18

Time-Dependent Perturbation Theory

18.1. The Problem

Except for the problem of magnetic resonance, we have avoided studying phenomena governed by a time-dependent Hamiltonian. Whereas in the time-independent case the problem of solving the equation

$$i\hbar|\dot{\psi}\rangle = H|\psi\rangle \tag{18.1.1}$$

reduced to solving the eigenvalue problem of H, in the time-dependent case a frontal attack on the full time-dependent Schrödinger equation becomes inevitable.

In this chapter we consider the perturbative solution to a class of phenomena described by

$$H(t) = H^0 + H^1(t) \tag{18.1.2}$$

where H^0 is a time-independent piece whose eigenvalue problem has been solved and H^1 is a small time-dependent perturbation. For instance, H^0 could be the hydrogen atom Hamiltonian and H^1 the addition due to a weak external electromagnetic field. Whereas in the time-independent case one is interested in the eigenvectors and eigenvalues of H, the typical question one asks here is the following. If at $t=0$ the system is in the eigenstate $|i^0\rangle$ of H^0, what is the amplitude for it to be in the eigenstate $|f^0\rangle$ $(f \neq i)$ at a later time t? Our goal is to set up a scheme in which the answer may be computed in a perturbation series in powers of H^1. To zeroth order, the answer to the question raised is clearly zero, for the only effect of H^0 is to multiply $|i^0\rangle$ by a phase factor $\exp(-iE_i^0 t/\hbar)$, which does not alter its orthogonality to $|f^0\rangle$. But as soon as we let H^1 enter the picture, i.e., work to nonzero order, the eigenstates of H^0 cease to be stationary and $|i^0\rangle$ can evolve into a state with a projection along $|f^0\rangle$.

The next section begins with a simple derivation of the first-order transition amplitude for the process $i \to f$ and is followed by several applications and discussions of special types of perturbations (sudden, adiabatic, periodic, etc.). In Section 3 the expressions for the transition amplitude to any order are derived, following a scheme more abstract than the one used in Section 2. Sections 4 and 5 are concerned with electromagnetic interactions. Section 4 contains a brief summary of relevant concepts from classical electrodynamics, followed by a general discussion of several fine points of the electromagnetic interaction at the classical and quantum levels. It therefore has little to do with perturbation theory. However, it paves the way for the last section, in which first-order perturbation theory is applied to the study of the interaction of atoms with the electromagnetic field. Two illustrative problems are considered, one in which the field is treated classically and the other in which it is treated quantum mechanically.

18.2. First-Order Perturbation Theory

Our problem is to solve Eq. (18.1.1) to first order in H^1. Since the eigenkets $|n^0\rangle$ of H^0 form a complete basis, we can always expand

$$|\psi(t)\rangle = \sum_n c_n(t)|n^0\rangle \tag{18.2.1}$$

To find $c_n(t)$ given $c_n(0)$ is equivalent to finding $|\psi(t)\rangle$ given $|\psi(0)\rangle$. Now $c_n(t)$ changes with time because of H^0 and H^1. Had H^1 been absent, we would know

$$c_n(t) = c_n(0)\, e^{-iE_n^0 t/\hbar} \tag{18.2.2}$$

Let us use this information and write

$$|\psi(t)\rangle = \sum_n d_n(t)\, e^{-iE_n^0 t/\hbar}|n^0\rangle \tag{18.2.3}$$

If d_n changes with time, it is because of H^1. So we expect that the time evolution of d_n can be written in a nice power series in H^1. The equation of motion for $d_f(t)$ is found by operating both sides of Eq. (18.2.3) with $(i\hbar\partial/\partial t - H^0 - H^1)$ to get

$$0 = \sum_n [i\hbar\dot{d}_n - H^1(t)d_n]\, e^{-iE_n^0 t/\hbar}|n^0\rangle \tag{18.2.4}$$

and then dotting with $\langle f^0|\exp(iE_f^0 t/\hbar)$:

$$i\hbar\dot{d}_f = \sum_n \langle f^0|H^1(t)|n^0\rangle\, e^{i\omega_{fn}t} d_n(t) \tag{18.2.5a}$$

where

$$\omega_{fn}=\frac{E_f^0-E_n^0}{\hbar} \tag{18.2.5b}$$

Notice that H^0 has been eliminated in Eq. (18.2.5), which is exact and fully equivalent to Eq. (18.1.1). Let us now consider the case where at $t=0$, the system is in the state $|i^0\rangle$, i.e.,

$$d_n(0)=\delta_{ni} \tag{18.2.6}$$

and ask what $d_f(t)$ is. To *zeroth order*, we ignore the right-hand side of Eq. (18.2.5a) completely, because of the explicit H^1, and get

$$\dot{d}_f=0 \tag{18.2.7}$$

in accordance with our expectations. To *first order*, we use the zeroth-order d_n in the right-hand side because H^1 is itself of first order. This gives us the first-order equation

$$\dot{d}_f(t)=\frac{-i}{\hbar}\langle f^0|H^1(t)|i^0\rangle\, e^{i\omega_{fi}t} \tag{18.2.8}$$

the solution to which, with the right initial conditions, is

$$d_f(t)=\delta_{fi}-\frac{i}{\hbar}\int_0^t \langle f^0|H^1(t')|i^0\rangle\, e^{i\omega_{fi}t'}\,dt' \tag{18.2.9}$$

Since we now know d to first order, we can feed it into the right-hand side of Eq. (18.2.5a) to get an equation for d that is good to second order. Although we can keep going to any desired order in this manner, we stop with the first, since a more compact scheme for calculating transition amplitudes to any desired order will be set up in the next section. At this point we merely note that the first-order calculation is reliable if $|d_f(t)| \ll 1 (f\neq i)$. If this condition is violated, our calculation becomes internally inconsistent, for we can no longer approximate $d_n(t)$ by δ_{ni} in the right-hand side of Eq. (18.2.5a).

Let us apply our first-order result to a simple problem. Consider a one-dimensional harmonic oscillator in the ground state $|0\rangle$‡ of the unperturbed Hamiltonian at $t=-\infty$. Let a perturbation

$$H^1(t)=-e\mathscr{E}X\, e^{-t^2/\tau^2} \tag{18.2.10}$$

‡ We shall denote the nth unperturbed state by $|n\rangle$ and not $|n^0\rangle$ in this discussion.

be applied between $t=-\infty$ and $+\infty$. What is the probability that the oscillator is in the state $|n\rangle$ at $t=\infty$? According to Eq. (18.2.9), for $n\neq 0$,

$$d_n(\infty)=\frac{-i}{\hbar}\int_{-\infty}^{\infty}(-e\mathscr{E})\langle n|X|0\rangle\, e^{-t^2/\tau^2}\, e^{in\omega t}\, dt \tag{18.2.11}$$

Since

$$X=\left(\frac{\hbar}{2m\omega}\right)^{1/2}(a+a^\dagger)$$

only $d_1(\infty)\neq 0$. We find that it is (using $a^\dagger|0\rangle=|1\rangle$)

$$\begin{aligned} d_1(\infty)&=\frac{ie\mathscr{E}}{\hbar}\left(\frac{\hbar}{2m\omega}\right)^{1/2}\int_{-\infty}^{\infty}e^{-t^2/\tau^2}\, e^{i\omega t}\, dt \\ &=\frac{ie\mathscr{E}}{\hbar}\left(\frac{\hbar}{2m\omega}\right)^{1/2}\cdot(\pi\tau^2)^{1/2}\, e^{-\omega^2\tau^2/4} \end{aligned} \tag{18.2.12}$$

Thus the probability of the transition $0\rightarrow 1$ is‡

$$P_{0\rightarrow 1}=|d_1|^2=\frac{e^2\mathscr{E}^2\pi\tau^2}{2m\omega\hbar}\, e^{-\omega^2\tau^2/2} \tag{18.2.13}$$

This result will be used shortly.

Exercise 18.2.1. Show that if $H^1(t)=-e\mathscr{E}X/[1+(t/\tau)^2]$, then, to first order,

$$P_{0\rightarrow 1}=\frac{e^2\mathscr{E}^2\pi^2\tau^2}{2m\omega\hbar}\, e^{-2\omega\tau}$$

*Exercise 18.2.2.** A hydrogen atom is in the ground state at $t=-\infty$. An electric field $\mathbf{E}(t)=(\mathbf{k}\mathscr{E})\, e^{-t^2/\tau^2}$ is applied until $t=\infty$. Show that the probability that the atom ends up in any of the $n=2$ states is, to first order,

$$P(n=2)=\left(\frac{e\mathscr{E}}{\hbar}\right)^2\left(\frac{2^{15}a_0^2}{3^{10}}\right)\pi\tau^2\, e^{-\omega^2\tau^2/2}$$

where $\omega=(E_{2lm}-E_{100})/\hbar$. Does the answer depend on whether or not we incorporate spin in the picture?

We now turn our attention to different types of perturbations.

‡ Since $d_n(t)$ and $c_n(t)$ differ only by a phase factor, $P(n)=|c_n|^2=|d_n|^2$.

The Sudden Perturbation

Consider a system whose Hamiltonian changes abruptly over a small time interval ε. What is the change in the state vector as $\varepsilon \to 0$? We can find the answer without resorting to perturbation theory. Assuming that the change occurred around $t=0$, we get, upon integrating Schrödinger's equation between $t=-\varepsilon/2$ and $\varepsilon/2$,

$$|\psi(\varepsilon/2)\rangle - |\psi(-\varepsilon/2)\rangle = |\psi_{\text{after}}\rangle - |\psi_{\text{before}}\rangle = \frac{-i}{\hbar}\int_{-\varepsilon/2}^{\varepsilon/2} H(t)|\psi(t)\rangle\, dt \tag{18.2.14}$$

Since the integrand on the right-hand side is finite, the integral is of order ε. In the limit $\varepsilon \to 0$, we get

$$|\psi_{\text{after}}\rangle = |\psi_{\text{before}}\rangle \tag{18.2.15}$$

An instantaneous change in H produces no instantaneous change in $|\psi\rangle$.‡ Now the limit $\varepsilon \to 0$ is unphysical. The utility of the above result lies in the fact that it is an excellent approximation if H changes over a time that is very small compared to the natural time scale of the system. The latter may be estimated semiclassically; several examples follow in a moment. For the present, let us consider the case of an oscillator to which is applied the perturbation in Eq. (18.2.10). It is clear that whatever be the time scale of this system, the change in the state vector must vanish as τ, the width of the Gaussian pulse, vanishes. This means in particular that the system initially in the ground state must remain there after the pulse, i.e., the $0 \to 1$ transition probability must vanish. This being an exact result, we expect that if the transition probability is calculated perturbatively, it must vanish to any given order. (This is like saying that if an analytic function vanishes identically, then so does every term in its Taylor expansion.) Turning to the first-order probability for $0 \to 1$ in Eq. (18.2.13), we see that indeed it vanishes as τ tends to zero.

A more realistic problem, where ε is fixed, involves a $1s$ electron bound to a nucleus of charge Z which undergoes β decay by emitting a *relativistic* electron and changing its charge to $(Z+1)$. The time the emitted electron takes to get out of the $n=1$ shell is

$$\tau \simeq a_0/Zc \tag{18.2.16}$$

whereas the characteristic time for the $1s$ electron is

$$T \simeq \frac{\text{size of state}}{\text{velocity of } e^-} \simeq \frac{a_0}{Z} \Big/ Z\alpha c = \frac{a_0}{Z^2 \alpha c} \tag{18.2.17}$$

so that

$$\tau/T = Z\alpha$$

‡ We are assuming H is finite in the integral $(-\varepsilon/2, \varepsilon/2)$. If it has a delta function spike, it can produce a change in $|\psi\rangle$, see Exercise 18.2.6.

For Z small, we may apply the sudden approximation and conclude that the state of the atomic electron is the same just before and just after β decay. Of course, this state is not an eigenstate of the charge $(Z+1)$ ion, but rather a superposition of such states (see Exercise 18.2.4).

*Exercise 18.2.3.** Consider a particle in the ground state of a box of length L. Argue on semiclassical grounds that the natural time period associated with it is $T \simeq mL^2/\hbar\pi$. If the box expands symmetrically to double its size in time $\tau \ll T$ what is the probability of catching the particle in the ground state of the new box? (See Exercise (5.2.1).)

*Exercise 18.2.4.** In the β decay H^3 (two neutrons + one proton in the nucleus) $\rightarrow (He^3)^+$ (two protons + one neuron in the nucleus), the emitted electron has a kinetic energy of 16 keV. Argue that the sudden approximation may be used to describe the response of an electron that is initially in the $1s$ state of H^3. Show that the amplitude for it to be in the ground state of $(He^3)^+$ is $16(2)^{1/2}/27$. What is the probability for it to be in the state

$$|n=16, l=3, m=0\rangle \text{ of } (He^3)^+?$$

Exercise 18.2.5. An oscillator is in the ground state of $H=H^0+H^1$, where the time-independent perturbation H^1 is the linear potential $(-fx)$. If at $t=0$, H^1 is abruptly turned off, show that the probability that the system is in the nth eigenstate of H^0 is given by the Poisson distribution

$$P(n)=\frac{e^{-\lambda}\lambda^n}{n!}, \quad \text{where} \quad \lambda=\frac{f^2}{2m\omega^3\hbar}$$

Hint: Use the formula

$$\exp[A+B]=\exp[A]\exp[B]\exp[-\tfrac{1}{2}[A,B]]$$

where $[A, B]$ is a c number.

*Exercise 18.2.6.** Consider a system subject to a perturbation $H^1(t)=H^1\delta(t)$. Show that if at $t=0^-$ the system is in the state $|i^0\rangle$, the amplitude to be in a state $|f^0\rangle$ at $t=0^+$ is, to first order,

$$d_f=\frac{-i}{\hbar}\langle f^0|H^1|i^0\rangle \qquad (f\neq i)$$

Notice that (1) the state of the system *does* change instantaneously; (2) Even though the perturbation is "infinite" at $t=0$, we can still use first-order perturbation theory if the "area under it" is small enough.

The Adiabatic Perturbation

We now turn to the other extreme and consider a system whose Hamiltonian $H(t)$ changes very slowly from $H(0)$ to $H(\tau)$ in a time τ. If the system starts out at $t=0$ in an eigenstate $|n(0)\rangle$ of $H(0)$, where will it end at time τ? The *adiabatic theorem* asserts that if the rate of change of H is slow enough, the system will end

up in the corresponding eigenket $|n(\tau)\rangle$ of $H(\tau)$.‡ Rather than derive the theorem and the precise definition of "slow enough" we consider a few illustrative examples.

Consider a particle in a box of length $L(0)$. If the box expands slowly to a length $L(\tau)$, the theorem tells us that a particle that was in the nth state of the box of length $L(0)$ will now be in the nth state of the box of length $L(\tau)$. But how slow is slow enough?

There are two ways to estimate this. The first is a semiclassical method and goes as follows. The momentum of the particle is of the order (dropping factors of order unity like π, n, etc.)

$$p \simeq \frac{\hbar}{L} \tag{18.2.18}$$

and the time it takes to finish one full oscillation is of the order

$$T \simeq \frac{L}{v} = \frac{mL}{p} \simeq \frac{mL^2}{\hbar} \tag{18.2.19}$$

We can say the expansion or contraction is slow if the fractional change in the length of the box per cycle is much smaller than unity:

$$\frac{|\Delta L|_{\text{per cycle}}}{L} \simeq \frac{|dL/dt| mL^2/\hbar}{L} = \frac{mL}{\hbar}\left|\frac{dL}{dt}\right| \ll 1 \tag{18.2.20}$$

This can also be written as

$$\frac{v_{\text{walls}}}{v_{\text{particle}}} \ll 1 \tag{18.2.21}$$

The second approach is less intuitive§ and it estimates T as

$$T \sim \frac{1}{\omega_{\min}} \tag{18.2.22}$$

‡ This is again a result that is true to any given order in perturbation theory. We shall exploit this fact in a moment.

§ The logic behind this approach and its superiority over the intuitive one will become apparent shortly in an example where we recover the results of time-independent perturbation theory from the time-dependent one.

where $\omega_{\min}$ is the smallest of the transition frequencies between the initial state i and any *accessible* final state f‡; it is the smallest of

$$\omega_{fi}=\frac{E_f^0-E_i^0}{\hbar} \tag{18.2.23}$$

In the present case, since $E_n^0=(n^2\hbar^2\pi^2/2mL^2)$, energy differences are of the order $\hbar^2/mL^2$ and

$$T\sim\frac{1}{\omega_{\min}}\simeq\frac{mL^2}{\hbar} \tag{18.2.24}$$

which coincides with Eq. (18.2.19). This is not surprising, for we can also write T in Eq. (18.2.19) as

$$T\simeq\frac{mL^2}{\hbar}\simeq\frac{1}{E_i^0/\hbar}\sim\frac{1}{\omega_i} \tag{18.2.25}$$

Thus T in Eq. (18.2.19) is $\sim\hbar/E_i^0$, while T in eq. (18.2.24) is $\sim\hbar/|E_f^0-E_i^0|_{\min}$. Since the energy levels of a quantum system are all of the same order of magnitude (say a Rydberg or $\hbar\omega$), energies and energy differences are of the same order of magnitude and the two estimates for T are equivalent, unless *the levels are degenerate or nearly so*. In this case, it is $T\sim 1/\omega_{\min}$ that is to be trusted, for it exposes the instability of a degenerate or nearly degenerate system. An explicit example that follows later will illustrate this.

