

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



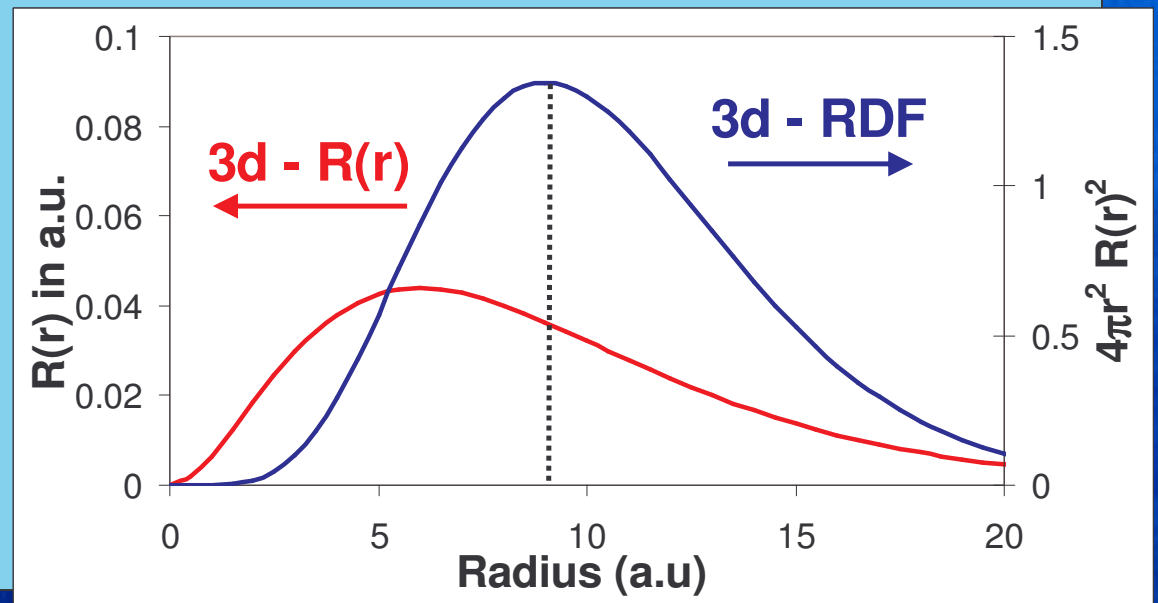
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d orbitals – wave functions

- 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

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

- 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



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 $3d, 4d, 5d$ orbitals using boundary surfaces

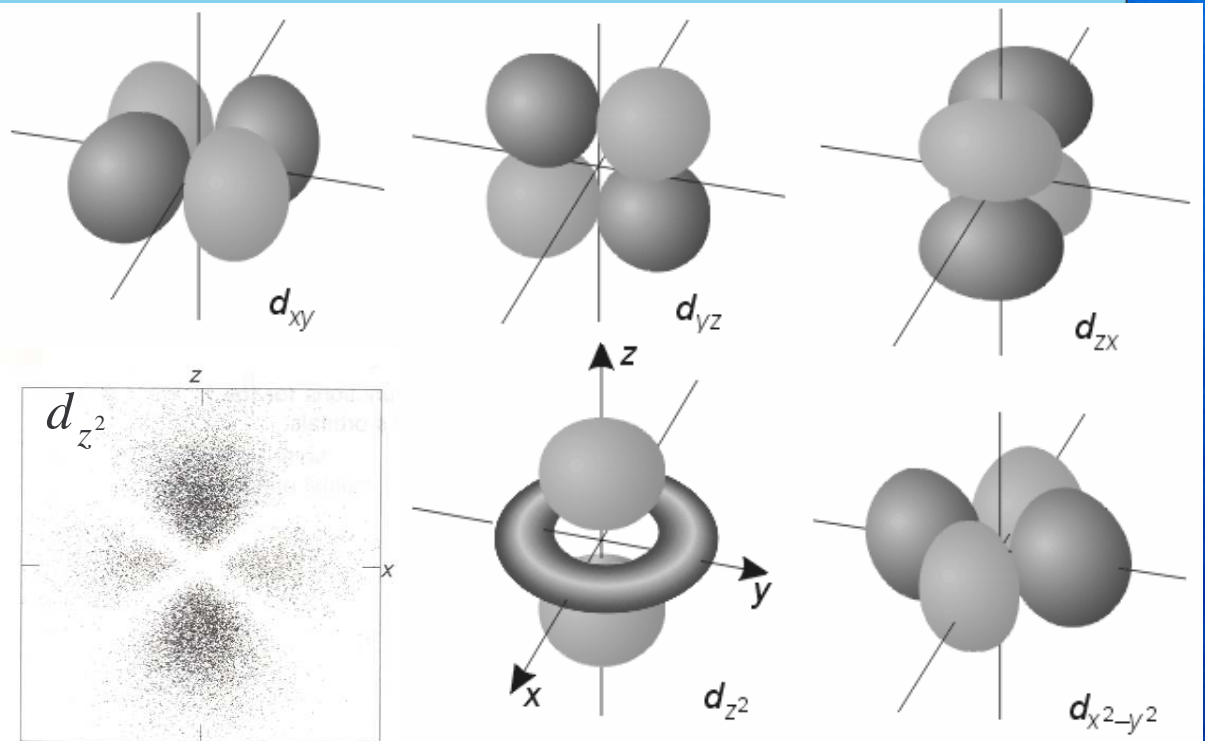
- Five different angular functions e.g. $Y(d_{xz}) = \left(\frac{15}{16\pi}\right)^{1/2} \sin(\theta)\cos(\theta)\cos(\phi)$

