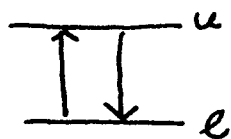


I. The Absorption and Emission of Radiation (spectroscopy)



Bohr spectral condition for atoms, molecules

$$\Delta E = E_u - E_e = h\nu = \frac{hc}{\lambda} = \hbar\omega$$

quantized levels

whether absorption or emission.

Contrast resonant processes vs non-resonant processes (e.g. scattering)

More detailed quantum mechanical treatments:

- a) semi-classical theory (classical radiation)
- b) fully quantum theory (quantized radiation)

Schrodinger equation (time-dependent)

$$\hat{H} \Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t}$$

$$\hat{H} = \underbrace{\hat{H}_0}_{\text{isolated system}} + \hat{H}'(t)$$

interaction with radiation

$$\hat{H}' = 0 \text{ solutions } \Psi_n(x,t) = e^{-iE_n t/\hbar} \Psi_n(x)$$

$$\text{where } \hat{H}_0 \Psi_n(x) = E_n \Psi_n(x)$$

Now turn on field: try $\Psi(x,t) = \sum_n c_n(t) \Psi_n(x,t)$

$$\sim \Psi(x,t) = \sum_n c_n(t) e^{-iE_n t/\hbar} \Psi_n(x)$$

Initial condition:

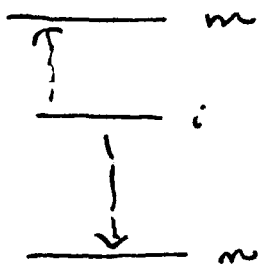
$$c_i(0) = 1$$

$$|c_n(t)|^2$$

prob of finding system in n.

Exact solution: two-level problem (Burneth)

Perturbative solution: may other levels $m \neq i$



$$P_{m \leftarrow i} = |c_m(t)|^2 \quad R_{m \leftarrow i}(t) = \frac{d}{dt} P_{m \leftarrow i}(t)$$

Answer depends on form of \mathcal{H}' .

$$\mathcal{H}'(t) = -\vec{\mu} \cdot \vec{E} - \vec{\mu}_m \cdot \vec{B} - \frac{1}{6} \vec{Q} : \vec{\nabla} \vec{E} + \dots$$

\vec{E} \vec{B} \rightarrow

$\vec{\mu} \cdot \vec{E}$: electric dipole
 $\vec{\mu}_m \cdot \vec{B}$: magnetic dipole
 $\vec{Q} : \vec{\nabla} \vec{E}$: electric quadrupole

dominant unless $\omega \rightarrow \infty$

Notation $(X)_{mi} = \int_{-\infty}^{\infty} \psi_m^* \hat{X} \psi_i d\tau \equiv \langle \psi_m | X | \psi_i \rangle = \langle m | X | i \rangle$

$\vec{\mu} = \sum_{\mu=eR} e_i \vec{R}_i$ $\vec{E} = \vec{E}^0 \cos \omega t$ ignore spative dimension $r \gg \text{size}$
 $\omega = 2\pi\nu$

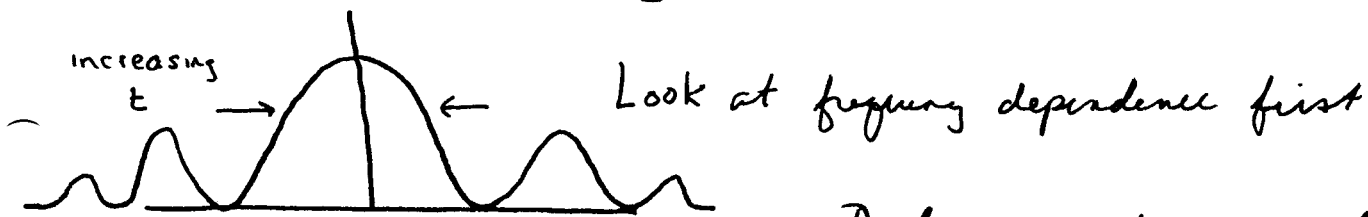
Let $\vec{E} = E_x \hat{i}$

$E_m > E_i$ $\omega_{mi} = (E_m - E_i) / \hbar > 0$ $\nu_{mi} = \frac{E_m - E_i}{h}$
 "resonant frequency"

$$P_{m \leftarrow i} = \frac{|\langle \mu_x \rangle_{mi}|^2 E_x^0{}^2}{\hbar^2} \frac{\sin^2 \left[\frac{(\omega - \omega_{mi}) t}{2} \right]}{(\omega - \omega_{mi})^2}$$

