Molecular Orbitals in Inorganic Chemistry

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Rm 110F (Chemistry)
Outline

- Correlation diagrams (from last lecture)
- LCAO theory
- Orbital size matters
- Where to put the FO energy levels
- The splitting energy
- Rules for combining FOs
- Origin of the splitting “rules”: making connections with QM
Analysis

MO diagram for H$_2$O
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 H\textsubscript{2}O bent?

![Diagram of H\textsubscript{2}O molecule with bond distances and angles]

C\textsub{2v} \quad \approx 105^\circ \quad \text{start with high symmetry}

H-O-H angle

D\textsub{sh} \quad 180^\circ \quad \text{end with lower symmetry}

From: http://www.dundee.ac.uk/museum/scientists.htm
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)

Fig 21 Walsh Diagram
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

≈105° H-O-H angle H₂O 180°
Energy of MOs

then examine how MOs change under geometric distortion

$\pi_u$ / $\sigma_g^+$ or $3a_1$ / $4a_1$ special

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

Important!
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

Fig 22
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

_self-study questions_

Fig 22
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 & symmetry breaking underlies many theories in physics and chemistry.

Noether’s Theorem

- 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
- Superconductivity
- Magnetism
- Field theory

Heisenberg Uncertainty Principle

Emmy Noether

Key Points

- 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
forming simple MOs

- combine the orbitals of each fragment
- add once “as is”, add once with phase inverted
- draw a “cartoon” and write an equation

\[
\psi_1^{sa} + \psi_1^{sb} = \frac{1}{\sqrt{2}} (\psi_1^{sa} + \psi_1^{sb})
\]

\[
\psi_{\sigma^*} = \frac{1}{\sqrt{2}} (\psi_1^{sa} - \psi_1^{sb})
\]

See slide in your notes from your Chemical Bonding course
LCAOs

- theory: linear combination of atomic orbitals
- so don’t combine AOs on different centers!

\[ \psi_\Gamma = N (c_1 \psi_1 + c_2 \psi_2 + \cdots + c_n \psi_n) = N \sum c_i \psi_i \]

Important!

LCAO
- don't combine components

real MO

often we work backwards!
- from computed MO to understand the bonding
LCAOs

C’s are represented in the size of the AO contributions

$\psi_\Gamma = N(c_1\psi_1 + c_2\psi_2 + \cdots c_n\psi_n) = N \sum c_i\psi_i$

see LiH from your 1st year Molecular Structure course!

Important!

Antibonding MO: higher E FO makes larger contribution

Bonding MO: lower E FO makes larger contribution

Fig. 4
LCAOs

C’s are represented in the size of the AO contributions

more ionic  more covalent

larger energy gap between the FOs
= more ionic the bond
= greater the disparity in contributions
MO diagrams are built by combining fragment orbitals

- fragment orbitals can be simple atomic orbitals
- or they can be more complex fragments (covered later)

where to put atomic fragment orbital energy levels?

- relative electronegativity ordering of first row (expected to know)
- transition metals and main group elements tend to be electropositive
- reference is H 1sAO

<table>
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<tr>
<th></th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
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<td>1.57</td>
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<td>3.04</td>
<td>3.44</td>
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<td>1.31</td>
<td>1.61</td>
<td>1.91</td>
<td>2.19</td>
<td>2.58</td>
<td>2.19</td>
</tr>
</tbody>
</table>

Pauling electronegativity

Important!

valence pAO relative to valence H1sAO

Fig.5
FO Positioning

atomic orbitals s-p gap increases along the periodic table
2s AOs only interact for adjacent atoms
2p AO always interact

Important!

Problematic

last year: some problems
this year: a few examples!

Fig. 6

![Graph showing average orbital ionization energies for 2nd Row Elements]
Orbital Interactions: CN⁻

See the on-line tutorial!

Important!

Fig. 7
Nitrogen is more electronegative than Carbon: N2p lie below C2p
Orbital Interactions: CN$^-$

- N is further along PT than C
- N has larger sp gap
- C has smaller sp gap
- pAO interactions not drawn in because we are focusing on sAOs

Fig. 7
Orbital Interactions: CN^–

- C is next to N on the PT so the 2s AOs interact.

