17 Time-Dependent Perturbations. Field Quantization and Second Quantization

In the usual quantum framework, the electromagnetic field acting on matter is considered a perturbation. Since the radiation field oscillates, we need tools for the treatment of time-dependent perturbations. The theory developed in Section 17.1 will allow us to deal more generally with the problem of a quantum system subject to a time-dependent perturbation.

We then apply the theory to the interaction of atomic matter with the radiation field and derive what are known in quantum theory as radiative corrections. Section 17.2 is devoted to a detailed discussion of atomic transitions – both induced and spontaneous – with some important applications. The formal introduction of field quantization in Section 17.3 allows us to push the theory beyond the usual limits of QM and to make contact with (nonrelativistic) quantum electrodynamics (QED) and quantum optics.

Section 17.4 presents an alternative, direct derivation of the radiative corrections using SED, where the matter–field interaction is present ab initio. In the same spirit, Section 17.5 provides a physical justification for the quantization of the field (done formally in QED), by deriving the conventionally postulated field operators and their basic commutators.

The chapter ends with a brief introduction to second quantization, an elegant and powerful formalism for describing and analyzing quantum many-body systems.

17.1 Time-Dependent Perturbation Theory

We saw in Chapter 13 that a quantum system changes its state when it is perturbed. Assuming that the state ψ_n is one of the eigenstates of $\widehat{H}_0$, the state Ψ, an eigenstate of the perturbed Hamiltonian $\widehat{H} = \widehat{H}_0 + V$, is written in the general form

$$\Psi_n = \psi_n + \sum_k C_{nk}\psi_k,$$

where the coefficient $C_{nk} = \langle\psi_k|\Psi_n\rangle$ gives the amplitude of the state k of $\widehat{H}_0$ contained in Ψ_n. Therefore, $P_{n\to k} \equiv |C_{nk}|^2$ is the probability that the state of the system changes from ψ_n to Ψ_k as a result of the perturbation. This example shows that one of the most important effects of a perturbation is to produce transitions between states.

So far we have dealt with time-independent perturbations; we will now extend the theory to the time-dependent case by writing the Schrödinger equation

$$i\hbar\frac{\partial\Psi}{\partial t} = \widehat{H}\Psi = (\widehat{H}_0 + \widehat{\mathcal{H}}(t))\Psi, \tag{17.1}$$

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where $\widehat{\mathcal{H}}(t)$ represents the perturbative Hamiltonian. We know that the general solution of the unperturbed problem

$$i\hbar\frac{\partial\psi}{\partial t} = \widehat{H}_0\psi \tag{17.2}$$

can be written in the form

$$\psi(x,t) = \sum_k C_k e^{-iE_kt/\hbar}\varphi_k(x), \tag{17.3}$$

where φ_k are the eigenfunctions of $\widehat{H}_0$ and E_k are the corresponding eigenvalues and the coefficients C_k of the expansion are given by

$$C_k = \int \varphi_k^*(x)\psi(x,0)\,dx. \tag{17.4}$$

To solve Eq. (17.1) we apply the method of variation of parameters, which consists in writing the solutions in the form (17.3), but with the constants C_k replaced by respective functions of time to be determined,

$$\Psi = \sum_k C_k(t)e^{-iE_kt/\hbar}\varphi_k(x). \tag{17.5}$$

Substituting into Eq. (17.1) and simplifying gives

$$i\hbar\sum_k \dot{C}_k(t)e^{-iE_kt/\hbar}\varphi_k(x) = \sum_k C_k(t)e^{-iE_kt/\hbar}\widehat{\mathcal{H}}(t)\varphi_k(x),$$

and multiplying by φ_l^* and integrating over x, we get

$$\dot{C}_l(t) = -\frac{i}{\hbar}\sum_k C_k(t)e^{i(E_l-E_k)t/\hbar}\mathcal{H}_{lk}, \tag{17.6}$$

where

$$\mathcal{H}_{lk} = \int \varphi_l^*\widehat{\mathcal{H}}(t)\varphi_k dx. \tag{17.7}$$

Integrating (17.6) over time, assuming that the perturbation is applied at time $t = 0$, we obtain

$$C_l(t) = C_l(0) - \frac{i}{\hbar}\sum_k \int_0^t C_k(t')e^{i\omega_{lk}t'}\mathcal{H}_{lk}dt', \tag{17.8}$$

where $\omega_{kn} = (E_k - E_n)/\hbar$. From (17.4) it follows that the initial value of $C_l(t)$ is

$$C_l(0) = \int \varphi_l^*(x)\Psi(x,0)dx. \tag{17.9}$$

We will limit ourselves to the special case in which the system, before being perturbed, is in an eigenstate of $\widehat{H}_0$, $\Psi(x,0) \equiv \Psi_n(x,0) = \varphi_n(x)$; it follows from (17.9) that $C_k(0) = \delta_{nk}$. Since $\Psi_n(t)$ is the wave function we are looking for, we add the index n to the coefficients of the expansion (17.5) and write

$$\Psi_n(t) = \sum_k C_{nk}(t)e^{-iE_kt/\hbar}\varphi_k(x), \quad C_{nk}(0) = \delta_{nk}. \tag{17.10}$$

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To solve the system of integral equations (17.8), which is exact, we perform a perturbative expansion of the coefficients,

$$C_{nk}(t) = C_{nk}(0) + C_{nk}^{(1)}(t) + C_{nk}^{(2)}(t) + \cdots . \tag{17.11}$$

Substituting into Eq. (17.8) gives

$$\begin{aligned} C_{nl}(t) &= C_{nl}(0) - \frac{i}{\hbar}\sum_k \int_0^t \left(C_{nk}(0) + C_{nk}^{(1)}(t') + \cdots .\right) e^{i\omega_{lk}t'}\mathcal{H}_{lk}dt' \\ &= C_{nl}(0) - \frac{i}{\hbar}\int_0^t e^{i\omega_{ln}t'}\mathcal{H}_{ln}dt' - \frac{i}{\hbar}\sum_k \int_0^t \left(C_{nk}^{(1)}(t') + \cdots .\right) e^{i\omega_{lk}t'}\mathcal{H}_{lk}dt', \end{aligned} \tag{17.12}$$

from which it follows that

$$C_{nk}^{(1)}(t) = -\frac{i}{\hbar}\int_0^t e^{i\omega_{kn}t'}\mathcal{H}_{kn}(t')dt', \tag{17.13}$$

$$\begin{aligned} C_{nl}^{(2)}(t) &= -\frac{i}{\hbar}\sum_k \int_0^t \left(C_{nk}^{(1)}(t') + \cdots .\right) e^{i\omega_{lk}t'}\mathcal{H}_{lk}dt' \\ &= \left(-\frac{i}{\hbar}\right)^2 \sum_k \int_0^t dt' \int_0^{t'} dt'' e^{i\omega_{lk}t'}\mathcal{H}_{lk}(t')e^{i\omega_{kn}t''}\mathcal{H}_{kn}(t''), \end{aligned} \tag{17.14}$$

and so on. $C_{nl}^{(2)}(t)$ is often rewritten in a more convenient form, taking into account that the unperturbed states, eigenstates of $\widehat{H}_0$, form a complete basis,

$$\begin{aligned} C_{nl}^{(2)}(t) &= \left(-\frac{i}{\hbar}\right)^2 \sum_k \int_0^t dt' \int_0^{t'} dt'' \\ &\quad \times \langle l|\, e^{iE_l t'/\hbar}\hat{\mathcal{H}}(t')e^{-iE_k t'/\hbar}\,|k\rangle\,\langle k|\, e^{iE_k t''/\hbar}\hat{\mathcal{H}}(t'')e^{-iE_n t''/\hbar}\,|n\rangle \\ &= \left(-\frac{i}{\hbar}\right)^2 \sum_k \int_0^t dt' \int_0^{t'} dt'' \\ &\quad \times \langle l|\, e^{i\widehat{H}_0 t'/\hbar}\hat{\mathcal{H}}(t')e^{-i\widehat{H}_0 t'/\hbar}\,|k\rangle\langle k|\, e^{i\widehat{H}_0 t''/\hbar}\hat{\mathcal{H}}(t'')e^{-i\widehat{H}_0 t''/\hbar}\,|n\rangle\,, \end{aligned} \tag{17.15}$$

that is,

$$C_{nk}^{(2)}(t) = -\frac{1}{\hbar^2}\int_0^t dt' \int_0^{t'} dt''\,\langle k|\, e^{i\widehat{H}_0 t'/\hbar}\hat{\mathcal{H}}(t')e^{i\widehat{H}_0(t''-t')/\hbar}\hat{\mathcal{H}}(t'')e^{-i\widehat{H}_0 t''/\hbar}\,|n\rangle\,. \tag{17.16}$$

In Eq. (17.15), the matrix elements of the interaction Hamiltonian appear in the Heisenberg picture relative to the unperturbed Hamiltonian, that is, in the interaction representation, as briefly explained in Section 8.6.6. The first-order approximation, which is sufficient in many cases of interest, is valid as long as the coefficients $C_{nk}(t)$ do not differ much from their initial value.

Equations (17.13)–(17.16) show that the perturbation produces transitions to the states k connected to the initial state n by the matrix of the perturbing potential or its products. After an important example of induced vibrations, we will separately consider two general cases of great interest.

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Exercise E17.1. Rabi oscillations in EPR

Use Eq. (17.6) to study the time evolution of the population of the two energy levels in electron (paramagnetic) spin resonance.

Solution. As shown in Section 14.3.3, resonant transitions occur when electrons are subject to a constant magnetic field $B_z = B_0$ and a perpendicular field $\boldsymbol{B}_1$ that oscillates with frequency very close to the transition frequency between levels.

Here, in contrast to Section 14.3.3, we consider the uniform field as part of the unperturbed Hamiltonian and the oscillating field as a perturbation. The unperturbed Hamiltonian is then

$$\widehat{H}_0 = 2\frac{e_0 B_0}{2mc}\widehat{S}_z = 2\omega_L \widehat{S}_z = \tfrac{1}{2}\hbar\omega_0 \hat{\sigma}_z, \tag{17.17}$$

where $\omega_L = e_0 B_0/2mc$ is the Larmor frequency and $\omega_0 = 2\omega_L$ twice this frequency (or cyclotron frequency); the unperturbed eigenenergies are $E_1 = \frac{1}{2}\hbar\omega_0$, $E_2 = -\frac{1}{2}\hbar\omega_0$, and the unperturbed states are the eigenvectors of $\widehat{S}_z$.

Using the rotating-wave approximation (RWA), we assume that the rotating field of interest (the other component is neglected) rotates against the clock in the xy-plane and has the form

$$\boldsymbol{B}_1(t) = B_1\left(\mathbf{i}\cos\omega t + \mathbf{j}\sin\omega t\right), \tag{17.18}$$

so that the perturbation Hamiltonian is

$$\hat{\mathcal{H}}(t) = \omega_B\left(\cos\omega t\,\widehat{S}_x + \sin\omega t\,\widehat{S}_y\right), \tag{17.19}$$

or, in explicit matrix form (compare with Eq. (14.52)),

$$\hat{\mathcal{H}}(t) = \tfrac{1}{2}\hbar\omega_B \begin{pmatrix} 0 & e^{-i\omega t} \\ e^{i\omega t} & 0 \end{pmatrix}, \tag{17.20}$$

with $\omega_B = 2\mu_0 B_1/\hbar$.

As only two levels are active, the system of Eq. (17.6) is reduced to

$$\begin{aligned} i\hbar\frac{dC_1}{dt} &= C_1\mathcal{H}_{11}e^{i\omega_{11}t} + C_2\mathcal{H}_{12}e^{i\omega_{12}t}, \\ i\hbar\frac{dC_2}{dt} &= C_1\mathcal{H}_{21}e^{i\omega_{21}t} + C_2\mathcal{H}_{22}e^{i\omega_{22}t}, \end{aligned} \tag{17.21}$$

with $\omega_{11} = \omega_{22} = 0$ and $\omega_{12} = -\omega_{21} = \omega_0$. From Eq. (17.20), the nondiagonal matrix elements of $\hat{\mathcal{H}}(t)$ are $\mathcal{H}_{12} = \mathcal{H}_{21}^* = \frac{1}{2}\hbar\omega_B e^{-i\omega t}$, so that

$$\frac{dC_1}{dt} = -\tfrac{1}{2}i\omega_B e^{-i(\omega-\omega_0)t}C_2, \tag{17.22}$$

$$\frac{dC_2}{dt} = -\tfrac{1}{2}i\omega_B e^{i(\omega-\omega_0)t}C_1. \tag{17.23}$$

To solve this system it is convenient to decouple the equations; this is easily done by deriving the first and in the second substituting the result to eliminate C_2. This gives

$$\frac{d^2C_1}{dt^2} + i(\omega-\omega_0)\frac{dC_1}{dt} + \left(\tfrac{1}{2}\omega_B\right)^2 C_1 = 0, \tag{17.24}$$

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the general solution of which is

$$C_1 = Ce^{-i(\omega-\omega_0)t/2} \sin\left(\tfrac{1}{2}\Omega t + \alpha\right), \tag{17.25}$$

$$\Omega^2 = (\omega - \omega_0)^2 + \omega_B^2. \tag{17.26}$$

The coefficient C_2 follows immediately from Eq. (17.22),

$$C_2 = \frac{C}{\omega_B} e^{i(\omega-\omega_0)t/2} \left[i\Omega \cos\left(\tfrac{1}{2}\Omega t + \alpha\right) + (\omega - \omega_0) \sin\left(\tfrac{1}{2}\Omega t + \alpha\right)\right]. \tag{17.27}$$

The quantities $|C_1(t)|^2$ and $|C_2(t)|^2$ determine the instantaneous populations of the respective levels. If initially only the lower level is populated ($C_1 = 0, C_2 = 1$), we must put $\alpha = 0$, $C = -i\omega_B/\Omega$, and we are left with

$$|C_1(t)|^2 = 1 - |C_2(t)|^2 = \left(\frac{\omega_b}{\Omega}\right)^2 \sin^2 \tfrac{1}{2}\Omega t.$$

These results show that transitions between the two states occur periodically with a frequency Ω that depends on the coupling, as follows from (17.26). These transitions are known as Rabi oscillations. At resonance, $\omega = \omega_0$, and Ω reaches its minimum value, $\Omega_{\text{res}} = \omega_B$; in this case both levels are populated on average with equal probability,

$$|C_1(t)|^2 = \sin^2 \tfrac{1}{2}\Omega t, \quad |C_2(t)|^2 = \cos^2 \tfrac{1}{2}\Omega t.$$

17.1.1 Perturbations acting for finite times

We now consider the case of a potential V applied to the system at $t = 0$ and disappearing after some time. For times t sufficiently larger than the duration of V (e.g., for $t = \infty$), the coefficients C will have reached their final value and the wave function will be a superposition of eigenstates of the original Hamiltonian $\widehat{H}_0$, $\Psi_n = \sum_k C_{nk}(\infty) e^{-iE_k t/\hbar} \varphi_k(x)$. Since $C_{nk}(\infty)$ is the amplitude of the state k contained in Ψ_n, the transition probability from the initial state n to the state k during the perturbation is to first order given by Eq. (17.13),

$$w_{nk} = |C_{nk}^{(1)}(\infty)|^2 = \frac{1}{\hbar^2} \left| \int_0^\infty V_{kn} e^{i\omega_{kn}t} dt \right|^2, \quad k \neq n. \tag{17.28}$$

Suppose that the potential V changes very little over time intervals of the order of ω_{kn}^{-1}; in this case, due to the oscillations of the integrand, the integral is small. We conclude that when a perturbation varies adiabatically, that is, very slowly, a system in a nondegenerate stationary state remains in it. If there is degeneracy between states k and n, the previous argument does not hold, because $\omega_{kn} = 0$ and transitions between these states will occur since they do not imply an energy exchange. In this case, the preceding theory is not satisfactory, but the problem can be solved explicitly starting from the exact equation (17.8) (see problem P17.1).

The opposite extreme case, corresponding to a pulse of height V and width Δt in the limit where Δt tends to zero but the area $V\Delta t$ remains constant, is more difficult to

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analyze, but allows us to observe an interesting phenomenon. Assuming that the pulse is applied at time t_1, we obtain directly from Eq. (17.13) with $\int_0^\infty dt \Rightarrow \int_{t_1}^{t_1+\Delta t} dt$, that

$$C_{nk}^{(1)} = \frac{V_{kn}}{\hbar\omega_{kn}} e^{i\omega_{kn}t_1}\left(1 - e^{i\omega_{kn}\Delta t}\right), \quad \omega_{kn} \neq 0. \tag{17.29}$$

The second term of this expression gives the (first-order) coefficients of the expansion of Ψ_n at time $t + \Delta t$ of the complete Hamiltonian $\widehat{H}$ in terms of the eigenfunctions φ_n of $\widehat{H}_0$ and, therefore, does not contribute to the transitions between the states n and k. The transition probability from the initial state n to the state k is then given by the first term in Eq. (17.29) and is

$$w_{nk} = \frac{|V_{kn}|^2}{\hbar^2\omega_{kn}^2} = \frac{|V_{kn}|^2}{(E_n - E_k)^2}. \tag{17.30}$$

We can verify that Eq. (17.30) is correct by analyzing the meaning of each of the two terms in Eq. (17.29). In general, whatever the size of the pulse, if we know the eigenfunctions Ψ_k of $\widehat{H}$ and φ_n of $\widehat{H}_0$, we can calculate the transition probability between these states by using the formula

$$w_{nk} = \left|\int \Psi_k^* \varphi_n dx\right|^2. \tag{17.31}$$

In the particular case of a small pulse, the eigenvalues of $\widehat{H}$ essentially coincide with those of $\widehat{H}_0$, so we can write $\widehat{H}_0\varphi_n = E_n\varphi_n$ and $\widehat{H}\Psi_k \approx E_k\Psi_k$; from the first of these equations and the conjugate of the second, it follows that

$$\begin{aligned}\int (\varphi_n \widehat{H}^* \Psi_k^* - \Psi_k^* \widehat{H}_0\varphi_n)dx &= \int (\Psi_k^* \widehat{H}\varphi_n - \Psi_k^* \widehat{H}_0\varphi_n)dx = \int \Psi_k^* V\varphi_n dx \\ &= \int (\varphi_n E_k\Psi_k^* - \Psi_k^* E_n\varphi_n)dx = (E_k - E_n)\int \Psi_k^*\varphi_n dx,\end{aligned} \tag{17.32}$$

and from here we get to first order

$$\int \Psi_k^*\varphi_n dx = \frac{\int \Psi_k^* V\varphi_n dx}{E_k - E_n} \simeq \frac{\int \varphi_k^* V\varphi_n dx}{E_k - E_n} = \frac{V_{kn}}{\hbar\omega_{kn}}, \tag{17.33}$$

since for a small perturbation the eigenfunctions of $\widehat{H}$ and $\widehat{H}_0$ are equal to zero order; from here Eq. (17.30) follows immediately. The term we neglected when we took $\Psi_k^* \to \varphi_k^*$ corresponds to the additional term in (17.29), which we must also neglect there when calculating w_{nk}.

Let us now consider the case of a potential V which is switched on at $t = 0$ and switched off after a long time t. From Eqs. (17.11) and (17.13), it follows that

$$C_{nn} = 1 - \frac{i}{\hbar}\int_0^t V_{nn}dt = 1 - \frac{iV_{nn}}{\hbar}t \simeq e^{-iV_{nn}t/\hbar}, \tag{17.34}$$

which shows that the first-order energy correction is V_{nn}, in agreement with the time-independent perturbation theory. Analogously,

$$C_{nk} = -\frac{iV_{kn}}{\hbar}\int_0^t e^{i\omega_{kn}t'}dt' = \frac{V_{kn}}{\hbar\omega_{kn}}(1 - e^{i\omega_{kn}t}). \tag{17.35}$$

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As before, the second term of this expression is the one that transforms the stationary states of $\widehat{H}_0$ into the corresponding stationary states of $\widehat{H}$. Taking this into account, the term $C_{nk}^{(1)} = V_{kn}/\hbar\omega_{kn} = V_{kn}/(E_k - E_n)$ gives the first-order correction to the wave function, in correspondence with the time-independent perturbation theory. The transition probability between states n and k at time t is given by

$$w_{nk} = |C_{nk}|^2 = \frac{|V_{kn}|^2}{\hbar^2\omega_{kn}^2}\left|1 - e^{i\omega_{kn}t}\right|^2 = \frac{4|V_{kn}|^2}{\hbar^2}\frac{\sin^2\frac{1}{2}\omega_{kn}t}{\omega_{kn}^2}. \tag{17.36}$$

For nondegenerate states, w_{nk} remains small for all time if $|V_{kn}|$ is small; conversely, if $|V_{kn}|$ is large, (17.36) holds only for times small enough for $|V_{kn}|t \ll \hbar$ to hold. If the state is degenerate, then the amplitude of the transition between degenerate states ($\omega_{kn} = 0$) increases with time, and the previous expression holds only for short times, as in the previous case of large perturbations. From this we conclude that the smallest perturbation is sufficient to produce transitions between the different degenerate states.

