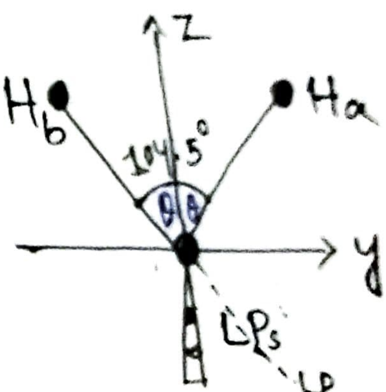
Tutorial-6

Q-1



$\phi_a = N\left[\sin\theta \cdot \psi_{2p_y} + \cos\theta \cdot \psi_{2p_z} - \alpha \cdot \psi_{2s}\right]$

$\phi_b = N\left[\cos\theta \cdot \psi_{2p_z} - \sin\theta \cdot \psi_{2p_y} - \alpha \psi_{2s}\right]$

Now; $\langle \phi_a | \phi_b \rangle = 0$

$\Rightarrow N^2\left[\cos^2\theta \langle \psi_{2p_z} | \psi_{2p_z}\rangle - \sin^2\theta \langle \psi_{2p_y} | \psi_{2p_y}\rangle + \alpha^2 \langle \psi_{2s} | \psi_{2s}\rangle\right] = 0$

$\Rightarrow N^2\left[(\cos^2\theta - \sin^2\theta) + \alpha^2\right] = 0$

$\Rightarrow \cos 2\theta + \alpha^2 = 0$

$\Rightarrow \alpha^2 = 0.25038 \quad (2\theta = 104.5°)$

$\Rightarrow \alpha = 0.5001$

So $N^2 = \dfrac{1}{\cos^2\theta + \sin^2\theta + \alpha^2} = \dfrac{1}{(0.61)^2 + (0.79)^2 + (0.50)^2}$

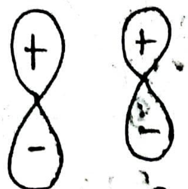
$= 0.8957$

$\phi_a = 0.89\left[0.61\, \psi_{2p_z} + 0.79\, \psi_{2p_y} - 0.5\, \psi_{2s}\right]$

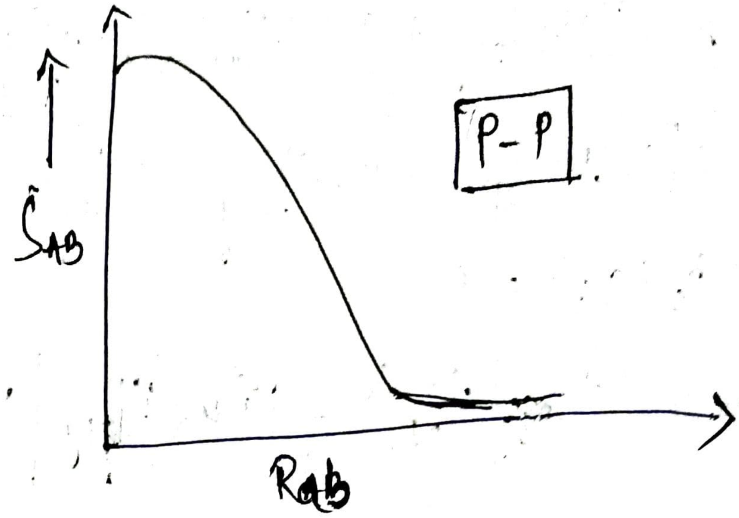
$\phi_b = 0.89\left[0.61\, \psi_{2p_z} - 0.79\, \psi_{2p_y} - 0.5\, \psi_{2s}\right]$

Q-2) a, b, c.

(i)



p p.



