

Chapter 9

Approximation Methods for Stationary States

9.1 Introduction

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

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

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

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

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

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

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

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

9.2 Time-Independent Perturbation Theory

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

$$\hat{H} = \hat{H}_0 + \hat{H}_p, \quad (9.2)$$

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

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

Thus the eigenvalue problem (9.1) becomes

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

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

9.2.1 Nondegenerate Perturbation Theory

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

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

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

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

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

$$| \psi_n \rangle = | \phi_n \rangle + \lambda | \psi_n^{(1)} \rangle + \lambda^2 | \psi_n^{(2)} \rangle + \dots. \quad (9.7)$$

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

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

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

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

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

- Zero order in λ :

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

- First order in λ :

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

- Second order in λ :

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

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

$$\langle\phi_n | \psi_n\rangle = 1. \quad (9.12)$$

Substituting (9.7) into (9.12) we get

$$\lambda \langle\phi_n | \psi_n^{(1)}\rangle + \lambda^2 \langle\phi_n | \psi_n^{(2)}\rangle + \dots = 0; \quad (9.13)$$

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

$$\langle\phi_n | \psi_n^{(1)}\rangle = \langle\phi_n | \psi_n^{(2)}\rangle = \dots = 0. \quad (9.14)$$

First-order correction

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

$$E_n^{(1)} = \langle\phi_n | \hat{W} | \phi_n\rangle, \quad (9.15)$$

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

$$E_n = E_n^{(0)} + \langle\phi_n | \hat{H}_p | \phi_n\rangle. \quad (9.16)$$

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

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

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

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

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

which, when substituted into (9.17), leads to

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

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

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

Second-order correction

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

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

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

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

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

$$E_n = E_n^{(0)} + \langle\phi_n | \hat{H}_p | \phi_n\rangle + \sum_{m \neq n} \frac{|\langle\phi_m | \hat{H}_p | \phi_n\rangle|^2}{E_n^{(0)} - E_m^{(0)}} + \dots \quad (9.23)$$

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

Validity of the time-independent perturbation theory

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

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

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

Example 9.1 (Charged oscillator in an electric field)

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

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

Solution

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

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

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

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

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

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

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

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

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

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

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

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

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

Solution

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

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

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

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

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

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

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

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

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

$$\langle n+1 | \hat{X} | n \rangle = \sqrt{n+1} \frac{\sqrt{\hbar}}{2m\omega}, \quad \langle n-1 | \hat{X} | n \rangle = \sqrt{n} \frac{\sqrt{\hbar}}{2m\omega}, \quad (9.29)$$

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

we can reduce (9.28) to

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

hence the energy is given to second order by

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

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

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

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

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

$$|\psi_n\rangle = |n\rangle + \frac{q\mathcal{E}}{\hbar\omega} \frac{\sqrt{\hbar}}{2m\omega} \{ \sqrt{n} |n-1\rangle - \sqrt{n+1} |n+1\rangle \}, \quad (9.34)$$

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

Example 9.2 (The Stark effect)

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

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

Solution

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

$$\hat{H}_0 = \frac{\hat{p}^2}{2\mu} - \frac{e^2}{r}. \quad (9.35)$$

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

$$\langle r\theta\phi | nlm \rangle = \psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi). \quad (9.36)$$

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

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

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

The term

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

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

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

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

$$\alpha = -2 \frac{\Delta E}{\mathcal{E}^2}. \quad (9.40)$$

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

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

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

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

hence

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

where

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

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

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

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

$$\alpha \leq \frac{16}{3} a_0^3. \quad (9.46)$$

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

9.2.2 Degenerate Perturbation Theory

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

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

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

$$\hat{H}_0 | \phi_{n_\alpha} \rangle = E_n^{(0)} | \phi_{n_\alpha} \rangle \quad (\alpha = 1, 2, \dots, f), \quad (9.48)$$

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

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

$$| \psi_n \rangle = \sum_{\alpha=1}^f a_\alpha | \phi_{n_\alpha} \rangle. \quad (9.49)$$

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

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

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

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

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

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

or to

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

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

$$\sum_{\alpha=1}^f (\hat{H}_{p_{\beta\alpha}} - E_n^{(1)} \delta_{\alpha, \beta}) a_\alpha = 0 \quad (\beta = 1, 2, \dots, f), \quad (9.54)$$

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

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

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

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

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

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

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

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

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

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

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

$$E_{n\alpha} = E_n^{(0)} + E_{n\alpha}^{(1)} \quad (\alpha = 1, 2, \dots, f) \quad (9.58)$$

and the corresponding eigenvectors are given to zero order by

$$|\psi_{n\alpha}\rangle = \sum_{\beta=1}^f a_{\alpha\beta} |\phi_{n\beta}\rangle. \quad (9.59)$$

Example 9.3 (The Stark effect of hydrogen)

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

Solution

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

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

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

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

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

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

$$H_p = \begin{pmatrix} \langle 1 | \hat{H}_p | 1 \rangle & \langle 1 | \hat{H}_p | 2 \rangle & \langle 1 | \hat{H}_p | 3 \rangle & \langle 1 | \hat{H}_p | 4 \rangle \\ \langle 2 | \hat{H}_p | 1 \rangle & \langle 2 | \hat{H}_p | 2 \rangle & \langle 2 | \hat{H}_p | 3 \rangle & \langle 2 | \hat{H}_p | 4 \rangle \\ \langle 3 | \hat{H}_p | 1 \rangle & \langle 3 | \hat{H}_p | 2 \rangle & \langle 3 | \hat{H}_p | 3 \rangle & \langle 3 | \hat{H}_p | 4 \rangle \\ \langle 4 | \hat{H}_p | 1 \rangle & \langle 4 | \hat{H}_p | 2 \rangle & \langle 4 | \hat{H}_p | 3 \rangle & \langle 4 | \hat{H}_p | 4 \rangle \end{pmatrix} \quad (9.62)$$

or as

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

The diagonalization of this matrix leads to the following eigenvalues:

$$E_{2_1}^{(1)} = -3e\mathcal{E}a_0, \quad E_{2_2}^{(1)} = E_{2_3}^{(1)} = 0, \quad E_{2_4}^{(1)} = 3e\mathcal{E}a_0. \quad (9.64)$$

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

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

The corresponding eigenvectors to zeroth order are

$$|\psi_2\rangle_1 = \frac{1}{\sqrt{2}}(|200\rangle + |210\rangle), \quad |\psi_2\rangle_2 = |211\rangle, \quad (9.66)$$

$$|\psi_2\rangle_3 = |21-1\rangle, \quad |\psi_2\rangle_4 = \frac{1}{\sqrt{2}}(|200\rangle - |210\rangle). \quad (9.67)$$

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

9.2.3 Fine Structure and the Anomalous Zeeman Effect

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

9.2.3.1 Spin-Orbit Coupling

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

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

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

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

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

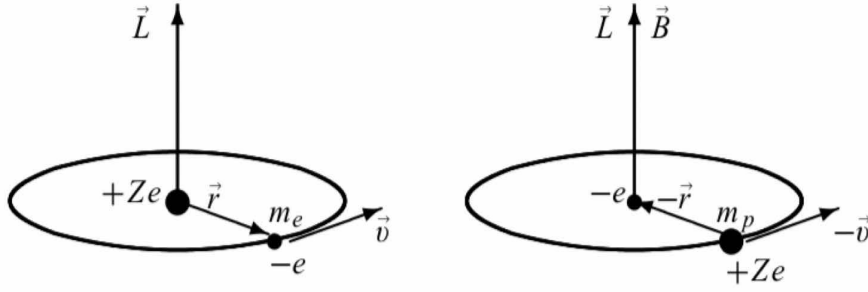


Figure 9.1 (Left) An electron moving in a circular orbit as seen by the nucleus. (Right) The same motion as seen by the electron within its rest frame; the electron sees the nucleus moving in a circular orbit around it.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

where $E_n^{(0)} = -e^2/(2a_0 n^2) = -(13.6/n^2)$ eV are the energy levels of hydrogen and $E_{SO}^{(1)}$ is the energy due to spin-orbit interaction:

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

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

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

we can rewrite (9.79) as

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

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

or

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

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

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

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

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

9.2.3.2 Relativistic Correction

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

$$\sqrt{\hat{p}^2 c^2 + m_e^2 c^4} - m_e c^2 \simeq \frac{\hat{p}^2}{2m_e} - \frac{\hat{p}^4}{8m_e^3 c^2} + \dots \quad (9.85)$$

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

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

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

$$E_R^{(1)} = \langle n l j m_j | \hat{H}_R | n l j m_j \rangle = -\frac{1}{8m_e^3 c^2} \langle n l j m_j | \hat{p}^4 | n l j m_j \rangle. \quad (9.87)$$

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

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

An insertion of this value in (9.87) leads to

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

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

Remark

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

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

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

9.2.3.3 The Fine Structure of Hydrogen

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Problem 9.2

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

where $\lambda \ll 1$.