The transition probability between states n and k per unit time is defined as

$$W_{nk} \equiv \frac{|C_{nk}|^2}{t} = \frac{4|V_{kn}|^2}{\hbar^2}\frac{\sin^2\frac{1}{2}\omega_{kn}t}{\omega_{kn}^2 t}. \tag{17.37}$$

This function is only significantly different from zero for $|\omega_{kn}|t \leq \pi$, that is, $|E_n - E_k|t \leq \pi\hbar$, and approaches zero with time as shown in Fig. 17.1. Thus, while for very short times the perturbation can cause transitions between states whose energies differ by an arbitrary amount, as time progresses, the most favored transitions are those between states of increasingly closer energies, until at $t \to \infty$ the net transition is between states of equal energy. In this limit, the function behaves like a Dirac delta function,

$$\lim_{t\to\infty}\frac{\sin^2\omega t}{\pi t\omega^2} = \delta(\omega). \tag{17.38}$$

To convince ourselves of this, we first note that if $\omega \neq 0$, the limit is zero, but for $\omega = 0$ it has an infinite value; in addition, the function is normalized to unity,

$$\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\sin^2\omega t}{\omega^2 t}d\omega = 1.$$

It is clear from Fig. 17.1 that in the limit $t \to \infty$, the behavior of the function is precisely that of $\delta(\omega)$. Therefore, we can write

$$\lim_{t\to\infty}\frac{\sin^2\frac{1}{2}\omega_{kn}t}{\omega_{kn}^2 t} = \frac{\pi}{4}\delta(\tfrac{1}{2}\omega_{kn}) = \tfrac{1}{2}\pi\hbar\delta(E_n - E_k).$$

Substituting this result into Eq. (17.37), we get for the probability per unit time at large times

$$W_{nk} = \frac{2\pi}{\hbar}|V_{kn}|^2\delta(E_n - E_k). \tag{17.39}$$

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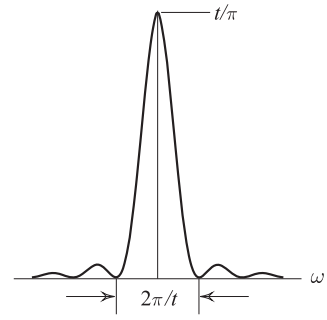


Figure 17.1 A constant perturbation V is applied during a time t. The graph shows how the transition probability per unit time between two states varies as a function of ω and becomes very sharp around $\omega = 0$ for large times.

17.1.2 Fermi's golden rule

The most important use of Eq. (17.39) is when the state k belongs to a set of final states in the continuum; for example, in problems of scattering by a short-range potential V (where the final state corresponds to a range of free particles), or when an essentially free particle is produced as the result of the interaction. In such cases, within a small interval ΔE_k of final energies there is a number $\Delta N(E_k)$ of states with different momentum, polarization, and so on, which must be taken into account. Our interest must then not be in W_{nk}, but in the quantity $\sum_{\Delta E_k} W_{nk}$ to which all final states with energy within ΔE_k contribute. If the number of states with energy in the interval $(E_k, E_k + dE_k)$ is $dN(E_k)$, we write

$$W_{nk} \to \sum_{\Delta E_k} W_{nk} \to \int_{\Delta N(E_k)} W_{nk} dN(E_k). \tag{17.40}$$

On the other hand, if $\rho(E_k)$ is the density of final states with energy E_k, that is, if the number of states $dN(E_k)$ is given by

$$dN(E_k) = \rho(E_k) dE_k, \tag{17.41}$$

(17.40) is written

$$W_{nk} = \frac{2\pi}{\hbar} \int_{E_k - \frac{1}{2}\Delta E_k}^{E_k + \frac{1}{2}\Delta E_k} |V_{nk}|^2 \delta(E_n - E_k) \rho(E_k) dE_k, \tag{17.42}$$

that is,

$$W_{nk} = \frac{2\pi}{\hbar} |V_{nk}|^2 \rho(E_k), \quad E_k = E_n. \tag{17.43}$$

This formula was called the *golden rule* by Fermi because of its numerous and important applications in the theory of transitions. Comparing Eq. (17.43) with (17.39), we see that the infinitely narrow density $\delta(E_n - E_k)$ has been replaced by the realistic density $\rho(E_k)$ of finite width. Equation (17.43) is also valid for describing first-order transitions in the reverse sense, that is, from the continuum to a stationary state. An important application of the golden rule will be discussed in Section 18.2.

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17.1.3 Periodic perturbations: Resonant transitions

An important use of time-dependent perturbation theory is for periodic potentials of the form $V\cos\omega t$, which can be expressed as linear combinations of the complex Hamiltonians

$$\widehat{\mathcal{H}}^{\pm} = \widehat{V}^{\pm} e^{\pm i\omega t}. \tag{17.44}$$

As we will see in what follows, each of these two terms produces a different effect, so there is no interference between them and they can be considered separately (as was done in Exercise E17.1). Substituting into the general formula (17.13), we obtain for the coefficient of the perturbative expansion to first order

$$C_{nk}^{(1)}(t) = -\frac{i}{\hbar} V_{kn}^{\pm} \int_0^t e^{i(\omega_{kn}\pm\omega)t'} dt'. \tag{17.45}$$

From this it follows that all the results of the previous section apply to the present case with the substitution $\omega_{kn} \to \omega_{kn} \pm \omega$. In particular, the transition probability per unit time is

$$W_{nk} = \frac{2\pi}{\hbar} |V_{nk}^{\pm}|^2 \rho(E_k), \tag{17.46}$$

where the energies of the system in the initial and final states are related by $\omega_{kn} \pm \omega = 0$, that is,

$$E_k = E_n \mp \hbar\omega. \tag{17.47}$$

Equation (17.37) is written in this case (for finite time) as

$$W_{nk}^{\pm} = \frac{4}{\hbar^2} |V_{kn}^{\pm}|^2 \frac{\sin^2 \frac{1}{2}(\omega_{kn} \pm \omega)t}{(\omega_{kn} \pm \omega)^2 t}. \tag{17.48}$$

If one of the conditions $\omega_{kn} \pm \omega \simeq 0$ is fulfilled, the corresponding probability $W_{nk}^{\pm}$ increases with time and the transition becomes highly probable. In these cases we speak of resonant transitions, which are the ones most favored by the system.

Exercise E17.2. Power absorbed by a canonical ensemble of molecules
Consider a system of molecules that is perturbed by a field of frequency ω. The unperturbed state i with energy E_i contributes to the system with weight w_i. Find an expression in the Heisenberg description for the average power that the system absorbs from the field.

Solution. With the perturbation potential written in the form $\widehat{\mathcal{H}}(t) = V\cos\omega t$, it follows from the preceding discussion that the probability per unit time of a transition from state n to state k is given by

$$W_{nk} = \frac{1}{4}\frac{2\pi}{\hbar^2} |V_{nk}|^2 \left[\delta(\omega_{kn} - \omega) + \delta(\omega_{kn} + \omega)\right]. \tag{17.49}$$

Since $\hbar\omega_{kn} W_{nk}$ is the corresponding average energy absorbed per second, summing over k, we obtain the average power absorbed by the system due to all transitions induced by the perturbation. We can calculate the average power change in two equivalent ways:

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(a) by summing over the absorptions from state n and subtracting the emissions leading to state n, or

(b) by summing over the absorptions from state n formally described by the two contributions V^+, V^-. Equation (17.50) shows the formal equivalence of the two methods.

Since state n occurs with probability w_n, the total average power absorbed by the system is

$$\begin{aligned}\overline{\dot{W}}_{\text{abs}} &= \sum_n w_n \sum_k \hbar\omega_{kn} W_{nk} \\ &= \frac{\pi}{2\hbar} \sum_{k,n} w_n \omega_{kn} |V_{nk}|^2 [\delta(\omega_{kn} - \omega) + \delta(\omega_{kn} + \omega)] \\ &= \frac{\pi\omega}{2\hbar} \sum_{k,n} (w_n - w_k) |V_{nk}|^2 \delta(\omega_{kn} - \omega). \end{aligned} \tag{17.50}$$

This result is expressed in Schrödinger's description. To move to the Heisenberg description we write the delta function in terms of an integral over time and combine with the matrix elements of $\widehat{V}$ in the following form,

$$\begin{aligned} |\widehat{V}_{nk}|^2 \delta(\omega_{kn} - \omega) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle n|\widehat{V}|k\rangle\langle k|\widehat{V} \exp\,[i(\omega_{kn} - \omega)t]|n\rangle dt \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle n|\widehat{V}|k\rangle\langle k| \exp\,(i\frac{E_k}{\hbar}t)\widehat{V} \exp\,(-i\frac{E_n}{\hbar}t)|n\rangle \exp(-i\omega t)dt \\ = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle n|\widehat{V}|k\rangle\langle k| \exp\,(i\frac{\widehat{H}_0}{\hbar}t)\widehat{V} \exp\,(-i\frac{\widehat{H}_0}{\hbar}t)|n\rangle \exp\,(-i\omega t)dt, \end{aligned} \tag{17.51}$$

where $\widehat{H}_0$ is the Hamiltonian of the unperturbed system. This result can be rewritten directly in terms of the matrix elements of $\widehat{V}$ in the Heisenberg description, $\widehat{V}_H \equiv V(t) = \exp\,(i\widehat{H}_0 t/\hbar)\widehat{V} \exp\,(-i\widehat{H}_0 t/\hbar)$. Recalling Heisenberg's general equation of evolution

$$i\hbar \frac{d\hat{F}_H}{dt} = \left[\hat{F}_H, \hat{H}_H\right], \tag{17.52}$$

we get

$$\overline{\dot{W}}_{\text{abs}} = \frac{\omega}{4\hbar} \sum_{n,k} \int_{-\infty}^{\infty} (w_n - w_k)\langle n|\widehat{V}(0)|k\rangle\langle k|\widehat{V}(t)|n\rangle \exp\,(-i\omega t)dt. \tag{17.53}$$

To give a more condensed form to this expression we note that

$$\sum_{n,k} w_n \langle n|\widehat{V}(0)|k\rangle\langle k|\widehat{V}(t)|n\rangle = \sum_n w_n \langle n|\widehat{V}(0)\widehat{V}(t)|n\rangle \equiv \langle \widehat{V}(0)\widehat{V}(t)\rangle, \tag{17.54}$$

where $\langle\widehat{A}\rangle$ represents the average $\sum_n w_n\langle n|\widehat{A}|n\rangle$, as explained in Chapter 15. Analogously,

$$\sum_{n,k} w_k \langle n|\widehat{V}(0)|k\rangle\langle k|\widehat{V}(t)|n\rangle = \sum_k w_k \langle k|\widehat{V}(t)\widehat{V}(0)|k\rangle = \langle \widehat{V}(t)\widehat{V}(0)\rangle. \tag{17.55}$$

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Therefore,

$$\overline{W}_{\text{abs}} = \frac{\omega}{4\hbar}\int_{-\infty}^{\infty}\left\langle \widehat{V}(0)\widehat{V}(t) - \widehat{V}(t)\widehat{V}(0)\right\rangle \exp(-i\omega t)dt. \tag{17.56}$$

One particular case deserves special consideration. As we have seen in Chapter 15, in a canonical ensemble at temperature T the weights w_k are given by the Maxwell–Boltzmann distribution, that is, $w_k = C\exp(-E_k/kT)$, so that

$$w_n - w_k = w_n[1 - \exp(-\hbar\omega_{kn}/kT)]. \tag{17.57}$$

Substituting in Eq. (17.53) and proceeding as before, we get

$$\overline{\dot{W}}_{\text{abs}} = \frac{\omega}{4\hbar}[1 - \exp(-\hbar\omega/kT)]\int_{-\infty}^{\infty}\langle \widehat{V}(0)\widehat{V}(t)\rangle \exp(-i\omega t)dt. \tag{17.58}$$

17.2 Radiative Transitions

Any periodic perturbation, whatever its physical nature, tends to produce resonant transitions between the various atomic states. The case of greatest interest to us here – though not the only physically interesting one – is when the perturbation is due to an external electromagnetic field. In such a case $\hbar\omega$ is the energy associated with the mode of frequency ω, which is added to or subtracted from the initial atomic energy to obtain the energy of the final state of the atom, as follows from Eq. (17.47). In the first case, that is, when $E_k = E_n + \hbar\omega$, which corresponds to the perturbation $\widehat{\mathcal{H}}^-$, the atom absorbs the energy $\hbar\omega$ from the field (this is the induced absorption). On the contrary, in the case where the perturbation is described by $\widehat{\mathcal{H}}^+$, we have $E_k = E_n - \hbar\omega$, which means that the atom gives off the energy $\hbar\omega$ to the field, giving rise to an induced emission. With the methods developed in Section 17.1, we can study such resonant atomic transitions induced by an external radiation field.

17.2.1 Induced emission and absorption of radiation

We saw in Section 12.7 that by neglecting the quadratic effects of the electromagnetic field (assuming that the field is not too strong relative to the energies involved), the Hamiltonian of the minimal interaction between an atomic electron and the field, reduced to its linear term, is

$$\widehat{\mathcal{H}} = -\frac{e}{mc}\boldsymbol{A}(\boldsymbol{r},t)\cdot\widehat{\boldsymbol{p}}, \tag{17.59}$$

with the Coulomb gauge $\nabla\cdot\boldsymbol{A} = 0$, so $\boldsymbol{A}$ and $\widehat{\boldsymbol{p}}$ commute. In source-free regions, the vector potential of a field mode of frequency ω can be written in the form

$$\boldsymbol{A} = \boldsymbol{A}_-(\boldsymbol{r})e^{-i\omega t} + \boldsymbol{A}_+(\boldsymbol{r})e^{i\omega t}, \tag{17.60}$$

where $\boldsymbol{A}_+ = \boldsymbol{A}_-^*$, since $\boldsymbol{A}$ is real. According to the previous section, the first term corresponds to energy absorption and the second to energy emission. The $\boldsymbol{A}_+, \boldsymbol{A}_-$ are solutions of the Helmholtz equation,

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$$\nabla^2 \boldsymbol{A}_\pm + \frac{\omega^2}{c^2}\boldsymbol{A}_\pm = 0.$$

Atomic transitions are known to involve polarized field modes. We therefore take a component along a given polarization $\boldsymbol{\epsilon}$ and write

$$\boldsymbol{A} = A_0\boldsymbol{\epsilon}[e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)} + e^{-i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}], \tag{17.61}$$

where $\boldsymbol{A}_0$ is a real and constant vector and $\boldsymbol{k}$ the wave vector along the direction of propagation and perpendicular to $\boldsymbol{\epsilon}$ (the free electromagnetic field, by being massless admits only two degrees of polarization). The corresponding electric and magnetic vectors are

$$\boldsymbol{E} = -\frac{1}{c}\frac{\partial \boldsymbol{A}}{\partial t} = -2A_0 k\boldsymbol{\epsilon}\sin(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t), \tag{17.62}$$

$$\boldsymbol{B} = \nabla \times \boldsymbol{A} = 2A_0(\boldsymbol{\epsilon}\times\boldsymbol{k})\sin(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t), \tag{17.63}$$

which, after averaging over time, gives an energy density per unit volume,

$$u = \frac{1}{8\pi}\overline{\left(\boldsymbol{E}^2 + \boldsymbol{B}^2\right)}^t = \frac{A_0^2}{2\pi}k^2, \tag{17.64}$$

from which the energy content is

$$\mathcal{E} = Vu = \frac{A_0^2 V}{2\pi}k^2, \tag{17.65}$$

if u is considered homogeneous. This energy is associated to the single frequency $\omega = kc$, so that we can use Planck's formula for the spectral energy density, Eq. (2.22), and write

$$\rho(\omega) = \frac{\omega^2}{2\pi^2 c^3}\mathcal{E}. \tag{17.66}$$

Note that we have divided by two, since in (2.22) the two possible polarizations are considered, while here we have set a direction for $\boldsymbol{\epsilon}$. With $\mathcal{E}$ given by (17.65), we get

$$\rho(\omega) = \frac{V\omega^4}{4\pi^3 c^5}A_0^2. \tag{17.67}$$

In the (quantum) literature it is common to find these results expressed in terms of photons, associating the energy $\mathcal{E}$ contained in V with an average number N of photons of frequency ω, that is, $\mathcal{E} = N\hbar\omega$. Although this language is foreign to the present treatment, which describes the field in classical (nonquantized) terms, we use it here for later convenience and express the energy density as

$$\rho\,(\omega) = \frac{\hbar\omega^3}{2\pi^2 c^3}N. \tag{17.68}$$

It is important to distinguish between the spectral energy density $\rho(\omega)$ and the energy density of final states $\rho(E_k)$, as is discussed in what follows.

Coming back to our subject we will first discuss induced emission processes. The corresponding interaction Hamiltonian is, from (17.59)–(17.61),

$$\widehat{\mathcal{H}}^+ = -\frac{e}{mc}\boldsymbol{A}_+(\boldsymbol{r},t)\cdot\widehat{\boldsymbol{p}} = \widehat{V}^+ e^{i\omega t}, \tag{17.69}$$

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where

$$\widehat{V}^{+} = -\frac{e}{mc} A_0 e^{-ik\cdot r} \boldsymbol{\epsilon} \cdot \widehat{\boldsymbol{p}}. \tag{17.70}$$

Equation (17.46) gives, for the probability of emission per unit time,

$$W_{nk}^{\mathrm{em}} = \frac{2\pi}{\hbar} |\langle n|\widehat{V}^{+}|k\rangle|^2 \rho(E_k) = \frac{2\pi e^2 A_0^2}{m^2 \hbar c^2} |\langle n|e^{-i\mathbf{k}\cdot\mathbf{r}} \boldsymbol{\epsilon} \cdot \widehat{\boldsymbol{p}}|k\rangle|^2 \rho(E_k). \tag{17.71}$$

Since the system emits a photon, there will be more photons in the final state. Normalizing within a box of volume V, the number of photons contained in d^3p is

$$d^3n = \frac{V}{(2\pi\hbar)^3} d^3p = \frac{Vp^2}{(2\pi\hbar)^3} dp d\Omega_p. \tag{17.72}$$

We now rewrite this expression in the form

$$d^3n = \frac{Vp^2}{(2\pi\hbar)^3} \frac{dp}{d\mathcal{E}} d\Omega_p d\mathcal{E}.$$

The density of final states within the solid angle $d\Omega_p$ is obtained from Eq. (17.41), which gives

$$d\rho(\mathcal{E}) = \frac{d^3n}{d\mathcal{E}} = \frac{Vp^2}{(2\pi\hbar)^3} \frac{dp}{d\mathcal{E}} d\Omega_p. \tag{17.73}$$

This expression is used as a starting point to calculate the density of final states in the continuum in each particular case. Since for photons, as is our case, $dp/d\mathcal{E} = d(\mathcal{E}/c)/d\mathcal{E} = 1/c$ and $p = \hbar\omega/c$, we have

$$d\rho(\mathcal{E}) = \frac{Vp^2}{8\pi^3\hbar^3 c} d\Omega_p = \frac{V\omega^2}{8\pi^3\hbar c^3} d\Omega_p. \tag{17.74}$$

Substituting this result into Eq. (17.71) and using (17.67), we get

$$dW_{nk}^{\mathrm{em}} = \frac{\pi e^2 \rho(\omega)}{m^2\hbar^2\omega^2} \left| \langle n|e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \boldsymbol{\epsilon} \cdot \widehat{\boldsymbol{p}}|k\rangle \right|^2 d\Omega_p. \tag{17.75}$$

