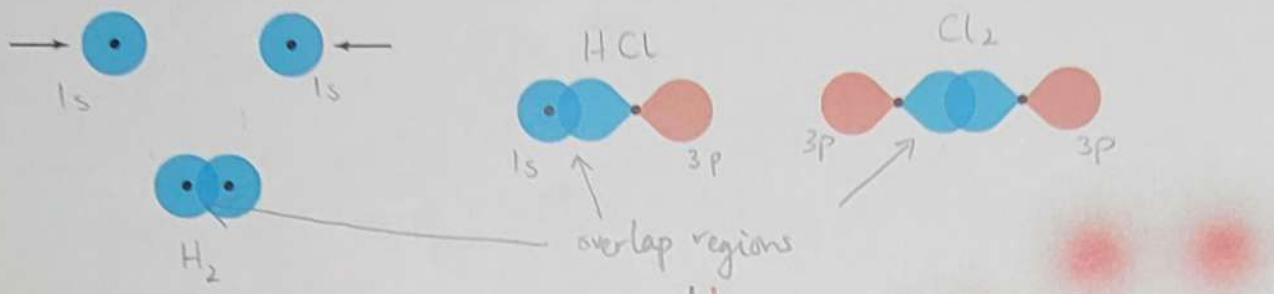
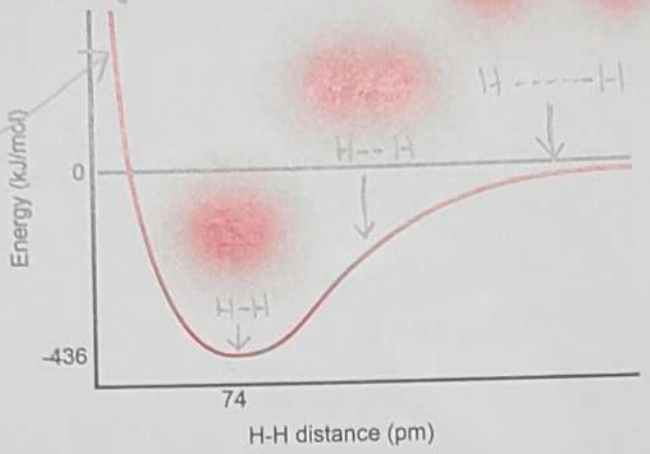
Valence bond theory

Covalent bonds form through sharing of electrons by adjacent atoms.

Can occur when orbitals on the two atoms overlap → valence bond theory



The energy of the system depends on the quality of the overlap between orbitals



If the distance is too close, repulsive forces between nuclei increases the energy of the system

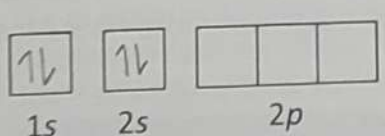
Hybrid Orbitals

To apply the ideas of orbital overlap and valence-bond theory to polyatomic molecules, we need to introduce the concept of **hybrid atomic orbitals (HAOs)**.

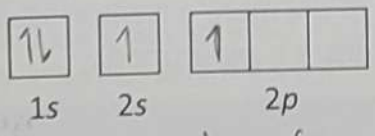
Mix (combine, hybridize) n atomic orbitals to make n hybrid orbitals

sp hybrid orbitals

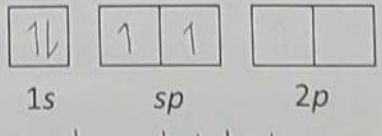
Consider beryllium: in its ground electronic state, it would not be able to form bonds because it has no singly-occupied orbitals:



