} &= \sum_{m \neq n} \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)} + \int \frac{H'_{E,n}}{E_n^{(0)} - E^{(0)}} \psi_E^{(0)} dE^{(0)} \\ E_n^{(2)} &= \sum_{m \neq n} \frac{|H'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}} + \int \frac{|H'_{E,n}|^2}{E_n^{(0)} - E^{(0)}} dE^{(0)}\end{aligned}\quad (9.37)$$

where $H'_{E,n} \equiv \langle \psi_E^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle$. The integrals in these equations are over the range of continuum-state energies (for example, from zero to infinity for the hydrogen atom). The existence of continuum states in the unperturbed problem makes evaluation of $E_n^{(2)}$ even harder.

Comparison of the Variation and Perturbation Methods

The perturbation method applies to all the bound states of a system. Although the variation theorem stated in Section 8.1 applies only to the lowest state of a given symmetry, we can use the linear variation method to treat excited bound states.

Perturbation calculations are often hard to do because of the need to evaluate the infinite sums over discrete states and integrals over continuum states that occur in the second-order and higher-order energy corrections.

In the perturbation method, one can calculate the energy much more accurately (to order $2k + 1$) than the wave function (to order k). The same situation holds in the variation method, where one can get a rather good energy with a rather inaccurate wave function. If one calculates properties other than the energy, the results will generally not be as reliable as the calculated energy.

The Variation–Perturbation Method

The variation–perturbation method allows one to accurately estimate $E^{(2)}$ and higher-order perturbation-theory energy corrections for the ground state of a system without evaluating the infinite sum in (9.36). The method is based on the inequality

$$\langle u | \hat{H}^0 - E_g^{(0)} | u \rangle + \langle u | \hat{H}' - E_g^{(1)} | \psi_g^{(0)} \rangle + \langle \psi_g^{(0)} | \hat{H}' - E_g^{(1)} | u \rangle \geq E_g^{(2)} \quad (9.38)$$

where u is any well-behaved function that satisfies the boundary conditions and where the subscript g refers to the ground state. For the proof of (9.38), see *Hameka*, Section 7-9. By taking u to be a trial function with parameters that we vary to minimize the left side of (9.38), we can estimate $E_g^{(2)}$. The function u turns out to be an approximation to $\psi_g^{(1)}$, the first-order correction to the ground-state wave function, and u can then be used to estimate $E_g^{(3)}$ also. Similar variational integrals can be used to find higher-order corrections to the ground-state energy and wave function.

9.3 Perturbation Treatment of the Helium-Atom Ground State

The helium atom has two electrons and a nucleus of charge $+2e$. We shall consider the nucleus to be at rest (Section 6.6) and place the origin of the coordinate system at the nucleus. The coordinates of electrons 1 and 2 are (x_1, y_1, z_1) and (x_2, y_2, z_2) ; see **Fig. 9.1**.

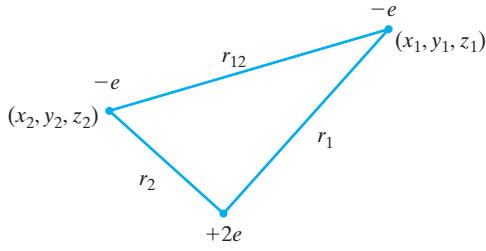


FIGURE 9.1 Interparticle distances in the helium atom.

If we take the nuclear charge to be $+Ze$ instead of $+2e$, we can treat heliumlike ions such as H^- , Li^+ , and Be^{2+} . The Hamiltonian operator is

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad (9.39)$$

where m_e is the mass of the electron, r_1 and r_2 are the distances of electrons 1 and 2 from the nucleus, and r_{12} is the distance from electron 1 to 2. The first two terms are the operators for the electrons' kinetic energy [Eq. (3.48)]. The third and fourth terms are the potential energies of attraction between the electrons and the nucleus. The final term is the potential energy of interelectronic repulsion [Eq. (6.58)]. Note that the potential energy of a system of interacting particles cannot be written as the sum of potential energies of the individual particles. The potential energy is a property of the system as a whole.

The Schrödinger equation involves six independent variables, three coordinates for each electron. In spherical coordinates, $\psi = \psi(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$.

The operator ∇_1^2 is given by Eq. (6.6) with r_1, θ_1, ϕ_1 replacing r, θ, ϕ . The variable r_{12} is $r_{12} = [(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2]^{1/2}$, and by using the relations between Cartesian and spherical coordinates, we can express r_{12} in terms of $r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2$.

Because of the $e^2/4\pi\epsilon_0 r_{12}$ term, the Schrödinger equation for helium cannot be separated in any coordinate system, and we must use approximation methods. The perturbation method separates the Hamiltonian (9.39) into two parts, $\hat{H}^0$ and $\hat{H}'$, where $\hat{H}^0$ is the Hamiltonian of an exactly solvable problem. If we choose

$$\hat{H}^0 = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_2} \quad (9.40)$$

$$\hat{H}' = \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad (9.41)$$

then $\hat{H}^0$ is the sum of two hydrogenlike Hamiltonians, one for each electron:

$$\hat{H}^0 = \hat{H}_1^0 + \hat{H}_2^0 \quad (9.42)$$

$$\hat{H}_1^0 \equiv -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1}, \quad \hat{H}_2^0 \equiv -\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_2} \quad (9.43)$$

The unperturbed system is a helium atom in which the two electrons exert no forces on each other. Although such a system does not exist, this does not prevent us from applying perturbation theory to this system.

Since the unperturbed Hamiltonian (9.42) is the sum of the Hamiltonians for two independent particles, we can use the separation-of-variables results of Eqs. (6.18) to (6.24) to conclude that the unperturbed wave functions have the form

$$\psi^{(0)}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) = F_1(r_1, \theta_1, \phi_1)F_2(r_2, \theta_2, \phi_2) \quad (9.44)$$

and the unperturbed energies are

$$E^{(0)} = E_1 + E_2 \quad (9.45)$$

$$\hat{H}_1^0 F_1 = E_1 F_1, \quad \hat{H}_2^0 F_2 = E_2 F_2 \quad (9.46)$$

Since $\hat{H}_1^0$ and $\hat{H}_2^0$ are hydrogenlike Hamiltonians, the solutions of (9.46) are the hydrogenlike eigenfunctions and eigenvalues. From Eq. (6.94), we have

$$E_1 = -\frac{Z^2}{n_1^2} \frac{e^2}{8\pi\epsilon_0 a_0}, \quad E_2 = -\frac{Z^2}{n_2^2} \frac{e^2}{8\pi\epsilon_0 a_0} \quad (9.47)$$

$$E^{(0)} = -Z^2 \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right) \frac{e^2}{8\pi\epsilon_0 a_0}, \quad \begin{array}{l} n_1 = 1, 2, 3, \dots \\ n_2 = 1, 2, 3, \dots \end{array} \quad (9.48)$$

where a_0 is the Bohr radius. Equation (9.48) gives the zeroth-order energies of states with both electrons bound to the nucleus. The He atom also has continuum states.

The lowest level has $n_1 = 1, n_2 = 1$, and its zeroth-order wave function is [Eq. (6.104)]

$$\psi_{1s^2}^{(0)} = \frac{1}{\pi^{1/2}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr_1/a_0} \cdot \frac{1}{\pi^{1/2}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr_2/a_0} = 1s(1)1s(2) \quad (9.49)$$

where $1s(1)1s(2)$ denotes the product of hydrogenlike $1s$ functions for electrons 1 and 2, and where the subscript indicates that both electrons are in hydrogenlike $1s$ orbitals. (Note that the procedure of assigning electrons to orbitals and writing the atomic wave function as the product of one-electron orbital functions is an *approximation*.) The energy of this unperturbed ground state is

$$E_{1s^2}^{(0)} = -Z^2(2) \frac{e^2}{8\pi\epsilon_0 a_0} \quad (9.50)$$

The quantity $-e^2/8\pi\epsilon_0 a_0$ is the ground-state energy of the hydrogen atom (taking the nucleus to be infinitely heavy) and equals -13.606 eV [Eqs. (6.105)–(6.108)]. If the electron mass m_e in a_0 is replaced by the reduced mass for ${}^4\text{He}$, $-e^2/8\pi\epsilon_0 a_0$ is changed to -13.604 eV, and we shall use this number to (partly) correct for the nuclear motion in He. For helium, $Z = 2$ and (9.50) gives $-8(13.604 \text{ eV}) = -108.83$ eV:

$$E_{1s^2}^{(0)} = -108.83 \text{ eV} \quad (9.51)$$

How does this zeroth-order energy compare with the true helium ground-state energy? The experimental first ionization energy of He is 24.587 eV. The second ionization energy of He is easily calculated theoretically, since it is the ionization energy of the hydrogenlike ion He^+ and is equal to $2^2(13.604 \text{ eV}) = 54.416$ eV. If we choose the zero of energy as the completely ionized atom [this choice is implicit in (9.39)], then the ground-state energy of the helium atom is $-(24.587 + 54.416) \text{ eV} = -79.00$ eV. The zeroth-order energy (9.51) is in error by 38%. We should have expected such a large error, since the perturbation term $e^2/4\pi\epsilon_0 r_{12}$ is not small.

The next step is to evaluate the first-order perturbation correction to the energy. The unperturbed ground state is nondegenerate, and use of (9.22) and (9.49) gives

$$\begin{aligned} E^{(1)} &= \langle \psi^{(0)} | \hat{H}' | \psi^{(0)} \rangle \\ E^{(1)} &= \frac{Z^6 e^2}{(4\pi\epsilon_0)\pi^2 a_0^6} \int_0^{2\pi} \int_0^{2\pi} \int_0^\pi \int_0^\pi \int_0^\infty \int_0^\infty e^{-2Zr_1/a_0} e^{-2Zr_2/a_0} \frac{1}{r_{12}} r_1^2 \sin \theta_1 \\ &\quad \times r_2^2 \sin \theta_2 dr_1 dr_2 d\theta_1 d\theta_2 d\phi_1 d\phi_2 \quad (9.52) \end{aligned}$$

The volume element for this two-electron problem contains the coordinates of both electrons; $d\tau = d\tau_1 d\tau_2$. The integral in (9.52) can be evaluated by using an expansion of $1/r_{12}$ in terms of spherical harmonics, as outlined in Prob. 9.14. One finds

$$E^{(1)} = \frac{5Z}{8} \left(\frac{e^2}{4\pi\epsilon_0 a_0} \right) \quad (9.53)$$

Recalling that $\frac{1}{2}e^2/4\pi\epsilon_0 a_0$ equals 13.604 eV when the ^4He reduced mass is used, and putting $Z = 2$, we find for the first-order perturbation energy correction for the helium ground state:

$$E^{(1)} = \frac{10}{4}(13.604 \text{ eV}) = 34.01 \text{ eV}$$

Our approximation to the energy is now

$$E^{(0)} + E^{(1)} = -108.83 \text{ eV} + 34.01 \text{ eV} = -74.82 \text{ eV} \quad (9.54)$$

which, compared with the experimental value of -79.00 eV , is in error by 5.3%.

To evaluate the first-order correction to the wave function and higher-order corrections to the energy requires evaluating the matrix elements of $1/r_{12}$ between the ground unperturbed state and all excited states (including the continuum) and performing the appropriate summations and integrations. No one has yet figured out how to evaluate directly all the contributions to $E^{(1)}$. Note that the effect of $\psi^{(1)}$ is to mix into the wave-function contributions from other configurations besides $1s^2$. We call this *configuration interaction*. The largest contribution to the true ground-state wave function of helium comes from the $1s^2$ configuration, which is the unperturbed (zeroth-order) wave function.

$E^{(2)}$ for the helium ground state has been calculated using the variation-perturbation method, Eq. (9.38). Scherr and Knight used 100-term trial functions to get extremely accurate approximations to the wave-function corrections through sixth order and thus to the energy corrections through thirteenth order [C. W. Scherr and R. E. Knight, *Rev. Mod. Phys.*, **35**, 436 (1963)]. For calculations of the energy corrections through order 401, see J. D. Baker et al., *Phys. Rev. A*, **41**, 1247 (1990). The second-order correction $E^{(2)}$ turns out to be -4.29 eV , and $E^{(3)}$ is $+0.12 \text{ eV}$. Through third order, we have for the ground-state energy

$$E \approx -108.83 \text{ eV} + 34.01 \text{ eV} - 4.29 \text{ eV} + 0.12 \text{ eV} = -78.99 \text{ eV}$$

which is close to the experimental value -79.00 eV . Including corrections through thirteenth order, Scherr and Knight obtained a ground-state helium energy of $-2.90372433(e^2/4\pi\epsilon_0 a_0)$, which is close to the value $-2.90372438(e^2/4\pi\epsilon_0 a_0)$ obtained from the purely variational calculations described in the next section.

