Molecular Orbitals in Inorganic Chemistry

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Rm 110F (MSRH)

Feedback from Lecture 1

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

Challenging material

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

We will cover all of these

most people are: confident or can with notes

pure metals solids semi-conductors
not covered

practice this

Fig. 1

Revision

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

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 focussing on exactly these things!

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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>
</tr>
</thead>
<tbody>
<tr>
<td>A(_1)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A(_2)</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>B(_1)</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>B(_2)</td>
<td>1</td>
<td>-1</td>
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</table>

Fragments

map onto each other under the symmetry operations
H atoms map onto each other
O atom maps onto its self
H\(_2\) and O atom are the fragments
use place holders!

Set Up MO Diagram

vertical axis: Energy
add H 1s reference level
reproduce the whole of the molecular structure in the MO

fragment orbitals
H\(_2\) orbitals
O atom orbitals

Fig. 4

Fig. 5

Fig. 6
Set Up MO Diagram

vertical axis: Energy
position AOs
O more electronegative => so valence orbitals lie below H 1s reference orbital

Fig. 6

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 H₂ =>stabilisation and destabilisation are less ie splitting energy is less
more on this next lecture!

Fig. 6

Fragment Orbital Symmetry

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

Lecture 1
No change under σᵥ

Γ

C₂  E  C₂ σᵥ(xz)  σᵥ(yz)
1  1  1  1

a₁

Short-Cut!
totally bonding orbitals are always totally symmetric
which is the first symmetry label listed for all point groups
for C₂, this is the a₁ irreducible representation

Important!

Short Cuts!

look in the last columns of the character table
find Tᵥ, Tₓ, Tz
sometimes also written as just x, y, z
gives you the axis symmetry label

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

Add symmetry labels to MO diagram

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
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

Stage One
MO Diagram

Evaluate splitting
FOs closer in energy interact more
destabilisation is always larger

more on this next lecture!

THEN MOs on the diagram

Stage One
MO Diagram

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

Stage One
MO Diagram

Annotate your diagrams!
Important!
do not repeat information

2a is the O 1sAO which is not shown because this is a valence MO diagram

FOs are closer in energy and so the interaction between the orbitals is larger for the b\textsubscript{1} MO

antibonding MO is always destabilised more than the bonding MO is stabilised
Stage One
MO Diagram

add the electrons!
fill sequentially

Stage Two: 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!

a_1 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

antibonding due to increased out-of-phase interaction

occupied unoccupied antibonding MO

ψ(3a_1) + ψ(4a_1) = 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

**Fig 14**

form \( \psi_{(3a_1)} + \psi_{(4a_1)} \)

**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

**Fig 14**

Form \( \psi_{(3a_1)} + \psi_{(4a_1)} \)

- Bonding due to increased in-phase interaction
- "Non-bonding" or slightly antibonding MO

**Mixing**

**strong mixing:**
- 4a<br> MO unoccupied
- 3a<br> MO non-bonding
- In HOMO/LUMO region
- Close in energy
- Occupied MO is stabilised

**Fig 15**

Extra lines shown to show the main mixing interaction

**Final MO Diagram of H₂O**

- antibonding MO is always destabilised more than the bonding MO is stabilised
- The 4a<br> lies above the 2b<br> because there is strong directional antibonding interaction in the 4a<br> and weaker less directional overlapping in the 2b<br> MO

**Fig 15**

- Significant mixing drives 3a<br> down in energy and changes the shape of the MO
- The orbitals are closer in energy and such interaction between the orbitals is larger for the 1b<br> than the 2a<br> MO
“Real” MOs

- Computed molecular orbitals
- We have “solved” the Schrödinger equation!!!

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 delocalised 1b\(_1\), 3a\(_1\) and 1b\(_2\) MOs

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

Analysis

- MO diagrams are transferable:
  - One diagram is good for many molecules or fragments!
  - Molecules BeH\(_2\) (homework), H\(_2\)S fragments CH\(_2\) (lecture 4), NH\(_2\)
  - We can even treat metal fragments: MH\(_2\)

- General formula AH\(_2\):
  - A = main group element, M = metal
  - Slight modifications:
    - Different numbers of electrons
    - Slightly different position of the fragment orbitals
Walsh diagram: change one geometric parameter and examine changes in MOs and energies

typically start from the highest symmetry
I've constructed the MO diagram for linear H\textsubscript{2}O for you (Self-study for you to reproduce)

example: Why is H\textsubscript{2}O bent?

start with high symmetry
end with lower symmetry

Qualitative not Quantitative!

(2a\textsubscript{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
then examine how MOs change under geometric distortion

(1b₁) destabilised

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

Fig 21

(2b₁) stabilised

socratic quiz!

WHZ9KBWC3

Fig 21
Energy of MOs

then examine how MOs change under geometric distortion

/ or 3a₁/4a₁ special
as planar molecule 1πₓ and 3σᵣ⁺ cannot mix (not same symmetry)
when molecule distorts they become the same symmetry: mixing occurs
1πₓ goes to 3a₁
3σᵣ⁺ goes to 4a₁
on mixing the 1πₓ (3a₁) is stabilised

Important!

Walsh Diagram

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

Change of Axes

When the symmetry point group changes the axial definition changes!
z-axis reorientated
orbital remains the same
only labels change
then follow with mixing

Symmetry Breaking

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 Breaking

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.

- General relativity
- Standard model of particle physics
- Higgs particle
- Superconductivity
- Magnetism
- Serous Stuff!

Key Points

- Be able to form MO diagrams for molecules with the general formula AH₂ and AH₃ (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!!