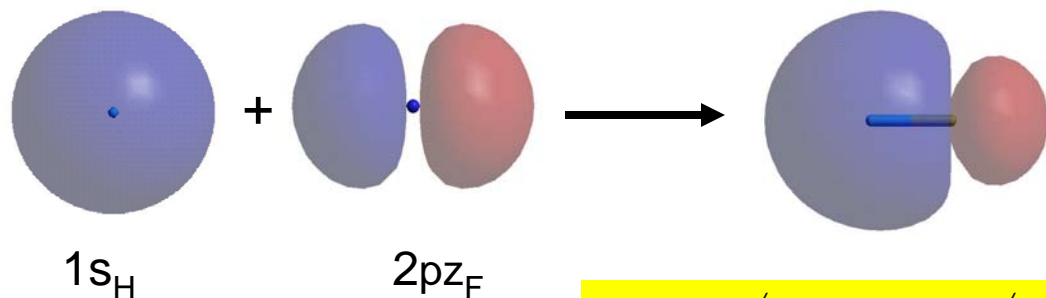


## Diatomic molecules: Heteronuclear molecules

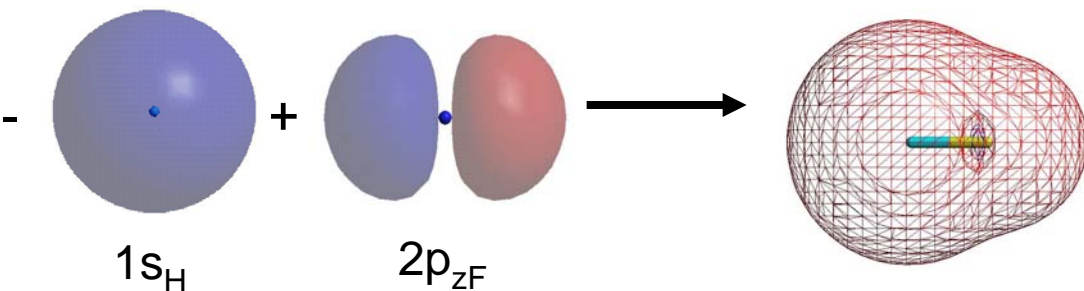
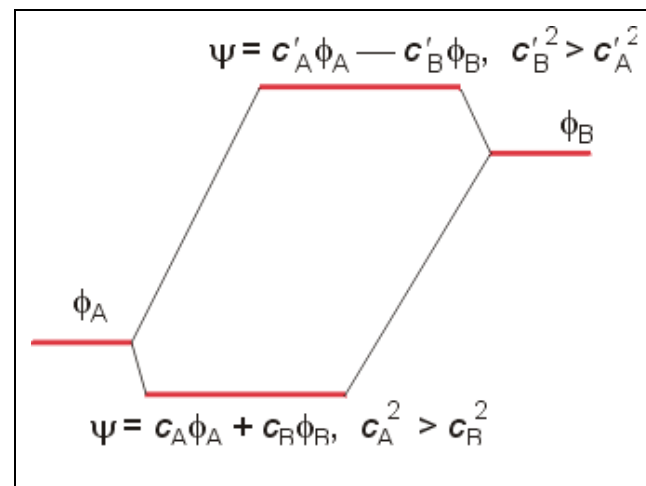
In heteronuclear diatomic molecules, the relative contribution of atomic orbitals to each MO is not equal. Some MO's will have more contribution from AO's on one atom than from AO's on the other. **This means that the coefficients in the MO will not be the same!** For example, in hydrogen fluoride (HF), some orbitals are derived more from H than F and vice versa. The more the contribution from AO's on a given atom, the higher the coefficient in front of the AO in the MO.

The combinations of  $\sigma$  symmetry: (note that the 1s orbital on H is closer in energy to the  $2p_z$  orbital on F so we will look at that combination because there will be more interaction)



This MO is more F-like

$$2\sigma = (\sqrt{0.1} 1s_H + \sqrt{0.9} 2p_{zF})$$

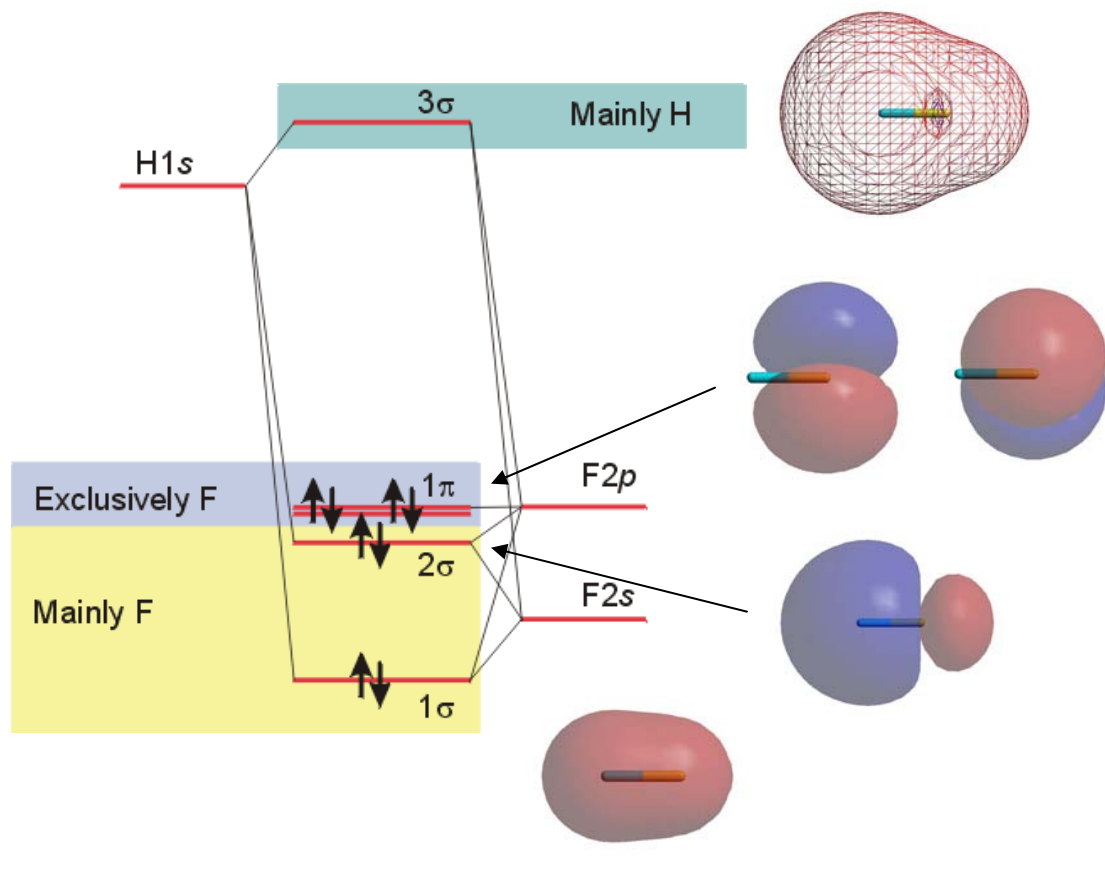


This MO is more H-like

$$3\sigma^* = (\sqrt{0.9} 1s_H - \sqrt{0.1} 2p_{zF})$$

Because the contributions are not equal, the MO diagram will be skewed.

