FORBIDDEN TRANSITIONS IN THE HARMONIC OSCILLATOR AND HYDROGEN

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Post date: 8 November 2021.

The stimulated emission rate in a system perturbed by an electromagnetic wave of form

$$\mathbf{E} = E_0 \hat{\mathbf{n}} \cos\left(\mathbf{k}\cdot\mathbf{r} - \omega t\right) \tag{1}$$

due to the first-order term in $\mathbf{k}\cdot\mathbf{r}$ turned out to be

$$R_{b\to a} = \frac{dP_{a\to b}}{dt} = \left(\frac{1}{2} q \frac{\omega}{\hbar c}\right)^2 \frac{\pi}{\epsilon_0} \rho(\omega) \left|\left\langle a \left| \left(\hat{\mathbf{k}}\cdot\mathbf{r}\right)\left(\hat{\mathbf{n}}\cdot\mathbf{r}\right) \right| b \right\rangle\right|^2 \tag{2}$$

To find the spontaneous emission rate, we can follow the same argument that we used earlier when neglecting $\mathbf{k}\cdot\mathbf{r}$. [The earlier argument included an average over all directions of polarization and propagation of the electromagnetic wave, but we'll neglect that here.] To recap, the idea is that we assume that the stimulated emission rate is $R_{b\to a} = B_{ba}\rho(\omega)$ and then using results from statistical mechanics to show that the spontaneous emission rate A (to use Einstein's notation) is

$$A = \frac{\hbar\omega^3}{\pi^2 c^3} B_{ba} \tag{3}$$

From above, we can read off B_{ba} as

$$B_{ba} = \left(\frac{1}{2} q \frac{\omega}{\hbar c}\right)^2 \frac{\pi}{\epsilon_0} \left|\left\langle a \left| \left(\hat{\mathbf{k}}\cdot\mathbf{r}\right)\left(\hat{\mathbf{n}}\cdot\mathbf{r}\right) \right| b \right\rangle\right|^2 \tag{4}$$

so the spontaneous emission rate is

$$A = \frac{q^2\omega^5}{4\pi\hbar\epsilon_0 c^5} \left|\left\langle a \left| \left(\hat{\mathbf{k}}\cdot\mathbf{r}\right)\left(\hat{\mathbf{n}}\cdot\mathbf{r}\right) \right| b \right\rangle\right|^2 \tag{5}$$

As I noted in the earlier post, this answer differs from the one in Griffiths because of the factor of 4 in the denominator. To proceed with the next example, however, I'll use Griffiths's answer, so I'll take the spontaneous emission rate to be

$$A = \frac{q^2\omega^5}{\pi\hbar\epsilon_0 c^5}\left|\left\langle a\left|\left(\hat{\mathbf{k}}\cdot\mathbf{r}\right)\left(\hat{\mathbf{n}}\cdot\mathbf{r}\right)\right|b\right\rangle\right|^2 \tag{6}$$

We can get explicit expressions for A in different systems if we can work out the matrix element $\left\langle a\left|\left(\hat{\mathbf{k}}\cdot\mathbf{r}\right)\left(\hat{\mathbf{n}}\cdot\mathbf{r}\right)\right|b\right\rangle$.

Example 1. Consider first a one-dimensional harmonic oscillator. To do this properly, we must average the matrix element over all polarization directions $\hat{\mathbf{n}}$ and propagation directions $\hat{\mathbf{k}}$. We can do this by using spherical coordinates and taking

$$\hat{\mathbf{k}} = \hat{\mathbf{z}} \tag{7}$$

$$\hat{\mathbf{n}} = \cos\phi\hat{\mathbf{x}} + \sin\phi\hat{\mathbf{y}} \tag{8}$$

$$\mathbf{r} = x\sin\theta\hat{\mathbf{y}} + x\cos\theta\hat{\mathbf{z}} \tag{9}$$

That is, the wave propagates along the z axis and is polarized in the xy plane (since $\hat{\mathbf{k}}$ and $\hat{\mathbf{n}}$ must be perpendicular). The oscillator lies along the r direction with its displacement from equilibrium given by x.

The operator is

$$\left(\hat{\mathbf{k}}\cdot\mathbf{r}\right)\left(\hat{\mathbf{n}}\cdot\mathbf{r}\right) = x^2\left(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}\right)\left(\hat{\mathbf{n}}\cdot\hat{\mathbf{r}}\right) \tag{10}$$

The oscillator wave functions don't depend on $\left(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}\right)\left(\hat{\mathbf{n}}\cdot\hat{\mathbf{r}}\right)$; they depend only on x, the position of the particle. We can therefore take $\left(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}\right)\left(\hat{\mathbf{n}}\cdot\hat{\mathbf{r}}\right)$ outside the matrix element. We can now average $\left|\left(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}\right)\left(\hat{\mathbf{n}}\cdot\hat{\mathbf{r}}\right)\right|^2$ over all values of θ and ϕ. It might seem that we're changing the direction of $\mathbf{r}$ in doing this which we don't want to do, since we're considering the oscillator to lie in a fixed direction. However, for the purposes of the average, what's important is that we average over propagation and polarization directions *relative* to the direction of the oscillator, and that's what this calculation will do. Also note that for the purposes of the average over the angles, the value of x is a constant; we're freezing the oscillator at one particular position and averaging over propagation and polarization directions of the perturbing radiation. The average over x is done when we calculate the matrix element $\left\langle a\left|\left(\hat{\mathbf{k}}\cdot\mathbf{r}\right)\left(\hat{\mathbf{n}}\cdot\mathbf{r}\right)\right|b\right\rangle$ by integrating over the product of the initial and final wave functions.

