L4 Advanced Molecular Orbital Diagrams

More Complex Fragments

- Molecular orbital diagrams take two fragments and combine them to form a molecule. So far, we have examined diatomics with AO fragments and \( \text{EH}_2 \) with an atomic fragment and an \( \text{H}_2 \) fragment.
- Many molecular orbital diagrams are not made up from atomic orbitals, but from fragment orbitals.
- Fragments can contain symmetry related atoms (i.e., 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 MO are well known = molecular fragments (\( \text{H}_2\text{E} \) is a well known fragment)
- Example 1, \( \text{CH}_2\text{O} \), Figure 1:
  o Fragment (a) is preferable because it includes a single atom for which the orbitals are particularly easy to determine, and because the \( \text{H}_2\text{C} \) fragment is well known, and has the same symmetry as the molecule.

![Figure 1 Fragments CH\(_2\text{O}\)](image)

- Example 2, \( \text{BH}_3 \), Figure 2:
  o The best fragment pattern is \( \text{H}_3 \) and a central B atom because \( \text{H}_3 \) is well known and the three H atoms map onto each other under the molecular point group.

![Figure 2 Fragments BH\(_3\)](image)
In-Class Activity

• determine the symmetry fragments for $C_2H_4$

• determine the molecular fragments for $C_2H_4$

• which is the better one to use and why?

Orbital Symmetry

• the symmetry of MOs or fragment orbitals can be determined by looking at the phase-pattern.

• orbitals that have the same phase distribution as the $x$, $y$ and $z$ axes have the same symmetry as these axes.
  o for example the orbital in Figure 4 comes from a $D_{2h}$ molecule ($C_2H_4$), it has a phase distribution like the $z$-axis and hence this MO has $b_{1u}$ symmetry

• A new short-cut
  o To the right of the character table are given the Cartesian binary functions $x^2$, $y^2$, $z^2$, $xy$, $xz$, and $yz$, these are similar to the functions of the dAOs.
  o The symmetry of a dAO can be identified from the symmetry of the corresponding Cartesian function.
  o The $dx^2-y^2$ orbital has the symmetry of the $(x^2, y^2)$ pair, or sometimes the Cartesian function $x^2-y^2$ is explicitly given
  o for example the symmetry of the MO shown in Figure 5 from a $D_{2h}$ molecule ($C_2H_4$) is like the $dxz$ AO and hence has $b_{2g}$ symmetry

• the symmetry of any remaining MOs has to be worked out the long way (ie with a representation table (Lecture 1))
  o for example the symmetry of the MO shown in Figure 5 from a $D_{2h}$ molecule ($C_2H_4$) has to be worked out from a representation table

$$
\begin{array}{ccc|ccc}
D_{2h} & E & C_2(z) & C_2(y) & C_2(x) & i & \sigma(xy) & \sigma(xz) & \sigma(yz) \\
\hline
\Gamma & 1 & 1 & -1 & -1 & -1 & 1 & 1 & 1 \\
\end{array}
$$

Figure 3 Fragments $C_2H_4$

Figure 4 Using axial symmetry

Figure 5 Using dAO like symmetry

Figure 6 Using the representation table
In-Class Activity
• take the socrative quiz and determine the symmetry of these MOs identifying appropriate "short-cut". These are MOs from C₂H₄ which belongs to the D₂h point group. Assume the center of the axis system defined sits on the center of inversion for the molecule.

![Figure 7 Determining orbital symmetry via short-cuts](image)

On the Nature of Bonding and Antibonding MOs
• phase
  o bonding interactions have the SAME or in-phase overlap
  o antibonding interactions have OPPOSITE phase or out-of-phase overlap
  o in complex diagrams the MOs have both in-phase and out-of-phase interactions
• nodes
  o a node occurs where the phase changes, ie when the wave function goes to zero.
  o nodes at atoms are less important than nodes in the inter-nuclear region
  o for similar MOs the more nodes an orbital has the higher it’s energy and the greater the antibonding character
• there is a sliding scale, and the dominant interaction determines if the MO is defined as bonding, antibonding or "non-bonding"
  o closer interactions are stronger and dominate over distant interactions which are weaker because S_ab is very distant dependent
• consider the MO of Figure 8 it has in-phase bonding interactions between distant hydrogen atoms, and out-of-phase antibonding interactions between connected H and E sAOs, thus this orbital is more antibonding than bonding, and hence this MO is "antibonding" overall

In-Class Activity
• draw the MO 1 from Figure 7 and annotate your diagram identifying the bonding / antibonding interactions
• what is the expected order of relative energies (deepest/most bonding first) for the MOs given in Figure 7?
LCAO for complex MOs

- 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.

- **Figure 10** shows the gaussview display for an optimised di alkylthiocarbamate (H2CNS2) anion (a common ligand in TM chemistry)

- which are the **important MOs**?
  - the MOs below MO12 (-5.66 au) are core orbitals and we ignore these
  - the MOs above MO13 (-0.77 au) are valence orbitals and are of interest
  - note the jump in energy from the core to the valence orbitals
  - unoccupied orbitals are diffuse and do not have the same level of validity as occupied orbitals
  - the MOs roughly above the LUMO+4 are not of interest, here MO28 (+0.22 au) and above
  - thus the interesting MOs are the valence bonding MOs those between MO13 and MO28 some of these are represented in the Figures below.

