The Connection to Quantum Mechanics

Introduction

- now we will consider some of the components of a MO diagram to obtain a greater depth of understanding
- we will
  - provide some mathematical justification for the "rules" we have been using
  - consider which fragments to use in building a MO diagram
  - generate symmetry adapted fragment orbitals

Making Connections: Quantum Mechanics

- we can link qualitative MO theory to some real equations from QM
  - The Schrödinger (wave) equation is $H\Psi = E\Psi$
  - which includes the Hamiltonian operator for the molecule

$$H = T_n + T_e + V_{nn} + V_{ne} + V_{ee} \quad H_e = T_e + V_{ne} + V_{ee}$$

  - and the total wavefunction Ψ for the molecule which is composed of slater determinants of the individual MOs ψ_i
  - we can write a form of the Schrödinger equation called the Fock equation for each MO ψ_i

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

  - reminder: h is T_e+V_{ne} and V_{ee} is J and K, ε_i is the energy of the MO ψ_i
  - the MOs ψ_i are formed from a linear combination of the AOs where the coefficients c_n represent the size or contribution of each AO to the MO

$$\psi = \sum c_n \phi_n$$
$$\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + ...$$

  - inside the computer a computational chemistry code solves the Schrödinger equation for the molecule via a series of coupled Fock equations (one for each MO) and the *c's* are varied until the lowest possible E is obtained

Simple Example

- lets take a simple example to help understand what is happening, these are "motivational" justifications, the reality is more complicated!
- we can determine the expression for the coefficient c by examining the normalisation of the MOs
  - remember normalisation ensures only 1e per spin MO, meaning 2e per spatial MO.

$$require \quad \int \psi^{*}\psi d\tau = \langle \psi | \psi \rangle = 1 \quad given \quad \psi = c(\phi_a \pm \phi_b)$$

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

$$\langle \psi | \psi \rangle = c^2 (\underbrace{\langle \phi_a | \phi_a \rangle}_{=1} + \underbrace{\langle \phi_b | \phi_b \rangle}_{=1} \pm 2 \underbrace{\langle \phi_a | \phi_b \rangle}_{=S_{ab}})$$

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

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

$$\psi = \frac{1}{\sqrt{2(1 \pm S_{ab})}}(\phi_a \pm \phi_b)$$

- we can also simplify the expression for the energy

$$H\Psi = E\Psi$$

$$\text{premultiply both sides by } \Psi^* \text{ and integrate}$$

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

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

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

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

- now we can obtain expressions for the energy of the bonding and antibonding MOs

$$E = < \Psi^* | H | \Psi > \text{ and } \psi_+ = c_+(\phi_a + \phi_b)$$

$$< \Psi^* | H | \Psi >= c_+^2 < \phi_a + \phi_b | H | \phi_a + \phi_b >$$

$$= c_+^2 [< \phi_a | H | \phi_a > + < \phi_a | H | \phi_b > + < \phi_b | H | \phi_a > + < \phi_b | H | \phi_b >]$$

$$< \phi_a | H | \phi_a >= H_{aa} = \epsilon_a \text{ and} < \phi_b | H | \phi_b >= H_{bb} = \epsilon_b \text{ and } < \phi_a | H | \phi_b >= H_{ab} = H_{ba}$$

$$< \Psi^* | H | \Psi >= E_+ = c_+^2 [H_{aa} + 2H_{ab} + H_{bb}] = c_+^2 [\epsilon_a + \epsilon_b + 2H_{ab}]$$

$$\text{conversely for } \psi_- = c_-(\phi_a - \phi_b) \quad < \Psi^* | H | \Psi >= E_- = c_1^2 [\epsilon_a + \epsilon_b - 2H_{ab}]$$

$$\text{where } c^2 = \frac{1}{2(1 \pm S_{ab})}$$

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

- these are the important equations for us!

important

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

- now you can see why the splitting energy depends on the MO energy difference $\Delta\varepsilon = \varepsilon_b - \varepsilon_a$, the overlap S_{ab} and H_{ab}
  - the "rules" for splitting simply reflect the mathematics

