Appendix FF

Transition Probabilities for z-Polarized Light

We suppose that the electromagnetic radiation incident upon an atom is a superposition of plane waves. For each of these waves, the electric field can be written

$$\mathbf{E} = 2\mathbf{E}_0 \sin(\mathbf{k} \cdot \mathbf{r} - \omega t). \tag{FF.1}$$

The energy per unit volume of the radiation field associated with this monochromatic wave is

$$W = \epsilon_0 \mathbf{E}^2 = \epsilon_0 \, 4E_0^2 \sin^2(\mathbf{k} \cdot \mathbf{r} - \omega t).$$

Since the time average of the sine squared function in this last equation is 1/2, the average energy per volume is

$$W_{\text{av}} = 2\epsilon_0 E_0^2. \tag{FF.2}$$

Using the representation of the sine function given by Eq. (3.10), Eq. (FF.1) can be written

$$\mathbf{E} = -i\mathbf{E}_0 \mathrm{e}^{\mathrm{i}(\mathbf{k}\cdot\mathbf{r}-\omega t)} + i\mathbf{E}_0 \mathrm{e}^{-\mathrm{i}(\mathbf{k}\cdot\mathbf{r}-\omega t)}. \tag{FF.3}$$

For most applications, the coupling between the electrons and the radiation field is rather weak. The interaction can then be described by the Hamiltonian

$$H_{\text{int}} = \mathbf{E} \cdot (-\mathrm{e}\mathbf{r}), \tag{FF.4}$$

where $(-\mathrm{e}\mathbf{r})$ is the dipole moment of the electron. We shall consider radiation for which the electric field vector $\mathbf{E}$ is directed along the z-axis. Using Eq. (FF.3), the interaction Hamiltonian can then be written

$$H_{\text{int}} = -i(-ez)E_0 \, \mathrm{e}^{\mathrm{i}(\mathbf{k}\cdot\mathbf{r}-\omega t)} + i(-ez)E_0 \, \mathrm{e}^{-\mathrm{i}(\mathbf{k}\cdot\mathbf{r}-\omega t)}. \tag{FF.5}$$

The wave function of a hydrogen-like ion exposed to a time-dependent radiation field may be described by Eq. (4.17)

$$\psi(\mathbf{r}, t) = \sum_n c_n(t)\phi_n(\mathbf{r})\mathrm{e}^{-\mathrm{i}E_n t/\hbar}, \tag{FF.6}$$

where the coefficients $c_n(t)$ depend on time. The wave functions ϕ_n are eigenfunctions of the stationary atomic Hamiltonian

$$H_0 = \frac{-\hbar^2}{2m}\nabla^2 - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}. \tag{FF.7}$$

For simplicity, we assume that the eigenvalues E_n are nondegenerate. In order to be in a position to calculate the probability that the atom makes a transition from a level i to a level j, we suppose that at time, $t = 0$, the coefficient $c_i(0)$ is equal to one and all the other coefficients $c_j(0)$ are equal to zero. We wish to calculate the probability $|c_j(t)|^2$ that at a later time t the atom is in the state j. Substituting Eq. (FF.6) into the Schrödinger time-dependent equation,

$$i\hbar\frac{\partial\psi(\mathbf{r}, t)}{\partial t} = H\,\psi(\mathbf{r}, t), \tag{FF.8}$$

we obtain the following first-order differential equation for the coefficients $c_n(t)$

$$\sum_n \left(i\hbar \frac{dc_n}{dt} + E_n c_n \right) \phi_n(\mathbf{r})\, \mathrm{e}^{-\mathrm{i}E_n t/\hbar} = (H_0 + H_{\mathrm{int}}) \sum_n c_n \phi_n(\mathbf{r})\, \mathrm{e}^{-\mathrm{i}E_n t/\hbar}. \tag{FF.9}$$

