Molecular Orbitals in Inorganic Chemistry

Dr. P. Hunt
p.hunt@imperial.ac.uk
Rm 110F (MSRH)
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 AH₂ or linear AB or AH₃
Example:

**CH₂O**
- formaldehyde
- molecular fragments CH₂ and O
- symmetry fragments H₂ and CO
- use molecular fragments as there is a single atom

CH₂ fragment like H₂O will have the same MOs

H’s map onto each other under C₂

Fig. 1
**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

![Diagram of BH$_3$ molecule showing molecular orbitals](image)

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

C₂H₄

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

Fig. 3
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

Fig. 4
look at the phase pattern!

orbitals with the same phase pattern as a dAO have the same symmetry as the corresponding cartesian function

look at the last column on your character tables: it gives the symmetry label (IR) of the binary cartesian functions
if there are no short-cuts possible
=> use a representation table

<table>
<thead>
<tr>
<th>$D_{2h}$</th>
<th>E</th>
<th>$C_2(z)$</th>
<th>$C_2(y)$</th>
<th>$C_2(x)$</th>
<th>i</th>
<th>$\sigma(xy)$</th>
<th>$\sigma(xz)$</th>
<th>$\sigma(yz)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Fig. 6
test yourself!

socrative quiz

socrative quiz!

WHZ9KBWC3

determine the symmetry of these MOs

- these are MOs from C₂H₄ which belongs to the D₂h point group
- assume the centre of the axis system lies on the centre of inversion for the molecule
Bonding vs Anti-bonding

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

\[ \text{in-phase overlap} \]
\[ \text{out-of-phase overlap} \]
Bonding vs Anti-bonding

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

**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 where phase changes in the internuclear region)
More Complex MOs

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

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

Important!
This MO has only sAOs so interactions are stronger than $\pi$ or p interactions

![Diagram](image)

- orbitals are close $\Rightarrow$ strong (antibonding) interaction
- orbitals are far apart $\Rightarrow$ weak (bonding) interaction

Fig. 8
In-Class Activity

test yourself!

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

\[ \text{S}_2\text{C}=\text{NR}_2 \]
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

Fig. 11
"built" from EH₂ FOs
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

MO15

combined “b1” MOs from EH$_2$ fragments

"built" from EH$_2$ FOs

larger contribution

MO15
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
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

combined "a_1" MOs from EX_2 and EH_2 fragments

larger contribution

orientation!!
draw what you see, FO does not lie along the bonds
complex molecules are built up by combining a series of fragments

1. know the BH$_2$ fragment

2. combine two BH$_2$ fragments => intermediate MO diagram

3. add H$_2$ across centre => final MO diagram

3 fragments!! form intermediate MO diagram
Diborane

We could expect the bonding in $\text{B}_2\text{H}_6$ 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
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
Setting Up

- **determine molecular shape**
- **identify the point group of the molecule:** $D_{2h}$
  - Convince yourself of this for homework

- **define the axial system**
- **find all of the symmetry elements**
  - 3 $C_2$ axes
  - 3 $\sigma$ planes
  - Centre of inversion, $i$
  - Convince yourself of this for homework

Fig. 15
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
treat two BH$_2$ fragments first

- know orbitals for EH$_2$
- 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 $b_2$ orbital
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
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 pσ vs pπ

make an educated guess that can be justified

exact ordering will require computation

Fig. 16
Symmetry Labels?

totally bonding MO

Fig. 16
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
totally bonding MO

which symmetry label is associated with each of the axes?

- x-axis = b$_3$u
- y-axis = b$_2$u
- z-axis = b$_1$u
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 = \( b_{1u} \)
- 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 = b₃u
- y-axis = b₂u
- z-axis = b₁u

which MOs have the same phase pattern as dAOs?

final MO: use representation table

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>E</th>
<th>C₂(z)</th>
<th>C₂(y)</th>
<th>C₂(x)</th>
<th>i</th>
<th>σ(xy)</th>
<th>σ(xz)</th>
<th>σ(yz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Γ</td>
<td></td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

b₁u symmetry
use the molecular fragments because it is easier to work out the interactions of degenerate fragments

two BH₂ fragments

we already know MOs for AH₂ from H₂O

add H₂ across

MOs for H₂ are very simple!

Fig. 15
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

---

- Fig. 19
**MO Diagram**

- **Combine orbitals of the same symmetry**

- **b\textsubscript{3u}**
  - there is only one b\textsubscript{3u} orbital on B\textsubscript{2}H\textsubscript{4} fragment
  - the energy levels are almost degenerate, stabilisation is large

- **exact energy ordering difficult to predict, require a calculation**

- **the a\textsubscript{g} FOs are further apart in energy and interact strongly, there are two nodal planes**

- **the b\textsubscript{3u} FOs are close in energy and interact strongly, they have a single nodal plane**

---

**Fig. 19**
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.
**MO Diagram**

**Configuration**
- 10e from B$_2$H$_4$ fragment and 2e from 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!**
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
4 of the occupied MOs are non-bonding with respect to the bridging H atoms
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
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 BH₂ units (and H₂)

low energy for a LUMO

can accept electrons without destabilising the molecule

B₂H₆²⁻ is stable!
Analysis

Qualitative MO diagram

Exact ordering can vary

Fig. 19

Fig. 20
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 $B_2H_6$ with respect to VSEPR theory, delocalisation, and MO theory. Be able to justify the stability of $B_2H_6^{2-}$

- be able to form a MO diagram for $A_2H_2$, $A_2H_4$, $A_2H_6$ and analyse the MO diagram for information relating to structure and bonding
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/

Hunt Research Group

The Hunt Research Group is a theoretical and computational chemistry group which carries out theoretical development and computational modelling.

Our research is focused towards understanding the chemistry and physics associated with solvents and solvation, particularly as this applies to ionic-liquids and deep eutectic solvents.

We study the making and breaking of molecules. This includes catalytic mechanisms (for group II and frustrated Lewis acid-base pairs) and chemical decomposition (for green fuels, bio-fuels and ionic-liquids).

Overarching all of these areas is a specialisation in hydrogen-bonding, acid-base interactions and an expertise in the MO theory of bonding. We have developed the Effective MO Method for interrogating the electronic structure of liquids and study charge partitioning and interactions within molecules.

July 2019

Molecular orbital of the month This is a MO from SnOTf4. OTf is a triflate anion (SO3CF3)− which coordinates to the central tin (Sn) metal through oxygen atoms. SnOTf4 is a novel catalyst for activating methane and thus producing useful molecules like methanol.

Using methane from biomass or natural gas sources as a feedstock to build more complex molecules is a promising area. We also have the advantage of replacing transition metals with less expensive and more abundant main group metals. This new catalyst is unusual in that the ligand has a larger effect on reactivity than the central metal.
In-Class Activity

draw the LCAO for MO14, M24 and MO25

MO 14

MO 24
HOMO

MO 25
LUMO