Extra for experts (NOT examined)

- we want to find the minimum energy, ie the first derivative is zero
- we use a **variational** process to vary the c_i's until the ∂E/∂c=0 for all c_i's

$$E(c_a, c_b) = \frac{<\psi|H|\psi>}{<\psi|\psi>} = \frac{c_a^2 H_{aa} + c_b^2 H_{bb} + c_a c_b H_{ab}}{c_a^2 S_{aa} + c_b^2 S_{bb} + c_a c_b S_{ab}}$$

$$\text{and differentiate } \frac{\partial E}{\partial C_a} \text{ and } \frac{\partial E}{\partial C_b}$$

- taking the derivative, remembering quotient rule $(\frac{F}{G})' = \frac{F'G - G'F}{G^2}$
- delivers a set of coupled equations, ie dependent on all c_i's, the best way to deal with this is to arrange the equations into a matrix form

$$\frac{\partial}{\partial c_a}(<\psi|H|\psi> - E<\psi|\psi>) \text{ and } \frac{\partial}{\partial c_a b}(<\psi|H|\psi> - E<\psi|\psi>)$$

$$\text{leads to}$$

$$c_a H_{aa} + c_b H_{ab} = E(c_a S_{aa} + c_b S_{ab}) \text{ and } c_a H_{ab} + c_b H_{bb} = E(c_a S_{ab} + c_b S_{bb})$$

$$H_{aa} = \epsilon_a \;\; H_{bb} = \epsilon_b \;\; H_{ab} = H_{ba}$$

$$S_{ab} = 0 \;\; S_{aa} = S_{bb} = 1$$

$$\text{secular (set of coupled) equations to solve}$$

$$\begin{pmatrix} \epsilon_a - E & H_{ab} \\ H_{ab} & \epsilon_b - E \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix}$$

$$\text{determinant must be zero}$$

$$(\epsilon_a - E)(\epsilon_b - E) - H_{ab}^2 = 0$$

$$E^2 - (\epsilon_a + \epsilon_b)E + (\epsilon_a \epsilon_b - H_{ab}^2) = 0$$

$$\text{solution for a quadratic } ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{(b^2 - 4ac)}}{2a}$$

$$a = 1 \;\; b = -(\epsilon_a + \epsilon_b) \;\; c = (\epsilon_a \epsilon_b - H_{ab}^2)$$

$$E_\pm = \frac{(\epsilon_a + \epsilon_b) \pm \sqrt{(\epsilon_a + \epsilon_b)^2 - 4(\epsilon_a \epsilon_b - H_{ab})}}{2}$$

$$\begin{aligned}(\epsilon_a + \epsilon_b)^2 - 4(\epsilon_a \epsilon_b - H_{ab}) &= \epsilon_a^2 + \epsilon_b^2 + 2\epsilon_a \epsilon_b - 4\epsilon_a \epsilon_b + 4H_{ab} \\ &= \epsilon_a^2 + \epsilon_b^2 - 2\epsilon_a \epsilon_b + 4H_{ab} \\ &= (\epsilon_a - \epsilon_b)^2 + 4H_{ab}\end{aligned}$$

$$E_\pm = \frac{(\epsilon_a + \epsilon_b)}{2} \pm \sqrt{\left(\frac{\epsilon_a - \epsilon_b}{2}\right)^2 + H_{ab}^2}$$

$$\Delta\epsilon = \epsilon_a - \epsilon_b$$

$$E_\pm = \frac{(\epsilon_a + \epsilon_b)}{2} \pm \sqrt{\left(\frac{\Delta\epsilon}{2}\right)^2 + H_{ab}^2}$$

- if you look at this energy, if $\varepsilon_a = \varepsilon_b$ then 2ε/2=ε and of course in this situation Δε=0 which re-generates for us the simple equation I showed above.

