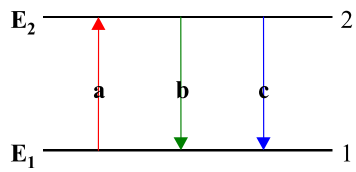
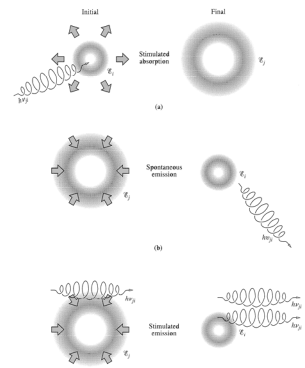
Absorption & Stimulated Emission



a *absorption*

b *spontaneous emission*

c *stimulated emission*

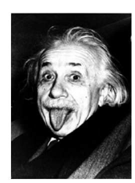


$$\frac{dN_1}{dt} = N_1 B_{12}\rho(\nu) \qquad \textit{Absorption}$$

$$\frac{dN_2}{dt} = N_2 B_{21}\rho(\upsilon) \qquad \textit{Stimulated emission}$$

$$\frac{dN_2}{dt} = N_2 A_{21} \qquad \textit{Spontaneous emission}$$

Einstein approach



Recall;

$$-\frac{dN_2}{dt} = W_{21}N_2 + A_{21}N_2 = B_{21}\rho(\nu)N_2 + A_{21}N_2$$

$$-\frac{dN_1}{dt} = W_{12}N_1 = B_{12}\rho(\nu)N_1$$

At thermal equilibrium; $dN_2/dt = dN_1/dt$

$$\therefore\ [B_{21}\rho(\nu) + A_{21}]N_2^e = B_{12}\rho(\nu)N_1^e \quad ; \quad \frac{N_2^e}{N_1^e} = e^{-h\nu/kT}$$

$$\Rightarrow \qquad \rho(\nu) = \frac{N_2A_{21}}{N_1B_{12} - N_2B_{21}} = \frac{A_{21}/B_{21}}{\left(\frac{N_1}{N_2}\right)\frac{B_{12}}{B_{21}} - 1}$$

$$\boxed{\rho(\nu) = \frac{A_{21}/B_{21}}{\frac{B_{12}}{B_{21}}e^{h\nu/kT} - 1}}$$

Compare this expression with the Planck blackbody radiation law;

$$\rho(\nu) = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1}$$

We get ;

$$B_{12} = B_{21}$$
$$\frac{A_{21}}{B_{21}} = \frac{8\pi\, hn^3 \nu^3}{c^3}$$

These results are due to Einstein (1917) so *A* and *B* are called *the Einstein coefficients*

Notes:

- **$B_{21} = B_{12}$ so the stimulated absorption & emission rates per atom are equal – as expected from the form of the electric dipole transition matrix element. (This can be obtained by demanding $\rho(\nu) \rightarrow \infty$ as $T \rightarrow \infty$)**
- **$A_{21}/B_{21} \propto \nu^3$, so *the spontaneous emission rate increases as the cube of the energy* $h\nu$. (R-J law at high temp. limit)**
- **The ratio of probabilities of spontaneous to stimulated emission is $\frac{A_{21}}{B_{21}\rho(\nu)} = \frac{1}{e^{h\nu/kT} - 1}$**
- **so if $h\nu >> kT$ spontaneous emission is much more likely than stimulated emission. But if $h\nu << kT$ then stimulated emission is much more likely – this is the secret of the *maser,* which is *microwave amplification by stimulated emission of radiation*.**

If we know B, we can get A and τ_{sp}=1/A

How do we relate Einstein coefficients to atomic parameters?

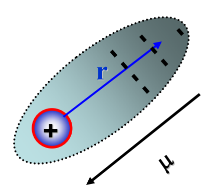
➡ ***We need Q.M.***

ELECTRIC DIPOLE MOMENT

In what way, light (quanta) and atoms interact?

Predominantly through electric dipole orientation in field

$$H'(r,t) = e\vec{r}.\vec{E}(\vec{r},t) \equiv -\vec{\mu}.\vec{E}(r,t)$$
$$= \vec{\mu}.\vec{E}_o \sin \omega t$$



$$H_{21}^{'o} = \vec{E}_o.\vec{\mu}_{21} \quad , \quad \vec{\mu}_{21} = -e\int u_2^*(r)\,\vec{r}\,u_1(r)dV$$

The electric dipole matrix element μ_{21} may be evaluated once the wave function of the atoms are known

Parity Selection Rule

Atom has spherical symmetry; $H_0(\vec{r}) = H_0(-\vec{r})$

The eigen-function (wave function) would be either symmetric or anti-symmetric, we say the eigen-function has a well-defined parity.