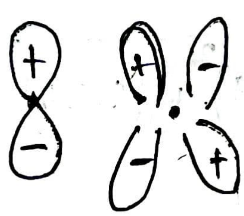
$$\psi_{bonding} = (\psi_p + \psi_p)\cdot\frac{1}{\sqrt{2(1+S_{ab})}}$$

$$\psi_{Antibonding} = (\psi_p - \psi_p)\cdot\frac{1}{\sqrt{2(1-S_{ab})}}$$

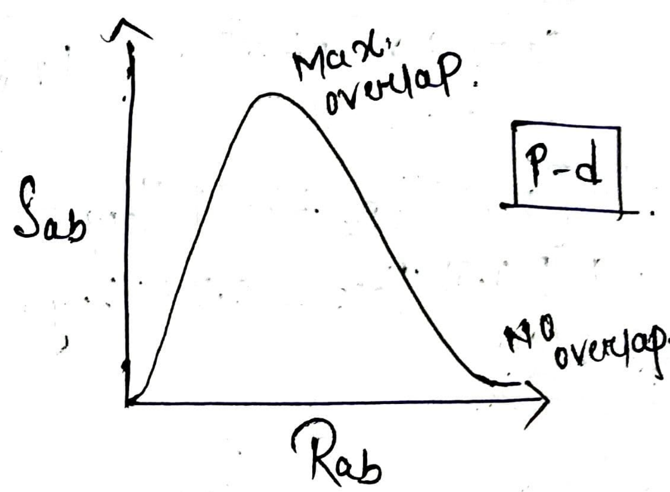
$\psi_{b.o.}$ =  π_u

$\psi_{a.b}$ =  π_g^*

(ii).



p d.

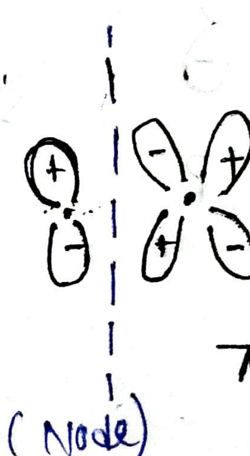


$$\psi_{b.o} = C_\alpha \psi_p + C_\beta \psi_d.$$

$$\psi_{a.o.} = C'_\alpha \cdot \psi_p - C'_\beta \cdot \psi_d.$$

$\psi_{b.o.}$ = 

π (symmetry can't assign)

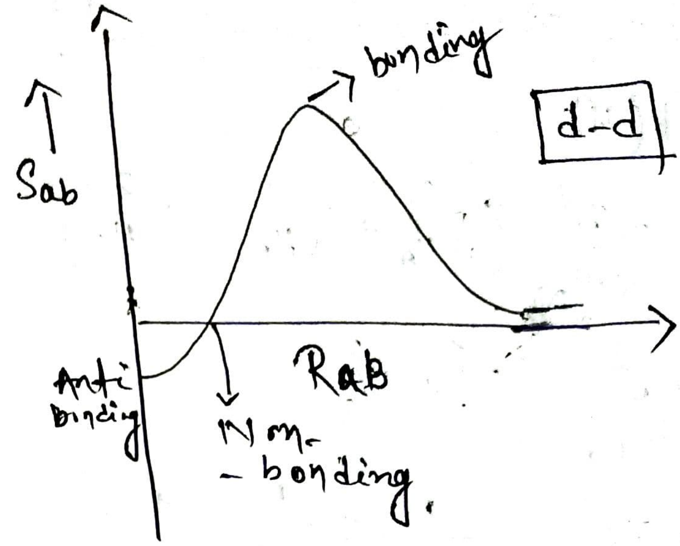
$\psi_{a.b}$ = 

(Node)

π^* (symmetry can't assign.)

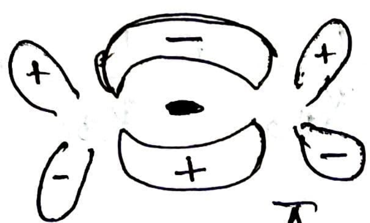
(iii)

d d



$\psi_{b.o} = C_\alpha \cdot \psi_d + C_\beta \cdot \psi_d$

$\psi_{a.b} = C'_\alpha \cdot \psi_d - C'_\beta \cdot \psi_d$.