Now we focus on the matrix element. The values of $\boldsymbol{r}$ that contribute significantly to the integral are of the order of the atomic radius a or less, due to the exponentially decreasing shape of the wave functions. This means that if k is not too large, we can approximate the exponential in (17.75) to unity. This is the long-wavelength approximation, and as already mentioned in Section 2.2, it is perfectly valid for light atoms and radiation in the visible range; characteristic values are $a \sim 10^{-8}$ cm; $\lambda = 1/k \sim 10^{-5}$ cm, that is, $ka \sim 10^{-3}$. We can therefore consider the field to be independent of the coordinates,

$$\boldsymbol{A}_{+}(r,t) = A_0 \widehat{\boldsymbol{\epsilon}} e^{i\omega t}.$$

This uniform field inside the atom corresponds to the (time-dependent) interaction potential $V = -e\boldsymbol{E}_{+} \cdot \boldsymbol{r} = -\boldsymbol{E}_{+} \cdot \boldsymbol{d}$ describing the coupling of the atomic electric dipole $\boldsymbol{d} = e\boldsymbol{r}$ to the electric field. We see therefore that the long-wavelength approximation leads to the electric dipole transitions discussed previously. Eq. (17.75) is then reduced to

$$dW_{nk}^{\mathrm{em}} = \frac{\pi e^2 \rho(\omega)}{m^2\hbar^2\omega^2} |\langle n|\boldsymbol{\epsilon} \cdot \widehat{\boldsymbol{p}}|k\rangle|^2 d\Omega_p. \tag{17.76}$$

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We use the Heisenberg equation to calculate $\langle k|\widehat{\boldsymbol{p}}|n\rangle = (m/i\hbar)\langle k|\,[\boldsymbol{r}, H]\,|n\rangle$ and get

$$\langle k|\boldsymbol{\epsilon}\cdot\widehat{\boldsymbol{p}}|n\rangle = im\omega_{nk}\langle k|\boldsymbol{\epsilon}\cdot\boldsymbol{r}|n\rangle. \tag{17.77}$$

Further, taking into account that the atom resonates precisely at the transition frequency, $\omega = \omega_{nk}$, we get

$$dW_{nk}^{\mathrm{em}} = \frac{\pi e^2}{\hbar^2}\rho(\omega)|\langle n|\boldsymbol{\epsilon}\cdot\boldsymbol{r}|k\rangle|^2 d\Omega_p. \tag{17.78}$$

When considering photons emitted with any polarization, one must average over the two possible values of $\boldsymbol{\epsilon}$, giving them equal weight. The average of $|\langle n|\boldsymbol{\epsilon}\cdot\boldsymbol{r}|k\rangle|^2$ can be written as $\sum_{ij}\overline{\epsilon_i\epsilon_j}\langle n|x_i|k\rangle\langle k|x_j|n\rangle$, with

$$\overline{\epsilon_x} = \overline{\epsilon_y} = \overline{\epsilon_z} = 0, \qquad \overline{\epsilon_x^2} = \overline{\epsilon_y^2} = \overline{\epsilon_z^2} = \tfrac{1}{3}\overline{\epsilon^2} = \tfrac{1}{3}. \tag{17.79}$$

Moreover, transitions with different polarizations are uncorrelated, so

$$\overline{\epsilon_i\epsilon_j} = \tfrac{1}{3}\delta_{ij}, \tag{17.80}$$

whence

$$\sum_{ij}\overline{\epsilon_i\epsilon_j}\langle n|x_i|k\rangle\langle k|x_j|n\rangle = \tfrac{1}{3}\sum_i\langle n|x_i|k\rangle\langle k|x_i|n\rangle = \tfrac{1}{3}|\langle n|\boldsymbol{r}|k\rangle|^2. \tag{17.81}$$

Substituting this result into Eq. (17.78) gives

$$dW_{nk}^{\mathrm{em}} = \frac{\pi e^2}{3\hbar^2}\rho(\omega)|\langle n|\boldsymbol{r}|k\rangle|^2 d\Omega. \tag{17.82}$$

Since the radiation is assumed to be isotropic, we can immediately perform the angular integration and thus obtain the probability of a dipolar transition per unit time from state n to state k with emission of frequency $\omega = \omega_{nk}$ in any direction and with any polarization,

$$W_{nk}^{\mathrm{em}} = \frac{4\pi^2 e^2}{3\hbar^2}\rho(\omega)|\langle n|\boldsymbol{r}|k\rangle|^2. \tag{17.83}$$

It is clear from the preceding that the derivation of the formulas for induced absorption follows a similar pattern. Again assuming that the field is isotropic, we obtain for the probability of absorption of a photon of frequency $\omega = \omega_{nk}$ in any direction and with any polarization, since $|\langle n|\boldsymbol{r}|k\rangle|^2 = |\langle k|\boldsymbol{r}|n\rangle|^2$,

$$W_{nk}^{\mathrm{abs}} = \frac{4\pi^2 e^2}{3\hbar^2}\rho(\omega)|\langle n|\boldsymbol{r}|k\rangle|^2. \tag{17.84}$$

17.2.2 Selection rules for dipole transitions

Equations (17.83) and (17.84) are important results: they show that an external radiation field has the same capacity to induce atomic emissions and absorptions, and they allow us to calculate the transition probability per unit time – which determines the intensity of the corresponding spectral lines – as a function of the spectral density of the field and the atom's electric dipole moment.

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Note that for electric dipole transitions to occur, $\langle n|\boldsymbol{r}|k\rangle$ must be different from zero. These selection rules for allowed transitions play an important role in determining the shape of atomic and molecular spectra and thus provide useful information about the system, such as the symmetries and the associated conservation laws.

For example, in Chapter 12 we obtained $|\Delta l| = 1, \quad |\Delta m| = 0, 1$, which tells us that for central problems (where the orbital angular momentum is a conserved quantity) the angular momentum of the atom or molecule must change by one (in units of $\hbar$) at each transition; this is due to the fact that the emitted or absorbed photon carries an angular momentum (spin) equal to 1. In Section 9.3 we obtained $|\Delta n| = 1$ for the harmonic oscillator, due to the fact that a linear system oscillating at frequency ω only interacts with field modes of that frequency. If the potential $V(x)$ is an even function of x (which is often the case), only dipole transitions between eigenstates of different parity are allowed, due to the odd parity of the dipole moment, as illustrated in Section 2.5 (see Exercise 17.44).

17.2.3 Multipole transitions

To study the effect of the higher multipole moments, we do a Taylor series expansion of the exponential in (17.75),

$$e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} = 1 - i\boldsymbol{k}\cdot\boldsymbol{r} - \tfrac{1}{2}(\boldsymbol{k}\cdot\boldsymbol{r})^2 + \ldots \tag{17.85}$$

The first term corresponds to the dipole; for the second term we need to calculate the matrix element of the operator

$$(\boldsymbol{\epsilon}\cdot\widehat{\boldsymbol{p}})(\boldsymbol{k}\cdot\boldsymbol{r}) = \tfrac{1}{2}\left[(\boldsymbol{\epsilon}\cdot\widehat{\boldsymbol{p}})(\boldsymbol{k}\cdot\boldsymbol{r}) + (\boldsymbol{\epsilon}\cdot\boldsymbol{r})(\boldsymbol{k}\cdot\boldsymbol{p})\right] + \tfrac{1}{2}(\boldsymbol{k}\times\boldsymbol{\epsilon})\cdot(\boldsymbol{r}\times\widehat{\boldsymbol{p}}). \tag{17.86}$$

In the first term we replace the matrix element of $\widehat{\boldsymbol{p}}$ by that of $\boldsymbol{r}$ as before (with the auxiliary introduction of a sum over intermediate states) and in the last term we introduce the magnetic vector using (17.63) instead of the product $\boldsymbol{k}\times\boldsymbol{\epsilon}$, and the orbital angular momentum instead of $\boldsymbol{r}\times\widehat{\boldsymbol{p}}$. This gives an expression of the form

$$\langle(\boldsymbol{\epsilon}\cdot\widehat{\boldsymbol{p}})(\boldsymbol{k}\cdot\boldsymbol{r})\rangle = C_1\langle(\boldsymbol{\epsilon}\cdot\widehat{\boldsymbol{r}})(\boldsymbol{k}\cdot\boldsymbol{r})\rangle + C_2\langle\boldsymbol{B}\cdot\hat{\boldsymbol{L}}\rangle. \tag{17.87}$$

The first term obviously refers to the effect of the electric quadrupole moment ($E2$ transitions), while the second generates transitions due to the magnetic dipole moment of the atom ($M1$ transitions). In general, if the transitions are due to a moment of order 2^l, the transitions are El or Ml, depending on the case.

Continuing with this procedure, we could, in principle, calculate the transition probabilities associated with any multipole and the corresponding selection rules. This is a subject for more advanced or specialized texts and we will not insist on it here. However, we can estimate the relative order of magnitude of the different contributions without the need for explicit calculations. We do this by expanding the exponential in the form

$$e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} = \sum(-i)^l j_l(kr)P_l(\cos\theta), \tag{17.88}$$

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where θ is the angle formed by the vectors $\boldsymbol{k}$ and $\boldsymbol{r}$. For small values of the argument we can approximate the spherical Bessel functions as

$$j_l(kr) = \frac{(kr)^l}{(2l+1)!!} + \dots \tag{17.89}$$

Since $ka \ll 1$, only the lowest multipoles contribute significantly to the transition probability. For example, in the frequent case cited above with $ka \simeq 10^{-3}$, if we take the transition probability $E1$ as 1, that of the quadrupole transition will be $(10^{-3})^2$, a million times smaller. Therefore, the spectral lines produced by multipole transitions are much fainter, and normally visible only when the corresponding dipole transitions are absent, i.e., when they are excluded by a selection rule.

17.2.4 The Einstein A and B coefficients

In 1916, Einstein published an elegant derivation of Planck's distribution law as an additional argument in favor of his photonic theory of the radiation field, based on a statistical study of equilibrium between matter and radiation. Schematically, this important part of the derivation goes as follows.

Consider, for simplicity, an ensemble of two-level atoms with $E_n > E_k$, subject to a radiation field with spectral density $\rho(\omega)$.[1] The resonant field-atom interaction produces transitions between states k and n, at the frequency $\omega = |\omega_{kn}|$; each atom is in one of the two possible stationary states. When equilibrium has been reached at temperature T, there are N_n and N_k atoms in states n and k, respectively, with the relative populations given by the Boltzmann factor,[2]

$$N_n/N_k = e^{-(E_n-E_k)/kT}. \tag{17.90}$$

Transitions from k to n take place when the atom absorbs energy from the field and becomes excited. Since these processes can only occur in the presence of the field, Einstein proposed to write the mean number $dn_{\rm abs}$ of field- induced absorptions occurring during dt in the form

$$dn_{\rm abs} = N_k B_{kn} \rho(\omega, T) dt. \tag{17.91}$$

The absorption probability per unit time and unit spectral density of the field, B_{kn}, is an intrinsic property of the atom and can only be determined through the quantum study of the atom-field interaction.

We can treat the downward transitions in a similar way, by writing the mean number of field-induced emissions during dt as $N_n B_{nk} \rho(\omega, T) dt$. To this we must add the number of spontaneous emissions, those that occur in the absence of an external field, which Einstein wrote as $N_n A_{nk} dt$, where A_{nk} is the probability per unit time that an atom will decay freely from n to k. This is a "spontaneous" (i.e., not induced) process, independent of the external field. Consequently, the total number of emissions during dt is

$$dn_{\rm em} = [N_n B_{nk} \rho(\omega, T) + N_n A_{nk}] dt. \tag{17.92}$$

[1] There may of course be other energy levels, but our focus will be on the transitions between levels E_n and E_k. A modern quantum-mechanical approach to the two-level atom is discussed in Section 3.

[2] We take the degeneracy to be 1 for simplicity; the result is essentially independent of this consideration.

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In equilibrium, the average number of absorptions during dt must be equal to the average number of emissions, so that[3]

$$N_k B_{kn} \rho = N_n B_{nk} \rho + N_n A_{nk}. \tag{17.93}$$

If we introduce Eq. (17.72), which holds in thermal equilibrium, we get

$$e^{-E_k/kT} B_{kn} \rho = e^{-E_n/kT} (B_{nk} \rho + A_{nk}). \tag{17.94}$$

Assuming that ρ grows indefinitely with increasing temperature T (which is not only intuitively clear, but is also confirmed by the final result), (17.94) gives

$$B_{kn} = B_{nk}, \tag{17.95}$$

which means that the probabilities of induced energy absorption or emission are equal. This is a first important prediction of the theory, which is confirmed by the quantum treatment of the problem, as shown at the end of the previous section. Taking this into account, we obtain from (17.94) that

$$\rho = \frac{A_{nk}/B_{nk}}{e^{(E_n - E_k)/kT} - 1}. \tag{17.96}$$

Using Wien's displacement law

$$\rho(\omega, T) = \omega^3 f(\omega/T), \tag{17.97}$$

where f is a universal function, we infer that

$$\frac{A_{nk}}{B_{nk}} = \lambda \omega^3 \tag{17.98}$$

and

$$E_n - E_k = \hbar \omega, \tag{17.99}$$

where λ and $\hbar$ are coefficients to be determined. Note that with this derivation, Bohr's hypothesis about atomic transitions between energy levels is no longer a hypothesis. Substituting these results in (17.96) we get

$$\rho = \frac{\lambda \omega^3}{e^{\hbar\omega/kT} - 1}. \tag{17.100}$$

By comparing with the Rayleigh–Jeans approximate formula $\rho = (\omega^2/\pi^2 c^3) kT$, which is known to work well at high temperatures, we get

$$\lambda = \frac{\hbar}{\pi^2 c^3}, \tag{17.101}$$

which introduced into (17.100) gives Planck's blackbody radiation law. Further, from (17.98) and (17.101) we get

$$A_{nk} = \frac{\hbar \omega^3}{\pi^2 c^3} B_{nk}. \tag{17.102}$$

This result is extremely important because it shows that when a quantum system responds to an external electromagnetic field ($B_{nk} \neq 0$), it will also decay without

[3] This property is called detailed balance, because it leads to a state of equilibrium at each frequency separately; historically, this notion was introduced by Einstein precisely in this context.

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external intervention ($A_{nk} \neq 0$), emitting energy until it reaches its ground state. This proves that the excited states of an atomic system are unstable, i.e., they decay "spontaneously."

The above was the first derivation of the Planck distribution free from logical inconsistencies or arbitrary adjustments. The lack of quantum formalism in 1916 prevented Einstein from establishing the formulas for the A and B coefficients separately.

17.2.5 Spontaneous emission of radiation: a semiclassical approach

In Section 2.1 the quantum-mechanical formulas for the induced transition probabilities were derived by considering the external radiation field as a perturbation. According to Eqs. (17.83) and (17.84), the Einstein B coefficient, which gives the probability of induced transitions per unit time and per unit spectral density, is

$$B_{nk} = \frac{4\pi^2 e^2}{3\hbar^2} |\langle k|\boldsymbol{r}|n\rangle|^2. \tag{17.103}$$

However, the Schrödinger equation dictates that the excited states are stationary in the absence of an external field, so there is no spontaneous decay in QM. This contradiction cannot be resolved within the Schrödinger formalism, which does not take full account of radiative interactions. In Sections 17.3 and 17.4 it is shown that a proper treatment of the matter-field system, including the vacuum field, satisfactorily resolves the contradiction. As shown in the following exercise, a partial solution is obtained by using semiclassical arguments to derive a formula for the A coefficient of spontaneous decay, assuming that it is due to the radiation reaction of the electron.

Exercise E17.3. Semiclassical approach to spontaneous emission
Use the classical Larmor formula for the power radiated by a nonrelativistic point charge, to derive a quantum expression for the Einstein A coefficient.

Solution. The classical formula for the average energy emitted per unit time by an electric dipole $e\boldsymbol{r}$ is

$$\frac{d\mathcal{E}}{dt} = \frac{2e^2}{3c^3} \overline{(\ddot{\boldsymbol{r}})^2}^t, \tag{17.104}$$

where the symbol $^{-t}$ means time averaging. To give this expression a quantum form we proceed as follows.

We consider an ensemble of atoms that can make transitions between states k and n, and describe the state of such an ensemble as a superposition of both states, $\psi = C_n\psi_n + C_k\psi_k$, with $|C_n|^2 + |C_k|^2 = 1$. We then replace the acceleration $\ddot{\boldsymbol{r}}$ by its expectation value, which is given by

$$\begin{aligned} \langle\psi|\ddot{\boldsymbol{r}}|\psi\rangle &= \int (C_n^*\psi_n^* + C_k^*\psi_k^*)\ddot{\boldsymbol{r}}(C_n\psi_n + C_k\psi_k)d^3x \\ &= |C_n|^2\langle n|\ddot{\boldsymbol{r}}|n\rangle + |C_k|^2\langle k|\ddot{\boldsymbol{r}}|k\rangle + C_n^*C_k\langle n|\ddot{\boldsymbol{r}}|k\rangle + C_nC_k^*\langle k|\ddot{\boldsymbol{r}}|n\rangle. \end{aligned} \tag{17.105}$$

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Applying the Heisenberg equation twice, we get

$$\langle n|\ddot{\boldsymbol{r}}|k\rangle = -\left(\frac{E_n - E_k}{\hbar}\right)^2 \langle n|\boldsymbol{r}|k\rangle = -\omega^2\langle n|\boldsymbol{r}|k\rangle, \tag{17.106}$$

where $\omega = \omega_{nk}$. Atomic states usually have well-defined parity, even or odd, so the integrand in

$$\langle n|x_i|n\rangle = \int_{-\infty}^{\infty} \psi_n^* x_i \psi_n dx_i \tag{17.107}$$

($i = 1, 2, 3$) is odd and the integral vanishes. This means that normally an atom has no dipole electric moment in its ground state. The preceding expectation value reduces therefore to (there are two equivalent contributions)

$$\langle\psi|\ddot{\boldsymbol{r}}|\psi\rangle = 2\mathrm{Re}\left(C_n^* C_k\right)\langle n|\ddot{\boldsymbol{r}}|k\rangle. \tag{17.108}$$

Since the coefficients are of order unity, we can write

$$|\langle\psi|\ddot{\boldsymbol{r}}|\psi\rangle|^2 = C_0^2|\langle n|\ddot{\boldsymbol{r}}|k\rangle|^2, \tag{17.109}$$

where C_0^2 is a real constant of the order of unity. Substituting in Eq. (17.104) we get

$$d\mathcal{E} = \frac{2e^2\omega^4}{3c^3}C_0^2|\langle n|\boldsymbol{r}|k\rangle|^2 dt. \tag{17.110}$$

On the other hand, the mean energy radiated during dt is the energy $\hbar\omega$ radiated in each transition multiplied by the mean number of transitions $A_{nm}dt$, so that

$$A_{nk} = \frac{2e^2\omega^3 C_0^2}{3\hbar c^3}|\langle k|\boldsymbol{r}|n\rangle|^2. \tag{17.111}$$

With B_{nk} given by (17.103), we get

$$A_{nk} = \frac{\hbar\omega^3}{2\pi^2 c^3}\frac{C_0^2}{2}B_{nk}, \tag{17.112}$$

which compares well with the exact result, Eq. (17.102), except for the indeterminate numerical factor of order 1. In Sections 17.3 and 17.4 we return to this point to show that a complete treatment of the matter–field system gives the correct formulas for the A and B coefficients, with $C_0^2 = 2$.

Before concluding this section, we note that since A_{nk} is the probability per unit time for a spontaneous transition to occur between states n and k, its inverse is the mean time it takes for such a transition to occur. This quantity is defined as the mean lifetime $T_{n\to k}$ of the excited state n,

$$T_{n\to k} = A_{nk}^{-1}. \tag{17.113}$$

However, it is often the case that the system can decay from state n to any one of several states k, in which case each different decay mode contributes to shortening the mean lifetime. In such a case the mean lifetime of the excited state n takes the form

$$T_n = \left(\sum_{E_k < E_n} A_{nk}\right)^{-1}. \tag{17.114}$$

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Radiative lifetimes of excited atomic states fall typically in the range of $10^{-8} - 10^{-10}$ s, with the exception of metastable states (states that do not decay via a dipole transition), which can have lifetimes on the order of seconds or longer.

In what follows we apply these results to a specific example for illustrative purposes.

Exercise E17.4. Mean lifetimes for an infinite well

Using the electric dipole selection rules for a 1D infinite well, find the mean lifetime for spontaneous transitions from the excited state $n = 4$.

Solution. We saw in Chapter 5 that the eigenfunctions of $\widehat{H}$ in this case are $\varphi_n = \sqrt{\frac{2}{a}} \sin \frac{\pi n}{a} x$. This gives for the matrix element of x

$$\langle n'|x|n\rangle = \int \varphi_{n'} x \varphi_n dx = \frac{4a}{\pi^2} \frac{nn'}{(n^2 - n'^2)^2} [(-1)^{n-n'} - 1].$$

Therefore, spontaneous dipole emissions exist for all $n > n'$ such that $\Delta n \equiv n - n' =$ odd.

