

Chem1101 – Semester 1

Filling Energy Levels in Atoms Larger than Hydrogen

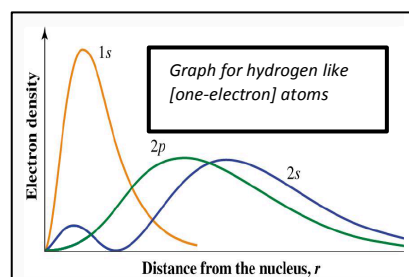
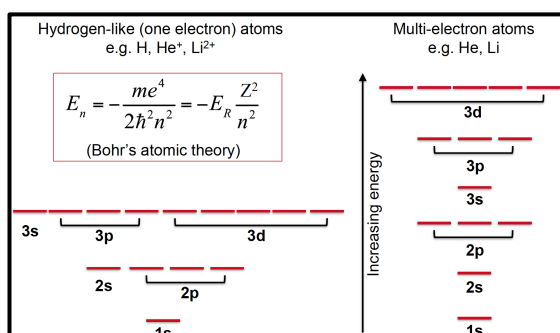
Write the electronic configuration of atoms and ions from the s and p blocks

Explain orbital shielding, and its effects

- Using the atomic orbitals obtained for the hydrogen atom, we fill orbitals beginning with the lowest energy. For helium (2 electrons),
 - Electron 1 - 1s orbital ($n=1, l=0, m_l=0$) with $m_s = -\frac{1}{2}$ (or $+\frac{1}{2}$)
 - Electron 2 - 1s orbital ($n=1, l=0, m_l=0$) with $m_s = -\frac{1}{2}$ (or $+\frac{1}{2}$)
- The ground state electron configuration of He is: $1s^2$, for H: $1s^1$

For multi-electron systems, n is no longer sufficient to predict energy levels. We now need to consider:

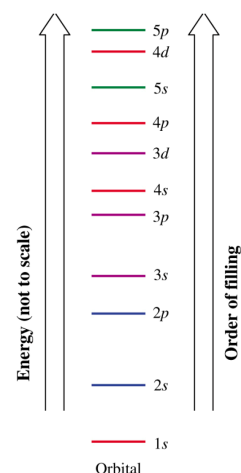
1. Electron-electron repulsion:	<ul style="list-style-type: none"> When we have more than one electron, the electrons within an orbital repel each other
2. Orbital Shielding:	<ul style="list-style-type: none"> When an orbital is occupied, it shields the interaction of the outer orbital with the nucleus. This alters the energy levels of the orbitals. Orbital shielding depends on the shape of the orbital: $s < p < d < f$ Orbitals of equal n nearest the nucleus have lowest energy: $s < p < d < f...$



- After He, the $n=1$ (1s) orbital is full.
- For a **1-electron atom**, 2s and 2p have the same energy [i.e. degenerate]
- For **multi electron atoms**, electrons in orbitals closer to the nucleus **shield** electrons that are further away. Shielding has the effect of decreasing the positive attraction from the nucleus, raising its energy.
- The 2s orbital has a lobe closer to the nucleus than the 2p orbital, so it is **less shielded**, and therefore has **lower energy**, hence will be filled first

Explain orbital shielding, and its effects cont.

- As the **angular momentum quantum number, l , increases**, the orbitals extend further from the nucleus. This means that the energy of an orbital **increases with l for a given n** .
- This effect is big enough that the energy of the **4s orbital is lower than 3d**. The order of increasing energies and of filling is shown in the diagram at right.



Paraphrase the Pauli exclusion principle, Aufbau principle, and Hund's rule

Pauli Exclusion Principle:	No two electrons in an atom may be in the same quantum state {i.e. no 2 electrons can have the same 4 quantum numbers - n, l, m_l, m_s }
Aufbau Principle:	Electrons in atoms tend to exist in the lowest possible energy configuration (or ground state)
Hund's Rule:	<ul style="list-style-type: none"> The lowest energy electron configuration in orbitals of equal energy is the one with the maximum number of unpaired electrons with parallel spins. Maximise number of parallel unpaired electron spins in degenerate [i.e. same energy] orbitals

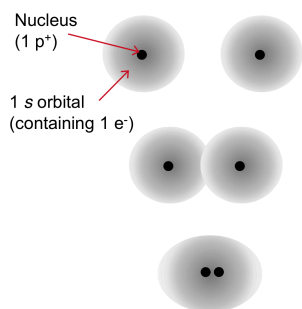
Identify any element from the electronic configuration of its atom or ion

Recognise the consequences of Hund's rule on the detailed electronic configuration of an atom

Having one electron in each p-orbital will keep the electrons as far from each other as possible to account for the repulsive potential energy between electrons.

Bonding – Molecular Orbitals (MO) theory

Explain how electron sharing leads to lowering of electronic energy in terms of increasing the de Broglie wavelength.



