Molecular Orbitals in Inorganic Chemistry

Prof. P. Hunt
p.hunt@imperial.ac.uk
Rm 110F (MSRH)
Feedback from Lecture 1

- Finding symmetry elements
- Finding point group
- Drawing MO diagram of a diatomic
- MO mixing?

Challenging material

Most people are: confident or can with notes

Dominant by far!
- 3 or more atoms
- Heteronuclear
- MO mixing

Labelling MOs
- Relative E of AOs
- MO diagrams
- MOs for metals

“Dotted” lines
- Numbering MOs
- Orbital overlaps
- Bonding/antibonding

Practice this
- Point groups
- Finding improper rotations
- Visualising symmetry operations

Minimise this!
- “Memorise”

We will cover all of these

Pure metals
- Solids
- Semi-conductors

Not covered

😀

We will cover all of these 😊
Lecture 2 Outline

L2 build a MO diagram to show you the process

- quick revision
- stage 1: basic MO diagram for H₂O
- stage 2: include MO mixing
- real MOs (how good are qualitative diagrams)
- Walsh or correlation diagrams

L3 come back and look closely at the details

3 or more atoms
hetero-nuclear
AO energy
MO mixing
labelling MOs

We will spend the next two lectures focusing on exactly these things!
MO are combinations of AOs

details: Foundation from last year

atomic orbitals
- radial and angular components
- radial: as quantum shell increases
  - inner nodes
  - radius max density increases
- cartoons represent outer portion
- shaded part represents negative part of function
- angular nature represented by the lobes

the “Orbitron”
- link from my website
Setting Up

- determine the shape of the molecule
- find the point group of the molecule: $C_{2v}$
- define the axial system
- find all of the symmetry elements

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>E</th>
<th>$C_2$</th>
<th>$\sigma_v(xz)$</th>
<th>$\sigma'_v(yz)$</th>
<th>$h=4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A$_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>z</td>
</tr>
<tr>
<td>A$_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>B$_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>x</td>
</tr>
<tr>
<td>B$_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>y</td>
</tr>
</tbody>
</table>

Fig. 4

your character tables
map onto each other under the symmetry operations

✧ H atoms map onto each other
✧ O atom maps onto its self
✧ $\text{H}_2$ and O atom are the fragments

use place holders!
map onto each other under the symmetry operations

- H atoms map onto each other
- O atom maps onto itself
- H₂ and O atom are the fragments

use place holders!

fragment orbitals

- H₂ orbitals
- O atom orbitals

reproduce the whole of the molecular structure in the MO

Fig. 6
Set Up MO Diagram

- **vertical axis: Energy**
- Add H 1s reference level

Fig. 6
Set Up MO Diagram

- **Vertical axis:** Energy
- **Position AOs**
  - O more electronegative
  - => so valence orbitals lie below H 1s reference orbital

![Diagram](attachment:image.png)
Set Up MO Diagram

**vertical axis: Energy**

**position AOs**

✧ O more electronegative
  => so valence orbitals lie below H 1s reference orbital

✧ H atoms are further apart than in H$_2$
  => stabilisation and destabilisation are less ie splitting energy is less

more on this next lecture!
How does each orbital transform under the symmetry operations of the group?

✦ orbital is unchanged ⇒ character = 1
✦ a sign change ⇒ character = -1
✦ check against the character table

Totally bonding orbitals are always totally symmetric

✦ which is the first symmetry label listed for all point groups
✦ for $C_{2v}$ this is the $a_1$ irreducible representation

\[ \chi = 1 \]

Short-Cut!
Short Cuts!

Look in the last columns of the character table:
✧ find $T_x$, $T_y$, $T_z$
✧ sometimes also written as just $x$, $y$, $z$
✧ gives you the axis symmetry label

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>E</th>
<th>$C_2$</th>
<th>$\sigma_v(xz)$</th>
<th>$\sigma_v'(yz)$</th>
<th>$h=4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$T_z$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>$T_x$</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$T_y$</td>
</tr>
</tbody>
</table>

Important!

