2.1 - 2.3

3. Semiclassical atom-radiation interaction

Treat atom quantum-mechanically
light classically.

Wavefunction for all Z electrons

$$\Psi(\underbrace{\vec{r}_1, \vec{r}_2, \dots, \vec{r}_Z}_{\vec{r}}, t)$$

shorthand notation

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

In general, $\hat{H}$ can be time-dependent.

First consider $\hat{H} = \hat{H}_A$ just atom, no light
(time independent)

Solutions: stationary states

$$\Psi(\vec{r},t) = \psi_i(\vec{r})\, e^{-iE_i t/\hbar}$$

$$\hat{H}_A \psi_i = E_i \psi_i$$

capital Ψ time-dependent
small ψ eigenstates

Dirac notation: $\hat{H}_A |i\rangle = E_i |i\rangle$

Consider two levels

$|2\rangle$ ——— E_2

$|1\rangle$ ——— E_1

$E_2 - E_1 = \hbar\omega_0$ def.

Light hits the atom

$$\vec{E}(\vec{r},t) = \vec{E}_0 \cos(\vec{k}\cdot\vec{r} - \omega t) \quad \text{(running wave)}$$

3-2 Now the Hamiltonian is

$$\hat{H} = \hat{H}_A + \hat{H}_I$$

interaction Hamiltonian - time-dependent

Write the general state as

$$\Psi(\vec{r},t) = C_1(t)\,\Psi_1(\vec{r},t) + C_2(t)\,\Psi_2(\vec{r},t)$$

Normalization $\Rightarrow$ $|C_1(t)|^2 + |C_2(t)|^2 = 1$

at all times t

Insert into Schrödinger eq

$$(\hat{H}_A + \hat{H}_I)(C_1\Psi_1 + C_2\Psi_2) = i\hbar\frac{\partial}{\partial t}(C_1\Psi_1 + C_2\Psi_2)$$

$$C_1\hat{H}_I\Psi_1 + C_2\hat{H}_I\Psi_2 = i\hbar\Psi_1\frac{\partial C_1}{\partial t} + i\hbar\Psi_2\frac{\partial C_2}{\partial t}$$

Multiply from left by Ψ_1^* and integrate

[or Dirac notation: $\langle 1|e^{iE_1t/\hbar}$ from left]

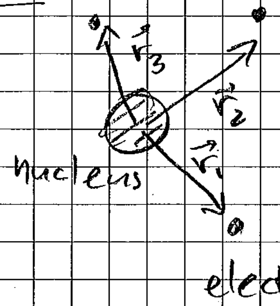
& use $\int \Psi_1^*\Psi_2 = \langle 1|2\rangle = 0$

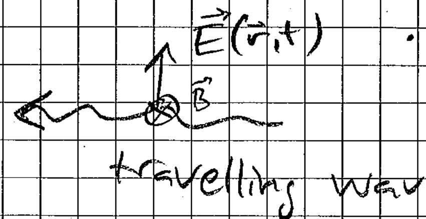
$$\boxed{\begin{aligned} &C_1\langle 1|\hat{H}_I|1\rangle + C_2\underbrace{e^{it(E_1-E_2)/\hbar}}_{=e^{i\omega_0 t}}\langle 1|\hat{H}_I|2\rangle = i\hbar\frac{\partial C_1}{\partial t} \\ &C_2\langle 2|\hat{H}_I|2\rangle + C_1 e^{-i\omega_0 t}\langle 2|\hat{H}_I|1\rangle = i\hbar\frac{\partial C_2}{\partial t}\end{aligned}}$$

Can in principle be solved if we know ψ_1, ψ_2, $\hat{H}_I$

Form of the semi-classical interaction Hamiltonian

Atom:





$$\vec{E}(\vec{r},t) = \vec{E}_0 \cos(kz-\omega t) \qquad \vec{B} = \vec{B}_0 \cos(kz-\omega t)$$

