

Molecular Geometry

Molecular Geometry

Molecular geometry is the 3-dimensional representation of a molecule focused upon the arrangement of bonded atoms around a central atom.

Valence-shell electron-pair repulsion (VSEPR)

Things to note

Geometry is focused upon the central atom (you may have multiple central atoms in a molecule and therefore multiple shapes).

Lone pairs of electrons take-up more space and therefore compress the angle.

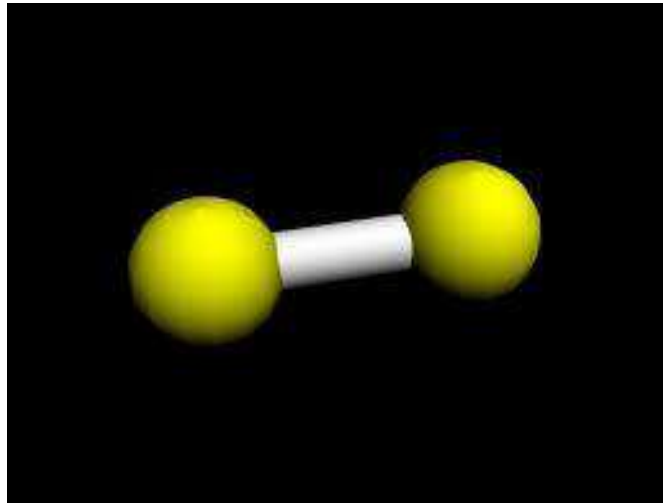
Lone pairs of electrons are not part of the central atom shape (the 3-D part).

Basic

A molecule with no central atom because it is just two atoms bonded together is linear.

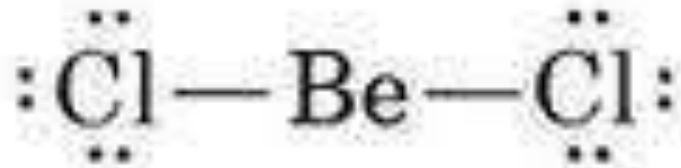
H_2 , or Cl_2

The angle is 180.

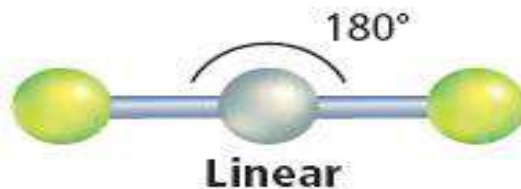


Central Atoms

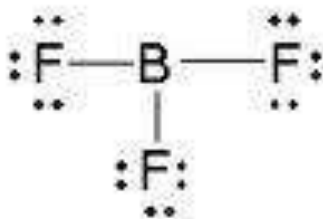
First identify the central atom and then count bonded clouds and non-bonded clouds from the Lewis Structure.



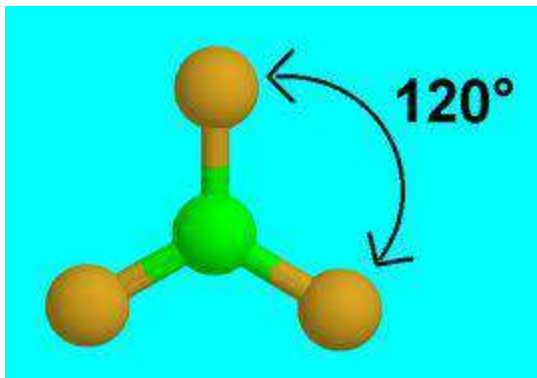
Be has 2 shared clouds, no unshared clouds.
This will be linear with a bond angle of 180° .



The next geometry has 3 shared clouds and 0 unshared clouds.



The molecular geometry is trigonal planar. It has three triangles and a flat shape. The bond angle is 120° .