- Two angular nodes planes

→ orthogonal to s and p

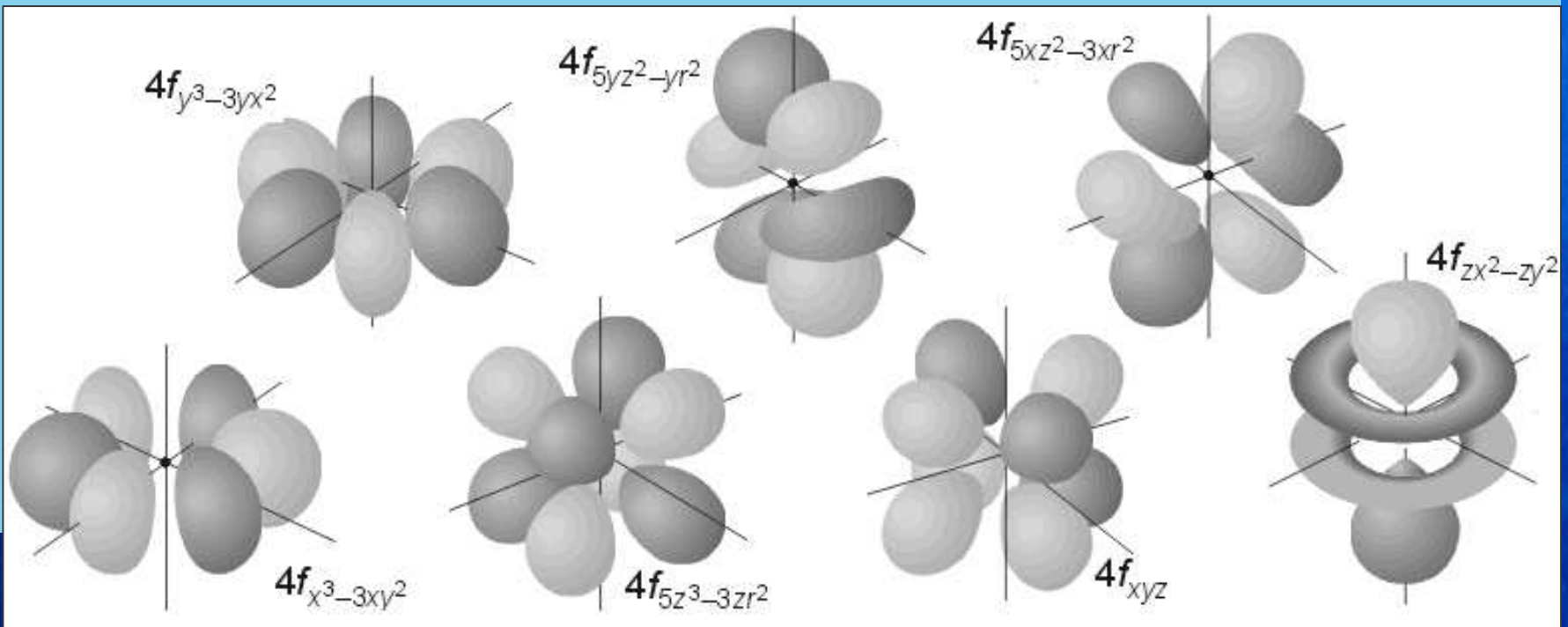
e.g. d_{xy} Nodal planes in yz and xz

(+ve lobe points between + x and + y axes)



