Moleuclar Orbital Theory

Lecture 7

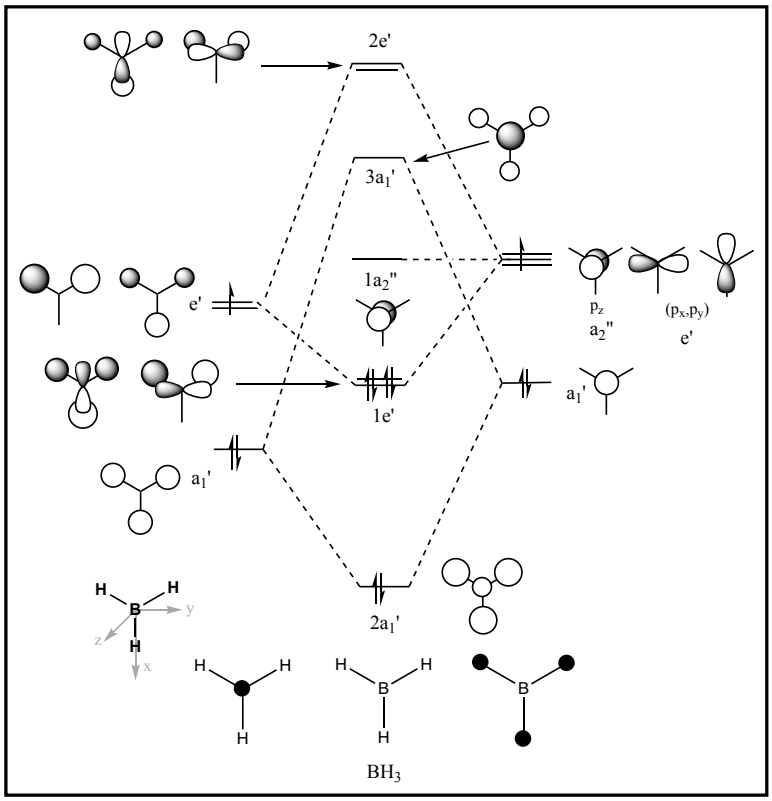
Outline

- interpreting EH_3 MO diagrams
- some mathematical (QM) justifications
- choosing the chemical fragments
- analysing the bonding/anti-bonding character
- LCAO for real MOs

BH3 and NH3

BH_3

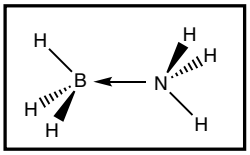
- planar D_{3h}
- vibronic coupling does not occur
- there is no electronic stablisation on lowering the symmetry
- the $a_2'' \rightarrow a_1'$ is empty!
- no MO mixing occurs



BH3 and NH3

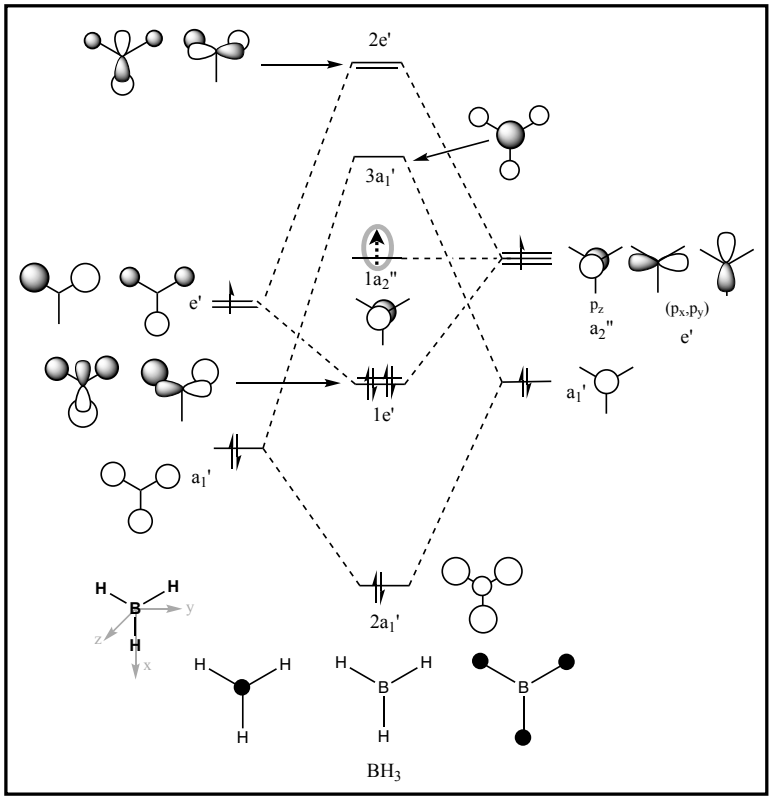
BH_3 Lewis Acid

- a_2'' is a non-bonding MO
- low in energy
- occupation does not destablise the molecule



Lewis Adduct

- occupation stabilises BH_3!
- presence of base reduces symmetry to C_{3v}
- once the $a_2'' \rightarrow a_1'$ starts to "fill up" mixing can occur!
- the larger the e-donation, the larger the distortion
- can measure "donation" by this distortion



Making Connections with QM

- link qualitative arguments to mathematics
- solve Schrödinger equation

$H\Psi = E\Psi$ — whole molecule eqn.

$H = T_n + T_e + V_{ee} + V_{en} + V_{nn}$

$\Psi = N|\psi_1\psi_2...\psi_n|$

$F\psi_i = \epsilon_i\psi_i$ — individual orbitals eqn.

$F = h_i + \sum_j^n 2J_j - K_j$

coupled equations with Fock operators

$\psi = \sum c_n\phi_n$

$\psi = c_a\phi_a \pm c_b\phi_b$

$\psi = c(\phi_a \pm \phi_b)$

expand our MO in terms of the FOs

Reminder from QM:

- determine the expression for c

$$require \quad \int \psi^* \psi d\tau = \langle \psi | \psi \rangle = 1$$

$$\psi = c(\phi_a \pm \phi_b)$$

$$\langle \psi | \psi \rangle = \langle c(\phi_a \pm \phi_b) | c(\phi_a \pm \phi_b) \rangle$$

$$\langle \psi | \psi \rangle = c^2 \left[\underbrace{\langle \phi_a | \phi_a \rangle}_{=1} + \underbrace{\langle \phi_b | \phi_b \rangle}_{=1} \pm 2 \underbrace{\langle \phi_a | \phi_b \rangle}_{=S_{ab}} \right]$$

$$1 = \langle \psi | \psi \rangle = c^2 2(1 \pm S_{ab})$$

$$c^2 = \frac{1}{2(1 \pm S_{ab})} \quad \therefore c = \frac{1}{\sqrt{2(1 \pm S_{ab})}}$$

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AOs are normalised

AOs on same atom are orthogonal but not for different atoms!

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AOs are normalised

AOs on same atom are orthogonal but not for different atoms!

important for later

Reminder from QM:

- rearrange the Schrödinger equation

cannot divide by wavefunction! in QM we premultiply and integrate

$$H\Psi = E\Psi$$

premultiply both sides by Ψ^* and integrate

$$\int \Psi^* H \Psi d\tau = \int \Psi^* E \Psi d\tau$$

$$E = \frac{\int \Psi^* H \Psi d\tau}{\int \Psi^* \Psi d\tau}$$

$$\text{if} \int \Psi^* \Psi d\tau = < \Psi^* | \Psi > = 1$$

$$E = \int \Psi^* H \Psi d\tau = < \Psi^* | H | \Psi >$$

Making Connections with QM

ready to solve!

two important pieces of information

$$E = \langle \psi | H | \psi \rangle \quad and \quad \psi = c(\phi_a \pm \phi_b)$$

$$\psi_+ = c_+(\phi_a + \phi_b)$$

$$\langle \psi | H | \psi \rangle = c_+^2 \langle \phi_a + \phi_b | H | \phi_a + \phi_b \rangle$$

$$\langle \psi | H | \psi \rangle = c_+^2 \left[\langle \phi_a | H | \phi_a \rangle + \langle \phi_a | H | \phi_b \rangle + \langle \phi_b | H | \phi_a \rangle + \langle \phi_b | H | \phi_b \rangle \right]$$

$$\langle \phi_a | H | \phi_a \rangle = H_{aa} \quad assume \quad H_{ab} = H_{ba}$$

$$\langle \psi | H | \psi \rangle = c_+^2 \left[H_{aa} + 2H_{ab} + H_{bb} \right]$$

$$E_+ = \langle \psi | H | \psi \rangle$$

$$E_+ = \frac{H_{aa} + 2H_{ab} + H_{bb}}{2(1 + S_{ab})} \qquad E_- = \frac{H_{aa} - 2H_{ab} + H_{bb}}{2(1 - S_{ab})}$$

