An introduction to Molecular Orbital Theory

6 Lecture Course
Prof S.M.Draper
SNIAMS Institute 2.5
smdraper@tcd.ie

Objectives of the course

- Wave mechanics / Atomic orbitals (AOs)
  - The basis for rejecting classical mechanics (the Bohr Model) in the treatment of electrons
  - Wave mechanics and the Schrödinger equation
  - Representation of atomic orbitals as wave functions
  - Electron densities and radial distribution functions
  - Understanding the effects of shielding and penetration on AO energies

- Bonding
  - Review VSEPR and Hybridisation
  - Linear combination of molecular orbitals (LCAO), bonding / antibonding
  - Labelling of molecular orbitals (MOs) (σ, π and g, u)
  - Homonuclear diatomic MO diagrams – mixing of different AO’s
  - More complex molecules (CO, H₂O ….)
  - MO diagrams for Transition metal complexes

Lecture schedule

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Literature

- Book Sources: all titles listed here are available in the Hamilton Library
  - 3. Inorganic Chemistry (Prentice Hall) C. Housecroft, A. G. Sharpe – comprehensive text with very accessible language. CD contains interactive energy diagrams
- Additional sources: [http://winter.group.shef.ac.uk/orbitron/](http://winter.group.shef.ac.uk/orbitron/) - gallery of AOs and MOs
Tutorials

- Tutorials are NOT for the lecturer to give you another lecture and provide answers to potential exam questions
- If you come to tutorials with this attitude you will be disappointed.

- To make the MOST from your tutorials recognise that they are YOUR chance to understand the material and to ask questions

You MUST attempt the sheets BEFORE the tutorial and read the through the lectures preceding it

Where it All Began

Lecture 1 The Bohr Model

Prof. S.M. Draper
SNIAMS Rm 2.5
smdraper@tcd.ie

Bohr model of the atom (1913)
http://www.youtube.com/watch?V=R7OKDh65GCM

Assumptions
1) Rutherford (1912) model of the atom (Planetary model with central nucleus + electrons in orbit)
2) Planck (1901), Einstein (1905) – the energy electromagnetic waves is quantised into packets called photons (particle like property).

Adsorption / Emission spectra for Hydrogen

Johann Balmer (1885) measured line spectra for hydrogen
364.6 nm (uv), 410.2 nm (uv), 434.1 nm (violet), 486.1 nm (blue), and 656.3 nm (red).

Balmer discovered these lines occur in a series - both absorption and emission - where \( \alpha \) is the Rydberg constant (3.29 \( \times 10^{15} \) Hz)

\[ \alpha = \frac{1}{\lambda^2} \]

Balmer series \( n_2 = 2 \) and \( n_1 = n_1 + 1, n_1 + 2, n_1 + 3 \ldots \)
Other series for \( n_1 = 1 \) (Lyman – UV), \( n_1 = 3 \) (Paschen – IR) etc.
Electrons must have specific energies – no model of the atom to explain this.
Bohr model of the atom

Speed of electromagnetic waves (c) is constant (ν and λ vary)

\[ c = \nu \lambda, \quad \nu = h \lambda, \quad E = h \nu, \quad E = h c / \lambda. \]

As frequency increases, wavelength decreases. Given \( \lambda \rightarrow \nu \)

e.g. radio waves: \( \lambda = 0.1 \text{ m} \)  
X-rays: \( \lambda = 1 \times 10^{-12} \text{ m} \)
\( \nu = 3 \times 10^9 \text{ Hz} \)  
\( \nu = 3 \times 10^{20} \text{ Hz} \)
\( E = 2 \times 10^{-24} \text{ J} \)  
\( E = 2 \times 10^{-13} \text{ J} \)

\( E \) – energy (J), \( h \) – Planck’s constant (J s), \( \nu \) – frequency (Hz), \( c \) – speed of light (m\(^{-1}\)), \( \lambda \) – wavelength (m)

Bohr model

Electron assumed to travel in circular orbits.

- Only orbits with quantised angular momentum are allowed (as observed in spectra)
  \[ mvr = \left( \frac{h}{2\pi} \right) \]

- Classical electrodynamic theory rejected (charged particles undergoing acceleration must emit radiation)

- Radiation is absorbed or emitted only when electrons jump from one orbit to another

where \( a \) and \( b \) represent the energy of the initial and final orbits

Bohr model – calculating the energy and radius

will not be examined

- Energy
  \[ -\frac{Ze^2}{8\varepsilon_0 r} = \frac{1}{2} m v^2 = E \]

- Quantised angular momentum
  \[ mvr = \left( \frac{h}{2\pi} \right) \]

- Combining the two
  \[ \frac{1}{2} m v^2 = \frac{-Ze^2}{2m\varepsilon_0 r} = \frac{-n^2 h^2}{8\varepsilon_0 m} = \frac{-Ze^2}{8\varepsilon_0 r} = E \]

- Rearranging to give \( r \)
  \[ r^2 = \frac{n^2 h^2}{8\varepsilon_0 m \left( -\frac{Ze^2}{m^2} \right)} \]

- Substitute \( r \) into energy gives
  \[ \frac{-Ze^2}{8\varepsilon_0 r} = \frac{-n^2 h^2 \varepsilon_0}{8\pi m^2 \varepsilon_0^2} \]

- Energy is dependent on \( I \) and \( Z^2 \) (2s and 2p the same – only true for 1 electron systems)
  \[ \frac{I}{n^2} \]
Taking Important findings: Energy levels of Hydrogen

Substitute quantised momentum into energy expression and rearrange in terms of \( r \) (radius) (see previous slide)

\[
r = \frac{n^2 \hbar^2 c^2}{\pi m Z e^2} = \frac{n^2 a_0}{Z}
\]

\( a_0 \) (Bohr) radius of the 1s electron on Hydrogen 52.9 pm \((n=1, Z=1)\)

Radius \((r)\) depends on \( Z \)

Substitute \( r \) back into energy expression gives

\[
E_n = -\frac{mZ^2 e^4}{8\pi^2 \hbar^2 c^2} = \frac{13.6056 \times Z^2}{n^2} (\text{eV})
\]

Energy of 1s electron in H is 13.6056 eV = 0.5 Hartree \((1\text{eV} = 1.602 \times 10^{-19} \text{J})\)

Energy \((E)\) depends on \( Z \)

Radius of orbits

For hydrogen \((Z=1)\)

\[
r = n^2 a_0 \quad E_n = -\frac{13.6056}{n^2}
\]

\[
\begin{array}{c|c|c}
 n & \text{energy (eV)} & r \text{ (pm)} \\
 1 & -13.6056 & 52.9 \\
 2 & -3.4014 & 211 \\
 3 & -1.5117 & 476 \\
 4 & -0.8504 & 847 \\
 5 & -0.3779 & 1322 \\
 \infty & 0.0000 & \infty \\
\end{array}
\]

Note. The spacing reflects the radius of the orbit – not the energy.

Energy levels of Hydrogen

For hydrogen \((Z=1)\)

\[
r = n^2 a_0 \quad E_n = -\frac{13.6056}{n^2}
\]

\[
\begin{array}{c|c|c|c|c|c}
 n & \text{energy (eV)} & r (pm) & \text{nucleus} \\
 1 & -13.6056 & 52.9 & \infty & 0.0000 & \infty \\
 2 & -3.4014 & 211 & \infty & 0.0000 & \infty \\
 3 & -1.5117 & 476 & \infty & 0.0000 & \infty \\
 4 & -0.8504 & 847 & \infty & 0.0000 & \infty \\
 5 & -0.3779 & 1322 & \infty & 0.0000 & \infty \\
\end{array}
\]

Note. The spacing reflects the energy not the radius of the orbit.