Let us consider one more example of the adiabatic theorem, an oscillator subject to the perturbation

$$H^1(t)=-e\mathscr{E}X\,e^{-t^2/\tau^2} \tag{18.2.26}$$

between $-\infty\le t\le\infty$. We expect that if τ, which measures the time over which H^1 grows from 0 to its peak, tends to infinity, the change in the system will be adiabatic. Thus, if a system starts in the ground state of $H(-\infty)=H^0$ at $t=-\infty$, it will end up in the ground state of $H(\infty)=H(-\infty)=H^0$. Our first-order formula, Eq. (18.2.13), for $P_{0\to 1}$ conforms with this expectation and vanishes exponentially as $\omega\tau\to\infty$. Our formula also tells us what large τ means: it means

$$\omega\tau\gg 1,\qquad \tau\gg 1/\omega \tag{18.2.27}$$

This is what we would expect from the semiclassical estimate or the estimate $T\sim 1/\omega_{\min}$ and the condition $\tau\gg T$.

The adiabatic theorem suggests a way of recovering the results of time-independent perturbation theory from time-dependent theory. Consider a Hamiltonian $H(t)$

‡ This is a state for which $\langle f^0|H^1|i^0\rangle\neq 0$.

which changes continuously from H^0 at $t=-\infty$ to H^0+H^1 at $t=0$:

$$H(t)=H^0+e^{t/\tau}H^1, \qquad -\infty \le t \le 0 \tag{18.2.28}$$

As τ, the rise time of the exponential, goes to infinity, the adiabatic theorem assures us that an eigenstate $|n^0\rangle$ of H^0 at $t=-\infty$ will evolve into the eigenstate $|n\rangle$ of H at $t=0$. If we calculate the state at $t=0$ to a *given order* in *time-dependent* theory and let $\tau\to\infty$, we should get the *time-independent* formula for the state $|n\rangle$ *to that order*. To first order, we know that the projection of the state at $t=0$ along $|m^0\rangle$ $(m\neq n)$ is

$$\begin{aligned} d_m(0) &= \frac{-i}{\hbar}\int_{-\infty}^{0} \langle m^0|H^1|n^0\rangle\, e^{t/\tau}\, e^{i\omega_{mn}t}\, dt \\ &= \frac{(-i/\hbar)\langle m^0|H^1|n^0\rangle}{1/\tau + i\omega_{mn}} \end{aligned} \tag{18.2.29}$$

If we now let $\tau\to\infty$, we regain the familiar result

$$\langle m^0|n\rangle = \frac{\langle m^0|H^1|n^0\rangle}{E_n^0 - E_m^0} \tag{18.2.30}$$

In practice, $\tau\to\infty$ is replaced by some large τ. Equation (18.2.29) tells us what large τ means: it is defined by

$$|1/\tau| \ll |\omega_{\min}|$$

or

$$\tau \gg 1/\omega_{\min} \tag{18.2.31}$$

Thus we see that $T\simeq 1/\omega_{\min}$ is indeed the reliable measure of the natural time scale of the system. In particular, if the system is degenerate (or nearly so), $T\to\infty$ and it becomes impossible, in practice, to change the state of the system adiabatically.

Let us wind up the discussion on the adiabatic approximation by observing its similarity to the WKB approximation. The former tells us that if the Hamiltonian changes *in time* from H^0 to H^0+H^1, the eigenstate $|n^0\rangle$ evolves smoothly into its counterpart $|n\rangle$ in the limit $\tau/T\to\infty$, where τ is the duration over which the Hamiltonian changes and T is the *natural time scale* for the system. The latter tells us that if the potential changes *in space* from V^0 to V^1, a plane wave of momentum $p^0=[2m(E-V^0)]^{1/2}$ evolves smoothly into a plane wave of momentum $p^1=[2m(E-V^1)]^{1/2}$ in the limit $L/\lambda\to\infty$, where L is the *length* over which V changes and $\lambda=2\pi\hbar/p$ is *natural length scale* for the system.

We shall return to adiabatic evolutions in Chapter 21.

The Periodic Perturbation

Consider a system that is subject to a periodic perturbation, say an atom placed between the plates of a condenser connected to an alternating current (ac) source or in the way of a monochromatic light beam. While in reality these perturbations vary as sines and cosines, we consider here the case

$$H^1(t) = H^1 e^{-i\omega t} \tag{18.2.32}$$

Which is easier to handle mathematically. The sines and cosines can be handled by expressing them in terms of exponentials.

Let us say the system comes into contact with this perturbation at $t=0$. The amplitude for transition from $|i^0\rangle$ to $|f^0\rangle$ in time t $(i \neq f)$ is

$$d_f(t) = \left(\frac{-i}{\hbar}\right) \int_0^t \langle f^0|H^1|i^0\rangle \, e^{i(\omega_{fi}-\omega)t'} \, dt' \tag{18.2.33}$$

$$= \frac{-i}{\hbar} \langle f^0|H^1|i^0\rangle \frac{e^{i(\omega_{fi}-\omega)t}-1}{i(\omega_{fi}-\omega)} \tag{18.2.34}$$

The probability for the transition $i \to f$ is

$$P_{i\to f} = |d_f|^2 = \frac{1}{\hbar^2} |\langle f^0|H^1|i^0\rangle|^2 \left\{\frac{\sin[(\omega_{fi}-\omega)t/2]}{(\omega_{fi}-\omega)\frac{1}{2}t}\right\}^2 t^2 \tag{18.2.35}$$

Since the function $(\sin^2 x)/x^2$ is peaked at the origin and has a width $\Delta x \simeq \pi$, we find that the system likes to go to states f such that

$$|(\omega_{fi}-\omega)t/2| \lesssim \pi$$

or

$$E_f^0 t = (E_i^0 t + \hbar\omega t) \pm 2\hbar\pi$$

or

$$E_f^0 - E_i^0 = \hbar\omega \pm \frac{2\hbar\pi}{t} = \hbar\omega\left(1 \pm \frac{2\pi}{\omega t}\right) \tag{18.2.36}$$

For small t, the system shows no particular preference for the level with $E_f^0 = E_i^0 + \hbar\omega$. Only when $\omega t \gg 2\pi$ does it begin to favor $E_f^0 = E_i^0 + \hbar\omega$. The reason is simple. You and I know the perturbation has a frequency ω, say, because we set the dial on the ac source or tuned our laser to frequency ω. But the system goes by what it knows, starting from the time it made contact with the perturbation. In the beginning, it will not even know it is dealing with a periodic perturbation; it must wait a few cycles to get the message. Thus it can become selective only after a few cycles, i.e., after $\omega t \gg 2\pi$. What does it do meanwhile? It Fourier-analyzes the pulse

into its frequency components and its transition amplitude to a state with $E_f^0 = E_i^0 + \hbar\omega_{fi}$ is proportional to the Fourier component at $\omega = \omega_{fi}$. The t' integral in Eq. (18.2.33) is precisely this Fourier transform.‡

What happens if we wait a long time? To find out, we consider the case of a system exposed to the perturbation from $t = -T/2$ to $T/2$ and let $T \to \infty$. Equation (18.2.33) becomes

$$d_f = \lim_{T\to\infty} \frac{-i}{\hbar} \int_{-T/2}^{T/2} H_{fi}^1 e^{i(\omega_{fi}-\omega)t'} \, dt' \tag{18.2.37}$$

$$= \frac{-2\pi i}{\hbar} H_{fi}^1 \delta(\omega_{fi} - \omega) \tag{18.2.38}$$

and

$$P_{i\to f} = \frac{4\pi^2}{\hbar^2} |H_{fi}^1|^2 \delta(\omega_{fi} - \omega)\delta(\omega_{fi} - \omega) \tag{18.2.39}$$

We handle the product of δ functions as follows:

$$\delta\delta = \lim_{T\to\infty} \delta(\omega_{fi} - \omega) \frac{1}{2\pi} \int_{-T/2}^{T/2} e^{i(\omega_{fi}-\omega)t} \, dt \tag{18.2.40}$$

Since the δ function in front of the integral vanishes unless $\omega_{fi} = \omega$, we may set $\omega_{fi} = \omega$ in the integral to obtain

$$\delta\delta = \delta(\omega_{fi} - \omega) \lim_{T\to\infty} \frac{T}{2\pi} \tag{18.2.41}$$

Feeding this into Eq. (18.2.39) for $P_{i\to f}$, and dividing by T, we get the *average transition rate*:

$$R_{i\to f} = \frac{P_{i\to f}}{T} = \frac{2\pi}{\hbar} |\langle f^0 | H^1 | i^0 \rangle|^2 \delta(E_f^0 - E_i^0 - \hbar\omega) \tag{18.2.42}$$

This is called *Fermi's golden rule* and has numerous applications, some of which will be discussed later in this chapter and in the next chapter. You may be worried about the δ function in $R_{i\to f}$ and in particular whether first-order perturbation theory is to be trusted when the rate comes out infinite! As we will see, in all practical applications the δ function will get integrated over for one reason or another. The validity of the first-order formula will then depend only on the area under the δ function. (Recall Exercise 18.2.6.)

‡ The inability of a system to assign a definite frequency to an external perturbation until many cycles have elapsed is a purely classical effect. The quantum mechanics comes in when we relate frequency to energy.

18.3. Higher Orders in Perturbation Theory‡

In Section 18.2 we derived a formula for the transition amplitude from $|i^0\rangle$ to $|f^0\rangle$ to first order in perturbation theory. The procedure for going to higher orders was indicated but not pursued. We address that problem here, using a more abstract formalism, desirable for its compactness and the insight it gives us into the anatomy of the perturbation series.

The basic idea behind the approach is the same as in Section 18.2: we want to isolate the time evolution generated by H^1, for H^0 by itself causes no transitions between its own eigenstates $|i^0\rangle$ and $|f^0\rangle$. To do this, we must get acquainted with other *equivalent* descriptions of quantum dynamics besides the one we have used so far. The description we are familiar with is called the *Schrödinger picture*. In this picture the state of the particle is described by a vector $|\psi_S(t)\rangle$. (We append a subscript S to all quantities that appear in the Schrödinger picture to distinguish them from their counterparts in other pictures.) The physics is contained in the inner products $\langle\omega_S|\psi_S(t)\rangle$ which give the probabilities

$$P(\omega, t)=|\langle\omega_S|\psi_S(t)\rangle|^2 \tag{18.3.1}$$

for obtaining the result ω when Ω is measured. Here $|\omega_S\rangle$ is the normalized eigenket of the operator $\Omega_S(X_S, P_S)$ with eigenvalue ω. Since X_S and P_S are time independent so are Ω_S and $|\omega_S\rangle$. Thus the physics is contained in the dot product of the moving ket $|\psi_S(t)\rangle$ with the stationary kets $|\omega_S\rangle$.

The time evolution of $|\psi_S(t)\rangle$ is given in general by

$$i\hbar\frac{d}{dt}|\psi_S(t)\rangle=H_S|\psi_S(t)\rangle \tag{18.3.2a}$$

and in our problem by

$$i\hbar\frac{d}{dt}|\psi_S(t)\rangle=[H_S^0+H_S^1(t)]|\psi_S(t)\rangle \tag{18.3.2b}$$

The expectation values change according to

$$i\hbar\frac{d}{dt}\langle\Omega_S\rangle=\langle[\Omega_S, H_S]\rangle \tag{18.3.3}$$

If we define a propagator $U_S(t, t_0)$ by

$$|\psi_S(t)\rangle=U_S(t, t_0)|\psi_S(t_0)\rangle \tag{18.3.4}$$

‡ This section may be skimmed through by a reader pressured for time.

it follows from Eq. (18.3.2) [because $|\psi_S(t_0)\rangle$ is arbitrary] that

$$i\hbar \frac{dU_S}{dt} = H_S U_S \tag{18.3.5}$$

Here are some formulas (true for all propagators U) that will be useful in what follows (recall Eq. (4.3.16)):

$$\begin{aligned} U^\dagger U &= I \\ U(t_3, t_2)U(t_2, t_1) &= U(t_3, t_1) \\ U(t_1, t_1) &= I \\ U^\dagger(t_1, t_2) &= U(t_2, t_1) \end{aligned} \tag{18.3.6}$$

The Interaction Picture

Since $U_S(t, t_0)$ is a unitary operator, which is the generalization of the rotation operator to complex spaces, we may describe the time evolution of state vectors as "rotations" in Hilbert space.‡ The rotation is generated by $U_S(t, t_0)$ or equivalently, by $H_S(t) = H_S^0 + H_S^1(t)$. Imagine for a moment that H_S^1 is absent. Then the rotation will be generated by $U_S^0(t)$, which obeys

$$i\hbar \frac{dU_S^0}{dt} = H_S^0 U_S^0 \tag{18.3.7}$$

the formal solution to which is $U_S^0(t, t_0) = e^{-iH_S^0(t-t_0)/\hbar}$. If $H_S^1(t)$ is put back in, both H_S^0 and $H_S^1(t)$ jointly produce the rotation U_S.

These pictorial arguments suggest a way to freeze out the time evolution generated by H_S^0. Suppose we switch to a frame that rotates at a rate that U_S^0 (or H_S^0) by itself generates. In this frame the state vector moves because $H_S^1 \neq 0$. Let us verify this conjecture. To neutralize the rotation induced by U_S^0, i.e., to see things from the rotating frame, we multiply $|\psi_S(t)\rangle$ by $(U_S^0)^\dagger$ to get

$$|\psi_I(t)\rangle = [U_S^0(t, t_0)]^\dagger |\psi_S(t)\rangle \tag{18.3.8a}$$

The ket $|\psi_I(t)\rangle$ is the state vector in the rotating frame, or in the *interaction picture*. If we set $t = t_0$ in the above equation, we did

$$|\psi_I(t_0)\rangle = |\psi_S(t_0)\rangle \tag{18.3.8b}$$

‡ In this section we use the word "rotation" in this generalized sense, and not in the sense of a spatial rotation.

i.e., the interaction and Schrödinger kets coincide at $t=t_0$, which is that instant we switch to the moving frame. The time evolution of $|\psi_I(t)\rangle$ is as follows‡:

$$\begin{aligned} i\hbar\frac{d}{dt}|\psi_I(t)\rangle &= i\hbar\frac{dU_S^{0\dagger}}{dt}|\psi_S\rangle + U_S^{0\dagger}i\hbar\frac{d|\psi_S\rangle}{dt} \\ &= -U_S^{0\dagger}H_S^0|\psi_S\rangle + U_S^{0\dagger}(H_S^0+H_S^1)|\psi_S\rangle \\ &= U_S^{0\dagger}H_S^1|\psi_S\rangle \\ &= U_S^{0\dagger}H_S^1U_S^0U_S^{0\dagger}|\psi_S\rangle \\ &= U_S^{0\dagger}H_S^1U_S^0|\psi_1(t)\rangle \end{aligned}$$

Now

$$(U_S^0)^\dagger H_S^1(t)U_S^0 = H_I^1(t) \tag{18.3.9}$$

is the perturbing Hamiltonian as seen in the rotating frame. So we can write

$$i\hbar\frac{d}{dt}|\psi_I(t)\rangle = H_I^1(t)|\psi_I(t)\rangle \tag{18.3.10}$$

So, as we anticipated, the time evolution of the state vector in the interaction picture is determined by the perturbing Hamiltonian, H_I^1. Despite the fact that the state vector now rotates at a different rate, the physical predictions are the same as in the Schrödinger picture. This is because $P(\omega, t)$ depends only on the inner product between the state vector and the eigenket of Ω with eigenvalue ω, and the inner product between two vectors is unaffected by going to a rotating frame. However, both the state vector and the eigenket appear different in the interaction picture. Just as

$$|\psi_S(t)\rangle \to U_S^{0\dagger}(t, t_0)|\psi_S(t)\rangle = |\psi_I(t)\rangle$$

so does

$$|\omega_S\rangle \to U_S^{0\dagger}(t, t_0)|\omega_S\rangle = |\omega_I(t)\rangle \tag{18.3.11}$$

However,

$$\langle\omega_S|\psi_S(t)\rangle = \langle\omega_I(t)|\psi_I(t)\rangle \tag{18.3.12}$$

The time-dependent ket $|\omega_I(t)\rangle$ is just the eigenket of the time-dependent operator

$$\Omega_I(t) = U_S^{0\dagger}\Omega_S U_S^0 \tag{18.3.13}$$

which is just Ω as seen in the rotating frame:

$$\Omega_I(t)|\omega_I(t)\rangle = U_S^{0\dagger}\Omega_S U_S^0 U_S^{0\dagger}|\omega_S\rangle = U_S^{0\dagger}\Omega_S|\omega_S\rangle = \omega|\omega_I(t)\rangle \tag{18.3.14}$$

‡ Whenever the argument of any U is suppressed, it may be assumed to be (t, t_0).