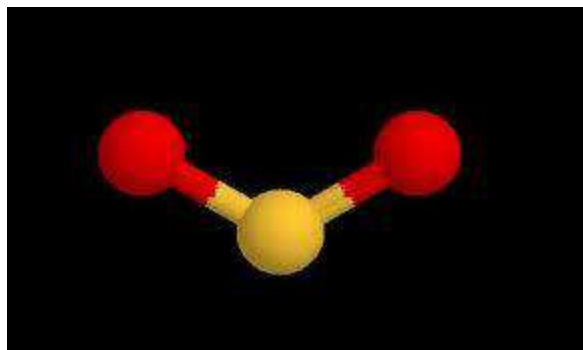


The 3 shared and 0 unshared pairs is a parent shape to 2 shared and 1 unshared pair of electrons.

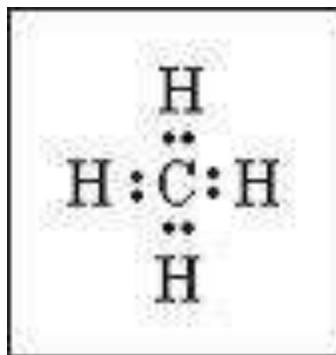
The unshared pair of electrons will compress the bond angle.



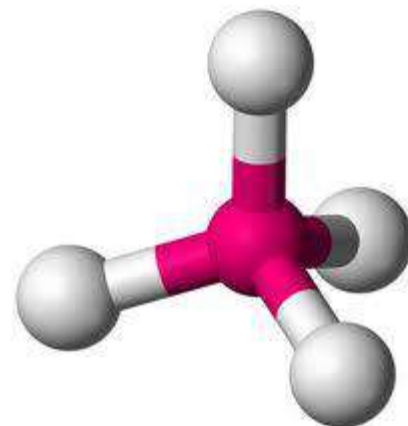
The molecular geometry is bent, with a bond angle less than 120°.



4 shared, 0 unshared



Tetrahedral with 109.5° bond angle

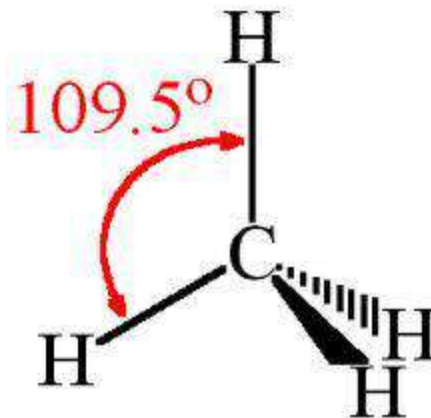


This is three dimensional.

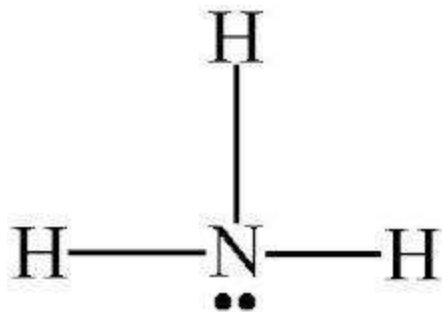
The hash marks indicate into

The paper, and the dark

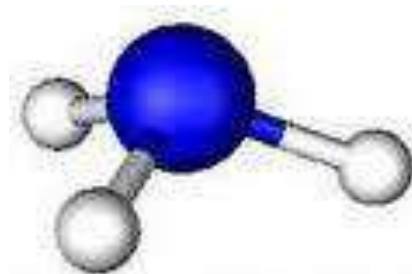
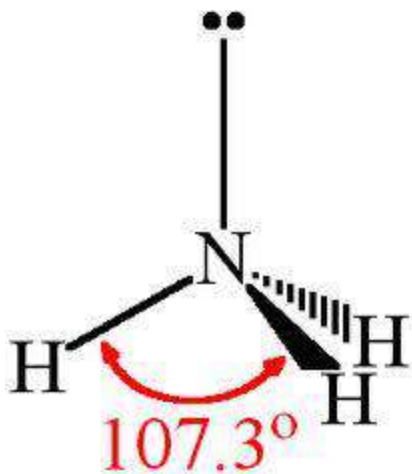
Out of the paper.