On the right-hand side of this equation, we have written the Hamiltonian H as the sum of a stationary term H_0 and a dynamic term H_{int} corresponding to the interaction of the electron with an oscillating electromagnetic field. Since ϕ_n is an eigenfunction of H_0 corresponding to the eigenvalue E_n, the second term on the left-hand side of the equation cancels with the first term on the right to give

$$\sum_n i\hbar \frac{dc_n}{dt} \phi_n(\mathbf{r})\, \mathrm{e}^{-\mathrm{i}E_n t/\hbar} = H_{\mathrm{int}} \sum_n c_n \phi_n(\mathbf{r})\, \mathrm{e}^{-\mathrm{i}E_n t/\hbar}. \tag{FF.10}$$

The assumption that H_{int} is small means that the coefficients $c_n(t)$ evolve slowly with time. It is thus reasonable to approximate the coefficients c_n on the right-hand side of the above equation with their initial values. Since $c_i(0) = 1$ and all the other coefficients are zero, we get

$$\sum_n i\hbar \frac{dc_n}{dt} \phi_n(\mathbf{r})\, \mathrm{e}^{-\mathrm{i}E_n t/\hbar} = H_{\mathrm{int}} \phi_i(\mathbf{r})\, \mathrm{e}^{-\mathrm{i}E_i t/\hbar}. \tag{FF.11}$$

We may now single out the term on the left-hand side corresponding to the level j by multiplying the equation through on the left by the function $\phi_j^*(r)$ and integrating to obtain

$$\sum_n i\hbar \frac{dc_n}{dt} \mathrm{e}^{-\mathrm{i}E_n t/\hbar} \int \phi_j^*(r) \phi_n(\mathbf{r})\, \mathrm{d}V = \mathrm{e}^{-\mathrm{i}E_i t/\hbar} \int \phi_j^*(r) H_{\mathrm{int}} \phi_i(\mathbf{r})\, \mathrm{d}V. \tag{FF.12}$$

The eigenfunctions of H_0 have the property that they form an orthogonal set of functions. This means that if n is not equal to j, the integral, $\int \phi_j^*(r)\phi_n(\mathbf{r})dV$, which appears on the left is equal to zero. For the case, $n = j$, the functions can be normalized so that the integral is equal to one. Using this property of the wave functions, Eq. (FF.12) can be written

$$i\hbar \frac{\mathrm{d}c_j}{\mathrm{d}t} = \mathrm{e}^{\mathrm{i}(E_j t - E_i)t/\hbar} \int \phi_j^*(r) H_{\mathrm{int}} \phi_i(\mathbf{r})\, \mathrm{d}V. \tag{FF.13}$$

The factor, $(E_j - E_i)/\hbar$, which appears in the exponential term may be identified as the angular frequency of the transition

$$\omega_{ij} = \frac{E_j - E_i}{\hbar}. \tag{FF.14}$$

Multiplying Eq. (FF.13) through by $-\mathrm{i}\mathrm{d}t/\hbar$ and integrating from 0 to t, we obtain the following equation for the coefficient c_j as a function of time

$$c_j(t) = -\frac{\mathrm{i}}{\hbar} \int_0^t \mathrm{e}^{\mathrm{i}\omega_{ij} t'} \left[\int \phi_j^*(\mathbf{r}) H_{\mathrm{int}} \phi_i(\mathbf{r})\, \mathrm{d}V \right] \mathrm{d}t'. \tag{FF.15}$$

In order to solve this last equation for c_j, we must use the explicit form of the interaction Hamiltonian. Substituting Eq. (FF.5) into Eq. (FF.15) and performing the integrations over t', we obtain

$$\begin{aligned} c_j(t) = & -\left[\frac{1 - \mathrm{e}^{\mathrm{i}(\omega_{ij} - \omega)t}}{\hbar(\omega_{ij} - \omega)} \right] \mathrm{i}E_0 \int \phi_j^*(\mathbf{r})(-ez)\, \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \phi_i(\mathbf{r})\, \mathrm{d}V \\ & + \left[\frac{1 - \mathrm{e}^{\mathrm{i}(\omega_{ij} + \omega)t}}{\hbar(\omega_{ij} + \omega)} \right] \mathrm{i}E_0 \int \phi_j^*(\mathbf{r})(-ez)\, \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \phi_i(\mathbf{r})\, \mathrm{d}V. \end{aligned} \tag{FF.16}$$

