



# Bonding in Molecules

## Covalent Bonding

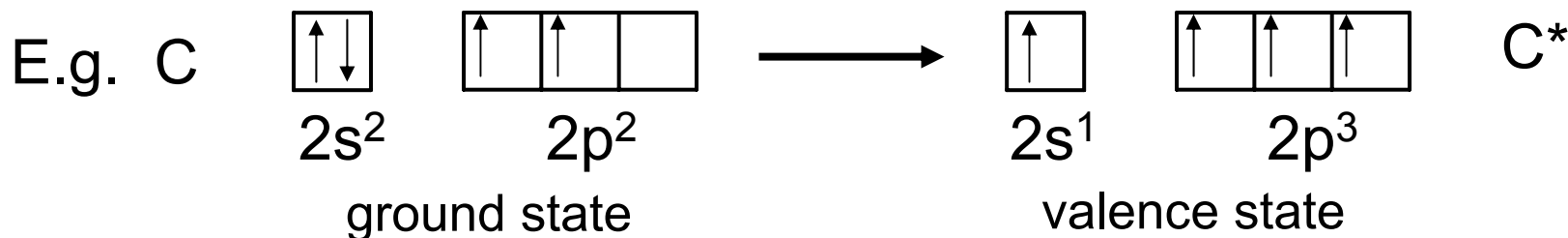
The term *covalent* implies sharing of electrons between atoms.

Valence electrons and valence shell orbitals

- Only valence electrons are used for bonding:  $ns$ ,  $np$ ,  $nd$
- “Core” electrons are held too tightly (too low in energy)
- Filled  $nd$  orbitals are considered core electrons

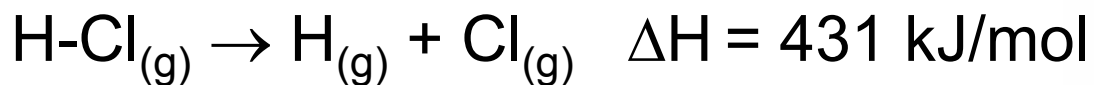
### Valence state electron configurations and Promotion Energies

- The *promotion energy* is the energy required to promote electrons from the ground state to a “valence state”, which is one type of excited state configuration that is used for bonding.

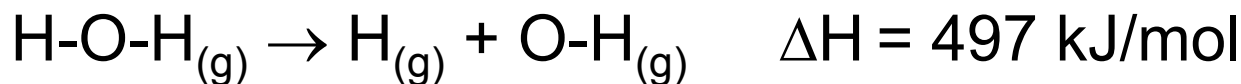


# Chem 59-250 Bond Energy, $E_{A-B}$

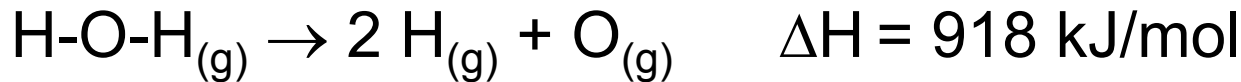
Diatomic:



Polyatomic:

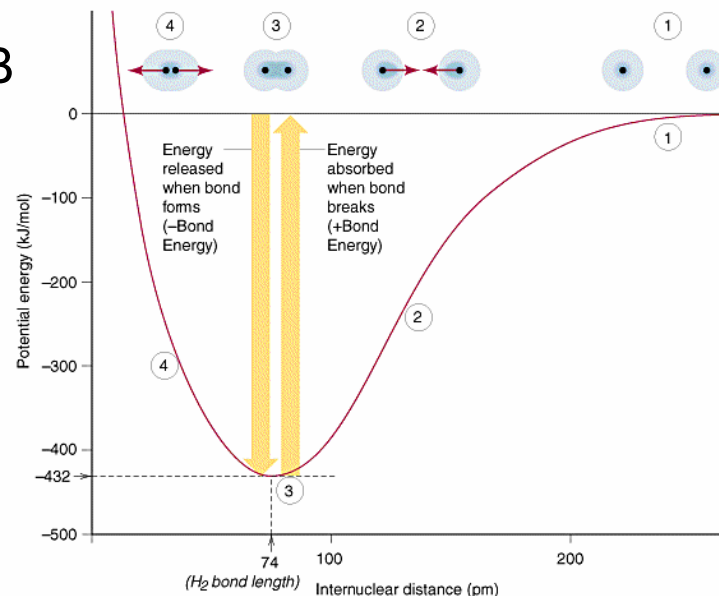


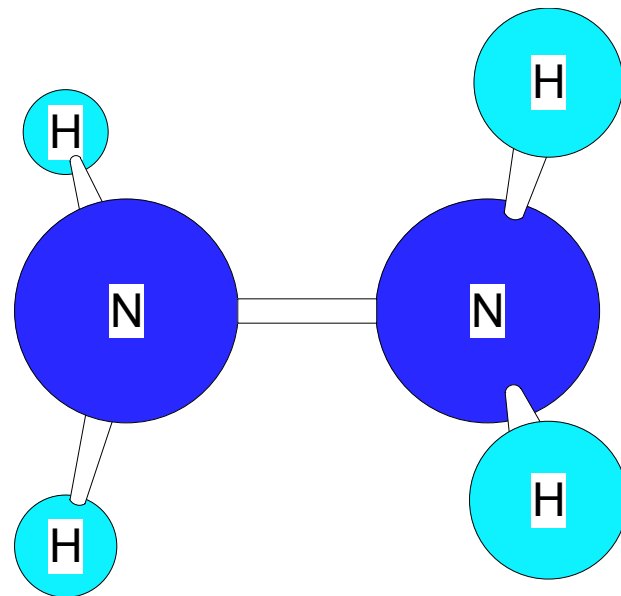
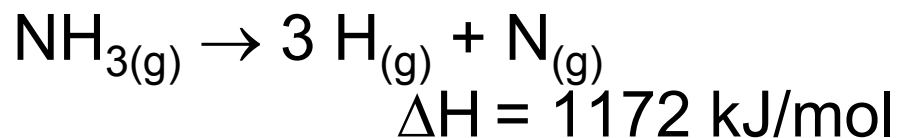
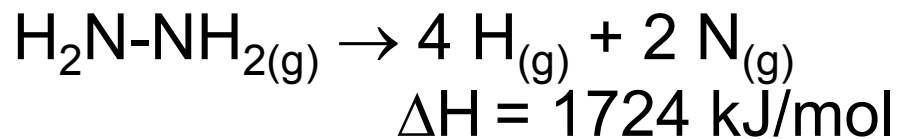
Thus:



Average O-H bond energy =  $918 / 2$

$$E_{\text{O-H}} = 459 \text{ kJ/mol}$$





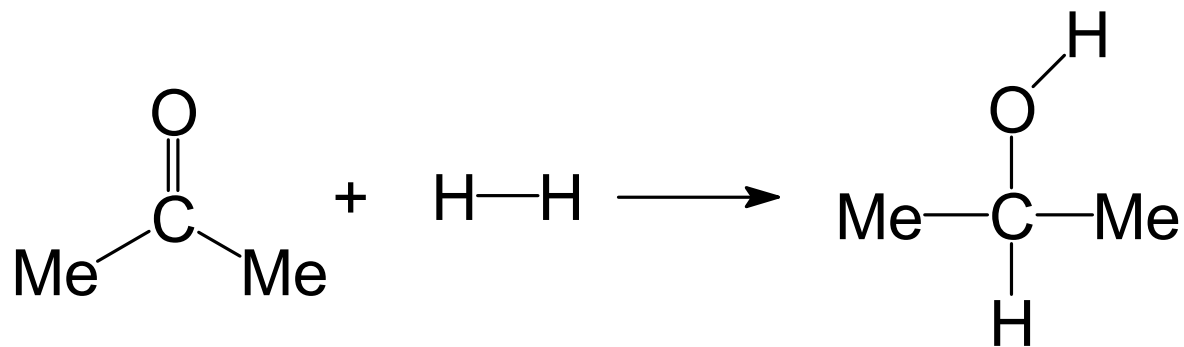
Thus average N-H bond energy =  $1172 / 3$

$$E_{\text{N-H}} = 391 \text{ kJ/mol}$$

Since  $1724 = 4 E_{\text{N-H}} + E_{\text{N-N}}$

We can estimate N-N bond energy to be:

$$1724 - 4(391) = 160 \text{ kJ/mol}$$



$$E_{\text{H-H}} = 436 \text{ kJ/mol}$$

$$E_{\text{C-H}} = 414 \text{ kJ/mol}$$

$$E_{\text{C=O}} = 745 \text{ kJ/mol}$$

$$E_{\text{C-O}} = 351 \text{ kJ/mol}$$

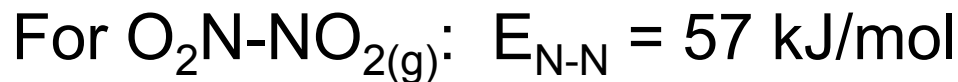
$$E_{\text{O-H}} = 464 \text{ kJ/mol}$$

$$\Delta H_{\text{rxn}} = \sum E(\text{bonds broken}) - \sum E(\text{bonds formed})$$

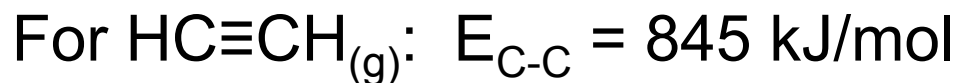
$$\Delta H_{\text{rxn}} = (436 + 745) - (414 + 351 + 464) \text{ kJ/mol}$$

$$\Delta H_{\text{rxn}} = -48 \text{ kJ/mol}$$

Remember that such calculated bond energies can change:

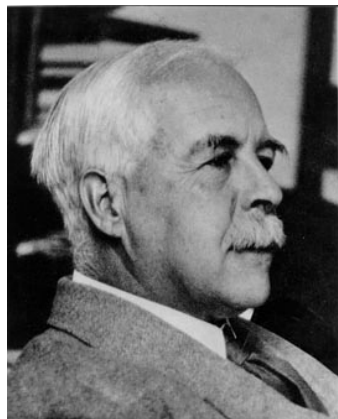


They are only a rough approximation and predictions must be made cautiously. There are, however, some typical trends such as:





*Localized* implies that electrons are confined to a particular bond or atom.

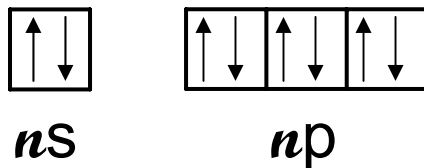


G.N. Lewis

The Lewis approach to bonding

Pairs of electrons are localized in bonds or as non-bonding “lone pairs” on atoms. Each bond is formed by a pair of electrons shared by two atoms.

*Octet rule*: most main group atoms will tend to end up with an  $ns^2 np^6$  electron configuration.



This is mostly true for the molecules of organic chemistry not necessarily for inorganic compounds.



