Chapter 10

Time-Dependent Perturbation Theory

10.1 Introduction

We have dealt so far with Hamiltonians that do not depend explicitly on time. In nature, however, most quantum phenomena are governed by time-dependent Hamiltonians. In this chapter we are going to consider approximation methods treating Hamiltonians that depend explicitly on time.

To study the structure of molecular and atomic systems, we need to know how electromagnetic radiation interacts with these systems. Molecular and atomic spectroscopy deals in essence with the absorption and emission of electromagnetic radiation by molecules and atoms. As a system absorbs or emits radiation, it undergoes transitions from one state to another.

Time-dependent perturbation theory is most useful for studying processes of absorption and emission of radiation by atoms or, more generally, for treating the transitions of quantum systems from one energy level to another.

10.2 The Pictures of Quantum Mechanics

As seen in Chapter 2, there are many representations of wave functions and operators in quantum mechanics. The connection between the various representations is provided by unitary transformations. Each class of representation, also called a *picture*, differs from others in the way it treats the time evolution of the system.

In this section we look at the pictures encountered most frequently in quantum mechanics: the Schrödinger picture, the Heisenberg picture, and the interaction picture. The Schrödinger picture is useful when describing phenomena with time-independent Hamiltonians, whereas the interaction and Heisenberg pictures are useful when describing phenomena with time-dependent Hamiltonians.

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*:

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

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

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

with

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

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

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

and satisfies these properties:

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

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

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

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 $\mid \psi(t)\rangle_H$:

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

where $\mid \psi(t)\rangle$ 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 $\mid \psi(t)\rangle = \hat{U}(t) \mid \psi(0)\rangle$, with $\hat{U}(t) = e^{-it\hat{H}/\hbar}$. Thus, we can rewrite (10.8) as

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

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

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

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

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

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 $\mid \psi(0)\rangle_H = \mid \psi(0)\rangle$ 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

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

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

$$\boxed{\frac{d\hat{A}_H}{dt} = \frac{1}{i\hbar}\left[\hat{A}_H, \hat{H}\right].} \tag{10.13}$$

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

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

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):

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

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

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

with

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

we can rewrite (10.15) as

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

or

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

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

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

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 $\hat{H}_0$:

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

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 $\hat{H}_0$:

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

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 Hamilonian $\hat{H}_0$ whose solutions—the eigenvalues E_n and eigenstates $\mid \psi_n\rangle$—are known,

$$\hat{H}_0 \mid \psi_n\rangle = E_n \mid \psi_n\rangle, \tag{10.23}$$

and whose most general state vectors are given by stationary states

$$\mid \Psi_n(t)\rangle = e^{-it\hat{H}_0/\hbar} \mid \psi_n\rangle = e^{-iE_nt/\hbar} \mid \psi_n\rangle. \tag{10.24}$$

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 $\hat{H}_0$:

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

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

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

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 $\mid \psi_i\rangle$ of $\hat{H}_0$, what is the probability that the system will be found at a later time in another unperturbed eigenstate $\mid \psi_f\rangle$?

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 $\mid \Psi(t)\rangle$ in terms of an expansion coefficient $c_n(t)$:

$$\mid \Psi(t)\rangle = \sum_n c_n(t) e^{-iE_nt} \mid \psi_n\rangle, \tag{10.27}$$

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):

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

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

$$\mid \Psi(t)\rangle_I = e^{it\hat{H}_0/\hbar} \mid \Psi(t)\rangle = e^{it\hat{H}_0/\hbar}\hat{U}(t, t_i) \mid \Psi(t_i)\rangle = e^{it\hat{H}_0/\hbar}\hat{U}(t, t_i)e^{-i\hat{H}_0t_i/\hbar} \mid \Psi(t_i)\rangle_I, \tag{10.29}$$

or as

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

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

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

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

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

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

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

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:

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

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

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

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):

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

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

where we have used the fact that

$$\langle\psi_f\mid\hat{V}_I(t')\mid\psi_i\rangle=\langle\psi_f\mid e^{iH_0t'/\hbar}\hat{V}(t')e^{-iH_0t'/\hbar}\mid\psi_i\rangle=\langle\psi_f\mid V(t')\mid\psi_i\rangle\exp\left(i\omega_{fi}t'\right), \tag{10.37}$$

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

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

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

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

where

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

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

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

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

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

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

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

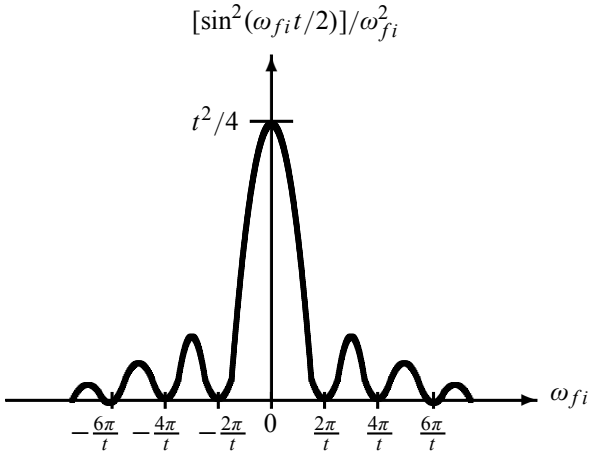

Figure 10.1 Plot of $[\sin^2(\omega_{fi}t/2)]/\omega_{fi}^2$ versus ω_{fi} for a fixed value of t; $\omega_{fi} = (E_f - E_i)/2$.

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 $\mid \psi_f \rangle$ 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 $t \to \infty$ the transition probability takes the shape of a delta function, as we are going to see.

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

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

to write the following expression:

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

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

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

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

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

The delta term $\delta(E_f - E_i)$ guarantees the conservation of energy: in the limit $t \to \infty$, 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 $\mid \psi_i\rangle$ into a continuum of final states $\mid \psi_f\rangle$. 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):

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

or

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

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):

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

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

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

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

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

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

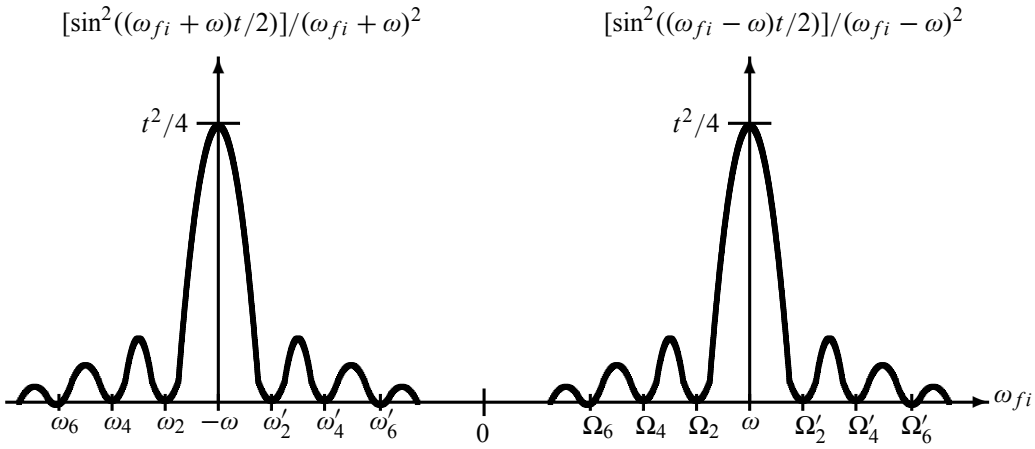

Figure 10.2 Plot of $[\sin^2((\omega_{fi} \pm \omega)t/2)]/(\omega_{fi} \pm \omega)^2$ versus ω_{fi} for a fixed value of t, where $\omega_n = -\omega - n\pi/t$, $\omega_n' = -\omega + n\pi/t$, $\Omega_n = \omega - n\pi/t$, and $\Omega_n' = \omega + n\pi/t$.

value is $P_{if}(t) = (t^2/4\hbar^2)|\langle\psi_f \mid \hat{v}^\dagger \mid \psi_i\rangle|^2$. 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 $t \to \infty$ to

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

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

$$E_f = E_i - \hbar\omega, \tag{10.55}$$

$$E_f = E_i + \hbar\omega. \tag{10.56}$$

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.

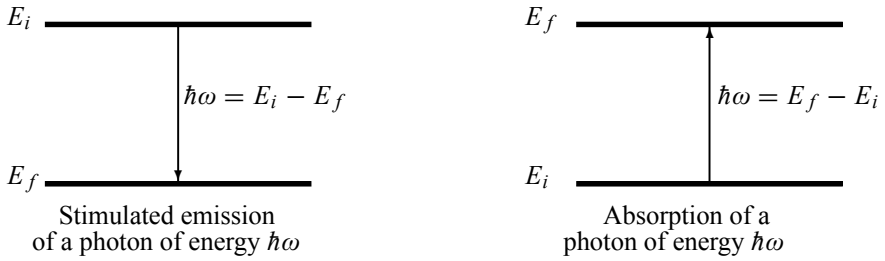

Figure 10.3 Stimulated emission and absorption of a photon of energy $\hbar\omega$.

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:

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

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

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

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

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

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

where

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

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

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

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

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

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

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

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

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

a way that the wave function at a given time is continuously and smoothly converted into an eigenstate of the corresponding Hamiltonian at a later time. This result is the basis of an important theorem of quantum mechanics, known as the *adiabatic theorem*, which states that: if a system is initially in the nth state and if its Hamiltonian evolves slowly with time, it will be found at a later time in the nth state of the new (instantaneous) Hamiltonian. That is, *the system will make no transitions*; it simply remains in the nth state of the new Hamiltonian.

Let us now discuss the adiabatic approximation for those cases where the Hamiltonian splits into a time-independent part $\hat{H}_0$ and a time-dependent part $\hat{V}(t)$, which is small enough so that perturbation theory applies and which is turned on and off very slowly. If $\hat{V}(t)$ is turned on at $t = 0$ and off at time t in a slow and smooth way, it will change very little in the time interval $0 \leq t' \leq t$. The term $\partial\langle\psi_f \mid V(t') \mid \psi_i\rangle/\partial t'$ will be almost constant, so we can take it outside the integral sign in (10.65):

$$P_{if}(t) \simeq \frac{1}{\hbar^2\omega_{fi}^2}\left|\frac{\partial}{\partial t}\langle\psi_f \mid \hat{V}(t) \mid \psi_i\rangle\right|^2 \left|\int_0^t e^{i\omega_{fi}t'}dt'\right|^2, \tag{10.66}$$

or

$$P_{if}(t) \simeq \frac{4}{\hbar^2\omega_{fi}^4}\left|\frac{\partial}{\partial t}\langle\psi_f \mid \hat{V}(t) \mid \psi_i\rangle\right|^2 \sin^2\left(\frac{\omega_{fi}t}{2}\right). \tag{10.67}$$

The adiabatic approximation is valid only when the time change in the energy of the perturbation during one period of oscillation is very small compared with the energy difference $|E_f - E_i|$ between the initial and final states:

$$\left|\frac{1}{\omega_{fi}}\frac{\partial}{\partial t}\langle\psi_f \mid \hat{V}(t) \mid \psi_i\rangle\right| \ll |E_f - E_i|. \tag{10.68}$$

Since $\sin^2\alpha \ll 1$ we see from (10.67) that, in the adiabatic approximation, the transition probability is very small, $P_{if} \ll 1$. In fact, if the rate of change of $\hat{V}(t)$, and hence of $\hat{H}(t)$, is very small, we will have $\partial\langle\psi_f \mid \hat{V}(t) \mid \psi_i\rangle/\partial t \to 0$, which in turn implies that the transition probability is practically zero: $P_{if} \to 0$. Once more, we see that *no transition occurs when the perturbation is turned on and off adiabatically*. That is, if a system is initially (at $t = 0$) in the nth state $\mid \psi_n(0)\rangle$ of $\hat{H}_0$ with energy $E_n(0)$, then at the end (at time t) of an *adiabatic perturbation* $\hat{V}(t)$, it will be found in the nth state $\mid \psi_n(t)\rangle$ of the new Hamiltonian ($\hat{H} = \hat{H}_0 + \hat{V}(t)$) with energy $E_n(t)$. As an illustrative example, consider a particle in a harmonic oscillator potential whose constant is being changed *very slowly* from k to, say, $3k$; if the particle is initially in the second excited state, it will remain in the second excited state of the new oscillator.

Note that the transition probability (10.67) was derived by making use of two approximations: the perturbation theory approximation and the adiabatic approximation. It should be stressed, however, that when the perturbation is not weak, but switched on adiabatically, we can still use the adiabatic approximation but no longer in conjunction with perturbation theory.

10.4.2 Sudden Approximation

Again, let us start with a brief discussion of the sudden approximation without invoking perturbation theory. If the Hamiltonian of a system changes abruptly (over a very short time interval) from one form to another, we would expect the wave function not to change much, yet its

expansion in terms of the eigenfunctions of the initial and final Hamiltonians may be different. Consider, for instance, a system which is initially ($t < 0$) in an eigenstate $\mid \psi_n\rangle$ of the Hamiltonian $\hat{H}_0$:

$$\hat{H}_0 \mid \psi_n\rangle = E_n^{(0)} \mid \psi_n\rangle, \qquad \mid \psi_n(t)\rangle = e^{iE_n^{(0)}t/\hbar} \mid \psi_n\rangle. \tag{10.69}$$

At time $t = 0$ we assume that the Hamiltonian is suddenly changed from $\hat{H}_0$ to $\hat{H}$ and that it preserves this new form (i.e., $\hat{H}$) for $t > 0$; it should be stressed that the difference between the two Hamiltonians $\hat{H} - \hat{H}_0$ does not need to be small. Let $\mid \phi_n\rangle$ be the eigenfunctions of $\hat{H}$:

$$\hat{H} \mid \phi_n\rangle = E_n \mid \phi_n\rangle, \qquad \mid \phi_n(t)\rangle = e^{iE_nt/\hbar} \mid \phi_n\rangle. \tag{10.70}$$

The state of the system is given for $t > 0$ by

$$\mid \Phi(t)\rangle = \sum_n c_n e^{iE_nt/\hbar} \mid \phi_n\rangle. \tag{10.71}$$

If the system is initially in an eigenstate $\mid \psi_m\rangle$ of $\hat{H}_0$, the continuity condition at $t = 0$ dictates that the system remains in this state just after the change takes place:

$$\mid \Phi(0)\rangle = \sum_n c_n \mid \phi_n\rangle = \mid \psi_m\rangle \quad \Longrightarrow \quad c_n = \langle \phi_n \mid \psi_m\rangle. \tag{10.72}$$

The probability that a sudden change in the system's Hamiltonian from $\hat{H}_0$ to $\hat{H}$ causes a transition from the mth state of $\hat{H}_0$ to the nth state of $\hat{H}$ is

$$\boxed{P_{mn} = |\langle \phi_n \mid \psi_m\rangle|^2.} \tag{10.73}$$

We should note that the sudden approximation is applicable only for transitions between discrete states.

Let us now look at the sudden approximation within the context of perturbation theory. Consider a system which is subjected to a perturbation that is small and switched on suddenly. When $\hat{V}(t)$ is instantaneously turned on, the term $e^{i\omega_{fi}t'}$ in (10.65) does not change much during the switching-on time. We can therefore take $e^{i\omega_{fi}t'}$ outside the integral sign,

$$P_{if} \simeq \frac{1}{\hbar^2\omega_{fi}^2} \left| e^{i\omega_{fi}t} \right|^2 \left| \int_0^t \frac{\partial}{\partial t'} \langle \psi_f \mid \hat{V}(t') \mid \psi_i\rangle dt' \right|^2 \tag{10.74}$$

hence the transition probability is given within the sudden approximation by

$$P_{if}(t) \simeq \frac{|\langle \psi_f \mid \hat{V}(t) \mid \psi_i\rangle|^2}{\hbar^2\omega_{fi}^2}. \tag{10.75}$$

To conclude, notice that both (10.73) and (10.75) give the transition probability within the sudden approximation. Equation (10.73) represents the exact formula, where the change in the Hamiltonians, $\hat{H} - \hat{H}_0$, may be large, but equation (10.75) gives only an approximate result, for it was derived from a first-order perturbative treatment, where we assumed that the change $\hat{H} - \hat{H}_0$ is small, yet sudden.

Example 10.2
A particle is initially ($t < 0$) in the ground state of an infinite, one-dimensional potential well with walls at $x = 0$ and $x = a$.

(a) If the wall at $x = a$ is moved *slowly* to $x = 8a$, find the energy and wave function of the particle in the new well. Calculate the work done in this process.

(b) If the wall at $x = a$ is now *suddenly* moved (at $t = 0$) to $x = 8a$, calculate the probability of finding the particle in (i) the ground state, (ii) the first excited state, and (iii) the second excited state of the new potential well.

