Physics of Atoms and Molecules.

Atoms — many electron; Molecules — many atoms

QM

SM

Bare ionic pot $\sum_{N} \frac{-1}{(r - R_N)}$

core electron + valence electron

C: 1s (2) 2s, 2p (4) : total 6

B: 1s (2) 2s, 2p (3) : total 5

Look at the periodic table

Many electron : Pot seen by one is <u>screened by others</u>

$\Rightarrow$ effective pot.

$$-\frac{1}{r} \longrightarrow -\frac{e^{-\alpha m r}}{r} \quad \text{Yukawa pot.}$$

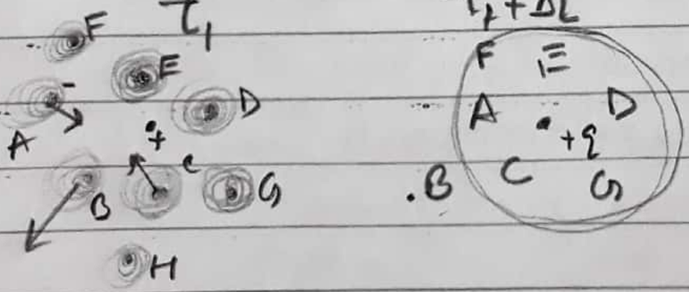
m mass, α scaling constant.

$$= \frac{-1}{r\,\varepsilon(r)}, \quad \varepsilon(r) = e^{\alpha m r} \rightarrow \text{Screening}$$

effectively shortens the range

Note: Screening is a result of dynamic nature of electrons

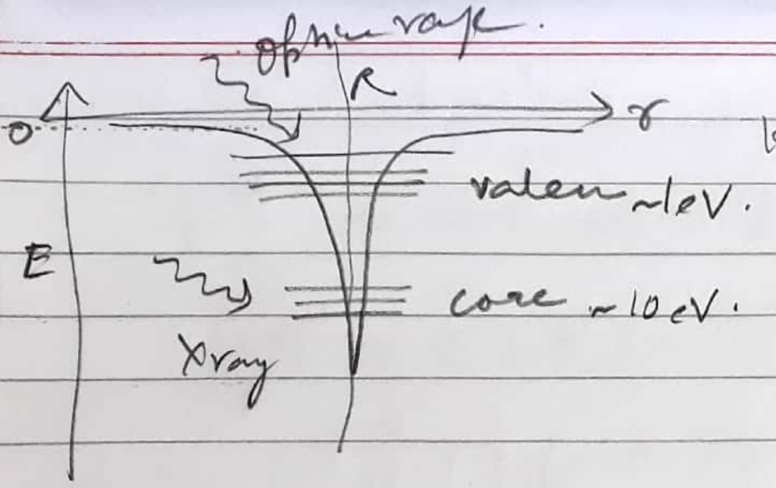
Since, if no charge moves then no screening!

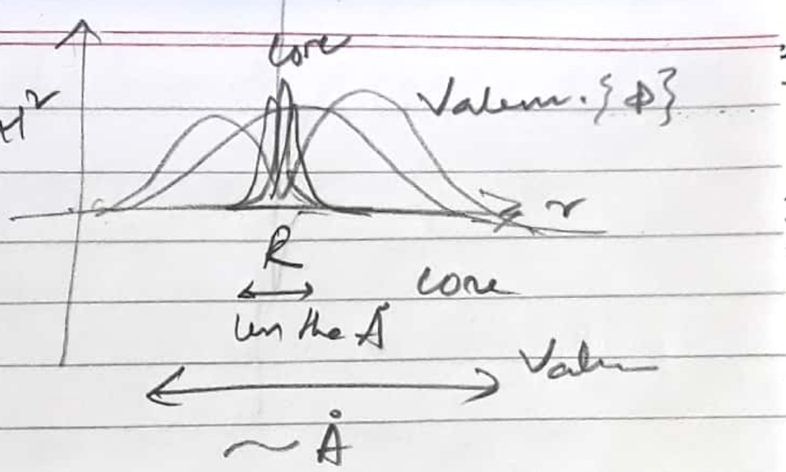


So our simplest description of many electrons:

Independent electron moving in screened potential due to others.

All many electrons effect goes into screening.

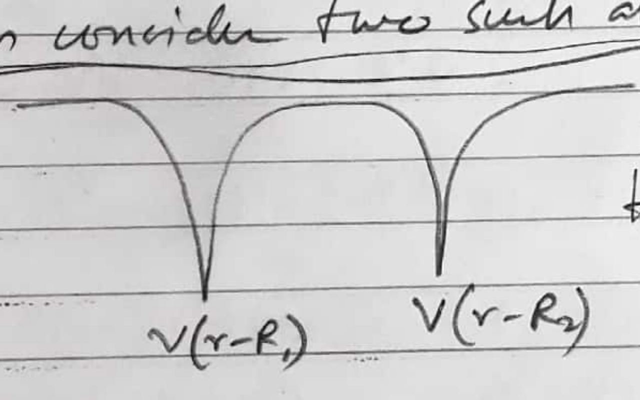




Valence: $\{\phi_n\}, \{E_n\}$ Valence electrons takes part in inter-atomic interactions.