The perturbation-theory series expansion for the He-atom energy can be proved to converge [R. Ahlrichs, *Phys. Rev. A*, **5**, 605 (1972)].

An exact wave function and energy cannot be found for the two-electron ground-state He atom, but remarkably, there exists a two-electron problem for which the exact ground-state solution of the Schrödinger equation has been found. This is a hypothetical atom (called the *Hooke's-law atom* or *harmonium*) with Hamiltonian operator

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 + \frac{1}{2}k(r_1^2 + r_2^2) + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

where r_1 and r_2 are the distances of the electrons from the origin. For certain values of the force-constant k , exact ground-state wave functions and energies have been found. See en.wikipedia.org/wiki/Hooke's_atom.

9.4 Variation Treatments of the Ground State of Helium

In the last section, we wrote the helium-atom Hamiltonian as $\hat{H} = \hat{H}^0 + \hat{H}'$, where the ground-state eigenfunction $\psi_g^{(0)}$ of $\hat{H}^0$ is (9.49). What happens if we use the zeroth-order perturbation-theory ground-state wave function $\psi_g^{(0)}$ as the variation function ϕ in the variational integral? The variational integral $\langle \phi | \hat{H} | \phi \rangle = \langle \phi | \hat{H} \phi \rangle$ then becomes

$$\begin{aligned} \langle \phi | \hat{H} | \phi \rangle &= \langle \psi_g^{(0)} | (\hat{H}^0 + \hat{H}') \psi_g^{(0)} \rangle = \langle \psi_g^{(0)} | \hat{H}^0 \psi_g^{(0)} + \hat{H}' \psi_g^{(0)} \rangle \\ &= \langle \psi_g^{(0)} | E_g^{(0)} \psi_g^{(0)} \rangle + \langle \psi_g^{(0)} | \hat{H}' \psi_g^{(0)} \rangle = E_g^{(0)} + E_g^{(1)} \end{aligned} \quad (9.55)$$

since $\hat{H} \psi_g^{(0)} = E_g^{(0)} \psi_g^{(0)}$, $\langle \psi_g^{(0)} | \psi_g^{(0)} \rangle = 1$, and $E_g^{(1)} = \langle \psi_g^{(0)} | \hat{H}' | \psi_g^{(0)} \rangle$ [Eq. (9.22)]. Use of $\psi_g^{(0)}$ as the variation function gives the same energy result as in first-order perturbation theory.

Now consider variation functions for the helium-atom ground state. If we used $\psi_g^{(0)}$ [Eq. (9.49)] as the trial function, we would get the first-order perturbation result, -74.82 eV. To improve on this result, we introduce a variational parameter into (9.49). We try the normalized function

$$\phi = \frac{1}{\pi} \left(\frac{\zeta}{a_0} \right)^3 e^{-\zeta r_1/a_0} e^{-\zeta r_2/a_0} \quad (9.56)$$

which is obtained from (9.49) by replacing the true atomic number Z by a variational parameter ζ (zeta). ζ has a simple physical interpretation. Since one electron tends to screen the other from the nucleus, each electron is subject to an effective nuclear charge somewhat less than the full nuclear charge Z . If one electron fully shielded the other from the nucleus, we would have an effective nuclear charge of $Z - 1$. Since both electrons are in the same orbital, they will be only partly effective in shielding each other. We thus expect ζ to lie between $Z - 1$ and Z .

We now evaluate the variational integral. To expedite things, we rewrite the helium Hamiltonian (9.39) as

$$\begin{aligned} \hat{H} &= \left[-\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\zeta e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{\zeta e^2}{4\pi\epsilon_0 r_2} \right] + (\zeta - Z) \frac{e^2}{4\pi\epsilon_0 r_1} + (\zeta - Z) \frac{e^2}{4\pi\epsilon_0 r_2} \\ &\quad + \frac{e^2}{4\pi\epsilon_0 r_{12}} \end{aligned} \quad (9.57)$$

where the terms involving zeta were added and subtracted. The terms in brackets in (9.57) are the sum of two hydrogenlike Hamiltonians for nuclear charge ζ . Moreover, the trial function (9.56) is the product of two hydrogenlike $1s$ functions for nuclear charge ζ . Therefore, when these terms operate on ϕ , we have an eigenvalue equation, the eigenvalue being the sum of two hydrogenlike $1s$ energies for nuclear charge ζ :

$$\left[-\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\zeta e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{\zeta e^2}{4\pi\epsilon_0 r_2} \right] \phi = -\zeta^2 (2) \frac{e^2}{8\pi\epsilon_0 a_0} \phi \quad (9.58)$$

Using (9.57) and (9.58), we have

$$\begin{aligned} \int \phi^* \hat{H} \phi \, d\tau &= -\zeta^2 \frac{e^2}{4\pi\epsilon_0 a_0} \int \phi^* \phi \, d\tau + \frac{(\zeta - Z)e^2}{4\pi\epsilon_0} \int \frac{\phi^* \phi}{r_1} \, d\tau \\ &\quad + \frac{(\zeta - Z)e^2}{4\pi\epsilon_0} \int \frac{\phi^* \phi}{r_2} \, d\tau + \frac{e^2}{4\pi\epsilon_0} \int \frac{\phi^* \phi}{r_{12}} \, d\tau \end{aligned} \quad (9.59)$$

Let f_1 be a normalized $1s$ hydrogenlike orbital for nuclear charge ζ , occupied by electron 1. Let f_2 be the same function for electron 2:

$$f_1 = \frac{1}{\pi^{1/2}} \left(\frac{\zeta}{a_0} \right)^{3/2} e^{-\zeta r_1/a_0}, \quad f_2 = \frac{1}{\pi^{1/2}} \left(\frac{\zeta}{a_0} \right)^{3/2} e^{-\zeta r_2/a_0} \quad (9.60)$$

Noting that $\phi = f_1 f_2$, we now evaluate the integrals in (9.59):

$$\begin{aligned} \int \phi^* \phi d\tau &= \int \int f_1^* f_2^* f_1 f_2 d\tau_1 d\tau_2 = \int f_1^* f_1 d\tau_1 \int f_2^* f_2 d\tau_2 = 1 \\ \int \frac{\phi^* \phi}{r_1} d\tau &= \int \frac{f_1^* f_1}{r_1} d\tau_1 \int f_2^* f_2 d\tau_2 = \int \frac{f_1^* f_1}{r_1} d\tau_1 \\ &= \frac{1}{\pi} \frac{\zeta^3}{a_0^3} \int_0^\infty e^{-2\zeta r_1/a_0} \frac{r_1^2}{r_1} dr_1 \int_0^\pi \sin \theta_1 d\theta_1 \int_0^{2\pi} d\phi_1 = \frac{\zeta}{a_0} \end{aligned}$$

where the Appendix integral (A.8) was used. Also,

$$\int \frac{\phi^* \phi}{r_2} d\tau = \int \frac{f_2^* f_2}{r_2} d\tau_2 = \int \frac{f_1^* f_1}{r_1} d\tau_1 = \frac{\zeta}{a_0}$$

since it doesn't matter whether the label 1 or 2 is used on the dummy variables in the definite integral. Finally, we must evaluate $(e^2/4\pi\epsilon_0) \int (\phi^* \phi / r_{12}) d\tau$. This is the same as the integral (9.52) that occurred in the perturbation treatment, except that Z is replaced by ζ . Hence, from (9.53)

$$\frac{e^2}{4\pi\epsilon_0} \int \frac{\phi^* \phi}{r_{12}} d\tau = \frac{5\zeta e^2}{32\pi\epsilon_0 a_0}$$

The variational integral (9.59) thus has the value

$$\int \phi^* \hat{H} \phi d\tau = \left(\zeta^2 - 2Z\zeta + \frac{5}{8}\zeta \right) \frac{e^2}{4\pi\epsilon_0 a_0} \quad (9.61)$$

As a check, if we set $\zeta = Z$ in (9.61), we get the first-order perturbation-theory result, (9.50) plus (9.53).

We now vary ζ to minimize the variational integral:

$$\begin{aligned} \frac{\partial}{\partial \zeta} \int \phi^* \hat{H} \phi d\tau &= \left(2\zeta - 2Z + \frac{5}{8} \right) \frac{e^2}{4\pi\epsilon_0 a_0} = 0 \\ \zeta &= Z - \frac{5}{16} \end{aligned} \quad (9.62)$$

As anticipated, the effective nuclear charge lies between Z and $Z - 1$. Using (9.62) and (9.61), we get

$$\int \phi^* \hat{H} \phi d\tau = \left(-Z^2 + \frac{5}{8}Z - \frac{25}{256} \right) \frac{e^2}{4\pi\epsilon_0 a_0} = -\left(Z - \frac{5}{16} \right)^2 \frac{e^2}{4\pi\epsilon_0 a_0} \quad (9.63)$$

Putting $Z = 2$, we get as our approximation to the helium ground-state energy $-(27/16)^2 (e^2/4\pi\epsilon_0 a_0) = -(729/256) 2(13.604 \text{ eV}) = -77.48 \text{ eV}$, as compared with the true value of -79.00 eV . Use of ζ instead of Z has reduced the error from 5.3% to 1.9%. In accord with the variation theorem, the true ground-state energy is less than the variational integral.

How can we improve our variational result? We might try a function that had the general form of (9.56), that is, a product of two functions, one for each electron:

$$\phi = u(1)u(2) \quad (9.64)$$

However, we could try a variety of functions u in (9.64), instead of the single exponential used in (9.56). A systematic procedure for finding the function u that gives the lowest value of the variational integral will be discussed in Section 11.1. This procedure shows that for the best possible choice of u in (9.64) the variational integral equals -77.86 eV, which is still in error by 1.5%. We might ask why (9.64) does not give the true ground-state energy, no matter what form we try for u . The answer is that, when we write the trial function as the product of separate functions for each electron, we are making an approximation. Because of the $e^2/4\pi\epsilon_0 r_{12}$ term in the Hamiltonian, the Schrödinger equation for helium is not separable, and the true ground-state wave function cannot be written as the product of separate functions for each electron. To reach the true ground-state energy, we must go beyond a function of the form (9.64).

The Bohr model gave the correct energies for the hydrogen atom but failed when applied to helium. Hence, in the early days of quantum mechanics, it was important to show that the new theory could give an accurate treatment of helium. The pioneering work on the helium ground state was done by Hylleraas in the years 1928–1930. To allow for the effect of one electron on the motion of the other, Hylleraas used variational functions that contained the interelectronic distance r_{12} . One function he used is

$$\phi = N[e^{-\zeta r_1/a_0}e^{-\zeta r_2/a_0}(1 + br_{12})] \quad (9.65)$$

where N is the normalization constant and ζ and b are variational parameters. Since

$$r_{12} = [(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2]^{1/2} \quad (9.66)$$

the function (9.65) goes beyond the simple product form (9.64). Minimization of the variational integral with respect to the parameters gives $\zeta = 1.849$, $b = 0.364/a_0$, and a ground-state energy of -78.7 eV, in error by 0.3 eV. The $1 + br_{12}$ term makes the wave function larger for large values of r_{12} . This is as it should be, because the repulsion between the electrons makes it energetically more favorable for the electrons to avoid each other. Using a more complicated six-term trial function containing r_{12} , Hylleraas obtained an energy only 0.01 eV above the true ground-state energy.

Hylleraas's work has been extended by others. Using a 1078-term variational function, Pekeris found a ground-state energy of $-2.903724375(e^2/4\pi\epsilon_0 a_0)$ [C. L. Pekeris, *Phys. Rev.*, **115**, 1216 (1959)]. With relativistic and nuclear-motion corrections added, this gave for E_i , the ionization energy of helium, $E_i/hc = 198310.69$ cm $^{-1}$, compared with the experimental value 198310.67 cm $^{-1}$. Using an improved variational function, Frankowski and Pekeris bettered Pekeris's result by obtaining the energy $-2.90372437703(e^2/4\pi\epsilon_0 a_0)$, a result believed to be within $10^{-11}(e^2/4\pi\epsilon_0 a_0)$ of the true nonrelativistic, infinite-nuclear-mass ground-state energy [K. Frankowski and C. L. Pekeris, *Phys. Rev.*, **146**, 46 (1966)]. Drake and Yan used linear variational functions containing r_{12} to calculate the ground-state energy and many excited-state energies of He that are thought to be accurate to 1 part in 10^{14} or better [G. W. F. Drake and Z.-C. Yan, *Chem. Phys. Lett.*, **229**, 486 (1994); *Phys. Rev. A*, **46**, 2378 (1992)]. These workers similarly calculated Li variational energies for the ground state and two excited states with 1 part in 10^9 accuracy or better [Z.-C. Yan and G. W. F. Drake, *Phys. Rev. A*, **52**, 3711 (1995)]. Adding in relativistic and nuclear motion corrections, Drake and Yan found good agreement between theoretically calculated and experimental spectroscopic transition frequencies of He and Li. By doing a series of variational calculations with increasing numbers of terms in the variation function and extrapolating to the limit of an infinite number of terms, Drake and co-workers found the following ground-state,

nonrelativistic, infinite-nuclear-mass He energy: $-2.90372437703411959831 (e^2/4\pi\epsilon_0 a_0)$, which is believed accurate to 21 significant figures [G. W. F. Drake et al., *Phys. Rev. A*, **65**, 054501 (2002)].