For the case $E_j < E_i$, the angular frequency ω_{ij}, which is given by (FF.14), is negative and the transition $i \to j$ corresponds to stimulated emission. When the frequency ω of the incident radiation is near $-\omega_{ij}$, the denominator of the second term in Eq. (FF.16) will become very small and the second term will be much larger than the first. It is usually true that for emission processes the first term may be neglected. Similarly, the first term in Eq. (FF.16) provides a good approximate description of absorption.

We shall consider stimulated emission in some detail. Factoring $\mathrm{e}^{\mathrm{i}(\omega_{ij}+\omega)t/2}$ from the second term of Eq. (FF.16), we may write this contribution to c_j as

$$c_j(t) = \mathrm{e}^{\mathrm{i}(\omega_{ij}+\omega)t/2}\left[\frac{\mathrm{e}^{\mathrm{i}(\omega_{ij}+\omega)t/2} - \mathrm{e}^{-\mathrm{i}(\omega_{ij}+\omega)t/2}}{\hbar(\omega_{ij}+\omega)}\right] \times \mathrm{i}E_0 \int \phi_j^*(\mathbf{r})(-ez)\,\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}}\phi_i(\mathbf{r})\,\mathrm{d}V. \tag{FF.17}$$

The representation of the sine function in terms of exponentials given by Eq. (3.10) may then be used to write Eq. (FF.17) in the following way

$$c_j(t) = \mathrm{e}^{\mathrm{i}(\omega_{ij}+\omega)t/2}\,\frac{\sin[(\omega_{ij}+\omega)t/2]}{\hbar[(\omega_{ij}+\omega)/2]}\,E_0 \int \phi_j^*(\mathbf{r})(-ez)\,\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}}\phi_i(\mathbf{r})\,\mathrm{d}V. \tag{FF.18}$$

The transition probability per time is $|c_j(t)|^2/t$. Using Eq. (FF.18), the transition probability per time may be written

$$|c_j(t)|^2/t = \frac{t\sin^2[(\omega_{ij}+\omega)t/2]}{\hbar^2[(\omega_{ij}+\omega)t/2]^2}\,E_0^2\,\left|\int \phi_j^*(\mathbf{r})(-ez)\,\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}}\phi_i(\mathbf{r})\,\mathrm{d}V\right|^2. \tag{FF.19}$$

Eq. (FF.19) gives the probability per time that radiation of a single frequency ω will be emitted. According to Eq. (FF.2), the energy per volume of the wave is equal to $2\epsilon_0 E_0^2$. In order to be in a position to integrate over the entire spectrum of frequencies, we set this expression for the energy equal to the amount of energy of a continuous spectrum in the range between ω and $\omega + \mathrm{d}\omega$

$$2\epsilon_0 E_0^2 = \rho(\omega)\,\mathrm{d}\omega. \tag{FF.20}$$

where, as before, $\rho(\omega)$ is the energy density per frequency range. Solving the above equation for E_0^2, gives

$$E_0^2 = \frac{1}{2\epsilon_0}\rho(\omega)\,\mathrm{d}\omega. \tag{FF.21}$$

We now substitute this expression for E_0^2 into Eq. (FF.19) and integrate over a range of frequencies that includes the resonant frequency $-\omega_{ij}$ to obtain

$$|c_j(t)|^2/t = \frac{1}{2\epsilon_0\hbar^2}\left|\int \phi_j^*(\mathbf{r})(-ez)\,\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}}\phi_i(\mathbf{r})\,\mathrm{d}V\right|^2 \times \int_{\omega_1}^{\omega_2} \rho(\omega)\left[\frac{\sin\big((\omega_{ij}+\omega)t/2)\big)}{\big((\omega_{ij}+\omega)t/2\big)}\right]^2 t\,\mathrm{d}\omega. \tag{FF.22}$$