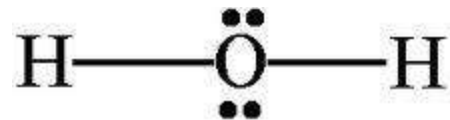
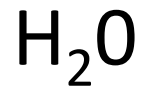
3 shared clouds, 1 unshared cloud



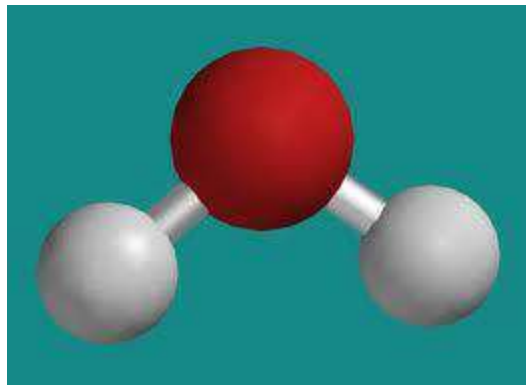
Trigonal pyramidal (not flat), bond angle 107.3°



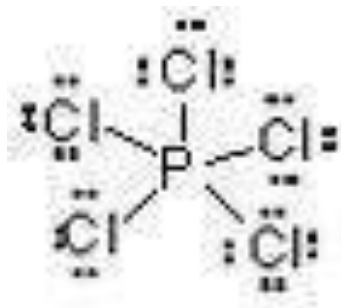
2 shared clouds and 2 unshared clouds



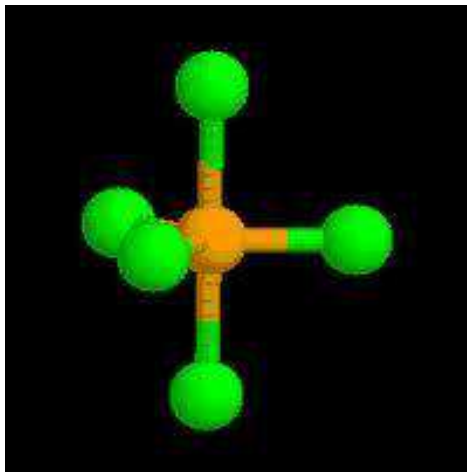
Bent (again), bond angle is 104.5° (different)