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

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

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

Solution

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

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

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

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

and its eigenstates by

$$|\phi_1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad |\phi_2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad |\phi_3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad |\phi_4\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}. \quad (9.260)$$

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

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

or

$$(E_0 + \lambda E_0 - E)(8E_0 - E) \lceil (3E_0 - E)(7E_0 - E) - 4\lambda^2 E_0^2 \rceil = 0, \quad (9.262)$$

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

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

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

$$E_3 \simeq (3 - \lambda^2)E_0, \quad E_4 \simeq (7 + \lambda^2)E_0. \quad (9.264)$$

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

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

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

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

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

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

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

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

and

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

because

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

Similarly, since

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

we can ascertain that

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

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

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

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

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

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

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

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

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

and hence

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

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

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

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

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

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

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

The diagonalization of (9.312) yields the following eigenvalues:

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

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

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

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

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

Problem 9.5

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

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

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

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

Solution

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

$$|\phi_1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad |\phi_2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad |\phi_3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad |\phi_4\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}. \quad (9.316)$$

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

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

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

or

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

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

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

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

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

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

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

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

where

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

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

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

Similarly, we can show that

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

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

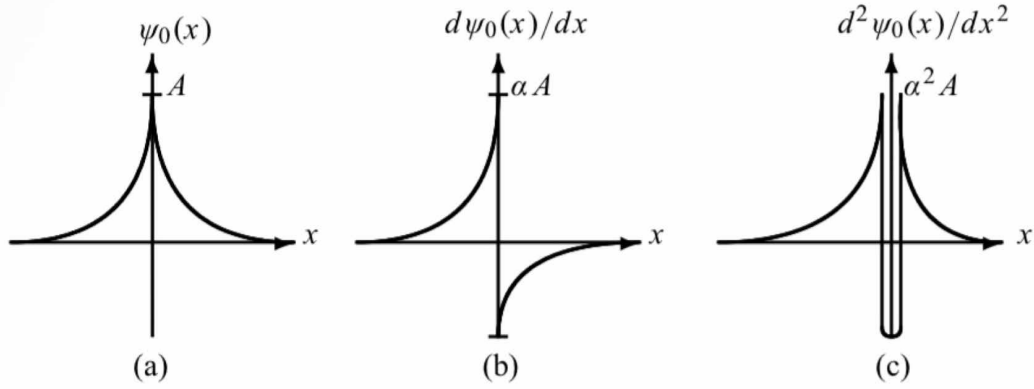


Figure 9.9 Shapes of $\psi_0(x) = Ae^{-\alpha|x|}$, $d\psi_0(x)/dx$, and $d^2\psi_0(x)/dx^2$.

So the diagonalization of

$$V = \begin{pmatrix} 0 & \lambda E_0 & 0 \\ \lambda E_0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (9.327)$$

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

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

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

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

Problem 9.6

Use the variational method to estimate the energy of the ground state of a one-dimensional harmonic oscillator by making use of the following two trial functions:

$$(a) \psi_0(x, \alpha) = Ae^{-\alpha|x|}, \quad (b) \psi_0(x, \alpha) = A/(x^2 + \alpha),$$

where α is a positive real number and where A is the normalization constant.

Solution

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

The normalization constant A can be calculated at once:

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

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

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

10.2.1 The Schrödinger Picture

In describing quantum dynamics, we have been using so far the Schrödinger picture in which *state vectors depend explicitly on time, but operators do not*:

$$\boxed{i\hbar \frac{d}{dt} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle,} \quad (10.1)$$

where $|\psi(t)\rangle$ denotes the state of the system in the Schrödinger picture. We have seen in Chapter 3 that the time evolution of a state $|\psi(t)\rangle$ can be expressed by means of the propagator, or time-evolution operator, $\hat{U}(t, t_0)$, as follows:

$$\boxed{|\psi(t)\rangle = \hat{U}(t, t_0) |\psi(t_0)\rangle,} \quad (10.2)$$

with

$$\hat{U}(t, t_0) = e^{-i(t-t_0)\hat{H}/\hbar}. \quad (10.3)$$

The operator $\hat{U}(t, t_0)$ is unitary,

$$\hat{U}^\dagger(t, t_0)\hat{U}(t, t_0) = I, \quad (10.4)$$

and satisfies these properties:

$$\hat{U}(t, t) = I, \quad (10.5)$$

$$\hat{U}^\dagger(t, t_0) = \hat{U}^{-1}(t, t_0) = \hat{U}(t_0, t), \quad (10.6)$$

$$\hat{U}(t_1, t_2)\hat{U}(t_2, t_3) = \hat{U}(t_1, t_3). \quad (10.7)$$

10.2.2 The Heisenberg Picture

In this picture the time dependence of the state vectors is completely frozen. The Heisenberg picture is obtained from the Schrödinger picture by applying $\hat{U}$ on $|\psi(t)\rangle_H$:

$$|\psi(t)\rangle_H = \hat{U}^\dagger(t) |\psi(t)\rangle = |\psi(0)\rangle, \quad (10.8)$$

where $|\psi(t)\rangle$ and $\hat{U}^\dagger(t)$ can be obtained from (10.2) and (10.3), respectively, by setting $t_0 = 0$: $\hat{U}^\dagger(t) = \hat{U}^\dagger(t, t_0 = 0) = e^{it\hat{H}/\hbar}$ and $|\psi(t)\rangle = \hat{U}(t) |\psi(0)\rangle$, with $\hat{U}(t) = e^{-it\hat{H}/\hbar}$. Thus, we can rewrite (10.8) as

$$\boxed{|\psi(t)\rangle_H = e^{it\hat{H}/\hbar} |\psi(t)\rangle.} \quad (10.9)$$

As $|\psi\rangle_H$ is frozen in time we have: $d|\psi\rangle_H/dt = 0$. Let us see how the expectation value of an operator $\hat{A}$ in the state $|\psi(t)\rangle$ evolves in time:

$$\langle\psi(t)|\hat{A}|\psi(t)\rangle = \langle\psi(0)|e^{it\hat{H}/\hbar}\hat{A}e^{-it\hat{H}/\hbar}|\psi(0)\rangle = \langle\psi(0)|\hat{A}_H(t)|\psi(0)\rangle = {}_H\langle\psi|\hat{A}_H(t)|\psi\rangle_H, \quad (10.10)$$

where $\hat{A}_H(t)$ is given by

$$\boxed{\hat{A}_H(t) = \hat{U}^\dagger(t)\hat{A}\hat{U}(t) = e^{it\hat{H}/\hbar}\hat{A}e^{-it\hat{H}/\hbar}.} \quad (10.11)$$

Equation (10.10) shows that the expectation value of an operator is the same in both the Schrödinger and the Heisenberg pictures. From (10.10) and (10.11) we see that both the Schrödinger and the Heisenberg pictures coincide at $t = 0$, since $|\psi(0)\rangle_H = |\psi(0)\rangle$ and $\hat{A}_H(0) = \hat{A}$.