When the initial state is $n = 4$, the emission spectrum will have as dominant lines those corresponding to the frequencies $3\omega_1, 5\omega_1, 7\omega_1, 15\omega_1$, where $\omega_1 = E_1/\hbar = \pi^2\hbar/2ma^2$, see Eq. (4.73). The lines produced by higher-order transitions are superimposed on this spectrum, but are much fainter.

The initial state $n = 4$ can decay either to the state $n = 3$, or directly to the ground state ($n = 1$), so that its total probability of decay is the sum of the probabilities of each of the possible transitions (because they are mutually exclusive events), $A_{4\text{tot}} = A_{43} + A_{41}$. Therefore, the mean lifetime of the state $n = 4$ is, according to Eq. (17.114),

$$T_4 = (A_{43} + A_{41})^{-1},$$

with $A_{4k} = \frac{4e^2\omega^3}{3\hbar c^3} |\langle k|x|4\rangle|^2$.

17.2.6 A basic introduction to the laser

An important application of the previous results is the laser. We have seen in Section 17.2.1 that an electromagnetic field of frequency ω stimulates atomic emissions of that frequency. Therefore, by bringing atoms into a suitable excited state and exposing them to a field of frequency equal to the emission frequency, it is possible to generate intense, coherent and (practically) monochromatic light. The device developed on this basis is the laser (acronym for Light Amplification by Stimulated Emission of Radiation).

As an example, consider a gas laser using a He–Ne mixture; these gases are used because the 2^1s_0 and 2^3s_1 levels of He[4] coincide with the excited levels $(2p)^5(5s)$ and $(2p)^5(4s)$ of Ne, respectively, and since He is easily excited and eventually decays into

[4] The notation for the electronic configuration of atoms is explained in Section 16.1. Essentially it is ${}^{2s+1}L_j$, plus the atomic shell (a number).

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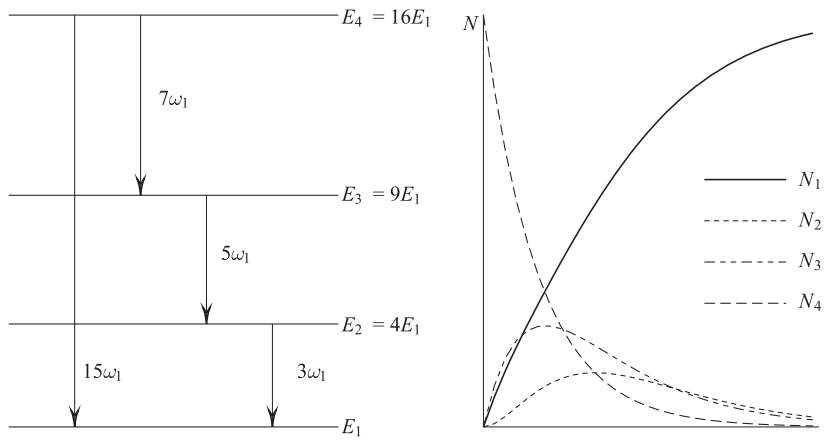


Figure 17.2 (a) Transitions between energy levels in a He–Ne laser. (b) Diagram of a He–Ne laser tube, 9–10 inches long. Before the invention of low-cost diode lasers, red He–Ne lasers were widely used in barcode scanners.

such states, collisions with Ne will transfer energy to it and leave many of its atoms in the said excited states (see Fig. 17.2). Thus, after an electric discharge, the population of excited Ne atoms will be abnormally high – an effect called population inversion. The Ne atoms decay to the $(2p)^5(4p)$ and $(2p)^5(3p)$ states ($5s \rightarrow 4p$ and $4s \rightarrow 3p$ transitions); the emitted light is reflected by mirrors at either end of the laser as shown schematically in Fig. 17.2, creating a strong field of the appropriate frequency to further stimulate emission. The process is self-stimulating, until finally the light becomes intense enough to escape through one of the mirrors, which is semi-transparent. The red emission line at 632.8 nm has a high spectral purity, long coherence length, and excellent spatial quality, making this laser a useful source for holography and as a wavelength reference for spectroscopy, albeit at the cost of very low efficiency (less than 0.025%).

Shortly after the successful operation of the first ruby and He–Ne lasers in 1960, it was demonstrated that a semiconductor diode could function as a laser. In light-emitting diodes (LEDs), which are driven either by voltage or by optical pumping, a photon of energy equal to the recombination energy between electrons and electron holes (see Section 6.3) can cause recombination by stimulated emission; the gain increases as the number of electrons and holes injected across the diode junction increases. The size of LEDs, their efficiency, and their ability to produce light of different wavelengths, make them extremely useful; but unlike a laser, the light emitted by an LED is neither spectrally coherent nor highly monochromatic.

As already explained, stimulated or induced emission was unknown in Einstein's time; in fact, it was only with his work of 1916 that the term appeared – along with the notion of spontaneous emission – as another product of Einstein's intuition, which, despite its importance, as we have just seen, is almost never cited. In a peculiar twist of meaning, recognition of his introduction of stimulated emission often leads to Einstein being credited as the inventor of the laser. (Just as the "invention" of the atomic bomb is often attributed to him as a result of his famous mass-energy equivalence formula $E = mc^2$.)

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17.2.7 The photoelectric effect

Another example of important application of time-dependent perturbation theory is the photoelectric effect, a process in which an atom absorbs a photon of sufficient energy to be ionized. In order not to complicate matters, we will only consider the case of an H atom in the ground state, whose ionization energy is $I = Z^2me^4/2\hbar^2 \approx 13.6$ eV, and photons with $\hbar\omega \gg I$. From this relation and from the conservation of energy, which we can write in the approximate form $\hbar\omega \simeq p^2/2m$ (assuming W to be negligible in Einstein's equation $\hbar\omega - W \simeq p_{max}^2/2m$), it follows that the speed at which the electron is ejected from the atom must be high enough for it to ensure that

$$\frac{v}{c} \gg \frac{Ze^2}{\hbar c} = Z\alpha \quad \left(v = \frac{p}{m}\right). \tag{17.115}$$

We will assume that the radiation field can be described classically, while the electron obeys quantum laws. This approach differs substantially from the one discussed in Section 2.3.1, where it was shown that Einstein used the photoelectric effect precisely to support his fundamental proposal that the field must be quantized. The present calculation shows that the photoelectric effect can also be explained as being generated by the interaction of the quantized atom with the classical radiation field. The point of such a calculation is that the fundamental equation of the photoelectric effect – an example of Einstein's heuristic view – namely $\hbar\omega = T_{\max} + W$, can be rewritten in the form

$$T_{\max} + W = E_{\text{out}} - E_{\text{in}}, \tag{17.116}$$

where E_{out} and E_{in} are the final and initial atomic electron energies, respectively, so that $E_{\text{out}} - E_{\text{in}}$ is the energy available for the photoelectric effect. Writing it in terms of the Bohr transition frequency $\hbar\omega$, gives Einstein's formula. However, in writing the fundamental postulate in the form of (17.116), the quantization of the field is not used, but the Schrödinger equation enters instead. Several authors, including Mandel, Sudarshan, and Wolf (1964) and Lamb and Scully (1968), have argued that the correct form of this equation is precisely (17.116) and not Einstein's original, which happens to be derived, a consequence of the quantization of matter. Regardless of which principle one takes, the preceding discussion shows that it is legitimate to consider a classical radiation field and use perturbation theory to derive the probability of the photoelectric effect, which we will do here.

By considering the atom initially in its ground state, which we denote by $|0\rangle$, the wave function is

$$\langle r|0\rangle = \psi_{100}(r) = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Zr/a_0}. \tag{17.117}$$

Since the emitted electron has a very large energy relative to the ionization energy, we can consider it to be free, so the wave function of the final state, which we denote by $|p\rangle$, is

$$\langle r|p\rangle = \frac{1}{\sqrt{V}} \exp\left(\frac{i\boldsymbol{p}\cdot\boldsymbol{r}}{\hbar}\right). \tag{17.118}$$

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A more precise theory would have to take into account that the electron is not really free but moves in the Coulomb field of the ionized atom. With the previously discussed meaning of the quantity N, the transition probability per unit time is (see Eq. (17.46))

$$W = \frac{2\pi}{\hbar}|\langle p|V^-|0\rangle|^2\rho(E_p) = \frac{4\pi^2e^2N}{m^2V\omega}|\langle p|e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\epsilon}\cdot\widehat{\boldsymbol{p}}|0\rangle|^2\rho(E_p). \tag{17.119}$$

The density of final states $\rho(E_p)$ refers in this case to that of free electrons, for which $dE = vdp$ (both classically and relativistically), resulting in (see Section 7.1.5)

$$d\rho(E_p) = \frac{Vp^2}{8\pi^3\hbar^3}\frac{dp}{dE_p}d\Omega = \frac{Vm^2v}{8\pi^3\hbar^3}d\Omega, \tag{17.120}$$

whence

$$dW = \frac{Ne^2v}{2\pi\hbar^3\omega}|\langle p|e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\epsilon}\cdot\widehat{\boldsymbol{p}}|0\rangle|^2d\Omega. \tag{17.121}$$

The integral in the matrix element

$$\begin{aligned}\langle p|e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\widehat{\boldsymbol{p}}|0\rangle &= -i\hbar\sqrt{\frac{Z^3}{\pi Va_0^3}}\int\exp\left[-i\left(\boldsymbol{p}/\hbar-\boldsymbol{k}\right)\cdot\boldsymbol{r}\right]\nabla\exp\left(-\frac{Zr}{a_0}\right)d^3r\\ &= \sqrt{\frac{Z^3}{\pi Va_0^3}}(\boldsymbol{p}-\hbar\boldsymbol{k})\int\exp\left[-\frac{Zr}{a_0}-i(\frac{\boldsymbol{p}}{\hbar}-\boldsymbol{k})\cdot\boldsymbol{r}\right]d^3r\end{aligned} \tag{17.122}$$

is solved using the formula

$$\int e^{-br+i\boldsymbol{q}\cdot\boldsymbol{r}}d^3r = \frac{4\pi}{q}\int_0^\infty re^{-br}\sin qrdr = \frac{8\pi b}{(b^2+q^2)^2}, \tag{17.123}$$

where $b = Z/a_0$ and

$$\boldsymbol{q} = (\boldsymbol{k}-\frac{\boldsymbol{p}}{\hbar}). \tag{17.124}$$

Since $\boldsymbol{\epsilon}\cdot\boldsymbol{k} = 0$, we get

$$\langle p|e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\epsilon}\cdot\widehat{\boldsymbol{p}}|0\rangle = 8\sqrt{\frac{\pi a_0^3}{Z^3V}}\frac{\boldsymbol{\epsilon}\cdot\boldsymbol{p}}{\left(1+\frac{a_0^2q^2}{Z^2}\right)^2}, \tag{17.125}$$

and substituting into Eq. (17.121), we finally have

$$\frac{dW}{d\Omega} = \frac{32e^2a_0^3v}{Z^3\hbar^3\omega}\frac{(\boldsymbol{\epsilon}\cdot\boldsymbol{p})^2}{(1+a_0^2q^2/Z^2)^4}\frac{N}{V}. \tag{17.126}$$

To give this result a more convenient form we observe that from $\hbar\omega \approx p^2/2m$ it follows that $p^2 \approx 2m\hbar\omega = 2mc\hbar k \gg p\hbar k$, thus $mc \gg p$; from this same relation it also follows that $2\hbar k/p = p/mc = v/c$. Since $p \gg \hbar k$, we can write from (17.124)

$$q^2 \approx (p^2/\hbar^2) - 2(pk\cos\theta/\hbar) = (p^2/\hbar^2)(1-\frac{v}{c}\cos\theta), \tag{17.127}$$

where θ is the angle between $\boldsymbol{k}$ and $\boldsymbol{p}$. Further, from condition (17.115) it follows that $pa_0/Z\hbar = (1/Z\alpha)(v/c) \gg 1$, so that

$$1+\frac{q^2a_0^2}{Z^2} \simeq \frac{q^2a_0^2}{Z^2} = \frac{p^2a_0^2}{Z^2\hbar^2}\left(1-\frac{v}{c}\cos\theta\right). \tag{17.128}$$

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On the other hand, $\boldsymbol{\epsilon} \cdot \boldsymbol{p} = p \sin\theta \sin\phi$, where ϕ is the angle between $\boldsymbol{\epsilon}$ and the component of $\boldsymbol{p}$ perpendicular to $\boldsymbol{k}$. Substituting all these expressions into equation (17.126), we get

$$\frac{d\sigma}{d\Omega} \equiv \frac{(dW/d\Omega)}{j_{\text{inc}}} = \frac{V}{Nc}\frac{dW}{d\Omega} = \frac{32\alpha\hbar}{mck}\left(\frac{\hbar Z}{a_0 p}\right)^5 \frac{\sin^2\theta \sin^2\phi}{\left(1 - \frac{v}{c}\cos\theta\right)^4}. \tag{17.129}$$

We have divided $dW/d\Omega$ by the incident photon flux $j_{\text{inc}} = v_{\text{inc}}\rho_{\text{inc}} = c(N/V)$ to obtain the mean number of photoelectrons emitted in the element of solid angle $d\Omega$ per unit of incident flux. This quantity, which we have denoted as $d\sigma/d\Omega$, is called the differential cross section (of the photoelectric effect in this case). Due to the normalization introduced by dividing by j_{inc}, the differential cross section is independent of the illumination intensity and other incidental details of the experimental setup, so it is used as a properly normalized measure of the effective cross section.[5] The expressions obtained show that at low energies the photoelectrons are emitted preferentially in the polarization direction (in which $(\boldsymbol{\epsilon} \cdot \boldsymbol{p})^2$ takes its maximum value p^2), of the absorbed electric field. As the energy increases, the denominator $\left(1 - \frac{v}{c}\cos\theta\right)^4$ shifts this maximum in the forward direction (defined by the photoelectron). Furthermore, the cross section increases with the atomic number as Z^5 and decreases with the energy of the incident photon as $k^{-1}p^{-5} \sim \omega^{-7/2}$. All of these quantum predictions for the photoelectric effect are well verified in experiment.

17.3 Radiative Corrections: The Full Picture

We have seen in Section 17.2 that QM leads naturally to Einstein's (stimulated transition) B coefficients, but to obtain a reasonably approximate formula for the (spontaneous transition) A coefficients we resorted to arguments borrowed from classical physics. We will now proceed to derive the A_{nk} from a fundamental theory.

17.3.1 Dirac: The Formal Field Quantization

In 1927, Dirac was able to weave the photon concept into the fabric of the new QM and to describe the interaction of photons with matter. He found that the formula for the spontaneous transitions could be obtained by using a quantized field instead of a classical field to perturb the atomic electron. Dirac took the phases and energies of the field modes and interpreted them as operators related by commutators. Nowadays it is more common to quantize the (complex) Fourier amplitudes of the vector potential. The quantization of the field is thus formally achieved by replacing the classical oscillators describing the field by quantum oscillators, that is, by rewriting Eq. (17.61) in the form

$$\widehat{\boldsymbol{A}} = \widehat{a}\,\boldsymbol{\epsilon} A_-(\boldsymbol{r})e^{-i\omega t} + \widehat{a}^\dagger \boldsymbol{\epsilon} A_+(\boldsymbol{r})e^{i\omega t}, \tag{17.130}$$

[5] This important concept is discussed in detail in Section 18.1.

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where $A_{\pm}(\boldsymbol{r}) = A_0 e^{\mp i\boldsymbol{k}\cdot\boldsymbol{r}}$, the operators $\widehat{a}$ and $\widehat{a}^{\dagger}$ (corresponding to the mode of frequency ω) satisfy the commutators

$$[a, \widehat{a}^{\dagger}] = 1, \tag{17.131}$$

and operators pertaining to different field modes commute with each other. Note that these are the same as the lowering and raising operators used in Section 9.4 to describe the (mechanical) HO of frequency ω. In the present case, it is appropriate to speak of annihilation and creation because that is what $\widehat{a}$ and $\widehat{a}^{\dagger}$ do: applying $\widehat{a}$ decreases the number of photons by 1, and applying $\widehat{a}^{\dagger}$ increases it by 1. As in the case of the HO, n successive applications of $\widehat{a}$ to an initially excited state $|n\rangle$ of a given mode of the field eventually produces the state with zero photons, that is, the electromagnetic vacuum (or vacuum fluctuations, as it is called in quantum theory). Conversely, n successive applications of $\widehat{a}^{\dagger}$ to a field mode initially in the vacuum state $|0\rangle$ will bring the field to the excited state $|n\rangle$.

The issue of spontaneous transitions is solved as follows. As we can see from Eq. (17.130), $\boldsymbol{A}_-$ is accompanied by $\widehat{a}$ and $\boldsymbol{A}_+$ is accompanied by $\widehat{a}^{\dagger}$, so using Eq. (17.68), we can replace N by the expectation value $\langle N|\widehat{a}^{\dagger}\widehat{a}|N\rangle = N$ in Eq. (17.84) for the probability of resonant absorption of photons in the form

$$W_{nk}^{\text{abs}} = \frac{4e^2\omega^3}{3\hbar c^3} N |\langle n|\boldsymbol{r}|k\rangle|^2, \tag{17.132}$$

while in the formula for the probability of emission, Eq. (17.83), we must introduce $\langle N|\widehat{a}\,\widehat{a}^{\dagger}|N\rangle = \langle N|\widehat{a}^{\dagger}\widehat{a} + 1|N\rangle = N + 1$,

$$W_{nk}^{\text{em}} = \frac{4e^2\omega^3(N+1)}{3\hbar c^3} |\langle n|\boldsymbol{r}|k\rangle|^2. \tag{17.133}$$

In the absence of an external field, that is, with zero photons ($N = 0$), this gives

$$W_{nk}^{\text{em}}(N=0) \equiv A_{nk} = \frac{4e^2\omega^3}{3\hbar c^3} |\langle n|\boldsymbol{r}|k\rangle|^2 = \frac{\hbar\omega^3}{\pi^2 c^3} B_{nk}, \tag{17.134}$$

in exact agreement with Eq. (17.102). This result confirms that the quantization of the radiation field – involved in the transition to quantum electrodynamics (QED) – is sufficient to obtain the coefficient for the spontaneous decay of atomic excited states, among other important phenomena that will be discussed in what follows.

We thus see that if the quantum properties of the field are properly taken into account, one obtains a theory that is free of difficulties (well, not absolutely free, as will be discussed later). Formally, we can say that we have a complete quantum theory.

Note that the transformation of the vector potential $\boldsymbol{A}$ into an operator transforms Maxwell's equations from relations between functions into (equivalent) relations between operators. The vectors $\boldsymbol{E}$ and $\boldsymbol{B}$ also become operators (linear in $\widehat{a}$ and $\widehat{a}^{\dagger}$) which do not commute with each other or with the field Hamiltonian $(1/8\pi)\,(\widehat{\boldsymbol{E}}^2 + \widehat{\boldsymbol{B}}^2)$, which now takes the form

$$\widehat{H}_{\mathbf{k}\lambda} = \hbar\omega \left(\hat{a}^{\dagger}_{\mathbf{k}\lambda}\hat{a}_{\mathbf{k}\lambda} + \tfrac{1}{2}\right) \tag{17.135}$$

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for every field mode of frequency ω, propagation direction $\mathbf{k}$ and polarization λ. The step from classical electrodynamics to QED is thus entirely analogous and just as fundamental (and therefore has similar implications) as the step from classical mechanics to QM.

An exposition of the physical rationale for this transformation is left for Section 17.4.

Exercise E17.5. Field commutators in the Coulomb gauge

Find the values of the field commutators, $\left[\hat{A}_i(\boldsymbol{r}), \hat{A}_j(\boldsymbol{r}')\right]$, $\left[\hat{A}_i(\boldsymbol{r}), \hat{E}_j(\boldsymbol{r}')\right]$, where i, j refer to the Cartesian field components in the Coulomb gauge, expressed in terms of the annihilation and creation operators $\widehat{a}$ and $\widehat{a}^\dagger$ of different field modes (m, n).

Solution. Let us consider two linear field operators $\hat{F}$ and $\hat{G}$, represented by

$$F_i = \sum_m \left[f_{im}\hat{a}_m + f^*_{im}\hat{a}^\dagger_m \right], \tag{17.136}$$

$$G_j = \sum_n \left[g_{jn}\hat{a}_n + g^*_{jn}\hat{a}^\dagger_n \right]. \tag{17.137}$$

Their commutator is $\left[\hat{F}_i, \hat{G}_j\right]$.