ground state
no unpaired electrons

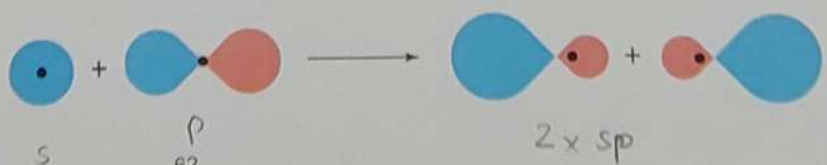


Imagine promotion of an electron from 2s → 2p



rewrite orbital diagram to show hybrid orbitals

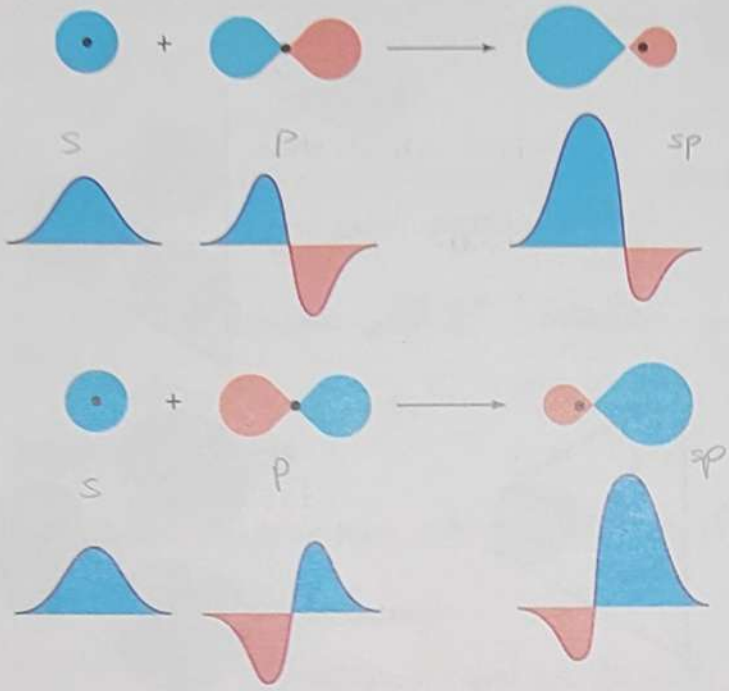
Mixing the *s* and *p* orbitals yields two degenerate orbitals



sp hybrid orbitals have two lobes: 1 large, 1 small

Phase

Note that orbitals, atomic and hybrid alike, have lobes of different colours. This difference in **phase** arises from the wave nature of the electron. Regions where the wave function is positive are represented by one colour (here **blue**), negative by another (here **red**).



phase changes when crossing a node

we will use the concept of orbital addition again when creating molecular orbitals

Orbitals are usually drawn in simplified form, and hybrid orbitals are no exception:

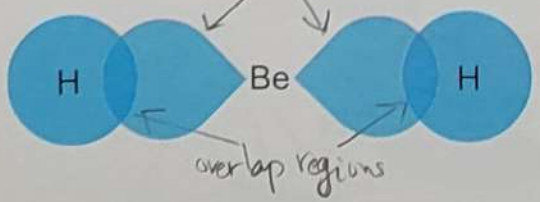
calculated HAO

simplified HAO

very simplified HAO

These two degenerate *sp* orbitals align themselves 180° from each other, and 90° from the two remaining unhybridized *p* orbitals.

large lobes of sp hybrid orbitals

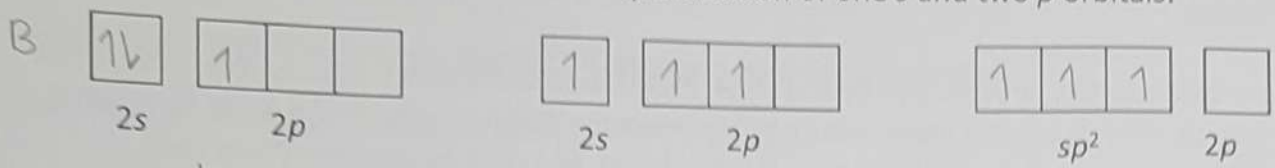


H 1s orbital

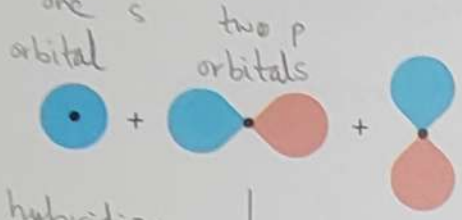
H 1s orbital

(the small back-lobes of hybrid orbitals and other p-orbitals are not shown)

Three sp^2 hybrid orbitals are formed from hybridization of one *s* and two *p* orbitals:

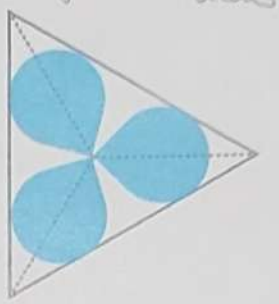


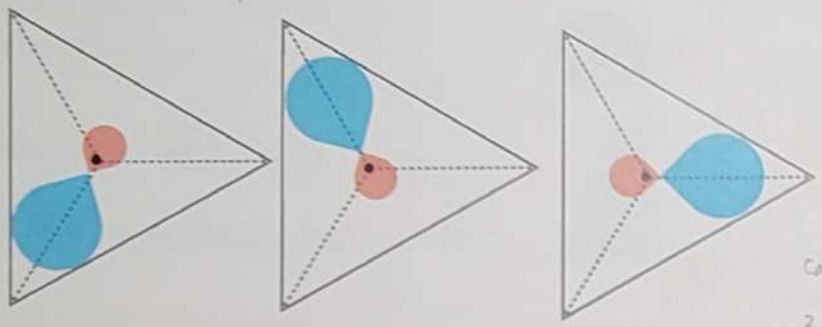
ground state promote electron from 2s → 2p rewrite orbital diagram to show hybrid orbitals



sp^2 hybrid orbitals shown together (large lobes only)