Solution
For $t < 0$ the particle was in a potential well with walls at $x = 0$ and $x = a$, and hence

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}, \qquad \psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right) \qquad (0 \le x \le a). \tag{10.76}$$

(a) When the wall is moved slowly, the adiabatic theorem dictates that the particle will make no transitions; it will be found at time t in the ground state of the new potential well (the well with walls at $x = 0$ and $x = 8a$). Thus, we have

$$E_1(t) = \frac{\pi^2\hbar^2}{2m(8a)^2} = \frac{\pi^2\hbar^2}{128ma^2}, \qquad \psi_1'(x) = \sqrt{\frac{2}{8a}}\sin\left(\frac{\pi x}{8a}\right) \qquad (0 \le x \le a). \tag{10.77}$$

The work needed to move the wall is

$$\Delta W = E_1(t) - E_1 = \frac{\pi^2\hbar^2}{m(8a)^2} - \frac{\pi^2\hbar^2}{2ma^2} = -\frac{63\pi^2\hbar^2}{128ma^2}. \tag{10.78}$$

(b) When the wall is moved rapidly, the particle will find itself instantly (at $t \ge 0$) in the new potential well; its energy levels and wave function are now given by

$$E_n' = \frac{n^2\pi^2\hbar^2}{2m(8a)^2} = \frac{n^2\pi^2\hbar^2}{128ma^2}, \qquad \psi_n'(x) = \sqrt{\frac{2}{8a}}\sin\left(\frac{n\pi x}{8a}\right) \qquad (0 \le x \le 8a). \tag{10.79}$$

The probability of finding the particle in the ground state of the new box potential can be obtained from (10.73): $P_{11} = |\langle\psi_1' \mid \psi_1\rangle|^2$, where

$$\langle\psi_1' \mid \psi_1\rangle = \int_0^a \psi_1'^*(x)\psi_1(x)\,dx = \frac{2}{\sqrt{8}a}\int_0^a \sin\left(\frac{\pi x}{8a}\right)\sin\left(\frac{\pi x}{a}\right)dx = \frac{16}{63\pi}\sqrt{4-2\sqrt{2}}; \tag{10.80}$$

hence

$$P_{11} = \left|\langle\psi_1' \mid \psi_1\rangle\right|^2 = \left(\frac{16}{63\pi}\right)^2(4-2\sqrt{2}) = 0.0077 \simeq 0.7\%. \tag{10.81}$$

The probability of finding the particle in the first excited state of the new box potential is given by $P_{12} = \left|\langle\psi_2' \mid \psi_1\rangle\right|^2$, where

$$\langle\psi_2' \mid \psi_1\rangle = \int_0^a \psi_2'^*(x)\psi_1(x)\,dx = \frac{2}{\sqrt{8}a}\int_0^a \sin\left(\frac{\pi x}{4a}\right)\sin\left(\frac{\pi x}{a}\right)dx = \frac{8}{15\pi}; \tag{10.82}$$

hence

$$P_{12} = \left|\langle\psi_2' \mid \psi_1\rangle\right|^2 = \left(\frac{8}{15\pi}\right)^2 = 0.1699 \simeq 17\%. \tag{10.83}$$

A similar calculation leads to

$$P_{13} = \left|\langle \psi_3' \mid \psi_1 \rangle\right|^2 = \left| \frac{2}{\sqrt{8}a} \int_0^a \sin\left(\frac{3\pi x}{8a}\right) \sin\left(\frac{\pi x}{a}\right) dx \right|^2 = \left| \frac{16}{55\pi} \sqrt{4+2\sqrt{2}} \right|^2 \simeq 24.2\%. \tag{10.84}$$

These calculations show that the particle is most likely to be found in higher excited states; the probability of finding it in the ground state is very small.

10.5 Interaction of Atoms with Radiation

One of the most important applications of time-dependent perturbation theory is to study the interaction of atomic electrons with an external electromagnetic radiation. Such an application reveals a great deal about the structure of atoms. For simplicity, we assume that only one atomic electron is involved in the interaction and that the electron spin is neglected. We also assume that the nucleus is infinitely heavy.

In the absence of an external perturbation, the Hamiltonian of the atomic electron is $\hat{H}_0 = \vec{P}^2/(2m_e) + V_0(\vec{r})$, where m_e is the mass of the electron and $V_0(\vec{r})$ is the static potential due to the interaction of the electron with the other electrons and with the nucleus.

Now, if electromagnetic radiation of vector potential $\vec{A}(\vec{r},t)$ and electric potential $\phi(\vec{r},t)$ is applied on the atom, the Hamiltonian due to the interaction of the electron (of charge $-e$) with the radiation is given by

$$\begin{aligned} H &= \frac{1}{2m_e}\left(\vec{P} + \frac{e}{c}\vec{A}(\vec{r},t)\right)^2 - e\phi(\vec{r},t) + V_0(\vec{r}) \\ &= H_0 - e\phi(\vec{r},t) + \frac{e}{2m_e c}\left[2\vec{A}\cdot\vec{P} - i\hbar\vec{\nabla}\cdot\vec{A}\right] + \frac{e^2\vec{A}^2}{2m_e c^2}, \end{aligned} \tag{10.85}$$

where we have used the relation $\vec{P}\cdot\vec{A} = \vec{A}\cdot\vec{P} - i\hbar\vec{\nabla}\cdot\vec{A}$. Since $\phi(\vec{r},t) = 0$ for radiation with no electrostatic source and since $\vec{\nabla}\cdot\vec{A} = 0$ (Coulomb gauge), and neglecting the term in $\vec{A}^2$, we may write (10.85) as

$$\hat{H} = \hat{H}_0 + \frac{e}{m_e c}\vec{A}\cdot\vec{P} = \hat{H}_0 + \hat{V}(t), \tag{10.86}$$

where

$$\hat{V}(t) = \frac{e}{m_e c}\vec{A}(\vec{r},t)\cdot\vec{P}. \tag{10.87}$$

This term, which gives the interaction between the electron and the radiation, is small enough (compared to $\hat{H}_0$) to be treated by perturbation theory. We are going to use perturbation theory to study the effect of $\hat{V}(t)$ on the atom. In particular, we will focus on the transitions that are induced as a result of this perturbation.

At this level, we cannot proceed further without calculating $\vec{A}(\vec{r},t)$. In what follows, we are going to show that, using $\vec{A}(\vec{r},t)$ for an electromagnetic radiation, we obtain a $\hat{V}(t)$ which has the structure of a harmonic perturbation: $\hat{V}(t) = \hat{v}e^{-i\omega t} + \hat{v}^\dagger e^{i\omega t}$. Therefore, by analogy with a harmonic perturbation, we would expect the atom to emit or absorb photons and then undergo transitions from one state to another. For the sake of completeness, we are going to determine $\vec{A}(\vec{r},t)$ in two different ways: by treating the radiation *classically* and then *quantum*

mechanically. We are going to show that, unlike a quantum treatment, a classical treatment allows only a description of stimulated emission and absorption processes, but not spontaneous emission. Spontaneous emission turns out to be a purely quantum effect.

10.5.1 Classical Treatment of the Incident Radiation

A *classical*[1] treatment of the incident radiation is valid only when *large* numbers of photons contribute to the interaction with the atom (recall that quantum mechanical effects are generally encountered only when a *finite* number of photons are involved).

From classical electrodynamics, if we consider the incident radiation to be a plane wave of polarization $\vec{\varepsilon}$ that is propagating along the direction $\vec{n}$, the vector potential $\vec{A}(\vec{r},t)$ is given by

$$\vec{A}(\vec{r},t) = \vec{A}_0(\vec{r})e^{-i\omega t} + \vec{A}_0^*(\vec{r})e^{i\omega t} = A_0\vec{\varepsilon}\left[e^{i(\vec{k}\cdot\vec{r}-\omega t)} + e^{-i(\vec{k}.\vec{r}-\omega t)}\right], \tag{10.88}$$

with $\vec{k} = k\vec{n}$. Since $\vec{A}(\vec{r},t)$ satisfies the wave equation $\vec{\nabla}^2\vec{A} - (1/c^2)\partial^2\vec{A}/\partial t^2 = 0$, we have $k = \omega/c$. The Coulomb gauge condition $\vec{\nabla}\cdot\vec{A} = 0$ yields $\vec{k}\cdot\vec{A}_0 = 0$; that is, $\vec{A}(\vec{r},t)$ lies in a plane perpendicular to the wave's direction of propagation, $\vec{n}$. The electric and magnetic fields associated with the vector potential (10.88) can be obtained at once:

$$\vec{E}(\vec{r},t) = -\frac{1}{c}\frac{\partial\vec{A}}{\partial t} = \frac{i\omega}{c}A_0\vec{\varepsilon}\left[-e^{i(\vec{k}\cdot\vec{r}-\omega t)} + e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right], \tag{10.89}$$

$$\vec{B}(\vec{r},t) = \vec{\nabla}\times\vec{A} = i(\vec{k}\times\vec{\varepsilon})A_0\left[-e^{i(\vec{k}\cdot\vec{r}-\omega t)} + e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right] = \vec{n}\times\vec{E}. \tag{10.90}$$

These two relations show that $\vec{E}$ and $\vec{B}$ have the same magnitude, $|\vec{E}| = |\vec{B}|$.

The energy density (or energy per unit volume) for a single photon of the incident radiation can be obtained from (10.89) and (10.90):

$$u = \frac{1}{8\pi}(|\vec{E}|^2 + |\vec{B}|^2) = \frac{1}{4\pi}|\vec{E}|^2 = \frac{\omega^2}{\pi c^2}|A_0|^2\sin^2(\vec{k}\cdot\vec{r} - \omega t). \tag{10.91}$$

Averaging this expression over time, we see that the energy of a single photon per unit volume, $\hbar\omega/V$, is given by $(\omega^2/2\pi c^2)|A_0|^2 = \hbar\omega/V$ and hence $|A_0|^2 = 2\pi\hbar c^2/(\omega V)$, which, when inserted into (10.88), leads to

$$\vec{A}(\vec{r},t) = \sqrt{\frac{2\pi\hbar c^2}{\omega V}}\left[e^{i(\vec{k}\cdot\vec{r}-\omega t)} + e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right]\vec{\varepsilon}. \tag{10.92}$$

Having specified $\vec{A}(\vec{r},t)$ by means of a classical treatment, we can now rewrite the potential (10.87) as

$$\hat{V}(t) = \frac{e}{m_e c}\left(\frac{2\pi\hbar c^2}{\omega V}\right)^{1/2}\vec{\varepsilon}\cdot\vec{P}\left[e^{i(\vec{k}\cdot\vec{r}-\omega t)} + e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right] = \hat{\upsilon}e^{-i\omega t} + \hat{\upsilon}^\dagger e^{i\omega t}, \tag{10.93}$$

where

$$\hat{\upsilon} = \frac{e}{m_e}\left(\frac{2\pi\hbar}{\omega V}\right)^{1/2}\vec{\varepsilon}\cdot\vec{P}e^{i\vec{k}\cdot\vec{r}}, \qquad \hat{\upsilon}^\dagger = \frac{e}{m_e}\left(\frac{2\pi\hbar}{\omega V}\right)^{1/2}\vec{\varepsilon}\cdot\vec{P}e^{-i\vec{k}\cdot\vec{r}}. \tag{10.94}$$

[1] A *classical* treatment of the electric and magnetic fields, $\vec{E}(\vec{r},t)$ and $\vec{B}(\vec{r},t)$, and their corresponding electric and vector potentials, $\phi(\vec{r},t)$ and $\vec{A}(\vec{r},t)$, means that they are described by *continuous* fields.

The structure of (10.93) is identical with (10.50); that is, *the interaction of an atomic electron with radiation has the structure of a harmonic perturbation*. By analogy with (10.50) we can state that the term $e^{-i\omega t}$ in (10.93) gives rise to the *absorption* of the incident photon of energy $\hbar\omega$ by the atom, and $e^{i\omega t}$ to the *stimulated emission* of a photon of energy $\hbar\omega$ by the atom. That is, the absorption process occurs when the atom receives a photon from the radiation, and the stimulated emission when the radiation receives or gains a photon from the decaying atom. At this level, we cannot afford not to mention an important application of stimulated emission. In this process we start with one (incident) photon and end up with two: the incident photon plus the photon given by the atom resulting from its transition to a lower energy level. What would happen if we had a large number of atoms in the same excited state? A single external photon would trigger an avalanche, or chain reaction, of photons released by these atoms in a very short time and all having the same frequency. This would lead to an *amplification* of the electromagnetic field. How does this take place? When the incident photon interacts with the first atom, it will produce two photons, which in turn produce four photons; these four photons then produce eight photons (after they interact with four different atoms), and so on. This process is known as the *amplification by stimulated emission of the* (incident) *radiation*. Two such radiation amplifications have been achieved experimentally and have led to enormous applications: one in the microwave domain, known as *maser* (microwave amplification by stimulated emission of radiation); the other in the domain of light waves, called *laser* (light amplification by stimulated emission of radiation).

Following the approach that led to the transition rates (10.54) from (10.50), we can easily show that the transition rates for the stimulated emission and absorption corresponding to (10.93) are given by

$$\boxed{\Gamma_{i\to f}^{emi} = \frac{4\pi^2 e^2}{m_e^2 \omega V} \left| \langle \psi_f \mid e^{-i\vec{k}\cdot\vec{r}}\, \vec{\varepsilon}\cdot\vec{P} \mid \psi_i \rangle \right|^2 \delta(E_f - E_i + \hbar\omega),} \tag{10.95}$$

$$\boxed{\Gamma_{i\to f}^{abs} = \frac{4\pi^2 e^2}{m_e^2 \omega V} \left| \langle \psi_f \mid e^{i\vec{k}\cdot\vec{r}}\, \vec{\varepsilon}\cdot\vec{P} \mid \psi_i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega).} \tag{10.96}$$

These relations represent the expressions for the transition rates when the radiation is treated classically.

What would happen when there is no radiation? If $\vec{A} = 0$ (i.e., the atom is placed in a vacuum), equations (10.95) and (10.96) imply that no transition will occur since, as equation (10.87) shows, if $\vec{A} = 0$ the perturbation will be zero; hence $\Gamma_{i\to f}^{emi} = 0$ and $\Gamma_{i\to f}^{abs} = 0$. As a result, the classical treatment cannot account for *spontaneous* emission which occurs even in the absence of an external perturbing field. This implies, for instance, that a hydrogen atom in an $n \geq 2$ energy eigenstate remains in this eigenstate unless it is perturbed by an external field. This is in complete disagreement with experimental observations, which show that atoms in the $n \geq 2$ states undergo *spontaneous emissions*; they emit electromagnetic radiation *even when no external perturbation is present*. The spontaneous emission is *a purely quantum effect*.

10.5.2 Quantization of the Electromagnetic Field

We have seen that a classical treatment of radiation leads to transition rates that account only for the processes of absorption and stimulated emission; spontaneous emission of photons by atoms is a typical phenomenon that a classical treatment fails to explain, let alone predict. The

classical treatment is valid only when very large numbers of photons contribute to the radiation; that is, when the intensity of the radiation is so high that only its wave aspect is important. At very low intensities, however, the particle nature of the radiation becomes nonnegligible. In this case we have to consider a quantum mechanical treatment of the electromagnetic radiation. To obtain a quantum description of the radiation, we would necessarily need to replace the various fields (such as $\vec{E}(\vec{r},t)$, $\vec{B}(\vec{r},t)$, and the potential vector $\vec{A}(\vec{r},t)$) with operators.

In the absence of charges and currents, the electric and magnetic fields are fully specified by the vector potential $\vec{A}(\vec{r},t)$. Since $\vec{A}(\vec{r},t)$ is transverse (perpendicular to the wave vector $\vec{k}$), it has only two nonzero components along the directions of two polarization (unit) vectors, $\vec{\varepsilon}_1$ and $\vec{\epsilon}_2$, which lie in a plane perpendicular to $\vec{k}$. We can thus expand $\vec{A}(\vec{r},t)$ in a Fourier series as follows:

$$\vec{A}(\vec{r},t)=\frac{1}{\sqrt{V}}\sum_{\vec{k}}\sum_{\lambda=1}^{2}\left[A_{\lambda,\vec{k}}\vec{\varepsilon}_{\lambda}e^{i(\vec{k}\cdot\vec{r}-\omega_k t)}+A^{*}_{\lambda,\vec{k}}\vec{\varepsilon}^{\,*}_{\lambda}e^{-i(\vec{k}\cdot\vec{r}-\omega_k t)}\right], \tag{10.97}$$

where we have assumed that the electromagnetic field is confined to a large volume V with periodic boundary conditions. We are going to see that, by analogy with the quantization of a classical harmonic oscillator, *the quantization of radiation can be achieved by writing the electromagnetic field in terms of creation and annihilation operators*.

The Hamiltonian of the complete system (atom and the external radiation) is $\hat{H}=\hat{H}_0+\hat{H}_r+V(t)$, where $\hat{H}_0$ is the Hamiltonian of the unperturbed atom, $\hat{H}_r$ is the Hamiltonian of the electromagnetic field, and $\hat{V}(t)$ is the interaction of the atom with the radiation. To find $\hat{H}_r$ we need to quantize the energy of the electromagnetic field which can be obtained from (10.97):

$$\mathcal{H}_r=\frac{1}{8\pi}\int d^3r\left(\vec{E}^2(\vec{r},t)+\vec{B}^2(\vec{r},t)\right)=\frac{V}{8\pi c^2}\sum_{\vec{k}}\sum_{\lambda=1}^{2}(\hbar\vec{k})^2A^{*}_{\lambda,\vec{k}}A_{\lambda,\vec{k}}, \tag{10.98}$$

with $|\vec{\varepsilon}_\lambda|^2=1$, where we have used $\omega_k=ck$, $\vec{E}(\vec{r},t)=-(1/c)\partial\vec{A}/\partial t$, and $\vec{B}(\vec{r},t)=\vec{\nabla}\times\vec{A}$. Instead of the two variables $A_{\lambda,\vec{k}}$ and $A^{*}_{\lambda,\vec{k}}$, we can introduce a new set of two canonically conjugate variables:

$$Q_{\lambda,\vec{k}}=\frac{1}{\sqrt{4\pi c^2}}\left(A^{*}_{\lambda,\vec{k}}+A_{\lambda,\vec{k}}\right),\qquad P_{\lambda,\vec{k}}=\frac{i\omega_k}{\sqrt{4\pi c^2}}\left(A^{*}_{\lambda,\vec{k}}-A_{\lambda,\vec{k}}\right). \tag{10.99}$$

Combining (10.98) and (10.99) we can write

$$H_r=\sum_{\vec{k}}\sum_{\lambda=1}^{2}\left(\frac{1}{2}P^2_{\lambda,\vec{k}}+\frac{\omega_k^2}{2}Q^2_{\lambda,\vec{k}}\right). \tag{10.100}$$

This expression has the structure of a Hamiltonian of a collection of independent harmonic oscillators. This is compatible with the fact that electromagnetic waves in a vacuum result from the (harmonic) oscillations of the electromagnetic field; hence they can be described by means of a linear superposition of independent vibrational modes. To quantize (10.100) we simply need to find the operators $\hat{Q}_{\lambda,\vec{k}}$ and $\hat{P}_{\lambda\vec{k}}$ that correspond to the variables $Q_{\lambda,\vec{k}}$ and $P_{\lambda\vec{k}}$, respectively, such that they obey the canonical commutation relations:

$$\left[\hat{Q}_{\lambda_1\vec{k}_1},\ \hat{P}_{\lambda_2\vec{k}_2}\right]=i\hbar\delta_{\lambda_1,\lambda_2}\delta_{\vec{k}_1,\vec{k}_2}. \tag{10.101}$$

Following the same quantization procedure of a classical harmonic oscillator, and introducing the lowering and raising operators

$$\hat{a}_{\lambda,\vec{k}} = \sqrt{\frac{\omega_k}{2\hbar}}\hat{Q}_{\lambda,\vec{k}} + \frac{i}{\sqrt{2\hbar\omega_k}}\hat{P}_{\lambda,\vec{k}}, \qquad \hat{a}^{\dagger}_{\lambda,\vec{k}} = \sqrt{\frac{\omega_k}{2\hbar}}\hat{Q}_{\lambda,\vec{k}} - \frac{i}{\sqrt{2\hbar\omega_k}}\hat{P}_{\lambda,\vec{k}}, \tag{10.102}$$

which lead to $\hat{Q}_{\lambda,\vec{k}} = \sqrt{\hbar/2\omega_k}(\hat{a}^{\dagger}_{\lambda,\vec{k}} + \hat{a}_{\lambda,\vec{k}})$ and $\hat{P}_{\lambda,\vec{k}} = i\sqrt{\hbar\omega_k/2}(\hat{a}^{\dagger}_{\lambda,\vec{k}} - \hat{a}_{\lambda,\vec{k}})$, we can show that the Hamiltonian operator corresponding to (10.100) is given by

$$\hat{H}_r = \sum_{\vec{k}}\sum_{\lambda=1}^{2}\hbar\omega_k\left(\hat{N}_{\lambda,\vec{k}} + \frac{1}{2}\right), \tag{10.103}$$

with $\hat{N}_{\lambda,\vec{k}} = \hat{a}^{\dagger}_{\lambda,\vec{k}}\hat{a}_{\lambda,\vec{k}}$.