10.2.2.1 The Heisenberg Equation of Motion

Let us now derive the equation of motion that regulates the time evolution of operators within the Heisenberg picture. Assuming that $\hat{A}$ does not depend explicitly on time (i.e., $\partial \hat{A} / \partial t = 0$) and since $\hat{U}(t)$ is unitary, we have

$$\begin{aligned} \frac{d\hat{A}_H(t)}{dt} &= \frac{\partial \hat{U}^\dagger(t)}{\partial t} \hat{A} \hat{U}(t) + \hat{U}^\dagger(t) \hat{A} \frac{\partial \hat{U}(t)}{\partial t} = -\frac{1}{i\hbar} \hat{U}^\dagger \hat{H} \hat{U} \hat{U}^\dagger \hat{A} \hat{U} + \frac{1}{i\hbar} \hat{U}^\dagger \hat{A} \hat{U} \hat{U}^\dagger \hat{H} \hat{U} \\ &= \frac{1}{i\hbar} [\hat{A}_H, \hat{U}^\dagger \hat{H} \hat{U}], \end{aligned} \quad (10.12)$$

where we have used (10.3) to write $\partial \hat{U}(t) / \partial t = \hat{H} \hat{U} / i\hbar$ and $\partial \hat{U}^\dagger(t) / \partial t = -\hat{U}^\dagger \hat{H} / i\hbar$. Since $\hat{U}(t)$ and $\hat{H}$ commute, we have $\hat{U}^\dagger(t) \hat{H} \hat{U}(t) = H$; hence we can rewrite (10.12) as

$$\boxed{\frac{d\hat{A}_H}{dt} = \frac{1}{i\hbar} [\hat{A}_H, \hat{H}].} \quad (10.13)$$

This is the *Heisenberg equation of motion*. It plays the role of the Schrödinger equation within the Heisenberg picture. Since the Schrödinger and Heisenberg pictures are equivalent, we can use either picture to describe the quantum system under consideration. The Heisenberg equation (10.13), however, is in general difficult to solve.

Note that the structure of the Heisenberg equation (10.13) is similar to the classical equation of motion of a variable A that does not depend explicitly on time $dA/dt = \{A, H\}$, where $\{A, H\}$ is the Poisson bracket between A and H (see Chapter 3).

10.2.3 The Interaction Picture

The interaction picture, also called the *Dirac picture*, is useful to describe quantum phenomena with Hamiltonians that depend explicitly on time. In this picture *both state vectors and operators evolve in time*. We need, therefore, to find the equation of motion for the state vectors and for the operators.

10.2.3.1 Equation of Motion for the State Vectors

State vectors in the interaction picture are defined in terms of the Schrödinger states $|\psi(t)\rangle$ by

$$\boxed{|\psi(t)\rangle_I = e^{it\hat{H}_0/\hbar} |\psi(t)\rangle.} \quad (10.14)$$

If $t = 0$ we have $|\psi(0)\rangle_I = |\psi(0)\rangle$. The time evolution of $|\psi(t)\rangle$ is governed by the Schrödinger equation (10.1) with $\hat{H} = \hat{H}_0 + \hat{V}$ where $\hat{H}_0$ is time independent, but $\hat{V}$ may depend on time.

To find the time evolution of $|\psi(t)\rangle_I$, we need the time derivative of (10.14):

$$\begin{aligned} i\hbar \frac{d|\psi(t)\rangle_I}{dt} &= -\hat{H}_0 e^{it\hat{H}_0/\hbar} |\psi(t)\rangle + e^{it\hat{H}_0/\hbar} \left(i\hbar \frac{d|\psi(t)\rangle}{dt} \right) \\ &= -\hat{H}_0 |\psi(t)\rangle_I + e^{it\hat{H}_0/\hbar} \hat{H} |\psi(t)\rangle, \end{aligned} \quad (10.15)$$

where we have used (10.1). Since $\hat{H} = \hat{H}_0 + \hat{V}$ and

$$e^{iH_0t/\hbar} \hat{V} = (e^{it\hat{H}_0/\hbar} \hat{V} e^{-it\hat{H}_0/\hbar}) e^{it\hat{H}_0/\hbar} = \hat{V}_I(t) e^{it\hat{H}_0/\hbar}, \quad (10.16)$$

with

$$\hat{V}_I(t) = e^{it\hat{H}_0/\hbar} \hat{V} e^{-it\hat{H}_0/\hbar}, \quad (10.17)$$

we can rewrite (10.15) as

$$i\hbar \frac{d}{dt} |\psi(t)\rangle_I = -\hat{H}_0 |\psi(t)\rangle_I + \hat{H}_0 e^{it\hat{H}_0/\hbar} |\psi(t)\rangle + \hat{V}_I(t) e^{it\hat{H}_0/\hbar} |\psi(t)\rangle, \quad (10.18)$$

or

$$\boxed{i\hbar \frac{d}{dt} |\psi(t)\rangle_I = \hat{V}_I(t) |\psi(t)\rangle_I.} \quad (10.19)$$

This is the Schrödinger equation in the interaction picture. It shows that the time evolution of the state vector is governed by the interaction $\hat{V}_I(t)$.

10.2.3.2 Equation of Motion for the Operators

The interaction representation of an operator $\hat{A}_I(t)$ is given, as shown in (10.17), in terms of its Schrödinger representation by

$$\boxed{\hat{A}_I(t) = e^{i\hat{H}_0t/\hbar} \hat{A} e^{-i\hat{H}_0t/\hbar}.} \quad (10.20)$$

Calculating the time derivative of $\hat{A}_I(t)$ and since $\partial \hat{A} / \partial t = 0$, we can show the time evolution of $\hat{A}_I(t)$ is governed by $\hat{H}_0$:

$$\boxed{\frac{d\hat{A}_I(t)}{dt} = \frac{1}{i\hbar} [\hat{A}_I(t), \hat{H}_0].} \quad (10.21)$$

This equation is similar to the Heisenberg equation of motion (10.13), except that $\hat{H}$ is replaced by $\hat{H}_0$. The basic difference between the Heisenberg and interaction pictures can be inferred from a comparison of (10.9) with (10.14), and (10.11) with (10.20): in the Heisenberg picture it is $\hat{H}$ that appears in the exponents, whereas in the interaction picture it is $\hat{H}_0$ that appears.

In conclusion, we have seen that, within the Schrödinger picture, the states depend on time but not the operators; in the Heisenberg picture, only operators depend explicitly on time, state vectors are frozen in time. The interaction picture, however, is intermediate between the Schrödinger and the Heisenberg pictures, since both state vectors and operators evolve with time.

10.3 Time-Dependent Perturbation Theory

We consider here only those phenomena that are described by Hamiltonians which can be split into two parts, a time-independent part $\hat{H}_0$ and a time-dependent part $\hat{V}(t)$ that is small compared to $\hat{H}_0$:

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t), \quad (10.22)$$

where $\hat{H}_0$, which describes the system when unperturbed, is assumed to have exact solutions that are known. Such splitting of the Hamiltonian is encountered in the following typical problem. Consider a system which, when unperturbed, is described by a time-independent Hamiltonian $\hat{H}_0$ whose solutions—the eigenvalues E_n and eigenstates $|\psi_n\rangle$ —are known,

$$\hat{H}_0 |\psi_n\rangle = E_n |\psi_n\rangle, \quad (10.23)$$

and whose most general state vectors are given by stationary states

$$|\Psi_n(t)\rangle = e^{-it\hat{H}_0/\hbar} |\psi_n\rangle = e^{-iE_n t/\hbar} |\psi_n\rangle. \quad (10.24)$$

In the time interval $0 \leq t \leq \tau$ we subject the system to an external time-dependent perturbation, $\hat{V}(t)$, that is small compared to $\hat{H}_0$:

$$\hat{V}(t) = \begin{cases} \hat{V}(t), & 0 \leq t \leq \tau, \\ 0, & t < 0, \quad t > \tau. \end{cases} \quad (10.25)$$

During the time interval $0 \leq t \leq \tau$, the Hamiltonian of the system is $\hat{H} = \hat{H}_0 + \hat{V}(t)$ and the corresponding Schrödinger equation is

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = (\hat{H}_0 + \hat{V}(t)) |\Psi(t)\rangle, \quad (10.26)$$

where $\hat{V}(t)$ characterizes the interaction of the system with the external source of perturbation.

