

Inorganic Chemistry (CY11001)

Chemical Bonding: Part-II

**Covering: Linear Combination of Atomic Orbitals (LCAO),
MO for Homonuclear and Heteronuclear diatomic molecules**

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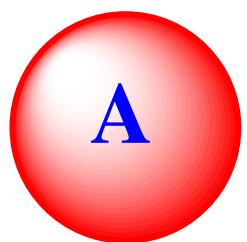
High Pressure Lab (Ground Floor)

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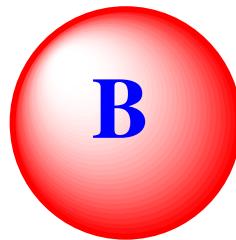
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Linear Combination of Atomic Orbitals (LCAO)

The wave function for the molecular orbitals can be approximated by taking linear combinations of atomic orbitals.



$$\Psi_A$$



$$\Psi_B$$

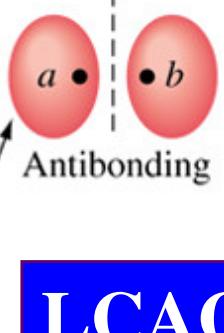
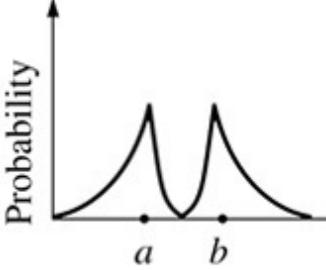
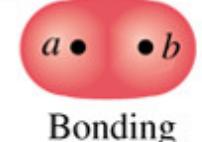
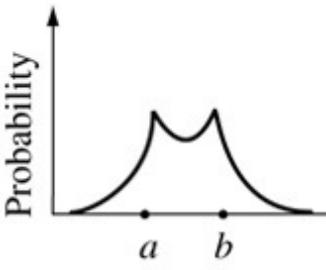
$$\Psi_{AB} = N(c_A \Psi_A + c_B \Psi_B)$$

c – extent to which each AO contributes to the MO
 N = Normalization const

$$\Psi^2_{AB} = (c_A^2 \Psi_A^2 + 2c_A c_B \Psi_A \Psi_B + c_B^2 \Psi_B^2)$$

Probability density

Overlap integral

<p>$1s_a$ and $1s_b$</p> <p>1s orbitals of two widely separated hydrogen atoms</p>	<p>Nodal plane</p>  <p>Antibonding</p>	 <p>Probability</p> <p>a b</p> <p>σ^*_{1s}</p>	<p>Energy level diagram</p>
<p>$1s_a$ and $1s_b$</p> <p>Molecular orbitals of H_2 molecule</p>	 <p>Bonding</p>	 <p>Probability</p> <p>a b</p> <p>σ_{1s}</p>	<p>Electron charge density (probability) along a line joining two hydrogen nuclei: a and b</p>

H_2

11.4 eV

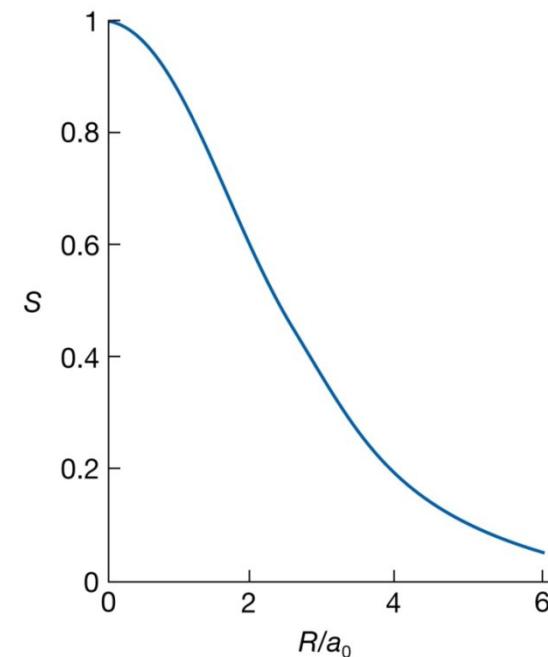
109 nm

The overlap integral

■ The extent to which two atomic orbitals on different atom overlaps : the overlap integral

$$S = \int \psi_A \psi_B d\tau$$

- ◆ There is nothing magic about the molecule being bonded
 - Electrons preferentially spend time between the two nuclei. They act as electrostatic “glue”



- ◆ The extent to which orbitals overlap can be evaluated using an overlap integral S .
 - $S = 0$ indicates that the orbitals do not overlap/interact with one another
 - S depends on the symmetry of the orbital