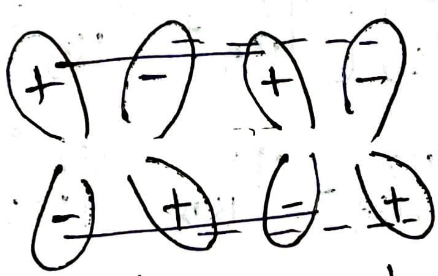
$\psi_{b.o}$ = 

π_u

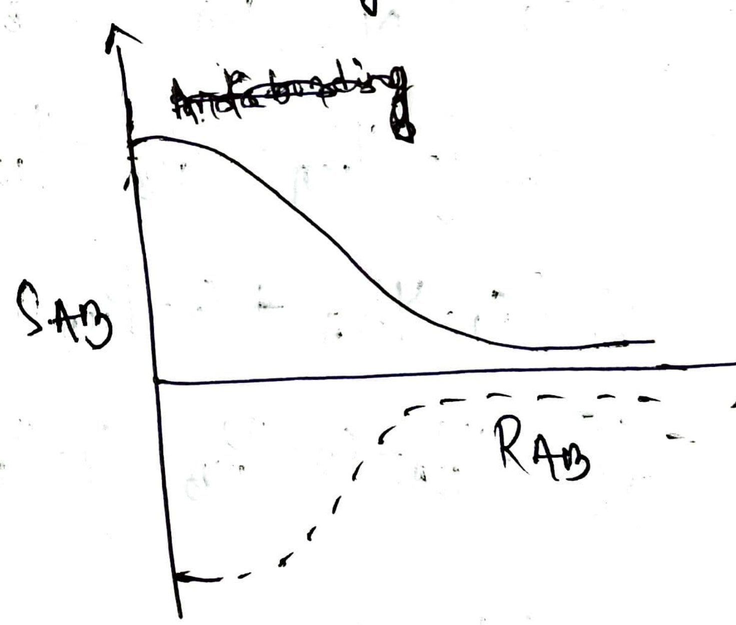
$\psi_{a.b}$ = 

π_g^* (Node)

(iv)



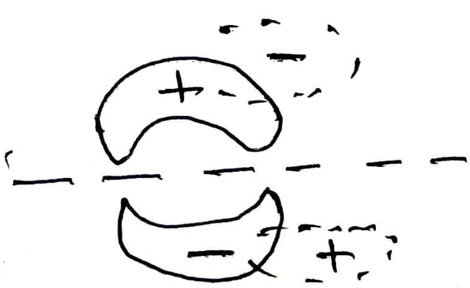
d d.



$\psi_{b.o} = C_\alpha \cdot \psi_d + C_\beta \cdot \psi_d$

$\psi_{a.o} = C'_\alpha \cdot \psi_d - C'_\beta \cdot \psi_d$.

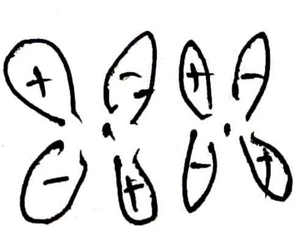
$\psi_{b.o}$



δ_g

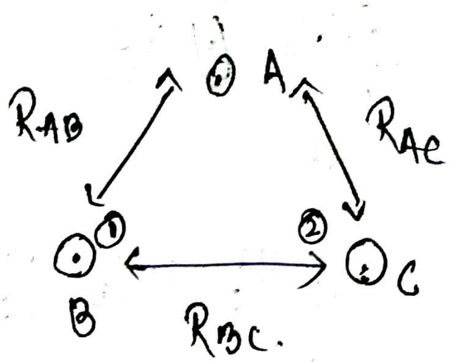
one bond at front & one at back.

