Where have we been?

Lectures 1 and 2

Bohr’s Model/ Wave Mechanics/ Radial and Angular Wavefunctions/ Radial Distribution Functions/ s and 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

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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
  - Radial wave functions same for all $3d$ orbital
  - Max probability at $r = 9 \ a_0$
- AOs with no nodes have max probability at same radius as Bohr model
- $4d$ orbital has 1 node

$$R(3d) = \frac{1}{9\sqrt{30}} \left( \frac{Z}{a_0} \right)^{3/2} (\rho r)^2 e^{-\rho r/2}$$
$d$ orbitals – angular functions

- Angular functions same for $d_{xy}$, $d_{yz}$, $d_{xz}$, $d_{z^2}$, $d_{x^2-y^2}$ irrespective of $n$
  → same shape for 3$d$, 4$d$, 5$d$ orbitals using boundary surfaces

- Five different angular functions e.g.
  $$Y(d_{xz}) = \left( \frac{15}{16\pi} \right)^{1/2} \sin(\theta)\cos(\theta)\cos(\phi)$$

- Two angular nodes planes
  → orthogonal to $s$ and $p$
  e.g. $d_{xy}$ Nodal planes in yz and xz
  (+ve lobe points between +x and +y axes)
**f orbitals**

- Almost no covalent bonding because metal orbitals are so contracted → shape not really important

- $l = 3$ → Seven different angular functions for each n ($n \geq 4$)
  - f block is 14 element wide, same shape for 4f, 5f etc
  - Radial functions same for all nf orbitals
  - Three angular nodes (nodal planes) → orthogonal to s, p and d orbitals
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 \( n - l - 1 \)
    - \( n = 3 \quad 3s \rightarrow 2 \text{ nodes} \quad 3p \rightarrow 1 \text{ node} \quad 3d \rightarrow 0 \text{ nodes} \)
    - \( 3s \) 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 \( Z_{\text{eff}} = Z - S \)
    \( S \) = a screening or shielding constant

- Li atom – why is the electronic configuration \( 1s^2 2s^1 \) and not \( 1s^2 2p^1 \)?
  - \( 1s \) electrons shield the valence electron from the nuclear charge
  - \( 2s \) penetrates more effectively → feels a greater nuclear charge
  - \( 2p \) penetrates less effectively
  - \( 2s \) is filled first

- \( E(1s) < E(2s) < E(2p) \)
- \( E(ns) < E(np) < E(nd) \)
• Shielding and penetration  \( \rightarrow \)  \( E(\text{ns}) < E(\text{np}) < E(\text{nd}) < E(\text{nf}) \)

• This gives rise to the electronic configuration of atoms and the order of elements in the periodic table

• Orbitals 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)

• \( E(\text{4s}) < E(\text{3d}) \)
  K, Ca

• \( E(\text{6s}) < E(\text{5d}) \approx E(\text{6f}) \)
  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 given n shell have the same energy

- Penetration follows $s > p > d > f$

- 3d shielded very effectively by orbitals of $n \leq 3$

- 3d almost does not change in energy with Z until $Z = 19$

- 4s filled, $n = 4$ does not shield 3d effectively $\rightarrow$ energy drops

- Similar pattern for 4d and 4f
The Transition Metal Hiccup!

- For K and Ca the $E(3d) > E(4s)$ so 4s filled first,
- At Sc the $E(3d) < E(4s)$ (but very close)
- For Transition metals $E(3d) < E(4s)$ so the 4s electrons are lost first when ionized

Energy

\[
\begin{align*}
4p & \{ \quad \quad \quad \quad \quad \\
3d & \{ \quad \quad \quad \quad \quad \\
4s & \quad \quad \quad \quad \quad \\
\end{align*}
\]

Increasing $Z$
Drawing representations of AO’s

- Need to be able to draw AOs when considering their interactions i.e. when they form molecular orbitals (MOs).
  - Simple diagrams are all you need !!!!
Making Bonds
Localised Bond Pictures
Revising JF Lewis Bonding / VSEPR

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

Each H has a share in the 2 electrons → H – H

E.g. $H_2$  H • + × H → H • H

H •
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.

- Diatomics
  - \( F_2 \)
    
    \[
    \begin{array}{c}
    \text{F} \\
    \text{F}
    \end{array}
    \]
    
    + \[
    \begin{array}{c}
    \times \\
    \times
    \end{array}
    \]
    
    $\rightarrow$ \[
    \begin{array}{c}
    \text{F} \\
    \times
    \end{array}
    \]
    
    2 electrons shared $\rightarrow$ bond order = 1
    
    $F - F$

  - \( O_2 \)
    
    \[
    \begin{array}{c}
    \text{O} \\
    \times
    \end{array}
    \]
    
    + \[
    \begin{array}{c}
    \times \\
    \times
    \end{array}
    \]
    
    $\rightarrow$ \[
    \begin{array}{c}
    \times \\
    \times
    \end{array}
    \]
    
    4 electrons shared $\rightarrow$ bond order = 2
    
    $O = O$
Lewis bonding – polyatomics (H₂O)

- Oxygen (Group 16) has 8 electrons, each hydrogen (Group 1) has 1 electron
- Oxygen has two lone pairs

\[
\begin{align*}
2 \text{H} & \quad \text{O} \\
\text{XX} & \quad \text{XX} \\
\text{XX} & \quad \text{XX}
\end{align*}
\]

- 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 \(\rightarrow\) 4 directions to consider
  - Accommodate 4 directions \(\rightarrow\) Tetrahedral shape
  - \(\text{H}_2\text{O}\) is bent with H-O-H angle of 104.5°
  - Compares with a perfect tetrahedral of 109.45° \(\rightarrow\) lone pair repulsion
Lewis bonding – polyatomics (ethene)

4 electrons shared between the Carbon atoms $\rightarrow$ bond order = 2 $\rightarrow$ C = C
Each Carbon –hydrogen bond involves the sharing of electrons $\rightarrow$ C – H

- Shape – VSEPR
  - Electrons repel each other
  - Carbon atoms have 3 directions – bond to C and two bonds to two H
  - Accommodate 3 bond direction $\rightarrow$ 120° in a plane (molecule is flat)
Lewis structures – that break the Octet Rule

- Some structures do not obey the 8 electron rule. These usually contain a 3rd row element as the central atom e.g. PF₅

\[
\begin{array}{c}
\text{F} \\
\quad \times \\
\text{F} \times \text{P} \times \text{F} \\
\quad \times \times \times \\
\end{array}
\quad \begin{array}{c}
\text{F} \\
\quad \times \\
\text{P} & 90^\circ & \text{F} \\
\quad \times \times \times \\
\text{F} & \text{F} & \text{F}
\end{array}
\]

(only the electrons round the P are shown for clarity)

- F atoms have 3 lone pairs (6 electrons) + 2 in each bond \( \rightarrow 8 \)
- P atom has 5 bond pairs with 2 electrons each \( \rightarrow 10 \) electrons!
- Overall 5 directions to accommodate \( \rightarrow \) trigonal bipyramidal
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 AOs
  - ON THE SAME ATOM

- Use Lewis model (number of electron pairs) \( \rightarrow \) hybridisation \( \rightarrow \) shape.
  - E.g. BeH\(_2\), Be – Group 2
  
  \[
  \text{H} \times \text{Be} \times \text{H}
  \]

- Correctly predicted by VSEPR to be linear – can we explain it using AOs
- Not if we think the Be electrons are in 2s spherical orbitals
  - Mix one s with one \( p_z \) orbital \( \rightarrow \) two \( sp \) hybrid orbitals