423 Molecular Orbital Theory Assignment

Set: 13th March 2026. Due: **25th March 5pm**

Hand-in as a PDF file on Nuku (the Assignment in the 423 folder). Diagrams and text need to be legible to me and photographs/scans clear please!

Q1. Draw a MO diagram for C_{2v} $ClBH_2$. Use the BH_2 fragment orbitals given in **Figure 1**. The Cl pAOs will have an energy between the $1b_1$ and $2a_1$ FOs and the Cl sAO will interact with the $1a_1$ FO. Explicitly demonstrate MO mixing by drawing out and combining the relevant MOs, discuss MO mixing with respect to these MOs. Depict the mixed MOs on your MO diagram.

15 marks

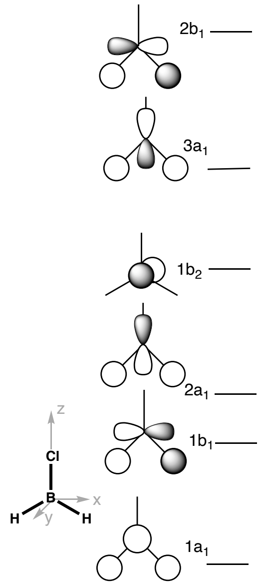


Figure 1 $ClBH_2$ fragment orbitals

Q2 Consider three oxygen atoms arranged in an equilateral triangle, that belong to the D_{3h} point group, **Figure 2**. In the following show your working at all stages.

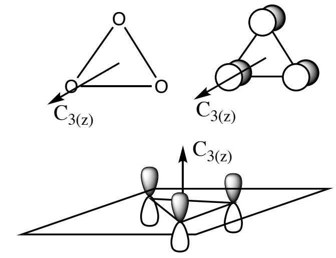


Figure 2 O_3 pAOs

i) Determine the reducible representation for the three p_π orbitals
ii) Write down the reduction and projection formulae. Briefly explain the terms in both formulae.
iii) Use the reduction formula to determine the symmetry of the p_π based symmetry adapted fragment orbitals.
iv) Use the projection formula to determine the wave function of the p_π based symmetry adapted fragment orbitals.
v) Draw an energy level diagram for the p_π based symmetry adapted fragment orbitals. Draw the fragment orbitals and write the associated equation beside each energy level. Label the symmetry of each orbital.

10 marks

Q3 Draw LCAOs for the computed MOs of borazine shown in **Figure 3**. On your diagrams annotate features important for evaluating the MO bonding character.

