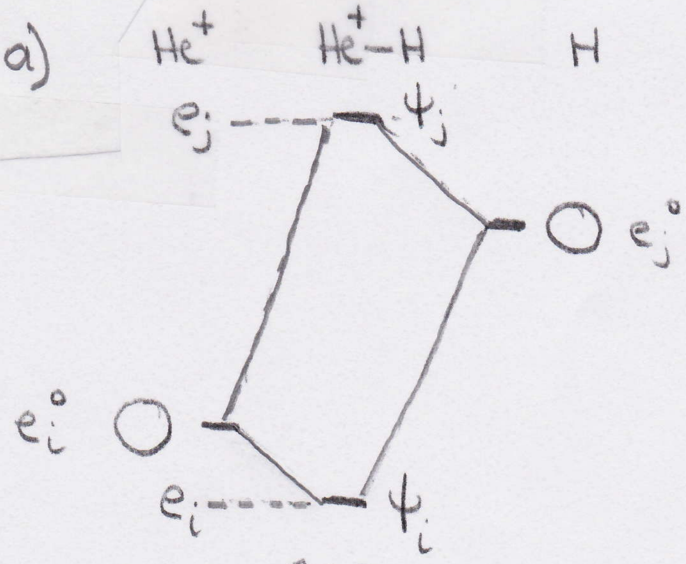
Answers - Chapter 3

1. a)



$$e_i \propto e_i^\circ + \frac{\tilde{S}_{ij}^{\,2}}{e_i^\circ - e_j^\circ} = \frac{(+)^2}{(-)} = (-) \therefore \text{stabilization}$$

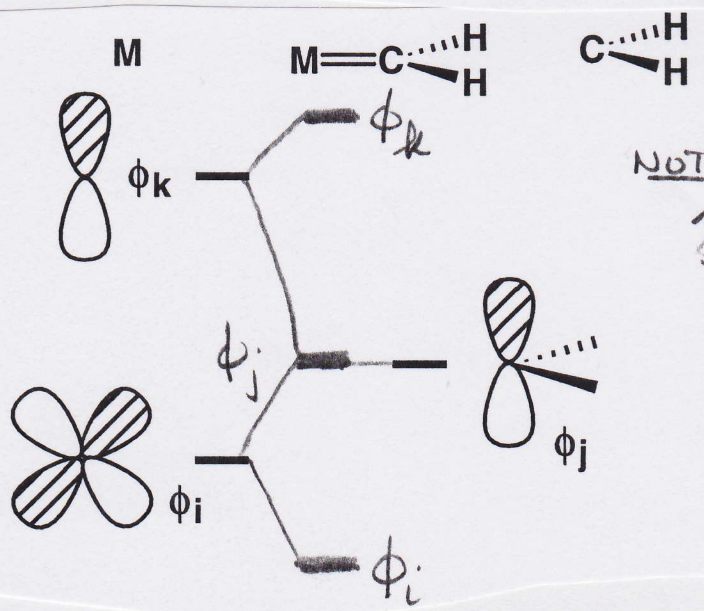
$$e_j \propto e_j^\circ + \frac{S_{ij}^{\,2}}{e_j^\circ - e_i^\circ} = \frac{(+)^2}{(+)} = (+) \therefore \text{destabilization}$$

$$\psi_i = \psi_i^\circ + t_{ji}^{(1)}\psi_j^\circ \qquad t_{ji}^{(1)} \propto \frac{-\tilde{S}_{ij}}{e_i^\circ - e_j^\circ} = \frac{(-)}{(-)} = (+)$$

$\therefore \psi_i =$ 

$$\psi_j = \psi_j^\circ + t_{ij}^{(1)}\psi_i^\circ \qquad t_{ij}^{(1)} \propto \frac{-\tilde{S}_{ij}}{e_j^\circ - e_i^\circ} = \frac{(-)}{(+)} = (-)$$

$\therefore \psi_j =$ 



NOTE!

$\tilde{S}_{ij} = (+)$

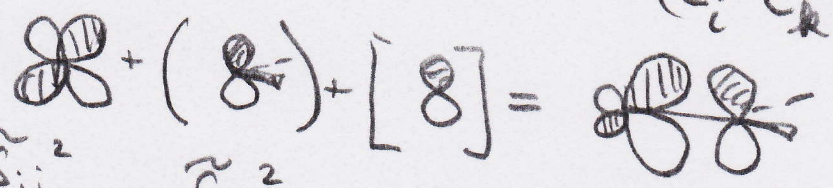
$\tilde{S}_{kj} = (+)$

$$e_i \propto \frac{\tilde{S}_{ij}^{\,2}}{e_i^\circ - e_j^\circ} = \frac{(+)}{(-)} = (-)$$

$$t^{(1)}_{ji} \propto \frac{-\tilde{S}_{ij}}{e_i^\circ - e_j^\circ} = \frac{(-)}{(-)} = (+)$$

$$\phi_i \approx \phi_i^\circ + t^{(1)}_{ji}\phi_j^\circ + t^{(2)}_{ki}\phi_k^\circ$$

$$t^{(2)}_{ki} \propto \frac{\tilde{S}_{ij}\,\tilde{S}_{kj}}{(e_i^\circ - e_k^\circ)(e_i^\circ - e_j^\circ)} = \frac{(+)(+)}{(-)(-)} = (+)$$