Additional example for CO in your notes.

Self-study document on web-site:
- links to revision from last year
- includes more complex details from this year
- emphasis is on interpretation as well as construction.
In-Class Activity

Where would you put the FOs for the MO diagram of MgCl$_2$?

- Once you have completed the quiz then:
  - Draw the fragments for the MO diagram

  socrative quiz!

  WHZ9KBWC3
How far apart are the MOs placed??

**Splitting energy**
- destabilisation is larger than stabilisation energy

\[ E = \Delta E_s + \Delta E_d \]

![Diagram showing splitting energy](image)
Splitting Energy

Depends on 3 quantities

- **energy difference between FO:**
  \[ \Delta \varepsilon = \varepsilon_i - \varepsilon_j \]

- **orbital coupling:**
  \[ H_{ij} = \langle \psi_i | H | \psi_j \rangle \] (molecule mediated orbital overlap)

- **extent of orbital overlap:**
  \[ S_{ij} = \langle \psi_i | \psi_j \rangle \] (direct orbital overlap)

**Important!**
Go back to the Schrödinger equation

\[ \langle \psi_i | H | \psi_j \rangle = \int \psi_i H \psi_j d\tau \]

- solving gives the energy of MOs

Interaction of orbital(i) with orbital(j) modified by the local environment (H)

"overlap" mediated by the molecule

Direct orbital overlap

Fig.9
Degenerate orbitals have the largest splitting. Sliding the scale as FO shift apart, the splitting energy is reduced. Eventually, a point is reached at which there is no interaction.

- Form ionic compound.
Orbital Overlap

$S_{ab}$ overlap depends on:
- Relative location
- Orientation
- Diffusivity

Sigma orbitals overlap better than pi orbitals:
- $s_{\sigma} > p_{\sigma} > sp_{\sigma} > p_{\pi}$

Orbitals orientated toward each other overlap better.

Diffuse orbitals have poor overlap.

Better overlap:
- Larger overlap, smaller splitting.
- Reduced overlap $S << 1$

Negative and positive overlap cancel out $S = 0$.

Strong overlap $\Delta E$ decreases.

For more information, see Fig. 11.
Making Connections with QM

- link qualitative arguments to mathematics
- solved in your Chemical Bonding course
- solve Schrödinger equation

\[ E \psi = H \psi \]

Expand our MO in terms of the FOs:

\[
\psi = \sum c_n \phi_n \\
\psi = c_a \phi_a \pm c_b \phi_b \\
\psi = c(\phi_a \pm \phi_b)
\]

\[ H = T_n + T_e + V_{ee} + V_{en} + V_{nn} \]

Course cross-over material: I expect you to be able to carry out the derivations!

See slides in your notes from your Chemical Bonding course.
Reminder from QM:

determine the expression for $c$

\[ \int \psi^* \psi \, d\tau = \langle \psi | \psi \rangle = 1 \]

\[ \psi = c (\phi_a \pm \phi_b) \]

\[ \langle \psi | \psi \rangle = \langle c (\phi_a \pm \phi_b) | c (\phi_a \pm \phi_b) \rangle \]

\[ \langle \psi | \psi \rangle = c^2 \left[ \frac{\langle \phi_a | \phi_a \rangle + \langle \phi_b | \phi_b \rangle}{=1} \pm 2 \frac{\langle \phi_a | \phi_b \rangle}{=S_{ab}} \right] \]

\[ 1 = \langle \psi | \psi \rangle = c^2 \cdot 2 \left( 1 \pm S_{ab} \right) \]

\[ c^2 = \frac{1}{2 \left( 1 \pm S_{ab} \right)} \]

\[ \therefore c = \frac{1}{\sqrt{2 \left( 1 \pm S_{ab} \right)}} \]

\[ \psi = \frac{1}{\sqrt{2 \left( 1 \pm S_{ab} \right)}} (\phi_a \pm \phi_b) \]

AOs are normalised as well!

important for later
Reminder from QM:

