

Atomic transitions 6

From the previous section the transition rate is

$$R_{a \rightarrow b} = \frac{\pi e^2}{3\epsilon_0 \hbar^2} |\langle \psi_b | \mathbf{r} | \psi_a \rangle|^2 \rho(\omega_0)$$

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

$$R_{a \rightarrow b} = \frac{e^2 \omega_0^3}{3\pi \epsilon_0 \hbar c^3} |\langle \psi_b | \mathbf{r} | \psi_a \rangle|^2 \frac{1}{\exp\left(\frac{\hbar \omega_0}{kT}\right) - 1} \quad (1)$$

Interchange ψ_a and ψ_b by the identity

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

to obtain

$$\begin{array}{ccc} R_{a \rightarrow b} & = & R_{b \rightarrow a} \\ \text{absorption} & & \text{stimulated} \\ \text{rate} & & \text{emission} \\ & & \text{rate} \end{array}$$

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

$$A_{b \rightarrow a} = R_{b \rightarrow a} \left[\exp\left(\frac{\hbar \omega_0}{kT}\right) - 1 \right] = \frac{e^2 \omega_0^3}{3\pi \epsilon_0 \hbar c^3} |\langle \psi_a | \mathbf{r} | \psi_b \rangle|^2 \quad (2)$$

Verify dimensions.

$$A_{b \rightarrow a} \propto \frac{\frac{e^2}{\text{C}^2} \frac{\omega_0^3}{\text{s}^{-3}}}{\frac{\epsilon_0}{\text{C}^2 \text{J}^{-1} \text{m}^{-1}} \frac{\hbar}{\text{J s}} \frac{c^3}{\text{m}^3 \text{s}^{-3}}} \times \frac{|\langle \psi_a | \mathbf{r} | \psi_b \rangle|^2}{\text{m}^2} = \text{s}^{-1}$$

We will now show why

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

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

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

Hence

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

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

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

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

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

Here is Einstein coefficient $B_{b \rightarrow a}$ for comparison with “Einstein coefficients” in Wikipedia.

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

Eigenmath script