By analogy to the harmonic oscillator, the operators $\hat{a}_{\lambda,\vec{k}}$ and $\hat{a}^{\dagger}_{\lambda,\vec{k}}$ obey the following commutation relations:

$$\left[\hat{a}_{\lambda_1,\vec{k}_1},\ \hat{a}^{\dagger}_{\lambda_2,\vec{k}_2}\right] = \delta_{\lambda_1,\lambda_2}\delta_{\vec{k}_1,\vec{k}_2}, \qquad \left[\hat{a}_{\lambda_1,\vec{k}_1},\ \hat{a}_{\lambda_2,\vec{k}_2}\right] = \left[\hat{a}^{\dagger}_{\lambda_1,\vec{k}_1},\ \hat{a}^{\dagger}_{\lambda_2,\vec{k}_2}\right] = 0, \tag{10.104}$$

and serve respectively to *annihilate* and *create* a photon of wave number $\vec{k}$ and polarization λ. The eigenvalues of $\hat{N}_{\lambda,\vec{k}}$ are $n_{\lambda,\vec{k}} = 0, 1, 2, \ldots$; by analogy with the harmonic oscillator, its eigenvectors are

$$|\, n_{\lambda,\vec{k}}\rangle = \frac{1}{\sqrt{n_{\lambda,\vec{k}}!}}\left(\hat{a}^{\dagger}_{\lambda\vec{k}}\right)^{n_{\lambda,\vec{k}}}\ |\, 0\rangle, \tag{10.105}$$

where $|\, 0\rangle$ is the state with no photons, the vacuum state, and $|\, n_{\lambda,\vec{k}}\rangle$ is a state of the electromagnetic field with $n_{\lambda,\vec{k}}$ photons with wave vector $\vec{k}$ and polarization λ. The number $n_{\lambda,\vec{k}}$ therefore represents the *occupation number* mode. The actions of $\hat{a}_{\lambda,\vec{k}}$ and $\hat{a}^{\dagger}_{\lambda,\vec{k}}$ on $|\, n_{\lambda,\vec{k}}\rangle$ are given by

$$\hat{a}_{\lambda,\vec{k}}\,|\, n_{\lambda,\vec{k}}\rangle = \sqrt{n_{\lambda,\vec{k}}}\,|\, n_{\lambda,\vec{k}} - 1\rangle, \qquad \hat{a}^{\dagger}_{\lambda,\vec{k}}\,|\, n_{\lambda,\vec{k}}\rangle = \sqrt{n_{\lambda,\vec{k}} + 1}\,|\, n_{\lambda,\vec{k}} + 1\rangle. \tag{10.106}$$

The eigenstates of the Hamiltonian (10.103) can be inferred from (10.105):

$$|n_{\lambda_1\vec{k}_1},\ n_{\lambda_2\vec{k}_2},\ n_{\lambda_3\vec{k}_3}, \ldots\rangle = \prod_j |n_{\lambda_j\vec{k}_j}\rangle, \tag{10.107}$$

with the energy eigenvalues (of the radiation)

$$E_r = \sum_{\vec{k}}\sum_{\lambda}\hbar\omega_k\left(n_{\lambda\vec{k}} + \frac{1}{2}\right). \tag{10.108}$$

The state $|n_{\lambda_1\vec{k}_1},\ n_{\lambda_2\vec{k}_2},\ n_{\lambda_3\vec{k}_3}, \ldots\rangle$ describes an electromagnetic field with $n_{\lambda_1\vec{k}_1}$ photons in the mode $(\lambda_1, \vec{k}_1)$ (i.e., $n_{\lambda_1\vec{k}_1}$ photons with wave vector $\vec{k}_1$ and polarization λ_1), $n_{\lambda_2\vec{k}_2}$ photons in the

mode $(\lambda_2, \vec{k}_2)$, and so on. Substituting (10.99) into (10.102), we get $\hat{a}_{\lambda,\vec{k}} = \sqrt{\omega_k/(2\pi\hbar c^2)}\hat{A}_{\lambda,\vec{k}}$ and $\hat{a}^\dagger_{\lambda,\vec{k}} = \sqrt{\omega_k/(2\pi\hbar c^2)}\hat{A}^\dagger_{\lambda,\vec{k}}$; hence

$$\hat{A}_{\lambda,\vec{k}} = \sqrt{\frac{2\pi\hbar c^2}{\omega_k}}\hat{a}_{\lambda,\vec{k}}, \qquad \hat{A}^\dagger_{\lambda,\vec{k}} = \sqrt{\frac{2\pi\hbar c^2}{\omega_k}}\hat{a}^\dagger_{\lambda,\vec{k}}. \tag{10.109}$$

An insertion of these two relations into (10.97) gives the vector potential operator:

$$\hat{\vec{A}}(\vec{r},t) = \sum_{\vec{k}}\sum_{\lambda=1}^{2}\sqrt{\frac{2\pi\hbar c^2}{\omega_k V}}\left[\hat{a}_{\lambda,\vec{k}}e^{i(\vec{k}\cdot\vec{r}-\omega_k t)}\,\vec{\varepsilon}_\lambda + \hat{a}^\dagger_{\lambda,\vec{k}}e^{-i(\vec{k}\cdot\vec{r}-\omega_k t)}\,\vec{\varepsilon}^{\,*}_\lambda\right]. \tag{10.110}$$

The interaction $\hat{V}(t)$ as given by (10.87) reduces to $\hat{V}(t) = (e/m_e c)\hat{\vec{A}}(\vec{r},t)\cdot\vec{P}$ or

$$\hat{V}(t) = \frac{e}{m_e}\sum_{\vec{k}}\sum_{\lambda}\sqrt{\frac{2\pi\hbar}{\omega_k V}}\left[\hat{a}_{\lambda,\vec{k}}e^{i\vec{k}\cdot\vec{r}}\vec{\varepsilon}_\lambda\cdot\vec{P}e^{i\omega_k t} + \hat{a}^\dagger_{\lambda,\vec{k}}e^{i\vec{k}\cdot\vec{r}}\vec{\varepsilon}^{\,*}_\lambda\cdot\vec{P}e^{-i\omega_k t}\right], \tag{10.111}$$

or

$$\hat{V}(t) = \sum_{\vec{k}}\sum_{\lambda=1}^{2}\left(\hat{v}_{\lambda,\vec{k}}e^{i\omega_k t} + \hat{v}^\dagger_{\lambda,\vec{k}}e^{-i\omega_k t}\right), \tag{10.112}$$

where

$$\hat{v}_{\lambda,\vec{k}} = \frac{e}{m_e}\sqrt{\frac{2\pi\hbar}{\omega_k V}}\hat{a}_{\lambda,\vec{k}}e^{i\vec{k}\cdot\vec{r}}\vec{\varepsilon}_\lambda\cdot\vec{P}, \qquad \hat{v}^\dagger_{\lambda,\vec{k}} = \frac{e}{m_e}\sqrt{\frac{2\pi\hbar}{\omega_k V}}\hat{a}^\dagger_{\lambda,\vec{k}}e^{-i\vec{k}\cdot\vec{r}}\vec{\varepsilon}^{\,*}_\lambda\cdot\vec{P}. \tag{10.113}$$

The terms $\hat{v}_{\lambda,\vec{k}}$ and $\hat{v}^\dagger_{\lambda,\vec{k}}$ correspond to the absorption (annihilation) and emission (creation) of a photon by the atom, respectively. As in the classical case, the interaction (10.112) has the structure of a *harmonic* perturbation.

Remark
The quantization of the radiation is achieved by writing the electromagnetic field in terms of creation and annihilation operators, by analogy with the harmonic oscillator. This process, which is called *second quantization*, leads to the replacement of the various *fields* (such as the vector potential $\vec{A}(\vec{r},t)$, the electric field $\vec{E}(\vec{r},t)$, and the magnetic field $\vec{B}(\vec{r},t)$) by operator quantities, which in turn are expressed in terms of creation and annihilation operators. For instance, the Hamiltonian and the vector potential of the radiation are given in the second quantization representation by equations (10.103) and (10.110), respectively.

10.5.3 Transition Rates for Absorption and Emission of Radiation

Before the atom and the radiation interact, their initial state is given by $|\,\Phi_i\rangle = |\,\psi_i\rangle\,|\,n_{\lambda,\vec{k}}\rangle$, where $|\,\psi_i\rangle$ is the state of the unperturbed atom and $|\,n_{\lambda,\vec{k}}\rangle$ is the state vector of the radiation. After the interaction takes place, the state of the system is given by $|\,\Phi_f\rangle = |\,\psi_f\rangle\,|\,n_{\lambda,\vec{k}}\rangle_f$.

Let us look first at the case of emission of a photon. If after interaction the atom emits a photon, the final state of the system will be given by $|\,\Phi_f\rangle = |\,\psi_f\rangle\,|\,n_{\lambda,\vec{k}}+1\rangle$, since the electromagnetic field gains a photon; hence its state changes from $|\,n_{\lambda,\vec{k}}\rangle \to |\,n_{\lambda,\vec{k}}+1\rangle$.

Formally, this process can be achieved by creating a photon, that is, by applying $\hat{v}^{\dagger}_{\lambda,\vec{k}}$ or $\hat{a}^{\dagger}_{\lambda,\vec{k}}$ on the photonic state $\mid n_{\lambda,\vec{k}}\rangle$:

$$\begin{aligned}\langle \Phi_f \mid \hat{v}^{\dagger}_{\lambda,\vec{k}} \mid \Phi_i\rangle &= \frac{e}{m_e}\sqrt{\frac{2\pi\hbar}{\omega_k V}}\langle \psi_f \mid e^{-i\vec{k}\cdot\vec{r}}\vec{\varepsilon}^{\,*}_{\lambda}\cdot\hat{\vec{P}} \mid \psi_i\rangle\langle n_{\lambda,\vec{k}}+1|\hat{a}^{\dagger}_{\lambda,\vec{k}}|n_{\lambda,\vec{k}}\rangle \\ &= \frac{e}{m_e}\sqrt{\frac{2\pi\hbar}{\omega_k V}}\sqrt{n_{\lambda\vec{k}}+1}\langle \psi_f \mid e^{-i\vec{k}\cdot\vec{r}}\vec{\varepsilon}^{\,*}_{\lambda}\cdot\hat{\vec{P}} \mid \psi_i\rangle. \end{aligned} \tag{10.114}$$

When $n_{\lambda\vec{k}} = 0$ (i.e., no radiation), equation (10.114) shows that *even in the absence of an external radiation*, the theory can describe events where there is emission of a photon. This is called *spontaneous emission*. This phenomenon cannot be described by means of a classical treatment of radiation. But if $n_{\lambda\vec{k}} \neq 0$, then $n_{\lambda\vec{k}}$ is responsible for *induced* or *stimulated* emissions; the bigger $n_{\lambda\vec{k}}$, the bigger the emission probability.

In the case of a photon absorption, the system undergoes a transition from an initial state $\mid \Phi_i\rangle = \mid \psi_i\rangle \mid n_{\lambda,\vec{k}}\rangle$ to the final state $\mid \Phi_f\rangle = \mid \psi_f\rangle \mid n_{\lambda,\vec{k}}-1\rangle$. This can be achieved formally by applying the annihilation operator $\hat{a}_{\lambda,\vec{k}}$ on $\mid n_{\lambda,\vec{k}}\rangle$:

$$\begin{aligned}\langle \Phi_f \mid \hat{v}_{\lambda,\vec{k}} \mid \Phi_i\rangle &= \frac{e}{m_e}\sqrt{\frac{2\pi\hbar}{\omega_k V}}\langle \psi_f \mid e^{i\vec{k}\cdot\vec{r}}\vec{\varepsilon}_{\lambda}\cdot\hat{\vec{P}} \mid \psi_i\rangle\langle n_{\lambda,\vec{k}}-1|\hat{a}_{\lambda,\vec{k}}\mid n_{\lambda,\vec{k}}\rangle \\ &= \frac{e}{m_e}\sqrt{\frac{2\pi\hbar}{\omega_k V}}\sqrt{n_{\lambda,\vec{k}}}\langle \psi_f \mid e^{i\vec{k}\cdot\vec{r}}\vec{\varepsilon}_{\lambda}\cdot\hat{\vec{P}} \mid \psi_i\rangle. \end{aligned} \tag{10.115}$$

The transition rates corresponding to the emission or absorption of a photon of energy $\hbar\omega_k = \hbar ck$, wave number $\vec{k}$, and polarization λ can be obtained, by analogy with (10.95) and (10.96), from (10.114) and (10.115):

$$\boxed{\Gamma^{emi}_{i\to f} = \frac{4\pi^2 e^2}{m_e^2\omega_k V}\left(n_{\lambda,\vec{k}}+1\right)\left|\langle \psi_f \mid e^{-i\vec{k}\cdot\vec{r}}\vec{\varepsilon}^{\,*}_{\lambda}\cdot\vec{P} \mid \psi_i\rangle\right|^2\delta(E_f - E_i + \hbar\omega_k),} \tag{10.116}$$

$$\boxed{\Gamma^{abs}_{i\to f} = \frac{4\pi^2 e^2}{m_e^2\omega_k V}n_{\lambda,\vec{k}}\left|\langle \psi_f \mid e^{i\vec{k}\cdot\vec{r}}\vec{\varepsilon}_{\lambda}\cdot\vec{P} \mid \psi_i\rangle\right|^2\delta(E_f - E_i - \hbar\omega_k).} \tag{10.117}$$

10.5.4 Transition Rates within the Dipole Approximation

Approximate expressions of the transition rates (10.116) and (10.117) can be obtained by expanding $e^{\pm i\vec{k}\cdot\vec{r}}$:

$$e^{\pm i\vec{k}\cdot\vec{r}} = 1 \pm i\vec{k}\cdot\vec{r} - \frac{1}{2}(\vec{k}\cdot\vec{r}) \mp \cdots = 1 \pm i\frac{\omega}{c}\vec{n}\cdot\vec{r} - \frac{1}{2}\frac{\omega^2}{c^2}(\vec{n}\cdot\vec{r})^2 \mp \cdots. \tag{10.118}$$

This expansion finds its justification in the fact that $(\vec{k}\cdot\vec{r})$ is a small quantity, since the wavelength of the radiation (visible or ultraviolet) is very large compared to the atomic size: $kr = 2\pi a_0/\lambda \sim 2\pi \times 10^{-10}\,\mathrm{m}/10^{-6}\,\mathrm{m} \sim 10^{-3}$. In the case of nuclear radiation (such as γ radiation), kr is also in the range of 10^{-3}, with $r_{nucleus} \sim 10^{-15}$ m.

