12.6: Electromagnetic Radiation

Let us use the previous results to investigate the interaction of an atomic electron with classical (i.e., non-quantized) electromagnetic radiation.

The unperturbed Hamiltonian of the system is

$$H_0 = \frac{p^2}{2\,m_e} + V_0(r). \tag{12.6.1}$$

Now, the standard classical prescription for obtaining the Hamiltonian of a particle of charge q in the presence of an electromagnetic field is

$$\begin{aligned} \mathbf{p} &\rightarrow \mathbf{p} + q\,\mathbf{A}, \\ H &\rightarrow H - q\,\phi, \end{aligned}$$

where $\mathbf{A}(\mathbf{r})$ is the vector potential, and $\phi(\mathbf{r})$ the scalar potential. Note that

$$\begin{aligned} \mathbf{E} &= -\nabla\phi - \frac{\partial\mathbf{A}}{\partial t}, \\ \mathbf{B} &= \nabla\times\mathbf{A}. \end{aligned}$$

This prescription also works in quantum mechanics. Thus, the Hamiltonian of an atomic electron placed in an electromagnetic field is

$$H = \frac{(\mathbf{p} - e\,\mathbf{A})^2}{2\,m_e} + e\,\phi + V_0(r), \tag{12.6.2}$$

where $\mathbf{A}$ and ϕ are functions of the position operators. The previous equation can be written

$$H = \frac{\left(p^2 - e\,\mathbf{A}\cdot\mathbf{p} - e\,\mathbf{p}\cdot\mathbf{A} + e^2\,A^2\right)}{2\,m_e} + e\,\phi + V_0(r). \tag{12.6.3}$$

Now,

$$\mathbf{p}\cdot\mathbf{A} = \mathbf{A}\cdot\mathbf{p}, \tag{12.6.4}$$

provided that we adopt the Coulomb gauge $\nabla\cdot\mathbf{A} = 0$. Hence,

$$H = \frac{p^2}{2\,m_e} - \frac{e\,\mathbf{A}\cdot\mathbf{p}}{m_e} + \frac{e^2\,A^2}{2\,m_e} + e\,\phi + V_0(r). \tag{12.6.5}$$

Suppose that the perturbation corresponds to a linearly polarized, monochromatic, plane-wave. In this case,

$$\begin{aligned} \phi &= 0, \\ \mathbf{A} &= A_0\,\epsilon\,\cos(\mathbf{k}\cdot\mathbf{r} - \omega t)\,, \end{aligned}$$

where $\mathbf{k}$ is the wavevector (note that $\omega = k\,c$), and ϵ a unit vector that specifies the direction of polarization (i.e., the direction of $\mathbf{E}$). Note that $\epsilon\cdot\mathbf{k} = 0$. The Hamiltonian becomes

$$H = H_0 + H_1(t), \tag{12.6.6}$$

with

$$H_0 = \frac{p^2}{2\,m_e} + V_0(r), \tag{12.6.7}$$

and

$$H_1 \simeq -\frac{e\,\mathbf{A}\cdot\mathbf{p}}{m_e}, \tag{12.6.8}$$

where the A^2 term, which is second order in A_0, has been neglected.

The perturbing Hamiltonian can be written

$$H_1=-\frac{e\,A_0\,\epsilon\cdot\mathbf{p}}{2\,m_e}[\exp(\mathrm{i}\,\mathbf{k}\cdot\mathbf{r}-\mathrm{i}\,\omega t)+\exp(-\mathrm{i}\,\mathbf{k}\cdot\mathbf{r}+\mathrm{i}\,\omega t)]\,. \tag{12.6.9}$$

This has the same form as Equation ([e13.51]), provided that

$$V^{\dagger}=-\frac{e\,A_0\,\epsilon\cdot\mathbf{p}}{2\,m_e}\exp(\mathrm{i}\,\mathbf{k}\cdot\mathbf{r}\,). \tag{12.6.10}$$

It follows from Equations ([e13.53]), ([e13.63]), and ([e13.79]) that the transition probability for radiation induced absorption is

$$P^{abs}_{i\to f}(t)=\frac{t^{\,2}}{\hbar^{\,2}}\,\frac{e^{\,2}\,|A_0|^{\,2}}{4\,m_e^2}\,\,|\langle f|\epsilon\cdot\mathbf{p}\,\,\exp(\,\mathrm{i}\,\mathbf{k}\cdot\mathbf{r})|i\rangle|^{\,2}\,\mathrm{sinc}^2[(\omega-\omega_{fi})\,t/2]. \tag{12.6.11}$$

Now, the mean energy density of an electromagnetic wave is

$$u=\frac{1}{2}\left(\frac{\epsilon_0\,|E_0|^{\,2}}{2}+\frac{|B_0|^{\,2}}{2\,\mu_0}\right)=\frac{1}{2}\,\epsilon_0\,|E_0|^{\,2}, \tag{12.6.12}$$

where $E_0=A_0\,\omega$ and $B_0=E_0/c$ are the peak electric and magnetic field-strengths, respectively. It thus follows that

$$P^{abs}_{i\to f}(t)=\frac{t^{\,2}\,e^{\,2}}{2\,\epsilon_0\,\hbar^{\,2}\,m_e^2\,\omega^{\,2}}\,\,|\langle f|\epsilon\cdot\mathbf{p}\,\,\exp(\,\mathrm{i}\,\mathbf{k}\cdot\mathbf{r})|i\rangle|^{\,2}\,u\,\mathrm{sinc}^2[(\omega-\omega_{fi})\,t/2]. \tag{12.6.13}$$

Thus, not surprisingly, the transition probability for radiation induced absorption (or stimulated emission) is directly proportional to the energy density of the incident radiation.