The angular average is thus

$$\left|\left(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}\right)\left(\hat{\mathbf{n}}\cdot\hat{\mathbf{r}}\right)\right|^2_{ave} = \frac{1}{4\pi}\int_0^{\pi}\int_0^{2\pi}(\cos\theta)^2(\sin\theta\sin\phi)^2\sin\theta d\phi d\theta \tag{11}$$

$$= \frac{1}{4\pi}\int_0^{\pi}\sin^3\theta\left(1-\sin^2\theta\right)d\theta\int_0^{2\pi}\sin^2\phi d\phi \tag{12}$$

$$= \frac{1}{15} \tag{13}$$

It remains to work out $\left\langle a\left|x^2\right|b\right\rangle$. It's easiest to do this using the raising and lowering operators as we did earlier. In terms of these operators, we have

$$x^2 = \frac{\hbar}{2m\omega_o}\left(a_+^2 + a_+a_- + a_-a_+ + a_-^2\right) \tag{14}$$

Since we're interested in emission, we want only those matrix elements $\left\langle a\left|x^2\right|b\right\rangle$ where state a has a lower energy than state b. The only component of x^2 that will give this is the operator $\frac{\hbar}{2m\omega_o}a_-^2$, which converts a state with energy $\hbar\omega_o\left(n+\frac{1}{2}\right)$ to a state with energy $\hbar\omega_o\left(n-2+\frac{1}{2}\right)$ where ω_o is the frequency of the oscillator. Since $a_-\psi_n = \sqrt{n}\psi_{n-1}$, we get

$$\left\langle n-2\left|x^2\right|n\right\rangle = \frac{\hbar}{2m\omega_o}\sqrt{n(n-1)} \tag{15}$$

The energy of the emitted photon is equal to the energy difference between the two states, so

$$\hbar\omega = \hbar\omega_o\left(n+\frac{1}{2}\right) - \hbar\omega_o\left(n-2+\frac{1}{2}\right) = 2\hbar\omega_o \tag{16}$$

$$\omega_o = \frac{\omega}{2} \tag{17}$$

Putting it all into 6 we get

$$A_f = \frac{q^2\omega^5}{\pi\hbar\epsilon_0 c^5}\left(\frac{1}{15}\right)\left(\frac{\hbar}{m\omega}\sqrt{n(n-1)}\right)^2 \tag{18}$$

$$= \frac{\hbar q^2\omega^3 n(n-1)}{15\pi\epsilon_0 m^2 c^5} \tag{19}$$

$$= \frac{8\hbar q^2\omega_o^3 n(n-1)}{15\pi\epsilon_0 m^2 c^5} \tag{20}$$

The spontaneous emission rate for a one-dimensional oscillator if we ignore $\mathbf{k}\cdot\mathbf{r}$ is given in Griffiths as his equation 9.63:

$$A_a = \frac{nq^2\omega_o^2}{6\pi\epsilon_0 mc^3} \tag{21}$$

so the ratio is

$$\frac{A_f}{A_a} = \frac{16\hbar\omega_o(n-1)}{5mc^2} \tag{22}$$

This ratio is very small if $\hbar\omega_o \ll mc^2$, that is, if the energy of one quantum in the oscillator is much less than its relativistic mass-energy. For this reason, the transitions involving the first-order $\mathbf{k}\cdot\mathbf{r}$ are referred to as *forbidden* transitions, even though they *do* occur, albeit with a much smaller rate.

Example 2. In the hydrogen atom, we found that transition by spontaneous emission between two states, both with $\ell = 0$, is not allowed. What happens if we consider forbidden transitions between, say, the 2S state and the 1S state? For both these states, the hydrogen wave functions are independent of angle, so the matrix element is

$$\left\langle a \left| \left(\hat{\mathbf{k}}\cdot\mathbf{r}\right)\left(\hat{\mathbf{n}}\cdot\mathbf{r}\right) \right| b \right\rangle = \int dr\psi_a^*\psi_b r^2 \int_0^\pi \int_0^{2\pi} \left(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}\right)\left(\hat{\mathbf{n}}\cdot\hat{\mathbf{r}}\right)\sin\theta d\phi d\theta \tag{23}$$

The angular integral comes out to

$$\int_0^\pi \int_0^{2\pi} \left(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}\right)\left(\hat{\mathbf{n}}\cdot\hat{\mathbf{r}}\right)\sin\theta d\phi d\theta = \hat{\mathbf{k}}\cdot\hat{\mathbf{n}} = 0 \tag{24}$$

since the propagation and polarization directions are always perpendicular. Therefore, there are no forbidden transitions between 2S and 1S.