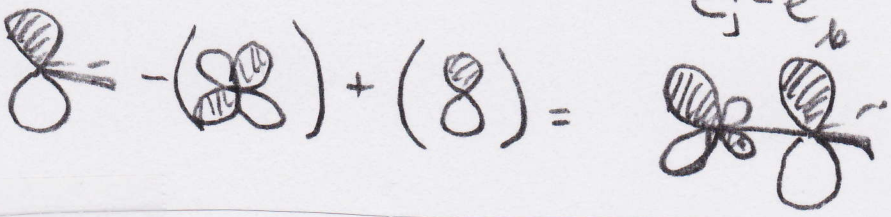
$\phi_i =$ 

$$e_j \propto \frac{\tilde{S}_{ij}^{\,2}}{e_j^\circ - e_i^\circ} + \frac{\tilde{S}_{jk}^{\,2}}{e_j^\circ - e_k^\circ} = \frac{(+)}{(+)} + \frac{(+)}{(-)} \approx 0$$

$$\phi_j \approx \phi_j^\circ + t^{(1)}_{ij}\phi_j^\circ + t^{(1)}_{kj}\phi_k$$

$$t^{(1)}_{ij} \propto \frac{-\tilde{S}_{ij}}{e_j^\circ - e_i^\circ} = \frac{(-)}{(+)} = (-)$$

$$t^{(1)}_{kj} \propto \frac{-\tilde{S}_{kj}}{e_j^\circ - e_k^\circ} = \frac{(-)}{(-)} = (+)$$

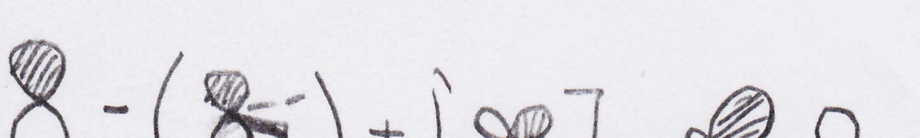
$\phi_j =$ 

$$e_k \propto \frac{\tilde{S}_{kj}^{\,2}}{e_k^\circ - e_j^\circ} = \frac{(+)}{(+)} = (+)$$

$$t^{(1)}_{jk} \propto \frac{-\tilde{S}_{kj}}{e_k^\circ - e_j^\circ} = \frac{(-)}{(+)} = (-)$$

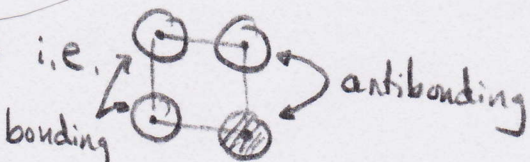
$$\phi_k \approx \phi_k^\circ + t^{(1)}_{jk}\phi_j^\circ + t^{(2)}_{ik}\phi_i^\circ$$

$$t^{(2)}_{ik} \propto \frac{\tilde{S}_{ij}\,\tilde{S}_{kj}}{(e_k^\circ - e_i^\circ)(e_k^\circ - e_j^\circ)} = \frac{(+)(+)}{(+)(+)} = (+)$$

$\phi_k =$ 

c)

<u>note</u> $\langle \psi_i^\circ | \psi_\ell^\circ \rangle = 0$ i.e.,



likewise $\langle \psi_j^\circ | \psi_k^\circ \rangle = 0$ $\therefore$ we only have degenerate interactions to worry about

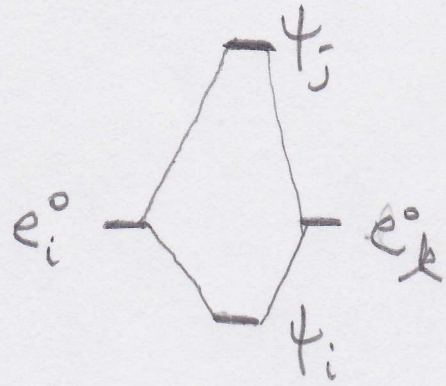
$\therefore t_{\ell i}^{(1)} = 0,\ t_{ji}^{(2)} = 0$, etc.