Energy of emission is \( E_{\text{initial}} - E_{\text{final}} \)

Balmer series \((\Rightarrow n_{\text{final}}=2)\)

\[
\begin{array}{c|c|c|c|c|c}
 n & \text{energy (eV)} & r (pm) & \text{nucleus} \\
 3 & -1.5117 & 476 & \text{n} & \text{in} & \text{it} \\
 4 & -0.8504 & 847 & \text{n} & \text{in} & \text{it} \\
 5 & -0.3779 & 1322 & \text{n} & \text{in} & \text{it} \\
 \infty & 0.0000 & \infty & \text{n} & \text{in} & \text{it} \\
\end{array}
\]

Emission spectra

Same form as fitted to emission spectra.

Balmer series \((\Rightarrow n_{\text{final}}=2)\)

\[
\begin{array}{c|c|c|c|c|c}
 n=3 & n=2 & \text{E} & \text{nm} \\
 5 & 4 & \Rightarrow & 656 & \text{nm} \\
 4 & 3 & \Rightarrow & 486 & \text{nm} \\
 3 & 2 & \Rightarrow & 434 & \text{nm} \\
\end{array}
\]

\( n = 13.6056 \text{ eV} / c = 3.29 \times 10^{15} \text{Hz} \)

Note. The spacing reflects the energy not the radius of the orbit.
Problems with the Bohr Model

- Only works for 1 electron systems
  - E.g. H, He⁺, Li²⁺
- Splitting of lines in a magnetic field
  - Modified Bohr-Sommerfield (elliptical orbits - not satisfactory)
- Electrons were found to exhibit wave-like properties
  - E.g. can be diffracted as they pass through a crystal (like x-rays)
  - Considered as classical particles in Bohr model

Wave / particle duality
http://www.youtube.com/watch?v=IsA_oIXdF_8

de Broglie (1923)
By this time it was accepted that EM radiation can have wave and particle properties (photons)
de Broglie proposed that particles could have wave properties (wave / particle duality). Particles could have an associated wavelength ($\lambda$)

$$E = mc^2, \quad \lambda = \frac{h}{p}$$

No experimental at time.

1925 Davisson and Germer showed electrons could be diffracted according to Bragg's Law (used for X-ray diffraction)
Numerically confirm de Broglie’s equation

Wave Mechanics

- For waves: it is not possible to determine the position and momentum of the electron simultaneously – Heisenberg ‘Uncertainty principle’
- Use probability of finding an electron from $\psi^2$ (actually $\psi^* \psi$ – but functions we will deal with are real)

Where $\psi$ is a wave function and a solution of the Schrödinger equation (1927). The time-independent form of the Schrödinger equation for the hydrogen atom is:

$$\frac{-\hbar^2}{8\pi^2 m} \nabla^2 \psi - \frac{e^2}{4\pi\epsilon_0 r} \psi = \frac{E}{\hbar^2} \psi, \quad \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Wave mechanics and atoms

- What does this mean for atoms
- Electrons in “orbits” must have an integer number of wavelengths
- E.g. n=4 and n=5 are allowed
  - These create continuous or standing waves (like on a guitar string)
- E.g. n=4.33 is not allowed
  - The wavefunction is not continuous
- The wave nature of electrons brings in the quantized nature of the orbital energies.
Atomic solutions of the Schrödinger equation for H

- Schrödinger equation can be solved exactly for one electron systems
  - Solved by trial and error manipulations for more electrons
- Solutions give rise to 3 quantum numbers which describe a three dimensional space called an atomic orbital: \( n, l, m \) (and spin quantum number describing the electron)
  - principal quantum number, defines the orbital size with values \( 1 \) to \( \infty \)
  - azimuthal or angular momentum quantum number, defines shape. For a given value of \( n \), \( l \) has values \( 0 \) to \( (n-1) \)
  - magnetic quantum number, defines the orbital orientation. For a given value of \( l \), \( m_l \) has values from \( +l \) through \( 0 \) to \( -l \)

Solutions of the Schrödinger equation for H

\[
\begin{array}{cccccc}
 n & 1 & 2 & 2 & 2 & 2 \\
l & 0 & 0 & 1 & 1 & 1 \\
m_l & 0 & 0 & -1 & 0 & 1 \\
\hline
\text{Orbital} & 1s & 2s & 2p & 2p & 2p \\
\end{array}
\]

\[
\begin{array}{cccccccc}
 n & 3 & 3 & 3 & 3 & 3 & 3 & 3 \\
l & 0 & 0 & 1 & 1 & 1 & 2 & 2 & 2 & 2 \\
m_l & 0 & -1 & 0 & 1 & -2 & -1 & 0 & 1 & 2 \\
\hline
\text{Orbital} & 3s & 3p & 3p & 3p & 3d & 3d & 3d & 3d & 3d \\
\end{array}
\]

An introduction to Molecular Orbital Theory

Lecture 2 – Representing atomic orbitals - The Schrödinger equation and wavefunctions.

Last Lecture

- Recap of the Bohr model
  - Electrons
  - Assumptions
  - Energies / emission spectra
  - Radii
- Problems with Bohr model
  - Only works for 1 electron atoms
  - Cannot explain splitting by a magnetic field
- Wave-particle duality
- Wave mechanics
  - Schrödinger
  - Solutions give quantum number \( n, l, m_l \) → atomic orbitals
Representations of Orbitals:

For an atomic system containing one electron (e.g., H, He+ etc.). The wavefunction, \( \Psi \), is a solution of the Schrödinger equation.

It describes the behaviour of an electron in a region of space called an atomic orbital (\( \phi \cdot \text{phi} \)).

Each wavefunction (\( \phi \)) has two parts:
- radial part – which changes as a function of distance from the nucleus
- angular part – which changes as a function of shape

\[ \psi_{\text{ext}} = \psi_{\text{radial}}(r) \psi_{\text{angular}}(\theta, \phi) \]

Orbitals have
- SIZE determined by the radial part of the wavefunction
- SHAPE determined by the angular part (spherical harmonics)
- ENERGY determined by the Schrödinger equation. Calculated exactly for one electron systems and by trial and error for more complex systems).

Polar Coordinates

- To describe the wavefunction of atomic orbitals we must describe it in three dimensional space
- For an atom it is more appropriate to use spherical polar coordinates:

\[ r, \theta, \phi \]

Location of point P
Cartesian = x, y, z

Graphical representation of Radial Wavefunction

- \( R(r) \) of the 1s orbital of H

\[ R(r) = 2e^{-r} \]

it decays exponentially with \( r \)

it has a maximum at \( r = 0 \)

- \( R(r) \) has no physical meaning
- \( R(r)^2 \) does. It represents the probability but….
- Misleading – does not take into account the volume
- \( R(r)^2 \) increases toward \( r = 0 \)
- In reality the volume is very small so probability of being at small \( r \) is small

Angular component is a constant \( \Rightarrow \) Spherical
Radial distribution functions (RDF)
• Probability of an electron at a radius \( r \) (RDF) is given by probability of an electron at a point which has radius \( r \) multiplied by the volume at a radius of \( r \)
  - Consider a sphere – volume as we move at a small slice is \( 4\pi r^2 \delta r \)
    - By differentiation, the volume of a sphere = \( \frac{4}{3}\pi r^3 \)
  • RDF\((r) = \frac{4\pi r^2 R(r)^2}{\rho} \)
  • Maximum for 1s at a = 0 (like Bohr!)

