

# PHY403 - ATOMIC & MOLECULAR PHYSICS.

## Ext books:

- ① Bransden and Joachain, Physics of Atoms & Molecules. (advanced)
- ② Demtröder, Atoms, Molecules & Photons. (intermediate)

Instructor: Dr. Ramandeep Johel

## Grading/Weightage:

4 quizzes      40% (10% each)      2 before & 2 after MidSem.

| MidSem      20%

| EndSem      40%

No graded assignments.

(1)

Lecture-1 (Hamiltonian of 2 e<sup>-</sup> atom)  
 (07/09)

We will use atomic units  $m_e = 1$ ,  $\hbar = 1$  and  $\frac{e^2}{4\pi\epsilon_0} = 1$

This implies that in Bohr's model

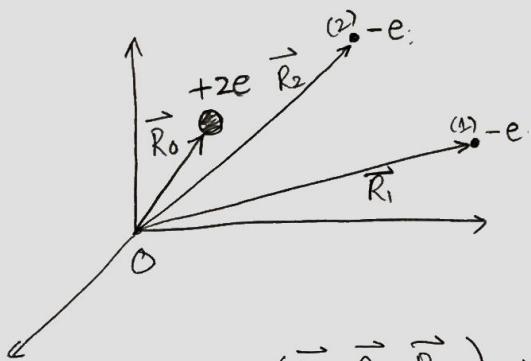
$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 1$$

$$E_n = -\frac{me^4}{32\pi^2\hbar^2\epsilon_0^2} \frac{1}{n^2} = -\frac{1}{2n^2} \text{ a.u.}$$

$$1 \text{ a.u.} = 27.2 \text{ eV}$$

$$E_1 = -0.5 \text{ a.u.} = -13.6 \text{ eV}$$

Let's now come at the problem of the Helium atom



$\vec{R}_0$ : P.V. of +2e nucleus  
 $\vec{R}_1$ : P.V. of e<sup>-</sup><sub>1</sub>  
 $\vec{R}_2$ : P.V. of e<sup>-</sup><sub>2</sub>

Instead of using  $(\vec{R}_0, \vec{R}_1, \vec{R}_2)$ , we shift to another set of vectors  $(\vec{R}, \vec{r}_1, \vec{r}_2)$  where  $\vec{R}$  = P.V. of COM,  $\vec{r}_1 = \vec{R}_1 - \vec{R}_0$  and  $\vec{r}_2 = \vec{R}_2 - \vec{R}_0$   
 (separation v b/w e<sup>-</sup> and 2e<sup>+</sup>)

$$\vec{R} = \frac{M\vec{R}_0 + m\vec{R}_1 + m\vec{R}_2}{M+2m}$$

$+2e \rightarrow M$   
 $-e \rightarrow m$

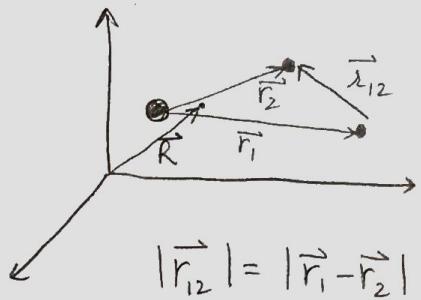
(2)

The Hamiltonian of the system is given by

$$\hat{H} = \hat{T} + \hat{V}$$

$$\hat{V}_g = -\frac{ze^2}{4\pi\epsilon_0 r_1} - \frac{ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

$$\hat{T} = -\frac{\hbar^2}{2m} \nabla_{R_1}^2 - \frac{\hbar^2}{2m} \nabla_{R_2}^2 - \frac{\hbar^2}{2M} \nabla_{R_0}^2$$



$$(\vec{R}_0, \vec{R}_1, \vec{R}_2) \longrightarrow (\vec{R}, \vec{r}_1, \vec{r}_2)$$

$$M\vec{R}_0 + m\vec{R}_1 + m\vec{R}_2 = (M+2m)\vec{R}$$

$$\begin{aligned}\vec{r}_1 &= \vec{R}_1 - \vec{R}_0 & \vec{r}_2 &= \vec{R}_2 - \vec{R}_0 \\ \downarrow & & \downarrow & \\ \vec{r}_1 &= \vec{r}_1 + \vec{R}_0 & \vec{r}_2 &= \vec{r}_2 + \vec{R}_0\end{aligned}$$

$$M\vec{R}_0 + m\vec{r}_1 + m\vec{r}_2 + 2m\vec{R}_0 = (M+2m)\vec{R}$$

$$(M+2m)\vec{R}_0 = (M+2m)\vec{R} - m(\vec{r}_1 + \vec{r}_2)$$

$$\Rightarrow \vec{R}_0 = \vec{R} - \frac{m}{(M+2m)}(\vec{r}_1 + \vec{r}_2)$$

$$\begin{aligned}\vec{R}_1 &= \vec{R}_0 + \vec{r}_1 = \vec{R} - \frac{m}{(M+2m)}(\vec{r}_1 + \vec{r}_2) + \frac{(M+2m)}{(M+2m)}\vec{r}_1 \\ &= \vec{R} + \frac{(M+2m)}{(M+2m)}(-m\vec{r}_1 - m\vec{r}_2 + M\vec{r}_1 + 2m\vec{r}_1)\end{aligned}$$

$$\vec{R}_1 = \vec{R} + \frac{(m+M)\vec{r}_1 - m\vec{r}_2}{(M+2m)}$$

$$\vec{R}_2 = \vec{r}_2 + \vec{R}_0 = \vec{R} + \frac{(m+M)\vec{r}_2 - m\vec{r}_1}{(M+2m)}$$

→ Wasn't really needed!

(3)

Since we are doing a  $(\vec{R}_0, \vec{r}_1, \vec{r}_2) \rightarrow (\vec{R}, \vec{r}_1, \vec{r}_2)$  transformation,  
we only need  $\vec{R}(\vec{R}_0, \vec{r}_i)$  and  $\vec{r}_i(\vec{R}_0, \vec{r}_i)$

$$\vec{R} = \frac{M\vec{R}_0 + m\vec{r}_1 + m\vec{r}_2}{(M+2m)} \quad \vec{r}_1 = \vec{R}_1 - \vec{R}_0 \quad \vec{r}_2 = \vec{R}_2 - \vec{R}_0$$

$$\Rightarrow X = \frac{MX_0 + mX_1 + mX_2}{(M+2m)} \quad x_1 = X_1 - X_0 \quad x_2 = X_2 - X_0$$

Now

$$\frac{\partial}{\partial X_0} = \frac{\partial}{\partial X} \frac{\partial X}{\partial X_0} + \frac{\partial}{\partial x_1} \frac{\partial x_1}{\partial X_0} + \frac{\partial}{\partial x_2} \frac{\partial x_2}{\partial X_0}$$

$$= \frac{M}{(M+2m)} \frac{\partial}{\partial X} - \frac{\partial}{\partial x_1} - \frac{\partial}{\partial x_2} \Rightarrow \vec{\nabla}_{R_0} = \frac{M}{M+2m} \vec{\nabla}_R - \vec{\nabla}_{r_1} - \vec{\nabla}_{r_2}$$

$$\frac{\partial}{\partial X_1} = \frac{m}{(M+2m)} \frac{\partial}{\partial X} + \frac{\partial}{\partial x_1} \Rightarrow \vec{\nabla}_{R_1} = \frac{m}{M+2m} \vec{\nabla}_R + \vec{\nabla}_{r_1}$$

$$\frac{\partial}{\partial X_2} = \frac{m}{(M+2m)} \frac{\partial}{\partial X} + \frac{\partial}{\partial x_2} \Rightarrow \vec{\nabla}_{R_2} = \frac{m}{M+2m} \vec{\nabla}_R + \vec{\nabla}_{r_2}$$

$$\bullet \nabla_{R_0}^2 = \left( \frac{M}{M+2m} \right)^2 \vec{\nabla}_R^2 + \vec{\nabla}_{r_1}^2 + \vec{\nabla}_{r_2}^2 - \frac{2M}{(M+2m)} \left[ \vec{\nabla}_R \cdot \vec{\nabla}_{r_1} + \vec{\nabla}_R \cdot \vec{\nabla}_{r_2} \right]$$

$$- 2 \vec{\nabla}_{r_1} \cdot \vec{\nabla}_{r_2}$$

$$\bullet \nabla_{R_1}^2 = \left( \frac{m}{M+2m} \right)^2 \vec{\nabla}_R^2 + \vec{\nabla}_{r_1}^2 + \frac{2m}{(M+2m)} \vec{\nabla}_R \cdot \vec{\nabla}_{r_1}$$

$$\bullet \nabla_{R_2}^2 = \left( \frac{m}{M+2m} \right)^2 \vec{\nabla}_R^2 + \vec{\nabla}_{r_2}^2 + \frac{2m}{(M+2m)} \vec{\nabla}_R \cdot \vec{\nabla}_{r_2}$$

$$\Rightarrow \hat{T} = -\frac{\hbar^2}{2M} \left( \frac{M^2}{(M+2m)^2} \nabla_R^2 + \nabla_{r_1}^2 + \nabla_{r_2}^2 - \frac{2M}{(M+2m)} \vec{\nabla}_R \cdot (\vec{\nabla}_{r_1} + \vec{\nabla}_{r_2}) - 2\vec{\nabla}_{r_1} \cdot \vec{\nabla}_{r_2} \right)$$

$$= -\frac{\hbar^2(M+2m)}{2(M+2m)^2} \nabla_R^2 - \frac{\hbar^2}{2} (\nabla_{r_1}^2 + \nabla_{r_2}^2) \underbrace{\left( \frac{1}{M} + \frac{1}{m} \right)}_{\frac{1}{\mu}} - \frac{\hbar^2}{M} \vec{\nabla}_{r_1} \cdot \vec{\nabla}_{r_2}$$

$$\Rightarrow \boxed{\hat{T} = \underbrace{-\frac{\hbar^2}{2(M+2m)} \nabla_R^2}_{\text{COM-part}} - \underbrace{\frac{\hbar^2}{2\mu} (\nabla_{r_1}^2 + \nabla_{r_2}^2)}_{r_1, r_2 \text{ part}} - \underbrace{\frac{\hbar^2}{M} \vec{\nabla}_{r_1} \cdot \vec{\nabla}_{r_2}}_{Y_\mu}}$$

Since we are using atomic units  $\hbar=1$  &  $\frac{e^2}{4\pi\epsilon_0} = 1$

$$\therefore \hat{T} = \underbrace{-\frac{\nabla^2}{2(M+2m)}}_{\text{COM-part}} - \underbrace{\frac{(\nabla_{r_1}^2 + \nabla_{r_2}^2)}{2\mu}}_{r_1, r_2 \text{ part}} - \underbrace{\frac{\vec{\nabla}_{r_1} \cdot \vec{\nabla}_{r_2}}{M}}_{Y_\mu}$$

$$\hat{V} = -\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

$\downarrow$   
makes KE non-separable.  
in  $\vec{r}_1$  and  $\vec{r}_2$

The energy eigenvalue eq<sup>n</sup>

$$\hat{H} \psi(\vec{R}, \vec{r}_1, \vec{r}_2) = E_{\text{tot}} \psi(\vec{R}, \vec{r}_1, \vec{r}_2)$$

$\downarrow$   
can be solved for separable wavefn  $\Phi(\vec{R}) \psi(\vec{r}_1, \vec{r}_2)$

Then for the COM co-ordinate, we can separate out the eq<sup>n</sup>

$$\boxed{-\frac{\nabla_R^2 \Phi(\vec{R})}{2(M+2m)} = E_{\text{COM}} \Phi(\vec{R})}$$

ONLY K.E. TERM  
like a free particle motion

For the relative co-ordinate  $(\vec{r}_1, \vec{r}_2)$ , the eq<sup>n</sup> is given by (5)

$$\left[ -\frac{1}{2\mu} (\nabla_{r_1}^2 + \nabla_{r_2}^2) - \frac{1}{M} \vec{\nabla}_{r_1} \cdot \vec{\nabla}_{r_2} + V(\vec{r}_1, \vec{r}_2) \right] \psi(\vec{r}_1, \vec{r}_2) = E_{\text{rel}} \psi(\vec{r}_1, \vec{r}_2)$$

However, now the wave fn can't be further separated due to interaction terms.

$$E_{\text{tot}} = E_{\text{rel}} + E_{\text{com}}$$

Now the actual problem to solve is the  $(\vec{r}_1, \vec{r}_2)$  energy eigenvalue eq<sup>n</sup>.

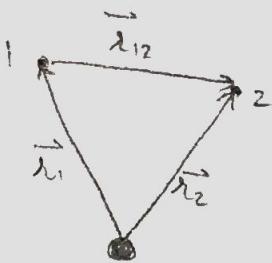
Now if we make the approximation that -

1st approximation  $M \rightarrow \infty \Rightarrow \frac{1}{M} \vec{\nabla}_{r_1} \cdot \vec{\nabla}_{r_2} \rightarrow 0$  and  $\mu \rightarrow m$

This simplifies the eq<sup>n</sup> greatly

$$-\left[ \frac{(\nabla_{r_1}^2 + \nabla_{r_2}^2)}{2m} + \frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{r_{12}} \right] \psi(\vec{r}_1, \vec{r}_2) = E_{\text{rel}} \psi(\vec{r}_1, \vec{r}_2)$$

Lecture - 2 (Independent Particle Model)



$$\vec{r}_{12} = |\vec{r}_1 - \vec{r}_2|$$

The eigenfs of the He atom problem can be either

- space symmetric
- space anti-symmetric

$$\psi_s(\vec{r}_1, \vec{r}_2) = \psi_s(\vec{r}_2, \vec{r}_1) \quad \text{symmetric (para states)}$$

$$\psi_A(\vec{r}_1, \vec{r}_2) = -\psi_A(\vec{r}_2, \vec{r}_1) \quad \text{anti-symmetric (ortho states)}$$

The Hamiltonian of the relative co-ords part in the He atom was approximated as

$$H = \underbrace{-\frac{\nabla_{r_1}^2}{2} - \frac{Z}{r_1} - \frac{\nabla_{r_2}^2}{2} - \frac{Z}{r_2}}_{\substack{\uparrow \text{Hydrogenic} \\ \text{Hamiltonian}}} + \underbrace{\frac{1}{r_{12}}}_{\substack{\downarrow \text{perturbation.}}}$$

2nd Approximation (very crude, only for the moment)

The contribution of perturbation  $\frac{1}{r_{12}}$  is very small.

This gives

$$H = h_1 + h_2$$

and we know how to solve for hydrogenic Hamiltonians

$$E = E_1 + E_2$$

For this Hamiltonian, we separate the wavefn  $\psi = \psi_1(\vec{r}_1) \psi_2(\vec{r}_2)$  (2)  
and we get the Hydrogenic solns

$$(h_1 + h_2)\psi_1 \psi_2 = (E_1 + E_2)\psi_1 \psi_2$$

$$\Rightarrow \hat{h}_1 \psi_{n_1 l_1 m_1} = E_{n_1} \psi_{n_1 l_1 m_1}$$

$$\text{and } \hat{h}_2 \psi_{n_2 l_2 m_2} = E_{n_2} \psi_{n_2 l_2 m_2} \quad \text{where } E = E_{n_1} + E_{n_2}$$

$$E_{n_1} = -\frac{Z^2}{2n_1^2} \quad E_{n_2} = -\frac{Z^2}{2n_2^2} \Rightarrow E = -\frac{Z^2}{2} \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right)$$

We'll call this the 0<sup>th</sup> order approximation

$$\begin{aligned} E^{(0)} &= -2 \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right) \\ (Z=2) \end{aligned}$$

For ground state  
( $n_1=1, n_2=1$ )

Is this allowed?

$e^-$ s are fermions, so  
they shouldn't be in the  
same state.

Allowed because we also have spin!

$$E_{1,1}^{(0)} = -4 \text{ a.u.} = -4 (13.6 \times 2) \text{ eV} = -\underline{\underline{108.8 \text{ eV}}}$$

0 eV	$\text{He}^{2+} + 2e^-$
-	-79 eV (experimental value)
-	-108.8 eV (from our approx.)

This model is known as independent particle model. The wavefn's are supposed to be symm. or antisymm. since switching  $\vec{r}_1$  &  $\vec{r}_2$  doesn't change the Energy eigenvalue eqn.

$$\text{so, } \psi_{\pm}^{(0)}(\vec{r}_1, \vec{r}_2) = \psi^{(0)}(\vec{r}_1, \vec{r}_2) - \psi^{(0)}(\vec{r}_2, \vec{r}_1)$$

$$= \psi_{n_1 l_1 m_1}^{(0)}(\vec{r}_1) \psi_{n_2 l_2 m_2}^{(0)}(\vec{r}_2) - \psi_{n_1 l_1 m_1}^{(0)}(\vec{r}_2) \psi_{n_2 l_2 m_2}^{(0)}(\vec{r}_1)$$

+ → Symm.  
- → Anti-symm.

For G.S.  $\psi_+^{(0)} = 2\psi_{100}(\vec{r}_1) \psi_{100}(\vec{r}_2)$  and  $\psi_-^{(0)} = 0$

# Lecture-3 (Introducing Spin)

(10/09)

Spatial wave function  $\begin{cases} \xrightarrow{\text{symmetric}} \\ \xrightarrow{\text{anti-symmetric}} \end{cases}$

$$\psi(\vec{r}_1, \vec{r}_2) \xrightarrow{\text{exchange}} \psi(\vec{r}_2, \vec{r}_1)$$

Since we are dealing with indistinguishable particles here

$$\psi(\vec{r}_2, \vec{r}_1) = e^{i\alpha} \psi(\vec{r}_1, \vec{r}_2)$$

exchanging again

$$\psi(\vec{r}_2, \vec{r}_1) = e^{2i\alpha} \psi(\vec{r}_1, \vec{r}_2) \Rightarrow \underline{e^{i\alpha} = \pm 1}$$

## Independent particle model

$$E_{n_1, n_2}^{(0)} = -2 \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right) \text{ a.u.}$$

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{n_1 l_1 m_1}(\vec{r}_1) \psi_{n_2 l_2 m_2}(\vec{r}_2) \pm \psi_{n_1 l_1 m_1}(\vec{r}_2) \psi_{n_2 l_2 m_2}(\vec{r}_1)$$

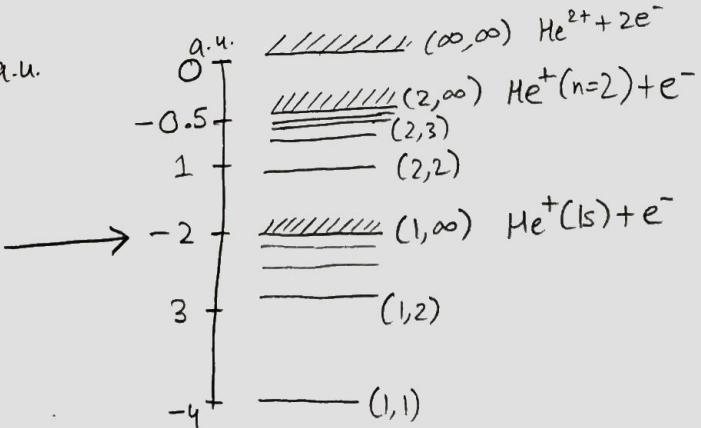
If  $n_i, l_i, m_i$  all are same for both  $e^-$ s, only the symmetric wavefn survives.

Let's say now that  $(n_1, l_1, m_1) = (1, 0, 0)$  and  $(n_2, l_2, m_2) = (n, l, m)$

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1) \psi_{nlm}(\vec{r}_2) \pm \psi_{100}(\vec{r}_2) \psi_{nlm}(\vec{r}_1)$$

$$E_{1, n}^{(0)} = -2 \left( 1 + \frac{1}{n^2} \right) \text{ a.u.}$$

INDEPENDENT PARTICLE  
MODEL SPECTRUM



(2)

Approximations made so far & possible corrections.

① the nucleus is infinitely heavy ( $M \rightarrow \infty$ )

$$\Rightarrow \lim_{M \rightarrow \infty} \mu = m \quad \lim_{M \rightarrow \infty} \frac{1}{M} \vec{\nabla}_1 \cdot \vec{\nabla}_2 = 0$$

(mass polarization)

Since  $E_\infty = -\frac{me^4}{4\pi^2 k^2 e^2 n^2}$ , i.e.  $E_\infty \propto m$

we can estimate the correction  $E_\mu = \frac{\mu}{m} E_\infty$  where  $\frac{\mu}{m} = 1 - \frac{m}{M} \Rightarrow 0 < \frac{\mu}{m} < 1$

This raises the energy levels! (since energies are  $< 0$ )

To account for correction in mass polarization term, we can use first order perturbation theory -

$$\Delta E_{mp} = -\frac{1}{M} \langle \Psi | \vec{\nabla}_1 \cdot \vec{\nabla}_2 | \Psi \rangle = -\frac{1}{M} \langle \Psi | \vec{p}_1 \cdot \vec{p}_2 | \Psi \rangle \\ = -\frac{1}{M} \langle \Psi_0^{(1)} | \vec{p}_1 | \Psi_0^{(1)} \rangle \circ \langle \Psi_0^{(2)} | \vec{p}_2 | \Psi_0^{(2)} \rangle$$

(for ground state,  $\langle \vec{p} \rangle = 0$  anyway)

② Our model is non-relativistic. Hence, we'd need to include relativistic corrections.

Introducing Spin in independent particle model.

$$\Psi = \psi(\vec{r}_1, \vec{r}_2) \chi(1, 2) \xrightarrow{\text{spin}}$$

For a single electron spin  $S = \frac{1}{2} \Rightarrow$  eigenvalues of  $S_z$   $m_S = \pm \frac{1}{2}$

But we have an addition of two spins here -

$$\vec{S} = \vec{S}_1 + \vec{S}_2$$

$$S_z \in \{ |S_1 - S_2|, \dots, |S_1 + S_2| \}$$

$$S_1, S_2 = \frac{1}{2}$$

$$m_s = m_1 + m_2$$

$$m_s \in \{ -S, \dots, S \}$$

So, for  $S_1 = S_2 = \frac{1}{2} \Rightarrow S \in \{ 0, 1 \}$

(3)

$$S=0 \Rightarrow m=0 \quad \text{SINGLET}$$

$$S=1 \Rightarrow m \in \{-1, 0, 1\} \quad \text{TRIPLET}$$

For triplet,  $m=1 \Rightarrow | \uparrow \uparrow \rangle$

$$m=-1 \Rightarrow | \downarrow \downarrow \rangle$$

$$m=0 \Rightarrow \frac{1}{\sqrt{2}} [ | \uparrow \downarrow \rangle + | \downarrow \uparrow \rangle ]$$

$$\text{For singlet} \Rightarrow \frac{1}{\sqrt{2}} [ | \uparrow \downarrow \rangle - | \downarrow \uparrow \rangle ]$$

You can find coeffs.  
using Clebsch-Gordan  
coeff. method

However, since we are dealing with fermions, the TOTAL WAVE FN  
must be anti-symmetric.

