

Physics 221B
Spring 2011
Notes 40
Emission and Absorption of Radiation

In these notes we will examine some simple examples of the interaction of the quantized radiation field with matter. We will mostly be concerned with the emission, absorption, and scattering of radiation by atomic systems. These notes continue with the notation developed in Notes 37 and 39.

We begin with the Hamiltonian for the combined matter-field system, which is

$$H = H_{\text{matter}} + H_{\text{em}}, \quad (1)$$

which is a quantized version of the classical Hamiltonian presented in Sec. 37.16. The quantized field Hamiltonian was presented in Eq. (39.14), which we reproduce here,

$$H_{\text{em}} = \sum_{\lambda} \hbar \omega_k a_{\lambda}^{\dagger} a_{\lambda}, \quad (2)$$

where we use box normalization. The classical matter Hamiltonian was presented in Eq. (37.96), which we transcribe over into a quantum operator and augment with terms for spins interacting with the magnetic field,

$$H_{\text{matter}} = \sum_{\alpha} \frac{1}{2m_{\alpha}} \left[\mathbf{p}_{\alpha} - \frac{q_{\alpha}}{c} \mathbf{A}(\mathbf{x}_{\alpha}) \right]^2 + \sum_{\alpha < \beta} \frac{q_{\alpha} q_{\beta}}{|\mathbf{x}_{\alpha} - \mathbf{x}_{\beta}|} - \sum_{\alpha} \boldsymbol{\mu}_{\alpha} \cdot \mathbf{B}(\mathbf{x}_{\alpha}). \quad (3)$$

In this Hamiltonian, \mathbf{x}_{α} and \mathbf{p}_{α} are taken as operators with the usual commutation relations, and $\boldsymbol{\mu}_{\alpha}$ is the magnetic moment of particle α , related to the spin in the usual way. The spin-dependent terms are exactly the ones we have always used, except that now the magnetic field \mathbf{B} itself is quantized.

The total Hamiltonian (1) involves both the matter and field degrees of freedom, and acts on the total ket space

$$\mathcal{E} = \mathcal{E}_{\text{matter}} \otimes \mathcal{E}_{\text{em}}, \quad (4)$$

where \mathcal{E}_{em} is the Fock space described in Notes 39, and where $\mathcal{E}_{\text{matter}}$ is the usual ket space for nonrelativistic particles, possibly with spin.

Most of the following discussion works for any nonrelativistic system (atom, molecule, nucleus, solid), but when it is necessary to be specific, we will for simplicity take the matter Hamiltonian to be that of a hydrogen-like atom with a single electron,

$$H_{\text{matter}} = \frac{1}{2m} \left[\mathbf{p} + \frac{e}{c} \mathbf{A}(\mathbf{x}) \right]^2 - \frac{Ze^2}{|\mathbf{x}|} + \frac{e}{mc} \mathbf{S} \cdot \mathbf{B}(\mathbf{x}). \quad (5)$$

In this Hamiltonian we assume for simplicity that the nucleus is infinitely massive, and we set $q = -e$ and $g = 2$ for the electron charge and g -factor.

The total Hamiltonian, including the matter and field terms, is complicated, and cannot be solved exactly even in simple models. Therefore we must resort to perturbation theory. We begin by expanding the total Hamiltonian into three terms, $H = H_0 + H_1 + H_2$, where

$$\begin{aligned} H_0 &= \frac{\mathbf{p}^2}{2m} - \frac{Ze^2}{|\mathbf{x}|} + \sum_{\lambda} \hbar\omega_{\lambda} a_{\lambda}^{\dagger} a_{\lambda}, \\ H_1 &= \frac{e}{mc} [\mathbf{p} \cdot \mathbf{A}(\mathbf{x}) + \mathbf{S} \cdot \mathbf{B}(\mathbf{x})], \\ H_2 &= \frac{e^2}{2mc^2} \mathbf{A}(\mathbf{x})^2, \end{aligned} \quad (6)$$

which is basically an expansion in the coupling between the matter and the field. This Hamiltonian represents the interaction of a hydrogen-like atom with an electromagnetic field. It is easy to show that as an order of magnitude, $H_1 \ll H_0$ and $H_2 \ll H_1$ if the electric fields associated with the light waves are small in comparison to the electric fields felt by the electron due to the nucleus, that is, if $E_{\text{wave}} \ll E_{\text{nucleus}}$. In most practical situations, this condition is met; however, in certain modern experiments involving high intensity laser light, this condition is not met, and different approximation methods must be used. In our initial applications, we will be doing first order perturbation theory, and we will be able to neglect H_2 ; but in second order calculations it is necessary to treat terms involving both H_1^2 and H_2 .

We note that the unperturbed Hamiltonian H_0 in Eq. (6) is the sum of a Hamiltonian for the matter and one for the field, with no interaction. This Hamiltonian is therefore solvable, and the unperturbed eigenkets are simply tensor products of atomic eigenkets with field eigenkets. Denoting the states of the atom by capital letters such as $|X\rangle$, we can write a typical eigenstate of H_0 in the form $|X\rangle | \dots n_{\lambda} \dots \rangle$.

Our first application will be the spontaneous emission of a photon by an atom in an excited state. We will use box normalization for this calculation. Let $|A\rangle$ and $|B\rangle$ be two discrete (bound) states of the atom, with $E_A < E_B$, and suppose at $t = 0$ the atom is in the upper state $|B\rangle$. Suppose furthermore that at $t = 0$ the electromagnetic field is in the vacuum state $|0\rangle$ (no photons). We will be interested in time-dependent transitions to the state in which the atom is in the lower state $|A\rangle$, and a photon has been emitted, so that the field contains one photon. Since the wave vector \mathbf{k} of the outgoing photon in the final state is continuously variable (after $V \rightarrow \infty$), we have an example of a time-dependent perturbation problem with a continuum of final states. As explained in Sec. 32.11, the transition rate can be written

$$w = \frac{2\pi}{\hbar^2} \sum_f |\langle f | H_1 | i \rangle|^2 \delta(\omega_{fi}), \quad (7)$$

where we sum over some set of final states f . Here ω_{fi} is the Einstein or resonance frequency connecting the initial and final states,

$$\omega_{fi} = \frac{E_f - E_i}{\hbar}. \quad (8)$$

As usual, the δ -function in Eq. (7) enforces energy conservation, in this case, $E_f = E_i$.

The initial state is a tensor product of the atomic state $|B\rangle$ with the vacuum state $|0\rangle$ for the field,

$$|i\rangle = |B\rangle|0\rangle, \quad (9)$$

with an energy $E_i = E_B$ (the energy of the atomic state B). A specific final state is specified by the mode $\lambda = (\mathbf{k}, \mu)$ of the outgoing photon; thus, the sum on f in Eq. (7) is equivalent to a sum on λ . The final state of the electromagnetic field can be written as $a_\lambda^\dagger|0\rangle$, so the final state of the whole matter-field system is

$$|f\rangle = |A\rangle a_\lambda^\dagger|0\rangle. \quad (10)$$

The energy of the final state is $E_f = E_A + \hbar\omega_k$, where the k -subscript on ω_k is understood to refer to the k contained in $\lambda = (\mathbf{k}, \mu)$. The Einstein frequency is

$$\omega_{fi} = \frac{\hbar\omega_k - (E_B - E_A)}{\hbar} = \omega_k - \omega_{BA} = c(k - k_{BA}), \quad (11)$$

where ω_{BA} and k_{BA} are respectively the frequency and wavenumber associated with the energy difference $E_B - E_A$.