How does $\hat{V}(t)$ affect the system? When the system interacts with $\hat{V}(t)$, it either absorbs or emits energy. This process inevitably causes the system to undergo transitions from one unperturbed eigenstate to another. The main task of time-dependent perturbation theory consists of answering this question: If the system is initially in an (unperturbed) eigenstate $|\psi_i\rangle$ of $\hat{H}_0$, what is the probability that the system will be found at a later time in another unperturbed eigenstate $|\psi_f\rangle$?

To prepare the ground for answering this question, we need to look for the solutions of the Schrödinger equation (10.26). The standard method to solve (10.26) is to expand $|\Psi(t)\rangle$ in terms of an expansion coefficient $c_n(t)$:

$$|\Psi(t)\rangle = \sum_n c_n(t) e^{-iE_n t} |\psi_n\rangle, \quad (10.27)$$

and then insert this into (10.26) to find $c_n(t)$ to various orders in the approximation. Instead of following this procedure, and since we are dealing with time-dependent potentials, it is more convenient to solve (10.26) in the interaction picture (10.19):

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle_I = \hat{V}_I(t) |\Psi(t)\rangle_I, \quad (10.28)$$

where $|\Psi(t)\rangle_I = e^{it\hat{H}_0/\hbar} |\Psi(t)\rangle$ and $\hat{V}_I(t) = e^{it\hat{H}_0/\hbar} \hat{V}(t) e^{-it\hat{H}_0/\hbar}$. The time evolution equation $|\Psi(t)\rangle = \hat{U}(t, t_i) |\Psi(t_i)\rangle$ may be written in the interaction picture as

$$|\Psi(t)\rangle_I = e^{it\hat{H}_0/\hbar} |\Psi(t)\rangle = e^{it\hat{H}_0/\hbar} \hat{U}(t, t_i) |\Psi(t_i)\rangle = e^{it\hat{H}_0/\hbar} \hat{U}(t, t_i) e^{-it_i\hat{H}_0/\hbar} |\Psi(t_i)\rangle_I, \quad (10.29)$$

or as

$$| \Psi(t) \rangle_I = \hat{U}_I(t, t_i) | \Psi(t_i) \rangle_I, \quad (10.30)$$

where the time evolution operator is given in the interaction picture by

$$\hat{U}_I(t, t_i) = e^{it\hat{H}_0/\hbar} \hat{U}(t, t_i) e^{-i\hat{H}_0 t_i/\hbar}. \quad (10.31)$$

Inserting (10.30) into (10.28) we end up with

$$i\hbar \frac{d\hat{U}_I(t, t_i)}{dt} = \hat{V}_I(t) \hat{U}_I(t, t_i). \quad (10.32)$$

The solutions of this equation, with the initial condition $\hat{U}_I(t_i, t_i) = \hat{I}$, are given by the *integral equation*

$$\hat{U}_I(t, t_i) = 1 - \frac{i}{\hbar} \int_{t_i}^t \hat{V}_I(t') \hat{U}_I(t', t_i) dt'. \quad (10.33)$$

Time-dependent perturbation theory provides *approximate* solutions to this integral equation. This consists in assuming that $\hat{V}_I(t)$ is *small and then proceeding iteratively*. The first-order approximation is obtained by inserting $\hat{U}_I(t', t_i) = 1$ in the integral sign of (10.33), leading to $\hat{U}_I^{(1)}(t, t_i) = 1 - (i/\hbar) \int_{t_i}^t \hat{V}_I(t') dt'$. Substituting $\hat{U}_I(t', t_i) = \hat{U}_I^{(1)}(t', t_i)$ in the integral sign of (10.33) we get the second-order approximation:

$$\hat{U}_I^{(2)}(t, t_i) = 1 - \frac{i}{\hbar} \int_{t_i}^t \hat{V}_I(t') dt' + \left(-\frac{i}{\hbar}\right)^2 \int_{t_i}^t \hat{V}_I(t_1) dt_1 \int_{t_i}^{t_1} \hat{V}_I(t_2) dt_2. \quad (10.34)$$

The third-order approximation is obtained by substituting $\hat{U}_I^{(2)}(t, t_i)$ into (10.33), and so on. A repetition of this iterative process yields

$$\begin{aligned} \hat{U}_I(t, t_i) = & 1 - \frac{i}{\hbar} \int_{t_i}^t \hat{V}_I(t') dt' + \left(-\frac{i}{\hbar}\right)^2 \int_{t_i}^t \hat{V}_I(t_1) dt_1 \int_{t_i}^{t_1} \hat{V}_I(t_2) dt_2 + \dots \\ & + \left(-\frac{i}{\hbar}\right)^n \int_{t_i}^t \hat{V}_I(t_1) dt_1 \int_{t_i}^{t_1} \hat{V}_I(t_2) dt_2 \int_{t_i}^{t_2} \hat{V}_I(t_3) dt_3 \dots \int_{t_i}^{t_{n-1}} \hat{V}_I(t_n) dt_n + \dots \end{aligned} \quad (10.35)$$

This series, known as the *Dyson series*, allows for the calculation of the state vector up to the desired order in the perturbation.

We are now equipped to calculate the transition probability. It may be obtained by taking the matrix elements of (10.35) between the eigenstates of $\hat{H}_0$. Time-dependent perturbation theory, where one assumes knowledge of the solutions of the unperturbed eigenvalue problem (10.23), deals in essence with the calculation of the transition probabilities between the unperturbed eigenstates $|\psi_n\rangle$ of the system.

10.3.1 Transition Probability

The transition probability corresponding to a transition from an initial unperturbed state $|\psi_i\rangle$ to another unperturbed state $|\psi_f\rangle$ is obtained from (10.35):

$$P_{if}(t) = \left| \langle \psi_f | \hat{U}_I(t, t_i) | \psi_i \rangle \right|^2 = \left| \langle \psi_f | \psi_i \rangle - \frac{i}{\hbar} \int_0^t e^{i\omega_{fi}t'} \langle \psi_f | \hat{V}(t') | \psi_i \rangle dt' \right|^2$$

$$+ \left(-\frac{i}{\hbar} \right)^2 \sum_n \int_0^t e^{i\omega_{fn}t_1} \langle \psi_f | \hat{V}(t_1) | \psi_n \rangle dt_1 \int_0^{t_1} e^{i\omega_{ni}t_2} \langle \psi_n | \hat{V}(t_2) | \psi_i \rangle dt_2 + \dots \Big|^2, \quad (10.36)$$

where we have used the fact that

$$\langle \psi_f | \hat{V}_I(t') | \psi_i \rangle = \langle \psi_f | e^{iH_0 t'/\hbar} \hat{V}(t') e^{-iH_0 t'/\hbar} | \psi_i \rangle = \langle \psi_f | V(t') | \psi_i \rangle \exp(i\omega_{fi}t'), \quad (10.37)$$

where ω_{fi} is the transition frequency between the initial and final levels i and f :

$$\omega_{fi} = \frac{E_f - E_i}{\hbar} = \frac{1}{\hbar} (\langle \psi_f | \hat{H}_0 | \psi_f \rangle - \langle \psi_i | \hat{H}_0 | \psi_i \rangle). \quad (10.38)$$