Wave functions of Hydrogen 2s and 3s orbitals
For H 2s\((r) = \frac{1}{2\sqrt{2}} (2-r)e^{(-r/2)} \) For H 3s\((r) = \frac{1}{9\sqrt{3}} \left[ 6 - 4r + \left( \frac{2}{3} r \right)^2 \right] e^{(-r/3)} \)

 exponential decreases more slowly than 1s, \( e^{(-r/n)} \) the larger \( n \) the more diffuse the orbital

\( 2s \) at \( 2r = 0 \) (i.e. \( r = 2 \) a.u.)

\( 3s \) changes sign twice with two nodes \( (r = 1.9, 7.1 \) a.u.\)

\( \Rightarrow \) Caused by the order of the polynomial!

What does a negative sign mean?
• The absolute sign of a wave function is not important.
  - The wave function has
  - the electron density is related to the square of the wave function
  - This is the same irrespective of the sign
• Wavefunction signs matter when two orbitals interact with each other (see later)
• Some books have the 2s as opposite sign – you can see that the electron density \( R(r) \) is the same

Wave functions of 2s and 3s orbitals
<table>
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<th>2s((r))</th>
<th>3s((r))</th>
</tr>
</thead>
<tbody>
<tr>
<td>General</td>
<td>( \frac{1}{2\sqrt{2}} \left( \frac{Z}{n\rho_0} \right)^{1/2} (2 - \rho r)e^{(-\rho r/2)} )</td>
<td>( \frac{1}{9\sqrt{3}} \left( \frac{Z}{n\rho_0} \right)^{1/2} (6 - 6\rho r + (\rho r)^2) e^{(-\rho r/2)} )</td>
</tr>
<tr>
<td>( \rho = \frac{2\rho}{n\rho_0} )</td>
<td>( \rho = \frac{2\rho}{n\rho_0} )</td>
<td></td>
</tr>
<tr>
<td>For H</td>
<td>( 2s \Rightarrow Z=1, n=2, \rho=1 )</td>
<td>( 3s \Rightarrow Z=1, n=3, \rho=2/3 )</td>
</tr>
</tbody>
</table>

\( \frac{1}{2\sqrt{2}} (2-r)e^{(-r/2)} \)
\( \frac{1}{9\sqrt{3}} \left[ 6 - 4r + \left( \frac{2}{3} r \right)^2 \right] e^{(-r/3)} \)

The form of the wave functions is the important concept – not the precise equation
Note \( R(r) \) has functional form
Normalisation constant * polynomial (increasing order with \( n \)) * exponential (-\( r/\rho \))
Radial Nodes

- The point at which \( R(r) = 0 \) (not including the origin) is called a radial node.
- Number of radial node = \( n - l - 1 \)
  - \( 1s = 1 - 0 - 1 = 0 \)
  - \( 2s = 2 - 0 - 1 = 1 \)
  - \( 3s = 3 - 0 - 1 = 2 \)
  - \( 2p = 2 - 1 - 1 = 0 \)
  - \( 3p = 3 - 1 - 1 = 1 \)
  - \( 3d = 3 - 2 - 1 = 0 \)
- In general, the more nodes contained within e.g. a set of s orbitals, the higher the energy of the orbital – like a wave that crosses the x-axis many times.
- Why are there radial nodes?
  - Pauli exclusion principle dictates that no two electrons can have the same set of quantum numbers.
  - Actually - no two electrons can overlap (i.e. occupy the same space).
  - Overlap integral = \( \int \phi_A \phi_B \rho \, d\tau = 0 \) (analogous to normalisation).
  - Atomic orbitals are said to be Orthogonal.
  - Satisfied for AO’s with same \( l \) by having change(s) in the wave function sign.
  - Satisfied for AO’s with different \( l \) because the angular component ensures no overlap.

Orthogonal orbitals

- Radial nodes ensure that orbital of the same angular momentum (s-s, p-p, d-d) are orthogonal.
- E.g. 1s – 2s
- Need to take into account volume – Individual traces are \( 4\pi r^2 R(r) \)
- Product (green) is \( 4\pi R(1s)R(2s) \)
- Total area under the green line = 0
  - The two orbitals are orthogonal.

RDF’s of \( ns \) orbitals

- 1s - 1 peak: Maximum at \( r = a_0 \) - Bohr Model \( \rightarrow \) radius of \( a_0 \)
- 2s - 2 peaks: Maximum at \( r \approx 5 a_0 \) - Bohr Model \( \rightarrow \) radius of \( 4 a_0 \)
- 3s - 3 peaks: Maximum at \( r \approx 13 a_0 \) - Bohr Model \( \rightarrow \) radius of \( 9 a_0 \)

These maximum correspond to the distance from the nucleus at which the electron has the highest probability of being found i.e. the optimum size of a sphere of very small thickness in which to find an electron in a 1s, 2s or 3s orbital.

Representing atomic orbitals

- How do the radial wavefunctions and the RDF reflect experimental observations of electron density?
  - In 2D we can use dot diagrams to look at the whole wave function
    - s orbitals have spherical symmetry
    - The electron density is zero – radial nodes
    - The most probable point for locating an electron is the nucleus
    - The most probable shell at radius \( r \) for locating an electron increases from 1s to 2s to 3s orbitals.
Boundary Surfaces

- Represent the wave function/atomic orbital in 3D
  - Draw a 3D surface at a given value of $\phi$
  - Define the surface such that it encloses a space in which the electron spends most of its time
  - The surface now depicts outer shape and size of the orbital
  - The inner structure of the wave function is hidden beneath the surface

$p$ orbitals - wavefunctions

- There are three $p$ orbitals for each value of $n$ ($p_x, p_y, p_z$)
  - The radial function is the same for all $np$ orbitals
  - The angular terms are different → different shapes (orientations)
  - Angular terms are the same for different $n$ → $2p_x, 3p_x, 4p_x$ i.e. have same shape
- Wave function for $2p$ and $3p$ orbitals
  \[ R(r) = \frac{2Z}{\alpha_0} \rho^{\frac{3}{2}} e^{-\rho} \]
  \[ Y(\theta, \phi) = \frac{3}{4\pi} \rho Y_l^m(\theta, \phi) \]
  \[ R(2p) = \frac{1}{2\sqrt{6}} \left( \frac{Z}{\alpha_0} \right)^{\frac{3}{2}} \rho e^{-\rho/2} \]
  \[ R(3p) = \frac{1}{9\sqrt{6}} \left( \frac{Z}{\alpha_0} \right)^{\frac{3}{2}} (4-3\rho) \rho e^{-\rho/2} \]
Note the form of $R(r) →$ Constant $* \rho^{\frac{3}{2}} e^{-\rho} * \rho$ $* \text{exponential}$

$p$ orbitals – radial functions

- Radial wave function for hydrogen $p$ orbitals ($Z=1$)
  - For $2p$ $n = 2 \rightarrow \rho = 1$
  - For $3p$ $n = 3 \rightarrow \rho = 2/3$
  \[ R(2p) = \frac{1}{2\sqrt{6}} \rho e^{-\rho/2} \]
  \[ R(3p) = \frac{1}{9\sqrt{6}} \left( 4 - 2\rho \right) \rho e^{-2\rho/3} \]
- Polynomial $→$ nodes
  - Equation for no. of radial nodes
  - $n - l - 1 \rightarrow 2p = 0, 3p = 1$
  - Ensures $2p$ and $3p$ orthogonal
- All $p$ orbitals are multiplied by $\rho$
  - $R(r) = 0$ at $r = 0$
- Required to match the angular function $→$ angular node
**p orbitals – angular functions boundary surfaces**