Origin of the Splitting Energy

- assume that the interacting AOs () have energies () that are degenerate ie the same energy. To simplify even further we assume there is zero direct overlap (S_{ab}=0)

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

  - the "pictorial" representation of this result is shown in **Figure 1** below,

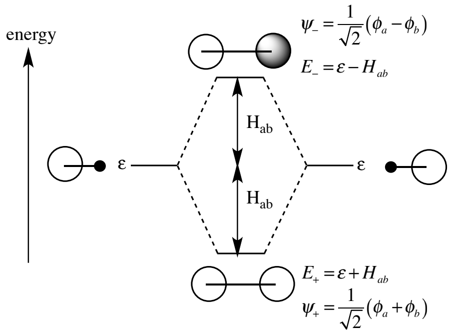


Figure 1 Splitting energy for degenerate FOs

  - by convention H_{ab} *(an energy) is negative*, ε is also negative, so adding two negative numbers means the energy goes down for E_+ and up for E_-
  - the important point is that the splitting energy is dependent on the orbital coupling H_{ab}
  - different sources use different sign conventions!

Antibonding is larger than Bonding

- now lets consider solutions to the Schrödinger equation where we allow the orbitals to overlap $S_{ij} \neq 0$, we will leave $\varepsilon = \varepsilon_a = \varepsilon_b$ (otherwise the equations are too complex!)

$$E_+ = \frac{2\epsilon + 2H_{ab}}{2(1+S_{ab})} = \frac{\epsilon + H_{ab}}{(1+S_{ab})} \text{ and } E_- = \frac{2\epsilon - 2H_{ab}}{2(1-S_{ab})} = \frac{\epsilon - H_{ab}}{(1-S_{ab})}$$

- the splitting energies are shown in **Figure 2**
  - including the effects of S_{ab} shifts the energy of both MOs up
  - we are already familiar with this effect in the "rule" that antibonding MOs are always destabilised more than bonding MOs are stabilised

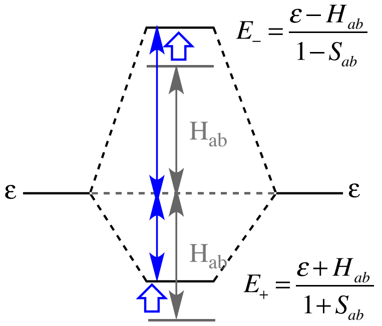


Figure 2 Splitting energy including overlap effects

- *think* about the equation by putting some numbers in, lets say S_{ab}=0.2 (overlap can vary between 0 and 1 but it is normally much smaller than 1).

  - the antibonding MO has an energy (ε-H_{ab}) multiplied by 1/0.8=1.25, the magnitude of the energy of destabilisation is increased.
  - the bonding MO has an energy of (ε+H_{ab}) multiplied by 1/1.2=0.83, the magnitude of the energy of stabilisation is decreased.

Different FO Energies reduce Splitting Energy

- now we release the degeneracy constraint, and allow the energy of the fragment orbitals to differ, $\varepsilon_a \neq \varepsilon_b$ but we assume S_{ab}=0 for simplicity
- the equations for this are more complex, they come from **second-order Rayleigh-Schrödinger perturbation theory**
- I'm not going to cover this theory here so I'm going to give you the solution in that the orbitals shift by:

$$E_{shift} = \frac{H_{ab}^2}{\Delta\epsilon}$$

- the new splitting energies are shown in **Figure 3**.
  - the energy of each MO is now dependent on the *square* of H_{ab}
  - and the energy is *inversely* proportional to the energy gap ($\Delta\varepsilon$)
- so for large $\Delta\varepsilon$ E_+ is very close to ε_a and E_- is very close to ε_b