The transition probability (10.36) can be written in terms of the expansion coefficients $c_n(t)$ introduced in (10.27) as

$$P_{if}(t) = \left| c_f^{(0)} + c_f^{(1)}(t) + c_f^{(2)}(t) + \dots \right|^2, \quad (10.39)$$

where

$$c_f^{(0)} = \langle \psi_f | \psi_i \rangle = \delta_{f,i}, \quad c_f^{(1)}(t) = -\frac{i}{\hbar} \int_0^t \langle \psi_f | \hat{V}(t') | \psi_i \rangle e^{i\omega_{fi}t'} dt', \dots \quad (10.40)$$

The first-order transition probability for $|\psi_i\rangle \rightarrow |\psi_f\rangle$ with $i \neq f$ (and hence $\langle \psi_f | \psi_i \rangle = 0$) is obtained by terminating (10.36) at the first order in $V_I(t)$:

$$P_{if}(t) = \left| -\frac{i}{\hbar} \int_0^t \langle \psi_f | \hat{V}(t') | \psi_i \rangle e^{i\omega_{fi}t'} dt' \right|^2. \quad (10.41)$$

In principle we can use (10.36) to calculate the transition probability to any order in $\hat{V}_I(t)$. However, terms higher than the first order become rapidly intractable. For most problems of atomic and nuclear physics, the first order (10.41) is usually sufficient. In what follows, we are going to apply (10.41) to calculate the transition probability for two cases, which will have later usefulness when we deal with the interaction of atoms with radiation: a *constant* perturbation and a *harmonic* perturbation.

10.3.2 Transition Probability for a Constant Perturbation

In the case where $\hat{V}$ does not depend on time, (10.41) leads to

$$P_{if}(t) = \frac{1}{\hbar^2} \left| \langle \psi_f | \hat{V} | \psi_i \rangle \int_0^t e^{i\omega_{fi}t'} dt' \right|^2 = \frac{1}{\hbar^2} \left| \langle \psi_f | \hat{V} | \psi_i \rangle \right|^2 \left| \frac{e^{i\omega_{fi}t} - 1}{\omega_{fi}} \right|^2, \quad (10.42)$$

which, using $|e^{i\theta} - 1|^2 = 4 \sin^2(\theta/2)$, reduces to

$$P_{if}(t) = \frac{4 \left| \langle \psi_f | \hat{V} | \psi_i \rangle \right|^2}{\hbar^2 \omega_{fi}^2} \sin^2 \left(\frac{\omega_{fi}t}{2} \right). \quad (10.43)$$

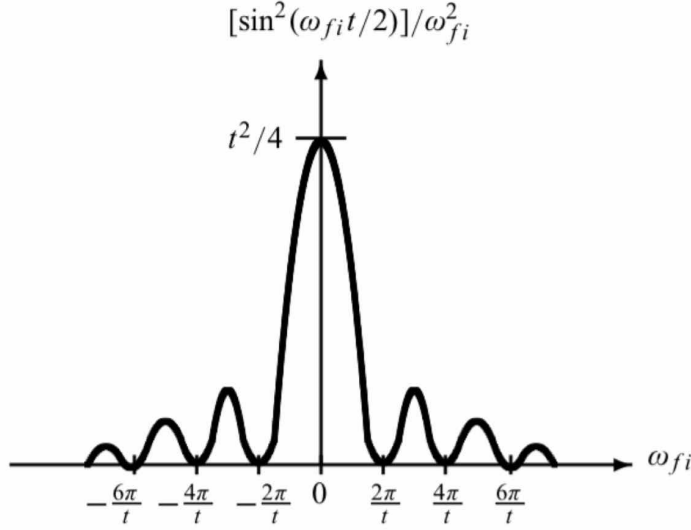


Figure 10.1 Plot of $[\sin^2(\omega_{fi}t/2)]/\omega_{fi}^2$ versus ω_{fi} for a fixed value of t ; $\omega_{fi} = (E_f - E_i)/2$.

As a function of time, this transition probability is an oscillating sinusoidal function with a period of $2\pi/\omega_{fi}$. As a function of ω_{fi} , however, the transition probability, as shown in Figure 10.1, has an interference pattern: it is appreciable only near $\omega_{fi} \simeq 0$ and decays rapidly as ω_{fi} moves away from zero (here, for a fixed t , we have assumed that ω_{fi} is a continuous variable; that is, we have considered a continuum of final states; we will deal with this in more detail in a moment). This means that the transition probability of finding the system in a state $|\psi_f\rangle$ of energy E_f is greatest only when $E_i \simeq E_f$ or when $\omega_{fi} \simeq 0$. The height and the width of the main peak, centered around $\omega_{fi} = 0$, are proportional to t^2 and $1/t$, respectively, so the area under the curve is proportional to t ; since most of the area is under the central peak, the transition probability is proportional to t . The transition probability therefore grows linearly with time. The central peak becomes narrower and higher as time increases; this is exactly the property of a delta function. Thus, in the limit $t \rightarrow \infty$ the transition probability takes the shape of a delta function, as we are going to see.

As $t \rightarrow \infty$ we can use the asymptotic relation (Appendix A)

$$\lim_{t \rightarrow \infty} \frac{\sin^2(yt)}{\pi y^2 t} = \delta(y) \quad (10.44)$$

to write the following expression:

$$\frac{1}{(\frac{1}{2}\omega_{fi})^2} \sin^2\left(\frac{\omega_{fi}t}{2}\right) = 2\pi t \hbar \delta(\hbar\omega_{fi}), \quad (10.45)$$

because $\delta(\omega_{fi}/2) = 2\hbar\delta(\hbar\omega_{fi})$. Now since $\hbar\omega_{fi} = E_f - E_i$ and hence $\delta(\hbar\omega_{fi}) = \delta(E_f - E_i)$, we can reduce (10.43) in the limit of long times to

$$P_{if}(t) = \frac{2\pi t}{\hbar} \left| \langle \psi_f | \hat{V} | \psi_i \rangle \right|^2 \delta(E_f - E_i). \quad (10.46)$$

The *transition rate*, which is defined as a transition probability per unit time, is thus given by

$$\Gamma_{if} = \frac{P_{if}(t)}{t} = \frac{2\pi}{\hbar} \left| \langle \psi_f | \hat{V} | \psi_i \rangle \right|^2 \delta(E_f - E_i). \quad (10.47)$$

The delta term $\delta(E_f - E_i)$ guarantees the conservation of energy: in the limit $t \rightarrow \infty$, the transition rate is nonvanishing only between states of equal energy. Hence a constant (time-independent) perturbation neither removes energy from the system nor supplies energy to it. It simply causes energy-conserving transitions.

Transition into a continuum of final states

Let us now calculate the total transition rate associated with a transition from an initial state $|\psi_i\rangle$ into a continuum of final states $|\psi_f\rangle$. If $\rho(E_f)$ is the density of final states—the number of states per unit energy interval—the number of final states within the energy interval E_f and $E_f + dE_f$ is equal to $\rho(E_f) dE_f$. The total transition rate W_{if} can then be obtained from (10.47):

$$W_{if} = \int \frac{P_{if}(t)}{t} \rho(E_f) dE_f = \frac{2\pi}{\hbar} |\langle \psi_f | \hat{V} | \psi_i \rangle|^2 \int \rho(E_f) \delta(E_f - E_i) dE_f, \quad (10.48)$$

or

$$W_{if} = \frac{2\pi}{\hbar} |\langle \psi_f | \hat{V} | \psi_i \rangle|^2 \rho(E_i). \quad (10.49)$$

This relation is called the *Fermi golden rule*. It implies that, in the case of a constant perturbation, if we wait long enough, the total transition rate becomes constant (time independent).

10.3.3 Transition Probability for a Harmonic Perturbation

Consider now a perturbation which depends harmonically on time (i.e., the time between the moments of turning the perturbation on and off):

$$\hat{V}(t) = \hat{v} e^{i\omega t} + \hat{v}^\dagger e^{-i\omega t}, \quad (10.50)$$

where $\hat{v}$ is a time-independent operator. Such a perturbation is encountered, for instance, when charged particles (e.g., electrons) interact with an electromagnetic field. This perturbation provokes transitions of the system from one stationary state to another.