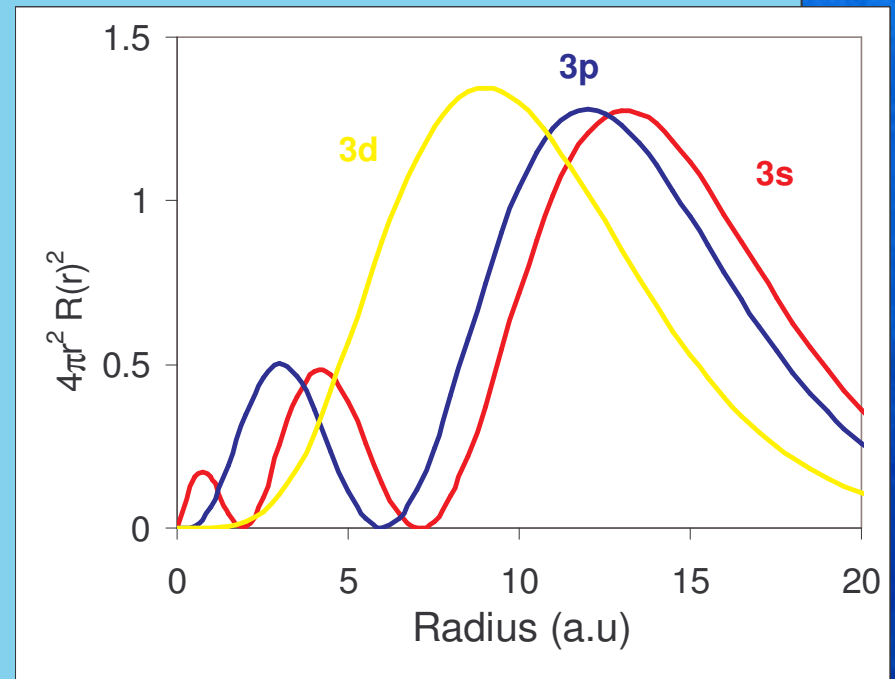
f orbitals

- Almost no covalent bonding because metal orbitals are so contracted → shape not really important
- $l = 3 \rightarrow$ 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 $n - l - 1$
 - $n = 3$ $3s \rightarrow 2$ 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

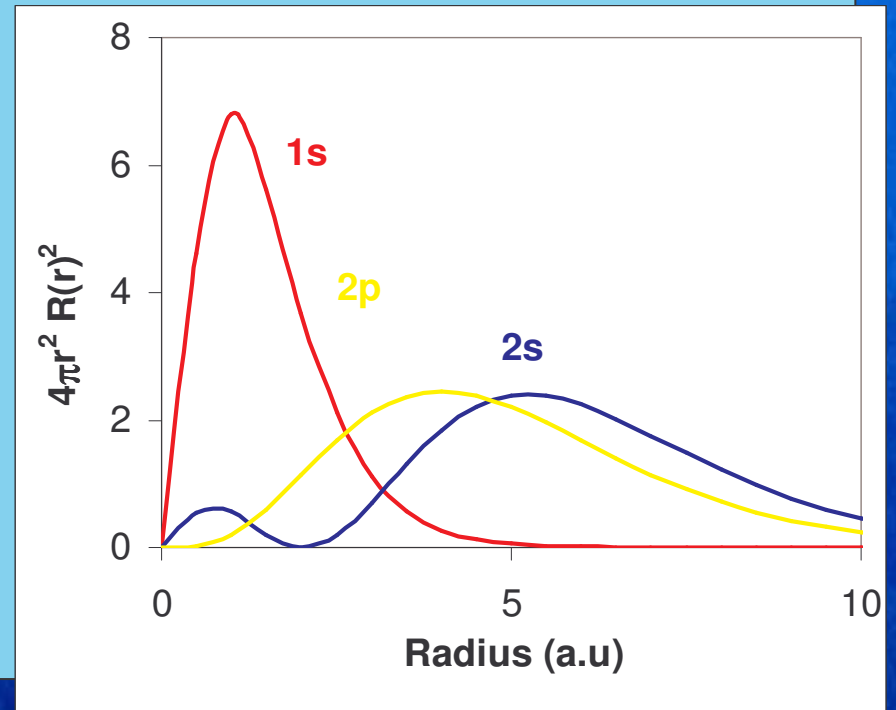
– Effective nuclear charge $Z_{\text{eff}} = Z - S$
S = a screening or shielding constant