- All p orbitals have the same shape
  \[ Y(p_x) = \left(\frac{3}{4\pi}\right)^{1/2} \cos(\theta) \]
- Angular function give rise to direction
  \[ Y(p_y) = \left(\frac{3}{4\pi}\right)^{1/2} \sin(\theta) \cos(\phi) \]
- Can represent p orbital as dot diagrams or boundary surfaces
  \[ Y(p_z) = \left(\frac{3}{4\pi}\right)^{1/2} \sin(\theta) \sin(\phi) \]
- 1 angular nodal plane \( p_x \) (yz plane), \( p_y \) (xz plane) \( p_z \) (xy plane)
  - Ensures that p orbitals are orthogonal to s orbitals

**p orbitals – RDF’s**

- Radial distribution function show probability at a given radius
- \( 2p \) function – no nodes, maximum at \( r = 4 \, a_0 \) (same as \( n=2 \) for Bohr model)
- \( 3p \) function – two peaks, maximum at \( r \approx 12 \, a_0 \) (not the same as Bohr)

**Where Have we Been? Last lectures**

- Solutions of the Schrödinger equation for atoms
  - Atomic orbitals (\( \phi \))
  - Defined three quantum number (\( n, l, m_l \))
- Defined polar coordinates \( \theta, \phi \) radial and angular terms
- Examined wavefunctions of the s orbitals
  - Angular term constant for s orbitals
  - Wavefunction as \( \text{constant} \times \text{polynomial} \times \text{exponential} \)
  - Decays as \( \text{the larger} \, n \, \text{the more diffuse the orbital} \)
  - Defined radial nodes and examined the number of radial nodes (polynomial \( \rightarrow n - l - 1 \))
  - Discussed the requirement for radial nodes \( \rightarrow \) Pauli exclusion principle
- p orbitals
  - Radial functions similar to s orbital (except additional \( r \)) \( R(0) = 0 \)
  - Angular terms define shapes \( p_x, p_y, \) and \( p_z \) – same for different \( n \)
  - Radial distribution function for p orbitals
**Where are we going?**

**Lecture 3**
- Brief wavefunction considerations: $d$ and $f$ orbitals
- Using wavefunctions and radial distribution functions (RDFs) to
  - compare atomic orbitals (AOs)
  - define penetration and shielding
  - explain the 'aufbau' building-up principle
- Revision
  - Localised bond pictures
  - Hybridisation

**d orbitals – wave functions**
- Five $d$ orbitals for each value of $n (n \geq 3) \rightarrow l = 2, m_l = -2, -1, 0, 1, 2$
- Wave functions slightly more complicated (constant * polynomial * $r^2$ * exp)
  - Radial wave functions same for all $3d$ orbital
    \[
    R(3d) = \frac{1}{9\sqrt{20}} \frac{Z}{r_0} \gamma_2 (\rho r)^2 e^{-r/\rho}
    \]
  - Max probability at $r = 9 a_0$
  - AO's with no nodes have max probability at same radius as Bohr model
  - $4d$ orbital has 1 node

**d orbitals – angular functions**
- Angular functions same for $d_{x^2}$, $d_{y^2}$, $d_{z^2}$, $d_{x^2-y^2}$, $d_{xy}$, $d_{xz}$, $d_{yz}$ irrespective of $n$
  - same shape for 3$d$, 4$d$, 5$d$ orbitals using boundary surfaces
Five different angular function e.g.
\[
Y(d_{x^2-y^2}) = \left(\frac{15}{16\pi}\right)^{1/2} \sin(\theta) \cos(\phi) \cos(\phi)
\]
- Two angular nodes planes $\rightarrow$ orthogonal to $s (0)$ and $p (1)$
  - $d_{x^2}$, Nodal planes in $xy$ and $xz$ (note: +ve lobe points between +x and +y axes)

**f orbitals**
- Almost no covalent bonding $\rightarrow$ shape not really important
- $l = 3$ $\rightarrow$ Seven different angular function for each $n (n \geq 4)$
  - $f$ block is 14 element wide, same shape for $4f$, $5f$ etc
  - Radial functions same for all $n^f$ orbitals
  - Three angular nodes (nodal planes) $\rightarrow$ orthogonal to $s$, $p$ and $d$ orbitals

**Note the functional form of $R(r) \rightarrow$ Constant * polynomial * $r^2$ * exponential**
Penetration

- RDF allow us to directly compare AOs on the same graph
- The RDFs of AOs within a given shell \((n)\) have different maxima
- Number of nodes \(n - l - 1\):
  - \(n = 3\) \(3s \rightarrow 2\) nodes \(3p \rightarrow 1\) node \(3d \rightarrow 0\) nodes
  - \(3s\) has a peak very close to the nucleus
  - \(3p\) has a peak close to the nucleus
- These close peaks have a very strong interaction with the nucleus
- \(3s\) is said to be the most penetrating
- Penetration \(3s > 3p > 3d\)

Multi-electron Atoms

- Multi-electron atoms are assumed to have hydrogen-like wave functions.
- Differences are the increase in atomic number and the effective nuclear charge.
- In reality the electrons repel each other and shield the nucleus
  - Effective nuclear charge \(Z_{\text{eff}} = Z - S\)
    - \(S\) is a screening or shielding constant
- Li atom – why is the electronic configuration \(1s^2 2s^1\) and not \(1s^2 2p^0\?
  - \(1s\) electrons shield the valence electron from the nuclear charge
  - \(2s\) penetrates more effectively
  - \(2p\) penetrates less effectively
  - \(2s\) is filled first
- \(E(1s) < E(2s) < E(2p)\)
- \(E(ns) < E(np) < E(nd) < E(nf)\)

Periodic Table

- Shielding and penetration \(\Rightarrow E(ns) < E(np) < E(nd) < E(nf)\)
- This gives rise to electronic configuration of atoms and the order of elements in the periodic table
  - Electrons are filled in order of increasing energy (Aufbau principle) and electrons fill degenerate (same energy) levels singularly first to give maximum spin (Hund’s rule)
    - \(E(4s) < E(3d)\)
      - K, Ca
    - \(E(6s) \approx E(5d)\)
      - La \([Xe]\) \(6s^2 5d^1\)
      - Ce \([Xe]\) \(6s^2 4f^2\)

More complex results of penetration and shielding

Energy levels vs atomic number

- For H \((Z=1)\) all orbitals within a principle QN have same energy
- For multi electron atoms penetration follows
  - \(s > p > d > f\)
- \(3d\) shielded very effectively by orbitals of \(n \leq 3\)
- \(s^2 3p^2 4d^1\)
- Similar pattern for \(4d\) and \(4f\)
The Transition Metal Hiccup!

