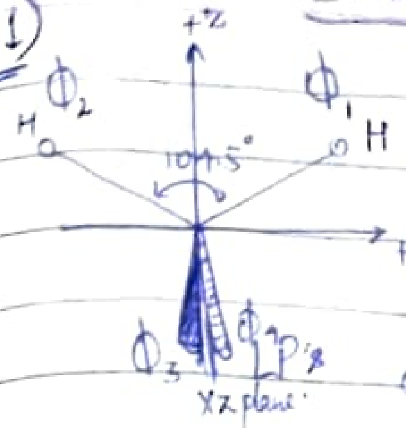
Kumar Satyam 200050064.

CH107 Tut-6.

Page No.

Date

Q1)



for Oxygen

	2s	$2p_x$	$2p_y$	$2p_z$
$\phi_1 =$	a_1	a_2	a_3	a_4
$\phi_2 =$	b_1	b_2	b_3	b_4
$\phi_3 =$	c_1	c_2	c_3	c_4
$\phi_4 =$	d_1	d_2	d_3	d_4

By Symmetry & orientations,

$a_1 = b_1$ $\quad c_1 = d_1$ $\quad a_2 = b_2 = 0$ $\quad c_2 = -d_2$

$a_3 = -b_3$ $\quad c_3 = d_3 = 0$ $\quad a_4 = b_4$ $\quad c_4 = d_4$

by Sum of Total Contributions,

$a_1^2 + c_1^2 = 1/2$ $\quad c_2 = -d_2 = 1/\sqrt{2}$ $\quad a_3 = -b_3 = 1/\sqrt{2}$

$a_4^2 + c_4^2 = 1/2$.

by Normalizn;

$a_1^2 + a_4^2 = 1/2$ $\quad c_1^2 + c_4^2 = 1/2$.

$\Rightarrow \boxed{a_1^2 = c_4^2}$ & $\boxed{a_4^2 = c_1^2}$

by Orthogonality of ϕ_1 & ϕ_3.

$a_1 c_1 + a_4 c_4 = 0$

Now

	2s	$2p_x$	$2p_y$	$2p_z$
ϕ_1	a_1	0	$1/\sqrt{2}$	a_4
ϕ_2	a_1	0	$-1/\sqrt{2}$	a_4
ϕ_3	c_1	$1/\sqrt{2}$	0	c_4
ϕ_4	c_1	$-1/\sqrt{2}$	0	c_4

Angle b/w ϕ_1 & ϕ_2 = 104.5°

$$\therefore \cos(104.5^\circ) = \frac{\frac{1}{\sqrt{2}} \cdot -\frac{1}{\sqrt{2}} + a_4^2}{\sqrt{\frac{1}{2} + a_4^2}\sqrt{\frac{1}{2} + a_4^2}} = \frac{a_4^2 - \frac{1}{2}}{a_4^2 + \frac{1}{2}}.$$

$\Rightarrow \boxed{a_4 = 0.5475}$

$\Rightarrow a_1 = 0.4748$

$\Rightarrow C_1 = 0.5475$

$\Rightarrow C_4 = -0.4748$

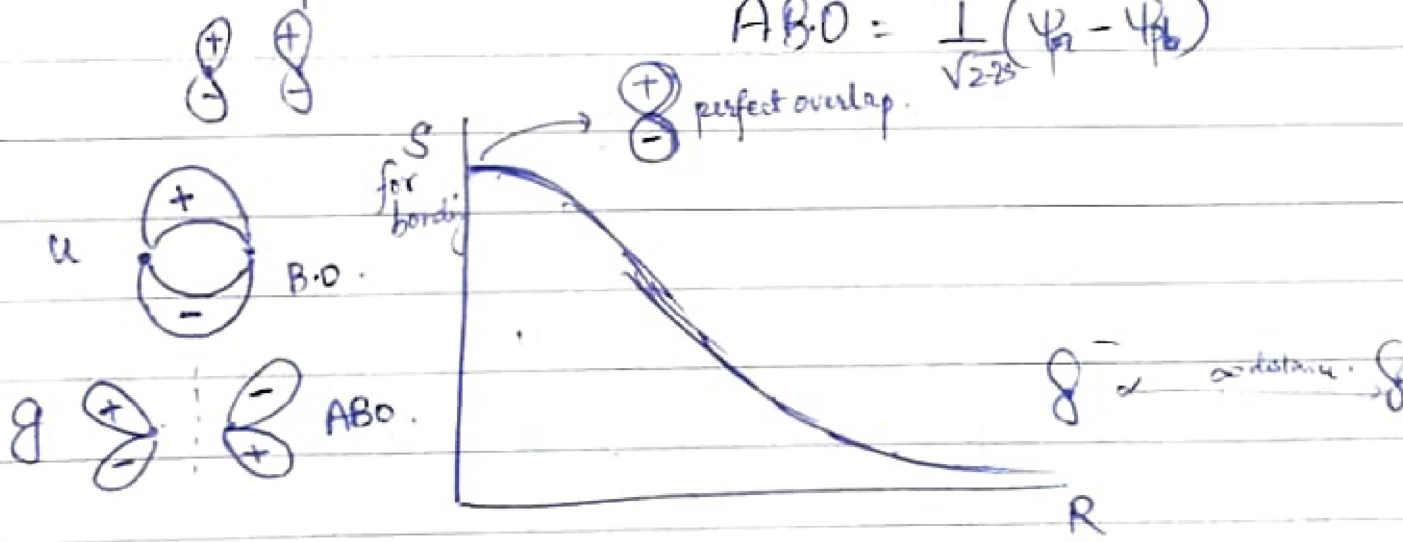
So finally.