- **rearrange the Schrödinger equation**

\[ H\psi = E\psi \]
\[ \psi^* H\psi = \psi^* E\psi \]
\[ \int \psi^* H \psi d\tau = E \int \psi^* \psi d\tau \]

because \( E \) is a number

\[ \int \psi^* H \psi d\tau = \langle \psi | H | \psi \rangle = E \]

require \[ \int \psi^* \psi d\tau = \langle \psi | \psi \rangle = 1 \]

\[ E = \langle \psi | H | \psi \rangle \]  

cannot divide by wavefunction!  
in QM we premultiply and integrate
Making Connections with QM

ready to solve!

\[ E = \langle \psi | H | \psi \rangle \quad \text{and} \quad \psi = c (\phi_a \pm \phi_b) \]

two important pieces of information
Making Connections with QM

ready to solve!

\[ E = \langle \psi | H | \psi \rangle \quad \text{and} \quad \psi = c \left( \phi_a \pm \phi_b \right) \]

\[ \psi_+ = c_+ \left( \phi_a + \phi_b \right) \]

\[ \langle \psi | H | \psi \rangle = c_+^2 \langle \phi_a + \phi_b | H | \phi_a + \phi_b \rangle \]

\[ \langle \psi | H | \psi \rangle = c_+^2 \left[ \langle \phi_a | H | \phi_a \rangle + \langle \phi_a | H | \phi_b \rangle + \langle \phi_b | H | \phi_a \rangle + \langle \phi_b | H | \phi_b \rangle \right] \]

\[ \langle \phi_a | H | \phi_a \rangle = H_{aa} \quad \text{assume} \quad H_{ab} = H_{ba} \]

\[ \langle \psi | H | \psi \rangle = c_+^2 \left[ H_{aa} + 2H_{ab} + H_{bb} \right] \]

\[ E_+ = \langle \psi | H | \psi \rangle \]

\[ E_+ = \frac{H_{aa} + 2H_{ab} + H_{bb}}{2\left(1 + S_{ab}\right)} \quad E_- = \frac{H_{aa} - 2H_{ab} + H_{bb}}{2\left(1 - S_{ab}\right)} \]

put in wavefunction
Making Connections with QM

ready to solve!

\[ E = \langle \psi | H | \psi \rangle \quad \text{and} \quad \psi = c(\phi_a \pm \phi_b) \]

\[ \psi_+ = c_+ (\phi_a + \phi_b) \]

\[ \langle \psi | H | \psi \rangle = c_+^2 \langle \phi_a + \phi_b | H | \phi_a + \phi_b \rangle \]

\[ \langle \psi | H | \psi \rangle = c_+^2 \left[ \langle \phi_a | H | \phi_a \rangle + \langle \phi_a | H | \phi_b \rangle + \langle \phi_b | H | \phi_a \rangle + \langle \phi_b | H | \phi_b \rangle \right] \]

\[ \langle \phi_a | H | \phi_a \rangle = H_{aa} \quad \text{assume} \quad H_{ab} = H_{ba} \]

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Making Connections with QM

ready to solve!

\[ E = \langle \psi | H | \psi \rangle \quad \text{and} \quad \psi = c ( \phi_a \pm \phi_b ) \]

\[ \psi_+ = c_+ ( \phi_a + \phi_b ) \]

\[ \langle \psi | H | \psi \rangle = c_+^2 \langle \phi_a + \phi_b | H | \phi_a + \phi_b \rangle \]

\[ \langle \psi | H | \psi \rangle = c_+^2 [ \langle \phi_a | H | \phi_a \rangle + \langle \phi_a | H | \phi_b \rangle + \langle \phi_b | H | \phi_a \rangle + \langle \phi_b | H | \phi_b \rangle ] \]

\[ \langle \phi_a | H | \phi_a \rangle = H_{aa} \quad \text{assume} \quad H_{ab} = H_{ba} \]

\[ \langle \psi | H | \psi \rangle = c_+^2 [ H_{aa} + 2H_{ab} + H_{bb} ] \]

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Making Connections with QM

ready to solve!