The time dependence of Ω_I may be calculated by combining Eq. (18.3.13), which defines it, and Eq. (18.3.7), which gives the time evolution of U_S^0:

$$i\hbar\frac{d\Omega_I}{dt}=i\hbar\frac{dU_S^{0\dagger}}{dt}\Omega_S U_S^0+U_S^{0\dagger}\Omega_S i\hbar\frac{dU_S^0}{dt}$$
$$=U_S^{0\dagger}[\Omega_S, H_S^0]U_S^0=[\Omega_I, H_I^0] \tag{18.3.15}$$

In the interaction picture, the operators evolve in response to the unperturbed Hamiltonian H_I^0.‡ Whereas in the Schrödinger picture, the entire burden of time evolution lies with the state vectors, in this picture it is shared by the state vectors and the operators (in such a way that the physics is the same).

Let us now address the original problem, of obtaining a perturbation series for the transition amplitude. We define a propagator $U_I(t, t_0)$ in the interaction picture:

$$|\psi_I(t)\rangle=U_I(t, t_0)|\psi_I(t_0)\rangle \tag{18.3.16}$$

which, because of Eq. (18.3.10), obeys

$$i\hbar\frac{dU_I}{dt}=H_I^1U_I \tag{18.3.17}$$

Once we find $U_I(t)$, we can always go back to $U_S(t)$ by using

$$U_S(t, t_0)=U_S^0(t, t_0)U_I(t, t_0) \tag{18.3.18}$$

which follows from Eqs. (18.3.8) and (18.3.16).

Since H_I^1 depends on time, the solution to Eq. (18.3.17) is not $U_I=\exp(-iH_I^1(t-t_0)/\hbar)$. A formal solution, with the right initial condition, is

$$U_I(t, t_0)=I-\frac{i}{\hbar}\int_{t_0}^{t}H_I(t')U_I(t', t_0)\,dt' \tag{18.3.19}$$

as may be readily verified by feeding it into the differential equation. Since U_I occurs on both sides, this is not really a solution, but an *integral equation*, equivalent to the differential equation (18.3.17), with the right initial condition built in. So we have not got anywhere in terms of the exact solution. But the integral equation provides a nice way to carry out the perturbation expansion. Suppose we want U_I to zeroth order. We drop anything with an H_I^1 in Eq. (18.3.19):

$$U_I(t, t_0)=I+O(H_I^1) \tag{18.3.20}$$

‡ Actually, $H_I^0=U_S^{0\dagger}H_S^0U_S^0=H_S^0$ since $[H_S^0, U_S^0]=0$ in this problem.

This is to be expected, for if we ignore H_I^1, the state vectors do not move in the interaction picture.

To first order, we can keep one only power of H_I^1. So we use the zeroth-order value for U_I in the right-hand side of Eq. (18.3.20) to get

$$U_I(t, t_0) = I - \frac{i}{\hbar}\int_{t_0}^{t} H_I^1(t')\,dt' + O(H_I^2) \tag{18.3.21}$$

Before going to the next order, let us compare this with Eq. (18.2.9) for the transition amplitude $d_f(t)$, computed to first order. Recall the definition of $d_f(t)$: it is the projection along $\langle f_S^0| \exp[iE_f^0(t-t_0)/\hbar]$ at time t, of a state that was initially (at $t = t_0$) $|i_S^0\rangle$‡:

$$\begin{aligned} d_f(t) &= \langle f_S^0| e^{iE_f^0(t-t_0)/\hbar} U_S(t, t_0)|i_S^0\rangle \qquad (18.3.22)\\ &= \langle f_S^0| U_S^{0\dagger}(t, t_0) U_S(t, t_0)|i_S^0\rangle \\ &= \langle f_S^0| U_I(t, t_0)|i_S^0\rangle \qquad (18.3.23)\end{aligned}$$

If we feed into this our first-order propagator given in Eq. (18.3.21), we get

$$\begin{aligned} d_f(t) &= \langle f_S^0| U_I(t, t_0)|i_S^0\rangle \\ &= \delta_{fi} - \frac{i}{\hbar}\int_{t_0}^{t} \langle f_S^0| H_I^1(t')|i_S^0\rangle\,dt' \\ &= \delta_{fi} - \frac{i}{\hbar}\int_{t_0}^{t} \langle f_S^0| U_S^{0\dagger}(t', t_0) H_S^1 U_S^0(t', t_0)|i_S^0\rangle\,dt' \\ &= \delta_{fi} - \frac{i}{\hbar}\int_{t_0}^{t} (H_S^1)_{fi}\, e^{i\omega_{fi}(t'-t_0)}\,dt' \qquad (18.3.24)\end{aligned}$$

which agrees with Eq. (18.2.9) if we set $t_0 = 0$.

Let us now turn to higher orders. By repeatedly feeding into the right-hand side of Eq. (18.3.19) the result for U_I to a known order, we can get U_I to higher orders:

$$\begin{aligned} U_I(t, t_0) = I &- \frac{i}{\hbar}\int_{t_0}^{t} H_I^1(t')\,dt' + (-i/\hbar)^2 \int_{t_0}^{t}\int_{t_0}^{t'} H_I^1(t')H_I^1(t'')\,dt'\,dt'' \\ &+ (-i/\hbar)^3 \int_{t_0}^{t}\int_{t_0}^{t'}\int_{t_0}^{t''} H_I^1(t')H_I^1(t'')H_I^1(t''')\,dt'\,dt''\,dt''' + \cdots \qquad (18.3.25)\end{aligned}$$

‡ We have set $t_0 = 0$ in Section 18.2.

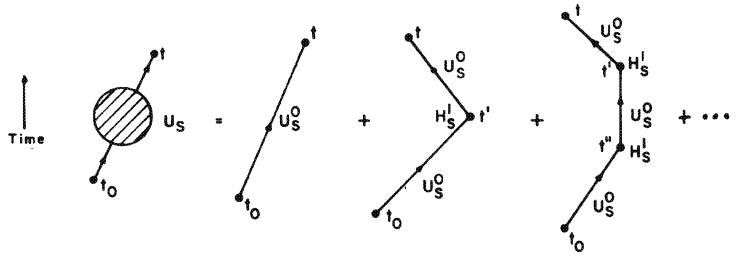

Figure 18.1. A pictorial representation of the perturbation series. The hatched circle represents the full propagator between times t_0 and t. The hatched circle is a sum of many terms, each of which corresponds to a different number of interactions with the perturbation, H_S^1. Between such interactions, the particle evolves in response to just H_S^0, i.e., is propagated by U_S^0.

Premultiplying by $U_S^0(t, t_0)$ and expressing H_I^1 in terms of H_S^1, we get the Schrödinger picture propagator

$$U_S(t, t_0) = U_S^0(t, t_0) - \frac{i}{\hbar}\int_{t_0}^{t} U_S^0(t, t_0)U_S^{0\dagger}(t', t_0)H_S^1 U_S^0(t', t_0)\,dt'$$
$$+(-i/\hbar)^2\int_{t_0}^{t}\int_{t_0}^{t'} U_S^0(t, t_0)U_S^{0\dagger}(t', t_0)H_S^1 U_S^0(t', t_0)U_S^{0\dagger}(t'', t_0)$$
$$\times H_S^1 U_S^0(t'', t_0)\,dt'\,dt'' + \cdots \tag{18.3.26}$$

$$U_S(t, t_0) = U_S^0(t, t_0) - \frac{i}{\hbar}\int_{t_0}^{t} U_S^0(t, t')H_S^1 U_S^0(t', t_0)\,dt'$$
$$+(-i/\hbar)^2\int_{t_0}^{t}\int_{t_0}^{t'} U_S^0(t, t')H_S^1 U_S^0(t', t'')H_S^1 U_S^0(t'', t_0)\,dt'\,dt'' + \cdots$$

The above series could be described by the following words. On the left-hand side we have the complete Schrödinger picture propagator and on the right-hand side a series expansion for it. The first term says the system evolves from t_0 to t in response to just U_S^0, i.e., in response to H_S^0. The second term, if we read it from right to left (imagine it acting on some initial state) says the following: the system evolves from t_0 to t': in response to U_S^0, there it interacts once with the perturbation and thereafter responds to U_S^0 alone until time t. The integral over t' sums over the possible times at which the single encounter with H_S^1 could have taken place. The meaning of the next and higher terms is obvious. These are represented schematically in Fig. 18.1.

If we consider specifically the transition from the state $|i^0\rangle$ to $|f^0\rangle$ (we drop the subscript S everywhere) we get

$$\langle f^0|U(t, t_0)|i^0\rangle = \delta_{fi}\,e^{-iE_f^0(t-t_0)/\hbar} + \frac{-i}{\hbar}\int_{t_0}^{t} e^{-iE_f^0(t-t')/\hbar}\langle f^0|H^1|i^0\rangle\, e^{-iE_i^0(t'-t_0)/\hbar}\,dt'$$
$$+\left(\frac{-i}{\hbar}\right)^2\int_{t_0}^{t}\int_{t_0}^{t'}\sum_n e^{-iE_f^0(t-t')/\hbar}\langle f^0|H^1|n^0\rangle$$
$$\times e^{-iE_n^0(t'-t'')/\hbar}\langle n^0|H^1|i^0\rangle\, e^{-iE_i^0(t''-t_0)/\hbar}\,dt'\,dt'' + \cdots \tag{18.3.27}$$

upon introducing a complete set of eigenstates of H^0 in the second-order term. The meaning of the first term is obvious. The second (reading right to left) says that between t_0 and t' the eigenstate $|i^0\rangle$ picks up just a phase (i.e., responds to H_S^0 alone). At t' it meets the perturbation, which has an amplitude $\langle f^0|H^1|i^0\rangle$ of converting it to the state $|f^0\rangle$. Thereafter it evolves as the eigenstate $|f^0\rangle$ until time t. The total amplitude to end up in $|f^0\rangle$ is found by integrating over the times at which the conversion could have taken place. Thus the first-order transition corresponds to a one-step process $i \to f$. At the second order, we see a sum over a complete set of states $|n^0\rangle$. It means the system can go from $|i^0\rangle$ to $|f^0\rangle$ via any *intermediate or virtual* state $|n^0\rangle$ that H^1 can knock $|i^0\rangle$ into. Thus the second-order amplitude describes a two-step process, $i \to n \to f$. Higher-order amplitudes have a similar interpretation.

The Heisenberg Picture

It should be evident that there exist not just two, but an infinite number of pictures, for one can go to frames rotating at various speeds. Not all these are worthy of study, however. We conclude this section with one picture that is very important, namely, the *Heisenberg picture*. In this picture, one freezes out the *complete time dependence* of the state vector. The Heisenberg state vector is

$$|\psi_H(t)\rangle = U_S^\dagger(t, t_0)|\psi_S(t)\rangle = |\psi_S(t_0)\rangle \tag{18.3.28}$$

The operators in this picture are

$$\Omega_H(t) = U_S^\dagger \Omega_S U_S \tag{18.3.29}$$

and obey

$$i\hbar \frac{d\Omega_H}{dt} = [\Omega_H, H_H] \tag{18.3.30}$$

*Exercise 18.3.1.** Derive Eq. (18.3.30).

Thus in the Heisenberg picture, the state vectors are fixed and the operators carry the full time dependence. (Since the interaction picture lies between this Heisenberg picture and the Schrödinger picture, in that the operators and the state vectors share the time dependence, it is also called the *intermediate picture*. Another name for it is the *Dirac picture*.)

Notice the similarity between Eq. (18.3.30) and the classical equation

$$\frac{d\omega}{dt} = \{\omega, \mathscr{H}\} \tag{18.3.31}$$

The Heisenberg picture displays the close formal similarity between quantum and classical mechanics: to every classical variable ω there is a quantum operator Ω_H, which obeys similar equations; all we need to do is make the usual substitution $\omega \to \Omega$, $\{\ \} \to (-i/\hbar)[\ ,\ ]$. The similarity between Eqs. (18.3.30) and (18.3.31) is even

more striking if we actually evaluate the commutators and Poisson bracket (PB). Consider, for example, the problem of the oscillator for which

$$H_H=\frac{P_H^2}{2m}+\frac{1}{2}m\omega^2X_H^2 \tag{18.3.32}$$

Since X_H, P_H are obtained from X_S, P_S by a unitary transformation, they satisfy the same commutation rules

$$[X_H(t),\,P_H(t)]=U_S^\dagger(t,\,t_0)[X_S,\,P_S]U_S(t,\,t_0)=U_S^\dagger i\hbar I U_S=i\hbar I \tag{18.3.33}$$

Note that the time arguments must be equal in X_H and P_H. Hence Eq. (18.3.33) is called the *equal-time commutation relation*. From Eq. (18.3.30),

$$\dot{X}_H=-\frac{i}{\hbar}[X_H,\,H_H]=\left(-\frac{i}{\hbar}\right)\frac{i\hbar P_H}{m}=\frac{P_H}{m} \tag{18.3.34a}$$

and likewise

$$\dot{P}_H=-m\omega^2X_H \tag{18.3.34b}$$

which are identical in form to the classical equations

$$\begin{aligned}\dot{x}&=\frac{\partial\mathscr{H}}{\partial p}=\frac{p}{m}\\ \dot{p}&=-\frac{\partial\mathscr{H}}{\partial x}=-m\omega^2x\end{aligned} \tag{18.3.35}$$

This is to be expected, because the recipe for quantizing is such that commutators and PB always obey the correspondence [recall Eq. (7.4.40)]

$$\{\omega,\,\lambda\}=\gamma\rightarrow-\frac{i}{\hbar}[\Omega,\,\Lambda]=\Gamma \tag{18.3.36}$$

Although the Heisenberg picture is not often used in nonrelativistic quantum mechanics, it is greatly favored in relativistic quantum field theory.

Exercise 18.3.2. In the paramagnetic resonance problem Exercise 14.4.3 we moved to a frame rotating in *real space*. Show that this is also equivalent to a Hilbert space rotation, but that it takes us neither to the interaction nor the Heisenberg picture, except at resonance. What picture is it at resonance? (If $\mathbf{B}=B_0\mathbf{k}+B\cos\omega t\,\mathbf{i}-B\sin\omega t\,\mathbf{j}$, associate B_0 with H_S^0 and B with H_S^1.)

18.4. A General Discussion of Electromagnetic Interactions

This section contains a summary of several concepts from electro-dynamics that are relevant for the next section. It also deals with certain subtle questions of basic interest, not directly linked to the rest of this chapter.

Classical Electrodynamics

Let us begin with an extremely concise review of this subject.‡ The response of matter to the electromagnetic field is given by the Lorentz force on a charge q:

$$\mathbf{F}=q\left(\mathbf{E}+\frac{\mathbf{v}}{c}\times\mathbf{B}\right) \tag{18.4.1}$$

The response of the fields to the charges is given by Maxwell's equations:

$$\nabla\cdot\mathbf{E}=4\pi\rho \tag{18.4.2}$$

$$\nabla\times\mathbf{E}+\frac{1}{c}\frac{\partial\mathbf{B}}{\partial t}=0 \tag{18.4.3}$$

$$\nabla\cdot\mathbf{B}=0 \tag{18.4.4}$$

$$\nabla\times\mathbf{B}-\frac{1}{c}\frac{\partial\mathbf{E}}{\partial t}=\frac{4\pi}{c}\mathbf{j} \tag{18.4.5}$$

where ρ and $\mathbf{j}$ are the charge and current densities bound by the continuity equation

$$\nabla\cdot\mathbf{j}+\frac{\partial\rho}{\partial t}=0 \tag{18.4.6}$$

Exercise 18.4.1. By taking the divergence of Eq. (18.4.5) show that the continuity equation must be obeyed if Maxwell's equations are to be mutually consistent.

The potentials $\mathbf{A}$ and ϕ are now introduced as follows. Equation (18.4.4), combined with the identity $\nabla\cdot\nabla\times\mathbf{A}\equiv 0$, tells us that $\mathbf{B}$ can be written as a curl

$$\mathbf{B}=\nabla\times\mathbf{A} \tag{18.4.7}$$

‡ For any further information see the classic, *Classical Electrodynamics* by J. D. Jackson, Wiley, New York (1975).