- 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

- $E(1s) < E(2s) < E(2p)$

- $E(ns) < E(np) < E(nd)$

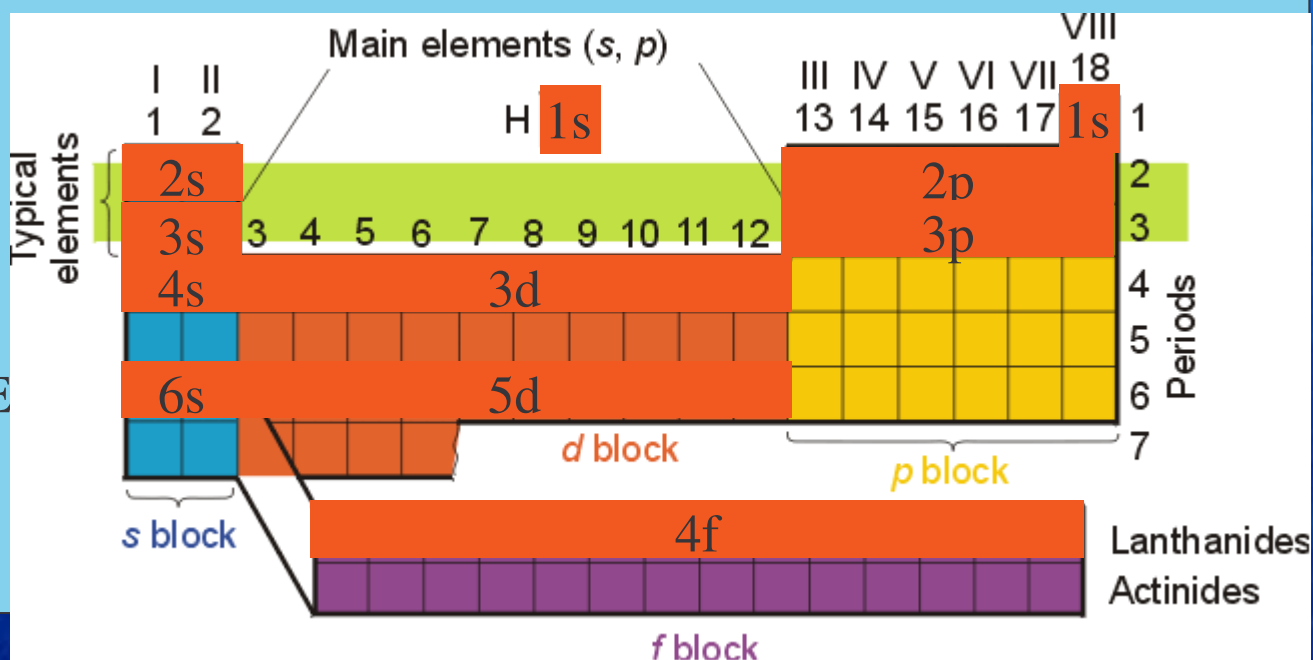


Periodic table

- Shielding and penetration → $E(ns) < E(np) < E(nd) < E(nf)$
- 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)