Fig. 7
look for similarities in the phase of orbitals and the cartesian axes

<table>
<thead>
<tr>
<th>\Gamma { \bigcirc }</th>
<th>E</th>
<th>C_2</th>
<th>\sigma_v(xz)</th>
<th>\sigma_v'(yz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\Gamma { \bigcirc }</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>\Gamma { \infty }</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>\Gamma { \leftrightarrow }</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

look for similarity in phase patterns!
look for similarities in the phase of orbitals and the cartesian axes

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>E</th>
<th>$C_2$</th>
<th>$\sigma_v(xz)$</th>
<th>$\sigma_{v}'(yz)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma{\bigcirc}$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma{\bigotimes}$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$\Gamma{\bigtriangleup}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Short-Cut!
Add symmetry labels to MO diagram
Form the MOs

Only fragment orbitals (FOs) of the same symmetry can combine
✦ for water: $a_1$ and $b_1$

FO can only combine ONCE
✦ more than one FO of same symmetry?
✦ then combine the lowest energy two
✦ leave the last one non-bonding (for now!)

Form MOs by
✦ “adding” FOs together “as is”
✦ “adding” FOs with ONE FO phase inverted

Important!

work out MOs first then the splitting

Fig 10
Stage One
MO Diagram

Evaluate splitting
- FOs far apart in energy interact only weakly
- in-phase interactions are bonding
- destabilisation is always larger

more on this next lecture!

THEN MOs on the diagram

Fig 11/12
Evaluate splitting
✧ FOs closer in energy interact more
✧ destabilisation is always larger

THEN MOs on the diagram

more on this next lecture!
Stage One
MO Diagram

Label MOs

✦ number within symmetry label
✦ count the core orbitals only if molecule is small

Fig 11/12
Stage One
MO Diagram

antibonding MO is always destabilised more than the bonding MO is stabilised

a_1 FO left non-bonding in the first stage diagram

FOs are closer in energy and so the interaction between the orbitals is larger for the b_1 MO

1a_1 is the O 1sAO which is not shown because this is a valence MO diagram

Annotate your diagrams!

Important!
do not repeat information
Stage One
MO Diagram

add the electrons!
✦ fill sequentially

antibonding MO is always destabilised more than the bonding MO is stabilised

a₁ FO left non-bonding in the first stage diagram

FOs are closer in energy and so the interaction between the orbitals is larger for the b₁ MO

1a₁ is the O 1sAO which is not shown because this is a valence MO diagram

2 valence e

6 valence e

Fig 11/12
Stage One MO Diagram

add the electrons!

add the missing e to your Fig 12!

antibonding MO is always destabilised more than the bonding MO is stabilised

add the missing e to your Fig 12!

a₁ FO left non-bonding in the first stage diagram

FOs are closer in energy and so the interaction between the orbitals is larger for the b₁ MO

1a₁ is the O 1sAO which is not shown because this is a valence MO diagram

Fig 11/12

add the electrons!

fill sequentially

2 valence e

6 valence e
Stage 2: MO Mixing

**necessary conditions**

✦ ONLY MOs of the same symmetry can mix
✦ to occur mixing MUST stabilise the total energy

**mixing tends to be large when:**

✦ MOs are close in energy
✦ one MO is non-bonding or unoccupied
✦ orbitals are in HOMO-LUMO region

**Important!**
**a₁ MO Mixing**

**mixing orbitals**
- “add” MOs together “as is”
- “add” MOs with ONE MO phase inverted
- inspect to determine which is the bonding mixed MO

\[
\psi_1 = \psi(3a₁) + \psi(4a₁)
\]