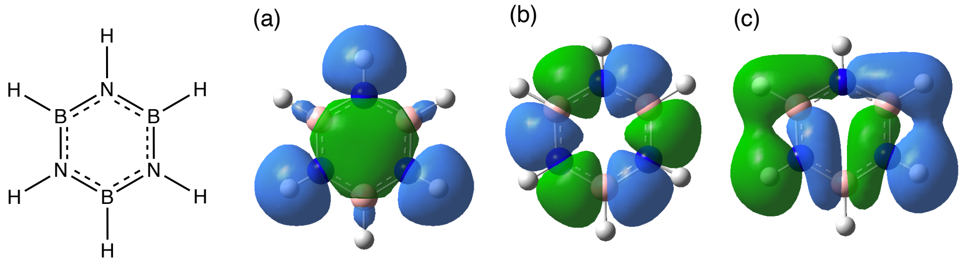
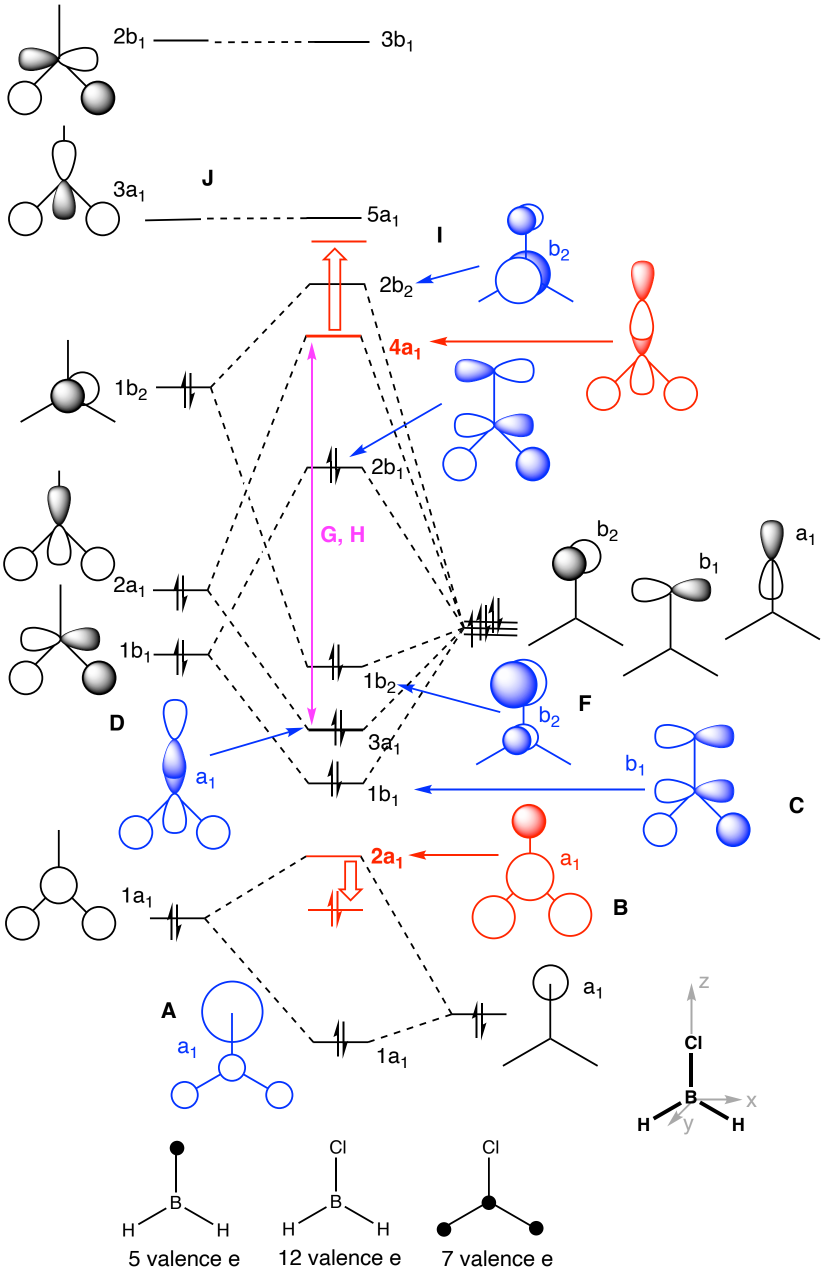


Figure 3 Borazine MOs

10 marks

Q1. Draw a MO diagram for C_{2v} $ClBH_2$. Use the BH_2 fragment orbitals given in **Figure 1**. The Cl pAOs will have an energy between the $1b_1$ and $2a_1$ FOs and the Cl sAO will interact with the a_1 FO. Explicitly demonstrate MO mixing by drawing out and combining the relevant MOs, discuss MO mixing with respect to these MOs. Depict the mixed MOs on your MO diagram.

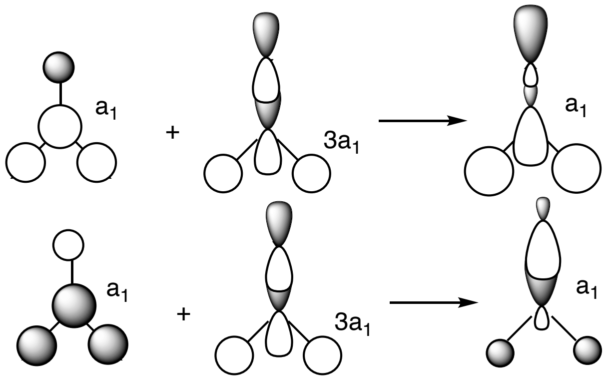
15 marks



- annotations!
  A the $1a_1$ a larger contribution from the Cl sAO as this AO is lower in energy and this MO is the bonding combination
  B the $2a_1$ a larger contribution from the BH_2 fragment orbital as this FO is higher in energy and this MO is the anti-bonding combination
  C Cl is electronegative and on the far right of the PT, it will have a large sp-gap
  D the differences in FO contributions are minor for the $1b_1$, $3a_1$ and $1b_2$ because the FOs are all very close in energy
  E the energy ordering of the $1b_1$ and $3a_1$ is difficult to predict, the FO for b_1 lie lower in energy but the FOs for a_1 have better overlap
  F the $1b_2$ will be higher in energy due to the "side on" or π overlap of the FOs
  G antibonding MOs are destabilised by more than bonding MOs are stabilised