The *electric dipole approximation* corresponds to keeping only the leading term in the expansion (10.118): $e^{\pm i\vec{k}\cdot\vec{r}} \simeq 1$; hence

$$\langle \psi_f \mid e^{\pm i\vec{k}\cdot\vec{r}}\vec{\varepsilon}_\lambda \cdot \vec{P} \mid \psi_i\rangle \simeq \vec{\varepsilon}_\lambda \cdot \langle \psi_f \mid \vec{P} \mid \psi_i\rangle. \tag{10.119}$$

This term gives rise to *electric dipole* or E1 transitions. To calculate this term, we need to use the relation

$$\left[\hat{X},\ \hat{H}_0\right] = \left[\hat{X},\ \frac{\hat{\vec{P}}^{\,2}}{2m_e} + \hat{V}(\vec{r})\right] = \left[\hat{X},\ \frac{\hat{P}_x^2}{2m_e}\right] = \frac{i\hbar}{m_e}\hat{P}_x, \tag{10.120}$$

which can be generalized to $[\vec{r},\ \hat{H}_0] = i\hbar\hat{\vec{P}}/m_e$. Hence, inserting $\hat{\vec{P}} = (m_e/i\hbar)[\vec{r},\ \hat{H}_0]$ into (10.119) and using $\hat{H}_0 \mid \psi_i\rangle = E_i \mid \psi_i\rangle$ and $\hat{H}_0 \mid \psi_f\rangle = E_f \mid \psi_f\rangle$, we have

$$\begin{aligned}\vec{\varepsilon}_\lambda \cdot \langle \psi_f \mid \vec{P} \mid \psi_i\rangle &= \frac{m_e}{i\hbar}\vec{\varepsilon}_\lambda \cdot \langle \psi_f \mid [\vec{r}, \hat{H}_0] \mid \psi_i\rangle = \frac{m}{i\hbar}(E_i - E_f)\vec{\varepsilon}_\lambda \cdot \langle \psi_f \mid \vec{r} \mid \psi_i\rangle \\ &= i m_e \omega_{fi}\vec{\varepsilon}_\lambda \cdot \langle \psi_f \mid \vec{r} \mid \psi_i\rangle.\end{aligned} \tag{10.121}$$

The substitution of this term into (10.119) leads to

$$\boxed{\langle \psi_f \mid e^{i\vec{k}\cdot\vec{r}}\vec{\varepsilon}_\lambda \cdot \vec{P} \mid \psi_i\rangle = i m_e \omega_{fi}\vec{\varepsilon}_\lambda \cdot \langle \psi_f \mid \vec{r} \mid \psi_i\rangle.} \tag{10.122}$$

Inserting (10.122) into (10.116) and (10.117), we obtain the transition rates, within the *dipole approximation*, for the emission and absorption of a photon of energy $\hbar\omega_k$ by the atom:

$$\boxed{\Gamma^{emi}_{i\to f} = \frac{4\pi^2 e^2 \omega_{fi}^2}{\omega_k V}(n_{\lambda,k} + 1)\left|\vec{\varepsilon}^{\,*}_\lambda \cdot \langle \psi_f \mid \vec{r} \mid \psi_i\rangle\right|^2 \delta(E_f - E_i + \hbar\omega_k),} \tag{10.123}$$

$$\boxed{\Gamma^{abs}_{i\to f} = \frac{4\pi^2 e^2 \omega_{fi}^2}{\omega_k V} n_{\lambda,k}\left|\vec{\varepsilon}_\lambda \cdot \langle \psi_f \mid \vec{r} \mid \psi_i\rangle\right|^2 \delta(E_f - E_i - \hbar\omega_k).} \tag{10.124}$$

10.5.5 The Electric Dipole Selection Rules

Since $\vec{r}$ is given in spherical coordinates by $\vec{r} = (r\sin\theta\cos\phi)\vec{i} + (r\sin\theta\sin\phi)\vec{j} + (r\cos\theta)\vec{k}$, we can write

$$\vec{\varepsilon}_\lambda \cdot \vec{r} = r(\varepsilon_x \sin\theta\cos\phi + \varepsilon_y \sin\theta\sin\phi + \varepsilon_z\cos\theta). \tag{10.125}$$

Using the relations $\sin\theta\cos\phi = -\sqrt{2\pi/3}(Y_{11} - Y_{1-1})$, $\sin\theta\sin\phi = i\sqrt{2\pi/3}(Y_{11} + Y_{1-1})$, and $\cos\theta = \sqrt{4\pi/3}\,Y_{10}$, we may rewrite (10.125) as

$$\vec{\varepsilon}_\lambda \cdot \vec{r} = \sqrt{\frac{4\pi}{3}}r\left(\frac{-\varepsilon_x + i\varepsilon_y}{\sqrt{2}}Y_{11} + \frac{\varepsilon_x + i\varepsilon_y}{\sqrt{2}}Y_{1-1} + \varepsilon_z Y_{10}\right), \tag{10.126}$$

which in turn leads to

$$\begin{aligned}\langle \psi_f \mid \vec{\varepsilon}_\lambda \cdot \vec{r} \mid \psi_i\rangle &= \sqrt{\frac{4\pi}{3}}\int_0^\infty r^3 R^*_{n_f l_f}(r) R_{n_i l_i}(r)\, dr \\ &\times \int Y^*_{l_f m_f}(\theta,\varphi)\left(\frac{-\varepsilon_x + i\varepsilon_y}{\sqrt{2}}Y_{11} + \frac{\varepsilon_x + i\varepsilon_y}{\sqrt{2}}Y_{1-1} + \varepsilon_z Y_{10}\right) Y_{l_i m_i}(\theta,\varphi) d\Omega,\end{aligned} \tag{10.127}$$

where we have used $\langle \vec{r} \mid \psi_i \rangle = R_{n_i l_i}(\vec{r}) Y_{l_i m_i}(\Omega)$ and $\langle \vec{r} \mid \psi_f \rangle = R_{n_f l_f}(\vec{r}) Y_{l_f m_f}(\Omega)$.

The integration over the angular degrees of freedom can be calculated by means of the Wigner–Eckart theorem; we have shown in Chapter 7 that

$$\int d\Omega\, Y^*_{l_f m_f} Y_{1m'} Y_{l_i m_i} = \langle l_f,\ m_f | Y_{1m'} | l_i,\ m_i \rangle$$
$$= \sqrt{\frac{3(2l_i+1)}{4\pi\,(2l_f+1)}} \langle l_i, 1;\ 0, 0 | l_f,\ 0 \rangle \langle l_i, 1;\ m_i, m' | l_f,\ m_f \rangle. \quad (10.128)$$

Inserting (10.128) into (10.123) and (10.124), we obtain $\Gamma^{emi}_{i\to f} \sim \langle l_i, 1;\ m_i, m' \mid l_f,\ m_f \rangle^2$ and $\Gamma^{abs}_{i\to f} \sim \langle l_i, 1;\ m_i, m' \mid l_f,\ m_f \rangle^2$. Thus the *dipole selection rules* are specified by the selection rules of the Clebsch–Gordan coefficient $\langle l_i, 1;\ m_i, m' \mid l_f,\ m_f \rangle$:

- The transition rates are zero unless the values of m_f and m_i satisfy the condition $m_i + m' = m_f$ or $m'_f - m_i = m'$. But since m' takes only three values, $m' = -1,\ 0,\ 1$, we have
$$m_f - m_i = -1,\ 0,\ 1. \quad (10.129)$$

- The permissible values of l_f must lie between $l_i - 1$ and $l_i + 1$ (i.e., $l_i - 1 \le l_f \le l_i + 1$), so we have $-1 \le l_f - l_i \le 1$ or
$$l_f - l_i = -1,\ 0,\ 1. \quad (10.130)$$
Note that, since the Clebsch–Gordan coefficient $\langle l_i, 1;\ m_i, m' \mid l_f,\ m_f \rangle$ vanishes for $l_i = l_f = 0$, no transition between $l_i = 0$ and $l_f = 0$ is allowed.

- Finally, since the coefficient $\langle l_i, 1;\ 0, 0 | l_f,\ 0 \rangle$ vanishes unless $(-1)^{l_i+1-l_f} = 1$ or $(-1)^{l_i-l_f} = -1$, then $(l_i - l_f)$ must be an odd integer:
$$l_f - l_i = \text{odd integer}. \quad (10.131)$$
This means that, in the case of electric dipole transitions, the final and initial states must have different parities. As a result, electric dipole transitions like 1s $\to$ 2s, 2p $\to$ 3p, etc., are *forbidden*, while transitions like 1s $\to$ 2p, 2p $\to$ 3s, etc., are allowed.

10.5.6 Spontaneous Emission

It is clear from (10.123) that the rate of emission of a photon from an atom is not zero even in the absence of an external radiation field ($n_{\lambda,\vec{k}} = 0$). This corresponds to the *spontaneous emission of a photon*. The total transition rate corresponding to spontaneous emission can be inferred from (10.123) by taking $n_{\lambda,\vec{k}} = 0$:

$$\Gamma^{emi}_{i\to f} = \frac{4\pi^2 \omega^2_{fi}}{\omega V} |\vec{\varepsilon}^*_\lambda \cdot \vec{d}_{fi}|^2 \delta(E_f - E_i + \hbar\omega), \quad (10.132)$$

where $\vec{d}_{fi}$ is the matrix element for the electron's electric dipole moment $\vec{d} = -e\vec{r}$:

$$\vec{d}_{fi} = \langle \psi_f \mid \vec{d} \mid \psi_i \rangle = -e \langle \psi_f \mid \vec{r} \mid \psi_i \rangle. \quad (10.133)$$

The relation (10.132) gives the transition probability per unit time corresponding to the transition of the atom from the initial state $|\ \psi_i\rangle$ to the final state $|\ \psi_f\rangle$ as a result of its spontaneous emission of a photon of energy $\hbar\omega$. Thus the final states of the system consist of products of discrete atomic states and a continuum of photonic states. The photon emitted will be detected in general as having a momentum in the momentum interval $(p,\ p+dp)$ located around $p = \hbar k = \hbar\omega/c$. The transition rate (10.132) needs then to be summed over the continuum of the final photonic states. The number of final photonic states within the unit volume V, whose momenta are within the interval $(p,\ p+dp)$, is given by

$$d^3n = \frac{Vd^3p}{(2\pi\hbar)^3} = \frac{Vp^2dp\,d\Omega}{(2\pi\hbar)^3} = \frac{V\hbar^3\omega^2}{(2\pi\hbar)^3c^3}d\Omega\,d\omega = \frac{V\omega^2}{(2\pi c)^3}d\Omega\,d\omega. \tag{10.134}$$

Thus, the transition rate corresponding to the emission of a photon in the solid angle $d\Omega$ is obtained by integrating (10.132) over $d\omega$:

$$\begin{aligned} dW^{emi}_{i\to f} &= \frac{V}{(2\pi)^3c^3}d\Omega\int\omega^2\Gamma^{emi}_{i\to f}d\omega = \frac{1}{2\pi c^3}|\vec{\varepsilon}^{\,*}_\lambda\cdot\vec{d}_{fi}|^2d\Omega\int\omega^2_{fi}\omega\delta(E_f-E_i+\hbar\omega)\,d\omega \\ &= \frac{1}{2\pi\hbar c^3}|\vec{\varepsilon}^{\,*}_\lambda\cdot\vec{d}_{fi}|^2d\Omega\int\omega^2_{fi}\omega\delta(\omega_{if}-\omega)\,d\omega, \end{aligned} \tag{10.135}$$

where we have used the fact $\delta(E_f - E_i + \hbar\omega) = (1/\hbar)\delta(\omega_{if} - \omega)$ with $\omega_{if} = (E_i - E_f)/\hbar$. Carrying out the integration, we can reduce (10.135) to

$$dW^{emi}_{i\to f} = \frac{\omega^3}{2\pi\hbar c^3}|\vec{\varepsilon}^{\,*}_\lambda\cdot\vec{d}_{fi}|^2d\Omega. \tag{10.136}$$

The transition rate (10.136) corresponds to a specific polarization; that is, the photon emitted travels along the direction $\vec{n}$ (since $\vec{k} = k\vec{n}$), which is normal to $\vec{\varepsilon}^{\,*}_\lambda$. To find the transition rate corresponding to any polarization, we need to sum over the two polarizations of the photon:

$$\sum_{\lambda=1}^{2}|\vec{\varepsilon}^{\,*}_\lambda\cdot\vec{d}_{fi}|^2 = |\varepsilon^*_1(d_{fi})_1|^2 + |\varepsilon^*_2(d_{fi})_2|^2 = |\vec{d}_{fi}|^2 - |(d_{fi})_3|^2. \tag{10.137}$$

Since the three directions of $\vec{d}_{fi}$ are equivalent, we have

$$\langle|(d_{fi})_1|^2\rangle = \langle|(d_{fi})_2|^2\rangle = \langle|(d_{fi})_3|^2\rangle = \frac{1}{3}\langle|\vec{d}_{fi}|^2\rangle. \tag{10.138}$$

Thus, an average over polarization yields

$$\sum_{\lambda=1}^{2}|\vec{\varepsilon}^{\,*}_\lambda\cdot\vec{d}_{fi}|^2 = |\vec{d}_{fi}|^2 - \frac{1}{3}|\vec{d}_{fi}|^2 = \frac{2}{3}|\vec{d}_{fi}|^2. \tag{10.139}$$

Substituting (10.139) into (10.136), we obtain the average transition rate corresponding to the emission of the photon into the solid angle $d\Omega$:

$$dW^{emi}_{i\to f} = \frac{\omega^3}{3\pi\hbar c^3}|\vec{d}_{fi}|^2d\Omega. \tag{10.140}$$

An integration over all possible (photonic) directions ($|\vec{d}_{fi}|^2$ is not included in the integration since we are integrating over the angular part of the photonic degrees of freedom only and not

over the electron's) yields $\int d\Omega = 4\pi$. Thus, the transition rate associated with the emission of the photon is

$$\boxed{W_{i\to f}^{emi} = \frac{4}{3}\frac{\omega^3}{\hbar c^3}\left|\vec{d}_{fi}\right|^2 = \frac{4}{3}\frac{\omega^3 e^2}{\hbar c^3}\left|\langle\psi_f \mid \vec{r}|\psi_i\rangle\right|^2,} \tag{10.141}$$

where $\omega = (E_f - E_i)/\hbar$.

The total *power (or intensity) radiated* by the electron is obtained by multiplying the total rates (10.141) by $\hbar\omega$:

$$\boxed{I_{i\to f} = \hbar\omega W_{i\to f}^{emi} = \frac{4}{3}\frac{\omega^4}{c^3}|\vec{d}_{fi}|^2 = \frac{4}{3}\frac{\omega^4 e^2}{c^3}\left|\langle\psi_f \mid \vec{r}|\psi_i\rangle\right|^2.} \tag{10.142}$$

The transition rates derived above, (10.141) and (10.142), were obtained for single-electron atoms. For atoms that have Z electrons, we must replace the dipole moment $\vec{d} = -e\vec{r}$ with the dipole moment of all Z electrons: $\vec{d} = -e\sum_{j=1}^{Z}\vec{r}_j$.

The mean lifetime τ of an excited state can be obtained by adding together the total transition probabilities per unit time (10.141) for all possible final states:

$$\boxed{\tau = \frac{1}{W} = \frac{1}{\sum_f W_{i\to f}}.} \tag{10.143}$$

Example 10.3

A particle of charge q and mass m is moving in a one-dimensional harmonic oscillator potential of frequency ω_0.

(a) Find the rate of spontaneous emission for a transition from an excited state $\mid n\rangle$ to the ground state.

(b) Obtain an estimate for the rate calculated in (a) and the lifetime of the state $\mid n\rangle$ when the particle is an electron and $\omega_0 = 3\times 10^{14}\,\mathrm{rad\,s^{-1}}$.

(c) Find the condition under which the dipole approximation is valid for the particle of (b).

Solution

(a) The spontaneous emission rate for a transition from an excited state $\mid n\rangle$ to $\mid 0\rangle$ is given by (10.141):

$$W_{n\to 0}^{emi} = \frac{4}{3}\frac{\omega^3 q^2}{\hbar c^3}\left|\langle 0 \mid \hat{X} \mid n\rangle\right|^2, \tag{10.144}$$

where $\omega = (E_n - E_0)/\hbar = (n+\frac{1}{2})\omega_0 - \frac{1}{2}\omega_0 = n\omega_0$. Since $\hat{a} \mid n\rangle = \sqrt{n} \mid n-1\rangle$ and $\hat{a}^\dagger \mid n\rangle = \sqrt{n+1} \mid n+1\rangle$, and since $\hat{X} = \sqrt{\hbar/(2m\omega_0)}(\hat{a}^\dagger + \hat{a})$, we have

$$\langle 0 \mid \hat{X} \mid n\rangle = \sqrt{\frac{\hbar}{2m\omega_0}}\langle 0 \mid \hat{a}^\dagger + \hat{a} \mid n\rangle = \sqrt{\frac{\hbar}{2m\omega_0}}\left[\sqrt{n+1}\delta_{0,n+1} + \sqrt{n}\delta_{0,n-1}\right]. \tag{10.145}$$

Thus only a transition from $\mid 1\rangle$ to $\mid 0\rangle$ is possible; hence $n = 1$, $\omega = \omega_0$, and $\langle 0 \mid \hat{X} \mid 1\rangle = \sqrt{\hbar/(2m\omega_0)}$. The emission rate (10.144) then becomes

$$W_{1\to 0}^{emi} = \frac{4}{3}\frac{\omega^3 q^2}{\hbar c^3}\left|\langle 0 \mid \hat{X} \mid 1\rangle\right|^2 = \frac{4}{3}\frac{\omega_0^3 q^2}{\hbar c^3}\frac{\hbar}{2m\omega_0} = \frac{2}{3}\frac{\omega_0^2 q^2}{mc^3}. \tag{10.146}$$

(b) If the particle is an electron, we have $q = -e$:

$$W_{1\to 0}^{emi} = \frac{2}{3}\frac{\omega_0^2 e^2}{m_e c^3} = \frac{2\alpha}{3}\frac{\omega_0^2 \hbar}{m_e c^2} = \frac{2\alpha}{3}\frac{\hbar c}{m_e c^2}\frac{\omega_0^2}{c}. \tag{10.147}$$

Using $m_e c^2 = 0.511\,\text{MeV}$, $\hbar c = 197.33\,\text{MeV fm}$, we have

$$W_{1\to 0}^{emi} = \frac{2\alpha}{3}\frac{\hbar c}{m_e c^2}\frac{\omega_0^2}{c} = \frac{2}{3\times 137}\frac{197.33\,\text{MeV fm}}{0.511\,\text{MeV}}\frac{9\times 10^{28}\,\text{s}^{-2}}{3\times 10^8\,\text{m s}^{-1}} = 5.6\times 10^5\,\text{s}^{-1}. \tag{10.148}$$

The lifetime of the $|\,1\rangle$ state is

$$\tau = \frac{1}{W_{1\to 0}^{emi}} = \frac{3}{2}\frac{m_e c^3}{\omega_0^2 e^2} = \frac{1}{5.6\times 10^5 sec^{-2}} = 0.18\times 10^{-5}\,\text{s}. \tag{10.149}$$

(c) For the dipole approximation to be valid, we need $kx \ll 1$, where x was calculated in (10.145) for $n = 1$: $x = \sqrt{\hbar/(2m_e\omega_0)}$. As for k, a crude estimate yields $k = \omega/c = (E_1 - E_0)/(\hbar c) = \omega_0/c$. Thus, we have

$$kx = \frac{\omega_0}{c}\sqrt{\frac{\hbar}{2m_e\omega_0}} = \sqrt{\frac{\hbar\omega_0}{2m_e c^2}} \ll 1 \qquad \Longrightarrow \qquad \hbar\omega_0 \ll 2m_e c^2. \tag{10.150}$$

This is indeed the case since $2m_e c^2 = 1.022\,\text{MeV}$ is very large compared to

$$\hbar\omega_0 = \hbar c\frac{\omega_0}{c} = 197.33\,\text{MeV fm}\times\frac{3\times 10^{14}\,\text{s}^{-1}}{3\times 10^8\,\text{m s}^{-1}} = 2.0\times 10^{-7}\,\text{MeV}. \tag{10.151}$$

10.6 Solved Problems

Problem 10.1

(a) Calculate the position and the momentum operators, $\hat{X}_H(t)$ and $\hat{P}_H(t)$, in the Heisenberg picture for a one-dimensional harmonic oscillator.

(b) Find the Heisenberg equations of motion for $\hat{X}_H(t)$ and $\hat{P}_H(t)$.