	2s	$2p_x$	$2p_y$	$2p_z$
$\phi_1 =$	0.4748	0	$1/\sqrt{2}$	0.5475
$\phi_2 =$	0.4748	0	$-1/\sqrt{2}$	0.5475
$\phi_3 =$	0.5475	$1/\sqrt{2}$	0	-0.4748
$\phi_4 =$	0.5475	$-1/\sqrt{2}$	0	-0.4748

Q2) (i) pp

$$B.O = \frac{1}{\sqrt{2+2S}}(\psi_a + \psi_b)$$

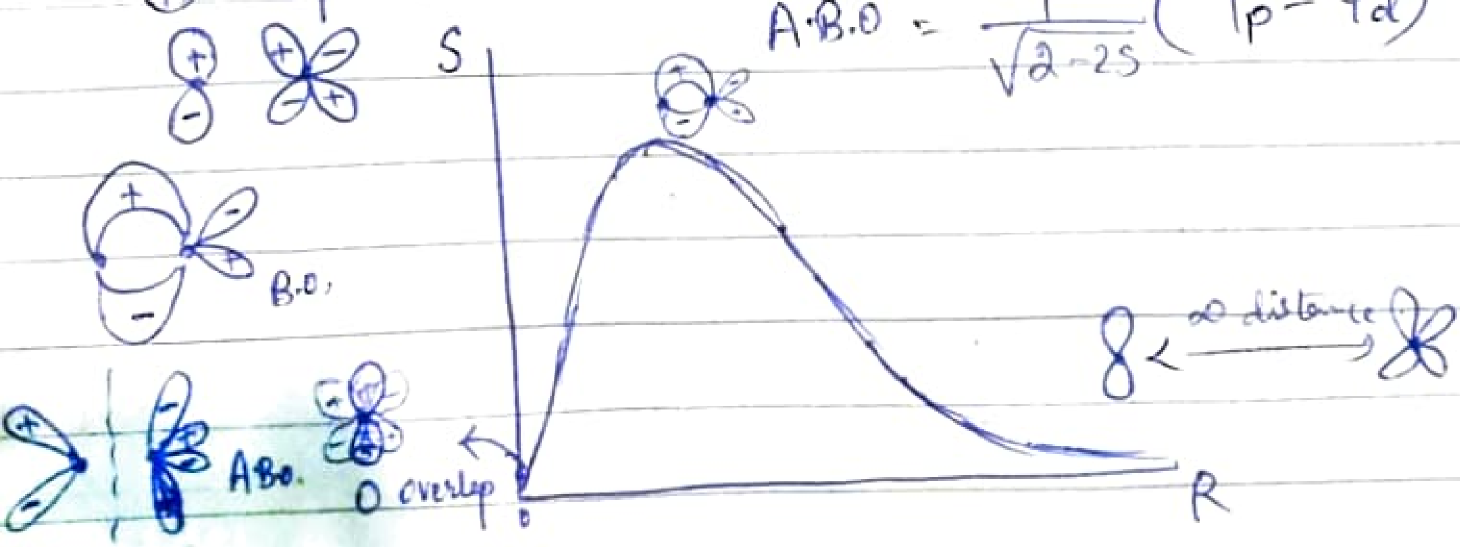
$$ABO = \frac{1}{\sqrt{2-2S}}(\psi_a - \psi_b)$$