$\psi_{a.o}$



δ_u^*

Q-3) H_3^+ molecular orbital :-



$\hat{H}(H_3^+)$

$$= -\frac{\hbar^2}{2m_N}\left(\nabla^2_{HA} + \nabla^2_{HB} + \nabla^2_{HC}\right)$$

$$-\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right)$$

$$-\frac{Ze^2}{4\pi\epsilon_0}\left(\frac{1}{r_{1A}} + \frac{1}{r_{1B}} + \frac{1}{r_{1C}} + \frac{1}{r_{2A}} + \frac{1}{r_{2B}} + \frac{1}{r_{2C}}\right)$$

$$+\frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_{12}}\right) + \frac{Z^2e^2}{4\pi\epsilon_0}\left(\frac{1}{R_{AB}} + \frac{1}{R_{BC}} + \frac{1}{R_{CA}}\right)$$

(a) $$\psi_{BMO} = \frac{1}{N}\left[\psi_{1sA} + \psi_{1sB} + \psi_{1sC}\right]\left[\psi_{1sA} + \psi_{1sB} + \psi_{1sC}\right]$$

or

$$\frac{1}{N}\left[-\psi_{1sA} - \psi_{1sB} - \psi_{1sC}\right]\left[-\psi_{1sA} - \psi_{1sB} - \psi_{1sC}\right]$$

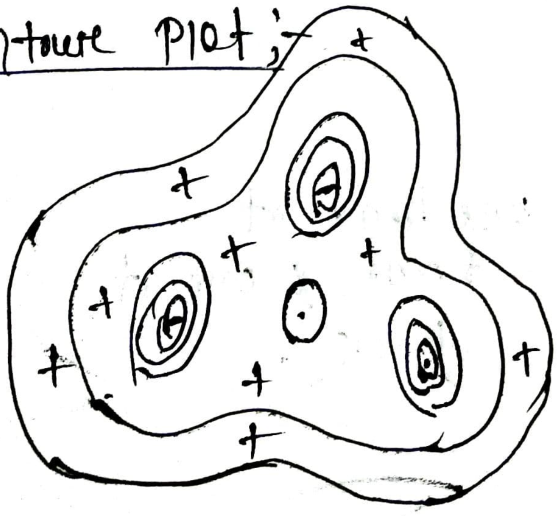
or

$$\frac{1}{N}\left[C_1\cdot\psi_{1sA} + C_2\cdot\psi_{1sB} + C_3\cdot\psi_{1sC}\right]\left[C_1\cdot\psi_{1sA} + C_2\cdot\psi_{1sB} + C_3\cdot\psi_{1sC}\right]$$

$$= \frac{1}{N}\left[-C_1\cdot\psi_{1sA} - C_2\cdot\psi_{1sB} - C_3\cdot\psi_{1sC}\right]\left[-C_1\cdot\psi_{1sA} - C_2\cdot\psi_{1sB} - C_3\cdot\psi_{1sC}\right]$$

where $C_1 = C_2 = C_3$.

Contoure plot ;-



(b) Spin wave function in ground state;-

$$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right] \quad \text{or} \quad \frac{1}{\sqrt{2}}\left[\alpha(2)\beta(1) - \alpha(1)\beta(2)\right]$$