The energy corrections are easy - see eq. 3.32 & 3.33 in the text:

From degenerate perturbation theory

$$e_j \,\&\, e_k = \pm(\tilde{H}_{ik} - e_i^\circ \hat{S}_{ik}) - \hat{S}_{ij}(\tilde{H}_{ik} - e_i^\circ \hat{S}_{ik})$$
$$= \pm(-) - (-)$$

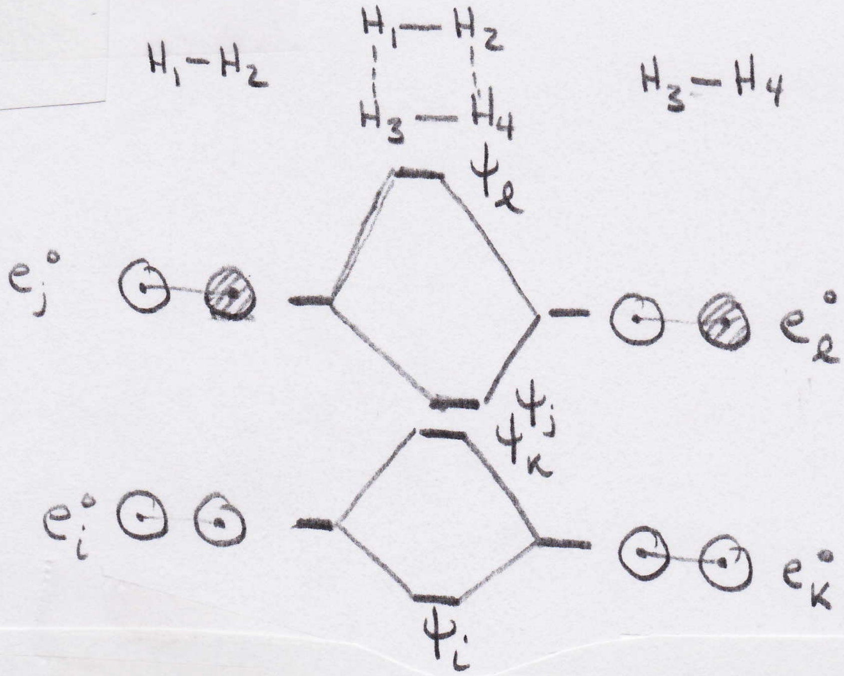
$\therefore$

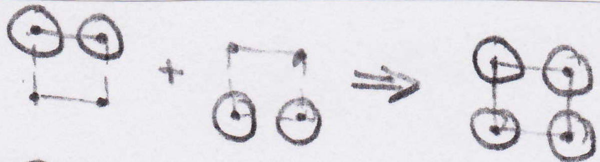


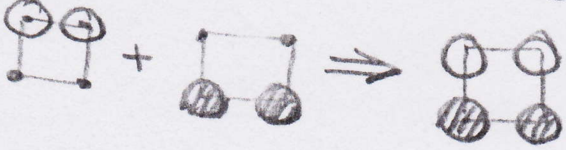
And the same application can be constructed for

$e_j \,\&\, e_\ell$

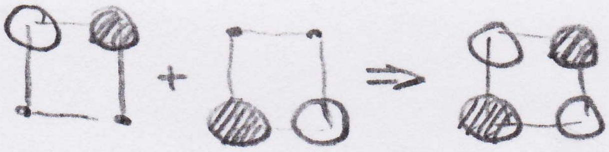
Therefore:



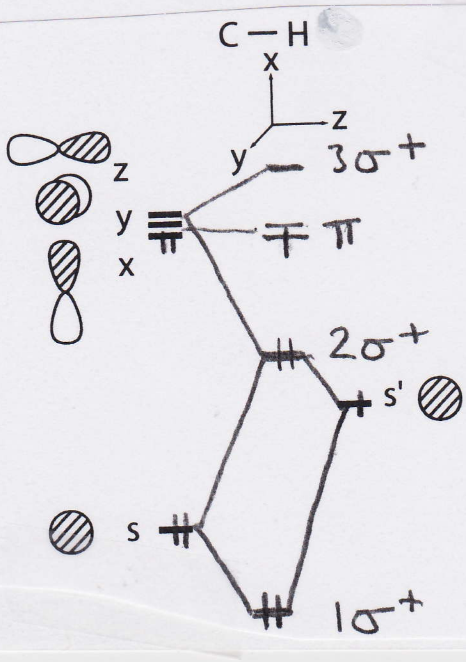
$\psi_i \propto \psi_i^\circ + \psi_k^\circ \equiv$ 

$\psi_k \propto \psi_i^\circ - \psi_k^\circ \equiv$ 

$\psi_j \propto \psi_j^\circ + \psi_l^\circ \equiv$ 

$\psi_l \propto \psi_j^\circ - \psi_l^\circ \equiv$ 

2.