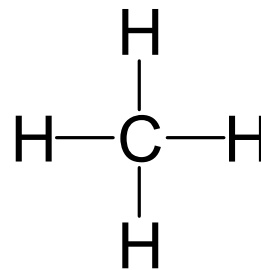
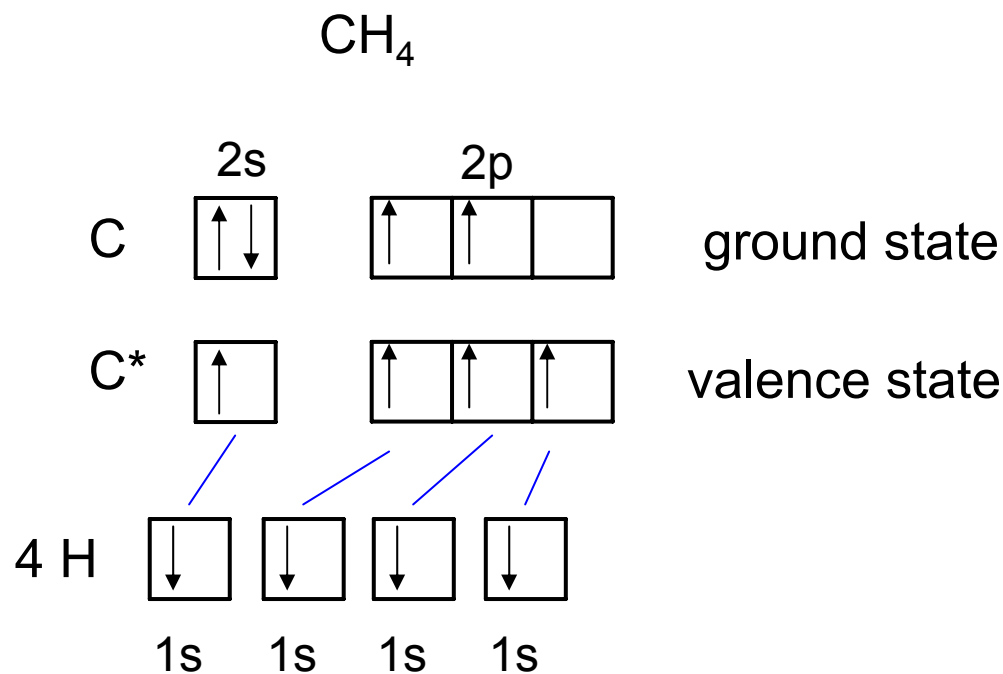
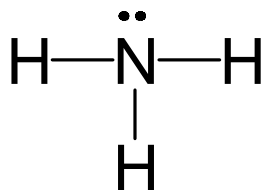
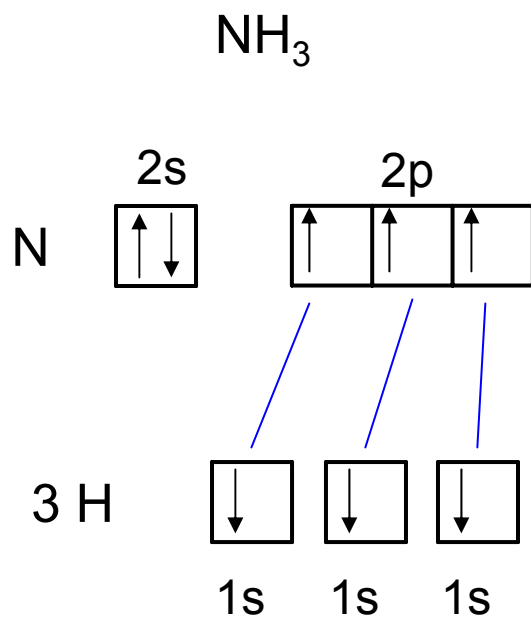
## Chem 59-250 Rules for drawing Lewis diagrams

- a. Pick the central atom.
  - Atoms that are present only once in the formula, especially heavy elements and metals, tend to be at the center of the structure.
  - Oxygen is often terminal and hydrogen almost always is.
  - Often the formula is written with the central atom first.  
(Sometimes there may be more than one central atom.)
- b. Write out the valence shell electron configurations for the neutral central atom and the "terminal" atoms in their ground states.
- c. If there is a negative charge distribute it among the terminal atoms in the first instance. Bear in mind that all the terminal atoms must make at least one covalent bond with the central atom, so do not create any noble gas configurations on them. Positive charge is best initially assigned by removing electrons from the central atom.
- d. The total number of unpaired electrons on the terminal atoms will have to match the number of unpaired electrons on the central atom to account for the bonds and leave no unpaired electrons. If this is not the case, once the first three steps have been carried out, there are two strategies available:
- e. Move electrons between the central atom and the terminal atoms as necessary. Make sure you keep track of the formal charges because you must be specific about their location. *Enclosing a Lewis structure in brackets with the charge outside is not acceptable.*
- f. If and only if the central atom comes from the second period or below (Na onwards,  $n=3$  and up), electrons can be placed into the  $nd$  subshell. (Whether the  $d$  orbitals play a significant role in bonding in main group compounds is debatable, but they do help to predict correct structure without invoking canonical structures with unreasonable charge separations.)



# Chem 59-250 Typical Lewis structural types:

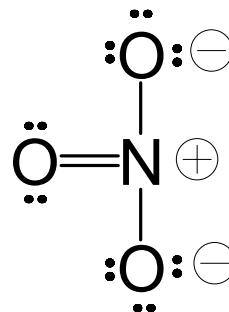
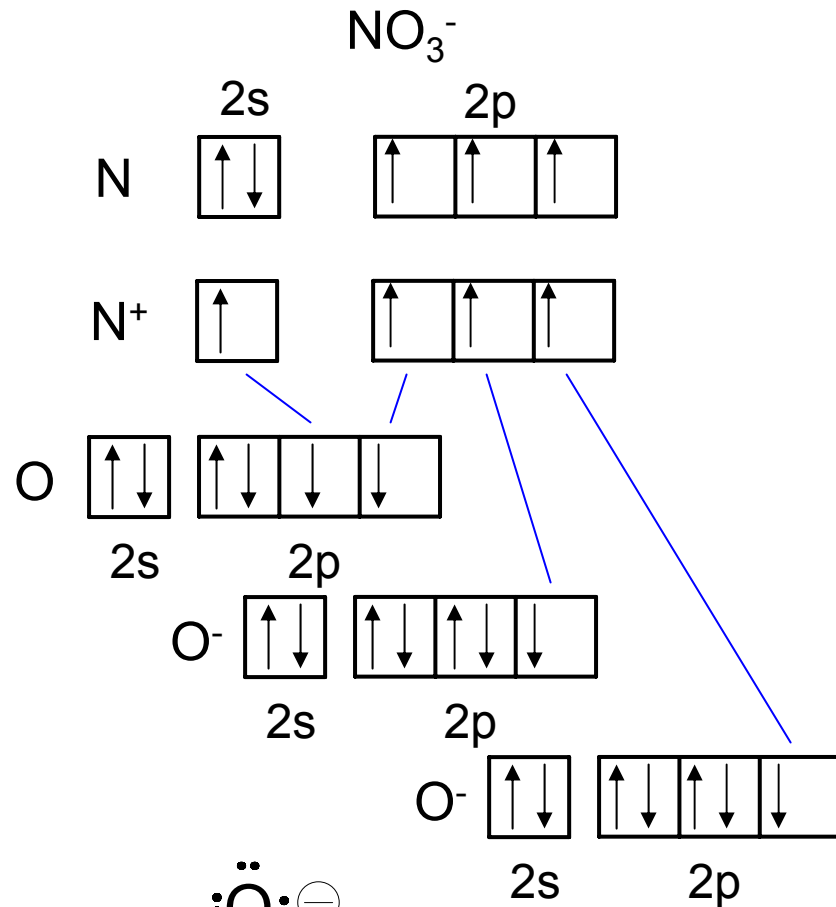
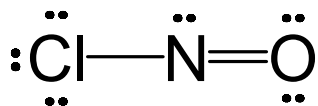
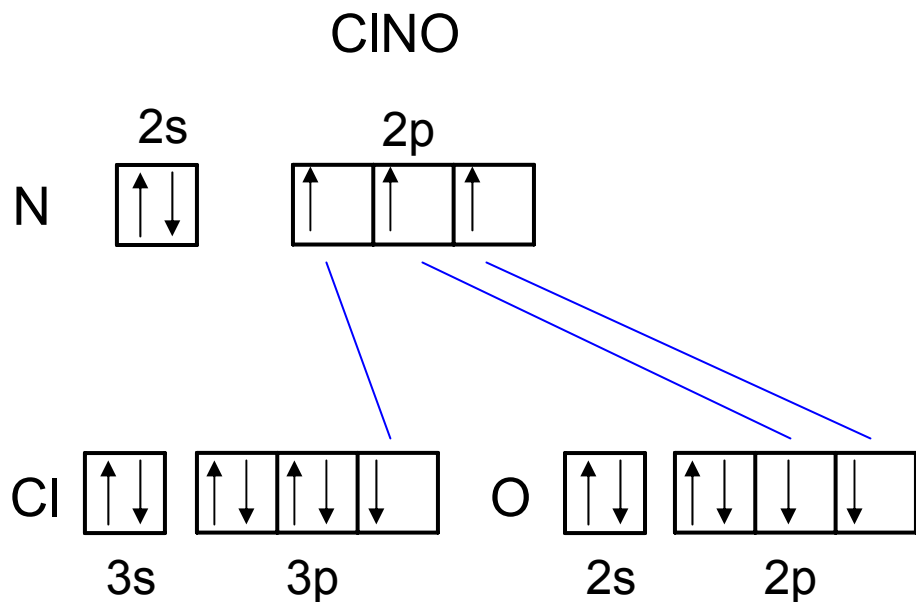
Molecules that conform to the "Octet Rule": saturated molecules



