Radiation and Absorption: Einstein A and B coefficients

We start from the atomic single-particle eigenvalues and eigenstates $E_n$ and $|n>$ and do a Golden Rule calculation with the perturbation: (note: $\hat{\epsilon}$ is the polarization of the vector potential.)

\[ V = -\frac{e}{mc}A \cos(k \cdot r - \omega t)\hat{\epsilon} \cdot \vec{p} \]

\[ = U(\vec{k})e^{-i\omega t} + U(-\vec{k})e^{i\omega t} \]

where $U(\vec{k}) = -\frac{eA}{2mc}\hat{\epsilon} \cdot \vec{p} e^{i\vec{k} \cdot \vec{r}}$

1. **Momentum matrix element; dipole matrix element.** Since we will consider transitions involving the photon energy in item 5 we use $E_n - E_m = \pm \hbar\omega$. We start from the commutator $\vec{p} = [H_0, \vec{r}] im/\hbar$. Then in the $\vec{k} \to 0$ limit, (Note: $\vec{p} = (i/2\hbar)[p^2, \vec{r}] = (im/\hbar)[H, \vec{r}]$.)

\[ <n|U(\vec{k} \to 0)|m> = -\frac{eA}{2mc}\frac{im}{\hbar}\hat{\epsilon} \cdot <n|[H_0, \vec{r}]|m> = -i\frac{eA}{2\hbar c}(E_n - E_m) <n|\hat{\epsilon} \cdot \vec{r}|m> \]

where $\vec{p}_{fi} = e <f|\vec{r}|i>$ is the dipole matrix element.

2. **Energy of $N$ mono-energetic photons each with energy $\hbar\omega$ in volume $V$.** We start by noting that $(\vec{E}, \vec{B}) = -(\omega/c)A \sin(k \cdot r - \omega t)(\hat{\epsilon}, \vec{k} \times \hat{\epsilon})$. Then

\[ N\hbar\omega = \int d^3r \frac{\omega}{2\pi} \int_0^{2\pi/\omega} dt \frac{E^2 + B^2}{8\pi} = V\frac{\omega^2 A^2}{8\pi c^2}. \]

3. **Photon density of states $\rho(\hbar\omega)$.**

\[ dN = V \frac{d^3k}{(2\pi)^3} \equiv \rho(\omega)d(\hbar\omega) \]

Hence $\rho(\hbar\omega) = \frac{V \omega^2}{(2\pi c)^3} \frac{d\Omega}{\hbar}$

4. **Einstein’s definition of $\rho_E$.** Since he got there first, Einstein could decide how he wanted to normalize the energy density. He defined $\rho_E$ as the total photon energy per unit volume in the frequency range $\nu$ to $\nu + d\nu$, in other words, he chose frequency and not energy (nor $\omega = 2\pi\nu$) as the scale to measure the density. Integrating over $\Omega$, $\rho_E d\nu \equiv 2(N/V)\hbar\omega \rho(\hbar\omega)d(\hbar\omega)$ where the factor of two results from summing over the two polarizations. Then we have that

\[ \rho_E = N\frac{2\hbar}{\pi} \left(\frac{\omega}{c}\right)^3. \]
5. Absorption rate. To be specific we consider the transition in which a photon of energy $\hbar \omega$ is absorbed by the $m$th level promoting the electron to the $n$th level: $E_n = E_m + h\omega$. Thus

$$w_{f\rightarrow i}^{abs} = \frac{2\pi}{\hbar} \sum_k |<n|U|m>|^2 \delta(E_n - E_m - \hbar\omega)$$

Note: $\sum_k = \int (d(h\omega)\rho(h\omega))$

Using that angular integral give \((8\pi/3)|\hat{\mu}_{fi}|^2\) and that \((A\omega/c)^2 = (8\pi\hbar\omega)(N/V)\)

$$, w_{f\rightarrow i}^{abs} = N \frac{4}{3\hbar} \left( \frac{\omega}{c} \right)^3 |\hat{\mu}_{fi}|^2.$$  

Note that the rate for emission is the same for absorption if we omit the possibility of spontaneous emission – that is, $N \rightarrow N + 1$.

6. Einstein B coefficient. Einstein defined the $B$ coefficient in term of the rate of absorption and the rate of stimulated emission by

$$w_{f\rightarrow i}^{abs} \equiv B_{if} \rho_E \quad \text{and} \quad w_{f\rightarrow i}^{em} \equiv B_{fi} \rho_E.$$  

Since the matrix element is the same in both calculations, $B_{if} = B_{fi}$.

7. Einstein A coefficient. As we already observed at the end of item 5, the spontaneous rate is simply the coefficient of $N$,

$$w_{f\rightarrow i}^{sp.em} \equiv A_{fi} = (4/3\hbar)(\omega/c)^3 |\hat{\mu}_{fi}|^2.$$  

8. Thermal equilibrium and Planck distribution law. In thermal equilibrium of a gas of atoms (say), the rates of emission and absorption must be equal. If $n_f$ and $n_i$ are the densities of atoms in the state $f$ and $i$, respectively, then in thermal equilibrium

$$n_f(A_{fi} + B_{fi} \rho_T) = n_i B_{if} \rho_T.$$  

Here $\rho_T$ is the energy density at finite temperature – that is, the thermal equivalent of $\rho_E$. In equilibrium at temperature $T$, the populations of atoms must be in the ratio given by the Boltzmann distribution $N_f/N_i = \exp(h\omega/k_BT)$. Using this, we can arrange the first equation in this section to yield

$$\rho_T = \frac{A_{fi}}{B_{fi} \exp(h\omega/k_BT) - 1}.$$  

At this stage we can follow two different routes depending on what we claim to know. On the one hand, if we claim to know the that the spontaneous rate is given by $w_{f\rightarrow i}^{abs}/N$, then

$$A_{fi}/B_{fi} = (2\hbar/\pi)(\omega/c)^3$$

and we can conclude that

$$\rho_T = \frac{2\hbar}{\pi} \left( \frac{\omega}{c} \right)^3 \frac{1}{\exp(h\omega/k_BT) - 1}.$$  

which is the famous Planck distribution law. On the other hand, if we claim to know the Planck law, then we can deduce the ratio $A_{if}/B_{if}$. Take your choice.