9.5 Perturbation Theory for a Degenerate Energy Level

We now consider the perturbation treatment of an energy level whose degree of degeneracy is d . We have d linearly independent unperturbed wave functions corresponding to the degenerate level. We shall use the labels $1, 2, \dots, d$ for the states of the degenerate level, without implying that these are necessarily the lowest-lying states. The unperturbed Schrödinger equation is

$$\hat{H}^0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)} \quad (9.67)$$

with

$$E_1^{(0)} = E_2^{(0)} = \dots = E_d^{(0)} \quad (9.68)$$

The perturbed problem is

$$\hat{H} \psi_n = E_n \psi_n \quad (9.69)$$

$$\hat{H} = \hat{H}^0 + \lambda \hat{H}' \quad (9.70)$$

As λ goes to zero, the eigenvalues in (9.69) go to the eigenvalues in (9.67); we have $\lim_{\lambda \rightarrow 0} E_n = E_n^{(0)}$. **Figure 9.2** shows this for a hypothetical system with six states and a threefold-degenerate unperturbed level. Note that the perturbation splits the degenerate energy level. In some cases the perturbation may have no effect on the degeneracy or may only partly remove the degeneracy.

As $\lambda \rightarrow 0$, the eigenfunctions satisfying (9.69) approach eigenfunctions satisfying (9.67). Does this mean that $\lim_{\lambda \rightarrow 0} \psi_n = \psi_n^{(0)}$? Not necessarily. If $E_n^{(0)}$ is nondegenerate, there is a unique normalized eigenfunction $\psi_n^{(0)}$ of $\hat{H}^0$ with eigenvalue $E_n^{(0)}$, and we can be sure that $\lim_{\lambda \rightarrow 0} \psi_n = \psi_n^{(0)}$. However, if $E_n^{(0)}$ is the eigenvalue of the d -fold degenerate level, then (Section 3.6) any linear combination

$$c_1 \psi_1^{(0)} + c_2 \psi_2^{(0)} + \dots + c_d \psi_d^{(0)} \quad (9.71)$$

is a solution of (9.67) with eigenvalue (9.68). The set of linearly independent normalized functions $\psi_1^{(0)}, \psi_2^{(0)}, \dots, \psi_d^{(0)}$, which we use as eigenfunctions corresponding to the states

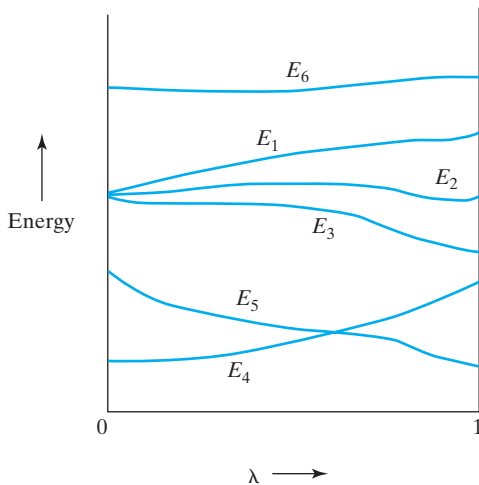


FIGURE 9.2 Effect of a perturbation on energy levels.

of the degenerate level, is not unique. Using (9.71), we can construct an infinite number of sets of d linearly independent normalized eigenfunctions for the degenerate level. As far as the unperturbed problem is concerned, one such set is as good as another. For example, for the three degenerate $2p$ states of the hydrogen atom, we can use the $2p_1$, $2p_0$, and $2p_{-1}$ functions; the $2p_x$, $2p_y$, and $2p_z$ functions; or some other set of three linearly independent functions constructed as linear combinations of the members of one of the preceding sets. For the perturbed eigenfunctions that correspond to the d -fold degenerate unperturbed level, all we can say is that as λ approaches zero they each approach a linear combination of unperturbed eigenfunctions:

$$\lim_{\lambda \rightarrow 0} \psi_n = \sum_{i=1}^d c_i \psi_i^{(0)}, \quad 1 \leq n \leq d \quad (9.72)$$

Our first task is thus to determine the **correct zeroth-order wave functions** (9.72) for the perturbation $\hat{H}'$. Calling these correct zeroth-order functions $\phi_n^{(0)}$, we have

$$\phi_n^{(0)} = \lim_{\lambda \rightarrow 0} \psi_n = \sum_{i=1}^d c_i \psi_i^{(0)}, \quad 1 \leq n \leq d \quad (9.73)$$

Each different function $\phi_n^{(0)}$ has a different set of coefficients in (9.73). The correct set of zeroth-order functions depends on what the perturbation $\hat{H}'$ is.

The treatment of the d -fold degenerate level proceeds like the nondegenerate treatment of Section 9.2, except that instead of $\psi_n^{(0)}$ we use $\phi_n^{(0)}$. Instead of Eqs. (9.13) and (9.14), we have

$$\psi_n = \phi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots, \quad n = 1, 2, \dots, d \quad (9.74)$$

$$E_n = E_d^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots, \quad n = 1, 2, \dots, d \quad (9.75)$$

where (9.68) was used. Substitution into $\hat{H}\psi_n = E_n\psi_n$ gives

$$\begin{aligned} (\hat{H}^0 + \lambda \hat{H}')(\phi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots) \\ = (E_d^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots)(\phi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots) \end{aligned}$$

Equating the coefficients of λ^0 in this equation, we get $\hat{H}^0 \phi_n^{(0)} = E_d^{(0)} \phi_n^{(0)}$. By the theorem of Section 3.6, each linear combination $\phi_n^{(0)}$ ($n = 1, 2, \dots, d$) is an eigenfunction of $\hat{H}^0$ with eigenvalue $E_d^{(0)}$, and this equation gives no new information.

Equating the coefficients of the λ^1 terms, we get

$$\begin{aligned} \hat{H}^0 \psi_n^{(1)} + \hat{H}' \phi_n^{(0)} &= E_d^{(0)} \psi_n^{(1)} + E_n^{(1)} \phi_n^{(0)} \\ \hat{H}^0 \psi_n^{(1)} - E_d^{(0)} \psi_n^{(1)} &= E_n^{(1)} \phi_n^{(0)} - \hat{H}' \phi_n^{(0)}, \quad n = 1, 2, \dots, d \end{aligned} \quad (9.76)$$

We now multiply (9.76) by $\psi_m^{(0)*}$ and integrate over all space, where m is one of the states corresponding to the d -fold degenerate unperturbed level under consideration; that is, $1 \leq m \leq d$. We get

$$\langle \psi_m^{(0)} | \hat{H}^0 | \psi_n^{(1)} \rangle - E_d^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = E_n^{(1)} \langle \psi_m^{(0)} | \phi_n^{(0)} \rangle - \langle \psi_m^{(0)} | \hat{H}' | \phi_n^{(0)} \rangle, \quad 1 \leq m \leq d \quad (9.77)$$

From Eq. (9.20), we have $\langle \psi_m^{(0)} | \hat{H}^0 | \psi_n^{(1)} \rangle = E_m^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle$. From (9.68), $E_m^{(0)} = E_d^{(0)}$ for $1 \leq m \leq d$, so $\langle \psi_m^{(0)} | \hat{H}^0 | \psi_n^{(1)} \rangle = E_d^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle$, and the left side of (9.77) equals zero. Equation (9.77) becomes

$$\langle \psi_m^{(0)} | \hat{H}' | \phi_n^{(0)} \rangle - E_n^{(1)} \langle \psi_m^{(0)} | \phi_n^{(0)} \rangle = 0, \quad m = 1, 2, \dots, d$$

corresponding to the root $E_n^{(1)}$, we solve (9.81) for $c_2, c_3, \dots, c_d$ in terms of c_1 and then find c_1 by normalization. Use of (9.79) in $\langle \phi_n^{(0)} | \phi_n^{(0)} \rangle = 1$ gives (Prob. 9.21)

$$\sum_{k=1}^d |c_k|^2 = 1 \quad (9.85)$$

For each root $E_n^{(1)}$, $n = 1, 2, \dots, d$, we have a different set of coefficients $c_1, c_2, \dots, c_d$, giving a different correct zeroth-order wave function.

In the next section, we shall show that

$$E_n^{(1)} = \langle \phi_n^{(0)} | \hat{H}' | \phi_n^{(0)} \rangle, \quad n = 1, 2, \dots, d \quad (9.86)$$

which is similar to the nondegenerate-case formula (9.22), except that the correct zeroth-order functions have to be used.

Using procedures similar to those for the nondegenerate case, one can now find the first-order corrections to the correct zeroth-order wave functions and the second-order energy corrections. For the results, see *Bates*, Volume I, pages 197–198; *Hameka*, pages 230–231.

As an example, consider the effect of a perturbation $\hat{H}'$ on the lowest degenerate energy level of a particle in a cubic box. We have three states corresponding to this level: $\psi_{211}^{(0)}$, $\psi_{121}^{(0)}$, and $\psi_{112}^{(0)}$. These unperturbed wave functions are orthonormal, and the secular equation (9.83) is

$$\begin{vmatrix} \langle 211 | \hat{H}' | 211 \rangle - E_n^{(1)} & \langle 211 | \hat{H}' | 121 \rangle & \langle 211 | \hat{H}' | 112 \rangle \\ \langle 121 | \hat{H}' | 211 \rangle & \langle 121 | \hat{H}' | 121 \rangle - E_n^{(1)} & \langle 121 | \hat{H}' | 112 \rangle \\ \langle 112 | \hat{H}' | 211 \rangle & \langle 112 | \hat{H}' | 121 \rangle & \langle 112 | \hat{H}' | 112 \rangle - E_n^{(1)} \end{vmatrix} = 0 \quad (9.87)$$

Solving this equation, we find the first-order energy corrections: $E_1^{(1)}, E_2^{(1)}, E_3^{(1)}$. The triply degenerate unperturbed level is split into three levels of energies (through first order): $(6h^2/8ma^2) + E_1^{(1)}$, $(6h^2/8ma^2) + E_2^{(1)}$, $(6h^2/8ma^2) + E_3^{(1)}$. Using each of the roots $E_1^{(1)}, E_2^{(1)}, E_3^{(1)}$, we get a different set of simultaneous equations (9.81). Solving each set, we find three sets of coefficients, which determine the three correct zeroth-order wave functions.

If you are familiar with matrix algebra, note that solving (9.83) and (9.81) amounts to finding the eigenvalues and eigenvectors of the matrix whose elements are $\langle \psi_m^{(0)} | \hat{H}' | \psi_i^{(0)} \rangle$.

9.6 Simplification of the Secular Equation

The secular equation (9.83) is easier to solve if some of the off-diagonal elements of the secular determinant are zero. In the most favorable case, all the off-diagonal elements are zero, and

$$\begin{vmatrix} H'_{11} - E_n^{(1)} & 0 & \cdots & 0 \\ 0 & H'_{22} - E_n^{(1)} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & H'_{dd} - E_n^{(1)} \end{vmatrix} = 0 \quad (9.88)$$

$$(H'_{11} - E_n^{(1)})(H'_{22} - E_n^{(1)}) \cdots (H'_{dd} - E_n^{(1)}) = 0$$

$$E_1^{(1)} = H'_{11}, \quad E_2^{(1)} = H'_{22}, \quad \dots, \quad E_d^{(1)} = H'_{dd} \quad (9.89)$$

Conversely, if we have, say, a fourfold-degenerate unperturbed level, and we happen to know that $\phi_1^{(0)}$ and $\phi_2^{(0)}$ are each linear combinations of $\psi_1^{(0)}$ and $\psi_2^{(0)}$ only, while $\phi_3^{(0)}$ and $\phi_4^{(0)}$ are each linear combinations of $\psi_3^{(0)}$ and $\psi_4^{(0)}$ only, we deal with two second-order secular determinants rather than a fourth-order secular determinant.