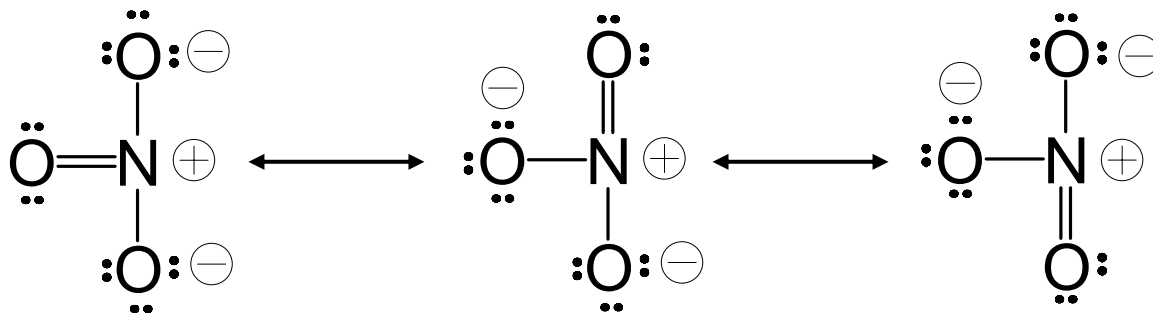
These are typical of the molecules of organic chemistry.



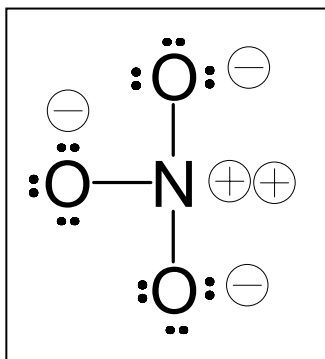
Molecules that conform to the "Octet Rule": unsaturated molecules.



*Resonance* implies that there is more than one possible way to distribute the valence electrons in a Lewis structure. For an adequate description, each “canonical” structure must be drawn.



If different equivalent resonance structures are possible, the molecule tends to be more stable than one would otherwise expect. This is a quantum mechanical effect that we will talk about later.



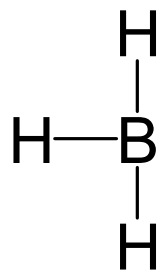
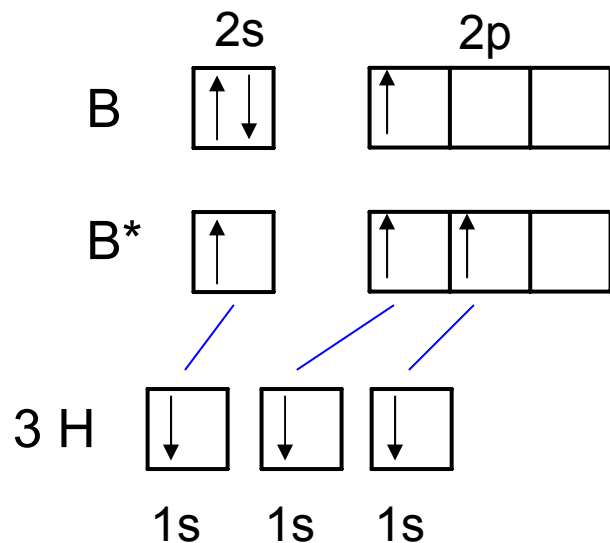
Less favourable  
canonical structure

**I expect you to be able to:**

Draw Lewis structures (including resonance structures when necessary), determine bond orders, determine and place formal charges.