We will work first on the matrix element. According to Eqs. (9), (10), and (6), we have

$$\langle f|H_1|i\rangle = \frac{e}{mc} \langle A|\langle 0|a_\lambda [\mathbf{p} \cdot \mathbf{A}(\mathbf{x}) + \mathbf{S} \cdot \mathbf{B}(\mathbf{x})]|B\rangle|0\rangle, \quad (12)$$

where $\mathbf{A}(\mathbf{x})$ and $\mathbf{B}(\mathbf{x})$ are the quantized fields, given in box-normalization form by Eqs. (39.18) and (39.20), but here evaluated at the particle position \mathbf{x} (which of course is an operator, unlike the label \mathbf{r}). The general structure of these equations is that both \mathbf{A} and \mathbf{B} consist of a Fourier series involving both annihilation and creation operators. That is, both fields have the form

$$\mathbf{A}, \mathbf{B} \sim \sum_{\lambda'} (\dots a_{\lambda'} \dots a_{\lambda'}^\dagger \dots), \quad (13)$$

where all inessential factors are suppressed and where we use λ' as the dummy index of summation to avoid confusion with the λ which represents the mode of the outgoing photon. Now we can see that all annihilation operators $a_{\lambda'}$ give zero, since they act on the vacuum $|0\rangle$ to the right in Eq. (12). As for the creation operators $a_{\lambda'}^\dagger$, these all give zero, too, except for the one term $\lambda' = \lambda$ in the λ' sum, because the operator $a_{\lambda'}^\dagger$ must create a photon that is then destroyed by the operator a_λ to the left in Eq. (12). In other words, the field matrix element has the form,

$$\langle 0|a_\lambda a_{\lambda'}^\dagger|0\rangle = \delta_{\lambda\lambda'}, \quad (14)$$

as follows from the commutation relations (39.4). Therefore the field scalar product kills the sum in Eq. (13), and leaves behind only the factors $\epsilon_\lambda^* e^{-i\mathbf{k}\cdot\mathbf{x}}$.

After the field scalar product has been taken, the matrix element is reduced to

$$\langle f|H_1|i\rangle = \frac{e}{mc} \sqrt{\frac{2\pi\hbar c^2}{V}} \frac{1}{\sqrt{\omega_k}} \langle A|[\mathbf{p} \cdot \epsilon_\lambda^* - i\mathbf{S} \cdot (\mathbf{k} \times \epsilon_\lambda^*)] e^{-i\mathbf{k}\cdot\mathbf{x}}|B\rangle. \quad (15)$$

Only an atomic matrix element remains, which we abbreviate by the definition,

$$M_{BA} = \frac{i}{\hbar} \langle B | [\mathbf{p} \cdot \boldsymbol{\epsilon}_\lambda + i\mathbf{S} \cdot (\mathbf{k} \times \boldsymbol{\epsilon}_\lambda)] e^{i\mathbf{k} \cdot \mathbf{x}} | A \rangle, \quad (16)$$

so that

$$\langle f | H_1 | i \rangle = \frac{e}{mc} \sqrt{\frac{2\pi\hbar c^2}{V}} \frac{1}{\sqrt{\omega_k}} i\hbar M_{BA}^*. \quad (17)$$

In manipulating M_{BA} , it is useful to note that $\boldsymbol{\epsilon} \cdot \mathbf{p}$ commutes with $e^{i\mathbf{k} \cdot \mathbf{x}}$, because of the transversality condition $\boldsymbol{\epsilon} \cdot \mathbf{k} = 0$. The matrix element M_{BA} depends on the quantum numbers of the atomic states A and B , and on the mode $\lambda = (\mathbf{k}, \mu)$ of the outgoing photon.

Now we can write the transition rate in the form,

$$w = \frac{2\pi}{\hbar^2} \sum_\lambda \frac{e^2}{m^2 c^2} \frac{2\pi\hbar c^2}{V} \frac{1}{\omega_k} \hbar^2 |M_{BA}|^2 \frac{1}{c} \delta(k - k_{BA}). \quad (18)$$

Which final states λ we sum over depends on what transition rate we wish to compute. To ask for fairly detailed information, suppose we want the differential transition rate per unit solid angle for photons of a given polarization μ going out in some specified direction. Then we do not sum on μ in Eq. (18) and we only sum over those wave numbers \mathbf{k} that lie in some small solid angle $\Delta\Omega$ surrounding the outgoing direction of interest. We should also replace the left hand side,

$$w \rightarrow \left(\frac{dw}{d\Omega} \right)_\mu \Delta\Omega, \quad (19)$$

where $(dw/d\Omega)_\mu$ is the transition probability per unit time per unit solid angle for photons of polarization μ , and we should replace the sum on the right hand side by

$$\sum_\lambda \rightarrow \sum_{\mathbf{k} \in \Delta\Omega} \rightarrow \frac{V}{(2\pi)^3} \Delta\Omega \int_0^\infty k^2 dk, \quad (20)$$

where as usual $V/(2\pi)^3$ is the density of states in \mathbf{k} -space.

Then the factors of V and $\Delta\Omega$ cancel, and the k -integration is easy to do because of the δ -function. The result is

$$\left(\frac{dw}{d\Omega} \right)_\mu = \frac{1}{2\pi} \frac{e^2}{m^2 c^3} \hbar\omega |M_{BA}|^2, \quad (21)$$

where now $\omega = \omega_{BA}$. Also, in this result the magnitude of \mathbf{k} that appears in M_{BA} is determined by conservation of energy, that is, it is given by $k = k_{BA} = \omega_{BA}/c$, so now M_{BA} depends only on the two atomic states A and B , and on the polarization μ and direction $\hat{\mathbf{k}}$ of the outgoing photon. Equation (21) gives us the intensity of the emitted radiation as a function of both photon polarization and direction. This result can be obtained from the semiclassical theory of radiation only in an ad hoc and convoluted manner, but it is perhaps the easiest calculation of quantum electrodynamics.

If we are only interested in the total rate of emission, regardless of direction or polarization, then we should sum the answer (21) over μ and integrate over solid angle of the outgoing photon. For this purpose it is convenient to introduce an abbreviation,

$$\overline{|M_{BA}|^2} = \frac{1}{2} \sum_\mu \frac{1}{4\pi} \int d\Omega |M_{BA}|^2, \quad (22)$$

which is the average of the square of the matrix element over polarizations and angles, and which depends only on the atomic states A and B . In terms of this quantity, the total transition rate can be written,

$$w = \frac{4e^2}{m^2c^3} \hbar\omega \overline{|M_{BA}|^2} = A_E, \quad (23)$$

where A_E is the Einstein A coefficient (defined to be the rate of spontaneous emission).

This is a good point to recall the various time scale arguments that went into the derivation of the formula (7), and to see how they actually work out in a real problem. According to the time-dependent perturbation theory as laid out in Notes 32, the δ -function in a formula like Eq. (7) is more properly the function Δ_t , defined by Eq. (32.42). This function is not infinitely narrow in energy or frequency, but rather has a width given by $\Delta\omega \sim 1/t$ or $\Delta E \sim \hbar/t$, where t is the elapsed time. This time should be long enough that ΔE is small in comparison to the energy scale of the summand in Eq. (7), because this allows us to replace the Δ_t function by a δ -function and the sum by an integral. But the time should also be short enough that the initial state is not significantly depleted of probability, because our model and approximations predict a probability that decreases linearly in time, something that leads to an absurdity after the life time of the state, when the probability becomes negative. For example, for the process of spontaneous emission, we obtained the formula (18). The summand in this formula depends on energy through the matrix element and through factors of ω and k , so it will be possible to replace the Δ_t function with a δ -function if $\Delta E \ll E$, where E is an energy characteristic of the atomic states A or B , or of the emitted photon. But since $E \sim \hbar\omega$, this means we must have $t \gg 1/\omega$, that is, the time must be much longer than an orbital period of the electron in the atom. On the other hand, in order that the initial state not be significantly depleted, we must have $t \ll 1/w$, where w is the total rate of emission, given by Eq. (23). In other words, t must be much less than the lifetime of the excited state. Altogether, the condition on the time is

$$\frac{1}{\omega} \ll t \ll \frac{1}{w}. \quad (24)$$

It is easy to find times that satisfy this condition in atomic transitions, because atomic time scales are always much shorter than lifetimes. In other applications, there may be more difficulty.

