Molecular Orbitals in Inorganic Chemistry

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Outline
- choosing fragments
- orbital symmetry (again!)
- bonding and antibonding character of orbitals
- complex MOs -> decompose into LCAOs
- a complex MO diagram: $B_2H_6$

Complex Fragments

MO diagrams combine two fragments

Symmetry Fragments
- atoms that transform onto each other under operations of the point group
- "equivalent atoms" in terms of NMR

Molecular Fragments
- small molecules for which the MOs are well known
  - like $AH_2$ or linear $AB$ or $AH_3$

Example:

CH$_2$O
formaldehyde
molecular fragments $CH_2$ and $O$
symmetry fragments $H_2$ and $CO$
use molecular fragments as there is a single atom

preferred

Fig. 1

CH$_2$ fragment like $H_2O$ will have the same MOs
H's map onto each other under $C_2$
**Example:**

BH$_3$
- boron trihydride
- molecular fragments H$_2$ and BH
- symmetry fragments H$_2$ and B
- use the symmetry fragments as there is a single atom

![Diagram of BH$_3$ with symmetry fragments and labels.]

- H$_2$ and BH fragments will have the same MOs as diatomics
- H's map onto each other under C$_2$

**In-Class Activity**

C$_2$H$_4$
- ethane
- determine the symmetry fragments
- determine the molecular fragments
- which is the better one to use and why?

![Diagram of C$_2$H$_4$ with symmetry and molecular fragments.]

**Orbital Symmetry**

- Short-cuts
  - look at the phase pattern!
  - orbitals with the same phase pattern as an axis have the same symmetry label as the axis

![Diagram showing D$_{2h}$ symmetry and orbitals.]

- same symmetry as the z-axis

**Orbital Symmetry**

- Short-cuts
  - look at the phase pattern!
  - orbitals with the same phase pattern as a dAO have the same symmetry as the corresponding cartesian function

![Diagram showing 2p$_z$ orbitals and symmetry labels.]

- same symmetry as the dxz AO
Orbital Symmetry

If there are no short-cuts possible
=> use a representation table

\[
\begin{array}{ccccccc}
D_{2h} & E & C_2(z) & C_2(y) & C_2(x) & i & \sigma(xy) & \sigma(xz) & \sigma(yz) \\
\Gamma & \{ \text{fig. 4} \} & 1 & 1 & -1 & -1 & -1 & 1 & 1 \end{array}
\]

Bonding vs Anti-bonding

**Bonding**
- bonding => in-phase overlap
- anti-bonding => out-of-phase overlap

**In-Class Activity**

test yourself!  
socrative quiz!

Fig. 6

\[
\begin{array}{ccc}
1 & 2 & 3 \\
\text{compare these MOs} & \text{determine the symmetry of these MOs} & \text{socrative quiz!}
\end{array}
\]

These are MOs from \(C_2H_4\) which belongs to the \(D_{2h}\) point group

Assume the centre of the axis system lies on the centre of inversion for the molecule

Nodes
- occur where phase changes
- raise the energy of an orbital, more nodes indicates increasing anti-bonding character
- nodes at atoms are less important
**More Complex MOs**

**Complex MO**
has both bonding and anti-bonding components

**Bonding character is a sliding scale**
- σ (s) interactions are much stronger than π (p) type interactions
  - the closer the orbitals the stronger the interaction
    (bonded vs non-bonded)

**In-Class Activity**

**test yourself!**

[Image of a diagram with MO1 identified, showing bonding and antibonding interactions]

**annotate a diagram of MO1 identifying the bonding/antibonding interactions**

**what is the relative energy ordering of these MOs?**

**HINTS**
- look at ALL of the interactions
- what is the type of interaction (s or p)?
- what is the distance between the interacting orbitals?
- for similar MOs how many nodes are there?

**LCAO for complex MOs**

in research we often work in "reverse"
- optimise a molecule
- confirm the minima (frequency analysis)
- compute the MOs

you will have seen the "MO window" for gaussview

**dithiocarbamate ligands**
- used as ligands for many TM and coinage metal complexes
- used in nanoparticle synthesis

this file is available on my web-site

**which MOs are important?**
- not the deep core orbitals: AO-like
  - “jump” in energy
- not the high energy unoccupied MOs: too diffuse
  - LUMO+4 and above
- yes to valence MOs!
- yes to lower energy unoccupied MOs

this file is available on my web-site
LCAO for complex MOs

decompose the real MOs into LCAO components
examine MO look for AO contributions
very small contributions are ignored
relate to known fragment orbitals
relative size is important

Look at Fig 11 in your notes

LCAO for complex MOs

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Fig. 11

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Fig. 11
Complex MO Diagrams

Complex molecules are built up by combining a series of fragments

1. know the BH₂ fragment

2. combine two BH₂ fragments
   => intermediate MO diagram

3. add H₂ across centre
   => final MO diagram

3 fragments!!
form intermediate MO diagram

Revision: MO checklist

Steps to construct a MO diagram

- determine the molecular shape and identify the point group of the molecule
- define the axial system and find all of the symmetry operations on the molecule
- identify the chemical fragments, and put them along the bottom of the diagram
- determine the energy levels and symmetry labels of the fragment orbitals
- combine fragment orbitals of the same symmetry, estimate the splitting energy and draw in the MO energy levels and MOs (in pencil)
- determine the number of electrons in each fragment and hence the central MO region, add them to the diagram
- identify if any MO mixing occurs, determine the mixed orbitals and redraw the MO diagram with shifted energy levels and the mixed MOs
- use this checklist!
- analyse the MO diagram

Diborane

We could expect the bonding in B₂H₆ to be similar to that of ethane

VSEPR theory does not work!
- make an ad-hoc correction
  - 3 center two electron “bent” bonds