The energy of the 4s and 3d orbitals

- For K and Ca the $E(3d) > E(4s)$.
- At Sc on the $E(3d) < E(4s)$ (but close)
  - If 4s electron go into 3d orbital the extra e-e repulsion and shielding cause the 3d to rise above 4s again – hence the strange energy level diagram
  - Result is that TM’s lose 4s electrons first when ionized

Energy

4p

3d

4s

K Ca Sc Ti Increasing Z

---

Making Bonds

Localised Bond Pictures

Revision of JF Lewis Bonding / VSEPR

- Localised view of bonding
  - Views covalent bonds as occurring between two atoms
  - Each bond is independent of the others
  - Each single bond is made up of two shared electrons
  - One electron is usually provided by each atom
  - Each 1st and 2nd row atom attains a noble gas configuration (usually)
  - Shape obtained by VSEPR (Valence Shell Electron Pair Repulsion)

e.g. $H_2$

\[ H \cdot + \times \ H \rightarrow \ \text{H-H} \]

Each H has a share of 2 electrons $\rightarrow$ H-H

---

Drawing representations of AO’s

- Need to be able to draw AO’s when considering their interactions i.e when they form MO’s
  - Diagrams help to visualise the 3D nature of AO’s
  - Simple drawings are all you need !!!!!

---

Lewis bonding

- Octet rule for main group elements / 18 electron rule for transition metals
  - All atoms have a share of 8 electrons (main group: $s + three \ p$ orbitals) or 18 electrons (TM: $s + three \ p + five \ d$ orbitals) to fill all their valence atomic orbitals. This makes them stable
  - Diatomics
    - $F_2$
    - $O_2$

\[ \text{F} \cdot + \times \text{F} \rightarrow \]

2 electrons shared $\rightarrow$ bond order = 1

\[ \text{F} = \text{F} \]

\[ \text{O} \cdot + \times \text{O} \rightarrow \]

4 electrons shared $\rightarrow$ bond order = 2

\[ \text{O} = \text{O} \]
Lewis bonding – polyatomics (H₂O)

- Oxygen (Group 16) has 6 valence electrons, each hydrogen (Group 1) has 1 electron
- Oxygen has two lone pairs

\[ \text{2H}^+ + \text{O}^2- \rightarrow \]

- Shape – VSEPR
  - Electrons repel each other (repulsion between lone pair electrons > repulsion between electrons in bonding pairs)
  - Oxygen has 2 bond pairs and 2 lone pairs → 4 directions to consider
  - Accommodate 4 directions → Tetrahedral shape
  - H₂O is bent with H-O-H angle of 104.5°
  - Compares with a perfect tetrahedral of 109.45° → lone pair repulsion

Lewis bonding – polyatomics (ethene)

- Used different symbols for electrons on adjacent atoms

\[ \text{4H}^+ + 2\times \text{C}^0 \rightarrow \]

- Carbon atoms share 4 electron bond order → C = C
- Carbon–hydrogen interactions share 2 electrons → C – H
- Shape – VSEPR
  - Electrons repel each other
  - Carbon atoms have 3 directions – bond to C and two bonds to H
  - Accommodate 3 bond direction → 120° in a plane (molecule is flat)

Lewis structures – breaking the octet rule

- Some structures to not obey the 8 electron rule.
  - e.g. PF₅

\[ \text{F} \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \times \time 59
An introduction to Molecular Orbital Theory

Lecture 4  Revision of hybridisation
Molecular orbital theory and diatomic molecules

Prof S.M. Draper
SNIAMS 2.5
smdraper@tcd.ie

Where did we go last lecture?

• d orbitals
  – Radial wavefunctions, nodes and angular wavefunctions (shapes)
• f orbitals
  – Radial wavefunctions, nodes and angular wavefunctions (shapes)
• Multi-electron atoms
  – Penetration and shielding
  – Atomic orbital energies, filling and the periodic table
• Valence bond theory (localised electron pairs forming bonds)
  – Lewis structures
    → number of electron pairs
    → bond order (electrons shares divided by 2)
  – VSEPR
    → repulsion of electron pairs (BP and LP)
    → molecular shape

Valence bond theory and hybridisation

• Valence bond theory (Linus Pauling)
  – Based on localised bonding
  – Hybridisation to give a geometry which is consistent with experiment.
  – Hybridisation constructs new hybrid atomic orbitals from the AO’s
• Use Lewis model (number of electron pairs) → hybridisation → shape.
  – E.g. BeH₂, Be – 1s² 2s²

\[
\text{H} \leftrightarrow \text{Be} \leftrightarrow \text{H}
\]

• Correctly predicted by VSEPR to be linear – can we explain it using AO’s
  – Mix S with pₓ orbital → two sp hybridized orbitals
**sp hybridisation**

- **sp hybridisation**
  - Mix and a and a p orbital – two combinations $s + p_z$ and $s - p_z$
  - Two AO’s $\rightarrow$ two hybrid AO’s
  - Relative sign is important when mixing orbitals
  - $sp$ therefore means that the hybrid orbital is 50% s and 50% p

$$\psi_{sp} = \frac{1}{\sqrt{2}}(\psi_{2s} - \psi_{2p_z})$$

**Hybridisation – $sp^2$ hybridisation**

- **Lewis structure $\rightarrow$ 3 directions**
- Molecular is planar
- Three directions each at 120°
  - mix one s with two p orbitals
  - $sp^2$ hybridisation

**Hybridisation – $sp^3$**

- **For tetrahedral molecules we have to mix the s with all the p orbitals ($sp^3$)**
  - This give rise 4 equally spaced orbitals e.g. methane

- $H_2O$ can also be thought of like this with two of the $sp^3$ orbitals occupied by lone pairs.

**Hybridisation – $\pi$ bonds**

- For ethene $sp^2$ hybridisation $\rightarrow$ bonding in three directions
  - Each local bond can hold 2 electrons
  - Have not accounted for the second pair of electrons shared by the C atoms
  - Creates a $\pi$ bond above and below the plane of the molecule
  - Could think of the C as going from $s^2 p^2 \rightarrow (sp^2)^2 p_z^1$
Hybridisation – $d$ orbitals

**Trigonal Bipyramidal**

*Sp$^d$* → 5 electron pairs

($s + px + py + pz + dz^2$)

Octahedra

*Sp$^d$* → 6 electron pairs

($s + px + py + pz + dz^2 + dx^2-y^2$)

Hybridisation – summary

<table>
<thead>
<tr>
<th>Hybridisation</th>
<th>Atomic orbitals that are mixed</th>
<th>Geometry</th>
<th>General formula</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>sp</em></td>
<td>$s + p$</td>
<td>linear</td>
<td>AB$_2$</td>
<td>BeH$_2$</td>
</tr>
<tr>
<td><em>sp$^2$</em></td>
<td>$s + p_x + p_y$</td>
<td>trigonal planar</td>
<td>AB$_3$</td>
<td>BF$_3$, CO$_3^{2-}$, C$_2$H$_4$</td>
</tr>
<tr>
<td><em>sp$^3$</em></td>
<td>$s + p_x + p_y + p_z$</td>
<td>tetrahedral</td>
<td>AB$_4$</td>
<td>SO$_4^{2-}$, CH$_4$, NH$_3$, H$_2$O,</td>
</tr>
<tr>
<td><em>sp$^d$</em></td>
<td>$s + p_x + p_y + p_z + dz^2$</td>
<td>Trigonal Bipyramidal</td>
<td>AB$_5$</td>
<td>PCl$_5$, SF$_4$</td>
</tr>
<tr>
<td><em>sp$^d$</em></td>
<td>$s + p_x + p_y + p_z + dz^2 + dx^2-y^2$</td>
<td>Square Pyramidal</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>sp$^d$</em></td>
<td>$s + p_x + p_y + p_z + dz^2 + dx^2-y^2$</td>
<td>Octahedral</td>
<td>AB$_6$</td>
<td>SF$_6$, [Ni(CN)$_4$]$_2^-$, [PtCl$_4$]$_2^-$</td>
</tr>
</tbody>
</table>