We see that time-dependent perturbation theory does not tell us about the behavior of the system on time scales comparable to or longer than the lifetime of an excited state. For example, our calculation of w only gives us the rate at which probability is depleted from the initial state at $t = 0$. It does not prove (although it suggests) that the probability in the initial state goes as e^{-wt} for times comparable to $1/w$. To deal with long time processes, more powerful methods are required than the time-dependent perturbation theory we have developed so far. We will have to worry about such longer time scales in later applications (to resonance fluorescence).

Next we consider the process of absorption, in which the atom is initially in the lower state $|A\rangle$, from which it absorbs a photon from the field and gets lifted into the higher state $|B\rangle$ (both assumed to be discrete). Since the field must contain some photons if one is to be absorbed, we assume the

initial state of the field is given by $|\dots n_\lambda \dots\rangle$, for some given list of occupation numbers $\{n_\lambda\}$. The atom can absorb a photon from any mode that initially has photons in it (but for long times, only those that nearly conserve energy will be important), so the state of the system after some time will be a linear combination of final states in which one of the modes has one fewer photon than in the initial state. In the following calculation, we let λ stand for the mode from which a photon has been absorbed, so that effectively λ also becomes a label of final states. That is, we take our initial and final states to be

$$\begin{aligned} |i\rangle &= |A\rangle|\dots n_\lambda \dots\rangle, \\ |f\rangle &= |B\rangle|\dots, n_\lambda - 1, \dots\rangle, \end{aligned} \quad (25)$$

where it is understood that all occupations numbers are identical in the initial and final states except in mode λ . The resonance frequency we will use is

$$\omega_{fi} = \frac{E_B - E_A - \hbar\omega_k}{\hbar} = \omega_{BA} - \omega_k = c(k_{BA} - k). \quad (26)$$

Now the matrix element has the form

$$\langle f|H_1|i\rangle = \frac{e}{mc} \langle B|\langle \dots, n_\lambda - 1, \dots|[\mathbf{p} \cdot \mathbf{A}(\mathbf{x}) + \mathbf{S} \cdot \mathbf{B}(\mathbf{x})]|A\rangle|\dots n_\lambda \dots\rangle, \quad (27)$$

where again the general structure of \mathbf{A} and \mathbf{B} is indicated by Eq. (13). We see now that the only term from the λ' sum in Eq. (13) that survives the field scalar product is the annihilation operator $a_{\lambda'}$ for $\lambda' = \lambda$, because this is the only operator that will lower the number of photons in mode λ by one. Furthermore, we have

$$a_\lambda|\dots n_\lambda \dots\rangle = \sqrt{n_\lambda}|\dots, n_\lambda - 1, \dots\rangle, \quad (28)$$

so after the field scalar product is taken, we are left with

$$\begin{aligned} \langle f|H_1|i\rangle &= \frac{e}{mc} \sqrt{\frac{2\pi\hbar c^2}{V}} \frac{\sqrt{n_\lambda}}{\sqrt{\omega_k}} \langle B|[\mathbf{p} \cdot \boldsymbol{\epsilon}_\lambda + i\mathbf{S} \cdot (\mathbf{k} \times \boldsymbol{\epsilon}_\lambda)] e^{i\mathbf{k} \cdot \mathbf{x}} |A\rangle \\ &= \frac{e}{mc} \sqrt{\frac{2\pi\hbar c^2}{V}} \frac{\sqrt{n_\lambda}}{\sqrt{\omega_k}} (-i\hbar) M_{BA}. \end{aligned} \quad (29)$$

The atomic matrix element is the same as in the process of emission, except it is complex conjugated. Finally, when we use this matrix element to compute the transition rate, we have

$$w = \frac{2\pi}{\hbar^2} \sum_\lambda \frac{e^2}{m^2 c^2} \frac{2\pi\hbar c^2}{V} \frac{n_\lambda}{\omega_k} \hbar^2 |M_{BA}|^2 \frac{1}{c} \delta(k - k_{BA}). \quad (30)$$

This would be fine if we had exact knowledge of the initial state of the electromagnetic field (if we knew it was in the pure state $|\dots n_\lambda \dots\rangle$, and if we knew exactly what all the n_λ were), but in practice we often do not have such information. Often we have only statistical information about the initial state of the field; this is certainly true for black body radiation, but it is also usually true

for other types of radiation fields, including laser light. Let us suppose, therefore, that we only know some probability distribution for the occupation numbers, say, $P(\{n_\lambda\})$, which is the probability for a specific list $\{n_\lambda\}$ of occupation numbers. For example, in thermal equilibrium (black body radiation), we would have

$$P(\{n_\lambda\}) = \frac{1}{Z} \exp\left(-\beta \sum_\lambda n_\lambda \hbar\omega_k\right). \quad (31)$$

Working with such a probability distribution is equivalent to working with a density operator for the electromagnetic field that is diagonal in the occupation number representation,

$$\rho = \sum_{\{n_\lambda\}} |\{n_\lambda\}\rangle P(\{n_\lambda\}) \langle\{n_\lambda\}|. \quad (32)$$

As explained in Notes 3, the absence of off-diagonal terms means that the relative phases between different occupation number states are random.

Under such a statistical assumption, we should replace w by its average over the probability distribution. This involves placing a sum over $\{n_\lambda\}$ times $P(\{n_\lambda\})$ before the right hand side of Eq. (30). But the only term in the right hand side that depends on $\{n_\lambda\}$ is the single factor of n_λ itself, which then gets replaced by its average,

$$\langle n_\lambda \rangle = \sum_{\{n_\lambda\}} P(\{n_\lambda\}) n_\lambda. \quad (33)$$

Finally, we can replace the sum on λ by the usual limit as $V \rightarrow \infty$,

$$\sum_\lambda \rightarrow \sum_\mu \frac{V}{(2\pi)^3} \int_0^\infty k^2 dk \int d\Omega_k, \quad (34)$$

where we sum over all states (the modes from which the photon could be absorbed) because we are only interested here in the total rate of absorption. As usual, the k -integral is trivial because of the δ -function. We obtain

$$w = \frac{1}{2\pi} \frac{e^2}{m^2 c^3} \hbar\omega \sum_\mu \int d\Omega_k \langle n_\lambda | M_{BA} |^2. \quad (35)$$

The average number of photons per mode $\langle n_\lambda \rangle$ is a function of λ , that is, in general it depends on k , $\hat{\mathbf{k}}$, and μ . But if the radiation is isotropic and unpolarized, then by definition $\langle n_\lambda \rangle$ depends only on the magnitude of the wave vector k (or equivalently, on the frequency ω). For simplicity, let us consider this case. Then $\langle n_\lambda \rangle$ can be taken out of the sum and integral in Eq. (35), and what remains is the average of the squared matrix element, as in Eq. (22). The result is

$$w_{\text{abs}} = \frac{4e^2}{m^2 c^3} \hbar\omega \overline{|M_{BA}|^2} \langle n_\lambda \rangle = A_E \langle n_\lambda \rangle, \quad (36)$$

which is the rate of absorption for isotropic, unpolarized radiation. It is just $\langle n_\lambda \rangle$ times the Einstein A -coefficient, a simple result.