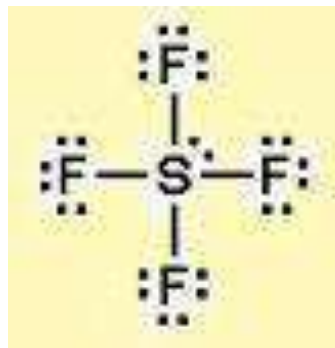
5 shared clouds, 0 unshared clouds



Trigonal bipyramidal, 90° and 120°



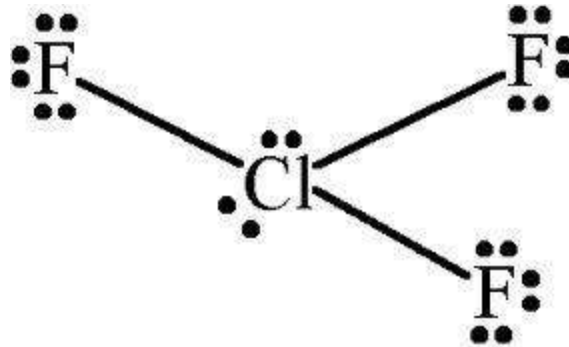
4 shared clouds, 1 unshared cloud



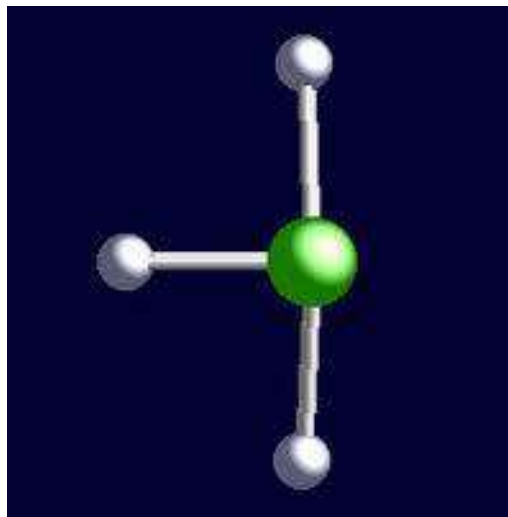
Seesaw



3 shared clouds, and 2 unshared clouds

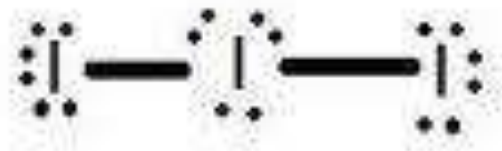


T-shaped

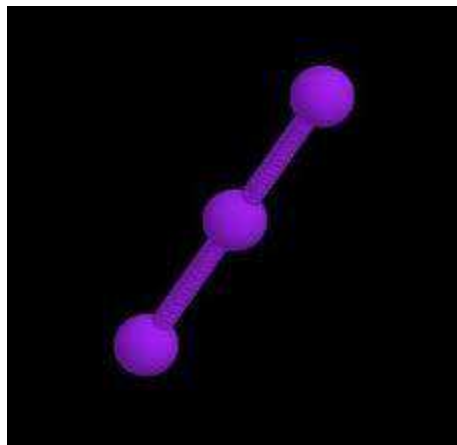


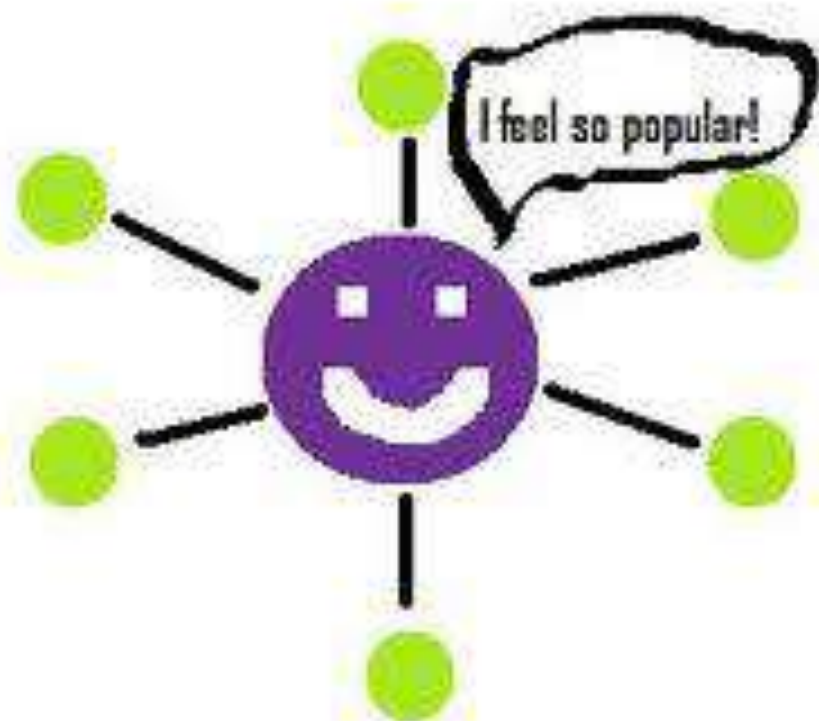
2 shared clouds and 3 unshared clouds

I_3^-

