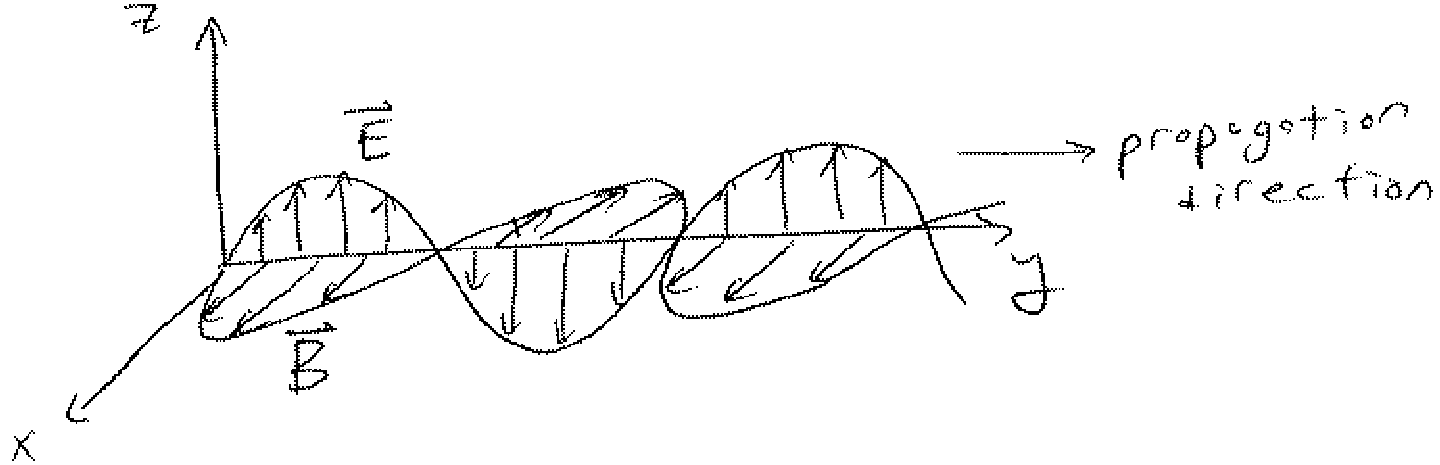
Physics 472 Lecture 21

Emission and Absorption of Radiation

Consider an electromagnetic wave incident on an atom/molecule:



For radiation in the visible range, or at lower frequencies, the wave-length is much greater than the size of an atom, so the spatial dependence of the field can be neglected. Moreover, the interaction of the field with the atom/molecule is typically dominated by the electric field

$$\vec{E} = E_0 \hat{z} \cos(\omega t)$$

$$\Rightarrow \boxed{H_1(t) = -q E_0 z \cos(\omega t)}$$

$$\equiv -q \int \vec{E} \cdot d\vec{r}$$

From our previous result, this leads to transition rates

$$\Gamma_{i \to m} = \frac{\pi}{\hbar} \frac{E_0^2}{2} |q \langle m | z | i \rangle|^2 \delta(E_m - E_i \pm \hbar\omega)$$

This is the result for a plane-polarized electromagnetic wave.

More generally, we would have

$$\vec{E}(t) = \vec{E}_0 \cos(\omega t),$$

$$H_1(t) = -q\, \vec{E}_0 \cdot \vec{r} \cos(\omega t)$$

$$\Gamma_{i \to m} = \frac{\pi}{2\hbar} \left| \langle m | q \vec{E}_0 \cdot \vec{r} | i \rangle \right|^2 \delta(E_m - E_i \pm \hbar\omega).$$

For unpolarized radiation,

$$\overline{E_x^2} = \overline{E_y^2} = \overline{E_z^2} = \frac{1}{3} \overline{\vec{E}^2}$$

$$\Gamma_{i \to m} = \frac{\pi}{6\hbar} \vec{E}_0^2 \left| \langle m | q \vec{r} | i \rangle \right|^2 \delta(E_m - E_i \pm \hbar\omega)$$

Furthermore, the energy density of an electromagnetic wave is

$$\rho = \frac{\vec{E}^2}{4\pi} = \frac{\vec{E}_0^2}{8\pi}$$

In general $\rho = \int_0^\infty \rho(\omega)\, d\omega$.

Integrating over the incident spectrum gives

$$\boxed{\Gamma^{(\pm)}_{i \to m} = \frac{4\pi^2}{3\hbar^2} \rho\left(\omega = \frac{E_m - E_i}{\hbar}\right) \vec{\wp}_{mi}^{\,2},}$$