Let us consider two such atoms in proximity:

let us see for 1 "independent" electron



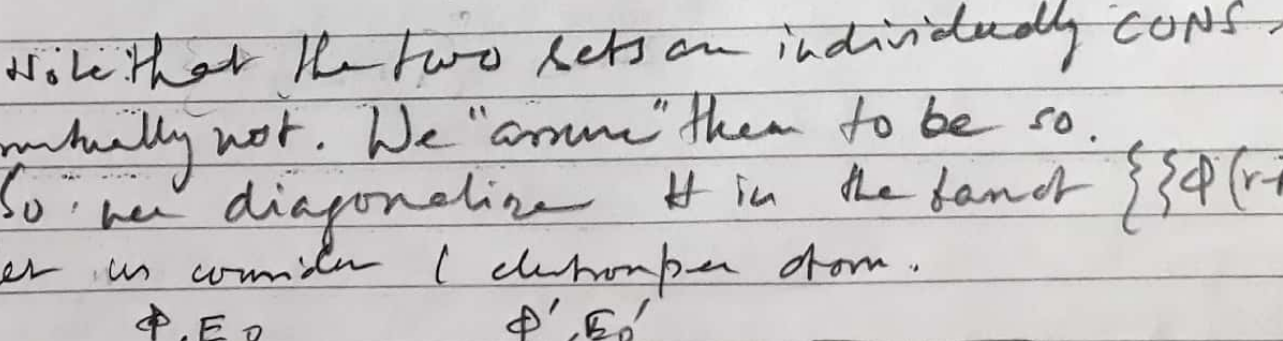
$$H = T + V$$

$$= -\frac{1}{2m}\nabla^2 + V(r-R_1) + V(r-R_2)$$

Let us "approximately" consider the state of an "independent" electron expressable in terms of the valence states of individual atoms. $\{\phi(r-R_1)\}, \{\phi(r-R_2)\}$

Note that the two sets are individually CONS but mutually not. We "assume" them to be so. So we diagonalize H in the basis of $\{\{\phi(r-R_1), \phi(r-R_2)\}\}$

Let us consider 1 electron per atom.



Let us seek solution in the basis of $\phi(r-R)$, $\phi'(r-R')$

$$\Psi = a\,\phi(r-R) + b\,\phi'(r-R') \quad ; \quad a^2+b^2=1$$

$$\hat{H}|\Psi\rangle = E|\Psi\rangle :$$

$$a\,\hat{H}|\phi(r-R)\rangle + b\,\hat{H}|\phi'(r-R')\rangle = E|\Psi\rangle$$

$\langle\phi(r-R)|$: both sides;

$$a\,\langle\phi(r-R)|\hat{H}|\phi(r-R)\rangle + b\,\langle\phi(r-R)|\hat{H}|\phi'(r-R')\rangle = aE$$

$\langle\phi'(r-R')|$: both side;

$$a\langle\phi'(r-R')|\hat{H}|\phi(r-R)\rangle + b\langle\phi'(r-R')|\hat{H}|\phi'(r-R')\rangle = bE$$

$$\begin{bmatrix} \langle\phi(r-R)|H|\phi(r-R')\rangle & \langle\phi|H|\phi'\rangle \\ \langle\phi'|H|\phi\rangle & \langle\phi'|H|\phi'\rangle \end{bmatrix}\begin{bmatrix} a \\ b \end{bmatrix} = E\begin{bmatrix} a \\ b \end{bmatrix}$$

$$\begin{aligned}\langle\phi|H|\phi\rangle &= \langle\phi|(KE+V+V')|\phi\rangle \\ &= \langle\phi|(KE+V)|\phi\rangle + \langle\phi|V'|\phi\rangle \\ &= E_0 + \alpha\end{aligned}$$

$$\begin{aligned}\langle\phi'|H|\phi'\rangle &= \langle\phi'|V|\phi'\rangle + E_0' \\ &= \alpha' + E_0'\end{aligned}$$

$$\langle\phi|H|\phi'\rangle = \beta$$

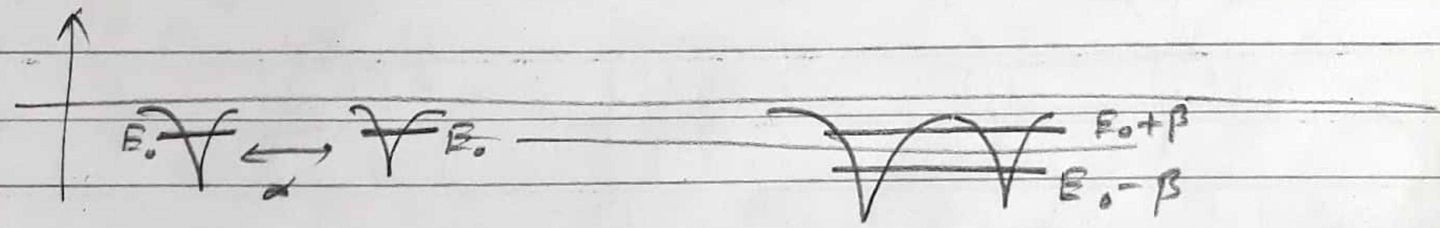
$$\langle\phi'|H|\phi\rangle = \beta^* \quad : \quad \begin{bmatrix} E_0+\alpha & \beta \\ \beta^* & E_0'+\alpha' \end{bmatrix}\begin{bmatrix} a \\ b \end{bmatrix} = E\begin{bmatrix} a \\ b \end{bmatrix}$$

$$\begin{bmatrix} E_0+\alpha & \beta \\ \beta^* & E_0'+\alpha' \end{bmatrix} \simeq \begin{bmatrix} E_0 & \beta \\ \beta^* & E_0' \end{bmatrix} \quad \because \text{ localised basis}$$

$$E = \frac{+(E_0+E_0') \pm \sqrt{(E_0-E_0')^2+4\beta^2}}{2}$$

$$= \frac{(E_0+E_0')}{2} \pm \beta\sqrt{1+\frac{(E_0-E_0')^2}{\beta^2}}$$

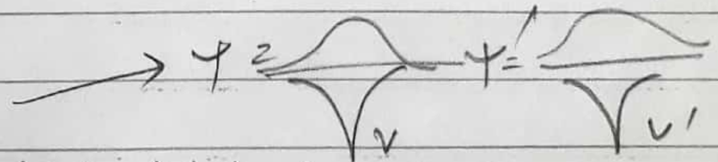
$\therefore$ If $E_0 = E_0'$ $\therefore$ $E = E_0 \pm \beta$