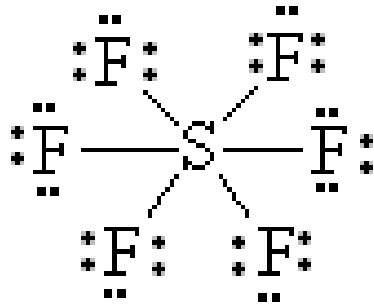


linear

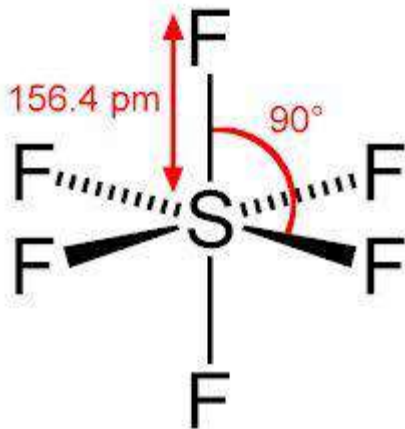




6 shared clouds, 0 unshared clouds

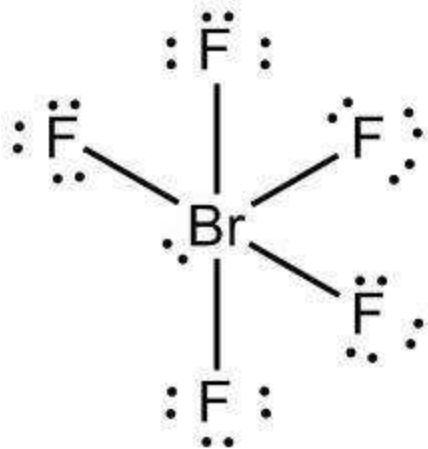


Octahedral, bond angle of 90°.

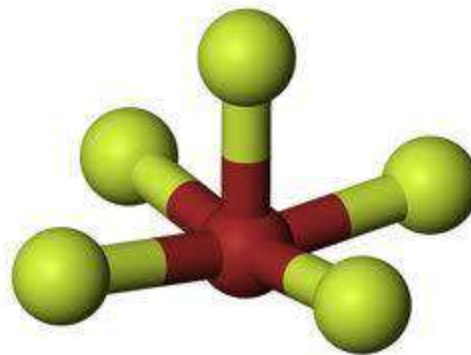
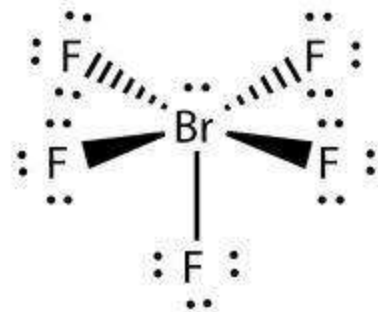


5 shared clouds, and 1 unshared cloud

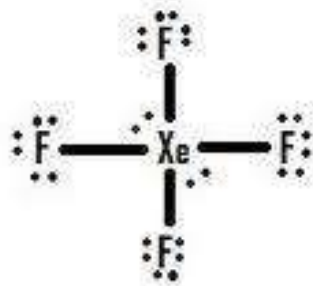
BrF_5



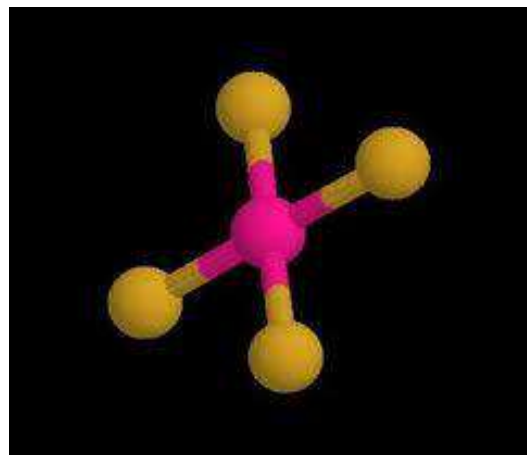
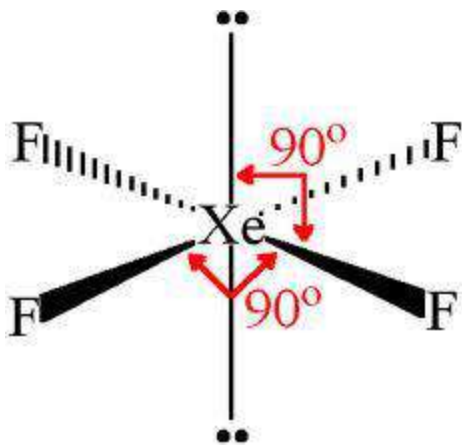
Square pyramidal