- to understand the bonding in this molecule, these MOs need to be decomposed into their fragment building blocks and analysed
  - first examine the orbitals looking for the AO composition
  - very small contributions are ignored
  - relate the orbital components to **fragment orbitals** you already know, in this case to those for the EH2 or EX2 fragment
  - pay attention to the **relative size** of the AO components

**Figure 11** Computed MOs 15, 16, 18 and 19 and their LCAO analogues
**Complex MO diagrams: B$_2$H$_6$**

- Complex molecules are often built up by combining a series of simpler fragments. To illustrate this we are going to form the MO diagram for B$_2$H$_6$.
- We will form an **intermediate MO diagram** from two BH$_2$ fragments and then add H$_2$ to form the final MO diagram for B$_2$H$_6$, **Figure 12**.
- One could expect B$_2$H$_6$ to be similar to C$_2$H$_6$, however boron is formally electron deficient. Each B atom has only 3 electrons, and cannot form 4 separate bonds. The VSEPR counting for B$_2$H$_6$ is shown below in **Figure 13**.

**Figure 13** VSEPR for C$_2$H$_6$ and B$_2$H$_6$

- To explain the deficiency of the VSEPR model with respect to B$_2$H$_6$ the idea of 3 centre–2 electron bonds was developed, with the B-H-B bridging bond (or “bent” bond) having 3 atomic centres but sharing only 2 electrons.
- However, MO theory can explain the bonding in B$_2$H$_6$ naturally and easily without making ad-hoc corrections.

**Combining two BH$_2$ fragments**

- The MOs for B$_2$H$_6$ are easily developed using the MO diagram checklist.
- **Determine the molecular shape and identify the point group of the molecule:** Convince yourself (at home) that this molecule has D$_{2h}$ symmetry, **Figure 14**.
- **Define the axial system and find all of the symmetry elements of the point group:** See **Figure 14**.
- **Identify the chemical fragments, and put them along the bottom of the diagram:** We will combine two BH$_2$ fragments to form B$_2$H$_4$ and then add an H$_2$ fragment across the centre.
• determine the energy levels and symmetry labels of the fragment orbitals

assess interactions for the orbitals which overlap when the fragments are brought together

• normally only fragment orbitals up to the LUMO+1 are included in the MO diagram, to work this out you need to know the configuration
  o the B atoms will contribute 6e and the 4H atoms 4e, so we fill the diagram with 10e.
• FIRST work out the MOs then analyse to work out the splitting energy
• there are two considerations when determining the splitting energy:
  o interactions between degenerate fragments are large.
  o but the BH₂ fragments are not directly bonded and are far apart in space, thus reducing interactions
  o note that σ, interactions are stronger than σp interactions, which are stronger than π interactions
  o however the directed σp interactions will also be strong
  o the exact energy ordering is difficult to predict without explicit calculation
• next we need to determine the symmetry of the MOs in Figure 15, add the labels into the boxes provided
  o label symmetry of the totally symmetric MO
  o label the symmetry of any orbitals with the same phase pattern as the x, y and z axes.
  o label the symmetry of any orbitals with the same phase pattern as a dAO.
  o there remains a single orbital with an unknown symmetry, and this has to be worked out the long way, Figure 16 what is the symmetry label of this MO?

Figure 15 Fragment orbitals for for B₂H₆

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>D_{2h}</td>
<td>E</td>
<td>C₂(z)</td>
<td>C₂(y) C₂(x)</td>
</tr>
<tr>
<td></td>
<td>i</td>
<td>σ(xy)</td>
<td>σ(xz)</td>
</tr>
</tbody>
</table>

Γ

\{  \begin{array}{cccccccc}
1 & 1 & -1 & -1 & -1 & -1 & 1 & 1 \\
\end{array} \}

Figure 16 Character table for fragment orbital
Adding the \( \text{H}_2 \) fragments

- We now combine \( \text{H}_2 \) with \( \text{B}_2\text{H}_4 \). The MOs just derived now form the FOs for the new MO diagram.
  - the \( \text{H}_2 \) fragment (Figure 17) has a bonding component that is totally symmetric (\( a_g \)) and an antibonding component has the same symmetry as the x-axis (\( b_{3u} \))
  - the \( \text{H}_2 \) fragment orbitals are not directly bonded, so will not exhibit a large splitting, they are sAOs but are neither strongly bonding or antibonding and so will lie near the non-bonding region of the \( \text{B}_2\text{H}_4 \) manifold of fragment orbitals, Figure 18

- combine fragment orbitals of the same symmetry, estimate the splitting energy and draw in the MO energy levels and MOs
  - the full MO diagram is shown in Figure 18
  - it will be sufficient for you to obtain the correct LCAO and a rough estimate of energy ordering based on the relative bonding antibonding character of the orbitals. Ordering that has been well explained with suitable arguments will be accepted in the exam!
  - calculations are required to obtain accurate energy ordering of the MOs,

**IMPORTANT**

![Figure 17 Fragment MOs for \( \text{H}_2 \)](image1)

![Figure 18 MO diagram for \( \text{B}_2\text{H}_6 \)](image2)
• determine the electronic configuration
  o the two boron atoms each contribute 3 valence electrons (2s^22p^1) while
    the six hydrogen atoms contribute 1e each giving a total of 6+6=12e.