Solution

In the Schrödinger picture, where the operators do not depend explicitly on time, the Hamiltonian of a one-dimensional harmonic oscillator is given by

$$\hat{H} = \frac{\hat{P}^2}{2m} + \frac{1}{2}m\omega^2\hat{X}^2. \tag{10.152}$$

(a) Using the commutation relations

$$[\hat{H},\ \hat{X}] = \frac{1}{2m}[\hat{P}^2,\ \hat{X}] = -\frac{i\hbar}{m}\hat{P}, \tag{10.153}$$

$$[\hat{H},\ \hat{P}] = \frac{1}{2}m\omega^2[\hat{X}^2,\ \hat{P}] = i\hbar m\omega^2\hat{X}, \tag{10.154}$$

along with

$$e^{\hat{A}}\hat{B}e^{-\hat{A}} = \hat{B} + [\hat{A},\ \hat{B}] + \frac{1}{2!}[\hat{A},\ [\hat{A},\ \hat{B}]] + \frac{1}{3!}[\hat{A},\ [\hat{A},\ [\hat{A},\ \hat{B}]]] + \cdots, \tag{10.155}$$

we may write (see Eq. (10.11))

$$\begin{aligned}\hat{X}_H(t) &= e^{it\hat{H}/\hbar}\hat{X}e^{-it\hat{H}/\hbar} = \hat{X} + \frac{it}{\hbar}[\hat{H},\ \hat{X}] + \frac{1}{2!}\left(\frac{it}{\hbar}\right)^2[\hat{H},\ [\hat{H},\ \hat{X}]] + \cdots \\ &= \hat{X} + \frac{t}{m}\hat{P} - \frac{(\omega t)^2}{2!}\hat{X} - \frac{(\omega t)^3}{3!}\frac{1}{m\omega}\hat{P} + \frac{(\omega t)^4}{4!}\hat{X} + \frac{(\omega t)^5}{5!}\frac{1}{m\omega}\hat{P} + \cdots \\ &= \hat{X}\left[1 - \frac{(\omega t)^2}{2!} + \frac{(\omega t)^4}{4!} + \cdots\right] + \frac{1}{m\omega}\hat{P}\left[(\omega t) - \frac{(\omega t)^3}{3!} + \frac{(\omega t)^5}{5!} + \cdots\right],\end{aligned} \tag{10.156}$$

or

$$\boxed{\hat{X}_H(t) = \hat{X}\cos(\omega t) + \frac{1}{m\omega}\hat{P}\sin(\omega t).} \tag{10.157}$$

A similar calculation yields (see Eq. (10.11))

$$\begin{aligned}\hat{P}_H(t) &= e^{it\hat{H}/\hbar}\hat{P}e^{-it\hat{H}/\hbar} = \hat{P} + \frac{it}{\hbar}[\hat{H},\ \hat{P}] + \frac{1}{2!}\left(\frac{it}{\hbar}\right)^2[\hat{H},\ [\hat{H},\ \hat{P}]] + \cdots \\ &= \hat{P}\left[1 - \frac{(\omega t)^2}{2!} + \frac{(\omega t)^4}{4!} + \cdots\right] - m\omega\hat{X}\left[(\omega t) - \frac{(\omega t)^3}{3!} + \frac{(\omega t)^5}{5!} + \cdots\right],\end{aligned} \tag{10.158}$$

or

$$\boxed{\hat{P}_H(t) = \hat{P}\cos(\omega t) - m\omega\hat{X}\sin(\omega t).} \tag{10.159}$$

(b) To find the equations of motion of $\hat{X}_H(t)$ and $\hat{P}_H(t)$, we need to use the Heisenberg equation $d\hat{A}_H(t)/dt = (1/i\hbar)[\hat{A}_H(t),\ \hat{H}]$ which, along with (10.153) and (10.154), leads to

$$\frac{d\hat{X}_H(t)}{dt} = \frac{1}{i\hbar}[\hat{X}_H(t),\ \hat{H}] = \frac{1}{i\hbar}e^{it\hat{H}/\hbar}[\hat{X},\ \hat{H}]e^{-it\hat{H}/\hbar} = \frac{1}{i\hbar}\frac{i\hbar}{m}e^{it\hat{H}/\hbar}\hat{P}e^{-it\hat{H}/\hbar}, \tag{10.160}$$

$$\frac{d\hat{P}_H(t)}{dt} = \frac{1}{i\hbar}[\hat{P}_H(t),\ \hat{H}] = \frac{1}{i\hbar}e^{it\hat{H}/\hbar}[\hat{P},\ \hat{H}]e^{-it\hat{H}/\hbar} = \frac{(-i\hbar m\omega^2)}{i\hbar}e^{it\hat{H}/\hbar}\hat{X}e^{-it\hat{H}/\hbar}, \tag{10.161}$$

or

$$\boxed{\frac{d\hat{X}_H(t)}{dt} = \frac{1}{m}\hat{P}_H(t), \qquad \frac{d\hat{P}_H(t)}{dt} = -m\omega^2\hat{X}_H(t).} \tag{10.162}$$

Problem 10.2
Using the expressions derived in Problem 10.1 for $\hat{X}_H(t)$ and $\hat{P}_H(t)$, evaluate the following commutators for a harmonic oscillator:

$$\left[\hat{X}_H(t_1), \hat{P}_H(t_2)\right], \quad \left[\hat{X}_H(t_1), \hat{X}_H(t_2)\right], \quad \left[\hat{P}_H(t_1), \hat{P}_H(t_2)\right].$$

Solution
Using (10.157) and (10.159) along with the commutation relations $[\hat{X},\ \hat{P}] = i\hbar$ and $[\hat{X},\ \hat{X}] = [\hat{P},\ \hat{P}] = 0$, we have

$$\begin{aligned}[\hat{X}_H(t_1),\ \hat{P}_H(t_2)] &= \left[\hat{X}\cos(\omega t_1) + \frac{1}{m\omega}\hat{P}\sin(\omega t_1),\ \hat{P}\cos(\omega t_2) - m\omega\hat{X}\sin(\omega t_2)\right] \\ &= [\hat{X},\ \hat{P}]\cos(\omega t_1)\cos(\omega t_2) - [\hat{P},\ \hat{X}]\sin(\omega t_1)\sin(\omega t_2) \\ &= i\hbar\left[\cos(\omega t_1)\cos(\omega t_2) + \sin(\omega t_1)\sin(\omega t_2)\right], \end{aligned} \tag{10.163}$$

or

$$\boxed{[\hat{X}_H(t_1),\ \hat{P}_H(t_2)] = i\hbar\cos\left[\omega(t_1 - t_2)\right].} \tag{10.164}$$

A similar calculation yields

$$\begin{aligned}[\hat{X}_H(t_1),\ \hat{X}_H(t_2)] &= \left[\hat{X}\cos(\omega t_1) + \frac{1}{m\omega}\hat{P}\sin(\omega t_1),\ \hat{X}\cos(\omega t_2) + \frac{1}{m\omega}\hat{P}\sin(\omega t_2)\right] \\ &= \frac{1}{m\omega}[\hat{X},\ \hat{P}]\cos(\omega t_1)\sin(\omega t_2) + \frac{1}{m\omega}[\hat{P},\ \hat{X}]\sin(\omega t_1)\cos(\omega t_2) \\ &= \frac{i\hbar}{m\omega}\left[\cos(\omega t_1)\sin(\omega t_2) - \sin(\omega t_1)\cos(\omega t_2)\right], \end{aligned} \tag{10.165}$$

or

$$\boxed{[\hat{X}_H(t_1),\ \hat{X}_H(t_2)] = -\frac{i\hbar}{m\omega}\sin\left[\omega(t_1 - t_2)\right].} \tag{10.166}$$

Similarly, we have

$$\begin{aligned}[\hat{P}_H(t_1),\ \hat{P}_H(t_2)] &= \left[\hat{P}\cos(\omega t_1) - m\omega\hat{X}\sin(\omega t_1),\ \hat{P}\cos(\omega t_2) - m\omega\hat{X}\sin(\omega t_2)\right] \\ &= -m\omega[\hat{P},\ \hat{X}]\cos(\omega t_1)\sin(\omega t_2) - m\omega[\hat{X},\ \hat{P}]\sin(\omega t_1)\cos(\omega t_2) \\ &= -i\hbar m\omega\left[\sin(\omega t_1)\cos(\omega t_2) - \cos(\omega t_1)\sin(\omega t_2)\right], \end{aligned} \tag{10.167}$$

or

$$\boxed{[\hat{P}_H(t_1),\ \hat{P}_H(t_2)] = -i\hbar m\omega\sin\left[\omega(t_1 - t_2)\right].} \tag{10.168}$$

Problem 10.3
Evaluate the quantity $\langle n \mid \hat{X}_H(t)\hat{X} \mid n\rangle$ for the nth excited state of a one-dimensional harmonic oscillator, where $\hat{X}_H(t)$ and $\hat{X}$ designate the position operators in the Heisenberg picture and the Schrödinger picture.

Solution
Using the expression of $\hat{X}_H(t)$ calculated in (10.157), we have

$$\langle n \mid \hat{X}_H(t)\hat{X} \mid n\rangle = \langle n \mid \hat{X}^2 \mid n\rangle\cos(\omega t) + \frac{1}{m\omega}\langle n \mid \hat{P}\hat{X} \mid n\rangle\sin(\omega t). \tag{10.169}$$

Since, for a harmonic oscillator, $\hat{X}$ and $\hat{P}$ are given by

$$\hat{X} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}^\dagger + \hat{a}), \qquad \hat{P} = i\sqrt{\frac{m\hbar\omega}{2}}(\hat{a}^\dagger - \hat{a}), \tag{10.170}$$

and $\hat{a}^\dagger \mid n\rangle = \sqrt{n+1} \mid n+1\rangle$ and $\hat{a} \mid n\rangle = \sqrt{n} \mid n-1\rangle$, we have

$$\langle n \mid \hat{X}^2 \mid n\rangle = \frac{\hbar}{2m\omega}\langle n \mid \hat{a}^{\dagger\,2} + \hat{a}^2 + \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a} \mid n\rangle = \frac{\hbar}{2m\omega}(2n+1), \quad (10.171)$$

$$\langle n \mid \hat{P}\hat{X} \mid n\rangle = \frac{i\hbar}{2}\langle n \mid \hat{a}^{\dagger\,2} + \hat{a}^2 - \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a} \mid n\rangle = -\frac{i\hbar}{2}, \quad (10.172)$$

since $\langle n \mid \hat{a}^{\dagger\,2} \mid n\rangle = \langle n \mid \hat{a}^2 \mid n\rangle = 0$, $\langle n \mid \hat{a}^\dagger\hat{a} \mid n\rangle = n$ and $\langle n \mid \hat{a}\hat{a}^\dagger \mid n\rangle = n+1$. Inserting (10.171) and (10.172) into (10.169), we obtain

$$\langle n \mid \hat{X}_H(t)\hat{X} \mid n\rangle = \frac{\hbar}{2m\omega}\Big[\,(2n+1)\cos(\omega t) - i\sin(\omega t)\Big]. \quad (10.173)$$

Problem 10.4
The Hamiltonian due to the interaction of a particle of mass m, charge q, and spin $\vec{S}$ with a magnetic field pointing along the z-axis is $\hat{H} = -(qB/mc)\hat{S}_z$. Write the Heisenberg equations of motion for the time-dependent spin operators $\hat{S}_x(t)$, $\hat{S}_y(t)$, and $\hat{S}_z(t)$, and solve them to obtain the operators as functions of time.

Solution
Let us write $\hat{H}$ in a lighter form $\hat{H} = \omega\hat{S}_z$ where $\omega = -qB/mc$. The commutation of $\hat{H}$ with the components of the spin operator can be inferred at once from $[\hat{S}_x,\ \hat{S}_z] = -i\hbar\hat{S}_y$ and $[\hat{S}_y,\ \hat{S}_z] = i\hbar\hat{S}_x$:

$$[\hat{S}_x,\ \hat{H}] = -i\hbar\omega\hat{S}_y, \qquad [\hat{S}_y,\ \hat{H}] = i\hbar\omega\hat{S}_x, \qquad [\hat{S}_z,\ \hat{H}] = 0. \quad (10.174)$$

The Heisenberg equations of motion for $\hat{S}_x(t)$, $\hat{S}_y(t)$, and $\hat{S}_z(t)$ can be obtained from $d\hat{A}_H(t)/dt = (1/i\hbar)[\hat{A}_H(t),\ \hat{H}] = (1/i\hbar)e^{it\hat{H}/\hbar}[\hat{A}(0),\ \hat{H}]e^{-it\hat{H}/\hbar}$ which, using (10.174), leads to

$$\begin{aligned}\frac{d\hat{S}_x(t)}{dt} &= \frac{1}{i\hbar}[\hat{S}_x(t),\ \hat{H}] = \frac{1}{i\hbar}e^{it\hat{H}/\hbar}[\hat{S}_x(0),\ \hat{H}]e^{-it\hat{H}/\hbar} \\ &= \frac{-i\hbar\omega}{i\hbar}e^{it\hat{H}/\hbar}\hat{S}_y(0)e^{-it\hat{H}/\hbar} = -\omega\hat{S}_y(t). \end{aligned} \quad (10.175)$$

Similarly, we have

$$\frac{d\hat{S}_y(t)}{dt} = \frac{1}{i\hbar}e^{it\hat{H}/\hbar}[\hat{S}_y(0),\ \hat{H}]e^{-it\hat{H}/\hbar} = \frac{i\hbar\omega}{i\hbar}e^{it\hat{H}/\hbar}\hat{S}_x(0)e^{-it\hat{H}/\hbar} = \omega\hat{S}_x(t), \quad (10.176)$$

$$\frac{d\hat{S}_z(t)}{dt} = \frac{1}{i\hbar}e^{it\hat{H}/\hbar}[\hat{S}_z(0),\ \hat{H}]e^{-it\hat{H}/\hbar} = 0. \quad (10.177)$$

To solve (10.175) and (10.176), we may combine them into two more conducive equations:

$$\frac{d\hat{S}_\pm(t)}{dt} = \pm i\omega\hat{S}_\pm(t), \quad (10.178)$$

where $\hat{S}_\pm(t) = \hat{S}_x(t) \pm i\hat{S}_y(t)$. The solutions of (10.178) are $\hat{S}_\pm(t) = \hat{S}_\pm(0)e^{\pm i\omega t}$ which, when combined with $\hat{S}_x(t) = \frac{1}{2}[\hat{S}_+(t) + \hat{S}_-(t)]$ and $\hat{S}_y(t) = \frac{1}{2i}[\hat{S}_+(t) - \hat{S}_-(t)]$, lead to

$$\hat{S}_x(t) = \hat{S}_x(0)\cos(\omega t) - \hat{S}_y(0)\sin(\omega t), \tag{10.179}$$

$$\hat{S}_y(t) = \hat{S}_y(0)\cos(\omega t) + \hat{S}_x(0)\sin(\omega t). \tag{10.180}$$

The solution of (10.177) is obvious:

$$\frac{d\hat{S}_z(t)}{dt} = 0 \qquad \Longrightarrow \qquad \hat{S}_z(t) = \hat{S}_z(0). \tag{10.181}$$

Problem 10.5

Consider a spinless particle of mass m, which is moving in a one-dimensional infinite potential well with walls at $x = 0$ and $x = a$.

(a) Find $\hat{X}_H(t)$ and $\hat{P}_H(t)$ in the Heisenberg picture.

(b) If at $t = 0$ the particle is in the state $\psi(x, 0) = [\phi_1(x) + \phi_2(x)]/\sqrt{2}$, where $\phi_1(x)$ and $\phi_2(x)$ are the ground and first excited states, respectively, with $\phi_n(x) = \sqrt{2/a}\sin(n\pi x/a)$, find the state vector $\psi(x, t)$ for $t > 0$ in the Schrödinger picture.

(c) Evaluate $\langle\psi(x, t) \mid \hat{X} \mid \psi(x, t)\rangle$ and $\langle\psi(x, t) \mid \hat{P} \mid \psi(x, t)\rangle$ as a function of time in the Schrödinger picture.

(d) Evaluate $\langle\psi(x, t) \mid \hat{X}_H(t) \mid \psi(x, t)\rangle$ and $\langle\psi(x, t) \mid \hat{P}_H(t) \mid \psi(x, t)\rangle$ as a function of time in the Schrödinger picture.

Solution

(a) Since the particle's Hamiltonian is purely kinetic, $\hat{H} = \hat{P}^2/2m$, we have $[\hat{H},\ \hat{P}] = 0$ and

$$[\hat{H},\ \hat{X}] = \frac{1}{2m}[\hat{P}^2,\ \hat{X}] = -\frac{i\hbar}{m}\hat{P}. \tag{10.182}$$

Using these relations along with (10.155), we obtain

$$\hat{X}_H(t) = e^{it\hat{H}/\hbar}\hat{X}e^{-it\hat{H}/\hbar} = \hat{X} + \frac{it}{\hbar}[\hat{H},\ \hat{X}] + \frac{1}{2!}\left(\frac{it}{\hbar}\right)^2[\hat{H},\ [\hat{H},\ \hat{X}]] + \cdots, \tag{10.183}$$

and since $[\hat{H},\ [\hat{H},\ \hat{X}]] = -(i\hbar/m)[\hat{H},\ \hat{P}] = 0$, we end up with

$$\hat{X}_H(t) = \hat{X} + \frac{t}{m}\hat{P}. \tag{10.184}$$

On the other hand, since $[\hat{H},\ \hat{P}] = 0$, we have

$$\hat{P} = \hat{P}_H(t). \tag{10.185}$$

(b) Since the energy of the nth level is given by $E_n = n^2\pi^2\hbar^2/(2ma^2)$, we have

$$\begin{aligned}\psi(x, t) &= \frac{1}{\sqrt{2}}\left[\phi_1(x)e^{-iE_1t/\hbar} + \phi_2(x)e^{-iE_2t/\hbar}\right] \\ &= \frac{1}{\sqrt{a}}\left[e^{-iE_1t/\hbar}\sin\left(\frac{\pi x}{a}\right) + e^{-iE_2t/\hbar}\sin\left(\frac{2\pi x}{a}\right)\right].\end{aligned} \tag{10.186}$$

(c) Using (10.186) we can write

$$\langle\psi(x,t)\mid\hat{X}\mid\psi(x,t)\rangle=\frac{1}{2}\Big[\langle\phi_1\mid\hat{X}\mid\phi_1\rangle+\langle\phi_2\mid\hat{X}\mid\phi_2\rangle+\langle\phi_1\mid\hat{X}\mid\phi_2\rangle e^{-i(E_2-E_1)t/\hbar}+\langle\phi_2\mid\hat{X}\mid\phi_1\rangle e^{i(E_2-E_1)t/\hbar}\Big]. \tag{10.187}$$

Since $\langle\phi_n|\hat{X}\mid\phi_n\rangle=a/2$ (Chapter 4) and

$$\langle\phi_1\mid\hat{X}\mid\phi_2\rangle=\langle\phi_2\mid\hat{X}\mid\phi_1\rangle=\frac{2}{a}\int_0^a x\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi x}{a}\right)dx=-\frac{16a}{9\pi^2}, \tag{10.188}$$

we can rewrite (10.187) as

$$\begin{aligned}\langle\psi(x,t)\mid\hat{X}\mid\psi(x,t)\rangle &= \frac{1}{2}\left[\frac{a}{2}+\frac{a}{2}-\frac{16a}{9\pi^2}\left(e^{-i(E_2-E_1)t/\hbar}+e^{i(E_2-E_1)t/\hbar}\right)\right]\\ &= \frac{a}{2}-\frac{16a}{9\pi^2}\cos\left(\frac{3\pi^2\hbar t}{2ma^2}\right),\end{aligned} \tag{10.189}$$

since $E_2-E_1=3\pi^2\hbar^2/(2ma^2)$.