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$$E = \langle \psi | H | \psi \rangle \quad and \quad \psi = c(\phi_a \pm \phi_b)$$

$$\psi_+ = c_+(\phi_a + \phi_b)$$

put in wavefunction

$$\langle \psi | H | \psi \rangle = c_+^2 \langle \phi_a + \phi_b | H | \phi_a + \phi_b \rangle$$

$$\langle \psi | H | \psi \rangle = c_+^2 \left[\langle \phi_a | H | \phi_a \rangle + \langle \phi_a | H | \phi_b \rangle + \langle \phi_b | H | \phi_a \rangle + \langle \phi_b | H | \phi_b \rangle \right]$$

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$$\langle \psi | H | \psi \rangle = c_+^2 \langle \phi_a + \phi_b | H | \phi_a + \phi_b \rangle$$

expand out brackets

$$\langle \psi | H | \psi \rangle = c_+^2 [\langle \phi_a | H | \phi_a \rangle + \langle \phi_a | H | \phi_b \rangle + \langle \phi_b | H | \phi_a \rangle + \langle \phi_b | H | \phi_b \rangle]$$

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simplify the notation

$$E_+ = \langle \psi | H | \psi \rangle$$

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replace c $\quad c^2 = \frac{1}{2(1+S_{ab})}$

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$$H_{aa} = \varepsilon_a \; and \; H_{bb} = \varepsilon_b$$

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Making Connections with QM

$$E_+ = \frac{\epsilon_a + \epsilon_b + 2H_{ab}}{2(1+S_{ab})} \quad E_- = \frac{\epsilon_a + \epsilon_b - 2H_{ab}}{2(1+S_{ab})}$$

- here I've provided a simplified rationalisation
- for those who want more, I've included a quantitative derivation in the notes!
  - will not be examined

Making Connections with QM

- set up model: diatomic
  - degenerate FOs $\varepsilon_a=\varepsilon_b=\varepsilon$
  - no overlap $S_{ab}=0$
  - non-zero coupling H_{ab} (H_{ab} is negative!)

insert into the equations

$$E_+ = \frac{\varepsilon_a + \varepsilon_b + 2H_{ab}}{2(1+S_{ab})} \quad and \quad E_- = \frac{\varepsilon_a + \varepsilon_b - 2H_{ab}}{2(1-S_{ab})}$$

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$$\text{assume } \epsilon_a = \epsilon_b = \epsilon \text{ and } S_{ab} = 0$$

$$E_+ = \frac{2\epsilon + 2H_{ab}}{2(1+0)}$$

$$E_+ = \epsilon + H_{ab}$$

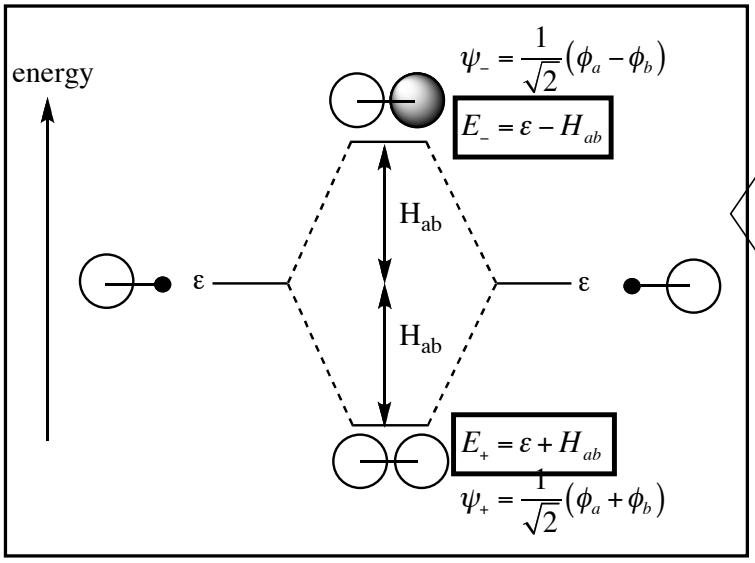
Making Connections with QM

set up model: diatomic

- degenerate FOs $\varepsilon_a=\varepsilon_b=\varepsilon$
- assume $S_{ab}=0$ (to simplify)
- non-zero coupling H_{ab} (H_{ab} is negative!)

insert into the equations

$$E_+ = \frac{\varepsilon_a + \varepsilon_b + 2H_{ab}}{2(1+S_{ab})} \quad and \quad E_- = \frac{\varepsilon_a + \varepsilon_b - 2H_{ab}}{2(1-S_{ab})}$$



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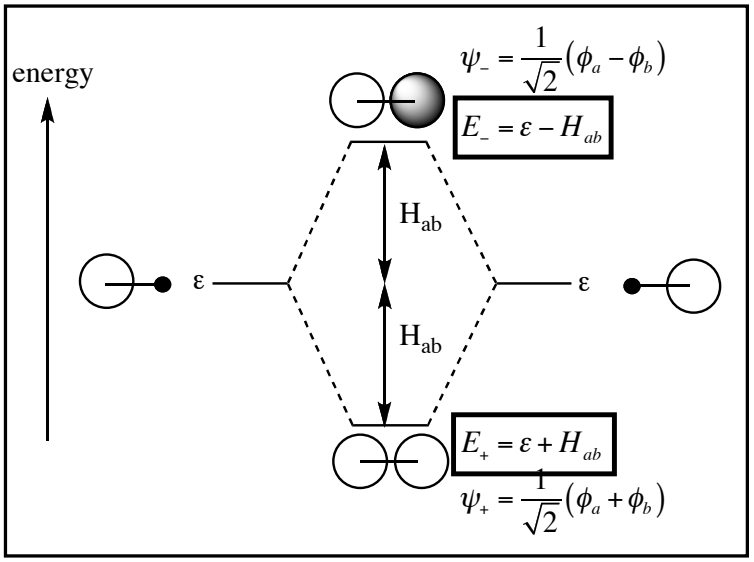

degenerate orbitals: splitting depends on H_{ab}

splitting is large!

Justified!

Making Connections with QM

modify model

- degenerate FOs $\varepsilon_a=\varepsilon_b=\varepsilon$
- overlap allowed $S_{ab} \neq 0$
- non-zero coupling H_{ab}

insert into the equations

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Making Connections with QM

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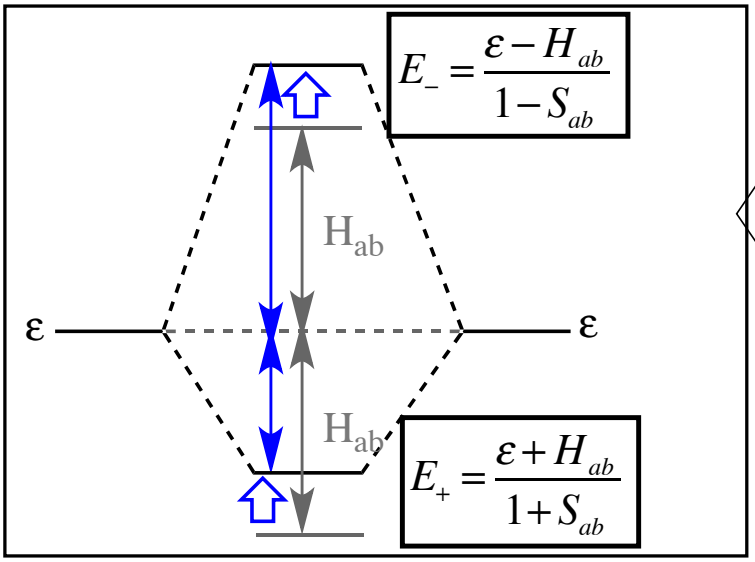