$\hbar = h/2\pi$

$\omega = 2\pi\nu$



peak at resonance \Rightarrow Bohr spectral condition

$\omega - \omega_{mi} \rightarrow$ one m picked out

$$\omega \rightarrow \omega_{mi} \quad P_{m \leftarrow i} \rightarrow \frac{|\langle \mu_x \rangle_{mi}|^2 E_x^0{}^2 t^2}{\hbar^2} \frac{t^2}{4}$$

$\sin^2 x \rightarrow x^2$

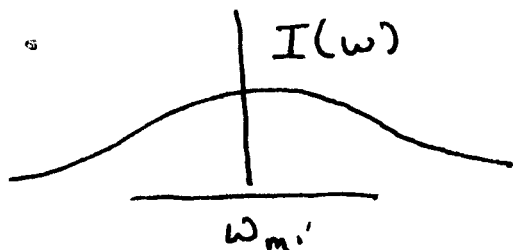
weird time dependence! $P_{m \leftarrow i} \propto t$

$$\left\{ \begin{array}{l} \text{exact 2-state solution: } P_{m \leftarrow i} = \sin^2 \frac{\omega_R t}{2} \\ \omega_R = \langle \mu_x \rangle_{mi} E_x^0 / \hbar \end{array} \right\}$$

Rabi frequency



Situation returns to normal if a range of radiation frequencies is used around ω_{mi} .



We can use $E(\omega) d\omega$ to specify intensity but it is more common to use the energy density distribution

$$I(\omega) \equiv c p(\nu) / 4\pi \quad \frac{\text{erg}}{\text{cm}^2 \cdot \text{s} \cdot \text{ster.}} \quad p(\nu) d\nu = p(\omega) d\omega = \frac{\text{energy}}{\text{Volume}} \quad \begin{matrix} \nu, \nu+d\nu \\ \omega, \omega+d\omega \end{matrix}$$

$$(p = \epsilon_0 E^2 / 2 \text{ mks})$$

$$\text{erg/cm}^3 \text{ s}^{-1}$$

$$P_{m \leftarrow i} = \left\{ \begin{array}{ll} \frac{2\pi}{3\hbar^2} p(\nu_{mi}) |\langle \mu \rangle_{mi}|^2 t & \text{cgs} \\ \frac{1}{6\epsilon_0 \hbar^2} p(\nu_{mi}) |\langle \mu \rangle_{mi}|^2 t & \text{mks} \end{array} \right\}$$

(unitless)

$\text{joule/m}^3 \text{ s}^{-1}$

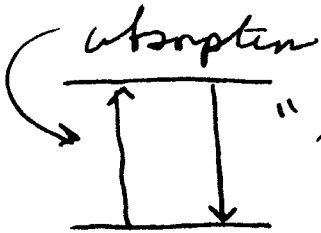
where we have assumed isotropic radiation
 $(E_x^0 = E_y^0 = E_z^0)$

$$|\langle \mu \rangle_{mi}|^2 = |\langle \mu_x \rangle_{mi}|^2 + |\langle \mu_y \rangle_{mi}|^2 + |\langle \mu_z \rangle_{mi}|^2$$

$\therefore R_{mi}$ is now time-independent

Notational Change

analysis works for absorption + emission



$$R_{u \leftarrow l} = R_{u \rightarrow l} = \frac{2\pi}{3\hbar^2} \rho(\nu_{ul}) \times |\langle \mu \rangle_{ul}|^2$$

(s⁻¹)

(equality holds for non-degenerate levels)

"transition dipole" independent of direction

Dipole Transitions E1

occur if $|\langle \mu \rangle_{ul}| \neq 0 \Rightarrow$ "selection rules"

Otherwise, probability of transition = 0 even at resonance.