e.g BF_3

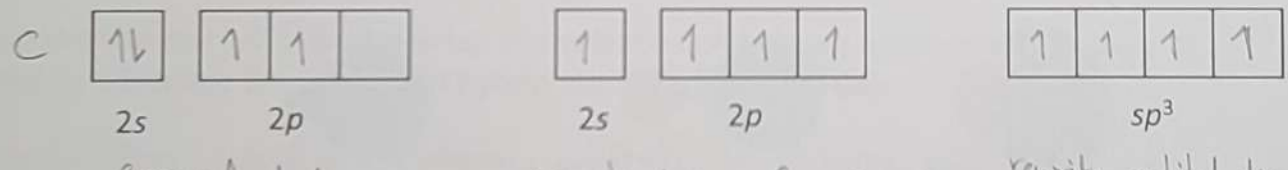




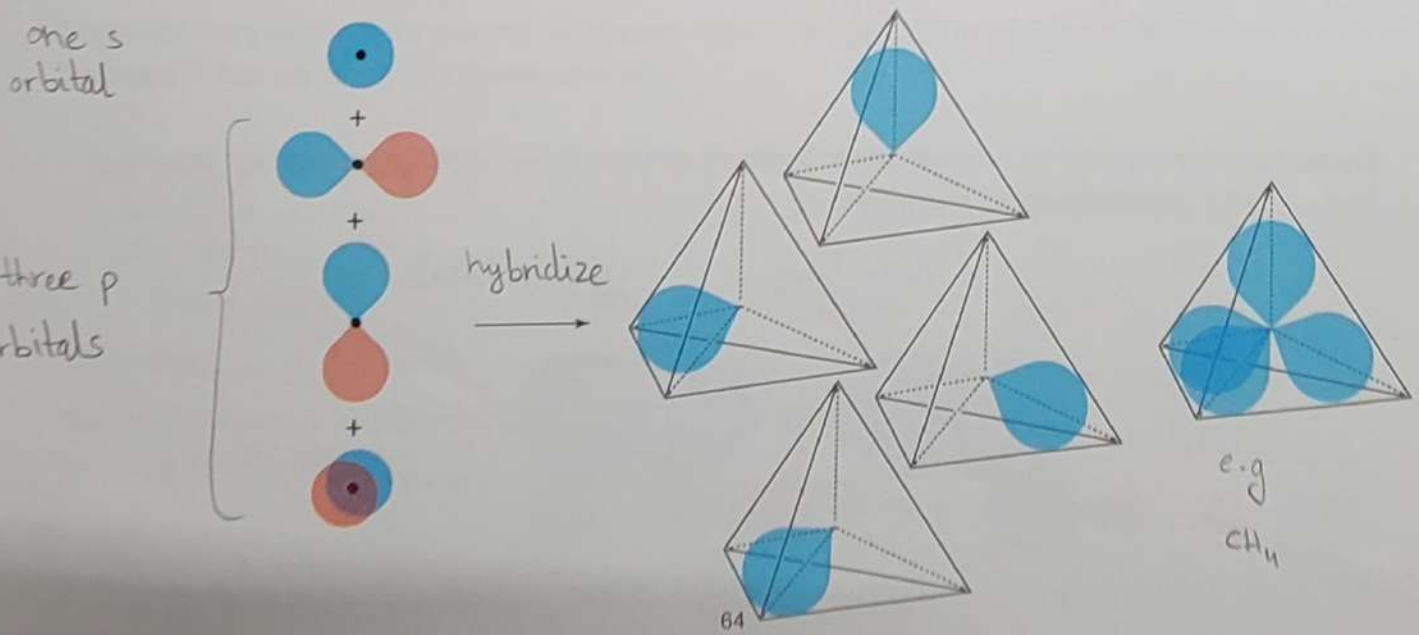
three sp^2 hybrid orbitals

calculated sp^2 hybrid orbitals

Four sp^3 hybrid orbitals are formed from hybridization of one *s* and three *p* orbitals:



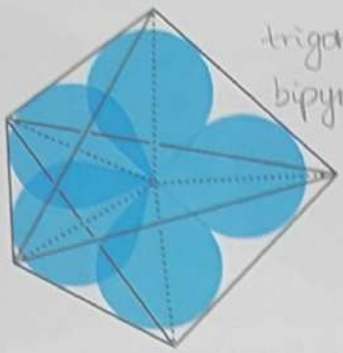
ground state promote electron from 2s → 2p rewrite orbital diagram to show hybrid orbitals



e.g CH_4

For geometries involving expanded octets on the central atom, we use *d* orbitals in our hybrids:

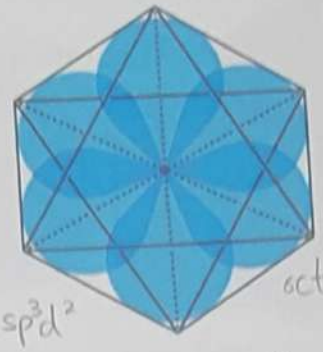
sp, p, p, d



trigonal bipyramidal

five sp^3d

s, p, p, p, d, d



octahedral

six sp^3d^2

Once you know the electron-domain geometry, you know the hybridization state of the atom:

2 electron domains = sp 3 electron domains = sp^2

4 electron domains = sp^3 5 = sp^3d 6 = sp^3d^2

Multiple Bonds

The covalent bonds we have seen so far are **sigma** (σ) bonds, characterized by:

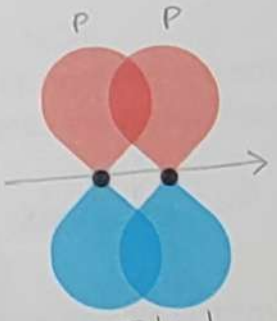
- head-to-head overlap
- cylindrical symmetry of electron density about the internuclear axis

To describe multiple bonding, we must invoke **pi** (π) bonds.