$S > 0$

Bonding

$S < 0$ anti



See next page
for clear sketch

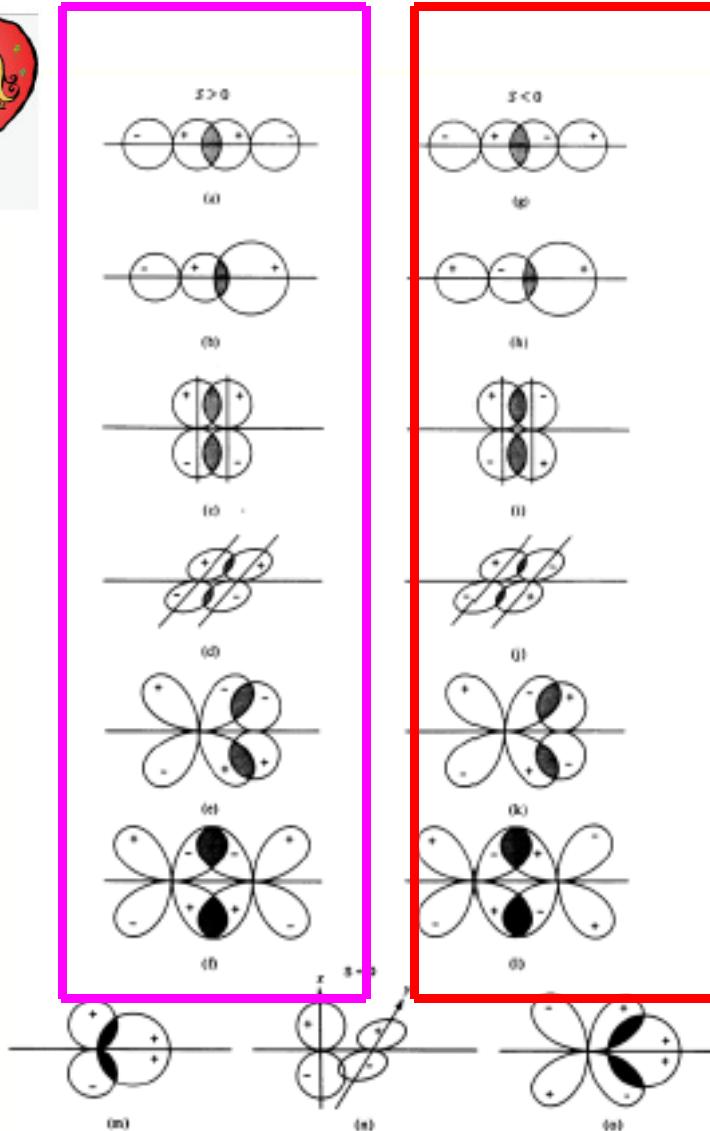


Fig. 5.8 Arrangement of atomic orbitals resulting in positive (a-f), negative (g-l), (m-o) overlap.

Bond strength depends on the degree of overlap

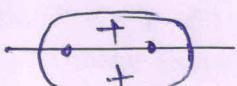
$S = 0$ nonbonding
(Huheey 158)



Bonding (non-bonding) / Antibonding MOs

①
Leesgo

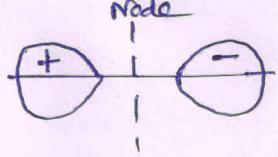
Lateral / side on overlap



6_s

bonding

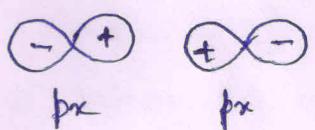
g



6_s^*

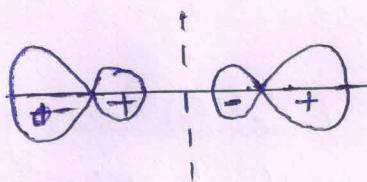
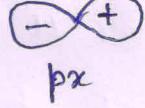
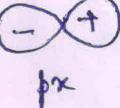
Antibonding

u



$6p_x$ or $6p_y$ bonding

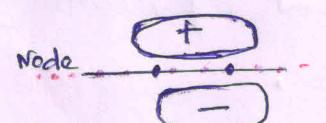
g



$6p_x^*$ or $6p_y^*$

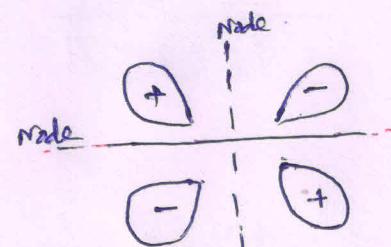
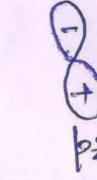
Antibonding

u



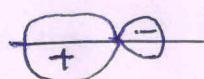
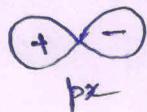
π_{p_z} bonding

u



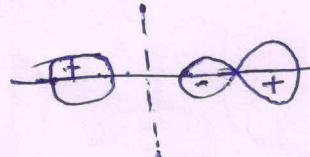
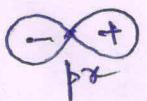
$\pi_{p_z}^*$ antibonding

g



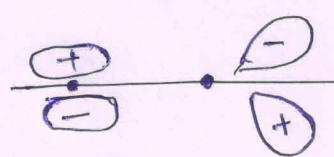
6

bonding



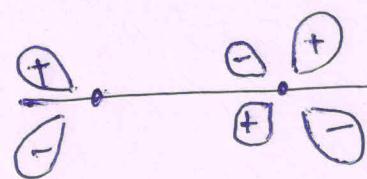
6^*

antibonding



π

bonding



π^* antibonding



- ⇒ In combination shown below any stabilization which occurs from overlapping + with + is destabilized by an equal amount of overlap of + with -.
- ⇒ There is no overall change in E & this situation is called NB.