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$$E_+ = \frac{\epsilon + H_{ab}}{1+S_{ab}}$$

eg if S_{ab}=0.2
E- divide by 0.8
E+ divide by 1.2

Making Connections with QM

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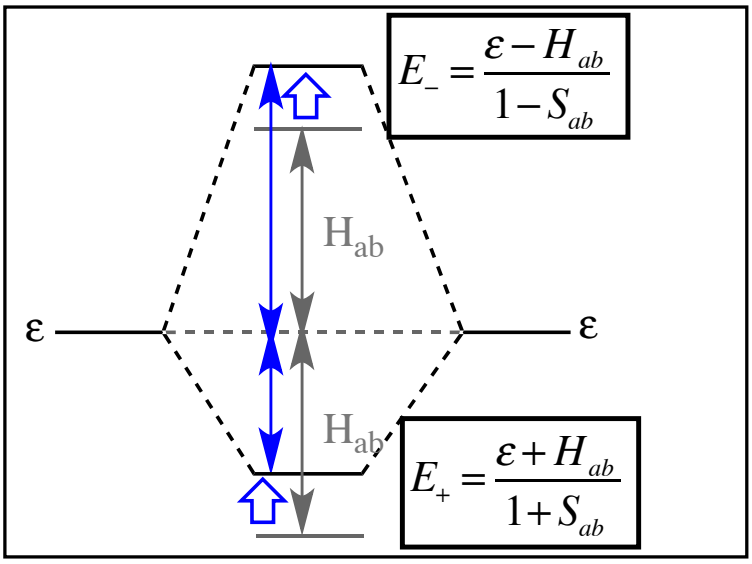
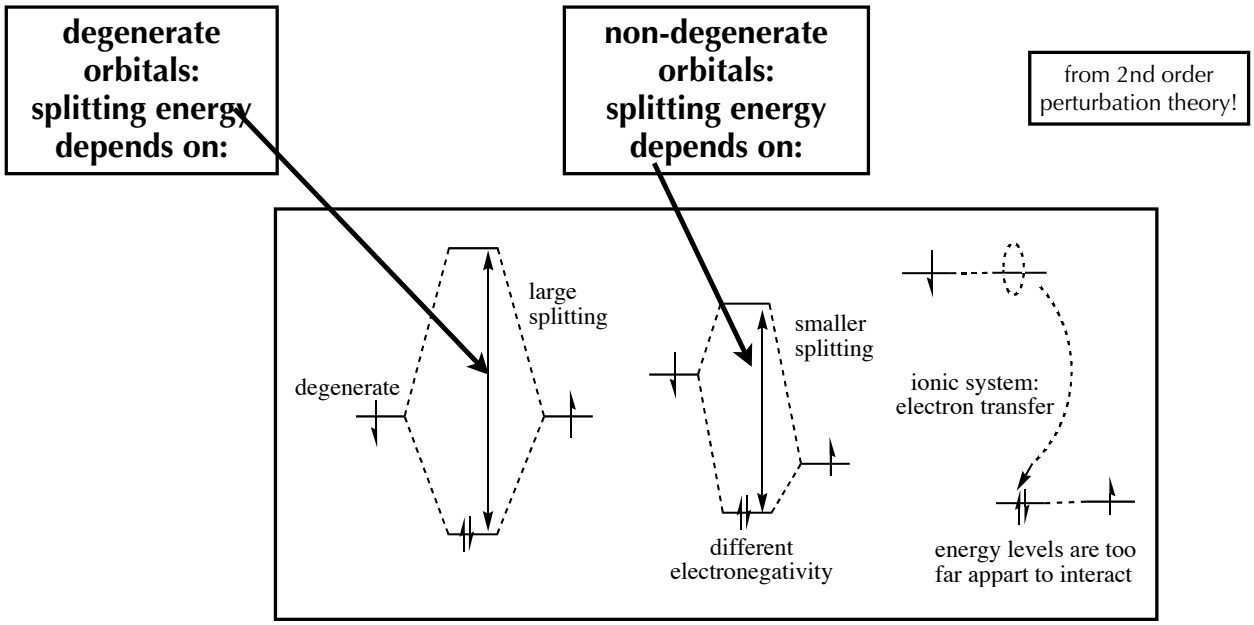


antibonding destabilisation is larger than bonding stabilisation

Justified!

Making Connections with QM

- **general rule: splitting energy decreases as the energy between the FO increases** **Justified!**



Complex Fragments

- **MO diagrams combine two fragments**

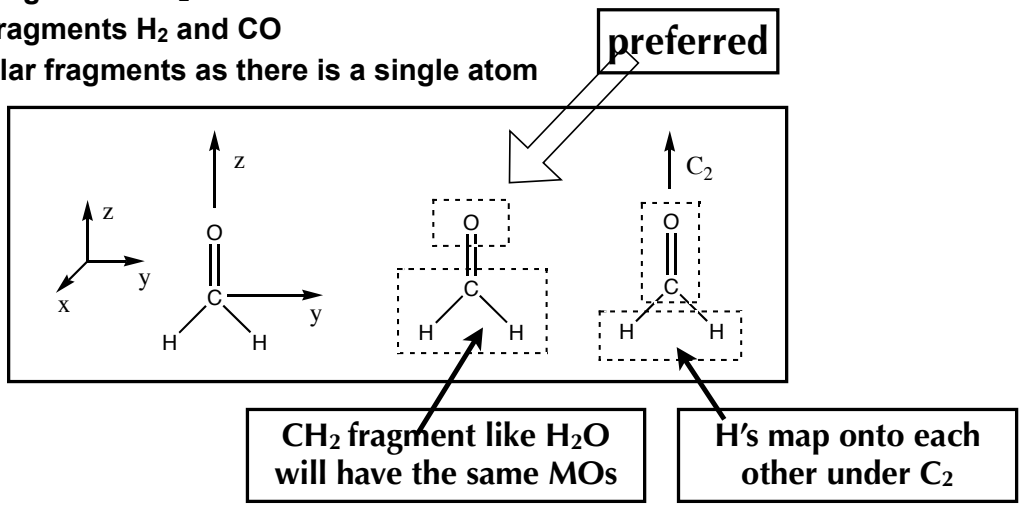
Symmetry Fragments **Molecular Fragments**

- **Symmetry fragments**
  - atoms that transform onto each other under operations of the point group
  - "equivalent atoms" in terms of NMR
  - these are the symmetry adapted FOs
  - if you are not deriving symmetry adapted FOs and you need the whole set for an more complex diagram in the test I will provide them!
- **Molecular fragments**
  - small molecules for which the MOs are well known
  - like linear AB or fragments from AH_2 , AH_3 , AH_4
  - (or ligand σ-orbitals! AL_2 , AL_3 , AL_4)
  - if you are not deriving FOs and you need the whole set of molecular FOs for a more complex diagram in the test I will provide them!

Example:

CH_2O

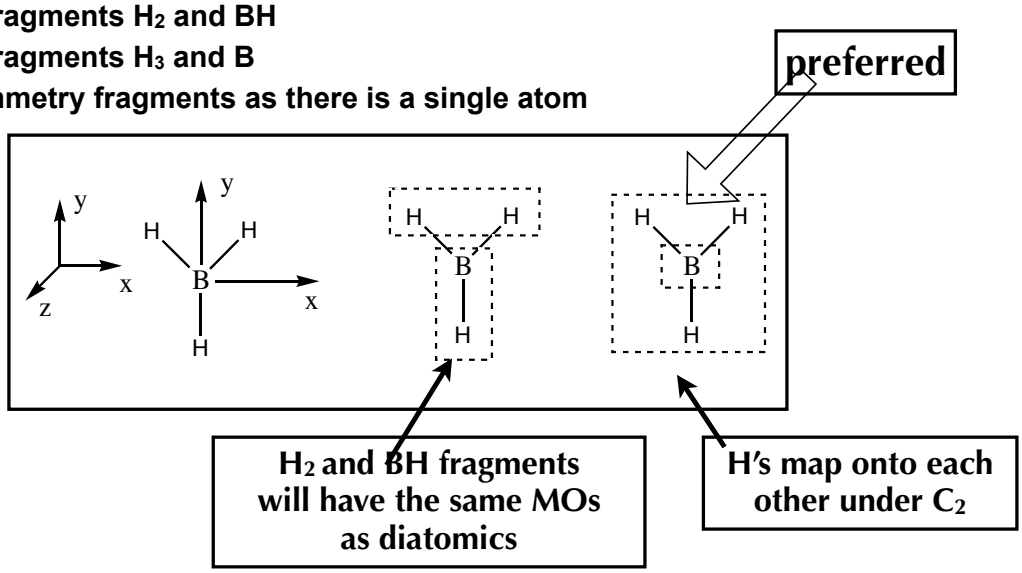
- formaldehyde
- molecular fragments CH_2 and O
- symmetry fragments H_2 and CO
- use molecular fragments as there is a single atom



Example:

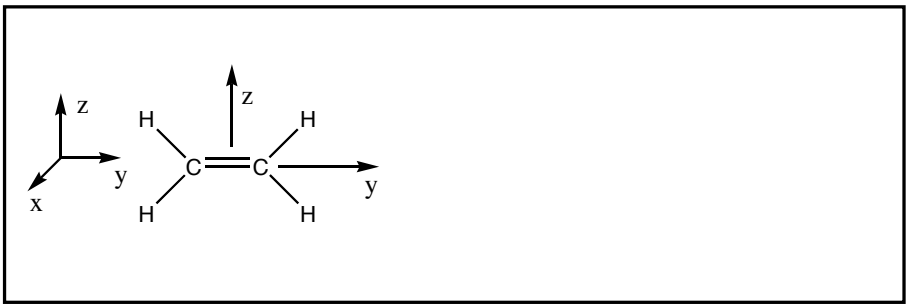
BH_3

- boron trihydride
- molecular fragments H_2 and BH
- symmetry fragments H_3 and B
- use the symmetry fragments as there is a single atom



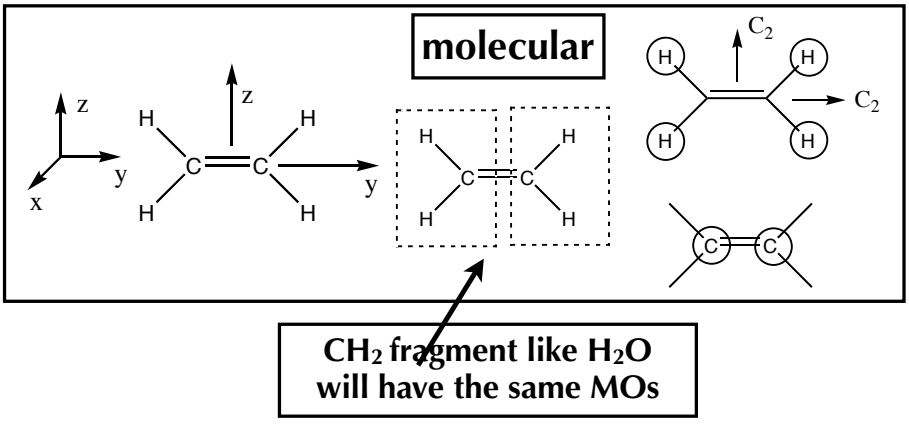
In-Class Activity-P1

- C_2H_4
  - ethane
  - determine the symmetry fragments
  - determine the molecular fragments
  - which is the better one to use and why?



In-Class Activity-P1

- C_2H_4
  - ethane
  - molecular fragments?



In-Class Activity-P1

- C_2H_4
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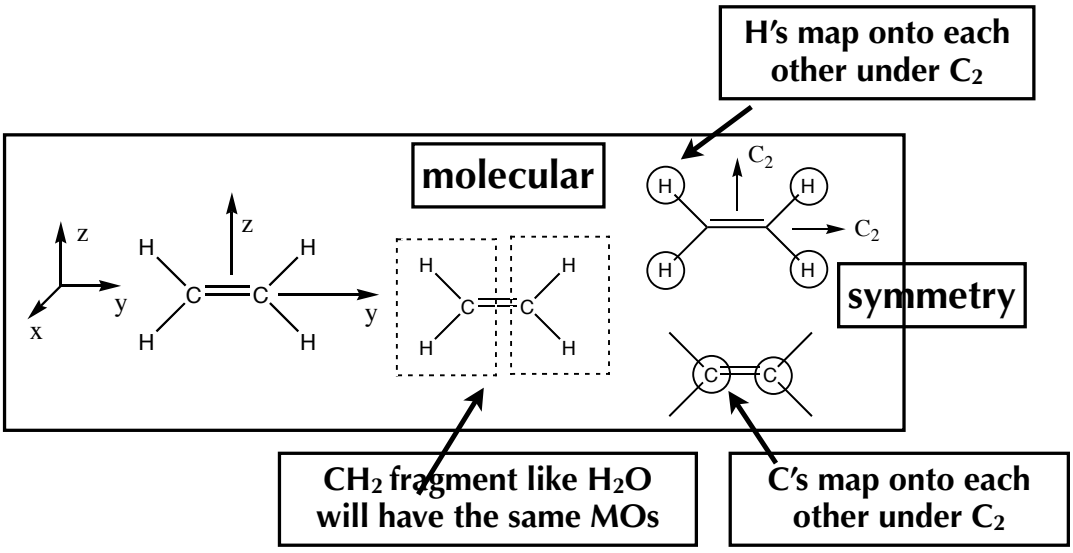
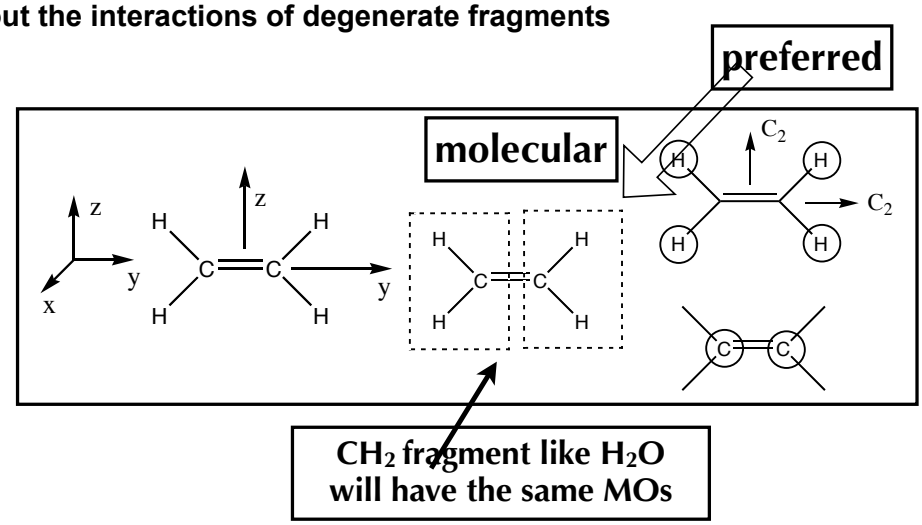
  - molecular fragments?
  - symmetry fragments?



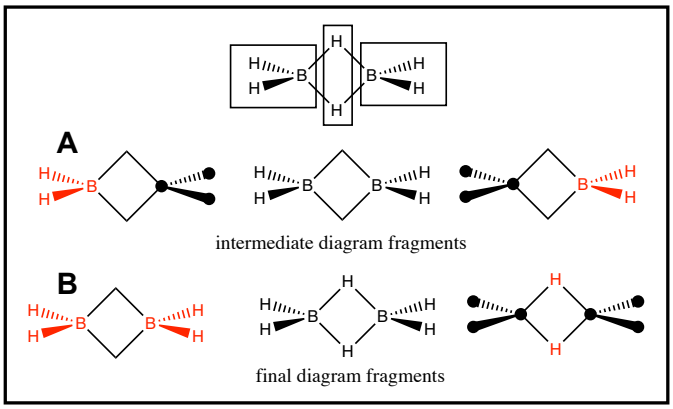
In-Class Activity-P1

- C_2H_4
  - ethane
  - molecular fragments?
  - symmetry fragments?
  - use the molecular fragments because it is easier to work out the interactions of degenerate fragments