Pi (π) bonds are characterized by:

side-to-side overlap

electron density above and below the internuclear axis



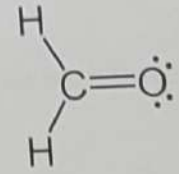
π bond

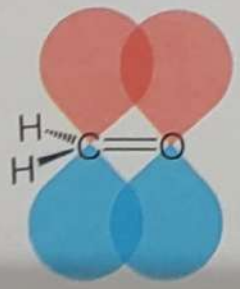
Single bonds are ***always*** σ bonds, because σ overlap is greater, resulting in a stronger bond and more energy lowering.

in a multiple bond, ONE of the bonds is a σ bond

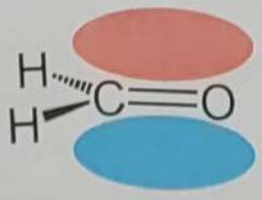
and the rest are π bonds

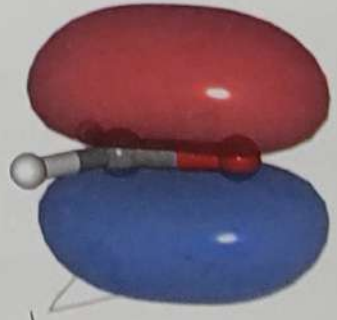
In a molecule like formaldehyde an sp^2 orbital on carbon overlaps in σ fashion with the corresponding orbital on the oxygen.





the unhybridized p orbitals overlap in π fashion





one π bond

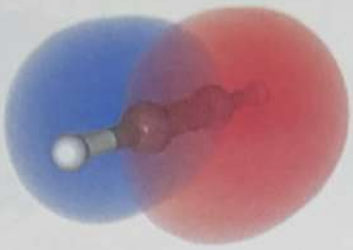
— = 1 σ

= = 1σ + 1π

≡ = 1σ + 2π

In triple bonds, e.g. acetylene, two *sp* orbitals form a σ bond between the carbons:

one pair of p orbitals overlapping in π fashion above plane

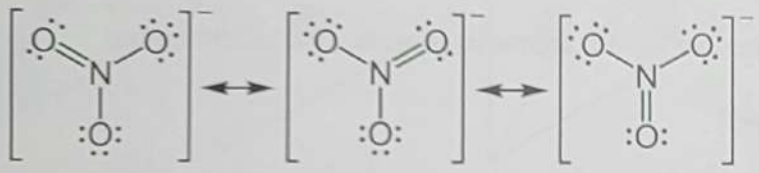


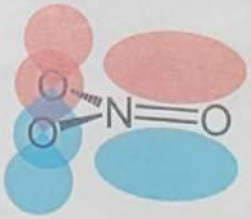
one pair of p orbitals overlapping in π fashion in plane

two π bonds

Delocalized π Bonding

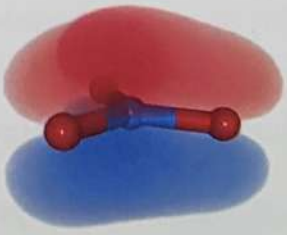
When writing Lewis structures for species like the nitrate ion, we draw resonance structures to more accurately reflect the structure of the molecule or ion.





In reality, each of the four atoms in the nitrate ion has a p orbital

The *p* orbitals on all three oxygens overlap with the *p* orbital on the central nitrogen

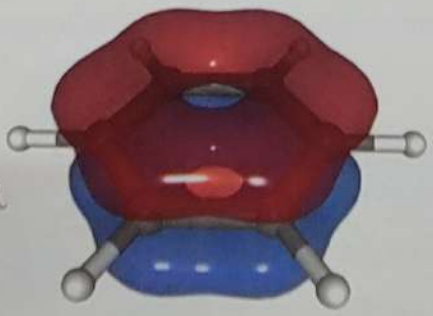


→ the π electrons are delocalized throughout the ion

Similarly for benzene, we can write two resonance forms:

Neither resonance structure completely describes the electrons in the π bonds.

→ the π electrons are delocalized throughout the ring



Molecular Orbitals

Some aspects of bonding are not explained by Lewis structures, VSEPR theory, and hybridization (valence bond theory), for example:

- why does O_2 interact with magnetic field?
- why are some molecules coloured?
- how do we explain metallic bonding?