How can we choose the right zeroth-order wave functions in advance and thereby simplify the secular equation? Suppose there is an operator $\hat{A}$ that commutes with both $\hat{H}^0$ and $\hat{H}'$. Then we can choose the unperturbed functions to be eigenfunctions of $\hat{A}$. Because $\hat{A}$ commutes with $\hat{H}'$, this choice of unperturbed functions will make the integrals H'_{ij} vanish if $\psi_i^{(0)}$ and $\psi_j^{(0)}$ belong to different eigenvalues of $\hat{A}$ [see Eq. (7.50)]. Thus, if the eigenvalues of $\hat{A}$ for $\psi_1^{(0)}, \psi_2^{(0)}, \dots, \psi_d^{(0)}$ are all different, the secular determinant will be in diagonal form, and we will have the right zeroth-order wave functions. If some of the eigenvalues of $\hat{A}$ are the same, we get block-diagonal rather than diagonal form. In general, the correct zeroth-order functions will be linear combinations of those unperturbed functions that have the same eigenvalue of $\hat{A}$. (This is to be expected since $\hat{A}$ commutes with $\hat{H} = \hat{H}^0 + \hat{H}'$, so the perturbed eigenfunctions of $\hat{H}$ can be chosen to be eigenfunctions of $\hat{A}$.) For an example, see Prob. 9.23.

9.7 Perturbation Treatment of the First Excited States of Helium

Section 9.3 applied perturbation theory to the ground state of the helium atom. We now treat the lowest excited states of He. The unperturbed energies are given by (9.48). The lowest unperturbed excited states have $n_1 = 1, n_2 = 2$ or $n_1 = 2, n_2 = 1$, and substitution in (9.48) gives

$$E^{(0)} = -\frac{5Z^2}{8} \left(\frac{e^2}{4\pi\epsilon_0 a_0} \right) = -\frac{20}{8} 2 \left(\frac{e^2}{8\pi\epsilon_0 a_0} \right) = -5(13.606 \text{ eV}) = -68.03 \text{ eV} \quad (9.92)$$

Recall that the $n = 2$ level of a hydrogenlike atom is fourfold degenerate, the $2s$ and three $2p$ states all having the same energy. The first excited unperturbed energy level of He is eightfold degenerate. The eight unperturbed wave functions are [Eq. (9.44)]

$$\begin{aligned} \psi_1^{(0)} &= 1s(1)2s(2), & \psi_2^{(0)} &= 2s(1)1s(2), & \psi_3^{(0)} &= 1s(1)2p_x(2), & \psi_4^{(0)} &= 2p_x(1)1s(2) \\ \psi_5^{(0)} &= 1s(1)2p_y(2), & \psi_6^{(0)} &= 2p_y(1)1s(2), & \psi_7^{(0)} &= 1s(1)2p_z(2), & \psi_8^{(0)} &= 2p_z(1)1s(2) \end{aligned} \quad (9.93)$$

where $1s(1)2s(2)$ signifies the product of a hydrogenlike $1s$ function for electron 1 and a hydrogenlike $2s$ function for electron 2. The explicit form of $\psi_8^{(0)}$, for example, is (Table 6.2)

$$\psi_8^{(0)} = \frac{1}{4(2\pi)^{1/2}} \left(\frac{Z}{a_0} \right)^{5/2} r_1 e^{-Zr_1/2a_0} \cos \theta_1 \cdot \frac{1}{\pi^{1/2}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr_2/a_0}$$

We chose to use the real $2p$ hydrogenlike orbitals, rather than the complex ones.

Since the unperturbed level is degenerate, we must solve a secular equation. The secular equation (9.83) assumes that the functions $\psi_1^{(0)}, \psi_2^{(0)}, \dots, \psi_8^{(0)}$ are orthonormal. This condition is met. For example,

$$\begin{aligned} \int \psi_1^{(0)*} \psi_1^{(0)} d\tau &= \iint 1s(1)^* 2s(2)^* 1s(1) 2s(2) d\tau_1 d\tau_2 \\ &= \int |1s(1)|^2 d\tau_1 \int |2s(2)|^2 d\tau_2 = 1 \cdot 1 = 1 \\ \int \psi_3^{(0)*} \psi_5^{(0)} d\tau &= \int |1s(1)|^2 d\tau_1 \int 2p_x(2)^* 2p_y(2) d\tau_2 = 1 \cdot 0 = 0 \end{aligned}$$

where the orthonormality of the hydrogenlike orbitals has been used.

The secular determinant contains $8^2 = 64$ elements. The operator $\hat{H}'$ is Hermitian, and $H'_{ij} = (H'_{ji})^*$. Also, since $\hat{H}'$ and $\psi_1^{(0)}, \dots, \psi_8^{(0)}$ are all real, we have $(H'_{ji})^* = H'_{ji}$, so $H'_{ij} = H'_{ji}$. The secular determinant is symmetric about the principal diagonal. This cuts the labor of evaluating integrals almost in half.

By using parity considerations, we can show that most of the integrals H'_{ij} are zero. First consider H'_{13} :

$$H'_{13} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} 1s(1)2s(2) \frac{e^2}{4\pi\epsilon_0 r_{12}} 1s(1)2p_x(2) dx_1 dy_1 dz_1 dx_2 dy_2 dz_2$$

An s hydrogenlike function depends only on $r = (x^2 + y^2 + z^2)^{1/2}$ and is therefore an even function. The $2p_x(2)$ function is an odd function of x_2 [Eq. (6.119)]. r_{12} is given by (9.66), and if we invert all six coordinates, r_{12} is unchanged:

$$r_{12} \rightarrow [(-x_1 + x_2)^2 + (-y_1 + y_2)^2 + (-z_1 + z_2)^2]^{1/2} = r_{12}$$

Hence, on inverting all six coordinates, the integrand of H'_{13} goes into minus itself. Therefore [Eq. (7.64)], $H'_{13} = 0$. The same reasoning gives $H'_{14} = H'_{15} = H'_{16} = H'_{17} = H'_{18} = 0$ and $H'_{23} = H'_{24} = H'_{25} = H'_{26} = H'_{27} = H'_{28} = 0$. Now consider H'_{35} :

$$H'_{35} = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} 1s(1)2p_x(2) \frac{e^2}{4\pi\epsilon_0 r_{12}} 1s(1)2p_y(2) dx_1 \cdots dz_2$$

Suppose we invert the x coordinates: $x_1 \rightarrow -x_1$ and $x_2 \rightarrow -x_2$. This transformation will leave r_{12} unchanged. The functions $1s(1)$ and $2p_y(2)$ will be unaffected. However, $2p_x(2)$ will go over to minus itself, so the net effect will be to change the integrand of H'_{35} into minus itself. Hence (Prob. 7.30), $H'_{35} = 0$. Likewise, $H'_{36} = H'_{37} = H'_{38} = 0$ and $H'_{45} = H'_{46} = H'_{47} = H'_{48} = 0$. By considering the transformation $y_1 \rightarrow -y_1$, $y_2 \rightarrow -y_2$, we see that $H'_{57} = H'_{58} = H'_{67} = H'_{68} = 0$. The secular equation is thus

$$\begin{vmatrix} b_{11} & H'_{12} & 0 & 0 & 0 & 0 & 0 & 0 \\ H'_{12} & b_{22} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & b_{33} & H'_{34} & 0 & 0 & 0 & 0 \\ 0 & 0 & H'_{34} & b_{44} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & b_{55} & H'_{56} & 0 & 0 \\ 0 & 0 & 0 & 0 & H'_{56} & b_{66} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & b_{77} & H'_{78} \\ 0 & 0 & 0 & 0 & 0 & 0 & H'_{78} & b_{88} \end{vmatrix} = 0$$

$$b_{ii} \equiv H'_{ii} - E^{(1)}, \quad i = 1, 2, \dots, 8$$

The secular determinant is in block-diagonal form and factors into four determinants, each of second order. We conclude that the correct zeroth-order functions have the form

$$\begin{aligned} \phi_1^{(0)} &= c_1\psi_1^{(0)} + c_2\psi_2^{(0)}, & \phi_2^{(0)} &= \bar{c}_1\psi_1^{(0)} + \bar{c}_2\psi_2^{(0)} \\ \phi_3^{(0)} &= c_3\psi_3^{(0)} + c_4\psi_4^{(0)}, & \phi_4^{(0)} &= \bar{c}_3\psi_3^{(0)} + \bar{c}_4\psi_4^{(0)} \\ \phi_5^{(0)} &= c_5\psi_5^{(0)} + c_6\psi_6^{(0)}, & \phi_6^{(0)} &= \bar{c}_5\psi_5^{(0)} + \bar{c}_6\psi_6^{(0)} \\ \phi_7^{(0)} &= c_7\psi_7^{(0)} + c_8\psi_8^{(0)}, & \phi_8^{(0)} &= \bar{c}_7\psi_7^{(0)} + \bar{c}_8\psi_8^{(0)} \end{aligned} \quad (9.94)$$

where the unbarred coefficients correspond to one root of each second-order determinant and the barred coefficients correspond to the second root.

The first determinant is

$$\begin{vmatrix} H'_{11} - E^{(1)} & H'_{12} \\ H'_{12} & H'_{22} - E^{(1)} \end{vmatrix} = 0 \quad (9.95)$$

We have

$$\begin{aligned} H'_{11} &= \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} 1s(1)2s(2) \frac{e^2}{4\pi\epsilon_0 r_{12}} 1s(1)2s(2) dx_1 \cdots dz_2 \\ H'_{11} &= \iint [1s(1)]^2 [2s(2)]^2 \frac{e^2}{4\pi\epsilon_0 r_{12}} d\tau_1 d\tau_2 \\ H'_{22} &= \iint [1s(2)]^2 [2s(1)]^2 \frac{e^2}{4\pi\epsilon_0 r_{12}} d\tau_1 d\tau_2 \end{aligned}$$

The integration variables are dummy variables and may be given any symbols whatever. Let us relabel the integration variables in H'_{22} as follows: We interchange x_1 and x_2 , interchange y_1 and y_2 , and interchange z_1 and z_2 . This relabeling leaves r_{12} [Eq. (9.66)] unchanged, so

$$H'_{22} = \iint [1s(1)]^2 [2s(2)]^2 \frac{e^2}{4\pi\epsilon_0 r_{12}} d\tau_2 d\tau_1 = H'_{11} \quad (9.96)$$

The same argument shows that $H'_{33} = H'_{44}$, $H'_{55} = H'_{66}$, and $H'_{77} = H'_{88}$.

We denote H'_{11} by the symbol J_{1s2s} :

$$H'_{11} = J_{1s2s} = \iint [1s(1)]^2 [2s(2)]^2 \frac{e^2}{4\pi\epsilon_0 r_{12}} d\tau_1 d\tau_2 \quad (9.97)$$

This is an example of a **Coulomb integral**, the name arising because J_{1s2s} is equal to the electrostatic energy of repulsion between an electron with probability density function $[1s]^2$ and an electron with probability density function $[2s]^2$.

The integral H'_{12} is denoted by K_{1s2s} :

$$H'_{12} = K_{1s2s} = \iint 1s(1)2s(2) \frac{e^2}{4\pi\epsilon_0 r_{12}} 2s(1)1s(2) d\tau_1 d\tau_2 \quad (9.98)$$

This is an **exchange integral**: The functions on the left and right of $e^2/4\pi\epsilon_0 r_{12}$ differ from each other by an exchange of electrons 1 and 2.

The general definitions of the Coulomb integral J_{mn} and the exchange integral K_{mn} are

$$J_{mn} \equiv \langle f_m(1)f_n(2) | e^2/4\pi\epsilon_0 r_{12} | f_m(1)f_n(2) \rangle \quad (9.99)$$

$$K_{mn} \equiv \langle f_m(1)f_n(2) | e^2/4\pi\epsilon_0 r_{12} | f_n(1)f_m(2) \rangle \quad (9.100)$$

where the integrals go over the full range of the spatial coordinates of electrons 1 and 2, and f_m and f_n are spatial orbitals.