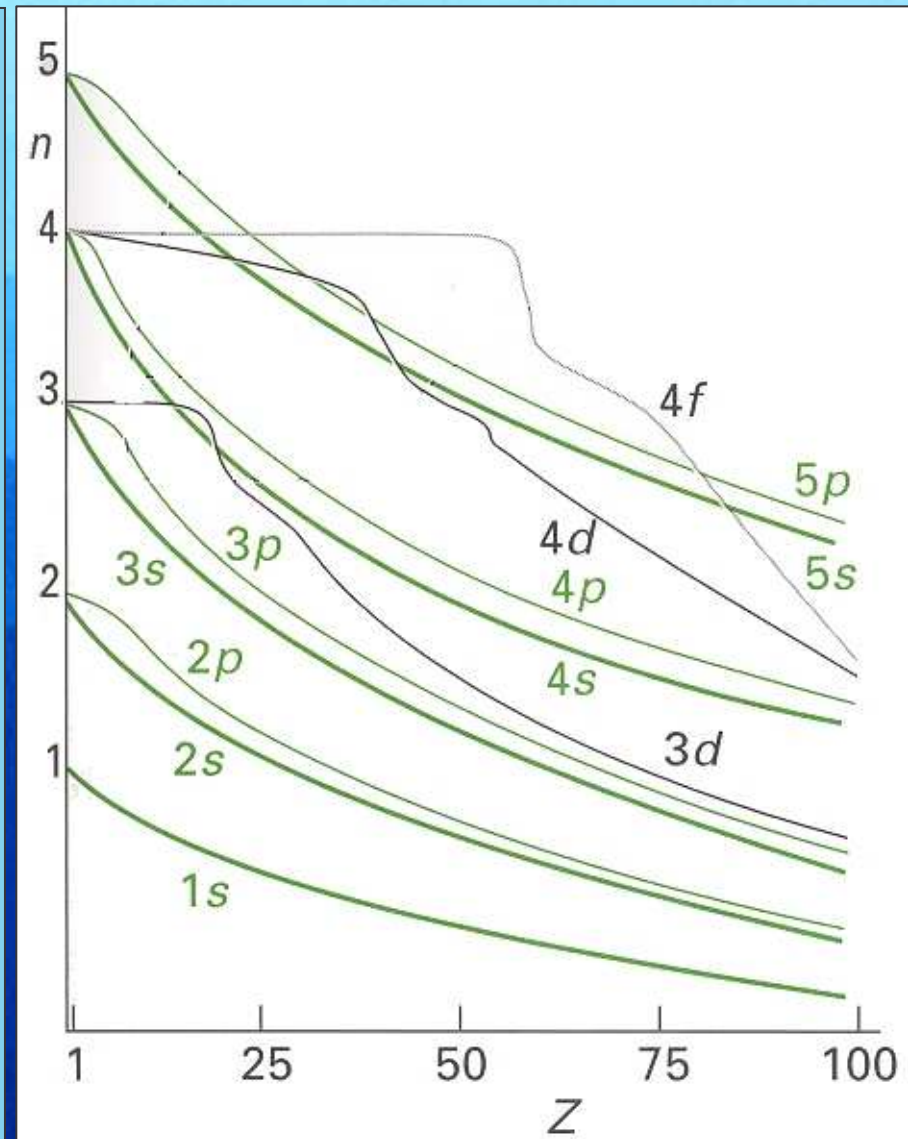
- $E(4s) < E(3d)$
K, Ca

- $E(6s) < E(5d) \approx E(4f)$
La [Xe] $6s^2 5d^1$
Ce [Xe] $6s^2 4f^2$



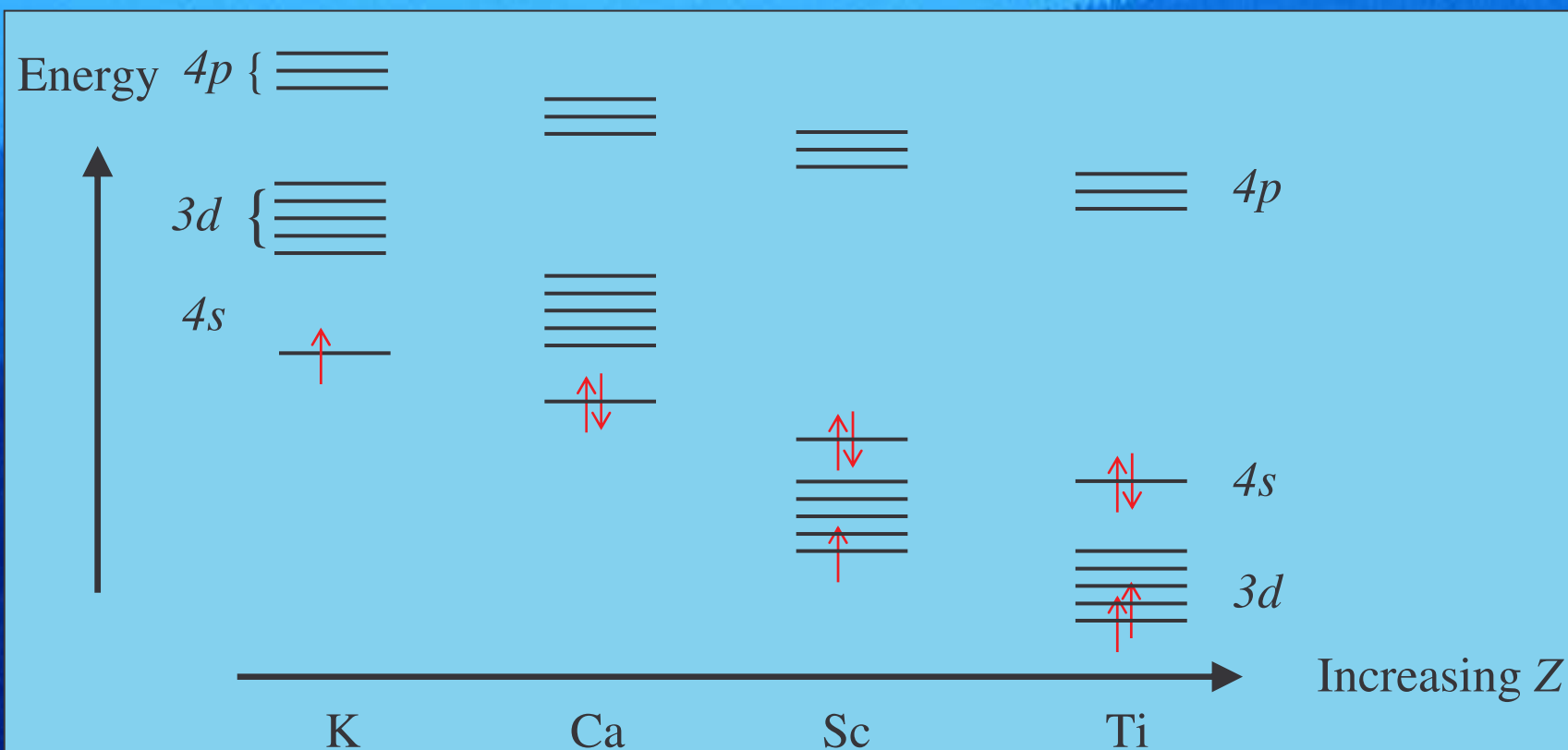
More complex results of penetration and shielding Energy levels vs atomic number

- 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 $4f$