Assume $\vec{E}_0 = E_0 \vec{e}_x$

But $\langle |\vec{r}_i| \rangle \approx a_B \approx 0{,}5\,\mathring{A}$ Bohr radius

for all electrons

$a_B \ll \lambda_{light}$

so we can put $z=0$ in expression for $\vec{E}$

Energy of electrons in field is

$$\mathcal{E} \approx \mathcal{E}_{ED} = e\vec{D}\cdot\vec{E}(\vec{r},t)$$

electric dipole approx.

where

$-e\vec{D}$ is dipole moment of atom

$$\vec{D} = \sum_{\alpha=1}^{Z} \vec{r}_\alpha = \text{C.M.} = (X, Y, Z); \quad \begin{cases} X = \sum_{\alpha=1}^{Z} x_\alpha \\ Y = \sum y_\alpha \end{cases}$$

$$\hat{H}_I = \hat{H}_{ED} = e\vec{D}\cdot\vec{E}_0 \cos\omega t = eE_0 X \cos\omega t$$

X is the x coordinate of the c.m. of electrons!

3-4 Note that

$$\hat{H}_{ED}(\{-\vec{r}_\alpha\}) = -\hat{H}_{ED}(\{\vec{r}_\alpha\})$$

$\hat{H}_{ED}$ has <u>odd</u> parity.

Therefore $\langle i|\hat{H}_{ED}|i\rangle =$

$$= \int d\vec{r}_1 .. d\vec{r}_Z \, |\Psi_i(\vec{r}_1, \ldots, \vec{r}_Z)|^2 \hat{H}_{ED}(\vec{r}_1 \ldots \vec{r}_Z) = 0$$

In general

$\langle i|\hat{H}_{ED}|j\rangle = 0$ if $|i\rangle$ and $|j\rangle$

have the <u>same parity</u>

that is, if both are odd

or both are even functions

<u>Assume</u> that $|1\rangle$ and $|2\rangle$ have opposite parity

(= dipole-allowed transition)

$$\Rightarrow \langle 1|\hat{H}_{ED}|1\rangle = \langle 2|\hat{H}_{ED}|2\rangle = 0$$

$$\langle 1|\hat{H}_{ED}|2\rangle = (\langle 2|\hat{H}_{ED}|1\rangle)^* \neq 0$$

$$\boxed{\langle 1|\hat{H}_{ED}|2\rangle = \underbrace{eE_0X_{12}}_{=\hbar\Omega} \cos(\omega t)}$$

where $X_{12} = \langle 1|X|2\rangle$

$$= \int d\vec{r}_1 \cdots d\vec{r}_Z \, \Psi_1^*(\vec{r}_1, \ldots, \vec{r}_Z) \left(\sum_{\alpha=1}^{Z} x_\alpha\right) \Psi_2(\vec{r}_1, \ldots, \vec{r}_Z)$$

$$\boxed{\Omega = eE_0 X_{12}/\hbar}$$

is called the <u>Rabi frequency</u> (Loudon: V)

Note: $|1\rangle$ and $|2\rangle$ bound states

$\Rightarrow$ ψ_1 and ψ_2 real functions

$\Rightarrow$ Ω real.

Time development of atom:

$$\boxed{\begin{aligned} i\frac{\partial C_1}{\partial t} &= e^{-i\omega_0 t} C_2 \, \Omega \cos \omega t \\ i\frac{\partial C_2}{\partial t} &= e^{i\omega_0 t} C_1 \, \Omega \cos \omega t \end{aligned}}$$

Usually $\Omega \ll \omega_0$

3-6 Calculate Einstein coefficients!