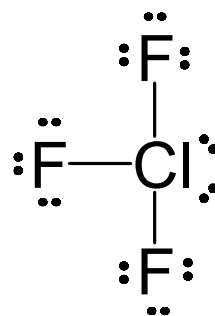
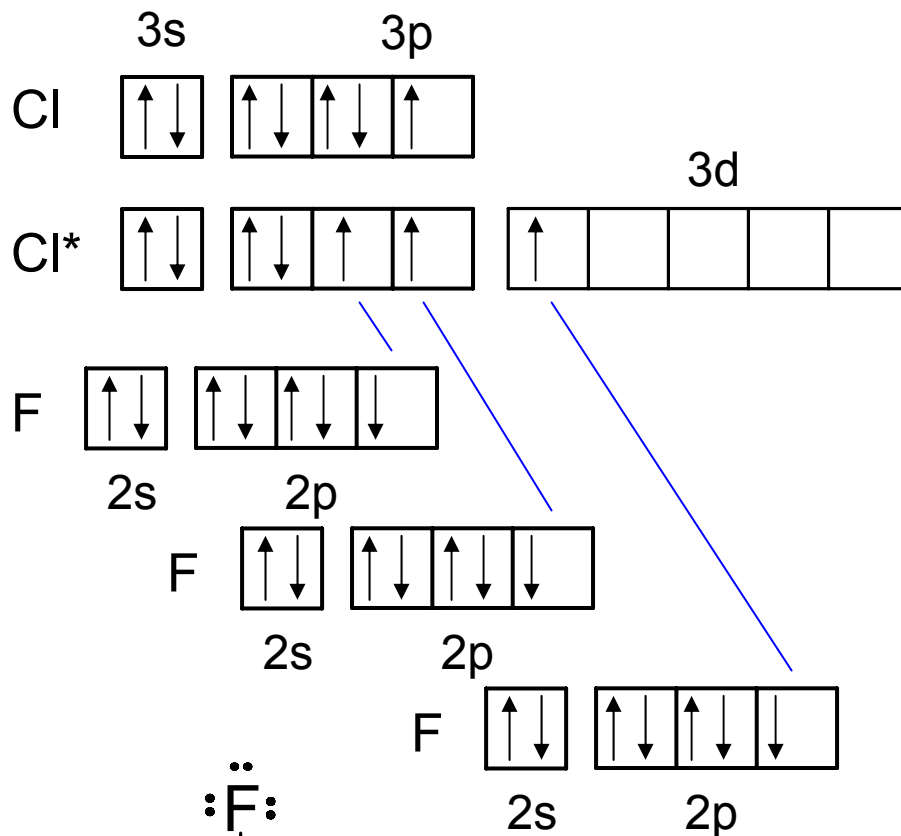


Electron-deficient molecules



"Lewis acids"

Expanded valence shell molecules



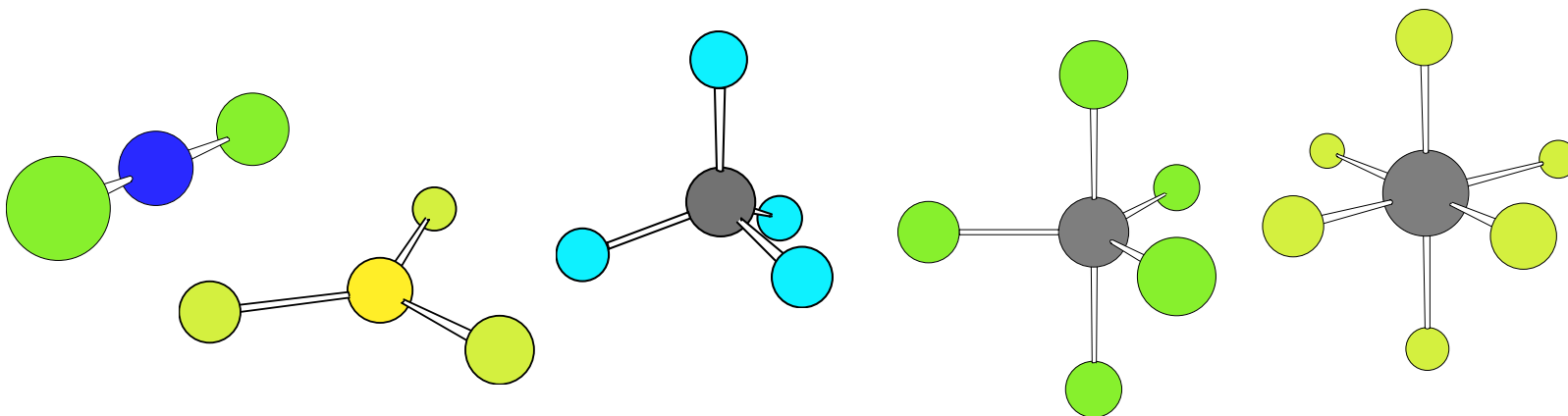
"Hypervalent molecules"

## Valence Shell Electron Pair Repulsion Theory

A basic geometry can be assigned to each non-terminal atom based on the number of “objects” attached to it. Objects include bonded atoms (single, double, triple, partial bonds) and “lone pairs” of electrons.

VSEPR theory lets us predict the shape of a molecule based on the electron configurations of the constituent atoms. It is based on maximizing the distance between points on a spherical surface.

| Number of Objects | 2      | 3               | 4           | 5                     | 6          |
|-------------------|--------|-----------------|-------------|-----------------------|------------|
| Geometry          | linear | trigonal planar | tetrahedral | trigonal bipyramidal* | Octahedral |



The geometry around an atom is described by the general formula:

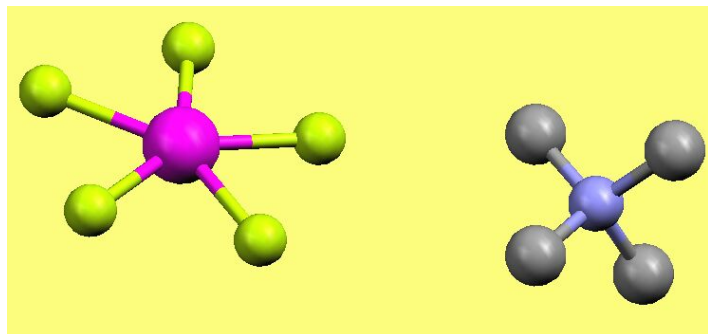
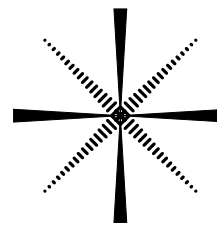
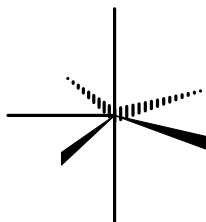
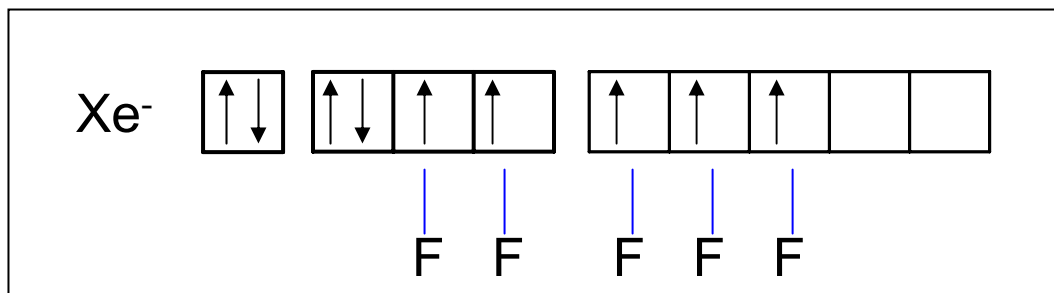