$e_s = e_s^\circ + e_s^{(2)}$ $\quad e_s^{(2)} \propto \frac{\tilde{S}_{ss'}^{\,2}}{e_s^\circ - e_{s'}^\circ} = \frac{(+)}{(-)} = (-)$

$e_{s'} = e_{s'}^\circ + e_{s'}^{(2)}$ $\quad e_{s'}^{(2)} \propto \frac{\tilde{S}_{ss}^{\,2}}{e_{s'}^\circ e_s^\circ} + \frac{\tilde{S}_{s'z}^{\,2}}{e_{s'}^\circ - e_z^\circ} = \frac{(+)}{(+)} + \frac{(+)}{(-)} \approx 0$ (but prob + as I've drawn it)

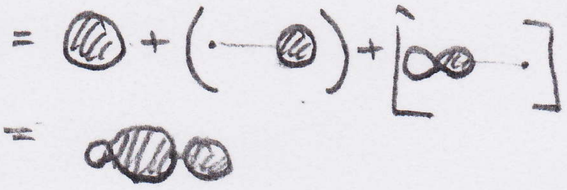
$e_{x,y} = e_{x,y}^\circ$

$e_z = e_z^\circ + e_z^{(2)}$ $\quad e_z^{(2)} \propto \frac{\tilde{S}_{s'z}^{\,2}}{e_z^\circ - e_{s'}^\circ} = \frac{(+)}{(+)} = (+)$

$\psi_{1\sigma^+} \approx \psi_s^\circ + t_{s's}^{(1)} \psi_{s'}^\circ + t_{zs}^{(2)} \psi_z^\circ$ $\quad t_{s's}^{(1)} \propto \frac{-\tilde{S}_{s's}}{e_s^\circ - e_{s'}^\circ} = \frac{(-)(+)}{(-)} = (+)$

$t_{zs}^{(2)} \propto \frac{\tilde{S}_{ss'} \tilde{S}_{s'z}}{(e_s^\circ - e_z^\circ)(e_s^\circ - e_{s'}^\circ)} = \frac{(+)(+)}{(-)(-)} = (+)$

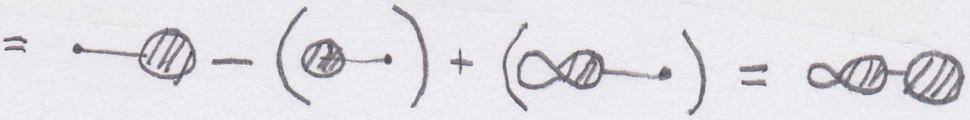
$\psi_{1\sigma^+} =$



$\psi_{2\sigma^+} \approx \psi_{s'}^\circ + t_{ss'}^{(1)} \psi_s^\circ + t_{zs'}^{(1)} \psi_z^\circ$ $\quad t_{ss'}^{(1)} \propto \frac{-\tilde{S}_{ss'}}{e_{s'}^\circ - e_s^\circ} = \frac{(-)(+)}{(+)} = (-)$

$t_{zs'}^{(1)} \propto \frac{-\tilde{S}_{s'z}}{e_{s'}^\circ - e_z^\circ} = \frac{(-)(+)}{(-)} = (+)$

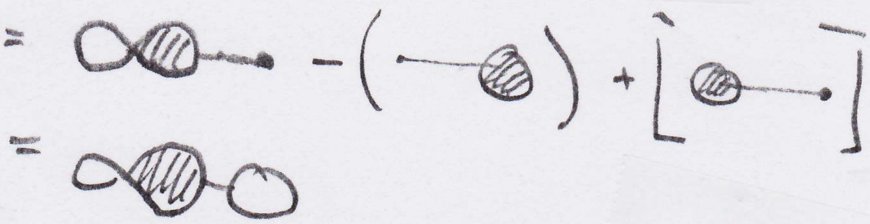
$\psi_{2\sigma^+} =$



$\psi_{3\sigma^+} \approx \psi_z^\circ + t_{s'z}^{(1)} \psi_{s'}^\circ + t_{sz}^{(2)} \psi_s^\circ$ $\quad t_{s'z}^{(1)} \propto \frac{-\tilde{S}_{s'z}}{e_z^\circ - e_{s'}^\circ} = \frac{(-)(+)}{(+)} = (-)$

$t_{sz}^{(2)} \propto \frac{\tilde{S}_{ss'} \tilde{S}_{zs'}}{(e_z^\circ - e_s^\circ)(e_z^\circ - e_{s'}^\circ)} = \frac{(+)(+)}{(+)(+)} = (+)$