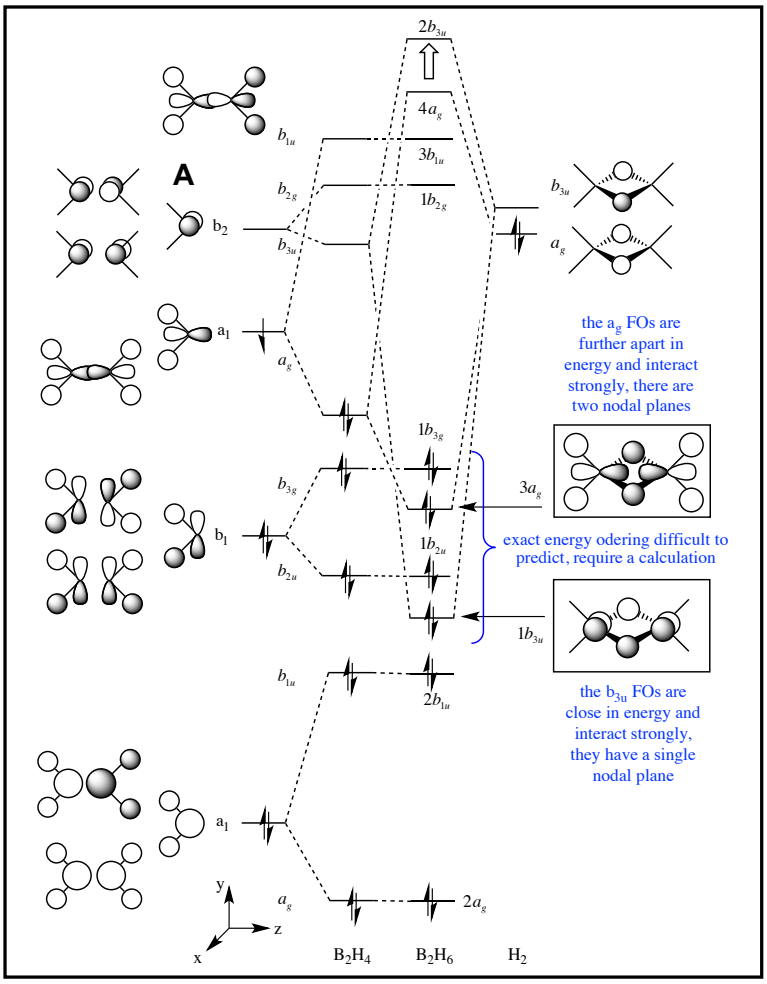


Intermediate MO Diagrams

- more complex molecules can be built up from multiple fragments
- B_2H_6 can be built from an intermediate MO diagram
  - first combine two BH_2 fragments
  - then combine the bridging H_2 fragment with B_2H_4

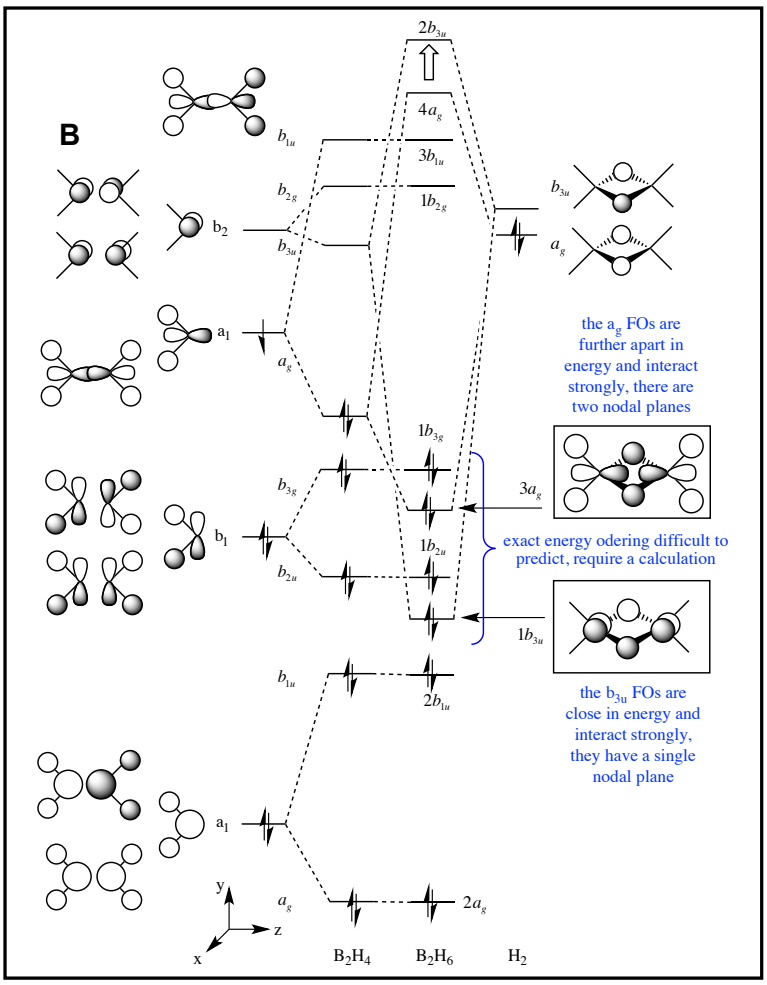


MO Diagram B_2H_6



MO Diagram B_2H_6

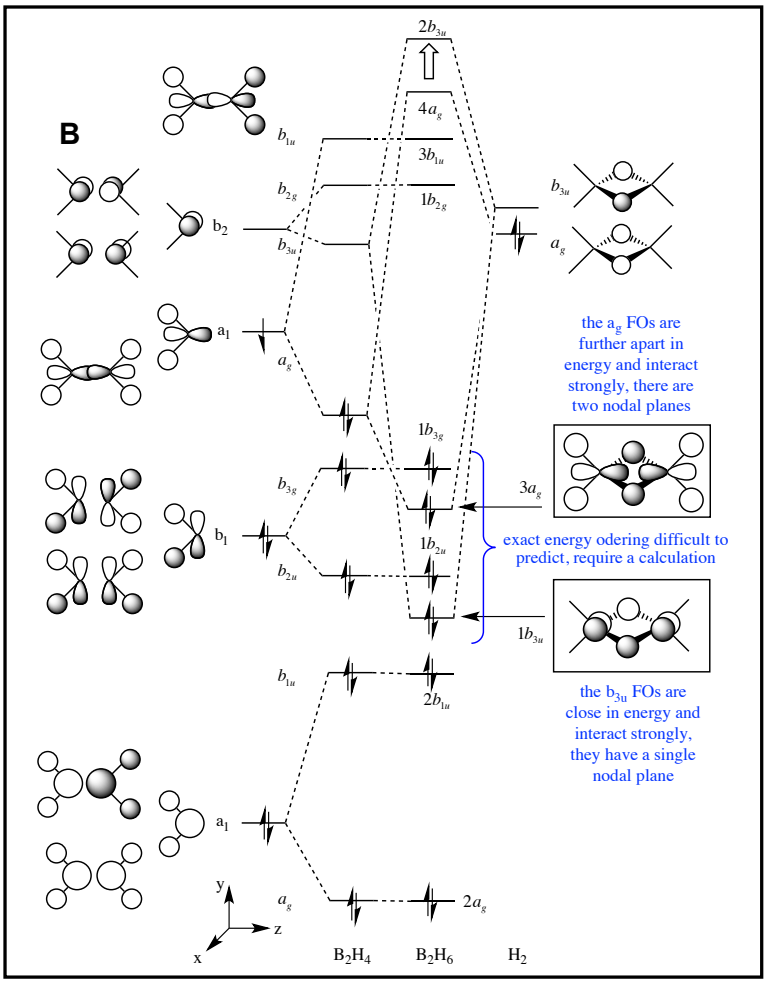
see Fig 13 in the notes



MO Diagram B_2H_6

How to build the MO diagram for B_2H_4?

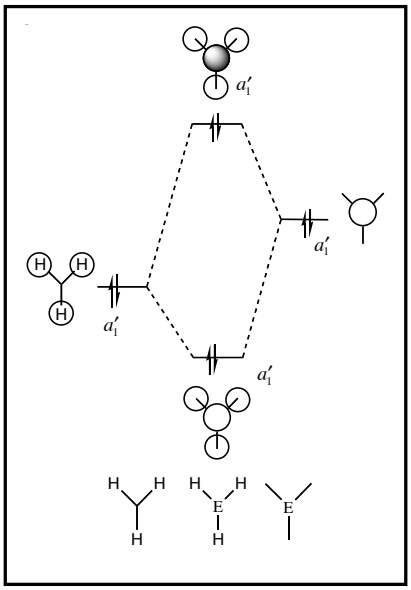
See the additional materials for this lecture



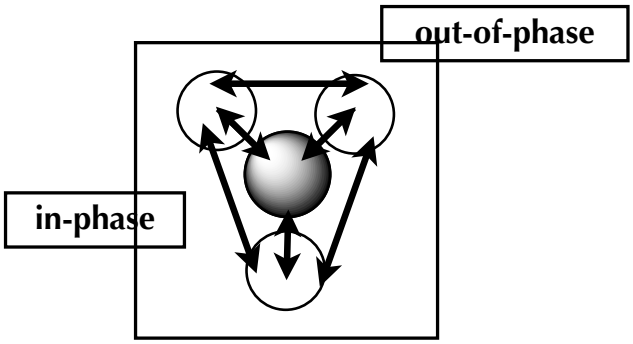
Nature of Bonding / Antibonding

Bonding

- bonding => in-phase overlap
- anti-bonding => out-of-phase overlap
- most orbitals contain BOTH bonding and antibonding interactions!