$\therefore$  If spatial part is symmetric  $\Psi_s$ , then we need to multiply by anti-symm.  
spin.  
(singlet)

If spatial part is anti-symm.  $\Psi_A$ , then need to multiply by symm. spin.  
(triplet)

$$\text{So } \underline{\Psi_s \cdot \frac{1}{\sqrt{2}} [ | \uparrow \downarrow \rangle - | \downarrow \uparrow \rangle ]} \text{ or } \underline{\Psi_A \cdot \begin{bmatrix} \text{triplet} \\ \text{states} \end{bmatrix}}$$

Therefore, we see in that some sense, Pauli exclusion principle couples  
the spatial d.o.f. with spin d.o.f.

The singlet states are also referred to as para states and triplet states as  
ortho states.

## Lecture - 4 (Pert. Theory on Ind. Particle model) (13/09)

In the last lecture, we introduced the spin wavefns.

$\chi \rightarrow$  singlet (AS)  
 $\chi \rightarrow$  triplet (S)

So, when we write the entire wavefn (which should be AS), it is

$$\Psi = \underbrace{\psi(r_1, r_2)}_{\text{Spatial}} \underbrace{\chi}_{\text{Spin}}$$

If  $\psi \rightarrow$  AS,  $\chi \rightarrow$  S  
 If  $\psi \rightarrow$  S,  $\chi \rightarrow$  AS

Then the ground state wavefn can be written as -

$$\Psi = \underbrace{\psi_{100}(r_1) \psi_{100}(r_2)}_{\text{Symmetric spatial part}} + \frac{1}{\sqrt{2}} [|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle]$$

antisymmetric spin part

Let's now discuss the wavefn and energies for excited states

$$E_{n_1, n_2} = -\frac{Z^2}{2} \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right)$$

	$n_1$	$n_2$	State
Ground	1	1	$(1s)^2$
First excited	1	2	$1s\ 2s$ and $1s\ 2p$

So,  $E_{1,2} = -2 \left( \frac{1}{1} + \frac{1}{4} \right) = -\frac{5}{2} = -2.5 \text{ au} = -6 \text{ eV}$

So, for first excited states are -

$$\Psi_{1,2}^{(\text{singlet})} = \frac{1}{\sqrt{2}} \left[ \psi_{100}(r_1) \psi_{2l_2m_2}(r_2) + \psi_{2l_2m_2}(r_1) \psi_{100}(r_2) \right] \chi_{s=0, m_s=0}$$

$$\Psi_{1,2}^{(\text{triplet})} = \frac{1}{\sqrt{2}} \left[ \psi_{100}(r_1) \psi_{2l_2m_2}(r_2) + \psi_{2l_2m_2}^{(r_1)} \psi_{100}(r_2) \right] \chi_{s=1, m_s}$$

(2)

Let's now improve our approximation by adding corrections to independent particle model.

$$\hat{H} = \hat{H}^{(0)} + \frac{1}{r_{12}} \xrightarrow{\text{perturbation (e-e repulsion term)}}$$

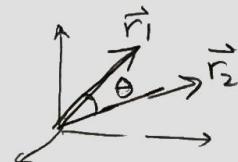
hydrogenic Hamiltonian  
for independent part. model

So, let's now use perturbation theory to find the energy corrections

$$E_0^{(1)} = \langle \Psi_g | \hat{H}' | \Psi_g \rangle \quad \text{where} \quad \Psi_g = \psi_{100}(r_1) \psi_{100}(r_2) \chi_{0,0}$$

$$= \frac{Z^3}{\pi} e^{-2Z(r_1+r_2)} \chi_{0,0}$$

$$\Rightarrow E_0^{(1)} = \int d\vec{r}_1 d\vec{r}_2 \underset{\substack{\parallel \\ 1}}{\langle \chi_{0,0} | \chi_{0,0} \rangle} \left( \frac{Z^3}{\pi} \right)^2 e^{-2Z(r_1+r_2)} \frac{1}{r_{12}}$$



$$\cos \theta = \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2)$$

One can write the expansion of  $\frac{1}{|\vec{r}_1 - \vec{r}_2|}$  using Yem's

$$= \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta}$$

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{\ell=0}^{\infty} \frac{(r_c)^\ell}{(r_s)^{\ell+1}} P_\ell(\cos \theta) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} \frac{4\pi}{2\ell+1} \frac{(r_c)^\ell}{(r_s)^{\ell+1}} Y_{em}^*(\theta_1, \phi_1) Y_{em}(\theta_2, \phi_2)$$

$$\Rightarrow E_0^{(1)} = \frac{Z^6}{\pi^2} \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} \frac{(4\pi)^2}{(2\ell+1)} \int dr_1 r_1^2 \int dr_2 r_2^2 e^{-2Z(r_1+r_2)} \frac{(r_c)^\ell}{(r_s)^{\ell+1}}$$

multiplied by  $4\pi (\chi_{0,0})^2 = 1$

$$\cdot \int d\Omega_1 \underbrace{Y_{em}^*(\theta_1, \phi_1) \chi_{0,0}}_{S_{\ell,0} S_{m,0}} \int d\Omega_2 \underbrace{\chi_{0,0} Y_{em}(\theta_2, \phi_2)}_{S_{\ell,0} S_{m,0}}$$

$$d^3r = r^2 \sin \theta dr d\theta d\phi$$

(3)

$\Rightarrow$  Only  $l=0, m=0$  term survives

$$\begin{aligned}
 E^{(0)} &= 16Z^5 \int_0^\infty dr_1 r_1^2 \int_0^\infty dr_2 r_2^2 e^{-2z(r_1+r_2)} \frac{1}{r_s} \\
 &= 16Z^5 \int_0^\infty dr_1 r_1^2 e^{-2zr_1} \left[ \frac{1}{r_s} \int_0^{r_1} dr_2 r_2^2 e^{-2zr_2} + \int_{r_1}^\infty dr_2 r_2^2 e^{-2zr_2} \right] \\
 &= \underline{\frac{5Z}{8} \text{ a.u.}}
 \end{aligned}$$

$$\Rightarrow E = E^{(0)} + E^{(1)} = -Z^2 + \frac{5}{8}Z = -2.75 \text{ a.u.} = -74.8 \text{ eV (for He)}$$

Important points:

$$\begin{aligned}
 \bullet \quad \frac{1}{|\vec{r}_1 - \vec{r}_2|} &= \sum_{l,m} \frac{4\pi}{2l+1} \frac{r_s l}{r_s^{l+1}} Y_{lm}^*(\theta_1, \phi_1) Y_{lm}(\theta_2, \phi_2) \quad \text{Addition}^m \\
 \Rightarrow \bullet \quad \int d^3r_1 \int d^3r_2 \frac{e^{-2z(r_1+r_2)}}{|\vec{r}_1 - \vec{r}_2|} &= \int dr_1 r_1^2 \int dr_2 r_2^2 e^{-2z(r_1+r_2)} \frac{1}{r_s} = \frac{5}{32 \cdot 4 \cdot Z^5}
 \end{aligned}$$

# Expectation values of KE & PE and Virial Theorem.

Kinetic energy operator  $\rightarrow -\frac{\nabla^2}{2}$

In spherical polar co-ordinates

$$-\frac{\nabla^2}{2} = -\frac{1}{2} \left[ \frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} \right] + \hat{O}(\theta, \phi)$$

Calculating exp. value of KE for ground state

$$\phi(r_1, r_2) = \frac{z^3}{\pi} e^{-2z(r_1+r_2)}$$

$$\begin{aligned} \langle \phi | -\frac{\nabla^2}{2} | \phi \rangle &= -\frac{1}{2} \underbrace{\int d^3 r_2 e^{-2zr_2} \frac{z^3}{\pi}}_{\text{from } \phi} \int d^3 r_1 e^{-2zr_1} \nabla_1^2 e^{-2zr_1} \cdot \frac{z^3}{\pi} \\ &= -\frac{1}{2} \int d^3 r_1 \frac{z^3}{\pi} e^{-2zr_1} \left( \frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} \right) e^{-2zr_1} = -\frac{1}{2} \int d^3 r_1 e^{-2zr_1} \left( z^2 - \frac{2z}{r_1} \right) \cdot \frac{z^3}{\pi} \\ &= -\frac{4\pi z^3}{2} \int dr_1 r_1^2 e^{-2zr_1} \left( z^2 - \frac{2z}{r_1} \right) \\ &= -2z^3 \left[ z^2 \int_0^\infty dr_1 r_1^2 e^{-2zr_1} - 2z \int_0^\infty dr_1 r_1 e^{-2zr_1} \right] \\ &= -2z^3 \left[ z^2 \cdot \frac{2}{(2z)^3} - 2z \cdot \frac{1}{(2z)^2} \right] = -2z^3 \left[ \frac{1}{4z} - \frac{1}{2z} \right] \\ &= +\frac{2z^2}{4} = \frac{z^2}{2} \quad (\text{which we use in Variational method}) \end{aligned}$$

$$\langle \phi | V_1 | \phi \rangle = -z \langle \phi | \frac{1}{r_1} | \phi \rangle = -z \left( \frac{z^3}{\pi} \right) \underbrace{4\pi \int dr_1 r_1^2 \frac{e^{-2zr_1}}{r_1}}_{V(2z)^2} = -\underline{\underline{z^2}}$$

Another way to get this Virial Theorem

$$2\langle T \rangle = \langle x \frac{\partial V}{\partial x} \rangle \Rightarrow \text{for } V(x) = \alpha x^s \Rightarrow 2\langle T \rangle = \underline{s\langle V \rangle}$$

$$\text{For } s = -1 \text{ (Coulomb potn)}, \langle T \rangle = -\frac{1}{2} \langle V \rangle$$

(1)

Lecture-5 (Variational Method on Ind-Particle model)  
(14/109)

Solving the Hydrogenic atom by Variational Method.

$$\langle \hat{H} \rangle = \langle \psi_{\text{trial}} | \hat{H} | \psi_{\text{trial}} \rangle \geq E_{\text{ground}}$$

$$\text{So, } H[\psi] \geq E_{\text{ground}}$$

One can usually decide upon a tunable parameter  $\alpha$  in the wavefunction s.t.  $\psi \equiv \psi(\alpha)$  where  $\alpha$  is a parameter.

The way we can prove the lower bound on  $H[\psi]$  is

$$|\psi\rangle = \sum_i c_i |\psi_i\rangle \Rightarrow \langle \hat{H} \rangle_\psi = \sum_i |c_i|^2 E_i \geq \sum_i |c_i|^2 E_0 = E_0$$

$$\therefore \langle \hat{H} \rangle_\psi = \langle \psi | \hat{H} | \psi \rangle \geq E_0$$

Let's apply this to the He atom problem

$$\phi(\vec{r}_1, \vec{r}_2) = \frac{Z_{\text{eff}}^3}{\pi} e^{-Z_{\text{eff}}(r_1 + r_2)}$$

Now the Hamiltonian is given by

$$H = T_1 + T_2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

$$Z_{\text{eff}} = Z - \frac{S}{\text{shielding}}$$

$$\langle \phi | T_1 | \phi \rangle = \frac{Z_{\text{eff}}^2}{2} \quad \langle \phi | \frac{1}{r_{12}} | \phi \rangle = \frac{5}{8} Z_{\text{eff}}$$

$$\langle \phi | \frac{1}{r_1} | \phi \rangle = Z_{\text{eff}}$$

$$E[\phi] = Z_{\text{eff}}^2 - 2Z Z_{\text{eff}} + \frac{5}{8} Z_{\text{eff}}$$

$$\frac{\partial E}{\partial Z_{\text{eff}}} = 0 \Rightarrow Z_{\text{eff}}^* = \underbrace{(Z - 5/16)}_{\text{screening const.}}$$

and we can show that  $\frac{\partial^2 E}{\partial Z_{\text{eff}}^2} \Big|_{Z_{\text{eff}}^*} > 0$

→ How?

(2)

$$\therefore E(z_{\text{eff}}^*) = -\left(Z - \frac{5}{16}\right)^2 \text{ a.u.}$$

So, comparing our results, the ground state energies are as follows -

- Independent particle model  $E_0 = -\frac{Z^2}{2} \left(\frac{1}{\pi} + \frac{1}{\pi}\right) = -\frac{Z^2}{2}$
- Variational method approach  $E_0 = -\left(Z - \frac{5}{16}\right)^2$
- Perturbation theory  $E_0 = -Z^2 + \frac{5Z}{8}$

## Lecture-6 (Higher excited states)

(16/09)

### Excited states of He atom:

One  $e^-$  is in the ground state, and the second  $e^-$  has  $n_2 > 1$ .  
 $(n_1 = 1)$

The spatial wavefn in the case of excited states can be both symmetric or antisymmetric

$$\Psi_{\pm}^{(0)}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \left[ \psi_{100}(r_1) \psi_{nem}(r_2) \pm \psi_{100}(r_2) \psi_{nem}(r_1) \right]$$

$$E_{1,n}^{(0)} = -\frac{Z^2}{2} \left[ 1 + \frac{1}{n^2} \right] \quad \text{degenerate in } l \text{ & } m.$$

Exchange degeneracy:  $\Psi_+$  and  $\Psi_-$  states have the same energy.

Perturbation term is given by  $H' = \frac{1}{r_{12}}$

$$\text{So, } \delta E_{\pm}^{(1)} = \langle \Psi_{\pm}^{(0)} | H' | \Psi_{\pm}^{(0)} \rangle = J \pm K$$

$$J = \int d^3 r_1 d^3 r_2 |\psi_{100}(r_1)|^2 \frac{1}{r_{12}} |\psi_{nem}(r_2)|^2 \leftarrow \text{Coulomb integral}$$

$$K = \int \psi_{100}^*(r_1) \psi_{nem}^*(r_2) \frac{1}{r_{12}} \psi_{100}(r_2) \psi_{nem}(r_1) d^3 r_1 d^3 r_2 \uparrow \text{Exchange integral.}$$

how?  $J > 0, K > 0$  part independent of spin.

$$K = -\frac{1}{2} (1 + 4 \vec{S}_1 \cdot \vec{S}_2) K_{ne} \quad \vec{S}_1 \cdot \vec{S}_2 = \frac{1}{2} \vec{s}^2 - \frac{3}{4} = \frac{s(s+1)}{2} - \frac{3}{4}$$

$\psi_+ \leftrightarrow$  Spin singlet state ( $s=0$ )  $\Rightarrow \vec{S}_1 \cdot \vec{S}_2 = -\frac{3}{4}, K = +K_{ne}$

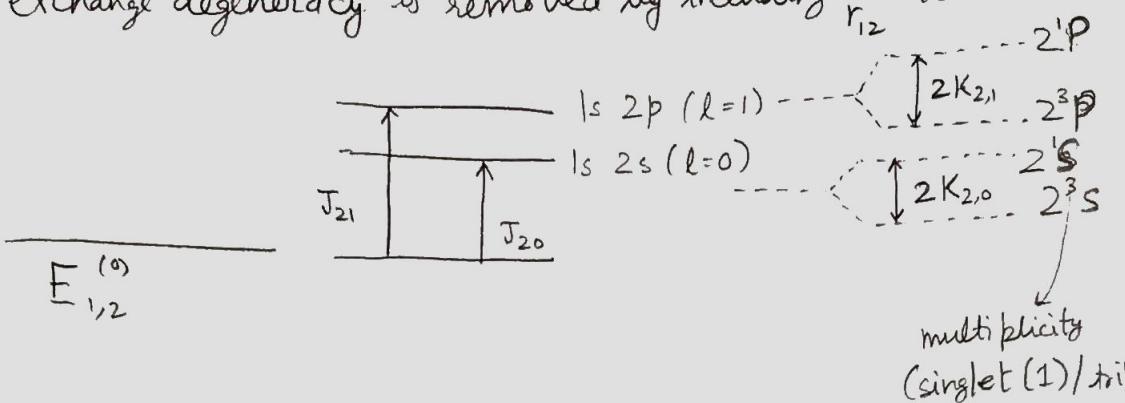
$\psi_- \leftrightarrow$  Spin triplet state ( $s=1$ )  $\Rightarrow \vec{S}_1 \cdot \vec{S}_2 = \frac{1}{4}, K = -K_{ne}$

$$\underline{\psi_+, \delta E_+^{(1)} = J + K_{ne}} \quad \text{and for } \underline{\psi_-, \delta E_-^{(1)} = J - K_{ne}}$$

(2)

Exchange integral gives rise to the exchange force in fermions.

The exchange degeneracy is removed by including  $\frac{1}{r_{12}}$  term.



Ques Is the effect of the exchange force (the K integral) more for small values of n and l. Why? ( $K_{nl} \propto \frac{1}{2l+1}$  ← which appears by expanding  $|\vec{r}_1 - \vec{r}_2|$  in terms of  $Y_{lm}$ )

shielding of nuclear charge:

Considering shielding of charge by  $e_2^-$  on  $e_1^-$  (in 1s)

$$P_{\text{charge}} = -e \Psi_{2(1s)}^* \Psi_{2(1s)}$$

$$\text{Pot}^n \text{ energy of } e_1 \Rightarrow V_{\text{eff}}(r_1) = -\frac{Ze^2}{4\pi\epsilon_0 r_1} + \int (-e)(-e \Psi_{2(1s)}^* \Psi_{2(1s)}) \frac{d^3 r_2}{4\pi G r_{12}}$$

$$\Psi_{1s} = \left(\frac{Z}{\pi}\right)^{1/2} e^{-Zr_1}$$

$$\Rightarrow \text{In atomic units } V_{\text{eff}}(r_1) = -\left(\frac{Z}{r_1} - \int d^3 r_2 \frac{\Psi_{2(1s)}^* \Psi_{2(1s)}}{r_{12}}\right)$$

$$\begin{aligned} \int d^3 r_2 \frac{\Psi_{2(1s)}^* \Psi_{2(1s)}}{|\vec{r}_1 - \vec{r}_2|} &= \frac{Z^3}{\pi} \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} Y_{lm}^*(\theta_1, \phi_1) \int d r_2 r_2^2 \frac{l}{r_2^{l+1}} e^{-2Zr_2} \int d\Omega_2 Y_{lm} \cdot \frac{Y_{lm}}{Y_{00}} \\ &= \frac{Z^3}{\pi} 4\pi \left[ \int_0^r dr_2 e^{-2Zr_2} \frac{r_2^2}{r_1} + \int_r^\infty dr_2 e^{-2Zr_2} \frac{1}{r_2} \right] \end{aligned}$$

$$4\pi \underbrace{\delta_{l0} \delta_{m0}}_{\delta_{00}}$$

CHECK  $\Rightarrow V_{\text{eff}}(r_1) = -\left[\frac{Z-1}{r_1} + \left(Z + \frac{1}{r_1}\right) e^{-2Zr_1}\right]$

In  $\lim r \rightarrow \infty$   $V_{\text{eff}} \sim -\frac{(Z-1)}{r_1}$  due to complete shielding

&  $\lim_{r \rightarrow 0} V_{\text{eff}} \sim -\frac{Z}{r_1}$

(1)

## Lecture-8 (Multi-Electron Systems)

(20/09)

### Multi-electron systems.

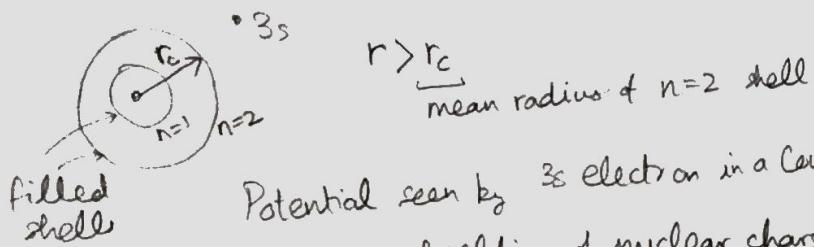
- " $\text{Na} \rightarrow 2, 8, 1$ "  
 $\underbrace{1s \quad 2s 2p}_{\text{filled}} \quad 3s \rightarrow \text{valence}$

Average electron distribution for filled shells spherically symmetric

C.t.  $L_{\text{total}} = 0$  and  $S_{\text{total}} = 0$

The  $3s$  electron moves in a spherically symmetric potential.

( $+Ze$  nucleus +  $-(z-1)e$  core electrons)



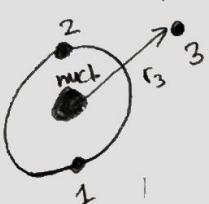
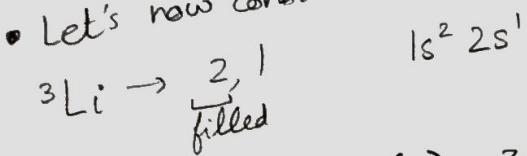
Potential seen by  $3s$  electron in a Coulomb potential, almost complete shielding of nuclear charge  $\Rightarrow Z_{\text{eff}}(r) \approx 1e$

However for  $r < r_c$ , the effective charge is a  $f^n$  of  $r$

$$\lim_{r \rightarrow 0} \phi_{3s}(r) \approx \frac{Ze^2}{r} \quad \text{and} \quad \lim_{r \rightarrow \infty} \phi_{3s}(r) \approx \frac{e^2}{r} \quad (\text{set } e=1)$$

Potential energy =  $-e\phi$

Let's now consider the Li atom with 3 electrons (Refer Demtroder)



$$V_{\text{eff}}(r_3) = -\frac{Ze^2}{r_3} + e^2 \left[ \frac{\int d\tau_1 |\Psi_{1(1s)}(r_1)|^2}{r_{31}} + \frac{\int d\tau_2 |\Psi_{2(2s)}(r_2)|^2}{r_{32}} \right]$$

nuclear.

how did we get this term?

$$P_{\text{charge}} = -e |\Psi_{i(1s)}|^2 \Rightarrow V_{\text{shield}(i)} = \int \frac{P_i}{r_{3i}} d\tau_i$$

Since  $\psi_{1s} = \left(\frac{Z_{\text{eff}}^3}{\pi}\right)^{1/2} e^{-Z_{\text{eff}}r}$  (2)  
 $Z_{\text{eff}} < 3$  (due to shielding)

$\Rightarrow \phi_{2s}(r) = \frac{e}{r} \left( 1 + 2 e^{-2Z_{\text{eff}}r/a_0} \left( \frac{r \cdot Z_{\text{eff}}}{a_0} + 1 \right) \right)$  Problem  
6.2  
Demtroder.  
 shielded pot

Variational Method applied to excited states. ( $n_1=1, n_2>1$ )

Consider the state  $\overset{2^3 S}{\underset{n}{\uparrow}} \xrightarrow{\text{multiplicity (spin)}} n_1=1, n_2=2 (l=0)$

The triplet spin represents symmetric spin wavefn.