H the $1b_1$ and $2b_1$ will have a smaller splitting energy because these MOs have side-on overlap while the $3a_1$ and $4a_1$ will have a larger splitting energy because these MOs have directed p-p overlap meaning the interaction will be stronger
I the $1b_2$ and $2b_2$ have different fragment coefficients because the contributing FOs are further apart in energy, the higher energy BH_2 b_1 contributes most to the antibonding MO, $2b_2$
J the higher energy BH_2 FOs remain non-bonding

- necessary conditions for MO mixing to occur:
  only MOs of the same symmetry can mix
  MOs cannot be from the same bonding-antibonding pair
  mixing must stabilise the total energy of the molecule
- mixing tends to be large or important when:
  MOs are close in energy
  one of the MOs is non-bonding or unoccupied
  MOs are in the HOMO-LUMO region
  MOs that mix form a new bonding/antibonding pair.
  the closer in energy the stronger mixing between MOs
- in this case the options are the $2b_1$ and $3b_1$ but they belong to the same BH_2 FO bonding and antibonding pair, and are far apart in energy
- the $3a_1$ and $4a_1$ belong to the same MO bonding and antibonding pair
- the other option is the $2a_1$ and $4a_1$ MOs, while the $2a_1$ is occupied the $4a_1$ is unoccupied, the energy difference is large so any splitting will be small.
- the mixing is shown below the top orbital is made less antibonding and the bottom orbital is significantly more antibonding.



MO diagram marks:
0.5 axial system defined in correct alignment and placed on the molecule
0.5 fragments and molecule along the bottom, placeholders present
1 energies, depicting and labelling FOs
3 for shapes of MOs, including size variations in MOs
1 correct symmetry labels MOs
2 MO energies roughly right
1 electronic configuration
3 for correct mixing MOs, rules for mixing
3 for a selection of annotations related to MOs and energies
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15 marks

Q2 Consider three oxygen atoms arranged in an equilateral triangle, that belong to the D_{3h} point group, **Figure 2**. In the following show your working at all stages.

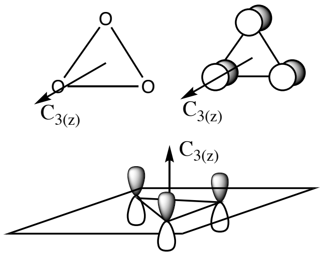


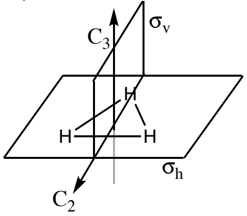
Figure 4 O_3 pAOs

find the character table

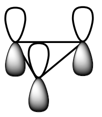
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	σ_v		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(T_x, T_y)	x^2-y^2, xy
A_1”	1	1	1	-1	-1	-1		
A_2”	1	1	-1	-1	-1	1	T_z	
E”	2	-1	0	-2	1	0	(R_x, R_y)	xz, yz

i) Determine the reducible representation for the three p_π orbitals
  - use all three pz orbitals as a basis
  - determine the number of orbitals that don't shift from one atomic center to another under the symmetry operations of the group, atoms that move contribute 0, for the atoms that move if the phase is unchanged an orbital contributes +1, if the phase changes the orbital contributes (-1).

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma(3p_z)$	3	0	-1	-3	0	1



selected elements from the D_{3h} point group



ii) Write down the reduction and projection formulae. Briefly explain the terms in both formulae.
  - this is straight from the notes, please see the relevant section

The Reduction formula

$$n_{IR} = \frac{1}{h}\sum_{Q} k \bullet \chi^{IR}(Q) \bullet \chi^{R}(Q)$$

h = number of operations in the group
Q = a particular symmetry operation
k = the number of operations of Q
$\chi^{IR}(Q)$ the character of the **I**rreducible **R**epresentation under Q
$\chi^{R}(Q)$ = the character of the **R**educible **R**epresentation under Q

The Projection Operator

$$P_\Gamma[\psi] = \frac{1}{h}\sum_Q \chi^{IR}(Q) \bullet Q[\psi]$$

h = number of operations in the group
Q = a particular symmetry operation
$P_\Gamma[\Psi]$= operate on an orbital function
$\chi^{IR}(Q)$= the character of the **I**rreducible **R**epresentation under Q

iii) Use the reduction formula to determine the symmetry of the p_π based symmetry adapted fragment orbitals.