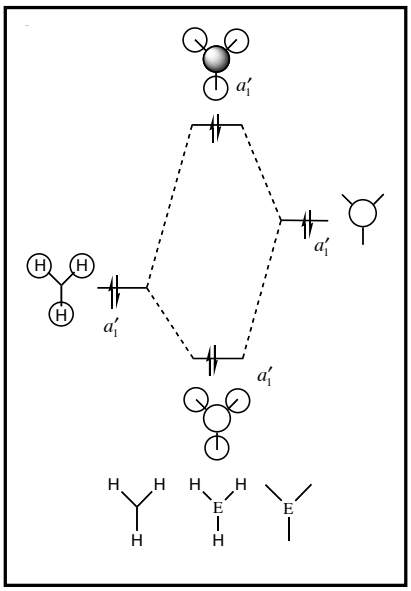
bonding/antibonding is a sliding scale!

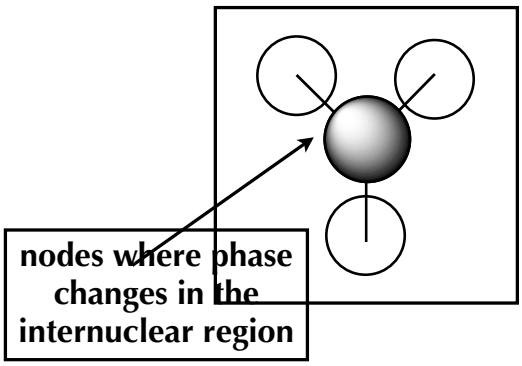


Nature of Bonding / Antibonding

Nodes

- occur where phase changes
- raises the energy of an orbital, more nodes indicates increasing anti-bonding character
- nodes at atoms are less important
- nodes along bonds are very important



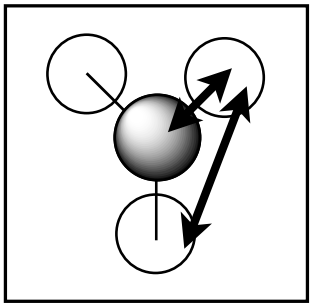


More Complex MOs

- **for each interaction comment on:**
  - antibonding or bonding?
  - through bond? then is it a short or long bond?
  - through space? then distance is important
  - type of interaction? s-s vs s-p and sigma vs pi
  - evaluate on scale from weak to strong

Important!

- **evaluate overall**
  - combine all the information!
  - the number and type of nodes present
  - number of each type of interaction
  - relative size of the contributing FOs

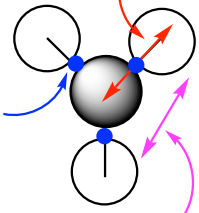


More Complex MOs

- **Students have had problems**
  - follow the rubric
  - include arrows and annotations
- **What your assessment should look like:**

out-of-phase so antibonding
through bond, short bond so strong
s-s interaction so strong
overall: strong antibonding interaction

internuclear (not atomic) nodes, stronger antibonding

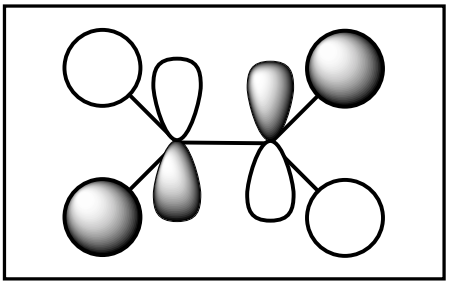


MO is overall: *strongly antibonding*
Due to internuclear nodes, strong through bond antibonding, moderated only weakly by slight long range through space bonding

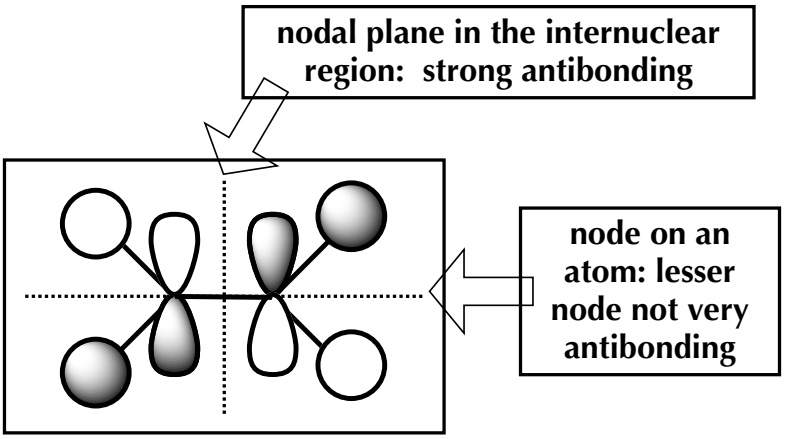
in-phase so bonding
through space, long distance so weak
long range s-s interaction so weak
overall: weak bonding interaction

In-Class Activity-P2

- **Draw this diborane LCAOs MO and annotate your diagram evaluating the bonding and antibonding interactions**



In-Class Activity-P2

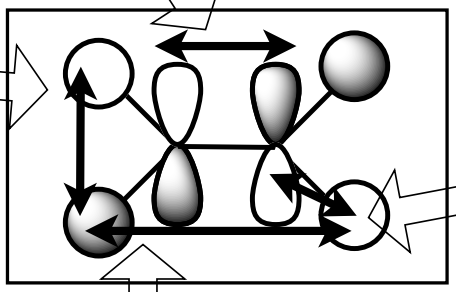


In-Class Activity-P2

A antibonding through bond (strong) π-type (weak): overall: *medium antibondng*

4 strong bonding interactions moderated by numerous medium/ weak antibonding contributions
overall: weak antibonding

B antibonding through space, atoms medium apart (medium) s-s weaker at long range (medium) overall: *medium antibonding*



D bodning through bond (strong) directed s-p overlap, but on slight angle (medium-strong) overall: *strong bondng*

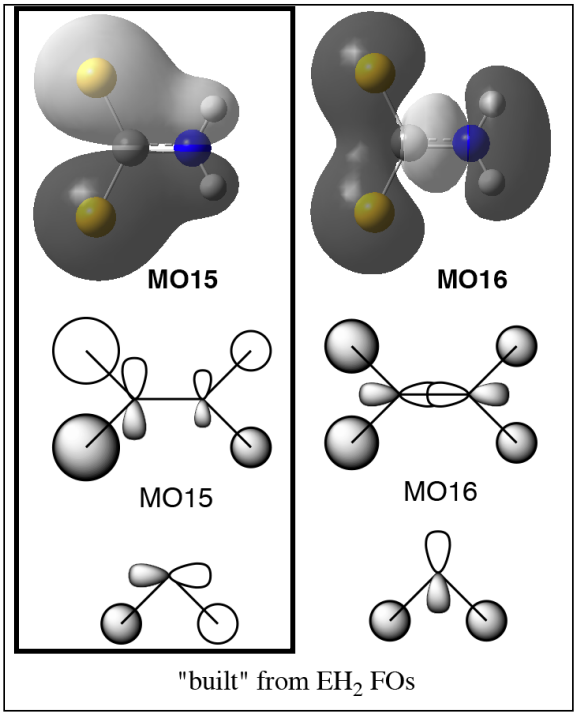
C antibonding through space, atoms very far apart (very weak) s-s weak when long range (weak) overall: *weak antibonding*

LCAO for complex MOs

- **in research we work "backwards" from the delocalised MOs**
- **decompose real MOs into LCAO components**
  - very small contributions are ignored
  - look for known fragment orbitals
  - relative size is important!
- **dithiocarbamate ligand**