(ii) p-d

$$B.O = \frac{1}{\sqrt{2+2S}}(\psi_p + \psi_d)$$

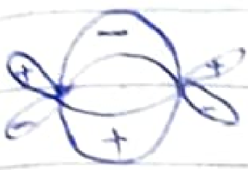
$$A.B.O = \frac{1}{\sqrt{2-2S}}(\psi_p - \psi_d)$$



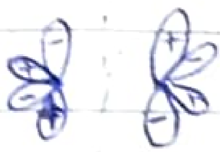
(iii) d-d. π

$$B.O. = \frac{1}{\sqrt{2+2S}}(\Psi_{d_a} - \Psi_{d_b})$$

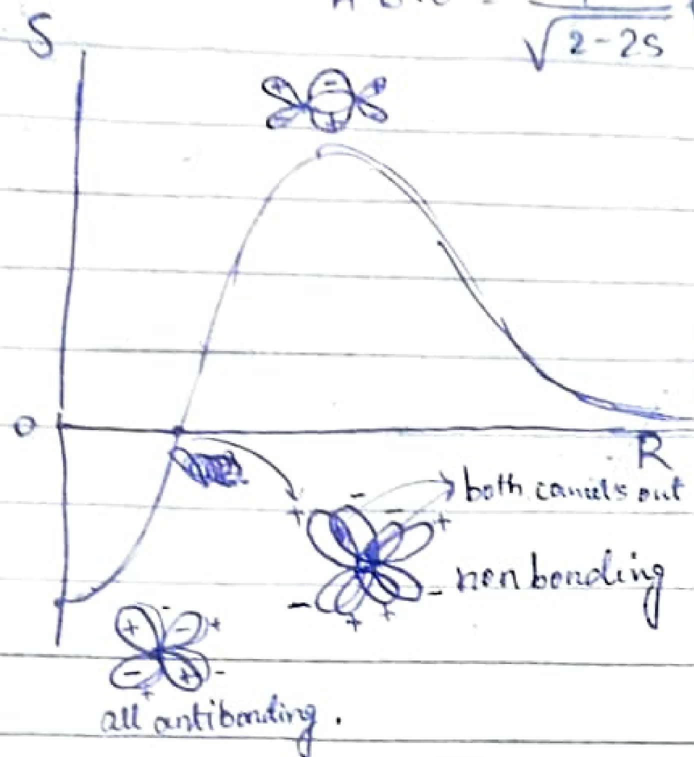
$$A.B.O. = \frac{1}{\sqrt{2-2S}}(\Psi_{d_a} + \Psi_{d_b})$$



B.O. (u)



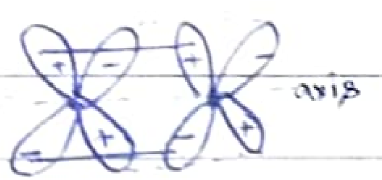
A.B.O. (g)