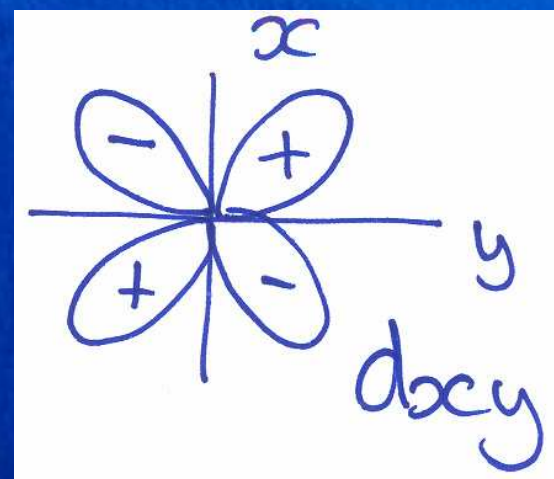
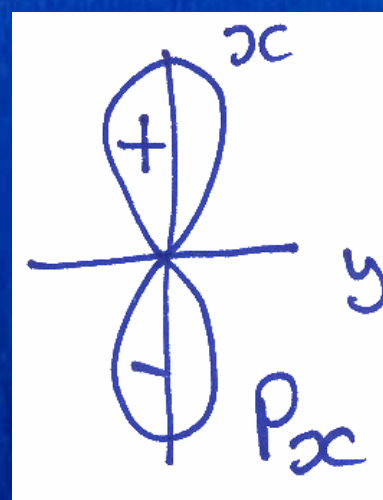
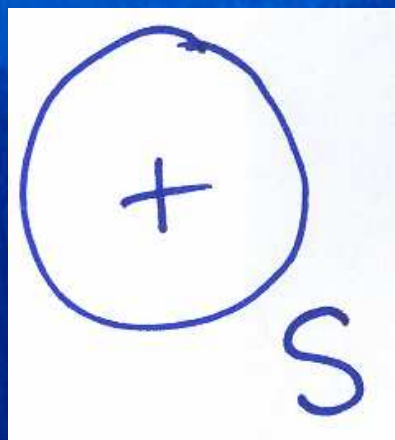
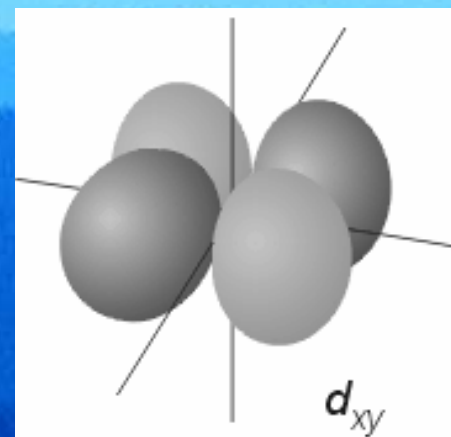
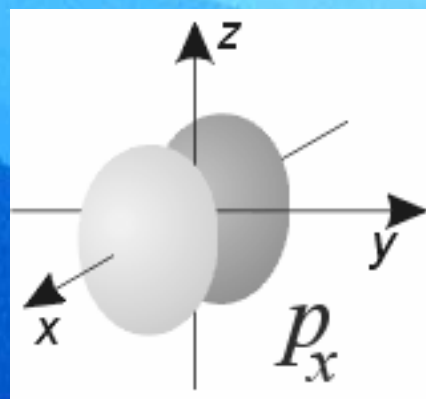
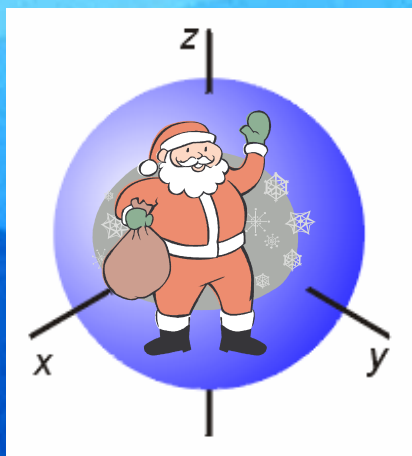
The Transition Metal Hiccup !