$=\sum \left\{ f_{im}g_{jn}\left[\hat{a}_m, \hat{a}_n\right] + f_{im}g^*_{jn}\left[\hat{a}_m, \hat{a}^\dagger_n\right] + f^*_{im}g_{jn}\left[\hat{a}^\dagger_m, \hat{a}_n\right] + f^*_{im}g^*_{jn}\left[\hat{a}^\dagger_m, \hat{a}^\dagger_n\right] \right\}$; with the usual commutation rules (see (17.131)) this reduces to

$$\left[\hat{F}_i, \hat{G}_j\right] = \sum_m \left[f_{im}g^*_{jm} - f^*_{im}g_{jm} \right]. \tag{17.138}$$

For $\hat{F}_i = \hat{A}_i(\boldsymbol{r})$ we have

$$f_{im} = A_{\omega_m}\epsilon_{im}e^{i\boldsymbol{k}_m\cdot\boldsymbol{r}}, \tag{17.139}$$

and similarly for the rest. Thus,

$$\left[\hat{A}_i(\boldsymbol{r}), \hat{A}_j(\boldsymbol{r}')\right] = -\sum_{\boldsymbol{k}\lambda} A^2_\omega \epsilon_i\epsilon_j (e^{i\boldsymbol{k}\cdot\boldsymbol{r}}e^{-i\boldsymbol{k}\cdot\boldsymbol{r}'} - e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}e^{i\boldsymbol{k}\cdot\boldsymbol{r}'}) = 0, \tag{17.140}$$

since the modes with $\boldsymbol{k}$ and $-\boldsymbol{k}$ contribute equally but with opposite sign.

Things change in the case of the commutator $\left[\hat{A}_i(\boldsymbol{r}), \hat{E}_j(\boldsymbol{r}')\right]$ due to the extra factor $i\omega$,

$$\begin{aligned}\left[\hat{A}_i(\boldsymbol{r}), \hat{E}_j(\boldsymbol{r}')\right] &= -\sum_{\boldsymbol{k}\lambda} i\omega A^2_\omega \epsilon_i\epsilon_j (e^{i\boldsymbol{k}\cdot\boldsymbol{r}}e^{-i\boldsymbol{k}\cdot\boldsymbol{r}'} + e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}e^{i\boldsymbol{k}\cdot\boldsymbol{r}'}) \\ &= -2i\sum_{\boldsymbol{k}\lambda} \frac{\hbar}{2\epsilon_o L^3}\epsilon_i\epsilon_j e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')}.\end{aligned}$$

The two polarization vectors and the normalized vector $\mathbf{k} = \boldsymbol{k}/|\boldsymbol{k}|$ form an orthonormal basis, so that $\sum_\lambda \epsilon_i\epsilon_j = \delta_{ij} - \frac{k_ik_j}{k^2} = \delta^\perp_{ij}$, and

$$\left[\hat{A}_i(\boldsymbol{r}), \hat{E}_j(\boldsymbol{r}')\right] = -2i\sum_{\boldsymbol{k}} \frac{\hbar}{2\epsilon_o L^3}\delta^\perp_{ij} e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')}.$$

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When there is a continuum of field modes, the sum is replaced by the corresponding integral; thus, $\left[\hat{A}_i(\boldsymbol{r}), \hat{E}_j(\boldsymbol{r}')\right] = \frac{\hbar}{i\epsilon_o}\frac{1}{(2\pi)^3}\int d^3k \delta_{ij}^{\perp} e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')}$. The function $\delta_{ij}^{\perp} = (\delta_{ij} - \frac{k_i k_j}{k^2})$ is the transverse delta in reciprocal space; in real space it is given by

$$\delta_{ij}^{\perp}(\boldsymbol{r}-\boldsymbol{r}') = \frac{1}{(2\pi)^3}\int d^3k \delta_{ij}^{\perp} e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')}$$

(see Mathematical Appendix A), and therefore

$$\left[\hat{A}_i(\boldsymbol{r}), \hat{E}_j(\boldsymbol{r}')\right] = \frac{\hbar}{i\epsilon_o}\delta_{ij}^{\perp}(\boldsymbol{r}-\boldsymbol{r}').$$

17.3.2 The two-level atom: Jaynes–Cummings model

We are now in a position to make a fully quantum treatment of atoms interacting with an electromagnetic field. To simplify the discussion, we will consider a two-level atom and restrict our attention to its dipole interaction with a single field mode $\boldsymbol{k}\lambda$ of frequency ω, which we take to be close to the atomic transition frequency ω_0. This would be the case, for example, if the atoms were exposed to a laser whose radiation can be regarded as monochromatic to a good approximation.

The Hamiltonian of the system composed of an atomic electron interacting with the quantized field mode in the Coulomb gauge ($\nabla \cdot \boldsymbol{A} = 0$) is then (see Section 12.7)

$$\widehat{H} = \widehat{H}_0 + \widehat{H}_{\mathrm{R}} + \widehat{H}_{\mathrm{I}}, \tag{17.141}$$

with

$$\widehat{H}_0 = \frac{\hat{\boldsymbol{p}}^2}{2m} + \hat{V}(r), \tag{17.142}$$

$$\widehat{H}_{\mathrm{R}} = \hbar\omega\left(\hat{a}_{\mathbf{k}\lambda}^{\dagger}\hat{a}_{\mathbf{k}\lambda} + \tfrac{1}{2}\right), \tag{17.143}$$

and, neglecting the quadratic term of the field as usual,

$$\widehat{H}_{\mathrm{I}} = -\frac{e}{mc}\hat{\boldsymbol{A}}\cdot\hat{\boldsymbol{p}}, \tag{17.144}$$

with

$$\hat{\boldsymbol{A}}(\boldsymbol{r},t) = \sqrt{\frac{2\pi\hbar c^2}{V\omega}}\boldsymbol{\epsilon}_{\mathbf{k}\lambda}\left(\hat{a}_{\mathbf{k}\lambda}e^{i\boldsymbol{k}\cdot\boldsymbol{r}-i\omega_k t} + \hat{a}_{\mathbf{k}\lambda}^{\dagger}e^{-i\boldsymbol{k}\cdot\boldsymbol{r}+i\omega_k t}\right), \tag{17.145}$$

where the coefficient has been selected such that the energy of the field mode is $\mathcal{E} = \hbar\omega$, hence,

$$\widehat{H}_{\mathrm{I}} = -\frac{e}{mc}\sqrt{\frac{2\pi\hbar c^2}{V\omega}}\left(\hat{a}_{\mathbf{k}\lambda}(t) + \hat{a}_{\mathbf{k}\lambda}^{\dagger}(t)\right)\hat{\boldsymbol{p}}\cdot\boldsymbol{\epsilon}_{\mathbf{k}\lambda}. \tag{17.146}$$

The $\hat{a}_{\mathbf{k}\lambda}$, $\hat{a}_{\mathbf{k}\lambda}^{\dagger}$ operate on the Hilbert space of the field oscillators, while particle operators act on their own Hilbert space, so that the Hilbert space of the whole system is the direct product of both spaces (now subspaces). Therefore, the components of the

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system's state vector will be written as products of two vectors, one in each of these subspaces. For the sake of simplicity, we will omit the indices $\mathbf{k}\lambda$ that denote the field mode.

If we call $|i\rangle$ the eigenstates of the atomic Hamiltonian, we can express the latter in the form

$$\widehat{H}_0 = \sum_i \sum_j |i\rangle \langle i| \widehat{H}_{\text{at}} |j\rangle \langle j| = \sum_{i,j} \left(\langle i| \widehat{H}_{\text{at}} |j\rangle\right) |i\rangle \langle j| = \sum_{i,j} E_j \delta_{ij} |i\rangle \langle j| \tag{17.147}$$

or, introducing the elementary operators $\hat{\sigma}_{ij} \equiv |i\rangle \langle j|$,

$$\widehat{H}_0 = \sum_i E_i |i\rangle \langle i| = \sum_i E_i \hat{\sigma}_{ii}. \tag{17.148}$$

The momentum operator in its turn takes the form

$$\hat{\boldsymbol{p}} = \sum_i \sum_j |i\rangle \langle i| \hat{\boldsymbol{p}} |j\rangle \langle j| = \sum_{i,j} \boldsymbol{p}_{ij} |i\rangle \langle j| = \sum_{i,j} \boldsymbol{p}_{ij} \hat{\sigma}_{ij}. \tag{17.149}$$

With this, the total Hamiltonian becomes

$$\widehat{H} = \sum_i E_i \hat{\sigma}_{ii} + \hbar\omega \left(\hat{a}^\dagger \hat{a} + \tfrac{1}{2}\right) - \hbar \sum_{i,j} C_{ij} \left(\hat{a} + \hat{a}^\dagger\right) \hat{\sigma}_{ij}, \tag{17.150}$$

where

$$C_{ij} = \frac{e}{m} \sqrt{\frac{2\pi}{V\hbar\omega}} \boldsymbol{p}_{ij} \cdot \boldsymbol{\epsilon} = ie \sqrt{\frac{2\pi}{V\hbar\omega}} \omega_{ij} \boldsymbol{x}_{ij} \cdot \boldsymbol{\epsilon}. \tag{17.151}$$

The last equality follows directly from the Heisenberg equations of motion, which give $p_{ij} = im\omega_{ij} x_{ij}$.

Our atom has only two active states, which we call $|1\rangle = |-\rangle$ and $|2\rangle = |+\rangle$, where $E_2 > E_1$ and $\omega_{21} = \omega_0 = (E_2 - E_1)/\hbar$. So the corresponding completeness relation reduces to $\hat{\sigma}_{11} + \hat{\sigma}_{22} = |+\rangle \langle +| + |-\rangle \langle -| = P_2 + P_1 = \mathbb{I}$, where P_i $(i = 1, 2)$ are projection operators, and from Eq. (17.148) we get

$$\begin{aligned} \sum_i E_i \hat{\sigma}_{ii} &= E_1 \hat{\sigma}_{11} + E_2 \hat{\sigma}_{22} = \tfrac{1}{2} E_1 \left(\mathbb{I} + \hat{\sigma}_{11} - \hat{\sigma}_{22}\right) + \tfrac{1}{2} E_2 \left(\mathbb{I} + \hat{\sigma}_{22} - \hat{\sigma}_{11}\right) \\ &= \tfrac{1}{2} (E_1 + E_2) + \tfrac{1}{2} (E_2 - E_1) \left(\hat{\sigma}_{22} - \hat{\sigma}_{11}\right), \end{aligned} \tag{17.152}$$

that is,

$$\sum_i E_i \hat{\sigma}_{ii} = E_0 \hat{\sigma}_0 + \tfrac{1}{2} \hbar\omega_0 \hat{\sigma}_3, \tag{17.153}$$

where E_0 is the mean energy of the two states; $\hat{\sigma}_0 \equiv \mathbb{I}$ is the unit matrix, and

$$\hat{\sigma}_3 = \hat{\sigma}_{22} - \hat{\sigma}_{11} = |+\rangle \langle +| - |-\rangle \langle -|. \tag{17.154}$$

Note that this operator describes the difference in population between states, since $\langle \hat{\sigma}_3 \rangle = P_2 - P_1$. Assuming (as is usual) $\boldsymbol{x}_{11} = \boldsymbol{x}_{22} = 0$, $\boldsymbol{x}_{12} = \boldsymbol{x}_{21}$, and hence $\boldsymbol{p}_{12} = -\boldsymbol{p}_{21}$, (17.149) reduces to

$$\sum_{i,j} C_{ij} \hat{\sigma}_{ij} = C_{12} \hat{\sigma}_{12} + C_{21} \hat{\sigma}_{21} = -C_{21} \left(\hat{\sigma}_{12} - \hat{\sigma}_{21}\right) = -C \hat{\sigma}_2, \tag{17.155}$$

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where

$$C = -iC_{21} = e\omega_0\sqrt{\frac{2\pi}{V\hbar\omega}}\boldsymbol{x}_{12}\cdot\boldsymbol{\epsilon} \tag{17.156}$$

and

$$\hat{\sigma}_2 = i\left(\hat{\sigma}_{12} - \hat{\sigma}_{21}\right) = i\left(|-\rangle\langle+| - |+\rangle\langle-|\right). \tag{17.157}$$

Thus, (17.150) takes the form

$$\widehat{H} = E_0\hat{\sigma}_0 + \tfrac{1}{2}\hbar\omega_0\hat{\sigma}_3 + \hbar\omega\left(\hat{a}^\dagger\hat{a} + \tfrac{1}{2}\right) + \hbar C\left(\hat{a} + \hat{a}^\dagger\right)\hat{\sigma}_2. \tag{17.158}$$

In most applications, the additive constants E_0 and $\frac{1}{2}\hbar\omega$ do not play a dynamical role, so that the Hamiltonian can be redefined by subtracting these quantities,[6]

$$\widehat{H} = \tfrac{1}{2}\hbar\omega_0\hat{\sigma}_3 + \hbar\omega\hat{a}^\dagger\hat{a} + i\hbar C\left(\hat{a} + \hat{a}^\dagger\right)\left(\hat{\sigma} - \hat{\sigma}^\dagger\right), \tag{17.159}$$

where

$$\hat{\sigma} \equiv \hat{\sigma}_{12} = |-\rangle\langle+|, \quad \hat{\sigma}^\dagger \equiv \hat{\sigma}_{21} = |+\rangle\langle-| \tag{17.160}$$

are the atomic raising and lowering operators, which act on states $|+\rangle$ and $|-\rangle$ as usual,

$$\hat{\sigma}\,|-\rangle = |-\rangle\langle+|-\rangle = 0, \quad \hat{\sigma}\,|+\rangle = |-\rangle\langle+|+\rangle = |-\rangle, \tag{17.161}$$

$$\hat{\sigma}^\dagger|-\rangle = |+\rangle\langle-|-\rangle = |+\rangle, \quad \hat{\sigma}^\dagger|+\rangle = |+\rangle\langle-|+\rangle = 0. \tag{17.162}$$

We note that

$$[\hat{\sigma}, \hat{\sigma}^\dagger] = -\hat{\sigma}_3; \quad [\hat{\sigma}, \hat{\sigma}_3] = 2\hat{\sigma}, \quad [\hat{\sigma}^\dagger, \hat{\sigma}_3] = -2\hat{\sigma}^\dagger, \tag{17.163}$$

and more generally,

$$[\hat{\sigma}_{ij}, \hat{\sigma}_{kl}] = [\,|i\rangle\langle j|\,, |k\rangle\langle l|\,] = \delta_{jk}\hat{\sigma}_{il} - \delta_{il}\hat{\sigma}_{kj}. \tag{17.164}$$

Since the field and particle operators at equal times act on different spaces, their commutators are zero, for example, $\left[\hat{\sigma}_{ij}(t), \hat{a}(t)\right] = 0$. However, this is no longer true at different times, due to the interaction between the parts of the system, and the commutation relations must then be derived using the equations of motion, which give

$$\dot{\hat{a}} = \frac{1}{i\hbar}[\hat{a}, \widehat{H}] = -i\omega\hat{a} + C\left(\hat{\sigma} - \hat{\sigma}^\dagger\right). \tag{17.165}$$

$$\dot{\hat{\sigma}} = \frac{1}{i\hbar}[\hat{\sigma}, \widehat{H}] = -i\omega_0\hat{\sigma} + C\left(\hat{a} + \hat{a}^\dagger\right)\hat{\sigma}_3, \tag{17.166}$$

$$\dot{\hat{\sigma}}_3 = \frac{1}{i\hbar}[\hat{\sigma}_3, \widehat{H}] = -2C\left(\hat{a} + \hat{a}^\dagger\right)\left(\hat{\sigma} + \hat{\sigma}^\dagger\right), \tag{17.167}$$

and their adjoints.

The interaction Hamiltonian in Eq. (17.159) has four terms,

$$\left(\hat{a} + \hat{a}^\dagger\right)\left(\hat{\sigma} - \hat{\sigma}^\dagger\right) = \hat{a}\hat{\sigma} - \hat{a}\hat{\sigma}^\dagger + \hat{a}^\dagger\hat{\sigma} - \hat{a}^\dagger\hat{\sigma}^\dagger. \tag{17.168}$$

[6] This simplification is common in the literature. However, it should be borne in mind that the term associated with the zero-point energy, which in some cases may play a physical role, has been omitted.

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From Eqs. (17.165) and (17.166) it follows that in the absence of coupling, $\hat{a}(t) = \hat{a}(0)e^{-i\omega t}$ and $\hat{\sigma}(t) = \hat{\sigma}(0)e^{-i\omega_0 t}$. Therefore, for sufficiently weak coupling, the terms $\hat{a}\hat{\sigma}$ and $\hat{a}^\dagger\hat{\sigma}^\dagger$ oscillate rapidly with frequency $\omega_0 + \omega$, while the terms $\hat{a}\hat{\sigma}^\dagger$ and $\hat{a}^\dagger\hat{\sigma}$ oscillate with significantly lower frequency $\omega_0 - \omega$, which vanishes at exact resonance. In the rotating-wave approximation introduced in Section 14.3.3, the nonresonant contributions are neglected and the Hamiltonian becomes reduced to

$$\widehat{H} = \tfrac{1}{2}\hbar\omega_0\hat{\sigma}_3 + \hbar\omega\hat{a}^\dagger\hat{a} + i\hbar C\left(\hat{a}^\dagger\hat{\sigma} - \hat{a}\hat{\sigma}^\dagger\right). \tag{17.169}$$

This is known as the Jaynes–Cummings model. The term $\hat{a}^\dagger\hat{\sigma}$ contains a field-creation operator and an atom-lowering operator; the interaction $\hat{a}\hat{\sigma}^\dagger$ in turn describes the annihilation of a photon and the excitation of the atom. In other words, atomic excitation always involves the annihilation of a photon (term $\hat{a}\hat{\sigma}^\dagger$) and de-excitation involves the production of a photon (term $\hat{a}^\dagger\hat{\sigma}$). This would not be the case if the previously neglected terms $\hat{a}\hat{\sigma}$ and $\hat{a}^\dagger\hat{\sigma}^\dagger$ were retained. Because of this property, at resonance ($\omega = \omega_0$) the operator

$$\hat{N}(t) = \tfrac{1}{2}\hat{\sigma}_3 + \hat{a}^\dagger(t)\hat{a}(t) \tag{17.170}$$

is an integral of motion, with eigenvalues $N \pm \frac{1}{2}$ (N is the number of equivalent photons). For more details see Milonni (2013), chapter 6.

The equations of motion of the Jaynes–Cummings model are the Heisenberg equations for the operators $\hat{a}, \hat{a}^\dagger, \hat{\sigma}_3, \hat{\sigma}$ and $\hat{\sigma}^\dagger$. Using the commutation relations established earlier, one obtains

$$\dot{\widehat{a}} = -i\omega a + C\hat{\sigma}, \tag{17.171}$$

$$\dot{\widehat{\sigma}} = -i\omega\sigma + C\hat{a}\hat{\sigma}_3, \text{ and} \tag{17.172}$$

$$\dot{\widehat{\sigma}}_3 = -2C\left(\hat{a}^\dagger\hat{\sigma} - \hat{a}\sigma^\dagger\right) \tag{17.173}$$

and their adjoints. These equations, as well as the Jaynes–Cummings model, are used in a wide variety of problems in atomic physics, solid-state physics, quantum information circuits, quantum optics, and related fields.

17.4 The Radiative Corrections According to SED. Atomic Lifetimes and Lamb Shift

In QED, the vacuum fluctuations are the source of radiative corrections in an already quantized system, that is, these corrections are considered to be a primary effect of the vacuum. In contrast, according to SED, the vacuum fluctuations are responsible for quantizing the system in the first place, so that the radiative corrections appear as a secondary effect of the fluctuating vacuum.

In the following, we will take advantage of the physical transparency of the SED framework to derive the formulas for the radiative corrections.