MO diagram for HF

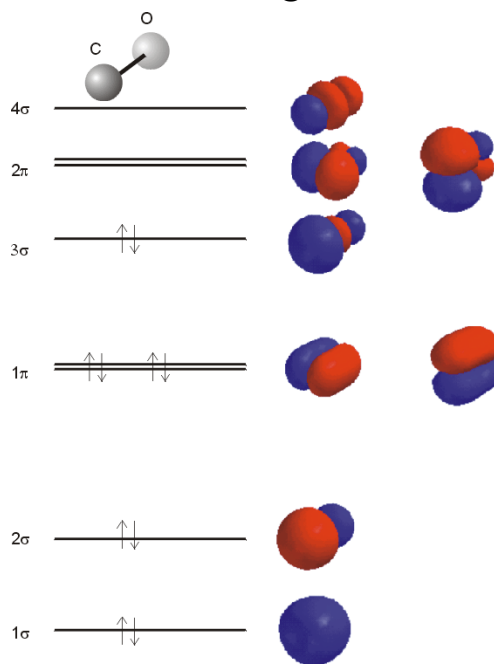
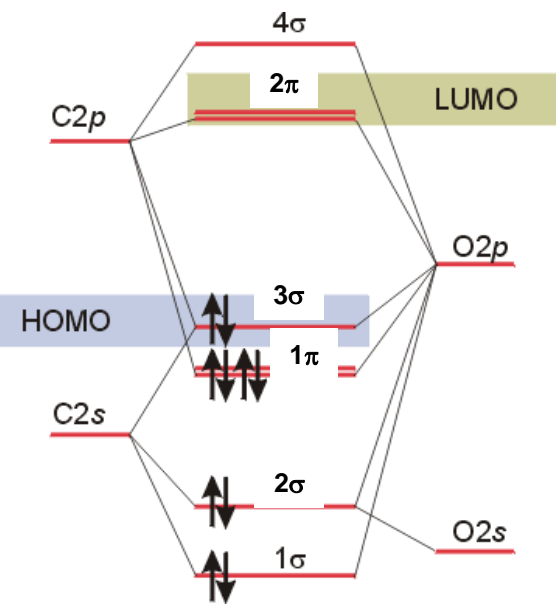


There is a little bit of mixing between the H 1s and the F 2s orbital but it interacts mostly with the 2p<sub>z</sub>.

F also has the 2p<sub>x</sub> and 2p<sub>y</sub> orbitals that cannot interact with the H 1s orbital because they have the wrong symmetry! If you try to combine these orbitals with the 1s on H, you will find that the overlap integral,  $S$ , is equal to 0. Thus these orbitals are exclusively found on the F atom and are called *non-bonding*. The energies of these orbitals do not change from the energies in the F atom.

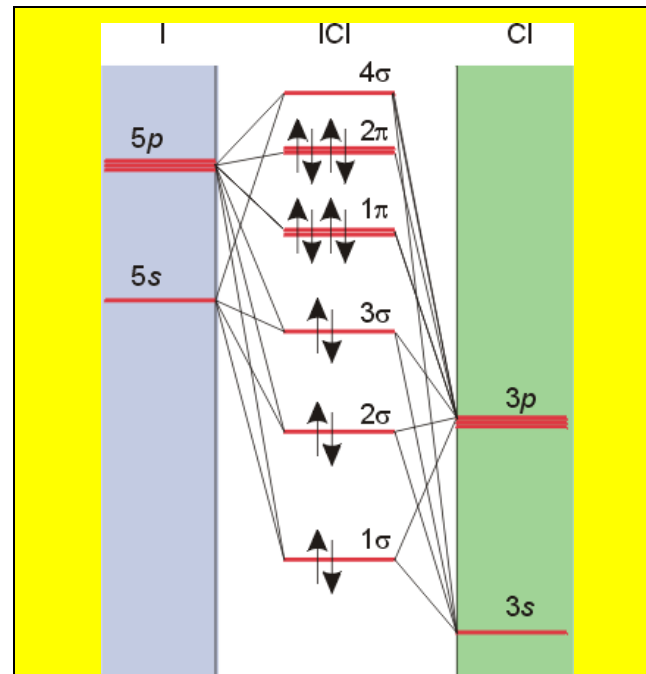
The orbitals that are derived mostly from F are going to be closer to the energies of the atomic orbitals of F and vice versa.

MO diagrams for other heteronuclear diatomics are formed in exactly the same way as that of H-F or those of the homonuclear diatomics: atomic orbitals of appropriate symmetry will interact to produce MO's. The orbitals that are closest in energy to one another will interact the most - i.e. there will be greater stabilization of the bonding MO and destabilization of the antibonding MO.



In this diagram, the labels are for the valence shell only - it ignores the 1s shell. The labels could also start at 3σ. Notice, there is no g or u because the molecule does not have a center of symmetry

Again, the MO's will have a larger contribution from one of the atoms. In CO, the HOMO has more of a contribution from C AO's, so CO acts as an electron donor through the carbon atom.

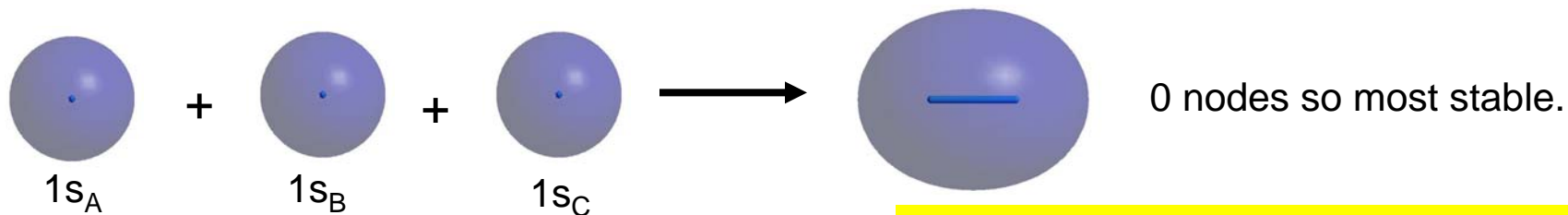


The relative energies of the AO's can be estimated based on the electronegativity of the atoms. More electronegative atoms will have more stable (lower) orbitals.

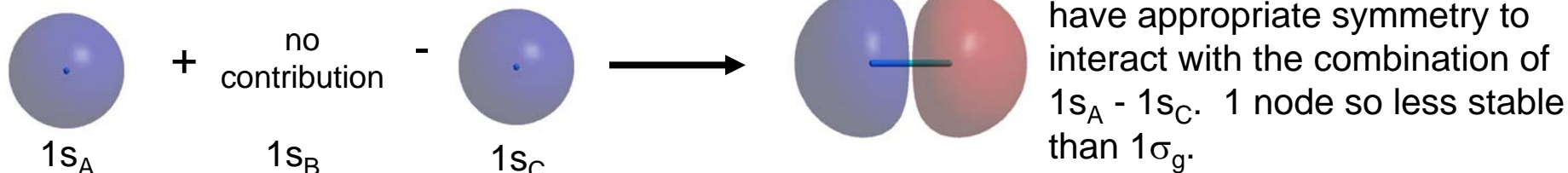
## Polyatomic molecules: The bonding in $H_3^+$

Each H atom has only a 1s orbital, so to obtain MO's for the  $H_3^+$  cation, we must make linear combinations of the three 1s orbitals.

Consider the situation where the H atoms arranged to make a linear geometry. **Note that atoms that are related by symmetry must be treated together.**



$$1\sigma_g = (\sqrt{0.25} 1s_A + \sqrt{0.5} 1s_B + \sqrt{0.25} 1s_C)$$



$$1\sigma_u = (\sqrt{0.5} 1s_A - \sqrt{0.5} 1s_C)$$



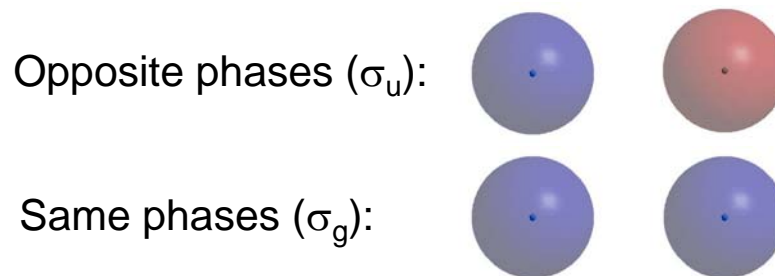
$$2\sigma_g^* = (-\sqrt{0.25} 1s_A + \sqrt{0.5} 1s_B - \sqrt{0.25} 1s_C)$$

## Polyatomic molecules: The bonding in $H_3^+$

For the linear cation, the MO diagram would then be:

**Note that the three H atoms are held together by a total of only two electrons.**

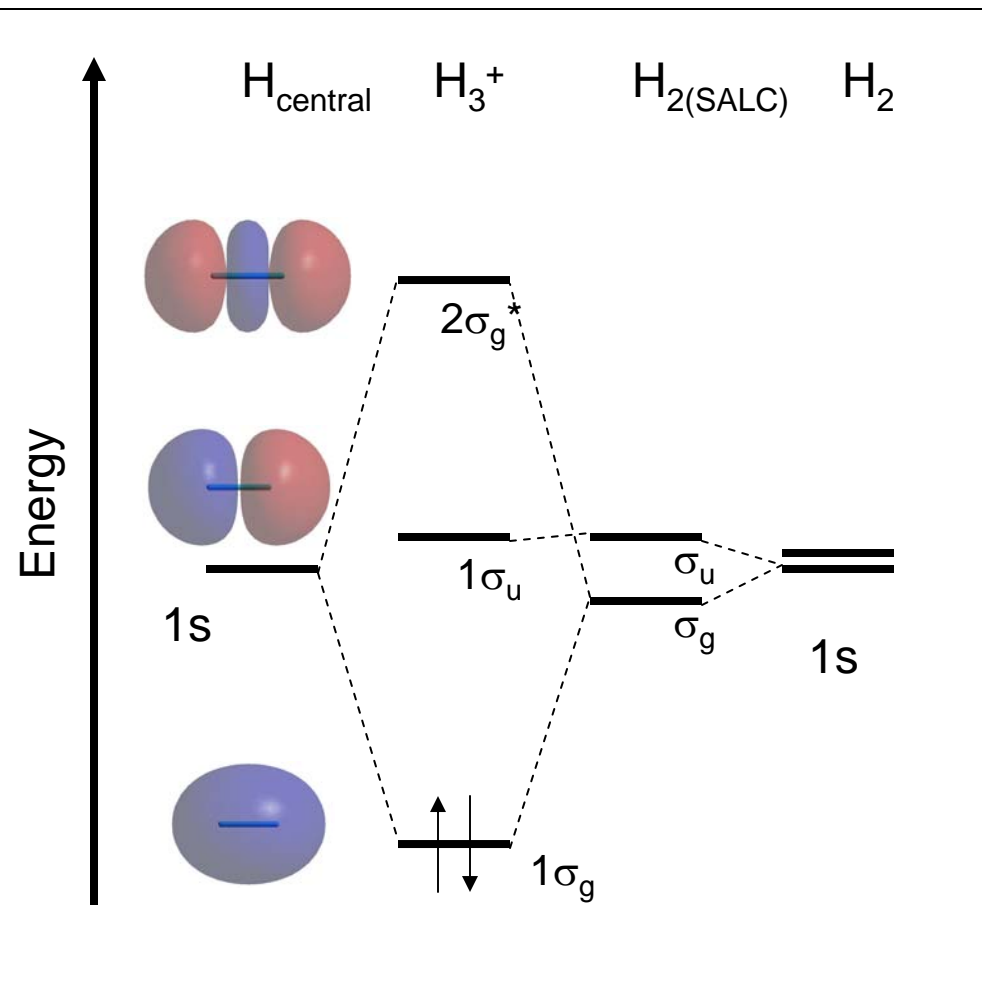
Since the terminal H atoms are symmetry related and must be considered as a pair, we must make symmetry adapted linear combinations (SALC's) of their orbitals to interact with the central atom:



**This is the approach that we must use for all polyatomic molecules.**

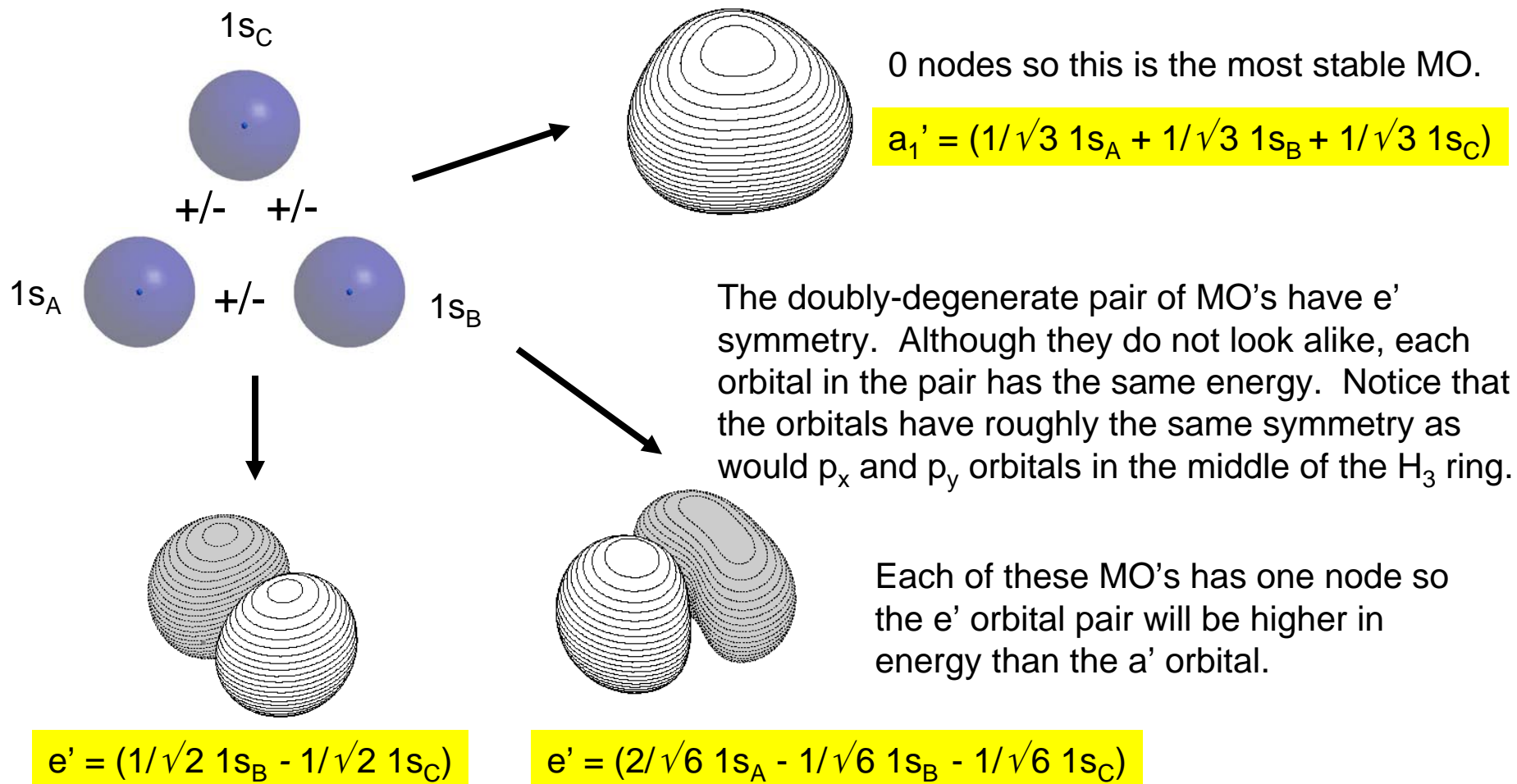
Note that the  $\sigma_u$  combination will be a little bit higher in energy than the  $\sigma_g$  so the non-bonding LUMO is a bit higher in energy than the AO in a free H atom.

BUT...since there are three atoms, a linear arrangement is not the only possibility!



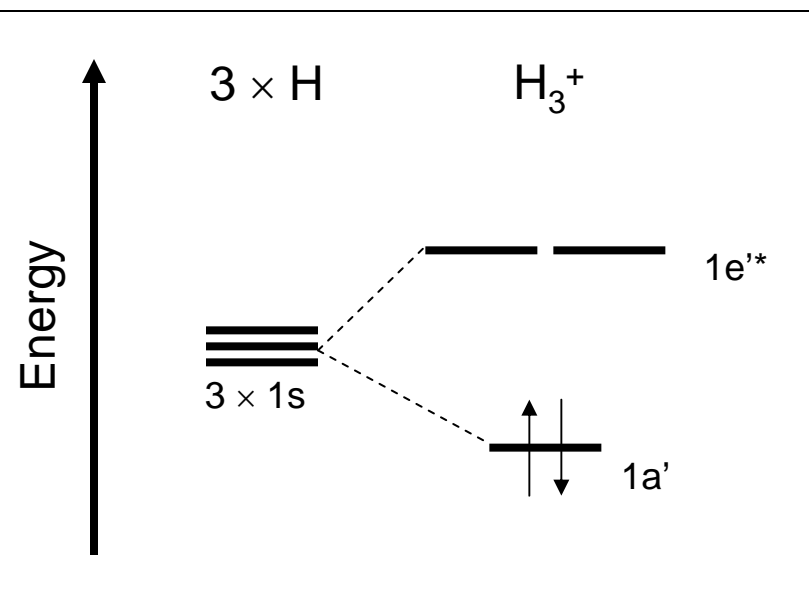
## Polyatomic molecules: The bonding in $H_3^+$

Consider the situation where the H atoms arranged in an equilateral triangular geometry. Note that now all the atoms are related by symmetry must be treated together as a set. The symmetry of this arrangement is  $D_{3h}$ , which tells us the symmetry of each of the orbitals and also that there must a pair of degenerate MO's.