Suppose that the incident radiation is not monochromatic, but instead extends over a range of frequencies. We can write

$$u=\int_{-\infty}^{\infty}\rho(\omega)\,d\omega, \tag{12.6.14}$$

where $\rho(\omega)\,d\omega$ is the energy density of radiation whose frequencies lie between ω and $\omega+d\omega$. Equation ([e13.80]) generalizes to

$$P^{abs}_{i\to f}(t)=\int_{-\infty}^{\infty}\frac{t^{\,2}\,e^{\,2}}{2\,\epsilon_0\,\hbar^{\,2}\,m_e^2\,\omega^{\,2}}\,\,|\langle f|\epsilon\cdot\mathbf{p}\,\,\exp(\,\mathrm{i}\,\mathbf{k}\cdot\mathbf{r})|i\rangle|^{\,2}\,\rho(\omega)\,\mathrm{sinc}^2[(\omega-\omega_{fi})\,t/2]\,d\omega. \tag{12.6.15}$$

Note, however, that the previous expression is only valid provided the radiation in question is *incoherent*: that is, provided there are no phase correlations between waves of different frequencies. This follows because it is permissible to add the intensities of incoherent radiation, whereas we must always add the amplitudes of coherent radiation . Given that the function $\mathrm{sinc}^2[(\omega-\omega_{fi})\,t/2]$ is very strongly peaked (see Figure [fsinc]) about $\omega=\omega_{fi}$ (assuming that $t\gg 2\pi/\omega_{fi}$), and

$$\int_{-\infty}^{\infty}\mathrm{sinc}^2(x)\,dx=\pi, \tag{12.6.16}$$

the previous equation reduces to

$$P^{abs}_{i\to f}(t)=\frac{\pi\,e^{\,2}\,\rho(\omega_{fi})}{\epsilon_0\,\hbar^{\,2}\,m_e^2\,\omega_{fi}^2}\,\,|\langle f|\epsilon\cdot\mathbf{p}\,\,\exp(\,\mathrm{i}\,\mathbf{k}\cdot\mathbf{r})|i\rangle|^{\,2}t. \tag{12.6.17}$$

Note that in integrating over the frequencies of the incoherent radiation we have transformed a transition probability that is basically proportional to $t^{\,2}$ [see Equation ([e13.80])] to one that is proportional to t. As has already been explained, the previous expression is only valid when $P^{abs}_{i\to f}\ll 1$. However, the result that

$$w^{abs}_{i\to f}\equiv\frac{dP^{abs}_{i\to f}}{dt}=\frac{\pi\,e^{\,2}\,\rho(\omega_{fi})}{\epsilon_0\,\hbar^{\,2}\,m_e^{\,2}\,\omega_{fi}^2}\,\,|\langle f|\epsilon\cdot\mathbf{p}\,\,\exp(\,\mathrm{i}\,\mathbf{k}\cdot\mathbf{r})|i\rangle|^{\,2} \tag{12.6.18}$$

is constant in time is universally valid. Here, $w^{abs}_{i\to f}$ is the transition probability per unit time interval, otherwise known as the *transition rate*. Given that the transition rate is constant, we can write (see Chapter [s2])

$$P_{i\rightarrow f}^{abs}(t+dt) - P_{i\rightarrow f}^{abs}(t) = \left[1 - P_{i\rightarrow f}^{abs}(t)\right]\, w_{i\rightarrow f}^{abs}\, dt: \tag{12.6.19}$$

that is, the probability that the system makes a transition from state i to state f between times t and $t+dt$ is equivalent to the probability that the system does not make a transition between times 0 and t and then makes a transition in a time interval dt—the probabilities of these two events are $1 - P_{i\rightarrow f}^{abs}(t)$ and $w_{i\rightarrow f}^{abs}\, dt$, respectively. It follows that

$$\frac{dP_{i\rightarrow f}^{abs}}{dt} + w_{i\rightarrow f}^{abs}\, P_{i\rightarrow f}^{abs} = w_{i\rightarrow f}^{abs}, \tag{12.6.20}$$

with the initial condition $P_{i\rightarrow f}^{abs}(0) = 0$. The previous equation can be solved to give

$$P_{i\rightarrow f}^{abs}(t) = 1 - \exp\left(-w_{i\rightarrow f}^{abs}\, t\right). \tag{12.6.21}$$

This result is consistent with Equation ([e13.86]) provided $w_{i\rightarrow f}^{abs}\, t \ll 1$: that is, provided that $P_{i\rightarrow f}^{abs} \ll 1$.

Using similar arguments to those given previously, the transition probability for stimulated emission can be shown to take the form

$$P_{i\rightarrow f}^{stm}(t) = 1 - \exp\left(-w_{i\rightarrow f}^{stm}\, t\right), \tag{12.6.22}$$

where the corresponding transition rate is written

$$w_{i\rightarrow f}^{stm} = \frac{\pi\, e^{\,2}\, \rho(\omega_{if})}{\epsilon_0\, \hbar^{\,2}\, m_e^2\, \omega_{if}^2}\, |\langle i|\epsilon\cdot\mathbf{p}\, \exp(\,\mathrm{i}\, \mathbf{k}\cdot\mathbf{r})|f\rangle|^{\,2}. \tag{12.6.23}$$

Contributors and Attributions

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