STIMULATED EMISSION OF RADIATION AT HIGH FREQUENCIES

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Section 9.2; Problem 9.21a.


In our treatment of stimulated emission of radiation, we assumed that the wavelength of the perturbing radiation was much greater than the size of the atom. For high frequency radiation, such as X-rays, this assumption is no longer valid, so we need to include the spatial variation of the wave in the calculation. In that case, we need to return to the original formula for the electric field:

\[ \mathbf{E} = E_0 \hat{n} \cos (\mathbf{k} \cdot \mathbf{r} - \omega t) \]  

where \( \mathbf{k} \) is the direction of propagation, \( \hat{n} \) is the direction of polarization and \( \omega = kc \) is the angular frequency. If we still assume that the wavelength is fairly large, so that \( kr = 2\pi r/\lambda \) is fairly small, we can use a first order approximation:

\[ \mathbf{E} = E_0 \hat{n} \left[ \cos (\omega t) + k \cdot \mathbf{r} \sin (\omega t) \right] \]

where the last line uses \( \sin x \approx x \) for small \( x \). The first term gives the transition rates we treated in the earlier post, so we’ll look at the second term here.

To get the perturbation \( H' \) to the hamiltonian, we can use the formula for the energy of a point charge in an electric field. The work done in moving a charge \( q \) from point \( \mathbf{a} \) to point \( \mathbf{b} \) is

\[ W = -q \int_{\mathbf{a}}^{\mathbf{b}} \mathbf{E} \cdot d\mathbf{r}' \]

If we take \( \mathbf{a} = 0 \) to be the centre of the atom and \( \mathbf{b} \) to be the field point \( \mathbf{r} \) then the energy due to the second term in \( H' \) is
$$H' = -qE_0 \sin(\omega t) \int_0^r (\mathbf{k} \cdot \mathbf{r'}) \hat{n} \cdot d\mathbf{r}'$$  \hspace{1cm} (5)$$

Since the integral doesn’t depend on the path, we can use a straight line from the origin out to point \( \mathbf{r} \). In that case, the direction of \( \mathbf{r}' \) is constant, so the angle \( \theta_k \) between \( \mathbf{k} \) and \( \mathbf{r}' \) is also constant, as is the angle \( \theta_n \) between \( \hat{n} \) and \( \mathbf{r}' \), so

$$\mathbf{k} \cdot \mathbf{r}' = (k \cos \theta_k) r'$$ \hspace{1cm} (6)$$
$$\hat{n} \cdot d\mathbf{r}' = (\cos \theta_n) dr'$$ \hspace{1cm} (7)$$

We then get

$$H' = -qE_0 k \sin(\omega t) \cos \theta_k \cos \theta_n \int_0^r r' dr'$$ \hspace{1cm} (8)$$
$$= -\frac{1}{2} qE_0 k \sin(\omega t) \cos \theta_k \cos \theta_n r^2$$ \hspace{1cm} (9)$$
$$= -\frac{1}{2} qE_0 \sin(\omega t) [kr \cos \theta_k] [r \cos \theta_n]$$ \hspace{1cm} (10)$$
$$= -\frac{1}{2} qE_0 \sin(\omega t) (\mathbf{k} \cdot \mathbf{r}) (\hat{n} \cdot \mathbf{r})$$ \hspace{1cm} (11)$$
$$= -\frac{1}{2} qE_0 \frac{\omega}{c} \sin(\omega t) (\mathbf{k} \cdot \mathbf{r}) (\hat{n} \cdot \mathbf{r})$$ \hspace{1cm} (12)$$

In the last line we used the relation \( k = \omega/c \). [Note that \( \hat{k} \) is a unit vector in the \( k \) direction which is not necessarily the \( z \) direction. The notation in Griffiths is confusing because he uses \( \hat{k} \) earlier in the chapter to refer to the \( z \) direction, but in this problem it refers to the \( k \) direction.]

The matrix element \( H'_{ba} \) is

$$H'_{ba} = -\frac{1}{2} qE_0 \frac{\omega}{c} \langle b | (\hat{k} \cdot \mathbf{r}) (\hat{n} \cdot \mathbf{r}) | a \rangle \sin(\omega t)$$ \hspace{1cm} (13)$$

This is the same situation as the one we looked at earlier, except here we have \( \sin(\omega t) \) instead of \( \cos(\omega t) \) and

$$V_{ba} = -\frac{1}{2} qE_0 \frac{\omega}{c} \langle b | (\hat{k} \cdot \mathbf{r}) (\hat{n} \cdot \mathbf{r}) | a \rangle$$ \hspace{1cm} (14)$$

We can work through the calculations, replacing the cosine by the sine to get
Keeping only the second term (because we’re considering only frequencies $\omega \approx \omega_0$), we get

$$c_b(t) = \frac{V_{ba}}{2i\hbar} \frac{e^{i(\omega_0-\omega)t} - 1}{\omega_0 - \omega}$$

(19)

$$c_b(t) = \frac{V_{ba} e^{i(\omega_0-\omega)t} - 1}{2i\hbar \omega_0 - \omega}$$

$$c_b(t) = \frac{V_{ba} e^{i(\omega_0-\omega)t/2} \sin \frac{(\omega_0-\omega)t}{2}}{\hbar \omega_0 - \omega}$$