- 2 separate atoms
- As atoms come together, electrons begin to be shared between two nuclei. **Wavelength is increased since electrons have more space to move around. Hence momentum decreases and kinetic energy is decreased (de Broglie)**
- When nuclei are too close together, nuclei repel each other

- The equilibrium (minimum energy) bond length is approximately 1 Å
- The **Ångström** (Å) is a distance unit used to discuss atomic distances. **1 Å is 10⁻¹⁰ m (=0.1 nm).**
- The **Bohr radius** is the most probable distance between a proton and electron in a H atom. [*i.e. the distance from nucleus to outside part of orbital*] The **Bohr radius = 0.53 Å.**

Recognize a σ orbital and a σ^* orbital

Molecular orbits arise from the mixing of orbital in different phases.

- When two 1s orbitals in the same phase, mix, the **bonding MO (σ)** is formed with **lower energy**
- When two 1s orbitals in opposite phase, mix, the **anti-bonding MO (σ^*)**, which has a **node**, forms with a higher energy

Bonds that result from sigma orbitals are called sigma bonds

Draw out ground state electronic configurations for molecules and molecular ions given their allowed energy levels

Atoms/molecules each have a maximum no. of 2 electrons in each molecular and atomic orbitals

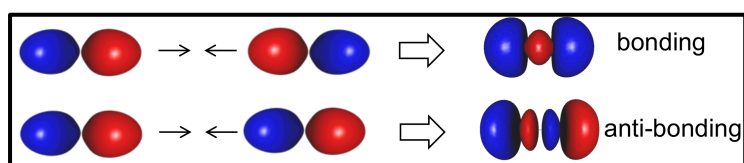
Total no. of atomic orbitals in component atoms = no. of molecular orbitals

i.e. 2 Hydrogen atoms are mixed to form 1 bonding orbital and 1 anti-bonding orbital

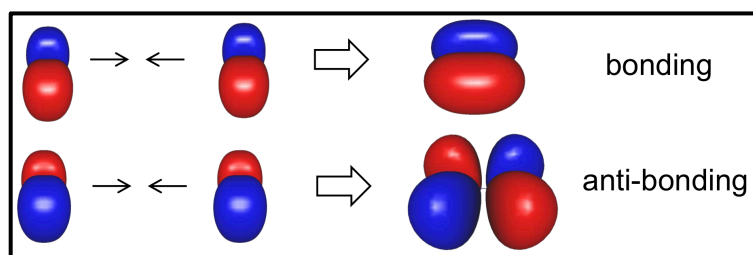
Recognise a bonding or antibonding orbital from the lobe representation

- P atomic orbitals give rise to **both σ and π molecular orbitals**
- There are 3 p orbitals in different orientations. When two these atoms approach, the p orbitals will interact differently**

1 pair of p orbitals will have an **end-on** interaction

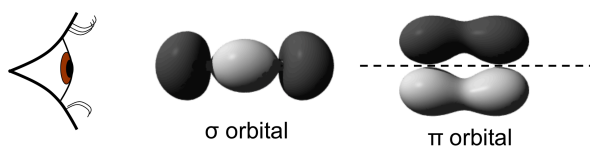


2 pairs of p orbitals will have a **side-on** interaction

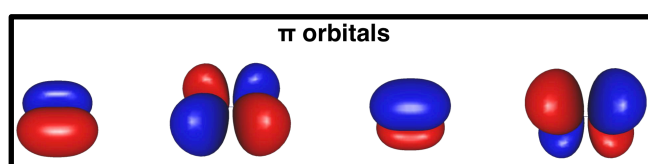
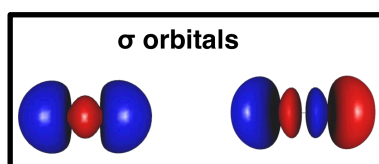


Recognize a π orbital, a π^* orbital and a non-bonding orbital

- Molecular orbitals are classified according to their symmetry
- Looking end-on, a molecular orbital may resemble an s-orbital, or a p-orbital.



- Those **without a node** in the plane containing both nuclei resemble an s-orbital and are denoted σ -orbitals.
- Those **with a node in the plane** containing both nuclei resemble a p-orbital and are denoted π -orbitals.



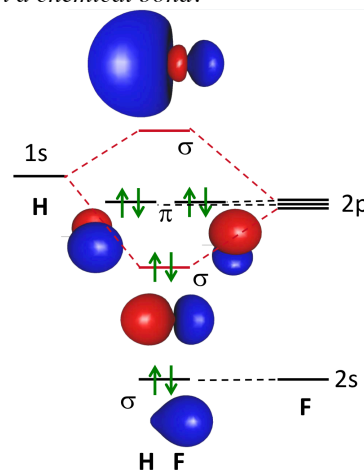
Distinguish between polar and apolar bonds in diatomic molecules and relate it to electron attraction of a nucleus (electronegativity)

Heteronuclear molecules: are formed through the mixing of different atomic orbitals gives rise to asymmetric molecular orbitals

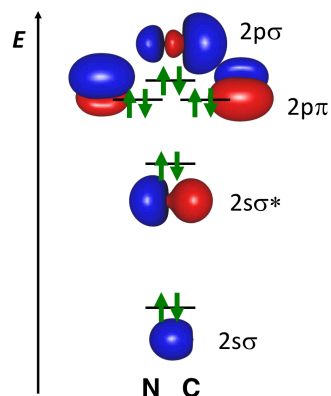
The bond between two elements with different electronegativities will be polar. The greater the difference, the more polar the bond becomes.