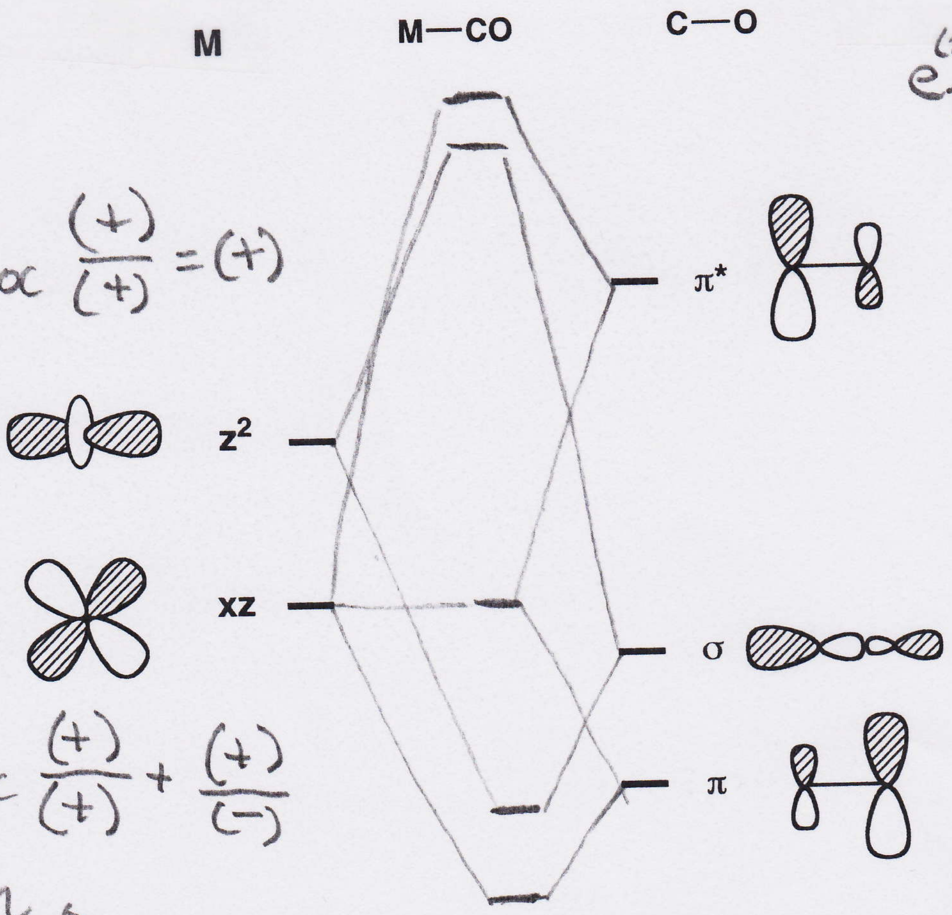
$\psi_{3\sigma^+} =$



3.

$$e^{(2)}_{\pi^*} \propto \frac{(+)}{(+)} = (+)$$

$$e^{(2)}_{z^2} \propto \frac{(+)}{(+)} = (+)$$



$$e^{(2)}_{\sigma} \propto \frac{(+)}{(-)} = (-)$$

$$e^{(2)}_{xz} \propto \frac{(+)}{(+)} + \frac{(+)}{(-)} \approx 0$$

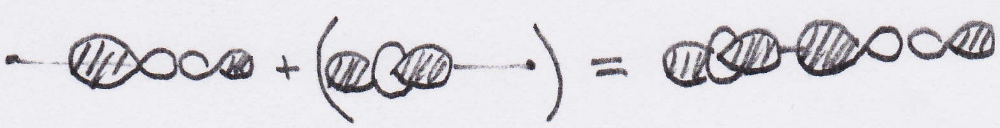
$$e^{(2)}_{\pi} \propto \frac{(+)}{(-)} = (-)$$

*** make sure that you understand that $\tilde{S}_{xz,\sigma} = \tilde{S}_{z^2,\pi} = \tilde{S}_{z^2,\pi^*} = 0 \leftarrow$ ***

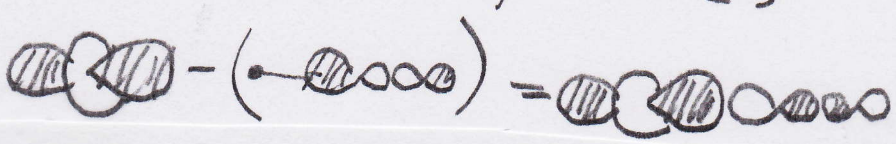
NOTE with the phases as drawn

$$\tilde{S}_{xz,\pi} \;\&\; \tilde{S}_{xz,\pi^*} \;\&\; \tilde{S}_{z^2,\sigma} = (+)$$

$$\psi_\sigma \approx \psi^0_\sigma + t^{(1)}_{z^2,\sigma}\psi_{z^2} \;;\; t^{(1)}_{z^2,\sigma} \propto \frac{-(+)}{(-)} = +$$