- 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



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 !!!!

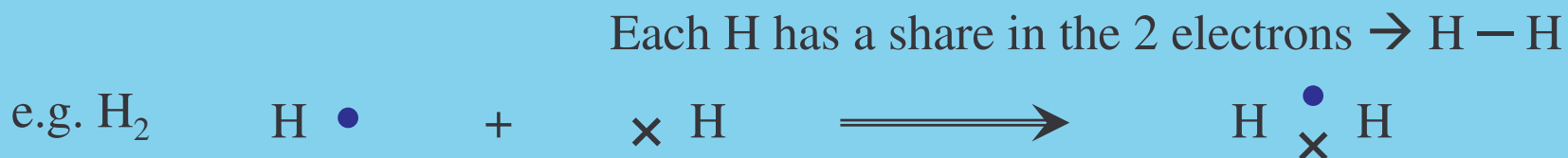


Making Bonds

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)



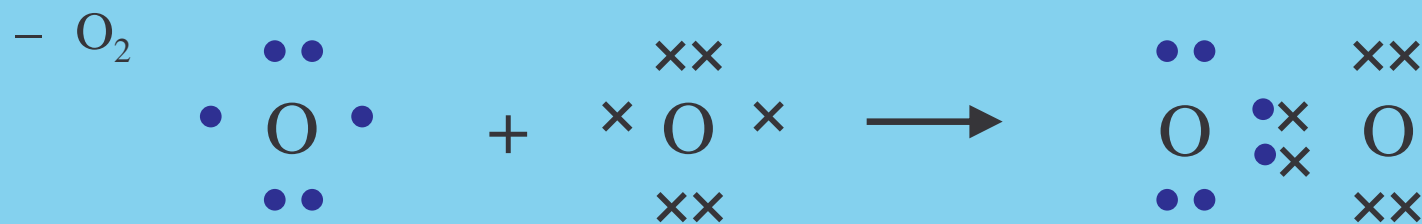
Lewis bonding

- 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



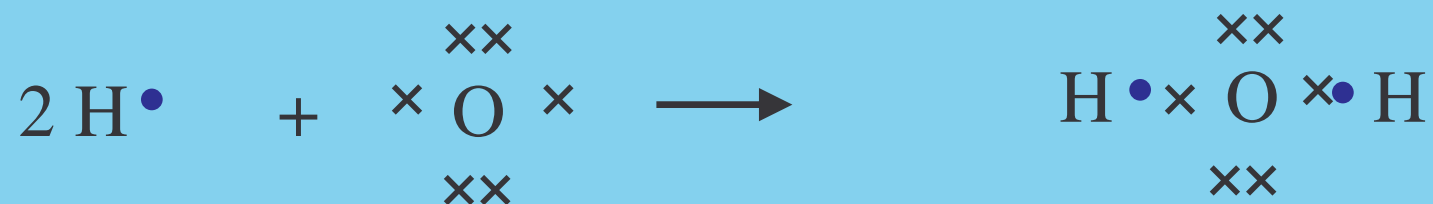
2 electrons shared \rightarrow bond order = 1
 $F - F$