A similar calculation which uses $\langle\phi_n|\hat{P}\mid\phi_n\rangle=0$ and

$$\langle\phi_1\mid\hat{P}\mid\phi_2\rangle=-i\hbar\frac{4\pi}{a}\int_0^a\sin\left(\frac{\pi x}{a}\right)\cos\left(\frac{2\pi x}{a}\right)dx=\frac{8i\hbar}{3a}=-\langle\phi_2\mid\hat{P}\mid\phi_1\rangle \tag{10.190}$$

leads to

$$\langle\psi(x,t)\mid\hat{P}\mid\psi(x,t)\rangle=\frac{1}{2}\Big[\langle\phi_1\mid\hat{P}\mid\phi_1\rangle+\langle\phi_2\mid\hat{P}\mid\phi_2\rangle+\langle\phi_1\mid\hat{P}\mid\phi_2\rangle e^{-i(E_2-E_1)t/\hbar}+\langle\phi_2\mid\hat{P}\mid\phi_1\rangle e^{i(E_2-E_1)t/\hbar}\Big], \tag{10.191}$$

or to

$$\langle\psi(x,t)\mid\hat{P}\mid\psi(x,t)\rangle=\frac{1}{2}\left[\frac{8i\hbar}{3a}e^{-i(E_2-E_1)t/\hbar}-\frac{8i\hbar}{3a}e^{i(E_2-E_1)t/\hbar}\right]=\frac{8\hbar}{3a}\sin\left(\frac{3\pi^2\hbar t}{2ma^2}\right). \tag{10.192}$$

(d) From (10.184) we have

$$\langle\psi(x,t)\mid\hat{X}_H(t)\mid\psi(x,t)\rangle=\langle\psi(x,t)\mid\hat{X}\mid\psi(x,t)\rangle+\frac{t}{m}\langle\psi(x,t)\mid\hat{P}\mid\psi(x,t)\rangle. \tag{10.193}$$

Inserting the expressions for $\langle\psi(x,t)\mid\hat{X}\mid\psi(x,t)\rangle$ and $\langle\psi(x,t)\mid\hat{P}\mid\psi(x,t)\rangle$ calculated in (10.189) and (10.192), we obtain

$$\langle\psi(x,t)\mid\hat{X}_H(t)\mid\psi(x,t)\rangle=\frac{a}{2}-\frac{16a}{9\pi^2}\cos\left(\frac{3\pi^2\hbar t}{2ma^2}\right)+\frac{8\hbar t}{3ma}\sin\left(\frac{3\pi^2\hbar t}{2ma^2}\right), \tag{10.194}$$

and $\langle\psi(x,t)\mid\hat{P}_H(t)\mid\psi(x,t)\rangle$ is given by (10.192):

$$\langle\psi(x,t)\mid\hat{P}_H(t)\mid\psi(x,t)\rangle=\langle\psi(x,t)\mid\hat{P}\mid\psi(x,t)\rangle=\frac{8\hbar}{3a}\sin\left(\frac{3\pi^2\hbar t}{2ma^2}\right), \tag{10.195}$$

since, as shown in (10.185), we have $\hat{P}_H(t)=\hat{P}$.

Problem 10.6
A particle, initially (i.e., $t \to -\infty$) 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., $t \to \infty$).

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

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

where

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

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

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

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

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

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

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., $t \to \infty$), 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):

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

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):

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

Since $\hat{a} \mid n\rangle = \sqrt{n} \mid n-1\rangle$ and $\hat{a}^\dagger \mid n\rangle = \sqrt{n+1} \mid n+1\rangle$, 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 $\langle n \mid \hat{x}^3|0\rangle$ are

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

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

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

$$P_{0\to 2} = 0 \tag{10.205}$$

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

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

Problem 10.8

A hydrogen atom, initially (i.e., $t \to -\infty$) 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., $t \to \infty$).

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

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

where

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

Since $z = r\cos\theta$ and

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

and using $\int_0^\pi \sin\theta\cos^2\theta\, d\theta = \int_{-1}^1 x^2 dx = \frac{2}{3}$, we have

$$\begin{aligned}\langle 210 \mid z \mid 100\rangle &= \int_0^\infty r^3 R_{21}^*(r) R_{10}(r) dr \int_0^\pi \sin\theta\cos^2\theta\, d\theta \int_0^{2\pi} d\phi \\ &= \frac{4\pi}{3}\frac{1}{4\pi a_0^4\sqrt{2}}\int_0^\infty r^4 e^{-3r/2a_0} dr = \frac{2^8 a_0}{3^5\sqrt{2}}. \end{aligned} \tag{10.210}$$

Inserting (10.208) and (10.210) into (10.207) we have

$$P_{1s\to 2p} = \frac{2^{15} e^2 E_0^2 \tau^2 a_0^2}{3^{10}\hbar^2}\left|\int_{-\infty}^{+\infty} \frac{e^{i\omega_{fi}t}}{\tau^2+t^2} dt\right|^2. \tag{10.211}$$

We may calculate this integral using the method of residues by closing the contour in the upper half of the t-plane. Since the infinite semicircle has no contribution to the integral, the pole at $t = i\tau$ gives

$$\begin{aligned}\int_{-\infty}^{+\infty} \frac{e^{i\omega_{fi}t}}{\tau^2+t^2} dt &= 2\pi i \,\text{Res}\left[\frac{e^{i\omega_{fi}t}}{\tau^2+t^2}\right]_{t=i\tau} = 2\pi i \lim_{t\to i\tau}\left[\frac{e^{i\omega_{fi}t}}{\tau^2+t^2}\times(t-i\tau)\right] \\ &= 2\pi i \lim_{t\to i\tau}\left[\frac{e^{i\omega_{fi}t}(t-i\tau)}{(t+i\tau)(t-i\tau)}\right] = \frac{\pi}{\tau}e^{-\omega_{fi}\tau}, \end{aligned} \tag{10.212}$$

where

$$\omega_{fi} = \frac{1}{\hbar}(E_f - E_i) = \frac{1}{\hbar}\left(E_{2p} - E_{1s}\right) = \frac{1}{\hbar}\left(\frac{1}{4}E_{1s} - E_{1s}\right) = -\frac{3}{4\hbar}E_{1s} = \frac{3R_y}{4\hbar}, \tag{10.213}$$

where R_y is the Rydberg constant: $R_y = 13.6\,\text{eV}$. Inserting (10.212) into (10.211), we obtain the transition probability

$$P_{1s\to 2p} = \frac{2^{15} e^2\pi^2 E_0^2 a_0^2}{3^{10}\hbar^2}\exp\left(-2\omega_{fi}\tau\right) = \frac{2^{15} e^2\pi^2 E_0^2 a_0^2}{3^{10}\hbar^2}\exp\left(-\frac{3R_y}{2\hbar}\tau\right). \tag{10.214}$$

Problem 10.9
A hydrogen atom is in its excited 2p state. Calculate the transition rate associated with the $2p \to 1s$ transitions (Lyman) and the lifetime of the 2p state.

Solution
The first expression of the total transition rate is given by (10.141):

$$W_{2p\to 1s} = \frac{4\omega_{2p\to 1s}^3}{3\hbar c^3}\left|\vec{d}_{2p\to 1s}\right|^2, \tag{10.215}$$

where

$$|\vec{d}_{2p\to 1s}|^2 = e^2|\langle 2p \mid \vec{\varepsilon}\cdot\vec{r} \mid 1s\rangle|^2 = e^2\left|\int_0^\infty r^3 R_{21}^* R_{10}(r)\, dr \int d\Omega\, Y_{1m}^*\vec{\varepsilon}\cdot\hat{r}\, Y_{00}\right|^2. \tag{10.216}$$

First, we need to calculate $\langle 2\mathrm{p} \mid \vec{\varepsilon} \cdot \vec{r} \mid 1\mathrm{s} \rangle$. The radial integral is given by

$$\int_0^\infty r^3 R_{21}^*(r) R_{10}(r)\, dr = \frac{1}{a_0^4\sqrt{6}} \int_0^\infty r^4 e^{-3r/2a_0} dr = \frac{2^8 a_0}{3^4\sqrt{6}}. \tag{10.217}$$

The angular part can be calculated from (10.127) as follows:

$$\begin{aligned}
\int d\Omega Y_{1m}^*(\Omega)\vec{\varepsilon}.\hat{r} Y_{00}(\Omega) &= \sqrt{\frac{4\pi}{3}} \int Y_{1m}^* \left(\frac{-\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{11} + \frac{\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{1-1} + \epsilon_z Y_{10} \right) Y_{00} d\Omega \\
&= \frac{1}{\sqrt{3}} \int Y_{1m}^* \left(\frac{-\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{11} + \frac{\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{1-1} + \epsilon_z Y_{10} \right) d\Omega \\
&= \frac{1}{\sqrt{3}} \left(\frac{-\epsilon_x + i\epsilon_y}{\sqrt{2}} \delta_{m,1} + \frac{\epsilon_x + i\epsilon_y}{\sqrt{2}} \delta_{m,-1} + \epsilon_z \delta_{m,0} \right),
\end{aligned} \tag{10.218}$$

since $\int Y_{1m}^*(\theta,\phi) Y_{l_i m_i}(\theta,\phi)\, d\Omega = \delta_{l_i,1}\delta_{m,m_i}$. An insertion of (10.217) and (10.218) into (10.216) leads to

$$|\vec{d}_{2\mathrm{p}\to 1\mathrm{s}}|^2 = 32 \left(\frac{2}{3}\right)^{10} e^2 a_0^2 \left[\frac{1}{2}(\epsilon_x^2 + \epsilon_y^2)(\delta_{m,-1} + \delta_{m,1}) + \epsilon_z^2 \delta_{m,0} \right], \tag{10.219}$$

which, when inserted into (10.215), leads to the total transition rate corresponding to a certain value of the azimuthal quantum number m:

$$W_{2\mathrm{p}\to 1\mathrm{s}} = \frac{4\omega_{2\mathrm{p}\to 1\mathrm{s}}^3}{3\hbar c^3} |\vec{d}_{fi}|^2 = \frac{128 e^2 a_0^2 \omega^3}{3\hbar c^3} \left(\frac{2}{3}\right)^{10} \left[\frac{1}{2}(\epsilon_x^2 + \epsilon_y^2)(\delta_{m,-1} + \delta_{m,1}) + \epsilon_z^2 \delta_{m,0} \right]. \tag{10.220}$$

Summing over the three possible m-states, $m = -1, 0, 1$,

$$\sum_{m=-1}^{1} \left[\frac{1}{2}(\epsilon_x^2 + \epsilon_y^2)(\delta_{m,-1} + \delta_{m,1}) + \epsilon_z^2 \delta_{m,0} \right] = \epsilon_x^2 + \epsilon_y^2 + \epsilon_z^2 = 1, \tag{10.221}$$

and since, as shown in (10.213), $\omega_{2\mathrm{p}\to 1\mathrm{s}} = (E_{2\mathrm{p}} - E_{1\mathrm{s}})/\hbar = 3R_y/(4\hbar) = 3e^2/(8\hbar a_0)$ (because the Rydberg constant R_y is equal to $e^2/(2\hbar a_0)$), we can reduce (10.220) to

$$W_{2\mathrm{p}\to 1\mathrm{s}} = \frac{128}{3\hbar c^3} \left(\frac{2}{3}\right)^{10} e^2 a_0^2 \omega_{2\mathrm{p}\to 1\mathrm{s}}^3 = \left(\frac{2}{3}\right)^8 \left(\frac{e^2}{\hbar c}\right)^4 \frac{c}{a_0} = \left(\frac{2}{3}\right)^8 \frac{c\alpha^4}{a_0}, \tag{10.222}$$

where $\alpha = e^2/(\hbar c) = 1/137$ is the fine structure constant and $a_0 = 0.529 \times 10^{-10}\,\mathrm{m}$ is the Bohr radius. The numerical value of the transition rate is

$$W_{2\mathrm{p}\to 1\mathrm{s}} = \left(\frac{2}{3}\right)^8 \frac{c\alpha^4}{a_0} \simeq \left(\frac{2}{3}\right)^8 \frac{3 \times 10^8\,\mathrm{m\,s^{-1}}}{137^4 \times 0.529 \times 10^{-10}\,\mathrm{m}} = 0.628 \times 10^9\,\mathrm{s^{-1}}. \tag{10.223}$$

The lifetime of the 2p state is then given by

$$\tau = \frac{1}{W_{2\mathrm{p}\to 1\mathrm{s}}} = \left(\frac{3}{2}\right)^8 \frac{a_0}{c\alpha^4} = \frac{1.5^8 \times 137^4 \times 0.529 \times 10^{-10}\,\mathrm{m}}{3 \times 10^8\,\mathrm{m\,s^{-1}}} = 1.6 \times 10^{-9}\,\mathrm{s}. \tag{10.224}$$

This value is in very good agreement with experimental data.

Remark

Another way of obtaining (10.222) is to use the relation

$$W_{2p\to 1s} = \frac{4e^2\omega_{2p\to 1s}^3}{3\hbar c^3}\frac{1}{3}\sum_{m=-1}^{1}|\langle 21m \mid \vec{r} \mid 100\rangle|^2$$
$$= \frac{4e^2\omega_{2p\to 1s}^3}{9\hbar c^3}\sum_{m=-1}^{1}\Big[|\langle 21m \mid \hat{x} \mid 100\rangle|^2 + |\langle 21m \mid \hat{y} \mid 100\rangle|^2 + |\langle 21m \mid \hat{z} \mid 100\rangle|^2\Big], \tag{10.225}$$

where we have averaged over the various transitions. Using the relations $x = r\sin\theta\cos\phi = -\sqrt{2\pi/3}\,r(Y_{11} - Y_{1-1})$, $y = r\sin\theta\sin\phi = i\sqrt{2\pi/3}\,r(Y_{11} + Y_{1-1})$, and $z = r\cos\theta = \sqrt{4\pi/3}\,rY_{10}$, we can show that

$$\langle 21m \mid \hat{x} \mid 100\rangle = -\frac{1}{\sqrt{4\pi}}\sqrt{\frac{2\pi}{3}}\int_0^\infty r^3 R_{21}^*(r)R_{10}(r)dr\int Y_{1m}^*(\Omega)\,(Y_{11} - Y_{1-1})\,d\Omega$$
$$= -\frac{1}{\sqrt{6}}\left[\frac{24}{\sqrt{6}}\left(\frac{2}{3}\right)^5 a_0\right](\delta_{m,1} - \delta_{m,-1}), \tag{10.226}$$

$$\langle 21m \mid \hat{y} \mid 100\rangle = \frac{i}{\sqrt{4\pi}}\sqrt{\frac{2\pi}{3}}\int_0^\infty r^3 R_{21}^*(r)R_{10}(r)dr\int Y_{1m}^*(Y_{11} + Y_{1-1})d\Omega$$
$$= \frac{i}{\sqrt{6}}\left[\frac{24}{\sqrt{6}}\left(\frac{2}{3}\right)^5 a_0\right](\delta_{m,1} + \delta_{m,-1}), \tag{10.227}$$

$$\langle 21m \mid \hat{z} \mid 100\rangle = \frac{1}{\sqrt{4\pi}}\sqrt{\frac{4\pi}{3}}\int_0^\infty r^3 R_{21}^*(r)R_{10}(r)dr\int Y_{1m}^*Y_{10}d\Omega$$
$$= \frac{1}{\sqrt{3}}\left[\frac{24}{\sqrt{6}}\left(\frac{2}{3}\right)^5 a_0\right]\delta_{m,0}. \tag{10.228}$$

A combination of the previous three relations leads to

$$\sum_{m=-1}^{1}|\langle 21m \mid \vec{r} \mid 100\rangle|^2 = 96a_0^2\left(\frac{2}{3}\right)^{10}\sum_m\left[\frac{1}{6}(\delta_{m,1} - \delta_{m,-1})^2 + \frac{1}{6}(\delta_{m,1} + \delta_{m,-1})^2 + \frac{1}{3}\delta_{m,0}^2\right]$$
$$= 96a_0^2\left(\frac{2}{3}\right)^{10}\sum_m\left[\frac{1}{6}(\delta_{m,1} + \delta_{m,-1}) + \frac{1}{6}(\delta_{m,1} + \delta_{m,-1}) + \frac{1}{3}\delta_{m,0}\right]$$
$$= \frac{96a_0^2}{3}\left(\frac{2}{3}\right)^{10}\sum_{m=-1}^{1}(\delta_{m,-1} + \delta_{m,1} + \delta_{m,0}) = 96\left(\frac{2}{3}\right)^{10}a_0^2. \tag{10.229}$$

Finally, substituting (10.229) into (10.225) and using $\omega_{2p\to 1s} = 3e^2/(8\hbar a_0)$, we obtain

$$W_{2p\to 1s} = \frac{128e^2a_0^2}{3\hbar c^3}\omega^3\left(\frac{2}{3}\right)^{10} = \left(\frac{2}{3}\right)^8\left(\frac{e^2}{\hbar c}\right)^4\frac{c}{a_0} = \left(\frac{2}{3}\right)^8\frac{c\alpha^4}{a_0}. \tag{10.230}$$

Problem 10.10

(a) Calculate the transition rate from the first excited state to the ground state for an isotropic (three-dimensional) harmonic oscillator of charge q.

(b) Find a numerical value for the rate calculated in (a) as well as the lifetime of the first excited state for the case of an electron (i.e., $m_e c^2 = 0.511\,\text{MeV}$) oscillating with a frequency of an optical radiation $\omega \simeq 10^{15}\,\text{rad}\,\text{s}^{-1}$.