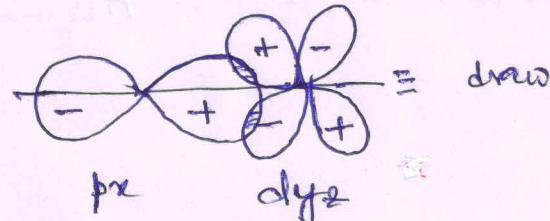
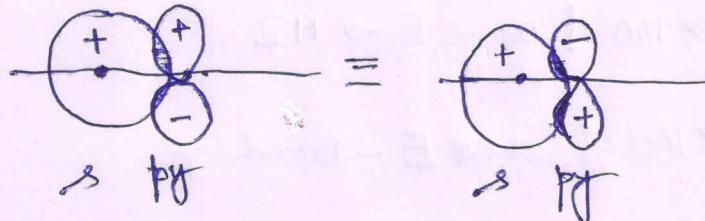
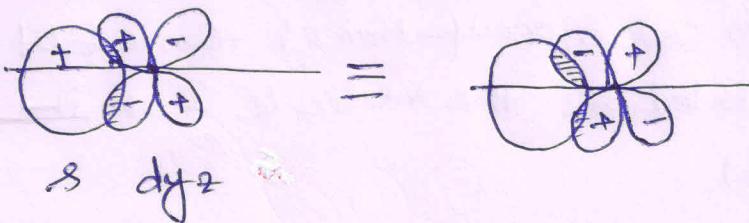
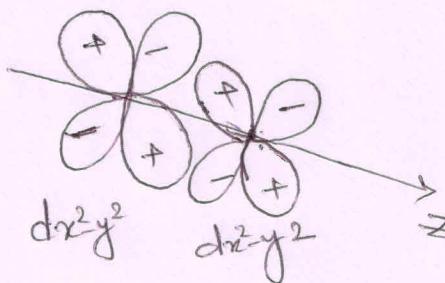
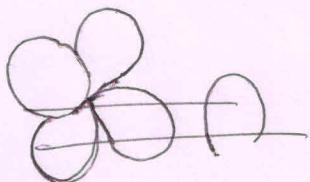


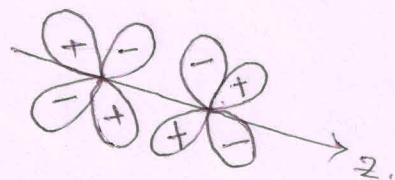
Fig: Non bonding combn of AOs



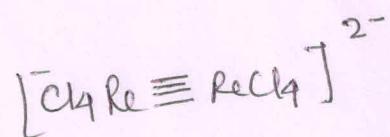
- So far we have seen s-s, p-p & s-p combinations of AOs. d-d combinations of AOs is also possible producing bonding & AB MOs which are called δ & δ^* respectively.



$\rightarrow \delta$ bonding



$\rightarrow \delta^*$ antibonding.

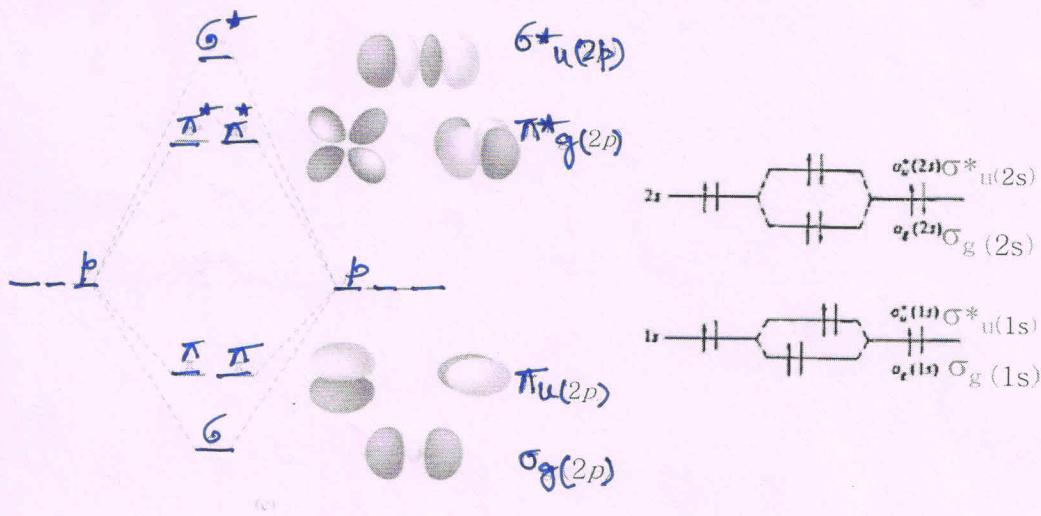


Homonuclear Diatomics

- MOs may be classified according to:
 - (i) Their symmetry around the molecular axis.
 - (ii) Their bonding and antibonding character.

The order of E of MOs are determined from spectroscopic data
- $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2px} < \pi 2p_y = \pi 2p_z < \pi^* 2p_y = \pi^* 2p_z < \sigma_{2px}^*$ $\longrightarrow O_2$ and heavier
- $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \pi 2p_y = \pi 2p_z < \sigma_{2px} < \pi^* 2p_y = \pi^* 2p_z < \sigma_{2px}^*$ $\longrightarrow B_2, C_2, N_2$

Place labels *g* or *u* in this diagram



All σ bonding MOs are gerade & all σ^* MOs are ungerade
All π bonding MOs are ungerade & all π^* MOs are gerade

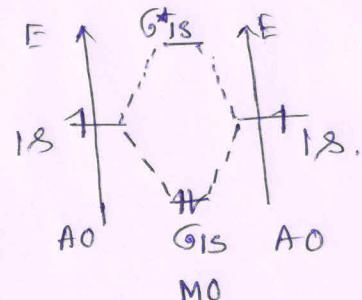


only for centrosym MOs.