The average number of photons in mode λ can be expressed macroscopically in terms of the energy density per unit frequency interval. This follows from writing out the energy density u (energy per unit volume) of the field in a box,

$$u = \frac{1}{V} \sum_{\lambda} \langle n_{\lambda} \rangle \hbar \omega_k \rightarrow \frac{1}{(2\pi)^3} \int_0^{\infty} k^2 dk \int d\Omega_k \sum_{\mu} \langle n_{\lambda} \rangle \hbar \omega_k, \quad (37)$$

where the limit $V \rightarrow \infty$ is indicated. But if the radiation is unpolarized and isotropic, then the entire summand/integrand becomes independent of $\hat{\mathbf{k}}$ and μ , and $\int d\Omega_k \sum_{\mu}$ can be replaced by 8π . Then switching to ω as a variable of integration, we have

$$u = \frac{\hbar}{\pi^2 c^3} \int_0^{\infty} d\omega \omega^3 \langle n_{\lambda} \rangle, \quad (38)$$

where it is understood that $\langle n_{\lambda} \rangle$ is a function only of ω . But this is equivalent to

$$\frac{du}{d\omega} = \frac{\hbar \omega^3}{\pi^2 c^3} \langle n_{\lambda} \rangle. \quad (39)$$

This is really an elementary result, which just amounts to counting states. Of course, if we use Eq. (39.71) for $\langle n_{\lambda} \rangle$, we obtain the usual Planck formula for $du/d\omega$.

Equations (36) and (39) show that the rate of absorption is proportional to $du/d\omega$. Following Einstein, we write this relationship in the form

$$w_{\text{abs}} = B_E \frac{du}{d\omega}, \quad (40)$$

which serves to define B_E , the Einstein B -coefficient. Now Eqs. (36), (39) and (40) can be used to obtain a relation between the Einstein A - and B -coefficients,

$$A_E = \frac{\hbar \omega^3}{\pi^2 c^3} B_E. \quad (41)$$

The relation between the Einstein A and B coefficients depends only on the counting of states in the electromagnetic field; it does not depend on the nature of the matter interacting with the radiation. Thus, Eq. (41) is valid for radiation interacting with any kind of matter (atoms in a gas, nuclei inside a star, etc). Equation (41) is of use in the semiclassical theory of radiation, in which B_E can be computed after a tricky and convoluted calculation, but A_E is impossible.

Finally, let us examine the process of emission in the presence of radiation. This is just like the spontaneous emission considered above, except the photon field is not assumed to be empty in the initial state. We let the initial and final states be

$$\begin{aligned} |i\rangle &= |B\rangle |\dots n_{\lambda} \dots\rangle, \\ |f\rangle &= |A\rangle |\dots, n_{\lambda} + 1, \dots\rangle, \end{aligned} \quad (42)$$

where it is understood that all occupation numbers are the same in the initial and final states, except in mode λ , which gains a photon. Now the matrix element for time-dependent perturbation theory has the form

$$\langle f | H_1 | i \rangle = \frac{e}{mc} \langle A | \langle \dots, n_{\lambda} + 1, \dots | (\mathbf{p} \cdot \mathbf{A} + \mathbf{S} \cdot \mathbf{B}) | B \rangle | \dots n_{\lambda} \dots \rangle, \quad (43)$$

and only the creation operator $a_{\lambda'}^\dagger$ for $\lambda' = \lambda$ survives in the sum (13). Also, we have

$$a_{\lambda}^\dagger |\dots n_{\lambda} \dots\rangle = \sqrt{n_{\lambda} + 1} |\dots, n_{\lambda} + 1, \dots\rangle, \quad (44)$$

so that when we compute the transition rate, we obtain

$$w_{\text{emiss}} = \frac{2\pi}{\hbar^2} \sum_{\lambda} \frac{e^2}{m^2 c^2} \frac{2\pi \hbar c^2}{V} \frac{n_{\lambda} + 1}{\omega_k} \hbar^2 |M_{BA}|^2 \frac{1}{c} \delta(k - k_{BA}), \quad (45)$$

which is exactly the same as the absorption rate (30) except for the replacement of n_{λ} by $n_{\lambda} + 1$. It is also the same as the rate of spontaneous emission (18), except for the replacement of 1 by $n_{\lambda} + 1$. Thus, the n_{λ} part is regarded as the rate of stimulated emission, and the 1 part is the rate of spontaneous emission.

If the sum on λ is taken over all photon states, then the result is the total rate of emission of the photon into any final state. Of course energy conservation restricts which final states the photon may go into, and the matrix element has a dependence on the direction of the outgoing photon, but there are still many possible final states. But because of the numerator in $n_{\lambda} + 1$, those states that are already populated by photons are more likely to receive the emitted photon. In this way, photon states that are already populated tend to become more populated; one can say that bosons not only can occupy the same state, they like to occupy the same state. The classical or semiclassical interpretation of this process is simple, for if we imagine an initial photon state that is already populated as a classical electromagnetic wave, assumed to be in resonance with the atomic transition, then the wave shakes the atom at its resonant frequency and stimulates the emission of a new photon with the same frequency, wave vector and polarization as the wave itself.

This is the basic principle of amplification in lasers and masers, which typically work by passing radiation through a cavity containing a population of atoms in an excited state. These atoms are stimulated to emit photons into one or a few states, which tends to increase the amplitude of the wave. However, stimulated emission is in competition with absorption, which according to Eq. (30) has a transition rate that is also proportional to n_{λ} . Of course, absorption removes photons from the wave. Therefore lasing normally requires a population inversion, to give the advantage to the process of emission.

The +1 in Eq. (44), representing the rate of spontaneous emission, is generally parasitic to laser operation, since the emitted photon is just as happy to go out in any direction or polarization. For proper laser operation, the population inversion must be sufficiently favorable to overcome these and other losses.

Let us now assume that the initial radiation field is represented by an isotropic and unpolarized ensemble $P(\{n_{\lambda}\})$, just as we did for absorption. Then we can average over the ensemble and sum over modes λ in Eq. (45), to obtain

$$w_{\text{emiss}} = A_E(\langle n_{\lambda} \rangle + 1) = B_E \frac{du}{d\omega} + A_E. \quad (46)$$

We see that the rate of stimulated emission is equal to the rate of absorption; this is called *detailed balance*, which means that transition rates between two microscopic states are equal. Detailed balance is not necessary to establish thermal equilibrium, but it generally holds in first order perturbation theory, due to the Hermiticity of the perturbing Hamiltonian H_1 .

We will now analyze the atomic matrix element M_{BA} , given by Eq. (16), which applies to both emission and absorption. First we note that the phase $\mathbf{k} \cdot \mathbf{x}$ in the exponent in Eq. (16) is small over the size of the atom. This follows easily in atomic units, in which the size of the atom is $a \sim 1/Z$, and the frequency of the emitted or absorbed radiation is $\omega \sim Z^2$. But since $k = \omega/c = \alpha\omega$ in atomic units, and since $x \sim a$, we have

$$\mathbf{k} \cdot \mathbf{x} \sim Z\alpha. \quad (47)$$

If Z is not too large, this is a small quantity. Similarly, we find that the term $i\mathbf{S} \cdot (\mathbf{k} \times \boldsymbol{\epsilon}_\lambda)$ in Eq. (16) is of order $Z\alpha$ relative to $\mathbf{p} \cdot \boldsymbol{\epsilon}_\lambda$. Therefore expanding in powers of k is equivalent to expanding in powers of $Z\alpha$. We write

$$M_{BA} = M_{BA}^{(0)} + M_{BA}^{(1)} + \dots \quad (48)$$

for this expansion, where

$$M_{BA}^{(0)} = \frac{i}{\hbar} \langle B | \boldsymbol{\epsilon}_\lambda \cdot \mathbf{p} | A \rangle, \quad (49)$$

$$M_{BA}^{(1)} = -\frac{1}{\hbar} \langle B | \mathbf{S} \cdot (\mathbf{k} \times \boldsymbol{\epsilon}_\lambda) + (\boldsymbol{\epsilon}_\lambda \cdot \mathbf{p})(\mathbf{k} \cdot \mathbf{x}) | A \rangle. \quad (50)$$

As we shall show, the term $M_{BA}^{(0)}$ is the electric dipole ($E1$) term, while the term $M_{BA}^{(1)}$ contains both the magnetic dipole ($M1$) term and the electric quadrupole ($E2$) term.