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17.4.1 Radiative transitions

In this section we will obtain a formula for the spontaneous transition probability, using the results of Section 10.3. To do this, we recall the SED evolution equation for a constant of motion $\xi(\boldsymbol{x}, \boldsymbol{p})$, Eq. (10.92),

$$\frac{d}{dt}\langle\xi\rangle = m\tau\left\langle \dddot{x}_i \frac{\partial\xi}{\partial p_i}\right\rangle - e^2\left\langle \frac{\partial\xi}{\partial p_i}\hat{\mathcal{D}}_i\right\rangle, \tag{17.174}$$

with

$$e^2\hat{\mathcal{D}}_i = D_{ij}^{px}\frac{\partial}{\partial x_j} + D_{ij}^{pp}\frac{\partial}{\partial p_j}. \tag{17.175}$$

Applied to the particle Hamiltonian $H(\boldsymbol{p},\boldsymbol{x}) = (1/2m)\boldsymbol{p}^2 + V(\boldsymbol{x})$, Eq. (17.174) gives, after integrating by parts the second term on the r.h.s.,

$$\frac{d}{dt}\langle H\rangle = \tau\langle\dddot{\boldsymbol{x}}\cdot\boldsymbol{p}\rangle + \frac{1}{m}\mathrm{tr}\left\langle D^{pp}\right\rangle, \tag{17.176}$$

where $\tau = 2e^2/3mc^3$. We will work in 1D, for simplicity in the exposition. To calculate the last term we use Eq. (10.84),

$$D^{pp}(t) = e^2\int_{-\infty}^{t} ds\left.\frac{\partial p(t)}{\partial p(s)}\right|_{x^{(0)}}\langle E(s)E(t)\rangle\,,$$

where the field correlation $\langle E(s)E(t)\rangle$ is given by

$$\langle E(s)E(t)\rangle = \varphi(t-s) = \frac{4\pi}{3}\int_0^\infty d\omega\rho(\omega)\cos\omega(t-s), \tag{17.177}$$

according to Eq. (10.46), and $\varphi(t-s)$ is the spectral energy function of the ZPF. This gives

$$D^{pp}(t) = e^2\int_{-\infty}^{t} ds\varphi(t-s)\left.\frac{\partial p(t)}{\partial p(s)}\right|_{x^{(0)}}, \tag{17.178}$$

where the derivative inside the integral, $\partial p(t)/\partial p(s) = \{x(s), p(t)\}$, must be replaced by the corresponding commutator divided by $i\hbar$, according to (10.125); hence,

$$D^{pp}(t) = \frac{e^2}{i\hbar}\int_{-\infty}^{t} ds\,\varphi(t-s)\left[\widehat{x}(s),\widehat{p}(t)\right]. \tag{17.179}$$

When the system in a stationary state n, Eq. (17.176), takes the form

$$\frac{d}{dt}\left\langle\hat{H}\right\rangle_n = \tau\left\langle n\left|\dddot{\hat{x}}\cdot\hat{p}\right|n\right\rangle + \frac{1}{m}\left\langle n\left|\hat{D}^{pp}\right|n\right\rangle, \tag{17.180}$$

with

$$\left\langle n\left|\hat{D}^{pp}\right|n\right\rangle = \frac{e^2}{i\hbar}\int_{-\infty}^{t} ds\,\varphi(t-s)\left\langle n\left|\left[\widehat{x}(s),\widehat{p}(t)\right]\right|n\right\rangle. \tag{17.181}$$

Writing the matrix elements of $\hat{x}(s), \hat{p(t)}$ as $x_{kn}(s) = x_{kn}\exp(i\omega_{kn}s)$, $p_{kn}(t) = im\omega_{kn}x_{kn}\exp(i\omega_{kn}t)$, we get

$$\left\langle n\left|\left[\widehat{x}(s),\widehat{p}(t)\right]\right|n\right\rangle = 2im\sum_k \omega_{kn}\left|x_{kn}\right|^2\cos\omega_{kn}(t-s), \tag{17.182}$$

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which, when introduced into (17.181), gives

$$\langle n \left| D^{pp} \right| n \rangle = \frac{2me^2}{\hbar} \sum_k \omega_{kn} \left| x_{kn} \right|^2 \int_{-\infty}^{t} ds\, \varphi(t-s) \cos \omega_{kn}(t-s). \tag{17.183}$$

Further, using (17.177) with $\rho_0(\omega) = \hbar\omega^3/2\pi^2c^3$ for the ZPF and taking into account that

$$\int_{-\infty}^{t} ds\, \cos\omega(t-s) \cos\omega_{kn}(t-s) = \frac{\pi}{2} \left[\delta(\omega - \omega_{kn}) + \delta(\omega + \omega_{kn})\right], \tag{17.184}$$

we finally obtain

$$\langle n \left| D^{pp} \right| n \rangle = -m^2\tau \sum_k \omega_{nk}^4 \left| x_{nk} \right|^2 \mathrm{sign}\omega_{nk}. \tag{17.185}$$

For the radiation reaction term in (17.180), again using $x_{kn}(t) = x_{kn} \exp(i\omega_{kn}t)$, we obtain

$$\tau(\hat{x}\,\hat{p})_{nn} = -m\tau \sum_k \omega_{nk}^4 \left| x_{nk} \right|^2. \tag{17.186}$$

Note that Eq. (17.185) contains a mixture of positive and negative terms, whereas in (17.186) all contributions have the same sign. The two contributions taken together give

$$\begin{aligned} \frac{d\langle H \rangle_n}{dt} &= -m\tau \sum_k \omega_{nk}^4 \left| x_{nk} \right|^2 (1 - \mathrm{sign}\omega_{kn}) \\ &= -2m\tau \sum_{k<n} \omega_{nk}^4 \left| x_{nk} \right|^2. \end{aligned} \tag{17.187}$$

This result confirms that while the ground state ($n = 0$) is strictly stationary – due to the equilibrium between the radiation reaction and the diffusive term – the excited states ($n > 0$) are not stationary; transitions from state n to lower-energy states k take place by the combined action of the ZPF and the radiation reaction (both factors contributing in equal measure), without the intervention of an external radiation field. Writing the average energy loss per unit time as

$$\frac{d\langle H \rangle_n}{dt} = \sum_{k<n} \hbar\omega_{nk} W_{nk}, \tag{17.188}$$

we get for the probability of spontaneous emissions from n to k per unit time

$$W_{nk} = \frac{4e^3}{3\hbar c^3} \omega_{nk}^3 \left| x_{nk} \right|^2, \tag{17.189}$$

in exact agreement with the QED result, Eq. (17.134). It is clear that these expressions have a meaning only in a statistical sense: they refer to an ensemble of systems prepared initially in the same excited state n, which have a certain probability per unit time to decay, determined by the specific properties of the system. However, which transition will occur in each instance, or which member of the ensemble will decay at a given time, is a matter of random circumstances.

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17.4.2 Breakdown of energy balance

One might now ask whether there is a background field $g(\omega)$ which, added to the ZPF, is capable of keeping the particles in an excited state n all the time. With the total field represented by a spectral energy density $\rho(\omega) = \rho_0(\omega)g(\omega)$, where $g(\omega) > 1$ is an even function of ω, Eq. (17.190) must be replaced by

$$\langle n \left| D^{pp} \right| n \rangle = -m^2\tau \sum_k g(\omega_{nk})\omega_{nk}^4 \left| x_{nk} \right|^2 \text{sign}\omega_{nk} \tag{17.190}$$

so that instead of (17.187) we have

$$\frac{d\langle H\rangle_n}{dt} = -m\tau \sum_k \omega_{nk}^4 \left| x_{nk} \right|^2 (1 - g(\omega_{kn})\text{sign}\omega_{kn}). \tag{17.191}$$

Note that the terms in parentheses have different signs depending on whether ω_{kn} refers to an upward or a downward transition (i.e., $k > n$ or $k < n$). Therefore, there is no way to satisfy detailed energy balance in general. However, as we will see later, there is one particular system that can remain in balance in an excited state, namely an ensemble of harmonic oscillators.

Exercise E17.6. Detailed energy balance condition for the harmonic oscillator
Determine the spectral density of the background field that can maintain an ensemble of oscillators in an excited state n.

Solution. The HO is exceptional in the sense that all the $|\omega_{nk}|$ contributing to the sum in (17.191) are equal in value and coincide with the oscillator frequency ω. Using the HO expressions

$$\left| x_{nk} \right|^2 = \frac{\hbar}{2m\omega}\left[(n+1)\delta_{k,n+1} + n\delta_{k,n-1}\right], \tag{17.192}$$

we obtain for first term on the right side of Eq. (17.191)

$$-m\tau \sum_k \omega_{nk}^4 \left| x_{nk} \right|^2 = -\tfrac{1}{2}\hbar\tau\omega^3(2n+1), \tag{17.193}$$

and for the second term

$$m\tau \sum_k \omega_{nk}^4 \left| x_{nk} \right|^2 g(\omega_{kn})\text{sign}\omega_{kn} = \tfrac{1}{2}\hbar\tau\omega^3 g_n(\omega). \tag{17.194}$$

Therefore,

$$\frac{d\langle H\rangle_n}{dt} = -\tfrac{1}{2}\hbar\tau\omega^3\left[2n + 1 - g_n(\omega)\right], \tag{17.195}$$

which indicates that detailed balance holds when $g_n(\omega) = 2n + 1$. In other words, if the HO in an excited state n is embedded in a field with spectral energy density

$$\rho(\omega) = \rho_0(\omega)(2n+1), \tag{17.196}$$

there are as many absorptions as there are emissions per unit time, all with the same frequency ω, so that the average energy of the oscillators does not change. This result should not come as a surprise, since this field has precisely an energy per normal mode

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$\hbar\omega(2n+1)/2$, equal to the energy of the mechanical oscillators with which it is in equilibrium.

It is important to note that even in the case where detailed balance holds, the excited states are *not* stationary (the energy is stationary, not the states): up and down transitions take place continuously, at a rate such that the average energy remains constant. In what follows, we derive the general formulas for the corresponding transition rates.

17.4.3 Atomic lifetimes

Consider an atom prepared in a state n, exposed to a radiation field with spectral energy density $\rho(\omega) = \rho_0(\omega)g(\omega)$ as earlier. It is convenient to separate the additional (external) field from the ZPF,

$$\rho(\omega)=\rho_0(\omega)+\rho_a(\omega), \quad \rho_a(\omega) = \rho_0(\omega)g_a(\omega), \tag{17.197}$$

so that Eq. (17.191) can be written as

$$\begin{aligned}\frac{d\langle H\rangle_n}{dt} &= -m\tau\sum_k \omega_{nk}^4 |x_{nk}|^2 \left[1-(1+g_a(\omega_{nk}))\mathrm{sign}\omega_{kn}\right] \\ &= m\tau\sum_k \omega_{nk}^4 |x_{nk}|^2 \left[(g_a)_{\omega_{kn}>0} - (2+g_a)_{\omega_{kn}<0}\right].\end{aligned} \tag{17.198}$$

The tern proportional to g_a represents the absorptions ($k > n$) and the second one, proportional to $2 + g_a$, the emissions ($k < n$). It is clear from this expression that there can only be absorption if there is an additional field, $\rho_a \neq 0$, which can therefore be identified with the *photonic* field. The emissions, on the other hand, can be either "spontaneous" (in the presence of only the ZPF, as in the previous section) or stimulated by the photonic field.

In terms of the A and B coefficients, Eq. (17.198) takes the form

$$\begin{aligned}\frac{d\langle H\rangle_n}{dt} &= \frac{d}{dt}\langle H\rangle_n^{\text{sp em}} + \frac{d}{dt}\langle H\rangle_n^{\text{ind em}} + \frac{d}{dt}\langle H\rangle_n^{\text{ind abs}} \\ &= \sum_{k>n}\hbar\omega_{kn}B_{kn}^{\text{abs}}\rho_a(\omega_{nk}) \\ &\quad -\sum_{k<n}\hbar\omega_{nk}\left[A_{nk}+B_{nk}^{\text{em}}\rho_a(\omega_{nk})\right],\end{aligned} \tag{17.199}$$

or, using (17.197),

$$\frac{d\langle H\rangle_n}{dt} = \sum_k \hbar|\omega_{nk}|\left[\left(B_{kn}^{\text{abs}}\rho_0 g_a\right)_{\omega_{kn}>0} - \left(A_{nk}+B_{nk}^{\text{em}}\rho_0 g_a\right)_{\omega_{kn}<0}\right], \tag{17.200}$$

whence

$$A_{nk} = \frac{4e^2\omega_{nk}^3}{3\hbar c^3}|x_{nk}|^2, \quad (n>k) \tag{17.201}$$

and

$$B_{kn}^{\text{abs}} = B_{nk}^{\text{em}} = \frac{4\pi^2 e^2}{3\hbar^2}|x_{nk}|^2 \equiv B_{nk}, \tag{17.202}$$

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in agreement with the respective qed formulas. Notice in particular the factor 2 in the relation

$$\frac{A_{nk}}{B_{nk}} = \frac{\hbar\,|\omega_{nk}|^3}{\pi^2 c^3} = 2\rho_0(\omega_{nk}). \tag{17.203}$$

The structure of Eq. (17.198) indicates that one should actually write $2\rho_0 = \rho_0(1 - \mathrm{sign}\omega_{\mathrm{kn}})$, $\omega_{\mathrm{kn}} < 0$, in order to keep track of the origin of each of the two terms: one is due to the vacuum fluctuations and the other to the Larmor radiation. They turn out to be of equal magnitude, as noted in relation to Eq. (17.187). In fact, it is precisely their equality that leads to the exact balance between them when the system is in its ground state.[7]

17.4.4 The Lamb shift

Another important radiative correction, which is considered a major success of QED despite its relative smallness, is the shift of some atomic energy levels due to a residual effect of the vacuum, known as the Lamb shift. The following is a rather straightforward and transparent calculation of the Lamb shift, using the SED tools.

To calculate the radiative energy shift we take $\mathcal{G} = xp$ in the equation of evolution for $\langle\mathcal{G}\rangle$, Eq. (10.86),

$$\frac{d}{dt}\langle xp\rangle = \left\langle \frac{dxp}{dt}\right\rangle_{\mathrm{nr}} + m\tau\left\langle \dddot{x}\frac{\partial xp}{\partial p}\right\rangle - e^2\left\langle \frac{\partial xp}{\partial p}\hat{\mathcal{D}}\right\rangle, \tag{17.204}$$

with $\hat{\mathcal{D}}$ given by Eq. (17.175), which gives

$$\frac{d}{dt}\langle xp\rangle_n = \frac{1}{m}\left\langle n\left|p^2\right|n\right\rangle + \langle n\,|xf|\,n\rangle + m\tau\,\langle n\,|x\,\dddot{x}|\,n\rangle + \left\langle n\left|D^{px}\right|n\right\rangle. \tag{17.205}$$

This equation is a time-dependent version of the classical virial theorem $\left\langle n\left|p^2/m\right|n\right\rangle - \langle n\,|r\cdot\nabla V|\,n\rangle = 0$, with two additional terms that represent radiative corrections to the average energy, given by $\delta E_n = -\frac{m\tau}{2}\langle n\,|x\,\dddot{x}|\,n\rangle - \frac{1}{2}\langle n\,|D^{px}|\,n\rangle$. The first term does not contribute under stationarity, since

$$\langle n\,|x\,\dddot{x}|\,n\rangle = -\tfrac{1}{2}\langle n\,|\dot{x}\,\ddot{x} + \ddot{x}\,\dot{x}|\,n\rangle = \frac{1}{2}\frac{d}{dt}\left\langle \dot{x}^2\right\rangle_n = 0. \tag{17.206}$$

Thus, the Lamb shift is due entirely to the additional fluctuations impressed upon the electrons through their dipolar coupling to the ZPF,

$$\delta E_n = -\frac{1}{2}\left\langle n\left|D^{px}\right|n\right\rangle = -\frac{1}{2}e\,\langle n\,|xE|\,n\rangle\,. \tag{17.207}$$

To calculate this term we write

$$D^{px}(t) = e\,\langle xE\rangle_0 = e^2\int_{-\infty}^{t} ds\,\left.\frac{\partial x(t)}{\partial p(s)}\right|_{x^{(0)}}\langle E(s)E(t)\rangle_0\,, \tag{17.208}$$

[7] It is often found in the literature that all spontaneous decay is attributed to one or the other of these two sources, more commonly to Larmor radiation. In QED the two contributions are equal, *provided* a symmetric operator order is used. Related discussions can be found in Davydov (2013), Dalibard et al. (1982), and Milonni (2013).

https://doi.org/10.1017/9781009679633.018 Published online by Cambridge University Press

which, after we write the Poisson bracket in terms of the commutator, gives

$$D^{px}(t) = \frac{e^2}{i\hbar}\int_{-\infty}^{t} ds\, \varphi(t-s)\,[\widehat{x}(s), \widehat{x}(t)]\,. \tag{17.209}$$

With the matrix elements of $\hat{x}$ given by $x_{kn}(t) = x_{kn}\exp(i\omega_{kn}t)$, we get

$$\langle n\,|[\widehat{x}(s), \widehat{x}(t)]|\,n\rangle = 2i\sum_k |x_{kn}|^2 \sin\omega_{kn}(t-s), \tag{17.210}$$

which when introduced into (17.209), gives

$$\left\langle n\left|D^{px}\right|n\right\rangle = \frac{2e^2}{\hbar}\sum_k |x_{kn}|^2 \int_{-\infty}^{t} ds\, \varphi(t-s)\sin\omega_{kn}(t-s).$$

Using (17.177) with $\rho_0(\omega) = \hbar\omega^3/2\pi^2c^3$ for the ZPF and taking into account that

$$\int_{-\infty}^{t} ds\, \cos(t-s)\sin\omega_{kn}(t-s) = \frac{\omega_{kn}}{\omega_{kn}^2 - \omega^2}, \tag{17.211}$$

we obtain

$$\delta E_n = -\frac{1}{2}\left\langle n\left|D^{px}\right|n\right\rangle = -\frac{2e^2}{3\pi c^3}\sum_k |x_{nk}|\,\omega_{kn}\int_0^\infty d\omega\,\frac{\omega^3}{\omega_{kn}^2-\omega^2}. \tag{17.212}$$

The *observable* Lamb shift $\delta E_{\mathrm{L}n}$ is obtained by subtracting from δE_n the free-particle contribution, δE_{fp}, obtained in the limit of continuous electron energies (when ω_{kn} can be ignored compared to ω in the denominator),

$$\delta E_{\mathrm{fp}} = \frac{2e^2}{3\pi c^3}\sum_m |\boldsymbol{x}_{nm}|^2\,\omega_{mn}\int_0^\infty d\omega\,\omega = \frac{e^2\hbar}{\pi mc^3}\int_0^\infty d\omega\,\omega. \tag{17.213}$$

The last equality follows from the Thomas–Reiche–Kuhn sum rule $\Sigma_m\,|\boldsymbol{x}_{nm}|^2\,\omega_{mn} = 3\hbar/2m$. Hence,

$$\delta E_{\mathrm{L}n} = \delta E_n - \delta E_{\mathrm{fp}} = -\frac{2e^2}{3\pi c^3}\sum_k |\boldsymbol{x}_{nk}|^2\,\omega_{kn}^3\int_0^\infty d\omega\,\frac{\omega}{\omega_{kn}^2-\omega^2}, \tag{17.214}$$

in accordance with the (nonrelativistic) QED formula. Note that the integral is logarithmically divergent. The problem is solved as in QED by introducing a cutoff frequency equal to the Compton frequency of the electron $\omega_C = mc^2/\hbar$, thus giving[8]

$$\delta E_{\mathrm{L}n} = \frac{2e^2}{3\pi c^3}\sum_k |\boldsymbol{x}_{nk}|^2\,\omega_{kn}^3\ln\left|\frac{mc^2}{\hbar\omega_{kn}}\right|. \tag{17.215}$$

The numerical evaluation of this result gives 1057.833 MHz (in units of h) or 4.372×10^{-6}eV for the energy difference between the $2s_{1/2}$ and $2p_{1/2}$ H levels, which corresponds almost exactly to the experimental value observed by Lamb.

[8] Note that the logarithmic divergence here is a result of the previous approximations. If no approximation is made in the radiation reaction term in the denominator of Eq. (17.214), instead of ω^2, ω^4 will appear, and the integral will converge (and lead to a correct prediction).

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17.4.5 External effects on the radiative corrections

We note from Eq. (17.208) that the Lamb shift is due to the coupling of the (instantaneous) electric dipole moment of the atom to the electric component of the background field. But the background field can be modified externally, for example, by placing the atom in a reflective cavity that changes the field's boundary conditions and thus affects the distribution of the normal field modes, or by adding a photonic field to the vacuum. As a result, the Lamb shift is modified accordingly (Problem P17.11).

From the formulas obtained for the emission and absorption probabilities in Section 17.4.3, it is clear that the atomic radiation lifetimes are also modified by the addition of a photonic field or by placing the atom in a reflective cavity.

Such "environmental" effects have been studied and tested experimentally for more than 50 years, leading to the development of *cavity quantum electrodynamics* (CQED). The techniques developed to create and measure CQED states are now being applied to the development of quantum computers and other modern systems. The calculations are typically done within the framework of QED, although they can usually be done more easily within the framework of SED, as shown earlier, which reproduces the (nonrelativistic) QED formulas with the advantage of physical transparency.

17.5 Canonical Field Quantization Clarified

In Section 17.3.1, the field was quantized *à la* Dirac, that is, by replacing the classical field variables a, a^* by the annihilation and creation operators $a, \widehat{a}^\dagger$ satisfying the commutator (17.131). This formal quantization procedure, introduced as a postulate, was instrumental in the development of QED and is used more generally to quantize other fields. In the following we give a physical rationale for the replacement of variables by operators to describe the quantized radiation field.