where

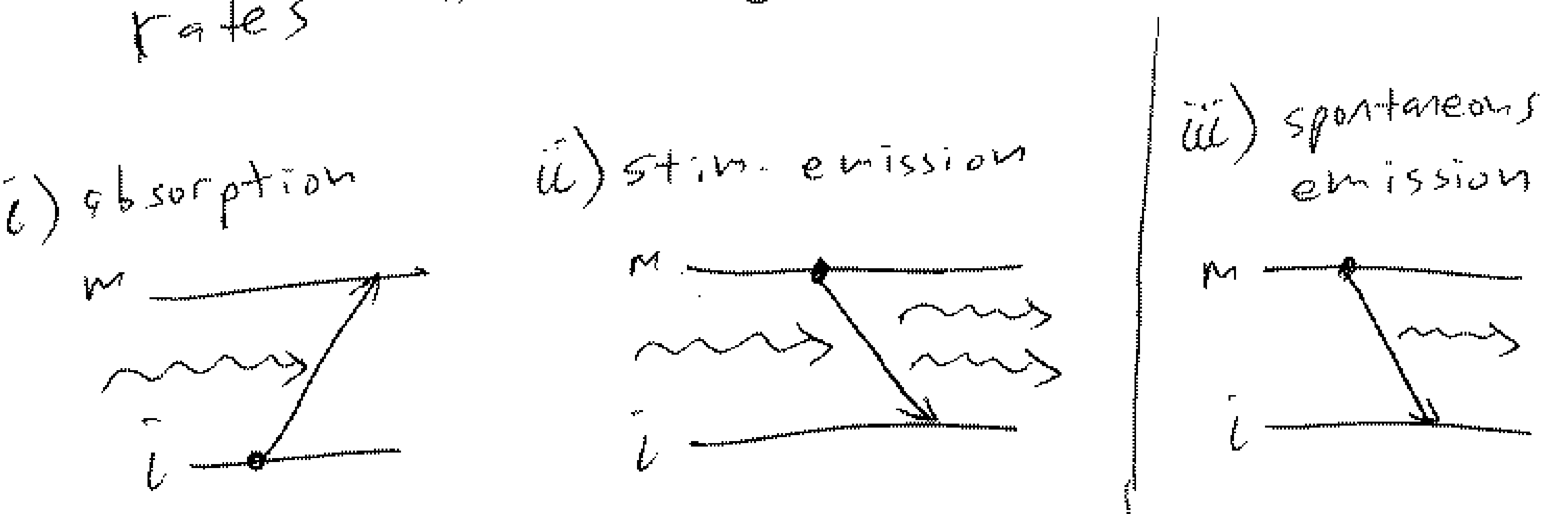
$$\vec{\wp}_{mi} = q \langle m | \vec{r} | i \rangle \text{ is}$$

the electric-dipole matrix element.

Spontaneous emission

So far, we have treated the atom (electron) quantum mechanically, but we have treated the electromagnetic field classically.

Thus we have found two processes, i) absorption and ii) stimulated emission, whose rates are equal:



If we include the quantum fluctuations

of the electromagnetic field, another process will also appear —

iii) Spontaneous emission, which can be thought of as emission stimulated by vacuum fluctuations. To treat this process from first principles would require quantum electrodynamics, which is outside the scope of this course. However, there is a thermodynamic argument due to Einstein that gives the correct result, so we will use that!

Einstein's A and B coefficients

Consider an ensemble of two-level atoms:

E_2 ——— $N_2(t)$

E_1 ——— $N_1(t)$

$E_2 - E_1 = \hbar\omega$

$\rho(\omega)$ = Energy density per frequency of EM field

$B_{12}\,\rho(\omega)$ is the probability per second for photon absorption

$B_{21}\,\rho(\omega)$ is the probability per second for stimulated emission

A_{21} is the probability per second for spontaneous emission

$$\frac{dN_1}{dt} = \left[A_{21} + B_{21}\rho(\omega)\right]N_2 - B_{12}\rho(\omega)N_1$$

$$\frac{dN_2}{dt} = B_{12}\rho(\omega)N_1 - \left[A_{21} + B_{21}\rho(\omega)\right]N_2$$

In equilibrium, $\dot{N}_1 = \dot{N}_2 = 0$.

$$\Rightarrow \quad \frac{N_1}{N_2} = \frac{A_{21} + B_{21}\rho(\omega)}{B_{12}\rho(\omega)}$$

On the other hand Boltzmann tell's us

$$\frac{N_1}{N_2} = \frac{e^{-E_1/k_BT}}{e^{-E_2/k_BT}} = e^{\hbar\omega/k_BT},$$

where T is the temperature.

Then

$$B_{12}\,\rho(\omega)\,e^{\hbar\omega/k_B T} = A_{21} + B_{21}\,\rho(\omega)$$

or

$$\rho(\omega) = \frac{A_{21}}{B_{12}\,e^{\hbar\omega/k_B T} - B_{21}}$$

On the other hand, we know that $\rho(\omega)$ is the Planck (black body) distribution

$$\rho(\omega) = \frac{\hbar}{\pi^2 c^3}\,\frac{\omega^3}{e^{\hbar\omega/k_B T} - 1}$$

This implies

$$B_{21} = B_{12} \quad \text{and} \quad \frac{A_{21}}{B_{12}} = \frac{\hbar\omega^3}{\pi^2 c^3}.$$

we have already calculated

$B_{12} = B_{21}$:

$$\Gamma_{12} \equiv B_{12}\rho(\omega) = \frac{4\pi^2}{3\hbar^2} \vec{\wp}_{12}^{\,2} \rho(\omega)$$

$$\Gamma_{21} \equiv B_{21}\rho(\omega) = \frac{4\pi^2}{3\hbar^2} \vec{\wp}_{12}^{\,2} \rho(\omega)$$

Thus

$$A_{21} = \frac{\hbar\omega^3}{\pi^2 c^3} B_{12} = \frac{4\omega^3 \vec{\wp}_{12}^{\,2}}{3\hbar c^3}$$

is the rate of <u>spontaneous emission</u>.