\[ E = \langle \psi | H | \psi \rangle \quad \text{and} \quad \psi = c (\phi_a \pm \phi_b) \]

\[ \psi_+ = c_+ (\phi_a + \phi_b) \]

\[ \langle \psi | H | \psi \rangle = c_+^2 \langle \phi_a + \phi_b | H | \phi_a + \phi_b \rangle \]

\[ \langle \psi | H | \psi \rangle = c_+^2 [ \langle \phi_a | H | \phi_a \rangle + \langle \phi_a | H | \phi_b \rangle + \langle \phi_b | H | \phi_a \rangle + \langle \phi_b | H | \phi_b \rangle ] \]

\[ \langle \phi_a | H | \phi_a \rangle = H_{aa} \quad \text{assume} \quad H_{ab} = H_{ba} \]

\[ \langle \psi | H | \psi \rangle = c_+^2 [ H_{aa} + 2H_{ab} + H_{bb} ] \]

\[ E_+ = \langle \psi | H | \psi \rangle \]

\[ E_+ = \frac{H_{aa} + 2H_{ab} + H_{bb}}{2(1+S_{ab})} \quad E_- = \frac{H_{aa} - 2H_{ab} + H_{bb}}{2(1-S_{ab})} \]

replace c
Making Connections with QM  

ready to solve!

\[ E = \langle \psi | H | \psi \rangle \quad \text{and} \quad \psi = c \left( \phi_a \pm \phi_b \right) \]

\[ \psi_+ = c_+ \left( \phi_a + \phi_b \right) \]

\[ \langle \psi | H | \psi \rangle = c_+^2 \left[ \langle \phi_a | H | \phi_a \rangle + \langle \phi_a | H | \phi_b \rangle + \langle \phi_b | H | \phi_a \rangle + \langle \phi_b | H | \phi_b \rangle \right] \]

\[ \langle \phi_a | H | \phi_a \rangle = H_{aa} \quad \text{assume} \quad H_{ab} = H_{ba} \]

\[ \langle \psi | H | \psi \rangle = c_+^2 \left[ H_{aa} + 2H_{ab} + H_{bb} \right] \]

\[ E_+ = \langle \psi | H | \psi \rangle \]

\[ E_+ = \frac{H_{aa} + 2H_{ab} + H_{bb}}{2(1 + S_{ab})} \]

\[ E_- = \frac{H_{aa} - 2H_{ab} + H_{bb}}{2(1 - S_{ab})} \]

DONE! (not quite!!)
Making Connections with QM

ready to solve!

\[ E = \langle \psi | H | \psi \rangle \quad \text{and} \quad \psi = c \left( \phi_a \pm \phi_b \right) \]

\[ \psi_+ = c_+ \left( \phi_a + \phi_b \right) \]

\[ \langle \psi | H | \psi \rangle = c_+^2 \langle \phi_a + \phi_b | H | \phi_a + \phi_b \rangle \]

\[ \langle \psi | H | \psi \rangle = c_+^2 \left[ \langle \phi_a | H | \phi_a \rangle + \langle \phi_a | H | \phi_b \rangle + \langle \phi_b | H | \phi_a \rangle + \langle \phi_b | H | \phi_b \rangle \right] \]

\[ \langle \phi_a | H | \phi_a \rangle = H_{aa} \quad \text{assume} \quad H_{ab} = H_{ba} \]

\[ \langle \psi | H | \psi \rangle = c_+^2 \left[ H_{aa} + 2H_{ab} + H_{bb} \right] \]

\[ E_+ = \langle \psi | H | \psi \rangle \]

\[ E_+ = \frac{\varepsilon_a + 2H_{ab} + \varepsilon_b}{2(1 + S_{ab})} \quad E_- = \frac{\varepsilon_a - 2H_{ab} + \varepsilon_b}{2(1 - S_{ab})} \]
Making Connections with QM

- set up model: diatomic
  - degenerate FOs $\varepsilon_a = \varepsilon_b = \varepsilon$
  - no overlap $S_{ab} = 0$
  - non-zero coupling $H_{ab}$ ($H_{ab}$ is negative!)