Substitution of (9.96) to (9.98) into (9.95) gives

$$\begin{vmatrix} J_{1s2s} - E^{(1)} & K_{1s2s} \\ K_{1s2s} & J_{1s2s} - E^{(1)} \end{vmatrix} = 0 \quad (9.101)$$

$$(J_{1s2s} - E^{(1)})^2 = (K_{1s2s})^2$$

$$E_1^{(1)} = J_{1s2s} - K_{1s2s}, \quad E_2^{(1)} = J_{1s2s} + K_{1s2s} \quad (9.102)$$

We now find the coefficients of the correct zeroth-order wave functions that correspond to these two roots. Use of $E_1^{(1)}$ in (9.81) gives

$$K_{1s2s}c_1 + K_{1s2s}c_2 = 0$$

$$K_{1s2s}c_1 + K_{1s2s}c_2 = 0$$

Hence $c_2 = -c_1$. Normalization gives

$$\langle \phi_1^{(0)} | \phi_1^{(0)} \rangle = \langle c_1 \psi_1^{(0)} - c_1 \psi_2^{(0)} | c_1 \psi_1^{(0)} - c_1 \psi_2^{(0)} \rangle = |c_1|^2 + |c_1|^2 = 1$$

$$c_1 = 2^{-1/2}$$

where the orthonormality of $\psi_1^{(0)}$ and $\psi_2^{(0)}$ was used. The zeroth-order wave function corresponding to $E_1^{(1)}$ is then

$$\phi_1^{(0)} = 2^{-1/2}(\psi_1^{(0)} - \psi_2^{(0)}) = 2^{-1/2}[1s(1)2s(2) - 2s(1)1s(2)] \quad (9.103)$$

Similarly, one finds the function corresponding to $E_2^{(1)}$ to be

$$\phi_2^{(0)} = 2^{-1/2}(\psi_1^{(0)} + \psi_2^{(0)}) = 2^{-1/2}[1s(1)2s(2) + 2s(1)1s(2)] \quad (9.104)$$

We have three more second-order determinants to deal with:

$$\begin{vmatrix} H'_{33} - E^{(1)} & H'_{34} \\ H'_{34} & H'_{33} - E^{(1)} \end{vmatrix} = 0 \quad (9.105)$$

$$\begin{vmatrix} H'_{55} - E^{(1)} & H'_{56} \\ H'_{56} & H'_{55} - E^{(1)} \end{vmatrix} = 0 \quad (9.106)$$

$$\begin{vmatrix} H'_{77} - E^{(1)} & H'_{78} \\ H'_{78} & H'_{77} - E^{(1)} \end{vmatrix} = 0 \quad (9.107)$$

Consider H'_{33} and H'_{55} :

$$H'_{33} = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} 1s(1)2p_x(2) \frac{e^2}{4\pi\epsilon_0 r_{12}} 1s(1)2p_x(2) dx_1 \cdots dz_2$$

$$H'_{55} = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} 1s(1)2p_y(2) \frac{e^2}{4\pi\epsilon_0 r_{12}} 1s(1)2p_y(2) dx_1 \cdots dz_2$$

These two integrals are equal—the only difference between them involves replacement of $2p_x(2)$ by $2p_y(2)$ —and these two orbitals differ only in their orientation in space. More formally, if we relabel the dummy integration variables in H'_{33} according to the scheme $x_2 \rightarrow y_2, y_2 \rightarrow x_2, x_1 \rightarrow y_1, y_1 \rightarrow x_1$, then r_{12} is unaffected and H'_{33} is transformed to H'_{55} . Similar reasoning shows $H'_{77} = H'_{33}$. Introducing the symbol J_{1s2p} for these Coulomb integrals, we have

$$H'_{33} = H'_{55} = H'_{77} = J_{1s2p} = \iint 1s(1)2p_z(2) \frac{e^2}{4\pi\epsilon_0 r_{12}} 1s(1)2p_z(2) d\tau_1 d\tau_2$$

Also, the exchange integrals involving the $2p$ orbitals are equal:

$$H'_{34} = H'_{56} = H'_{78} = K_{1s2p} = \iint 1s(1)2p_z(2) \frac{e^2}{4\pi\epsilon_0 r_{12}} 2p_z(1)1s(2) d\tau_1 d\tau_2$$

The three determinants (9.105) to (9.107) are thus identical and have the form

$$\begin{vmatrix} J_{1s2p} - E^{(1)} & K_{1s2p} \\ K_{1s2p} & J_{1s2p} - E^{(1)} \end{vmatrix} = 0$$

The determinant is similar to (9.101), and by analogy with (9.102)–(9.104), we get

$$E_3^{(1)} = E_5^{(1)} = E_7^{(1)} = J_{1s2p} - K_{1s2p} \quad (9.108)$$

$$E_4^{(1)} = E_6^{(1)} = E_8^{(1)} = J_{1s2p} + K_{1s2p} \quad (9.109)$$

$$\begin{aligned} \phi_3^{(0)} &= 2^{-1/2} [1s(1)2p_x(2) - 1s(2)2p_x(1)] \\ \phi_4^{(0)} &= 2^{-1/2} [1s(1)2p_x(2) + 1s(2)2p_x(1)] \\ \phi_5^{(0)} &= 2^{-1/2} [1s(1)2p_y(2) - 1s(2)2p_y(1)] \\ \phi_6^{(0)} &= 2^{-1/2} [1s(1)2p_y(2) + 1s(2)2p_y(1)] \\ \phi_7^{(0)} &= 2^{-1/2} [1s(1)2p_z(2) - 1s(2)2p_z(1)] \\ \phi_8^{(0)} &= 2^{-1/2} [1s(1)2p_z(2) + 1s(2)2p_z(1)] \end{aligned} \quad (9.110)$$

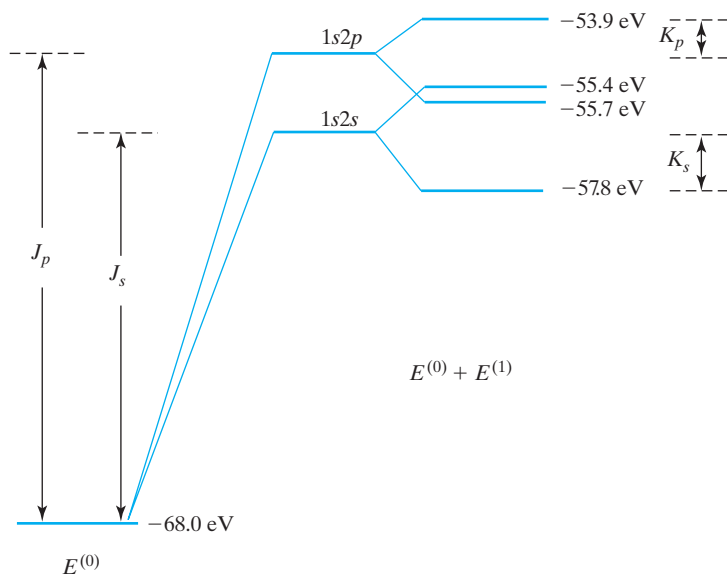
The electrostatic repulsion $e^2/4\pi\epsilon_0 r_{12}$ between the electrons has partly removed the degeneracy. The hypothetical eightfold-degenerate unperturbed level has been split into two nondegenerate levels associated with the configuration $1s2s$ and two triply degenerate levels associated with the configuration $1s2p$. It might be thought that higher-order energy corrections would further resolve the degeneracy. Actually, application of an external magnetic field is required to completely remove the degeneracy. Because the $e^2/4\pi\epsilon_0 r_{12}$ perturbation has not completely removed the degeneracy, any normalized linear combinations of $\phi_3^{(0)}$, $\phi_5^{(0)}$, and $\phi_7^{(0)}$ and of $\phi_4^{(0)}$, $\phi_6^{(0)}$, and $\phi_8^{(0)}$ can serve as correct zeroth-order wave functions.

To evaluate the Coulomb and exchange integrals in $E^{(1)}$ in (9.102) and (9.108), one uses the $1/r_{12}$ expansion given in Prob. 9.14. The results are

$$\begin{aligned} J_{1s2s} &= \left(\frac{17}{81}\right) \frac{Ze^2}{4\pi\epsilon_0 a_0} = 11.42 \text{ eV}, & J_{1s2p} &= \left(\frac{59}{243}\right) \frac{Ze^2}{4\pi\epsilon_0 a_0} = 13.21 \text{ eV} \\ K_{1s2s} &= \left(\frac{16}{729}\right) \frac{Ze^2}{4\pi\epsilon_0 a_0} = 1.19 \text{ eV}, & K_{1s2p} &= \left(\frac{112}{6561}\right) \frac{Ze^2}{4\pi\epsilon_0 a_0} = 0.93 \text{ eV} \end{aligned} \quad (9.111)$$

where we used $Z = 2$ and $e^2/8\pi\epsilon_0 a_0 = 13.606 \text{ eV}$. Recalling that $E^{(0)} = -68.03 \text{ eV}$ [Eq. (9.92)], we get (Fig. 9.3)

FIGURE 9.3 The first excited levels of the helium atom.



$$E^{(0)} + E_1^{(1)} = E^{(0)} + J_{1s2s} - K_{1s2s} = -57.8 \text{ eV}$$

$$E^{(0)} + E_2^{(1)} = E^{(0)} + J_{1s2s} + K_{1s2s} = -55.4 \text{ eV}$$

$$E^{(0)} + E_3^{(1)} = E^{(0)} + J_{1s2p} - K_{1s2p} = -55.7 \text{ eV}$$

$$E^{(0)} + E_4^{(1)} = E^{(0)} + J_{1s2p} + K_{1s2p} = -53.9 \text{ eV}$$

The first-order energy corrections seem to indicate that the lower of the two levels of the $1s2p$ configuration lies below the higher of the two levels of the $1s2s$ configuration. Study of the helium spectrum reveals that this is not so. The error is due to neglect of the higher-order perturbation-energy corrections.

Using the variation-perturbation method (Section 9.2), Knight and Scherr calculated the second- and third-order corrections $E^{(2)}$ and $E^{(3)}$ for these four excited levels. [R. E. Knight and C. W. Scherr, *Rev. Mod. Phys.*, **35**, 431 (1963); for energy corrections through 17th order, see F. C. Sanders and C. W. Scherr, *Phys. Rev.*, **181**, 84 (1969).] Figure 9.4 shows their results (which are within 0.1 eV of the experimental energies). Figure 9.4 shows that Fig. 9.3 is quite inaccurate. Since the perturbation $e^2/4\pi\epsilon_0 r_{12}$ is not really very small, a perturbation treatment that includes only the $E^{(1)}$ correction does not give accurate results.

The first-order correction to the wave function, $\psi^{(1)}$, will include contributions from other configurations (configuration interaction). When we say that a level belongs to the configuration $1s2s$, we are indicating the configuration that makes the largest contribution to the true wave function.

We started with the eight degenerate zeroth-order functions (9.93). These functions have three kinds of degeneracy. There is the degeneracy between hydrogenlike functions with the same n , but different l ; the $2s$ and the $2p$ functions have the same energy. There is the degeneracy between hydrogenlike functions with the same n and l , but different m ; the $2p_1$, $2p_0$, and $2p_{-1}$ functions have the same energy. (For convenience we used the real functions $2p_{x,y,z}$, but we could have started with the functions $2p_{1,0,-1}$.) Finally, there is the degeneracy between functions that differ only in the interchange of the two electrons between the orbitals; the functions $\psi_1^{(0)} = 1s(1)2s(2)$ and $\psi_2^{(0)} = 1s(2)2s(1)$ have the same energy. This last kind of degeneracy is called *exchange degeneracy*. When the interelectronic repulsion $e^2/4\pi\epsilon_0 r_{12}$ was introduced as a perturbation, the exchange degeneracy and the degeneracy associated with the quantum number l were removed. The degeneracy associated with m remained, however; each $1s2p$ helium level is triply degenerate, and we could just as well have used the $2p_1$, $2p_0$, and $2p_{-1}$ orbitals instead of the real orbitals in constructing the correct zeroth-order wave functions. Let us consider the reasons for the removal of the l degeneracy and the exchange degeneracy.