Try to solve eqs of motion for C_1, C_2

Start with $C_1(0)=0$, $C_2(0)=1$

i.e. atom in excited state

Note that $B_{12}\langle W(\omega_0)\rangle = \frac{|C_2|^2}{t}$

Rate of transition = increase in population / unit time

First approximation (short times): take $C_1(t)=1$

$$\frac{i\partial C_2(t)}{\partial t} = \underbrace{C_1}_{=1} \Omega e^{i\omega_0 t} \cos\omega t$$

$$C_2(t) = \frac{1}{i}\Omega \int_0^t dt' e^{i\omega_0 t'} \cos\omega t'$$

$$= \frac{\Omega}{i}\int_0^t dt' e^{i\omega_0 t'} \frac{1}{2}\left(e^{i\omega t'} + e^{-i\omega t'}\right)$$

$$= \frac{\Omega}{2i}\int_0^t dt' \left(e^{i(\omega_0+\omega)t'} + e^{i(\omega_0-\omega)t'}\right)$$

$$= \frac{\Omega}{2i}\left\{\frac{e^{i(\omega_0+\omega)t'}}{i(\omega_0+\omega)} + \frac{e^{i(\omega_0-\omega)t'}}{i(\omega_0-\omega)}\right\}_0^t$$

$$= \frac{\Omega}{2}\left\{\frac{1-e^{i(\omega_0+\omega)t}}{\omega_0+\omega} + \frac{1-e^{i(\omega_0-\omega)t}}{\omega_0-\omega}\right\}$$

the approximation can be improved by iteration. Can be shown: this is first order in Ω

If irradiance is not too large, 1st order will do.

$$C_2(t) = \frac{\Omega}{2}\left\{\cancel{\frac{1-e^{i(\omega_0+\omega)t}}{\omega_0+\omega}} + \frac{1-e^{i(\omega_0-\omega)t}}{\omega_0-\omega}\right\}$$

smaller
& oscillates fast

the rotating wave approximation (RWA):

$$\boxed{C_2(t) = \frac{\Omega}{2}\,\frac{1-e^{i(\omega_0-\omega)t}}{\omega_0-\omega}}$$

Good when $|\omega_0-\omega| \ll \omega_0+\omega$

$$|C_2(t)|^2 = \frac{\Omega^2}{(\omega_0-\omega)^2}\left|\frac{1-e^{i(\omega_0-\omega)t}}{2}\right|^2$$

$$= \Omega^2\,\frac{\sin^2\left(\frac{\omega_0-\omega}{2}t\right)}{(\omega_0-\omega)^2}$$

$$\approx \frac{\Omega^2 t^2}{4} \quad \text{when } \omega_0 \to \omega$$

contrary to the assumption $|C_2(t)|^2 \propto t$!

At odds with Einstein theory??

Solution: Consider a light beam containing a continuous range of frequencies ω that are also incoherent

Then

$$|C_2(t)|^2 = \sum_{\omega} \Omega^2\,\frac{\sin^2\left(\frac{\omega_0-\omega}{2}t\right)}{(\omega_0-\omega)^2}$$

and use
$$\begin{cases} \Omega^2 = \dfrac{e^2 E_0^2 X_{12}^2}{\hbar^2} \\ \int \langle W(\omega) \rangle d\omega = \frac{1}{2}\varepsilon_0 E_0^2 \\ \dfrac{\sin^2\left(\frac{\omega_0-\omega}{2}t\right)}{(\omega_0-\omega)^2} = \frac{\pi}{2} t\, \delta(\omega_0-\omega) \end{cases}$$

$\Rightarrow \ldots \Rightarrow \ldots$ (see Loudon, §2.3)

$$|c_2(t)|^2 = \frac{2e^2 X_{12}}{\hbar^2 \varepsilon_0} \langle W(\omega_0) \rangle \cdot \frac{1}{2}\pi t$$

$\Rightarrow \ldots \Rightarrow$

$$B_{12} = \frac{\pi e^2 D_{12}^2}{3\varepsilon_0 \hbar^2}$$

What about A_{21}?

In absence of coupling Ω, we have

$$i\frac{\partial c_2}{\partial t} = 0 = i\frac{\partial c_1}{\partial t}$$

no spontaneous emission in semiclassical theory!

(Have to wait until Chapter 4.)

Have to introduce by hand $A_{21} = \frac{1}{\tau_R}$

(next lecture.)