Feeding this into Eq. (18.4.3), we find that

$$\nabla \times \left(\mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} \right) = 0 \tag{18.4.8}$$

Based on the identity $\nabla \times \nabla \phi \equiv 0$, we deduce that $\mathbf{E} + (1/c)\partial \mathbf{A}/\partial t$ can be written as a gradient, or that

$$\mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} - \nabla \phi \tag{18.4.9}$$

If we replace $\mathbf{E}$ and $\mathbf{B}$ by the potentials in the other two Maxwell equations and use the identity $\nabla \times \nabla \times \mathbf{A} \equiv \nabla(\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A}$ (true in Cartesian coordinates) we get the equations giving the response of $\mathbf{A}$ and ϕ to the charges and currents:

$$\nabla^2 \phi + \frac{1}{c} \frac{\partial}{\partial t} (\nabla \cdot \mathbf{A}) = -4\pi \rho \tag{18.4.10}$$

$$\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} - \nabla \left(\nabla \cdot \mathbf{A} + \frac{1}{c} \frac{\partial \phi}{\partial t} \right) = -\frac{4\pi \mathbf{j}}{c} \tag{18.4.11}$$

Before attacking these equations, let us note that there exists a certain arbitrariness in the potentials $\mathbf{A}$ and ϕ, in that it is possible to change them (in a certain way) without changing anything physical. It may be readily verified that $\mathbf{A}$ and ϕ and

$$\mathbf{A}' = \mathbf{A} - \nabla \Lambda \tag{18.4.12}$$

$$\phi' = \phi + \frac{1}{c} \frac{\partial \Lambda}{\partial t} \tag{18.4.13}$$

where Λ is an arbitrary function, lead to the same fields $\mathbf{E}$ and $\mathbf{B}$.

*Exercise 18.4.2.** Calculate $\mathbf{E}$ and $\mathbf{B}$ corresponding to $(\mathbf{A}, \phi)$ and $(\mathbf{A}', \phi')$ using Eqs. (18.4.7) and (18.4.9) and verify the above claim.

Since the physics, i.e., the force law and Maxwell's equations, is sensitive only to $\mathbf{E}$ and $\mathbf{B}$, the transformation of the potentials, called a *gauge transformation*, does not affect it. This is known as *gauge invariance*, Λ is called the *gauge parameter*, and $(\mathbf{A}, \phi)$ and $(\mathbf{A}', \phi')$ are called *gauge transforms* of each other, or said to be *gauge equivalent*.

Gauge invariance may be exploited to simplify Eqs. (18.4.10) and (18.4.11). We consider the case of the free electromagnetic field ($\rho = \mathbf{j} = 0$), which will be of interest

in the next section. In this case the gauge freedom allows us (see following exercise) to choose $\mathbf{A}$ and ϕ such that

$$\nabla \cdot \mathbf{A} = 0 \tag{18.4.14}$$

$$\phi = 0 \tag{18.4.15}$$

This is called the *Coulomb gauge* and will be used hereafter. There is no residual gauge freedom if we impose the above Coulomb gauge conditions and the requirement that $|\mathbf{A}| \to 0$ at spatial infinity. The potential in the Coulomb gauge is thus unique and "physical" in the sense that for a given $\mathbf{E}$ and $\mathbf{B}$ there is a unique $\mathbf{A}$.

*Exercise 18.4.3.** Suppose we are given some $\mathbf{A}$ and ϕ that do not obey the Coulomb gauge conditions. Let us see how they can be transformed to the Coulomb gauge.

(1) Show that if we choose

$$\Lambda(\mathbf{r}, t) = -c \int_{-\infty}^{t} \phi(\mathbf{r}, t')\, dt'$$

and transform to $(\mathbf{A}', \phi')$ then $\phi' = 0$. $\mathbf{A}'$ is just $\mathbf{A} - \nabla\Lambda$, with $\nabla \cdot \mathbf{A}'$ not necessarily zero.

(2) Show that if we gauge transform once more to $(\mathbf{A}'', \phi'')$ via

$$\Lambda' = -\frac{1}{4\pi} \int \frac{\nabla \cdot \mathbf{A}'(\mathbf{r}', t)\, d^3\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}$$

then $\nabla \cdot \mathbf{A}'' = 0$. [Hint: Recall $\nabla^2(1/|\mathbf{r} - \mathbf{r}'|) = -4\pi\delta^3(\mathbf{r} - \mathbf{r}')$.]

(3) Verify that ϕ'' is also zero by using $\nabla \cdot \mathbf{E} = 0$.

(4) Show that if we want to make any further gauge transformations *within* the Coulomb gauge, Λ must be time independent and obey $\nabla^2\Lambda = 0$. If we demand that $|\mathbf{A}| \to 0$ at spatial infinity, $\mathbf{A}$ becomes unique.

In the Coulomb gauge, the equations of motion for the electromagnetic field (away from charges) simplify to

$$\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} = 0 \tag{18.4.16a}$$

$$\nabla \cdot \dot{\mathbf{A}} = 0 \tag{18.4.16b}$$

$$\nabla \cdot \mathbf{A} = 0 \tag{18.4.16c}$$

The first equation tells us that electromagnetic waves travel at the speed c. Of special interest to us are solutions to these equations of the form‡

$$\mathbf{A} = \mathbf{A}_0 \cos(\mathbf{k} \cdot \mathbf{r} - \omega t) \tag{18.4.17}$$

‡ Here $\mathbf{k}$ denotes the wave vector and not the unit vector along the z axis.

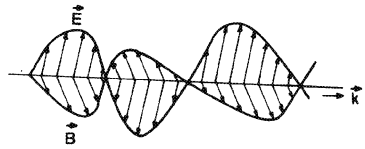

Figure 18.2. The electromagnetic wave at a given time. **E**, **B**, and **k** (the wave vector) are mutually perpendicular.

Feeding this into the wave equation we find

$$\omega^2 = k^2 c^2$$

or

$$\omega = kc \tag{18.4.18}$$

The gauge condition tells us that

$$0 = \nabla \cdot \mathbf{A} = -(\mathbf{k} \cdot \mathbf{A}_0) \sin(\mathbf{k} \cdot \mathbf{r} - \omega t)$$

or

$$\mathbf{k} \cdot \mathbf{A}_0 = 0 \tag{18.4.19}$$

This means that **A** must lie in a plane perpendicular to the direction of propagation, i.e., that electromagnetic waves are *transverse*. The electric and magnetic fields corresponding to this solution are

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} = -\left(\frac{\omega}{c}\right)\mathbf{A}_0 \sin(\mathbf{k} \cdot \mathbf{r} - \omega t) \tag{18.4.20}$$

$$\mathbf{B} = \nabla \times \mathbf{A} = -(\mathbf{k} \times \mathbf{A}_0) \sin(\mathbf{k} \cdot \mathbf{r} - \omega t) \tag{18.4.21}$$

Thus **E** and **B** are mutually perpendicular and perpendicular to **k** (i.e., they are also transverse)—see Fig. 18.2. They have the same magnitude:

$$|\mathbf{E}| = |\mathbf{B}| \tag{18.4.22}$$

The energy flow across unit area (placed normal to **k**) per second is (from any standard text)

$$|\mathbf{S}| = \frac{c}{4\pi} |(\mathbf{E} \times \mathbf{B})| = \frac{\omega^2}{4\pi c} |\mathbf{A}_0|^2 \sin^2(\mathbf{k} \cdot \mathbf{r} - \omega t) \tag{18.4.23a}$$

The time average over a cycle is

$$S_{\text{av}} = \frac{\omega^2}{8\pi c} |\mathbf{A}_0|^2 \tag{18.4.23b}$$

The energy per unit volume is

$$u = (1/8\pi) \cdot [|\mathbf{E}|^2 + |\mathbf{B}|^2] \tag{18.4.24}$$

Notice that $|\mathbf{S}|$ equals the energy density times the velocity of wave propagation.

The Potentials in Quantum Theory

We now ask if quantum mechanics also is invariant under gauge transformations of the potentials. Let us seek the answer to this question in the path integral approach. Recall that

$$U(\mathbf{r}t, \mathbf{r}'t') = N \sum_{\text{paths}} \exp[iS/\hbar] \tag{18.4.25}$$

where N is a normalization factor and the action

$$S = \int_{t'}^{t} \mathscr{L}\, dt'' = \int_{t'}^{t} \left(\frac{1}{2} m|\dot{\mathbf{r}}|^2 + \frac{q}{c} \mathbf{v} \cdot \mathbf{A} - q\phi \right) dt'' \tag{18.4.26}$$

is to be evaluated along each path P that connects $(\mathbf{r}', t')$ and $(\mathbf{r}, t)$. Suppose we perform a gauge transformation of the potentials. Then

$$S \to S_\Lambda = S - \int_{t'}^{t} \frac{q}{c} \left(\mathbf{v} \cdot \nabla\Lambda + \frac{\partial \Lambda}{\partial t''} \right) dt'' \tag{18.4.27}$$

But

$$\mathbf{v} \cdot \nabla\Lambda + \frac{\partial \Lambda}{\partial t''} = \frac{d\Lambda}{dt''} \tag{18.4.28}$$

is the *total derivative* along the trajectory. Consequently

$$S_\Lambda = S + \frac{q}{c} [\Lambda(\mathbf{r}', t') - \Lambda(\mathbf{r}, t)] \tag{18.4.29}$$

It is clear that S and S_Λ imply the same classical dynamics: varying S and varying S_Λ (to find the path of least actions) are equivalent, since S and S_Λ differ only by

$(q/c)\Lambda$ at the end points, and the latter are held fixed in the variation. Going on to the quantum case, we find from Eqs. (18.4.25) and (18.4.29) that

$$U \to U_\Lambda = U \cdot \exp\left\{\frac{iq}{\hbar c}[\Lambda(\mathbf{r}', t') - \Lambda(\mathbf{r}, t)]\right\} \tag{18.4.30}$$

Since

$$U(\mathbf{r}, t; \mathbf{r}', t') = \langle \mathbf{r}| U(t, t')|\mathbf{r}'\rangle \tag{18.4.31}$$

we see that effect of the gauge transformation is equivalent to a change in the coordinate basis:

$$|\mathbf{r}\rangle \to |\mathbf{r}_\Lambda\rangle = e^{(iq\Lambda/\hbar c)}|\mathbf{r}\rangle \tag{18.4.32}$$

which of course cannot change the physics. (Recall, however, the discussion in Section 7.4.) The change in the wave function under the gauge transformation is

$$\psi = \langle \mathbf{r}|\psi\rangle \to \psi_\Lambda = \langle \mathbf{r}_\Lambda|\psi\rangle = e^{-iq\Lambda(\mathbf{r},t)/\hbar c}\psi \tag{18.4.33}$$

This result may also be obtained within the Schrödinger approach (see the following exercise).

Exercise 18.4.4 (Proof of Gauge Invariance in the Schrödinger Approach). (1) Write H for a particle in the potentials $(\mathbf{A}, \phi)$.

(2) Write down H_Λ, the Hamiltonian obtained by gauge transforming the potentials.

(3) Show that if $\psi(\mathbf{r}, t)$ is a solution to Schrödinger's equation with the Hamiltonian H, then $\psi_\Lambda(\mathbf{r}, t)$ given in Eq. (18.4.33) is the corresponding solution with $H \to H_\Lambda$.

Although quantum mechanics is similar to classical mechanics in that it is insensitive to gauge transformations of the potentials, it is different in the status it assigns to the potentials. This is dramatically illustrated in the *Aharonov–Bohm effect*, depicted schematically in Fig. 18.3.‡ The experiment is just the double-slit experiment with one change: there is a small shaded region ($B \neq 0$) where magnetic fluxes comes out of the paper. (You may imagine a tiny solenoid coming out of the paper, inside which are confined the flux lines. These lines must of course return to the other end of the solenoid, but this is arranged not to happen in the experimental region.) The vector potential (in Coulomb gauge) is shown by closed loops surrounding the coil. At a classical level, this variation in the double-slit experiment is expected to make no change in the outcome, for there is no magnetic field along the classical paths P_1 and P_2. There is, of course, an $\mathbf{A}$ field along P_1 and P_2, but the potential has no direct significance in classical physics. Its curl, which is significant, vanishes there.

Consider now the quantum case. In the path integral approach, a particle emitted by the source has the following amplitude to end up at a point $\mathbf{r}$ on the screen, before $\mathbf{B}$ is turned on:

$$\psi(\mathbf{r}) \simeq \psi_{P_1}(\mathbf{r}) + \psi_{P_2}(\mathbf{r}) \tag{18.4.34}$$

‡ For the actual experiment see R. G. Chambers, *Phys. Rev. Lett.*, **5**, 3 (1960).

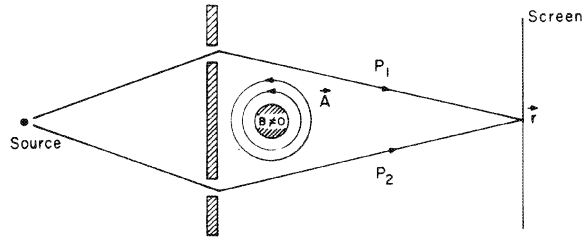

Figure 18.3. An experiment (schematic) that displays the Aharonov–Bohm effect. It is just the double-slit experiment but for the small coil coming out of the paper carrying magnetic flux (indicated by the shaded region marked $B \neq 0$).

where ψ_{P_i} $(i=1, 2)$ is the contribution from the classical path P_i and its immediate neighbors. The interference between these two contributions produces the usual interference pattern. Let us turn on **B**. Now each path gets an extra factor

$$\exp\left[\frac{iq}{\hbar c}\int_{t'}^{t}(\mathbf{v}\cdot\mathbf{A})\,dt''\right]=\exp\left(\frac{iq}{\hbar c}\int_{\text{source}}^{\mathbf{r}}\mathbf{A}\cdot d\mathbf{r}''\right) \tag{18.4.35}$$

Since $\nabla\times\mathbf{A}=0$ near P_1 and P_2, by Stoke's theorem the integral is the same for P_1 and its neighbors and P_2 and its neighbors. But the integral on P_1 is not the same as the integral on P_2, for these paths surround the coil and

$$\int_{P_2}\mathbf{A}\cdot d\mathbf{r}-\int_{P_1}\mathbf{A}\cdot d\mathbf{r}=\oint\mathbf{A}\cdot d\mathbf{r}=\int_S(\nabla\times\mathbf{A})\cdot d\mathbf{s}$$

$$=\int\mathbf{B}\cdot d\mathbf{s}=\Phi\neq 0 \tag{18.4.36}$$

where s is any surface bounded by the closed loop P_1+P_2, and Φ is the flux crossing it, i.e., coming out of the paper in Fig. 18.3. Bearing this in mind, we get

$$\psi(\mathbf{r})=\exp\left(\frac{iq}{\hbar c}\int_{P_1}\mathbf{A}\cdot d\mathbf{r}''\right)\psi_{P_1}(\mathbf{r})+\exp\left(\frac{iq}{\hbar c}\int_{P_2}\mathbf{A}\cdot d\mathbf{r}''\right)\psi_{P_2}(\mathbf{r}) \tag{18.4.37}$$

Pulling out an overall phase factor, which does not affect the interference pattern, we get

$$\psi(\mathbf{r})=\begin{pmatrix}\text{overall}\\ \text{factor}\end{pmatrix}\left[\psi_{P_1}(\mathbf{r})+\exp\left(\frac{iq}{\hbar c}\oint\mathbf{A}\cdot d\mathbf{r}\right)\psi_{P_2}(\mathbf{r})\right]$$

$$=\begin{pmatrix}\text{overall}\\ \text{factor}\end{pmatrix}[\psi_{P_1}(\mathbf{r})+\exp[iq\Phi/\hbar c]\psi_{P_2}(\mathbf{r})] \tag{18.4.38}$$

By varying **B** (and hence Φ) we change the relative phase between the contributions from the two paths and move the interference pattern up and down. Whenever $(q\Phi/\hbar c)=2n\pi$, the pattern will return to its initial form, as if there were no field.

In other words, an integral multiple of the *flux quantum*

$$\Phi_0 = \frac{2\pi\hbar c}{q} \tag{18.4.39}$$

will not make any observable difference to the quantum mechanics of the particle. This idea is very frequently invoked; we shall do so in Chapter 21.

Let us understand how the particle discerns the magnetic field even though the dominant paths all lie in the $\mathbf{B}=0$ region. Suppose I show you Fig. 18.3 but cover the region where the coil is (the shaded region marked $B\neq 0$); will you know there is magnetic flux coming out of the paper? Yes, because the circulating $\mathbf{A}$ lines will tell you that $\oint \mathbf{A}\cdot d\mathbf{r} = \int \mathbf{B}\cdot d\mathbf{s} \neq 0$.‡ The classical particle, however, moves along P_1 *or* P_2, and can have no knowledge of $\oint \mathbf{A}\cdot d\mathbf{r}$. The best it can do is measure $\nabla\times\mathbf{A}$ locally, and that always equals zero. The quantum particle, on the other hand, "goes along P_1 *and* P_2" (in the path integral sense) and by piecing together what happens along P_1 and P_2 (i.e., by comparing the relative phase of the contributions from the two paths) it can deduce not only the existence of $\mathbf{B}$, but also the total flux. Notice that although the particle responds to $\mathbf{A}$ and not directly to $\mathbf{B}$, the response is gauge invariant.