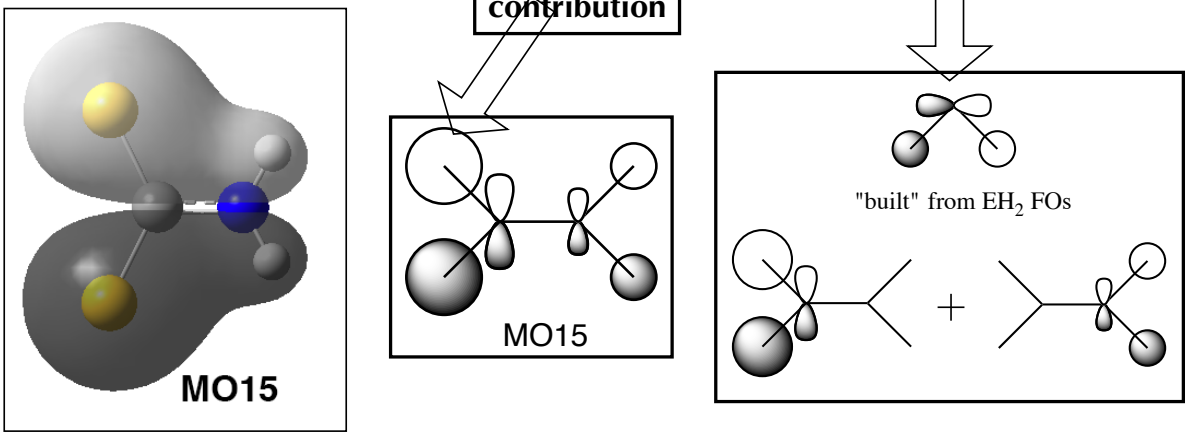
$S_2C{=}NR_2$

take a closer look at MO 15



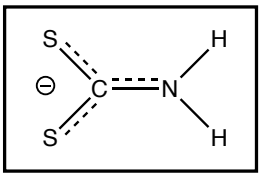
LCAO for complex MOs

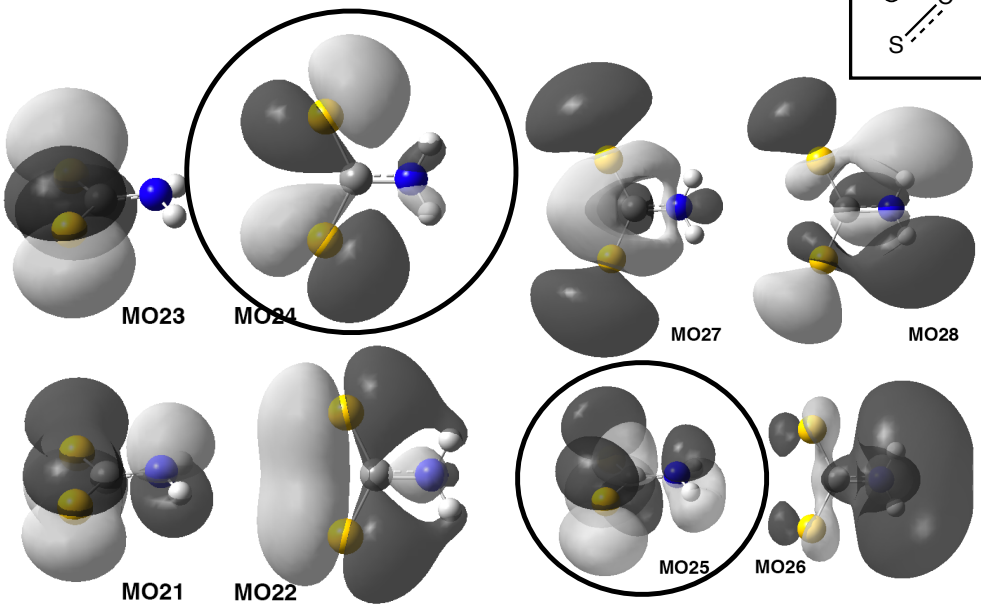
- **decompose the real MOs into LCAO components**
  - very small contributions are ignored
  - relate to known fragment orbitals
  - relative size is important



In-Class Activity-P3

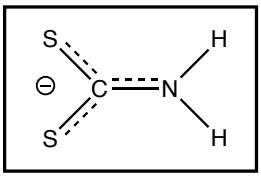
- **Draw LCAO for MO24 and MO25**

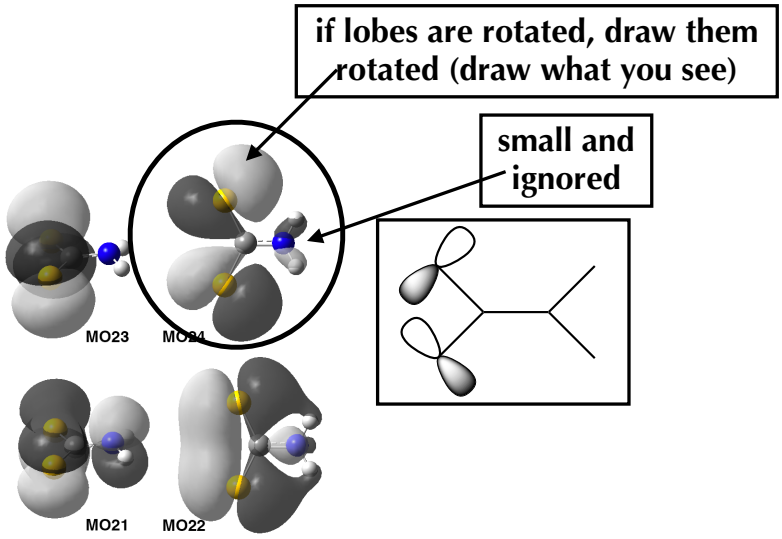




In-Class Activity-P3

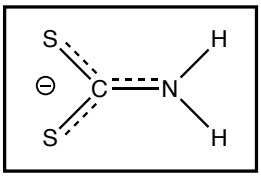
Draw LCAO for MO24 and MO25

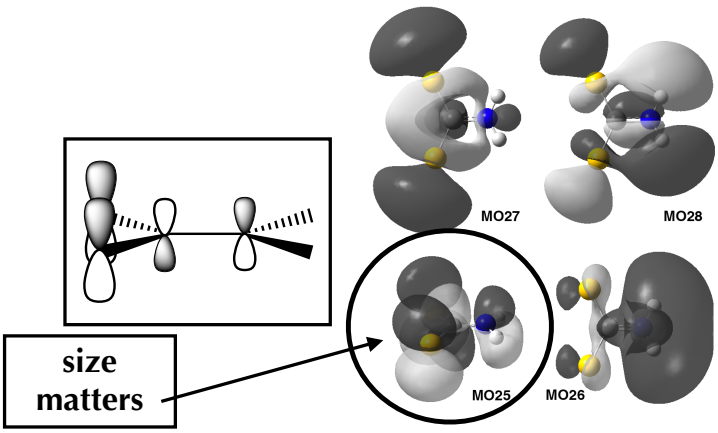




In-Class Activity-P3

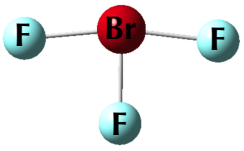
Draw LCAO for MO24 and MO25

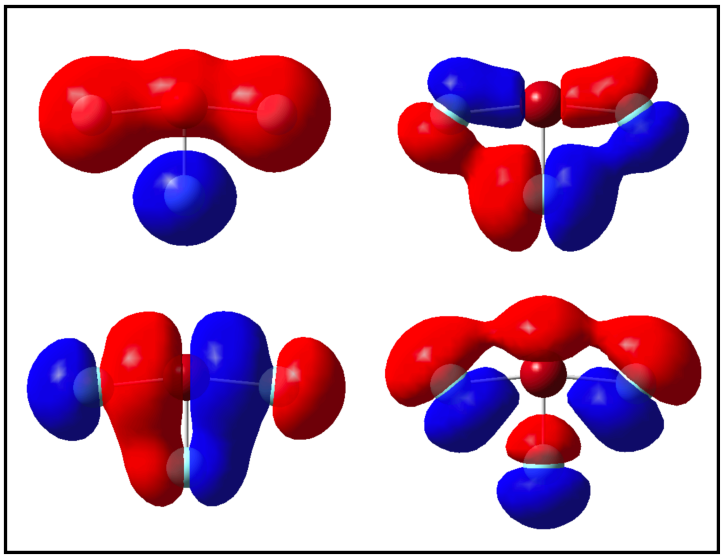




In-Class Activity P4

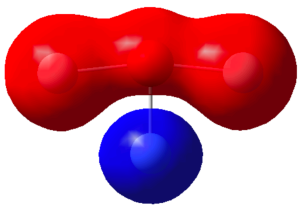
- Draw LCAOs for the computed MOs below.
- On your diagrams annotate features important for evaluating the MO bonding character