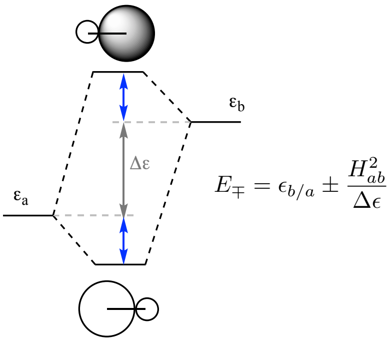


Figure 3 Splitting energy for non-degenerate FOs

- the orbital coefficients also differ

$$(\epsilon_a - E_-)c_a + H_{ab}c_b = 0$$

$$c_a = \frac{-H_{ab}c_b}{(\epsilon_a - E_-)}$$

$$\frac{c_a}{c_b} = \frac{-H_{ab}}{\epsilon_a - E_-}$$

$$\text{assume } |\Delta\epsilon| >> |H_{ab}| \quad E_- \approx \epsilon_b + \frac{H_{ab}^2}{\Delta\epsilon} \approx \epsilon_b$$

$$\frac{c_a}{c_b} = \frac{-H_{ab}}{(\epsilon_a - \epsilon_b)} = \frac{-H_{ab}}{\Delta\epsilon}$$

$$c_a \approx \frac{c_b}{\Delta\epsilon}$$

  - this makes sense orbital c_a is much smaller than c_b (since $\Delta\varepsilon$ is large) for the high energy E- orbital, which is mostly on the higher energy b fragment
- thus we have now provided a more quantitative argument based on QM for the initial qualitative assertion about MO splitting energies: "degenerate orbitals have a large splitting energy and for the rule that as the fragment orbitals shift apart in energy the splitting energy decreases" and for the rule for coefficients "the closest FO in energy contributes more to the MO"

More Complex Fragments

- molecular orbital diagrams take two fragments and combine them to form a molecule. So far, you have seen/examined
  - diatomic molecules with AO fragments
  - EH_2 with an atomic fragment and a H_2 fragment (Chem207 and additional resources in L5)
  - EH_3 with an atomic fragment and H_3 symmetry adapted fragment orbitals
  - ML_4 with ligand sigma-orital L_4 symmetry adapted fragment orbitals (L5 problems)
- many molecular orbital diagrams are not made up from atomic orbitals, but from fragment orbitals from a simple molecular fragment.
- fragments can contain symmetry related atoms (ie atoms that transform into each other under the symmetry operations of the group) = **symmetry fragments** OR they can be smaller molecular units for which the MOs are well known = **molecular fragments** (AB, AH_2, AH_3 and AH_4 are well known fragments)
- Example 1, CH_2O, **Figure 4**:
  - fragment (a) is preferable because it includes a single atom for which the orbitals are particularly easy to determine, and because the H_2C fragment is well known, and has the same symmetry as the molecule.

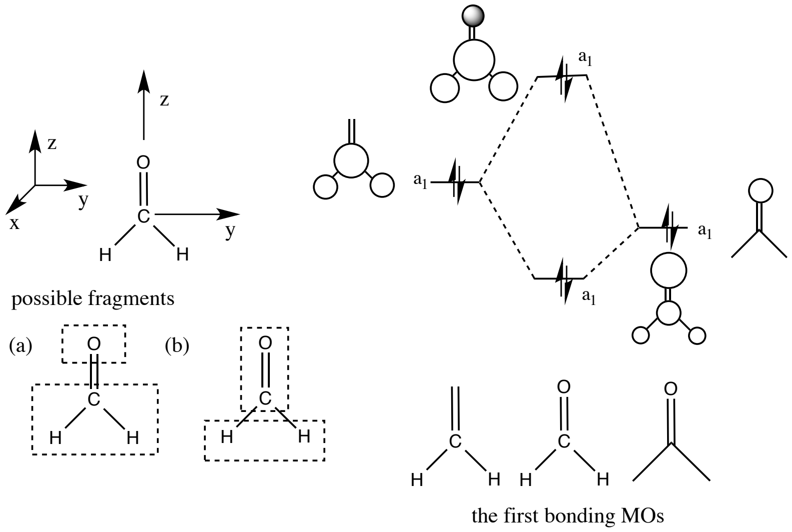


Figure 4 Fragments CH_2O

- Example 2, BH_3, **Figure 5**:
  - the best fragment pattern is H_3 and a central B atom because H_3 is well known and the three H atoms map onto each other under the molecular point group.