- Be smart! do not just go through all the IR sequentially!
- look at the character table and look for the IR that will give the all in-phase combination
  (a) this cannot be a_1' since under σ_h the pAOs will invert giving -1 character
  (b) under σ_h t the reducible rep has -3 so likely to be a_1" or a_2" or e"
  (c) try highest symmetry one first => a_1"

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1"	1	1	1	-1	-1	-1
$\Gamma(3p_z)$	3	0	-1	-3	0	1

$$n_{A_1''} = \frac{1}{12}\Big[(1\bullet1\bullet3) + (2\bullet1\bullet0) + (3\bullet1\bullet\text{-}1) + (1\bullet\text{-}1\bullet\text{-}3) + (2\bullet\text{-}1\bullet0) + (3\bullet\text{-}1\bullet1)\Big]$$

$$n_{A_1''} = \frac{1}{12}\Big[3 + 0 - 3 + 3 + 0 - 3\Big]=0$$

- this hasn't worked, so try the next one a_2"

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_2"	1	1	-1	-1	-1	1
$\Gamma(3p_z)$	3	0	-1	-3	0	1

$$n_{A_2''} = \frac{1}{12}\Big[(1\bullet1\bullet3) + (2\bullet1\bullet0) + (3\bullet\text{-}1\bullet\text{-}1) + (1\bullet\text{-}1\bullet\text{-}3) + (2\bullet\text{-}1\bullet0) + (3\bullet1\bullet1)\Big]$$

$$n_{A_1''} = \frac{1}{12}\Big[3 + 0 + 3 + 3 + 0 + 3\Big] = \frac{12}{12} = 1$$

- now we know that there is 1a_2" component we subtract this from the reducible representation

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma(3p_z)$	3	0	-1	-3	0	1
A_2"	1	1	-1	-1	-1	1
$\Gamma(3p_z) - A_2''$	2	-1	0	-2	1	0

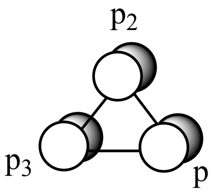
= E"

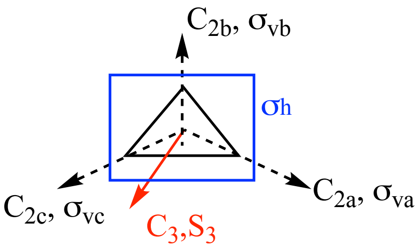
- this tells us that $\Gamma(3p_z) = a_2'' + e''$
- you should also do a check by adding the two IR and show you regenerate $\Gamma(3p_z)$

$\mathbf{D_{3h}}$	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_2''	1	1	-1	-1	-1	1
E"	2	-1	0	-2	1	0
$A_2'' + E''$	3	0	-1	-3	0	1

$=\Gamma(3p_z)$

iv) Use the projection formula to determine the wave function of the p_π based symmetry adapted fragment orbitals.





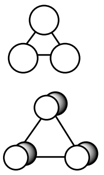
D_{3h}	E	C_3^1	C_3^2	C_{2a}	C_{2b}	C_{2c}	σ_h	S_3^1	S_3^{-1}	σ_{va}	σ_{vb}	σ_{vc}
$Q[p_1]$	p_1	p_2	p_3	$-p_1$	$-p_3$	$-p_2$	$-p_1$	$-p_2$	$-p_3$	p_1	p_3	p_2
A_2"	1	1	1	-1	-1	-1	-1	-1	-1	1	1	1
$\chi^{A2"}Q[p_1]$	p_1	p_2	p_3	p_1	p_3	p_2	p_1	p_2	p_3	p_1	p_3	p_2

$$
\begin{aligned}
P_{A2"}[p_1] &= \frac{1}{12}[p_1 + p_2 + p_3 + p_1 + p_3 + p_2 + p_1 + p_2 + p_3 + p_1 + p_3 + p_2] \\
&= \frac{1}{12}[4p_1 + 4p_2 + 4p_3] \\
&= \frac{1}{3}[p_1 + p_2 + p_3]
\end{aligned}
$$