We speak of "strong" or "dipole-allowed" transitions

Examples:

1) $O \text{---} \mu \text{---} O$ 1-D harmonic oscillator $E_n = h\nu(n + 1/2)$ $n = 0, 1, 2, \dots$
 $\mu = e(x - x_0)$ $\Delta n = n_u - n_l = 1 (\pm 1)$

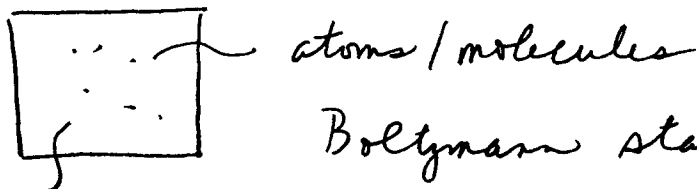
2) $O \text{---} O$ rigid rotor $E_J = hB J(J+1)$ $J = 0, 1, \dots$
 permanent moment μ $\Delta J = J_u - J_l = 1 (\pm 1)$

If $|\langle \mu \rangle_{ul}| = 0$, investigate higher-order effects.

According to QM, there are only 2 processes: absorption + stimulated emission. We will now see that basic QM misses a 3rd process: spontaneous emission!

II. Einstein A & B Coefficients

Ten years or so before quantum mechanics came on the scene, Einstein realized that there had to be another type of emission - called spontaneous emission - that is independent of any incident radiation field. Let us follow his reasoning.



Boltzmann statistics:

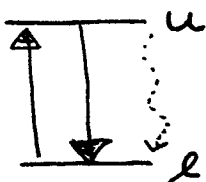
temperature T

$$P(E_n) = \frac{g_n e^{-E_n/kT}}{\sum_n g_n e^{-E_n/kT}} = \frac{1}{q}$$

degeneracy \rightarrow "partition function"

$P(E_n)$: prob. of finding any atom with energy E_n .

Let us consider two levels with no degeneracy:



At low densities, the populations in the two levels are determined by absorption & stimulated emission of radiation:

Still, Boltzmann tells us that $P(E_e) = \frac{e^{-E_e/kT}}{q}$

$$P(E_u) = \frac{e^{-E_u/kT}}{q}$$

$$\frac{n(E_u)}{n(E_e)} = e^{-(E_u - E_e)/kT} < 1$$

\rightarrow no. density (cm^{-3}) $E_u > E_e$

But, we now show that since $R_{u \rightarrow e} = R_{e \rightarrow u}$, a contradiction results:

$$\frac{dn_u}{dt} = R_{e \rightarrow u} n_e - R_{u \rightarrow e} n_u = 0 \text{ at equilibrium.}$$

$$\therefore n_u/n_e = \frac{R_{e \rightarrow u}}{R_{u \rightarrow e}} = 1 \text{ contradicts Boltzmann statistics}$$

To remove this contradiction, Einstein postulated the process of spontaneous emission.

Let's now look at all 3 processes, using Einstein's notation:

A. Non-degenerate case

— u Absorption Rate = $R_{u \leftarrow e} n_e \equiv B_{u \leftarrow e} p(\nu_{ue}) n_e$
 ($\text{cm}^{-3} \text{s}^{-1}$)

— e $B_{u \leftarrow e} = \frac{2\pi}{3h^2} | \langle \mu \rangle_{ue} |^2 \quad \text{cgs}$

Stimulated Emission Rate = $R_{u \rightarrow e} n_u \equiv B_{u \rightarrow e} p(\nu_{ue}) n_u$

$R_{u \leftarrow e} = R_{u \rightarrow e} \Rightarrow B_{u \rightarrow e} = B_{u \leftarrow e}$ { equality follows from derivation }

Now define spontaneous emission rate: $A_{u \rightarrow e} n_u$
 (no field dependence)

$\frac{dn_u}{dt} = B_{u \leftarrow e} p(\nu_{ue}) n_e - B_{u \rightarrow e} p(\nu_{ue}) n_u - A_{u \rightarrow e} n_u$

At equilibrium: $\frac{dn_u}{dt} = 0 \Rightarrow B_{u \leftarrow e} p(\nu_{ue}) n_e = B_{u \rightarrow e} p(\nu_{ue}) n_u + A_{u \rightarrow e} n_u$

$\frac{n_u}{n_e} = \frac{B_{u \leftarrow e} p(\nu_{ue})}{B_{u \rightarrow e} p(\nu_{ue}) + A_{u \rightarrow e}} \equiv e^{-h\nu_{ue}/kT}$
 arrows unnecessary Boltzmann statistics