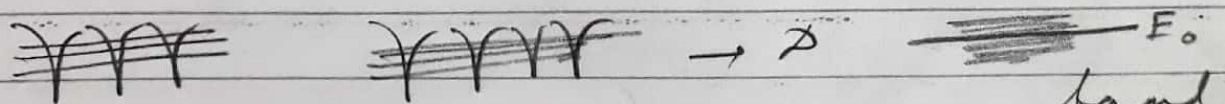
for
$E \doteqdot E_0 - \beta$; $a = -b = \frac{1}{\sqrt{2}}$ $\therefore$ $\psi = \frac{1}{\sqrt{2}}(\psi - \psi')$ 1 node

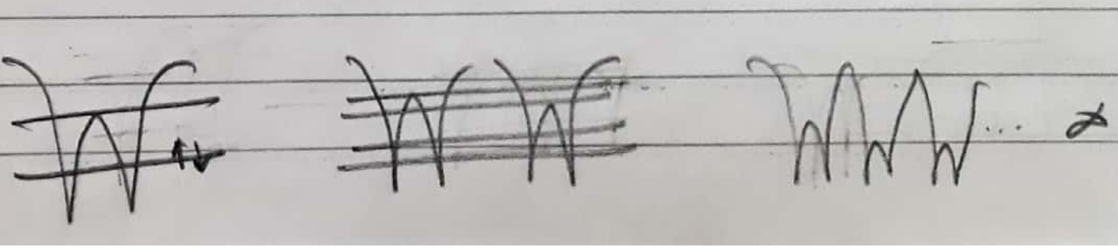
$E \doteqdot E_0 + \beta$: $a = b = \frac{1}{\sqrt{2}}$: $\psi = \frac{1}{\sqrt{2}}(\psi + \psi')$ 0 node

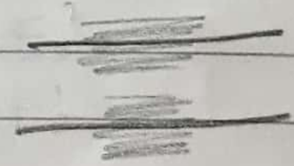
2) β must be −ve if



* Some confusion about $|\beta|$: A bit in details in next to next page







* Regarding confusion over β and $|\beta|$ in prior to prior page

$$E = \frac{1}{2}(E_0 + E_0') \pm \frac{1}{2}\sqrt{(E_0 - E_0')^2 + 4|\beta|^2}$$

$$= \frac{(E_0 + E_0')}{2} \pm \frac{2|\beta|}{2}\sqrt{1 + \frac{(E_0 - E_0')^2}{4|\beta|^2}}$$

let $E_0' = E_0$ then:

$$E = E_0 \pm |\beta| \;:$$

For $E = E_0 + |\beta|$ in $\begin{bmatrix} E_0 & \beta \\ \beta^* & E_0 \end{bmatrix}\begin{bmatrix} a \\ b \end{bmatrix} = E\begin{bmatrix} a \\ b \end{bmatrix}$

$$\begin{bmatrix} E_0 - (E_0 + |\beta|) & \beta \\ \beta^* & E_0 - (E_0 + |\beta|) \end{bmatrix}\begin{bmatrix} a \\ b \end{bmatrix} = 0$$

$$\Rightarrow \begin{bmatrix} -|\beta| & \beta \\ \beta^* & -|\beta| \end{bmatrix}\begin{bmatrix} a \\ b \end{bmatrix} = 0 \quad \Rightarrow \begin{bmatrix} -|\beta| & e^{i\theta}|\beta| \\ e^{-i\theta}|\beta| & -|\beta| \end{bmatrix}\begin{bmatrix} a \\ b \end{bmatrix} = 0$$

$$\Rightarrow \left.\begin{matrix} -a + e^{i\theta} b = 0 \\ e^{-i\theta} a - b = 0 \end{matrix}\right] \Rightarrow \Psi = a\Psi_0 + b\Psi_0' \;, \; a^2 + b^2 = 1$$

$$= \frac{1}{\sqrt{2}}\left[\Psi_0 + e^{-i\theta}\Psi_0'\right]$$

$$\therefore \; E = E_0 + |\beta| \;:\; \Psi = \frac{1}{\sqrt{2}}\left[\Psi_0 + e^{-i\theta}\Psi_0'\right]$$

for $E = E_0 - |\beta| \;:\; \Psi = \frac{1}{\sqrt{2}}\left[\Psi_0 - e^{-i\theta}\Psi_0'\right]$

N θ is determined by the sign of β. For example if β is $-$ve then θ is $180^\circ \Rightarrow e^{i\theta} = -1 \;\therefore$ the eng of the

$\Psi = \frac{1}{\sqrt{2}}\left[\Psi_0 + \Psi_0'\right]$ is $E = E_0 - |\beta|$ if $\beta < 0$

* say first →

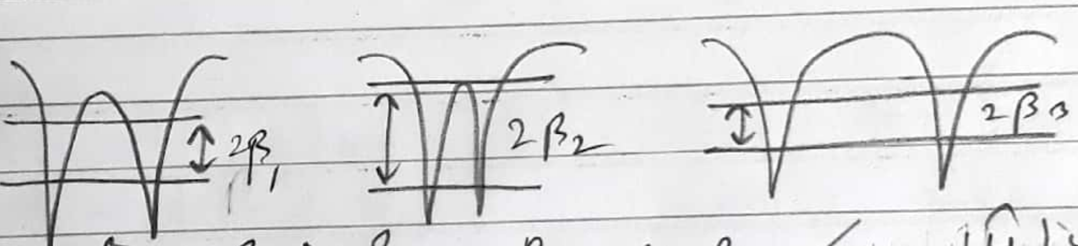
Born Oppenheimer Approximation:

Nuclear motion is much slower than the electronic motion:

: Electronic wave functions depend on nuclear position but not their velocities.