$\Rightarrow$  spatial part of wavefn  $\rightarrow$  anti-symmetric

$$\phi_{2^3s}(r_1, r_2) = N \left[ U_{1s}(r_1) V_{2s}(r_2) - U_{1s}(r_2) V_{2s}(r_1) \right]$$

$$U_{1s} \propto e^{-Z_i r}$$

$Z_i \rightarrow$  Zinner

$$V_{2s} \propto \left( 1 - \frac{Z_0 r}{2} \right) e^{-Z_0 r/2}$$

$Z_0 \rightarrow$  Zouter

$\langle E \rangle (Z_i, Z_o) =$  expectation value of  $E$  w.r.t. variable parameters  
 for wavefn  $\phi_{2^3s}$

Using variational method, we can check that for the given  
 wavefn,  $Z_i$  and  $Z_o$  are optimized to be  $Z_i = 2.01$  &  $Z_o = 1.53$

$$Z_{\text{eff}} \equiv Z - S$$

# Lecture-9 (Central Field Approx.)

(21/09)

Refer Bransden

(Notation)

Term value:

$$T = \frac{E}{hc}$$

If we have a transition b/w levels  $|i\rangle \rightarrow |k\rangle$

$$\bar{\nu} = T_i - T_k \quad \longrightarrow \text{wavenumber in } \text{cm}^{-1}$$

$$1 \text{ eV} = 8065.541 \text{ cm}^{-1}$$

## Multi-Electron systems. (contd.)

Let's first start with an observation:

For H-atom (coulomb pot<sup>n</sup> problem), for same  $n$  and different  $l$ , we have the same energy and a heavy dose of degeneracy exists for  $l \& m$ . No other spherically symmetric pot<sup>n</sup> has this property. (no degeneracy in  $m$  exists for other spherical symm. pot<sup>n</sup>s).

## CENTRAL FIELD APPROXIMATION

Let's review the idea of effective potentials due to shielding. The Hamiltonian can be written as-

$$H = \sum_{i=1}^N \left( -\frac{\nabla_i^2}{2} - \frac{Z}{r_i} \right) + \sum_{i \neq j} \frac{1}{r_{ij}}$$

since the Hamiltonian isn't separable, the eigenvalue  $\epsilon g^n$  also isn't.

$$\Rightarrow \hat{H} \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = E \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \quad \text{IGNORING SPIN}$$

For He atom ( $N=2$ ), the  $\frac{1}{r_{12}}$  can be treated as a perturbation.

However, for a multi- $e^-$  system, there is a cumulative effect of a lot of interaction terms. (we'll have  $\frac{n(n-1)}{2}$  terms).

The perturbation theory method won't work here because  $\sum_{i \neq j} \frac{1}{r_{ij}}$  might be significant enough.

So, we want to investigate a way to

$$\sum_{i \neq j} \frac{1}{r_{ij}} \longrightarrow \text{find the average effect of these terms!}$$

Central field Approximation comes to the rescue.

The effect of  $(N-1)$  electrons on the  $N^{\text{th}}$  electron can be given by

$$V(r_i) = -\frac{Z}{r_i} + \underbrace{S(r_i)}_{\substack{\text{average contribution} \\ \text{due to other } e^-}} \quad (\text{for each } e^-)$$

So, we can write the central field approximated Hamiltonian as

$$H_C = \sum_{i=1}^N \left[ -\frac{\nabla_i^2}{2} - \frac{Z}{r_i} + S(r_i) \right] = \sum_{i=1}^N H_C^{(i)}$$

This will allow us to write a separable eigenvalue eq" for  $\hat{H}_C = \sum_{i=1}^N \hat{H}_C^{(i)}$

spherically  
symmetric  
pot"

$$\left[ -\frac{\nabla_i^2}{2} + V(r_i) \right] U_{nlm_i}(\vec{r}_i) = E_{nl} U_{nlm_i}(\vec{r}_i)$$

Hence, we use separation of variables to do  $U_{nlm_i} = R_{nl}(r) Y_{lm_i}(\theta, \phi)$

(3)

This results in the radial & angular eq's - not Coulombic

$$\left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} + V(r) \right] R_{nl}(r) = E_{nl} R_{nl}(r)$$

However, the angular part has no pot<sup>n</sup>, so it's the same as for the H-atom (Coulomb pot<sup>n</sup>) problem.

$$\Rightarrow Y_{lm}(\theta, \phi) = \text{spherical Harmonics}$$

The potential  $V(r) = -\frac{Z}{r} + S(r)$  has a Coulombic part +  $\underbrace{S(r)}$   
↑  
can be thought of  
as the shielding  
fn.

which is what makes it different from H-atom problem.  
 For i<sup>th</sup> electron is  $E_{ni} l_i$ , so the total energy in Cf. approx is -

$$E_C = \sum_i E_{ni} l_i \quad \text{where} \quad \begin{array}{l} n=1, 2, 3, \dots \\ l=0, 1, 2, \dots, n-1 \\ m=-l, \dots, l \end{array}$$

Note that degeneracy in l is lifted, but exchange degeneracy still exists since we haven't talked about spin yet.

Form of  $S(r)$ ?  $\rightarrow$  not determined yet.

The effective pot<sup>n</sup> is given by  $V(r_i) = -\frac{Z}{r_i} + S(r_i)$

$$\begin{aligned} \text{As we've seen, } r_i \rightarrow 0 \Rightarrow V(r_i) \approx -\frac{Z}{r_i} \\ r_i \rightarrow \infty \Rightarrow V(r_i) \approx -\frac{Z-(N-1)}{r_i} \end{aligned} \quad \left. \begin{array}{l} \text{asymptotic behaviour} \\ \text{no. of } e^- \end{array} \right]$$

$$\begin{aligned} S=0 &\text{ in } \lim r \rightarrow \infty \\ S=N-1 &\text{ in } \lim r \rightarrow 0 \end{aligned}$$

For neutral atoms,  $N=Z$

$$Z_{\text{eff}} \equiv Z - S$$

The real problem is the evaluation for intermediate distances.

(4)

Shielding of charge distribution in He atom.

$$\begin{array}{c} \text{1} \\ \text{2} \\ \text{Nucleus} \end{array} \quad Q_{\text{eff}} = (Z - S) e \quad 0 \leq S \leq 1$$

↑  
charge dist.  
due to shielding

If we consider the shielding of charge by  $e^-_2$  on  $e^-_1$  is given -  
(in 1s)

$$P_{\text{charge}} = -e \psi_{2(1s)}^* \psi_{2(1s)}$$

$$\Rightarrow \text{Pot^n energy of } e^-_1 \text{ is } V_{\text{eff}}(r_1) = - \left( \frac{Z}{r_1} - \int d^3 r_2 \frac{\psi_{2(1s)}^* \psi_{2(1s)}}{|r_1 - r_2|} \right)$$

$$\psi_{1s} = \left( \frac{Z^3}{\pi} \right)^{1/2} e^{-Zr_2} \Rightarrow \int d^3 r_2 \left( \frac{Z^3}{\pi} \right) \frac{e^{-2Zr_2}}{|r_1 - r_2|}$$

$$\frac{1}{|r_1 - r_2|} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} \frac{4\pi}{2\ell+1} \frac{r_2^\ell}{r_2^{\ell+1}} Y_{\ell m}^*(\theta_1, \phi_1) Y_{\ell m}(\theta_2, \phi_2)$$

$$d^3 r_2 = \int dr_2 r_2^2 d\theta_2 d\phi_2 \sin\theta_2$$

$$I = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{(4\pi)^2}{2\ell+1} Y_{\ell m}^*(\theta_1, \phi_1) \int dr_2 r_2^2 \frac{r_2^\ell}{r_2^{\ell+1}} e^{-2Zr_2} \underbrace{\int d\Omega_2 Y_{\ell m}}_{S_{\ell m}}$$

$$= m \frac{(4\pi)^{3/2}}{r_1} Y_{00}^*(\theta_1, \phi_1) \int dr_2 r_2^2 \frac{1}{r_2} e^{-2Zr_2}$$

$$= 4\pi \left[ \int_0^{r_1} \frac{r_2^2}{r_1} e^{-2Zr_2} + \int_{r_1}^{\infty} r_2 e^{-2Zr_2} \right]$$

(2)

### Assignment - 0

$$1. (a) [L_3, r^2] \quad (b) [L_3, p^2]$$

$$r^2 = x_1^2 + x_2^2 + x_3^2$$

$$p^2 = p_1^2 + p_2^2 + p_3^2$$

$$[A, BC] = [A, B]C + B[A, C]$$

$$L_i = (\vec{r} \times \vec{p})_i \Rightarrow L_i = \epsilon_{ijk} r_j p_k$$

$$L_3 = r_1 p_2 - r_2 p_1 = x_1 p_2 - x_2 p_1$$

$$(a) [x p_y, x^2] + [x p_y, y^2] + [x p_y, z^2] - [y p_x, x^2] - [y p_x, y^2] \\ - [y p_x, z^2]$$

$$= [x p_y, x x] - [y p_x, y y] + [x p_y, y^2] - [y p_x, x^2]$$

$$(b) [x p_y, p^2] - [y p_x, p^2] = [x p_y, p_x^2] + [x p_y, p_y^2] - [y p_x, p_x^2] \\ - [y p_x, p_y^2]$$

$$2. \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$3. L^2 Y_{lm} = l(l+1) Y_{lm}$$

$$4. \psi_{1s} = \left(\frac{z^3}{\pi}\right)^{1/2} e^{-zr} \quad \text{Most probable distance? Max of radial pdf}$$

$$\text{Prob. density} = |\psi_{1s}|^2 = \frac{z^3}{\pi} e^{-2zr}$$

$$\text{Probability of finding electron b/w } r \text{ & } r+dr = \int_0^{2\pi} \int_0^\pi d\Omega \int_r^{r+dr} dr' r'^2 \frac{z^3}{\pi} e^{-2zr'} \frac{e^{-2zr}}{\pi}$$

$$= 4\pi \frac{z^3}{\pi} e^{-2zr} r^2 dr$$

$$\Rightarrow \rho(r) = 4z^3 e^{-2zr} r^2$$

$$\frac{\partial \rho}{\partial r} = 2re^{-2zr} - 2zr^2 e^{-2zr} = 0 \Rightarrow 2r = zr^2$$

$$\boxed{r = \frac{1}{z}}$$

5. two spin half particles.

(3)

$$\vec{S} = \vec{S}_1 + \vec{S}_2$$

$$S_1^z \psi_{s,m} = s(s+1) \psi_{s,m}$$

$$S_1^{(z)} \psi_{s,m} = m_s \psi_{s,m}$$

$$S \in \{ |s_1 - s_2|, \dots, |s_1 + s_2| \}$$

$$m_s \in \{-s, \dots, s\}$$

$$s_1 = \frac{1}{2}, s_2 = \frac{1}{2}$$

$$S \in \{0, 1\} \quad m_s \in \{-1, 0, 1\} \quad (\text{for } s=1)$$

$$m_s = 0 \quad (\text{for } s=0)$$

for  $s=0$

$$\Psi = \alpha |1\uparrow\downarrow\rangle + \beta |1\downarrow\uparrow\rangle$$

$$(m=0)$$

for  $s=1$

$$\Psi = |1\uparrow\uparrow\rangle \quad m_s = 1$$

$$\Psi = |1\downarrow\downarrow\rangle \quad m_s = -1$$

$$\Psi = \gamma |1\uparrow\downarrow\rangle + \delta |1\downarrow\uparrow\rangle \quad m_s = 0$$

$\alpha, \beta, \gamma, \delta$  to be determined via C-G coeff method.

### Assignment - 1

1. Independent particle model  $\Psi_g = \psi_{100}(r_1) \psi_{100}(r_2)$

symmetric  
spatial wavefn.

$$E_{n_1, n_2} = -\frac{Z_{eff}^2}{2} \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right)$$

$$\Delta E_{ionization} = + Z_{eff}^2 = 2.9$$

$$E_{1,1} = -\frac{Z_{eff}^2}{2} (1+1) = -Z_{eff}^2$$

$$Z_{eff} \approx 1.7$$

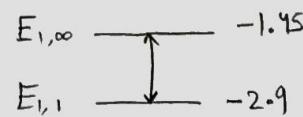
$$E_{ionized(2+)} = E_{\infty, \infty} = -\frac{Z_{eff}^2}{2} \left( \frac{1}{\infty} + \frac{1}{\infty} \right) = 0$$

$$\Rightarrow Z - S = 1.7$$

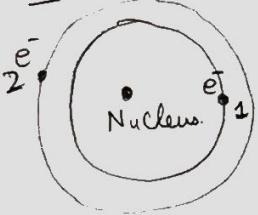
$$\text{so, } S \approx 2 - 1.7 = \underline{\underline{0.3}}$$

$$\Rightarrow E_{1,\infty} = -\frac{Z_{eff}^2}{2} \left( \frac{1}{\infty} + \frac{1}{1} \right) = -\frac{Z_{eff}^2}{2} = -\frac{2.9}{2} = -1.45 \quad E_{\infty, \infty} = 0$$

$$\Delta E_{ionization} (1,1 \rightarrow 1,\infty) = \underline{\underline{1.45}} \text{ a.u.}$$



2.



If screening is max. i.e.  $S = N - 1 = Z - 1$  (for neutral atoms) (4)

$$\text{then } Z_{\text{eff}} = Z - (Z - 1) = 1$$

$$E_{n_1, n_2} = -\frac{Z_{\text{eff}}^2}{2} \left( \frac{1}{n_1} + \frac{1}{n_2} \right) = -\frac{1}{2} \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right)$$

$$\text{In this case, } E_{1,1} = -\frac{1}{2} (1+1) = -1 \text{ a.u.}$$

$$E_{1,\infty} = -\frac{1}{2} (1+\frac{1}{\infty}) = -\frac{1}{2} \text{ a.u.}$$

$$\Rightarrow \Delta E_{\text{ionization}} = \frac{1}{2} \text{ a.u.}$$

3. we have three orthogonal states  $\langle \psi_i | \psi_j \rangle = \delta_{ij} \quad i, j \in \{a, b, c\}$

If the particles are distinguishable, then the wavefn is a product of all  $\psi_i$ 's

$$\underline{\Psi} = \underline{\psi_a(\vec{r}_1)} \underline{\psi_b(\vec{r}_2)} \underline{\psi_c(\vec{r}_3)}$$

For fermions, the state needs to be anti-symm. under  $\vec{r}_i \leftrightarrow \vec{r}_j$  exchange.

$$\Psi = \begin{vmatrix} \psi_a(\vec{r}_1) & \psi_b(\vec{r}_1) & \psi_c(\vec{r}_1) \\ \psi_a(\vec{r}_2) & \psi_b(\vec{r}_2) & \psi_c(\vec{r}_2) \\ \psi_a(\vec{r}_3) & \psi_b(\vec{r}_3) & \psi_c(\vec{r}_3) \end{vmatrix} = \psi_a(\vec{r}_1) (\psi_b(\vec{r}_2) \psi_c(\vec{r}_3) - \psi_b(\vec{r}_3) \psi_c(\vec{r}_2)) + \psi_b(\vec{r}_1) (\psi_a(\vec{r}_3) \psi_c(\vec{r}_2) - \psi_a(\vec{r}_2) \psi_c(\vec{r}_3)) + \psi_c(\vec{r}_1) (\psi_a(\vec{r}_2) \psi_b(\vec{r}_3) - \psi_a(\vec{r}_3) \psi_b(\vec{r}_2))$$

$$\underline{\Psi}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \sum_{i,j,k \in \{a,b,c\}} \epsilon_{ijk} \psi_i(\vec{r}_1) \psi_j(\vec{r}_2) \psi_k(\vec{r}_3)$$

4.



$$\langle \psi_n | \psi_m \rangle = 0$$

(5)

For distinguishable particles

$$\Psi = \psi_n(x_1) \psi_m(x_2)$$

For fermions

$$\Psi = \psi_n(x_1) \psi_m(x_2) - \psi_n(x_2) \psi_m(x_1)$$

D)  $\langle \Psi | \hat{x}_1 - \hat{x}_2 | \Psi \rangle = \langle \psi_n | \langle \psi_m |_{\hat{x}_2} (\hat{x}_1 - \hat{x}_2) | \psi_n \rangle | \psi_m \rangle_2$

$$= \langle \psi_n | \hat{x}_1 | \psi_n \rangle \langle \psi_m | \psi_m \rangle - \langle \psi_n | \psi_n \rangle \langle \psi_m | \hat{x}_2 | \psi_m \rangle$$

$$= \langle \psi_n | \hat{x}_1 | \psi_n \rangle - \langle \psi_m | \hat{x}_2 | \psi_m \rangle$$

$$\langle x | \psi_n \rangle = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

$$\langle \psi_n | \hat{x}_1 | \psi_n \rangle = \frac{2}{a} \int_0^a dx \sin^2\left(\frac{n\pi x}{a}\right)x = -\frac{a(1-2\pi^2 n^2 - 1)}{4\pi^2 n^2} = \frac{a}{2}$$

$$\Rightarrow (\langle \hat{x}_1 - \hat{x}_2 \rangle)^2 = 0$$

F)  $\langle \Psi | \hat{x}_1 - \hat{x}_2 | \Psi \rangle = (\langle \psi_n |_{\hat{x}_1} \langle \psi_m |_{\hat{x}_2} - \langle \psi_m |_{\hat{x}_1} \langle \psi_n |_{\hat{x}_2}) (\hat{x}_1 - \hat{x}_2)$   
 $\circ (|\psi_n\rangle_1 |\psi_m\rangle_2 - |\psi_m\rangle_1 |\psi_n\rangle_2)$

$$= \langle \psi_n | \hat{x}_1 | \psi_n \rangle + \langle \psi_m | \hat{x}_1 | \psi_m \rangle - \langle \psi_n | \hat{x}_2 | \psi_n \rangle + \langle \psi_m | \hat{x}_2 | \psi_m \rangle$$

$$= \frac{a}{2} + \frac{a}{2} - \frac{a}{2} - \frac{a}{2} = 0$$

$$\Rightarrow \langle (x_1 - x_2)^2 \rangle = 0$$

$$5. \quad \Psi_g = \psi_{100}(r_1) \psi_{100}(r_2) = \frac{Z^3}{\pi} e^{-Z(r_1+r_2)}$$

$$\langle \Psi_g | \frac{1}{|\vec{r}_1 - \vec{r}_2|} | \Psi_g \rangle = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} \left(\frac{Z^3}{\pi}\right)^2 \int d^3 r_1 \int d^3 r_2 \frac{r_1^l}{r_2^{l+1}} \exp \frac{Y_{lm}^*(\Theta_1, \Phi_1) Y_{lm}(\Theta_2, \Phi_2)}{r_1 r_2}$$

$$= \frac{Z^6}{\pi^2} \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{(4\pi)^2}{(2l+1)} \underbrace{\int d\Omega_1 Y_{00}^* Y_{lm} \int d\Omega_2 Y_{00} Y_{lm}}_{\delta_{l0} \delta_{m0}} \cdot \int dr_2 r_2^{2l} \int dr_1 r_1^{2l} \frac{r_1^l}{r_2^{l+1}} \exp$$

$$= \frac{Z^6}{\pi^2} (4\pi)^2 \int_0^\infty dr_1 r_1^2 \int_0^\infty dr_2 r_2^2 \frac{1}{r_1 r_2} \exp(-2z(r_1 + r_2))$$

$$= 16Z^2 \left[ \int_0^\infty dr_1 r_1^2 \left( \frac{1}{r_1} \int_0^{r_1} dr_2 r_2^2 e^{-2zr_2} + \int_{r_1}^\infty dr_2 r_2 e^{-2zr_2} \right) e^{-2zr_1} \right]$$

$$\bullet \frac{1}{r_1} \int_0^{r_1} dr_2 r_2^2 e^{-2zr_2} + \int_{r_1}^\infty dr_2 r_2 e^{-2zr_2}$$

$$= \frac{1}{r_1} \left( \frac{2}{z^3} - \left( \frac{z^2 r_1^2 + 2zr_1 + 2}{z^3} \right) e^{-2zr_1} \right) + \frac{(zr_1 + 1) e^{-2zr_1}}{z^2}$$

$$= \frac{2}{z^3 r_1} - \left( \frac{r_1}{z^2} + \frac{1}{z^2} + \frac{2}{z^3 r_1} \right) e^{-2zr_1} + \left( \frac{r_1}{z^2} + \frac{1}{z^2} \right) e^{-2zr_1}$$

$$= \frac{2}{z^3 r_1} - \left( \frac{1}{z^2} + \frac{2}{z^3 r_1} \right) e^{-2zr_1} = \frac{2}{z^3 r_1} (1 - e^{-2zr_1}) - \frac{e^{-2zr_1}}{z^2}$$

$$I = 16Z^2 \left[ \frac{2}{z^3} \int_0^\infty dr_1 (1 - e^{-2zr_1}) r_1 - \int_0^\infty dr_1 \frac{e^{-2zr_1}}{z^2} r_1^2 \right] \text{ divergent}$$


7.  $\Psi_g = \psi_{100}(r_1) \psi_{100}(r_2)$

$$\langle \psi_g |_1 \langle \psi_g |_2 (r_1^2 + r_2^2) | \psi_g \rangle_1 | \psi_g \rangle_2 = \langle \psi_g |_1 | r_1^2 | \psi_g \rangle_1 + \langle \psi_g |_2 | r_2^2 | \psi_g \rangle_2$$

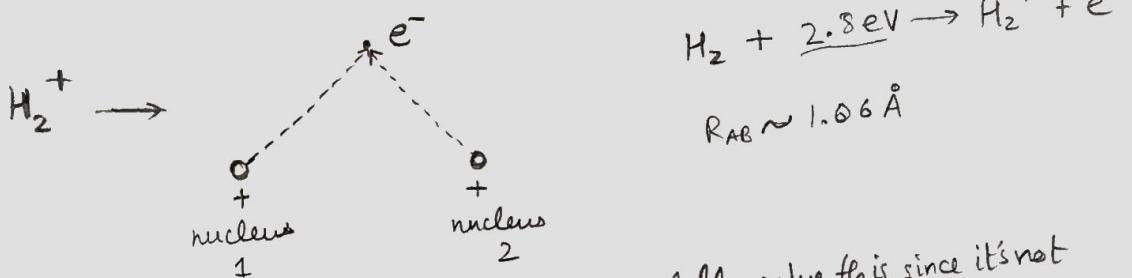
$$= 2 \langle \psi_{100} | r_1^2 | \psi_{100} \rangle = 2 \int \frac{z^3}{\pi} e^{-2zr} d^3r r^2$$

$$= \frac{2z^3}{\pi} 4\pi \int_0^\infty dr r^2 e^{-2zr} = 8z^3 \left( \frac{3}{4\pi z^5} \right) = \underline{\underline{\frac{6}{z^2}}}$$

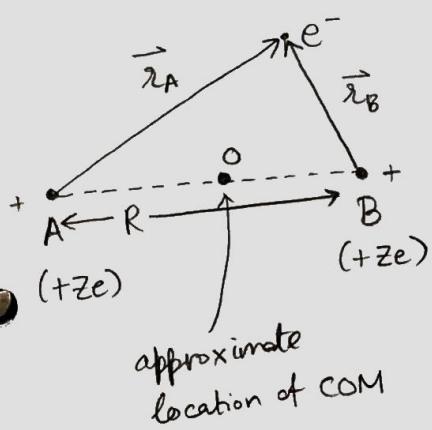
Lecture - 10  
(30/09/21)

Molecular systems.