Where X is a bonded atom, E is a lone pair and (m+n) is the number of objects (sometimes called the *steric number*, SN) around the central atom A.

| Number of Objects | 2      | 3   | 4  | 5   | 6  |
|-------------------|--------|---|--|---|--|
| Geometry          | linear | trigonal planar                               | tetrahedral  | trigonal bipyramidal  | Octahedral   |
| Formula (Shape)   | $AX_2$ | $AX_3$<br>(trig. planar)<br>$AX_2E$<br>(bent) | $AX_4$<br>(tetrahedral)<br>$AX_3E$<br>(pyramidal)<br>$AX_2E_2$<br>(bent) | $AX_5$<br>(t.b.p. or square pyramidal)<br>$AX_4E$<br>(seesaw)<br>$AX_3E_2$<br>(T-shaped)<br>$AX_2E_3$<br>(linear) | $AX_6$<br>(octahedral)<br>$AX_5E$<br>(square pyramidal)<br>$AX_4E_2$<br>(square planar)<br>$AX_3E_3$<br>(T-shaped) |



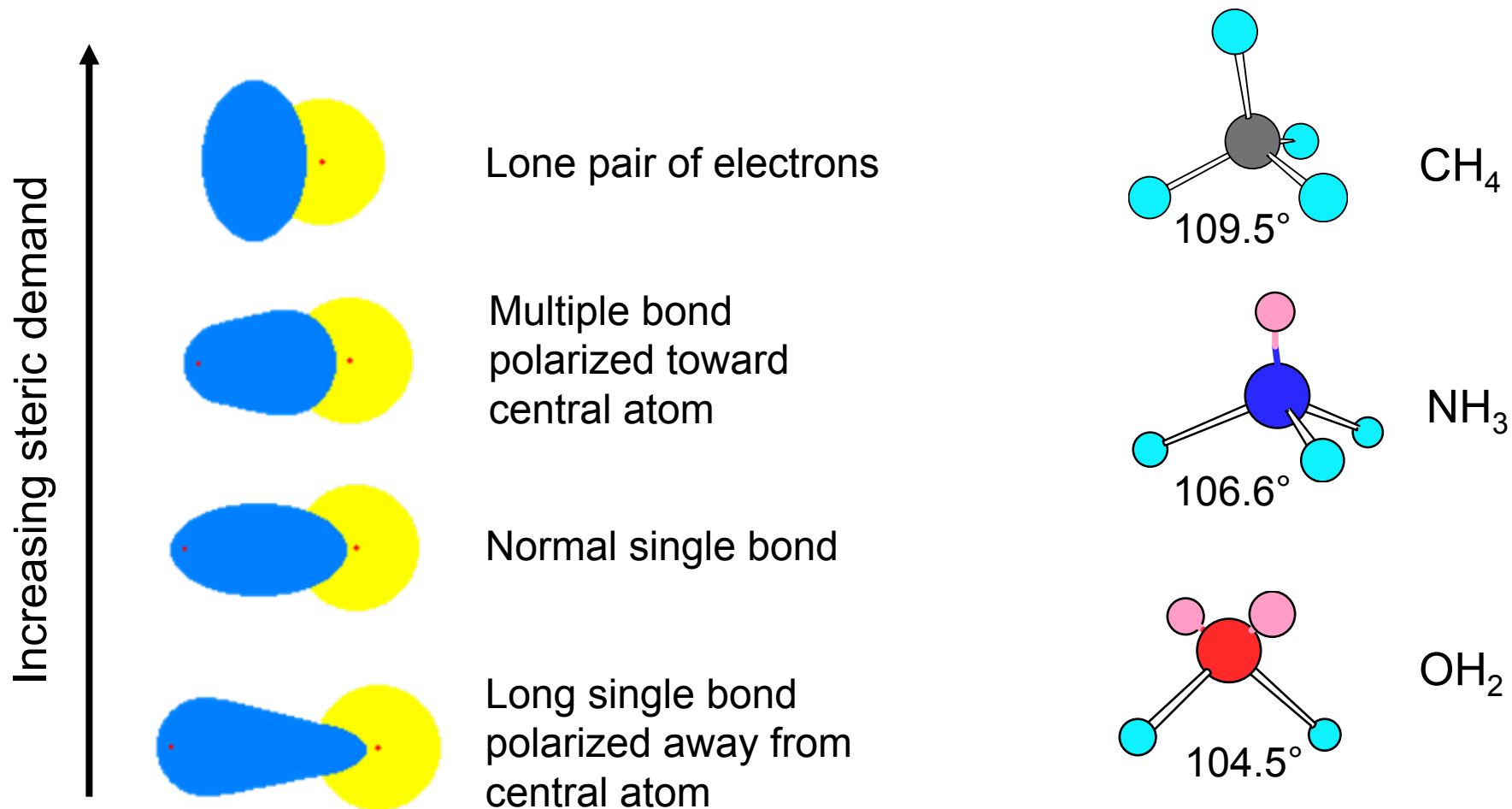
|                   |                        |                       |
|-------------------|------------------------|-----------------------|
| Number of Objects | 7                      | 8                     |
| Geometry          | pentagonal bipyramidal | square anti-prismatic |

 $\text{XeF}_5^-$  $\text{NMe}_4^+$ 

Xe is described as  $\text{AX}_5\text{E}_2$  and has a pentagonal planar shape derived from the pentagonal bipyramidal geometry.

## Refinement of VSEPR theory predicted geometries

The relative *steric* demand of objects is different and amount of repulsion caused by the object will alter the arrangement of the atoms around the central atom.