The interelectronic repulsion in helium makes the $2s$ orbital energy less than the $2p$ energy. Figures 6.9 and 6.8 show that a $2s$ electron has a greater probability than a $2p$ electron of being closer to the nucleus than the $1s$ electron(s). A $2s$ electron will not be as effectively shielded from the nucleus by the $1s$ electrons and will therefore have a lower energy than a $2p$ electron. [According to Eq. (6.94), the greater the nuclear charge, the lower the energy.] Mathematically, the difference between the $1s2s$ and the $1s2p$ energies results from the Coulomb integral J_{1s2s} being smaller than J_{1s2p} . These Coulomb integrals

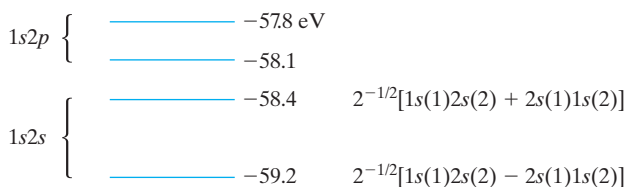


FIGURE 9.4 $E^{(0)} + E^{(1)} + E^{(2)} + E^{(3)}$ for the first excited levels of helium. Also shown are the correct zeroth-order wave functions for the $1s2s$ levels.

represent the electrostatic repulsion between the appropriate charge distributions. When the $2s$ electron penetrates the charge distribution of the $1s$ electron, it feels a repulsion from only the unpenetrated part of the $1s$ charge distribution. Hence the $1s$ – $2s$ electrostatic repulsion is less than the $1s$ – $2p$ repulsion, and the $1s2s$ levels lie below the $1s2p$ levels. The interelectronic repulsion in many-electron atoms lifts the l degeneracy, and the orbital energies for the same value of n increase with increasing l .

Now consider the removal of the exchange degeneracy. The functions (9.93) with which we began the perturbation treatment have each electron assigned to a definite orbital. For example, the function $\psi_1^{(0)} = 1s(1)2s(2)$ has electron 1 in the $1s$ orbital and electron 2 in the $2s$ orbital. For $\psi_2^{(0)}$ the opposite is true. The secular determinant was not diagonal, so the initial functions were not the correct zeroth-order wave functions. The correct zeroth-order functions do not assign each electron to a definite orbital. Thus the first two correct zeroth-order functions are

$$\phi_1^{(0)} = 2^{-1/2}[1s(1)2s(2) - 1s(2)2s(1)], \quad \phi_2^{(0)} = 2^{-1/2}[1s(1)2s(2) + 1s(2)2s(1)]$$

We cannot say which orbital electron 1 is in for either $\phi_1^{(0)}$ or $\phi_2^{(0)}$. This property of the wave functions of systems containing more than one electron results from the indistinguishability of identical particles in quantum mechanics and will be discussed further in Chapter 10. Since the functions $\phi_1^{(0)}$ and $\phi_2^{(0)}$ have different energies, the exchange degeneracy is removed when the correct zeroth-order functions are used.

9.8 Time-Dependent Perturbation Theory

In spectroscopy, we start with a system in some stationary state, expose it to electromagnetic radiation (light), and then observe whether the system has made a transition to another stationary state. The radiation produces a time-dependent potential-energy term in the Hamiltonian, so we must use the time-dependent Schrödinger equation. The most convenient approach here is an approximate one called time-dependent perturbation theory.

Let the system (atom or molecule) have the time-independent Hamiltonian $\hat{H}^0$ in the absence of the radiation (or other time-dependent perturbation), and let $\hat{H}'(t)$ be the time-dependent perturbation. The time-independent Schrödinger equation for the unperturbed problem is

$$\hat{H}^0\psi_k^0 = E_k^0\psi_k^0 \quad (9.112)$$

where E_k^0 and ψ_k^0 are the stationary-state energies and wave functions. The time-dependent Schrödinger equation (7.97) in the presence of the radiation is

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = (\hat{H}^0 + \hat{H}')\Psi \quad (9.113)$$

where the state function Ψ depends on the spatial and spin coordinates (symbolized by q) and on the time: $\Psi = \Psi(q, t)$. (See Chapter 10 for a discussion of spin coordinates.)

First suppose that $\hat{H}'(t)$ is absent. The unperturbed time-dependent Schrödinger equation is

$$-(\hbar/i)\partial\Psi^0/\partial t = \hat{H}^0\Psi^0 \quad (9.114)$$

The system's possible stationary-state state functions are given by (7.99) as $\Psi_k^0 = \exp(-iE_k^0 t/\hbar)\psi_k^0$, where the ψ_k^0 functions are the eigenfunctions of $\hat{H}^0$ [Eq. (9.112)]. Each Ψ_k^0 is a solution of (9.114). Moreover, the linear combination

$$\Psi^0 = \sum_k c_k \Psi_k^0 = \sum_k c_k \exp(-iE_k^0 t/\hbar)\psi_k^0 \quad (9.115)$$

with the c_k 's being arbitrary time-independent constants, is a solution of the time-dependent Schrödinger equation (9.114), as proved in the discussion leading to Eq. (7.100). The functions Ψ_k^0 form a complete set (since they are the eigenfunctions of the Hermitian operator $\hat{H}^0$), so any solution of (9.114) can be expressed in the form (9.115). Hence (9.115) is the general solution of the time-dependent Schrödinger equation (9.114), where $\hat{H}^0$ is independent of time.

Now suppose that $\hat{H}'(t)$ is present. The function (9.115) is no longer a solution of the time-dependent Schrödinger equation. However, because the unperturbed functions Ψ_k^0 form a complete set, the true state function Ψ can at any instant of time be expanded as a linear combination of the Ψ_k^0 functions according to $\Psi = \sum_k b_k \Psi_k^0$. Because $\hat{H}$ is time-dependent, Ψ will change with time and the expansion coefficients b_k will change with time. Therefore,

$$\Psi = \sum_k b_k(t) \exp(-iE_k^0 t/\hbar) \psi_k^0 \quad (9.116)$$

In the limit $\hat{H}'(t) \rightarrow 0$, the expansion (9.116) reduces to (9.115).

Substitution of (9.116) into the time-dependent Schrödinger equation (9.113) and use of (9.112) gives

$$\begin{aligned} -\frac{\hbar}{i} \sum_k \frac{db_k}{dt} \exp(-iE_k^0 t/\hbar) \psi_k^0 + \sum_k E_k^0 b_k \exp(-iE_k^0 t/\hbar) \psi_k^0 \\ = \sum_k b_k \exp(-iE_k^0 t/\hbar) E_k^0 \psi_k^0 + \sum_k b_k \exp(-iE_k^0 t/\hbar) \hat{H}' \psi_k^0 \\ -\frac{\hbar}{i} \sum_k \frac{db_k}{dt} \exp(-iE_k^0 t/\hbar) \psi_k^0 = \sum_k b_k \exp(-iE_k^0 t/\hbar) \hat{H}' \psi_k^0 \end{aligned}$$

We now multiply by ψ_m^{0*} and integrate over the spatial and spin coordinates. Using the orthonormality equation $\langle \psi_m^0 | \psi_k^0 \rangle = \delta_{mk}$, we get

$$-\frac{\hbar}{i} \sum_k \frac{db_k}{dt} \exp(-iE_k^0 t/\hbar) \delta_{mk} = \sum_k b_k \exp(-iE_k^0 t/\hbar) \langle \psi_m^0 | \hat{H}' | \psi_k^0 \rangle$$

Because of the δ_{mk} factor, all terms but one in the sum on the left are zero, and the left side equals $-(\hbar/i)(db_m/dt) \exp(-iE_m^0 t/\hbar)$. We get

$$\frac{db_m}{dt} = -\frac{i}{\hbar} \sum_k b_k \exp[i(E_m^0 - E_k^0)t/\hbar] \langle \psi_m^0 | \hat{H}' | \psi_k^0 \rangle \quad (9.117)$$

Let us suppose that the perturbation $\hat{H}'(t)$ was applied at time $t = 0$ and that before the perturbation was applied the system was in stationary state n with energy $E_n^{(0)}$. The state function at $t = 0$ is therefore $\Psi = \exp(-iE_n^0 t/\hbar) \psi_n^0$ [Eq. (7.99)], and the $t = 0$ values of the expansion coefficients in (9.116) are thus $b_n(0) = 1$ and $b_k(0) = 0$ for $k \neq n$:

$$b_k(0) = \delta_{kn} \quad (9.118)$$

We shall assume that the perturbation $\hat{H}'$ is small and acts for only a short time. Under these conditions, the change in the expansion coefficients b_k from their initial values at the time the perturbation is applied will be small. To a good approximation, we can replace the expansion coefficients on the right side of (9.117) by their initial values (9.118). This gives

$$\frac{db_m}{dt} \approx -\frac{i}{\hbar} \exp[i(E_m^0 - E_n^0)t/\hbar] \langle \psi_m^0 | \hat{H}' | \psi_n^0 \rangle \quad (9.119)$$

Let the perturbation $\hat{H}'$ act from $t = 0$ to $t = t'$. Integrating from $t = 0$ to t' and using (9.118), we get

$$b_m(t') \approx \delta_{mn} - \frac{i}{\hbar} \int_0^{t'} \exp[i(E_m^0 - E_n^0)t/\hbar] \langle \psi_m^0 | \hat{H}' | \psi_n^0 \rangle dt \quad (9.120)$$

Use of the approximate result (9.120) for the expansion coefficients in (9.116) gives the desired approximation to the state function at time t' for the case that the time-dependent perturbation $\hat{H}'$ is applied at $t = 0$ to a system in stationary state n . [As with time-independent perturbation theory, one can go to higher-order approximations (see *Fong*, pp. 234–244).]

For times after t' , the perturbation has ceased to act, and $\hat{H}' = 0$. Equation (9.117) gives $db_m/dt = 0$ for $t > t'$, so $b_m = b_m(t')$ for $t \geq t'$. Therefore, for times after exposure to the perturbation, the state function Ψ is [Eq. (9.116)]

$$\Psi = \sum_m b_m(t') \exp(-iE_m^0 t/\hbar) \psi_m^0 \quad \text{for } t \geq t' \quad (9.121)$$

where $b_m(t')$ is given by (9.120). In (9.121), Ψ is a superposition of the eigenfunctions ψ_m^0 of the energy operator $\hat{H}^0$, the expansion coefficients being $b_m \exp(-iE_m^0 t/\hbar)$. [Compare (9.121) and (7.66).] The work of Section 7.6 tells us that a measurement of the system's energy at a time after t' will give one of the eigenvalues E_m^0 of the energy operator $\hat{H}^0$, and the probability of getting E_m^0 equals the square of the absolute value of the expansion coefficient that multiplies ψ_m^0 ; that is, it equals $|b_m(t') \exp(-iE_m^0 t/\hbar)|^2 = |b_m(t')|^2$.

The time-dependent perturbation changes the system's state function from $\exp(-iE_n^0 t/\hbar) \psi_n^0$ to the superposition (9.121). Measurement of the energy then changes Ψ to one of the energy eigenfunctions $\exp(-iE_m^0 t/\hbar) \psi_m^0$ (reduction of the wave function, Section 7.9). The net result is a transition from stationary state n to stationary state m , the probability of such a transition being $|b_m(t')|^2$.

9.9 Interaction of Radiation and Matter

We now consider the interaction of an atom or molecule with electromagnetic radiation. A proper quantum-mechanical approach would treat both the atom and the radiation quantum mechanically, but we shall simplify things by using the classical picture of the light as an electromagnetic wave of oscillating electric and magnetic fields.

A detailed investigation, which we omit, shows that usually the interaction between the radiation's magnetic field and the atom's charges is much weaker than the interaction between the radiation's electric field and the charges, so we shall consider only the latter interaction. (In NMR spectroscopy the important interaction is between the magnetic dipole moments of the nuclei and the radiation's magnetic field. We shall not consider this case.)

Let the electric field $\mathcal{E}$ of the electromagnetic wave point in the x direction only. (This is plane-polarized radiation.) The electric field is defined as the force per unit charge, so the force on charge Q_i is $F = Q_i \mathcal{E}_x = -dV/dx$, where (4.24) was used. Integration gives the potential energy of interaction between the radiation's electric field and the charge as $V = -Q_i \mathcal{E}_x x$, where the arbitrary integration constant was taken as zero. For a system of several charges, $V = -\sum_i Q_i x_i \mathcal{E}_x$. This is the time-dependent perturbation $\hat{H}'(t)$. The space and time dependence of the electric field of an electromagnetic wave traveling in the z direction with wavelength λ and frequency ν is given by (see a first-year physics text) $\mathcal{E}_x = \mathcal{E}_0 \sin(2\pi\nu t - 2\pi z/\lambda)$, where $\mathcal{E}_0$ is the maximum value of $\mathcal{E}_x$ (the amplitude). Therefore,

$$\hat{H}'(t) = -\mathcal{E}_0 \sum_i Q_i x_i \sin(2\pi\nu t - 2\pi z_i/\lambda)$$

where the sum goes over all the electrons and nuclei of the atom or molecule.