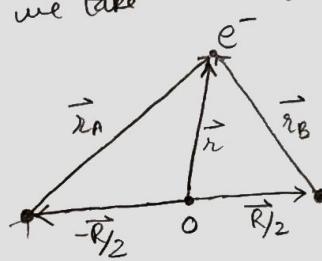
We'll begin with the study of  $H_2^+$  ion, which is the simplest molecular system.



We'll have to make approximations to meaningfully solve this since it's not an exactly solvable model.



If we take O as origin - (COM as origin)



So, our new co-ords are given by  $\vec{r}$  &  $\vec{R}$

$$\vec{r}_A = \vec{r} + \frac{\vec{R}}{2}$$

$$\vec{r}_B = \vec{r} - \frac{\vec{R}}{2}$$

$$\vec{r}_B = \vec{r} - \frac{\vec{R}}{2}$$

$$V(\vec{r}, \vec{R}) = \frac{z_A z_B}{R} - \frac{z_A}{r_A} - \frac{z_B}{r_B}, \quad KE = -\frac{\nabla_{\vec{r}_A}^2}{2M_A} - \frac{\nabla_{\vec{r}_B}^2}{2M_B} - \frac{\nabla_{\vec{r}}^2}{2m}$$

what co-ord. system are we writing this in?

$$V(\vec{r}, \vec{R}) = \frac{z_A z_B}{R} - \frac{z_A}{r_A} - \frac{z_B}{r_B}, \quad KE = -\frac{\nabla_{\vec{r}_A}^2}{2M_A} - \frac{\nabla_{\vec{r}_B}^2}{2M_B} - \frac{\nabla_{\vec{r}}^2}{2m}$$

(assuming  $z_A$  &  $z_B$  to be diff. in general)

$$H = K + V \Rightarrow H \psi(\vec{r}_A, \vec{r}_B, \vec{R}) = E \psi(\vec{r}_A, \vec{r}_B, \vec{R})$$

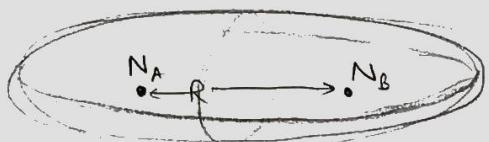
due to non-separability, this can't be solved exactly.

Approximation: Nuclei are very heavy compared to  $e^-$ .  $\therefore$  We can approximate

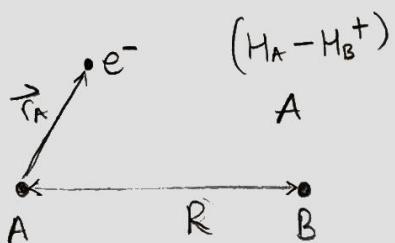
the nuclei to be almost fixed with distance  $\vec{R}$  b/w them. ( $\vec{R}$  now becomes a parameter.)

$$\Rightarrow KE \approx -\frac{\nabla_e^2}{2me} \quad (\text{Born-Oppenheimer approximation})$$

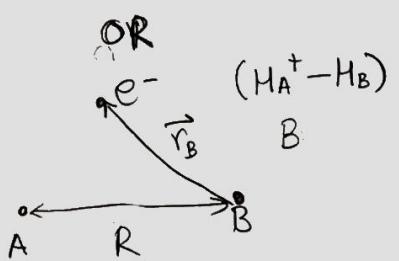
Schrödinger eqn then becomes separable in elliptical co-ordinate system.



We'll approximately solve using the Linear Combination of Atomic Orbitals (LCAO) method. The energy eigenvalues obtained will be dependent on the separation parameter  $\vec{R}$ .



We can think of this situation as a  $H^+$  ion bonded with H atom. So, we can either consider it as  $H_A^+ - H_B$  or  $H_A - H_B^+$ .



$\therefore$  the overall wavefn should be a linear comb. of both of these possibilities -

$$\psi = c_A \phi_A + c_B \phi_B$$

why is the state of  $H_A - H_B^+$  given by just  $\phi_A = \sqrt{Z_A^3/\pi} e^{-Z_A r_A}$

and state of  $H_A^+ - H_B$  by just  $\phi_B = \sqrt{Z_B^3/\pi} e^{-Z_B r_B}$ ? What about the other nucleus?

(3)

$$H = -\frac{\nabla^2}{2} + V \quad (\text{since } m_e = 1 \text{ in a.m.u})$$

$$\langle E \rangle = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

We now define the following terms -

$$H_{AA} = \langle \phi_A | H | \phi_A \rangle$$

$$\text{If nucleus A} = \text{nucleus B} \Rightarrow H_{AA} = H_{BB}$$

$$\text{and } Z_A = Z_B$$

$$\phi_A(r_A) = \sqrt{\frac{Z_A^3}{\pi}} e^{-Z_A r_A}$$

$$\phi_B(r_B) = \sqrt{\frac{Z_B^3}{\pi}} e^{-Z_B r_B}$$

In our system

$$Z_A = Z_B = 1$$

$$\therefore H_{AA} = \langle \phi_A | H | \phi_A \rangle = \langle \phi_B | H | \phi_B \rangle = H_{BB}$$

$$H_{AB} = \langle \phi_A | H | \phi_B \rangle = \langle \phi_B | H | \phi_A \rangle = H_{BA}$$

$$S = \langle \phi_A | \phi_B \rangle \quad (\text{overlap integral})$$

$$\begin{aligned} \Rightarrow \langle E \rangle &= \langle C_A \phi_A + C_B \phi_B | H | C_A \phi_A + C_B \phi_B \rangle / \langle C_A \phi_A + C_B \phi_B | C_A \phi_A + C_B \phi_B \rangle \\ &= \frac{C_A^2 H_{AA} + 2C_A C_B H_{AB} + C_B^2 H_{BB}}{C_A^2 + C_B^2 + 2C_A C_B S} \end{aligned}$$

Now we optimize

$$\frac{\partial \langle E \rangle}{\partial C_A} = 0 \quad \text{and} \quad \frac{\partial \langle E \rangle}{\partial C_B} = 0$$

These give the condition that

$$\begin{vmatrix} H_{AA} - \langle E \rangle & H_{AB} - \langle E \rangle S \\ H_{AB} - \langle E \rangle S & H_{BB} - \langle E \rangle \end{vmatrix} = 0$$

} Try out  
this calculation

$$\Rightarrow \langle E \rangle_1 = \frac{H_{AA} - H_{AB}}{1-S} \quad \langle E \rangle_2 = \frac{H_{AA} + H_{AB}}{1+S}$$

Putting these back into the linear eqns  $\Rightarrow C_A = \pm C_B$

This will give a symmetric & antisymmetric  $\Psi$

$$\text{Symm. } \Psi \sim (\phi_A + \phi_B)$$

$$\text{anti-sym. } \Psi \sim (\phi_A - \phi_B)$$

Optimization calculations:

$$\frac{\partial \langle E \rangle}{\partial C_A} = 0 \Rightarrow 2C_B [ (H_{AA}S - H_{AB})C_A^2 + C_B^2(H_{AB} - H_{BB}S) ] = 0$$

$$\frac{\partial \langle E \rangle}{\partial C_B} = 0 \Rightarrow 2C_A [ (H_{BB}S - H_{AB})C_B^2 + C_A^2(H_{AB} - H_{AA}S) ] = 0$$

Assuming  $C_A \neq 0, C_B \neq 0$

$$(H_{AA}S - H_{AB})C_A^2 = +C_B^2(H_{BB}S - H_{AB})$$

$$(H_{BB}S - H_{AB})C_B^2 = +C_A^2(H_{AA}S - H_{AB})$$

since  $H_{AA} = H_{BB}$  here, both eqns give  $C_A^2 = C_B^2 \Rightarrow C_A = \pm C_B$

$$\langle E \rangle_+ = \frac{C_A^2(H_{AA} + 2H_{AB} + H_{BB})}{2C_A^2(1+S)} = \frac{2C_A^2(H_{AA} + H_{AB})}{2C_A^2(1+S)} = \frac{H_{AA} + H_{AB}}{1+S}$$

$$\langle E \rangle_- = \frac{C_A^2(H_{AA} - 2H_{AB} + H_{BB})}{2C_A^2(1-S)} = \frac{H_{AA} - H_{AB}}{1-S}$$

$$\tilde{\Phi}_+ = \phi_A + \phi_B \Rightarrow \langle \tilde{\phi}_+ | \tilde{\phi}_+ \rangle = 2 + 2S \Rightarrow \phi_+ = \frac{1}{\sqrt{2+2S}} (\phi_A + \phi_B) \rightarrow \text{symmetric}$$

$$\tilde{\Phi}_- = \phi_A - \phi_B \Rightarrow \langle \tilde{\phi}_- | \tilde{\phi}_- \rangle = 2 - 2S \Rightarrow \phi_- = \frac{1}{\sqrt{2-2S}} (\phi_A - \phi_B) \rightarrow \text{anti-symmetric}$$

Lecture-11

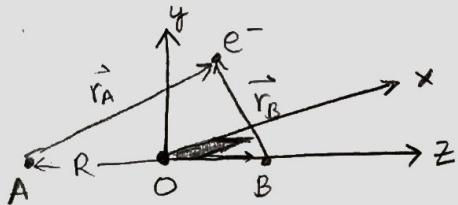
(01/10/21)

From last lecture, we saw that using LCAO for the hydrogen<sup>+</sup> molecule H<sub>2</sub><sup>+</sup>, we got two energy eigenstates. We started with  $\psi = C_A \phi_A + C_B \phi_B$

$$\psi = C_A \phi_A + C_B \phi_B \xrightarrow[\text{principle}]{\text{minimize } \langle E \rangle \text{ using variational}} \begin{cases} C_A = C_B, \phi_+ = \frac{1}{\sqrt{2+2S}} (\phi_A + \phi_B), E_+ = \frac{H_{AA} + H_{AB}}{1+S} \\ C_A = -C_B, \phi_- = \frac{1}{\sqrt{2-2S}} (\phi_A - \phi_B), E_- = \frac{H_{AA} - H_{AB}}{1-S} \end{cases}$$

Now, let's calculate H<sub>AA</sub>, S and H<sub>AB</sub>.

- $H_{AA} = \langle \phi_A | H | \phi_A \rangle = \int d\tau \phi_A \left( -\frac{\nabla^2}{2} - \frac{1}{r_A} \right) \phi_A - \underbrace{\int d\tau \phi_A \frac{1}{r_B} \phi_A}_{\substack{\text{Hydrogen atom} \\ \text{Hamiltonian}}} + \underbrace{\int \phi_A \frac{1}{R} \phi_A d\tau}_{\frac{1}{R}}$

Overlap integral S

$$S = \int d\tau \phi_A \phi_B = \frac{1}{\pi} \int d\tau e^{-(r_A + r_B)}$$

Two center integral

$d\tau = dx dy dz$   
with origin at O,  
z-axis || to R, and  
yz-plane containing  
the electron.

The co-ordinates used to evaluate the integral are elliptical co-ordinates.

$$\mu = \frac{r_A + r_B}{R}$$

$$v = \frac{r_A - r_B}{R}$$

$$\phi = \arctan \left( \frac{y}{x} \right)$$

$$\begin{aligned} 1 \leq \mu &\leq \infty & 0 \leq \phi &\leq 2\pi \\ -1 \leq v &\leq +1 \end{aligned}$$

$$\Rightarrow d\tau = \frac{R^3}{8} (\mu^2 - v^2) d\mu dv d\phi$$

$$\Rightarrow S = \frac{R^3}{8\pi} \int_1^\infty d\mu \int_{-1}^1 dv \int_0^{2\pi} d\phi e^{-\mu R} (\mu^2 - v^2)$$

(2)

This gives

$$S(R) = e^{-R} \left( 1 + R + \frac{R^2}{3} \right)$$

Using elliptical co-ordinates, we can also evaluate the "?" integral in  $H_{AA}$

$$* \langle \phi_A | \frac{1}{r_B} | \phi_A \rangle = \frac{1}{R} [ 1 - (1+R) e^{-2R} ]$$

We'll also require another such integral in evaluation of  $H_{AB}$

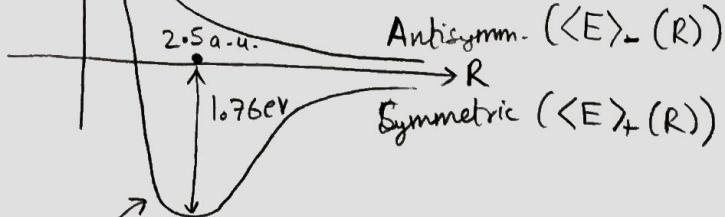
$$* \langle \phi_A | \frac{1}{r_A} | \phi_B \rangle = (1+R) e^{-R}$$

$$H_{AA} = -\frac{1}{2(1)^2} - \frac{1}{R} [ 1 - (1+R) e^{-2R} ] + \frac{1}{R} = H_{BB}$$

$$\begin{aligned} H_{AB} &= -\frac{1}{2} \langle \phi_A | \phi_B \rangle - \langle \phi_A | \frac{1}{r_A} | \phi_B \rangle + \frac{1}{R} \langle \phi_A | \phi_B \rangle \\ &= \left( \frac{1}{R} - \frac{1}{2} \right) e^{-R} \left( 1 + R + \frac{R^2}{3} \right) - (1+R) e^{-R} \end{aligned}$$

∴ We can use these to get the form of  $\langle E \rangle_+$  (or  $\langle E \rangle_s$ ) and  $\langle E \rangle_-$  (or  $\langle E \rangle_a$ ).

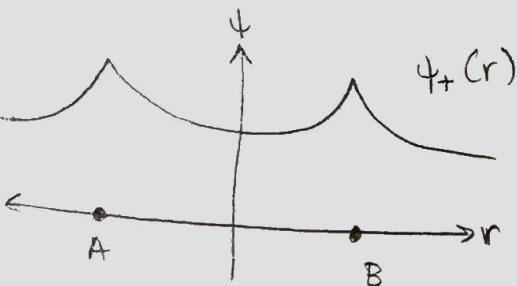
$\langle E \rangle$	Dissociation energy
LCAO	1.76 eV
Experiments	2.8 eV



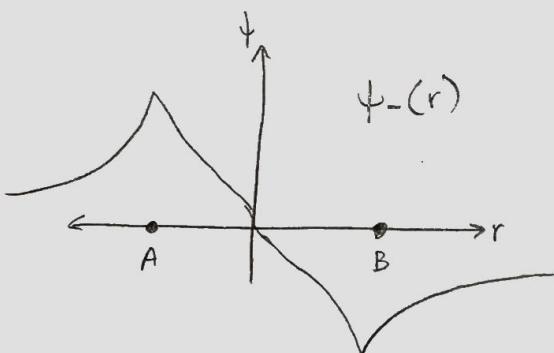
bound state at  $R = 2.5$  a.u.  $\Rightarrow$  stability of  $H_2^+$  system.

The symmetric combination leads to a bonding atomic orbital.

The anti-sym. combination leads to an anti-bonding orbital.



Bonding M.O.



Anti-Bonding M.O.

$$\langle E_{\pm} \rangle = E_H + \frac{1}{R} - \frac{(j \pm k)}{1 \pm S}$$

Lecture-12  
(04/10/21)

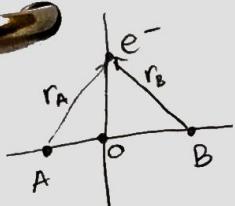
where  $j = \langle \phi_A | \frac{1}{r_B} | \phi_B \rangle = \frac{1}{R} (1 - (1+R)e^{-2R})$ ,  
 $k = \langle \phi_A | \frac{1}{r_A} | \phi_B \rangle = (1+R)e^{-R}$   
 $S = e^{-R}(1+R+\frac{R^2}{3})$

Evaluation of the integrals:

In the expression for  $H_{AA}$ -

$$H_{AA} = \underbrace{\int \phi_A \left( -\frac{\nabla^2}{2} - \frac{1}{r_A} \right) \phi_A d\tau}_{H_A} + \int \phi_A \frac{1}{R} \phi_A d\tau - \int d\tau \phi_A \frac{1}{r_B} \phi_A$$

$$\frac{1}{R} \langle \phi_A | \phi_A \rangle$$



Now in elliptical co-ords.-

$$\mu = \frac{r_A + r_B}{R}$$

$$r_A = \frac{R}{2} (\mu + v)$$

$$v = \frac{r_A - r_B}{R}$$

$$r_B = \frac{R}{2} (\mu - v)$$

$$\phi = \arctan \left( \frac{y}{x} \right)$$

$$d\tau = \frac{R^3}{8} (\mu^2 - v^2) d\mu dv d\phi$$

$(\mu + v)$

$$\langle \phi_A | \frac{1}{r_B} | \phi_A \rangle = \frac{1}{\pi} \int d\tau \frac{e^{-2r_A}}{r_B} = \frac{R^2}{48\pi} \int d\mu \int dv \int d\phi \frac{e^{-R(\mu+v)}}{R(\mu-v)/2} e^{-R(\mu+v)} \frac{(\mu+v)^2}{(\mu^2 - v^2)}$$

$$= \frac{R^2}{2} \int d\mu \int dv e^{-R(\mu+v)} \frac{(\mu+v)^2}{(\mu^2 - v^2)}$$

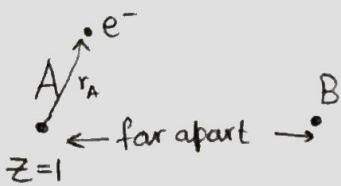
(4)

$$\bullet \left\langle \phi_A \left| \frac{1}{r_B} \right| \phi_A \right\rangle = \frac{R^2}{2} \int_1^\infty d\mu \int_{-1}^{+1} dv e^{-R(\mu+v)} \cdot (\mu+v) = \frac{1}{R} \left[ 1 - (1+R)e^{-2R} \right]$$

Similarly to calculate the term  $\left\langle \phi_A \left| \frac{1}{r_A} \right| \phi_B \right\rangle$  which appears in  $H_{AB}$ .

$$\bullet \left\langle \phi_A \left| \frac{1}{r_A} \right| \phi_B \right\rangle = \frac{R^3}{24} \int_1^\infty d\mu \int_{-1}^{+1} dv \frac{e^{-\mu R}}{\mu - v} (\mu - v) \\ = \frac{R^2}{2} \int_1^\infty d\mu \int_{-1}^{+1} dv e^{-\mu R} (\mu - v) = (1+R) e^{-R}$$

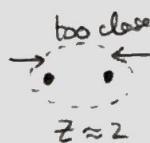
Another calculation to further get a better approximation, Coulson considered the effect of the  $H^+$  nucleus into the wavefn.



When A & B are far apart, the wavefn  $\phi_A$  of  $H_A - H_B^+$  can just be thought of as

$$\phi_A = \sqrt{\frac{Z^3}{\pi}} e^{-Zr_A}$$

with  $Z=1$



But if they get too close, the charge of nucleus A might look like charge of A&B combined, and thus as separation  $\downarrow$ ,  $Z \rightarrow 2$ .



But in eqn, they are neither too far nor too close, so  $1 < Z_{eff} < 2$ .

$\Rightarrow$  We can choose  $Z_{eff}$  as a variational parameter, s.t.

$$\phi_{A,B} = \sqrt{\frac{Z_{eff}^3}{\pi}} e^{-Z_{eff} r_{A,B}}$$

And then optimize  $\langle E \rangle$  for this new parameter as well  $\frac{\partial \langle E \rangle}{\partial Z_{eff}} = 0$ .

This gives  $Z_{eff} = 1.34$

# (H<sub>2</sub>) Hydrogen molecule

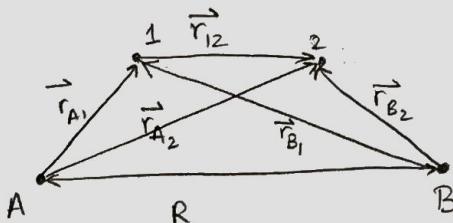
LECTURE - 13  
(05/10/2021)

①



The hydrogen molecule, is a more complicated multielectronic system, but is more stable than H<sub>2</sub><sup>+</sup>.

H<sub>2</sub> has two protons as nuclei & 2 electrons. The total wavefn also has to be anti-symmetric now.