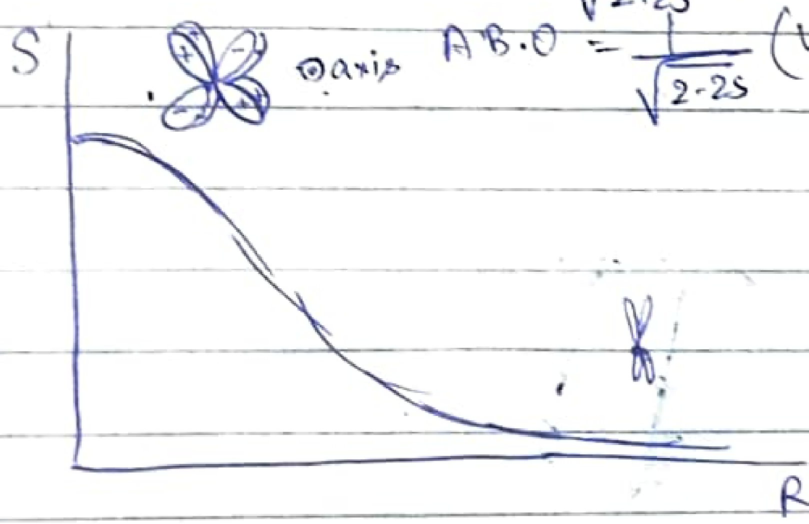
(iv) d-d δ

$$B.O. = \frac{1}{\sqrt{2+2S}}(\Psi_{d_a} + \Psi_{d_b})$$

$$A.B.O = \frac{1}{\sqrt{2-2S}}(\Psi_{d_a} - \Psi_{d_b})$$

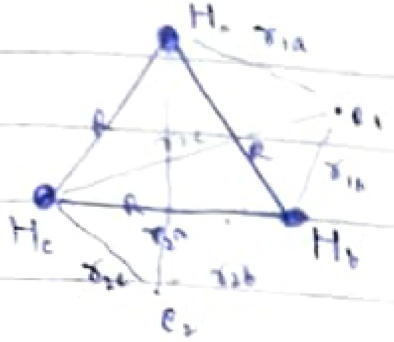


B.O. (g)



A.B.O (u)

Q.3) $H_3^{(+)}$



assume to be '0'

$$\hat{H} = \frac{-\hbar^2}{2m}\{\nabla_a^2 + \nabla_b^2 + \nabla_c^2\} + \frac{-\hbar^2}{2m}\{\nabla_{1e}^2 + \nabla_{2e}^2\} + (-Qe^2)\{\Sigma \frac{1}{r_{ia}}\}$$
$$+ (-Qe^2)\{\Sigma \frac{1}{r_{ib}}\} + (-Qe^2)\{\Sigma \frac{1}{r_{ic}}\} + \underbrace{(Qe^2)\{\frac{1}{r_{12}}\}}_{\text{Not a const}}$$
$$+ Qe^2\{\frac{3}{R}\}$$ constant for particular R

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + Qe^2\left(\frac{1}{r_{12}}\right) + Qe^2\left(\frac{3}{R}\right)$$

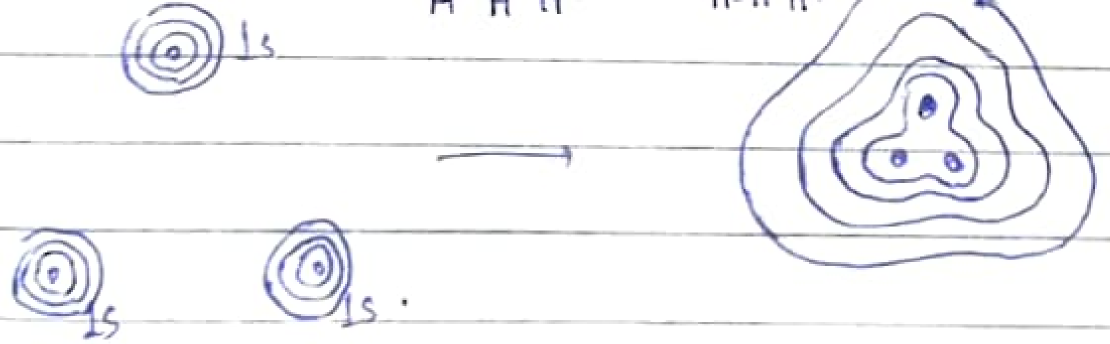
$$\hat{H}_1 = \frac{-\hbar^2}{2m}\nabla_{1e}^2 - Qe^2\left\{\sum_{a,b,c}\frac{1}{r_{1a}}\right\}$$
$$\hat{H}_2 = \frac{-\hbar^2}{2m}\nabla_{2e}^2 - Qe\left\{\sum_{a,b,c}\frac{1}{r_{2a}}\right\}$$

$\Psi_{lowest\ energy}$ is $\Psi_{bonding}(H_3^+)$

2) $\Psi_{bonding}(H_3^+) = \Psi_{bonding}(1) \cdot \Psi_{bonding}(2)$
$$= c^2(\Psi_{1s_a}^1 + \Psi_{1s_b}^1 + \Psi_{1s_c}^1)(\Psi_{1s_a}^2 + \Psi_{1s_b}^2 + \Psi_{1s_c}^2)$$
$$= c^2(\underline{\Psi_a^1\Psi_a^2} + \Psi_a^1\Psi_b^2 + \Psi_a^1\Psi_c^2 + \Psi_b^1\Psi_a^2 + \underline{\Psi_b^1\Psi_b^2} + \Psi_b^1\Psi_c^2 + \Psi_c^1\Psi_a^2 + \Psi_c^1\Psi_b^2 + \underline{\Psi_c^1\Psi_c^2})$$