\Rightarrow H_2^+ is more stable than H_2

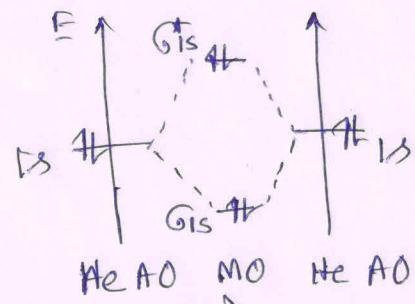


- The valence cell elec conf of H is $1S^1$.
- 2 H atoms comes to their equidist, the 2 $1S$ orbitals undergoes LACO to form MO
- Bond order = $\frac{2-0}{2} = 1$
- MO 'e' distribution of H_2 is $G_{1S}^2 G_{1S}^{*0}$
- MO 'e' distribution in H_2^+ is $G_{1S} G_{1S}^{*0}$
- $BO = \frac{1-0}{2} = \frac{1}{2}$
- Hence H_2^+ is less stable than H_2



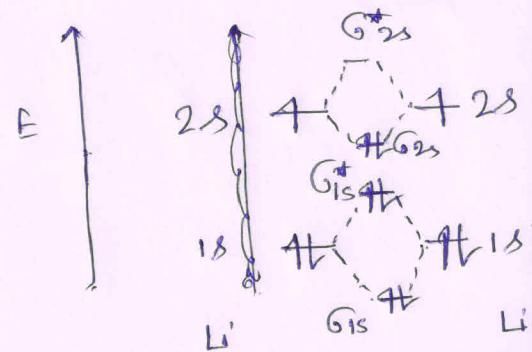
$\Rightarrow He_2$ is unknown but He_2^+ has been detected in discharge tube

- valence cell 'e' conf of He is $1S^2$
- MO 'e' distribution: $He_2 \rightarrow G_{1S}^2 G_{1S}^{*2}$
- $BO = \frac{2-2}{2} = \frac{0}{2} = 0$; so does not exist
- $He_2^+ \rightarrow G_{1S}^2 G_{1S}^{*1}$
- $BO = \frac{2-1}{2} = \frac{1}{2}$ (some bonding; so exist though unstable).



$\Rightarrow Li_2$

- 'e' conf: $1S^2 2S^1$
- MO 'e' dist: $G_{1S}^2 G_{1S}^{*2} G_{2S}^2 \equiv KK G_{2S}^2$
KK don't contribute to bonding.
- $BO = \frac{4-2}{2} = 1$



(4)

⇒ why noble gas are monoatomic?

- He, Ne, Ar, Kr, Xe, Rn

- Valence cell e^- conf He $\rightarrow 1s^2$; others: $ns^2 np^6$

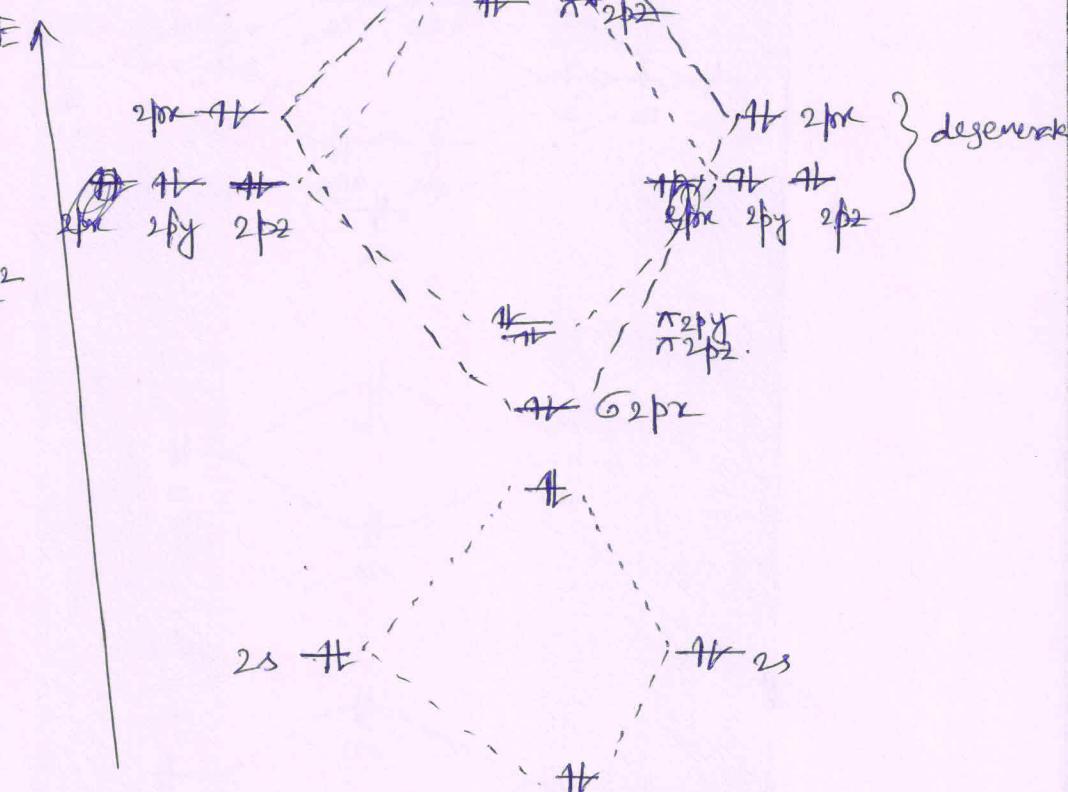
- Show MO for He_2 (before).