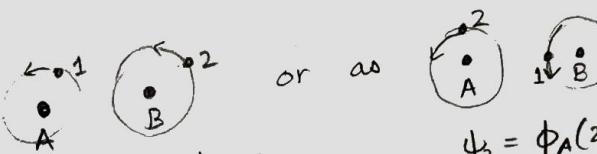
Again, in the Bohr-Oppenheimer approximation, we neglect KE of nuclei A & B

$$\Rightarrow H = -\frac{\nabla_1^2}{2} - \frac{1}{r_{A_1}} - \frac{1}{r_{B_1}} - \frac{\nabla_2^2}{2} - \frac{1}{r_{A_2}} - \frac{1}{r_{B_2}} + \frac{1}{r_{12}} + \frac{1}{R}$$

$\underset{\substack{\uparrow \\ \text{H}_2^+ \text{ Hamiltonians.}}}{= H_1 + H_2 + \frac{1}{r_{12}} - \frac{1}{R}}$

Heitler-London approximation (valence bond method)

H-L approximation uses the fact that we can consider the H<sub>2</sub> molecule as



$$\psi_1 = \phi_A(1) \phi_B(2)$$

$$\psi_2 = \phi_A(2) \phi_B(1)$$

Then for a general state, we can consider a linear combination

$$\psi = c_1 \psi_1 + c_2 \psi_2$$

optimize c<sub>i</sub> to get  $\langle E \rangle_{\min}$

$$\langle E \rangle = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

(2)

$$\text{Optimization } \frac{\partial \langle E \rangle}{\partial c_1} = 0, \quad \frac{\partial \langle E \rangle}{\partial c_2} = 0$$

$$\text{Now } \langle E \rangle = \frac{\langle \psi_1 | \hat{H} | \psi_1 + \psi_2 \rangle}{\langle \psi_1 + \psi_2 | \psi_1 + \psi_2 \rangle}$$

$$\langle E \rangle = \frac{c_1^2 H_{11} + c_2^2 H_{22} + 2c_1 c_2 H_{12}}{c_1^2 + c_2^2 + 2S^2 c_1 c_2}$$

$$\frac{\partial \langle E \rangle}{\partial c_1} = 0 \Rightarrow (H_{11} S^2 - H_{12}) c_1^2 + c_2^2 (H_{12} - H_{22} S^2) = 0$$

$$\frac{\partial \langle E \rangle}{\partial c_2} = 0 \Rightarrow (H_{22} S^2 - H_{12}) c_2^2 + c_1^2 (H_{12} - H_{11} S^2) = 0$$

where we have taken  $H_{12} = H_{21}$ ,  $H_{11} = H_{22}$

$$H_{11} = H_{22} = \langle \psi_1 | \hat{H} | \psi_1 \rangle \quad S^2 = \langle \psi_1 | \psi_2 \rangle = \langle \phi_A(1) \phi_B(2) | \phi_A(2) \phi_B(1) \rangle$$

$$H_{12} = H_{21} = \langle \psi_1 | \hat{H} | \psi_2 \rangle$$

This implies  $c_1 = \pm c_2$

$$\begin{cases} \langle E \rangle_+ &= \frac{H_{11} + H_{12}}{1 + S^2} \\ &(c_1 = c_2) \\ \langle E \rangle_- &= \frac{H_{11} - H_{12}}{1 - S^2} \\ &(c_1 = -c_2) \end{cases}$$

$$\Rightarrow \psi_+ = \frac{\psi_1 + \psi_2}{\sqrt{2(1+S^2)}} \quad \psi_- = \frac{\psi_1 - \psi_2}{\sqrt{2(1-S^2)}}$$

$$\text{If we now write } \hat{H} = \underbrace{\frac{-\nabla_1^2}{2} - \frac{1}{r_{A_1}} - \frac{1}{r_{B_1}}}_{H_1} - \underbrace{\frac{-\nabla_2^2}{2} - \frac{1}{r_{A_2}} - \frac{1}{r_{B_2}}}_{H_2} + \frac{1}{R} + \frac{1}{r_{12}}$$

$$\hat{H} = H_1 + H_2 + \frac{1}{R} + \frac{1}{r_{12}}$$

(can also be written as  $\hat{H} = H_1 + H_2 + \frac{1}{r_{12}} - \frac{1}{R}$  where  $H_i = \frac{-\nabla_i^2}{2} - \frac{1}{r_{A_i}} - \frac{1}{r_{B_i}} + \frac{1}{R}$   
is the  $H_2^+$  Hamiltonian)

Therefore,

$$H_{11} = \langle \psi_1 | H_1 | \psi_1 \rangle + \langle \psi_1 | H_2 | \psi_1 \rangle + \underbrace{\langle \psi_1 | \frac{1}{r_{12}} | \psi_1 \rangle}_{\text{the integral is over } \int d\tau_1 d\tau_2} + \frac{1}{R}$$

$$\Psi_1 = \phi_A(1) \phi_B(2), \quad \Psi_2 = \phi_A(2) \phi_B(1)$$

$$\Rightarrow H_{11} = \underbrace{\langle \phi_A(1) | H_1 | \phi_A(1) \rangle}_{1} \underbrace{\langle \phi_B(2) | \phi_B(2) \rangle}_{1} + \underbrace{\langle \phi_B(2) | H_2 | \phi_B(2) \rangle}_{1} \underbrace{\langle \phi_A(1) | \phi_A(1) \rangle}_{1} + \underbrace{\langle \psi_1 | \frac{1}{r_{12}} | \psi_1 \rangle}_{\text{we'll deal with this later.}} + \frac{1}{R}$$

- $\langle \phi_A(1) | H_1 | \phi_A(1) \rangle = \langle \phi_A(1) | -\frac{\nabla_1^2}{2} - \frac{1}{r_{A1}} | \phi_A(1) \rangle - \langle \phi_A(1) | \frac{1}{r_{B1}} | \phi_A(1) \rangle$

$$= -\frac{Z_A^2}{2} - \frac{1}{R} \left[ 1 - (1+R) e^{-2R} \right]$$

↑  
considering ground state

↑  
we calculated this in  
 $H_2^+$  calculation.



$$= -\frac{1}{2} - \frac{1}{R} \left[ 1 - (1+R) e^{-2R} \right] = \underline{E_H - P}$$

Similarly,

- $\langle \phi_B(2) | H_2 | \phi_B(2) \rangle = \langle \phi_B(2) | -\frac{\nabla_2^2}{2} - \frac{1}{r_{B2}} | \phi_B(2) \rangle - \langle \phi_B(2) | \frac{1}{r_{A2}} | \phi_B(2) \rangle$

calculated in  $H_2^+$

$\Rightarrow$  same as  $\langle \phi_A(1) | H_1 | \phi_A(1) \rangle$

$$\therefore = -\frac{1}{2} - \frac{1}{R} \left[ 1 - (1+R) e^{-2R} \right] = \underline{E_H - P}$$

(4)

$$\text{So, } H_{11} = 2E_H - P + \underbrace{\langle \psi_1 | \frac{1}{r_{12}} | \psi_1 \rangle}_{\text{Hydrogen}} + \frac{1}{R}$$

- $\langle \psi_1 | \frac{1}{r_{12}} | \psi_1 \rangle = \int d\tau_1 d\tau_2 \phi_A(1) \phi_B(2) \frac{1}{r_{12}} \phi_A(1) \phi_B(2)$
- $= \int d\tau_1 d\tau_2 \phi_A^2(1) \frac{1}{r_{12}} \phi_B^2(2) \rightarrow \text{interaction energy b/w charged distributions}$

Reminder:

$$\text{charge distribution of } e_1^- = -e |\phi_A(1)|^2$$

$$\text{charge distribution of } e_2^- = -e |\phi_B(2)|^2$$

$$\Rightarrow V_{\text{interaction}} = \int d\tau_1 (-e |\phi_A(1)|^2) \int d\tau_2 (-e |\phi_B(2)|^2) \cdot \frac{1}{4\pi\epsilon_0 r_{12}}$$

We'll denote  $\int d\tau_1 d\tau_2 \phi_A^2(1) \frac{1}{r_{12}} \phi_B^2(2) \equiv \underset{1}{(AA)} \underset{2}{|BB)}$

$$\therefore H_{11} = 2E_H - P + (AA|BB) + \frac{1}{R}$$

Let's move onto  $H_{12}$ .

$$H_{12} = \langle \psi_1 | H | \psi_2 \rangle = \langle \psi_1 | H_1 | \psi_2 \rangle + \langle \psi_1 | H_2 | \psi_2 \rangle + \langle \psi_1 | \frac{1}{r_{12}} | \psi_2 \rangle + \langle \psi_1 | \frac{1}{R} | \psi_2 \rangle$$

Similarly, here the term-

$$\begin{aligned} \langle \psi_1 | \frac{1}{r_{12}} | \psi_2 \rangle &= \int d\tau_1 d\tau_2 \phi_A(1) \phi_B(2) \frac{1}{r_{12}} \phi_A(2) \phi_B(1) \\ &= \int d\tau_1 d\tau_2 \phi_A(1) \phi_B(1) \frac{1}{r_{12}} \phi_A(2) \phi_B(2) \\ &\equiv (AB|AB) \end{aligned}$$

Lecture - 14  
 (07/10/21)

$H_2$  molecule: the Hamiltonian is of the form  $H = H_1 + H_2 + \frac{1}{r_{12}} + \frac{1}{R}$

$$H_1 = -\frac{\nabla_1^2}{2} - \frac{1}{r_{A_1}} - \frac{1}{r_{B_1}}$$

$$H_2 = -\frac{\nabla_2^2}{2} - \frac{1}{r_{A_2}} - \frac{1}{r_{B_2}}$$

Molecular orbital picture:

We constructed the molecular orbitals by  $\psi = \phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)$

which was a "product combination" of atomic orbitals.

We can instead also proceed via the "linear combination" of atomic orbitals (LCAO) route, like we did for  $H_2^+$  ion.

$$\sigma(1) = \frac{1}{\sqrt{2(1+s)}} (\phi_A(1) + \phi_B(1)) \rightarrow \text{Linear combination of orbitals of electron 1.} = \phi_+(1)$$

$$\sigma(2) = \frac{1}{\sqrt{2(1+s)}} (\phi_A(2) + \phi_B(2)) \rightarrow \text{Linear combination of orbitals of electron 2.} = \phi_+(2)$$

So, we can think of  $\sigma(1)$  as bonding orbital of  $e_1$  and  $\sigma(2)$  as bonding orbital of  $e_2$ . So, the net state of  $H_2$  atom would then be -

$$\underline{\psi = \sigma(1)\sigma(2)} \quad \longrightarrow \text{spatial part.}$$

Anti-symm. version  
of  $\psi^{MO}$ ?

Difference in MOT and LCAO-

- MOT - first take product of  $e_1$  &  $e_2$  eigenstates & then take linear combination.
- LCAO - first take linear comb. of  $e_1$  &  $e_2$  eigenstates, then take product.

(2)

Since we are taking a symmetric spatial wavefn, the total wavefn has to be anti-symmetric  $\Rightarrow$  spin wavefn is anti-symm.

$$\Psi(1,2) = \sigma(1)\sigma(2) \cdot \frac{1}{\sqrt{2}} (|1\uparrow\downarrow\rangle - |1\downarrow\uparrow\rangle)$$

So, while calculating  $\langle E \rangle$ , one should technically do an integral over the total wavefn  $\Psi$  (with spin), but the inner product of spin wavefn  $\langle \chi | \chi \rangle = 1$ .

$$\begin{aligned} \langle H \rangle &= \int d\tau \Psi(1,2) H \Psi(1,2) = \langle \chi | \chi \rangle \int d\tau \sigma(1)\sigma(2) H \sigma(1)\sigma(2) \\ &= \int d\tau \sigma(1)\sigma(2) \hat{H} \sigma(1)\sigma(2) \end{aligned}$$

$$\begin{aligned} \langle H \rangle &= \int d\tau_1 \sigma(1) \hat{H}_1 \sigma(1) \underbrace{\int d\tau_2 \sigma(2) \sigma(2)}_{\parallel} + \underbrace{\int d\tau_1 \sigma(1) \sigma(1)}_{\parallel} \underbrace{\int d\tau_2 \sigma(2) \hat{H}_2 \sigma(2)}_{\parallel} \\ &+ \int d\tau_1 d\tau_2 \sigma^2(1) \frac{1}{r_{12}} \sigma^2(2) + \frac{1}{R} \end{aligned}$$

$$\int d\tau_{1,2} \sigma(1,2) \hat{H}_{1,2} \sigma(1,2) \rightarrow \text{mean energy of } H_2^+ \text{ ion} = E_{H_2^+}$$

$$\int d\tau_1 d\tau_2 \sigma^2(1) \frac{1}{r_{12}} \sigma^2(2) \equiv J$$

$$\Rightarrow \langle E \rangle = E_{H_2^+} + E_{H_2^+} + J + \frac{1}{R} = 2E_{H_2^+} + J + \frac{1}{R}$$

$$\text{where } E_{H_2^+} = E_H + \frac{1}{R} - \frac{(j+k)}{1+s}$$

$$\text{where } j = \frac{1}{R} (1 - (1+R)e^{-2R})$$

$$k = (1+R)e^{-R}$$

$$s = e^{-R} \left(1 + R + \frac{R^2}{3}\right)$$

Let's now consider the  $\mathcal{J}$  integral

$$\mathcal{J} = \int d\tau_1 d\tau_2 \sigma(1)^2 \sigma(2)^2 \frac{1}{r_{12}}$$

$$= \frac{1}{4(1+s)^2} \int d\tau_1 d\tau_2 (\phi_A(1) + \phi_B(1))^2 \frac{1}{r_{12}} (\phi_A(2) + \phi_B(2))^2 \rightarrow 9 \text{ terms}$$

1 term:  $j' \equiv \int \phi_A^2(1) \frac{1}{r_{12}} \phi_B^2(2) d\tau_1 d\tau_2 = (AA|BB)$

2 terms:  $k' \equiv \int \phi_A(1) \phi_B(1) \frac{1}{r_{12}} \phi_A(2) \phi_B(2) d\tau_1 d\tau_2 = (AB|AB)$

4 terms:  $l \equiv \int \phi_A^2(1) \frac{1}{r_{12}} \phi_A(2) \phi_B(2) d\tau_1 d\tau_2 = (AA|AB)$

2 terms:  $m \equiv \int \phi_A^2(1) \frac{1}{r_{12}} \phi_A^2(2) d\tau_1 d\tau_2 = (AA|AA)$

### Lecture-15 (08/10/21)

Molecular Orbital Approximation / LCAO for  $H_2$ :

$$\begin{aligned} \sigma_{\text{symm}}(r_1, r_2) &= \sigma(1) \sigma(2) = \phi_+(1) \phi_+(2) \\ &= \frac{1}{2(1+s)} \underbrace{(\phi_A(1) + \phi_B(1))}_{H_2^+ \text{ wavefn } (1)} \underbrace{(\phi_A(2) + \phi_B(2))}_{H_2^+ \text{ wavefn } (2)} \rightarrow \text{wavefn used in MOT/LCAO} \end{aligned}$$

$$H = H_1 + H_2 + \frac{1}{r_{12}} - \frac{1}{R}$$

$$\text{where } H_1 = -\frac{\nabla_1^2}{2} - \frac{1}{r_{A_1}} - \frac{1}{r_{B_1}} + \frac{1}{R}$$

$H_1, H_2$  are now hydrogen molecule ion ( $H_2^+$ ) hamiltonians.

(4)

$$\Rightarrow H = 2\hat{H}(H_2^+) + \Delta E$$

$$\Delta E = \frac{1}{r_{12}} - \frac{1}{R}$$

$$\langle H \rangle = \int d\tau_1 d\tau_2 \sigma_{\text{symm}} \hat{H} \sigma_{\text{symm}}$$

This method gives  $\langle E \rangle \approx -2.7 \text{ eV}$  whereas  $E_{\text{exp}} = -4.7 \text{ eV}$ .

It also gives the incorrect expression for  $E(R \rightarrow \infty) \neq 2E_{\text{binding}}(H)$ .

### Heitler-London / Valence bond approximation

$$\Psi_1 = \phi_A(1) \phi_B(2), \quad \Psi_2 = \phi_A(2) \phi_B(1)$$

$$\Psi_{\pm} = N(\Psi_1 \pm \Psi_2) = N(\phi_A(1) \phi_B(2) \pm \phi_A(2) \phi_B(1))$$

$$\Psi_{s,a}^{\text{HL}} = \frac{1}{\sqrt{2(1 \pm S^2)}} (\phi_A(1) \phi_B(2) \pm \phi_A(2) \phi_B(1)) \rightarrow \text{wavefn used in H-L / VBT}$$

compared to the wavefn in MO approx-

$$\Psi_s^{\text{MO}} = \frac{1}{2(1+S)} \underbrace{(\phi_A(1) \phi_A(2) + \phi_B(1) \phi_B(2) + \phi_A(1) \phi_B(2) + \phi_A(2) \phi_B(1))}_{\downarrow}$$

these terms are missing in HL  
 (represents both e<sup>-</sup>s associated  
 to either A or B       $H_A^- - H_B^+$        $H_A^+ - H_B^- \Rightarrow$  ionic character)       $\Rightarrow$  causes overestimation due to equal emphasis to ionic & covalent character!

HL method thus gives a closer estimate of  $E \approx -3.14 \text{ eV}$

If instead tunable parameters are introduced for ionic & covalent configurations in MO method, we get a much better estimate of  $\approx -4.02 \text{ eV}$ .

Electron density distribution (H<sub>2</sub>)

We'll consider the symmetric (bonding) state.

For H<sub>2</sub> (VBT) wavefn

$$(\psi_+^{H_2})^2 = \frac{1}{2(1+s^2)} [\phi_A^2(1) \phi_B^2(2) + \phi_A^2(2) \phi_B^2(1) + 2\phi_A(1)\phi_B(1)\phi_A(2)\phi_B(2)]$$

Electron density of individual electrons -

$$\begin{aligned} p_1 &\equiv \overline{\int d\tau_2 \psi_+^2(1,2)} \\ &= \frac{1}{2(1+s^2)} \left[ \phi_A^2(1) \overline{\int d\tau_2 \phi_B^2(2)} + \phi_B^2(1) \overline{\int d\tau_2 \phi_B(2)} + 2\phi_A(1)\phi_B(1) \right. \\ &\quad \left. \overline{\int d\tau_2 \phi_A(2)\phi_B(2)} \right] \\ \Rightarrow p_1 &= \frac{1}{2(1+s^2)} \left[ \phi_A^2(1) + \phi_B^2(1) + 2\phi_A(1)\phi_B(1)s \right] \end{aligned}$$

S (overlap integral)

Similarly

$$\begin{aligned} p_2 &\equiv \overline{\int d\tau_1 \psi_+^2(1,2)} \\ p_2 &= \frac{1}{2(1+s^2)} \left[ \phi_A^2(2) + \phi_B^2(2) + 2\phi_A(2)\phi_B(2)s \right] \end{aligned}$$

Total P

$$P = p_1 + p_2 \stackrel{?}{=} \frac{1}{(1+s^2)} \left[ \phi_A^2(1) + \phi_B^2(1) + 2s\phi_A(1)\phi_B(1) \right]$$

how can we just add  
the charge densities over diff. co-ords?

For Molecular orbital method wavefn

$$\rho^{MO} = \frac{1}{(1+s)} [\phi_A^2(1) + \phi_B^2(1) + 2\phi_A(1)\phi_B(1)]$$

shouldn't this

$$\text{be } \frac{1}{2(1+s)^2}$$

In the middle where  $\phi_A(1) = \phi_B(1)$

we can see that  $\rho^{MO} = \frac{4\phi_A^2}{1+s}$  &  $\rho^{HL} = \frac{2\phi_A^2(1+s)}{(1+s^2)}$   
 $\Rightarrow \rho^{MO} > \rho^{HL}$

### Lecture-17

(12/10/2021)

Heitler-London (VB) method ignores the ionic character completely. (i.e. never do we consider a wavefn where both e<sup>-</sup>s belong to the same nucleus.)

The Molecular orbital / LCAO method on the other hand overemphasizes the ionic character. (since it gives equal contrib. to ionic & covalent.)  
 So, if we improve upon the wavefn by learning from both the methods -

$$\psi = N [\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1) + \lambda (\phi_A(1)\phi_A(2) + \phi_B(1)\phi_B(2))]$$

↑  
variable parameter  
for ionic parameter.

If we then do  $\frac{\partial \langle E \rangle}{\partial \lambda} = 0 \Rightarrow \lambda = \frac{1}{6} \Rightarrow 17\% \text{ ionic contribution}$

This results in  $\langle E \rangle \approx -4.02 \text{ eV}$

Using these methods, we write the ground state wavefn as -

$$\Psi_g = \frac{\Psi_+ + \Psi_-}{\sqrt{2}} \left[ \alpha(1)\beta(2) - \alpha(2)\beta(1) \right]$$

↑ bonding spatial wavefn      ↑ spin wavefn. (spin-singlet.)

Considering  $\Psi_+$  of HL method-

$$\Psi_g = \frac{1}{\sqrt{2(1+s^2)}} (\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)) \cdot \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

$$= \frac{1}{2\sqrt{1+s^2}} \left[ \phi_A(1)\alpha(1) \cdot \phi_B(2)\beta(2) + \phi_B(1)\alpha(1) \cdot \phi_A(2)\beta(2) \right. \\ \left. - \phi_A(1)\beta(1) \cdot \phi_B(2)\alpha(2) - \phi_B(1)\beta(1) \cdot \phi_A(2)\alpha(2) \right]$$

$$= \frac{1}{2\sqrt{1+s^2}} \begin{pmatrix} \phi_A(1)\alpha(1) & \phi_A(2)\alpha(2) \\ \phi_B(1)\beta(1) & \phi_B(2)\beta(2) \end{pmatrix} - \begin{pmatrix} \phi_A(1)\beta(1) & \phi_A(2)\beta(2) \\ \phi_B(1)\alpha(1) & \phi_B(2)\alpha(2) \end{pmatrix}$$

Slater determinants

①

### Practice for MidSem.

#### Assignment 0

4.  $\Psi_1 = \Psi_{1s}(r) = \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr}$

$$P(r, r+dr) = \left[ \int d\Omega |\Psi_{1s}|^2 \right] dr = dr \int_0^{2\pi} d\phi \int_0^\pi r^2 \sin\theta \left(\frac{Z^3}{\pi}\right) e^{-2Zr} \\ = r^2 dr \cdot \left(\frac{Z^3}{\pi}\right) e^{-2Zr} \cdot 4\pi = 4Z^3 r^2 e^{-2Zr} dr$$

Pradial ( $r$ ) =  $4Z^3 r^2 e^{-2Zr}$

Prob. of finding  $e^-$  inside Bohr radius ( $a_0 = 1 \text{ a.u.}$ )

$$P(0, a_0=1) = \int_0^1 dr 4Z^3 r^2 e^{-2Zr}$$

$$f(\alpha) = \int_0^1 dr e^{-\alpha r} = \left( \frac{e^{-\alpha r}}{-\alpha} \right) \Big|_0^1 = \frac{1}{\alpha} (e^0 - e^{-\alpha}) = \frac{1 - e^{-\alpha}}{\alpha}$$

$$\frac{\partial f}{\partial \alpha} = \int_0^1 dr (-r) e^{-\alpha r} \Rightarrow \frac{\partial^2 f}{\partial \alpha^2} = \int_0^1 dr (-r)^2 e^{-\alpha r} = \int_0^1 dr e^{-\alpha r} r^2$$

$$\frac{\partial f}{\partial \alpha} = \frac{\alpha (-e^{-\alpha} \cdot (-1)) - (1 - e^{-\alpha})}{\alpha^2} = \frac{\alpha e^{-\alpha} - 1 + e^{-\alpha}}{\alpha^2} \\ = \frac{(\alpha + 1)e^{-\alpha} - 1}{\alpha^2}$$

$$\frac{\partial^2 f}{\partial \alpha^2} = \frac{\alpha^2 [ -(\alpha + 1)e^{-\alpha} + e^{-\alpha} ] - 2\alpha [ (\alpha + 1)e^{-\alpha} - 1 ]}{\alpha^4}$$

$$= \frac{\alpha^2 [ -\alpha e^{-\alpha} - e^{-\alpha} + e^{-\alpha} ] - 2\alpha [ (\alpha + 1)e^{-\alpha} - 1 ]}{\alpha^4} \\ = \frac{-\alpha^2 e^{-\alpha} - 2[(\alpha + 1)e^{-\alpha} - 1]}{\alpha^3}$$