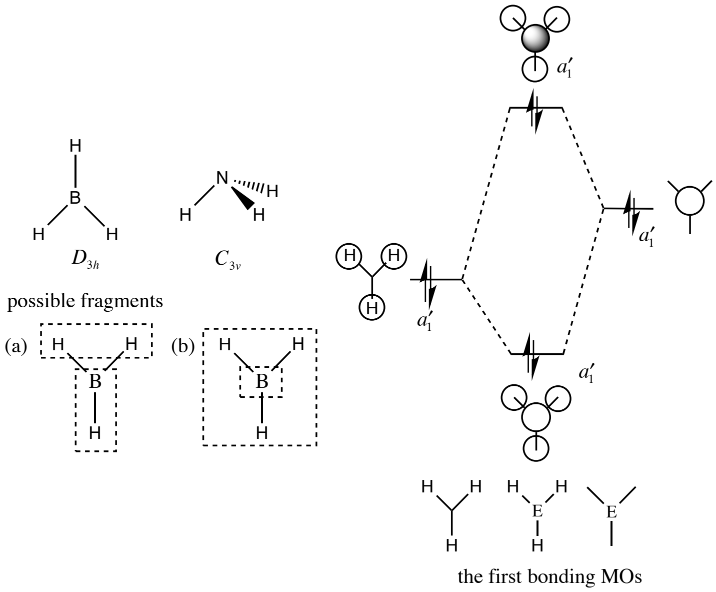


Figure 5 Fragments BH_3

In-Class Activity P1

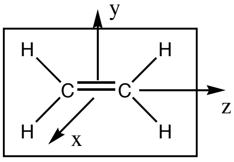
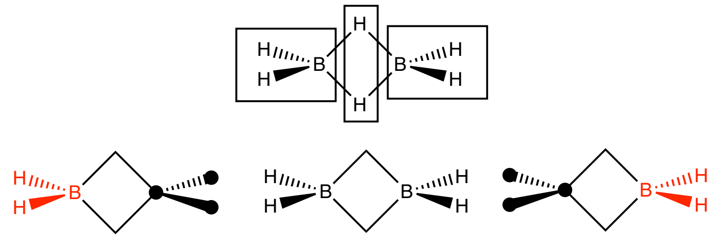


Figure 6 Fragments C_2H_4

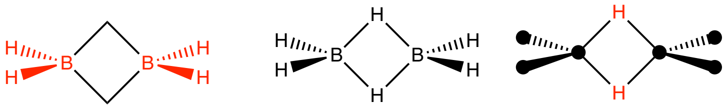
- determine the <u>symmetry fragments</u> for C_2H_4
- determine the <u>molecular fragments</u> for C_2H_4
- which is the better one to use and why?

Intermediate MO Diagrams (B_2H_6)

- complex molecules are often built up by combining a series of simpler fragments.
- for example the MO diagram for B_2H_6 can be formed in two steps,
  - an **intermediate MO diagram** is formed combining two BH_2 fragments
  - final MO diagram is formed adding H_2 to the intermediate MO diagram