4 electrons shared \rightarrow bond order = 2
 $O = O$

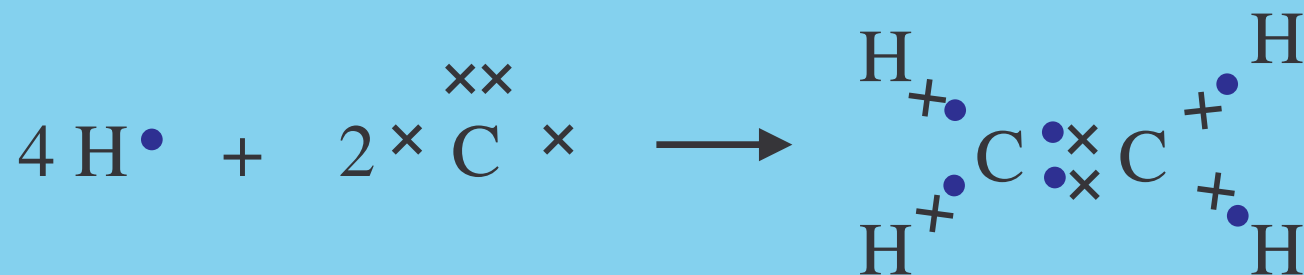
Lewis bonding – polyatomics (H₂O)

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



- 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)

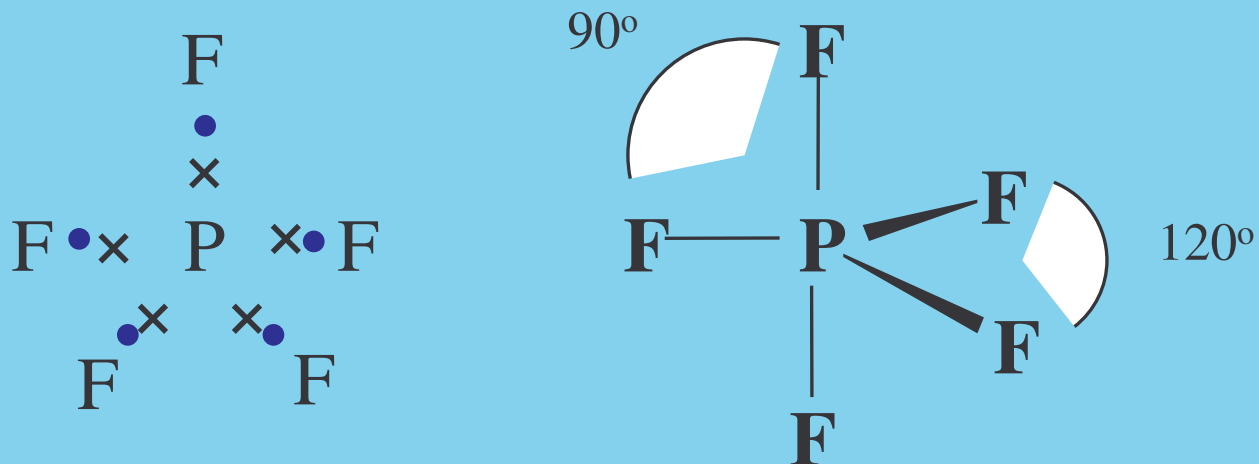


4 electrons shared between the Carbon atoms \rightarrow bond order = 2 \rightarrow C = C
Each Carbon –hydrogen bond involves the sharing of electrons \rightarrow C – H

- 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



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

- F atoms have 3 lone pairs (6 electrons) + 2 in each bond → 8
- P atom has 5 bond pairs with 2 electrons each → 10 electrons !
- Overall 5 directions to accommodate → 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) → hybridisation → shape.
 - E.g. BeH_2 , Be – Group 2



- 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 → two sp hybrid orbitals