Molecular orbital theory

- Molecule orbital theory (Robert Mullikan)
- Assumes electrons are delocalised
  - Different to Lewis and hybridisation (these are not MO)
  - Molecular orbitals are formed which involve all of the atoms of the molecule
  - Molecular orbital are formed by addition and subtraction of AO’s
  - Linear Combination of Atomic Orbitals (LCAO)
- Like hybrid AO’s but the MO involves the WHOLE molecule (hybridisation effects only the central atom)

Molecular orbital theory of H$_2$ - bonding

- H$_2$ molecule – interaction of two hydrogen 1s orbitals ($\psi_1$ and $\psi_2$)

  In phase interaction (same sign)

  $\psi_1 = (\psi_1 + \psi_2)$

  → Constructive interference

  Animation shows the in phase interaction of the s orbitals as they are brought together
Molecular orbital theory of H₂ - antibonding

- H₂ molecule – interaction of two hydrogen 1s orbitals (φₛ and φₗ)
  
  Out of phase interaction (opposite sign)
  \[ \varphi_2 = (\varphi_s - \varphi_l) \]
  Destructive interference

Animation shows the out of phase interaction (different colours) of the s orbitals as they are brought together

Interaction of 2 AO → 2 MO’s – A general rule is that n AO → n MO’s

Energy level diagram for H₂

- Interference between AO wave functions → bonding
  - Constructively → bonding interaction
  - Destructively → anti-bonding interaction

- Energy level diagram represents this interaction
  - Two s orbitals interaction to create a low energy bonding and high energy anti-bonding molecular orbital
  - Electrons fill the lowest energy orbital (same rules as for filling AO’s)
  - Bonding energy = 2 ΔE

Charge density associate with MO’s in H₂

- Charge density given by \( \varphi^2 \)
  
  - In phase interaction → enhance density between the atoms
    \[ \psi_1^2 = (\varphi_s + \varphi_l)^2 \quad \text{→} \quad \psi_1^2 = [\varphi_s]^2 + [\varphi_l]^2 + 2(\varphi_s\varphi_l) \]
    referred to a positive overlap (σ bonding) \( \psi_1 = \psi_\sigma \)

  - Out of phase interaction → reduced density between the atoms
    \[ \psi_2^2 = (\varphi_s - \varphi_l)^2 \quad \text{→} \quad \psi_2^2 = [\varphi_s]^2 + [\varphi_l]^2 - 2(\varphi_s\varphi_l) \]
    referred to a negative overlap (σ* anti-bonding) \( \psi_2 = \psi_{\sigma^*} \)

New wave functions must be normalised to ensure probability in 1!

What happens when the AO’s have different energies?

- Hypothetical molecule where the two s orbitals have different energies \( E(\varphi_s) < E(\varphi_l) \)

- What would the MO’s be like?
  - Bonding MO will be much more like the low energy orbital \( \varphi_s \)
  - Anti-bonding MO will be much more like high energy orbital \( \varphi_l \)

- We can say that the bonding MO is
  \[ \psi_\sigma = (C_s^+\varphi_s + C_l^-\varphi_l) \]

- Where the coefficients C, indicate the contribution of the AO to the MO

So for \( \varphi_\sigma \quad C_s^+ > C_l^- \)
Linear Combination of Atomic Orbitals - LCAO

- We wrote an equation using coefficients for the contribution of AO’s to the bonding MO, we can do the same for the anti-bonding MO
  \[ \psi_{n} = (C_{n}^{\sigma} \varphi_{n} + C_{n}^{\pi} \varphi_{n}) \quad \psi_{n} = (C_{n}^{\sigma} \varphi_{n} - C_{n}^{\pi} \varphi_{n}) \]
  where the coefficients are different this reflects the contribution to each MO
  \[ C_{n}^{\sigma} > C_{n}^{\pi} \quad C_{n}^{\sigma} < C_{n}^{\pi} \]

- The sign can be absorbed into the coefficient and we can write all of the MO’s in a general way
  \[ \psi_{n} = (C_{n}^{\sigma} \varphi_{n} + C_{n}^{\pi} \varphi_{n}) \]
  \[ n = 1 \]
  \[ \psi_{1} = (C_{1}^{\sigma} \varphi_{1} + C_{1}^{\pi} \varphi_{1}) \quad C_{a}^{1} = 0.8, C_{b}^{1} = 0.2 \]
  \[ n = 2 \]
  \[ \psi_{2} = (C_{2}^{\sigma} \varphi_{2} + C_{2}^{\pi} \varphi_{2}) \quad C_{a}^{2} = 0.2, C_{b}^{2} = -0.8 \]

- The coefficients contain information on both phase (sign) of the AO’s and how big their contribution (size) is to a particular MO

What interactions are possible?

- We have seen how s orbitals interact – what about other orbitals

  - If you have positive overlap reversing the sign \( \rightarrow \) negative overlap
    E.g. \( s + s \) and \( p_{x} + p_{x} \) \( \rightarrow \) +ve
    \( s - s \) and \( p_{x} - p_{x} \) \( \rightarrow \) -ve

  - Must define orientation and stick to it for all orbitals.
    Thus
    \( p_{x} + p_{x} \rightarrow \) -ve
    \( p_{x} - p_{x} \rightarrow \) +ve
    i.e. for sigma bond between P orbital need opposite sign coefficients!

What interactions are NOT possible?

- Some orbitals cannot interact – they give rise to zero overlap

  - Positive overlap (constructive interference) on one side is cancelled by negative overlap (destructive interference) on the other

  \( s + p_{x} \) positive overlap above the axis is cancelled by negative overlap below
  - Same is true for the other interactions below

LCAO

- Generally we can write
  \[ \psi_{n} = \sum_{x=a...}^{N_{b}AO's} C_{n}^{x} \varphi_{x} \]
  \( x = a, b, c \ldots \) (all of the AO’s in the molecule) \( n = 1, 2, 3 \ldots \) (the resulting MO’s)

  - So
    MO(1) = \[ \psi_{1} = C_{1}^{1} \varphi_{1} + C_{1}^{2} \varphi_{2} + C_{1}^{3} \varphi_{3} + \ldots \]
    MO(2) = \[ \psi_{2} = C_{2}^{1} \varphi_{1} + C_{2}^{2} \varphi_{2} + C_{2}^{3} \varphi_{3} + \ldots \]
    MO(3) = \[ \psi_{3} = C_{3}^{1} \varphi_{1} + C_{3}^{2} \varphi_{2} + C_{3}^{3} \varphi_{3} + \ldots \]
    \( C_{i}^{a} \) - coefficients for MO(1), \( C_{i}^{a} \) - coefficients for MO(2) etc.

- And an examination of the coefficients tells us the bonding characteristics of the MO’s
Labelling molecular orbitals

1) Symmetry Label

- $\sigma$: spherical symmetry along the bond axis - same symmetry as $s$ orbital - no nodes pass through the bond axis (can be at right angles $\rightarrow \sigma^*$)

- $\pi$: one nodal plane which passes through the bond axis

- $\delta$: two nodal plane which pass through the bond axis (end on $d_{xy}$ or $d_{-x^2+y^2}$)

2) Bonding and anti-bonding label (already met this label)

- Nothing if bonding (no nodes between bonded atoms)

- Additional $^*$ if a nodal plane exits between the atoms, that is if the wavefunction changes sign as you go from one atom to the other.