Now  $\alpha = 2Z$

$$\Rightarrow P(0, a_0=1) = -2Z^2 e^{-2Z} - 1 \cdot [ (2Z+1) e^{-2Z} - 1 ] \\ = \underline{\underline{e^{-2Z}(-2Z^2 - 2Z - 1 + e^{2Z})}}$$

For  $Z=1$

$$P = -2e^{-2} - 1(3e^{-2}-1) = -\frac{2e^{-2} - 3e^{-2} + 1}{1} = -5e^{-2} + 1$$
$$= \frac{1}{1} - \frac{5e^{-2}}{1} = 0.32$$

Assignment - 1

1. He  $\rightarrow$  Ind. Particle model

$$E = -\frac{Z^2}{2} \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) = -\frac{Z^2}{2} \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) = -Z^2 \text{ (for g.s.)}$$

$$E_{1,\infty} = -\frac{Z^2}{2} \left( \frac{1}{1} + \frac{1}{\infty} \right) = -\frac{Z^2}{2} \quad (\text{He}^+)$$

$$E_{\infty,\infty} = -\frac{Z^2}{2} \left( \frac{1}{\infty} + \frac{1}{\infty} \right) = 0 \Rightarrow \Delta E_{\text{He} \rightarrow \text{He}^+} = Z^2 = 20.9 \text{ a.u.}$$

$$\text{So, } E_{1,\infty} = -1.045 \text{ a.u.}$$

$$Z = \sqrt{2.9} \approx 1.7 \text{ ?? ?}$$

If we have total screening by one of the electrons, the  $Z=1$  ( $\lim_{r \rightarrow \infty}$ )

$$\text{So, } \Delta E_{\text{He} \rightarrow \text{He}^+} = -\frac{Z^2}{2} = -\frac{1}{2} = -0.5 \text{ a.u.}$$

$$\therefore \langle \Psi | \frac{1}{|\vec{r}_1 - \vec{r}_2|} | \Psi \rangle = \frac{Z^6}{\pi^2} \int d^3 r_1 d^3 r_2 e^{-2Z(r_1 + r_2)} \cdot \frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} Y_{lm}^*(\theta_1, \phi_1) Y_{lm}(\theta_2, \phi_2) \frac{r_1^l}{r_2^{l+1}}$$

$$\langle |\vec{r}_1 - \vec{r}_2| \rangle = \frac{Z^6}{\pi^3} \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} \int dr_1 r_1^2 e^{-2Zr_1} \int dr_2 r_2^2 e^{-2Zr_2} \left( \int d\Omega_1 Y_{lm}^*(\theta_1 \phi_1) Y_{lm}^*(\theta_2 \phi_2) \right) \frac{r_1^l}{r_2^{l+1}}$$

$$= \frac{Z^6}{\pi^2} (4\pi)^2 \int dr_1 dr_2 e^{-2Z(r_1 + r_2)} r_1^2 r_2^2 \cdot \frac{1}{r_2}$$

$$( \int d\Omega_2 Y_{lm}(\theta_2 \phi_2) Y_{lm}^*(\theta_1 \phi_1) ) \frac{(4\pi)}{8\pi r_1 r_2} \delta_{l0} \delta_{m0}$$

(3)

$$\int_0^\infty dr_1 r_1^2 e^{-2Zr_1} \left[ \int_0^{r_1} dr_2 \frac{r_2^2}{r_1} e^{-2Zr_2} + \int_{r_1}^\infty dr_2 \frac{r_2^2}{r_1} e^{-2Zr_2} \right]$$

$$= \int_0^\infty dr_1 r_1^2 e^{-2Zr_1} \int_{r_1}^\infty dr_2 r_2 e^{-2Zr_2} + \int_0^\infty dr_1 r_1 e^{-2Zr_1} \int_0^{r_1} dr_2 r_2^2 e^{-2Zr_2}$$

$$= \int_0^\infty dr_1 r_1^2 e^{-4Zr_1} \frac{(2Zr_1+1)}{4Z^2} + \int_0^\infty dr_1 r_1 \left[ \frac{e^{-2Zr_1}}{4Z^3} - \frac{(2Z^2r_1^2+2Zr_1+1)e^{-4Zr_1}}{4Z^3} \right]$$

$$= \int_0^\infty dr_1 \frac{e^{-4Zr_1}}{4Z^3} r_1 \left[ (2Z^2r_1^2+Zr_1) + e^{2Zr_1} - (2Z^2r_1^2+2Zr_1+1) \right]$$

$$= \int_0^\infty dr_1 \frac{e^{-4Zr_1}}{4Z^3} r_1 \left[ e^{2Zr_1} - Zr_1 - 1 \right]$$

$$= \frac{1}{4Z^3} \int_0^\infty dr_1 \left[ e^{-2Zr_1} r_1 - Zr_1^2 e^{-4Zr_1} - r_1 e^{-4Zr_1} \right]$$

$$I = \frac{1}{4Z^2} \cdot \frac{5}{32Z^2} = \frac{5}{32 \cdot 4Z^5}$$

$$\text{so, } \langle |\vec{r}_1 - \vec{r}_2| \rangle = \frac{Z^6}{\pi^2} (16\pi^2) \cdot I = \frac{Z^6}{\pi^2} 16\pi^2 \cdot \frac{5}{16 \cdot 8Z^5} = \frac{5Z}{8} \text{ a.u.}$$

Quiz-1

$$1. V_{\text{eff}(2)} = -\frac{Ze^2}{r_2} + e^2 \int dT_1 \frac{|\psi_{11}|^2}{r_{12}}$$

$$\int dT_1 \frac{Z^3}{\pi} \frac{e^{-2Zr_1}}{r_{12}} = \frac{Z^3}{\pi} \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{(4\pi)}{2l+1} Y_{lm} \int dT_1 r_1^2 e^{-2Zr_1} \frac{r_1^l}{r_{12}^{l+1}}$$

$$\int dT_1 Y_{lm}^*(\theta_1, \phi_1) \frac{Y_{lm}^*}{Y_{00}}$$

(4)

$$= \frac{Z^3}{\pi} 4\pi \int dr_1 r_1^2 e^{-2Zr_1} \frac{1}{r_2}$$

$$= 4Z^3 \left[ \int_0^{r_2} dr_1 r_1^2 e^{-2Zr_1} \cdot \frac{1}{r_2} + \int_{r_2}^{\infty} dr_1 r_1^2 \frac{e^{-2Zr_1}}{r_2} \right]$$

$$= \frac{1}{r_2} \left( -2Z^2 r_2^2 - 2Zr_2 - 1 \right) e^{-2Zr_2} + \frac{(2Z^2 r_2^2 + Zr_2) e^{-2Zr_2}}{r_2} + \frac{1}{r_2}$$

$$= \frac{1}{r_2} \left[ -\left(Z + \frac{1}{r_2}\right) r_2 e^{-2Zr_2} + 1 \right] = -\left(Z + \frac{1}{r_2}\right) e^{-2Zr_2} + \frac{1}{r_2}$$

$$\text{So, } V_{\text{eff}}(r_2) = e^2 \left[ -\frac{Z}{r_2} + \frac{1}{r_2} - \left(Z + \frac{1}{r_2}\right) e^{-2Zr_2} \right]$$

$$= -e^2 \left[ \frac{(Z-1)}{r_2} + \left(Z + \frac{1}{r_2}\right) e^{-2Zr_2} \right]$$

$$\langle \frac{V_{\text{eff}}}{-e^2} \rangle = \frac{Z^3}{\pi} \left[ \int_0^{\infty} dr_2 e^{-2Zr_2} \cdot \frac{(Z-1)}{r_2} + \int dr_2 (Z + \frac{1}{r_2}) e^{-4Zr_2} \right]$$

$$= 4Z^3 \left[ \int_0^{\infty} dr_2 r_2 e^{-2Zr_2} \cdot (Z-1) + \int_0^{\infty} dr_2 Z e^{-4Zr_2} r_2^2 + \int_0^{\infty} dr_2 e^{-4Zr_2} r_2 \right]$$

$$= 4Z^3 \left[ \frac{(Z-1)}{4Z^2} + \frac{1}{32Z^2} + \frac{1}{16Z^2} \right]$$

$$= (Z-1)Z + \frac{Z}{8} + 2\frac{Z}{8} = Z^2 - Z + \frac{3Z}{8} = Z^2 - \frac{5Z}{8} = Z \left(Z - \frac{5}{8}\right)$$

For  $Z=2$ ,

$$\langle \frac{V_{\text{eff}}}{-e^2} \rangle = Z^4 \left( \frac{16-5}{8} \right) = \frac{11}{4} \Rightarrow \underline{\underline{\langle V_{\text{eff}} \rangle = -\frac{11}{4} \text{ a.u.}}}$$

Post

Mid - Semester

Exams

## Lecture - 18

(26-10-2021)

Demtroder 5.4

The Hamiltonian for the non-relativistic hydrogen atom is -

$$H = \underbrace{-\frac{\nabla^2}{2} + \frac{Z}{r_1}}_{\downarrow} + \text{other correction terms (?)}$$

$H_{\text{non-rel.}}$

### Relativistic corrections in H-atom problem.

Free particle energy is given by  $E = \sqrt{p^2 c^2 + m^2 c^4}$

K.E of relativistic particle  $K = \sqrt{p^2 c^2 + m^2 c^4} - mc^2$

$$mc^2 \sqrt{1 + \frac{p^2}{m^2 c^2}} = mc^2 \left( 1 + \frac{1}{2} \frac{p^2}{m^2 c^2} - \frac{1}{8} \frac{p^4}{m^2 c^4} + \dots \right) \xrightarrow{\text{NR Kinetic energy}} O(p^6)$$

So, the leading term in relativistic KE is -

$$K = mc^2 + \frac{p^2}{2m} - \frac{1}{8} \frac{p^4}{m^3 c^2} + \dots - mc^2$$

$$K_{\text{NR}} = \frac{p^2}{2m}, \quad K_{\text{rel-corr.}} = \underline{\underline{-\frac{p^4}{8m^3 c^2}}}$$

Using  $\delta \hat{H} = -\frac{\hat{p}^4}{8m^3 c^2}$ , we can calculate  $\langle \psi | \delta \hat{H} | \psi \rangle$ , which is

the first order correction in energy of hydrogen atom problem -

$$\begin{aligned} \Rightarrow \delta E_{\text{nl}} &= \langle \psi_{\text{nlm}} | \delta \hat{H} | \psi_{\text{nlm}} \rangle = -\frac{\hbar^4}{8m^3 c^2} \int d^3 \vec{r} \psi_{\text{nlm}}^* \nabla^4 \psi_{\text{nlm}} \\ &= -E_n \cdot \frac{Z^2 \alpha^2}{n} \left( \frac{3}{4n} - \frac{1}{l+1/2} \right) \end{aligned}$$

$$\boxed{\alpha \equiv \frac{e^2}{4\pi\epsilon_0 k_c}}$$

The relativistic energy shift  $\delta E_{\text{rel}}$  is maximum for  $n=1$ .

For a given value of  $n$  though, the correction is maximum for  $l=0$ .

(intuitively, because this orbit is closest to nucleus)

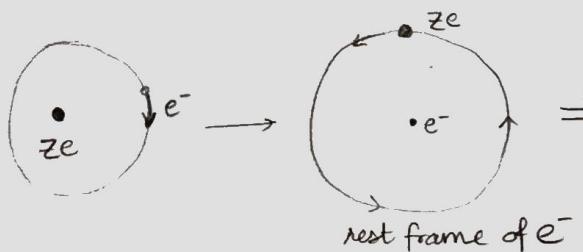
### SPIN-ORBIT COUPLING.

$$\vec{\mu}_s = -2 \frac{\mu_B}{\hbar} \vec{s}$$

magnetic spin moment

$$\vec{\mu}_e = -\frac{e}{2m} \vec{l} = -\frac{\mu_B}{\hbar} \vec{l}$$

orbital magnetic moment.



$$\Rightarrow \vec{B}_e = \frac{\mu_0 Ze}{4\pi m r^3} \vec{l} \quad (\text{from Biot-Savart's law.})$$

The spin of the electron interacts with the magnetic field present at the centre.

$$\text{Then } \delta E = -\vec{\mu}_s \cdot \vec{B}_e \sim \underline{\underline{\hat{S} \cdot \hat{L}}}$$

Lecture-19.

(28-10-21)

(Demtröder 5.5.4, 6.5)

$$\text{Since } \hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}} \Rightarrow \hat{J}^2 = \hat{L}^2 + \hat{S}^2 + 2 \hat{\vec{S}} \cdot \hat{\vec{L}}$$

$$\underline{\underline{\vec{S} \cdot \vec{L} = \frac{\hat{J}^2 - \hat{L}^2 - \hat{S}^2}{2}}}$$

$$\Rightarrow \text{So, } \delta \hat{H} \sim \underline{\underline{\frac{\hat{J}^2 - \hat{L}^2 - \hat{S}^2}{2}}}$$

For an eigenstate  $|\psi; n, l, j, s\rangle$

$s = \frac{1}{2}$

$$\delta E_{l,j} = \langle \psi; n, l, j, s | \delta \hat{H} | \psi; n, l, j, s \rangle \sim \frac{\hbar^2}{2} [j(j+1) - l(l+1) - s(s+1)]$$

$$\Rightarrow E_{n,l,j} = E_n + \left( \frac{a}{2} [j(j+1) - l(l+1) - s(s+1)] \right) \quad \text{where } a = \frac{\mu_0 Ze^2 \hbar^2}{8\pi m_e^2 r^3}$$

In both spin-orbit coupling and relativistic corrections-

Relativistic correction

$$E_n = -E_0 \frac{Z^2}{n^2}$$

$$\text{So, } \delta E_{\text{rel.}} = +E_0 \frac{Z^4 \alpha^2}{n^3} \left( \frac{3}{4n} - \frac{1}{l+\frac{1}{2}} \right)$$

$$E_{n,l} = E_n + \delta E_{\text{rel.}} = E_n \left( 1 - Z^2 \alpha^2 \left( \frac{3}{4n} - \frac{1}{l+\frac{1}{2}} \right) \right) \quad \text{where } E_n = -E_0 \frac{Z^2}{n^2}$$

## ② Spin-orbit coupling.

$$E_{n,l,s} = E_n + \delta E_{\text{so}}$$

$$\delta E_{\text{so}} = -\frac{E_n}{2} Z^2 \alpha^2 \left[ \frac{j(j+1) - l(l+1) - s(s+1)}{nl(l+\frac{1}{2})(l+\frac{1}{2})} \right]$$

$$\Rightarrow E_{n,l,s} = E_n \left[ 1 - \frac{Z^2 \alpha^2}{2} \frac{(j(j+1) - l(l+1) - s(s+1))}{nl(l+\frac{1}{2})(l+\frac{1}{2})} \right]$$

Combining these, we get the full fine structure energy shift-

$$E_{n,j} = E_n \left[ 1 + \frac{Z^2 \alpha^2}{n} \left( \frac{1}{j+\frac{1}{2}} - \frac{3}{4n} \right) \right]$$

The dependence on  $l$  cancels out!

## Addition of angular momentum.

In absence of any coupling,  $\vec{L}$  and  $\vec{s}$  are good q. nos. & we have a degeneracy of  $(2l+1) \times (2s+1)$  for given  $n, l, s$ .

However, if we include S-O coupling, then the energy eigenvalue is a fn of quantum number  $j$  of total ang. mom  $\vec{J}$ .

Say we have angular momenta  $\vec{l}_1$  and  $\vec{l}_2$

$$(\vec{l}_1)^2 |l_1, m_1\rangle = l_1(l_1+1)\hbar^2 |l_1, m_1\rangle, (\vec{l}_1)_z |l_1, m_1\rangle = m_1\hbar |l_1, m_1\rangle$$

$$(\vec{l}_2)^2 |l_2, m_2\rangle = l_2(l_2+1)\hbar^2 |l_2, m_2\rangle, (\vec{l}_2)_z |l_2, m_2\rangle = m_2\hbar |l_2, m_2\rangle$$

$$-l_i \leq m_i \leq +l_i$$

Total angular momentum-

$$\vec{J} = \vec{l}_1 + \vec{l}_2$$

$$\Rightarrow j \in \{|l_1 - l_2|, \dots, l_1 + l_2\} \quad \text{and } m_j \in \{-j, -j+1, \dots, j\}$$

$$|l_1, m_1\rangle \otimes |l_2, m_2\rangle$$

new basis states  $\rightarrow (2l_1+1) \cdot (2l_2+1)$  combinations.

For spin-orbit coupling

$$\vec{J} = \vec{l} + \vec{s}$$

$$j \in \{|l-s|, \dots, l+s\}$$

$$m_j \in \{-j, \dots, +j\}$$

$$\vec{l}^2 |l, m_l\rangle = l(l+1)\hbar^2 |l, m_l\rangle, L_z |l, m_l\rangle = m_l\hbar |l, m_l\rangle$$

$$\vec{s}^2 |s, m_s\rangle = s(s+1)\hbar^2 |s, m_s\rangle, S_z |s, m_s\rangle = m_s\hbar |s, m_s\rangle$$

$$l = 0, 1, 2, 3, 4, \dots$$

$$\begin{array}{ccccc} \text{Label} & S & P & D & F \\ & & & & G \end{array}$$

Spectroscopic notn

$${}^{2s+1} L_J$$

(1)

Lecture - 20.  
(29-10-21)

$$\vec{J} = \vec{L} + \vec{S} \quad (\text{addition of any momentum})$$

$$j \in \{|l-s|, \dots, |l+s|\} \quad (\text{decreases in steps of unity})$$

$$\text{For } s=\frac{1}{2} \Rightarrow j=l \pm \frac{1}{2} \quad (\text{for } l \geq 1. \text{ for } l=0, j=\frac{1}{2})$$

For each  $j$  value,  $\exists (2j+1)$  components of  $m_j$  values.

$$m_j \in \{-j, \dots, +j\}$$

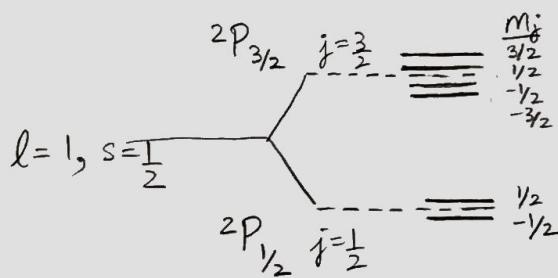
$$l=2 \quad s=\frac{1}{2}$$

$$j \in \{|2+1|, \dots, |2-1|\} = \{1, 2, 3\}$$

$$l=1 \quad s=\frac{1}{2}$$

$$j \in \{\frac{1}{2}, \frac{3}{2}\}$$

$\downarrow$  4  $m_j$  values  
2  $m_j$  values



External  $\vec{B}$  field splits degeneracies.

Centroid of split levels weighted by their degeneracies is at the same level as the unsplit energy  $\Rightarrow$

$$\boxed{\frac{1}{N} \sum_{j=1}^N (2j+1) E_j = E(n, l, s)}$$

$$\Delta E_j \sim [j(j+1) - l(l+1) - s(s+1)]$$

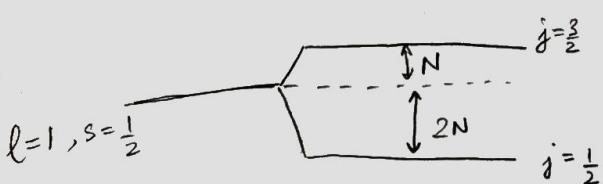
$$\Delta E_{3/2} = N \left[ \frac{3}{2} \cdot \frac{5}{2} - 2 \cdot 1 - \frac{1}{2} \cdot \frac{3}{2} \right] = N$$

$$\Delta E_{1/2} = N \left[ \cancel{\frac{1}{2}} \cdot \cancel{\frac{3}{2}} - 2 \cdot 1 - \cancel{\frac{1}{2}} \cdot \cancel{\frac{3}{2}} \right] = -2N$$

# of fine structure splittings is given by -

$$2s+1 \quad \text{if } l > s$$

$$2l+1 \quad \text{if } s > l$$



$$\begin{aligned} & \sum_i (\text{deg})_i \cdot (\Delta E)_i \\ &= 4 \cdot (N) + 2(-2N) \\ &= 0 = \Delta E_{\text{weighted}}. \end{aligned}$$

## Lecture-21

(01-11-2021)

(Potential in diatomic molecules, rotational & vibrational spectra)

If we consider the diatomic molecule as made up of dipoles, then the interaction potential obtained is known as the van-der Waals interaction potential

$$V_{\text{vdw}} = -\frac{C_6}{R^6}$$

$C_6 = -C_1 \alpha_A \alpha_B \rightarrow$  vander Waals constant.

This accommodates the attractive behaviour of molecules.

However, for small values of  $R$ , we know that  $\text{pot}^n$  must be repulsive, and hence we use the empirical Lenard-Jones potential

$$E_{\text{pot}^n}^{\text{LJ}}(R) = \frac{a}{R^{12}} - \frac{b}{R^6}$$

$R_e$  is defined s.t.

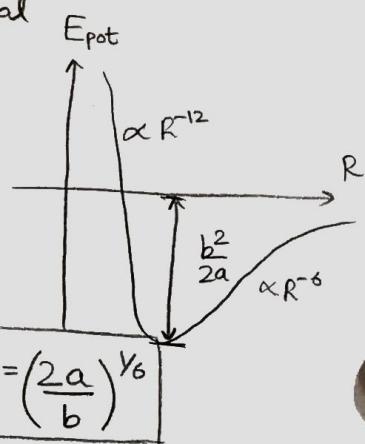
$$\left. \frac{\partial E}{\partial R} \right|_{R_e} = 0$$

$$\left. \frac{\partial E}{\partial R} \right|_{R_e} = -\frac{12a}{R_e^{13}} + \frac{6b}{R_e^7} = 0$$

$$\frac{12a}{R_e^6} = 6b \Rightarrow R_e = \left(\frac{2a}{b}\right)^{1/6}$$

$$E(R_e) = \frac{\alpha b^2}{4a^2} - \frac{bb}{2a} = -\frac{b^2}{2a}$$

$$E(R_e) = -\frac{b^2}{2a}$$



Morse potential.