4 shared clouds, and 2 unshared clouds



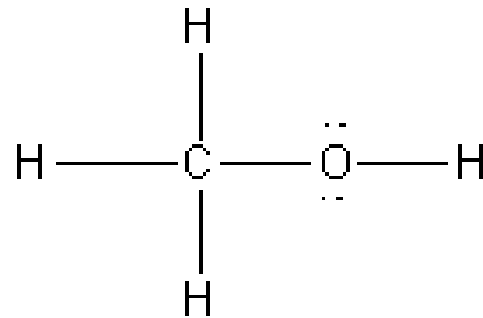
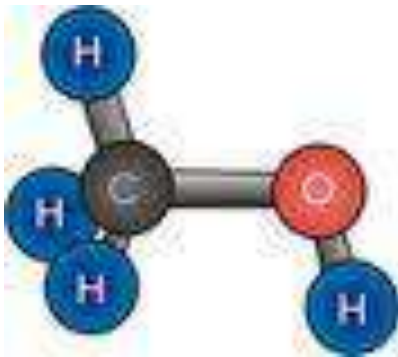
Square planar



Multiple Central Atoms

More complex molecules will have several central atoms.

For each central atom, there maybe a different geometry.



Dipole Moments

Previously we have discussed electronegativity which results in unequal sharing of electrons.

The distribution of electrical charge led to partial charges on either element.

With a dipole moment, we return to that concept, but apply it over the entire molecule.

Dipole moments apply to polar covalent compounds.

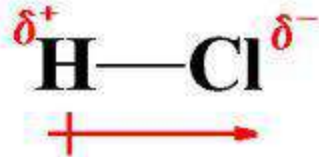
Non-polar covalent compounds have an equal distribution of electrons and therefore no partial charges on any of the atoms.

Determining Dipole Moments

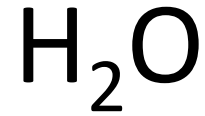
Need the electronegativity differences and the molecular geometry to determine the dipole moment.

Linear Example

The dipole arrow head points in the direction towards the negative charge.

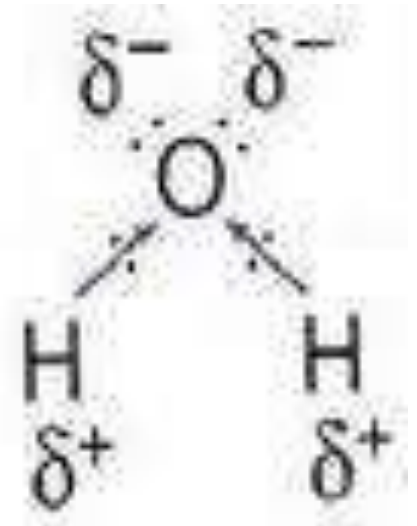


**Dipole Moment has a
Magnitude and a Direction**



The negative charge is on the oxygen, so the arrows point away from the hydrogen towards the oxygen.

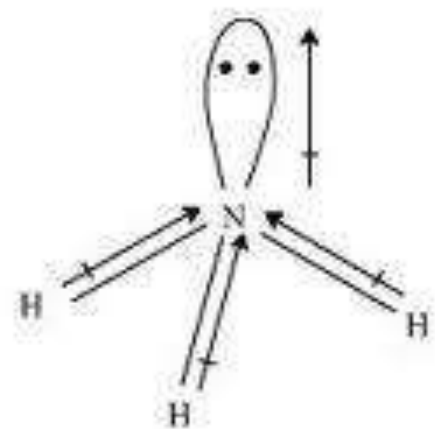
The net dipole extends from the top of the oxygen.



Ammonia

Again the dipole moment is the result of adding the arrows pointing towards the nitrogen.

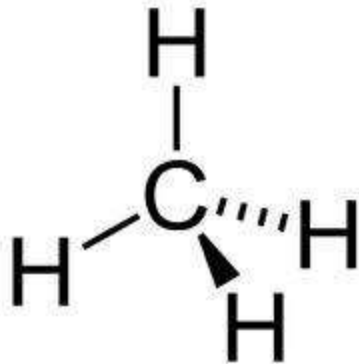
Therefore the resulting dipole arrow is from the nitrogen to the lone pair of electrons.