The transition probability corresponding to this perturbation can be obtained from (10.41):

$$P_{if}(t) = \frac{1}{\hbar^2} \left| \langle \psi_f | \hat{v} | \psi_i \rangle \int_0^t e^{i(\omega_{fi} + \omega)t'} dt' + \langle \psi_f | \hat{v}^\dagger | \psi_i \rangle \int_0^t e^{i(\omega_{fi} - \omega)t'} dt' \right|^2. \quad (10.51)$$

Neglecting the cross terms, for they are negligible compared with the other two (because they induce no lasting transitions), we can rewrite this expression as

$$P_{if}(t) = \frac{1}{\hbar^2} \left| \langle \psi_f | \hat{v} | \psi_i \rangle \right|^2 \left| \frac{e^{i(\omega_{fi} + \omega)t} - 1}{\omega_{fi} + \omega} \right|^2 + \frac{1}{\hbar^2} \left| \langle \psi_f | \hat{v}^\dagger | \psi_i \rangle \right|^2 \left| \frac{e^{i(\omega_{fi} - \omega)t} - 1}{\omega_{fi} - \omega} \right|^2, \quad (10.52)$$

which, using $|e^{i\theta} - 1|^2 = 4 \sin^2(\theta/2)$, reduces to

$$P_{if}(t) = \frac{4}{\hbar^2} \left[\left| \langle \psi_f | \hat{v} | \psi_i \rangle \right|^2 \frac{\sin^2((\omega_{fi} + \omega)t/2)}{(\omega_{fi} + \omega)^2} + \left| \langle \psi_f | \hat{v}^\dagger | \psi_i \rangle \right|^2 \frac{\sin^2((\omega_{fi} - \omega)t/2)}{(\omega_{fi} - \omega)^2} \right]. \quad (10.53)$$

As displayed in Figure 10.2, the transition probability peaks either at $\omega_{fi} = -\omega$, where its maximum value is $P_{if}(t) = (t^2/4\hbar^2) |\langle \psi_f | \hat{v} | \psi_i \rangle|^2$, or at $\omega_{fi} = \omega$, where its maximum

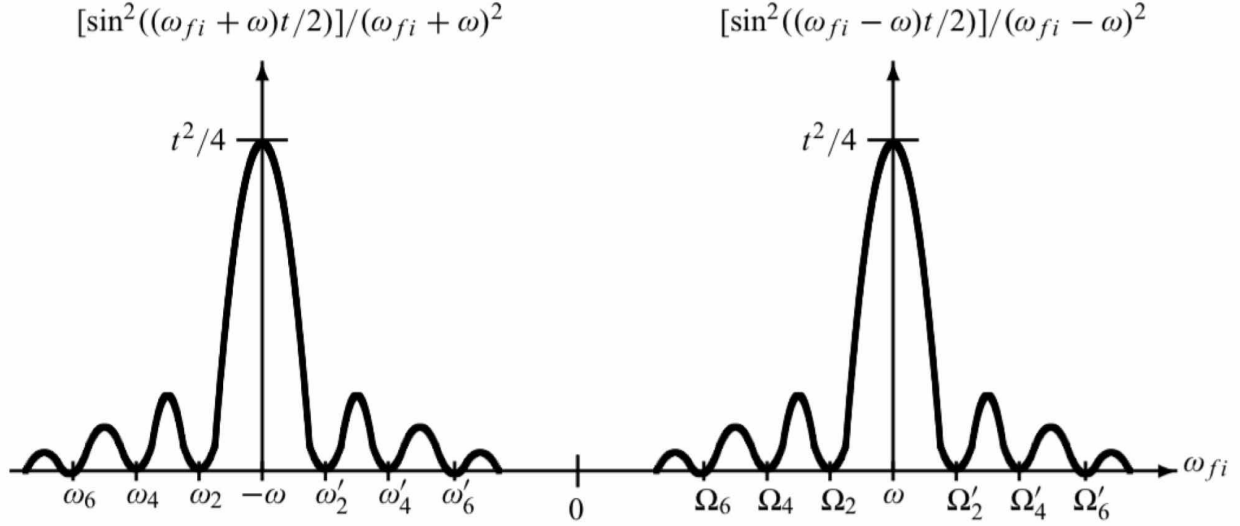


Figure 10.2 Plot of $[\sin^2((\omega_{fi} \pm \omega)t/2)]/(\omega_{fi} \pm \omega)^2$ versus ω_{fi} for a fixed value of t , where $\omega_n = -\omega - n\pi/t$, $\omega'_n = -\omega + n\pi/t$, $\Omega_n = \omega - n\pi/t$, and $\Omega'_n = \omega + n\pi/t$.

value is $P_{if}(t) = (t^2/4\hbar^2)|\langle\psi_f | \hat{v}^\dagger | \psi_i\rangle|^2$. These are conditions for resonance; this means that the probability of transition is greatest only when the frequency of the perturbing field is close to $\pm\omega_{fi}$. As ω moves away from $\pm\omega_{fi}$, P_{fi} decreases rapidly.

Note that the expression (10.53) is similar to that derived for a constant perturbation, as shown in (10.43). Using (10.45) we can reduce (10.53) in the limit $t \rightarrow \infty$ to

$$\Gamma_{if} = \frac{2\pi}{\hbar} \left| \langle\psi_f | \hat{v} | \psi_i\rangle \right|^2 \delta(E_f - E_i + \hbar\omega) + \frac{2\pi}{\hbar} \left| \langle\psi_f | \hat{v}^\dagger | \psi_i\rangle \right|^2 \delta(E_f - E_i - \hbar\omega). \quad (10.54)$$

This transition rate is nonzero only when either of the following two conditions is satisfied:

$$E_f = E_i - \hbar\omega, \quad (10.55)$$

$$E_f = E_i + \hbar\omega. \quad (10.56)$$

These two conditions cannot be satisfied simultaneously; their physical meaning can be understood as follows. The first condition $E_f = E_i - \hbar\omega$ implies that the system is initially excited, since its final energy is smaller than the initial energy; when acted upon by the perturbation, the system deexcites by giving up a photon of energy $\hbar\omega$ to the potential $\hat{V}(t)$ as shown in Figure 10.3. This process is called *stimulated emission*, since the system easily emits a photon of energy $\hbar\omega$. The second condition, $E_f = E_i + \hbar\omega$ shows that the final energy of the system is larger than its initial energy. The system then *absorbs* a photon of energy $\hbar\omega$ from $\hat{V}(t)$ and ends up in an excited state of (higher) energy E_f (Figure 10.3). We may thus view the terms $e^{i\omega t}$ and $e^{-i\omega t}$ in $\hat{V}(t)$ as responsible, respectively, for the emission and the absorption of a photon of energy $\hbar\omega$.

In conclusion, the effect of a harmonic perturbation is to transfer to the system, or to receive from it, a photon of energy $\hbar\omega$. In sharp contrast, a constant (time-independent) perturbation neither transfers energy to the system nor removes energy from it.

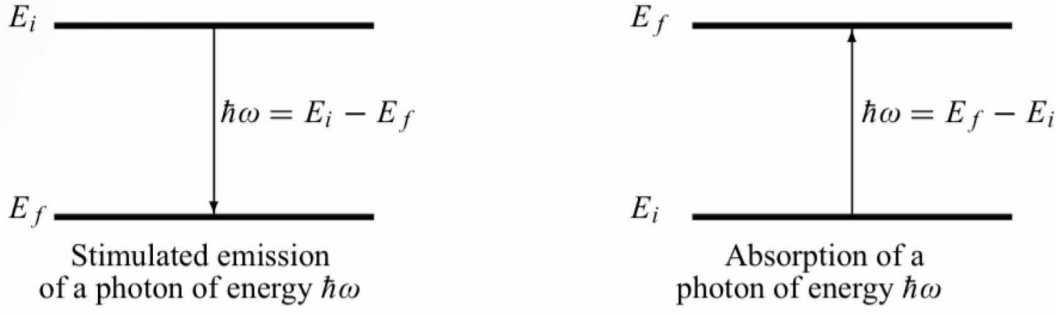


Figure 10.3 Stimulated emission and absorption of a photon of energy $\hbar\omega$.