Defining ω and ω_{mn} as

$$\omega \equiv 2\pi\nu, \quad \omega_{mn} \equiv (E_m^0 - E_n^0)/\hbar \quad (9.122)$$

and substituting $\hat{H}'(t)$ into (9.120), we get the coefficients in the expansion (9.116) of the state function Ψ as

$$b_m \approx \delta_{mn} + \frac{i\mathcal{E}_0}{\hbar} \int_0^{t'} \exp(i\omega_{mnt}) \left\langle \psi_m^0 \left| \sum_i Q_i x_i \sin(\omega t - 2\pi z_i/\lambda) \right| \psi_n^0 \right\rangle dt$$

The integral $\langle \psi_m^0 | \sum_i \dots | \psi_n^0 \rangle$ in this equation is over all space, but significant contributions to its magnitude come only from regions where ψ_m^0 and ψ_n^0 are of significant magnitude. In regions well outside the atom or molecule, ψ_m^0 and ψ_n^0 are vanishingly small, and such regions can be ignored. Let the coordinate origin be chosen within the atom or molecule. Since regions well outside the atom can be ignored, the coordinate z_i can be considered to have a maximum magnitude of the order of one nm. For ultraviolet light, the wavelength λ is on the order of 10^2 nm. For visible, infrared, microwave, and radio-frequency radiation, λ is even larger. Hence $2\pi z_i/\lambda$ is very small and can be neglected, and this leaves $\sum_i Q_i x_i \sin \omega t$ in the integral.

Use of the identity (Prob. 1.29) $\sin \omega t = (e^{i\omega t} - e^{-i\omega t})/2i$ gives

$$b_m(t') \approx \delta_{mn} + \frac{\mathcal{E}_0}{2\hbar} \left\langle \psi_m^0 \left| \sum_i Q_i x_i \right| \psi_n^0 \right\rangle \int_0^{t'} [e^{i(\omega_{mn}+\omega)t} - e^{i(\omega_{mn}-\omega)t}] dt$$

Using $\int_0^{t'} e^{at} dt = a^{-1}(e^{at'} - 1)$, we get

$$b_m(t') \approx \delta_{mn} + \frac{\mathcal{E}_0}{2\hbar i} \left\langle \psi_m^0 \left| \sum_i Q_i x_i \right| \psi_n^0 \right\rangle \left[\frac{e^{i(\omega_{mn}+\omega)t'} - 1}{\omega_{mn} + \omega} - \frac{e^{i(\omega_{mn}-\omega)t'} - 1}{\omega_{mn} - \omega} \right] \quad (9.123)$$

For $m \neq n$, the δ_{mn} term equals zero.

As noted at the end of Section 9.8, $|b_m(t')|^2$ gives the probability of a transition to state m from state n . There are two cases where this probability becomes of significant magnitude. If $\omega_{mn} = \omega$, the denominator of the second fraction in brackets is zero and this fraction's absolute value is large (but not infinite; see Prob. 9.27). If $\omega_{mn} = -\omega$, the first fraction has a zero denominator and a large absolute value.

For $\omega_{mn} = \omega$, Eq. (9.122) gives $E_m^0 - E_n^0 = h\nu$. Exposure of the atom to radiation of frequency ν has produced a transition from stationary state n to stationary state m , where (since ν is positive) $E_m^0 > E_n^0$. We might suppose that the energy for this transition came from the system's absorption of a photon of energy $h\nu$. This supposition is confirmed by a fully quantum-mechanical treatment (called *quantum field theory*) in which the radiation is treated quantum mechanically rather than classically. We have **absorption** of radiation with a consequent increase in the system's energy.

For $\omega_{mn} = -\omega$, we get $E_n^0 - E_m^0 = h\nu$. Exposure to radiation of frequency ν has induced a transition from stationary state n to stationary state m , where (since ν is positive) $E_n^0 > E_m^0$. The system has gone to a lower energy level, and a quantum-field-theory treatment shows that a photon of energy $h\nu$ is emitted in this process. This is **stimulated emission** of radiation. Stimulated emission occurs in lasers.

A defect of our treatment is that it does not predict **spontaneous emission**, the emission of a photon by a system not exposed to radiation, the system falling to a lower energy level in the process. Quantum field theory does predict spontaneous emission.

Note from (9.123) that the probability of absorption is proportional to $|\langle \psi_m^0 | \sum_i Q_i x_i | \psi_n^0 \rangle|^2$. The quantity $\sum_i Q_i x_i$ is the x component of the system's electric-dipole-moment operator $\hat{\mu}$ (see Section 14.2 for details), which is [Eqs. (14.14) and (14.15)]

$\hat{\mu} = \mathbf{i} \sum_i Q_i x_i + \mathbf{j} \sum_i Q_i y_i + \mathbf{k} \sum_i Q_i z_i = \mathbf{i} \hat{\mu}_x + \mathbf{j} \hat{\mu}_y + \mathbf{k} \hat{\mu}_z$, where $\mathbf{i}, \mathbf{j}, \mathbf{k}$ are unit vectors along the axes and $\hat{\mu}_x, \hat{\mu}_y, \hat{\mu}_z$ are the components of $\hat{\mu}$. We assumed polarized radiation with an electric field in the x direction only. If the radiation has electric-field components in the y and z directions also, then the probability of absorption will be proportional to

$$|\langle \psi_m^0 | \hat{\mu}_x | \psi_n^0 \rangle|^2 + |\langle \psi_m^0 | \hat{\mu}_y | \psi_n^0 \rangle|^2 + |\langle \psi_m^0 | \hat{\mu}_z | \psi_n^0 \rangle|^2 = |\langle \psi_m^0 | \hat{\mu} | \psi_n^0 \rangle|^2$$

where Eq. (5.25) was used. The integral $\langle \psi_m^0 | \hat{\mu} | \psi_n^0 \rangle = \mu_{mn}$ is the **transition (dipole) moment**.

When $\mu_{mn} = 0$, the transition between states m and n with absorption or emission of radiation is said to be **forbidden**. **Allowed** transitions have $\mu_{mn} \neq 0$. Because of approximations made in the derivation of (9.123), forbidden transitions may have some small probability of occurring.

Consider, for example, the particle in a one-dimensional box (Section 2.2). The transition dipole moment is $\langle \psi_m^0 | Qx | \psi_n^0 \rangle$, where Q is the particle's charge and x is its coordinate and where $\psi_m^0 = (2/l)^{1/2} \sin(m\pi x/l)$ and $\psi_n^0 = (2/l)^{1/2} \sin(n\pi x/l)$. Evaluation of this integral (Prob. 9.28) shows it is nonzero only when $m - n = \pm 1, \pm 3, \pm 5, \dots$ and is zero when $m - n = 0, \pm 2, \dots$. The **selection rule** for a charged particle in a one-dimensional box is that the quantum number must change by an odd integer when radiation is absorbed or emitted.

Evaluation of the transition moment for the harmonic oscillator and for the two-particle rigid rotor gives the selection rules $\Delta v = \pm 1$ and $\Delta J = \pm 1$ stated in Sections 4.3 and 6.4.

The quantity $|b_m|^2$ in (9.123) is sharply peaked at $\omega = \omega_{mn}$ and $\omega = -\omega_{mn}$, but there is a nonzero probability that a transition will occur when ω is not precisely equal to $|\omega_{mn}|$, that is, when $h\nu$ is not precisely equal to $|E_m^0 - E_n^0|$. This fact is related to the energy–time uncertainty relation (5.15). States with a finite lifetime have an uncertainty in their energy.

Radiation is not the only time-dependent perturbation that produces transitions between states. When an atom or molecule comes close to another atom or molecule, it suffers a time-dependent perturbation that can change its state. Selection rules derived for radiative transitions need not apply to collision processes, since $\hat{H}'(t)$ differs for the two processes.

Summary

For a system whose time-independent Schrödinger equation is $(\hat{H}^0 + \hat{H}')\psi_n = E_n\psi_n$, perturbation theory expresses the energies and wave functions of the nondegenerate levels as $E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \dots$ and $\psi_n = \psi_n^{(0)} + \psi_n^{(1)} + \psi_n^{(2)} + \dots$, where the unperturbed wave functions $\psi_n^{(0)}$ and energies $E_n^{(0)}$ satisfy $\hat{H}^0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$. The first-order energy correction is $E_n^{(1)} = \int \psi_n^{(0)*} \hat{H}' \psi_n^{(0)} d\tau$. The second-order energy correction is given by (9.35). The first-order correction to the wave function is $\psi_n^{(1)} = \sum_{m \neq n} a_m \psi_m^{(0)}$, where the expansion coefficients a_m are given by (9.26). For a degenerate level with degree of degeneracy d , we have $\psi_n = \phi_n^{(0)} + \psi_n^{(1)} + \dots$, where the correct zeroth-order wave functions are $\phi_n^{(0)} = \sum_{i=1}^d c_i \psi_i^{(0)}$ for $n = 1, \dots, d$. The first-order energy corrections for the degenerate level are found from the secular equation $\det[\langle \psi_m^{(0)} | \hat{H}' | \psi_i^{(0)} \rangle - E_n^{(1)} \delta_{mi}] = 0$, and then the coefficients c_i are found by solving (9.81).

Perturbation theory was applied to the helium atom, with $\hat{H}'$ taken as $e^2/4\pi\epsilon_0 r_{12}$. The unperturbed ground-state wave function is $\psi^{(0)} = 1s(1)1s(2)$. The first-order energy correction was calculated for the ground state. Degenerate perturbation theory was applied to the first group of helium excited states. We found that the $1s2s$ configuration

gives rise to two nondegenerate energy levels with correct zeroth-order wave functions $[1s(1)2s(2) \pm 1s(2)2s(1)]/\sqrt{2}$; the $1s2p$ configuration gives rise to two triply degenerate levels with correct zeroth-order wave functions $[1s(1)2p(2) \pm 1s(2)2p(1)]/\sqrt{2}$, where $2p$ can be $2p_x$, $2p_y$, or $2p_z$. (These conclusions will be modified when electron spin is taken into account in Chapter 10.) The $1s2s$ levels lie below the $1s2p$ levels.

Time-dependent perturbation theory shows that, when an atom or molecule in a stationary state is exposed to electromagnetic radiation of frequency ν , the molecule may make a transition between two stationary states m and n whose energy difference is $h\nu$, provided the transition dipole moment $\langle \psi_m^0 | \hat{\mu} | \psi_n^0 \rangle$ is nonzero for states m and n .

Problems

Sec.	9.2	9.3	9.4	9.5	9.6	9.7	9.8	general
Probs.	9.1–9.11	9.12–9.16	9.17	9.18–9.22	9.23	9.24–9.26	9.27–9.29	9.30–9.31

- 9.1** Consider a one-particle, one-dimensional system with $V = \infty$ for $x < 0$ and for $x > l$ and $V = C$ for $0 \leq x \leq l$, where C is a constant. (a) Sketch V for $C > 0$. (b) Treat the system as a perturbed particle in a box and find $E_n^{(1)}$ for the state with quantum number n .
- 9.2** (a) For the perturbed particle in a box of Prob. 9.1, find $E_n^{(2)}$ for the state with quantum number n . (b) Find $\psi_n^{(1)}$ for this system. (c) Use the results of Prob. 4.52 to explain why the results of Prob. 9.1 and 9.2 make sense.
- 9.3** For the anharmonic oscillator with Hamiltonian (9.3), evaluate $E^{(1)}$ for the first excited state, taking the unperturbed system as the harmonic oscillator. What is $E^{(0)}$?
- 9.4** Consider the one-particle, one-dimensional system with potential-energy

$$V = V_0 \quad \text{for} \quad \frac{1}{4}l < x < \frac{3}{4}l, \quad V = 0 \quad \text{for} \quad 0 \leq x \leq \frac{1}{4}l \quad \text{and} \quad \frac{3}{4}l \leq x \leq l$$

and $V = \infty$ elsewhere, where $V_0 = \hbar^2/ml^2$. Treat the system as a perturbed particle in a box.