- Show MO diagram for Ne_2

- MO 'e' dirn is:

$KK \ 6s^2, 6^*s^2, 6^*2px^2,$
 $\pi 2py^2 \} \ \pi^* 2py^2 \}$
 $\pi 2p_z^2 \}, \pi^* 2p_z^2 \}$

$$BO = \frac{8-8}{2} = 0$$



⇒ Draw MO diagram of O_2 & predict may character of it. Find BO & may character of O_2^+, O_2^- & O_2^{2-}

- valence cell e^- conf O $\rightarrow 1s^2 2s^2 2p^4$

- show MO (from Lee 106)
see next page.

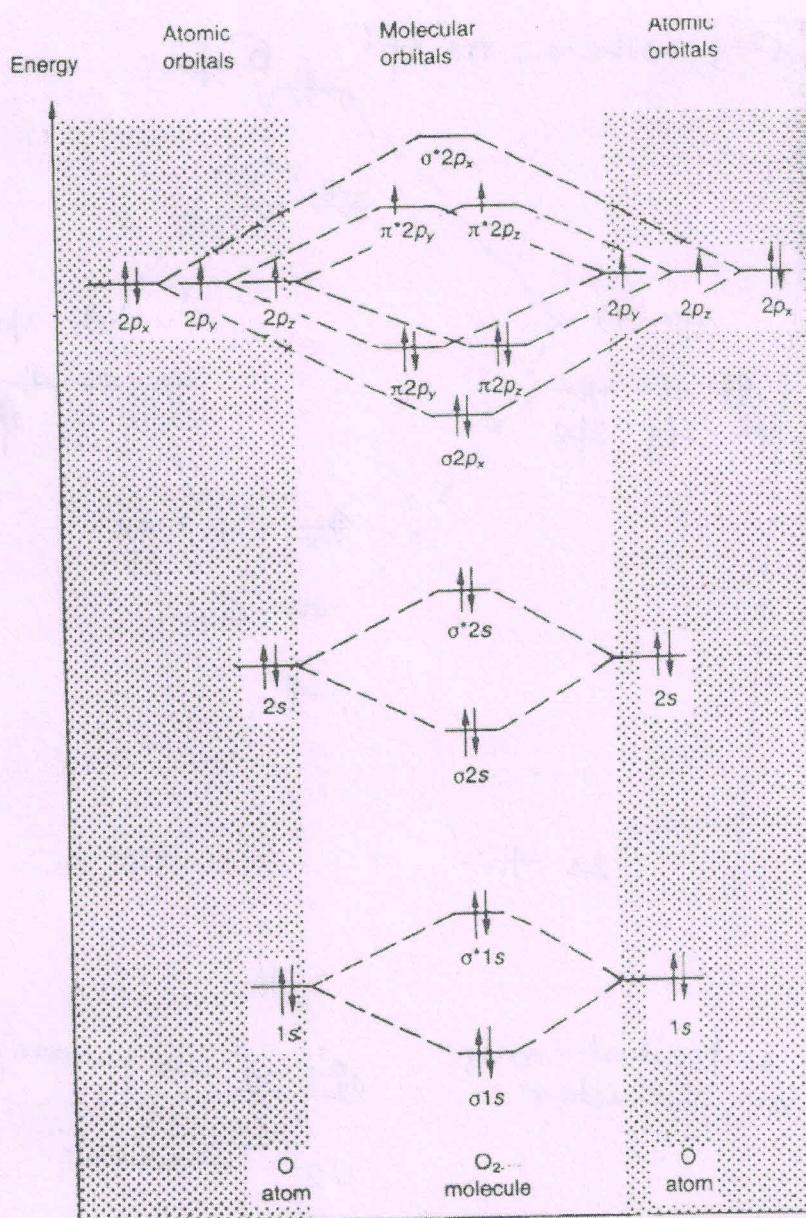
- MO 'e' dirn:

$O_2: KK, 6^*2s^2, 6^*2s^2, 6^2_{2px}, \pi 2py^2, \pi 2p_z^2, \pi^* 2py^1, \pi^* 2p_z^1, 6^*2px^0 \left| BO = \frac{8-4}{2} = 2 \right. \mu_s = \sqrt{n(n+2)} = 2\sqrt{2} BM = 2.84 BM$

$O_2^+: KK, 6^*2s^2, 6^*2s^2, 6^2_{2px}, \pi 2py^2, \pi^* 2py^1, \pi 2p_z^2, \pi^* 2p_z^0, 6^*2px^0 \left| BO = \frac{8-3}{2} = 2.5 \right.$