Ionic terms like $H^- H^+ H^+$

covalent terms with ionic too $H-H\ H^+$



b) Since Ψ in prev part is Symmetric wrt exchange operator

$$\therefore \Psi_{\substack{\text{with spin}\\ \text{bonding}}} = c^2(\psi_a^1+\psi_b^1+\psi_c^1)(\psi_a^2+\psi_b^2+\psi_c^2)\left[\frac{1}{\sqrt{2}}\alpha(1)\beta(2)-\frac{1}{\sqrt{2}}\alpha(2)\beta(1)\right]$$

antisymmetric spin part

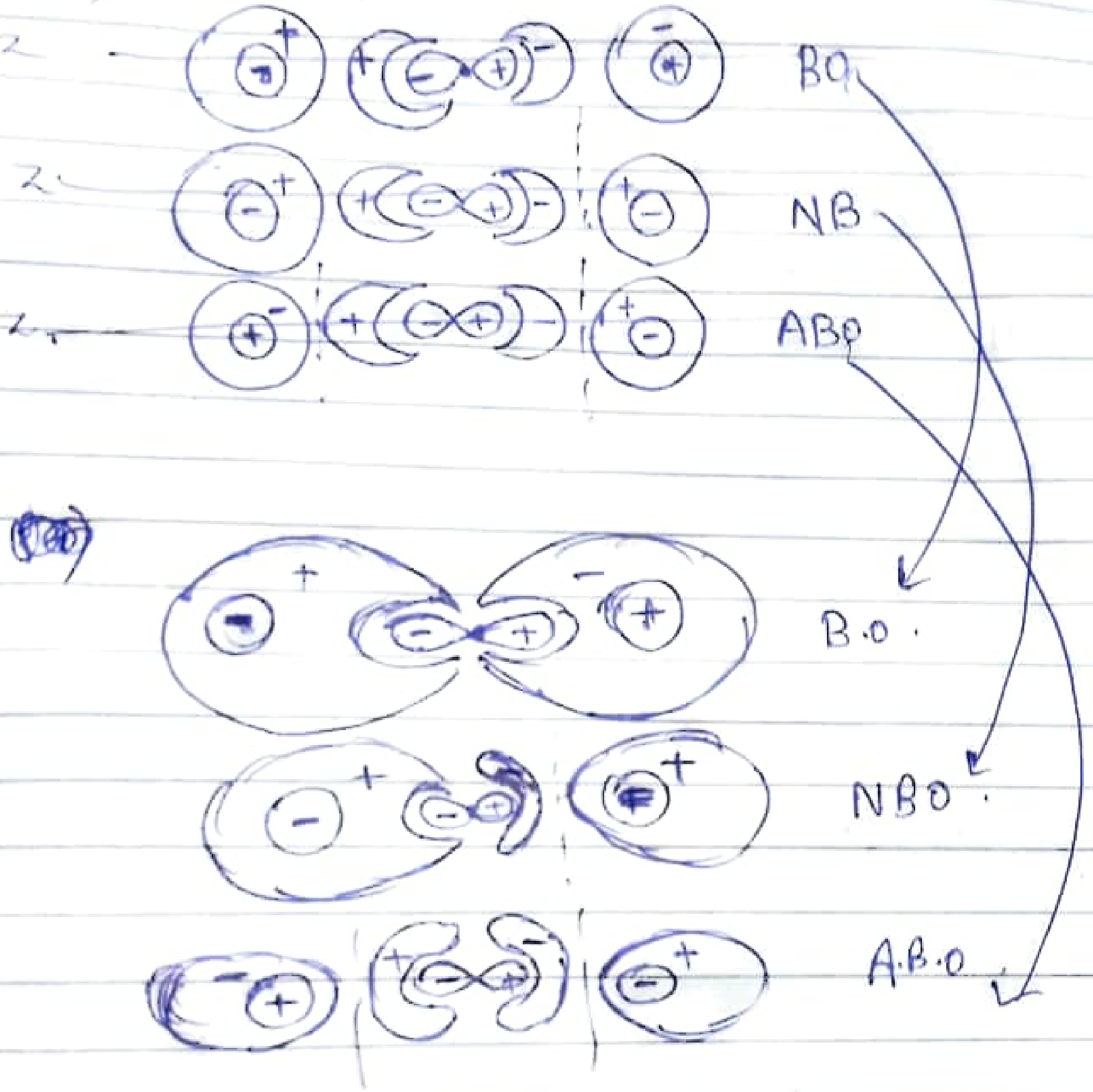
in ground state only $\Psi_{bonding}$ will be occupied by $2e^-$.