Polyatomic molecules: The bonding in  $H_3^+$

For the triangular cation, the MO diagram would then be:

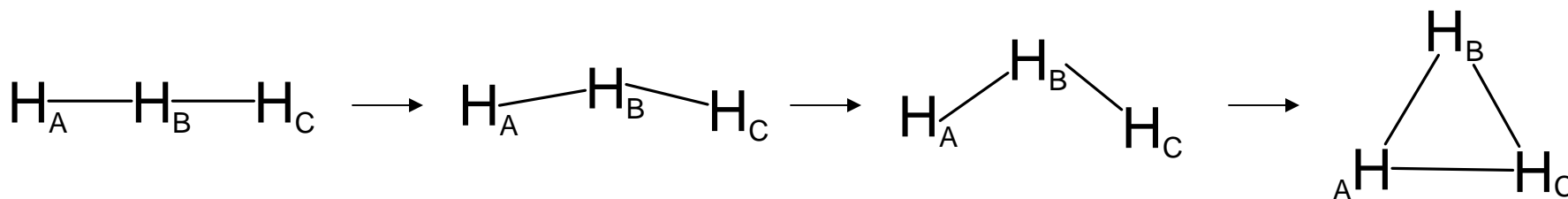


Notice that the  $e'$  pair must have identical energies and that the pair is less stable than either the free atoms or the  $a'$  MO so it can be called anti-bonding.

Again, the three H atoms are held together by a total of only two electrons.

Furthermore, there is no central atom and each H is related by symmetry. Because of this, the use of SALC's and MO theory can provide us with a much better model of the bonding than we could get from VBT and the localized model of bonding.

BUT...in theory, we could have any arrangement in between the linear and the triangular, so how do we find out which geometry is the most stable?

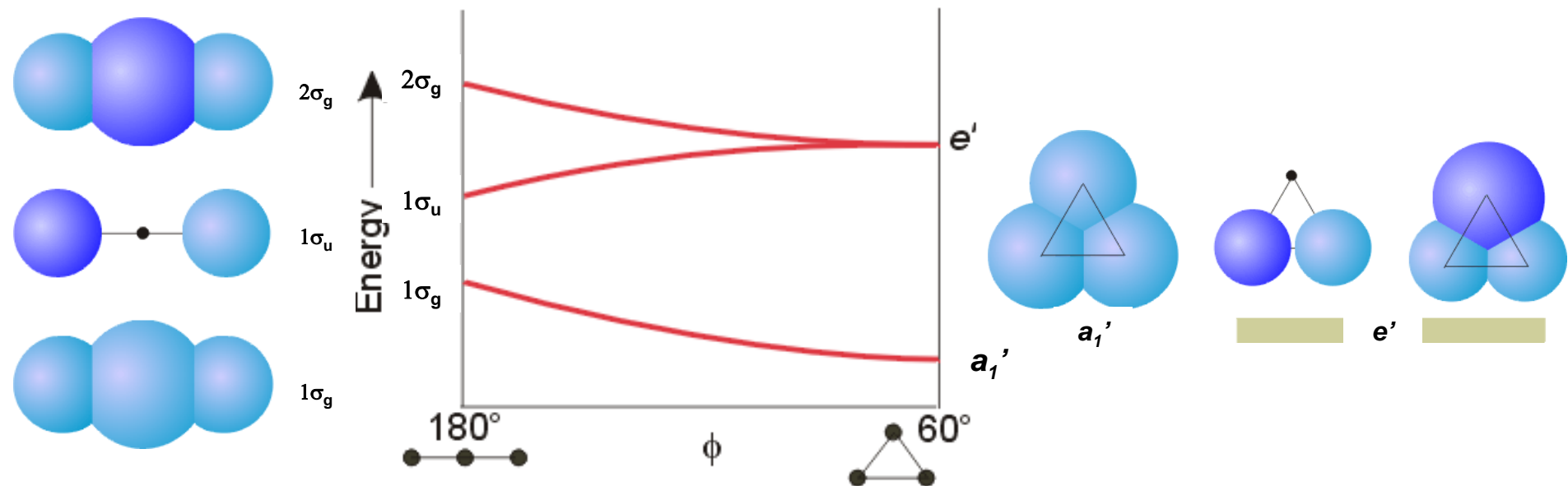




## Polyatomic molecules: The bonding in $H_3^+$

We can use a **Walsh diagram** to compare and assess the relative energies of different possible structures. In a Walsh diagram, the relative energies of important MO's are plotted as the value of a metrical parameter (e.g. bond lengths or angles) is changed. *The amount of stabilization or destabilization of the MO's is based on the amount of increase or decrease in the in-phase overlap of the AO's used to make each molecular orbital.*

Walsh diagram for  $D_{\infty h}$  to  $D_{3h}$



In the example of  $H_3^+$  there are only two electrons, thus we only have to examine how the energy of the lowest orbital ( $1\sigma$  to  $a_1'$ ) varies with the change in angle. From the diagram we can see that the energy decreases from  $D_{\infty h}$  to  $D_{3h}$  so the electronic energy of the triangular arrangement will be lower than that of the linear arrangement. This means that the triangular form will be the most stable arrangement. If there were more electrons, we would have to consider how the energies change for any orbital that might be populated with electrons.



# Molecular Orbital Theory

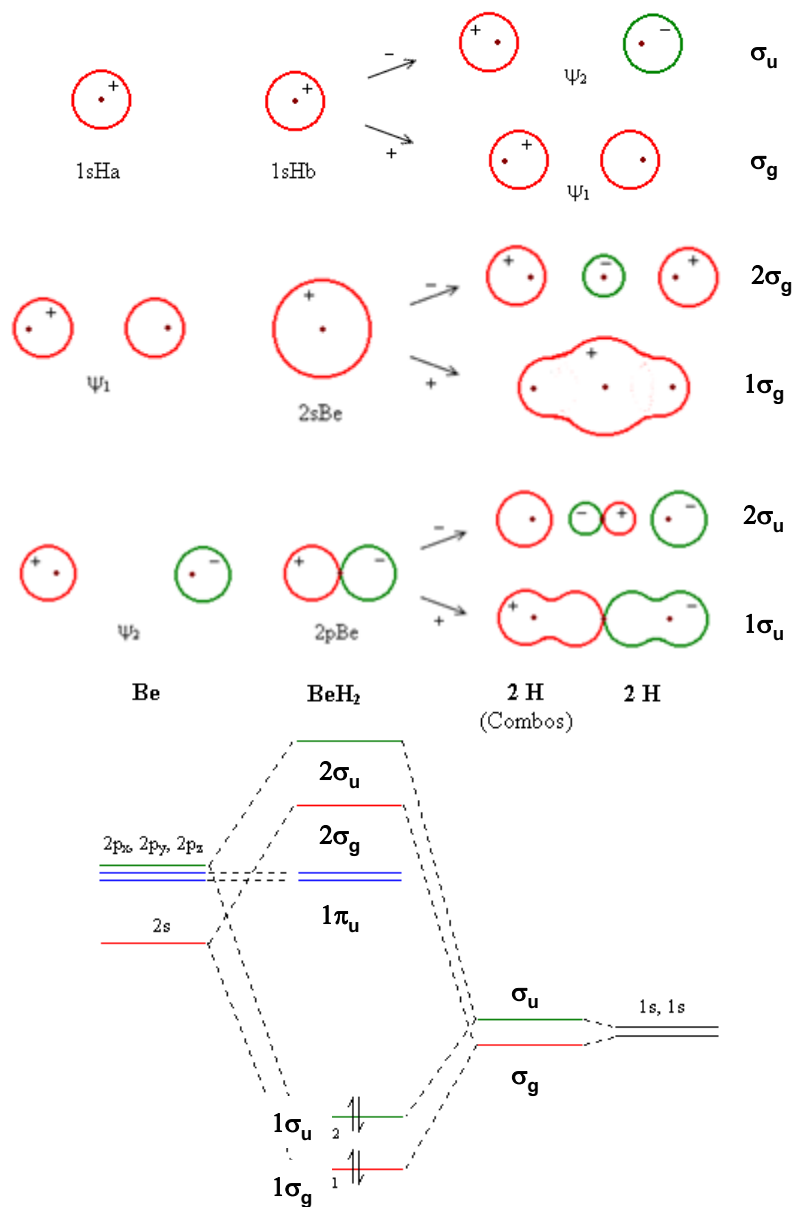
## Polyatomic molecules

The steps you can use to build a MO diagram for any polyatomic molecule are:

1. Determine the symmetry of the molecule and figure out which atoms are symmetry related.
2. Make appropriate symmetry adapted linear combinations of atomic orbitals for the symmetry related atoms.
3. Estimate the energies of the AO's using the electronegativities of the atoms.
4. Use symmetry to determine which orbitals can interact with each other to form bonding and anti-bonding MO's. Those that can't interact will be non-bonding.
5. Arrange MO's in order of increasing energy based on the number of nodes and use the available electrons to fill the lowest energy orbitals.

For simple molecules, you can draw pictures of the SALC's and MO's (as shown) in the example. For more complicated molecules, it is easier to just use symmetry and character tables.

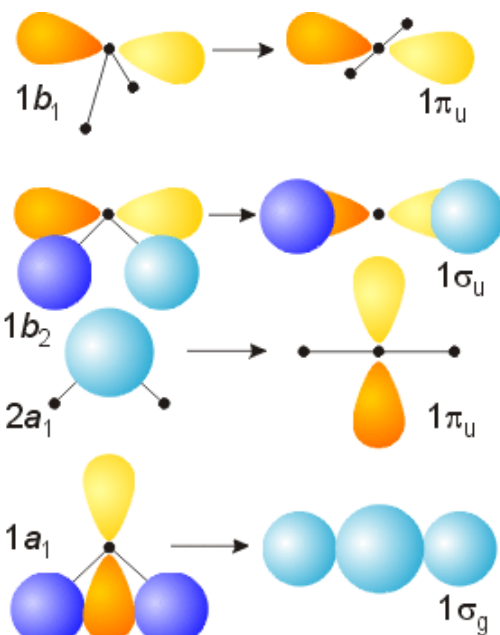
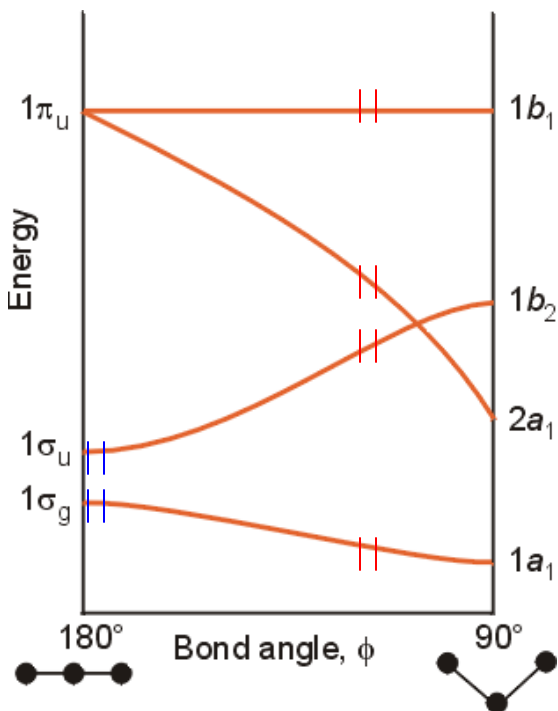
e.g.  $\text{BeH}_2$



# Molecular Orbital Theory

## Polyatomic molecules

If you are trying to estimate the appropriate geometry for a triatomic molecule using a Walsh diagram, all that is necessary is to correctly determine the number of electrons that will populate the orbitals in the diagram. Then you can estimate which electron configuration will provide the lowest overall energy (and thus the most stable geometry).



E.g.'s:

There are 4 valence electrons in  $\text{BeH}_2$  so these electrons can fill the  $1\sigma_g$  and the  $1\sigma_u$  orbitals in the diagram (shown in blue). The lowest energy combination is obtained when the bond angle is  $180^\circ$ .

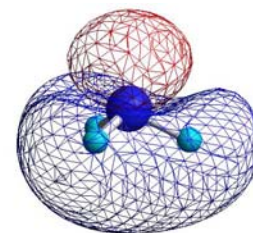
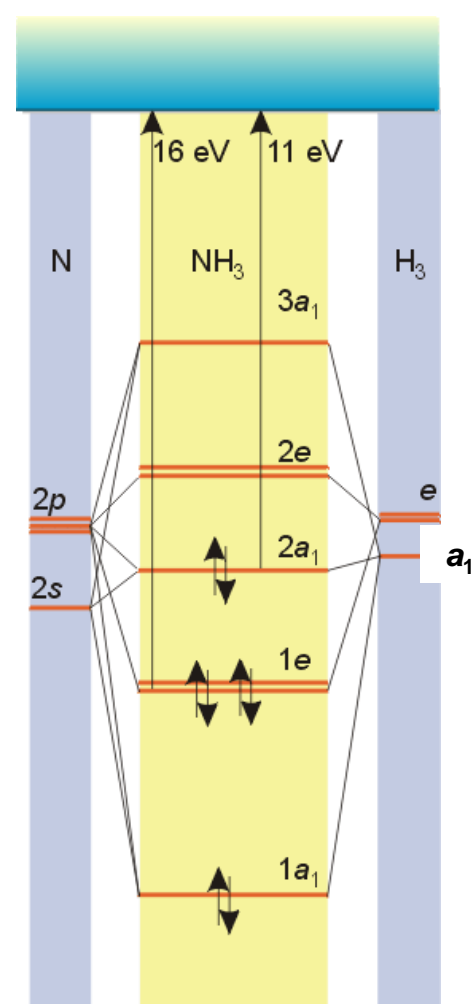
In  $\text{H}_2\text{O}$ , there are 8 valence electrons which will fill up all four orbitals in the diagram. Since the energy of the  $1b_1$  orbital doesn't change as the angle is changed, the overall energy is mostly determined by the relative energies of the  $2a_1$  and the  $1b_2$ . A reasonable guess is shown in red.

Orbital overlap analyses such as these allow for the prediction of molecular geometry using the delocalized model for covalent bonding in the same way that VSEPR is used in the localized approach.

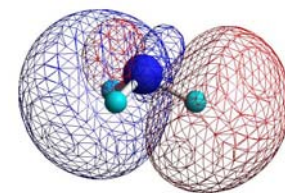
E.g. Building a MO diagram for  $\text{NH}_3$ :

1. The point group is  $C_{3v}$ .
2. All H's are related so these must be split into SALC's of a and e symmetry (these have exactly the same shape as those in the example for  $\text{H}_3^+$ , but the point group that must be used for  $\text{NH}_3$  is  $C_{3v}$ ).
3.  $\chi_{\text{N}} \approx 3$  and  $\chi_{\text{H}} \approx 2.2$  so the energy levels of the AO's on N will be lower than those on the H atoms.
4. From the  $C_{3v}$  character table, the symmetry of the AO's on N are:  $A_1(2s)$ ,  $A_1(2p_z)$ , and  $E(2p_x, 2p_y)$ . Each of these orbitals can interact with the SALC's from the H atoms.
5. Fill the MO's with the 8 valence electrons.

In  $\text{NH}_3$ , the HOMO is a mostly nitrogen-based orbital that corresponds to the lone pair of electrons from VBT. This is why ammonia acts as a Lewis base at the N atom. The LUMO is the  $2e$  level that has more H character - this shows why  $\text{NH}_3$  can also act as a Lewis acid through the H atoms.