$O_2^-: KK, 6^*2s^2, 6^*2s^2, 6^2_{2px}, \pi 2py^2, \pi 2p_z^2, \pi^* 2py^2, \pi^* 2p_z^1, 6^*2px^0 \left| BO = \frac{8-5}{2} = 1.5 \right.$

$O_2^=: KK, 6^*2s^2, 6^*2s^2, 6^2_{2px}, \pi 2py^2, \pi 2p_z^2, \pi^* 2py^2, \pi^* 2p_z^2, 6^*2px^0 \left| BO = \frac{8-6}{2} = 1 \right.$



$$\begin{array}{lll}
 \text{BO} & \text{BL(pm)} & \text{BE(kJ/mol)} \\
 \text{O}_2 \rightarrow 2 \rightarrow 120.7 \rightarrow 193 & & \\
 \text{O}_2^+ \rightarrow 2.5 \rightarrow 111.6 \rightarrow 643 & & \\
 \text{O}_2^- \rightarrow 1.5 \rightarrow 135 \rightarrow 395 & & \\
 \text{O}_2^{2-} \rightarrow 1 \rightarrow 149 \rightarrow - & &
 \end{array}$$

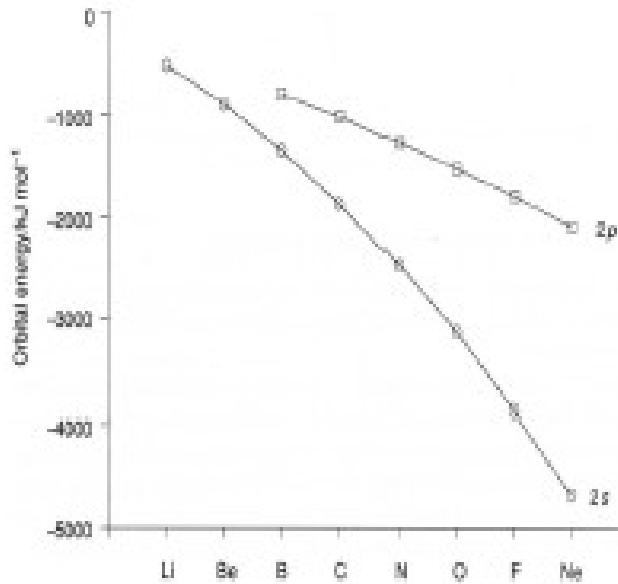
⇒ Discuss BO of F₂ molecule :

- Valence shell is config of 'F' $\rightarrow 1s^2 2s^2 2p^5$
- Show MO diagram (similar above)
- MO's distribution : $\sigma_{1s}^2, \sigma_{1s}^*, 6_{2s}^2, 6_{2s}^*, 6_{2p_x}^2, 6_{2p_x}^*, \pi_{2p_y}^2, \pi_{2p_y}^*, \pi_{2p_z}^2, 6_{2p_z}^*$
- $BO = \frac{8-6}{2} = 1$

Orbital Mixing

- ◆ Orbitals with similar energy interact, if they have the appropriate symmetries
- ◆ The σ_{2p} and σ_{2s} orbitals are symmetry related and give rise to two new orbitals, one with higher and one with lower energy