One dimensional example;

$$\mu_{21} = -e\int u_2(x)\, x\, u_1(x)dx = 0$$

If u_1 and u_2 have the same parity either both ODD or both EVEN

$$u_n(\vec{r}) = u_n(-\vec{r}) \qquad \Rightarrow \text{even parity}$$

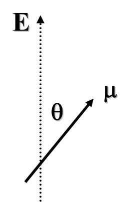
$$u_n(\vec{r}) = -u_n(-\vec{r}) \qquad \Rightarrow \text{odd parity}$$

$$\mu_{21} = -e\int u_2(x)\, x\, u_1(x)dx \neq 0$$

If u_1 and u_2 have different parity

Thus , electric dipole transitions only occur between states of opposite parity, e.g. (1s)→(2p)

Lets calculate W_{12}



$$W_{12} = \frac{\pi\left|H_{21}^{'o}\right|^2}{2\hbar^2}\delta(\Delta\omega)$$

$$\left|H_{21}^{'o}\right|^2 = \left|E_0 \cdot \mu_{21}\right|^2 = E_o^{\,2}\left|\mu_{21}\right|^2 \cos^2\theta$$

where θ is the angle between $\vec{E}_o$ and $\vec{\mu}$

For randomly oriented atoms, the average $\left|H_{21}^{'o}\right|^2$ **is**

$$\left\langle \left|H_{21}^{'o}\right|^2 \right\rangle = E_o^{\,2}\left|\mu_{21}\right|^2 \left\langle \cos^2\theta \right\rangle$$

We average $\cos^2\theta$ from $0 \le \theta \le \pi$

$$\left\langle \cos^2\theta \right\rangle = \frac{1}{4\pi}\int \cos^2\theta\, d\Omega = \frac{1}{4\pi}\int_0^{\pi}\int_0^{2\pi} \cos^2\theta \sin\theta\, d\theta\, d\varphi = \frac{1}{3}$$

$$\left\langle \left|H_{21}^{'o}\right|^2 \right\rangle = E_o^{\,2}\left|\mu_{21}\right|^2 \left\langle \cos^2\theta \right\rangle = \frac{1}{3}E_o^{\,2}\left|\mu_{21}\right|^2$$

Induced transition rate

$$W_{12} = \frac{\pi}{6}\frac{E_o^{\,2}|\mu_{21}|^2}{\hbar^2}\delta(\Delta\omega)$$

$$\because \quad I = \frac{n\varepsilon_0 c_0}{2}E_0^2$$

$$I = \frac{c}{n}\rho$$

$$\therefore \quad W_{12} = \frac{\pi}{3n^2\varepsilon_0 c_0\hbar^2}|\mu_{21}|^2 I\,\delta(\Delta\omega) = \frac{\pi}{3n^2\varepsilon_0\hbar^2}|\mu_{21}|^2\rho\,\delta(\Delta\omega) = W_{21}$$

$$since \quad \mu_{12} = \mu_{21}^* \quad \Rightarrow \quad |\mu_{12}| = |\mu_{21}|$$

Or;

$$W_{12} = \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{21}|^2\rho\,\delta(\Delta\nu)$$

The presence of $\delta(\nu-\nu_o)$ implies the atomic system would not respond to off resonance $(\nu \neq \nu_o)$ radiation, which is of course not realistic.

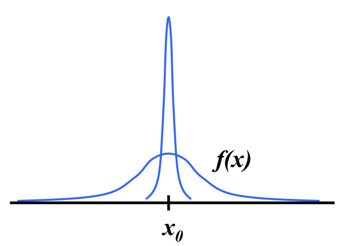
Einstein coefficients

If the radiation is not monochromatic, but due to blackbody
We can replace ρ by $\rho_\omega d\omega$ and integrate over dω. We get;

$$W = \frac{\pi}{3n^2\varepsilon_0\hbar^2}|\mu|^2\int_0^\infty \rho_\omega\,\delta(\omega-\omega_0)\,d\omega \qquad using \quad \int_0^\infty f(x)\delta(x-x_0) = f(x_0)$$

$$= \frac{\pi}{3n^2\varepsilon_0\hbar^2}|\mu|^2\rho_{\omega_0} \equiv B\rho_{\omega_0}$$

$$\therefore B = \frac{2\pi^2}{3n^2\varepsilon_o h^2}|\mu|^2$$



$$\because \frac{A}{B} = \frac{8\pi h\nu_o^{\,3}n^3}{c^3}$$

$$A = \frac{1}{\tau_{sp}} = \frac{16\pi^3\nu_o^{\,3}n|\mu|^2}{3h\varepsilon_o c^3}$$

Numerical

$$A = \frac{16\pi^3 \nu_o^{\,3} n |\mu|^2}{3h\varepsilon_o c^3} \approx 2.83\times 10^{46}\,\frac{|\mu|^2}{\lambda^3} = \frac{1}{\tau_{sp}}$$

We took $n \approx 1$, let $\lambda = 500$ nm and $\mu = e\,a = (1.6\times10^{-19})\,(10^{-10}) = 1.6\times10^{-29}$ C.m
Where a is the radius of atom.