: Nuclear motion such as rotation vibration are impacted by smooth smeared out potential due to fast moving electrons.

→ Note



since $\beta_2 > \beta_1 > \beta_3$ Recall $\beta = \langle \psi_R | \hat{H} | \psi_{R'} \rangle$

BO Approximation rescues us!

time and length scales:

$\Delta p \, \Delta x = \Delta E \, \Delta t \geq \hbar/2$

$\downarrow$ Å (10^{-10} m) $\quad \downarrow$ (1–10) eV $\approx 10^{-18}$ J $\quad \downarrow \sim 10^{-34}$ J-s

$\therefore \Delta t \approx 10^{-16}$ s $\quad 10^{-15}$ s → Femto Second!

$\Delta E_{nuclear} \sim 0.001 \, \Delta E_e$

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Let us remind ourselves about light: EM wave.

$$\vec{E}(r,t) = -\nabla\phi(\vec{r},t) - \frac{\partial}{\partial t}\vec{A}(\vec{r},t)$$
$$\vec{B}(r,t) = \nabla\times\vec{A}(\vec{r},t)$$

Invariant if
$\vec{A}\to\vec{A}+\nabla\chi$
$\phi\to\phi-\frac{\partial\chi}{\partial t}$, any analytic fn

In free space: MW Eqn:

MW1 $\boxed{\nabla\cdot E = 0}$ since $\phi=0$; MW2 $\boxed{\nabla\cdot B=0}$ (always); MW3 $\boxed{\nabla\times E = -\frac{\partial B}{\partial t}}$; MW4 $\boxed{\nabla\times B = 0 + \frac{1}{c^2}\frac{\partial E}{\partial t}}$

MW4 $\mu_0 J$; $J=0$ in free sp.

Convenient choice:

MW2 $\to$ $\nabla\cdot A=0$ (Coulomb Gauge)
MW1 $\to$ $\phi=0$

Remember that you have ∞ # of choices of A and ϕ to render same $\vec{E}$ and $\vec{B}$

MW3 $\to$ $\nabla\times\left(-\frac{\partial A}{\partial t}\right) = -\frac{\partial}{\partial t}(\nabla\times A)$

MW4 $\to$ $\nabla\times(\nabla\times A) = \frac{1}{c^2}\frac{\partial}{\partial t}\left(-\frac{\partial}{\partial t}A\right)$

$$\Rightarrow \underbrace{\vec{\nabla}(\vec{\nabla}\cdot\vec{A})}_{=0 \text{ by choice}} - \nabla^2 A = -\frac{1}{c^2}\frac{\partial^2 A}{\partial t^2}$$

$$\Rightarrow \nabla^2 A = \frac{1}{c^2}\frac{\partial^2 A}{\partial t^2} \Rightarrow \vec{A}(r,t) = 2\vec{A}_0(\omega)\cos(\vec{k}\cdot\vec{r}-\omega t+\delta_\omega)$$

$\to [e^{ik\cdots} + cc]$

$\omega = kc$

$$\Rightarrow \vec{E}(r,t) = -2\omega\vec{A}_0(\omega)\sin(\vec{k}\cdot\vec{r}-\omega t+\delta\omega)$$

$\therefore$ $\vec{E}_0(\omega) = -2\omega A_0(\omega)\hat{E}$

$$\vec{B}(r,t) = 2A_0(\omega)(\vec{k}\times\hat{E})\sin(\vec{k}\cdot\vec{r}-\omega t+\delta\omega)$$

EM wave
$|E|/|B| = c$

Energy density:

$$= \frac{1}{2}\left(\epsilon_0 |E|^2 + |B|^2/\mu_0\right) \text{ of EM field.}$$

$$= 4\epsilon_0 \omega^2 A_0^2(\omega)\sin^2(\vec{k}\cdot\vec{r} - \omega t + \delta_\omega) \quad \text{instantaneous}$$

Time Ave over $(2\pi/\omega)$: $\varphi(\omega) = 2\epsilon_0 \omega^2 A_0^2(\omega)$.

$$\varphi(\omega) = 2\epsilon_0 \omega^2 A_0^2(\omega) = n(\omega)\hbar\omega$$

↳ # density of photon with each with energy $h\nu = \hbar\omega$

$$\therefore A_0(\omega) = \sqrt{\frac{n(\omega)\hbar}{2\epsilon_0\omega}}$$

$$\Rightarrow E_0(\omega) = \sqrt{\frac{n(\omega)\hbar\omega}{2\epsilon_0}}$$

Intensity : $I(\omega) = \varphi(\omega)\, c = 2\epsilon_0 \omega^2 c A_0^2(\omega)$

Rate of energy flow through unit cross section $\perp$ to $\vec{k}$:

$$(\vec{E}\times\vec{B})/\mu_0 \to \text{Ave over } \left(\frac{2\pi}{\omega}\right) \Rightarrow I(\omega)$$

$$= 2\epsilon_0 \omega^2 c A_0^2(\omega) \quad \text{same as}$$

Charge particle in EM field:

L Eq: $\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0$

To get $\vec{F} = q(E + \vec{v}\times\vec{B}) = q\left[-\nabla\phi - \frac{\partial A}{\partial t} + \vec{v}\times(\nabla\times\vec{A})\right]$

a possible choice of L is $L = \frac{1}{2}mv^2 - q\phi + q\vec{v}\cdot\vec{A}$

So that Generalize Momenta $p_i = \frac{\partial L}{\partial \dot{q}_i} \Rightarrow \vec{p} = m\vec{v} + q\vec{A}$

$\therefore H = \frac{1}{2m}(\hat{p} - q\vec{A})\cdot(\hat{p} - q\vec{A}) + q\phi$. * Done later as well from L to H

$= \frac{\hat{p}^2}{2m} - \frac{q}{2m}(\vec{A}\cdot\vec{p} + \vec{p}\cdot\vec{A}) + \frac{q^2}{2m}\vec{A}\cdot\vec{A} + q\phi$.