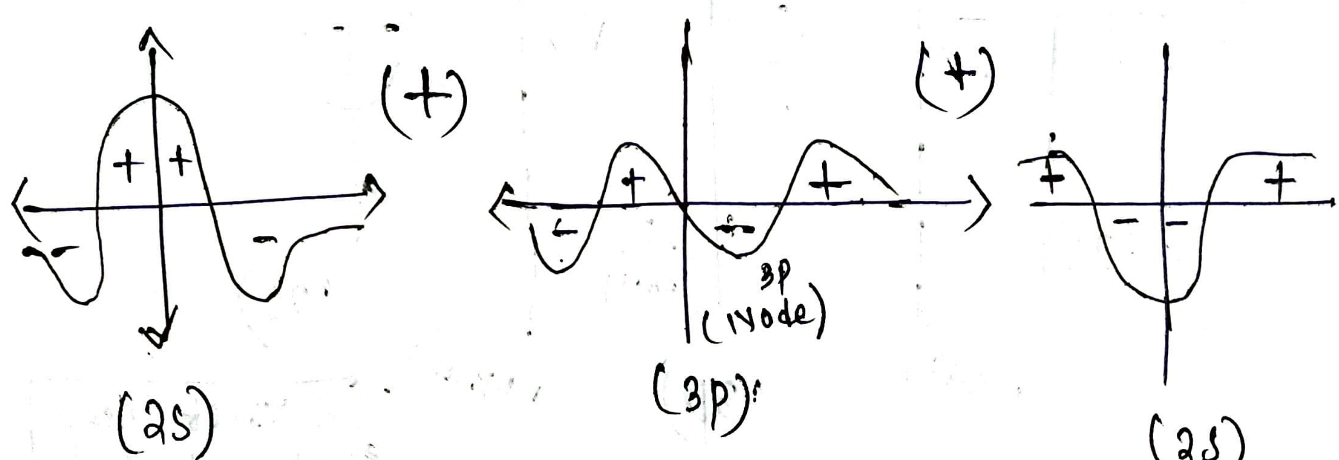
(c) Slater determinant;-

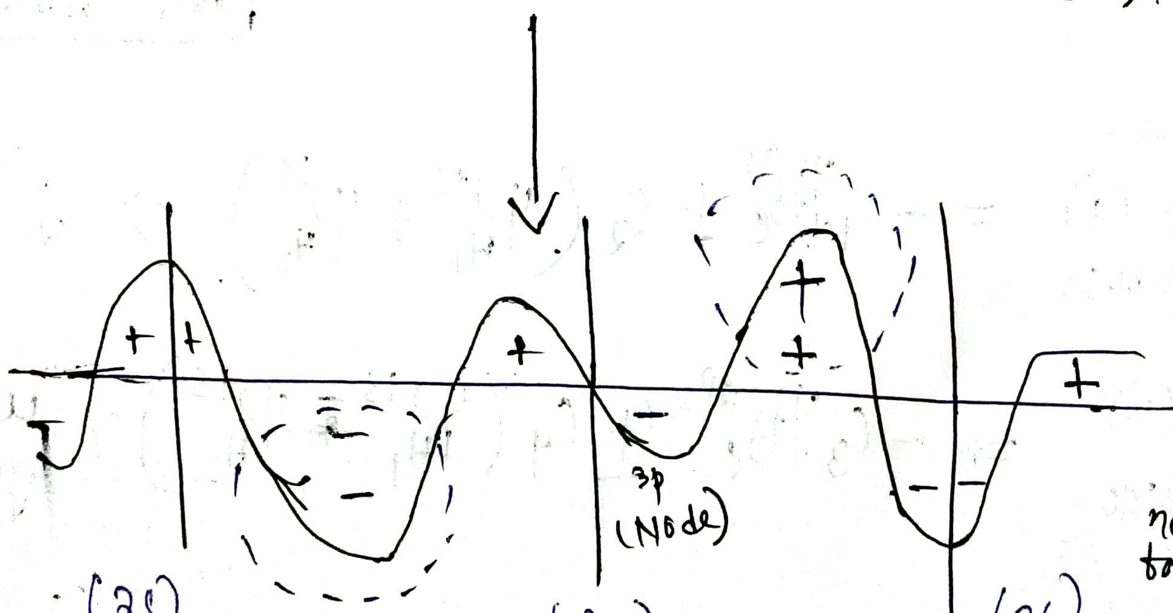
$$\frac{1}{\sqrt{2}}\begin{vmatrix} \psi_{MO}(1)\,\alpha(1) & \psi_{MO}(1)\,\beta(1) \\ \psi_{MO}(2)\,\alpha(2) & \psi_{MO}(2)\,\beta(2) \end{vmatrix}$$

(Q-4)