- (a) Find the first-order energy correction for the general stationary state with quantum number n . (b) For the ground state and for the first excited state, compare $E^{(0)} + E^{(1)}$ with the true energies $5.750345\hbar^2/ml^2$ and $20.23604\hbar^2/ml^2$. Explain why $E^{(0)} + E^{(1)}$ for each of these two states is the same as obtained by the variational treatment of Probs. 8.2a and 8.18.
- 9.5** For the perturbed particle in a box of Prob. 9.4, explain (without doing any calculations) why we expect $E^{(1)}$ to be greatest for the $n = 1$ state.
- 9.6** For the perturbed particle in a box of Prob. 9.4, find the first-order correction to the wave function of the stationary state with quantum number n .
- 9.7** Consider the perturbed particle in a box of Prob. 9.4. (a) Explain why $\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle = 0$ when $n = 1$ and m is an even integer. (b) Use a computer to evaluate $E^{(2)}$ for the ground state by summing over odd values of m in (9.35). Keep adding terms until the last added term is negligibly small in magnitude. Compare $E^{(0)} + E^{(1)} + E^{(2)}$ with the true ground-state energy $5.750345\hbar^2/ml^2$.
- 9.8** Consider a one-particle, one-dimensional system with

$$V = V_0 \quad \text{for} \quad (0.25 + c)l < x < (0.75 + c)l,$$

$$V = 0 \quad \text{for} \quad 0 \leq x \leq (0.25 + c)l \quad \text{and} \quad (0.75 + c)l \leq x \leq l,$$

and $V = \infty$ elsewhere. V_0 and c are constants and $0 \leq c \leq 0.25$. (a) Take the unperturbed system as a particle in a one-dimensional box and find $E^{(1)}$ in terms of V_0 and c . (b) Plot $E^{(1)}/V_0$ versus c for the ground state.

- 9.9** Assume that the charge of the proton is distributed uniformly throughout the volume of a sphere of radius 10^{-13} cm. Use perturbation theory to estimate the shift in the ground-state hydrogen-atom energy due to the finite proton size. The potential energy experienced by the electron when it has penetrated the nucleus and is at distance r from the nuclear center is $-eQ/4\pi\epsilon_0 r$, where Q is the amount of proton charge within the sphere of radius r . The

evaluation of the integral is simplified by noting that the exponential factor in ψ is essentially equal to 1 within the nucleus.

- 9.10** True or false? The second-order correction $E^{(2)}$ to the ground-state energy is never positive.
- 9.11** For an anharmonic oscillator with $\hat{H} = -(\hbar^2/2m)d^2/dx^2 + \frac{1}{2}kx^2 + cx^3$, take $\hat{H}'$ as cx^3 . (a) Find $E^{(1)}$ for the state with quantum number v . (b) Find $E^{(2)}$ for the state with quantum number v . You will need the following integral (Levine, *Molecular Spectroscopy*, p. 154):

$$\begin{aligned} \langle \psi_v^{(0)} | x^3 | \psi_v^{(0)} \rangle &= [(v+1)(v+2)(v+3)/8\alpha^3]^{1/2} \delta_{v',v+3} \\ &\quad + 3[(v+1)/2\alpha]^{3/2} \delta_{v',v+1} + 3(v/2\alpha)^{3/2} \delta_{v',v-1} \\ &\quad + [v(v-1)(v-2)/8\alpha^3]^{1/2} \delta_{v',v-3} \end{aligned}$$

where the $\psi^{(0)}$'s are harmonic-oscillator wave functions and α is defined by (4.31). (c) Which unperturbed states contribute to $\psi_v^{(1)}$?

- 9.12** When Hylleraas began his calculations on helium, it was not known whether the isolated hydride ion H^- was a stable entity. Calculate the ground-state energy of H^- predicted by the trial function (9.56). Compare the result with the ground-state energy of the hydrogen atom, -13.60 eV, and show that this simple variation function (erroneously) indicates H^- is unstable with respect to ionization into a hydrogen atom and an electron. (More complicated variational functions give a ground-state energy of -14.35 eV.)
- 9.13** There is more than one way to divide a Hamiltonian $\hat{H}$ into an unperturbed part $\hat{H}^0$ and a perturbation $\hat{H}'$. Instead of the division (9.40) and (9.41), consider the following way of dividing up the helium-atom Hamiltonian:

$$\begin{aligned} \hat{H}^0 &= -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \left(Z - \frac{5}{16} \right) \frac{e^2}{4\pi\epsilon_0 r_1} - \left(Z - \frac{5}{16} \right) \frac{e^2}{4\pi\epsilon_0 r_2} \\ \hat{H}' &= -\left(\frac{5}{16} \right) \frac{e^2}{4\pi\epsilon_0 r_1} - \left(\frac{5}{16} \right) \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \end{aligned}$$

What are the unperturbed wave functions? Calculate $E^{(0)}$ and $E^{(1)}$ for the ground state. (See Section 9.4.)

- 9.14** One can show that (see Eyring, Walter, and Kimball, p. 369)

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} [Y_l^m(\theta_1, \phi_1)]^* Y_l^m(\theta_2, \phi_2) \quad (9.124)$$

where $r_{<}$ means the smaller of r_1 and r_2 , and $r_{>}$ is the larger of r_1 and r_2 . Substitute this expansion into (9.52). Then multiply the right side by $Y_0^0(\theta_1, \phi_1)[Y_0^0(\theta_2, \phi_2)]^*(4\pi)$, which from (5.101) equals 1. Use the orthonormality of the spherical harmonics [Eq. (7.27)] to evaluate the angular integrals in terms of Kronecker deltas. Perform the sums to show that

$$E^{(1)} = \frac{16Z^6 e^2}{4\pi\epsilon_0 a_0^6} \int_0^\infty \int_0^\infty e^{-2Zr_1/a_0} e^{-2Zr_2/a_0} \frac{1}{r_{>}} r_1^2 r_2^2 dr_1 dr_2$$

Next, integrate first over r_1 and write the r_1 integral as the sum of integrals from 0 to r_2 and from r_2 to ∞ . In the range $0 \leq r_1 \leq r_2$, we have $r_{>} = r_2$; in the range $r_2 \leq r_1 \leq \infty$, we have $r_{>} = r_1$. Use indefinite integrals in the Appendix to do the r_1 integrals to obtain r_2 integrals, which are evaluated using an Appendix integral. Show that the result is (9.53).

- 9.15** Most (but not all) of the effect of nuclear motion in helium can be corrected for by replacing the electron's mass m_e by the reduced mass (6.59) in the expression for the energy. The energy of helium is proportional to what power of m_e ? [See Eq. (9.63).] Use of μ instead of m_e multiplies the energies calculated on the basis of infinite nuclear mass by what factor?
- 9.16** Use (9.53) to estimate $\langle 1/r_{12} \rangle^{-1}$ for the ground-state He atom.

- 9.17 Calculate $\langle r_1 \rangle$ for the helium trial function (9.56). To save time, use the result of Prob. 6.23.
- 9.18 A certain unperturbed system has a doubly degenerate energy level for which the perturbation integrals have the values $H'_{11} = 4b$, $H'_{12} = 2b$, $H'_{22} = 6b$, where b is a positive constant, $H'_{jk} \equiv \langle \psi_j^{(0)} | \hat{H}' | \psi_k^{(0)} \rangle$, and $\langle \psi_j^{(0)} | \psi_k^{(0)} \rangle = \delta_{jk}$. (a) In terms of b , find the $E^{(1)}$ values for the perturbed system. (b) Find the normalized correct zeroth-order wave functions.
- 9.19 Explain why without solving for the $E^{(1)}$ values in Prob. 9.18, we can be certain that the sum of the $E^{(1)}$ values is $10b$.
- 9.20 Show that the secular equation (9.82) can be written as

$$\det[\langle \psi_m^{(0)} | \hat{H} | \psi_i^{(0)} \rangle - (E_n^{(0)} + E_n^{(1)})\delta_{mi}] = 0$$

- 9.21 Verify the normalization condition (9.85) for the coefficients in a correct zeroth-order wave function.
- 9.22 (a) For a particle in a square box of length l with origin at $x = 0$, $y = 0$, write down the wave functions and energy levels. (b) If the system of (a) is perturbed by

$$\hat{H}' = b \quad \text{for} \quad \frac{1}{4}l \leq x \leq \frac{3}{4}l \quad \text{and} \quad \frac{1}{4}l \leq y \leq \frac{3}{4}l$$

where b is a constant and $\hat{H}' = 0$ elsewhere, find $E^{(1)}$ for the ground state. For the first excited energy level, find the $E^{(1)}$ values and the correct zeroth-order wave functions.

- 9.23 For a hydrogen atom perturbed by a uniform applied electric field in the z direction, the perturbation Hamiltonian is

$$\hat{H}' \equiv e\mathcal{E}z = e\mathcal{E}r \cos \theta$$

where $\mathcal{E}$ is the magnitude of the electric field. Consider the effect of $\hat{H}'$ on the $n = 2$ energy level, which is fourfold degenerate. Since $\hat{H}'$ commutes with the angular-momentum operator $\hat{L}_z$, the ideas of Section 9.6 lead us to set up the secular determinant using the complex hydrogen-atom orbitals $2s$, $2p_1$, $2p_0$, and $2p_{-1}$, which are eigenfunctions of $\hat{L}_z$. Set up the secular determinant using the fact that matrix elements of $\hat{H}'$ between states with different values of the quantum number m will vanish. Also, use parity considerations to show that certain other integrals are zero (see Prob. 7.29). Evaluate the nonzero integrals, and find the first-order energy corrections and the correct zeroth-order wave functions. *Hint:* Choose the order of the orbitals so as to make the secular determinant block diagonal.

- 9.24 Consider the perturbation treatment of the helium configurations $1s3s$, $1s3p$, and $1s3d$. Without setting up the secular equation, but simply by analogy to the results of Section 9.7, write down the 18 correct zeroth-order wave functions. How many energy levels correspond to each of these three configurations, and what is the degeneracy of each energy level? The levels of which configuration lie lowest? highest?
- 9.25 We have considered helium configurations in which only one electron is excited. Get a rough estimate of the energy of the $2s^2$ configuration from Eq. (9.48). Compare this with the ground-state energy of the He^+ ion to show that the $2s^2$ helium configuration is unstable with respect to ionization to He^+ and an electron. If we had obtained a more accurate estimate of the $2s^2$ energy by including the first-order energy correction, would this increase or decrease our estimate of the $2s^2$ energy?
- 9.26 For helium the first-order perturbation energy correction is $e^2/4\pi\epsilon_0 r_{12}$ averaged over the correct unperturbed wave function. Show that if we evaluate $\langle e^2/4\pi\epsilon_0 r_{12} \rangle$ using the incorrect zeroth-order functions $1s(1)2s(2)$ or $1s(2)2s(1)$, we get J_{1s2s} in each case. Now show that when we use the correct functions (9.103) and (9.104) to evaluate $\langle e^2/4\pi\epsilon_0 r_{12} \rangle$, we get $J_{1s2s} \pm K_{1s2s}$ (as found from the secular equation). The exchange-integral contribution to the energy thus arises from the indistinguishability of electrons in the same atom.
- 9.27 Evaluate $\lim_{s \rightarrow 0} (e^{as} - 1)/s$. [s corresponds to $\omega_{mn} \pm \omega$ in (9.123).]
- 9.28 Evaluate $\langle \psi_m^0 | Qx | \psi_n^0 \rangle$ for the particle in a one-dimensional box.
- 9.29 Find the selection rules for a charged particle in a three-dimensional box exposed to unpolarized radiation.

- 9.30** (a) Set f in (7.41) equal to $\hat{B}S$ and operate on each side of the resulting equation with $\hat{A}$. Then multiply by R^* and integrate over all space to obtain the sum rule

$$\sum_i \langle R | \hat{A} | g_i \rangle \langle g_i | \hat{B} | S \rangle = \langle R | \hat{A} \hat{B} | S \rangle$$

where the functions g_i form a complete, orthonormal set, the functions R and S are any two well-behaved functions, the operators $\hat{A}$ and $\hat{B}$ are linear, and the sum is over all members of the complete set. [See also Eq. (7.111). For other sum rules, see A. Dalgarno, *Rev. Mod. Phys.*, **35**, 522 (1963).] (b) An approximate way to evaluate $E_n^{(2)}$ in (9.35) is to replace $E_n^{(0)} - E_m^{(0)}$ by ΔE , where ΔE is some sort of average excitation energy for the problem, whose value can be roughly estimated from the spacings of the unperturbed levels. Use the sum rule of (a) to show that this replacement gives

$$E_n^{(2)} \approx \frac{1}{\Delta E} [\langle n | (\hat{H}')^2 | n \rangle - \langle n | \hat{H}' | n \rangle^2]$$

where n stands for $\psi_n^{(0)}$.

- 9.31** True or false: (a) Every linear combination of solutions of the time-dependent Schrödinger equation is a solution of this equation. (b) Every linear combination of solutions of the time-independent Schrödinger equation is a solution of this equation. (c) The nondegenerate perturbation-theory formula $E^{(1)} = \langle \psi^{(0)} | \hat{H}' | \psi^{(0)} \rangle$ applies only to the ground state. (d) The exact ground-state He-atom wave function has the form $f(1)f(2)$, where $f(i)$, $i = 1, 2$, is a function of the coordinates of electron i .