**Electronegativity is a measure of how strongly an atom attracts the electrons in a chemical bond.*

- Diatomic molecules with apolar bonds experience symmetrical forces, but the bonding electrons of other diatomic molecules such as HF have polar covalent bonds and thus experience asymmetrical attractive forces caused by the uneven distribution of the bonding electrons.
- The effective nuclear charge of F is significantly greater than H [as a result of a greater no. of protons] and thus the shared electrons would feel a stronger attraction towards the fluorine nucleus.
- Thus the bonding orbital is more like fluorine and the anti-bonding orbital is more like hydrogen
- Stability of the HF molecule can be achieved by having the electrons closer towards the fluorine nucleus resulting in the unequal distribution of electron density.

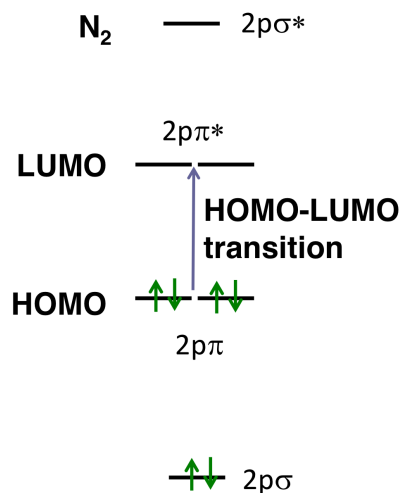


- CN^- is **isoelectronic** with N_2 (same number of electrons)
- Note: the lower-lying orbitals are polarised towards N since it is more electronegative than C. This allows it to draw electrons more strongly in the molecular orbital
- This unequal distribution of electrons creates a net polarisation of charge, which creates a **molecular dipole**.



Recall the meaning of HOMO and LUMO and determine the lowest energy electronic transition

- **HOMO** = Highest Occupied Molecular Orbital
- **LUMO** = Lowest Unoccupied Molecular Orbital
- The **lowest energy electronic transition** of a molecule is the **HOMO-LUMO transition**.



Band Theory - MO in Solids

Recall that the number of molecular orbitals increases with the number of atoms in a molecule

As the number of atoms in the molecule increases, so does the number of molecular orbitals

Recognise that in covalent networks:

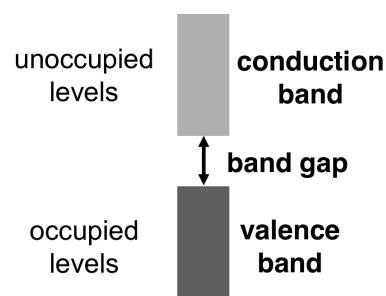
- interactions of σ -orbitals gives rise to a **valence bands**,
- interactions of σ^* orbitals give rise to a **conduction band**

Use, define and explain the concepts of conduction band, valence band, band gap, hole, acceptor level, donor level, n-doping and p-doping

Valence Band: Band of occupied orbitals

Conduction band: Band of unoccupied orbitals

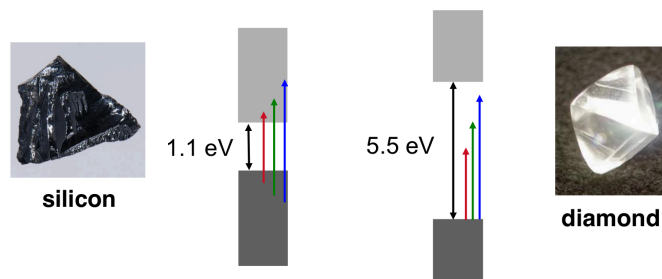
Band Gap: The minimum energy a network solid must absorb to promote an electron from the valence band to the conduction band.



Explain the relationship between band gap and electrical and optical properties

A large band gap will cause a greater absorption of visible light, resulting in the material composed of that element appearing black/opaque. [e.g. graphite, silicon]

Elements with atoms that have a little to no energy band gap, will be able to allow visible light to pass through easily, making the material composed of the element appear transparent [e.g. diamond]



	Graphite	Diamond
Apperance	Black/opaque	Transparent and clear
Electrical Conductivity	Highly conductive along 2 directions due to horizontal plane structure	insulator
Density	low (2.27 g cm^{-3})	High (3.51 g cm^{-3})
B.P & M.P.	sublimes at 3948K	melts at 3823K
Hardness	Soft solid	Hard solid