Two 2s and one 3p ;-

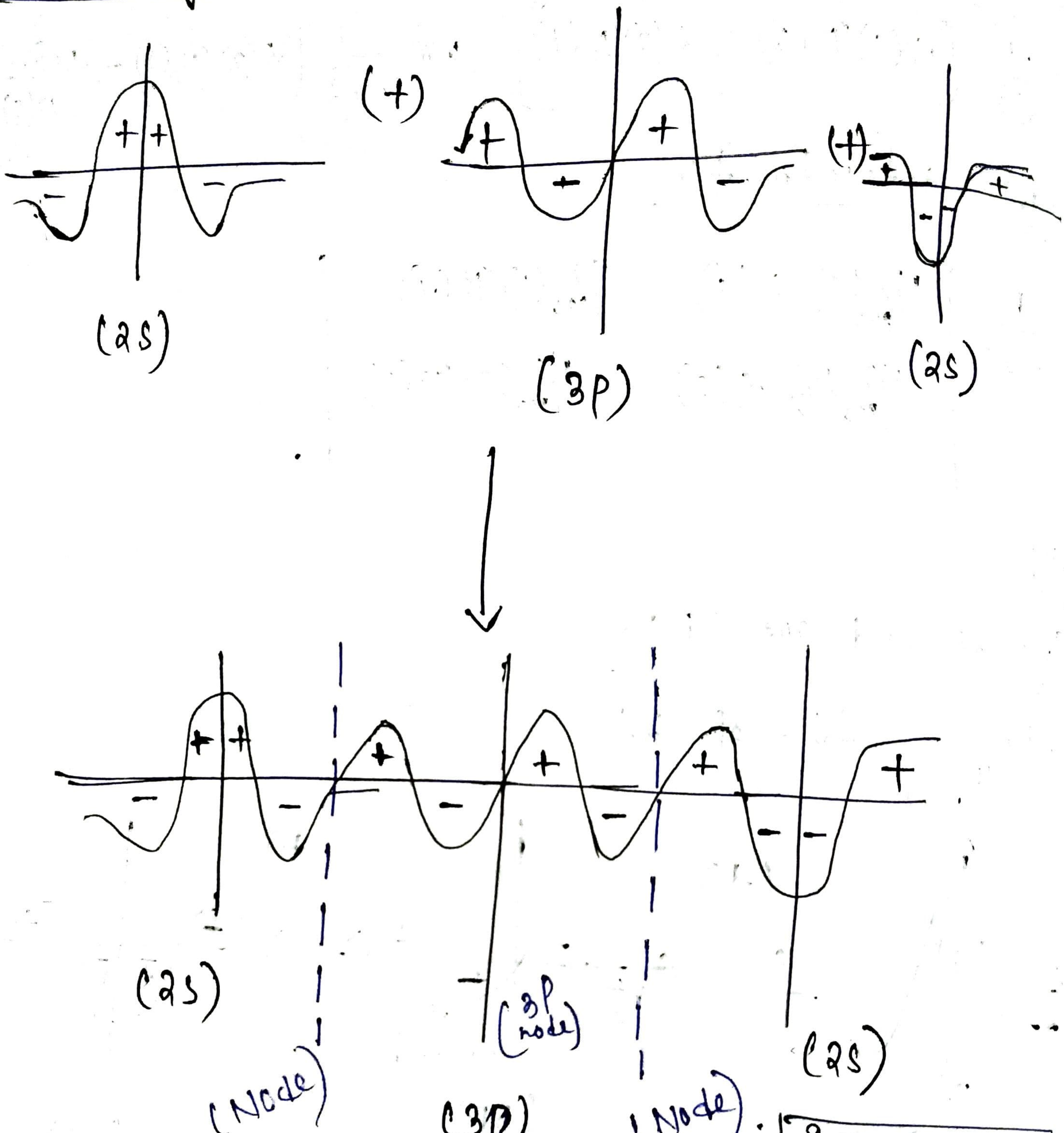
Bonding   2s — 3p — 2s





No new node formed.

