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 b is the upper level and

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

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

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

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

$$\underset{\substack{\text{absorption}\\ \text{rate}}}{R_{a\to b}} = \underset{\substack{\text{stimulated}\\ \text{emission}\\ \text{rate}}}{R_{b\to a}}$$

For the spontaneous emission rate $A_{b\to a}$ we have (more on this in a moment)

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

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

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

Here is Einstein coefficient $B_{b\to a}$ for comparison with "Einstein coefficients" in Wikipedia.

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