$\therefore$ TD Sch Eq^n: $\frac{\partial\Psi(r)}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + \frac{i\hbar q}{m}(\vec{A}\cdot\vec{\nabla} + \vec{\nabla}\cdot\vec{A})\right.$ "0 Coulomb Gauge"

$\left. + \frac{q^2}{2m}\vec{A}\cdot\vec{A} + q\phi\right]\Psi(r,t)$

Eq^n remain invariant if

$\vec{A} \to \vec{A} + \nabla\chi$

$\phi \to \phi - \frac{\partial}{\partial t}\chi$

$\Psi \to \Psi\exp\left[iq\frac{\chi}{\hbar}\right]$

(Show yourself)

$\Rightarrow$ Different choice of gauge $\Rightarrow$ Different phase factor of Ψ

$\to$ Geometric phase

$\to$ AB effect.

In an evolving scenario
How different choice of gauge
mean different route of evolution.
And different route of evolution leads to different geometric phase of electron

in parameter space.

** Recall, formulation of the H for quantum particles in EM field.

$L = \frac{1}{2}mv^2 - q\phi + q\vec{v}\cdot\vec{A} \Rightarrow p = m\vec{v} + qA$

p → Gauge dependent; $m\vec{v}$ → kinetic momentum is gauge invariant and physically measurable

$H = \sum_i \dot{q}_i p_i - L$

$= v\cdot p - L \Rightarrow \left(\frac{p - qA}{m}\right)p - \frac{1}{2}m\left(\frac{p-qA}{m}\right)^2 + q\phi - q\left(\frac{p-qA}{m}\right)\cdot A$

(writing everything in terms of generalized momenta)

$= \frac{1}{2m}\left[(p-qA)\left[2p - p + qA - 2qA\right]\right] + q\phi$

$= \frac{1}{2m}(p-qA)(p-qA) + q\phi$

Not $q\phi_0$ as ϕ_0 denotes ϕ_{20}

TDSE: $$i\hbar \frac{\partial}{\partial t}\Psi(r,t) = \underbrace{\left[-\frac{\hbar^2}{2m}\nabla^2 + q\phi_0\right]}_{H_0}\Psi + \underbrace{\frac{i\hbar q}{m}\vec{A}\cdot\nabla\Psi}_{H'}$$

we have put $\vec{A}\cdot\vec{A} \to 0$ assuming that $|A_0| \ll E_0$ the unperturbed energies of e in atoms and molecules.

We will therefore treat H' also perturbatively

Consider TD Ψ: $$\Psi(r,t) = \sum_k C_k(t)\,\phi_k(\vec{r})\,e^{-iE_k t/\hbar}$$

Where $H_0\phi_k = E_k\phi_k$

$$\therefore\ i\hbar\sum_k \dot{C}_k(t)e^{-iE_k t/\hbar}\phi_k + i\hbar\sum_l C_l(t)\phi_l\left(-\frac{iE_l}{\hbar}\right)e^{-iE_l t/\hbar}$$
$$= \sum_m C_m(t)E_m\phi_m e^{-iE_m t/\hbar} + \sum_n C_n(t)H'\phi_n e^{-iE_n t/\hbar}$$

$\int \phi_b^*(r)\,dr$ on both sides;

$$i\hbar\dot{C}_b(t)e^{-iE_b t/\hbar} + E_b C_b(t)e^{-iE_b t/\hbar} = E_b C_b(t)e^{-iE_b t/\hbar}$$
$$+ \sum_n C_n(t)\langle\phi_b|H' e^{-iE_n t/\hbar}|\phi_n\rangle$$

$$\Rightarrow \boxed{\dot{C}_b(t) = \frac{-e}{m}\sum_n C_n(t)\langle\phi_b|\vec{A}\cdot\nabla|\phi_n\rangle e^{i\omega_{bn}t}}\ ;\ \omega_{bn} = \frac{E_b - E_n}{\hbar}$$
$(q = -e)$

Determine evolution of Ψ as H' is switched on. (1)

Now let us consider a generic light pulse given by:

$$\vec{A}(r,t) = \hat{E}\int_0^{\infty} A_0(\omega)\cos(\vec{k}\cdot\vec{r} - \omega t + \delta\omega)\, d\omega \qquad \cos x \to \tfrac{1}{2}[e^{ix}+e^{-ix}]$$

° if $A_0(\omega)=\delta(\omega-\omega_0)$ then it is a monochromatic light

if $A_0(\omega)=1$ for all ω then it is sharp delta pulse in time.

Let the system be at state "a" given by Φ_a and E_a at $t \ll 0$

Also, since $\langle H'\rangle \ll \langle H_0\rangle$ it is reasonable to assume that over considerably large interval of time the evolution of $C_b(t)$ for $b \neq a$ will be contributed by the initial "a" state.