• identify if any MO mixing occurs, determine the mixed orbitals and redraw
  the MO diagram with shifted energy levels and the mixed MOs
  o no mixing is expected for this molecule
  o the 2a_g is a deep orbital and 3a_g MOs is too far apart in energy
  o the 2b_1u and 3b_1u are also too far apart in energy

• use the MO diagram check-list!
  o ie check the MO diagram, does it have all the required components?

• analysis of the MO diagram
  o this is an area where students have not performed well in the past, just
    drawing the MO diagram is not enough!
  o four of the MOs, 2a_g, 2b_1u, 1b_2u and 1b_3g are "non-bonding" with respect
    to the H_2 fragment. The 2a_g B_2H_4 fragment orbital lies too deep in energy
    to interact, and the 2b_1u, 1b_2u and 1b_3g fragment orbitals are of the wrong
    symmetry to interact with the H_2 fragment orbitals. These MOs all
    describe bonding within each of the terminal BH_2 units.
  o two of the MOs, the 1b_3u and 3a_g, primarily describe bonding in the
    bridging region and have strong interactions between the B atoms and the
    bridging H_2 fragment
  o the next 1b_2g MO is unoccupied and "non-bonding" with respect to the H_2
    fragment. It is antibonding between the boron atoms, but these are not
    particularly close and the antibonding nature of this MO is small. Thus
    the LUMO is relatively low in energy and if two electrons were added
    because of its non-bonding character the molecule would not be strongly
    destabilised. Thus we expect that B_2H_6^2- to be relatively easily formed,
    and once formed will be stable, which is the case.
  o in the MO picture of bonding in B_2H_6, there has been no need to treat
    B_2H_6 in any special way, no special bonding modes such as 3 center 2
    electron bonds have need to be invoked.

• the computed orbitals for HOMO and three lower energy orbitals are shown
  in Figure 19

![Figure 19](image)

Figure 19 the (a) HOMO b_3g, (b)HOMO-1 3a_g (c)HOMO-2 b_2u and (d)HOMO-3 b_3u
Special Comment
- Some text books can differ in the ordering of the energy levels for $\text{B}_2\text{H}_6$!
- Some text books simplify the interactions for $\text{B}_2\text{H}_6$ by showing a modified orbital diagram, in which all the orbitals that don't interact with the H$_2$ fragment are grouped at lower energy.
- Other text books may also show a larger MO energy splitting for the 3a$_g$ and 4a$_g$ orbitals, thus putting the 3a$_g$ MO below the 1b$_{3u}$ MO.
- These are all equally valid approximations if starting from a qualitative MO approach.
- Often for complex molecules we cannot tell the exact ordering of the MOs using qualitative MO theory alone. However, once we have carried out a calculation we have well defined energy ordering and we can understand how the bonding and antibonding interactions arise.

Key Points
- Be able to differentiate between symmetry and molecular fragments and be able to choose the fragments which make generating a MO diagram easier.
- Be able to use information from the character tables to quickly determine the symmetry of MOs, for example using the phase of the axes and the dAOs.
- Be able to explain the bonding/antibonding qualities of a set of MOs, and annotate a diagram showing the key characteristics / important interactions.
- Be able to present (complicated) computed MOs in terms of a LCAOs.
- Be able to discuss the bonding in $\text{B}_2\text{H}_6$ with respect to the VSEPR theory, delocalisation, and MO theory. Be able to justify the stability of $\text{B}_2\text{H}_6^{2-}$.
- Be able to form a MO diagram for molecules with the general formula $\text{A}_2\text{H}_2$, $\text{A}_2\text{H}_4$, $\text{A}_2\text{H}_6$ and analyse it for information relating to the structure and chemistry of the molecule under consideration.

Self-Study Problems / Exam Preparation
- Construct and annotate a valence MO diagram for $\text{H}_2\text{CN}^-$. Use your diagram to explain why the neutral radical is more stable than the anion.
- Optimise $\text{H}_2\text{CN}^-$, carry out a frequency analysis to confirm you have a minima, compute the MOs and generate LCAOs diagrams for each computed MO, compare these to your predicted MOs.
- Construct and **annotate** a valence MO diagram for $\text{I}_3^-$ ($D_{\infty h}$ point group). Use as fragments the two terminal I atoms (I—●—I) and a central I atom (●—I—●), assume that the MOs do not undergo mixing (old exam question)
  - What are the other possible fragments? Why are the suggested fragments the best fragments to use?
  - With reference to your MO diagram explain if $\text{I}_3^+$ is linear or bent and why
- Compute the MOs for $\text{I}_3^-$ and generate LCAOs diagrams for each computed MO, compare these to your predicted MOs.