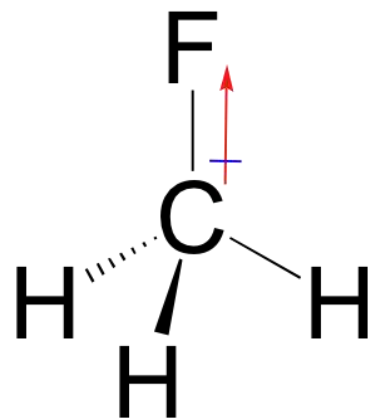
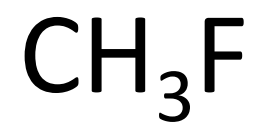


Dipole moment in NH₃



Methane is nonpolar, so it will not have a dipole.





VALENCE BOND (VB) THEORY

VSEPR models while helpful, are not robust enough to explain all aspects of covalent bonding.

Two areas in which VSEPR fails are bond length and bond enthalpy (energy).

VSEPR predicts all single bonds are of equal length and equal energy (enthalpy).

But... H_2 has a bond enthalpy of 436.4 kJ/mol and a bond length of 74pm while F_2 has a bond enthalpy of 150.6 kJ/mol and a bond length of 142pm.

Valence bond (VB) theory is one of two theories that uses quantum mechanics to explain bonding.

VB theory uses orbital overlapping to explain how bonds form between atoms.

For hydrogen, it is two “1s” orbitals overlapping to form the bond.

For fluorine, it is two “2p” orbitals overlapping to form the bond.

This works for same element bonding, but a new concept was developed using VB theory for unlike elements.

Hybridization

It was expected from Lewis Structures that a bond involving an s-orbital versus a p-orbital would have different energies, but this is not the case.

Different energy is associated with the type of elements involved and the number of electrons shared but not the orbitals involved.

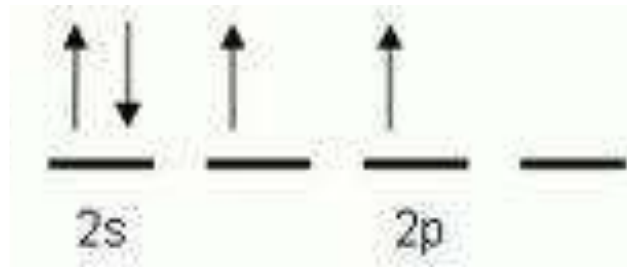
The solution is a merging of s-orbitals and p-orbitals as required from the Lewis Structure.

The s and p character is distributed over the merged hybridized orbitals.

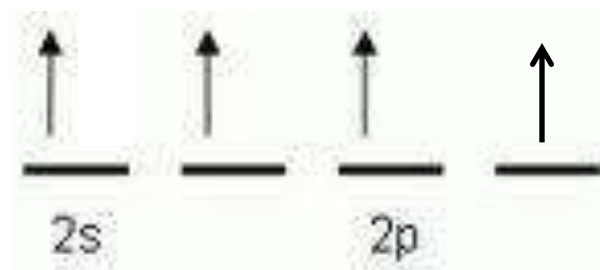
The more p's used, the less s character the hybridized orbitals have.

CH₄ as an example

The valence orbital notation for carbon is:



For hybridization to occur, 1 of the 2s electrons is promoted to the empty p orbital.

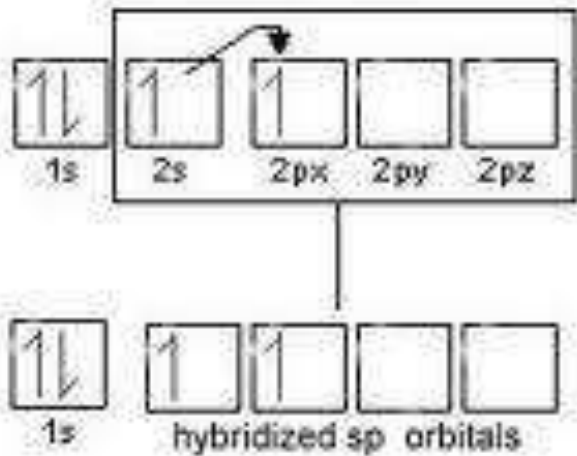


The promotion of the electron from the s-orbital to the p-orbital does require energy, but the energy is generally gained back from the resulting bond.