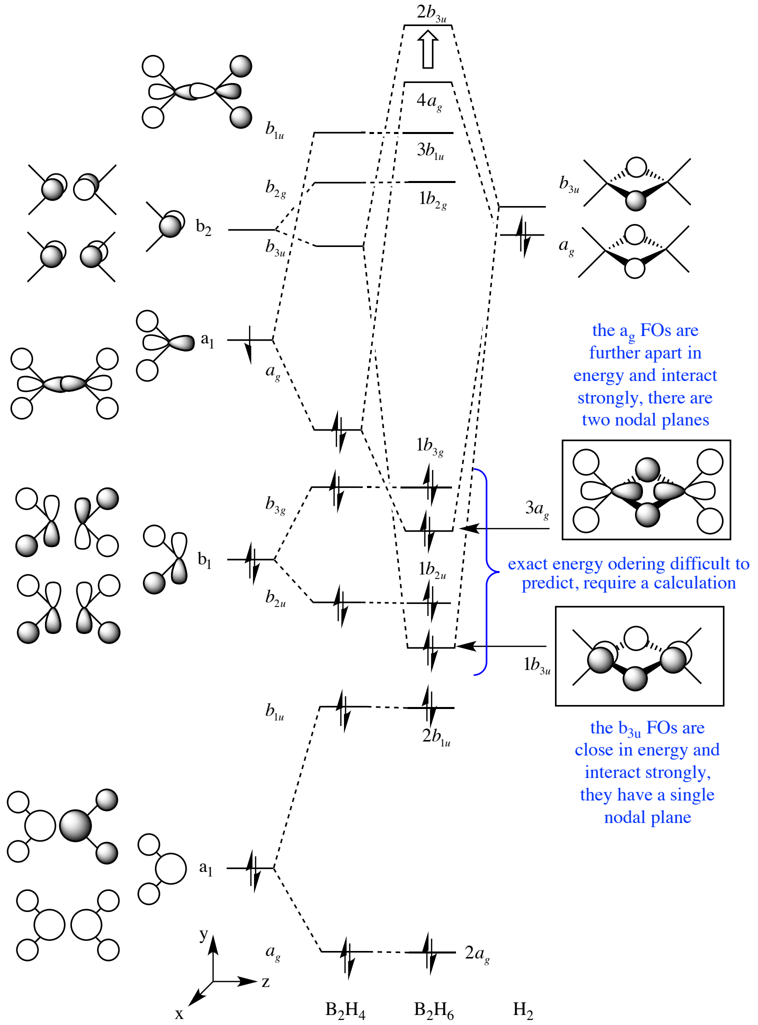
intermediate diagram fragments



final diagram fragments

Figure 7 (a) axial symmetry (b) dAO like symmetry

- the MOs derived for the intermediate MO diagram become the FOs (along with those for H_2) in the new final MO diagram,
- to see how to build the B_2H_6 MO diagram look at the additional materials online for this lecture.



the a_g FOs are further apart in energy and interact strongly, there are two nodal planes

exact energy odering difficult to predict, require a calculation

the b_{3u} FOs are close in energy and interact strongly, they have a single nodal plane

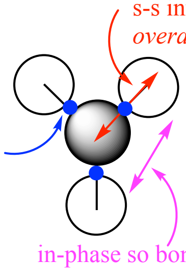
Figure 8 MO diagram for B_2H_6

On the Nature of Bonding and Antibonding MOs

- there is a sliding scale, and a range of interactions needs to be evaluated to determine if a MO is defined as bonding, antibonding or "non-bonding"
- number and type of nodes for the whole molecule
  - a **node** occurs where the phase changes, ie when the wave function goes to zero.
  - nodes at atoms are less important than nodes in the inter-nuclear region
  - for similar MOs the more nodes an orbital has the higher it's energy and the greater the antibonding character
- reminder: phase
  - bonding interactions are in-phase overlap
  - antibonding interactions are out-of-phase overlap
  - in complex diagrams the MOs have both in-phase and out-of-phase interactions
  - there is now a *sliding scale* with completely bonding and completely antibonding as the extremes

important

- for *EACH set of orbital interactions* (symmetry related) *annotate*:
  - phase: bonding or antibonding
  - through bond? a short of long bond?
  - through space? then distance is important
  - type of interaction? s-s vs s-p and sigma vs pi
  - assess each set of interactions on sliding scale weak-medium-strong
- make an overall assessment of the MOs overall character
  - combine all the information!
  - number of nodes and each set of orbital interactions
  - take into account the *number* of each interactions
  - take into account the *relative size* of the FOs
- as an example consider the MO of **Figure 9**



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

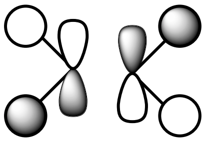
in-phase so bonding
through space, long distance so weak
long range s-s interaction so weak
overall: weak bonding interaction