Solve for $p(\nu_{ue})$: $B_{u \leftarrow e} p(\nu_{ue}) = [B_{u \rightarrow e} p(\nu_{ue}) + A_{u \rightarrow e}] e^{-h\nu_{ue}/kT}$

$p(\nu_{ue}) [B_{u \leftarrow e} - B_{u \rightarrow e} e^{-h\nu_{ue}/kT}] = A_{u \rightarrow e} e^{-h\nu_{ue}/kT}$

$p(\nu_{ue}) = \frac{A_{u \rightarrow e}}{(B_{u \leftarrow e} e^{h\nu_{ue}/kT} - B_{u \rightarrow e})}$

At complete thermal equilibrium, the atoms are in equilibrium with the radiation field, which is called "thermal radiation" and designated $P_T(\nu)$ in energy density terms.

In 1900, Planck derived a formula for $P_T(\nu)$, now known as the black body formula. This formula is approximated by certain solids + high density gases.

Laboratory Realization

black \rightarrow \boxed{T} \rightarrow $I_T(\nu) d\nu = \frac{c}{4} P_T(\nu) d\nu$

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

For consistency:

$$p(\nu_{ue}) = \frac{A_{ue}}{B_{ue} e^{h\nu_{ue}/kT} - B_{u \rightarrow e}} = \frac{8\pi h \nu_{ue}^3}{c^3} \times \frac{1}{e^{h\nu_{ue}/kT} - 1}$$

$$\Rightarrow 1) B_{ue} = B_{u \rightarrow e} \quad (\text{true, according to QM})$$

$$2) \frac{A_{ue}}{B_{ue}} = \frac{8\pi h \nu_{ue}^3}{c^3}$$

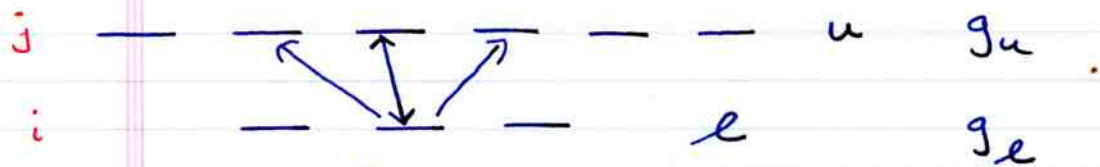
Now, if we use our quantum mechanical expression for B_{ue} :

$$B_{ue} = \frac{2\pi}{3\hbar^2} |\mu_{ue}|^2, \quad \text{we obtain}$$

$$A_{ue} (s^{-1}) = \frac{8\pi h \nu_{ue}^3}{c^3} B_{ue} = \frac{32\pi^3 \nu_{ue}^3}{3\hbar c^3} |\mu_{ue}|^2$$

$$= \frac{4\omega_{ue}^3}{3\hbar c^3} |\mu_{ue}|^2 \quad \left[\frac{\omega_{ue}}{3\pi \epsilon_0 \hbar c^3} |\mu_{ue}|^2; \text{ mks} \right]$$

Degenerate Case



$|\langle \mu \rangle_{ujl}|^2$ independent of direction S_{ue} "strength"

Define $|\langle \mu \rangle_{u \leftarrow l}|^2 \equiv \frac{1}{g_l} \sum_j \sum_i |\langle \mu \rangle_{ujl}|^2$

"transition dipole"

average for lower states

[given system in one of lower states]

$$|\langle \mu \rangle_{u \rightarrow l}|^2 = \frac{1}{g_u} \sum_j \sum_i |\langle \mu \rangle_{ujl}|^2$$

average for upper states

$$S_{ue} = g_l |\langle \mu \rangle_{u \leftarrow l}|^2 = g_u |\langle \mu \rangle_{u \rightarrow l}|^2 \text{ not equal}$$

$$g_l B_{u \leftarrow l} = g_u B_{u \rightarrow l}$$

Similar derivation leads to

$$\frac{A_{ue}}{B_{u \rightarrow l}} = 8\pi h \nu_{ue}^3 / c^3$$

$$A_{ue} = \frac{32\pi^3 \nu_{ue}^3}{3hc^3} |\langle \mu \rangle_{u \rightarrow l}|^2 \text{ for an average state in } u \text{ manifold}$$

Although Einstein used the special case of thermal equilibrium, we now know from QED that the result is true for most situations. We will consider the result to be general.