A much better approximation to molecular potential is given by the empirical Morse pot<sup>n</sup>, which matches closely to real pot<sup>n</sup>.

$$E_{\text{Morse}}(R) = E_D [1 - e^{-a(R-R_e)}]^2$$

$E_D \equiv$  dissociation energy

$R_e \equiv$  equilibrium value of  $R$

$$\lim_{R \rightarrow 0} E_{\text{pot}}(R) = E_D (1 - e^{aR_e})^2$$

$$\lim_{R \rightarrow \infty} E_{\text{pot}}(R) = E_D$$

### Rotation and Vibration of Diatomic molecules.

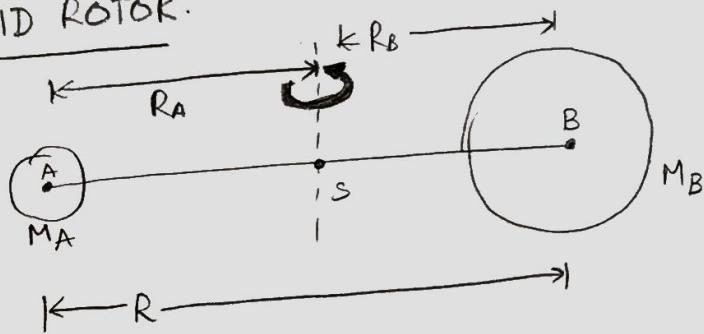
$$\hat{H} = -\frac{\hbar^2}{2} \sum_{k=1}^2 \frac{1}{M_k} \nabla_k^{(n)} \cdot \nabla_k^{(n)} - \frac{\hbar^2}{2m_e} \sum_{j=1}^N \nabla_j^{(e)} \cdot \nabla_j^{(e)}$$

$$+ \frac{e^2}{4\pi\epsilon_0} \left[ \frac{z_1 z_2}{R} + \sum_{ij} \frac{1}{r_{ij}} - \sum_i \left( \frac{z_1}{r_{i1}} + \frac{z_2}{r_{i2}} \right) \right]$$

We also include motion of nucleus & they are no longer rigid.

One can solve this by considering  $\hat{T}_{\text{nuclei}}$  ( $\hat{T}_{\text{nuclei}} \ll \hat{H}^{(0)}$ ) as a perturbation and using first order perturbation theory with  $\hat{H}^{(0)}$  wavefn's.

### RIGID ROTOR:



$$I = M_A R_A^2 + M_B R_B^2$$

$$= \mu R^2$$

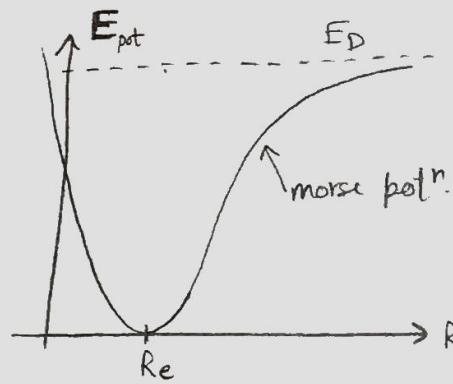
$$\mu = \frac{M_A M_B}{M_A + M_B}, \quad M_A R_A = M_B R_B$$

$$E_{\text{rot}^n} = \frac{1}{2} I \omega^2 = \frac{J^2}{2I} \quad (\text{classically})$$

For quantum,  $J^2 \rightarrow \hat{J}^2 \Rightarrow$  on the eigenstates of ang. mom<sup>n</sup>,

$$E_{\text{rot}^n} = \frac{j(j+1)\hbar^2}{2\mu R^2}$$

$$j = 0, 1, 2, \dots$$



We usually use waves in spectroscopy, so-

$$\frac{E_{\text{rot}}}{hc} = \varepsilon_j = \frac{j(j+1)h}{8\pi^2\mu R^2 c} = B j(j+1) \text{ cm}^{-1}$$

where  $B = \frac{h}{8\pi^2\mu R^2 c} \rightarrow \text{rot}^n \text{ constant.}$

The energy separation b/w  $j$  &  $j+1$  levels -

$$\Delta E_j = E_{\text{rot}}(j+1) - E_{\text{rot}}(j) = \frac{(j+1)h^2}{\mu R^2} \quad \begin{matrix} \text{increases linearly} \\ \text{with } j \end{matrix}$$

$$= 2B(j+1)hc$$

Lecture - 22  
(02 - 11 - 2021)

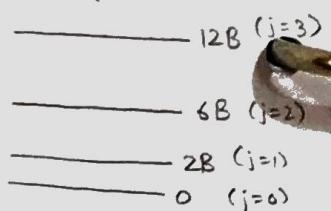
Book : Fundamentals of molecular spectroscopy - Banwell. (Section 2.3)

Problem: We are given wavenumbers of absorption lines in rot<sup>n</sup> spectrum of HCl.

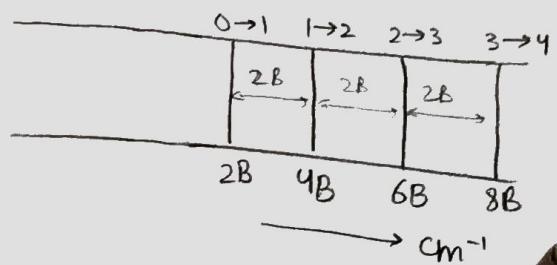
The lines correspond to transitions b/w  $j$  &  $j+1$

because of the [selection rule  $\Delta j = \pm 1$ ]

$$E = B j(j+1)$$



$$\overline{\nu}_{j \rightarrow j+1} = \varepsilon_{j+1} - \varepsilon_j = B(j+1)(j+2) - B j(j+1) = \underline{2B(j+1)}$$



If we observe the following lines-

<u>lines</u>	1	2	3	4	5
$\text{cm}^{-1}$	$x_1$	$x_2$	$x_3$	$x_4$	$x_5$

should ideally be the same

$$\langle \Delta x \rangle = \frac{1}{4} \sum_{i=1}^4 (x_{i+1} - x_i)$$

$$\text{Then } \langle \Delta x \rangle \stackrel{!}{=} 2B = \frac{2h}{48\pi^2 \mu R^2 c} \quad (\text{For a pure rot}^n \text{ spectrum})$$

$$\Rightarrow I = \frac{h}{4\pi^2 c \langle \Delta x \rangle}$$

$$\text{Given that we have a HCl molecule, } \mu = \frac{M_H M_{\text{Cl}}}{M_H + M_{\text{Cl}}} = \frac{35 \times 1}{35 + 1} \times \underbrace{1.66 \times 10^{-27}}_{1 \text{ a.u.}} \text{ kg}$$

$$\therefore R_e = \sqrt{\frac{I}{\mu}}$$

Important: Homonuclear Diatomic molecules ( $H_2, N_2, \dots$ ) do not show rotational spectrum, since they don't have any dipole moment & don't interact with radiation.

Heteronuclear molecules however have a dipole moment, and hence a rot<sup>n</sup> spectrum.

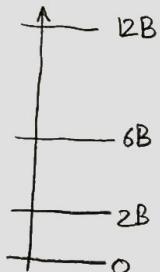
Probability of rotational spectrum transitions-

Prob. of transition decides the intensity of the spectral line.

We want to see if probability of transition  $0 \rightarrow 1$  is same as probability of transition  $1 \rightarrow 2$ .

The intrinsic probability of transitions is identical & doesn't depend on the energy levels. However, this is not the only deciding factor.

The occupation probability of energy levels plays an important role in the value of transition prob. & hence intensity of line.



At equilibrium, the occupation probability is given by Boltzmann distribution

$$N_j \propto e^{-\beta E_j}$$

$$\Rightarrow \frac{N_j}{N_0} = e^{-\beta(E_j - E_0)} = e^{-\beta E_j} \quad \text{since } E_0 = 0$$

At 300K, and the typical value of  $B \approx 2 \text{ cm}^{-1}$ , then  $P(j=1)$

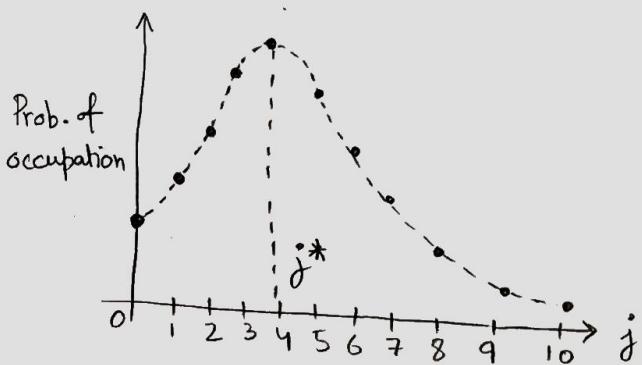
$$P(j=1) = \frac{N_1}{N_0} = e^{-\beta E_1} = e^{-\beta(Bhc j(j+1))} \Big|_{j=1} = e^{-2\beta Bhc} \approx 0.98$$

However, the occupation prob. also depends on the degeneracy of rot<sup>n</sup> levels.

Each level is  $(2j+1)$ -fold degenerate.

$$\therefore \text{Probability of occupation} \propto (2j+1) \cdot e^{-\beta E_j}$$

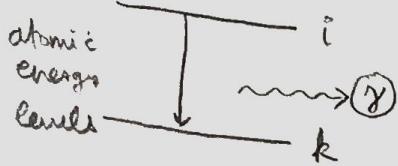
$$E_j = Bhc j(j+1)$$



It is maximum at some intermediate value of  $j^*$ . So the spectral line is max. for that transition

$$j^* \rightarrow j^* + 1$$

## LIGHT-MATTER INTERACTION



$$E_i - E_k = h\nu = h\omega$$

conservation of energy.

$i \rightarrow k$  atomic transition

Can be electronic, vibrational or rotational energy level transitions.

However, not all transitions allowed by conservation of energy are observed.

There exist certain selection rules which determine if a transition is allowed or not.

e.g. Rot<sup>h</sup> levels  $J \rightarrow J \pm 1$  or  $\Delta J = \pm 1$

Another conservation law is the conservation of angular momentum!

Broad topics in this -

- Einstein's A & B coeffs.
- Line broadening, line width.
- Two level atom in radiation field.

(Demtroder ch-7)

Einstein's coefficients

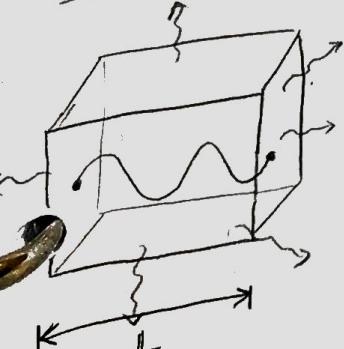
Atom + thermal radiation field

$$\text{Cavity modes: } k_x = \frac{\pi n_x}{L}, k_y = \frac{\pi n_y}{l}, k_z = \frac{\pi n_z}{\ell}$$

$$\Rightarrow |\vec{k}| = \frac{\pi}{L} \sqrt{n_x^2 + n_y^2 + n_z^2} \Rightarrow \lambda = \frac{2\pi}{k} = \frac{2L}{\pi \sqrt{n_1^2 + n_2^2 + n_3^2}}$$

$(n_1, n_2, n_3) \rightarrow$  mode of a cavity radiation field.

$\Rightarrow$  wavevector  $\vec{k}$  is quantized.



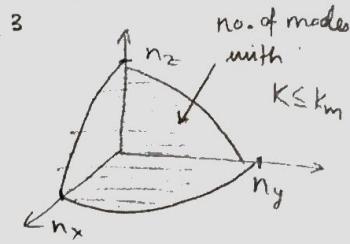
Spectral mode density  $\equiv$  No. of modes per unit volume per unit frequency range,  $\Delta\nu = 1\text{s}^{-1}$

$$n(\nu) = \frac{8\pi\nu^2}{c^3} \Rightarrow \text{No. of modes} = n(\nu)d\nu = \frac{8\pi\nu^2 d\nu}{c^3}$$

b/w  $\nu$  &  $\nu + d\nu$

Spectral energy density

$$\boxed{\omega_\nu = n_\nu \bar{\omega}_\nu (k_B T)} \rightarrow \text{average energy per mode}$$



$$\bar{\omega}_\nu (k_B T) = \sum (\text{energy of mode}) \cdot (\text{probability of mode})$$

$$\bar{\omega}_\nu = \sum_{n=0}^{\infty} E_n e^{-E_n \beta} = \frac{1}{Z} \cdot \left( -\frac{\partial Z}{\partial \beta} \right) = -\frac{\partial \ln Z}{\partial \beta}$$

$$= -\frac{\partial}{\partial \beta} \left( h\nu\beta - \ln(e^{h\nu\beta} - 1) \right) = -\left( h\nu - \frac{1}{e^{h\nu\beta} - 1} \cdot e^{h\nu\beta} \cdot h\nu \right) = \frac{h\nu}{e^{h\nu\beta} - 1}$$

$$\Rightarrow \omega_\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{h\nu\beta} - 1} \rightarrow \text{Planck's law.}$$

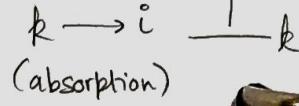
For Planck

$$Z = \sum_{n=0}^{\infty} e^{-\frac{n h\nu}{k_B T}} = \frac{e^{-h\nu/k_B T}}{e^{h\nu/k_B T} - 1}$$

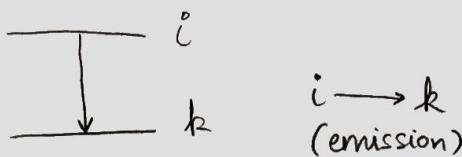
Light Matter Interaction - 3 processes.

① Stimulated absorption

$$\frac{dP_{ki}^{(\text{abs})}}{dt} \equiv \text{probability of absorption transition per second.}$$



$$\frac{dP_{ki}^{(\text{abs})}}{dt} = B_{ki} \omega_\nu$$



② Stimulated emission

$$\frac{dP_{ik}^{(\text{emis.})}}{dt} = B_{ik} \omega_\nu$$

( $\propto \omega_\nu$  since radiation field is involved)

③ Spontaneous emission: (not induced by radiation field)

$$\frac{dP_{ik}}{dt}^{\text{(spont. em.)}} = A_{ik} \quad \rightarrow \text{not dependent on } \omega_v$$

Stationary condition -

$$B_{ki} \omega_v N_k = (B_{ik} \omega_v + A_{ik}) \cdot N_i$$

total absorption rate = total emission rate

$$\text{At thermal eqm, } \frac{N_i}{N_k} = \frac{g_i}{g_k} e^{-\beta(E_i - E_k)}$$

i.  $\dots N_i$  atoms  
k.  $\dots N_k$  atoms  
This occurs in the first place because higher excited states are unstable, not because of external perturbations

$g_i, g_k$  are the degeneracies of each energy level.

$$B_{ki} \omega_v = (B_{ik} \omega_v + A_{ik}) \frac{g_i}{g_k} e^{-\beta(E_i - E_k) \underbrace{\hbar\nu}_{\text{h}\nu}}$$

$$\omega_v (B_{ki} - B_{ik} \frac{g_i}{g_k} e^{-\beta h\nu}) = A_{ik} \frac{g_i}{g_k} e^{-\beta h\nu}$$

$$\Rightarrow \omega_v = \frac{\frac{A_{ik}}{B_{ik}}}{\frac{g_k}{g_i} \frac{B_{ki}}{B_{ik}} e^{\beta h\nu} - 1}$$

Equating this with Planck's law,  $\omega_v = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\beta h\nu} - 1}$

By comparing the two, we get

$$\frac{A_{ik}}{B_{ik}} = \frac{8\pi h\nu^3}{c^3} \quad \text{and} \quad \frac{g_k B_{ki}}{g_i B_{ik}} = 1$$

$$\Rightarrow B_{ik} = \frac{g_k}{g_i} B_{ki} \quad \text{and} \quad A_{ik} = \frac{8\pi h\nu^3}{c^3} B_{ik}$$

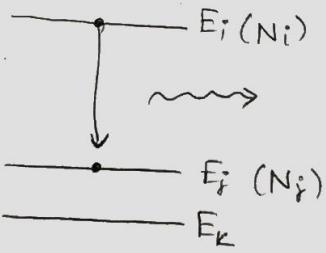
## Lifetimes of excited states.

Fluorescence transition: spontaneous emission.  $E_i \rightarrow E_j$

Since  $\frac{dP_{ij}}{dt}^{(\text{spont.})} = A_{ij} \Rightarrow \frac{dN_i}{dt} = -N_i A_{ij}$

↑  
- since # of particles decrease.

$$\Rightarrow dN_i = -N_i A_{ij} dt$$



If it decays into states lower than  $E_j$ , then  $A_i \equiv \sum_j A_{ij}$

and  $dN_i = -N_i A_i dt$

$$\Rightarrow N_i(t) = N_i(0) e^{-A_i t}$$

The lifetime is  $\tau_i \equiv 1/A_i \Rightarrow N_i(\tau_i) = N_i(0)/e$

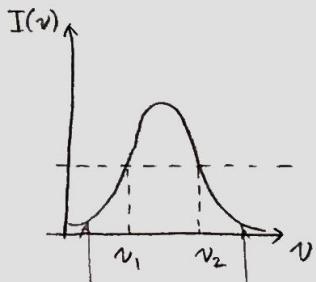
No. of particles that decay down to g.s. in  $dt$  time  $\frac{dN_i}{dt} dt$ . But all of them have lived for time  $t$ . So, the total time they all have lived is  $t \cdot dN_i$ .  
 $\Rightarrow \tau = \frac{1}{N_0} \int_{t=0}^{t=\infty} dN_i \cdot t$

If we have additional relaxation process, with prob./sec.  $= R_i$ , then

$$N_i(t) = N_i(0) e^{-i(A_i + R_i)t} \Rightarrow \tau_i = \frac{1}{R_i + A_i} \Rightarrow \frac{1}{\tau_i} = \frac{1}{\tau_{\text{spont}}} + R_i$$

## Line profiles of spectral lines.

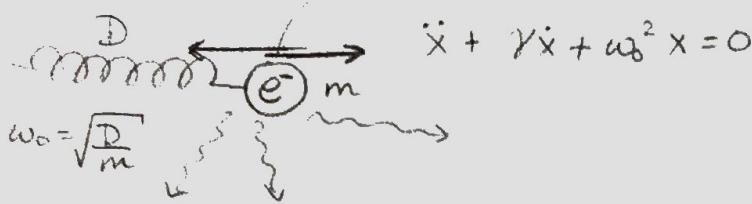
As one might expect,  $\Delta E = E_i - E_k = h\nu$  doesn't give rise to a sharp spectral line with a fixed definite frequency. This gives a line profile to a spectral line.



$$\text{Linewidth} \equiv v_2 - v_1 = \delta v \quad (\text{FWHM})$$

outside range is called line wings.

Natural linewidth.  $\rightarrow$  excited state  $e^-$



Starting with  $x(t=0) = x_0$  and  $\dot{x}(t=0) = -x_0 \cdot \gamma/2$

$$x(t) = x_0 e^{-(\gamma/2)t} \left[ \cos(\omega t) + \frac{\gamma}{2\omega} \sin(\omega t) \right] \quad \text{with } \omega = \sqrt{\omega_0^2 - (\frac{\gamma}{2})^2}$$

Since  $\gamma \ll \omega_0$  in most cases,

$$x(t) \approx x_0 e^{-(\gamma/2)t} \cos(\omega t) \quad \begin{matrix} \rightarrow \text{time dependent} \\ \text{amplitude} \Rightarrow \text{spread in emitted radiation} \end{matrix}$$

Fourier transform of  $x(t)$  gives  $A(\omega)$

$$A(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dt e^{-i\omega t} x(t) = \frac{1}{\sqrt{2\pi}} \int_0^{\infty} dt e^{-i\omega t} (x_0 e^{-\gamma t/2} \cos(\omega t))$$

$$= \frac{x_0}{\sqrt{8\pi}} \left[ \frac{1}{i(\omega_0 - \omega) + \gamma/2} + \frac{1}{i(\omega_0 + \omega) + \gamma/2} \right]$$

$$\approx \frac{x_0}{\sqrt{8\pi}} \cdot \frac{1}{i(\omega_0 - \omega) + \gamma/2} \quad \text{near } \omega \approx \omega_0$$

$$\Rightarrow P_{\omega}(\omega) \propto |A(\omega)|^2 = \frac{C}{(\omega - \omega_0)^2 + (\gamma/2)^2} \quad \rightarrow \text{Lorentzian profile}$$

Demanding  $\int_0^{\infty} P_{\omega}(\omega) d\omega = P_0 \Rightarrow$

$$P_{\omega}(\omega) = P_0 \frac{\gamma/2\pi}{(\omega - \omega_0)^2 + (\gamma/2)^2}$$

If the profile is given by  $P_{\omega}(\omega)$ , then FWHM is  $\delta\omega = \gamma$

$$\text{i.e. FWHM } (P_{\omega}(\omega)) = \delta\omega = \gamma \Rightarrow \underline{\underline{\delta\nu = \gamma/2\pi}}$$

$\uparrow$   
natural linewidth!

Since we have an intrinsic broadness due to Heisenberg's uncertainty principle

i.e.  $\Delta E \Delta t \geq \hbar$  but  $\Delta t \sim T$

So, the min. uncertainty that inherently exists is  $\Delta E = \frac{\hbar}{T}$

$$\Rightarrow \Delta v = \frac{\Delta E}{\hbar} = \frac{\hbar}{T h} = \frac{1}{2\pi T} = \delta v$$

Assuming  $\delta v = \frac{1}{2\pi T}$  for natural line width as well  $\Rightarrow \delta v = \frac{1}{2\pi T} = \frac{\gamma}{2\pi}$

$$\therefore T_i = \frac{1}{A_i} \text{ and } \delta v = \frac{1}{2\pi T_i} \Rightarrow \boxed{\delta v = \frac{A_i}{2\pi} = \frac{1}{2\pi T_i}}$$

↑                      ↑  
 from  $N_i(t) = N_0 e^{-A_i t}$       from Heisenberg's  
 uncertainty principle

$$\text{and for natural broadening, } \delta v = \frac{\gamma}{2\pi} = \frac{A_i}{2\pi} = \frac{1}{2\pi T_i} \Rightarrow A_i = \frac{1}{T_i} = \gamma$$

### Collision Broadening.

$\exists$  molecular interactions in liquids and gases. More severe interactions in liquids compared to gases, so more broadening in liquids.

Becomes important near  $R_{coll.}$  &  $T_{coll} = R_{coll}/v_e$ .

$$\langle T \rangle = \frac{d}{v} = \left(\frac{V}{N}\right)^{1/3} \cdot \frac{1}{v} = \frac{n^{-1/3}}{v} \quad \langle T \rangle \neq T_{coll}$$

↑  
 mean collision time



$$d = \left(\frac{V}{N}\right)^{1/3} = \frac{1}{n^{1/3}}$$

↑  
 avg. distance b/w atoms

The intensity of spectral lines actually depends on a number of factors -

- ① Transition probability.
- ② Population of states.
- ③ Path length of the sample.