Solution

As mentioned in Chapter 6, the ground state of an isotropic harmonic oscillator is a 1s state, $(n, l, m) = (0, 0, 0)$, whose energy and wave function are $E_0 = 3\hbar\omega/2$ and

$$\psi_{000}(r,\ \theta,\ \phi) = R_{00}(r)Y_{00}(\theta,\ \phi) = \frac{2}{\sqrt{\sqrt{\pi}}}\left(\frac{m\omega}{\hbar}\right)^{3/4} e^{-m\omega r^2/2\hbar} Y_{00}(\theta,\ \phi), \tag{10.231}$$

and the first excited state is a $1p$ state $(n, l, m) = (1, 1, m)$ whose energy and wave function are $E_1 = 5\hbar\omega/2$ and

$$\psi_{11m}(r,\ \theta,\ \phi) = R_{11}(r)Y_{1m}(\theta,\ \phi) = \sqrt{\frac{8}{3\sqrt{\pi}}}\left(\frac{m\omega}{\hbar}\right)^{5/4} r e^{-m\omega r^2/2\hbar} Y_{1m}(\theta,\ \phi). \tag{10.232}$$

Using $\int_0^\infty x^4 e^{-x^2} dx = \frac{3}{8}\sqrt{\pi}$ along with a change of variable $x = \sqrt{m\omega/\hbar}\, r$, we have

$$\int_0^\infty r^3 R_{11}^*(r) R_{10}(r)\, dr = 4\sqrt{\frac{2}{3\pi}}\left(\frac{m\omega}{\hbar}\right)^2 \int_0^\infty r^4 e^{-m\omega r^2/\hbar}\, dr = \sqrt{\frac{3\hbar}{2m\omega}}. \tag{10.233}$$

(a) The transition rate for a $1\text{p} \to 1\text{s}$ transition is given by

$$\begin{aligned} W_{1\text{p}\to 1\text{s}} &= \frac{4q^2\omega_{1\text{p}\to 1\text{s}}^3}{3\hbar c^3}\frac{1}{3}\sum_{m=-1}^{1} |\langle 11m \mid \vec{r} \mid 000\rangle|^2 \\ &= \frac{4q^2\omega_{1\text{p}\to 1\text{s}}^3}{9\hbar c^3}\sum_{m=-1}^{1}\Big[\, |\langle 11m \mid \hat{x} \mid 000\rangle|^2 + |\langle 11m \mid \hat{y} \mid 000\rangle|^2 + |\langle 21m \mid \hat{z} \mid 000\rangle|^2\Big]. \end{aligned} \tag{10.234}$$

Since $x = r\sin\theta\cos\phi = -\sqrt{2\pi/3}\, r(Y_{11} - Y_{1-1})$, $y = r\sin\theta\sin\phi = i\sqrt{2\pi/3}\, r(Y_{11} + Y_{1-1})$, and $z = r\cos\theta = \sqrt{4\pi/3}\, r Y_{10}$, and using (10.233), we can show by analogy with (10.226) to (10.228) that

$$\begin{aligned} \langle 11m \mid \hat{x} \mid 000\rangle &= -\frac{1}{\sqrt{4\pi}}\sqrt{\frac{2\pi}{3}}\int_0^\infty r^3 R_{11}^*(r) R_{00}(r)\, dr \int Y_{1m}^*(\Omega)\,(Y_{11} - Y_{1-1})\, d\Omega \\ &= -\frac{1}{\sqrt{6}}\sqrt{\frac{3\hbar}{2m\omega}}(\delta_{m,1} - \delta_{m,-1}), \end{aligned} \tag{10.235}$$

$$\begin{aligned} \langle 11m \mid \hat{y} \mid 000\rangle &= \frac{i}{\sqrt{4\pi}}\sqrt{\frac{2\pi}{3}}\int_0^\infty r^3 R_{11}^*(r) R_{00}(r)\, dr \int Y_{1m}^*(Y_{11} + Y_{1-1})\, d\Omega \\ &= \frac{i}{\sqrt{6}}\sqrt{\frac{3\hbar}{2m\omega}}(\delta_{m,1} + \delta_{m,-1}), \end{aligned} \tag{10.236}$$

$$\langle 11m \mid \hat{z} \mid 000\rangle = \frac{1}{\sqrt{4\pi}}\sqrt{\frac{4\pi}{3}}\int_0^\infty r^3 R_{11}^*(r)R_{00}(r)\,dr\int Y_{1m}^* Y_{10}\,d\Omega = \frac{1}{\sqrt{3}}\sqrt{\frac{3\hbar}{2m\omega}}\delta_{m,0}. \tag{10.237}$$

A combination of the previous three relations leads to

$$\begin{aligned}\sum_{m=-1}^{1}|\langle 11m \mid \vec{r} \mid 000\rangle|^2 &= \frac{3\hbar}{2m\omega}\sum_m\left[\frac{1}{6}(\delta_{m,1}-\delta_{m,-1})^2+\frac{1}{6}(\delta_{m,1}+\delta_{m,-1})^2+\frac{1}{3}\delta_{m,0}^2\right]\\ &= \frac{\hbar}{2m\omega}\sum_{m=-1}^{1}(\delta_{m,-1}+\delta_{m,1}+\delta_{m,0}) = \frac{3\hbar}{2m\omega}.\end{aligned} \tag{10.238}$$

Substituting (10.238) into (10.234), and using $\omega_{1\mathrm{p}\to 1\mathrm{s}} = (E_1 - E_0)/\hbar = (\frac{5}{2} - \frac{3}{2})\omega = \omega$, we obtain

$$W_{1\mathrm{p}\to 1\mathrm{s}} = \frac{4q^2\omega_{1\mathrm{p}\to 1\mathrm{s}}^3}{9\hbar c^3}\frac{3\hbar}{2m\omega} = \frac{2q^2\omega^2}{3mc^3}. \tag{10.239}$$

(b) In the case of an electron ($q = -e$ and $m_e c^2 = 0.511\,\mathrm{MeV}$) which is oscillating with a frequency of $\omega \simeq 10^{15}\,\mathrm{s}^{-1}$, the transition rate is

$$\begin{aligned}W_{1\mathrm{p}\to 1\mathrm{s}} &= \frac{2e^2\omega^2}{3m_e c^3} = \frac{2\alpha}{3}\left(\frac{\hbar c}{m_e c^2}\right)\frac{\omega^2}{c}\\ &= \frac{2}{3}\frac{1}{137}\left(\frac{197\,\mathrm{MeV\ fm}}{0.511\,\mathrm{MeV}}\right)\frac{10^{30}\,\mathrm{s}^{-2}}{3\times 10^8\,\mathrm{m\,s}^{-1}} \simeq 0.64\times 10^7\,\mathrm{s}^{-1},\end{aligned} \tag{10.240}$$

where $\alpha = e^2/(\hbar c) = 1/137$ is the fine structure constant. The lifetime of the 1p state for the oscillator is given by

$$\tau = \frac{1}{W_{1\mathrm{p}\to 1\mathrm{s}}} = \frac{3m_e c^3}{2e^2\omega^2} \simeq \frac{1}{0.64\times 10^7\,\mathrm{s}^{-1}} = 1.56\times 10^{-7}\,\mathrm{s}. \tag{10.241}$$

Problem 10.11
Show that free electrons can neither emit nor absorb photons.

Solution
If the electron is *free* both before and after it interacts with the photon, its initial and final wave functions are given by *plane* waves: $\psi_i(\vec{r}) = (2\pi)^{-3/2}e^{i\vec{k}_i\cdot\vec{r}}$ and $\psi_f(\vec{r}) = (2\pi)^{-3/2}e^{i\vec{k}_f\cdot\vec{r}}$. Let us assume, for argument sake, that a free electron can absorb and emit a photon; the corresponding absorption and emission transition rates would be given as follows (see (10.95) and (10.96)):

$$\Gamma_{i\to f}^{abs} = \frac{4\pi^2 e^2}{m_e^2\omega V}\left|(\vec{\varepsilon}\cdot\vec{k}_i)\langle\psi_f \mid e^{i\vec{k}\cdot\vec{r}} \mid \psi_i\rangle\right|^2\delta(E_f - E_i - \hbar\omega), \tag{10.242}$$

$$\Gamma_{i\to f}^{emi} = \frac{4\pi^2 e^2}{m_e^2\omega V}\left|(\vec{\varepsilon}\cdot\vec{k}_i)\langle\psi_f \mid e^{-i\vec{k}\cdot\vec{r}} \mid \psi_i\rangle\right|^2\delta(E_f - E_i + \hbar\omega), \tag{10.243}$$

where we have used $\vec{P}\,\psi_i(\vec{r}) = \vec{k}_i\,\psi_i(\vec{r})$. Since

$$\langle \psi_f \mid e^{\pm i\vec{k}\cdot\vec{r}} \mid \psi_i \rangle = \frac{1}{(2\pi)^2}\int d^3r\, e^{i(\vec{k}_i - \vec{k}_f \pm \vec{k})\cdot\vec{r}} = \delta(\vec{k}_i - \vec{k}_f \pm \vec{k}), \tag{10.244}$$

the delta functions $\delta(\vec{k}_i - \vec{k}_f \pm \vec{k})$ give the conservation laws of the linear momentum for both the absorption and emission processes.

Let us show first that a free electron cannot absorb a photon. For this, we are going to show that the momentum conservation condition $\delta(\vec{k}_i - \vec{k}_f + \vec{k})$ is incompatible with the energy conservation condition $\delta(E_f - E_i - \hbar\omega)$. Combining equations (10.242) and (10.244), we see that the absorption rate is proportional to the product of two delta functions: $\Gamma^{abs}_{i\to f} \sim \delta(\vec{k}_i - \vec{k}_f + \vec{k})\delta(E_f - E_i - \hbar\omega)$, one pertaining to the conservation of momentum

$$\delta(\vec{k}_i - \vec{k}_f + \vec{k}) \quad \Longrightarrow \quad \vec{p}_i - \vec{p}_f + \vec{p}_{photon} = 0, \tag{10.245}$$

the other dealing with the conservation of energy

$$\delta(E_f - E_i - \hbar\omega) \quad \Longrightarrow \quad E_f - E_i - cp_{photon} = 0, \tag{10.246}$$

where $\vec{p}_i = \hbar\vec{k}_i$ and E_i are the initial momentum and energy of the electron, $\vec{p}_f = \hbar\vec{k}_f$ and E_f are its final momentum and energy, and $\vec{p}_{photon} = \hbar\vec{k}$ and cp_{photon} are the linear momentum and energy of the absorbed photon. We are now ready to show that the condition (10.245) is incompatible with (10.246). If we work within the rest frame of the initial electron, we have $\vec{p}_i = 0$. Thus, on the one hand, (10.245) leads to $\vec{p}_{photon} = \vec{p}_f$ and, on the other hand, (10.246) leads to $E_f = cp_{photon}$ or $p_f^2/2m_e = cp_{photon}$. Indeed, conditions (10.245) and (10.246) are contradictory since, inserting $\vec{p}_i = 0$ and $\vec{p}_{photon} = \vec{p}_f$ into (10.246), we end up with $p_f^2/2m_e = cp_f$ or $p_f = 2m_ec$. This suggests either that $v_f = 0$ and this is meaningless since, as $\vec{p}_{photon} = \vec{p}_f$, the speed of the photon would also be zero; or that $v_f = 2c$ and this is impossible. So both results are impossible. In summary, having started with the assumption that a free electron can absorb a photon (10.242), we have ended up with a momentum conservation law and an energy conservation law that are contradictory. Thus, a free electron cannot absorb a photon.

Following the same procedure, we can also show that the assumption of a free electron emitting a photon leads to a momentum conservation law and an energy conservation law that are incompatible; thus, a free electron cannot emit a photon.

Problem 10.12

A hydrogen atom in its ground state is placed in an oscillating electric field $\vec{\mathcal{E}}(t) = \vec{\mathcal{E}}_0\sin(\omega t)$ of angular frequency ω with $\hbar\omega > m_ee^4/(2\hbar^2)$.

(a) Find the transition rate (probability per unit time) that the atom will be ionized.

(b) Use the expression derived in (a) to find the maximum transition rate.

Solution

After ionization we assume the electron to be in free motion: its energy is purely kinetic $E_k = \hbar^2k^2/2m_e$ and its wave function is a plane wave $\psi_k(\vec{r}) = (2\pi)^{-3/2}e^{i\vec{k}\cdot\vec{r}}$. Since the perturbation resulting from the interaction of the hydrogen's electron with the external field $\vec{\mathcal{E}}(t)$ is *harmonic*,

$$\hat{V}(t) = -e\vec{r}\cdot\vec{\mathcal{E}}(t) = -e\vec{r}\cdot\vec{\mathcal{E}}_0\sin(\omega t) = \frac{e}{2i}\vec{r}\cdot\vec{\mathcal{E}}_0e^{-i\omega t} - \frac{e}{2i}\vec{r}\cdot\vec{\mathcal{E}}_0e^{i\omega t}, \tag{10.247}$$

we can infer, by analogy with the method that led to (10.54) from (10.50), the transition rate for the ionization of the hydrogen atom:

$$\Gamma_{0k} = \frac{2\pi}{\hbar}\left|\frac{e}{2i}\langle\psi_k|\vec{r}\cdot\vec{\mathcal{E}}_0 \mid 100\rangle\right|^2\delta(E_k - E_0 + \hbar\omega) + \frac{2\pi}{\hbar}\left|-\frac{e}{2i}\langle\psi_k|\vec{r}\cdot\vec{\mathcal{E}}_0 \mid 100\rangle\right|^2\delta(E_k - E_0 - \hbar\omega), \tag{10.248}$$

where $E_0 = -m_e e^4/2\hbar^2 = -13.6\,\text{eV}$ is the ground state energy and $E_k = \hbar^2 k'/2m_e$ is the final energy of the electron. The first delta term, $\delta(E_k - E_0 + \hbar\omega)$, in (10.248) does not contribute, since if $\hbar\omega = E_0 - E_k$ the ionization could not take place because the electric field would not be strong enough to ionize the atom. The transition rate (10.248) then becomes

$$\Gamma_{0k} = \frac{\pi e^2}{2\hbar}\left|\langle\psi_k|\vec{r}\cdot\vec{\mathcal{E}}_0 \mid 100\rangle\right|^2\delta(E_k - E_0 - \hbar\omega). \tag{10.249}$$

To calculate $\langle\psi_k|\vec{r}\cdot\vec{\mathcal{E}}_0 \mid 100\rangle$, let us take $\vec{k}$ along the z-axis and hence $\vec{k}\cdot\vec{r} = kr\cos\theta$ and $\psi_k(\vec{r}) = (2\pi)^{-3/2}e^{ikr\cos\theta}$. Taking (θ,ϕ) and (α,β) as the respective polar angles of $\vec{r}$ and $\vec{\mathcal{E}}_0$, we have $\vec{r} = r(\sin\theta\cos\phi\vec{i} + \sin\theta\sin\phi\vec{j} + \cos\theta\vec{k})$ and $\vec{\mathcal{E}}_0 = \mathcal{E}_0(\sin\alpha\cos\beta\vec{i} + \sin\alpha\sin\beta\vec{j} + \cos\alpha\vec{k})$; hence

$$\begin{aligned}\vec{r}\cdot\vec{\mathcal{E}}_0 &= r\mathcal{E}_0(\sin\theta\cos\phi\sin\alpha\cos\beta + \sin\theta\sin\phi\sin\alpha\sin\beta + \cos\theta\cos\alpha)\\ &= r\mathcal{E}_0\Big[\sin\theta\sin\alpha\cos(\phi-\beta) + \cos\theta\cos\alpha\Big].\end{aligned} \tag{10.250}$$

Since $\psi_{1S} = (\pi a_0^3)^{-1/2}e^{-r/a_0}$ and $d^3r = r^2dr\sin\theta\cos\phi\,d\theta\,d\phi$, we have

$$\begin{aligned}\langle\psi_k|\vec{r}\cdot\vec{\mathcal{E}}_0 \mid 100\rangle &= \frac{1}{(2\pi)^{3/2}}\frac{1}{\sqrt{\pi a_0^3}}\int d^3r\,(\vec{r}\cdot\vec{\mathcal{E}}_0)e^{-ikr\cos\theta - r/a_0}\\ &= \frac{\mathcal{E}_0}{\sqrt{8\pi^4 a_0^3}}\int_0^\infty r^3e^{-r/a_0}dr\int_0^\pi\sin\theta e^{-ikr\cos\theta}d\theta\int_0^{2\pi}\Big[\sin\theta\sin\alpha\cos(\phi-\beta) + \cos\theta\cos\alpha\Big]d\phi\\ &= \frac{2\pi\,\mathcal{E}_0\cos\alpha}{\sqrt{8\pi^4 a_0^3}}\int_0^\infty r^3e^{-r/a_0}\,dr\int_0^\pi\sin\theta\cos\theta e^{-ikr\cos\theta}\,d\theta,\end{aligned} \tag{10.251}$$

where we have used $\int_0^{2\pi}\cos(\phi-\beta)d\phi = 0$, since $\int_0^{2\pi}\cos\phi\,d\phi = 0$ and $\int_0^{2\pi}\sin\phi\,d\phi = 0$. A change of variable $x = \cos\theta$ and an integration by parts leads to

$$\begin{aligned}\int_0^\pi\sin\theta\cos\theta e^{-ikr\cos\theta}d\theta &= \int_{-1}^1 xe^{-ikrx}dx = \frac{1}{-ikr}xe^{-ikrx}\Big|_{-1}^1 - \frac{1}{(-ikr)^2}e^{-ikrx}\Big|_{-1}^1\\ &= \frac{i}{kr}\Big[e^{-ikr} + e^{ikr}\Big] + \frac{1}{k^2r^2}\Big[e^{-ikr} - e^{ikr}\Big].\end{aligned} \tag{10.252}$$