The term occurring in the denominator of the integrand will be zero when the frequency ω is equal to $-\omega_{ij}$. This frequency, which makes the largest contribution to the transition probability, will be denoted by ω^*. Using Eq. (FF.14), we may write

$$\omega^* = -\omega_{ij} = \frac{E_i - E_j}{\hbar}\,. \tag{FF.23}$$

For an emission process, E_i will be greater than E_j and ω^* will be positive. According to Eq. (4.44), ω^* is then equal to the transition frequency. Substituting ω^* for $-\omega_{ij}$ in Eq. (FF.22), we get

$$|c_j(t)|^2/t = \frac{1}{2\epsilon_0\hbar^2}\left|\int \phi_j^*(\mathbf{r})(-ez)\,\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}}\phi_i(\mathbf{r})\,\mathrm{d}V\right|^2 \times \int_{\omega_1}^{\omega_2} \rho(\omega)\left[\frac{\sin((\omega-\omega^*)t/2))}{((\omega-\omega^*)t/2)}\right]^2 t\,\mathrm{d}\omega. \tag{FF.24}$$

The function within square brackets in this last equation is similar to the function occurring within square brackets in Eq. (3.44), which is represented by the dotted line in Fig. 3.13. Both functions have well-defined maxima. The function within square brackets in Eq. (FF.24) has its maximum value for $\omega = \omega^*$, and the function is zero when the frequency ω differs from ω^* by an integral number of multiples of $2\pi/t$

$$\omega - \omega^* = n\,\frac{2\pi}{t}\,. \tag{FF.25}$$

For large values of t, the function within square brackets becomes very sharply peaked. The function $\rho(\omega)$ can then be approximated by its value at the transition frequency $\omega = \omega^*$ and brought outside the integral to give

$$|c_j(t)|^2/t = \frac{1}{2\epsilon_0\hbar^2}\,\rho(\omega^*)\left|\int \phi_j^*(\mathbf{r})(-ez)\,\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}}\phi_i(\mathbf{r})\,\mathrm{d}V\right|^2 \times \int_{\omega_1}^{\omega_2}\left[\frac{\sin((\omega-\omega^*)t/2)}{((\omega-\omega^*)t/2)}\right]^2 t\,\mathrm{d}\omega. \tag{FF.26}$$

In the limit of large t, the integral has the value 2π, and we obtain

$$|c_j(t)|^2/t = \frac{\pi}{\epsilon_0\hbar^2}\,\rho(\omega^*)\left|\int \phi_j^*(\mathbf{r})(-ez)\,\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}}\phi_i(\mathbf{r})\,\mathrm{d}V\right|^2. \tag{FF.27}$$

In deriving this result, we have not made any assumptions concerning the wavelength of the light. A very useful approximation can be obtained by taking advantage of the fact that the size of the atom is much smaller than the wavelength of visible or even ultraviolet light. The wavelength of visible light is between 400 and 700 nm, while the wavelength of ultraviolet light is between 10 and 400 nm. By comparison, the size of an atom is about 0.1 nm. The dependence of the incident wave upon the spatial coordinates occurs through the factor $\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}}$ in Eq. (FF.27). Since the magnitude of the wave vector $\mathbf{k}$ is $2\pi/\lambda$, $\mathbf{k}\cdot\mathbf{r}$ will not change appreciably over the size of the atom. It follows that we can approximate the exponential function by the first term in its Taylor series expansion

$$\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}} = 1 - \mathrm{i}\mathbf{k}\cdot\mathbf{r} + \cdots, \tag{FF.28}$$

This is called the *electric dipole approximation*. Replacing the exponential function with 1 in Eq. (FF.27) and denoting the transition frequency by ω as in the text, we obtain

$$|c_j(t)|^2/t = \frac{\pi}{\epsilon_0\hbar^2}\,\rho(\omega)\left|\int \phi_j^*(\mathbf{r})(-ez)\,\phi_i(\mathbf{r})\,\mathrm{d}V\right|^2. \tag{FF.29}$$