$\therefore$ In the RHS of expression of $\dot{C}_b(t)$ we can replace sum, or in other words use $C_n(t) \simeq C_n(t \ll 0) = \delta_{na}$

$$\therefore\ C_b(t) = -\frac{e}{m}\int_0^t \langle\Phi_b|\vec{A}\cdot\nabla|\Phi_a\rangle e^{i\omega_{ba}t'}dt'$$

Now for the generic light pulse:

$$C_b(t) = -\frac{e}{m}\int_0^{\infty} d\omega\, A_0(\omega)\Big[e^{i\delta\omega}\langle\Phi_b|e^{i\vec{k}\cdot\vec{r}}\hat{E}\cdot\nabla|\Phi_a\rangle\int_0^t e^{i(\omega_{ba}-\omega)t'}dt'$$
$$+ e^{-i\delta\omega}\langle\Phi_b|e^{-i\vec{k}\cdot\vec{r}}\hat{E}\cdot\nabla|\Phi_a\rangle\int_0^t e^{i(\omega_{ba}+\omega)t'}dt'\Big]$$

$$= -\frac{e}{2m}\int_0^{\infty}\cdots\Big[\cdots\left[e^{i(\omega_{ba}-\omega)t'}\right]_0^t\frac{1}{(\omega_{ba}-\omega)} + \cdots\left[e^{i(\omega_{ba}+\omega)t'}\right]_0^t\frac{1}{(\omega_{ba}+\omega)}\Big]$$

Note $|c_x(t)|^2 \leq 1$

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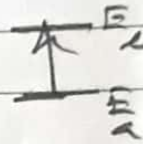
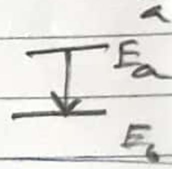
As $\omega \to \omega_{ba}$ the 1st term diverges
At $\omega \to \omega_{ab}$ the 2nd " " } both cannot

$\omega \to \omega_{ba} \Rightarrow E_b = E_a + \hbar\omega \Rightarrow$ Absorption 

$\omega \to \omega_{ab} \Rightarrow E_b = E_a - \hbar\omega \Rightarrow$ Emission 

Absorption: $\omega \longrightarrow \omega_{ba}$

$$|c_b(t)|^2 = \frac{e^2}{4m^2}\left(\int d\omega\, e^{i\delta_\omega}\right)\left(\int d\omega'\, e^{-i\delta_{\omega'}}\right);$$

δ_ω are all random. In normal light source

then the $\omega \neq \omega'$ term would average out to zero

retain only the $\omega = \omega'$ term.

product of sum $\longrightarrow$ sum of product.

$$= \frac{e^2}{4m^2}\int_0^\infty d\omega\, |A_0(\omega)|^2 \left|\langle \phi_b | e^{i\mathbf{k}\cdot\mathbf{r}}\, \hat{\varepsilon}\cdot\mathbf{p} | \phi_a\rangle\right|^2 \left|\int_0^t e^{i(\omega_{ba}-\omega)t'} dt'\right|^2$$

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Let us focus on the last term:

$$\left|\int_0^t e^{i(\omega_{ba}-\omega)t'}\,dt'\right|^2 = \left|\frac{1}{(\omega_{ba}-\omega)}\left(e^{i(\omega_{ba}-\omega)t}-1\right)\right|^2$$

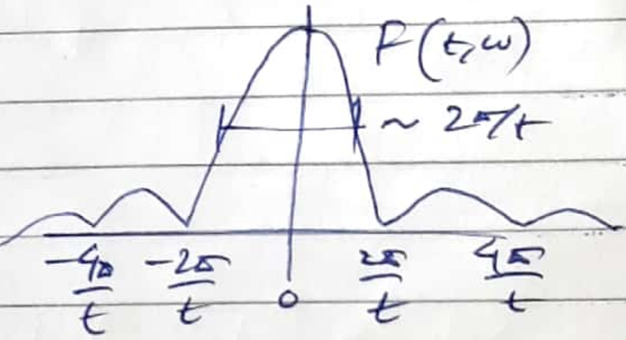
$$= \frac{1}{(\omega_{ba}-\omega)^2}\left(1-\left(e^{i(\omega_{ba}-\omega)t}+e^{-i(\omega_{ba}-\omega)t}\right)+1\right)$$

$$= \frac{1}{(\omega_{ba}-\omega)^2}\left(2-2\cos(\omega_{ba}-\omega)t\right)$$

$$= \frac{4\sin^2\frac{1}{2}(\omega_{ba}-\omega)t}{(\omega_{ba}-\omega)^2} = \frac{t^2\sin^2\left(\frac{\omega_{ba}-\omega}{2}\right)}{\left(\frac{\omega_{ba}-\omega}{2}\right)^2}$$

Define $F(t,\omega) = \dfrac{1-\cos\omega t}{\omega^2}$ $\therefore$ $|\cdots|^2 = 2F(t,\omega_{ba}-\omega)$

$$\int_{-\infty}^{+\infty} F(t,\omega)\,d\omega = \int_{-\infty}^{+\infty}\frac{2\sin^2\frac{\omega}{2}t}{\omega^2}\,d\omega$$



$$= t\int_{-\infty}^{\infty}\frac{\sin^2\left(\frac{\omega t}{2}\right)}{\left(\frac{\omega t}{2}\right)^2}\,d\left(\frac{\omega t}{2}\right)$$

$$= t\int_{-\infty}^{+\infty}\frac{\sin^2 x}{x^2}\,dx = \pi t \Rightarrow F(t,\omega) \underset{t\to\infty}{\sim} \pi t\,\delta(\omega)$$

$$\therefore |c_b(t)|^2 = \frac{e^2}{\cancel{4}2m^2}\int_0^\infty d\omega\,|A_0(\omega)|^2|M_{ba}|^2\,\cancel{2}\underbrace{F(t,\omega_{ba}-\omega)}_{\pi t\,\delta(\omega_{ba}-\omega)}\,d\omega$$

$$= \frac{e^2}{2m^2}|A_0(\omega_{ba})|^2|M_{ba}|^2\pi t \to \propto t$$ linearly increase with time.