Last Lecture

- Hybridisation $\rightarrow$ combining AO’s on one atom to $\rightarrow$ hybrid orbitals $\rightarrow$ hybridisation made consistent with structure

- Molecular orbital theory (delocalised view of bonding)
  - LCAO – all AO’s can contribute to a MO
  - n AO’s $\rightarrow$ n MO’s
  - Filled in same way as AO’s
  - Example of $H_2$

- Molecular orbitals for AO’s of different energy

- Linear Combination of Atomic Orbitals (LCAO)
  - Use of coefficient to describe (i) phase of interaction and (ii) size of contribution of a given AO
    $\psi_n = \sum_{\phi_n} C_n^* \phi_n$
Labelling molecular orbitals

3) Is there a centre of inversion? i.e. is it Centrosymmetric?
   - The final label indicates whether the MO has a centre of inversion

\[ p_x + p_x \]  \[ p_x - p_x \]

As you go from one side of wave function through the centre of the bond, the sign of the wavefunction reverses
\[ \rightarrow \] not centrosymmetric
\[ \rightarrow u = \text{ungerade or odd} \]

\[ \pi \]
\[ \pi^* \]

MO's sometimes labelled with the type of AO forming them e.g. \( \sigma \) or \( \sigma^* \)

2nd row Homonuclear Diatomics

- Li-Li \( \rightarrow \) Ne-Ne
  - Possible interactions between 1s, 2s and 2p
    - \( \sigma \) bonding - s and s, p_x and p_x
    - \( \pi \) bonding - p_x and p_x, p_y and p_y

Objectives – a fundamental understanding

- Wave mechanics / Atomic orbitals
  - The flaws in classical quantum mechanics (the Bohr Model) in the treatment of electrons
  - Wave mechanics and the Schrödinger equation
  - Representations of atomic orbitals including wave functions
  - Electron densities and radial distribution functions
  - Understanding shielding and penetration in terms of the energies of atomic orbitals

- Bonding
  - Revision of VSEPR and Hybridisation
  - Linear combination of molecular orbitals (LCAO), bonding / antibonding
  - Labelling of molecular orbitals (s, p and g, u)
  - Homonuclear diatomic MO diagrams
  - MO diagrams for Inorganic Complexes

Energy level diagram for \( \text{O}_2 \)

- 2s and 2p energies sufficiently different to give little interaction between each other – NO MIXING
  - Simple picture of the MO
    - Unpaired electrons \( \rightarrow \) Paramagnetic
    - Label MO’s starting from the bottom although often only valence orbitals
    - Energy difference too big to interact with valence orbitals
    - 1s AO’s very small \( \rightarrow \) very small overlap in lower levels (small \( \Delta E \))
Other possible interactions

- Can $\sigma$ interactions between $s$ and $p_z$ be important?
  - Depends on energy difference between $s$ and $p_z$.
  - If large then no effect.

- How does the energy of the 2s and 2p vary with Z (shielding / penetration)?

  Energy
  - Gap increases – 2p more effectively shielded - critical point between O and N.

MO diagram for N$_2$

- 2s and 2p energies sufficiently close for interaction → more complex.
  - 1$\pi$ and 2$\sigma$ shift to lower energy.
  - 3$\sigma$ shifted 4$\sigma$ shifted to high energy.
  - 3$\sigma$ now above 1$\pi$.
  - $\pi$ levels unaffected.

Making sense of N$_2$

- Take basic model for oxygen – no s p interaction.
  - Examine how the MO’s can interact.
  - $\pi$ and $\sigma$ cannot interact → zero overlap $\Rightarrow$ $\pi$ level remain the same.
  - Examine $\sigma$ – $\sigma$ interactions.

Bonding interactions can interact with each other 1$\sigma_u$ and 3$\sigma_u$.

Thus 1$\sigma_u$ goes down in energy and 3$\sigma_u$ goes up in energy.

Making sense of N$_2$

- Now examine the anti-bonding interaction (2$\sigma^*$ and 4$\sigma^*$).

Thus 2$\sigma^*$ goes down in energy and 4$\sigma^*$ goes up in energy.

For bonding with anti-bonding (1$\sigma$ – 4$\sigma$ or 2$\sigma$ – 3$\sigma$) the sign changes on one wave function $\Rightarrow$ zero overlap.
MO diagrams for 2nd row diatomics

- The effect of the overlap between 2s and 2p is greatest for the Li. The MO diagram changes systematically as you go across the periodic table.

- s–p mixing \( \rightarrow \) \( \text{B}_2 \) – paramagnetic and \( \text{C}_2 \) diamagnetic.

MO diagram for CO

- Same orbitals as homonuclear diatomics isoelectronic with \( \text{N}_2 \).
  - Different energies give rise to significant \( 2s \)-\( 2p \) mixing.
  - As heteronuclear diatomic the orbitals have either C or O character.

- \( 1\sigma \): \( \pi \) bond (uneven – more oxygen).
- \( 2\sigma \): Primarily oxygen (\( p_z \)).
- \( 3\sigma \): Primarily carbon (\( p_z \)).
- \( 2\pi^* \): Uneven – more carbon.
- \( 4\sigma \): C-O bonding (more C).

Homonuclear Diatomic MO energy diagrams

- No mixing \( \text{Li}_2 \) to \( \text{O}_2 \):
  - \( 2\sigma^* \)
  - \( 2\pi \)
  - \( 1\pi_u \)
  - \( 3\sigma g \)
  - \( 4\sigma^* u \)

- Mixing \( \text{N}_2 \) to \( \text{Ne}_2 \):
  - \( 2\sigma^* \)
  - \( 1\pi_u \)
  - \( 3\sigma^* \)
  - \( 4\sigma^* \)
  - \( 1\sigma_g \)

What about triatomic molecules? MO treatment of BeH\(_2\)

- VSEPR \( \rightarrow \) linear molecule, \( \text{H} \rightarrow \text{Be} \rightarrow \text{H} \): \( \text{Be} \) \( 1s^2 \) \( 2s^2 \) \( 2p^0 \), \( \text{H} \) \( 1s^1 \).
- Examine interaction of 6 AO with each other: 2 H \( 1s \), Be \( 2s \) and \( 2p_x \), Be \( 2p_y \), Be \( 2p_z \) \( \rightarrow \) 6 MO’s.

Interaction between H \( 1s \) and Be \( 2s \):
- Bonding
- Anti-bonding

Interaction between H \( 1s \) and Be \( 2p_z \):
- Bonding
- Anti-bonding

Each of these is delocalised over three atoms and can hold up to two electrons.

\( p_z \) and \( p_y \) have zero overlap \( \rightarrow \) non bonding.
An introduction to Molecular Orbital Theory

Lecture 6 More complex molecules, CO and bonding in transition metal complexes

Prof. S.M.Draper
SNIAMS 2.5
smdraper@tcd.ie
Last lecture

- LCAO
  - Interaction of AO’s with different energy → lower AO has bigger contribution
  - Representing contribution as coefficient

- AO interactions that were possible → MO’s
  - positive, negative and zero overlap
  - labelling of MO’s (σ, π, *)

- 2nd row homonuclear diatomics
  - 2s – 2p mixing occurs up to N → energy different too big after this (O₂, F₂)
  - Difference in MO diagram for N₂ and O₂

- Molecular orbital treatment of BeH₂

MO treatment of H₂O

- H₂O is not linear – but why?
  - We will examine the MO’s for a non linear tri-atomic and find out.
  - What orbitals are involved – 2 H 1s O 2s O 2pₓ O 2px and O 2pz

- Let’s start by creating MO’s from the hydrogen 1s orbitals.