Remark

For transitions into a continuum of final states, we can show, by analogy with the derivation of (10.49), that (10.54) leads to the absorption and emission transition rates:

$$W_{if}^{abs} = \frac{2\pi}{\hbar} \left| \langle \psi_f | \hat{V}^\dagger | \psi_i \rangle \right|^2 \rho(E_f) \Big|_{E_f=E_i+\hbar\omega}, \quad (10.57)$$

$$W_{if}^{emi} = \frac{2\pi}{\hbar} \left| \langle \psi_f | \hat{V} | \psi_i \rangle \right|^2 \rho(E_f) \Big|_{E_f=E_i-\hbar\omega}. \quad (10.58)$$

Since the perturbation (10.50) is Hermitian, $\langle \psi_f | \hat{V} | \psi_i \rangle = \langle \psi_i | \hat{V}^\dagger | \psi_f \rangle^*$, we have $|\langle \psi_f | \hat{V} | \psi_i \rangle|^2 = |\langle \psi_f | \hat{V}^\dagger | \psi_i \rangle|^2$; hence

$$\frac{W_{if}^{abs}}{\rho(E_f) \Big|_{E_f=E_i+\hbar\omega}} = \frac{W_{if}^{emi}}{\rho(E_f) \Big|_{E_f=E_i-\hbar\omega}}. \quad (10.59)$$

This relation is known as the condition of *detailed balancing*.

Example 10.1

A particle, which is initially ($t = 0$) in the ground state of an infinite, one-dimensional potential box with walls at $x = 0$ and $x = a$, is subjected for $0 \leq t \leq \infty$ to a perturbation $\hat{V}(t) = \hat{x}^2 e^{-t/\tau}$. Calculate to first order the probability of finding the particle in its first excited state for $t \geq 0$.

Solution

For a particle in a box potential, with $E_n = n^2 \pi^2 \hbar^2 / (2ma^2)$ and $\psi_n(x) = \sqrt{2/a} \sin(n\pi x/a)$, the ground state corresponds to $n = 1$ and the first excited state to $n = 2$. We can use (10.41) to obtain

$$P_{12} = \frac{1}{\hbar^2} \left| \int_0^\infty \langle \psi_2 | \hat{V}(t) | \psi_1 \rangle e^{i\omega_{21}t} dt \right|^2 = \frac{1}{\hbar^2} \left| \langle \psi_2 | \hat{x}^2 | \psi_1 \rangle \right|^2 \left| \int_0^\infty e^{-(1/\tau - i\omega_{21})t} dt \right|^2, \quad (10.60)$$

where

$$\langle \psi_2 | \hat{x}^2 | \psi_1 \rangle = \int_0^a x^2 \psi_2^*(x) \psi_1(x) dx = \frac{2}{a} \int_0^a x^2 \sin\left(\frac{2\pi x}{a}\right) \sin\left(\frac{\pi x}{a}\right) dx = -\frac{16a^2}{9\pi^2}, \quad (10.61)$$

$$\left| \int_0^t e^{-(1/\tau - i\omega_{21})t} dt \right|^2 = \left| \frac{e^{-(1/\tau - i\omega_{21})t} - 1}{1/\tau - i\omega_{21}} \right|^2 = \frac{1 + e^{-2t/\tau} - 2e^{-t/\tau} \cos(\omega_{21}t)}{\omega_{21}^2 + 1/\tau^2}, \quad (10.62)$$

which, in the limit $t \rightarrow \infty$, reduces to

$$\left| \int_0^\infty e^{-(1/\tau - i\omega_{21})t} dt \right|^2 = \left[\omega_{21}^2 + \frac{1}{\tau^2} \right]^{-1} = \left[\frac{9\pi^4 \hbar^2}{4m^2 a^4} + \frac{1}{\tau^2} \right]^{-1}, \quad (10.63)$$

since $\omega_{21} = (E_2 - E_1)/\hbar = 3\pi^2 \hbar / (2ma^2)$. A substitution of (10.61) and (10.63) into (10.60) leads to

$$P_{12} = \left(\frac{16a^2}{9\pi^2 \hbar} \right)^2 \left[\frac{9\pi^4 \hbar^2}{4m^2 a^4} + \frac{1}{\tau^2} \right]^{-1}. \quad (10.64)$$

10.4 Adiabatic and Sudden Approximations

In discussing the time-dependent perturbation theory, we have dealt with phenomena where the perturbation $\hat{V}(t)$ is small, but we have paid no attention to the rate of change of the perturbation. In this section we want to discuss approximation methods treating phenomena where $\hat{V}(t)$ is not only small but also switched on either *adiabatically* (slowly) or *suddenly* (rapidly). We assume here that $\hat{V}(t)$ is switched on at $t = 0$ and off at a later time t (the turning on and off may be smooth or abrupt).

Since $e^{i\omega_{fi}t} = (1/i\omega_{fi}) \partial e^{i\omega_{fi}t} / \partial t$ an integration by parts yields

$$\begin{aligned} -\frac{i}{\hbar} \int_0^t \langle \psi_f | \hat{V}(t') | \psi_i \rangle e^{i\omega_{fi}t'} dt' &= -\frac{1}{\hbar\omega_{fi}} \int_0^t \langle \psi_f | \hat{V}(t') | \psi_i \rangle \left(\frac{\partial}{\partial t'} e^{i\omega_{fi}t'} \right) dt' \\ &= -\frac{1}{\hbar\omega_{fi}} \langle \psi_f | \hat{V}(t) | \psi_i \rangle e^{i\omega_{fi}t} \Big|_{t=0} + \frac{1}{\hbar\omega_{fi}} \int_0^t e^{i\omega_{fi}t'} \left(\frac{\partial}{\partial t'} \langle \psi_f | \hat{V}(t') | \psi_i \rangle \right) dt' \\ &= \frac{1}{\hbar\omega_{fi}} \int_0^t e^{i\omega_{fi}t'} \left(\frac{\partial}{\partial t'} \langle \psi_f | \hat{V}(t') | \psi_i \rangle \right) dt', \end{aligned} \quad (10.65)$$

where we have used the fact that $\hat{V}(t)$ vanishes at the limits (when it is switched on at $t = 0$ and off at time t). The calculation of the integral depends on the rate of change of $\hat{V}(t)$. In what follows we are going to consider the cases where the interaction is switched on slowly or rapidly.

10.4.1 Adiabatic Approximation

First, let us discuss briefly the adiabatic approximation without combining it with perturbation theory. This approximation applies to phenomena whose Hamiltonians evolve *slowly* with time; we should highlight the fact that the adiabatic approximation does not require the Hamiltonian to split into an unperturbed part $\hat{H}_0$ and a weak time-dependent perturbation $\hat{V}(t)$. Essentially, it consists in approximating the solutions of the Schrödinger equation at every time by the stationary states (energy E_n and wave functions ψ_n) of the instantaneous Hamiltonian in such

Problem 10.6

A particle, initially (i.e., $t \rightarrow -\infty$) in its ground state in an infinite potential well whose walls are located at $x = 0$ and $x = a$, is subject at time $t = 0$ to a time-dependent perturbation $\hat{V}(t) = \varepsilon \hat{x} e^{-t^2}$ where ε is a small real number. Calculate the probability that the particle will be found in its first excited state after a sufficiently long time (i.e., $t \rightarrow \infty$).

