Atomic transitions 6

From the previous section the transition rate is

$$R_{a\to b} = \frac{\pi e^2}{3\varepsilon_0\hbar^2}\left|\langle\psi_b|\mathbf{r}|\psi_a\rangle\right|^2\rho(\omega_0)$$

where $E_b > E_a$ and

$$\omega_0 = \frac{E_b - E_a}{\hbar}$$

Interchange ψ_a and ψ_b by the identity

$$\left|\langle\psi_a|\mathbf{r}|\psi_b\rangle\right|^2 = \left|\langle\psi_b|\mathbf{r}|\psi_a\rangle\right|^2$$

to obtain

$$R_{b\to a} = \frac{\pi e^2}{3\varepsilon_0\hbar^2}\left|\langle\psi_a|\mathbf{r}|\psi_b\rangle\right|^2\rho(\omega_0)$$

By Planck's law

$$\rho(\omega_0) = \frac{\hbar\omega_0^3}{\pi^2 c^3}\frac{1}{\exp\left(\frac{\hbar\omega_0}{kT}\right) - 1}$$

Hence the absorption rate is

$$R_{a\to b} = \frac{e^2\omega_0^3}{3\pi\varepsilon_0\hbar c^3}\left|\langle\psi_b|\mathbf{r}|\psi_a\rangle\right|^2\frac{1}{\exp\left(\frac{\hbar\omega_0}{kT}\right) - 1} \tag{1}$$

and the stimulated emission rate is

$$R_{b\to a} = \frac{e^2\omega_0^3}{3\pi\varepsilon_0\hbar c^3}\left|\langle\psi_a|\mathbf{r}|\psi_b\rangle\right|^2\frac{1}{\exp\left(\frac{\hbar\omega_0}{kT}\right) - 1}$$

The spontaneous emission rate is

$$A_{b\to a} = R_{b\to a}\left[\exp\left(\frac{\hbar\omega_0}{kT}\right) - 1\right] = \frac{e^2\omega_0^3}{3\pi\varepsilon_0\hbar c^3}\left|\langle\psi_a|\mathbf{r}|\psi_b\rangle\right|^2 \tag{2}$$

Verify dimensions.

$$A_{b\to a} \propto \frac{\underset{\mathrm{C}^2}{e^2}\quad\underset{\mathrm{s}^{-3}}{\omega_0^3}}{\underset{\mathrm{C}^2\,\mathrm{J}^{-1}\,\mathrm{m}^{-1}}{\epsilon_0}\quad\underset{\mathrm{J\,s}}{\hbar}\quad\underset{\mathrm{m}^3\,\mathrm{s}^{-3}}{c^3}} \times \underset{\mathrm{m}^2}{\left|\langle\psi_a|\mathbf{r}|\psi_b\rangle\right|^2} = \mathrm{s}^{-1}$$

We will now show why

$$A_{b\to a} = R_{b\to a}\left[\exp\left(\frac{\hbar\omega_0}{kT}\right) - 1\right]$$

Let N_a be the number of atoms in the lower state and let N_b be the number of atoms in the upper state. From thermodynamics

$$\frac{N_a}{N_b} = \exp\left(\frac{\hbar\omega_0}{kT}\right)$$

At thermal equilibrium

$$N_a R_{a\to b} = N_b(A_{b\to a} + R_{b\to a})$$

Hence

$$\frac{N_a}{N_b} = \frac{A_{b\to a} + R_{b\to a}}{R_{a\to b}} = \exp\left(\frac{\hbar\omega_0}{kT}\right)$$

Solve for $A_{b\to a}$.

$$A_{b\to a} = R_{a\to b}\exp\left(\frac{\hbar\omega_0}{kT}\right) - R_{b\to a}$$

Noting that $R_{a\to b} = R_{b\to a}$ we have

$$A_{b\to a} = R_{b\to a}\left[\exp\left(\frac{\hbar\omega_0}{kT}\right) - 1\right]$$