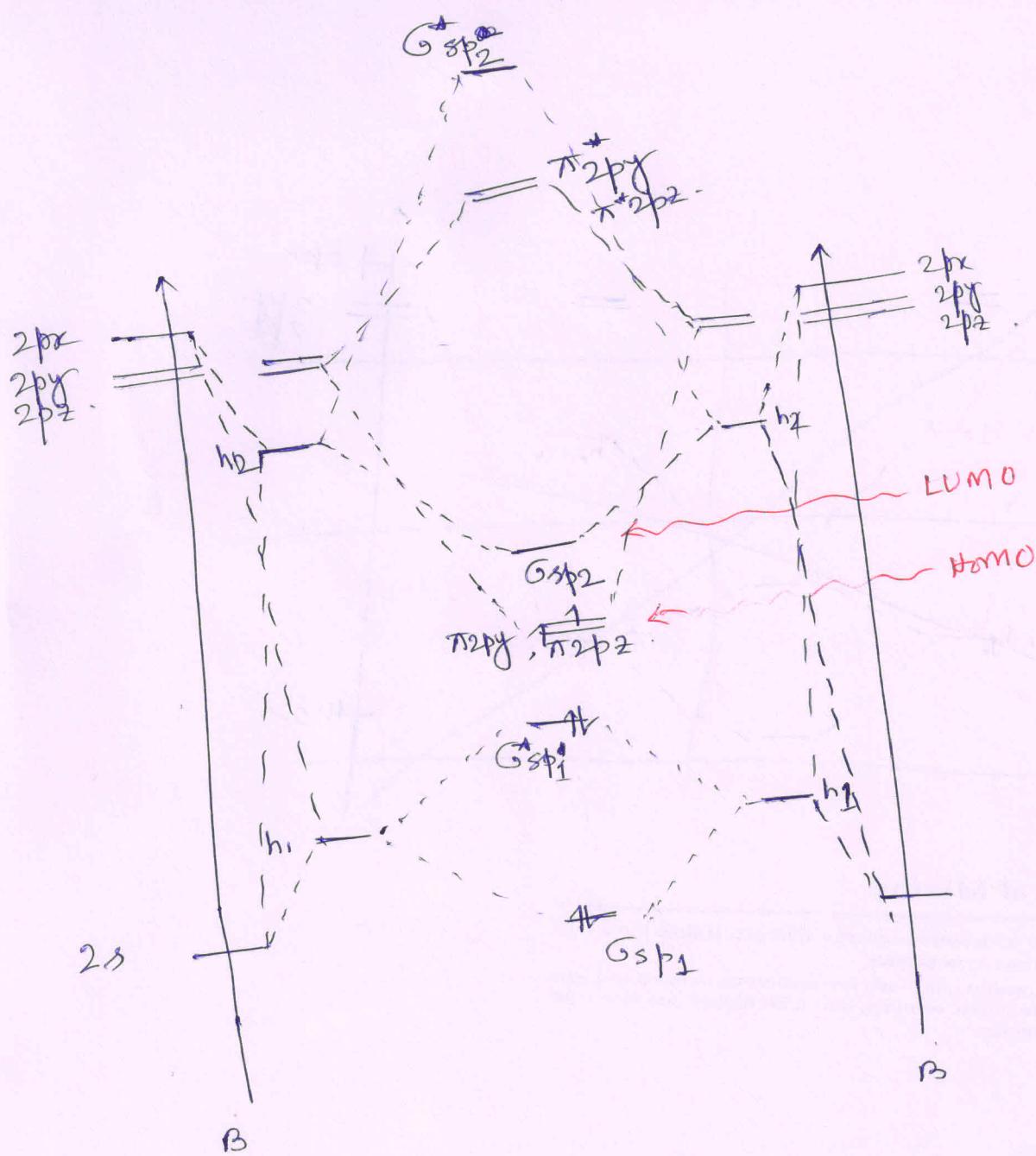
Li : 200 kJ/mol
F: 2500 kJ/mol



s & p mixing orbitals

* Explain {B₂ is paramagnetic & C₂ is dia.}

(5)



$${}^5\text{B} \rightarrow 1s^2 2s^2 2p^1; (3 \text{ valence } e' \times 2) = 6$$

Mixing: KK, $\sigma_{sp_1}^2$, $\sigma_{sp_1}^2$, $\pi_{2p_1}^1$, $\pi_{2p_1}^1$, $\sigma_{sp_2}^0$, $\pi_{2p_2}^0$, $\pi_{2p_2}^0$, $\sigma_{sp_2}^0$.

$$\text{BO} = \frac{4-2}{2} = 1 \text{ (paramagnetic)}$$

without Mixing: $\underbrace{1s^2, 1s^2}_{KK}, 2s^2, 2s^2, \pi_{2p_2}^0, \pi_{2p_2}^0, \sigma_{sp_2}^0$.

should be diamagnetic but it is PARAMAG

⑥

\Rightarrow Similar $s\&p$ orbital mixing for C₂

would be MO : KK, $6s^2$, $6^{*}s^2$, $62p_z^2$ $\pi 2p_y^1$ $\pi 2p_z^1$ | should be PARAMAG but NO