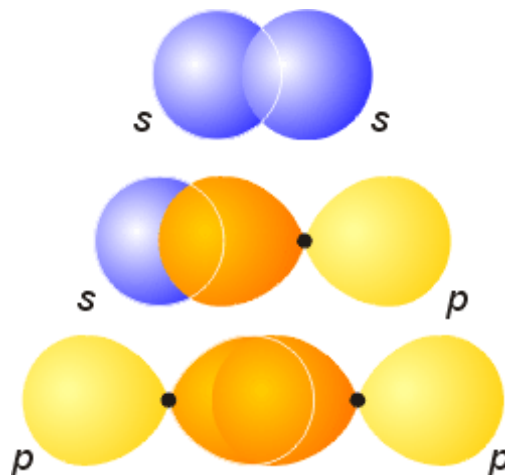


# Valence Bond Theory

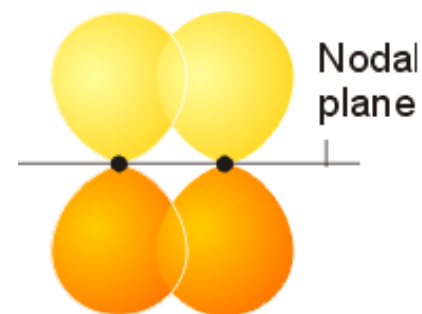
Valence bond theory (VBT) is a localized quantum mechanical approach to describe the bonding in molecules. VBT provides a mathematical justification for the Lewis interpretation of electron pairs making bonds between atoms. VBT asserts that electron pairs occupy *directed* orbitals localized on a particular atom. The directionality of the orbitals is determined by the geometry around the atom which is obtained from the predictions of VSEPR theory.

In VBT, a bond will be formed if there is overlap of appropriate orbitals on two atoms and these orbitals are populated by a maximum of two electrons.

$\sigma$  bonds:  
symmetric about  
the internuclear  
axis



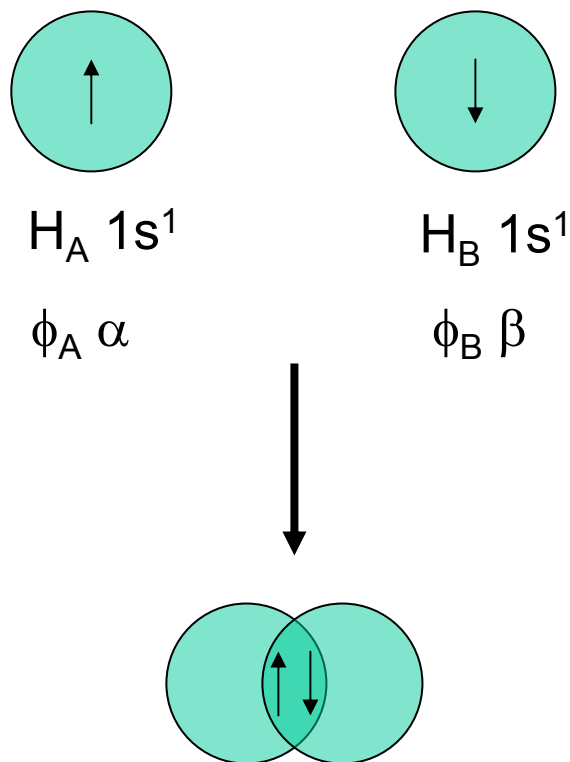
$\pi$  bonds: have  
a node on the  
inter-nuclear axis  
and the sign of  
the lobes  
changes across  
the axis.



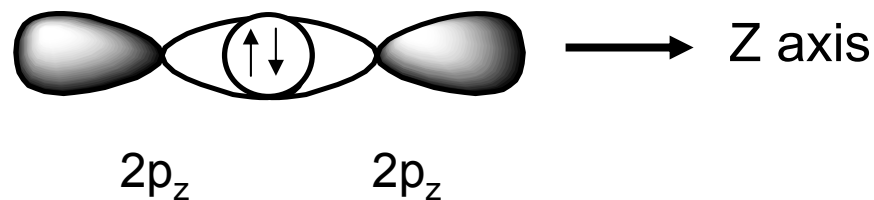
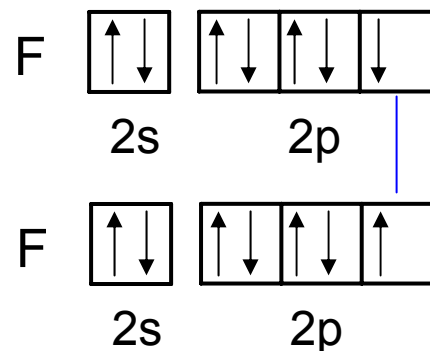


# Chem 59-250 Valence Bond Theory

Valence bond theory treatment of bonding in  $\text{H}_2$  and  $\text{F}_2$  – the way we will use it.



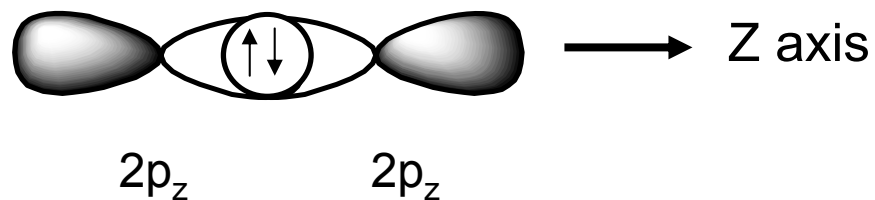
This gives a  $1s-1s$   $\sigma$  bond between the two H atoms.



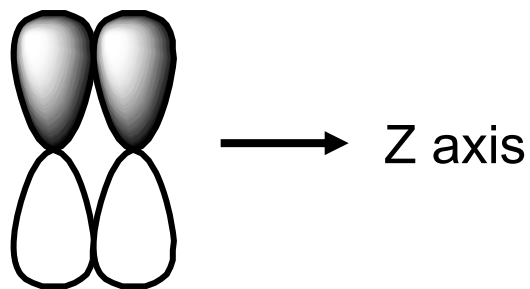
This gives a  $2p-2p$   $\sigma$  bond between the two F atoms.

*For the simple VBT treatment of covalent bonding, we will ignore the anti-bonding combinations and any ionic contributions to bonding.*

Valence bond theory treatment of bonding in O<sub>2</sub>

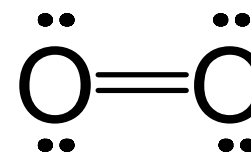
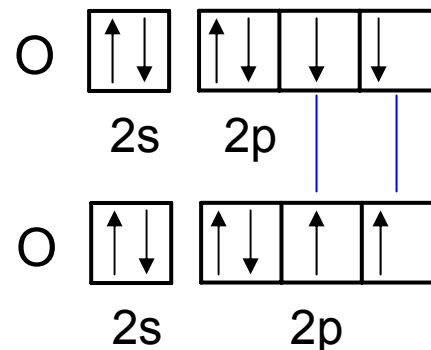


This gives a 2p-2p  $\sigma$  bond between the two O atoms.