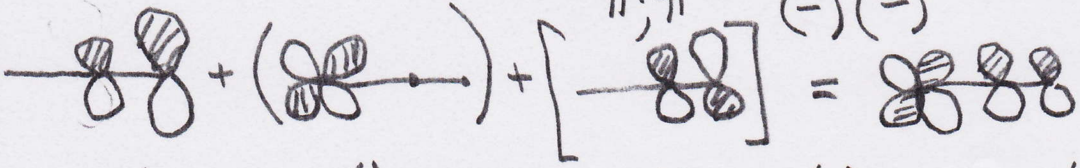
= 

$$\psi_{z^2} \approx \psi^0_{z^2} + t^{(1)}_{\sigma,z^2}\psi^0_{\sigma} \;;\; t^{(1)}_{\sigma,z^2} \propto \frac{-(+)}{(+)} = (-)$$

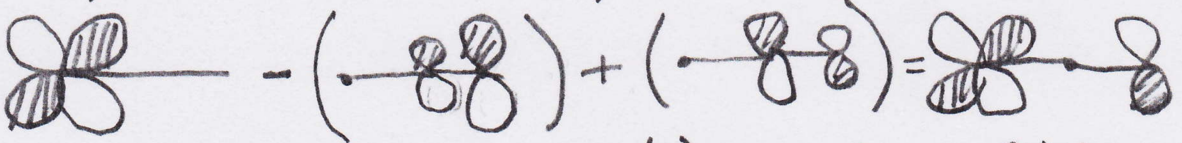
= 

$$\psi_{\pi} \approx \psi^{\circ}_{\pi} + t^{(1)}_{xz,\pi}\,\psi^{\circ}_{xz} + t^{(2)}_{\pi^*,\pi}\,\psi^{\circ}_{\pi^*}\ ;\quad t^{(1)}_{xz,\pi} \propto \frac{-(+)}{(-)} = (-)$$

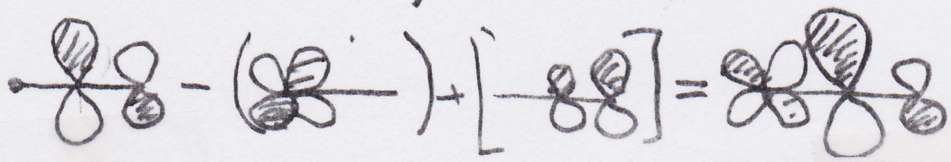
$$t^{(2)}_{\pi^*,\pi} \propto \frac{(+)(+)}{(-)(-)} = (+)$$

$\psi_{\pi} =$ 

$$\psi_{xz} \approx \psi^{\circ}_{xz} + t^{(1)}_{\pi,xz}\,\psi^{\circ}_{\pi} + t^{(1)}_{\pi^*,xz}\,\psi^{\circ}_{\pi^*}\ ;\quad t^{(1)}_{\pi,xz} \propto \frac{-(+)}{(+)} = (-)\ ;\quad t^{(1)}_{\pi^*,xz} \propto \frac{-(+)}{(-)} = (-)$$

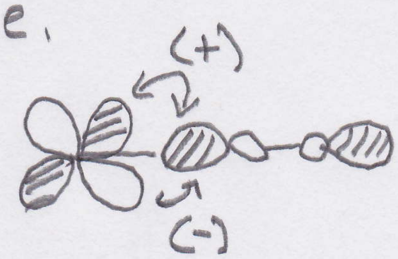
$\psi_{xz} =$ 

$$\psi_{\pi^*} \approx \psi^{\circ}_{\pi^*} + t^{(1)}_{xz,\pi^*}\,\psi^{\circ}_{xz} + t^{(2)}_{\pi,\pi^*}\,\psi^{\circ}_{\pi}\ ;\quad t^{(1)}_{xz,\pi^*} \propto \frac{-(+)}{(+)} = (-)\quad t^{(2)}_{\pi,\pi^*} \propto \frac{(+)(+)}{(+)(+)} = (+)$$

$\psi_{\pi^*} =$ 

There are two points that are worth re-imphazing:

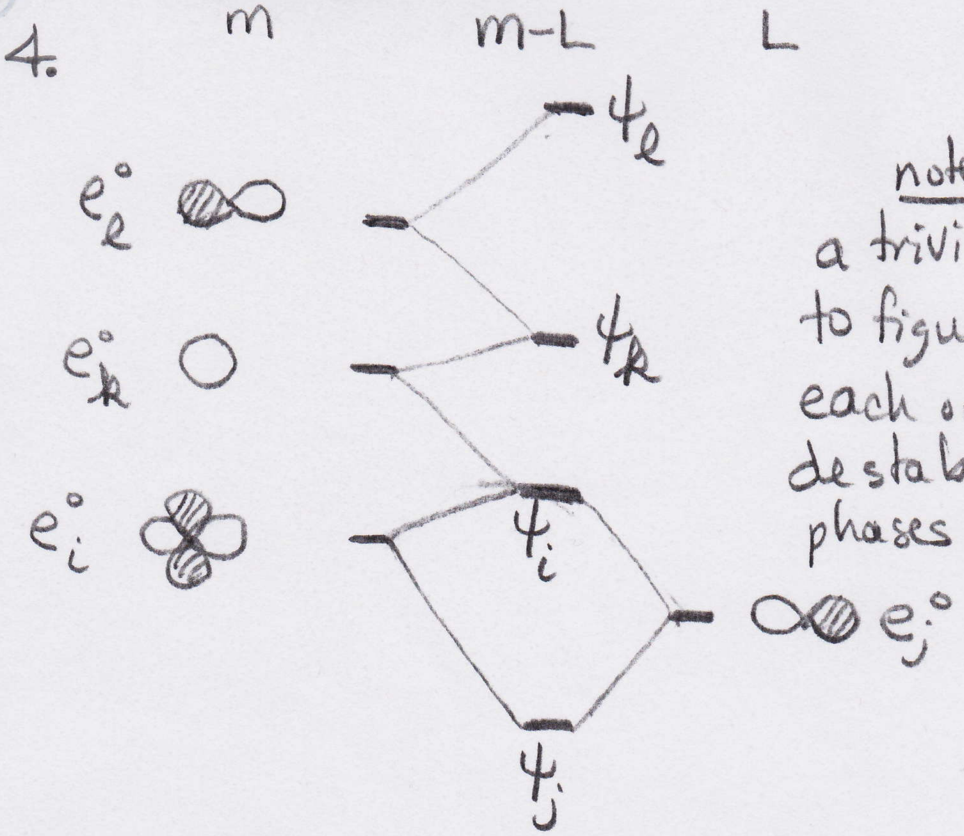
1. If you start with 5 orbitals, then you must end up with 5 and only 5 resultant MOs.
2. Symmetry, as we shall formalize in the next chapter, plays an important role. When $\tilde{S}_{ij} = 0$, there is <u>no</u> interaction, i.e.



positive and negative regions of overlap cancell eachother, ∴

$$\tilde{S}_{xz,\sigma} = 0$$

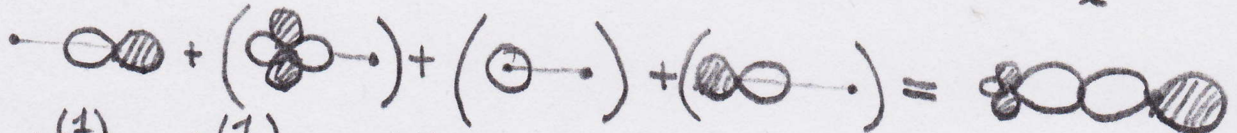
4.



__note__: It should be a trivial exercise by now to figure out whether or not each orbital is stabilized or destabilized! Notice the phases are such that S_{ij}, S_{kj} & $S_{\ell j}$ are __positive__

$$\psi_j \propto \psi_j^\circ + t_{ij}^{(1)}\psi_i^\circ + t_{kj}^{(1)}\psi_k^\circ + t_{\ell k}^{(1)}\psi_\ell^\circ$$

$$t_{ij}^{(1)} \propto \frac{-S_{ij}}{e_j^\circ - e_i^\circ} = (+) \quad t_{kj}^{(1)} \propto \frac{-\tilde{S}_{kj}}{e_j^\circ - e_k^\circ} = (+) \quad t_{\ell j}^{(1)} \propto \frac{-\tilde{S}_{\ell j}}{e_j^\circ - e_\ell^\circ} = (+)$$

$\therefore \psi_j \propto$ 

__note__ $t_{ij}^{(1)} > t_{kj}^{(1)} > t_{\ell j}^{(1)}$ because of energy difference

$$\psi_i \propto \psi_i^\circ + t_{ji}^{(1)}\psi_j^\circ + t_{ki}^{(2)}\psi_k^\circ + t_{\ell i}^{(2)}\psi_\ell^\circ$$