$$|C_b(t)|^2 = \frac{e^2}{2m^2} |A_0(\omega_{ba})|^2 |M_{ba}|^2 \pi t$$

$$= \frac{\pi}{2} \left| \frac{e A_0(\omega_{ba})}{m} \right|^2 |M_{ba}|^2 t$$

Recall, $I(\omega) = 2 \epsilon_0 \omega^2 c A_0^2(\omega) \rightarrow$ the intensity of the incident radiation.

$$|C_b(t)|^2 = \frac{\pi}{2} \left(\frac{e^2 I(\omega_{ba})}{2 \epsilon_0 \omega_{ba}^2 c m^2} \right) |M_{ba}|^2 t$$

$$= \frac{\pi e^2}{4 \epsilon_0 c m^2} \left(\frac{I(\omega_{ba})}{\omega_{ba}^2} \right) |M_{ba}|^2 t$$

$$= \left(\frac{\pi^2}{m^2 c} \right) \left(\frac{e^2}{4\pi \epsilon_0} \right) \left(\frac{I(\omega_{ba})}{\omega_{ba}^2} \right) |M_{ba}|^2 t$$

Transition rate: $W_{b \leftarrow a} = \frac{d}{dt} |C_b(t)|^2 = \left(\frac{\pi^2}{m^2 c} \right) \left(\frac{e^2}{4\pi \epsilon_0} \right) \frac{I(\omega_{ba})}{\omega_{ba}^2} |M_{ba}|^2$

Rate of absorption of energy by the system from the field (of the incident radiation): $\hbar \omega_{ba} W_{ba}$

assumed that one transition absorbs one quanta of energy $\hbar\omega$. (one photon process)

Absorption cross section: $\sigma = \frac{\text{Absorbed energy}}{\text{incident energy}}$

$$\sigma = \frac{\hbar \omega_{ba} W_{ba}}{I(\omega_{ba})} = \frac{\hbar \omega_{ba} W_{ba}}{\hbar \omega_{ba} \, n(\omega_{ba}) c} = \frac{W_{ba}}{n(\omega_{ba}) c}$$

$$= \frac{\text{rate of absorption of photon}}{\text{rate of incidence of photon}}$$

$$\sigma = \frac{W_{ba}}{n(\omega_{ba})\,c} = \frac{(\#/T)}{(\#/V)(L/T)} = \frac{V}{L} = L^2 \text{ area}$$

∴ "cross section"

Amplitude is governed by $|M_{ba}|^2$

$$M_{ba} = \langle \phi_b | e^{-i\vec{k}\cdot\vec{r}}\, \hat{E}\cdot\nabla | \phi_a \rangle$$

$$= \int_{-\infty}^{+\infty} \psi_b^*(\vec{r})\, e^{-i\vec{k}\cdot\vec{r}}\, \hat{E}\cdot\left(\nabla \psi_a(\vec{r})\right) dr$$

$$= \int_{-\infty}^{+\infty} \psi_b^* \Big(1 + \underbrace{i\vec{k}\cdot r}_{\to\ \frac{2\pi}{\lambda} r} + \frac{1}{2!}(i\vec{k}\cdot\vec{r})^2 + \cdots\Big)\, \hat{E}\cdot(\nabla \psi_a)\, dr$$

$\approx \mathring{A}$; $\lambda \approx 10^3$ nm

∴ $|\vec{k}\cdot\vec{r}|$ in atomic length scale : 10^{-4}

$$\approx \int \psi_b^* (1)\, \hat{E}\cdot\nabla\psi_a\, dr$$

→ Approx valid at atomic length scale

$$= \frac{i}{\hbar}\, \hat{\varepsilon}\cdot\langle \phi_b | \hat{p} | \phi_a \rangle$$

Now we use: $\hat{p} = m(i\hbar)^{-1}[\vec{r}, H]$ check by applying own bound states.

$$\Rightarrow \langle \phi_b | \hat{p} | \phi_a \rangle = m(i\hbar)^{-1}\langle \phi_b | (\hat{r} H_0 - H_0 \hat{r}) | \phi_a \rangle$$

$$= m(i\hbar)^{-1}(E_a - E_b)\langle \phi_b | \hat{r} | \phi_a \rangle$$

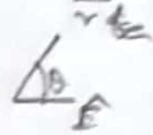
$$= m(i\hbar)^{-1}(E_a - E_b)\, \vec{r}_{ba}$$ → Dipole element

$$\therefore M^D_{ba} = \frac{m(-\omega_{ba})}{\hbar}\, \hat{E}\cdot\vec{r}_{ba} \qquad \omega_{ba} = \frac{E_b - E_a}{E}$$

$$\therefore W^{D}_{ba} = \left(\frac{\pi^2}{m^2 c}\right)\left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{I(\omega_{ba})}{\omega_{ba}^2}|M_{ba}|^2$$

$$= \left(\frac{\pi^2}{m^2 c}\right)\left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{I(\omega_{ba})}{\omega_{ba}^2}\frac{m^2\omega_{ba}^2}{\hbar^2}|\hat{E}\cdot\vec{r}_{ba}|^2$$

$$= \frac{\pi^2}{c\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right) I(\omega_{ba})\,|\vec{r}_{ba}|^2\cos^2\theta$$



for unpolarized light $\cos^2\theta$ has to be averaged over all solid angle: $\frac{1}{4\pi}\int \cos^2\theta \sin\theta\, d\theta\, d\phi$

$$W^{D}_{ba} = \frac{1}{3}\frac{\pi^2}{c\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right) I(\omega_{ba})|\vec{r}_{ba}|^2$$