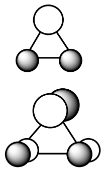
D_{3h}	E	C_3^1	C_3^2	C_{2a}	C_{2b}	C_{2c}	σ_h	S_3^1	S_3^{-1}	σ_{va}	σ_{vb}	σ_{vc}
$Q[p_1]$	p_1	p_2	p_3	$-p_1$	$-p_3$	$-p_2$	$-p_1$	$-p_2$	$-p_3$	p_1	p_3	p_2
E"	2	-1	-1	0	0	0	-2	1	1	0	0	0
$\chi^{E"}Q[p_1]$	$2p_1$	$-p_2$	$-p_3$	0	0	0	$2p_1$	$-p_2$	$-p_3$	0	0	0

$$
\begin{aligned}
P_{E2}[p_1] &= \frac{1}{12}[2p_1 - p_2 - p_3 + 2p_1 - p_2 - p_3] \\
&= \frac{1}{12}[4p_1 - 2p_2 + 2p_3] \\
&= \frac{1}{6}[2p_1 - p_2 - p_3]
\end{aligned}
$$

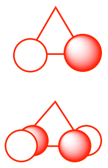
- now you need to guess an orthogonal partner, you already know the orbital shapes for the H_3 system



$\psi_{a_2''} = \frac{1}{3}\left[\phi_{p_1} + \phi_{p_2} + \phi_{p_3}\right]$



$\psi_{e"} = \frac{1}{6}\left[2\phi_{p_1} - \phi_{p_2} - \phi_{p_3}\right]$



$\psi_{e"} = \frac{1}{2}\left[\phi_{p_2} - \phi_{p_3}\right]$

guess wavefunction

- if you look directly down from above on the pAO system it looks just like the sAO system, (except that in the pAO system reflection in the sh plane alters the phase!). The first two orbitals have already been derived, we guess that the third will look like the last sAO MO but with a node in sh plane and a change of phase. Then we need to check that the two e” MOs are orthogonal: which is true!

- we have the two equations

$$\psi^1_{1e''} = 2\phi_{p1} - \phi_{p2} - \phi_{p3}$$
$$\psi^2_{1e''} = \phi_{p2} - \phi_{p3}$$

- now show they are orthogonal

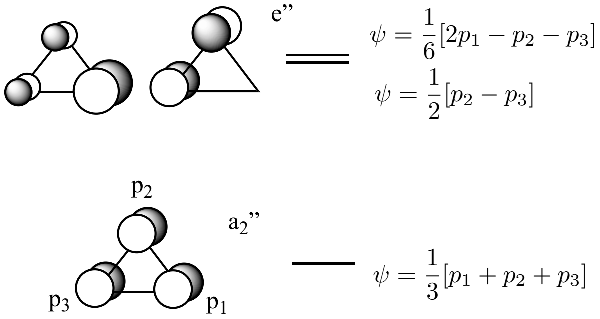
$$\begin{aligned}\int \psi^1_{1e''} \cdot \psi^2_{1e''} d\tau &= \int (2\phi_{p1} - \phi_{p2} - \phi_{p3}) \cdot (\phi_{p2} - \phi_{p3}) d\tau \\ &= \underbrace{\int 2\phi_{p1}\phi_{p2} d\tau}_{=2s} - \underbrace{\int 2\phi_{p1}\phi_{p3} d\tau}_{=2s} - \underbrace{\int \phi_{p2}\phi_{p2} d\tau}_{=1} + \underbrace{\int \phi_{p2}\phi_{p3} d\tau}_{=s} - \underbrace{\int \phi_{p3}\phi_{p2} d\tau}_{=s} + \underbrace{\int \phi_{p3}\phi_{p3} d\tau}_{=1} \\ &= 2s - 2s - 1 + s - s + 1 \\ &= 0\end{aligned}$$

- where we have used the fact that the atomic orbitals are normalised

$$\int \phi_i \bullet \phi_j d\tau = s_{ij} \quad and \quad \int \phi_i \bullet \phi_i d\tau = 1$$