We can use molecular orbital (MO) theory to explain some of these observations.

electrons in atoms are found in atomic orbitals

electrons in molecules are found in molecular orbitals

Molecular orbitals have some characteristics are similar to those of atomic orbitals.

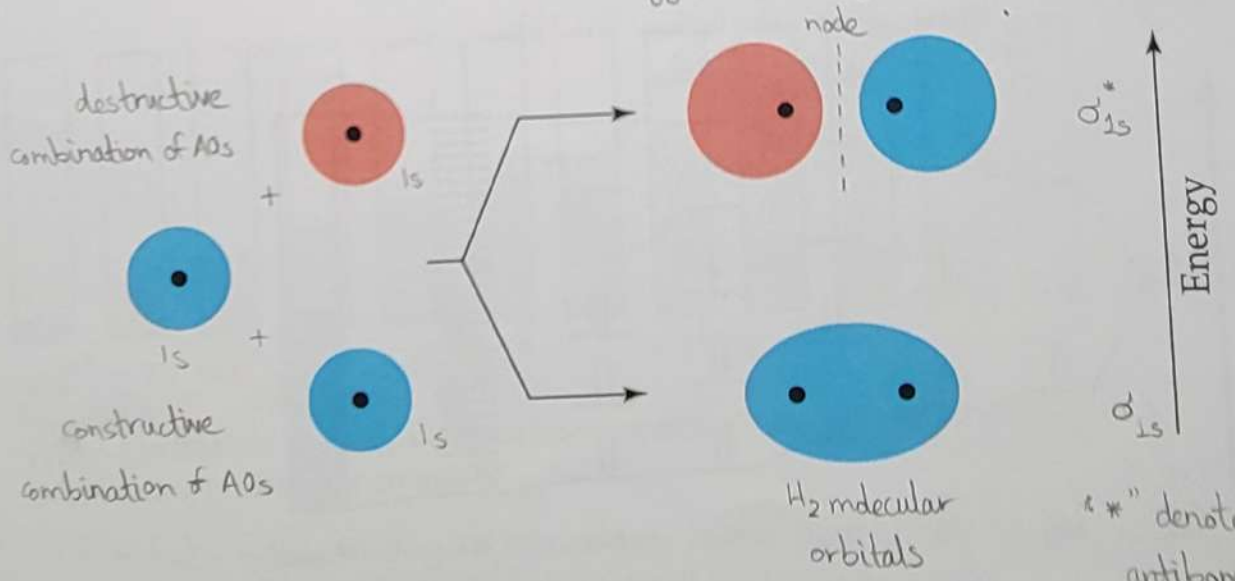
- each contain 2 electrons with opposite spin
- each has a definite energy
- electron density distribution can be visualized with contour diagrams

However, unlike atomic orbitals, molecular orbitals are associated with an entire molecule

The hydrogen molecule

When *n* AOs overlap, *n* MOs form. For H_2, 1*s* (H) + 1*s* (H) must result in 2 MOs:

A molecular orbital energy level diagram:

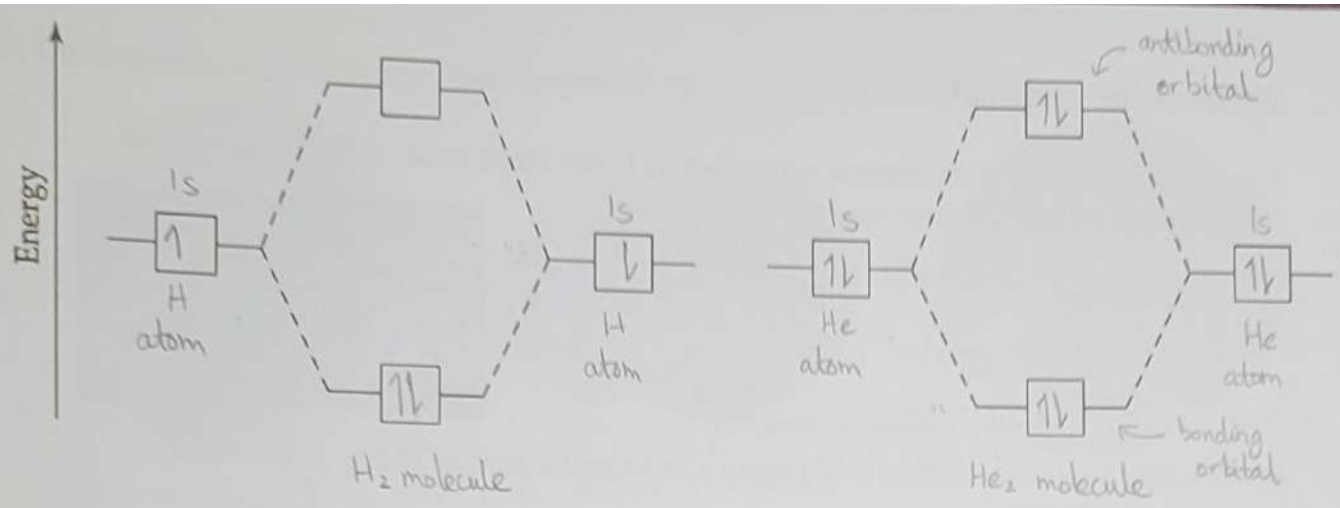


H_2 molecular orbitals

"*" denotes an antibonding orbital

Both bonding and antibonding molecular orbitals have electron density centered around the internuclear axis