(20)

The transition probability for stimulation by a monochromatic plane wave is therefore

$$P_{a\rightarrow b} = |c_b|^2$$

(21)

$$P_{a\rightarrow b} = \left( \frac{1}{2} q E_0 \frac{\omega}{\hbar c} \right)^2 |\langle b | (\hat{k} \cdot \hat{r}) (\hat{n} \cdot \hat{r}) | a \rangle|^2 \frac{\sin^2 \frac{(\omega_0-\omega)t}{2}}{(\omega_0 - \omega)^2}$$

(22)

In the problem, however, we’re interested in the transition probability for an atom subject to radiation over a range of frequencies. The energy density in an electromagnetic wave can be found from the average magnitude of the Poynting vector $\mathbf{S}$, which gives the amount of energy per unit area per unit time crossing a surface. In a unit time over a unit area, a volume of $c$ crosses the surface, so the energy density $u$ is $\langle S \rangle$:

$$u = \frac{1}{2} \varepsilon_0 E_0^2$$

(23)

If we have a range of frequencies, then we need to replace $u$ (which is for a single frequency) by $\rho(\omega) \, d\omega$, where $\rho(\omega)$ is the density of radiation with frequencies in the range $[\omega, \omega + d\omega]$. We can then integrate over all frequencies to get the new transition probability:
\begin{equation}
P_{a \rightarrow b} = \left( \frac{1}{2} \frac{q \omega}{\hbar c} \right)^2 \frac{2}{\epsilon_0} \left| \langle b | (\hat{k} \cdot \mathbf{r}) (\hat{n} \cdot \mathbf{r}) | a \rangle \right|^2 \int_0^\infty \rho(\omega) \frac{\sin^2 \left( \frac{\omega_0 - \omega}{2} t \right)}{(\omega_0 - \omega)^2} d\omega
\end{equation}

We can make a couple of approximations to evaluate the integral. First, since the integrand peaks around \( \omega = \omega_0 \), we can take \( \rho(\omega) \approx \rho(\omega_0) \) over the region where the integrand is significantly greater than zero. This means we can take \( \rho(\omega_0) \) as a constant and take it outside the integral. Second, again because the remaining term in the integrand peaks around \( \omega = \omega_0 \), we can extend the lower limit on the integrand to \(-\infty\). Then we can transform the integral using the substitution \( x = \frac{(\omega_0 - \omega)t}{2} \), so that \( d\omega = -\frac{2 dx}{t} \) and \((\omega_0 - \omega)^2 = \frac{4x^2}{t^2}\). Therefore

\begin{equation}
\int_0^\infty \rho(\omega) \frac{\sin^2 \left( \frac{\omega_0 - \omega}{2} t \right)}{(\omega_0 - \omega)^2} d\omega \approx \rho(\omega_0) \frac{2}{t} \int_{-\infty}^\infty \frac{\sin^2 x}{x^2} dx
\end{equation}

\begin{equation}
= \rho(\omega_0) \frac{\pi t}{2}
\end{equation}

Plugging this back into \ref{eq:24} we get

\begin{equation}
P_{a \rightarrow b} = \left( \frac{1}{2} \frac{q \omega}{\hbar c} \right)^2 \frac{2}{\epsilon_0} \rho(\omega_0) \left| \langle b | (\hat{k} \cdot \mathbf{r}) (\hat{n} \cdot \mathbf{r}) | a \rangle \right|^2 t \tag{27}
\end{equation}

The transition rate for stimulated absorption is

\begin{equation}
R_{a \rightarrow b} = \frac{dP_{a \rightarrow b}}{dt} = \left( \frac{1}{2} \frac{q \omega}{\hbar c} \right)^2 \frac{2}{\epsilon_0} \rho(\omega_0) \left| \langle b | (\hat{k} \cdot \mathbf{r}) (\hat{n} \cdot \mathbf{r}) | a \rangle \right|^2 \tag{28}
\end{equation}

Because the term \( \left| \langle b | (\hat{k} \cdot \mathbf{r}) (\hat{n} \cdot \mathbf{r}) | a \rangle \right|^2 \) is the same as \( \left| \langle a | (\hat{k} \cdot \mathbf{r}) (\hat{n} \cdot \mathbf{r}) | b \rangle \right|^2 \) (the operators \( \langle \hat{k} \cdot \mathbf{r} \rangle \langle \hat{n} \cdot \mathbf{r} \rangle \) are just real multipliers so \( \langle b | (\hat{k} \cdot \mathbf{r}) (\hat{n} \cdot \mathbf{r}) | a \rangle = \langle a | (\hat{k} \cdot \mathbf{r}) (\hat{n} \cdot \mathbf{r}) | b \rangle^* \) so the moduli are equal), the transition rate is the same for both absorption and emission:

\begin{equation}
R_{a \rightarrow b} = R_{b \rightarrow a} \tag{29}
\end{equation}

[We’ll see how to get the transition rate for spontaneous emission in a future post. However, the result \ref{eq:27} leads to a different result than that given in Griffiths, in that there is an extra factor of \( \frac{1}{4} \) in my answer. This appears to have crept in while doing the integral in \ref{eq:9} and Griffiths’s answer would seem to regard \( k \cdot r \) as a constant in the integration. I can’t see why you would assume this, but any comments are welcome.]
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