Solution

The transition probability from the ground state $n = 1$ (where $t \rightarrow -\infty$) to the first excited state $n = 2$ (where $t \rightarrow \infty$) is given by (10.41):

$$P_{1 \rightarrow 2} = \frac{1}{\hbar^2} \left| \int_{-\infty}^{+\infty} \langle \psi_2 | \hat{V}(t) | \psi_1 \rangle e^{i\omega_{21}t} dt \right|^2, \quad (10.196)$$

where

$$\omega_{21} = \frac{E_2 - E_1}{\hbar} = \frac{4\pi^2\hbar}{2ma^2} - \frac{\pi^2\hbar}{2ma^2} = \frac{3\pi^2\hbar}{2ma^2}, \quad (10.197)$$

$$\langle \psi_2 | \hat{V}(t) | \psi_1 \rangle = \frac{2\varepsilon}{a} e^{-t^2} \int_0^a x \sin\left(\frac{2\pi x}{a}\right) \sin\left(\frac{\pi x}{a}\right) dx = -\frac{16\varepsilon a}{9\pi^2} e^{-t^2}, \quad (10.198)$$

since $E_n = n^2\pi^2\hbar^2/(2ma^2)$ and $\psi_n(x) = \sqrt{2/a} \sin(n\pi x/a)$. Inserting (10.197) and (10.198) into (10.196), we have

$$P_{1 \rightarrow 2} = \left(\frac{16\varepsilon a}{9\pi^2\hbar} \right)^2 \left| \int_{-\infty}^{+\infty} e^{i\omega_{21}t - t^2} dt \right|^2. \quad (10.199)$$

A variable change $y = t - \frac{i}{2}\omega_{21}$ yields $i\omega_{21}t - t^2 = -\omega_{21}^2/4 - y^2$ and $dt = dy$:

$$P_{1 \rightarrow 2} = \left(\frac{16\varepsilon a}{9\pi^2\hbar} \right)^2 \left| e^{-\omega_{21}^2/4} \int_{-\infty}^{+\infty} e^{-y^2} dy \right|^2 = \pi \left(\frac{16\varepsilon a}{9\pi^2\hbar} \right)^2 \exp\left(-\frac{9\pi^4\hbar^2}{8m^2a^4}\right), \quad (10.200)$$

since $\omega_{21} = 3\pi^2\hbar/(2ma^2)$.

Problem 10.7

A particle is initially (i.e., $t = 0$) in its ground state in a one-dimensional harmonic oscillator potential. At $t = 0$ a perturbation $\hat{V}(x, t) = V_0 \hat{x}^3 e^{-t/\tau}$ is turned on. Calculate to first order the probability that, after a sufficiently long time (i.e., $t \rightarrow \infty$), the system will have made a transition to a given excited state; consider all final states.

Solution

The transition probability from the ground state $n = 0$ to an excited state n is given by (10.41):

$$P_{0 \rightarrow n} = \frac{1}{\hbar^2} \left| \int_0^{+\infty} \langle n | \hat{V}(t) | 0 \rangle e^{i\omega_{n0}t} dt \right|^2 = \frac{V_0^2}{\hbar^2} \left| \langle n | \hat{x}^3 | 0 \rangle \right|^2 \left| \int_0^{+\infty} e^{-(1/\tau - in\omega)t} dt \right|^2, \quad (10.201)$$

where $\omega_{n0} = \frac{E_n - E_0}{\hbar} = n\omega$ (since $E_n = \hbar\omega(n + \frac{1}{2})$) and the time integration was calculated in (10.63):

$$\left| \int_0^{\infty} e^{-(1/\tau - in\omega)t} dt \right|^2 = \frac{1}{n^2\omega^2 + 1/\tau^2}. \quad (10.202)$$

Since $\hat{a} | n \rangle = \sqrt{n} | n-1 \rangle$ and $\hat{a}^\dagger | n \rangle = \sqrt{n+1} | n+1 \rangle$, and since $\hat{X}^3 = (\hbar/2m\omega)^{3/2}(\hat{a}^\dagger + \hat{a})(\hat{a}^2 + \hat{a}^{\dagger 2} + 2\hat{a}^\dagger \hat{a} + 1)$, the only terms that survive in $\langle n | \hat{X}^3 | 0 \rangle$ are

$$\langle n | \hat{X}^3 | 0 \rangle = \left(\frac{\hbar}{2m\omega} \right)^{3/2} \langle n | \hat{a}^{\dagger 3} + \hat{a} \hat{a}^{\dagger 2} + \hat{a}^\dagger | 0 \rangle = \left(\frac{\hbar}{2m\omega} \right)^{3/2} (\sqrt{6} \delta_{n,3} + 3 \delta_{n,1}). \quad (10.203)$$

This implies that the particle can be found after a long duration only either in the first or in the third excited state.

Inserting (10.202) and (10.203) into (10.201), we can verify that the probabilities corresponding to the transitions from the ground state to the first, the second and the third excited states are given, respectively, by

$$P_{0 \rightarrow 1} = \frac{V_0^2}{\hbar^2} \left| \langle 1 | \hat{X}^3 | 0 \rangle \right|^2 \left| \int_0^{+\infty} e^{-(1/\tau - i\omega)t} dt \right|^2 = \left(\frac{\hbar}{2m\omega} \right)^3 \frac{9V_0^2}{(\hbar\omega)^2 + \hbar^2/\tau^2}, \quad (10.204)$$

$$P_{0 \rightarrow 2} = 0 \quad (10.205)$$

$$P_{0 \rightarrow 3} = \frac{V_0^2}{\hbar^2} \left| \langle 3 | \hat{X}^3 | 0 \rangle \right|^2 \left| \int_0^{+\infty} e^{-(1/\tau - 3i\omega)t} dt \right|^2 = \left(\frac{\hbar}{2m\omega} \right)^3 \frac{6V_0^2}{(3\hbar\omega)^2 + \hbar^2/\tau^2}. \quad (10.206)$$

Therefore the system cannot undergo transitions to the second excited state nor to excited states higher than $n = 3$; that is, $P_{0 \rightarrow 2} = 0$, since $\langle 2 | \hat{X}^3 | 0 \rangle = 0$ and $P_{0 \rightarrow n} = 0$ when $n > 3$, since $\langle n | \hat{X}^3 | 0 \rangle = 0$ for $n > 3$.

Problem 10.8

A hydrogen atom, initially (i.e., $t \rightarrow -\infty$) in its ground state, is placed starting at time $t = 0$ in a time-dependent electric field pointing along the z -axis $\vec{E}(t) = E_0 \tau \vec{k} / (\tau^2 + t^2)$, where τ is a constant having the dimension of time. Calculate the probability that the atom will be found in the 2p state after a sufficiently long time (i.e., $t \rightarrow \infty$).

Solution

Since the potential resulting from the interaction of the hydrogen's electron with the external field $\vec{E}(t)$ is $V(t) = -e\vec{r} \cdot \vec{E}(t)$, we can use (10.41) to write the transition probability from the 1s state to 2p as

$$P_{1s \rightarrow 2p} = \frac{1}{\hbar^2} \left| \int_{-\infty}^{+\infty} \langle 210 | V(t) | 100 \rangle e^{i\omega_{fi}t} dt \right|^2, \quad (10.207)$$

where

$$\langle 210 | V(t) | 100 \rangle = \langle 210 | (-e\vec{r} \cdot \vec{E}) | 100 \rangle = -\frac{eE_0\tau}{\tau^2 + t^2} \langle 210 | z | 100 \rangle. \quad (10.208)$$

Since $z = r \cos \theta$ and

$$\psi_{1s} = R_{10}(r)Y_{00}(\Omega) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}, \quad \psi_{2p} = R_{21}(r)Y_{10}(\Omega) = \frac{1}{\sqrt{8\pi a_0^3}} \frac{r}{2a_0} e^{-r/2a_0} \cos \theta, \quad (10.209)$$