The 4 orbitals combine into sp^3 hybridized orbitals.

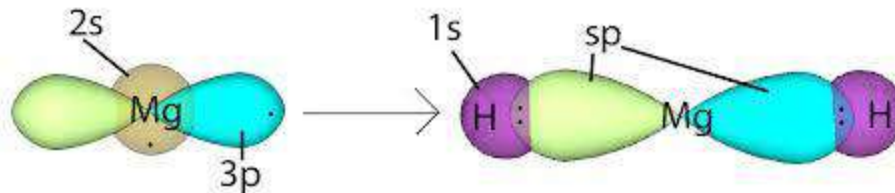
One molecular geometry associated with this hybridization is tetrahedral.

Other hybridizations

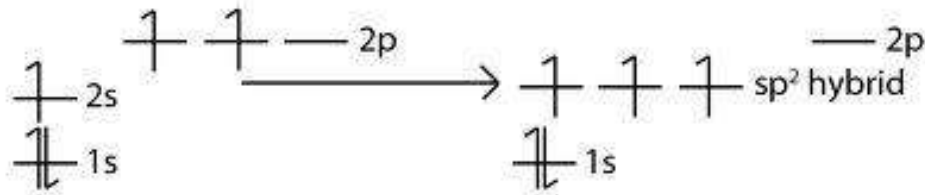


This is an example of an sp hybridization. Two of the p-orbitals are not hybridized.

Geometry is generally linear.



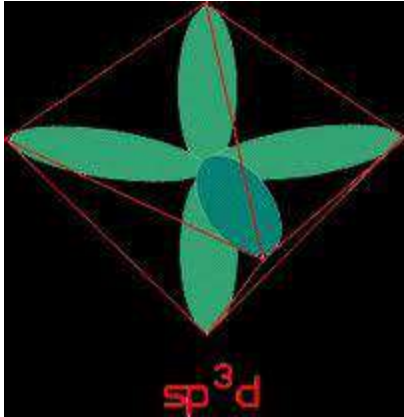
Other hybridizations



sp^2 hybridization, generally the geometry is trigonal planar.

One p -orbital is not hybridized.

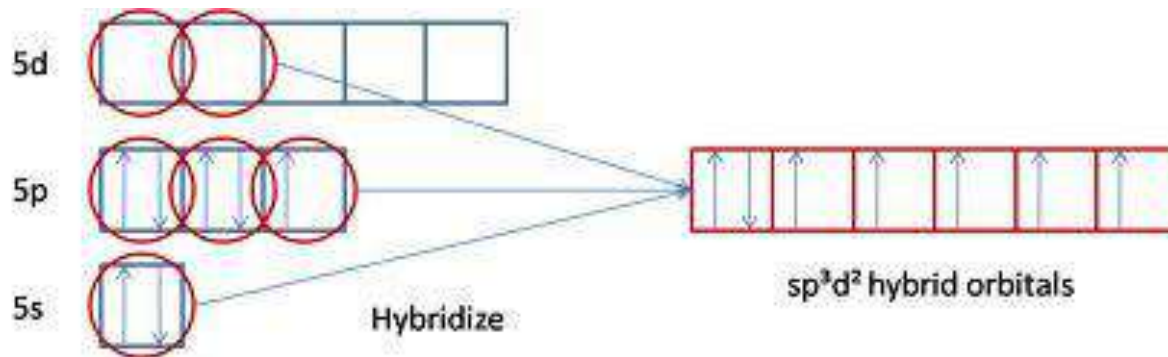
Other hybridizations



In this hybridization, you must be using an element from the 3rd period so that d-orbitals with higher energy are available for hybridization.

Trigonal bipyramidal

Other Hybridization



- This is using two d-orbitals and leaving three behind.
- This is the hybridization associated with octahedral.

To note

All of the previous hybridizations are for single bonds (or head-to-head orbital overlap which will soon be called sigma bonds).

Hybridization is used to explain covalent bonding.

It mixes non-equivalent orbitals

The formation of the hybrid orbitals requires an input of energy.