Antibonding:-



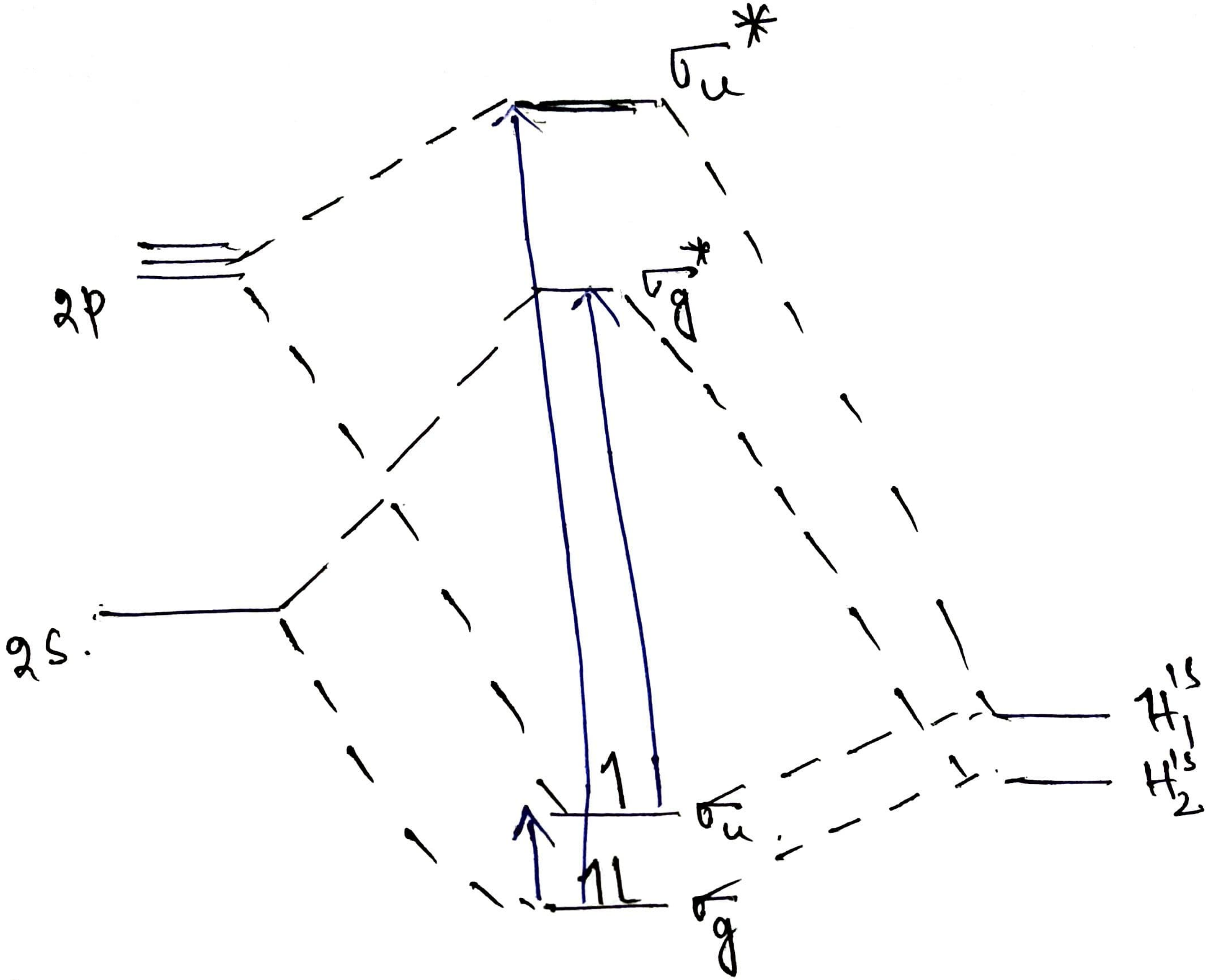
$\boxed{\text{2 No. of new nodes formed.}}$

(Q-5)

(a) $$\psi^{(1)}_{B.M.O.} = -C_1 \cdot \psi_{Be}^{2s} \pm C_2 \left(\psi_{H_1}^{1s} + \psi_{H_2}^{1s}\right) \rightarrow \text{'g' symmetry}$$

$$\psi^{(2)}_{BMO} = -C_3 \cdot \psi_{Be}^{2p_z} \pm C_4 \left(\psi_{H_1}^{1s} - \psi_{H_2}^{1s}\right) \rightarrow \text{"u" symmetry}$$

(b).



Total no. of spectral band = 3

Relative intensity = 2 : 2 : 1 = $\boxed{1 : 1 : 0.5}$.