When we insert this integral into (10.251), we still need to calculate four radial integrals which can be carried out by parts:

$$\int_0^\infty re^{\pm ikr - r/a_0}dr = \frac{1}{\pm ik - 1/a_0}re^{\pm ikr - r/a_0}\Big|_0^\infty - \frac{1}{(\pm ik - 1/a_0)^2}e^{\pm ikr - r/a_0}\Big|_0^\infty = \frac{a_0^2}{(\pm ia_0k - 1)^2}, \tag{10.253}$$

$$\begin{aligned}\int_0^\infty r^2 e^{\pm ikr - r/a_0} dr &= \frac{1}{\pm ik - 1/a_0} r^2 e^{\pm ikr - r/a_0}\Big|_0^\infty - \frac{2}{\pm ik - 1/a_0}\int_0^\infty r e^{\pm ikr - r/a_0} dr \\ &= -\frac{2}{(\pm ik - 1/a_0)^2} r e^{\pm ikr - r/a_0}\Big|_0^\infty + \frac{2}{(\pm ik - 1/a_0)^3} e^{\pm ikr - r/a_0}\Big|_0^\infty \\ &= -\frac{2a_0^3}{(\pm i a_0 k - 1)^3}. \end{aligned} \tag{10.254}$$

Inserting (10.252) to (10.254) into (10.251), we obtain

$$\begin{aligned}\langle \psi_k | \vec{r}\cdot\vec{\mathcal{E}}_0 \mid 100\rangle &= \frac{2\pi\mathcal{E}_0\cos\alpha}{\sqrt{8\pi^4 a_0^3}}\left[\frac{a_0^2}{k^2(-ia_0k-1)^2} - \frac{a_0^2}{k^2(ia_0k-1)^2} - \frac{2ia_0^3}{k(ia_0k-1)^3}\right. \\ &\qquad \left. - \frac{2ia_0^3}{k(-ia_0k-1)^3}\right] \\ &= -\frac{16\mathcal{E}_0\cos\alpha}{\pi\sqrt{2a_0^5}}\frac{ia_0^6 k}{(a_0^2k^2+1)^3}. \end{aligned} \tag{10.255}$$

A substitution of this expression into (10.249) leads to

$$\Gamma_{0k} = \frac{\pi e^2}{2\hbar}\frac{128\mathcal{E}_0^2\cos^2\alpha}{\pi^2 a_0^5}\frac{k^2 a_0^{12}}{(a_0^2k^2+1)^6}\delta(E_k - E_0 + \hbar\omega). \tag{10.256}$$

This relation gives the transition rate for a single final state ψ_k corresponding to a given k. We need to sum over all final states of the electron. These represent a continuum; we must then integrate over all directions of emission and over all possible momenta:

$$\begin{aligned}\Gamma_0 &= \int \Gamma_{0k}\, d^3k = \int k^2 dk \int_0^\pi \Gamma_{0k}\sin\alpha\, d\alpha \int_0^{2\pi} d\beta \\ &= 2\pi\frac{64e^2\mathcal{E}_0^2 a_0^7}{\pi\hbar}\int \frac{k^4\delta(E_k - E_0 - \hbar\omega)}{(a_0^2k^2+1)^6}dk\int_0^\pi \sin\alpha\cos^2\alpha\, d\alpha \\ &= \frac{256e^2\mathcal{E}_0^2 a_0^7}{3\hbar}\int\frac{k^4\delta(E_k - E_0 - \hbar\omega)}{(a_0^2k^2+1)^6}dk, \end{aligned} \tag{10.257}$$

where we have used $\int_0^\pi \sin\alpha\cos^2\alpha\, d\alpha = \int_{-1}^1 x^3 dx = \frac{2}{3}$. The integration over k can be converted into an integration over the final energy E_k: since $E_k = \hbar^2k^2/(2m_e)$, a change of variable $k = \sqrt{2m_eE_k/\hbar^2}$, and hence $k\,dk = (m_e/\hbar^2)dE_k$, reduces (10.257) to

$$\begin{aligned}\Gamma_0 &= \frac{256e^2\mathcal{E}_0^2 a_0^7}{3\hbar}\int\frac{k^3\delta(E_k - E_0 - \hbar\omega)}{(a_0^2k^2+1)^6}k\,dk \\ &= \frac{m_e}{\hbar^2}\frac{256e^2\mathcal{E}_0^2 a_0^7}{3\hbar}\int\frac{(2m_eE_k/\hbar^2)^{3/2}\delta(E_k - E_0 - \hbar\omega)}{\left(2m_ea_0^2E_k/\hbar^2+1\right)^6}dE_k \\ &= \frac{256e^2m_e\mathcal{E}_0^2 a_0^7}{3\hbar^3}\frac{(2m_e/\hbar^2)^{3/2}(E_0+\hbar\omega)^{3/2}}{\left[2m_ea_0^2(E_0+\hbar\omega)/\hbar^2+1\right]^6}. \end{aligned} \tag{10.258}$$

This relation can be simplified if we use $E_0 = -m_e e^4/(2\hbar^2) = -\hbar\omega_0$, which gives $E_0 + \hbar\omega = \hbar(\omega - \omega_0) = \hbar\omega_0(\omega/\omega_0 - 1)$. Since $a_0 = \hbar^2/(m_e e^2)$, we have $\hbar\omega_0 a_0^2 = m_e e^4 \hbar^4/(2\hbar^2 m_e^2 e^4) = \hbar^2/(2m_e)$ and hence $2m_e a_0^2(E_0 + \hbar\omega)/\hbar^2 = 2m_e\hbar\omega_0 a_0^2(\omega/\omega_0 - 1)/\hbar^2 = \omega/\omega_0 - 1$. Thus, inserting the expressions $E_0 + \hbar\omega = \hbar\omega_0(\omega/\omega_0 - 1)$ and $2m_e a_0^2(E_0 + \hbar\omega)/\hbar^2 + 1 = \omega/\omega_0$ into (10.258), we obtain

$$\Gamma_0 = \frac{256 e^2 m_e \mathcal{E}_0^2 a_0^7}{3\hbar^3} \frac{(2m_e/\hbar^2)^{3/2}(\hbar\omega_0)^{3/2}(\omega/\omega_0 - 1)^{3/2}}{(\omega/\omega_0)^6}. \tag{10.259}$$

Finally, since $(2m_e/\hbar^2)^{3/2}(\hbar\omega_0)^{3/2} = (2m_e/\hbar^2)^{3/2}(m_e e^4/2\hbar^2)^{3/2} = m_e^3 e^6/\hbar^6$ and using $a_0^4 = \hbar^8/(m^4 e^8)$, we can write (10.259) as

$$\Gamma_0 = \frac{256\mathcal{E}_0^2 a_0^3}{3\hbar}\left(\frac{\omega_0}{\omega}\right)^6\left(\frac{\omega}{\omega_0} - 1\right)^{3/2}. \tag{10.260}$$

If the frequency of the oscillating electric field is smaller than or equal to ω_0, the atom will not be ionized; at $\omega = \omega_0$ the probability of ionization will be zero.

(b) The maximum transition rate is obtained by taking the derivative of (10.260):

$$\frac{d\Gamma_0}{d\omega} = 0 \Longrightarrow \frac{2}{\omega}\left(\frac{\omega}{\omega_0} - 1\right) = \frac{1}{2\omega_0} \Longrightarrow \omega = \frac{4}{3}\omega_0. \tag{10.261}$$

Inserting $\omega = \frac{4}{3}\omega_0$ into (10.260) we obtain the maximum transition rate

$$\Gamma_{0max} = \frac{256\mathcal{E}_0^2 a_0^3}{3\hbar}\left(\frac{3}{4}\right)^6\left(\frac{4}{3} - 1\right)^{3/2} = \frac{\mathcal{E}_0^2 a_0^3}{\hbar}\frac{3^{7/2}}{2^4}. \tag{10.262}$$

10.7 Exercises

Exercise 10.1
Consider a spinless particle of mass m in a one-dimensional infinite potential well with walls at $x = 0$ and $x = a$ which is initially (i.e., at $t = 0$) in the state $\psi(x, 0) = [\phi_1(x) + \phi_3(x)]/\sqrt{2}$, where $\phi_1(x)$ and $\phi_3(x)$ are the ground and second excited states, respectively, with $\phi_n(x) = \sqrt{2/a}\,\sin(n\pi x/a)$.

(a) What is the state vector $\psi(x, t)$ for $t > 0$ in the Schrödinger picture.

(b) Evaluate $\langle\hat{X}\rangle$, $\langle\hat{P}\rangle$, $\langle\hat{X}^2\rangle$, and $\langle\hat{P}^2\rangle$ as functions of time for $t > 0$ in the Schrödinger picture.

(c) Repeat part (b) in the Heisenberg picture: i.e., evaluate $\langle\hat{X}\rangle_H$, $\langle\hat{P}\rangle_H$, $\langle\hat{X}^2\rangle_H$, and $\langle\hat{P}^2\rangle_H$ as functions of time for $t > 0$.

Exercise 10.2
Evaluate the expectation value $\langle\hat{X}_H(t)\hat{P}\rangle_3$ for the third excited state of a one-dimensional harmonic oscillator.

Exercise 10.3
Evaluate the expectation value $\langle\hat{X}\hat{P}_H(t)\rangle_n$ for the nth excited state of a one-dimensional harmonic oscillator.

Exercise 10.4
Consider a one-dimensional harmonic oscillator which is initially (i.e., at $t = 0$) in the state $\mid \psi(0)\rangle = (\mid 0\rangle + \mid 1\rangle)/\sqrt{2}$, where $\mid 0\rangle$ and $\mid 1\rangle$ are the ground and first excited states, respectively.

(a) What is the state vector $\mid \psi(t)\rangle$ for $t > 0$ in the Schrödinger picture?

(b) Evaluate $\langle \hat{X} \rangle$, $\langle \hat{P} \rangle$, $\langle \hat{X}^2 \rangle$, and $\langle \hat{P}^2 \rangle$ as functions of time for $t > 0$ in the Schrödinger picture.

(c) Repeat part (b) in the Heisenberg picture.

Exercise 10.5

(a) Calculate the coordinate operator $\hat{X}_H(t)$ for a free particle in one dimension in the Heisenberg picture.

(b) Evaluate the commutator $[\hat{X}_H(t),\ \hat{X}_H(0)]$.

Exercise 10.6
Consider the Hamiltonian $H = -(eB/mc)\hat{S}_x = \omega \hat{S}_x$.

(a) Write down the Heisenberg equations of motion for the time-dependent operators $\hat{S}_x(t)$, $\hat{S}_y(t)$, and $\hat{S}_z(t)$.

(b) Solve these equations to obtain S_x, S_y, S_z as functions of time.

Exercise 10.7
Evaluate the quantity $\langle n \mid \hat{P}_H(t)\hat{P} \mid n \rangle$ for the nth excited state of a one-dimensional harmonic oscillator, where $\hat{P}_H(t)$ and $\hat{P}$ designate the momentum operators in the Heisenberg picture and the Schrödinger picture, respectively.

Exercise 10.8
The Hamiltonian due to the interaction of a particle of mass m, charge q (the charge is negative), and spin $\vec{S}$ with a magnetic field pointing along the y-axis is $\hat{H} = -(qB/mc)\hat{S}_y$.

(a) Use the Heisenberg equation to calculate $d\hat{S}_x/dt$, $d\hat{S}_y/dt$, and $d\hat{S}_z/dt$.

(b) Solve these equations to obtain the components of the spin operator as functions of time.

Exercise 10.9
A particle is initially (i.e., when $t < 0$) in its ground state in a one-dimensional harmonic oscillator potential. At $t = 0$ a perturbation $\hat{V}(x, t) = V_0 \hat{x}^2 e^{-t/\tau}$ is turned on. Calculate to first order the probability that, after a sufficiently long time (i.e., $t \to \infty$), the system will have made a transition to a given excited state; consider all final states.

Exercise 10.10
A particle, initially (i.e., when $t < 0$) in its ground state in an infinite potential well whose walls are located at $x = 0$ and $x = a$, is subject, starting at time $t = 0$, to a time-dependent perturbation $\hat{V}(t) = V_0 \hat{x}^2 e^{-t^2}$ where V_0 is a small parameter. Calculate the probability that the particle will be found in its second excited state at $t = +\infty$.

Exercise 10.11
Find the intensity associated with the transition 3s $\to$ 2p in the hydrogen atom.

Exercise 10.12
A hydrogen atom in its ground state is placed in a region where, at $t = 0$, a time-dependent electric field is turned on:

$$\vec{E}(t) = E_0(\vec{i} + \vec{j} + \vec{k})e^{-t/\tau},$$

where τ is a positive real number. Using first-order time-dependent perturbation theory, calculate the probability that, after a sufficiently long time (i.e., $t \gg \tau$), the atom is to be found in each of the $n = 2$ states (i.e., consider the transitions to all the states in the $n = 2$ level). *Hint:* You may use: $\int_0^\infty r^3 R_{21}^*(r) R_{10}(r)\, dr = (24a_0/\sqrt{6})\left(\frac{2}{3}\right)^5$.

Exercise 10.13
(a) Calculate the reduced matrix element $\langle 1 \parallel Y_1 \parallel 2\rangle$. *Hint:* For this, you may need to calculate $\langle 1,\ 0|Y_{10}|2,\ 0\rangle$ directly and then from the Wigner–Eckart theorem.

(b) Using the Wigner–Eckart theorem and the relevant Clebsch–Gordan coefficients from tables, calculate $\langle 1,\ m|Y_{1m'}|2,\ m''\rangle$ for all possible values of m, m', and m''.

(c) Using the results of part (b), calculate the 3d $\rightarrow$ 2p transition rate for the hydrogen atom in the dipole approximation; give a numerical value. *Hint:* You may use the integral $\int_0^\infty r^3 R_{21}^*(r) R_{32}(r)\, dr = (64a_0/15\sqrt{5})\left(\frac{6}{5}\right)^5$ and the following Clebsch–Gordan coefficients:

$$\langle j, 1;\ m, 0|(j-1),\ m\rangle = -\sqrt{(j-m)(j+m)/[j(2j+1)]},$$
$$\langle j, 1;\ (m-1), 1|(j-1),\ m\rangle = \sqrt{(j-m)(j-m+1)/[2j(2j+1)]}, \text{ and}$$
$$\langle j, 1;\ (m+1), -1|(j-1),\ m\rangle = \sqrt{(j+m)(j+m+1)/[2j(2j+1)]}.$$

Exercise 10.14
A particle is initially in its ground state in an infinite one-dimensional potential box with sides at $x = 0$ and $x = a$. If the wall of the box at $x = a$ is *suddenly* moved to $x = 10a$, calculate the probability of finding the particle in

(a) the fourth excited ($n = 5$) state of the new box and

(b) the ninth ($n = 10$) excited state of the new box.

Exercise 10.15
A particle of mass m in the ground state of a one-dimensional harmonic oscillator is placed in a perturbation $\hat{V}(t) = -V_0\hat{x}e^{-t/\tau}$. Calculate to first-order perturbation theory the probability of finding the particle in its first excited state after a long time.

Exercise 10.16
A particle, initially (i.e., when $t < 0$) in its first excited state in an infinite potential well whose walls are located at $x = 0$ and $x = a$, is subject, starting at time $t = 0$, to a time-dependent perturbation $\hat{V}(t) = V_0\tau\hat{x}/(t^2 + \tau^2)$ where V_0 is a small real number. Calculate the probability that the particle will be found in its second excited state at $t = +\infty$.

Exercise 10.17
A one-dimensional harmonic oscillator has its spring constant suddenly reduced by half.

(a) If the oscillator is initially in its ground state, find the probability that the oscillator remains in the ground state.

(b) Find the work associated with this process.

Exercise 10.18
(a) Find the total transition rate associated with the decay of a harmonic oscillator, of charge q and mass m, from the nth excited state to the state just below.

(b) Find the power radiated by this oscillator as a result of its decay.

(c) Find the lifetime of the nth excited state.

(d) Estimate the order of magnitudes for the transition rate, the power, and the lifetime of the fifth excited state ($n = 5$) in the case of a harmonically oscillating electron (i.e., $q = e$) for the case of an optical radiation $\omega \simeq 10^{15}\,\mathrm{rad\,s^{-1}}$.

Exercise 10.19

Assuming that $\langle \psi_f \mid \vec{r} \mid \psi_i \rangle$ is roughly equal to the size of the system under study, use a crude calculation to estimate the mean lifetime of

(a) an electric dipole transition in an atom where $\hbar\omega \sim 10\,\mathrm{eV}$ and

(b) an electric dipole transition in a nucleus where $\hbar\omega \sim 1\,\mathrm{MeV}$.

Exercise 10.20

A particle is initially (i.e., when $t < 0$) in its ground state in the potential $V(x) = -V_0\delta(x)$ with $V_0 > 0$.

(a) If the strength of the potential is changed *slowly* to $3V_0$, find the energy and wave function of the particle in the new potential.

(b) Calculate the work done with this process. Find a numerical value for this work in MeV if this particle were an electron and $V_0 = 200$ MeV fm.

(c) If the strength of the potential is changed *suddenly* to $3V_0$, calculate the probability of finding the particle in the ground state of the new potential.

Exercise 10.21

A hydrogen atom in its ground state is placed at time $t = 0$ in a uniform electric field in the y-direction, $\vec{E}(t) = E_0\vec{j}e^{-t^2/\tau^2}$. Calculate to first-order perturbation theory the probability that the atom will be found in any of the $n = 2$ states after a sufficiently long time ($t = +\infty$).

Exercise 10.22

A particle, initially (i.e., when $t < 0$) in its ground state in an infinite potential well with its walls at $x = 0$ and $x = a$, is subject, starting at time $t = 0$, to a time-dependent perturbation $\hat{V}(t) = V_0\hat{x}\delta(x - 3a/4)e^{-t/\tau}$ where V_0 is a small parameter. Calculate the probability that the particle will be found in its first excited state ($n = 2$) at $t = +\infty$.

Exercise 10.23

Consider an isotropic (three-dimensional) harmonic oscillator which undergoes a transition from the second to the first excited state (i.e., $2\mathrm{s} \rightarrow 1\mathrm{p}$).

(a) Calculate the transition rate corresponding to $2\mathrm{s} \rightarrow 1\mathrm{p}$.

(b) Find the intensity associate with the $2\mathrm{s} \rightarrow 1\mathrm{p}$ transition.

Exercise 10.24

Consider a particle which is initially (i.e., when $t < 0$) in its ground state in a three-dimensional box potential

$$V(x, y, z) = \begin{cases} 0, & 0 < x < a,\ 0 < y < 2a,\ 0 < z < 4a, \\ +\infty, & \text{elsewhere.} \end{cases}$$

(a) Find the energies and wave functions of the ground state and first excited state.

(b) This particle is then subject, starting at time $t = 0$, to a time-dependent perturbation $\hat{V}(t) = V_0\hat{x}\hat{z}e^{-t^2}$ where V_0 is a small parameter. Calculate the probability that the particle will be found in the first excited state after a long time $t = +\infty$.