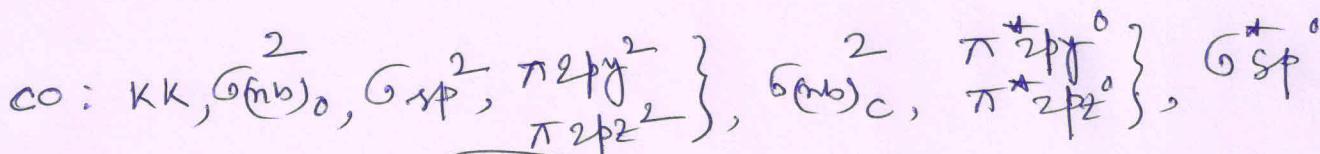
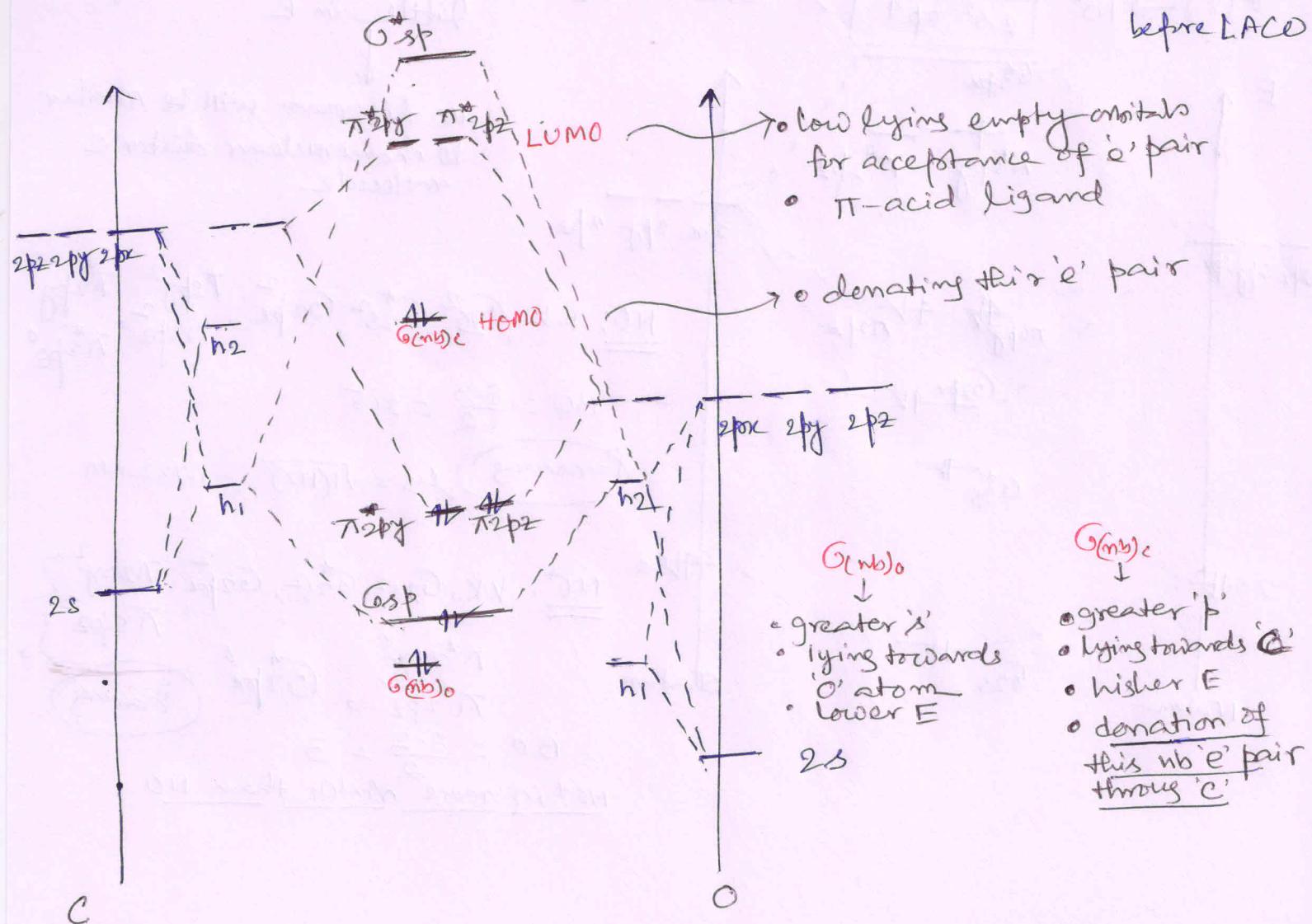
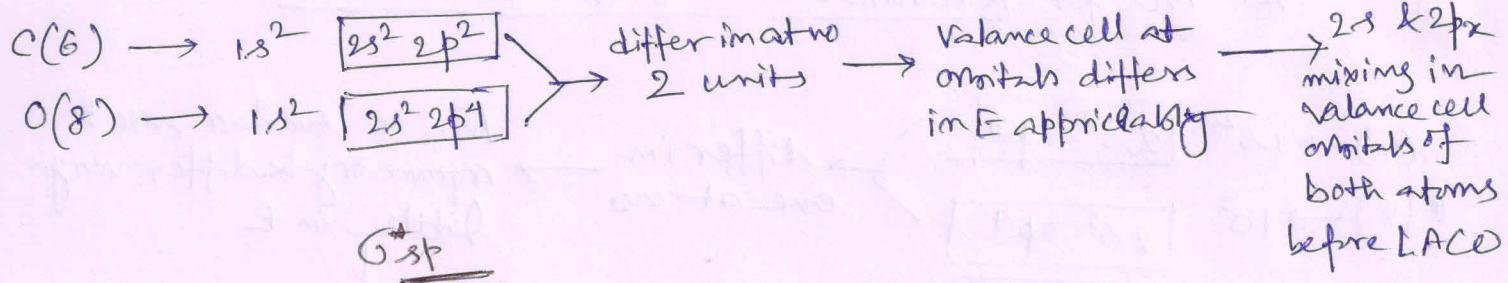
C₆ $\rightarrow 2s^2 2p^2$
(valence cell)

modified MO : KK, $6sp_1^2$, $6^{*}sp_1^2$, $\pi 2p_y^2$ $\pi 2p_z^2$ $6sp_2^0$, $\pi^{*}2p_y^0$ $\pi^{*}2p_z^0$ |
HOMO LUMO $6p_2^0$

Thus DIAMAGNETIC.

Show MO (similar to B₂)

⇒ Draw MO diagram for CO & indicate BO & magnetic nature



$$BO = \frac{6-0}{2} = 3 \text{ (diamagnetic)}$$

- Thus CO is reactive & readily forms complex compounds by denating (nb) e^- pair through C

Bond Order vs. Bond Length & Energy

Species	Bond order	Bond length/pm	Bond energy/kJ mol ⁻¹
H ₂ ⁺	1/2	105.2	256
H ₂	1	74.1	432
H ₂ ⁻	1/2	—	100–200
He ₂	0	297	0.1*
Li ₂	1	267.3	101
Be ₂	0	—	4
B ₂	1	159	289
C ₂	2	124.25	599
N ₂	3	109.8	942
O ₂	2	120.7	493
O ₂ ⁺	2 1/2	111.6	643
O ₂ ⁻	1 1/2	135	305
O ₂ ²⁻	1	149	—
F ₂	1	141.2	155
Ne ₂	0	310	0.2*

*Van der Waal forces.