JF Chemistry CH1101

The Electronic Theory of Chemistry

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Structure and Bonding

Part 2

Lewis Dot Diagrams

VSEPR Theory

Lewis Dot Diagrams

What is a bond?

-Sharing of electrons

-Covalent bond, bonding electrons localised, or fixed, between two atoms

Electrons that are not shared are localised as lone pairs

Lewis theory states that all atoms are trying to achieve a noble gas configuration ⇒ OCTET rule

Some rules for Lewis dot diagrams:

Only use valence electrons

Under most circumstances symmetrical geometry is correct!

Oxygen is commonly and Hydrogen always peripheral

Arrange electrons so that all non-H atoms obtain an octet (exceptions for elements in the 3rd and 4th row)

Lewis Dot Diagrams – Complex Structures

1 – Determine the total number of valence electrons

Neutral complexes sum the valence electrons

Cationic complexes *subtract* the charge

Anionic complexes *add* the charge

2 – Draw the skeletal structure with single bonds. (H is NEVER a central atom)

3 – Place pairs of electrons around the outermost atom

4 – Place any surplus electrons on the central atom

5 – If the central atom does NOT have 8 electrons form a double bond

Formal Charge

Lewis diagrams represent how the electrons are distributed in a molecule.

Formal charge is an “electron bookkeeping” of the valence electrons

1. All unshared electrons are assigned to the atom on which they are found
2. For any bond, half the number of electrons are assigned to each atom
3. Subtraction of the number of assigned electrons from the number of electrons in the isolated atom

In examples where two (or more) formulae are possible we chose the Lewis structure where

1. Atoms bear formal charges closest to zero
2. Any negative charge resides on the most electronegative atoms

REMEMBER FORMAL CHARGES DO NOT REPRESENT REAL CHARGES ON ATOMS

Bond Polarity

Difference in electronegativity gives an indication to the bond polarity.

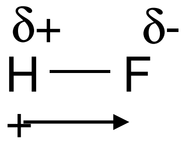
If the electronegativity difference is zero – nonpolar covalent bond

If the electronegativity difference is small (1.6) polar covalent bond

If the electronegativity difference is large (greater than 1.6) ionic bond

H 2.1; Li 1.0; F 4.0

Compound	F_2	HF	LiF
Electronegativity difference	0	1.9	3.0
Type of bond	Nonpolar	Polar	Ionic



Valence Shell Electron Pair Repulsion Theory

Electrons in bonds and lone pairs repel each other so try to be as far away from each other as possible

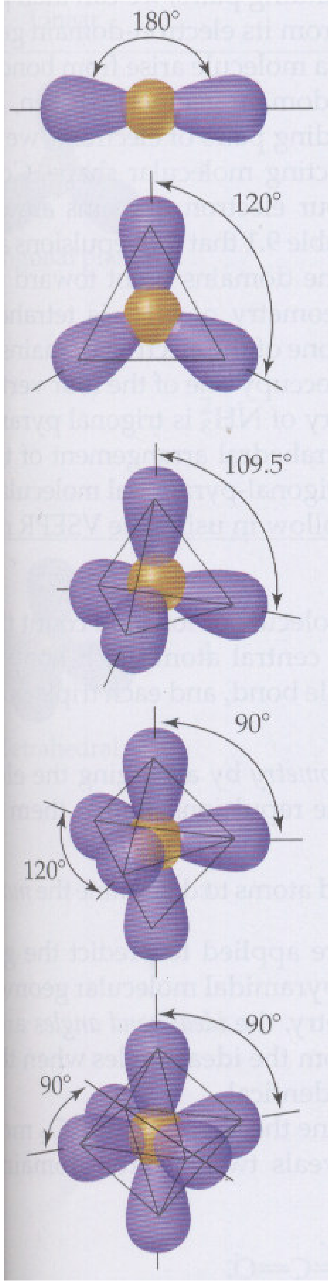
VSEPR theory starts with information of electron geometry (Lewis structures) and gives us molecular geometry

1. Draw the correct Lewis structure
2. Determine the number of regions of electron density (bonds and lone pairs)
3. Determine the electron geometry
4. Determine the molecular geometry

   lone pair-lone pair > lone pair-bond pair > bond pair-bond pair

Valence Shell Electron Pair Repulsion Theory

Electron geometry



2 Linear

3 Trigonal Planar

4 Tetrahedral

5 Trigonal Bipyramidal

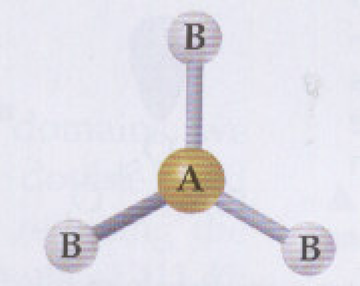
6 Octahedral

Valence Shell Electron Pair Repulsion Theory

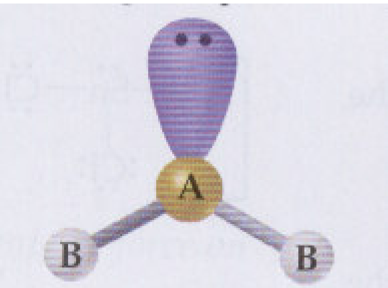
Electron Geometry = 2 Molecular Geometry = Linear

Linear

Electron Geometry = 3 Molecular Geometry =Trigonal Planar or Bent (V-shaped)

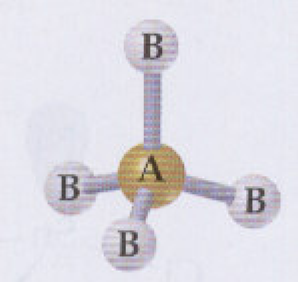


Trigonal planar

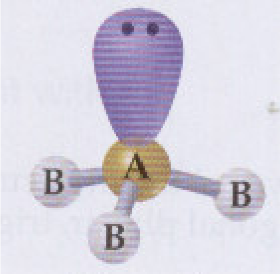


Bent

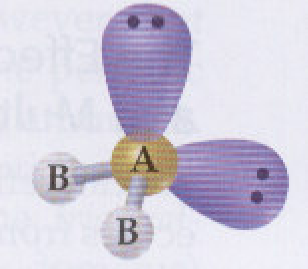
Electron Geometry = 4 Molecular Geometry =Tetrahedral, Trigonal Pyramidal or Bent (V-shaped)



Tetrahedral



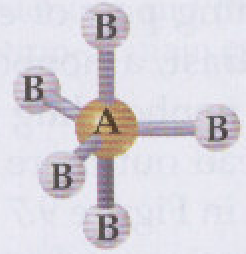
Trigonal pyramidal



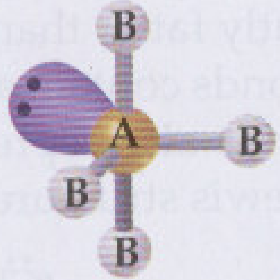
Bent

Valence Shell Electron Pair Repulsion Theory

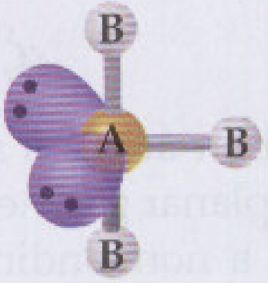
Electron Geometry = 5 Molecular Geometry = Trigonal Bipyramidal, Seesaw (disphenoidal), T-shaped, Linear



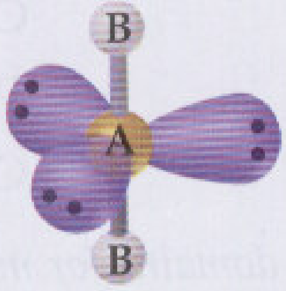
Trigonal bipyramidal



Seesaw

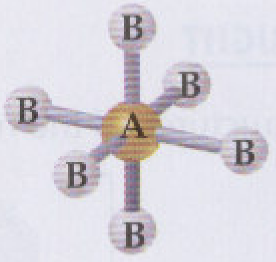


T-shaped

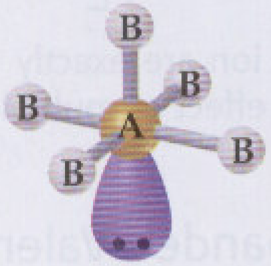


Linear

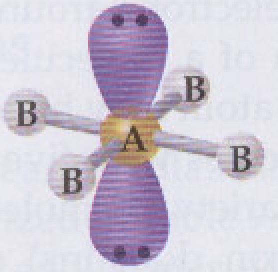
Electron Geometry = 6 Molecular Geometry = Octahedral, Square Pyramidal, Square Planar



Octahedral



Square pyramidal



Square planar

Valence Shell Electron Pair Repulsion Theory

Some subtleties

1. multiple bond exerts a greater repulsive force on adjacent electron domains than single bonds
2. Electronegative substituents prefer axial positions in a trigonal bipyramid
3. As the central atom gets larger so does the lone pair, so any bond pairs get forced closer together
4. The more electronegative an atom, the further away from the central atom the bonding pair will be so smaller angles are tolerated

NH_3	107	NCl_3	107	NF_3	102
PH_3	94				
AsH_3	92				
SbH_3	91				

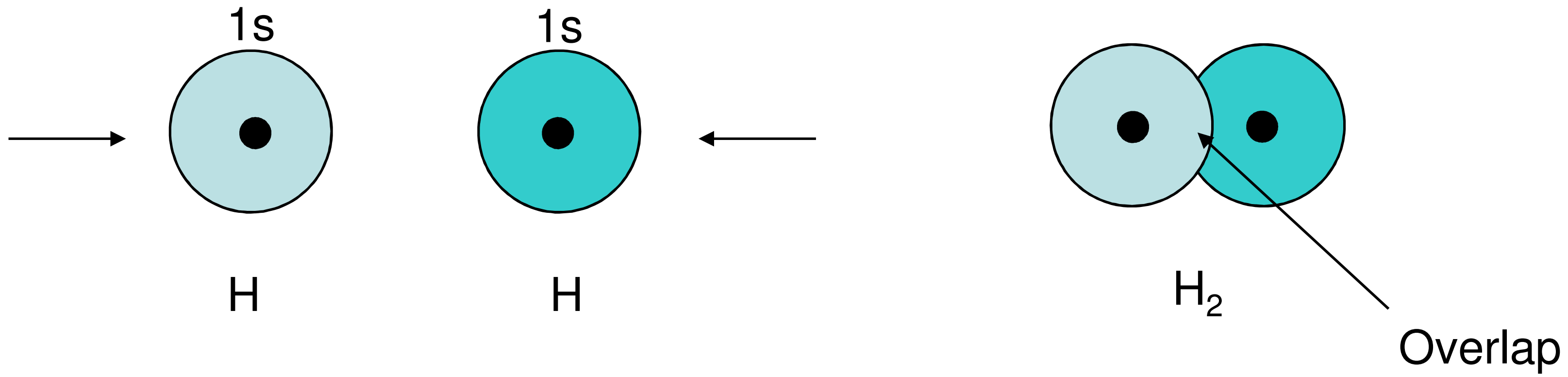
Bonding Theories

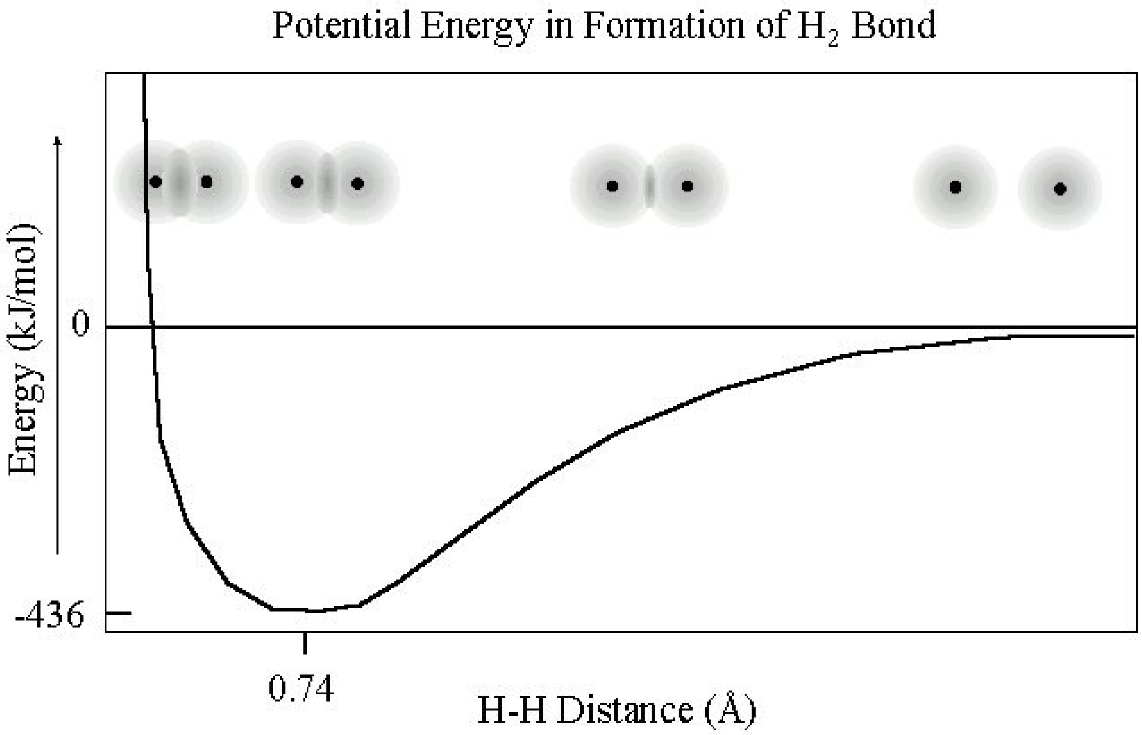
Valence Shell Electron Pair Repulsion Theory predicts the shapes of molecules but does not say why a bond exists.

How can we use atomic orbitals to explain bonding and to account for the molecular geometries? The combination of Lewis bonding and atomic orbitals is called **Valence-Bond** theory.

Lewis theory – electrons are shared between two atoms.

Valence bond theory – the buildup of electron density is visualised as occurring when the atomic orbital of one atom merges with the other causing overlap.



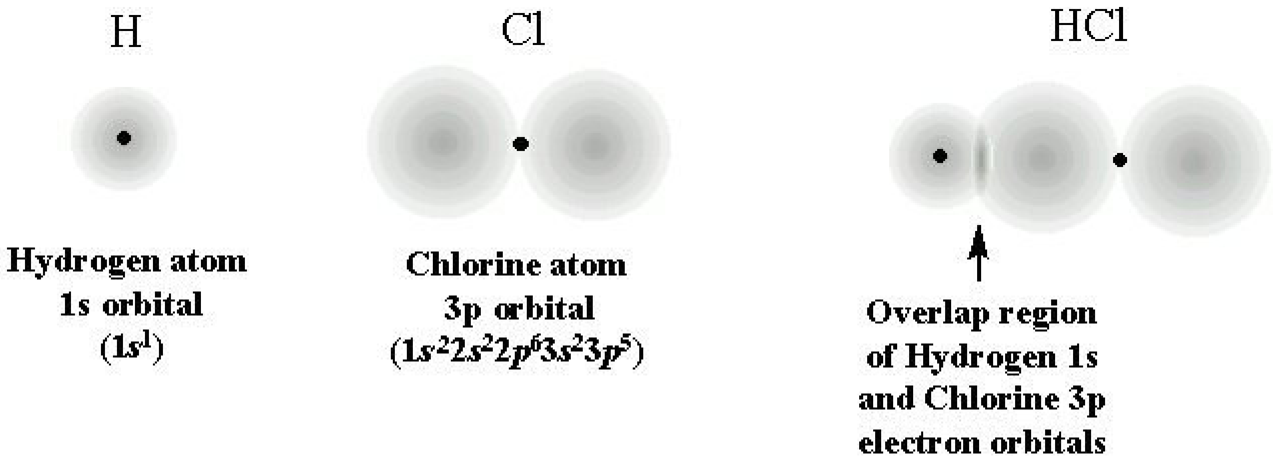


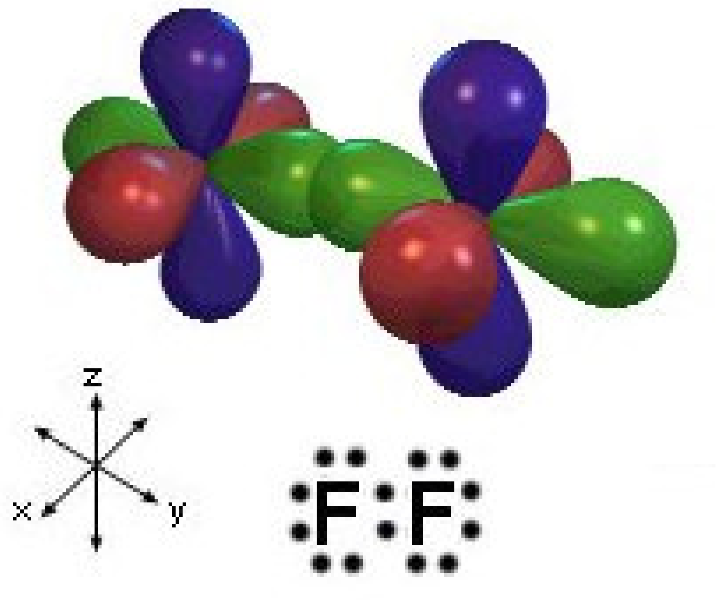
As the 1s orbitals of the hydrogen start to overlap there is a reduction in the energy of the system due to the increase in electron density between the two positively charged nuclei

As the distance decreases further, repulsion between the nuclei becomes significant at short distances. The internuclear distance at the minimum potential energy corresponds to the observed bond length

The observed bond length is the distance at which the attractive forces (nuclei for bonding electrons) is balanced by the repulsive force (nuclei vs. nuclei and electron vs. electron)

Valence-Bond Theory





Overlap of two p_y orbitals in F_2

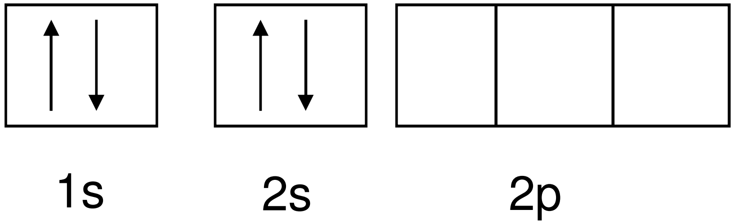
Hybrid Orbitals

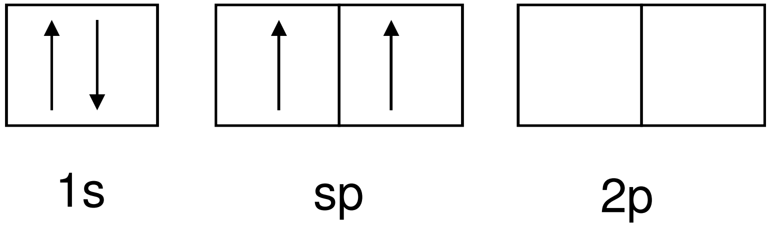
For polyatomic atoms we need to explain bonds *and* geometry

We can assume that atomic orbitals mix to form new orbitals called HYBRID orbitals. The total number of atomic orbitals always equals the total number of hybrid orbitals

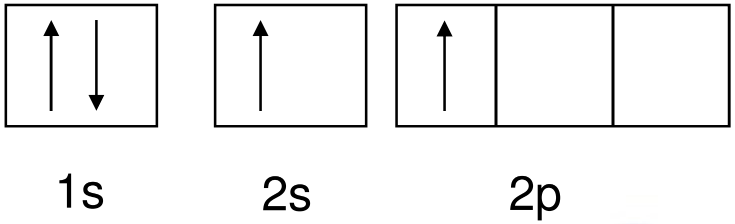
BeF$_2$: F has one unpaired electron, Be doesn’t

Ground state Be

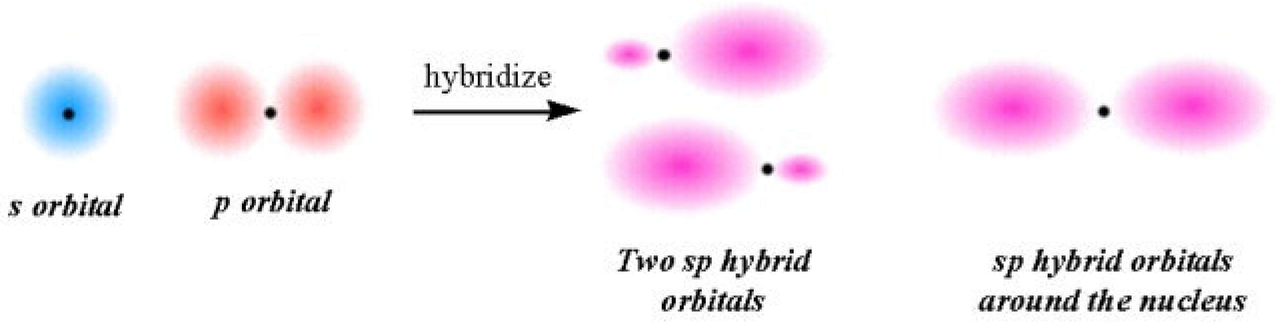




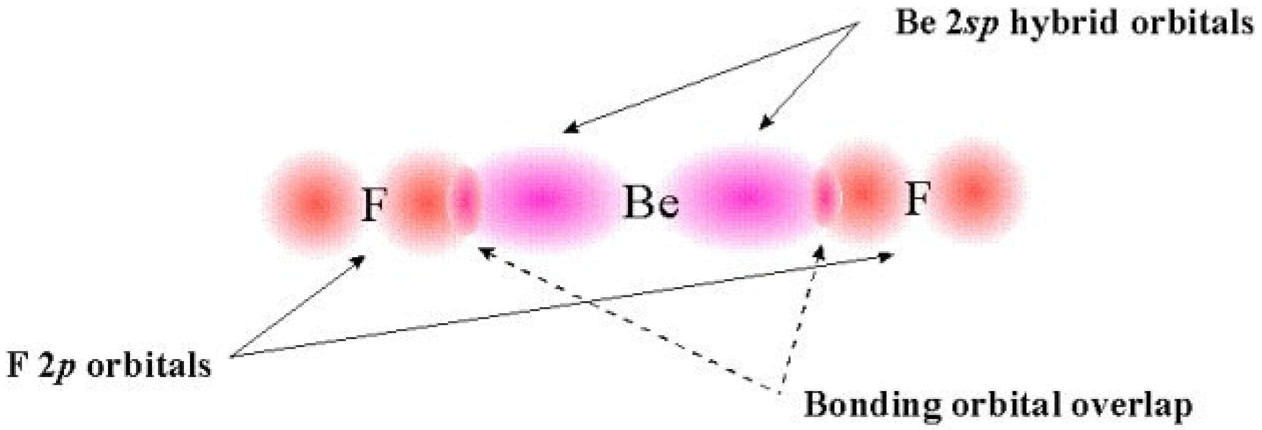
sp hybridisation



Promote one 2s electron



Hybrid Orbitals



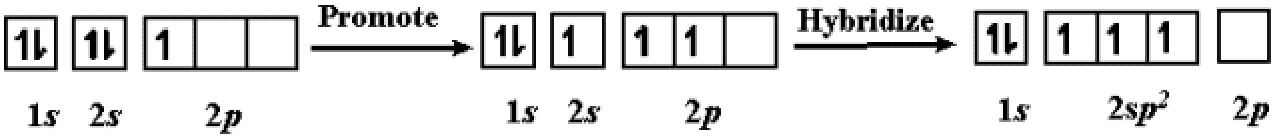
By combining an s and a p orbital the hybrid must be linear therefore the molecular geometry in BeF_2 must linear

the two steps often observed when constructing hybrid orbitals is to 1) promote a valence electron from the ground state configuration to a higher energy orbital, and then 2) hybridize the appropriate valence electron orbitals to achieve the desired valence electron geometry (i.e. the correct number of hybrid orbitals for the appropriate valence electron geometry)

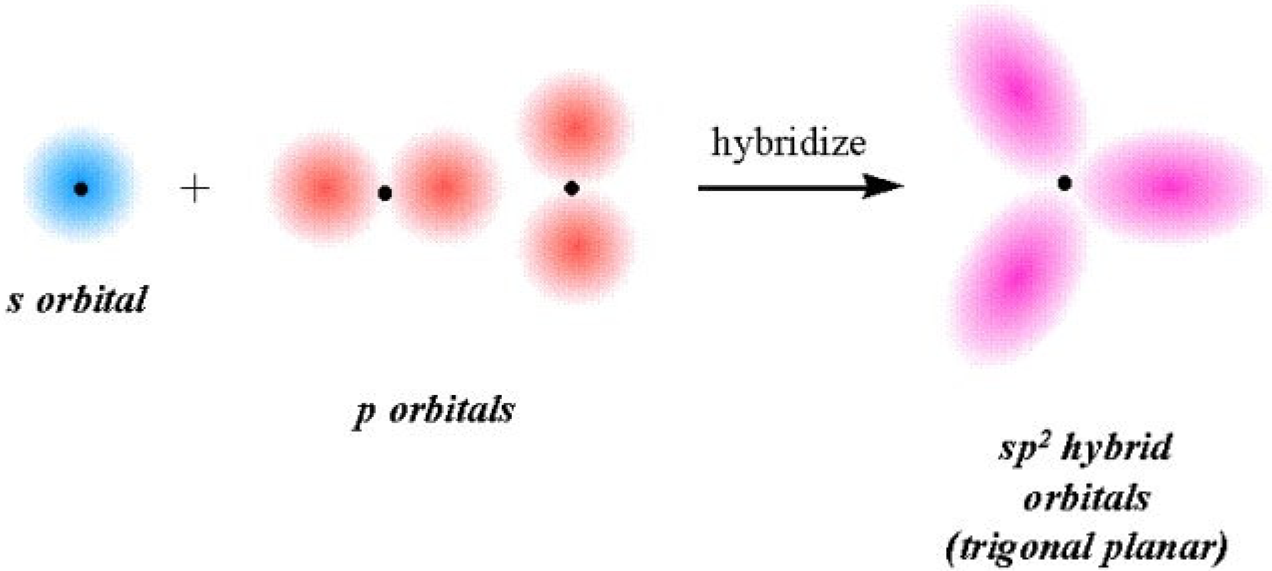
Hybrid Orbitals - sp^2

BF_3

Boron electron configuration:



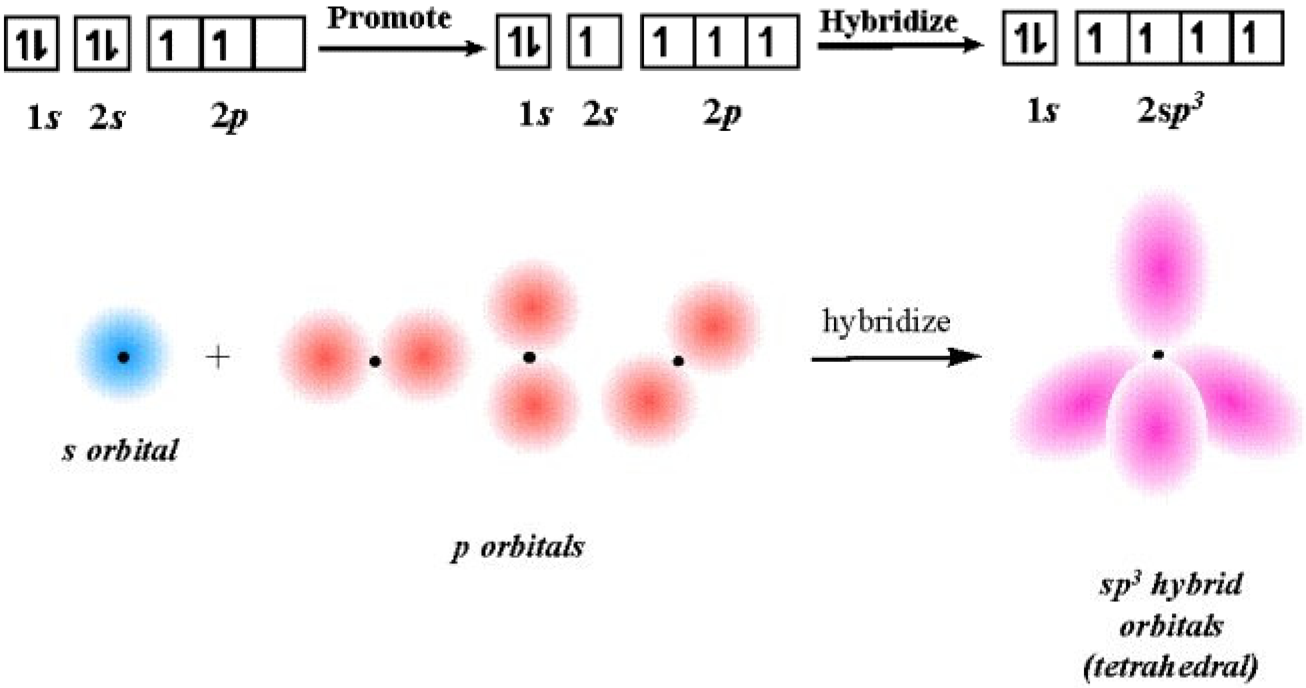
•The three *sp^2 hybrid orbitals have a trigonal planar arrangement to minimize electron repulsion*



NOTE: sp^2 refers to a hybrid orbital being constructed from one s orbital and two p orbitals.

Hybrid Orbitals – sp^3

CH_4

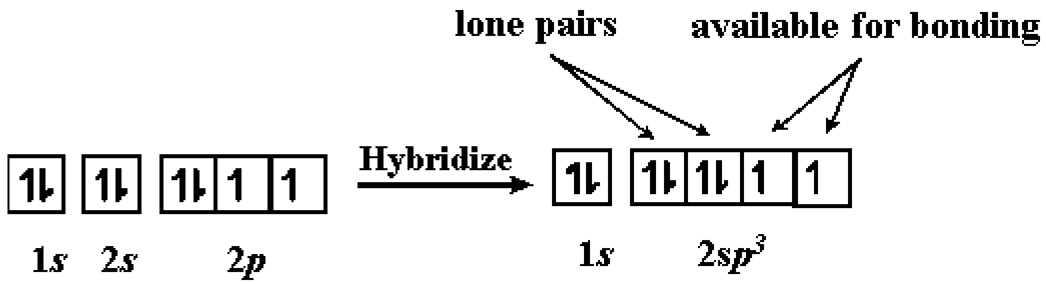


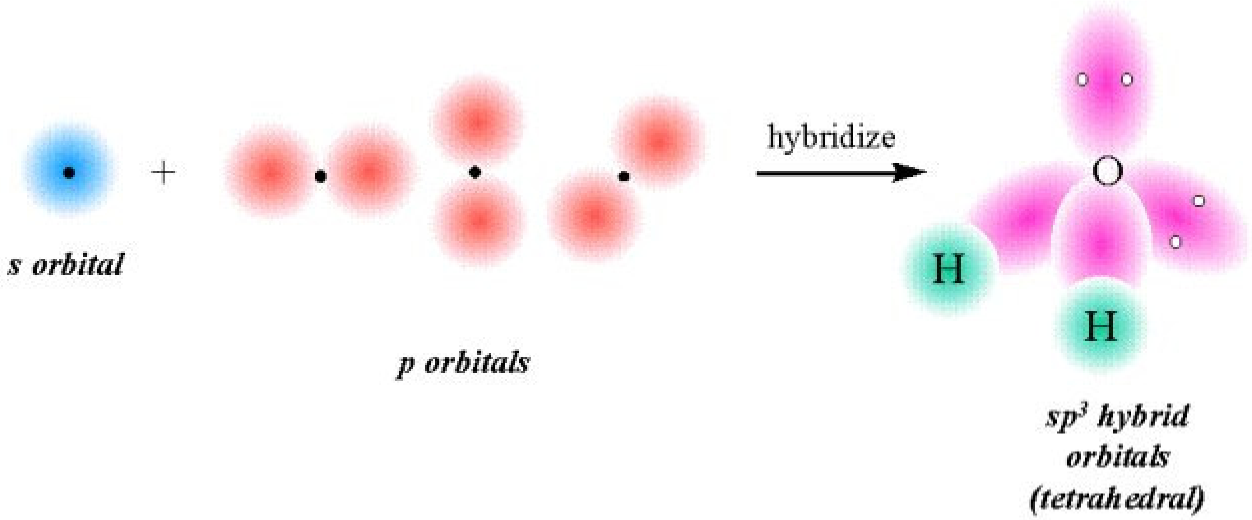
•Using **valence bond theory**, we would describe the bonds in methane as follows: each of the carbon *sp*^{3} hybrid orbitals can overlap with the 1s orbitals of a hydrogen atom to form a bonding pair of electrons

Hybrid Orbitals – sp^3

Water?

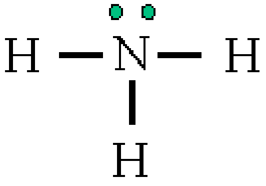
O



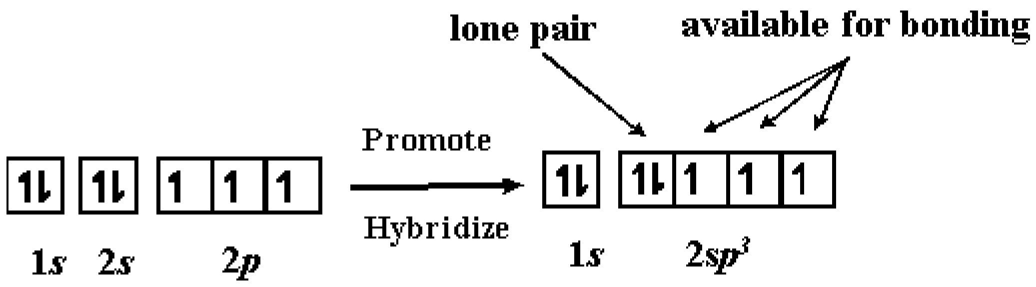


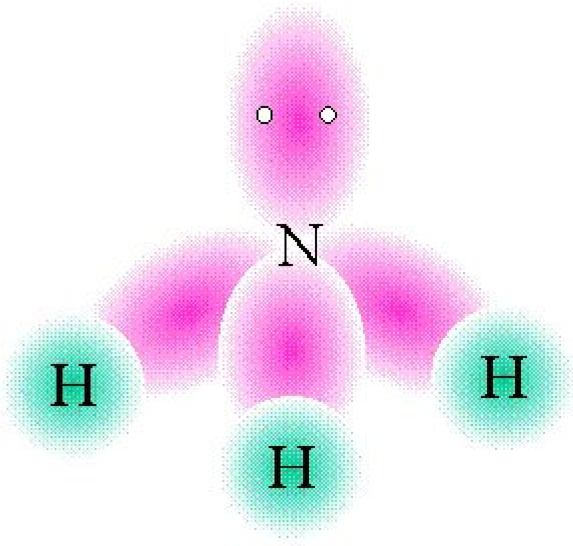
Hybrid Orbitals – sp^3

Ammonia?



VSEPR indicates *tetrahedral geometry* with one non-bonding pair of electrons (structure itself will be *trigonal pyramidal*)



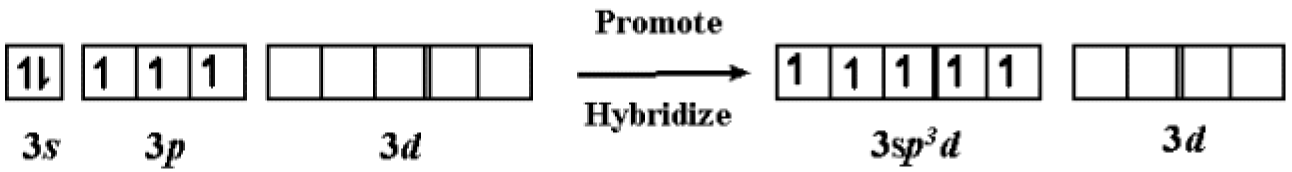


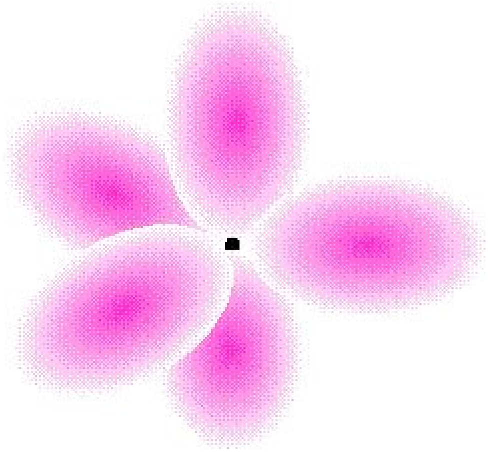
sp^3 hybrid orbitals (tetrahedral)

Hybrid Orbitals – d orbital involvement

Atoms in the third period and higher can utilize *d* orbitals to form hybrid orbitals

PF_5





Trigonal Bipyramidal

Similarly hybridizing one *s*, three *p* and two *d* orbitals yields six identical hybrid *sp^3d^2 orbitals. These would be oriented in an octahedral geometry.*

Hybrid Orbitals - Summary

Steps in predicting the hybrid orbitals used by an atom in bonding:

1. Draw the Lewis structure
2. Determine the electron geometry using the VSEPR model
3. Specify the hybrid orbitals needed to accommodate the electron pairs in the geometric arrangement

Valence Electron Pair Geometry	**Number of Orbitals**	**Hybrid Orbitals**
Linear	2	*sp*
Trigonal Planar	3	sp^2
Tetrahedral	4	sp^3
Trigonal Bipyramidal	5	sp^3d
Octahedral	6	sp^3d^2

These bonds are called sigma (σ) bonds

Hybrid Orbitals – Multiple Bonds?

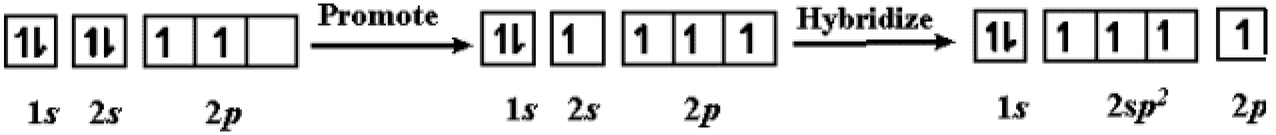
Sideways overlap of two p-orbitals will give a different type of bond - π (pi) bond.

Covalent bond that in which the overlap extends above and below the internuclear axis. There is no probability of finding the electrons on the internuclear axis.

π-bonds are generally weaker than σ-bonds as the overlap is sideways rather than direct

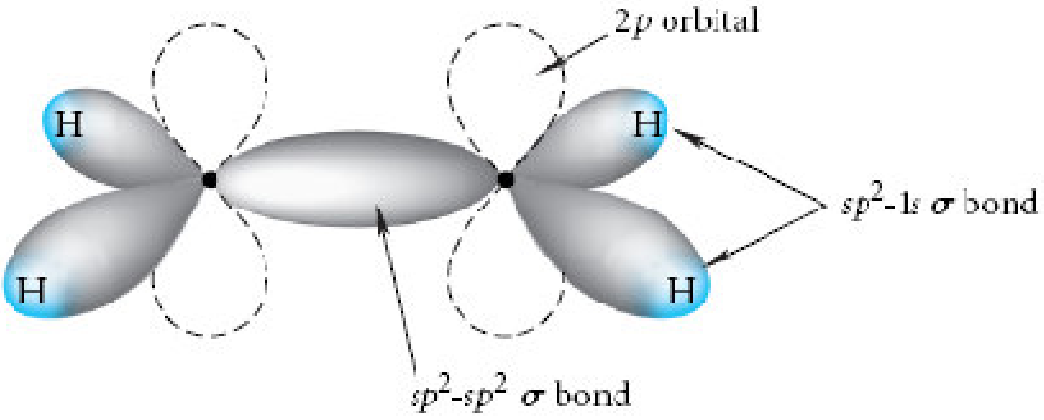
In most cases single bonds are σ-type whilst double and triple bonds are π-bonds

e.g. ethylene $H_2C{=}CH_2$



π-bond

σ-bonds

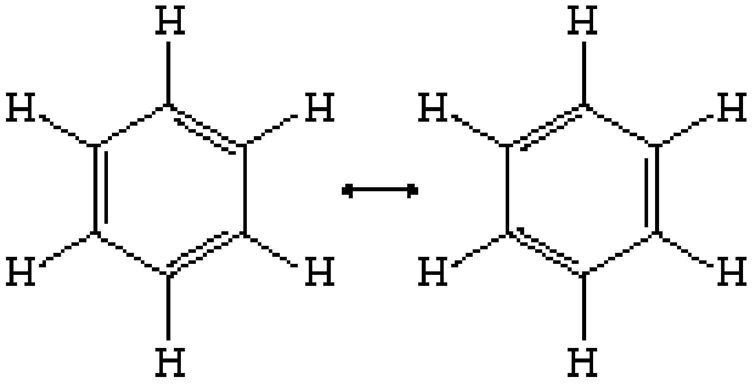


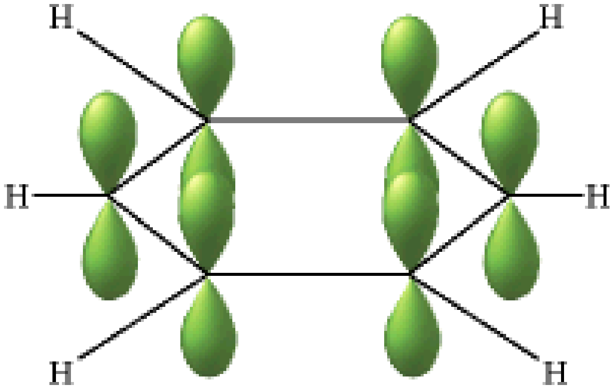
Same for HC≡CH

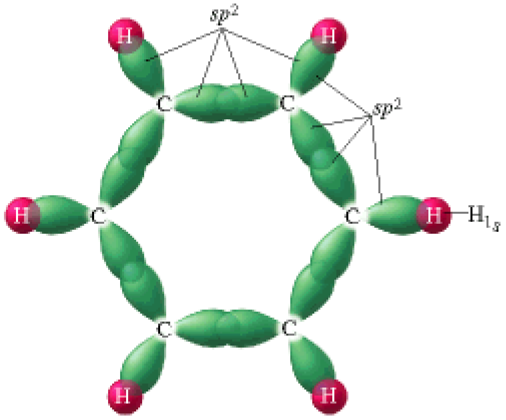
sp hybridised

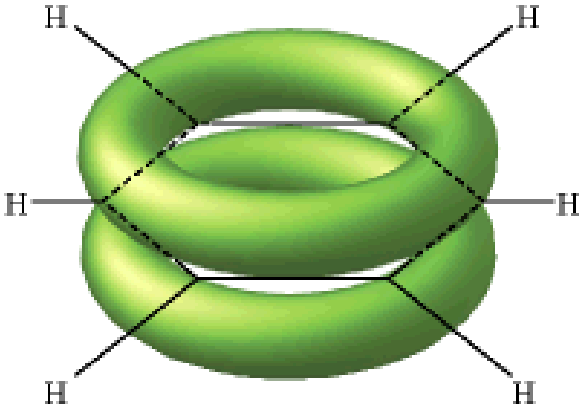
Hybrid Orbitals – Delocalised Bonding?

Benzene



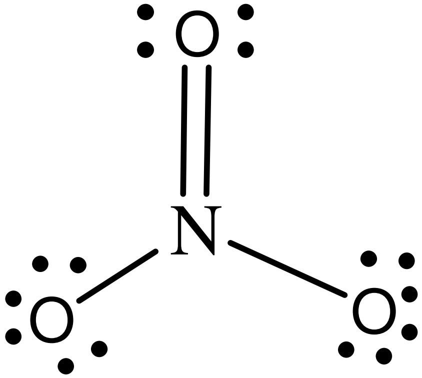


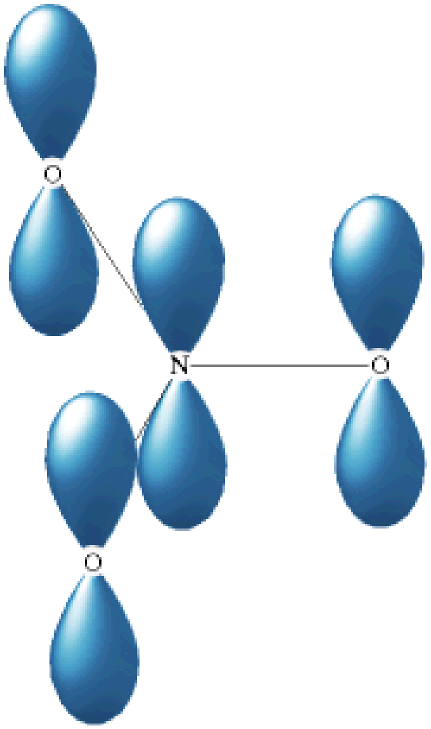


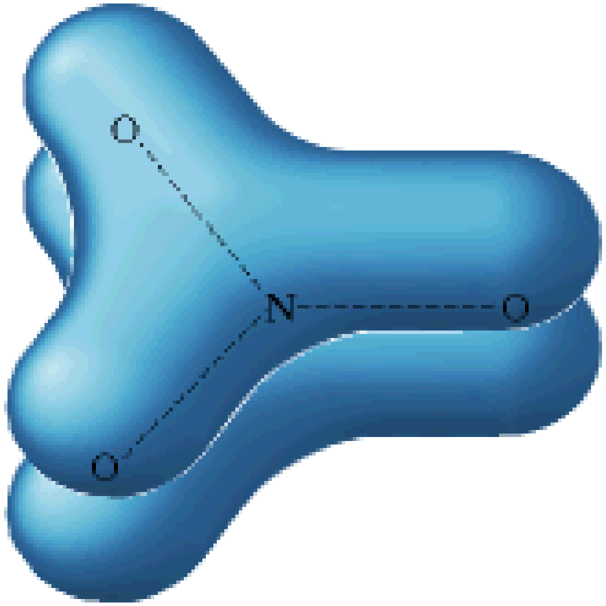


Hybrid Orbitals – Delocalised Bonding?

Nitrate ion

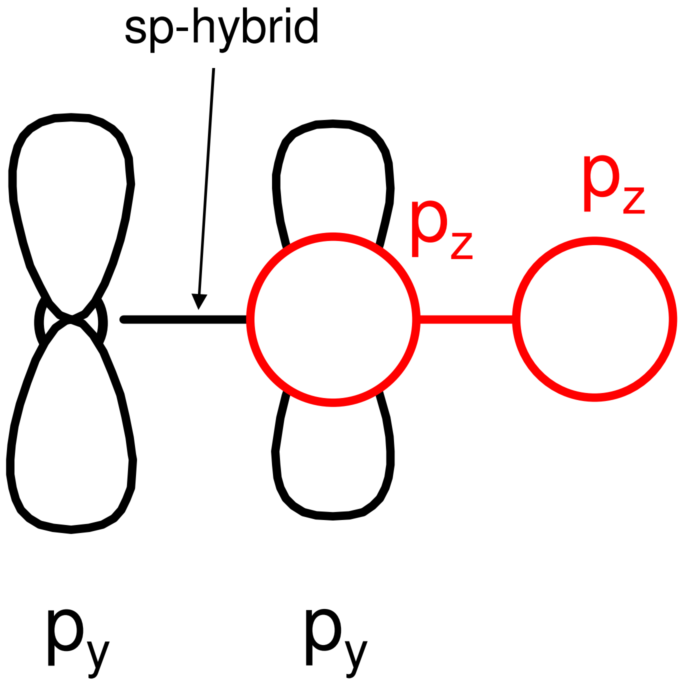






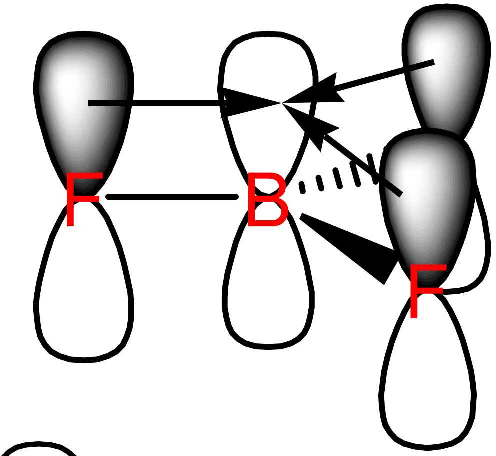
Hybrid Orbitals

CO_2

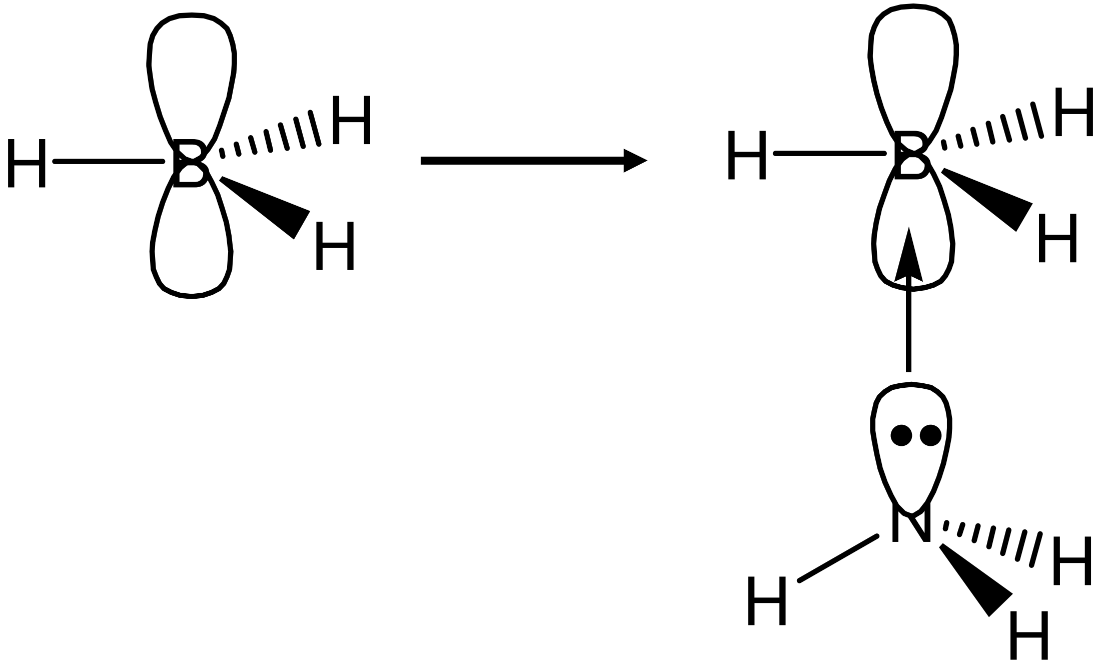


Hybrid Orbitals

BF_3: How can Boron obey the octet rule?



c.f. BH_3 - reactivity

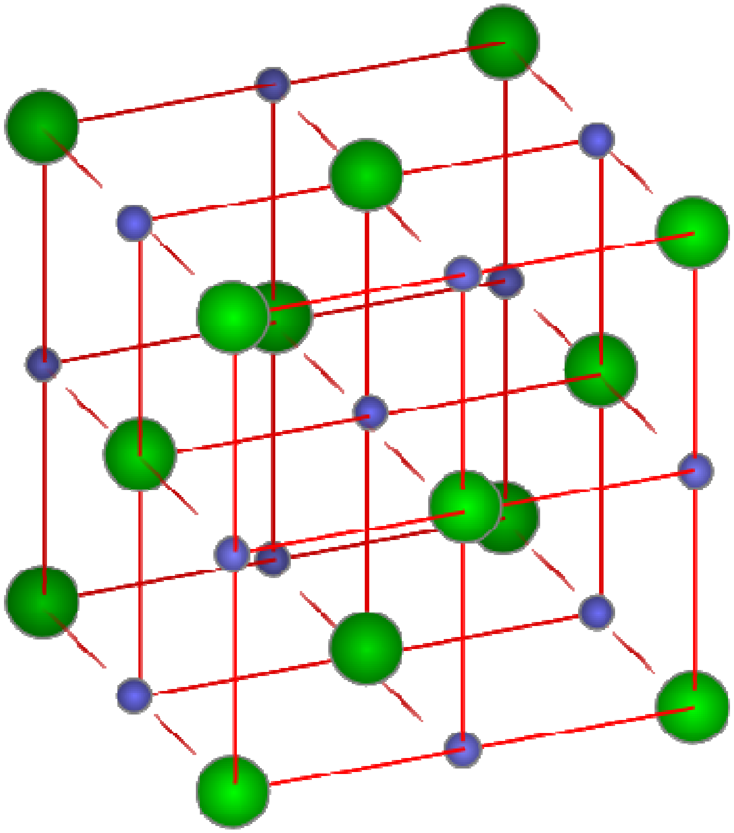


Ionic Solids

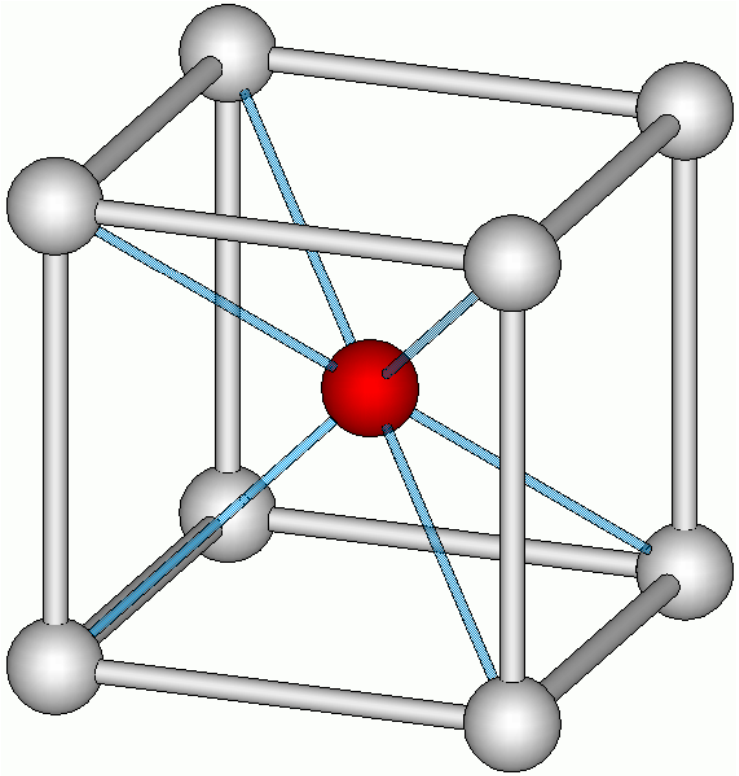
What are the structures of ionic solids e.g. NaCl?

- Can be thought of as effectively packed arrays of ions

- Efficient means maximising the contacts with oppositely charged ions



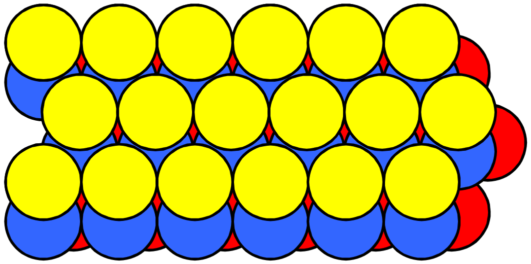
The structure of Sodium Chloride shows a coordination number of 6.



The structure of Cesium Chloride shows a coordination number of 8.

Ionic Solids

Many ionic compounds have structures based on close packing of the spherical anions



If we add a second layer of spheres these can sit on the depressions of the first layer

Adding a third layer gives two possibilities:

1. Spheres of Layer 3 may be placed directly over those of layer 1 – this is ABA or *hexagonal close packing*

2. Spheres of Layer 3 may be placed over the depressions in Layer 1 not covered by the spheres in Layer 2 – this is ABC or *cubic close packing*

CONCLUSIONS

❑ Every pair of bonded atoms shares one or more pairs of electrons. At least one pair of electrons is localised in the space between the atoms in a σ-bond.

❑ The geometry around an atom depends on the number of electrons (VSEPR).

❑ Hybrid Orbitals can explain multiple bonds and delocalisation

❑ Bond polarity and formal charges can be deduced