\[ E_+ = \frac{\varepsilon_a + \varepsilon_b + 2H_{ab}}{2(1 + S_{ab})} \quad \text{and} \quad E_- = \frac{\varepsilon_a + \varepsilon_b - 2H_{ab}}{2(1 - S_{ab})} \]

\[ \psi_+ = \frac{1}{\sqrt{2}}(\phi_a + \phi_b) \quad \psi_- = \frac{1}{\sqrt{2}}(\phi_a - \phi_b) \]

Fig. 13
set up model: diatomic

- degenerate FOs $\varepsilon_a = \varepsilon_b = \varepsilon$
- no overlap $S_{ab} = 0$
- non-zero coupling $H_{ab}$

Degenerate orbitals: splitting depends on $H_{ab}$

splitting is large!

Justified!
Making Connections with QM

modify model

- degenerate FOs $\varepsilon_a = \varepsilon_b = \varepsilon$
- overlap allowed $S_{ab} \neq 0$
- non-zero coupling $H_{ab}$

insert into the equations

$$E_+ = \frac{\varepsilon + \varepsilon + 2H_{ab}}{2(1 + S_{ab})}$$
and
$$E_- = \frac{\varepsilon + \varepsilon - 2H_{ab}}{2(1 - S_{ab})}$$

antibonding destabilisation is larger than bonding stabilisation

Justified!

See slides in your notes from your Chemical Bonding course
general rule: splitting energy decreases as the energy between the FO increases

degenerate orbitals: splitting energy depends on:

\[ H_{ab} = \langle \psi_a | H | \psi_b \rangle \]

non-degenerate orbitals: splitting energy depends on:

\[ \left( \frac{H_{ab}}{\Delta \varepsilon} \right)^2 \]

Fig. 10
Key Points

be able to explain LCAO, give the equation defining all the terms and illustrate LCAOs on a diagram

be able to explain and predict the relative size of FO contributions to a MO

be able to rationalise the position of FO energy levels

be able to define and illustrate the splitting energy

be able to discuss, employing equations, diagrams and examples $\Delta \varepsilon$, $S_{ab}$ and $H_{ab}$

be able to make a connection with QM including being able to derive the relevant equations

be able to compare and contrast the equations for $E_+$ and $E_-$ for different levels of approximation

be able to employ this knowledge in forming MO diagrams
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/
Removed Slides Follow
Generalise: linear combination of atomic orbitals

- $\Gamma$ = symmetry label of MO
- $N$ = normalisation coefficient
- $C_i$ tells us how large the contribution from each atomic orbital $\Psi_i$ will be

\[ \psi_\Gamma = N(c_1\psi_1 + c_2\psi_2 + \cdots c_n\psi_n) = N \sum c_i \psi_i \]

Solve Schrödinger Equation!

to determine $N$ and $C_i$
then examine how MOs change under geometric distortion

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

- $\downarrow$ O-H bonding overlap
- ALSO $\uparrow$ H-H through space antibonding
- net result destabilisation
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

- ↓ O-H antibonding overlap
  => stabilize
- also ↑ H···H through space antibonding
- => destabilize
- shorter distance overlap dominates
- => net result stabilisation

Fig 21
Making Connections with QM

\[
E_+ = \frac{\varepsilon + H_{ab}}{1 + S_{ab}} \quad E_- = \frac{\varepsilon - H_{ab}}{1 - S_{ab}}
\]

test!

- \( S_{ab} = 0.2 \)
- \((\varepsilon-H_{ab})*(1/0.8) = (\varepsilon-H_{ab})*1.25 \)
- = increase in destabilisation
- \((\varepsilon-H_{ab})*(1/1.2) = (\varepsilon-H_{ab})*0.83 \)
- = decrease in stabilisation

general rule: antibonding MOs are destabilised by more than bonding MOs are stabilised

Justified!
modify model

- $\epsilon_a \neq \epsilon_b$
- no overlap $S_{ab} = 0$

for non-degenerate orbitals the splitting energy depends on:

$$\frac{(H_{ab})^2}{\Delta \epsilon}$$

Important!

See slides in your notes from your Chemical Bonding course.

Course cross-over material: I expect you to be able to carry out the derivations!