$t^{(1)}_{ji} \propto \frac{-\tilde{S}_{ji}}{e_i^\circ - e_j^\circ} = (-)$ $\quad t^{(2)}_{ki} \propto \frac{\tilde{S}_{ij}\,\tilde{S}_{jk}}{(e_i^\circ - e_k^\circ)(e_i^\circ - e_j^\circ)} = \frac{(+)(+)}{(+)(-)} = (-)$

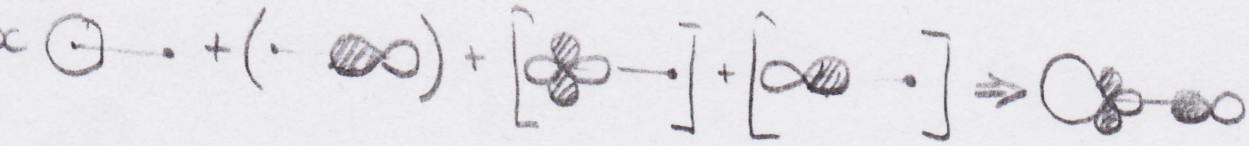
$t^{(2)}_{li} \propto \frac{\tilde{S}_{ij}\,\tilde{S}_{jl}}{(e_i^\circ - e_l^\circ)(e_i^\circ - e_j^\circ)} = (-)$ __note__ $t^{(2)}_{ki} > t^{(2)}_{li}$ again because of energy differences

$\psi_i \propto$ 

$$\psi_k \propto \psi_k^\circ + t^{(1)}_{jk}\psi_j^\circ + t^{(2)}_{ik}\psi_i^\circ + t^{(2)}_{lk}\psi_l^\circ$$

$t^{(1)}_{jk} \propto \frac{-\tilde{S}_{jk}}{e_k^\circ - e_j} = (-)$ $\quad t^{(2)}_{ik} \propto \frac{\tilde{S}_{ij}\,\tilde{S}_{kj}}{(e_k^\circ - e_i^\circ)(e_k^\circ - e_j^\circ)} = \frac{(+)(+)}{(+)(+)} = (+)$

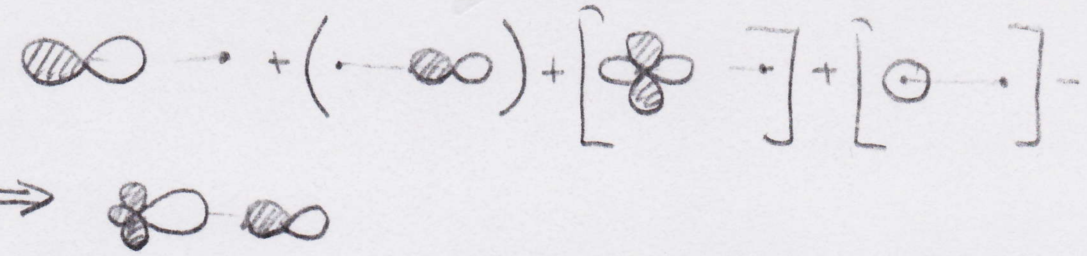
$t^{(2)}_{lk} \propto \frac{\tilde{S}_{kj}\,\tilde{S}_{lj}}{(e_k^\circ - e_l^\circ)(e_k^\circ - e_j^\circ)} = \frac{(+)(+)}{(-)(+)} = (-)$ __note__: $t^{(2)}_{ik} \approx t^{(2)}_{lk}$

$\therefore \psi_k \propto$ 

$$\psi_l \propto \psi_l^\circ + t^{(1)}_{jl}\psi_j^\circ + t^{(2)}_{il}\psi_i^\circ + t^{(2)}_{kl}\psi_k^\circ$$

$t^{(1)}_{jl} \propto \frac{-\tilde{S}_{jl}}{e_l^\circ - e_j^\circ} = (-)$ $\quad t^{(2)}_{il} \propto \frac{\tilde{S}_{ij}\,\tilde{S}_{lj}}{(e_l^\circ - e_i^\circ)(e_l^\circ - e_j^\circ)} = \frac{(+)(+)}{(+)(+)} = (+)$

$t^{(2)}_{kl} \propto \frac{\tilde{S}_{kj}\,\tilde{S}_{lj}}{(e_l^\circ - e_k^\circ)(e_l^\circ - e_j^\circ)} = \frac{(+)(+)}{(+)(+)} = (+)$ __note__ $t^{(2)}_{kl} > t^{(2)}_{il}$

$\psi_l \propto$ 

notice that ψ_j = M–L bonding

ψ_l = M–L antibonding

and ψ_i & ψ_k are basically M–L <u>nonbonding</u>