18.5. Interaction of Atoms with Electromagnetic Radiation

We will make no attempt to do justice to this enormous field. We will consider just two illustrative examples. The first is the photoelectric effect in hydrogen (in which the incident radiation knocks the electron out of the atom). The second is the *spontaneous* decay of hydrogen from an excited state to the ground state (decay in the absence of external fields), which can be understood only if the electromagnetic field is treated as a quantum system.

Photoelectric Effect in Hydrogen

Consider a hydrogen atom in its ground state $|100\rangle$ centered at the origin, and on which is incident the wave

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{A}_0 \cos(\mathbf{k}\cdot\mathbf{r} - \omega t) \tag{18.5.1}$$

For energies $\hbar\omega$ sufficiently large, the bound electron can be liberated and will come flying out. We would like to calculate the rate for this process using Fermi's

‡ This is like saying that you can infer the existence of a pole in the complex plane and its residue, without actually going near it, by evaluating $1/2\pi i \oint f(z)\,dz$ on a path that encloses it.

golden rule:

$$R_{i\to f}=\text{rate of transition } i\to f=\frac{2\pi}{\hbar}|\langle f^0|H^1|i^0\rangle|^2\delta(E_f^0-E_i^0-\hbar\omega) \quad (18.5.2)$$

Two points need to be explained before the application of this rule:

(1) For the final state, we must use a positive energy eigenstate of the Coulomb Hamiltonian $H^0=P^2/2m-e^2/r$. Now we argue on intuitive grounds that if the ejected electron is very energetic, we must be able to ignore the pull of the proton on it and describe it by a plane wave $|\mathbf{p}_f\rangle$ in Eq. (18.5.2), with negligible error. While this happens to be the case here, there is a subtle point that is worth noting. If we view the Coulomb attraction of the proton as a perturbation relative to the free-particle Hamiltonian $P^2/2m$, we can write the eigenstate of H^0 as a perturbation series:

$$|f^0\rangle=|\mathbf{p}_f\rangle+\text{higher-order terms}$$

We are certainly right in guessing that $|\mathbf{p}_f\rangle$ dominates the expansion at high energies. But we are assuming more: we are assuming that when we evaluate the matrix element in Eq. (18.5.2) the leading term $|\mathbf{p}_f\rangle$ will continue to dominate the higher-order terms. Clearly, the validity of this assumption depends also on the initial state $|i^0\rangle$ and the operator H^1. Now it turns out that if the initial state is an s state (as in the present case) the higher-order terms are indeed negligible in computing the matrix element, but not otherwise. For instance if the initial state is a p state, the contribution of the first-order term to the matrix element would be comparable to the contribution from the leading term $|\mathbf{p}_f\rangle$. For more details, you must consult a book that is devoted to the subject.‡

(2) The rule applied for potentials of the form $H^1(t)=H^1e^{-i\omega t}$, whereas here [recall Eq. (14.4.11)],§

$$\begin{aligned}H^1(t)&=\frac{-(-e)}{2mc}(\mathbf{A}\cdot\mathbf{P}+\mathbf{P}\cdot\mathbf{A})\\&=\frac{e}{mc}\mathbf{A}\cdot\mathbf{P}\quad(\text{because}\quad\nabla\cdot\mathbf{A}=0)\\&=\frac{e}{mc}\cos(\mathbf{k}\cdot\mathbf{r}-\omega t)\mathbf{A}_0\cdot\mathbf{P}\\&=\frac{e}{2mc}[e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}+e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)}]\mathbf{A}_0\cdot\mathbf{P}\end{aligned} \quad (18.5.3)$$

‡ For example, Section 70 of H. Bethe and E. Salpeter, *Quantum Mechanics of One and Two Electron Atoms*, Plenum, New York (1977). This is also a good place to look for other data on this subject. For instance if you want to know what the expectation value of r^{-4} is in the state $|nlm\rangle$ of hydrogen, you will find it here.

§ We do not include in H^1 the term proportional to $|\mathbf{A}|^2$, which is of second order. The spin interaction $-\gamma\mathbf{S}\cdot\mathbf{B}$ *is* of the first order, but negligible in the kinematical region we will focus on. This will be demonstrated shortly.

Of the two pieces, only the first has the correct time dependence to induce the transition $i \to f$ with $E_f > E_i$; the second will be killed by the energy-conserving delta function. Hereafter we ignore the second term and let

$$H^1(t) = \frac{e}{2mc} e^{i\mathbf{k}\cdot\mathbf{r}} \mathbf{A}_0 \cdot \mathbf{P}\, e^{-i\omega t}$$
$$= H^1 e^{-i\omega t} \tag{18.5.4}$$

With these two points out of the way, we can proceed to evaluate the transition matrix element in the coordinate basis:

$$H^1_{fi} = \frac{e}{2mc} \frac{1}{(2\pi\hbar)^{3/2}} \left(\frac{1}{\pi a_0^3}\right)^{1/2} \int e^{-i\mathbf{p}_f\cdot\mathbf{r}/\hbar}\, e^{i\mathbf{k}\cdot\mathbf{r}} \mathbf{A}_0 \cdot (-i\hbar\nabla)\, e^{-r/a_0}\, d^3\mathbf{r} \tag{18.5.5}$$

Consider the factor $e^{i\mathbf{k}\cdot\mathbf{r}}$. Recall from Chapter 5 that multiplication of a wave function by $e^{i\mathbf{p}_0\cdot\mathbf{r}/\hbar}$ adds to the state a momentum $\mathbf{p}_0$. Thus the factor $e^{i\mathbf{k}\cdot\mathbf{r}}$ represents the fact that a momentum $\hbar\mathbf{k}$ is imparted by the radiation to the atom.‡ For any transition *between atomic levels*, this momentum transferred is neglible compared to the typical momentum p of the electron. We see this as follows. The energy transferred is of the order of a Rydberg:

$$\hbar\omega \sim e^2/a_0 \tag{18.5.6}$$

so that the photon momentum is

$$\hbar k = \frac{\hbar\omega}{c} \simeq \frac{e^2}{a_0 c} \tag{18.5.7}$$

On the other hand, the typical momentum of the electron, estimated from the uncertainty principle, is

$$p \sim \frac{\hbar}{a_0} \tag{18.5.8}$$

Thus

$$\frac{\hbar k}{p} \simeq \frac{e^2}{\hbar c} \simeq \frac{1}{137} \tag{18.5.9}$$

In the present case $\hbar\omega$ is a lot higher because we have a liberated, high-energy electron. But there is still a wide range of ω over which $\hbar k/p \ll 1$. We will work in

‡ You may be worried that there is the $(-i\hbar\nabla)$ operator between $e^{i\mathbf{k}\cdot\mathbf{r}}$ and the atomic wave function. But since $\nabla\cdot\mathbf{A} = 0$, we can also write $\mathbf{A}\cdot\mathbf{P}$ as $\mathbf{P}\cdot\mathbf{A}$, in which case the $e^{i\mathbf{k}\cdot\mathbf{r}}$ will be right next to the atomic wave function.

this domain. In this domain, the ratio of the spin interaction we neglected, to the orbital interaction we are considering, is roughly

$$\frac{\langle (e/2mc)\mathbf{S}\cdot\mathbf{B}\rangle}{\langle (e/mc)\mathbf{A}\cdot\mathbf{P}\rangle}\simeq\frac{\langle \hbar\boldsymbol{\sigma}\cdot\nabla\times\mathbf{A}\rangle}{\langle \mathbf{A}\cdot\mathbf{P}\rangle}\simeq\frac{\hbar k}{p}\ll 1 \tag{18.5.10}$$

which justifies our neglect.

The domain we are working in may also be described by

$$ka_0\ll 1 \tag{18.5.11}$$

[Eq. (18.5.9)]. This means that the phase of the wave changes little over the size of the atom. Since the integral in Eq. (18.5.5) is rapidly cut off beyond $r\simeq a_0$ by the wave function e^{-r/a_0}, we may appropximate $e^{i\mathbf{k}\cdot\mathbf{r}}$ in the integral as

$$e^{i\mathbf{k}\cdot\mathbf{r}}\simeq 1 \tag{18.5.12}$$

This is called the *electric dipole approximation.*‡ The reason is that in this approximation, the atom sees a *spatially* constant electric field,

$$\begin{aligned}\mathbf{E}&=\frac{-1}{c}\frac{\partial\mathbf{A}}{\partial t}\\&=\frac{-1}{c}\frac{\partial}{\partial t}\left(\frac{\mathbf{A}_0}{2}e^{-i\omega t}\right)\S\\&=\frac{i\omega}{2c}\mathbf{A}_0\,e^{-i\omega t}\end{aligned} \tag{18.5.13}$$

and couples to it via its electric dipole moment $\boldsymbol{\mu}=-e\mathbf{R}$:

$$H^1(t)=-\boldsymbol{\mu}\cdot\mathbf{E}=\frac{i\omega e}{2c}\mathbf{A}_0\cdot\mathbf{R}\,e^{-i\omega t} \tag{18.5.14}$$

This must of course coincide with Eq. (18.5.3) in this approximation:

$$H^1(t)=\frac{e}{2mc}\mathbf{A}_0\cdot\mathbf{P}\,e^{-i\omega t} \tag{18.5.15}$$

‡ By keeping higher powers of $\mathbf{k}\cdot\mathbf{r}$ in the expansion, one gets terms known as electric quadrupole, magnetic dipole, electric octupole, magnetic quadrupole, etc. contributions.

§ We ignore the "wrong" frequency part of $\mathbf{A}$.

The equivalence of Eqs. (18.5.14) and (18.5.15) can be demonstrated in a general situation as follows. Since for any

$$H^0=\frac{|\mathbf{P}|^2}{2m}+V(\mathbf{R}) \tag{18.5.16a}$$

it is true that

$$[\mathbf{R}, H^0]=\frac{i\hbar}{m}\mathbf{P} \tag{18.5.16b}$$

we find

$$\begin{aligned}\langle f^0|\mathbf{P}|i^0\rangle &=\frac{m}{i\hbar}\langle f^0|\mathbf{R}H^0-H^0\mathbf{R}|i^0\rangle \\ &=\frac{m}{i\hbar}(E_i^0-E_f^0)\langle f^0|\mathbf{R}|i^0\rangle \\ &=im\omega\langle f^0|\mathbf{R}|i^0\rangle\end{aligned} \tag{18.5.17}$$

so that

$$\begin{aligned}\langle f^0|\frac{e}{2mc}\mathbf{A}_0\cdot\mathbf{P}|i^0\rangle &=\frac{ie\omega}{2c}\mathbf{A}_0\cdot\langle f^0|\mathbf{R}|i^0\rangle \\ &=\langle f^0|(-\boldsymbol{\mu}\cdot\mathbf{E})|i^0\rangle \quad \text{[by Eq. (18.5.14)]}\end{aligned} \tag{18.5.18}$$

Consider now the evaluation of the matrix element H_{fi}^1 in the dipole approximation:

$$H_{fi}^1=N\int e^{-i\mathbf{p}_f\cdot\mathbf{r}/\hbar}\mathbf{A}_0\cdot(-i\hbar\nabla)\,e^{-r/a_0}\,d^3\mathbf{r} \tag{18.5.19}$$

where N is a constant given by

$$N=\left(\frac{e}{2mc}\right)\left(\frac{1}{2\pi\hbar}\right)^{3/2}\left(\frac{1}{\pi a_0^3}\right)^{1/2} \tag{18.5.20}$$

If we integrate the ∇ by parts, we get

$$H_{fi}^1=N\mathbf{A}_0\cdot\mathbf{p}_f\int e^{-i\mathbf{p}_f\cdot\mathbf{r}/\hbar}\,e^{-r/a_0}\,d^3\mathbf{r} \tag{18.5.21}$$

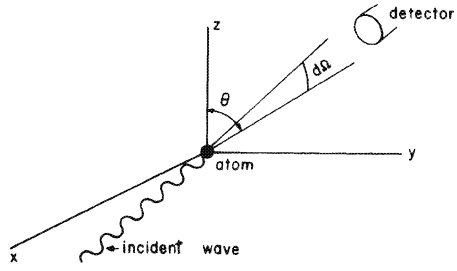

Figure 18.4. The photoelectric effect. In any realistic experiment, the resolution in energy and angle are finite. One asks how many electrons come into the cone of solid angle $d\Omega$ with magnitude of momentum between p and $p+dp$.

(It should now be clear why we prefer the $\mathbf{A}_0\cdot\mathbf{P}$ form of H^1 to the $\mathbf{A}_0\cdot\mathbf{R}$ form.) If we choose the z axis along $\mathbf{p}_f$, the $\mathbf{r}$ integral becomes

$$\begin{aligned}
&\int_0^\infty \int_{-1}^{1} \int_0^{2\pi} e^{-ip_f r\cos\theta/\hbar}\, e^{-r/a_0} r^2\, dr\, d(\cos\theta)\, d\phi \\
&= 2\pi \int_0^\infty \left(\frac{e^{-ip_f r/\hbar} - e^{ip_f r/\hbar}}{-ip_f r/\hbar} \right) e^{-r/a_0} r^2\, dr \\
&= \frac{2\pi\hbar i}{p_f} \left[-\frac{\partial}{\partial(1/a_0)} \right] \int_0^\infty \left[e^{-(1/a_0 + ip_f/\hbar)r} - e^{-(1/a_0 - ip_f/\hbar)r} \right] dr \\
&= \frac{8\pi/a_0}{[(1/a_0)^2 + (p_f/\hbar)^2]^2}
\end{aligned} \tag{18.5.22}$$

Feeding this into Eq. (18.5.5), and the resulting expression into the golden rule, we get the transition rate

$$\begin{aligned}
R_{i\to f} = \frac{2\pi}{\hbar} \left(\frac{e}{2mc} \right)^2 \frac{1}{8\pi^3\hbar^3} \frac{1}{\pi a_0^3} \frac{|\mathbf{A}_0\cdot\mathbf{p}_f|^2 64\pi^2 a_0^6}{[1+(p_f a_0/\hbar)^2]^4} \\
\times \delta(E_f^0 - E_i^0 - \hbar\omega)
\end{aligned} \tag{18.5.23}$$

Now the time has come to tackle the δ function. The δ function gives a singular probability distribution for finding a final electron in a state of *mathematically precise momentum* $\mathbf{p}_f$. This probability is of little interest in practice, where one sets up a detector with a finite opening angle $d\Omega$ and asks how many electrons come into it with magnitude of momentum between p_f and $p_f + dp_f$ (see Fig. 18.4). The δ function tells us that electron momenta are concentrated at

$$\frac{p_f^2}{2m} = E_i^0 + \hbar\omega$$

The contribution from this region is obtained by integrating the δ function over p_f. Using

$$\delta\left(\frac{p_f^2}{2m}-E_i^0-\hbar\omega\right)=\frac{m}{p_f}\,\delta\{p_f-[2m(E_i^0+\hbar\omega)]^{1/2}\} \tag{18.5.24}$$

we get the rate of transition into the detector to be

$$\begin{aligned} R_{i\to d\Omega}&=\frac{2\pi}{\hbar}\,|H_{fi}^1|^2 m p_f\,d\Omega \\ &=\frac{4a_0^3e^2p_f|\mathbf{A}_0\cdot\mathbf{p}_f|^2}{m\pi\hbar^4c^2[1+(p_fa_0/\hbar)^2]^4}\,d\Omega \end{aligned} \tag{18.5.25}$$

{In this and all following expressions, $p_f=[2m(E_i^0+\hbar\omega)]^{1/2}$.} Note that the rate depends only on the magnitude of the applied field $\mathbf{A}_0$, the angle between the polarization $\mathbf{A}_0$ and the outgoing momentum, and the magnitude of $\mathbf{p}_f$ or equivalently ω, the frequency of radiation. The formula above tells us that the electron likes to come parallel to $\mathbf{A}_0$, that is, to the electric field which rips it out of the atom. The direction of the incident radiation does not appear because we set $e^{i\mathbf{k}\cdot\mathbf{r}}=1$. If we keep the $e^{i\mathbf{k}\cdot\mathbf{r}}$ factor it will be seen that the electron momentum is also biased toward $\mathbf{k}$, reflecting the $\hbar\mathbf{k}$ momentum input.

*Exercise 18.5.1.** (1) By going through the derivation, argue that we can take the $e^{i\mathbf{k}\cdot\mathbf{r}}$ factor into account exactly, by replacing $\mathbf{p}_f$ by $\mathbf{p}_f-\hbar\mathbf{k}$ in Eq. (18.5.19).

(2) Verify the claim made above about the electron momentum distribution.