$A = 5.8\times10^{7}\ sec^{-1}$ ➡ $\tau_{sp} = 1.72\times10^{-8}$ sec

Transition rates; ***monochromatic radiation and atomic collision***

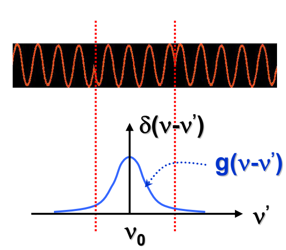
If an atom is permitted to interact with sinusoidal wave for a long time ($t \rightarrow \infty$), $W \propto \delta(\Delta\nu)$. In practice, an atom will change state by emission (spontaneous) or by collision with other atoms before $t \rightarrow \infty$. The sinusoidal wave would look quite different (which phase interrupted).

The monochromatic radiation becomes a narrow band radiation with a spectral distribution.

$$I_{\nu'}\, d\nu' = I\, g(\nu - \nu')\, d\nu'$$

Where $g(\nu-\nu')$ is the <u>normalized line shape function</u>;

$$\int_{-\infty}^{\infty} g(\nu - \nu')\, d\nu' = 1$$



The detailed functional shape of $g(\nu-\nu')$ <u>depends on the nature of collision process</u>.

For finite t, the system will respond to off resonance radiation.

Since any atomic system must decay one way or another (radiative, non-radiative, etc…) one must replace δ by line-shape functions which provide for finite response for off-resonance radiation.

So, $\delta(\nu-\nu_o)=g(\nu-\nu_o)$

$$\therefore \quad W_{12}=\frac{2\pi^2}{3n^2\varepsilon_o h^2}|\mu_{21}|^2\int Ig(\nu-\nu')\delta(\nu'-\nu_0)d\nu'$$

$$=\frac{2\pi^2}{3n\varepsilon_o c_0 h^2}|\mu_{21}|^2 I\, g(\Delta\nu) \qquad ; \qquad \Delta\nu=\nu-\nu_0$$

$$=\frac{2\pi^2}{3n^2\varepsilon_o h^2}|\mu_{21}|^2 \rho\, g(\Delta\nu)$$

$$since \quad \mu_{12}=\mu_{21}^* \quad \Rightarrow \quad |\mu_{12}|=|\mu_{21}|$$

$$\therefore \quad W_{12}=\frac{2\pi^2}{3n^2\varepsilon_o h^2}|\mu_{21}|^2 \rho\, g(\Delta\nu)=W_{21}$$

We can also write W in terms of spectral coefficient B, i.e. B_ν (Einstein coefficient per unit freq).

$$W=\frac{2\pi^2}{3n^2\varepsilon_o h^2}|\mu|^2 \rho\, g(\Delta\nu)\equiv B_\nu\,\rho$$

$$\therefore B_\nu=\frac{2\pi^2}{3n^2\varepsilon_o h^2}|\mu|^2 g(\Delta\nu)=B\,g(\Delta\nu)$$

Consider thermal equilibrium in every spectral range , we have;

$$\frac{A_\nu}{B_\nu}=\frac{A}{B}=\frac{8\pi h\nu^3 n^3}{c_0^3}$$

$$\Rightarrow \quad A_\nu=A\,g(\Delta\nu) \qquad , \qquad B_\nu=B\,g(\Delta\nu)$$

$$\int_0^\infty A_\nu d\nu=A\int_0^\infty g(\Delta\nu)d\nu=A$$

Therefore $g(\Delta\nu)$ is the spectrum of (spontaneously) radiated wave, and of the absorption and stimulated emission as well (for simple two-level system).

$g(\Delta\nu)d\nu$ gives the probability that spontaneously emitted photons has a frequency lying between ν and $\nu+d\nu$

Cause of Spontaneous Emission

Remember , Planck has to treat the normal modes of the cavity quantum mechanically, i.e. quantizing radiation as well. The allowed energy of a mode then behaves as a harmonic oscillator;

- **The energy cannot change continuously, but rather change by jumps of $h\nu$.**
- **The lowest energy level is not 0 but ($h\nu/2$). This energy ($h\nu/2$), which is the energy possessed by the mode at T=0 K, is called zero-point energy. Or , zero-point fluctuation energy.**

It is this zero-point energy that stimulates the spontaneous emission of atoms.

The full quantum theory will show that the radiation life time of the upper state τ_{sp} is same as the A derived by Einstein-Planck.

$$A = \frac{16\pi^3 \nu_o^3 n|\mu|^2}{3h\varepsilon_o c^3} = \frac{1}{\tau_{sp}}$$