Molecular Orbital Theory
- MOs are easily developed
- no special corrections required
- stability and bonding of diborane explained

Setting Up

determine molecular shape

Identify the point group of the molecule: D₂h
- convince yourself of this for homework

define the axial system

find all of the symmetry elements

3 C₂ axes
3 σ planes
 centre of inversion, i
- convince yourself of this for homework

convince yourself of this for homework
Revision: MO checklist

Steps to construct a MO diagram

1. Determine the molecular shape and identify the point group of the molecule.
2. Define the axial system and find all of the symmetry operations on the molecule.
3. Identify the chemical fragments, and put them along the bottom of the diagram.
4. Determine the energy levels and symmetry labels of the fragment orbitals.
5. Combine fragment orbitals of the same symmetry, estimate the splitting energy and draw in the MO energy levels and MOs (in pencil!).
6. Determine the number of electrons in each fragment and hence the central MO region, add them to the diagram.
7. Identify if any MO mixing occurs, determine the mixed orbitals and redraw the MO diagram with shifted energy levels and the mixed MOs.
8. Use this checklist!
9. Analyse the MO diagram.

Intermediate Diagram

Treat two BH₂ fragments first

- Know orbitals for BH₂
- Combine these two in intermediate diagram
- Include orbitals up to LUMO+1
- Requires electronic configuration of fragment
- B=3 valence e and 2H=2 valence e
- Fragment =5e therefore keep up to b₂ orbital

Form B₂H₄ Fragment

- Combine fragment orbitals of the same symmetry
- FIRST work out the MOs
- THEN the splitting energy:
  - Degenerate orbitals have a large interaction
  - But BH₂ units are NOT directly bonded and hence have a weaker interaction
  - Still moderated by overlap strength: s vs pₓ vs pᵧ
- Make an educated guess that can be justified
- Exact ordering will require computation

Fig. 16
Symmetry Labels?

totally bonding MO

which symmetry label is associated with each of the axes?

x-axis = $b_{3u}$
y-axis = $b_{2u}$
z-axis = $b_{1u}$

see the character table

which MOs have the same phase pattern as dAOs?
Symmetry Labels?
- totally bonding MO
- which symmetry label is associated with each of the axes?
  - x-axis = $b_u$
  - y-axis = $b_u$
  - z-axis = $b_u$
- which MOs have the same phase pattern as dAOs?
- final MO: use representation table

Set-Up
- Where will the $H_2$ orbitals lie?
- the H atoms are not directly bonded
  - means small splitting energy;
  - means fragments are almost non-bonding;
  - so they will lie near non-bonding orbitals of $B_2H_4$ fragment

MO Diagram
- Combine orbitals of the same symmetry
  - $a_g$
  - lowest $B_2H_4$ $a_g$ orbital is too deep and will not interact
  - the energy levels are not very close, but overlap is good
  - stabilisation is medium

Fragments:
- use the molecular fragments because it is easier to work out the interactions of degenerate fragments
  - two $BH_2$ fragments
  - we already know MOs for $AH_2$ from $H_2O$
  - add $H_2$ across
  - MOs for $H_2$ are very simple!
The MO Diagram

Combine orbitals of the same symmetry

$\text{b}_{3u}$
- There is only one $\text{b}_{3u}$ orbital on $\text{B}_{2}\text{H}_4$ fragment.
- The energy levels are almost degenerate, stabilisation is large.

The MO Diagram

Configuration

10e from $\text{B}_{2}\text{H}_4$ fragment and 2e from $\text{H}_2 = 12e$

Only MOs of the same symmetry mix

Must also be close in energy, greatest between occupied and unoccupied orbitals.

$a_g$ and $b_{1u}$?

- $b_{1u}$ too far apart in energy.
- $a_g$ both occupied.

No mixing!

Revision: MO checklist

Steps to construct a MO diagram

Determine the molecular shape and identify the point group of the molecule.

Define the axial system and find all symmetries of the molecule.

Identify the chemical fragments, and put them along the bottom of the diagram.

Determine the energy levels and labels of the fragment orbitals.

Combine fragment orbitals of the same symmetry, estimate the splitting energy and draw in the MO energy levels and MOs (in pencil!)

Determine the number of electrons in each fragment and hence the central MO region, add them to the diagram.

Identify any MO mixing occurs, determine the mixed orbitals and redraw the MO diagram with shifted energy levels and the mixed MOs.

Use this checklist!

Analyze the MO diagram.
Analysis

4 of the occupied MOs are non-bonding with respect to the bridging H atoms
2 of the occupied MOs describe bonding with the bridging H atoms natural description which doesn't require us to invoke "add-hoc" corrections to a theory
LUMO is essentially non-bonding between BH units (and H2)
low energy for a LUMO can accept electrons without destabilising the molecule
B2H62- is stable!
**Key Points**

- 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 quickly determine the symmetry of MOs using character tables and "short-cuts".
- Be able to explain the bonding/antibonding qualities of a set of MOs and annotate a diagram showing the key characteristics.
- Be able to represent complicated computed MOs in terms of LCAOs.
- Be able to discuss the bonding in $\text{B}_2\text{H}_6$ with respect to 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 $\text{A}_2\text{H}_2$, $\text{A}_2\text{H}_4$, $\text{A}_2\text{H}_6$ and analyse the MO diagram for information relating to structure and bonding.

**In-Class Activity**

Draw the LCAO for MO14, M24 and MO25.

**Finally**

See my web-site

Notes AND slides

Link to Panopto when it becomes available

Optional background support for beginners

Optional material to take you a little further

Links to interesting people and web-sites

Links to relevant research papers on MOs

Model answers!!

http://www.huntresearchgroup.org.uk/