→ sigma (σ) bonds



more stable than separate H atoms → molecule forms

less stable than separate He atoms → molecule does not form

Note similarity to mixing of atomic orbitals to make hybrid atomic orbitals: the difference here is that the orbitals used are on two different nuclei.

Bond order

Bond order = $\frac{1}{2}$ (no. of bonding electrons − no. of antibonding electrons)

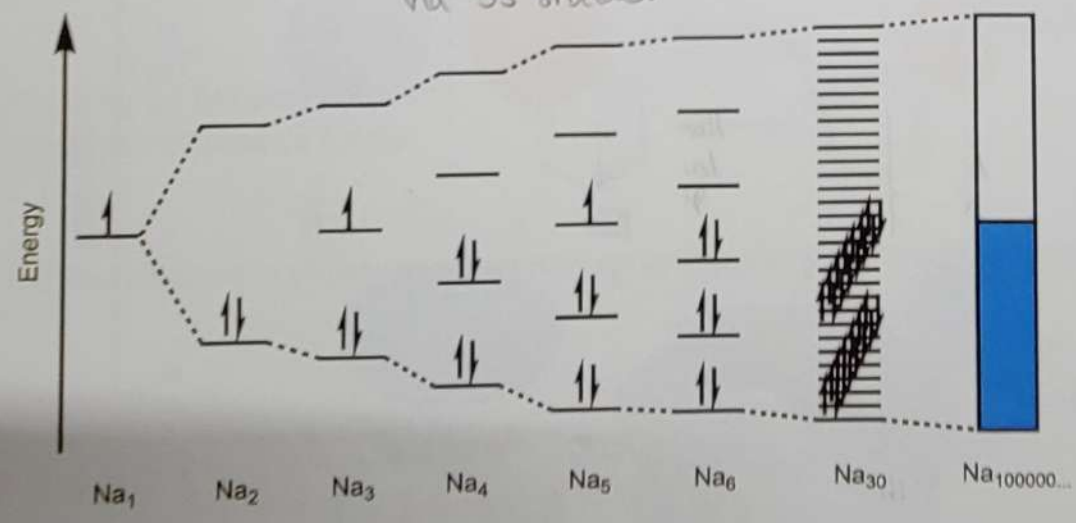
B.O. $H_2 = \frac{1}{2}(2-0) = 1$

B.O. $He_2 = \frac{1}{2}(2-2) = 0$

Band theory

We can apply the same reasoning to the combination of other orbitals to generate molecular orbitals for any molecule, but we are going to use MO theory to help us understand the bonding in metals, an important class of materials.

Imagine a linear chain of sodium (Na) atoms, which overlap via 3s orbitals:

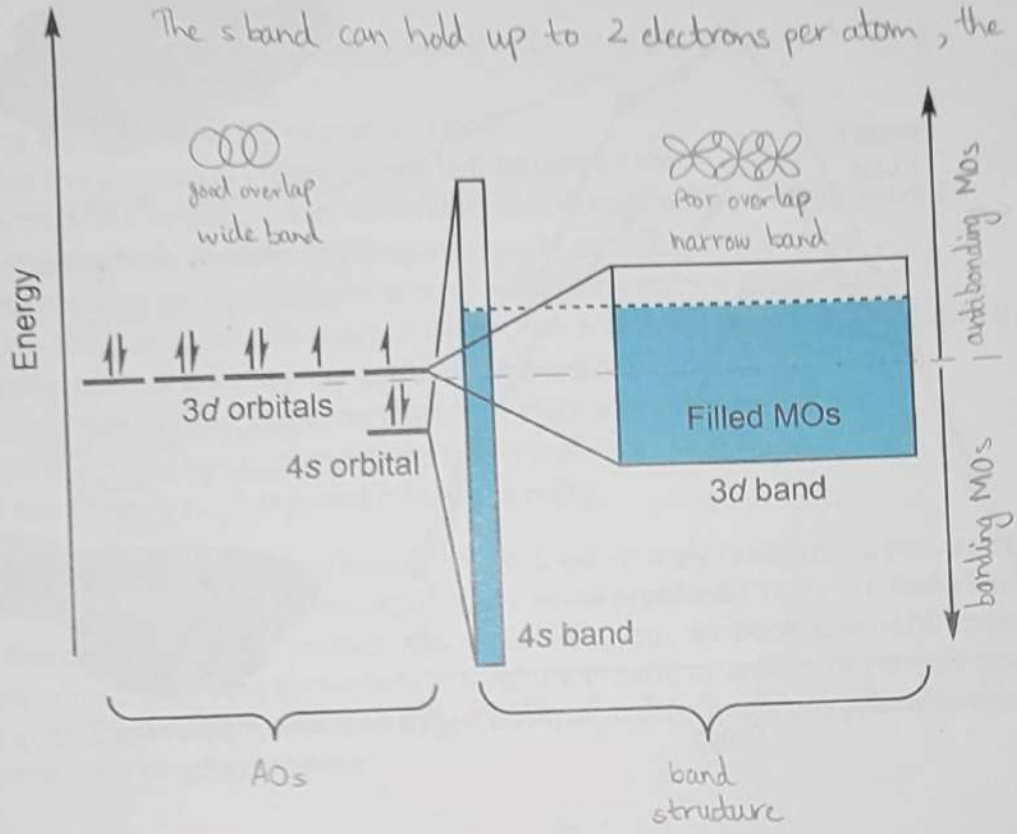


There are always as many MOs as AOs, and they are always half full since there is 1 3s electron per sodium atom.

Spacing between orbitals gets closer as we add atoms until they became effectively continuous: a band

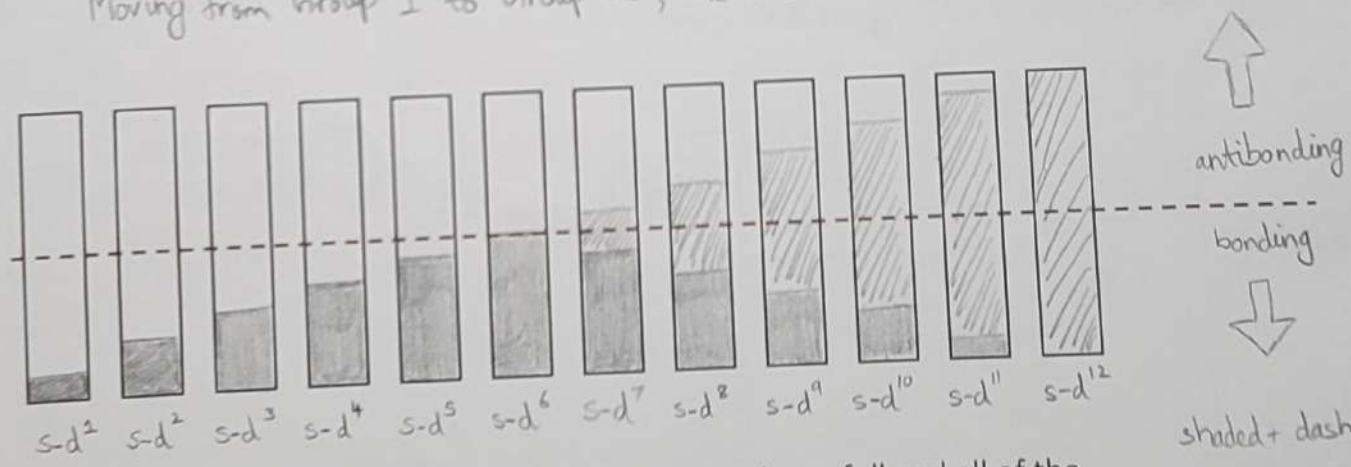
The energy differences between orbitals within a band are tiny, so electrons can readily move through the metal. Metals are hence excellent **conductors**.

For metals in groups 1-12, the s and d bands overlap.
The s band can hold up to 2 electrons per atom, the d band up to 10.



We can simplify the picture by imagining metals to have a single band that can accommodate 12 electrons per atom, the *s-d* band.

Moving from Group 1 to Group 12, the s-d bands fill with electrons:



When the band is half full, all of the bonding orbitals are full and all of the antibonding orbitals are empty.