- Taking the in-phase pair first- it will interact with O 2s and O 2pz (zero overlap with O 2px and O 2py)

- Problem - This is mixing three orbitals → must produce three orbital

MO’s of H₂O

- Three orbitals → three MO’s
  - Bonding
  - anti-bonding
  - approx. -2pz + H
  - approx. 2pₓ - 2s + H
  - approx. 2s + 2pz (a little) + H

MO’s of H₂O

- Out of phase H 1s orbitals
  - Only interact with px → 2 MO’s
  - Zero overlap with py

- Bonding
  - approx. 2pₓ + H
There are not two lone pairs!

Slightly bonding Pz
Non bonding Py

Very different to the VB concept of two identical sp^3 filled orbital

MO theory correct.

Energy level diagram for H_2O

\[ \text{H}_2\text{O} \]

\[ \text{O} \quad \text{H} \quad \text{O} \quad \text{H} \]


Comparison of H_2O and BeH_2

- Both cases of XA_2 \rightarrow same MO – different No of electrons
  - Bonding MO’s as a function of A-X-A bond angle

BeH_2 linear
BH_2 131°
CH_2 (t) 134°
CH_2 (s) 102°
NH_2 103°
OH_2 105°

π MO’s of Benzene

- π bonding is more important for reactivity – independent of σ (zero overlap)
  - six p_\text{x} orbitals \rightarrow combine to form six MO’s

- Different ways of arranging six px orbitals on a ring
  - Lowest energy – all in phase
  - Degenerate levels (1 nodal plane \rightarrow 2 nodes)
  - Degenerate levels (2 nodal planes \rightarrow 4 nodes)
  - Highest energy – all out of phase (3 nodal planes \rightarrow 6 nodes)
  - Energy increases with number of nodes – as in AO’s
  - Also the number of nodes on a ring must be even \rightarrow continuous wavefunction

- Lowest energy all in phase
  - All coefficients the same

π MO’s of Benzene

- Next occupied degenerate pair \rightarrow 1 nodal plane
  - Two ways of doing this – between atoms and through a pair of atoms
  - As the wavefunction goes through 0 (at the node) the smooth wavefunction has smaller coefficients next to the node zero at the node

- 2 electron per MO spread over 6 atoms
  - Compare with Lewis structure with individual double bonds
  - With local bonding have to resort to resonance structures to explain benzene
**MO diagram for CO**

- Same orbitals as homonuclear diatomics
  - different energies give rise to significant $2s - 2p$ mixing
  - confusing set of orbitals
  - $4\sigma$: C-O anti-bonding (more C)
  - $2\sigma^*$: $\pi^*$ (uneven – more carbon)
  - $3\sigma$: Primarily carbon ($p_z$)
  - $1\pi$: $\pi$ bond (uneven – more oxygen)
  - $2\sigma$: Primarily oxygen ($p_z$)
  - $1\sigma$: C-O bonding interaction (more O)

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**Interaction of the CO 3$\sigma$ with $d$ orbitals**

- Three sets of interaction based on symmetry of ligand AO’s
  - Generally applicable to $\sigma$ bonding TM ligands
  - $a_{1g}$ all ligand AO’s in phase
    - Interaction with $s$ orbital $\rightarrow$ 1
    - $t_{1u}$ ligands in one axis contribute
    - With opposite phase – one nodal plane
    - Interaction with $p$ orbitals $\rightarrow$ 3

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**The HOMO and LUMO of CO**

- For chemical reaction the HOMO (Highest Occupied Molecular Orbital) and the LUMO (Lowest unoccupied Molecular Orbital) are the most important.
  - HOMO – $3\sigma$
    - low energy Oxygen orbitals Come from standard $\pi$ interaction
    - makes $2\sigma$ mainly O $p_z$ in $3\sigma$ mainly C $p_z$
    - Some anti-bonding mixes in due to sp mixing
  - LUMO – $2\sigma^*$
    - comes from standard $\pi^*$ interaction
    - however lower oxygen orbital means $\pi$ has more oxygen and $\pi^*$ more carbon

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**Interaction of the CO 3$\sigma$ with $d$ orbitals**

- $e_g$ ligand phases have two nodal planes
  - Interact with $d$, $d_{z^2}$ $\rightarrow$ 2
  - Three remaining $d$ orbitals point between ligands
    - zero overlap ($t_{2g}$)
MO diagram for Tm (σ-L)_6

- Electrons from filled σ orbitals on the ligands fill all the bonding orbitals
- d electrons fill t^2g (non bonding) and e^* (antibonding)
- Example is d^6 - e^* g
- These are the orbitals considered in ligand field theory. Note the e^* g is anti-bonding!
- The size of ∆oct is important and it is decided by the π interaction

π interactions with TMs

- Orbitals with π character can interact with the t^2g d orbitals
  - Must be correct symmetry (t^2g) → 3 arrangements possible using d_ν, d_σ, d_π
- Two extreme situations
  - Ligand orbitals are low energy and filled (e.g. F)
  - Ligand orbitals are high energy and empty (e.g. CO)

Ligand Orbitals are high energy and empty: High ligand field situation

- Ligand orbitals are high energy and empty (e.g. CO 2π^*)
  - Filled orbitals interact in a π fashion
  - Bonding combinations are reduced in energy (like d orbitals)
  - Antibonding combination are raised in energy and empty (like ligand orbitals)
  - Strong interaction with empty orbitals with π interaction leads to increase in ∆oct (box shows the orbitals considered in ligand field theory)

Ligand orbitals are low energy and filled: Low ligand field situation

- Ligand orbitals are low energy and filled (e.g. F)
  - Filled orbitals interact in a π fashion
  - Bonding combinations are reduced in energy and filled (like ligand orbitals)
  - Antibonding combination are raised in energy and filled (like d orbitals)
  - Strong interaction with filled orbitals with π interaction leads to reduction in ∆oct (box shows the orbitals considered in ligand field theory)
1. Explain the MO approach for the interaction of
   a) two s orbitals of identical energy
   b) two s orbitals of slightly different energy
   c) two s orbital of very different energy.

2. Consider the bonding in the molecule O₂
   a) Draw a Lewis structure for O₂
   b) Determine the hybridization
   c) Perform an MO treatment of O₂
      (i) What orbitals are involved?
      (ii) what interactions are possible?
      (iii) what do the resulting MO’s look like?
      (iv) sketch an MO energy level diagram.
   d) What difference are there in the details of the bonding diagram between the Lewis and MO treatments

3. Consider the molecule BeH₂
   a) Draw a Lewis structure
   b) Determine the hybridization
   c) Perform an MO treatment of O₂
      (i) What orbitals are involved.
      (ii) Generate appropriate ‘ligand’ MO’s and interactions with the central atom
      (iii) what do the resulting MO’s look like?
      (iv) sketch an MO energy level diagram.
   d) What difference are there in the details of the bonding diagram between the Lewis and MO treatments

4. Perform the same analysis for BeH₂, HF, BH₃, and CH₄

5. Use molecular orbital theory to explain
   a) The splitting of the d orbitals by sigma interactions with ligands
   b) The effect of π interaction on the ligand field strength.