Fig 13

Occupied: \(\psi(3a₁)\)
Unoccupied: \(\psi(4a₁)\)
Antibonding due to increased out-of-phase interaction
In-Class Activity

mixing orbitals

✦ “add” MOs together “as is”
✦ “add” MOs with ONE MO phase inverted
✦ inspect to determine which is the bonding mixed MO

form
-ψ(3a_1) + ψ(4a_1)
**In-Class Activity**

**mixing orbitals**

- “add” MOs together “as is”
- “add” MOs with ONE MO phase inverted
- inspect to determine which is the bonding mixed MO

\[ \psi(3a_1) + \psi(4a_1) \]

form

\[ \psi(3a_1) - \psi(4a_1) \]

"non-bonding" or slightly antibonding MO

bonding due to increased in-phase interaction

Fig 14
Mixing

**strong mixing:**

- $4a_1$ MO unoccupied
- $3a_1$ MO non-bonding
- In HOMO/LUMO region
- Close in energy
- Occupied MO is stabilised

Significant mixing drives $3a_1$ MO down in energy and changes the shape of the MO.

Extra lines drawn to show the main mixing interaction.
Final MO Diagram of H$_2$O

- Antibonding MO is always destabilised more than the bonding MO is stabilised.
- The 4a$_1$ lies above the 2b$_1$ MO because there is strong directional antibonding overlap in the 4a$_1$ MO and weaker less directional overlap in the 2b$_1$ MO.
- b$_2$ FO left non-bonding as there is no other FO of this symmetry for it to interact with.
- FOs are closer in energy and so the interaction between the orbitals is larger for the 1b$_1$ than the 2a$_1$ MO.
- Significant mixing drives 3a$_1$ MO down in energy and changes the shape of the MO.
- 1a$_1$ is the O 1s AO which is not shown because this is a valence MO diagram.

Fig 15
“Real” MOs

we have “solved” the Schrödinger equation!!!

computed molecular orbitals

Fig 16
Experimental Evidence

Photoelectron spectrum
- energy required to eject an electron from its orbital

“traditional” theory:
- expect 2 equivalent bonds and 2 equivalent lone pairs for water = 2 lines in photo-electron spectrum

- have 3 lines in photo-electron spectrum which relate to delocalized $1b_1$, $3a_1$ and $1b_2$ MOs

Fig 17

BUT

Fig 5.13 from “Structure and Bonding” by J. Barrett

Fig 18
Delocalisation

- MOs are delocalised
  - not 2 center 2 electron
  - most of MOs extend over ALL atoms in molecule
  - there are no “bonds”

- Bonds represent a build up of the TOTAL electron density

- We keep ideas of hybridisation and 2c-2e bonds because they are USEFUL

(where have the bonds gone???)
MO diagrams are transferable
✦ one diagram is good for many molecules or fragments!
✦ molecules BeH₂ (homework), H₂S
✦ fragments CH₂ (lecture 4), NH₂
✦ we can even treat metal fragments: MH₂

general formula AH₂
✦ A=main group element, M=metal
✦ slight modifications:
✦ different numbers of electrons
✦ slightly different position of the fragment orbitals
Correlation Diagram

Walsh diagram: change one geometric parameter and examine changes in MOs and energies

- normally a bond distance or angle
- link the MOs for two extreme geometries

example: Why is $\text{H}_2\text{O}$ bent?

$$\begin{align*}
\text{C}_2\text{v} & \quad \approx 105^\circ \\
\text{D}_\infty & \quad 180^\circ 
\end{align*}$$

H-O-H angle

start with high symmetry

end with lower symmetry

Prof. A.D Walsh
University of Dundee
from: http://www.dundee.ac.uk/museum/scientists.htm

Fig 21
typically start from the highest symmetry

- I’ve constructed the MO diagram for linear H$_2$O for you (Self-study for you to reproduce)
then examine how MOs change under geometric distortion

Qualitative not Quantitative!
then examine how MOs change under geometric distortion

$2\sigma_g^+ (2a_1)$ stabilised

- BONDED overlap dominates
- directed O & H overlap is stronger in linear structure
- on bending ↓ O-H bonding overlap
- ALSO ↑ H···H through space bonding overlap
- net result small stabilisation

Fig 21
Energy of MOs

then examine how MOs change under geometric distortion

\( 1\sigma_u^+ (1b_1) \) destabilised

✦↓ O-H bonding overlap
✦ALSO ↑ H···H through space antibonding
✦net result destabilisation

Fig 21
Energy of MOs

then examine how MOs change under geometric distortion

\(1\pi_u (1b_2)\) no change

✦ non-bonding orbital
Energy of MOs

then examine how MOs change under geometric distortion

$2\sigma^+_{u}(2b_1)$ stabilised

socrative quiz!