First we work on $M_{BA}^{(0)}$. We invoke the following commutator, which is equivalent to the Heisenberg equations of motion for the operator \mathbf{x} ,

$$[\mathbf{x}, H_0] = \frac{i\hbar\mathbf{p}}{m} = i\hbar\dot{\mathbf{x}}. \quad (51)$$

Here H_0 can be taken to be the unperturbed atomic Hamiltonian seen in Eq. (6) since the field Hamiltonian will not contribute. Using Eq. (51) in Eq. (49), we find

$$\begin{aligned} M_{BA}^{(0)} &= \frac{m}{\hbar^2} \boldsymbol{\epsilon}_\lambda \cdot \langle B | \mathbf{x} H_0 - H_0 \mathbf{x} | A \rangle \\ &= \frac{m}{\hbar^2} (E_A - E_B) \boldsymbol{\epsilon}_\lambda \cdot \langle B | \mathbf{x} | A \rangle = -\frac{m\omega}{\hbar} \boldsymbol{\epsilon}_\lambda \cdot \langle B | \mathbf{x} | A \rangle, \end{aligned} \quad (52)$$

where $\omega = \omega_{BA} = (E_B - E_A)/\hbar$. The matrix element of \mathbf{x} is proportional to the matrix element of the electric dipole operator, defined by

$$\mathbf{D} = -e\mathbf{x}, \quad (53)$$

so we will henceforth refer to $M_{BA}^{(0)}$ as the electric dipole contribution to the matrix element. We will write this contribution as

$$M_{BA}^{E1} = -\frac{m\omega}{\hbar} \boldsymbol{\epsilon}_\lambda \cdot \langle B | \mathbf{x} | A \rangle. \quad (54)$$

Because the electric dipole term is the leading term in the expansion in kx , the assumption $kx \ll 1$ is sometimes called the electric dipole approximation.

As for $M_{BA}^{(1)}$, we work on the orbital part first [the second term in Eq. (50)]. We note that the two factors in this term can be written in any order, since

$$[\boldsymbol{\epsilon}_\lambda \cdot \mathbf{p}, \mathbf{k} \cdot \mathbf{x}] = -i\hbar \boldsymbol{\epsilon}_\lambda \cdot \mathbf{k} = 0, \quad (55)$$

because the light waves are transverse. We use the summation convention and break this term up into its symmetric and antisymmetric parts, finding,

$$\begin{aligned} M_{\text{orb}}^{(1)} &= -\frac{1}{\hbar} k_i \epsilon_j \langle B | x_i p_j | A \rangle \\ &= -\frac{1}{2\hbar} k_i \epsilon_j \langle B | x_i p_j - x_j p_i | A \rangle - \frac{1}{2\hbar} k_i \epsilon_j \langle B | x_i p_j + x_j p_i | A \rangle. \end{aligned} \quad (56)$$

The antisymmetric part can be written in terms of the orbital angular momentum,

$$-\frac{1}{2\hbar} k_i \epsilon_j \langle B | x_i p_j - x_j p_i | A \rangle = -\frac{1}{2\hbar} (\mathbf{k} \times \boldsymbol{\epsilon}) \cdot \langle B | \mathbf{x} \times \mathbf{p} | A \rangle, \quad (57)$$

which, when combined with the spin part of $M_{BA}^{(1)}$ [the first term in Eq. (50)], gives the magnetic dipole contribution to the matrix element,

$$M_{BA}^{M1} = -\frac{1}{2\hbar} (\mathbf{k} \times \boldsymbol{\epsilon}_\lambda) \cdot \langle B | \mathbf{L} + 2\mathbf{S} | A \rangle. \quad (58)$$

With the help of the commutation relations (51) and (55), the symmetric part of $M_{BA}^{(1)}$ can be transformed as follows:

$$\begin{aligned} -\frac{1}{2\hbar} k_i \epsilon_j \langle B | x_i p_j + p_i x_j | A \rangle &= \frac{im}{2\hbar^2} k_i \epsilon_j \langle B | x_i x_j H_0 - H_0 x_i x_j | A \rangle \\ &= -\frac{im\omega}{2\hbar} k_i \epsilon_j \langle B | x_i x_j | A \rangle, \end{aligned} \quad (59)$$

where we have swapped x_j and p_i in the second term of the first expression. In the final expression it is customary to replace the operator $x_i x_j$ by the electric quadrupole operator, defined by

$$Q_{ij} = x_i x_j - \frac{1}{3} r^2 \delta_{ij}, \quad (60)$$

since the extra term makes no contribution to the matrix element (because $\boldsymbol{\epsilon} \cdot \mathbf{k} = 0$), and since the tensor Q_{ij} , so defined, is a $k = 2$ irreducible tensor operator. The extra term in Eq. (60) has the effect of subtracting off the $k = 0$ component of the tensor product $x_i x_j$. Altogether, this gives the electric quadrupole contribution to the matrix element,

$$M_{BA}^{E2} = -\frac{im\omega}{2\hbar} k_i \epsilon_j \langle B | Q_{ij} | A \rangle. \quad (61)$$

In these operations on the atomic matrix element M_{BA} , we have been doing two things: one is to expand the matrix element in the small quantity $kx \ll 1$, and the other is to organize the

results into irreducible tensor operators. We have done this in an ad hoc manner for the first three terms ($E1$, $M1$ and $E2$) of the multipole expansion; these are the terms that are usually of most importance in atomic physics. However, in nuclear and molecular physics, one often has need to go to higher order in the multipole expansion, and one must be more systematic.

It is not necessary to expand in powers of kx in order to carry out the multipole expansion, and in some applications kx is not small. This is notably true in nuclear physics, where kx is not as favorable as in atomic applications. To carry out the multipole expansion without expanding in powers of kx , it is convenient to organize the photon states as eigenfunctions of (k, π, J^2, J_z) , rather than as eigenfunctions of (\mathbf{k}, Ω) as we have done. The eigenfunctions of (π, J^2, J_z) are known as *vector spherical harmonics*; they are a generalization of the ordinary spherical harmonics to vector fields. The theory of the vector spherical harmonics is essentially a straightforward application of rotation operators to the wave functions of a spin-1 particle, but it is sufficiently lengthy that we will not go into it in detail.

However, we remark that if kx is small, it means that the phase of the light wave is nearly constant over the spatial extent of the radiator, namely, the atom. We recall that in scattering theory we have s -wave scattering in the long wavelength limit, because the radiators stimulated by the incident wave are all in phase. Of course, in s -wave scattering, the scattered wave is isotropic and the cross section is independent of angle. In the case of a scalar wave, it is possible to radiate s -waves, but for transverse vector waves such as electromagnetic waves there are no s -waves. Instead, the lowest angular momentum state for the radiated waves is the $j = 1$ state, which comes in two varieties, odd and even parity, representing electric and magnetic dipole radiation. These give the simplest radiation patterns possible with electromagnetic waves. If kx is not small, it means that it is necessary to take into account the phase differences in the radiated wave across the radiator, which can be regarded as the effects of retardation.