HOMO

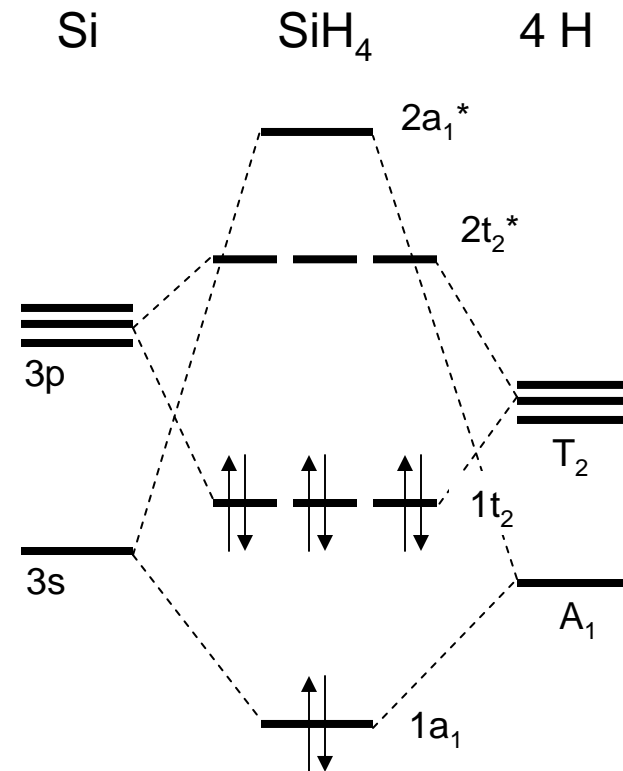


LUMO

E.g. Building a MO diagram for  $\text{SiH}_4$ :

1. The point group is  $T_d$ .
2. All H's are related so these must be split into SALC's of  $a_1$  and  $t_2$  symmetry (these are harder to draw, so it's easier to use a symmetry analysis of the four H atoms to get the SALC's for AO's of the H atoms).
3.  $\chi_{\text{Si}} \approx 1.9$  and  $\chi_{\text{H}} \approx 2.2$  so the energy levels of the AO's on the H atoms will be lower than those on the Si atom.
4. From the  $T_d$  character table, the symmetry of the AO's on Si are:  $A_1(3s)$ ,  $T_2(3p_x, 3p_y, 3p_z)$ . Each of these orbitals can interact with the SALC's from the H atoms.
5. Fill the MO's with the 8 valence electrons.

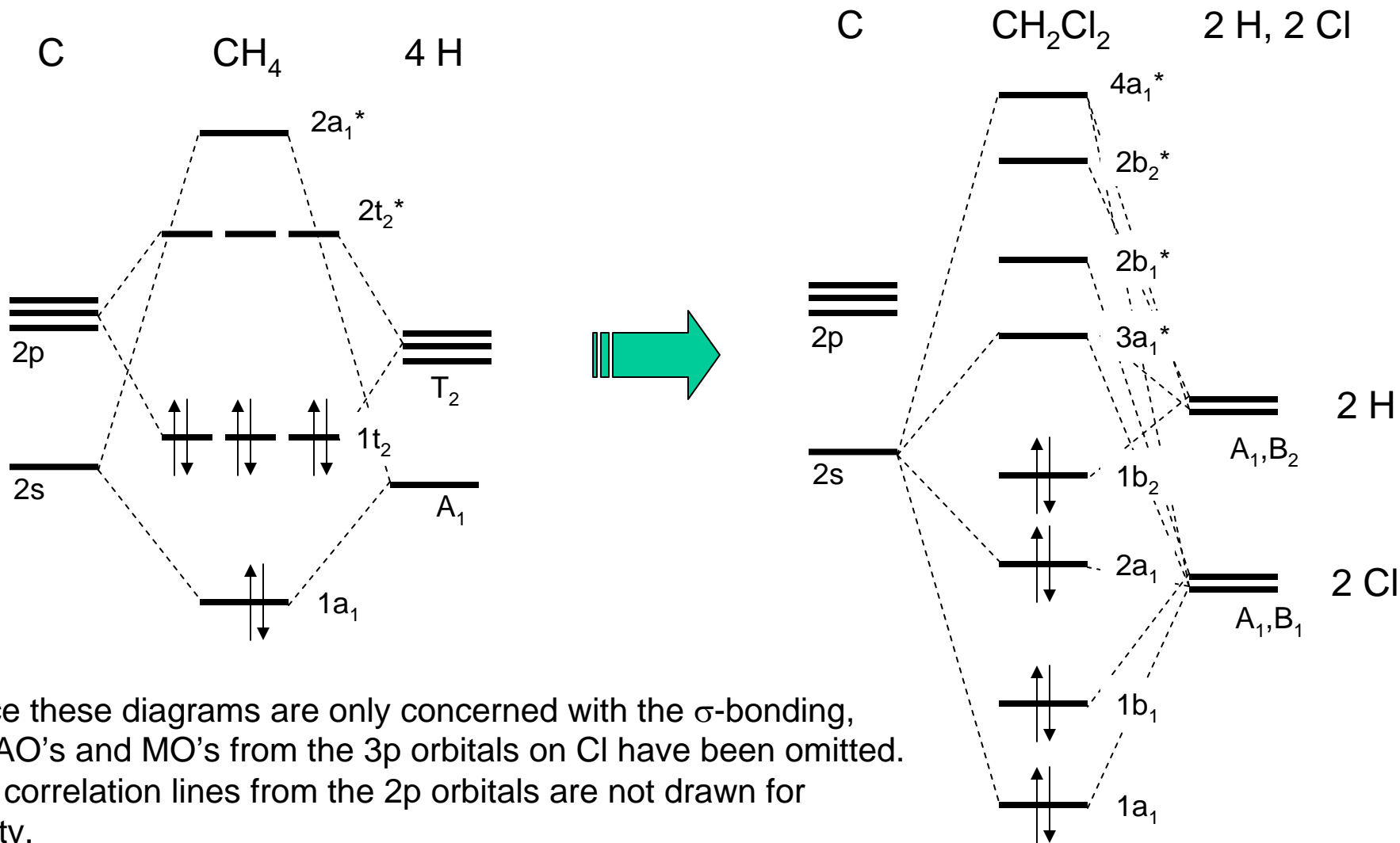
In  $\text{SiH}_4$ , the HOMO is a mostly based on the peripheral hydrogen atoms and the LUMO is dominated by Si so  $\text{SiH}_4$  will act as an electron donor through the H atoms and an electron acceptor at Si.



# Molecular Orbital Theory

## Polyatomic molecules

Consider what happens to the  $\sigma$ -bonding MO's if the symmetry is reduced from  $T_d$  to  $C_{2v}$ : there will no longer be triply-degenerate MO's. The four bonding orbitals are split into two sets - those with more H character (higher in energy) and those with more Cl character (lower in energy).



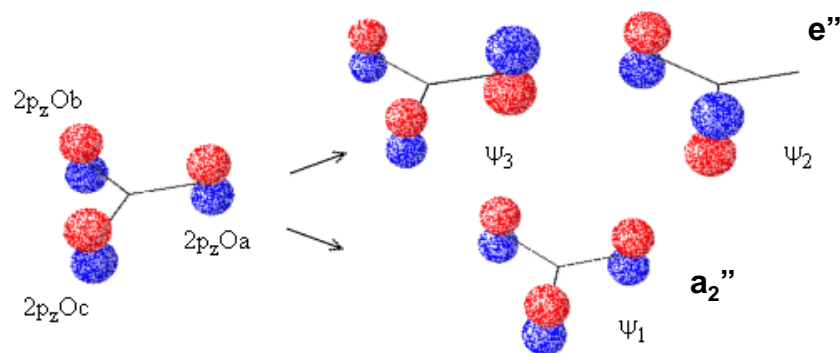
Since these diagrams are only concerned with the  $\sigma$ -bonding, the AO's and MO's from the 3p orbitals on Cl have been omitted. The correlation lines from the 2p orbitals are not drawn for clarity.

## Pi-bonding in polyatomic molecules

Molecular orbital theory considers  $\pi$ -bonding in exactly the same way as  $\sigma$ -bonding. Orbitals with appropriate symmetry will interact to form bonding and anti-bonding MO's. In contrast to Lewis theory or VBT, resonance structures are not needed to describe the  $\pi$ -bonding because the MO's are spread equally over the  $\pi$ -system of the entire molecule. Not surprisingly, the delocalized model of bonding provides a much better picture of the *delocalized*  $\pi$ -system.