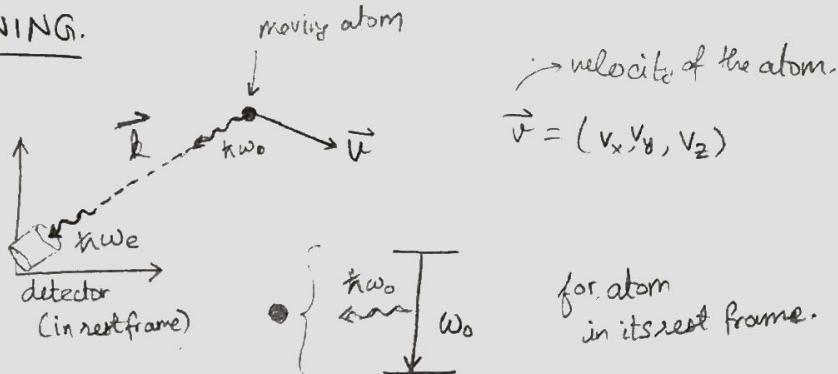
## Lecture - 26

(15-11-2021)

### DOPPLER BROADNING.

→ For emission -

$$\omega_e = \omega_0 + \vec{k} \cdot \vec{v}$$

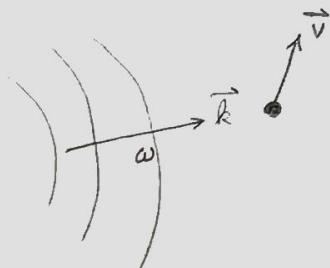


→ In absorption, assume that the radiation incident to the atom in observer's rest frame is  $(\vec{\omega}, \vec{k})$

$$\Rightarrow \omega' = \omega - \vec{k} \cdot \vec{v}$$

freq. observed  
in atom's rest frame

freq. of incident  
wave



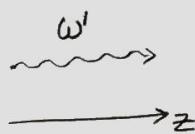
The absorption only occurs only if  $\omega' = \omega_0$

i.e. doppler shifted freq. = the transition gap.  $\Rightarrow \omega_a = \omega \stackrel{!}{=} \omega_0 + \vec{k} \cdot \vec{v}$   
so that  $\omega' = \omega_0 + \vec{k} \cdot \vec{v} - \vec{k} \cdot \vec{v}$

Let the wave travel in z-direction

$$\omega_a = \omega = \omega_0 + k_z v_z$$

$$= \omega_0 \left(1 + \frac{v_z}{c}\right)$$



• (in atom's rest frame)

At thermal eq<sup>n</sup>, the no. density of atoms in level  $|i\rangle$  with velocity b/w  $v_z$  &  $v_z + dv_z$

$$n_i(v_z) dv_z = \frac{N_i}{V_{mp} \sqrt{\pi}} e^{-(v_z/V_{mp})^2} dv_z$$

$$V_{mp} = \sqrt{\frac{2k_B T}{M}}$$

$$\text{where } N_i \equiv \int_{-\infty}^{\infty} dv_z n_i(v_z)$$

If  $v_z$  &  $dv_z$  are expressed in terms of  $\omega$  &  $d\omega$ -

$$v_z = \frac{c}{\omega_0}(\omega - \omega_0) \Rightarrow dv_z = \frac{c}{\omega_0} d\omega$$

$$n_i(v_z) dv_z = n_i(\omega) d\omega$$

$$= \frac{C N_i}{\omega_0 V_{mp} \sqrt{\pi}} e^{-\left(\frac{c(\omega-\omega_0)}{\omega_0 V_{mp}}\right)^2} d\omega$$

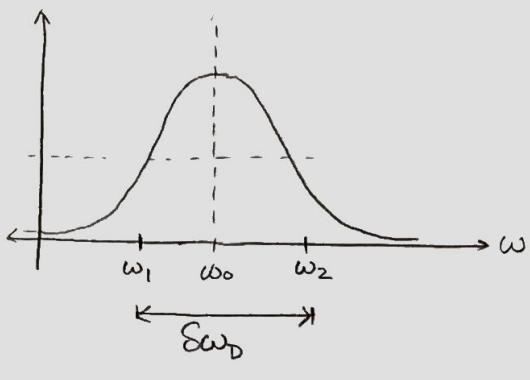
no. density of atoms that  
absorber emit radiation  
b/w  $\omega$  &  $\omega + d\omega$

Since spectral power density  $P(\omega) \propto n(\omega)$

Gaussian profile!

$$P(\omega) = P(\omega_0) e^{-\left(\frac{c}{\omega_0 V_{mp}}\right)^2 (\omega-\omega_0)^2}$$

→ intensity profile of Doppler-broadened lines



$$\Delta\omega_D = |\omega_1 - \omega_2|$$

$$\text{where } P(\omega_1) = P(\omega_2) = \frac{P(\omega_0)}{2}$$

Now,

$$\ln \left( \frac{P(\omega_0)}{P(\omega)} \right) = \left( \frac{c}{\omega_0 V_{mp}} \right)^2 (\omega - \omega_0)^2$$

$$\Rightarrow \ln \left( \frac{P(\omega_0)}{P(\omega_{1,2})} \right) = \ln 2 = \left( \frac{c}{\omega_0 V_{mp}} (\omega_{1,2} - \omega_0) \right)^2$$

$$\omega_1 - \omega_0 = - \frac{\omega_0 V_{mp}}{c} \sqrt{\ln 2}$$

$$\omega_2 - \omega_0 = + \frac{\omega_0 V_{mp}}{c} \sqrt{\ln 2}$$

$$\Delta\omega_D = \frac{N_0}{C} \sqrt{\frac{8 k_B T \ln 2}{m}}$$

$$\Delta\omega_D = \frac{2 \omega_0 V_{mp} \sqrt{\ln 2}}{c} = \frac{\omega_0}{c} \sqrt{\frac{8 k_B T \ln 2}{m}}$$

This also implies

$$\frac{c}{\omega_0 V_{mp}} = \frac{2 \sqrt{\ln 2}}{\Delta\omega_D} \approx \frac{1}{0.68 \Delta\omega_D}$$

$$\Rightarrow P(\omega) = P(\omega_0) e^{-[(\omega - \omega_0)/0.68 \Delta\omega_D]^2}$$

In visible range, the Doppler broadened line is two orders of magnitude larger than natural line width.

(1)

Lecture - 28  
 (18-11-2021)

Two-level quantum systems interacting with radiation.

$$\vec{E} = \vec{E}_0 e^{i(\vec{k} \cdot \vec{x} - \omega t)}, \quad \vec{B} = \vec{B}_0 e^{i(\vec{k} \cdot \vec{x} - \omega t)}$$

The interaction Hamiltonian, which acts as a perturbation is

$$\hat{H}' = -\vec{p} \cdot \vec{E} \quad \longrightarrow E_2$$

The unperturbed Hamiltonian's eigenfns are known-  $\longrightarrow E_1$

$$\hat{H}^0 \psi_1 = E_1 \psi_1 \quad \hat{H}^0 \psi_2 = E_2 \psi_2$$

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \quad \text{where } \psi_i \text{ are the spatial part of stationary solns.}$$

$$\psi_j^{(0)}(\vec{r}, t) = \psi_j(\vec{r}) e^{-i E_j t / \hbar} \quad \text{Define } \omega_j \equiv E_j / \hbar$$

The general soln of unperturbed  $\hat{H}^0$  is-

$$\psi^{(0)}(\vec{r}, t) = C_1 \psi_1 e^{-i \omega_1 t} + C_2 \psi_2 e^{-i \omega_2 t}$$

where

$$|C_1|^2 + |C_2|^2 = 1$$

Let us now introduce the new Hamiltonian-

$$\hat{H} = \hat{H}^{(0)} + \hat{H}'(t)$$

and the general soln now should have  $C_1$  &  $C_2$  as fns of time i.e.

$$C_1 \equiv C_1(t) \quad \& \quad C_2 \equiv C_2(t)$$

$$\Rightarrow \psi(\vec{r}, t) = C_1(t) \psi_1 e^{-i \omega_1 t} + C_2(t) \psi_2 e^{-i \omega_2 t}$$

(2)

Putting the  $\Psi(t)$  into  $i\hbar \frac{\partial \Psi(t)}{\partial t} = (\hat{H}^{(0)} + \hat{H}') \Psi(t) -$

$$i\hbar [ \dot{c}_1 e^{-i\omega_1 t} |\psi_1\rangle + \dot{c}_2 e^{-i\omega_2 t} |\psi_2\rangle ] = \hat{H}' [ c_1 e^{-i\omega_1 t} |\psi_1\rangle + c_2 e^{-i\omega_2 t} |\psi_2\rangle ]$$

Taking overlaps with  $\langle \psi_1 |$  &  $\langle \psi_2 |$

$$i\hbar e^{-i\omega_1 t} \dot{c}_1 = c_1 e^{-i\omega_1 t} H'_{11} + c_2 e^{-i\omega_2 t} H'_{12}$$

$$i\hbar e^{-i\omega_2 t} \dot{c}_2 = c_1 e^{-i\omega_1 t} H'_{21} + c_2 e^{-i\omega_2 t} H'_{22}$$

$$\Rightarrow \dot{c}_1 = -\frac{i}{\hbar} [ c_1 H'_{11} + c_2 H'_{12} e^{-i\Delta\omega_{21} t} ] \quad \Delta\omega_{21} \equiv \omega_2 - \omega_1$$

$$\dot{c}_2 = -\frac{i}{\hbar} [ c_1 H'_{21} e^{+i\Delta\omega_{21} t} + c_2 H'_{22} ]$$

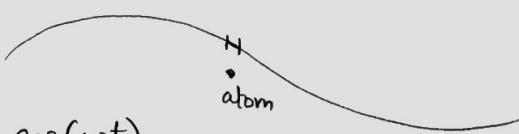
Dipole approximation:

$$\overrightarrow{E} \downarrow \Rightarrow \lambda \approx 100\text{nm}$$

whereas dim's of atom  $\approx 0.1\text{nm}$

$\therefore$  Over the spatial dim's of the atom

$$e^{i\vec{k} \cdot \vec{x}} \approx 1 \Rightarrow \vec{E} = \vec{E}_0 e^{-i\omega t} \equiv \vec{E}_0 \cos(\omega t)$$



$$\text{So, } \hat{H}' = -\vec{p} \cdot \vec{E} = -(-e\vec{r}) \cdot (\vec{E}) = e\vec{r} \cdot \vec{E} = e\hat{z} E_0 \cos(\omega t)$$

$$\text{Now, } H'_{11} \sim \langle \psi_1 | \hat{z} | \psi_1 \rangle = 0 = H'_{22}$$

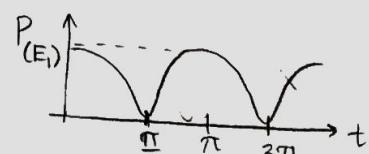
$\uparrow$  odd fn

(taking  $\vec{E}_0 = E_0 \hat{z}$ )  
for convenience

$$H'_{12} = e E_0 \langle \psi_1 | \hat{z} | \psi_2 \rangle \underset{\cos(\omega t)}{\equiv} \Omega_{12} \hbar \omega \cos(\omega t) \quad \Omega \text{ is the Rabi frequency.}$$

$$\Rightarrow \dot{c}_1 = -i [\Omega_{12} e^{-i\Delta\omega_{21} t} c_2] \cos(\omega t)$$

$$\dot{c}_2 = -i [\Omega_{12}^* e^{+i\Delta\omega_{21} t} c_1] \cos(\omega t)$$



$$\Omega T = \pi$$

$$T = \underline{\pi / \Omega}$$

Tutorial  
(22-11-2021)

Problem 1 For a thermal radiation field, find the average no. of photons in a mode at  $\lambda = 500 \text{ nm}$  for the sun. ( $T = 6000 \text{ K}$ )

$$\begin{aligned} \text{Mean no. of photons} = \langle n \rangle &= \frac{\sum_{n=0}^{\infty} n e^{-\beta h\nu}}{\sum_{n=0}^{\infty} e^{-\beta h\nu}} = \frac{\sum_{n=0}^{\infty} n e^{-\beta h\nu}}{e^{\beta h\nu} / (e^{\beta h\nu} - 1)} \\ &= \frac{1}{Z} \sum_{n=0}^{\infty} n e^{-\beta h\nu} = - \frac{\partial Z}{\partial \beta} \cdot \frac{1}{Z} \cdot \frac{1}{h\nu} \\ &= - \frac{\partial}{\partial \beta} (\ln Z) \cdot \frac{1}{h\nu} = \frac{h\nu}{e^{\beta h\nu} - 1} \cdot \frac{1}{h\nu} = \frac{1}{e^{\beta h\nu} - 1} \end{aligned}$$

So, 
$$\boxed{\langle n \rangle = \frac{1}{e^{h\nu/k_B T} - 1}}$$

$$\frac{h\nu}{k_B T} = \frac{hc}{\lambda k_B T} = \frac{hc}{(500 \text{ nm}) \cdot (6000 \text{ K}) k_B}$$

$$= \frac{1.44}{3} \times \frac{10^{-25}}{10^{-26}} = \frac{1.44}{3} \times 10 = \frac{14.4}{3} = 4.8$$

$$\Rightarrow \boxed{\langle n \rangle = 0.0083}$$

$$= \frac{1.44}{3 \times 10^4 \times 10^{-9} \times 1.35 \times 10^{-22}}$$

avg No. of photons in a mode of freq  $\nu$  is  $\langle n \rangle = \frac{1}{e^{\beta h\nu} - 1}$

No. of modes b/w freq.  $\nu$  &  $\nu + d\nu$  (per unit volume)  $N_\nu(\nu) d\nu = \frac{8\pi}{c^3} \nu^2 d\nu$

Total # of photons with freq. b/w  $\nu$  &  $\nu + d\nu = \frac{8\pi \nu^2}{c^3} \cdot \frac{1}{e^{\beta h\nu} - 1} \cdot d\nu$

$\Rightarrow$  spectral energy density = total energy per unit volume for freq. b/w  $\nu$  &  $\nu + d\nu$  =  $h\nu \cdot \frac{8\pi \nu^2}{c^3} \cdot \frac{1}{e^{\beta h\nu} - 1} d\nu$

Problem 2 Find the temperature at which mean photon no. at  $\lambda = 500\text{nm}$  would be unity = 1.

$$\Rightarrow 1 = \frac{1}{e^{hc/\lambda k_B T} - 1} \Rightarrow e^{hc/\lambda k_B T} = 2$$

$$\frac{hc}{\lambda k_B T} = \ln 2 \Rightarrow T = \frac{hc}{\lambda k_B \ln 2} \sim 4166\text{ K}$$

$$\frac{hc}{k_B} = \frac{1.986 \times 10^{-25}}{1.381 \times 10^{-23}} = 1.438 \times 10^{-2} = 0.01439$$

Problem 3. If rate of induced emission is  $x$  units, find the corresponding rate of spontaneous emission.

$$A_{ik} = \frac{8\pi v^3 h}{c^3} B_{ik} \underset{x}{\underset{\parallel}{\Rightarrow}} A_{ik} = \frac{8\pi v^3 h}{c^3} x$$

Problem 4 Mean lifetime  $\leftrightarrow$  natural linewidth?

$$\delta v = \frac{1}{2\pi\tau_i} \Rightarrow \tau_i = \frac{1}{2\pi\delta v_i}$$

$$\delta E \cdot \tau = \frac{h\nu}{2\pi} = \kappa \delta v \cdot \tau$$

$$\delta v = \frac{1}{2\pi\tau_i}$$

Since  $\tau_i = \frac{1}{\gamma}$  for natural line width,

$$\delta v_i = \frac{\gamma}{2\pi}$$

Problem 5. Einstein coefficient  $A_{ik}$  is given. Given no other relaxation process, how many atoms have decayed by  $t = 2T$ .

$$T = \frac{1}{A_{ik}} \quad \frac{N(t)}{N_0} = e^{-A_{ik}t} \Rightarrow \frac{N(2T)}{N_0} = e^{-2} = \frac{1}{e^2}$$

Book Q4.  $T = 1000\text{K}$  absorption  $T = 1.4\text{ns} \longrightarrow 186,204 \text{ cm}^{-1}$  (2)

$T = 1\text{ms} \longrightarrow 166,272 \text{ cm}^{-1}$  (1)

$$\Delta \bar{v} = \bar{v}_2 - \bar{v}_1 = \frac{1}{\lambda} \Rightarrow \lambda = \frac{1}{\bar{v}_2 - \bar{v}_1}$$

Now,  $\delta v_{\text{total}} = \frac{1}{2\pi T_1} + \frac{1}{2\pi T_2} = \frac{1}{2\pi} \left( \frac{1}{T_1} + \frac{1}{T_2} \right) = \text{natural line width}$

$$\omega_0 = 2\pi v = \frac{2\pi c}{\lambda} = 2\pi c (\bar{v}_2 - \bar{v}_1) = 2\pi v_0$$

$$\text{So, } \delta v_0 = \frac{v_0}{c} \sqrt{\frac{8k_B T}{m} \ln 2} = (\bar{v}_2 - \bar{v}_1) \sqrt{\frac{8k_B T}{m} \ln 2}$$

Book Q3  $T_k = 0.39\text{ms} = 390\mu\text{s}$

$T = 900\text{K}$

$$\Rightarrow \delta v_k = \frac{1}{2\pi T} \approx 410 \text{ Hz}$$

$k$

$i$

Let's say atom interacts with EM field for time  $\Delta t$ .

$$\text{Now } \Delta v \Delta t \geq \frac{1}{2\pi} \Rightarrow \Delta t \geq \frac{1}{2\pi \Delta v}$$

and we want  $\Delta v = 3\text{kHz}$

so, without interaction,  $\Delta t = T$  (lifetime)  $\longrightarrow 410\text{Hz}$

but with interaction  $\Delta t < T \longrightarrow \delta v \uparrow \Rightarrow 3000\text{Hz}$

$$\text{i.e. } \Delta t = \frac{1}{2\pi \cdot 3000} \approx 53\mu\text{s}$$

So, if the atom decays after  $53\mu\text{s}$ , then it will  $\longrightarrow 3000\text{Hz}$   $\xrightarrow{\text{zone}}$   
 zone which it travels before decaying  $= \langle v \rangle \Delta t = \sqrt{\frac{8k_B T}{\pi m}} \cdot \Delta t$

Lecture-29.  
(25-11-2021)

2 Two level quantum system

1

$$\begin{aligned}\dot{C}_1 &= -i\Omega_{12} \cos(\omega t) e^{-i\Delta\omega_{21}t} C_2(t) & \Delta\omega_{21} \equiv \Delta\omega \\ \dot{C}_2 &= -i\Omega_{12}^* \cos(\omega t) e^{+i\Delta\omega_{21}t} C_1(t)\end{aligned}$$

To zeroth order,  $C_1 = 1$  and  $C_2 = 0$ , so

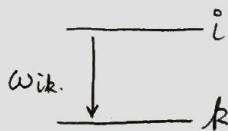
$$\begin{aligned}\dot{C}_2(t) &= -i\Omega_{21} \left( \frac{e^{i\omega t} + e^{-i\omega t}}{2} \right) e^{+i\Delta\omega_{21}t} \cdot 1 \\ \dot{C}_2(t) &= -\frac{i\Omega_{21}}{2} \left[ e^{i(\omega+\Delta\omega)t} + e^{-i(\omega-\Delta\omega)t} \right] \\ \Rightarrow C_2(t) &= -\frac{i}{2} \Omega_{21} \int_0^t dt \left[ e^{i(\omega+\Delta\omega)t} + e^{-i(\omega-\Delta\omega)t} \right] \\ &= -\frac{i}{2} \Omega_{21} \left[ \frac{e^{i(\omega+\Delta\omega)t} - 1}{i(\omega+\Delta\omega)} \quad \frac{e^{-i(\omega-\Delta\omega)t} - 1}{+i(\omega-\Delta\omega)} \right]\end{aligned}$$

Near  $\omega \approx \Delta\omega$ ,

$$\begin{aligned}C_2(t) &\approx -\frac{\Omega_{21}}{2} \frac{e^{-i(\omega-\Delta\omega)t} - 1}{(\omega-\Delta\omega)} = -\frac{\Omega_{21}}{2} \frac{e^{-i(\omega-\Delta\omega)t/2} \left[ e^{-i(\omega-\Delta\omega)\frac{t}{2}} - e^{+i(\omega-\Delta\omega)\frac{t}{2}} \right]}{(\omega-\Delta\omega)} \\ &= -\frac{\Omega_{21}}{2} \frac{e^{-i(\omega-\Delta\omega)t/2}}{(\omega-\Delta\omega)} \cdot \left( +2i \sin\left((\omega-\Delta\omega)\frac{t}{2}\right) \right) \\ &= i\Omega_{21} e^{-i(\omega-\Delta\omega)t/2} \sin\left((\omega-\Delta\omega)\frac{t}{2}\right) \cdot \frac{1}{(\omega-\Delta\omega)}\end{aligned}$$

$$\Rightarrow P_{1 \rightarrow 2} = |C_2(t)|^2 \approx \frac{|\Omega_{12}|^2}{(\omega-\Delta\omega)^2} \sin^2\left(\frac{(\omega-\Delta\omega)t}{2}\right)$$

### Spontaneous emission.



Average power radiated by spontaneous emission-

$$\langle P \rangle = N_i A_{ik} \hbar w_{ik}. \quad (1)$$

Emission is also modelled by an oscillating electric dipole. The power radiated by such a dipole is-

$$P = \frac{2}{3} \frac{\omega^4}{4\pi\epsilon_0 c^3} \langle \vec{p}^2 \rangle_{\text{time avg.}} \rightarrow \frac{p_0^2}{2} \quad \vec{P} = q\vec{r} = \vec{p}_0 \sin(\omega t)$$

$$P = \frac{1}{3} \frac{\omega^4}{4\pi\epsilon_0 c^3} p_0^2 \rightarrow \text{classical result}$$

Quantum mechanically,  $\langle \vec{P} \rangle = e \langle \vec{r} \rangle = e \int d\tau \psi_i^* \hat{r} \psi_i$

A more general integral which reduces to  $\langle \vec{r} \rangle$  for  $i=k$   $\Rightarrow \vec{M}_{ik} \equiv e \int d\tau \psi_i^* \vec{r} \psi_k$ .

This gives the power radiated b/w 2 levels -

$$\langle P_{ik} \rangle = \frac{4}{3} \frac{\omega_{ik}^4}{4\pi\epsilon_0 c^3} |M_{ik}|^2 \quad (2)$$

Comparing (1) & (2), we can write the Einstein coeffs. as

$$A_{ik} = \frac{2}{3} \frac{\omega_{ik}}{\epsilon_0 h c^3} |M_{ik}|^2 \rightarrow \text{dipole matrix element.}$$

Using now the relation b/w  $A_{ik}$  &  $B_{ik}$

$$B_{ik} = \frac{2\pi^2}{3\epsilon_0 h^2} |M_{ik}|^2$$

$|M_{ik}|^2 \rightarrow$  determines probability of transition  $\rightarrow$  further determines intensity of the spectral lines.