The total matrix element M_{BA} is a sum of terms in the multipole expansion, but if kx is small, there will be one term of leading order that dominates the others. Thus, in atomic transitions, the radiation is dominantly of one type ($E1$, $M1$, etc.), although higher order corrections are present, in general. The transition rate for the different multipole types is conveniently estimated by working in atomic units and expressing the dependence of w on Z and the fine structure constant $\alpha = 1/c$. For simplicity, we will ignore the dependence on the atomic quantum numbers, but if any of these are large, they should be taken into account, too. Then we find that the matrix element M_{BA}^{E1} of Eq. (54) is of order Z in atomic units, while the matrix elements M_{BA}^{M1} and M_{BA}^{E2} , given by Eqs. (58) and (61), are both of order αZ^2 . Therefore the spontaneous transition rate, given by Eq. (23), goes as $\alpha^3 Z^4$ for $E1$ transitions, and as $\alpha^5 Z^6$ for $M1$ and $E2$ transitions. We see that if Z is not too large, the condition (24) on time scales is easily met. In fact, for $Z \approx 1$ and for quantum numbers of order unity, the lifetimes for electric dipole transitions are of the order of $\alpha^3 \sim 10^{-6}$ times smaller than the orbital period of the electron. For example, in the $2p \rightarrow 1s$ transition in hydrogen (the fastest one), we can think of the electron as orbiting on the order of a million times before dropping

into the ground state. The factor becomes $\alpha^5 \sim 10^{-10}$ for $M1$ and $E2$ transitions that are even slower.

	T_q^k	k	π	Selection Rules
$E1$	\mathbf{x}	1	-	$\Delta j = 0, \pm 1, \Delta \ell = \pm 1$
$M1$	$\mathbf{L} + 2\mathbf{S}$	1	+	$\Delta j = 0, \pm 1, \Delta \ell = 0$
$E2$	Q_{ij}	2	+	$\Delta j = 0, \pm 1, \pm 2, \Delta \ell = 0, \pm 2$

Table 1. Multipole terms in the expansion of the transition matrix element. The order k and parity π of the irreducible tensor operator T_q^k are tabulated.

The operators that occur in the various multipole matrix elements (54), (58), and (61), can be expressed in terms of irreducible tensor operators T_q^k . These operators also have well defined transformation properties under conjugation by parity π . Table 1 summarizes the different operators we have considered and lists their k values and parities. The general rules are that an Ek or an Mk operator is an irreducible tensor operator (perhaps in Cartesian form) of order k , and that an Ek -operator has parity $(-1)^k$ and an Mk -operator has parity $(-1)^{k+1}$.

These operators are sandwiched between atomic states A and B , which are eigenstates of various angular momentum operators and also of parity (ignoring the weak interactions). The Wigner-Eckart theorem and rules of parity can be applied to the resulting matrix elements to obtain selection rules. For example, consider a model of hydrogen in which we include the fine structure corrections but ignore the hyperfine structure. Let us denote the upper state B by $|n\ell jm_j\rangle$ and the lower state A by $|n'\ell' j' m'_j\rangle$, so the different multipole contributions have the form $\langle n\ell jm_j | T_q^k | n'\ell' j' m'_j \rangle$. The selection rules for $E1$ transitions are familiar; the operator \mathbf{x} is a $k = 1$ irreducible tensor operator both under total rotations, generated by \mathbf{J} , and under purely orbital rotations, generated by \mathbf{L} . Therefore the Wigner-Eckart theorem gives the selection rules $\Delta j = 0, \pm 1$ and $\Delta \ell = 0, \pm 1$; but the case $\Delta \ell = 0$ is excluded by parity (otherwise known as Laporte's rule). For $M1$ transitions, the operator $\mathbf{L} + 2\mathbf{S}$ is a $k = 1$ irreducible tensor operator under total rotations, generated by \mathbf{J} , but is the sum of a $k = 1$ and a $k = 0$ operator under purely spatial rotations. Again, the Wigner-Eckart theorem gives $\Delta j = 0, \pm 1$ and $\Delta \ell = 0, \pm 1$, but this time parity excludes the case $\Delta \ell = \pm 1$. Similarly, for $E2$ transitions, the case $\Delta \ell = \pm 1$, which would be allowed by the Wigner-Eckart theorem, is excluded by parity. These rules are summarized in Table 1.

There are further restrictions imposed by the Wigner-Eckart theorem. For example, an $E2$ transition $j = \frac{1}{2} \rightarrow j = \frac{1}{2}$ is not allowed, because it is impossible to reach $j = \frac{1}{2}$ from $2 \otimes \frac{1}{2}$. Similarly, $\ell = 0 \rightarrow \ell = 0$ is impossible in $E2$ transitions. In hydrogen, only half-integral j are allowed, but in atoms with an even number of electrons, J is integral, and there are further rules of a similar sort. For example, $J = 0 \rightarrow J = 0$ is impossible in either $E1$ or $M1$ transitions.

An interesting case in hydrogen is the $2s_{1/2} \rightarrow 1s_{1/2}$ transition. Of course, the $2p$ states can make an $E1$ transition to the ground state, and do so with a lifetime on the order of 10^{-9} sec.

However, the $2s_{1/2} \rightarrow 1s_{1/2}$ is forbidden as an $E1$ transition, because of parity. It would appear from Table 1 that this transition is allowed as an $M1$ transition, but it turns out that the matrix element (58) vanishes because of the orthogonality of the radial wave functions. In detail, the story of the $M1$ transition in this case is somewhat complicated. It turns out that if the hydrogen atom is modeled with the Dirac equation, then the $M1$ matrix element does not exactly vanish, but it is higher order in powers of $v/c \sim \alpha$ than one would normally expect, and is very small. A similar result is obtained with the Schrödinger-Pauli theory, if we expand to higher order in kx and extract the $M1$ contribution from some higher order terms (although the Schrödinger-Pauli theory is not reliable for terms that are higher order in v/c). Suffice it to say that the $M1$ matrix element is very small. What about higher multipole moments in the $2s_{1/2} \rightarrow 1s_{1/2}$ transition? The $E2$ transition is forbidden in this case because it would be both a $j = \frac{1}{2} \rightarrow j = \frac{1}{2}$ and an $\ell = 0 \rightarrow \ell = 0$ transition. Similarly, we can see that all higher order multipole transitions are forbidden, because we cannot reach $j = \frac{1}{2}$ from $k \otimes \frac{1}{2}$, when $k \geq 2$. In fact, it turns out that the principal decay mode of the metastable $2s_{1/2}$ state is a two-photon decay to the $1s_{1/2}$ state, with a lifetime of about 10^{-1} sec.

Speaking of small effects, we may also notice that the $2s_{1/2}$ can decay to the $2p_{1/2}$ state by an $E1$ transition, since the latter is lower in energy by the (small) Lamb shift. But this rate is much smaller than the two-photon decay mentioned above, and does not contribute much to the overall decay rate. This transition is, however, important when driven by microwaves at or near the resonant frequency of 1.06 GHz. Indeed, Lamb and Retherford first used such microwave techniques in 1949 to make an unequivocal and high precision measurement of the Lamb shift.

Let us return now to the process of spontaneous emission, and consider the intensity of the emitted radiation as a function of angle and polarization. We will work this out only for electric dipole radiation, the most common case. We can imagine an experimental situation such as that illustrated in Fig. 1, which effectively measures the polarization μ and direction $\hat{\mathbf{k}}$ of the outgoing photon. In the following we will assume for simplicity that some state ($\mu = \pm 1$) of circular polarization is measured, but other states of polarization are only slightly more complicated to analyze.

We start with Eq. (21), into which we substitute Eq. (52) for the electric dipole approximation to the matrix element. This gives

$$\left(\frac{dw}{d\Omega}\right)_\mu = \frac{1}{2\pi} \frac{e^2 \omega^3}{\hbar c^3} |\boldsymbol{\epsilon}_\mu \cdot \mathbf{x}_{BA}|^2, \quad (62)$$

where $\boldsymbol{\epsilon}_\mu = \boldsymbol{\epsilon}_\mu(\hat{\mathbf{k}}) = \boldsymbol{\epsilon}_\lambda$, and where

$$\mathbf{x}_{BA} = \langle B | \mathbf{x} | A \rangle. \quad (63)$$

For simplicity we assume the atom is a hydrogen-like atom in the fine-structure model (we ignore hyperfine effects, etc.), and we take the upper and lower states to be $|B\rangle = |n\ell j m_j\rangle$ and $|A\rangle = |n'\ell' j' m'_j\rangle$, as above, so that

$$\mathbf{x}_{BA} = \langle n\ell j m_j | \mathbf{x} | n'\ell' j' m'_j \rangle. \quad (64)$$

(However, hardly anything changes if we use the eigenstates $|\alpha\pi L J M_J\rangle$ of a multi-electron atom.)