If we integrate $R_{i\to d\Omega}$ over all angles, we get the total rate for ionization. Choosing $\mathbf{A}_0$ along the z axis for convenience, we find

$$\begin{aligned} R_{i\to\text{all}}&=\frac{4a_0^3e^2p_f^3|\mathbf{A}_0|^2}{m\pi\hbar^4c^2[1+(p_fa_0/\hbar)^2]^4}\iint\cos^2\theta\,d(\cos\theta)\,d\phi \\ &=\frac{16a_0^3e^2p_f^3|\mathbf{A}_0|^2}{3m\hbar^4c^2[1+(p_fa_0/\hbar)^2]^4} \end{aligned} \tag{18.5.26}$$

Since this is the rate of ionization, and each ionization takes energy $\hbar\omega$ from the beam, the energy absorption rate is

$$\frac{dE_{\text{abs}}}{dt}=\hbar\omega\cdot R_{i\to\text{all}} \tag{18.5.27}$$

Now the beam brings in energy at the rate $\omega^2|\mathbf{A}_0|^2/8\pi c$ per unit area. Suppose we place, transverse to this beam, a perfectly absorbing disk of area σ. It will absorb

energy at the rate

$$\frac{dE_{\text{abs}}}{dt} = \frac{\sigma |\mathbf{A}_0|^2 \omega^2}{8\pi c} \tag{18.5.28}$$

By comparing Eqs. (18.5.27) and (18.5.28), we see that we can associate with the atom a *photoelectric cross section*

$$\sigma = \frac{8\pi c}{|\mathbf{A}_0|^2 \omega^2} \cdot \hbar\omega \cdot R_{i\to \text{all}} \tag{18.5.29}$$

$$= \frac{128 a_0^3 \pi e^2 p_f^3}{3m\hbar^3 \omega c[1 + p_f^2 a_0^2/\hbar^2]^4} \tag{18.5.30}$$

in the sense that if an ensemble of N (N large) nonoverlapping (separation $\gg a_0$) hydrogen atoms is placed in the way of the beam, the ensemble will absorb energy like a perfectly absorbent disk of area $N\sigma$. We can also associate a *differential cross section* $d\sigma/d\Omega$, with the energy flowing into a solid angle $d\Omega$:

$$\frac{d\sigma}{d\Omega} = \frac{8\pi c}{|\mathbf{A}_0|^2 \omega^2} \hbar\omega R_{i\to d\Omega}$$

$$= \frac{32 a_0^3 e^2 p_f^3 \cos^2\theta}{mc\omega\hbar^3[1 + p_f^2 a_0^2/\hbar^2]^4} \tag{18.5.31}$$

In the region where $p_f a_0/\hbar \gg 1$, the formula simplifies to

$$\frac{d\sigma}{d\Omega} = \frac{32 e^2 \hbar^5 \cos^2\theta}{mc\omega p_f^5 a_0^5} \tag{18.5.32}$$

*Exercise 18.5.2.** (1) Estimate the photoelectric cross section when the ejected electron has a kinetic energy of 10 Ry. Compare it to the atom's geometric cross section $\simeq \pi a_0^2$.

(2) Show that if we consider photoemission from the 1s state of a charge Z atom, $\sigma \propto Z^5$, in the limit $p_f a_0/Z\hbar \gg 1$.

Field Quantization‡

The general formalism, illustrated by the preceding example, may be applied to a host of other phenomena involving the interaction of atoms with radiation. The results are always in splendid agreement with experiment as long the electromagnetic field is of macroscopic strength. The breakdown of the above formalism for weak fields is most dramatically illustrated by the following example. Consider a hydrogen atom in free space (the extreme case of weak field) in the state $|2, l, m\rangle$. What is the rate of decay to the ground state? Our formalism gives an unambiguous answer of

‡ The treatment of this advanced topic will be somewhat concise. You are urged to work out the missing steps if you want to follow it in depth.

zero, for free space corresponds to $\mathbf{A}=0$ (in the Coulomb gauge), so that $H^1=0$ and the atom should be in the stationary state $|2, l, m\rangle$ forever. But it is found experimentally that the atom decays at a rate $R\simeq 10^9$ second^{-1}, or has a mean lifetime $\tau\simeq 10^{-9}$ second. In fact, all excited atoms are found to decay spontaneously in free space to their ground states. This phenomenon cannot be explained within our formalism.

So are we to conclude that our description of free space (which should be the simplest thing to describe) is inadequate? Yes! The description of free space by $\mathbf{A}=\dot{\mathbf{A}}=0$ is *classical*; it is like saying that the ground state of the oscillator is given by $x=p=0$. Now, we know that if the oscillator is treated quantum mechanically, only the *average* quantities $\langle 0|X|0\rangle$ and $\langle 0|P|0\rangle$ vanish in the ground state, and that there are nonzero fluctuations $(\Delta X)^2=\langle 0|X^2|0\rangle$ and $(\Delta P)^2=\langle 0|P^2|0\rangle$ about these mean values. In the same way, if the electromagnetic field is treated quantum mechanically, it will be found that free space (which is the ground state of the field) is described by $\langle\mathbf{A}\rangle=\langle\dot{\mathbf{A}}\rangle=0$ (where $\mathbf{A}$ and $\dot{\mathbf{A}}$ are *operators*)‡ with nonvanishing fluctuations $(\Delta\mathbf{A})^2$, $(\Delta\dot{\mathbf{A}})^2$. The free space is dormant only in the average sense; there are always quantum fluctuations of the fields about these mean values. It is these fluctuations that trigger spontaneous decay.

As long as we restrict ourselves to macroscopic fields, the quantum and classical descriptions of the field become indistinguishable. This is why in going from classical to quantum mechanics, i.e., in going from $\mathscr{H}^1=(e/mc)\mathbf{A}\cdot\mathbf{p}$ to $H^1=(e/mc)\mathbf{A}\cdot\mathbf{P}$, we merely promoted $\mathbf{p}$ to the operator $\mathbf{P}$, but let $\mathbf{A}$ continue to be the classical field. For this reason, this treatment is called the *semiclassical treatment*. We now turn to the full quantum mechanical treatment in which $\mathbf{A}$ will become an operator as well.

The basic idea behind quantizing the field is familiar: one finds a complete set of *canonical* coordinates and momenta to describe the classical field, and promotes them to operators obeying canonical commutation relations. One then takes $\mathscr{H}$, which is just the field energy written in terms of the canonical variables, and obtains H by the usual substitution rule. But there are many obstacles, as we shall see.

Let us start with the coordinaters of the field. If we decide to describe it in terms of the potentials, we have, at each point in space $\mathbf{r}$, four real coordinates $(\phi(\mathbf{r}), \mathbf{A}(\mathbf{r}))$.§ Now, we already know that these coordinates are not entirely physical, in that they can be gauge transformed with no observable consequences. For them to be physical, we must constrain them to a point where there is no residual gauge freedom, say by imposing the Coulomb gauge conditions. Although we shall do so eventually, we treat them as genuine coordinates for the present.

What are the momenta conjugate to these coordinates? To find out, we turn to the Lagrangian:

$$\mathscr{L}=\frac{1}{8\pi}\int[|\mathbf{E}|^2-|\mathbf{B}|^2]\,d^3\mathbf{r}=\frac{1}{8\pi}\int\left[\left|-\frac{1}{c}\frac{\partial\mathbf{A}}{\partial t}-\nabla\phi\right|^2-|\nabla\times\mathbf{A}|^2\right]d^3\mathbf{r}\| \tag{18.5.33}$$

‡ We depart from our convention here and denote classical and quantum field variables by the *same symbols*, because this is what everyone does in this case.

§ Now $\mathbf{r}$ is just a label on the field coordinates and not a dynamical variable.

‖ If you are unfamiliar with this $\mathscr{L}$: Recall that the field energy is $\int(1/8\pi)[|\mathbf{E}|^2+|\mathbf{B}|^2]\,d^3\mathbf{r}$, Eq. (18.4.24). Write this in the gauge $\phi=0$ and change the sign of the term that corresponds to "potential energy." The above result is just the generalization to the gauge with $\phi\neq 0$.

which, when varied with respect to the potentials, gives Maxwell's equations.‡ The momentum conjugate to each "coordinate" is the derivative of $\mathscr{L}$ with respect to the corresponding "velocity." It follows that the momentum conjugate to $\phi(\mathbf{r})$ vanishes (at each point $\mathbf{r}$ in space), for $\dot{\phi}(\mathbf{r})$ does not appear in $\mathscr{L}$. The fact that we are dealing with a coordinate whose conjugate momentum vanishes *identically* tells us that we can not follow the canonical route. But fortunately for us, we have the freedom to work in a gauge where $\phi=0$. So hereafter we can forget all about ϕ and its vanishing conjugate momentum. In particular, we can set $\phi=0$ in Eq. (18.5.33).

Consider now the coordinates $\mathbf{A}(\mathbf{r})$. To find $\Pi_i(\mathbf{r}_0)$, the momentum conjugate to $A_i(\mathbf{r}_0)$, we use the relation

$$\Pi_i(\mathbf{r}_0)=\frac{\partial \mathscr{L}}{\partial \dot{A}_i(\mathbf{r}_0)}$$

In differentiating $\mathscr{L}$ with respect to $\dot{A}_i(\mathbf{r}_0)$, we treat the integral in Eq. (18.5.33) over $\mathbf{r}$ as a sum over the continuous index $\mathbf{r}$. The partial derivative picks out just the term in the sum carrying the index $\mathbf{r}=\mathbf{r}_0$ (because the velocities at different points are independent variables) and gives§

$$\Pi_i(\mathbf{r}_0)=\frac{1}{4\pi c^2}\dot{A}_i(\mathbf{r}_0)=\frac{-E_i(\mathbf{r}_0)}{4\pi c} \tag{18.5.34}$$

or in vector form (dropping the subscript 0 on $\mathbf{r}$)

$$\boldsymbol{\Pi}(\mathbf{r})=\frac{1}{4\pi c^2}\dot{\mathbf{A}}=-\frac{\mathbf{E}}{4\pi c} \tag{18.5.35}$$

Note that $\boldsymbol{\Pi}$ is essentially the electric field.

The natural thing to do at this point would be to promote $\mathbf{A}$ and $\boldsymbol{\Pi}$ to quantum operators obeying canonical commutation rules, and obtain the quantum Hamiltonian H by the substitution rule. But if we did this, we would not be dealing with

‡ See for example, H. Goldstein, *Classical Mechanics*, Addison-Wesley, Reading, Massachusetts (1965), page 366.

§ A more formal treatment is the following. If, say, $\mathscr{L}=\sum_i \dot{q}_i^2$, then we know

$$p_j=\frac{\partial \mathscr{L}}{\partial \dot{q}_j}=\sum_i 2\dot{q}_i\frac{\partial \dot{q}_i}{\partial \dot{q}_j}=\sum_i 2\dot{q}_i\delta_{ij}=2\dot{q}_j$$

Likewise if

$$\mathscr{L}=\int \sum_i \dot{A}_i^2(\mathbf{r})\,d^3\mathbf{r}$$

$$\frac{\partial \mathscr{L}}{\partial \dot{A}_j(\mathbf{r}_0)}=\int \sum_i 2\dot{A}_i(\mathbf{r})\frac{\partial \dot{A}_i(\mathbf{r})}{\partial \dot{A}_j(\mathbf{r}_0)}\,d^3\mathbf{r}$$

$$=\int \sum_i 2\dot{A}_i(\mathbf{r})\delta_{ij}\delta^3(\mathbf{r}-\mathbf{r}_0)\,d^3\mathbf{r}=2\dot{A}_j(\mathbf{r}_0)$$

electrodynamics. The reason is classical and is as follows. Consider the Lagrangian in Eq. (18.5.33) with ϕ set equal to 0. By varying it with respect to the components of $\mathbf{A}$ we get the vector equation

$$\nabla^2\mathbf{A}-\frac{1}{c^2}\frac{\partial^2\mathbf{A}}{\partial t^2}-\nabla(\nabla\cdot\mathbf{A})=0 \tag{18.5.36}$$

which is just

$$\nabla\times\mathbf{B}-\frac{1}{c}\frac{\partial\mathbf{E}}{\partial t}=0$$

in the gauge with $\phi=0$. Two other equations

$$\nabla\cdot\mathbf{B}=0$$

$$\nabla\times\mathbf{E}+\frac{1}{c}\frac{\partial\mathbf{B}}{\partial t}=0$$

are identically satisfied if we write $\mathbf{E}$ and $\mathbf{B}$ in terms of $\mathbf{A}$. (Recall how the potentials were introduced in the first place.) As for the other Maxwell equation, Gauss's law,

$$\nabla\cdot\mathbf{E}=0$$

it does not follow from anything. (We would get this if we varied $\mathscr{L}$ with respect to ϕ, but we have eliminated ϕ from the picture.) It must therefore be appended as an *equation of constraint* on the momentum $\boldsymbol{\Pi}$, which is just $\mathbf{E}$ times a constant. (In contrast to an equation of motion, which has time derivatives in it, an equation of constraint is a relation among the variables at a given time. It signifies that the variables are not independent.) The constraint

$$\nabla\cdot\boldsymbol{\Pi}=0 \tag{18.5.37}$$

tells us that the components of momenta at nearby points are not independent. (Think of the derivatives in ∇ as differences.) We deduce an important feature of the constraint if we take the divergence of Eq. (18.5.36):

$$0=\nabla\cdot\nabla^2\mathbf{A}-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\nabla\cdot\mathbf{A}-\nabla^2\nabla\cdot\mathbf{A}\rightarrow\frac{\partial}{\partial t}(\nabla\cdot\boldsymbol{\Pi})=0 \tag{18.5.38}$$

In other words, the theory without the constraint has a conserved quantity $\nabla\cdot\boldsymbol{\Pi}$, and electrodynamics corresponds to the subset of trajectories in which this constant of motion is zero. Furthermore, if we limit ourselves to these trajectories, we see that $\nabla\cdot\mathbf{A}$ is also a constant of motion. [Write Eq. (18.5.37) as $\nabla\cdot\dot{\mathbf{A}}=0$.] We shall choose this constant to be zero, i.e., work in Coulomb gauge.

How are we to quantize this theory? One way is to ignore the constraints and to quantize the general theory and then try to pick out the subset of solutions (in

the quantum theory) that correspond to electrodynamics. This can be done but is very hard. Let us therefore tackle the constraints at the classical level. The first problem they pose is that they render the variables $\mathbf{A}$ and $\mathbf{\Pi}$ noncanonical, and we do not have a recipe for quantizing noncanonical variables. Let us verify that the constraints indeed imply that $\mathbf{A}$ and $\mathbf{\Pi}$ are noncanonical. Had they been canonical, they would have obeyed the generalizations of

$$\{q_i, p_j\} = \delta_{ij}$$

(with all other PB zero), namely,

$$\{A_i(\mathbf{r}), \Pi_j(\mathbf{r}')\} = \delta_{ij}\delta^3(\mathbf{r}-\mathbf{r}') \tag{18.5.39}$$

(with all other PB zero.) But if we take the divergence of $\mathbf{A}$ with respect to $\mathbf{r}$ or $\mathbf{\Pi}$ with respect to $\mathbf{r}'$, we get zero on the left-hand side but not on the right-hand side.

What we would like to do is the following. We would like to trade $\mathbf{A}$ and $\mathbf{\Pi}$ for a new set of variables that are fewer in number but have the constraints built into them. (This would be like trading the variables x, y, and z constrained by $x^2+y^2+z^2=a^2$ for the angles θ and ϕ on a sphere of radius a.) These variables and the corresponding momenta would be canonical and would automatically reproduce electrodynamics if we start with $\mathscr{H}$ written in terms of these. To quantize, we promote these variables to operators obeying canonical commutation rules. The Hamiltonian and other operators would then be obtained by the substitution rule.

Now the problem with the constraints

$$\nabla\cdot\mathbf{A}=0, \qquad \nabla\cdot\mathbf{\Pi}=0 \tag{18.5.40}$$

called *transversality constraints* (for a reason that will follow) is that they are not algebraic, but differential equations. To render them algebraic, we will trade $\mathbf{A}$ and $\mathbf{\Pi}$ for their Fourier transforms, since differential equations in coordinate space become algebraic when Fourier transformed. It is our hope that the algebraic constraints among the Fourier coefficients will be easier to implement. We will find that this is indeed the case. We will also find a bonus when we are done: the Fourier coefficients are normal coordinates; i.e., when we express the Hamiltonian

$$\mathscr{H}=\frac{1}{8\pi}\int[16\pi^2c^2|\mathbf{\Pi}|^2+|\nabla\times\mathbf{A}|^2]\,d^3\mathbf{r} \tag{18.5.41}$$

(which is obtained from $\mathscr{L}$ by changing the sign of the potential energy term and eliminating $\dot{\mathbf{A}}$ in favor of $\mathbf{\Pi}$) in terms of these, it becomes a sum over oscillator Hamiltonians of decoupled oscillators. This result could have been anticipated for the following reason. If we use the relation $|\nabla\times\mathbf{A}|^2=-\mathbf{A}\cdot\nabla^2\mathbf{A}$, valid when $\nabla\cdot\mathbf{A}=0$, we get

$$\mathscr{H}=\frac{1}{8\pi}\int\sum_i\sum_j[16\pi^2c^2\Pi_i(\mathbf{r})\delta_{ij}\Pi_j(\mathbf{r})-A_i(\mathbf{r})\nabla^2\delta_{ij}A_j(\mathbf{r})]\,d^3\mathbf{r} \tag{18.5.42}$$

which is of the same form as Eq. (7.1.10). [Remember that when we sandwich the derivative operator or the identity operator between two elements of function space, there will be only one (explicit) sum over the continuous index $\mathbf{r}$, the other one being eaten up by the delta functions in the matrix elements.] As the normal modes are the eigenvectors of ∇^2 (which we know are plane waves) the passage to the Fourier coefficients is the passage to normal coordinates.