$2p_y$                        $2p_y$  (the choice of  $2p_y$  is arbitrary)

This gives a 2p-2p  $\pi$  bond between the two O atoms. **In VBT,  $\pi$  bonds are predicted to be weaker than  $\sigma$  bonds because there is less overlap.**



Lewis structure

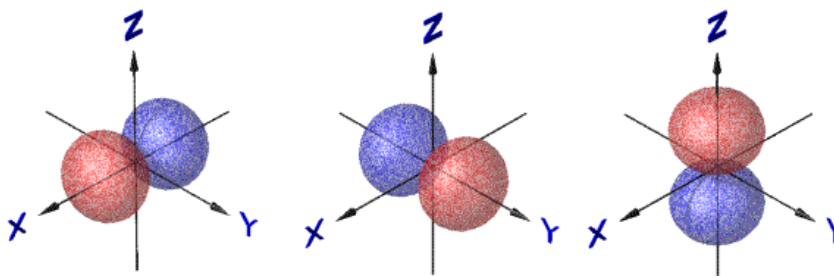
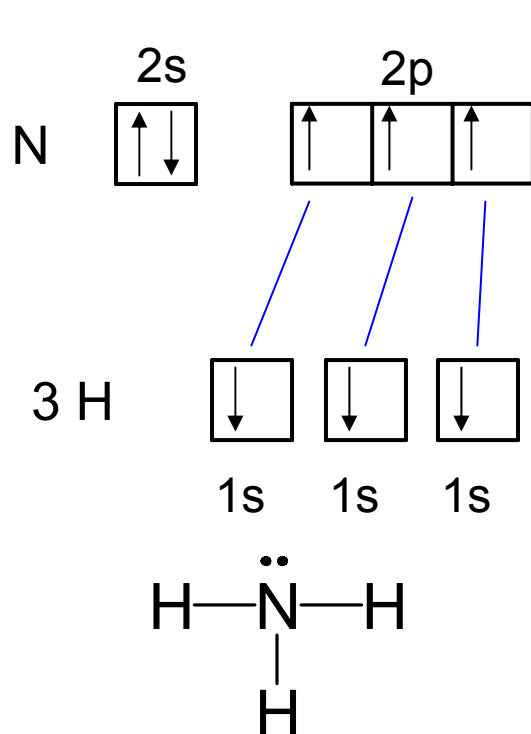
Double bond:  $\sigma$  bond +  $\pi$  bond  
 Triple bond:  $\sigma$  bond + 2  $\pi$  bond

The Lewis approach and VBT predict that O<sub>2</sub> is diamagnetic – this is wrong!

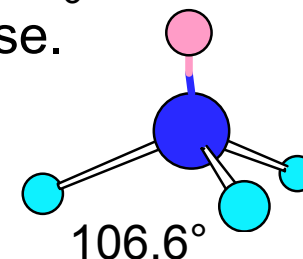
# Directionality

The bonding in diatomic molecules is adequately described by combinations of “pure” atomic orbitals on each atom. The only direction that exists in such molecules is the inter-nuclear axis and the geometry of each atom is undefined in terms of VSEPR theory (both atoms are terminal). This is not the case with polyatomic molecules and the orientation of orbitals is important for an accurate description of the bonding and the molecular geometry.

Examine the predicted bonding in ammonia using “pure” atomic orbitals:

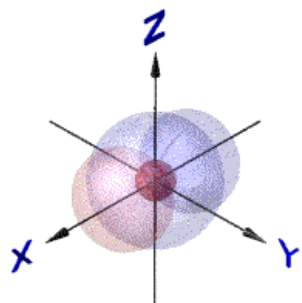


The 2p orbitals on N are oriented along the X, Y, and Z axes so we would predict that the angles between the 2p-1s  $\sigma$  bonds in  $\text{NH}_3$  would be  $90^\circ$ . We know that this is not the case.

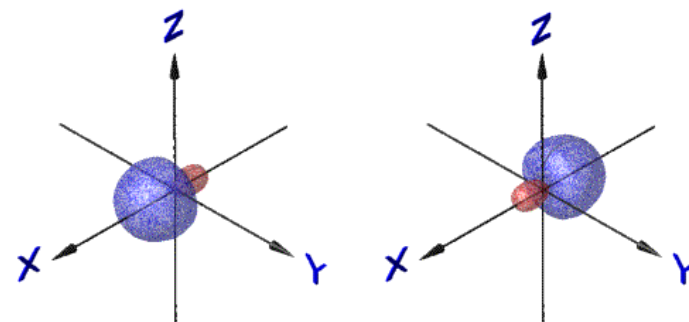
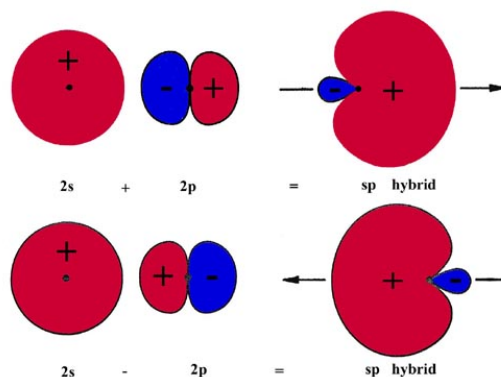


The problem of accounting for the true geometry of molecules and the directionality of orbitals is handled using the concept of *hybrid* orbitals. Hybrid orbitals are mixtures of atomic orbitals and are treated mathematically as linear combinations of the appropriate s, p and d atomic orbitals.

## Linear sp hybrid orbitals



A 2s orbital superimposed on a 2p<sub>x</sub> orbital



The two resultant sp hybrid orbitals that are directed along the X-axis (in this case)

$$\Psi_1 = \frac{1}{\sqrt{2}}\phi_s + \frac{1}{\sqrt{2}}\phi_p$$

$$\Psi_2 = \frac{1}{\sqrt{2}}\phi_s - \frac{1}{\sqrt{2}}\phi_p$$

The  $1/\sqrt{2}$  are normalization coefficients.