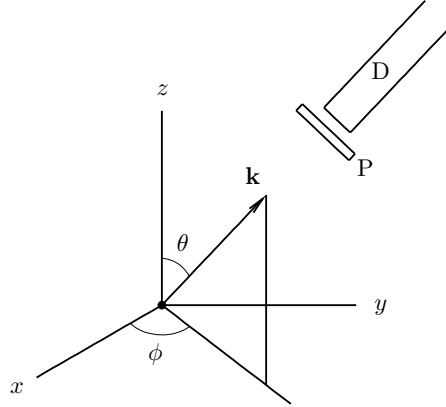


Fig. 1. Photons are emitted from a source of excited atoms at the origin of the coordinates. Photons emitted in a small solid angle around the direction \mathbf{k} are filtered by the polarizer P , which passes only one state of polarization, and are detected by the detector D .

It is convenient to expand \mathbf{x} in terms of the spherical basis as in Eq. (18.30),

$$\mathbf{x} = \sum_q \hat{\mathbf{e}}_q^* x_q, \quad (65)$$

because then the components x_q are components of a rank 1 irreducible tensor operator. We also use Eq. (39.33) to express ϵ_μ in terms of the spherical basis. Then we have

$$\epsilon_\mu \cdot \mathbf{x} = \sum_q x_q \hat{\mathbf{e}}_q^* \cdot [\mathbf{R}(\hat{\mathbf{k}}) \hat{\mathbf{e}}_\mu] = \sum_q x_q D_{q\mu}^1(\hat{\mathbf{k}}), \quad (66)$$

where $\mathbf{R}(\hat{\mathbf{k}})$ is defined by Eq. (39.31) and $D^1(\hat{\mathbf{k}})$ is the corresponding D -matrix, and where we use Eq. (18.54).

Now when we compute $\epsilon_\mu \cdot \mathbf{x}_{BA}$, we obtain a sum over the matrix elements of x_q , which can be transformed by the Wigner-Eckart theorem [see Eq. (18.79)]:

$$\begin{aligned} \epsilon_\mu \cdot \mathbf{x}_{BA} &= \sum_q \langle n\ell j m_j | x_q | n'\ell' j' m'_j \rangle D_{q\mu}^1(\hat{\mathbf{k}}) \\ &= \langle n\ell j || x || n'\ell' j' \rangle \sum_q \langle j m_j | j' 1 m'_j q \rangle D_{q\mu}^1(\hat{\mathbf{k}}). \end{aligned} \quad (67)$$

But by the selection rule (17.34) for the Clebsch-Gordan coefficients, only the term $q = m_j - m'_j$ survives in the sum. Therefore when we combine all the pieces together, we obtain the following expression for the differential transition rate for electric dipole transitions:

$$\left(\frac{dw}{d\Omega} \right)_\mu = \frac{1}{2\pi} \frac{e^2 \omega^3}{\hbar c^3} |\langle n\ell j || x || n'\ell' j' \rangle|^2 |\langle j m_j | j' 1 m'_j q \rangle|^2 |D_{q\mu}^1(\hat{\mathbf{k}})|^2, \quad (68)$$

where now it is understood that $q = m_j - m'_j$ (q is not summed over). This is a convenient expression, because the reduced matrix element shows the dependence of the transition rate on the manifolds

$(n\ell j)$ and $(n'\ell'j')$ of the initial and final states, the Clebsch-Gordan coefficient shows the dependence on the magnetic quantum numbers, and the D -matrix shows the dependence on the polarization and direction of the outgoing photon. Furthermore, writing the D -matrix in Euler angle form and using Eq. (13.57), we have

$$\left(\frac{dw}{d\Omega}\right)_\mu \sim |\hat{\mathbf{e}}_q^* \cdot \boldsymbol{\epsilon}_\mu(\hat{\mathbf{k}})|^2 = |D_{q\mu}^1(\phi, \theta, 0)|^2 = [d_{q\mu}^1(\theta)]^2, \quad (69)$$

where as illustrated in Fig. 1 (θ, ϕ) are the spherical angles of $\hat{\mathbf{k}}$ and where we suppress all leading factors and concentrate on the dependence on $\hat{\mathbf{k}}$ and μ . We see that the intensity of the emitted radiation is independent of the azimuthal angle ϕ , as we would expect since the initial and final states are eigenstates of J_z . Finally, we can invoke Eq. (13.61) for the reduced rotation matrix to determine the angular distribution as a function of θ for different choices of q and μ . The angular distribution is plotted in Fig. 2 for different cases. By the way, the quantity q has a simple interpretation, for if we write its definition in the form $m_j = m'_j + q$, we see that q is just the J_z quantum number of the emitted photon, since the total J_z of the combined matter-field system is conserved in the emission process.

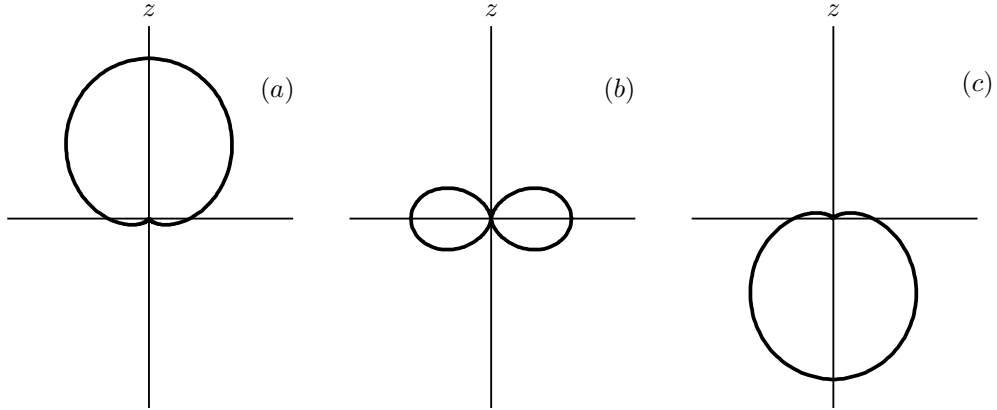


Fig. 2. Polar plots of intensity of electric dipole radiation for different cases. Case (a), $q = \mu = \pm 1$; case (b), $q = 0$, $\mu = \pm 1$; case (c), $q = -\mu = \pm 1$. Intensity is azimuthally symmetric.

The radiation patterns in Fig. 1 can be seen experimentally by placing the source (for example, a gas discharge tube) in a strong magnetic field, which will split the various magnetic substates of the otherwise degenerate initial and final states, so that a transition with a definite value of $\Delta m_j = -q$ can be observed. On the other hand, in many practical circumstances there is no magnetic field to split these substates, nor is the initial ensemble of atoms polarized. In such cases, the atom has an equal probability of being in any of the magnetic substates of the initial, degenerate atomic level; and all transitions to the various magnetic substates of the final, degenerate atomic level lie on top of one another (they have the same frequency), so the spectroscope simply sees a single line whose intensity is the superposition of the intensities of possibly several transitions. Furthermore, if the

initial state of the atom is unpolarized, then it has no preferred direction, and the emitted radiation is isotropic. In this case we might as well ask for the total transition rate (integrated over all solid angles and summed over polarizations). We will now analyze this case for electric dipole radiation.