With all these preliminaries out of the way, let us turn to the Fourier transform of the *unconstrained* A:

$$\mathbf{A}(\mathbf{r}) = \int [\mathbf{a}(\mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{r}} + \mathbf{a}^*(\mathbf{k})\, e^{-i\mathbf{k}\cdot\mathbf{r}}]\, d^3\mathbf{k} \tag{18.5.43}$$

This expansion deserves a few comments.

(1) Since we are Fourier transforming a vector $\mathbf{A}$, the Fourier coefficients are vectors $\mathbf{a}(\mathbf{k})$. [You may view Eq. (18.5.43) as giving three Fourier expansions, one for each component of $\mathbf{A}$.]

(2) Since $\mathbf{A}(\mathbf{r})$ is a *real* function, the Fourier coefficient at $\mathbf{k}$ and $-\mathbf{k}$ must be complex conjugates. Our expansion makes this apparent. Stated differently, one *real* vector function $\mathbf{A}$ in coordinate space cannot specify one *complex* vector function $\mathbf{a}(\mathbf{k})$ in $\mathbf{k}$ space: if we multiply both sides with $e^{-i\mathbf{k}_0\cdot\mathbf{r}}$ and integrate over $\mathbf{r}$, we find that this is indeed the case:

$$\int e^{-i\mathbf{k}_0\cdot\mathbf{r}}\mathbf{A}(\mathbf{r})\, d^3\mathbf{r} = (2\pi)^3[\mathbf{a}(\mathbf{k}_0) + \mathbf{a}^*(-\mathbf{k}_0)] \tag{18.5.44}$$

i.e., $\mathbf{A}(\mathbf{r})$ is seen to determine only the combination $\mathbf{a}(\mathbf{k}) + \mathbf{a}^*(-\mathbf{k})$. We shall exploit this point shortly.

(3) There is no time argument shown in Eq. (18.5.43) because we view it as linear relations between two sets of coordinates, such as the relations

$$x_1 = \frac{x_\mathrm{I} + x_\mathrm{II}}{2^{1/2}}$$

$$x_2 = \frac{x_\mathrm{I} - x_\mathrm{II}}{2^{1/2}}$$

which are understood to be true at all times. The discrete labels 1, 2, I, and II are replaced here by the continuous labels $\mathbf{r}$ and $\mathbf{k}$.

We similarly expand $\mathbf{\Pi}$ (before the transversality constraint is imposed) as

$$\mathbf{\Pi}(\mathbf{r}) = \frac{1}{4\pi i c}\int k[\mathbf{a}(\mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{r}} - \mathbf{a}^*(\mathbf{k})\, e^{-i\mathbf{k}\cdot\mathbf{r}}]\, d^3\mathbf{k} \tag{18.5.45}$$

The factor $(k/4\pi i c)$ is pulled out to simplify future manipulations. Note that the same function $\mathbf{a}(\mathbf{k})$ appears here. There is no conflict, since $\mathbf{\Pi}(\mathbf{r})$ determines a different

combination:

$$\int \boldsymbol{\Pi}(\mathbf{r})\, e^{-i\mathbf{k}_0\cdot\mathbf{r}}\, d^3\mathbf{r} = \frac{(2\pi)^3}{4\pi i c}\, k_0[\mathbf{a}(\mathbf{k}_0) - \mathbf{a}^*(-\mathbf{k}_0)] \tag{18.5.46}$$

It is clear that Eqs. (18.5.44) and (18.5.46) may be solved for $\mathbf{a}(\mathbf{k})$ in terms of $\mathbf{A}$ and $\boldsymbol{\Pi}$: the two real vector functions $\mathbf{A}(\mathbf{r})$ and $\boldsymbol{\Pi}(\mathbf{r})$ determine one complex vector function $\mathbf{a}(\mathbf{k})$. Consider now the vector $\mathbf{a}(\mathbf{k})$ at a given $\mathbf{k}$. We can expand it in terms of any three orthonormal vectors. Rather than choose them to be the unit vectors along the x, y, and z directions, let us choose them (with an eye on the constraints) as a function of $\mathbf{k}$, in the following way:

$$\left.\begin{matrix}\boldsymbol{\varepsilon}(\mathbf{k}1)\\ \boldsymbol{\varepsilon}(\mathbf{k}2)\end{matrix}\right\} \text{ orthonormal vectors in the plane perpendicular to } \mathbf{k}$$
$$\boldsymbol{\varepsilon}(\mathbf{k}3) \quad \text{a unit vector parallel to } \mathbf{k} \tag{18.5.47}$$

If we now expand $\mathbf{a}(\mathbf{k})$ (at each $\mathbf{k}$) as

$$\mathbf{a}(\mathbf{k}) = \sum_{\lambda=1}^{3} (c^2/4\pi^2\omega)^{1/2} a(\mathbf{k}\lambda)\boldsymbol{\varepsilon}(\mathbf{k}\lambda) \tag{18.5.48}$$

(where $\omega = kc$) and feed this into the expansions for $\mathbf{A}$ and $\boldsymbol{\Pi}$, we get

$$\mathbf{A}(\mathbf{r}) = \sum_{\lambda} \int \left(\frac{c^2}{4\pi^2\omega}\right)^{1/2} [a(\mathbf{k}\lambda)\boldsymbol{\varepsilon}(\mathbf{k}\lambda)\, e^{i\mathbf{k}\cdot\mathbf{r}} + a^*(\mathbf{k}\lambda)\boldsymbol{\varepsilon}(\mathbf{k}\lambda)\, e^{-i\mathbf{k}\cdot\mathbf{r}}]\, d^3\mathbf{k} \tag{18.5.49a}$$

$$\boldsymbol{\Pi}(\mathbf{r}) = \sum_{\lambda} \int \frac{1}{i}\left(\frac{\omega}{64\pi^4 c^2}\right)^{1/2} [a(\mathbf{k}\lambda)\boldsymbol{\varepsilon}(\mathbf{k}\lambda)\, e^{i\mathbf{k}\cdot\mathbf{r}} - a^*(\mathbf{k}\lambda)\boldsymbol{\varepsilon}(\mathbf{k}\lambda)\, e^{-i\mathbf{k}\cdot\mathbf{r}}]\, d^3\mathbf{k} \tag{18.5.49b}$$

These equations relate the old coordinates—three real components of $\mathbf{A}$ and three real components of $\boldsymbol{\Pi}$ at each point in $\mathbf{r}$ space—to three complex components of $\mathbf{a}$ at each point in $\mathbf{k}$ space. Since $\mathbf{A}$ and $\boldsymbol{\Pi}$ are canonical variables before we impose transversality, their PB are

$$\begin{aligned} \{A_i(\mathbf{r}), A_j(\mathbf{r}')\} &= 0 \\ \{\Pi_i(\mathbf{r}), \Pi_j(\mathbf{r}')\} &= 0 \\ \{A_i(\mathbf{r}), \Pi_j(\mathbf{r}')\} &= \delta_{ij}\delta^3(\mathbf{r}-\mathbf{r}') \end{aligned} \tag{18.5.50}$$

From these we may deduce (after some hard work) that

$$\begin{aligned} \{a(\mathbf{k}\lambda), a(\mathbf{k}'\lambda')\} &= 0 = \{a^*(\mathbf{k}\lambda), a^*(\mathbf{k}'\lambda')\} \\ \{a(\mathbf{k}\lambda), a^*(\mathbf{k}'\lambda')\} &= -i\delta_{\lambda\lambda'}\delta^3(\mathbf{k}-\mathbf{k}') \end{aligned} \tag{18.5.51}$$

We now address the problem of imposing the constraints, i.e., of regaining electrodynamics. The conditions $\nabla\cdot\mathbf{A}=0$ and $\nabla\cdot\mathbf{\Pi}=0$ tell us [when we apply them to Eqs. (18.5.43) and (18.5.45) and project both sides onto some given $\mathbf{k}$],

$$\mathbf{k}\cdot[\mathbf{a}(\mathbf{k})+\mathbf{a}^*(-\mathbf{k})]=0$$
$$\mathbf{k}\cdot[\mathbf{a}(\mathbf{k})-\mathbf{a}^*(-\mathbf{k})]=0$$

from which we deduce that

$$\mathbf{k}\cdot\mathbf{a}(\mathbf{k})=0 \tag{18.5.52}$$

The two differential equations of constraint have reduced, as anticipated, to (a complex) algebraic constraint. Imposing it on Eq. (18.5.48), we find [using $\mathbf{k}\cdot\boldsymbol{\varepsilon}$ ($\mathbf{k}$, 1 or 2) $=0$],

$$a(\mathbf{k}3)=0 \tag{18.5.53}$$

Thus the constraint tells us something very simple: every $a(\mathbf{k}3)$ is zero. (Since it forces $\mathbf{a}(\mathbf{k})$ to lie in a plane transverse to $\mathbf{k}$, we call it the transversality constraint). Implementation of the transversality constraint is very simple in momentum space: hereafter we let λ take on only the values 1 and 2. Also, setting $a(\mathbf{k}3)=0$ does not change the PB between the remaining a's. Equation (18.5.49) for $\mathbf{A}$ and $\mathbf{\Pi}$ continues to hold, with λ so restricted. However, these fields are now guaranteed to meet the transversality conditions.

Now for the other nice feature of these conditions. If we express $\mathscr{H}$ in terms of these, we get

$$\mathscr{H}=\sum_{\lambda=1}^{2}\int\omega[a^*(\mathbf{k}\lambda)a(\mathbf{k}\lambda)]\,d^3\mathbf{k} \tag{18.5.54}$$

Thus $a(\mathbf{k}\lambda)$ are normal coordinates in the sense that $\mathscr{H}$ contains no cross terms between a's carrying different labels. If we want to get the familiar oscillators, we define real variables

$$\begin{aligned} q(\mathbf{k}\lambda)&=\frac{1}{(2\omega)^{1/2}}[a(\mathbf{k}\lambda)+a^*(\mathbf{k}\lambda)] \\ p(\mathbf{k}\lambda)&=\frac{1}{i}\left(\frac{\omega}{2}\right)^{1/2}[a(\mathbf{k}\lambda)-a^*(\mathbf{k}\lambda)] \end{aligned} \tag{18.5.55}$$

which satisfy the canonical PB relations [as you may verify by combining Eqs. (18.5.51) and (18.5.55)]. In terms of these variables

$$\mathscr{H}=\sum_{\lambda}\int\left[\frac{1}{2}p^2(\mathbf{k}\lambda)+\frac{\omega^2}{2}q^2(\mathbf{k}\lambda)\right]d^3\mathbf{k} \tag{18.5.56}$$

Thus we find that the radiation field is equivalent to a collection of decoupled oscillators: there is an oscillator at each $\mathbf{k}$ and λ (=1 or 2) with frequency $\omega = kc$. The quantization of the radiation field then reduces to the quantization of the oscillator, which has already been accomplished in Chapter 7.

Since $q(\mathbf{k}\lambda)$ and $p(\mathbf{k}\lambda)$ are independent canonical coordinates describing the field, we can quantize the field by promoting these to operators Q and P obeying canonical commutation rules:

$$[Q(\mathbf{k}\lambda), P(\mathbf{k}'\lambda')] = i\hbar\{q, p\} = i\hbar\delta_{\lambda\lambda'}\delta^3(\mathbf{k}-\mathbf{k}')$$

with all other commutators vanishing. As in the case of a single oscillator, it proves useful to work with the combination

$$a(\mathbf{k}\lambda) = \left(\frac{\omega}{2\hbar}\right)^{1/2} Q + i\left(\frac{1}{2\omega\hbar}\right)^{1/2} P$$

and its adjoint

$$a^\dagger(\mathbf{k}\lambda) = \left(\frac{\omega}{2\hbar}\right)^{1/2} Q - i\left(\frac{1}{2\omega\hbar}\right)^{1/2} P \qquad (18.5.57)‡$$

which obey

$$[a(\mathbf{k}\lambda), a^\dagger(\mathbf{k}'\lambda')] = \delta_{\lambda\lambda'}\delta^3(\mathbf{k}-\mathbf{k}') \qquad (18.5.58)$$

and in terms of which $\mathbf{A}$ and $\boldsymbol{\Pi}$,§ which are now Hermitian operators, are given by

$$\mathbf{A} = \sum_\lambda \int \left(\frac{\hbar c^2}{4\pi^2\omega}\right)^{1/2} [a(\mathbf{k}\lambda)\boldsymbol{\varepsilon}(\mathbf{k}\lambda)\, e^{i\mathbf{k}\cdot\mathbf{r}} + a^\dagger(\mathbf{k}\lambda)\boldsymbol{\varepsilon}(\mathbf{k}\lambda)\, e^{-i\mathbf{k}\cdot\mathbf{r}}]\, d^3\mathbf{k} \qquad (18.5.59a)$$

$$\boldsymbol{\Pi} = \sum_\lambda \int \frac{1}{i}\left(\frac{\hbar\omega}{64\pi^4 c^2}\right)^{1/2} [a(\mathbf{k}\lambda)\boldsymbol{\varepsilon}(\mathbf{k}\lambda)\, e^{i\mathbf{k}\cdot\mathbf{r}} - a^\dagger(\mathbf{k}\lambda)\boldsymbol{\varepsilon}(\mathbf{k}\lambda)\, e^{-i\mathbf{k}\cdot\mathbf{r}}]\, d^3\mathbf{k} \qquad (18.5.59b)$$

To find H, we first symmetrize $\mathscr{H}$, i.e., $a^*a \to \frac{1}{2}(a^*a + aa^*)$, make the operator substitution, and use Eq. (18.5.58), to get

$$H = \sum_\lambda \int [a^\dagger(\mathbf{k}\lambda)a(\mathbf{k}\lambda) + \tfrac{1}{2}]\hbar\omega\, d^3\mathbf{k} \qquad (18.5.60)$$

‡ A small point, in case you are following all the details: a and $a^\dagger$ above are the operators corresponding to the classical variables $a/\hbar^{1/2}$ and $a^*/\hbar^{1/2}$. To see this, invert Eq. (18.5.55). All we need hereafter are Eqs. (18.5.57)-(18.5.59).

§ We use the same symbols for the classical and quantum variables in order to follow a widely used convention in this case. It should be clear from the context which is which.

Let us now consider the eigenstates of H. In the field ground state $|0\rangle$, all the oscillators are in their respective ground states. Thus any lowering operator will annihilate $|0\rangle$:

$$a(\mathbf{k}\lambda)|0\rangle = 0 \qquad \text{for all } \mathbf{k}, \lambda \tag{18.5.61}$$

The energy of this state, called the vacuum state or simply *vacuum*, is

$$E_0 = \sum_{\lambda} \int \frac{\hbar\omega}{2} d^3\mathbf{k} \tag{18.5.62}$$

which is the sum over the zero point energies of the oscillators. This constant energy E_0 has no physical consequences.

We now verify the results claimed earlier. In this ground state

$$\begin{aligned} \langle 0|\mathbf{A}|0\rangle &\sim \langle 0|(a + a^\dagger)|0\rangle = 0 \\ \langle 0|\mathbf{\Pi}|0\rangle &\sim \langle 0|(a - a^\dagger)|0\rangle = 0 \end{aligned} \tag{18.5.63}$$

In the above equation we have omitted a lot of irrelevant factors; only the central idea—that $\mathbf{A}$ and $\mathbf{\Pi}$ are linear combinations of creation and destruction operators and hence have no diagonal matrix elements in $|0\rangle$—is emphasized. On the other hand,

$$\begin{aligned} \langle 0||\mathbf{A}|^2|0\rangle &\neq 0 \\ \langle 0||\mathbf{\Pi}|^2|0\rangle &\neq 0 \end{aligned} \tag{18.5.64}$$

for the same reason that $\langle X^2\rangle \neq 0$, $\langle P^2\rangle \neq 0$ for a single oscillator.