Figure 9 MO with complex character

- there are no nodes on atoms, and there are nodes in the internuclear region this indicates the MO is highly antibonding
- has out-of-phase antibonding interactions between directly bonded atoms that are close together so strong and overlap is of s-s type the strongest possible, so overall a strong antibonding interaction for this component
- has in-phase bonding interactions which are through space and between *distant* H-atoms, overlap is also of s-s type, s-s becomes weak very rapidly so overall a weak bonding interaction for this component
- overall there is the same number of each type of interaction
- the the MOs overall assessment is for a strongly "antibonding" due to strong antibonding nodal character, strong antibonding through bond interactions, with only a weak through-space bonding component.

In-Class Activity P2

- draw and annotate a diagram evaluating the bonding / antibonding interactions of this MO:



LCAO for complex MOs

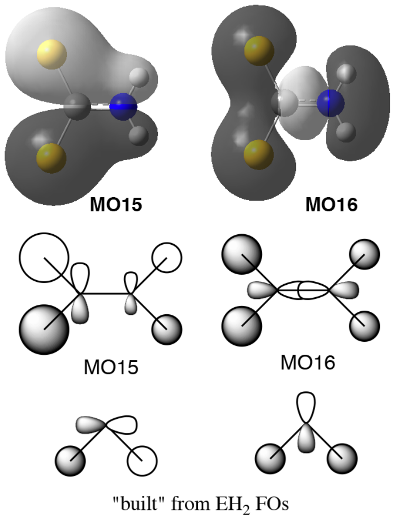


Figure 10 Computed MOs 15 and 16, for CS_2=NR_2 and their LCAO analogues

- in research we compute the structure (optimise) a molecule (carry out a frequency analysis to confirm it is a minima) and then study the MOs.
- to understand the bonding more complex MOs need to be decomposed into their fragment building blocks (LCAOs) and analysed
- very small contributions are ignored when working out LCAOs
- **Figure 10** shows some example orbitals from the dithiocarbamate ligand SC_2=NR_2
- we can relate the orbital components to fragment orbitals you already know, in this case to those for the EH_2
- do pay attention to the **relative size** of the AO components!
- **Figure 11** shows some more of the real MOs for SC_2=NR_2

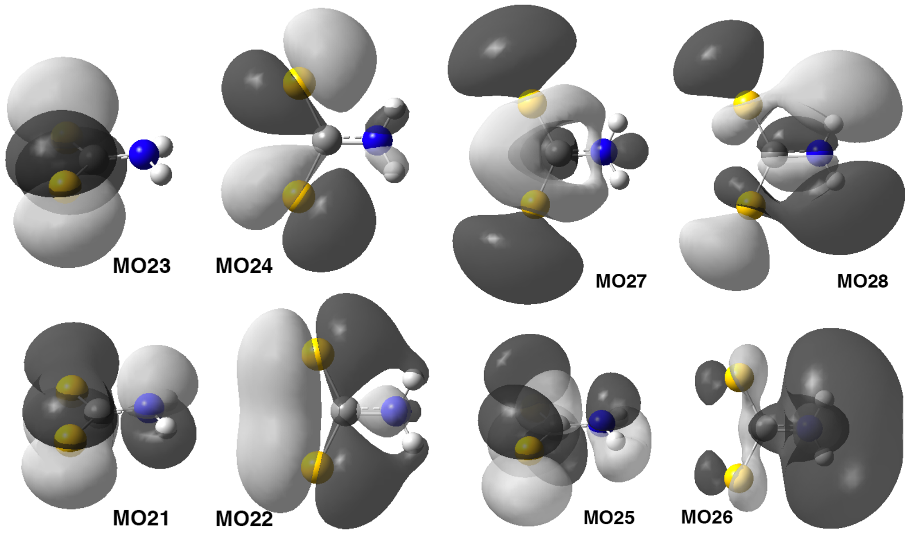


Figure 11 Other MOs including the HOMO 24 and LUMO 25

In-Class Activity P3

- draw the LCAO for MO24 and MO25

In-Class Activity P4

- draw LCAOs for the computed MOs of BrF_3 below, on your diagram annotate features important for evaluating the MO bonding character