We begin by computing the total transition rate. We could do this by integrating Eq. (68) over solid angles and summing it over polarizations, but it is just as easy to go back to Eq. (23), and to use the electric dipole expression (52) for the matrix element. Also, for simplicity, we will use the simple electrostatic, spinless model for the states $|n\ell m\rangle$ of the one-electron atom, that is, we will ignore the fine structure corrections. (Perhaps the spectroscope is cheap and cannot resolve the fine structure.) Then combining Eqs. (22) and (52), we have

$$\overline{|M_{BA}|^2} = \frac{m^2\omega^2}{\hbar^2} \frac{1}{8\pi} \sum_{\mu} \int d\Omega_k |\boldsymbol{\epsilon}_{\mu}(\hat{\mathbf{k}}) \cdot \mathbf{x}_{BA}|^2, \quad (70)$$

where now

$$\mathbf{x}_{BA} = \langle n\ell m | \mathbf{x} | n'\ell' m' \rangle. \quad (71)$$

Here the initial and final states are $|B\rangle = |n\ell m\rangle$ and $|A\rangle = |n'\ell' m'\rangle$, respectively. The polarization sum in Eq. (70) is easy if we use the completeness relation (37.53) for the polarization vectors. This gives

$$\sum_{\mu=\pm 1} |\boldsymbol{\epsilon}_{\mu}(\hat{\mathbf{k}}) \cdot \mathbf{x}_{BA}|^2 = |\mathbf{x}_{BA}|^2 - |\hat{\mathbf{k}} \cdot \mathbf{x}_{BA}|^2. \quad (72)$$

Next, the angular integration of this over Ω_k is easy, since the first term is independent of angle and the second term is just the angle average of one component of a vector. Thus we have

$$\int d\Omega_k (|\mathbf{x}_{BA}|^2 - |\hat{\mathbf{k}} \cdot \mathbf{x}_{BA}|^2) = \frac{8\pi}{3} |\mathbf{x}_{BA}|^2. \quad (73)$$

Altogether, Eq. (70) becomes

$$\overline{|M_{BA}|^2} = \frac{1}{3} \frac{m^2\omega^2}{\hbar^2} |\mathbf{x}_{BA}|^2. \quad (74)$$

As for the \mathbf{x}_{BA} , it is convenient to use it in complex conjugated form,

$$|\mathbf{x}_{BA}|^2 = |\langle B | \mathbf{x} | A \rangle|^2 = |\langle A | \mathbf{x} | B \rangle|^2 = |\mathbf{x}_{AB}|^2, \quad (75)$$

where

$$\mathbf{x}_{AB} = \langle n'\ell' m' | \mathbf{x} | n\ell m \rangle. \quad (76)$$

We expand \mathbf{x} in this expression in the spherical basis as in Eq. (65), so that

$$\mathbf{x}_{AB} = \sum_q \hat{\mathbf{e}}_q^* \langle A | x_q | B \rangle, \quad (77)$$

and so that

$$|\mathbf{x}_{AB}|^2 = \sum_q |\langle n'\ell' m' | x_q | n\ell m \rangle|^2. \quad (78)$$

But by Eq. (18.40), the quantity x_q can be expressed in terms of $Y_{1q}(\theta, \phi)$, where (θ, ϕ) are the spherical angles in \mathbf{x} -space. This causes the matrix element in Eq. (78) to factor into a radial part times an angular part,

$$\langle n' \ell' m' | x_q | n \ell m \rangle = I_r I_\Omega, \quad (79)$$

where

$$I_r = \int_0^\infty r^2 dr R_{n' \ell'}(r) r R_{n \ell}(r), \quad (80)$$

and

$$I_\Omega = \sqrt{\frac{4\pi}{3}} \int d\Omega Y_{\ell' m'}^*(\Omega) Y_{1q}(\Omega) Y_{\ell m}(\Omega). \quad (81)$$

We apply the 3- $Y_{\ell m}$ formula (17.43) to the latter, to obtain

$$I_\Omega = \sqrt{\frac{2\ell+1}{2\ell'+1}} \langle \ell 1 m q | \ell' m' \rangle \langle \ell' 0 | \ell 1 0 \rangle. \quad (82)$$

Then Eq. (78) becomes

$$|\mathbf{x}_{AB}|^2 = \frac{2\ell+1}{2\ell'+1} I_r^2 |\langle \ell' 0 | \ell 1 0 \rangle|^2 \sum_q \langle \ell' m' | \ell 1 m q \rangle \langle \ell 1 m q | \ell' m' \rangle, \quad (83)$$

which shows how the total transition rate depends on the magnetic quantum numbers of the transition.

Now, however, we assume that the initial state is unpolarized and that we don't care which final state the atom falls into. Then we obtain an effective value of $|\mathbf{x}_{AB}|^2$ by averaging over initial magnetic substates, and summing over final magnetic substates. This causes the replacement,

$$|\mathbf{x}_{AB}|^2 \rightarrow \frac{1}{2\ell+1} \sum_{mm'} |\mathbf{x}_{AB}|^2. \quad (84)$$

But when we use Eq. (83) in this, the q and mm' sums can be done,

$$\sum_{mm'} \sum_q \langle \ell' m' | \ell 1 m q \rangle \langle \ell 1 m q | \ell' m' \rangle = \sum_{m'} 1 = 2\ell' + 1, \quad (85)$$

where we use the orthonormality relation (17.33a) of the Clebsch-Gordan coefficients. Finally, putting all the pieces together and using Eq. (23), we find the effective Einstein A -coefficient for electric dipole radiation,

$$A^{E1} = \frac{4 e^2 \omega^3}{3 \hbar c^3} I_r^2 |\langle \ell' 0 | \ell 1 0 \rangle|^2. \quad (86)$$

At this point you may wish to look at Sakurai, *Modern Quantum Mechanics*, pp. 338–339, for his (brief) discussion of oscillator strengths and the Thomas-Rieche-Kuhn sum rule. Also, you may wish to plug in some numbers for typical atomic states in hydrogen; the radial integral I_r will just have to be done any way you can. Tables of dipole transition rates and further discussion are given in books such as Bethe and Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms*.

Problems

1. The perturbation expansion (6) is valid if $E_{\text{wave}} \ll E_{\text{nucleus}}$. Compute the energy flux (in watts per square cm) of light for which the rms electric field of the light wave is equal to the electric field strength due to the proton in a hydrogen atom at the Bohr radius. There is current experimental interest in the physics that arises at such high fields. The fields are created by focussing laser light onto a small region.

2. Compute the lifetime of the 21 cm transition in Hydrogen, $1s_{1/2} (f = 1) \rightarrow 1s_{1/2} (f = 0)$. Here f is the total angular momentum $\mathbf{F} = \mathbf{L} + \mathbf{S} + \mathbf{I}$, orbital plus spin for the electron plus spin for the proton. The splitting between the energy levels is given by Eq. (25.44), where g_N is the proton g -factor, μ_N and μ_B are the nuclear and Bohr magnetons, respectively, and a_0 is the Bohr radius. Assume the upper state is unpolarized (equal probabilities of being in the different magnetic substates). The lifetime is the inverse of the Einstein A coefficient. This lifetime determines the radio power radiated by galactic clouds of atomic hydrogen.

3. A hydrogen atom is at distance R from a hot blue star with radius a and surface temperature T , which radiates significantly in the ultraviolet. Assume $R \gg a$, so that the light coming from the star is concentrated in a narrow range of solid angles. Assume the surface of the star radiates as a blackbody. Assume the atom is unpolarized. When the atom absorbs a photon, taking it from the $1s$ state to the $2p$ state, it absorbs the photon momentum and suffers a recoil; then in short order ($\sim 10^{-9}$ sec), it reemits a photon and drops back into the ground state. But since the reemission of the photon is isotropic (for an unpolarized atom), the average momentum transferred by the emitted photon is zero. In this way, the atom feels an effective force because of the absorption of photons from star. Find an expression for this force in terms of R , a , T , and other appropriate parameters. Ignore all atomic states except the $1s$ and $2p$.