If we act on $|0\rangle$ with one of the raising operators, we get

$$a^\dagger(\mathbf{k}\lambda)|0\rangle = |\mathbf{k}\lambda\rangle \tag{18.5.65}$$

where the labels $\mathbf{k}$ and λ tell us that the oscillator bearing that label has gone to its first excited level. This state has energy $\hbar\omega = \hbar kc$ above E_0 as may be verified by letting H act on it and using Eqs. (18.5.58) and (18.5.61). What about the momentum content? Any standard textbook on electrodynamics will tell us that the momentum of the field is given, in classical physics, by

$$\mathscr{P} = \frac{1}{4\pi c} \int (\mathbf{E} \times \mathbf{B})\, d^3\mathbf{r} \tag{18.5.66}$$

If we calculate the corresponding quantum operator we will find that it is given by

$$\mathbf{P} = \sum_{\lambda} \int [a^\dagger(\mathbf{k}\lambda) a(\mathbf{k}\lambda)] \hbar\mathbf{k}\, d^3\mathbf{k} \tag{18.5.67}$$

It is clear on inspection or explicit operation that

$$\mathbf{P}|\mathbf{k}\lambda\rangle = \hbar\mathbf{k}|\mathbf{k}\lambda\rangle \tag{18.5.68}$$

Thus the state $|\mathbf{k}\lambda\rangle$ has momentum $\hbar\mathbf{k}$.

If we apply $a^\dagger(\mathbf{k}\lambda)$ on the vacuum n times, we will create a state with energy $n\hbar\omega$ and momentum $n\hbar\mathbf{k}$. This allows us to view the action of $a^\dagger(\mathbf{k}\lambda)$ as the creation of particles of momenta $\hbar\mathbf{k}$ and energy $\hbar\omega$. These particles, called photons, are massless since

$$m^2c^4 = E^2 - c^2p^2 = (\hbar\omega)^2 - (\hbar kc)^2 = 0 \tag{18.5.69}$$

In terms of photons, we have the correspondence

$$\left\{\begin{matrix}\text{quantum state} \\ \text{of field}\end{matrix}\right\} \leftrightarrow \left\{\begin{matrix}\text{quantum state of} \\ \text{each oscillator}\end{matrix}\right\} \leftrightarrow \left\{\begin{matrix}\text{number of photons} \\ \text{at each } \mathbf{k} \text{ and } \lambda\end{matrix}\right\}$$

For future use, let us obtain the wave function of the photon in the state $(\mathbf{k}, \lambda)$. We begin by deducing the normalization of the states. Combining Eqs. (18.5.65) and (18.5.58) we get

$$\begin{aligned}\langle \mathbf{k}'\lambda' | \mathbf{k}\lambda\rangle &= \langle 0|a(\mathbf{k}'\lambda')a^\dagger(\mathbf{k}\lambda)|0\rangle \\ &= \langle 0|a^\dagger a + \delta_{\lambda\lambda'}\delta^3(\mathbf{k}-\mathbf{k}')|0\rangle \\ &= \delta_{\lambda\lambda'}\delta^3(\mathbf{k}-\mathbf{k}')\end{aligned} \tag{18.5.70}$$

(assuming $\langle 0|0\rangle = 1$). The $\delta^3(\mathbf{k}-\mathbf{k}')$ factor and the fact that $\hbar\mathbf{k}$ is the momentum of the state tell us that the wave function corresponding to $|\mathbf{k}, \lambda\rangle$ is

$$\psi \sim \frac{1}{(2\pi)^{3/2}} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{18.5.71}$$

We use the $\sim$ sign instead of the $\rightarrow$ sign because λ has not entered the wave function yet. From the $\delta_{\lambda\lambda'}$ factor and the way λ entered the picture in the first place, we conclude that λ represents the polarization vector:

$$|\mathbf{k}\lambda\rangle \rightarrow \frac{\boldsymbol{\varepsilon}(\mathbf{k}\lambda)\, e^{i\mathbf{k}\cdot\mathbf{r}}}{(2\pi)^{3/2}} \tag{18.5.72}$$

You may be unhappy over the fact that unlike the $e^{i\mathbf{k}\cdot\mathbf{r}}/(2\pi)^{3/2}$ factor, which followed from analyzing the momentum content of the state [i.e., from the analysis of Eq. (18.5.68)], the $\boldsymbol{\varepsilon}$ was pulled out of a hat. It too may be deduced, starting with angular momentum considerations. We do not do so here.

Since the wave function of the photon is not a scalar, it has spin. Furthermore, since $\boldsymbol{\varepsilon}$ is a three-component object, the spin is unity. However, the requirement that $\mathbf{k}\cdot\boldsymbol{\varepsilon} = 0$ imposes a constraint on the possible orientations of photon spin. Consider, for example, a photon moving along the z axis. The condition $\mathbf{k}\cdot\boldsymbol{\varepsilon} = 0$ tells us that

$\boldsymbol{\varepsilon}$ cannot have a component along the z axis. What does this mean? The component of $\boldsymbol{\varepsilon}$ parallel to the z axis is characterized by the fact that it remains invariant under rotations around the z axis, i.e., transforms like an $s_z=0$ state. So we conclude that the photon can have only $s_z=\pm\hbar$, but not $s_z=0$. More generally, the spin of the photon can only take values $\pm\hbar$ parallel to its momentum. The component of spin parallel to momentum is called *helicity*. The transversality condition restricts the helicity to be $\pm\hbar$—it precludes helicity zero.‡

We consider one last feature of photons before turning to the problem that started this inquiry, namely, spontaneous decay. Consider a state with one photon in $(\mathbf{k}\lambda)$ and another in $(\mathbf{k}'\lambda')$:

$$|\mathbf{k}\lambda, \mathbf{k}'\lambda'\rangle = a^\dagger(\mathbf{k}\lambda)a^\dagger(\mathbf{k}'\lambda')|0\rangle \tag{18.5.73}$$

If we exchange the photon states we get the state

$$|\mathbf{k}'\lambda', \mathbf{k}\lambda\rangle = a^\dagger(\mathbf{k}'\lambda')a^\dagger(\mathbf{k}\lambda)|0\rangle \tag{18.5.74}$$

But since $[a^\dagger, a^\dagger]=0$, the two state vectors coincide, as they should for identical bosons.

Spontaneous Decay

Consider the spontaneous decay of the hydrogen atom from $|2lm\rangle$ to $|100\rangle$. The perturbing Hamiltonian is still given by the substitution rule

$$\mathscr{H}^1 = \frac{e}{mc}\mathbf{A}\cdot\mathbf{p} \to H^1 = \frac{e}{mc}\mathbf{A}\cdot\mathbf{P} \tag{18.5.75}$$

but the $\mathbf{A}$ in H^1 is now the operator in Eq. (18.5.59a).

The initial state of the system (atom + field) is

$$|i^0\rangle = |2lm\rangle \otimes |0\rangle \tag{18.5.76}$$

The final state is

$$|f^0\rangle = |100\rangle \otimes |\mathbf{k}\lambda\rangle \tag{18.5.77}$$

The perturbation H^1 is time independent ($\mathbf{A}$ is the operator in the Schrödinger picture) and

$$E_f^0 - E_i^0 = E_{100} + \hbar\omega - E_{2lm} \tag{18.5.78}$$

‡ The graviton, which is massless and has spin 2, also has only two helicity states, $\pm 2\hbar$. This is a general feature of massless bosons with spin.

From Fermi's golden rule, we get‡

$$R_{i\to f}=\frac{2\pi}{\hbar}\left|\langle f^0|\frac{e}{mc}\mathbf{A}\cdot\mathbf{P}|i^0\rangle\right|^2\delta(E_{100}+\hbar\omega-E_{2lm}) \tag{18.5.79}$$

Consider

$$\langle f^0|\mathbf{A}\cdot\mathbf{P}|i^0\rangle=\langle 100|\langle\mathbf{k}\lambda|\mathbf{A}|0\rangle\cdot\mathbf{P}|2lm\rangle \tag{18.5.80}$$

Now, $\mathbf{A}$ is a sum over a's and $a^\dagger$'s with different labels. The only relevant one is $a^\dagger(\mathbf{k}\lambda)$, which raises $|0\rangle$ to $|\mathbf{k}\lambda\rangle$. Thus, including the factors that accompany $a^\dagger(\mathbf{k}\lambda)$,

$$\langle\mathbf{k}\lambda|\mathbf{A}|0\rangle=\left(\frac{\hbar c^2}{4\pi^2\omega}\right)^{1/2}\boldsymbol{\varepsilon}(\mathbf{k}\lambda)\,e^{i\mathbf{k}\cdot\mathbf{r}} \tag{18.5.81}$$

so that

$$\langle f^0|\mathbf{A}\cdot\mathbf{P}|i^0\rangle=\left(\frac{\hbar c^2}{4\pi^2\omega}\right)^{1/2}\int\psi^*_{100}\,e^{i\mathbf{k}\cdot\mathbf{r}}\boldsymbol{\varepsilon}\cdot(-i\hbar\nabla)\psi_{2lm}\,d^3\mathbf{r}$$

In the dipole approximation, this becomes, upon using Eq. (18.5.17),§

$$\langle f^0|\mathbf{A}\cdot\mathbf{P}|i^0\rangle=\left(\frac{\hbar c^2}{4\pi^2\omega}\right)^{1/2}(im\omega)\int\psi^*_{100}\boldsymbol{\varepsilon}\cdot\mathbf{r}\psi_{2lm}\,d^3\mathbf{r} \tag{18.5.82}$$

From parity considerations, it is clear that only $l=1$ is relevant. Writing $\boldsymbol{\varepsilon}\cdot\mathbf{r}$ in the spherical basis (recall Exercise 15.3.2),

$$\begin{aligned}\boldsymbol{\varepsilon}\cdot\mathbf{r}&=\sum_{-1}^{+1}(-1)^q\varepsilon_1^q r_1^{-q}\\&=-\varepsilon_1^1 r_1^{-1}+\varepsilon_1^0 r_1^0-\varepsilon_1^{-1}r_1^{+1}\end{aligned} \tag{18.5.83}$$

where

$$\varepsilon_1^{\pm1}=\mp\frac{\varepsilon_x\pm i\varepsilon_y}{2^{1/2}},\qquad \varepsilon_1^0=\varepsilon_z \tag{18.5.84}$$

‡ In the photoelectric effect, the field is treated as an external time-dependent perturbation that acts on the atom, and the $\hbar\omega$ in the delta function reflects this time dependence. In the present case, the field is part of the system and the $\hbar\omega$ stands for the change in its energy.

§ We are unfortunately forced to use the symbol m for the mass as well as the z component of angular momentum. It should be clear from the context what m stands for.

and from Eq. (12.5.42),

$$r_1^{\pm 1}=\left(\frac{4\pi}{3}\right)^{1/2} rY_1^{\pm 1}, \qquad r_1^0=\left(\frac{4\pi}{3}\right)^{1/2} rY_1^0 \tag{18.5.85}$$

we get

$$\begin{aligned}\int \psi_{100}^* \boldsymbol{\varepsilon}\cdot\mathbf{r}\psi_{21m}\, d^3\mathbf{r} &= \left(\frac{4\pi}{3}\right)^{1/2} \int R_{10} r R_{21} r^2\, dr \\ &\quad \times\left[\int Y_0^{0*}(-\varepsilon_1^1 Y_1^{-1}+\varepsilon_1^0 Y_1^0-\varepsilon_1^{-1}Y_1^{+1})\, Y_1^m\, d\Omega\right] \\ &= \left(\frac{3}{2}\right)^{1/2} \frac{2^8}{3^5}\frac{a_0}{3^{1/2}}(+\varepsilon_1^1\delta_{m,+1}+\varepsilon_1^0\delta_{m,0}+\varepsilon_1^{-1}\delta_{m,-1}) \end{aligned} \tag{18.5.86}$$

The evaluation of the integrals (like so many other steps in this high-speed treatment) is left as an exercise. The modulus squared of the above quantity is

$$\frac{3}{2}\frac{2^{16}}{3^{10}}\frac{a_0^2}{3}[|\varepsilon_1^1|^2\delta_{m,-1}+|\varepsilon_1^0|^2\delta_{m,0}+|\varepsilon_1^{-1}|^2\delta_{m,1}]$$

If we average over the three initial m's (i.e., over an ensemble of such atoms randomly distributed with respect to m), this reduces to

$$\frac{3}{2}\frac{2^{16}}{3^{10}}\frac{a_0^2}{3}\frac{1}{3}(\varepsilon_x^2+\varepsilon_y^2+\varepsilon_z^2)=\frac{2^{15}a_0^2}{3^{11}} \tag{18.5.87}$$

Notice that the result is independent of the direction of $\boldsymbol{\varepsilon}$. This is to be expected since the atom has no sense of direction after the angular (m) averaging. The transition rate is

$$R_{\bar{i}\to f}=\frac{2\pi}{\hbar}\left(\frac{e}{mc}\right)^2\frac{\hbar c^2}{4\pi^2\omega}m^2\omega^2\frac{2^{15}a_0^2}{3^{11}}\delta(E_{100}+\hbar\omega-E_{21m}) \tag{18.5.88}$$

where $\bar{i}$ means the initial state is averaged over all orientations.

If we sum over all possible photon momenta and two possible polarizations at each momentum, we get, using

$$\int \delta(E_{100}+\hbar\omega-E_{21m})k^2\, dk\, d\Omega=\frac{4\pi k^2}{\hbar c}$$

where

$$k=\frac{\omega}{c}=\frac{E_{2lm}-E_{100}}{\hbar c}=\frac{e^2}{2a_0\hbar c}\left(1-\frac{1}{4}\right)=\frac{3e^2}{8a_0\hbar c}$$

the total decay rate

$$R_{i\to\text{all}}=\left(\frac{2}{3}\right)^8\alpha^5\frac{mc^2}{\hbar} \tag{18.5.89}$$

Recall that

$$\frac{mc^2}{\hbar}=\frac{mc^2c}{\hbar c}\simeq\frac{0.5\times10^6\text{ eV }c}{2000\text{ eV Å}}$$
$$\simeq0.25\times10^3\text{ Å}^{-1}\,c$$

Now $c=3\times10^{10}$ cm/sec $=3\times10^{18}$ Å/sec. So

$$\frac{mc^2}{\hbar}\simeq10^{21}\text{ sec}^{-1}$$

and

$$R_{i\to\text{all}}\simeq(0.67)^8\left(\frac{1}{137}\right)^5 10^{21}\text{ seconds}^{-1}$$
$$\simeq0.6\times10^9\text{ seconds}^{-1}$$

The corresponding mean lifetime is

$$\tau=1/R\simeq1.6\times10^{-9}\text{ seconds} \tag{18.5.90}$$

in excellent agreement with experiment.

Even if the fields are macroscopic, we can use the full quantum theory, though the semiclassical treatment will give virtually identical results. The relation of the two approaches may be described as follows. Consider a process in which an atom goes from the state i_a to the state f_a and the field goes from the state with n photons in $(\mathbf{k}, \lambda)$ to $n+1$ photons in $(\mathbf{k}, \lambda)$.‡ The result we get in the quantum mechanical treatment of this process, which involves the *emission* of a photon, will agree with the semiclassical calculation if we use a classical field $\mathbf{A}$ whose energy density§ is the same as that of $(n+1)$ photons in $(\mathbf{k}, \lambda)$. The 1 in $n+1$ is all important at small n, and contains the key to spontaneous decay. If we consider a process where a photon is *absorbed*, so that $n\to n-1$, the semiclassical method gives the correct answer if we

‡ We do not concern ourselves with other modes, which are spectators.
§ The wavelength and polarization are of course the same as that of the photons.

use a classical field **A** such that the energy density is that of the n photons. The appearance of the $(n+1)$ and n factors is easy to understand in the oscillator language. When a photon is created, the amplitude goes as

$$\langle n+1|a^\dagger|n\rangle = (n+1)^{1/2}\langle n+1|n+1\rangle \tag{18.5.91}$$

which gives the factor $(n+1)$ in the probability, while if it is destroyed,

$$\langle n-1|a|n\rangle = n^{1/2}\langle n-1|n-1\rangle \tag{18.5.92}$$

which gives a factor n in the probability.

It is conventional to separate the emission probability proportional to $n+1$ into the *probability for induced emission*, proportional to n, and the *probability for spontaneous emission*, proportional to 1. The induced emission is induced by the preexisting photons, and the spontaneous emission is—well, spontaneous.

The $(n+1)$ factor in the emission probability is a feature of bosons in general: the probability of a system emitting a boson into a quantum state already occupied by n bosons (of the same kind), is $(n+1)$ times larger than the probability of emission into that state if it is initially unoccupied. This principle is exploited in a laser, which contains a cavity full of atoms in an excited state, ready to emit photons of a fixed frequency but arbitrary directions for $\mathbf{k}$ and λ. The geometry of the cavity is such that photons of a certain $\mathbf{k}$ and λ get trapped in it. Consequently, these trapped photons stay back to influence more and more atoms to emit into the mode $(\mathbf{k}\lambda)$. This is why we call it *l*ight *a*mplification by *s*timulated *e*mission of *r*adiation. (This general principle, in modified form, is exploited in television also: this is the whole idea behind canned laughter.)