E.g. the  $\pi$ -bonding in  $\text{CO}_3^{-2}$

In the  $D_{3h}$  molecule, the  $2p_z$  orbitals on the O atoms give SALC's of the following form:



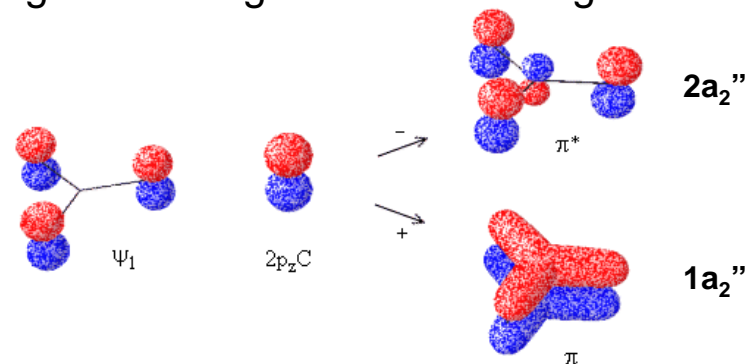
These are analogous to the SALC's we built for  $\text{H}_3^+$  and so the normalization coefficients are identical:

$$a_2'' = (1/\sqrt{3} 2p_{zA} + 1/\sqrt{3} 2p_{zB} + 1/\sqrt{3} 2p_{zC})$$

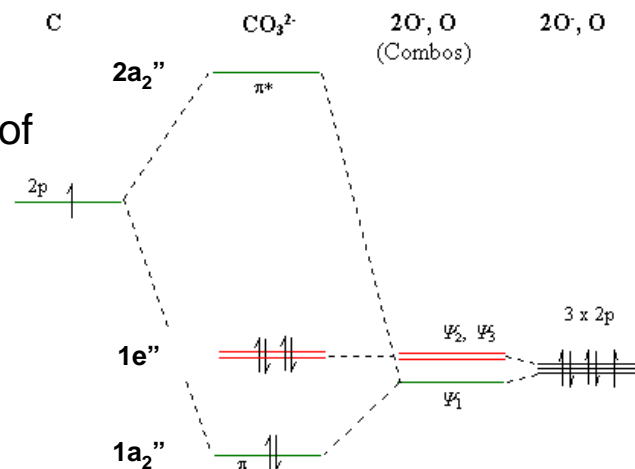
$$e'' = (1/\sqrt{2} 2p_{zB} - 1/\sqrt{2} 2p_{zC})$$

$$e'' = (2/\sqrt{6} 2p_{zA} - 1/\sqrt{6} 2p_{zB} - 1/\sqrt{6} 2p_{zC})$$

The  $2p_z$  orbital on C can only interact with the  $a_2''$  SALC to give bonding and anti-bonding MO's.



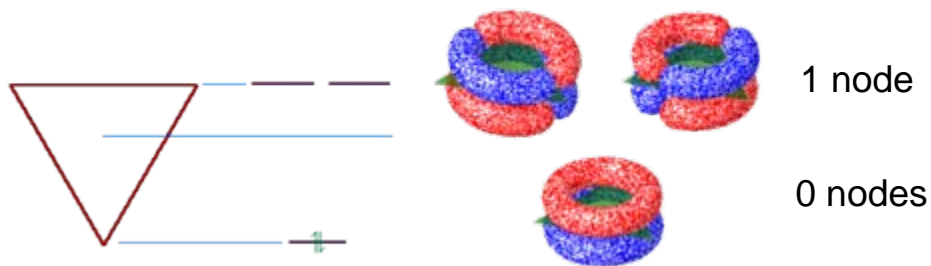
A MO diagram of the  $\pi$ -bonding:



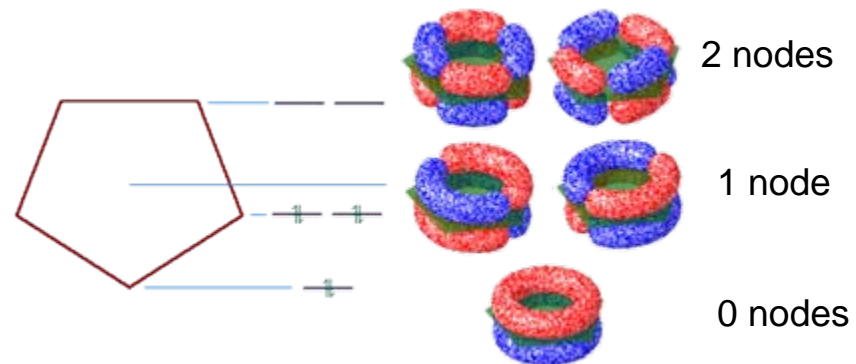
## Pi-bonding in aromatic molecules

The  $\pi$ -bonding in aromatic molecules is readily predicted using MO theory. Although the details of the treatment that predicts the energies is better left to a higher level course, the symmetry and relative energies of the MO's are easily understood from the number of nodes in each of the MO's.

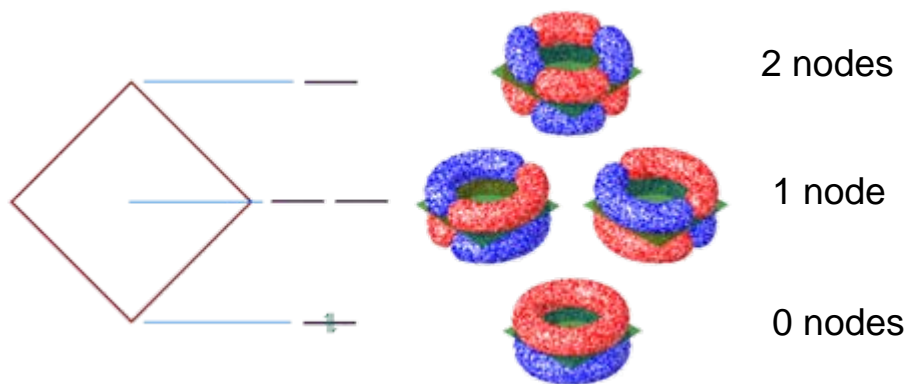
The  $\pi$ -bonding in  $C_3H_3^{+1}$  (aromatic)



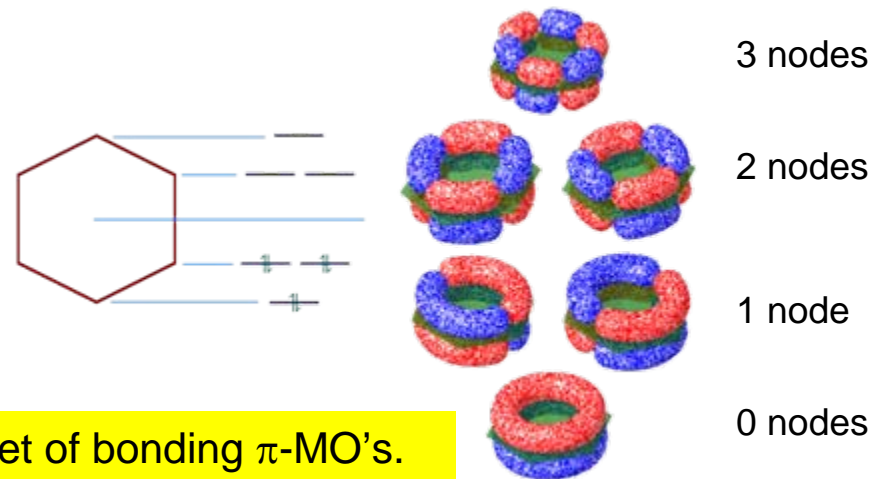
The  $\pi$ -bonding in  $C_5H_5^{-1}$  (aromatic)



The  $\pi$ -bonding in  $C_4H_4^{+2}$  (aromatic)



The  $\pi$ -bonding in  $C_6H_6$  (aromatic)

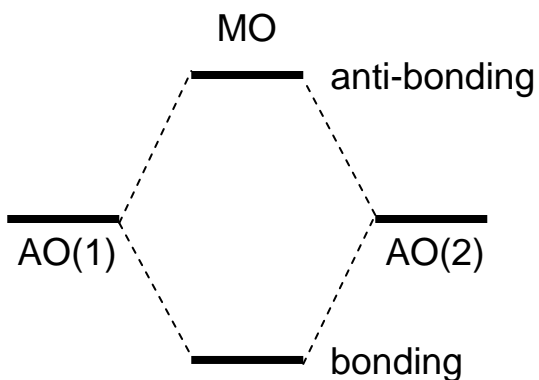


Aromatic compounds must have a completely filled set of bonding  $\pi$ -MO's. This is the origin of the Hückel  $(4N+2)$   $\pi$ -electron definition of aromaticity.