17.5.1 Describing a field component in interaction with matter

We have seen in previous sections that in radiative transitions, atomic matter interacts resonantly with field modes of well-defined frequencies ω_{nk}. Any radiative transition that changes the state of the atom is accompanied by a concomitant change in the state of the field involved. To describe the effect *on the radiation field* resulting from this process, we will focus on a *single* frequency $\omega_{nk} \equiv \omega$ of the field.[9]

We call $\mathrm{q_n}(t)$, $\mathrm{p_n}(t)$ the canonical variables of the field in a stationary state n and express them as linear combinations of the normal field amplitudes (a, a^*) introduced in Section 10.4.1.[10] Using roman letters to distinguish the field variables from those of the atomic system (which were expressed in italics), we have

[9] As in the case of QM, our aim is to reveal the quantization – in this case of the field modes – as the primary effect of this interaction; the secondary effects can then be treated as perturbations.

[10] This applies as long as there are no nonlinear effects, produced by nonlinear optical materials or at very high light intensities ($> 10^8\ \mathrm{Vm}^{-1}$) such as those provided by lasers. The first nonlinear optical effect to be predicted was two-photon absorption, by Maria Göppert Mayer for her PhD in 1931.

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$$\mathrm{q_n}(t) = \sum_{\mathrm{n'}} \mathrm{q_{nn'}} a_{n\mathrm{n'}} e^{-i\omega_{\mathrm{n'n}}t} + \mathrm{c.c.},\ \mathrm{p_n}(t) = \sum_{\mathrm{n'}} \mathrm{p_{nn'}} a_{\mathrm{nn'}} e^{-i\omega_{\mathrm{n'n}}t} + \mathrm{c.c.}, \tag{17.216}$$

where the amplitudes $a_{\mathrm{nn'}}, a^*_{\mathrm{nn'}}$ connect state n of the field with other possible states n' of the field, and $\mathrm{q_{nn'}}, \mathrm{p_{nn'}}$ are the respective *response coefficients*. Since the field oscillates with a single frequency ω, it follows that $\omega_{\mathrm{n'n}} = \pm\omega$ and consequently, only two terms connecting state n with a state n' are different from zero. Since there are no intermediate states, we denote the upper state (corresponding to $\omega_{\mathrm{n'n}} = +\omega$) by $\mathrm{n'} = \mathrm{n}+1$, and the lower state (corresponding to $\omega_{\mathrm{n'n}} = -\omega$) by $\mathrm{n'} = \mathrm{n}-1$, so that Eqs. (17.216) become

$$\mathrm{q_n}(t) = \mathrm{q_{nn+1}} a_+ e^{-i\omega t} + \mathrm{q_{nn-1}}\, a_- \mathrm{e}^{\mathrm{i}\omega t} + \mathrm{c.c.},\ \text{and} \tag{17.217}$$

$$\mathrm{p_n}(t) = -i\omega \mathrm{q_{nn+1}} a_+ e^{-i\omega t} + i\omega \mathrm{q_{nn-1}}\, a_- e^{i\omega t} + c.c. \tag{17.218}$$

From $\mathrm{p_n}(t) = \dot{\mathrm{q}}_\mathrm{n}(t)$, we have

$$\omega \mathrm{q_{nn+1}} - i\mathrm{p_{nn+1}} = 0, \qquad \omega \mathrm{q_{nn-1}} + i\mathrm{p_{nn-1}} = 0. \tag{17.219}$$

17.5.2 From field variables to field operators

In analogy with the procedure followed in Chapter 10, which led to the quantum mechanical canonical commutator $\left[\hat{x}, \hat{p}\right] = i\hbar$ we now take the Poisson bracket of the field variables given by Eqs. (17.217) and (17.218). The canonical Poisson bracket must satisfy

$$\{\mathrm{q_n}(t), \mathrm{p_n}(t)\}_{\{\mathrm{q,p}\}} = 1. \tag{17.220}$$

Since the normal amplitudes (a, a^*) are related to the (canonical) quadratures (q, p) by the transformation

$$\omega \mathrm{q} = \sqrt{\hbar\omega/2}(a + a^*),\ \mathrm{p} = -i\sqrt{\hbar\omega/2}(a - a^*), \tag{17.221}$$

the transformed Poisson bracket reads

$$\{\mathrm{q_n}(t), \mathrm{p_n}(t)\}_{\{a,a^*\}} \equiv \{\mathrm{q_n}(t), \mathrm{p_n}(t)\} = i\hbar. \tag{17.222}$$

From (17.217) and (17.218) we see that the only pairs of normal amplitudes involved in the Poisson bracket are $(a_+, a^*{}_+)$ and $(a_-, a^*{}_-)$; this gives explicitly

$$\sum_{n'=n\pm1} \left(\mathrm{q_{nn'}} \mathrm{p^*{}_{nn'}} - \mathrm{p_{nn'}} \mathrm{q^*{}_{nn'}}\right) = i\hbar. \tag{17.223}$$

By using Eq. (17.217) we get

$$\mathrm{q^*{}_{nn'}}(\omega_{\mathrm{n'n}}) = \mathrm{q_{n'n}}(\omega_{\mathrm{nn'}}),\ \mathrm{p^*{}_{nn'}}(\omega_{\mathrm{n'n}}) = \mathrm{p_{n'n}}(\omega_{\mathrm{nn'}}),\ a^*_{\mathrm{nn'}}(\omega_{\mathrm{n'n}}) = a_{\mathrm{n'n}}(\omega_{\mathrm{nn'}}), \tag{17.224}$$

so that Eq. (17.223) can be written in the alternative form

$$\sum_{n'=n\pm1} \left(\mathrm{q_{nn'}} \mathrm{p_{n'n}} - \mathrm{p_{nn'}} \mathrm{q_{n'n}}\right) = i\hbar. \tag{17.225}$$

By identifying $\mathrm{q_{nn'}}$ and $\mathrm{p_{n'n}}$ as the elements of matrices $\hat{\mathrm{q}}$ and $\hat{\mathrm{p}}$, respectively, Eq. (17.225) becomes

$$\left[\hat{\mathrm{q}}, \hat{\mathrm{p}}\right]_{\mathrm{nn}} = \left[\hat{\mathrm{q}}, \hat{\mathrm{p}}\right] = i\hbar, \tag{17.226}$$

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for any state n of the field. Therefore the canonical field commutator is the Poisson bracket of $\mathrm{q_n}(t), \mathrm{p_n}(t)$, with respect to the normal amplitudes $(a_{\pm}, a^*{}_{\pm})$ that take the field from any state n to states n±1.

From (17.219) we have $\mathrm{p_{nn'}} + i\omega_{\mathrm{n'n}}\mathrm{q_{nn'}} = 0$; therefore, the matrix $\hat{\mathrm{a}}$ and its adjoint, defined as

$$\hat{\mathrm{a}} = \frac{1}{\sqrt{2\hbar\omega}}(\omega\hat{\mathrm{q}} + i\hat{\mathrm{p}}),\ \hat{\mathrm{a}}^{\dagger} = \frac{1}{\sqrt{2\hbar\omega}}(\omega\hat{\mathrm{q}} - i\hat{\mathrm{p}}), \tag{17.227}$$

have off-diagonal elements $\mathrm{a_{nn'}}, \mathrm{a^*{}_{nn'}}$ immediately above and below the main diagonal, that is, they play the role of *annihilation* and *creation* operators respectively. Combining Eqs. (17.226) and (17.227) gives for their commutator

$$\left[\hat{\mathrm{a}}, \hat{\mathrm{a}}^{\dagger}\right] = 1, \tag{17.228}$$

which is exactly Eq. (17.131), the cornerstone of the quantum theory of radiation. Note, however, that, according to this result, it is not the mode amplitudes a, a^* that are quantized; rather, the operators $\hat{\mathrm{a}}, \hat{\mathrm{a}}^{\dagger}$ contain the *response coefficients* of the modes involved in the matter–field interaction.

17.5.3 The interaction Hilbert space

In principle, any problem involving matter–field interaction forces us to work in an extended Hilbert space which is the product of the particle and field Hilbert spaces. In principle this means introducing an infinite-dimensional Hilbert space to account for the continuous nature of the field spectrum. Fortunately, in practice, for the study of matter–field exchange processes the field components are limited to those that are relevant in each case, depending on the problem at hand, taking into account that different field components do not interact among themselves and remain uncorrelated. Therefore, it makes sense to complete the quantum field formalism by considering only one field component, as earlier, and introducing the state vectors living in a single Hilbert space, on which the respective $\hat{\mathrm{a}}, \hat{\mathrm{a}}^{\dagger}$ operators act. To each field mode corresponds a pair of operators $\hat{\mathrm{a}}, \hat{\mathrm{a}}^{\dagger}$ acting on its own Hilbert space, different from the Hilbert space of other field modes and of the particle interacting with it.

From here on, we will revert to conventional notation and write the field operators as $\hat{a}, \hat{a}^{\dagger}$ instead of $\hat{\mathrm{a}}, \hat{\mathrm{a}}^{\dagger}$; however, the reader should bear in mind the physical meaning of these operators, which, as seen earlier, represent the response of the field in matter–field exchange processes.

In Dirac's notation, $|\mathrm{n}\rangle$ stands for the state vector n, with $|0\rangle$ representing the ground state, and $\langle\mathrm{n}|$ stands for the adjoint of $|\mathrm{n}\rangle$. As we saw earlier the effect of $\hat{a}$ or $\hat{a}^{\dagger}$ on $|\mathrm{n}\rangle$ is to lower or raise the number n by one,

$$\hat{a}\,|\mathrm{n}\rangle = \sqrt{\mathrm{n}}\,|\mathrm{n}-1\rangle\,,\ \hat{a}^{\dagger}\,|\mathrm{n}\rangle = \sqrt{\mathrm{n}+1}\,|\mathrm{n}+1\rangle\,.$$

These are the basic elements used to describe how the field of frequency ω, interacting with matter, exchanges radiative energy in well-defined quantities $\pm\hbar\omega$.

By writing the Hamiltonian operator in *symmetrized* form,

$$\hat{\mathrm{H}} = \frac{1}{2}\left(\omega^2\hat{\mathrm{q}}^2 + \hat{\mathrm{p}}^2\right) = \frac{\hbar\omega}{2}\left(\hat{a}\hat{a}^{\dagger} + \hat{a}^{\dagger}\hat{a}\right), \tag{17.229}$$

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we get the well-known result for the expectation value of the energy,

$$\langle \mathrm{n}|\hat{\mathrm{H}}|\mathrm{n}\rangle = \mathcal{E}_{\mathrm{n}} = \left(\mathrm{n} + \frac{1}{2}\right)\hbar\omega, \tag{17.230}$$

so that the ground-state energy is indeed $\mathcal{E}_0 = \hbar\omega/2$, and $|\mathcal{E}_{\mathrm{n}} - \mathcal{E}_{\mathrm{n}\pm1}| = \hbar\omega$, as observed by Planck; see Section 2.9.

On its part, the *normal* operator order $\hat{a}^\dagger\hat{a}$ gives the total number n of photons available, that is, those that can be absorbed in *photodetection* processes, and conversely, the *antinormal* order $\hat{a}\hat{a}^\dagger$ gives the total probability of *photoemission* (both spontaneous and induced), as shown in Section 17.2.

Note that Eqs. (17.229)–(17.230), like all the previous ones, refer to a field component that exchanges energy *as a result of its interaction with quantized matter*; they tell us nothing about the (quantum or nonquantum) nature of the *free* radiation field. Consider, for example, the synchrotron radiation produced by highly accelerated orbiting electrons. When such radiation strikes a detector, a resonant interaction of the atoms of the detector at a well-defined frequency ω can lead to the absorption of a corresponding energy $\hbar\omega$; the energy absorbed by an atom is quantized, but we cannot ascertain that the energy emitted by the (free) accelerated electrons is.

By now the student may have realized that the image of an isolated atom or quantum particle in empty space is an entelechy, as previously discussed in Chapter 2. Even assuming that the system can be cooled to zero temperature, thereby eliminating the photonic radiation, the atom would still be surrounded by the field in its ground state, the ZPF. The inclusion of the ZPF transforms the apparently mechanical nature of quantum systems into a truly electrodynamic one, even in the absence of external fields. From the perspective gained by SED, we can say that quantum dynamics is a distinctive extension of classical physics into the stochastic domain. This counters the extended schizophrenic view of the world, in which its quantum and classical parts occupy mutually exclusive compartments (with the nanoworld somewhere in between).

17.6 *Second Quantization. An Introduction

Fully symmetrized or antisymmetrized wave functions correctly describe the behavior of the quantum system to which they refer, but, as we have seen in Chapter 15, they tend to be remarkably complex and unwieldy. It suffices to consider a case as simple as that of three equal particles, for the treatment of which it is necessary to deal with 6 (=3!) components of the wave function, to perceive the complexity that is soon reached when the number of particles increases. In addition to this practical difficulty, it turns out that for many purposes the wave function thus constructed contains much irrelevant or superfluous information, which, if eliminated, would simplify and clarify the description.

What we need in many cases is merely the description of a system containing identical particles that satisfy this or that statistics. The second-quantization method leads precisely to a synthetic description of the states of several identical particles, which makes it particularly suitable for carrying out the required calculations. What

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is being quantized are the fields that describe quantum particles, hence the name *second-quantization theory*. In fact, quantum field theory is a second-quantized theory.

A common way of second-quantizing Schrödinger's theory is to draw on the experience of using the creation and annihilation operators of the harmonic oscillator; however, in this brief introduction to the subject we will appeal to considerations that are more general in nature and therefore help to get a broader vision.

The starting point is the observation – which we will not prove here – that the Schrödinger equation can be derived from a Lagrangian density, that is, that there exists a Lagrangian density whose equations of motion (the corresponding Euler-Lagrange equations) are the Schrödinger equation and its adjoint. If we have a Lagrangian density[11] we can use it to construct the canonical momentum density conjugate to the generalized coordinate of the field. Using this procedure, it is found that by taking the wave function $\psi(x,t)$ as the generalized coordinate, the canonical conjugate momentum density becomes $\pi(x,t) = i\psi^*(x,t)$. As expected, the second-quantization method transforms *wave functions* into *operator*s, that is,

$$\psi(x,t) \to \widehat{\psi}(x,t),\ \pi(x,t) = i\psi^*(x,t) \to \widehat{\pi}(x,t) = i\widehat{\psi}^\dagger(x,t). \tag{17.231}$$

This is the standard procedure to quantize a field. However, since the commutation rules are different for bosonic and fermionic fields, one must study the two cases separately.

17.6.1 Second quantization of the Schrödinger field for bosons

The canonical variables $\widehat{\psi}(\boldsymbol{x},t)$ and $\widehat{\pi}(\boldsymbol{x}',t)$ for a bosonic field must satisfy the commutation rule (taking $\hbar = 1$)

$$\left[\widehat{\psi}(\boldsymbol{x},t), \widehat{\pi}(\boldsymbol{x}',t)\right] = i\delta(\boldsymbol{x}-\boldsymbol{x}'), \tag{17.232}$$

or equivalently with $\pi(\boldsymbol{x},t) = \psi^\dagger(\boldsymbol{x},t)$,

$$\left[\widehat{\psi}(\boldsymbol{x},t), \widehat{\psi}^\dagger(\boldsymbol{x}',t)\right] = \delta(\boldsymbol{x}-\boldsymbol{x}'). \tag{17.233}$$

In addition,

$$\left[\widehat{\psi}(\boldsymbol{x},t), \widehat{\psi}(\boldsymbol{x}',t)\right] = 0, \quad \left[\widehat{\psi}^\dagger(\boldsymbol{x},t), \widehat{\psi}^\dagger(\boldsymbol{x}',t)\right] = 0. \tag{17.234}$$

As the fields evolve, it may well happen that some variables become dependent on the others; for example, $\widehat{\psi}(\boldsymbol{x}',t')$ can depend on $\widehat{\psi}(\boldsymbol{x},t)$ for $t' > t$. The commutators for $t' \neq t$ will follow from the dynamics.

The quantized field $\widehat{\psi}(\boldsymbol{x},t)$ satisfies the Schrödinger equation

$$i\frac{\partial\widehat{\psi}(\boldsymbol{x},t)}{\partial t} = -\frac{1}{2m}\nabla^2\widehat{\psi}(\boldsymbol{x},t) + V(\boldsymbol{x})\widehat{\psi}(\boldsymbol{x},t) \equiv \widehat{\mathcal{H}}\widehat{\psi}(\boldsymbol{x},t), \tag{17.235}$$

where the operator $\widehat{\mathcal{H}}$ is the Hamiltonian density. Let us consider the eigenstates $u_k(\boldsymbol{x})$ of $\widehat{\mathcal{H}}$,

$$\widehat{\mathcal{H}}u_k(\boldsymbol{x}) = E_k u_k(\boldsymbol{x}), \tag{17.236}$$

[11] A field is a continuous system, so it is necessary to use the Lagrangian density and not simply the Lagrangian.

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as forming a complete orthonormal basis $\{u_k(\boldsymbol{x})\}$ that allows us to expand the $\widehat{\psi}$ state in the form

$$\widehat{\psi}(\boldsymbol{x},t)=\sum_k \widehat{a}_k u_k(\boldsymbol{x})e^{-iE_kt}. \tag{17.237}$$

The coefficients $\widehat{a}_k$ of the expansion are operators, in line with the operator structure of the field; they are given by

$$\widehat{a}_k=\int u_k^*(\boldsymbol{x})\widehat{\psi}(\boldsymbol{x},t)e^{iE_kt}d^3x. \tag{17.238}$$

The commutation rules (17.233) and (17.234) now allow us to determine the commutation rules for the coefficients $\widehat{a}_k$. Taking into account the orthonormality of $\{u_k(\boldsymbol{x})\}$ we have

$$\begin{aligned}\left[\widehat{a}_k,\widehat{a}_{k'}^\dagger\right]&=\int d^3x\int d^3x' u_k^*(\boldsymbol{x})u_{k'}(\boldsymbol{x}')e^{i(E_k-E_{k'})t}\left[\widehat{\psi}(\boldsymbol{x},t),\widehat{\psi}^\dagger(\boldsymbol{x}',t)\right]\\&=\int d^3x u_k^*(\boldsymbol{x})u_{k'}(\boldsymbol{x})e^{i(E_k-E_{k'})t}=\delta_{kk'};\end{aligned} \tag{17.239}$$

thus,

$$\left[\widehat{a}_k,\widehat{a}_{k'}^\dagger\right]=\delta_{kk'}. \tag{17.240}$$

Analogously, we get

$$[\widehat{a}_k,\widehat{a}_{k'}]=0,\quad \left[\widehat{a}_k^\dagger,\widehat{a}_{k'}^\dagger\right]=0. \tag{17.241}$$

These commutation rules are what we expected for bosonic fields. In fact, one can go the other way and postulate Eqs. (17.240) and (17.241), to derive the canonical rules (17.233) and (17.234). The two procedures are equivalent and it is a matter of taste rather than of principle which one is chosen. Given what we learned in Chapter 9, we know that the newly derived rules assign to the operators $\widehat{a}_k^\dagger$ and $\widehat{a}_k$ the character of creation and annihilation operators for bosons, respectively.

To determine the commutation rule for arbitrary times we make the following calculation, which is now direct,

$$\begin{aligned}\left[\widehat{\psi}(\boldsymbol{x},t),\widehat{\psi}^\dagger(\boldsymbol{x}',t')\right]&=\sum_{k,k'}\left[\widehat{a}_k,\widehat{a}_{k'}^\dagger\right]u_{k'}^*(\boldsymbol{x}')u_k(\boldsymbol{x})e^{-iE_kt+iE_{k'}t'}=\\&=\sum_k u_k^*(\boldsymbol{x}')u_k(\boldsymbol{x})e^{-iE_k(t-t')}.\end{aligned} \tag{17.242}$$

But this is precisely the expansion of the propagator (Green's function) of the Schrödinger equation for the problem at hand, as follows by comparison with Eq. (7.145). Taking $t=t'$, and remembering that $\sum_k u_k^*(\boldsymbol{x}')u_k(\boldsymbol{x})=\delta(\boldsymbol{x}-\boldsymbol{x}')$, we recover Eqs. (17.233) and (17.234).

