ATOMIC STRUCTURE NOTES

Hydrogenic Atoms

Orbital Angular Momentum & Electron Spin

Quantum Numbers –
Principal Quantum Number,   - Quantized Energy
Orbital Angular Momentum, *l*   - Quantized Orbital Angular Momentum
Magnetic Quantum Number, m_l. - Quantized Orientation of angular momentum.

The allowed energies are determined by n, and for a hydrogenic atom of atomic number Z:

$$E = -\frac{hcZ^2\Re}{n}$$

The zero energy is when electron and nucleus are widely separated. $1/n^2$ relationship for E indicates that the energy levels converge at high (less negative) energies. Zero energy = ionisation.

Electron Spin –
2 more Quantum Numbers are needed to define the state of an electron (spin).
s = spin angular momentum and always has a value of ½.
m_s = spin magnetic quantum number, and is either +½ or –½ .
These Quantum Numbers specify the orientation of the spin with respect to a chosen axis. Spin-up and Spin-down (α and β).

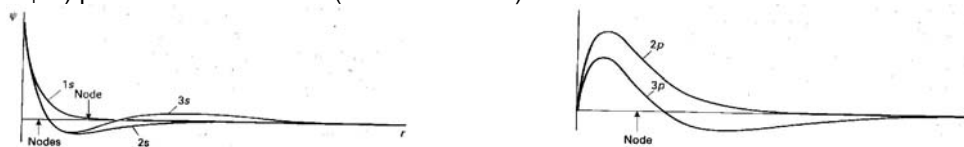### Shapes and Energies of Atomic Orbitals

Radial Shapes of Hydrogenic Orbitals –
A Hydrogenic orbital can be written as the product of a function R of the radius and a function Y of the angular coordinates. R determines variation with distance. Y expresses the shape of the orbital.
Where the radial wavefunction passes through zero is a radial node. Where the angular wavefunction passes thru zero is an angular node or nodal plane.
1s (n=1, l=0, m_l=0) decays exponentially with distance from the nucleus and never passes thru zero.
An orbital with Quantum Numbers n and l in general has n–*l*–1 radial nodes. Hence 2s (n=2, l=0 m_l=0) passes thru zero once (one radial node).
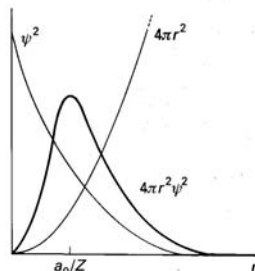

Multi-electron Atoms

Penetration & Screening

Shielding –
An electron is assumed to experience an effective nuclear charge (Z_{eff}) dependent on radius (location), n and *l* (differing radial distribution functions). The reduction of the true nuclear charge to the effective nuclear charge is called **shielding**. $Z_{eff} = Z - \sigma$.
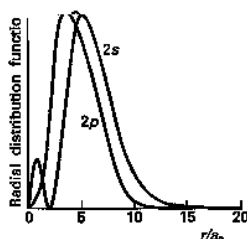
The closer to the nucleus that an electron can penetrate in an atom, the closer the value of Z_{eff} to Z, because the electron is repelled less by other electrons. For example, a 2s electron can penetrate, while a 2p electron is not as effective at this because it has a nodal plane through the nucleus. Therefore, it is more shielded from the nucleus by the electrons of the core. We can conclude that a 2s electron has lower energy (more bound) than a 2p, so for Lithium the ground state configuration must be $1s^2 2s^1$. It usually follows that: ns > np > nd > nf

Radial Distribution Functions

(for 1s orbital)

In general, the distance at which the electron is most likely to be found decreases with nuclear charge. The distance also increases as n increases since the higher the energy, the more likely the electron is to be further away. Maximum (most likely) position occurs at a_0/Z.

Although 2p is on average closer, the 2s has a higher probability of being close to the nucleus because of the inner maximum.

Periodicity

Ionic Radii

Metallic Radius = half the distance between nuclei of neighbouring atoms.

Covalent Radius = half the inter-nuclear separation of neighbouring atoms of the same element.

General Periodic Trends – descending a group atomic radii increase, and with s & p blocks they decrease from left to right across period.

Period 6 is different, due to lanthanide contraction. The 4f orbitals are being occupied by the lanthanides, and these have poor shielding properties. The repulsions being added on crossing the f-block fail to compensate for the increasing nuclear charge, so all the electrons are drawn inwards (Z_{eff} increases).

Similar reasoning behind the small increase in radius from Al to Ga – d-block with poor shielding.

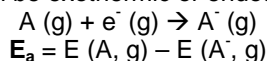Increase in radius of an anion is due to increased electron-electron repulsions.

Smaller radius of cations is due to less repulsion and also that there is a less in valence electrons (leaving a more compact core).

Ionization Energy

Follows pattern of Z_{eff}. Correlate with atomic radii – small radius = high E_I.

Electron Affinity

Electron-gain enthalpy - $\Delta_{eg}H$ is the standard enthalpy change per mole of atoms when a gas-phase atom gains an electron. Can be exothermic or endothermic.

$$A\ (g) + e^-\ (g) \rightarrow A^-\ (g)$$
$$E_a = E\ (A,\ g) - E\ (A^-,\ g)$$

A positive electron affinity indicates that the ion has a lower (more –ve), and so more favourable energy than the neutral atom. Its value is determined by the energy of the lowest unfilled orbital of the ground-state atom. An element has a high electron affinity if the additional electron can enter a shell where it experiences a strong effective nuclear charge. This is the case for elements in the top right of the periodic table.