WHZ9KBWC3
then examine how MOs change under geometric distortion

\(2\sigma_u^{-} (2b_1)\) stabilised

- \(\downarrow\) O-H antibonding overlap
  => stabilize
- also \(\uparrow\) H···H through space antibonding
- => destabilize
- shorter distance overlap dominates
- => net result stabilisation
Energy of MOs

then examine how MOs change under geometric distortion

\[ 1\pi_u / 3\sigma_g^+ \text{ or } 3a_1/4a_1 \text{ special} \]

- as planar molecule \( 1\pi_u \) and \( 3\sigma_g^+ \) cannot mix (not same symmetry)
- when molecule distorts they become the same symmetry: mixing occurs
  - \( 1\pi_u \) goes to \( 3a_1 \)
  - \( 3\sigma_g^+ \) goes to \( 4a_1 \)
  - on mixing the \( 1\pi_u \) (\( 3a_1 \)) is stabilised

Important!
Change of Axes

When the symmetry point group changes the axial definition changes!

✦ z-axis reoriented
✦ orbital remains the same
✦ only labels change
✦ then follow with mixing

Fig 22
**Orbital changes**
- AOs move with the atoms
- Form or shape of AOs remains constant
- !! except for MOs which undergo mixing

**Molecular stability**
- Examine how occupied MOs change under geometric distortion
- Look for occupied MOs which show a large change in energy
- These orbitals drive the change in shape

---

**Walsh Diagram**

**Fig 22**

**Self-study questions**
But how does the drop in symmetry start?

- nuclear vibrations provide infinitesimal distortion required for MO mixing
- vibronic coupling = coupling of electronic and nuclear motions
- breakdown of the Born-Oppenheimer approximation!
  ✦ collapse of a VERY fundamental approximation
  ✦ more common than you think!
  ✦ of which Jahn-Teller theorem is a special case
Symmetry & symmetry breaking underlies many theories in physics and chemistry. Noether's Theorem shows that a conservation law can be derived from any continuous symmetry. 

- Invariance with respect to translation gives the law of conservation of linear momentum.
- Invariance with respect to time translation gives the law of conservation of energy.

Serious Stuff!
- General relativity
- Standard model of particle physics
- Existence of Higgs particle
- Heisenberg Uncertainty Principle
- Field theory
- Magnetism
- Superconductivity

Emmy Noether
MO checklist

Steps to construct a MO diagram

✦ determine the molecular shape and identify the point group
✦ define the axial system and all of the symmetry operations
✦ identify the chemical fragments, put them on the bottom of the diagram
✦ determine the energy levels and symmetry labels of the fragment orbitals (use H1s as a reference)
✦ combine fragment orbitals of the same symmetry, determine the MOs and then estimate the splitting energy; 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
✦ annotate your diagram
✦ use the MO diagram to understand the structure, bonding and chemistry of the molecule

Very Important!

Steps we have used today to form a MO diagram
be able to form MO diagrams for molecules with the general formula $\text{AH}_2$ and $\text{AH}_3$ (tutorial) where A= main group element or a metal

be able to explain and illustrate MO mixing

be able to critically evaluate VSEPR theory, localised 2c-2e bonding and the delocalised MO picture of bonding

be able to describe how a PES is formed and be able to relate a spectrum to the MOs, and MO diagram of a molecule

be able to form correlation diagrams and explain why a particular geometry is more stable than another with reference to the stability of the MOs

be able to discuss symmetry breaking and vibronic coupling

be able to describe the process of forming a MO diagram (the MO checklist)
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/