The Hamiltonian of the system follows from its density,

$$\begin{aligned}\widehat{H}&=\int\widehat{\psi}^\dagger(\boldsymbol{x},t)\widehat{\mathcal{H}}\widehat{\psi}(\boldsymbol{x},t)d^3x\\&=\sum_{k,k'}\int d^3x\, e^{i(E_k-E_{k'})t}\,\widehat{a}_k^\dagger\widehat{a}_{k'}u_k^*(\boldsymbol{x})\widehat{\mathcal{H}}u_{k'}(\boldsymbol{x})\\&=\sum_{k,k'}e^{i(E_k-E_{k'})t}E_{k'}\widehat{a}_k^\dagger\widehat{a}_{k'}\int d^3x u_k^*(\boldsymbol{x}')u_k(\boldsymbol{x}),\end{aligned} \tag{17.243}$$

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whence

$$\widehat{H} = \sum_k E_k \widehat{a}_k^\dagger \widehat{a}_k. \tag{17.244}$$

This result, which holds for any external potential, describes the Hamiltonian as the energy of independent (noninteracting) particles, each one with its own energy E_k. We have thus obtained a description in terms of the states of the system instead of the modes of the field, just as when we quantized the radiation field in Section 17.3. If we introduce the number operators

$$\widehat{N}_k = \widehat{a}_k^\dagger \widehat{a}_k, \tag{17.245}$$

we see that they all commute with the Hamiltonian and with each other,

$$\left[\widehat{N}_k, \widehat{H}\right] = 0, \tag{17.246}$$

$$\left[\widehat{N}_k, \widehat{N}_{k'}\right] = 0. \tag{17.247}$$

This means that $\widehat{H}, \left\{\widehat{N}_k\right\}$ form a maximal set of commuting operators (MSCO) and can be used with a complete basis for describing the system. This basis is denoted by kets of the form $|n_1, n_2, n_3, \cdots\rangle$, each of which describes a state of $n = n_1 + n_2 + n_3 + \cdots$ particles, with n_1 particles in state 1, n_2 in state 2, etc., and $n_k = 0, 1, 2, 3, \cdots$. The set of numbers $\{n_1, n_2, n_3, \cdots | n = n_1 + n_2 + n_3 + \cdots\}$ is known as a partition of n, and the set of all possible partitions represents the set of possible states of the system. The space constructed on this basis is called *Fock space* or *space of occupation numbers*; the representation is called *number representation* and its vectors can be constructed using Eq. (7.145) to get

$$|n_1, n_2, n_3, \cdots\rangle = \frac{1}{(n_1! n_2! \cdots)^{1/2}} \left(\widehat{a}_1^\dagger\right)^{n_1} \left(\widehat{a}_2^\dagger\right)^{n_2} \cdots |0\rangle, \tag{17.248}$$

where the vacuum state $|0\rangle$ represents the state without particles. Since it is not possible to reduce any occupancy number from the empty state, it must be true that

$$\widehat{a}_k |0\rangle = 0. \tag{17.249}$$

Note the economy of the description, since $|n_1, n_2, n_3, \cdots\rangle$ specifies only the occupancy number in each energy eigenstate, independent of any spatial location.

Exercise E17.7. Heisenberg equation for the quantized boson field
Show that the Heisenberg equation for the Schrödinger field operator defined in Eq. (17.237) for bosons,

$$i\hbar \frac{\partial \widehat{\psi}}{\partial t} = \left[\widehat{\psi}, \widehat{H}\right], \tag{17.250}$$

where $\widehat{H}$ is the Hamiltonian operator given by (17.243), agrees with the Schrödinger equation for $\widehat{\psi}$. Derive the continuity equation for the particle density operator $\hat{\rho}(\boldsymbol{x}) = \hat{\psi}^\dagger \widehat{\psi}$. What does the result mean? With the particle number operator given by

$$\widehat{N} = \int \widehat{\psi}^\dagger(\boldsymbol{x}) \widehat{\psi}(\boldsymbol{x}) \mathrm{d}^3 x, \tag{17.251}$$

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show that $\widehat{N} = \sum_k \widehat{N}_k$, where $\widehat{N}_k = \widehat{a}_k^\dagger \widehat{a}_k$.

Solution. We have

$$\left[\widehat{\psi}(\boldsymbol{x}), \widehat{H}\right] = \int \left[\widehat{\psi}(\boldsymbol{x}), \widehat{\psi}^\dagger(\boldsymbol{x}')\widehat{\mathcal{H}}(\boldsymbol{x}')\widehat{\psi}(\boldsymbol{x}')\mathrm{d}^3x'\right], \tag{17.252}$$

where $\mathcal{H}$ represents the Hamiltonian density appearing in Eq. (17.235),

$$\widehat{\mathcal{H}}(\boldsymbol{x}) = -\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{x}). \tag{17.253}$$

The calculation is considerably simplified by applying the identity

$$\left[\widehat{A}, \widehat{B}\widehat{C}\right] = \widehat{B}\left[\widehat{A}, \widehat{C}\right] + \left[\widehat{A}, \widehat{B}\right]\widehat{C}, \tag{17.254}$$

which gives

$$\begin{aligned}\left[\widehat{\psi}(\boldsymbol{x}), \widehat{H}\right] = &\int \mathrm{d}^3x'\widehat{\psi}^\dagger(\boldsymbol{x}')\left[\widehat{\psi}(\boldsymbol{x}), \widehat{\mathcal{H}}(\boldsymbol{x}')\widehat{\psi}(\boldsymbol{x}')\right] \\ &+ \int \mathrm{d}^3x'\left[\widehat{\psi}(\boldsymbol{x}'), \widehat{\psi}^\dagger(\boldsymbol{x}')\right]\widehat{\mathcal{H}}(\boldsymbol{x}')\widehat{\psi}(\boldsymbol{x}').\end{aligned} \tag{17.255}$$

The first term on the right-hand side is zero, since

$$\left[\widehat{\psi}(\boldsymbol{x}), \widehat{\mathcal{H}}(\boldsymbol{x}')\widehat{\psi}(\boldsymbol{x}')\right] = \widehat{\mathcal{H}}(\boldsymbol{x}')\left[\widehat{\psi}(\boldsymbol{x}), \widehat{\psi}(\boldsymbol{x}')\right] = 0, \tag{17.256}$$

so that from (17.234) we get

$$\left[\widehat{\psi}(\boldsymbol{x}), \widehat{H}\right] = \int \mathrm{d}^3x'\delta(\boldsymbol{x}-\boldsymbol{x}')\widehat{\mathcal{H}}(\boldsymbol{x}')\widehat{\psi}(\boldsymbol{x}'), \tag{17.257}$$

that is, the Schrödinger equation

$$i\hbar\frac{\partial\widehat{\psi}}{\partial t} = \widehat{\mathcal{H}}(\boldsymbol{x})\widehat{\psi}(\boldsymbol{x}). \tag{17.258}$$

Note that this evolution equation is precisely the corresponding Heisenberg equation for the quantized field.

We now take the time derivative of the particle density $\hat{\rho}(\boldsymbol{x}) = \widehat{\psi}^\dagger\widehat{\psi}$ using the previous result,

$$\begin{aligned}\frac{d}{dt}\hat{\rho}(\boldsymbol{x}) &= \frac{d\widehat{\psi}^\dagger}{dt}\widehat{\psi} + \widehat{\psi}^\dagger\frac{d}{dt}\widehat{\psi} = -\frac{i\hbar}{2m}\left[\left(\nabla^2\widehat{\psi}^\dagger\right)\widehat{\psi} - \widehat{\psi}^\dagger\left(\nabla^2\widehat{\psi}\right)\right] \\ &= -\frac{i\hbar}{2m}\nabla\cdot\left[\left(\nabla\widehat{\psi}^\dagger\right)\widehat{\psi} - \widehat{\psi}^\dagger\left(\nabla\widehat{\psi}\right)\right],\end{aligned} \tag{17.259}$$

which leads to the continuity equation

$$\frac{d}{dt}\hat{\rho}(\boldsymbol{x}) = -\nabla\cdot\widehat{\boldsymbol{j}} \tag{17.260}$$

for the current density operator

$$\boldsymbol{j} = -\frac{i\hbar}{2m}\left[\widehat{\psi}^\dagger\left(\nabla\widehat{\psi}\right) - \left(\nabla\widehat{\psi}^\dagger\right)\widehat{\psi}\right]. \tag{17.261}$$

The equal-time particle density operators commute at any pair of points (see problem P17.12),

$$\left[\hat{\rho}(\boldsymbol{x}), \hat{\rho}(\boldsymbol{x}')\right] = 0. \tag{17.262}$$

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Because of its fundamental importance, this property could have been used as a requirement to quantize the field.

We now take the number operator

$$\widehat{N} = \int \widehat{\psi}^{\dagger}(x)\widehat{\psi}(x)\mathrm{d}^3x = \int \rho(x)\mathrm{d}^3x \tag{17.263}$$

and reduce this expression by steps similar to those that led to (17.244). It is sufficient to suppress the Hamiltonian operator, which leads to

$$\widehat{N} = \sum_k \widehat{N}_k = \sum_k \widehat{a}_k^{\dagger}\widehat{a}_k. \tag{17.264}$$

To determine $\dot{\widehat{N}}$ we must first determine $\widehat{a}_k(t) \equiv \widehat{a}_k e^{-iE_k t}$. This is easily done by considering Schrödinger's equation (17.258) and using Eq. (17.237),

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\sum_k \widehat{a}_k u_k(x)e^{-iE_k t} &= i\hbar\frac{\partial}{\partial t}\sum_k \widehat{a}_k(t)u_k(x) = i\hbar\sum_k \frac{d\widehat{a}_k(t)}{dt}u_k(x) \\ &= \sum_k \widehat{a}_k(t)\widehat{\mathcal{H}}(x)u_k(x) = \sum_k \widehat{a}_k(t)E_k u_k(x), \end{aligned} \tag{17.265}$$

that is,

$$i\hbar\frac{d\widehat{a}_k}{dt} = E_k\widehat{a}_k(t). \tag{17.266}$$

This equation describes the evolution of the field operator for a free field, that is, when the possible interactions between the particles that make up the system are not taken into account. By introducing such interactions, the equation is modified and the different modes (the k indices) interact and become coupled, so that the number of particles in each of the k states is no longer constant.

Note: Analogous results, mutatis mutandis, are obtained for fermions using anticommutators, as is demonstrated in the next section.

17.6.2 Second quantization of the Schrödinger–Pauli field for fermions

The quantization of the Schrödinger–Pauli field in the case of fermions is done in the same way as for bosons, with the only difference that the commutators are replaced by anticommutators.[12] If $\widehat{b}_k, \widehat{b}_k^{\dagger}$ are the operators for fermionic fields and their anticommutators are

$$\left\{\widehat{b}_k, \widehat{b}_{k'}^{\dagger}\right\} \equiv \widehat{b}_k\widehat{b}_{k'}^{\dagger} + \widehat{b}_{k'}^{\dagger}\widehat{b}_k, \tag{17.267}$$

the appropriate (anti)commutation rules are

[12] The observation that it is sufficient to replace commutators by anticommutators to make the transition from B–E to F–D statistics is due to the German mathematician and theoretical physicist Pascual Jordan (1902–1980).

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$$\left\{\widehat{b}_k, \widehat{b}_{k'}^\dagger\right\} = \delta_{kk'}, \tag{17.268}$$

$$\left\{\widehat{b}_k, \widehat{b}_{k'}\right\} = 0, \quad \left\{\widehat{b}_k^\dagger, \widehat{b}_{k'}^\dagger\right\} = 0. \tag{17.269}$$

Writing $\widehat{b}_k$ instead of $\widehat{a}_k$ everywhere leads to the theory for fermions, so the process will not be repeated here. From (17.269) it follows that

$$\left\{\widehat{b}_k, \widehat{b}_{k'}\right\} = \widehat{b}_k\widehat{b}_{k'} + \widehat{b}_{k'}\widehat{b}_k = 0, \tag{17.270}$$

and taking $k' = k$, we obtain $\widehat{b}_k^2 = 0$; similarly, $\left(\widehat{b}_k^\dagger\right)^2 = 0$. Now using (17.268) with $k' = k$ we can write the following equation for the number operator

$$\widehat{n}_k^2 = \widehat{b}_k^\dagger\widehat{b}_k\widehat{b}_k^\dagger\widehat{b}_k = \widehat{b}_k^\dagger\left(1 - \widehat{b}_k^\dagger\widehat{b}_k\right)\widehat{b}_k = n_k - \left(\widehat{b}_k^\dagger\right)^2\left(\widehat{b}_k\right)^2, \tag{17.271}$$

which means that

$$\widehat{n}_k^2 = \widehat{n}_k. \tag{17.272}$$

The eigenvalues of the number operator therefore satisfy the equation $n_k^2 - n_k = 0$, that is, the occupancy numbers n_k can only take the values 0, 1, as corresponds to the F-D statistics. Since the state vector is (taking into account that $n_k! = 1$ for fermions)

$$|n_1, n_2, n_3, \cdots\rangle = \left(\widehat{b}_1^\dagger\right)^{n_1}\left(\widehat{b}_2^\dagger\right)^{n_2}\cdots|0\rangle, \tag{17.273}$$

from the anticommutation of the operators it follows that $|n_1, n_2, n_3, \cdots\rangle$ is antisymmetric with respect to the permutation of pairs of particles (or labels). We also have that

$$\widehat{b}_k\,|n_1, n_2, \cdots n_k, \cdots\rangle = (-1)^{n_k}\sqrt{n_k}\,|n_1, n_2, \cdots 1 - n_k, \cdots\rangle, \tag{17.274}$$

$$\widehat{b}_k^\dagger\,|n_1, n_2, \cdots n_k, \cdots\rangle = (-1)^{n_k}\sqrt{1 - n_k}\,|n_1, n_2, \cdots 1 - n_k, \cdots\rangle. \tag{17.275}$$

These results exhibit $\widehat{b}_k^\dagger$ as a creation operator, since if the initial state is empty ($n_k = 0$), the final state will be complete ($n_k = 1$) and vice versa. Similarly, b_k acts as an annihilation operator.

17.6.3 The two quantum statistics

The formalism introduced earlier can be applied to derive the B-E and the F-D statistics, with the help of the density matrix formalism developed in Chapter 15; as this is a subject for a more advanced course, we will skip the derivation but present the main results because of their importance. Using the commutation rule $\left[\widehat{a}, \widehat{a}^\dagger\right] = 1$ in the B-E case and the anticommutation rule $\left\{\widehat{a}, \widehat{a}^\dagger\right\}$ in the F-D case, one obtains

$$\begin{aligned}\mathrm{tr}\left(e^{-\beta\widehat{H}}\widehat{a}^\dagger\widehat{a}\right) = \mathrm{tr}\left(\widehat{a}e^{-\beta\widehat{H}}\widehat{a}^\dagger\right) = e^{-\beta\hbar\omega}\mathrm{tr}\left(e^{-\beta\widehat{H}}\widehat{a}\widehat{a}^\dagger\right) \\ = e^{-\beta\hbar\omega}\mathrm{tr}\left(e^{-\beta\widehat{H}}\left(1 \mp \widehat{a}^\dagger\widehat{a}\right)\right),\end{aligned} \tag{17.276}$$

where the upper sign corresponds to fermions and the lower sign to bosons. From here it follows, multiplying by $e^{\beta\hbar\omega}$ and solving, that

$$(e^{\beta\hbar\omega} \pm 1)\mathrm{tr}\, e^{-\beta\widehat{H}}\widehat{a}^\dagger\widehat{a} = \mathrm{tr}\, e^{-\beta\widehat{H}} = Z_\pm, \tag{17.277}$$

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where Z is the partition function, so that

$$\overline{n} = \langle \widehat{a}^\dagger \widehat{a} \rangle = \frac{1}{Z_\pm} \mathrm{tr}\, e^{-\beta \widehat{H}} \widehat{a}^\dagger \widehat{a} = \frac{1}{e^{\beta\hbar\omega} \pm 1} = \frac{e^{-\beta\hbar\omega}}{1 \pm e^{-\beta\hbar\omega}}. \tag{17.278}$$

With the plus sign in the denominator, this formula applies to a gas of fermions, and with the minus sign, it applies to massless bosons, as discussed in Section 15.3.

Problems

P17.1 Show that an adiabatic perturbation produces periodic transitions in a system that has two degenerate states.

P17.2 Show that if the potential $V(t) = \hat{A}\delta(t)$ is applied to a system in its ground state, the probability of a transition to any excited state is

$$w = \frac{1}{\hbar^2} \left(\langle 0|A^2|0\rangle - \langle 0|A|0\rangle^2 \right). \tag{17.279}$$

P17.3 A harmonic oscillator in its ground state is perturbed by the sudden application of a uniform electric field of intensity ϵ (not necessarily small), which remains constant from that moment on. Show that the probability of transition to the excited state n is given by the Poisson distribution

$$W_{0n} = \frac{\xi_0^{2n}}{2^n n!} e^{-\xi_0^2/2}, \tag{17.280}$$

where $\xi_0 = x_0/\sqrt{\hbar/m\omega}$ and $x_0 = e\epsilon/m\omega^2$. Find the mean value of n.

P17.4 A physical system having only the states $|1\rangle$ and $|2\rangle$, degenerate and orthogonal, is perturbed by the action of a potential V that is applied in the interval $(0, T)$. Assuming (for simplicity) that the matrix elements of V are $V_{11} = V_{22} = 0$, $V_{12} = V_{21} = V_0$, determine the exact probability of the transition from $|1\rangle$ to $|2\rangle$, if the system was initially in the state $|1\rangle$. Then use perturbation theory to determine the effect of the perturbation to first order and compare the results. When is the perturbative solution valid?

P17.5 Calculate in detail the Einstein coefficient B for resonant absorption processes and show that the Einstein relation $B_{nk} = B_{kn}$ is satisfied.

P17.6 Show that the probability per unit time that an atom makes a spontaneous quadrupole transition between states n and n' is

$$A_{nn'}^{(2e)} = \frac{\omega_{nn'}^5}{90\hbar c^5} \sum_{i,j} \left| \langle n|Q_{ij}|n'\rangle \right|^2, \tag{17.281}$$

where Q_{ij} are the components of the electric quadrupole moment,

$$Q_{ij} = e\left(3x_i x_j - r^2\delta_{ij}\right), \quad i, j = 1, 2, 3. \tag{17.282}$$

P17.7 Find the selection rules for electrical quadrupole transitions of (a) particles confined in a 1D infinite rectangular well; (b) particles in a 1D HO well; (c) a flat rigid rotor.

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P17.8 Determine the direction in which an electron is most likely to be emitted by the absorption of 50-keV γ radiation.

P17.9 Calculate the probability of an electron in an atom making a transition between stationary states under the influence of a charged particle passing close to the atom.

P17.10 A 1D HO originally at rest is subjected to a force $f(t)$. Find the equation of motion of the center of the wave packet using first-order perturbation theory and compare with the exact result.

P17.11 The free-particle Lamb effect can be identified with the contribution of the (free-space) ZPF to the particle's energy, given by Eq. (17.213)

$$\delta E_{\text{fp}} = \frac{e^2\hbar}{\pi mc^3}\int_0^{\omega_C} d\omega\,\omega, \tag{17.283}$$

where the usual cutoff frequency $\omega_C = mc^2/\hbar$ (equal to Compton's frequency of the electron) has been introduced. Assume that the distribution of ZPF modes can be reduced by introducing the particle in a cavity that filters out all modes of frequency ω smaller than Ω without altering the isotropy of the field and write down the formula for the resulting energy shift.

(a) Estimate the minimum value of Ω needed to produce an energy shift of the order of the atomic Lamb effect.

(b) Estimate the size of the cavity needed to filter out the frequencies $\omega < \Omega$ and compare it with the size of the H atom. Considering 5 nm as the minimum size of current solid-state nanoelectronic devices, could such an energy shift be detectable? Discuss your answer.

P17.12 Use the fact that the normal field amplitudes used in Section 17.5 are independent from each other to prove that $\left[\hat{\mathrm{q}}, \hat{\mathrm{p}}\right]_{\mathrm{nn}'} = i\hbar\delta_{\mathrm{nn}'}$.

P17.13 By making repeated use of Eq. (17.254), determine the commutator of the densities $\left[\hat{\rho}(\boldsymbol{x}), \hat{\rho}(\boldsymbol{x}')\right]$, where $\hat{\rho}(\boldsymbol{x})$ is the boson density operator.

Bibliographical Notes

For physically transparent and accessible introductions to quantum electrodynamics, see Power (1964), Cohen-Tannoudji, Dupont-Roc, and Grynberg (1997), and Milonni (2013).

An alternative account of the photoelectric effect, showing that it can be explained equally well without invoking the photon, is Lamb and Scully (1969).

For calculations of radiative corrections in the SED framework with the advantage of added physical transparency, see, for example, Cetto and de la Peña (2012).

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