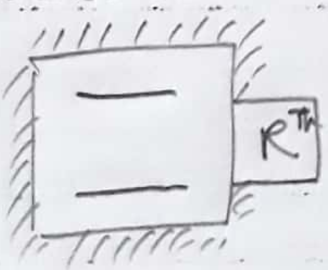
$$= \frac{1}{3}\frac{\pi}{c\hbar^2}\left(\frac{1}{4\pi\epsilon_0}\right) I(\omega_{ba})|\vec{D}_{ba}|^2 \; ; \; \vec{D}_{ba} = -e\vec{r}_{ba}$$

electron dipole moment of $-e\hat{r}$

Note that $|\vec{r}_{ba}| = |\vec{r}_{ab}|$, $\omega_{ba} = -\omega_{ab}$
and $I(\omega) \equiv I(|\omega|)$ actually.

$\therefore W^{D}_{ba} = W^{D}_{ab} \Rightarrow$ If levels "a" and "b" are equally occupied then they would remain equally occupied.

However this is a problem if you attach a thermal reservoir with such a two state system. Since



we know that in a canonical ensemble

$$\frac{N_a}{N_b} = e^{-(E_a - E_b)/kT} = e^{\omega_{ba}\hbar/kT}$$

N_a : instantaneous # of system in state "a"

N_b : # of system in state "b"
↳ (atom/mol)

Note that the process of response of matter in the presence of light ($I(\omega)$) that we have learned so far is called the "stimulated (st) absorption" process if $E_b > E_a$ and "stimulated emission" process if $E_b < E_a$.

Stimulated processes: $\dot{N}^{st}_{ba} = B_{ba} N_a \varphi(\omega_{ba})$

A coeff introduced by Einstein | # of atoms in state "a" | energy density

Note: $W^{st}_{ba} = \frac{\dot{N}^{st}_{ba}}{N_a} = B_{ba}\varphi(\omega_{ba})$

Similarly $\dot{N}^{st}_{ab} = B_{ab} N_b \varphi(\omega_{ba})$

As already discussed, if these are the only two processes then N_a and N_b would remain same if we start with $N_a = N_b$. Therefore there must be additional process of transition from "b" to "a" if $E_b > E_a$. Such a process cannot depend on presence of light (φ), since the heat exchange with the thermal reservoir will not necessarily happen at ω_{ba} or ω_{ab}. Thus the process must be spontaneous (sp).

At equilibrium $\dot{N}^{st}_{ba} = \dot{N}^{st}_{ab} + \dot{N}^{sp}_{ab}$ after Boltzmann distribution has been established (after long time) a strictly

$$\Rightarrow B_{ba} N_a \varphi(\omega_{ba}) = B_{ab} N_b \varphi(\omega_{ba}) + A_{ab} N_b$$

$$\frac{N_a}{N_b} = \frac{B_{ab}\varphi(\omega_{ba}) + A_{ab}}{B_{ba}\varphi(\omega_{ba})}$$ must be equal to $e^{\hbar\omega_{ba}/kT}$

AM

$$\frac{B_{ab}\,\varphi(\omega_{ba}) + A_{ab}}{B_{ba}\,\varphi(\omega_{ba})} = e^{\hbar\omega_{ba}/kT}$$

$$\Rightarrow \varphi(\omega_{ba}) = \frac{A_{ab}}{B_{ba}\,e^{\hbar\omega_{ba}/kT} - B_{ab}}$$

However, by Planck's law we know: $\varphi(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3}\left(\frac{1}{e^{\hbar\omega/kT}-1}\right)$

Recall Planck's law briefly → two direction of polarization

Energy density in the range ω, to $\omega + d\omega$: $\varphi(\omega)\,d\omega = \frac{2}{V}\left(\frac{\text{ph sp vol}}{h^3}\right) \times$ Bose factor $\times \hbar\omega$

# of photon in the range ω to $\omega + d\omega$ is given by $n(\omega)\,d\omega$

$$= \frac{2}{V}\left(\frac{V\,4\pi p^2\,dp}{h^3}\right)\left(\frac{1}{e^{\hbar\omega/kT}-1}\right)\hbar\omega, \quad p = \hbar k, \quad k = \omega/c$$

$$= \frac{2\times 4\pi\, k^2\,dk}{8\pi^3}\left(\frac{\hbar\omega}{e^{\hbar\omega/kT}-1}\right) = \frac{\hbar\omega^3\,d\omega}{\pi^2 c^3\left(e^{\hbar\omega/kT}-1\right)}$$

Recall: $W^{st}_{ba} = \frac{\dot N^{st}_{ba}}{N_a}$; Similarly for the spontaneous process $W^{sp}_{ab} = \frac{\dot N^{sp}_{ab}}{N_b} = A_{ab}$

$\therefore$ If $\frac{A_{ab}}{B_{ba}\,e^{\hbar\omega_{ba}/kT} - B_{ab}} = \frac{\hbar\omega^3_{ba}}{\pi^2 c^3}\left(\frac{1}{e^{\hbar\omega/kT}-1}\right)$

is possible only when:

$B_{ba} = B_{ab}$ and $\boxed{A_{ab} = \frac{\hbar\omega^3_{ba}}{\pi^2 c^3} B_{ab}} = \frac{\hbar\omega^3_{ba}}{\pi^2 c^3} W^{st}_{ab}$

$\overline{\varphi}$

$\Vert$

W^{sp}_{ab}

this trivially follows from $W_{ba} = W_{ab}$