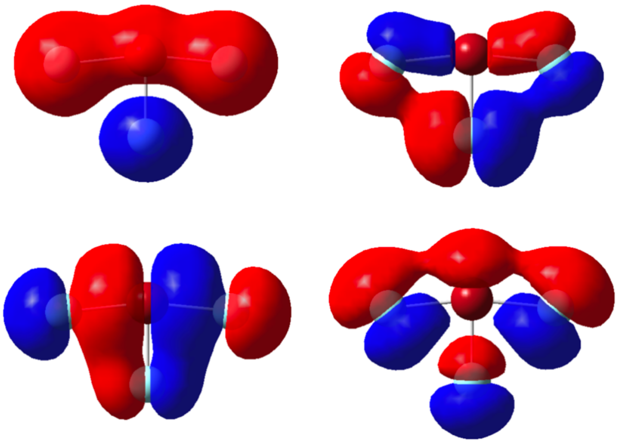


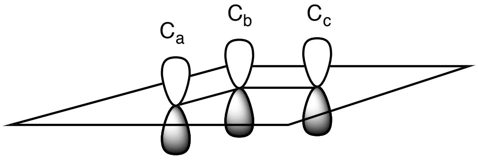
Figure 12 Selected computed MOs of BrF_3

Key Points

- be able to discuss employing equations, diagrams and examples $\Delta\varepsilon$, S_{ab} and H_{ab}, be able to employ this knowledge in forming MO diagrams
- be able to make a connection with quantum mechanics , 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, be able to annotate a diagram of the MO
- be able to represent complicated computed MOs in terms of LCAOs

Self-Study Problems / Test Preparation

- **Q1** QM related questions
  - assuming $\varepsilon_a \neq \varepsilon_b$ and $S_{ab}=0$, what happens to the MO energy levels as $\Delta\varepsilon$ gets larger?
  - when is S_{ab} likely to be small?
  - show that $c=1/\sqrt{2}$ when $S_{ab}=0$,
- **Q2** (*advanced for experts, not examined*) First, solve the secular determinant for 3 overlapping p_z orbitals on a 3-atom chain (energies and wavefunctions). Draw the relevant MOs based on your mathematical equations. Then, draw a MO diagram (using the processes described in this course) using two p_z AOs as one fragment and a single p_z AO as the other fragment. Finally, check your answers by computing the MOs of the allene anion $(C_3H_5)^-$. Compare the maths, MO theory and computational results.



$$\begin{vmatrix} H_{aa}-\varepsilon & H_{ab} & 0 \\ H_{ba} & H_{bb}-\varepsilon & H_{bc} \\ 0 & H_{cb} & H_{cc}-\varepsilon \end{vmatrix} = 0$$

Figure 13: Three atom conjugated chain Hückel problem

- **Q3** Draw LCAOs for the computed MOs of planar NO_3F shown below. On your diagrams annotate features important for evaluating the orbital bonding character.

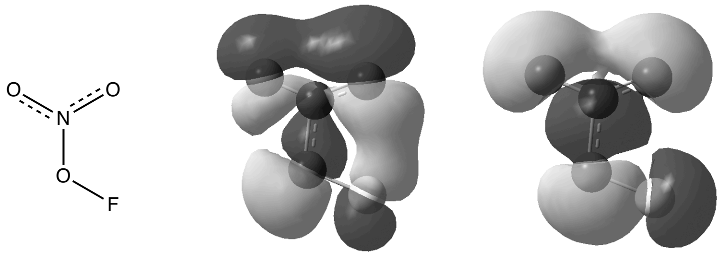


Figure 14: MOs from a calculation of NO_3F

- **Q4** Construct and annotate a valence MO diagram for $[H_2CN]^-$. Use your diagram to explain why the neutral radical is more stable than the anion