- and that the overlap between the orbitals is the same because the orbitals are all the same and they are all equally distant from each other ie $s_{12}=s_{21}=s_{13}=s_{23}$

v) Draw an energy level diagram for the p_π based symmetry adapted fragment orbitals. Draw the fragment orbitals and write the associated equation beside each energy level. Label the symmetry of each orbital.



$$\psi = \frac{1}{6}[2p_1 - p_2 - p_3]$$
$$\psi = \frac{1}{2}[p_2 - p_3]$$
$$\psi = \frac{1}{3}[p_1 + p_2 + p_3]$$

10 marks

Symmetry adapted FOs marks:
1 reducible representation
1 definitions
2 determining nIR
1 projection p1
2 projection tables
2 orthogonality
1 final diagram
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10 marks

Q3 Draw LCAOs for the computed MOs of borazine shown in **Figure 3**. On your diagrams annotate features important for evaluating the MO bonding character.

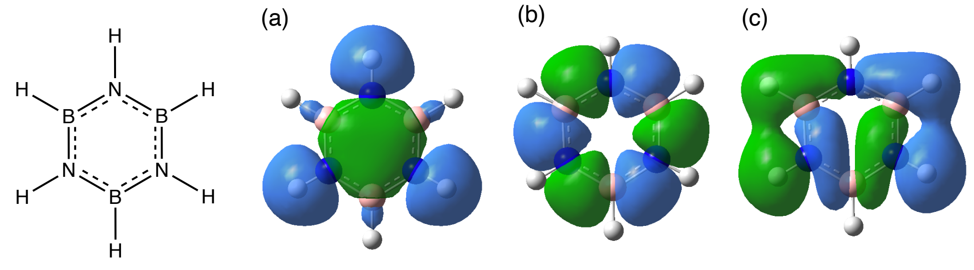
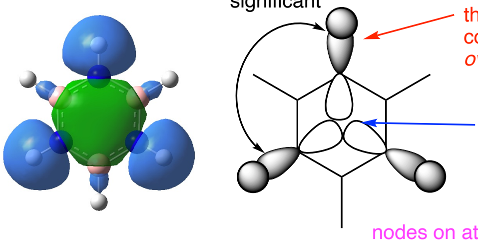


Figure 5 O_3 pAOs

10 marks

NET: stong bonding

too long range to be significant

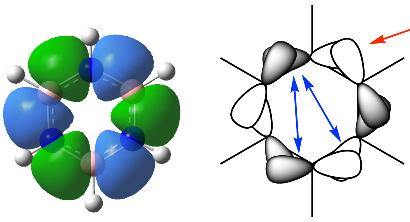


in-phase so bonding
through bond directd p-s, with large coefficients so strong
overall: strong bonding interaction

in-phase so bonding
through space very short distance and directed p-p, with large coefficients so strong
overall: strong bonding interaction

nodes on atomic centers are weaker

NET: stong bonding



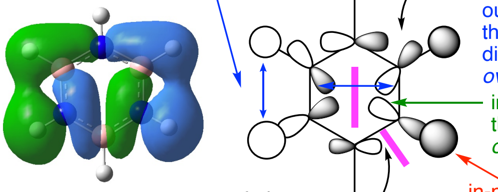
in-phase so bonding
through bond directd p-p, with large coefficients so strong
overall: strong bonding interaction

out-of-phase so antibonding
through space moderate distance with little direct overlap, weak
overall: weak antibonding interaction compensated for by through ring bonding

nodes on atomic centers are weaker

NET: weak bonding

in-phase so bonding
through space long range so weak
overall: weak bonding interaction



in-phase so bonding
through bond, but tilted overlap, moderate
overall: moderate bonding interaction

out-of-phase so antibonding
through space a moderate distance but directed overlap so moderate
overall: moderate antibonding interaction

in-phase so bonding
through bond but tilted overlap, moderate
overall: moderate bonding interaction

in-phase so bonding
through bond directd p-p, with large coefficients so strong
overall: strong bonding interaction

out-of-phase so antibonding
not directed and long distance so weak
overall: weak antibonding interaction

inter-nuclear nodes are stronger antibonding

LCAOs from MOs marks:

3 MO1
3 MO2
4 MO3
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10 marks