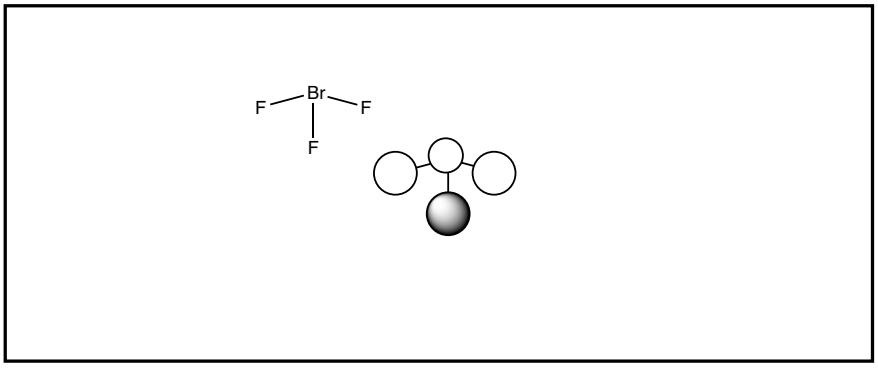




In-Class Activity P5

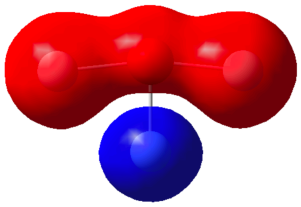
- Draw LCAOs for the computed MOs below.
- On your diagrams annotate features important for evaluating the MO bonding character

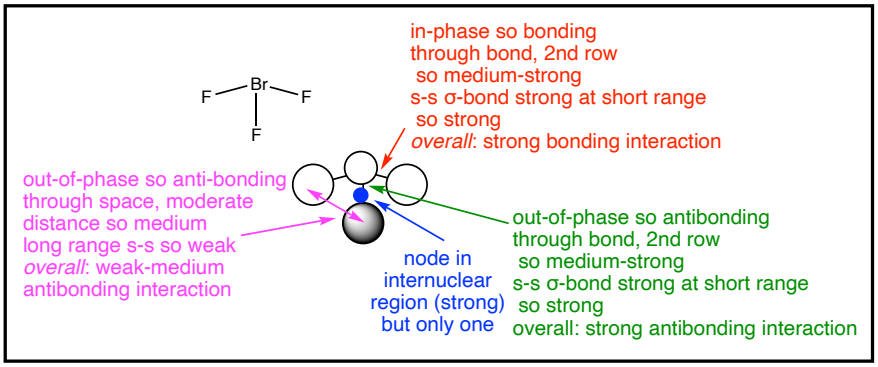




In-Class Activity P4

- Draw LCAOs for the computed MOs below.
- On your diagrams annotate features important for evaluating the MO bonding character

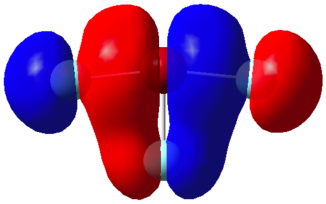


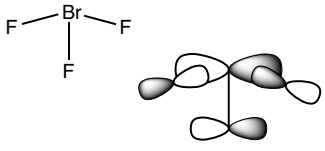


overall: 2 strong bonding interactions, 1 strong anti-bonding and 1 moderate antibonding, but sAOs, so moderate bonding

In-Class Activity P5

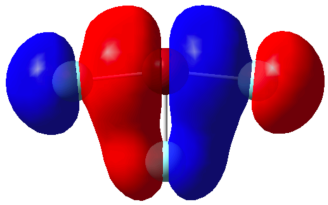
- Draw LCAOs for the computed MOs below.
- On your diagrams annotate features important for evaluating the MO bonding character

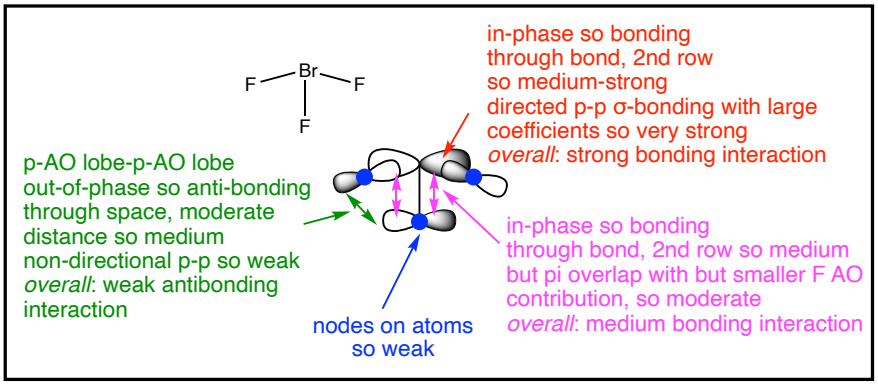




In-Class Activity P5

- **Draw LCAOs for the computed MOs below.**
- **On your diagrams annotate features important for evaluating the MO bonding character**

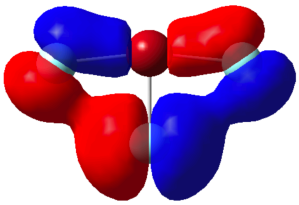


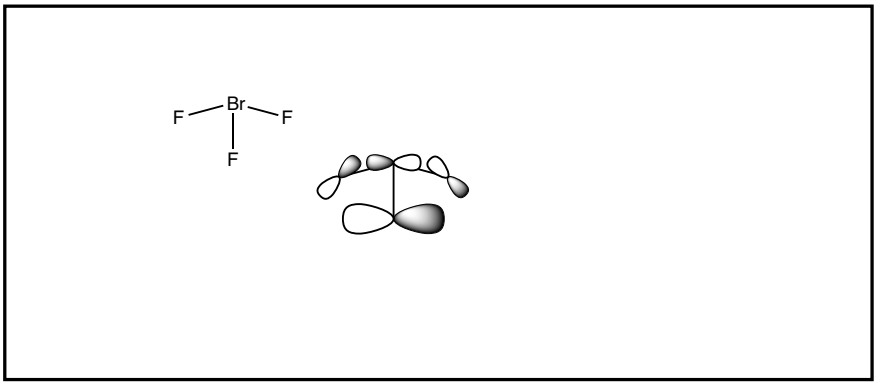


overall: 2 strong σ- & 1 medium π- bonding interactions, 2 weak antibonding, so strongly bonding

In-Class Activity P5

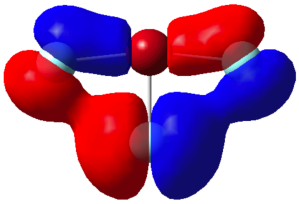
- **Draw LCAOs for the computed MOs below.**
- **On your diagrams annotate features important for evaluating the MO bonding character**

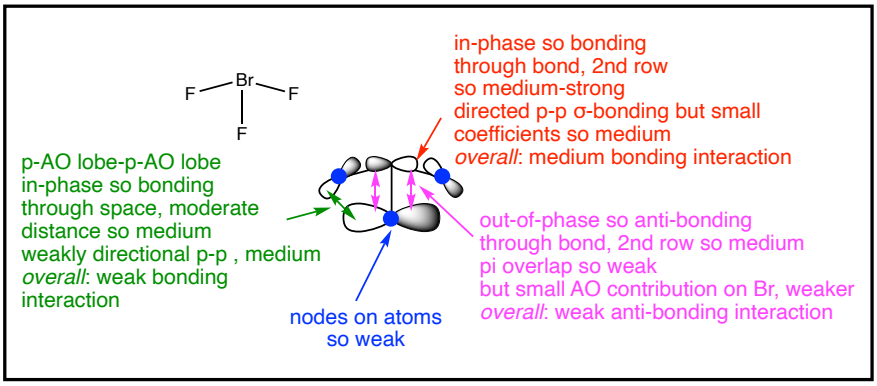




In-Class Activity P5

- **Draw LCAOs for the computed MOs below.**
- **On your diagrams annotate features important for evaluating the MO bonding character**





overall: 1 weak through-space and 2 moderate σ- bonding interactions, 1 weak π- antibonding, so weakly bonding

Key Points

- **be able to discuss, employing equations, diagrams and examples Δε, Sab and Hab, be able to employ this knowledge in forming MO diagrams**
- **be able to make a connection with QM, if given an equation be able to relate these to the "rules" and give relevant diagrams and examples**
- **be able to differentiate between symmetry and molecular fragments and be able to choose fragments that make generating the MO diagram easier**
- **be able to form and use intermediate MO diagrams**
- **be able to explain the LCAO acronym, give the general equation, describe each of the components and illustrate on a diagram**
- **be able to analyse and evaluate the bonding/antibonding qualities of a set of MOs and be able to annotate a diagram of the MO**
- **be able to represent complicated computed MOs in terms of LCAOs**