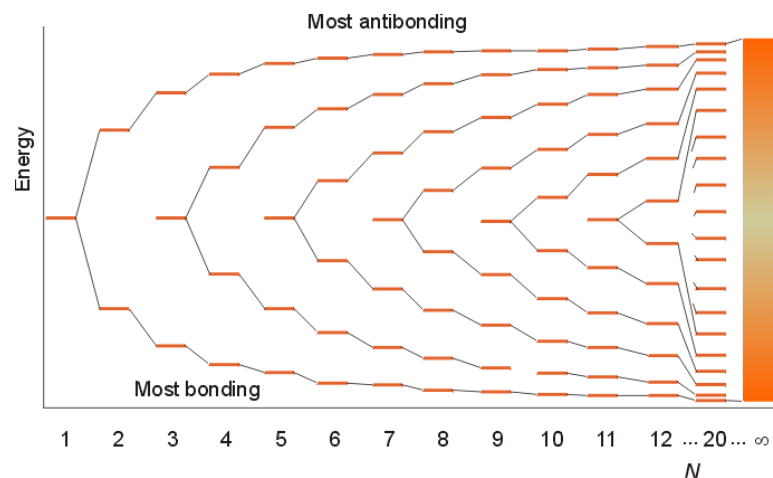


## “Infinite” polyatomic molecules

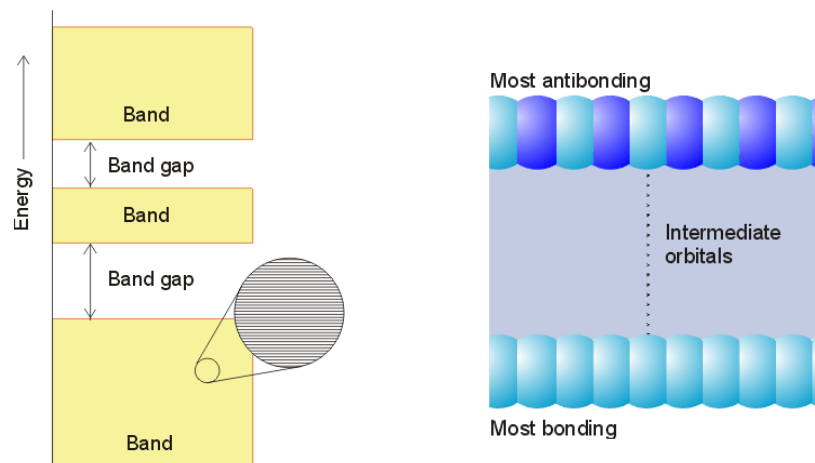
An adaptation of MO theory is also used to treat extended (essentially infinite) “molecular” systems such as pieces of a metal (or an alloy) or a molecule such as a diamond. Remember that whenever atomic orbitals have appropriate symmetry and energy, they will interact to form bonding and anti-bonding MO’s. We have only considered small molecules but there are essentially no limits to the number of atoms that can mix their corresponding AO’s together. This mixing **must** occur because of the Pauli exclusion principle (i.e. so that no two electrons in the solid have the same quantum numbers).



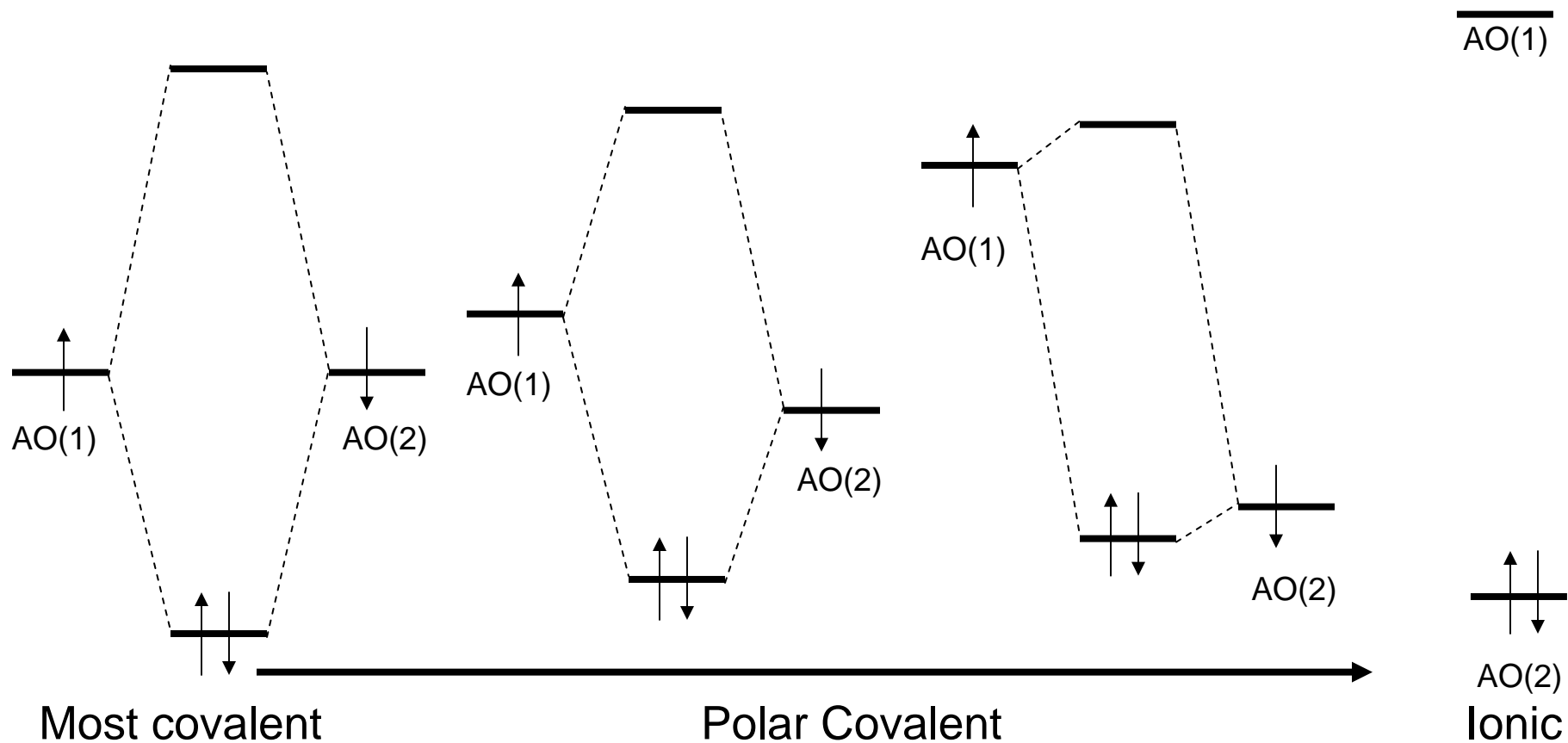
As the number of interacting atoms ( $N$ ) increases, the new bonding or anti-bonding MO’s get closer in energy.



In the extreme, the MO’s of a given type become so close in energy that they approximate a continuum of energy levels. Such sets of MO’s are known as **bands**. In any given band, the most stable MO’s have the most amount of bonding character and the highest energy MO’s are the most anti-bonding. The energy difference between adjacent bands is called the **band gap**.



Remember that the closer to AO's of appropriate symmetry are in energy, the more they interact with one another and the more stable the bonding MO that will be formed. This means that as the difference in electronegativity between two atoms increases, the stabilization provided by covalent bonding decreases (and the polarity of the bond increases). If the difference in energy of the orbitals is sufficiently large, then covalent bonding will not stabilize the interaction of the atoms. In that situation, the less electronegative atom will lose an electron to the more electronegative atom and two ions will be formed.



$\Delta\chi < 0.5$  : covalent

$2 > \Delta\chi > 0.5$  : polar

$\Delta\chi > 2$  : ionic