~~c)~~ $\cancel{\Psi = \frac{c^2}{\sqrt{2}}\left[\quad\right]}$

c) Write this in single slater determinant form

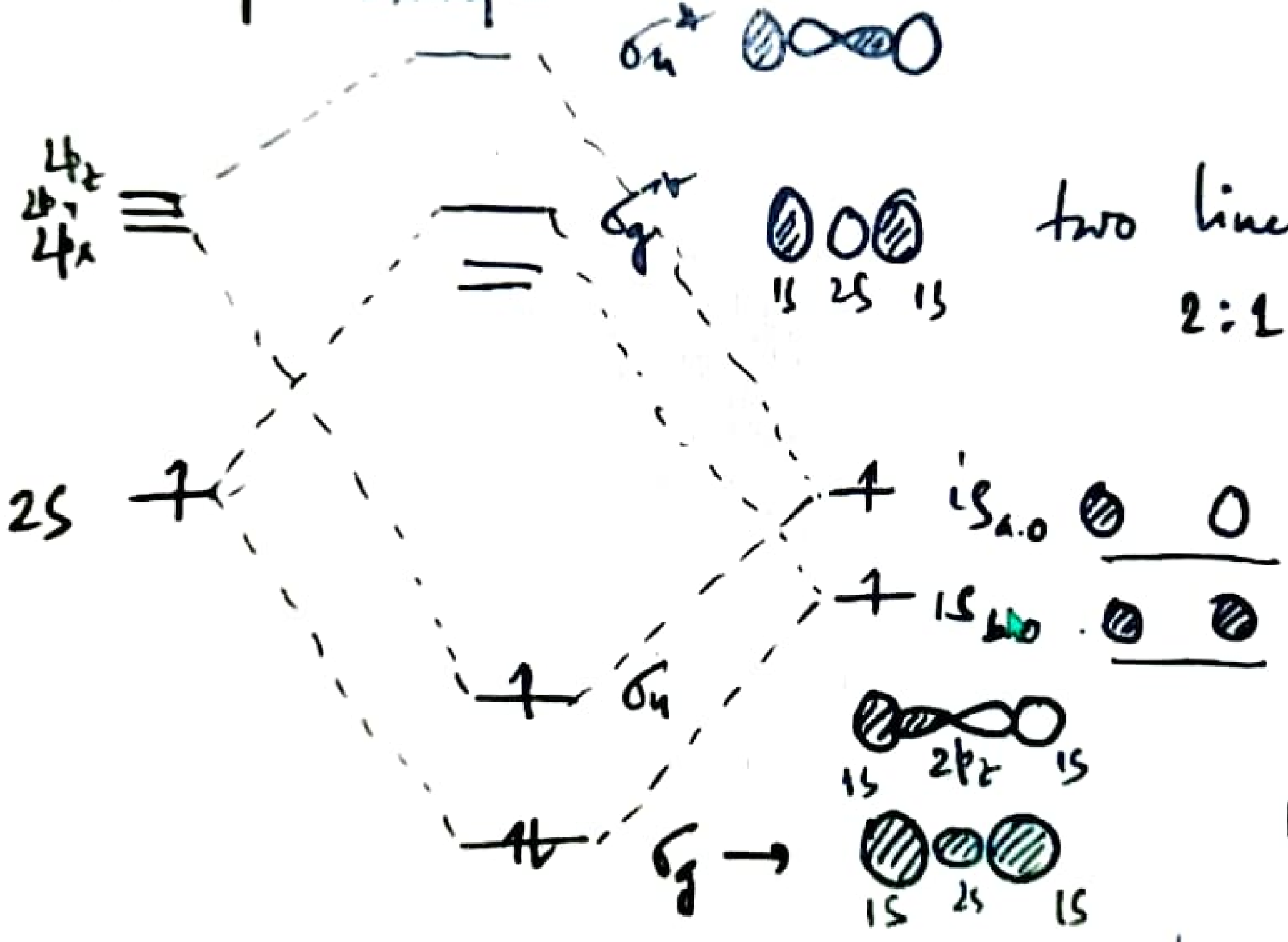
$$\Psi = \frac{c^2}{\sqrt{2}}\begin{vmatrix} \psi(1)\alpha(1) & \psi(1)\beta(1) \\ \psi(2)\alpha(2) & \psi(2)\beta(2) \end{vmatrix}$$

Q4)



We can do it graphically too.

5. Without s-p Mixing -



two lines with 2:1 intensity.