=> metal-metal bonding is maximized and metals are very hard

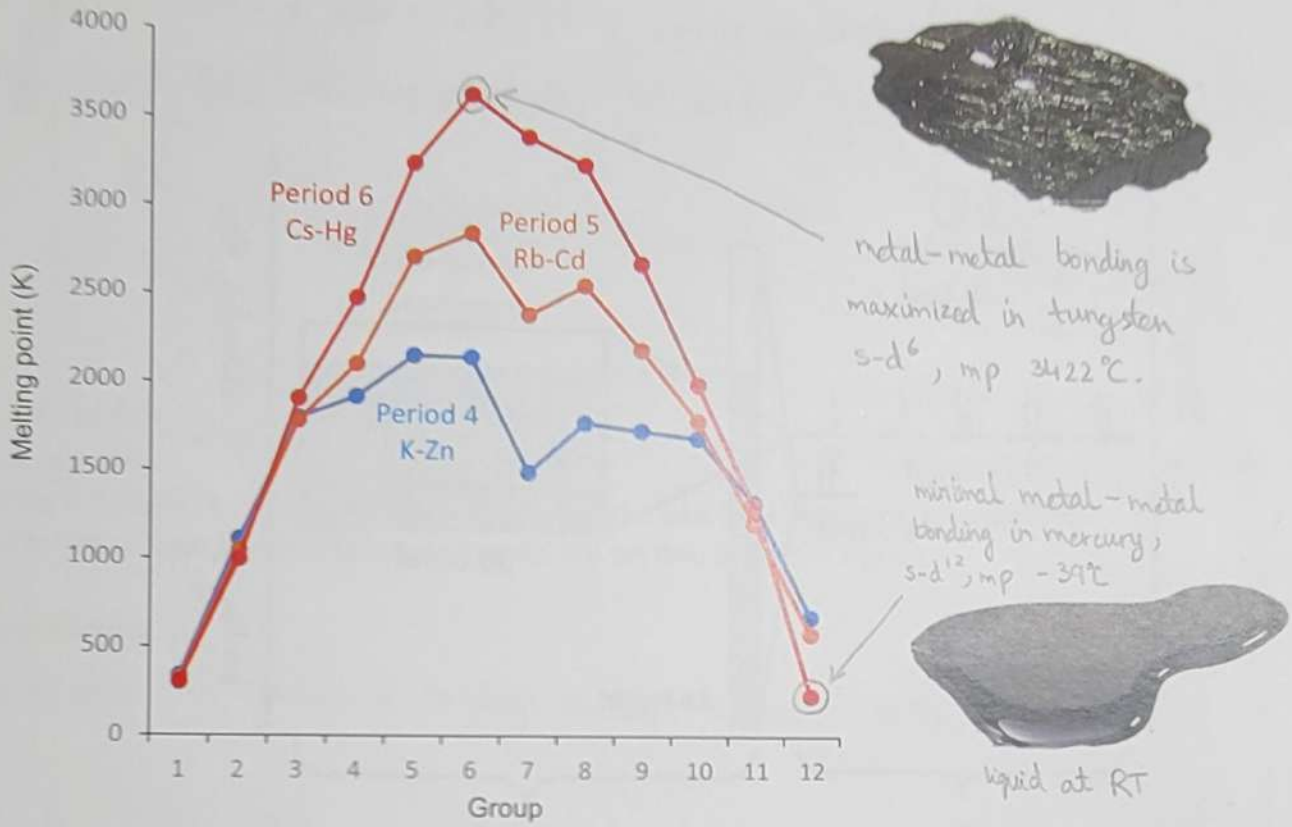
When the band is full, all of the bonding orbitals are full and all of the antibonding orbitals are also full, so the effects cancel each other out.

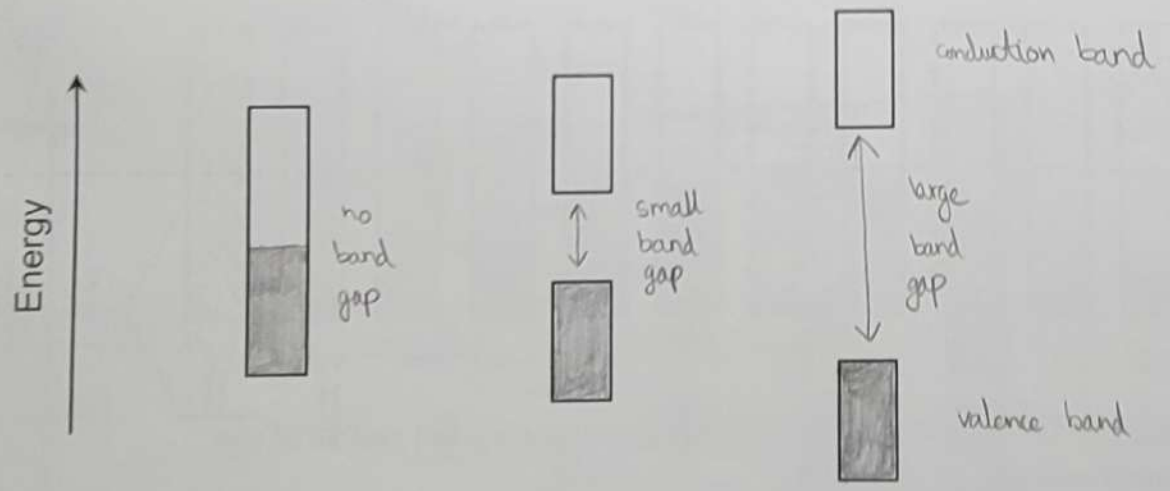
=> metal-metal bonding is minimized and metals are very soft

shaded + dashed = total electrons

shaded = bonding electrons

We can see this effect if we plot melting point against Group number:



Metals, semiconductors and insulators

Materials can conduct electricity if electrons can move easily from an occupied orbital to an unoccupied one. In metals, there is no gap between the **valence band** and the **conduction band**. **Semiconductors** have a small band gap and **insulators** have a large band gap: