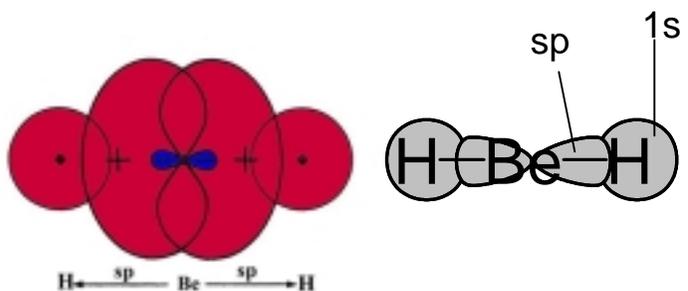


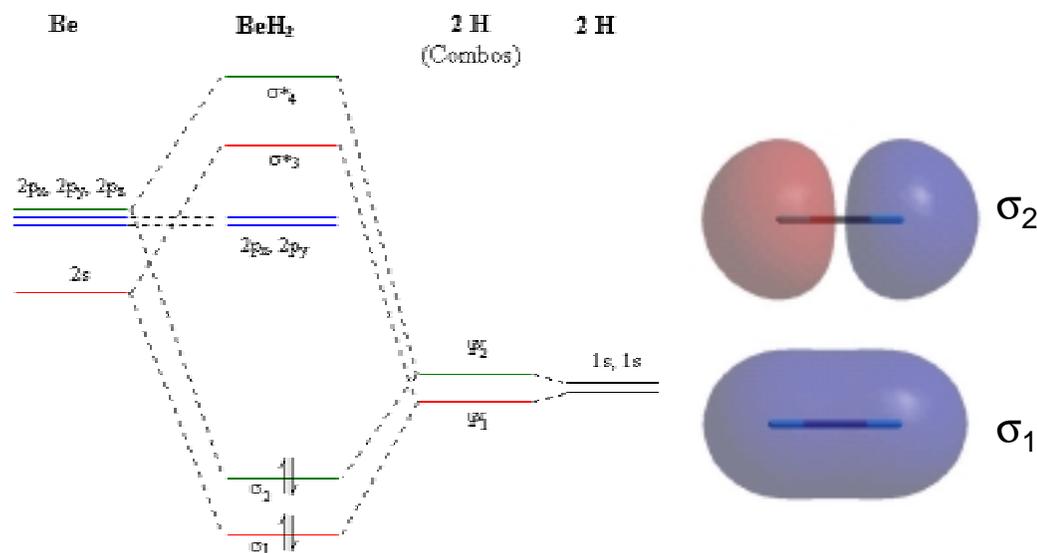
Chem 59-651 The Delocalized Approach to Bonding: Molecular Orbital Theory

The localized models for bonding we have examined (Lewis and VBT) assume that all electrons are restricted to specific bonds between atoms or in “lone pairs”. In contrast, the delocalized approach to bonding places the electrons in Molecular Orbitals (MO's) - orbitals that encompass the entire molecule and are not associated with any particular bond between two atoms. In most cases, MO theory provides us with a more accurate picture of the electronic structure of molecules and it gives us more information about their chemistry (reactivity).

Localized Bonding



Delocalized Bonding



Molecular orbitals are constructed from the available atomic orbitals in a molecule. This is done in a manner similar to the way we made hybrid orbitals from atomic orbitals in VBT. That is, we will make the MO's for a molecule from Linear Combinations of Atomic Orbitals (LCAO). In contrast to VBT, in MO theory the atomic orbitals will come from several or all of the atoms in the molecule. Once we have constructed the MO's, we can build an MO diagram (an energy level diagram) for the molecule and fill the MO's with electrons using the Aufbau principle.

Some basic rules for making MO's using the LCAO method:

- 1) n atomic orbitals must produce n molecular orbitals (e.g. 8 AO's must produce 8 MO's).
- 2) To combine, the atomic orbitals must be of the appropriate symmetry.
- 3) To combine, the atomic orbitals must be of similar energy.
- 4) Each MO must be normal and must be orthogonal to every other MO.

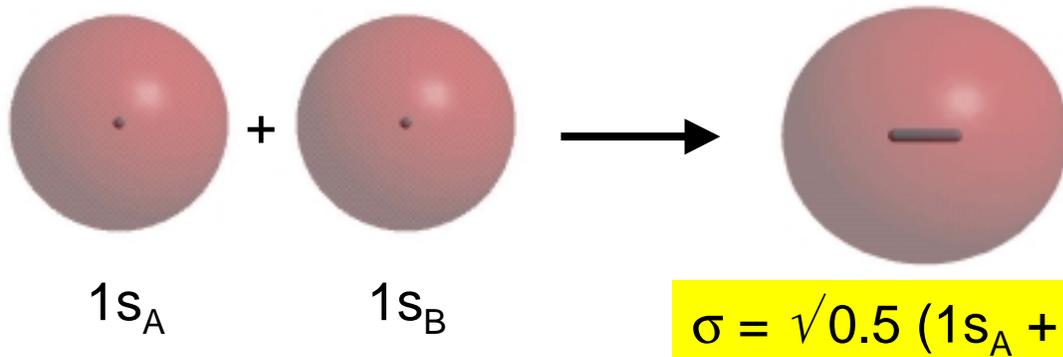




Diatomic molecules: The bonding in H₂

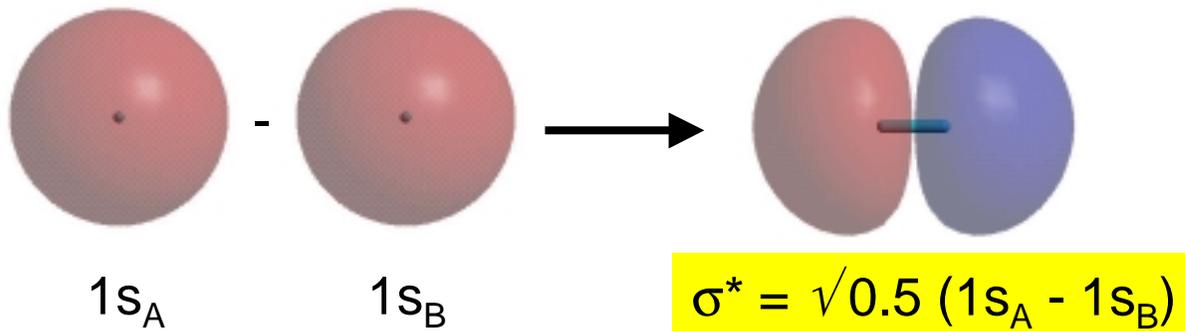
Each H atom has only a 1s orbital, so to obtain MO's for the H₂ molecule, we must make linear combinations of these two 1s orbitals.

Consider the addition of the two 1s functions (with the same phase):



This produces an MO around both H atoms and has the same phase everywhere and is symmetrical about the H-H axis. This is known as a *bonding* MO and is given the label σ because of its symmetry.

Consider the subtraction of the two 1s functions (with the same phase):



This produces an MO over the molecule with a node between the atoms (it is also symmetrical about the H-H axis). This is known as an *antibonding* MO and is given the label σ^* because of its symmetry. The star indicates antibonding.

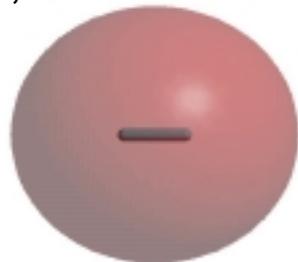
Remember that: -  is equivalent to: + 



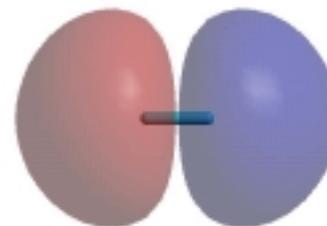
Diatomic molecules: The bonding in H_2

You may ask ... Why is σ called “bonding” and σ^* “antibonding”? What does this mean? How do you know the relative energy ordering of these MO’s?

Remember that each 1s orbital is an atomic wavefunction (ϕ_{1s}) and each MO is also a wave function, Ψ , so we can also write LCAO’s like this:



$$\sigma = \Psi_1 = \sqrt{0.5} (\phi_{1sA} + \phi_{1sB})$$



$$\sigma^* = \Psi_2 = \sqrt{0.5} (\phi_{1sA} - \phi_{1sB})$$

Remember that the square of a wavefunction gives us a probability density function, so the density functions for each MO are:

$$(\Psi_1)^2 = 0.5 [(\phi_{1sA} \phi_{1sA}) + \mathbf{2(\phi_{1sA} \phi_{1sB})} + (\phi_{1sB} \phi_{1sB})]$$

and $(\Psi_2)^2 = 0.5 [(\phi_{1sA} \phi_{1sA}) - \mathbf{2(\phi_{1sA} \phi_{1sB})} + (\phi_{1sB} \phi_{1sB})]$

The only difference between the two probability functions is in the cross term (in bold), which is attributable to the kind and amount of *overlap* between the two 1s atomic wavefunctions (the integral $\int (\phi_{1sA} \phi_{1sB}) \delta\tau$ is known as the “overlap integral”, S). In-phase overlap makes *bonding* orbitals and out-of-phase overlap makes *antibonding* orbitals...why?

Chem 59-651 Molecular Orbital Theory

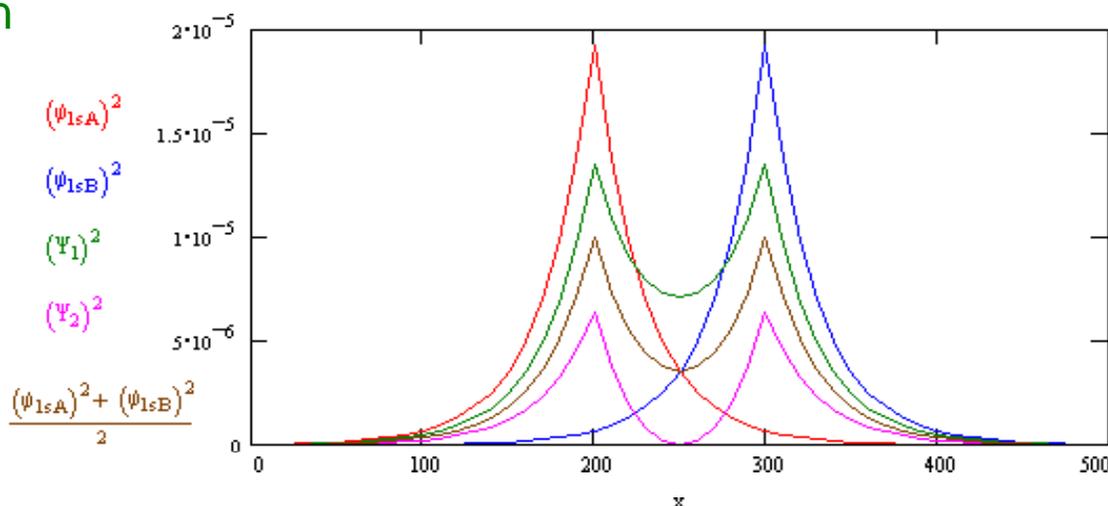


Diatomic molecules: The bonding in H_2

Consider the electron density between the two nuclei: the **red** curve is the probability density for H_A by itself, the **blue** curve is for H_B by itself and the **brown** curve is the density you would get for $\phi_{1sA} + \phi_{1sB}$ without any overlap: it is just $(\phi_{1sA})^2 + (\phi_{1sB})^2$ {the factor of $\frac{1}{2}$ is to put it on the same scale as the normalized functions}.

The function $(\Psi_1)^2$ is shown in **green** and has an extra $+ 2(\phi_{1sA} \phi_{1sB})$ of electron density than the situation where overlap is neglected.

The function $(\Psi_2)^2$ is shown in **pink** and has less electron density between the nuclei { $- 2(\phi_{1sA} \phi_{1sB})$ } than the situation where overlap is neglected.



$$(\Psi_1)^2 = 0.5 [(\phi_{1sA} \phi_{1sA}) + 2(\phi_{1sA} \phi_{1sB}) + (\phi_{1sB} \phi_{1sB})]$$

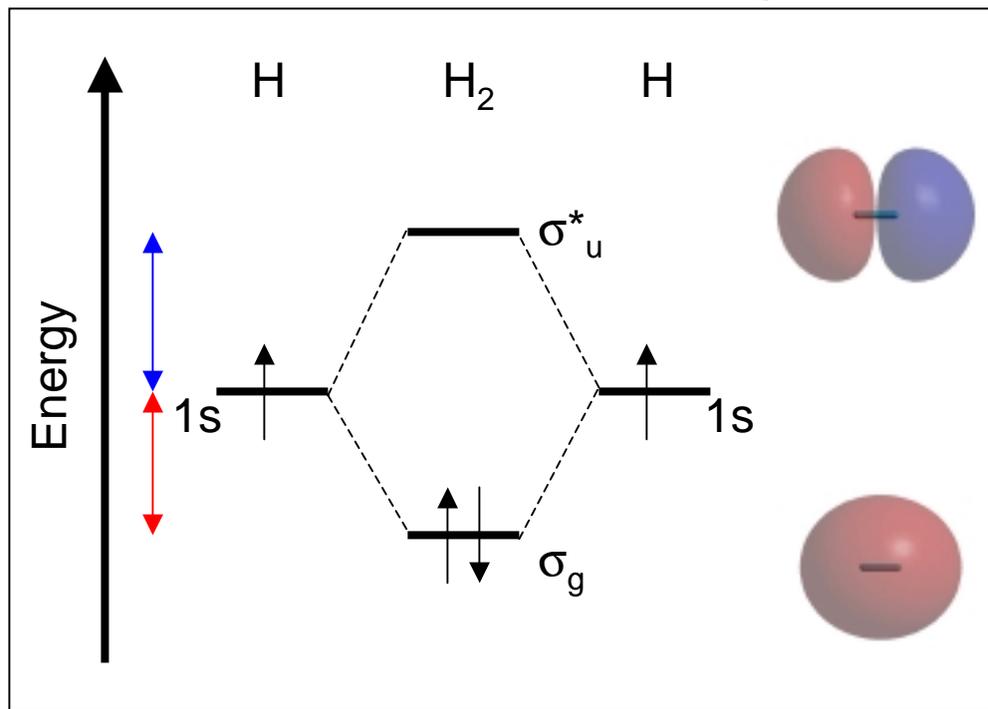
$$(\Psi_2)^2 = 0.5 [(\phi_{1sA} \phi_{1sA}) - 2(\phi_{1sA} \phi_{1sB}) + (\phi_{1sB} \phi_{1sB})]$$

The increase of electron density between the nuclei from the in-phase overlap reduces the amount of repulsion between the positive charges. This means that a bonding MO will be lower in energy (more stable) than the corresponding antibonding MO or two non-bonded H atoms.



Diatomic molecules: The bonding in H_2

So now that we know that the σ bonding MO is more stable than the atoms by themselves and the σ^* antibonding MO, we can construct the MO diagram.



To clearly identify the symmetry of the different MO's, we add the appropriate subscripts g (symmetric with respect to the inversion center) and u (anti-symmetric with respect to the inversion center) to the labels of each MO.

The electrons are then added to the MO diagram using the Aufbau principle.

Note:

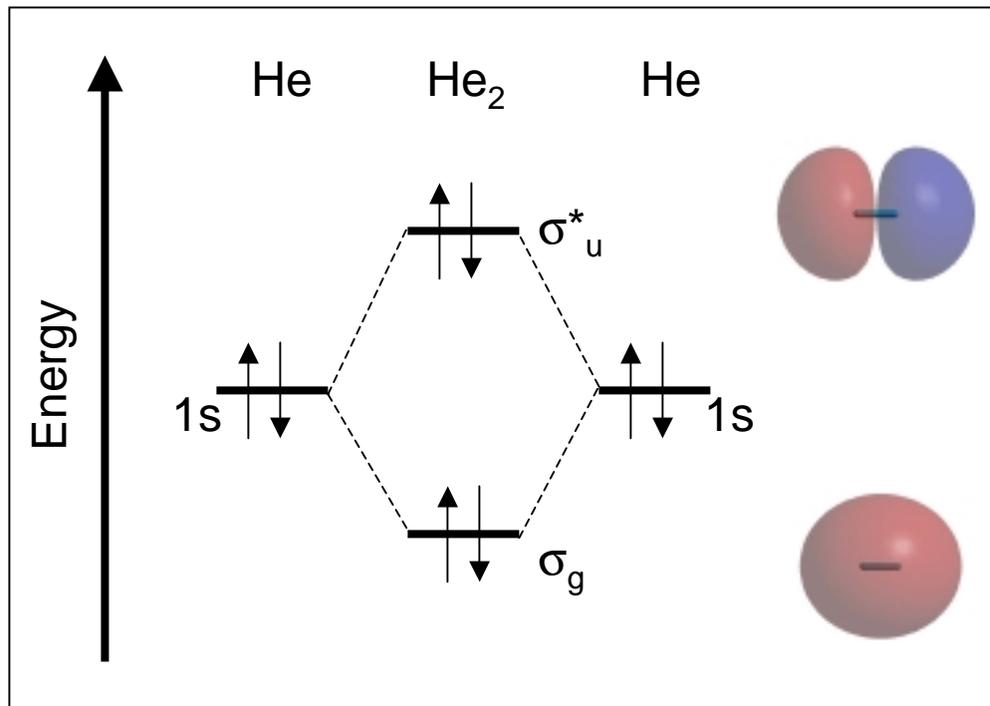
The amount of stabilization of the σ MO (indicated by the red arrow) is slightly less than the amount of destabilization of the σ^* MO (indicated by the blue arrow) because of the pairing of the electrons. For H_2 , the stabilization energy is 432 kJ/mol and the bond order is 1.

$$\text{Bond Order} = \frac{(\# \text{ of } e^- \text{ s in bonding MO's}) - (\# \text{ of } e^- \text{ s in antibonding MO's})}{2}$$

Chem 59-651 Molecular Orbital Theory

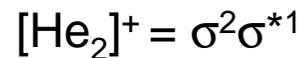
Diatomic molecules: The bonding in He₂

He also has only 1s AO, so the MO diagram for the molecule He₂ can be formed in an identical way, except that there are two electrons in the 1s AO on He.



The bond order in He₂ is $(2-2)/2 = 0$, so the molecule **will not exist**.

However the cation [He₂]⁺, in which one of the electrons in the σ^* MO is removed, would have a bond order of $(2-1)/2 = \frac{1}{2}$, so such a cation might be predicted to exist. The electron configuration for this cation can be written in the same way as we write those for atoms except with the MO labels replacing the AO labels:



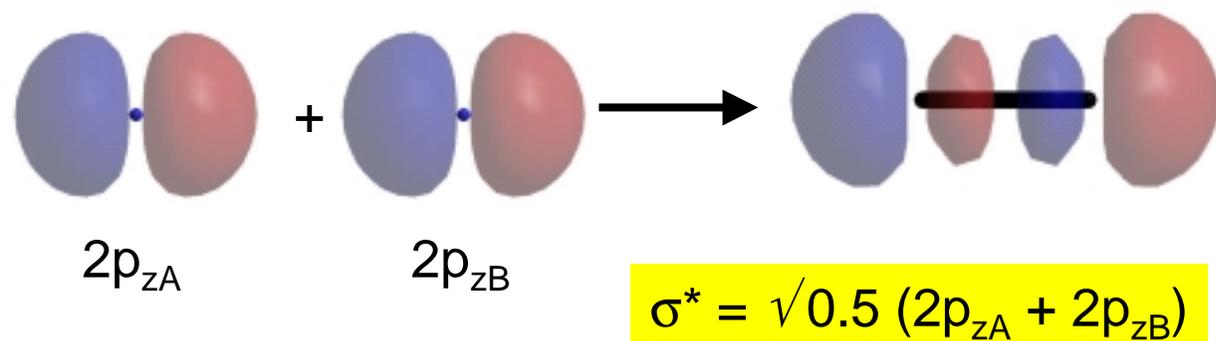
Molecular Orbital theory is powerful because it allows us to predict whether molecules should exist or not and it gives us a clear picture of the of the electronic structure of any hypothetical molecule that we can imagine.

Chem 59-651 Molecular Orbital Theory

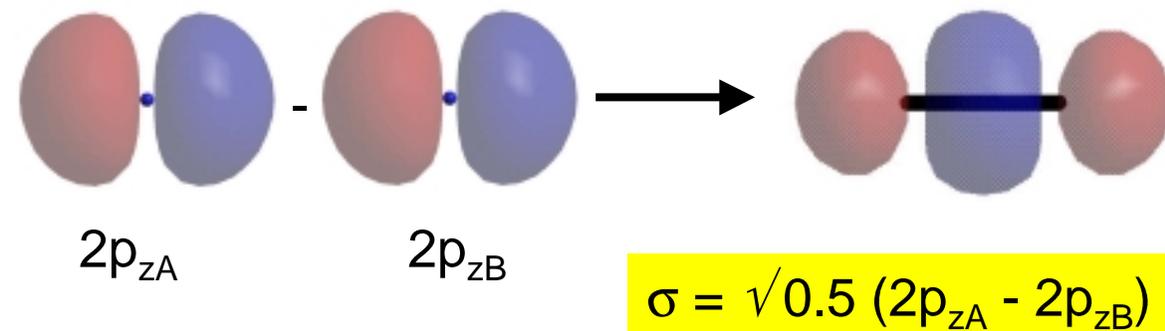
Diatomic molecules: The bonding in F_2

Each F atom has 2s and 2p valence orbitals, so to obtain MO's for the F_2 molecule, we must make linear combinations of each appropriate set of orbitals. In addition to the combinations of ns AO's that we've already seen, there are now combinations of np AO's that must be considered. The allowed combinations can result in the formation of either σ or π type bonds.

The combinations of σ symmetry:



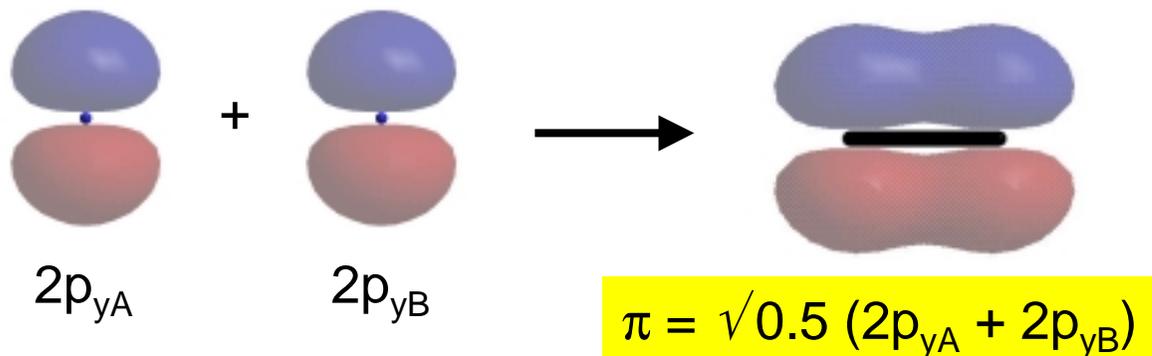
This produces an MO over the molecule with a node between the F atoms. This is thus an antibonding MO of σ_u^* symmetry.



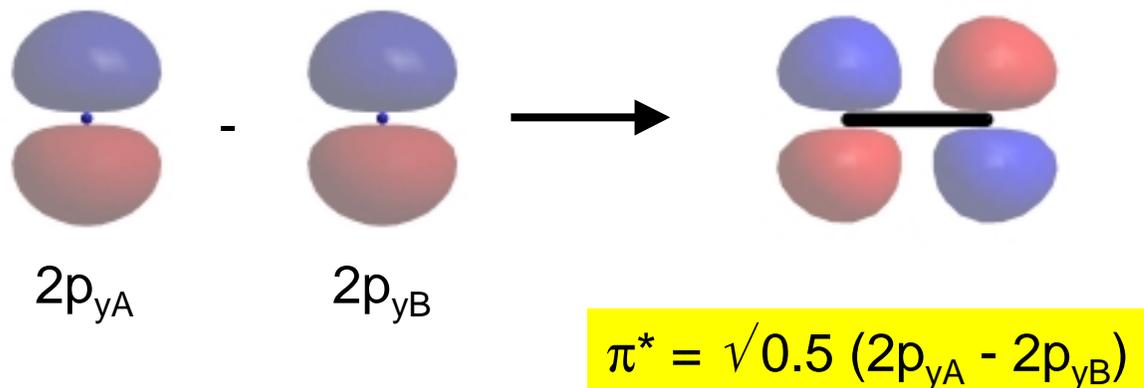
This produces an MO around both F atoms and has the same phase everywhere and is symmetrical about the F-F axis. This is thus a bonding MO of σ_g symmetry.

Diatomic molecules: The bonding in F₂

The first set of combinations of π symmetry:



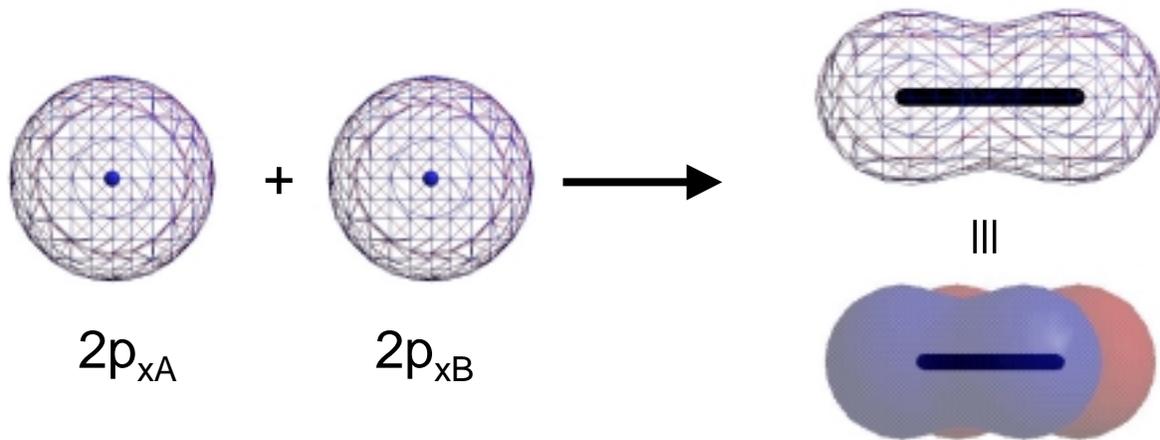
This produces an MO over the molecule with a node on the bond between the F atoms. This is thus a bonding MO of π_u symmetry.



This produces an MO around both F atoms that has two nodes: one on the bond axis and one perpendicular to the bond. This is thus an antibonding MO of π^*_g symmetry.

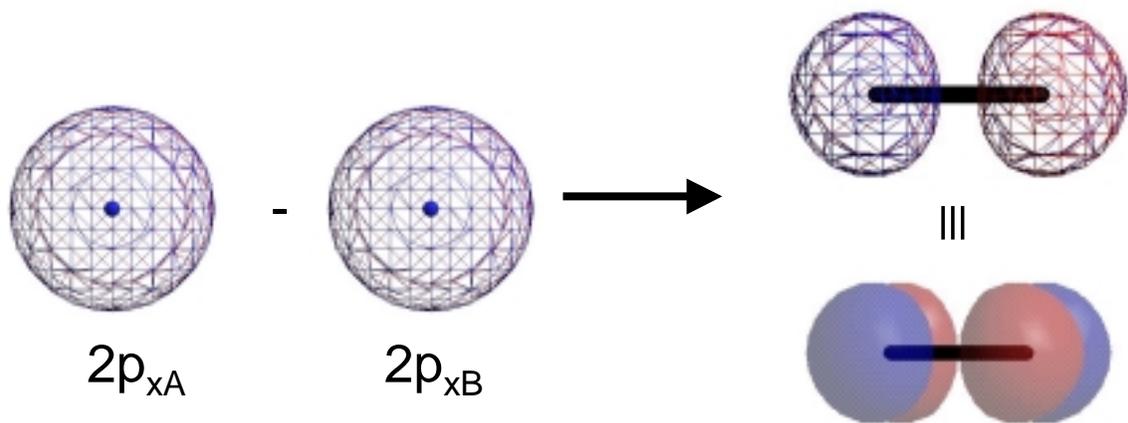
Diatomic molecules: The bonding in F_2

The second set of combinations with π symmetry (orthogonal to the first set):



This produces an MO over the molecule with a node on the bond between the F atoms. This is thus a bonding MO of π_u symmetry.

$$\pi = \sqrt{0.5} (2p_{xA} + 2p_{xB})$$

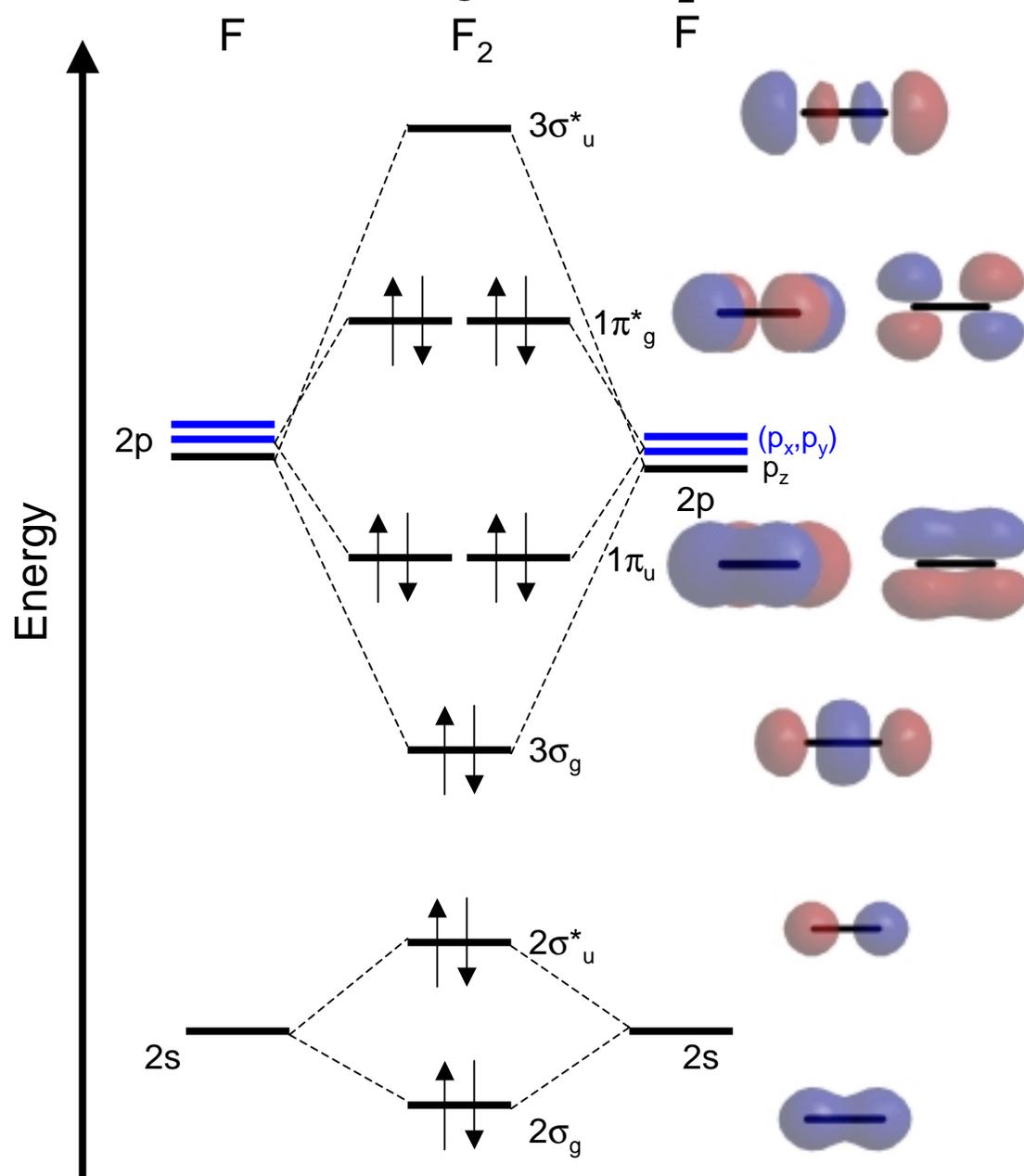


This produces an MO around both F atoms that has two nodes: one on the bond axis and one perpendicular to the bond. This is thus an antibonding MO of π_g^* symmetry.

$$\pi^* = \sqrt{0.5} (2p_{xA} - 2p_{xB})$$

Chem 59-651 Molecular Orbital Theory

MO diagram for F_2



You will typically see the diagrams drawn in this way. The diagram is only showing the MO's derived from the valence electrons because the pair of MO's from the 1s orbitals are much lower in energy and can be ignored.

Although the atomic 2p orbitals are drawn like this:  they are actually all the same energy and could be drawn like this: 

at least for two non-interacting F atoms.

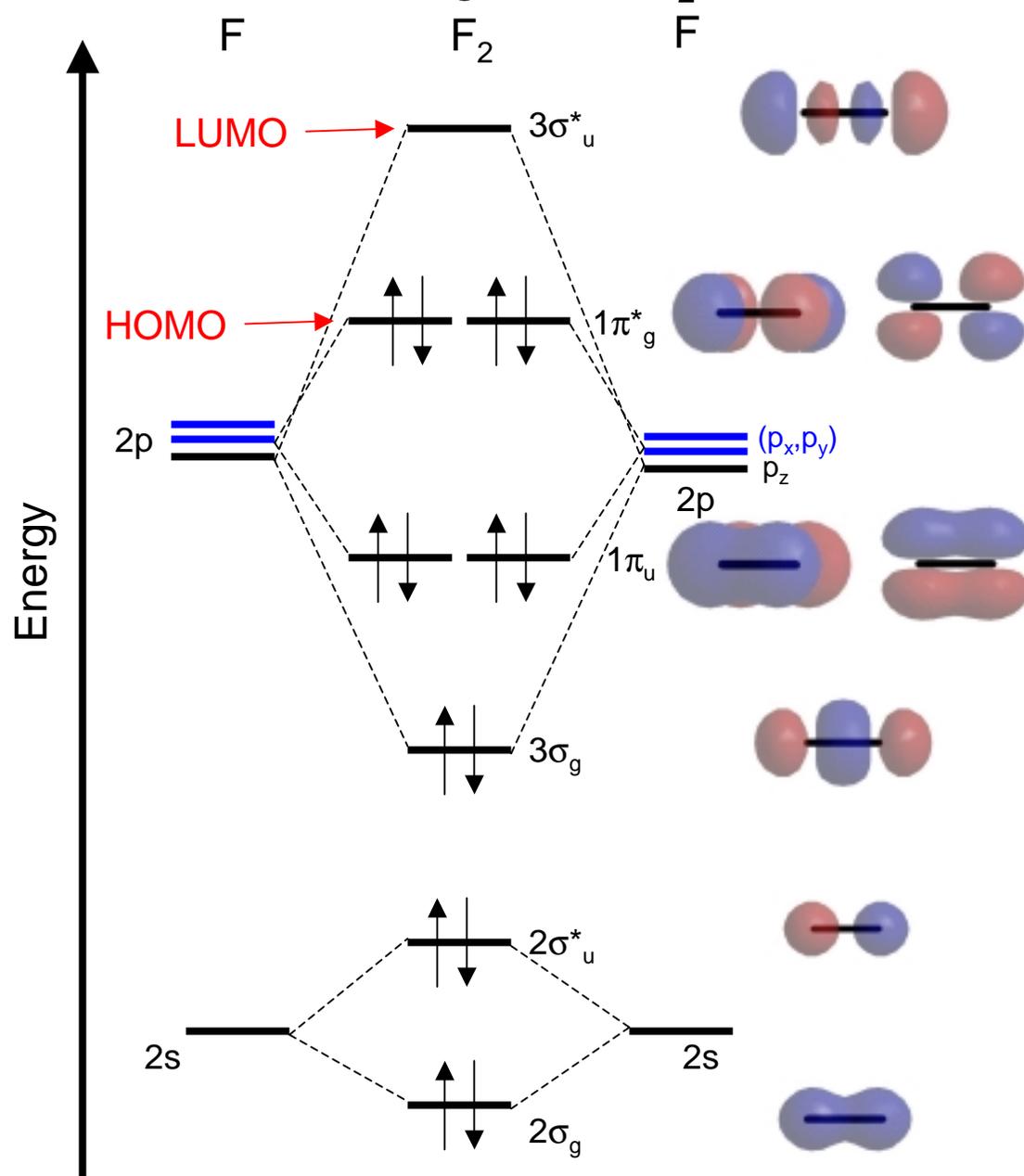
Notice that there is no mixing of AO's of the same symmetry from a single F atom because there is a sufficient difference in energy between the 2s and 2p orbitals in F.

Also notice that the more nodes an orbital of a given symmetry has, the higher the energy.

Note: The the sake of simplicity, electrons are not shown in the atomic orbitals.

Chem 59-651 Molecular Orbital Theory

MO diagram for F_2



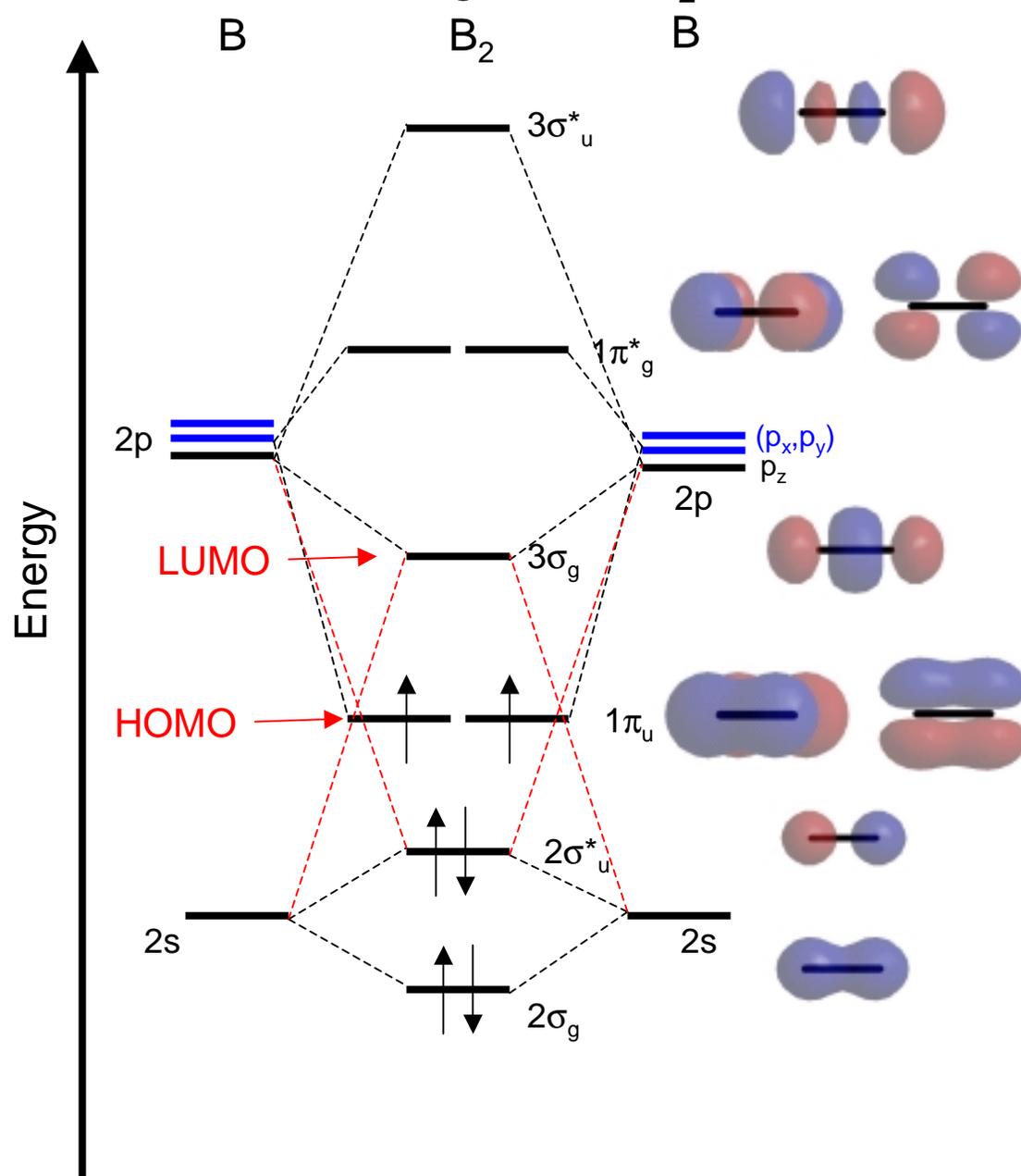
Another key feature of such diagrams is that the π -type MO's formed by the combinations of the p_x and p_y orbitals make degenerate sets (i.e. they are identical in energy).

The highest occupied molecular orbitals (HOMOs) are the $1\pi_g^*$ pair - these correspond to some of the "lone pair" orbitals in the molecule and this is where F_2 will react as an electron donor.

The lowest unoccupied molecular orbital (LUMO) is the $3\sigma_u^*$ orbital - this is where F_2 will react as an electron acceptor.

Chem 59-651 Molecular Orbital Theory

MO diagram for B₂

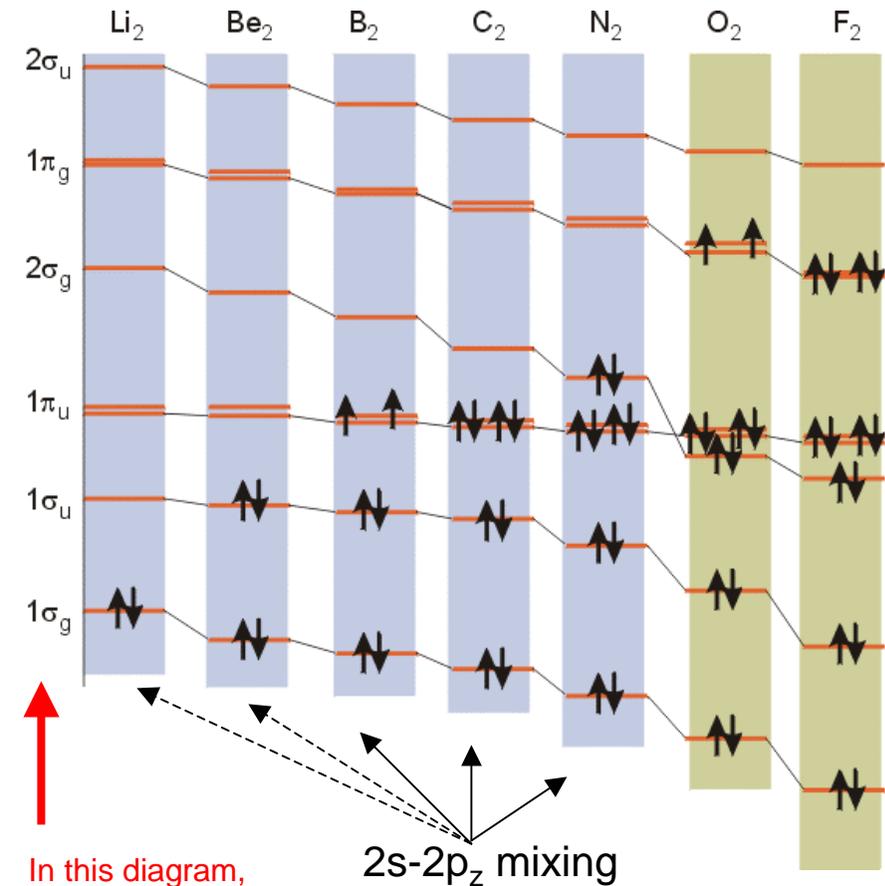


In the MO diagram for B₂, there are several differences from that of F₂. Most importantly, the ordering of the orbitals is changed because of mixing between the 2s and 2p_z orbitals. From Quantum mechanics: the closer in energy a given set of orbitals of the same symmetry, the larger the amount of mixing that will happen between them. This mixing changes the energies of the MO's that are produced.

The highest occupied molecular orbitals (HOMOs) are the 1π_u pair. Because the pair of orbitals is degenerate and there are only two electrons to fill, them, each MO is filled by only one electron - remember Hund's rule. Sometimes orbitals that are only half-filled are called "singly-occupied molecular orbitals" (SOMOs). Since there are two unpaired electrons, B₂ is a **paramagnetic** (triplet) molecule.

Chem 59-651 Molecular Orbital Theory

Diatatomic molecules: MO diagrams for Li_2 to F_2



In this diagram, the labels are for the valence shell only - they ignore the 1s shell. They should really start at $2\sigma_g$ and $2\sigma_u^*$.

Remember that the separation between the ns and np orbitals increases with increasing atomic number. This means that as we go across the 2nd row of the periodic table, the amount of mixing decreases until there is no longer any mixing; this happens at O_2 . At O_2 the ordering of the $3\sigma_g$ and the $1\pi_u$ MO's changes.

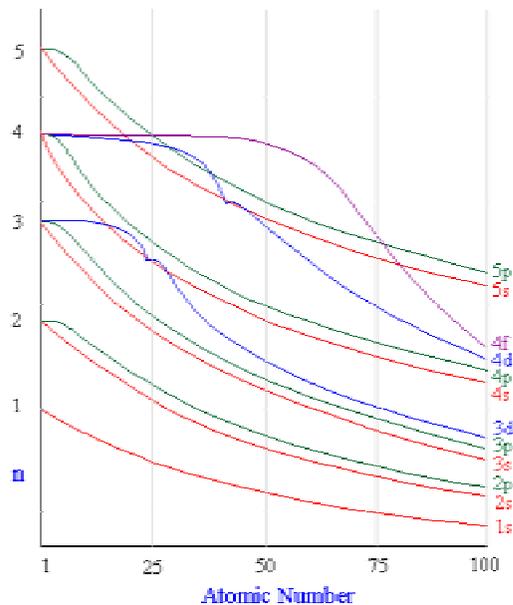
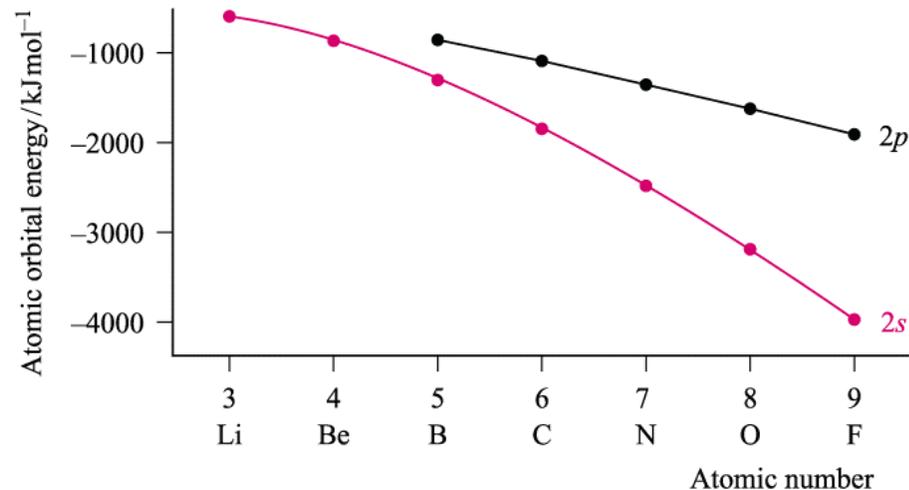
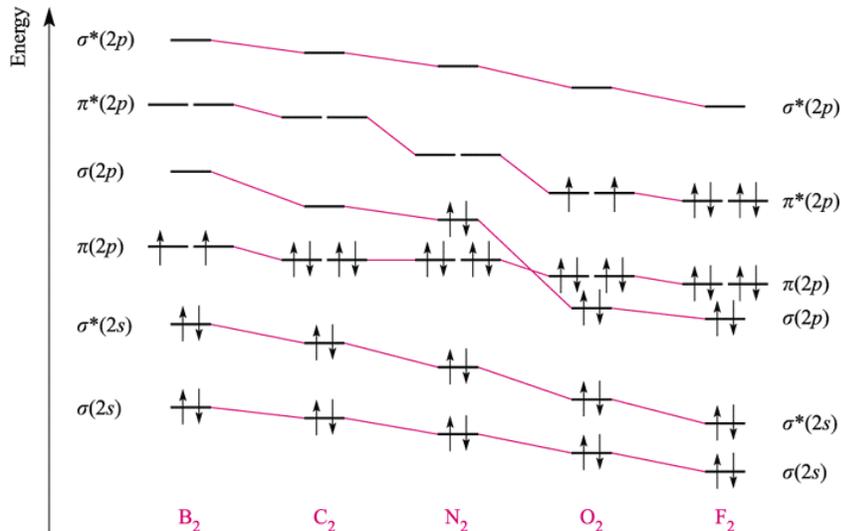
As we go to increasing atomic number, the effective nuclear charge (and electronegativity) of the atoms increases. This is why the energies of the analogous orbitals **decrease** from Li_2 to F_2 .

The trends in bond lengths and energies can be understood from the size of each atom, the bond order and by examining the orbitals that are filled.

Molecule	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond Order	1	0	1	2	3	2	1	0
Bond Length (Å)	2.67	n/a	1.59	1.24	1.01	1.21	1.42	n/a
Bond Energy (kJ/mol)	105	n/a	289	609	941	494	155	n/a
Diamagnetic (d)/ Paramagnetic (p)	d	n/a	p	d	d	p	d	n/a



Diatomic molecules: MO diagrams for B₂ to F₂ and beyond



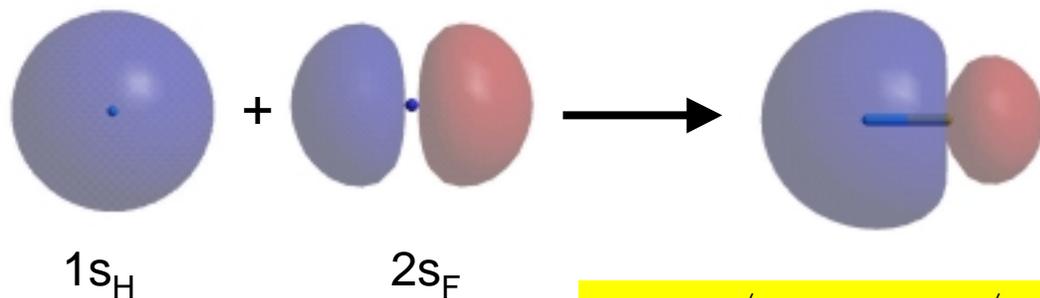
Remember that the separation between the ns and np orbitals increases with increasing atomic number. This means that as we go from the 2nd row of the periodic table to the 3rd row and below, there is no longer much mixing and all of the heavier homonuclear diatomic molecules (if they exist) should have MO diagrams similar to that of O₂.

Chem 59-651 Molecular Orbital Theory

Diatomic molecules: Heteronuclear molecules

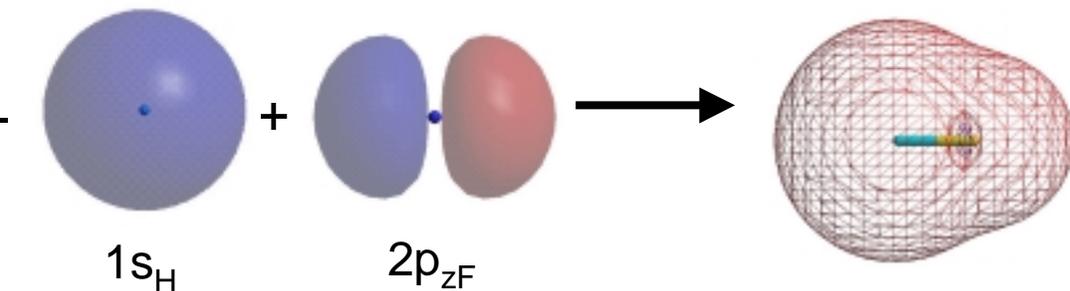
In heteronuclear diatomic molecules, the relative contribution of atomic orbitals to each MO is not equal. Some MO's will have more contribution from AO's on one atom than from AO's on the other. **This means that the coefficients in the MO will not be the same!** For example, in hydrogen fluoride (HF), 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 σ 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)



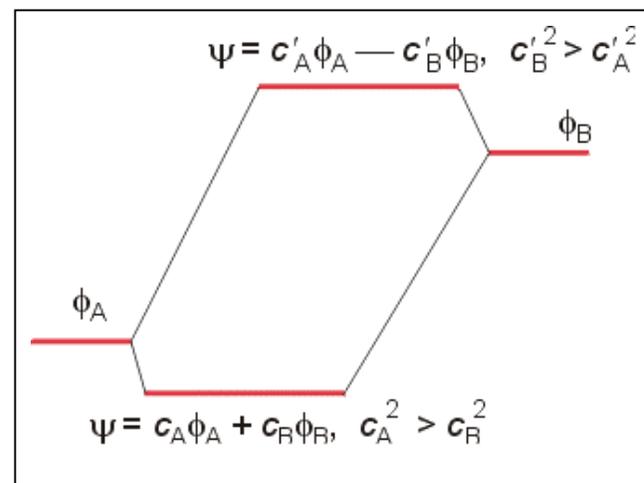
This MO is more F-like

$$\sigma_2 = (\sqrt{0.1} 1s_H + \sqrt{0.9} 2p_{zF})$$



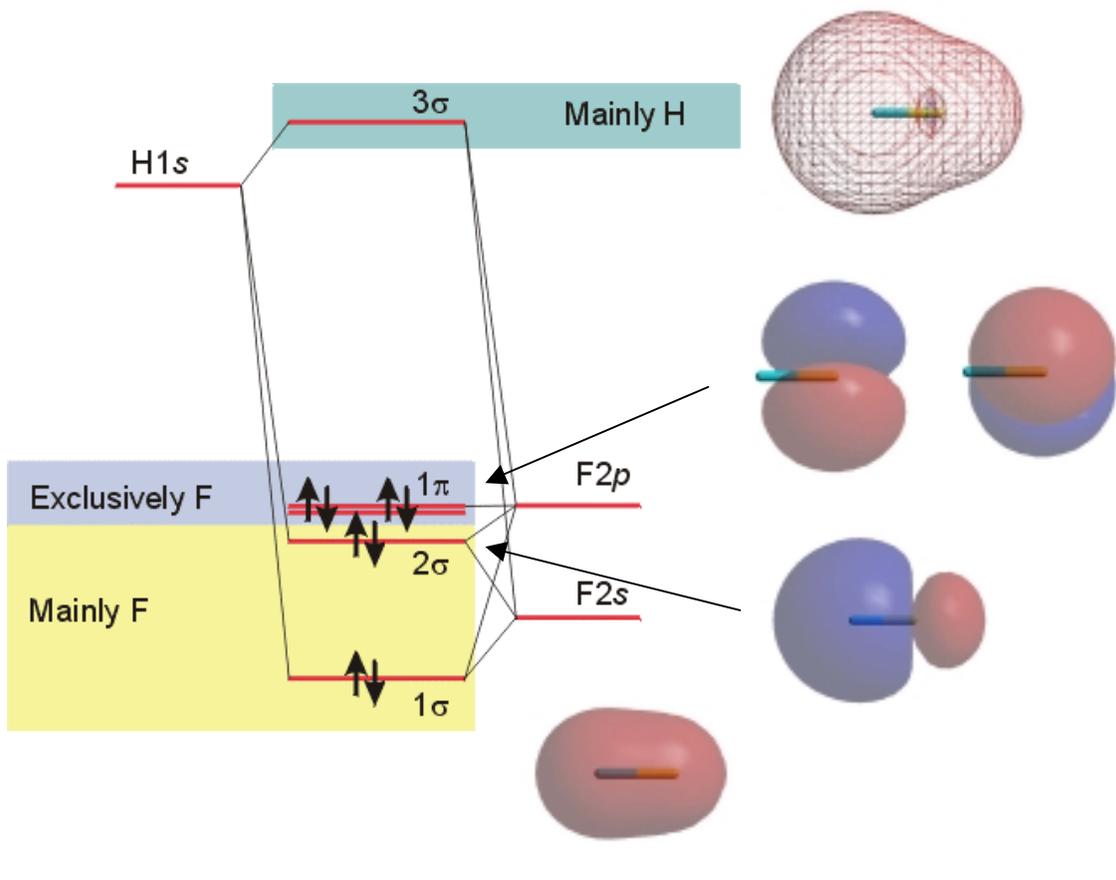
This MO is more H-like

$$\sigma_3^* = (\sqrt{0.9} 1s_H - \sqrt{0.1} 2p_{zF})$$



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

MO diagram for HF



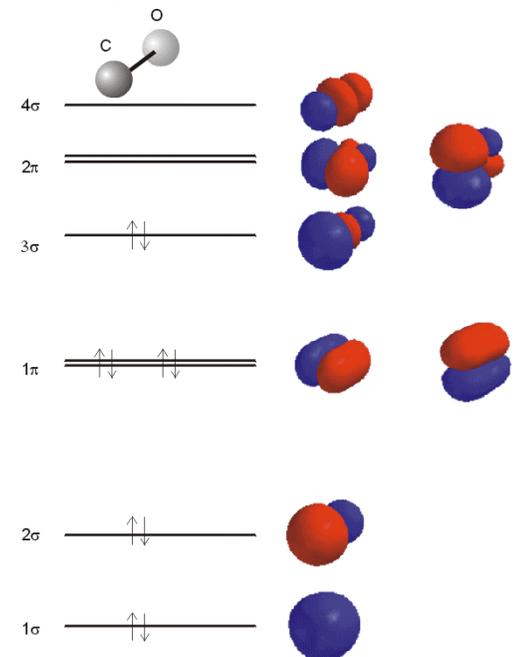
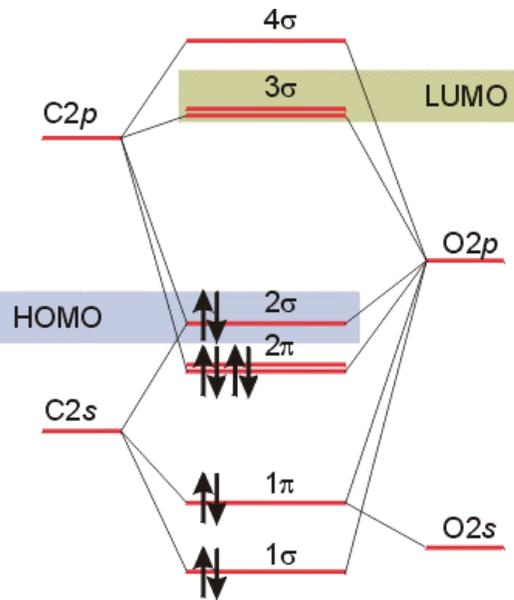
There is a little bit of mixing between the H 1s and the F 2s orbital but it interacts mostly with the 2p_z.

F also has the 2p_x and 2p_y 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.

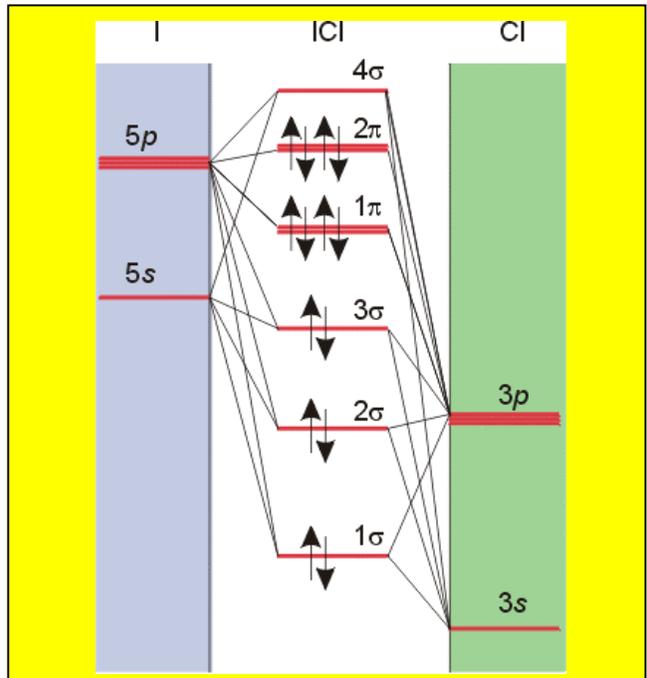
Chem 59-651 Molecular Orbital Theory

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 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 should really start at 3σ. Also note that there is a mistake in the labelling. 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.



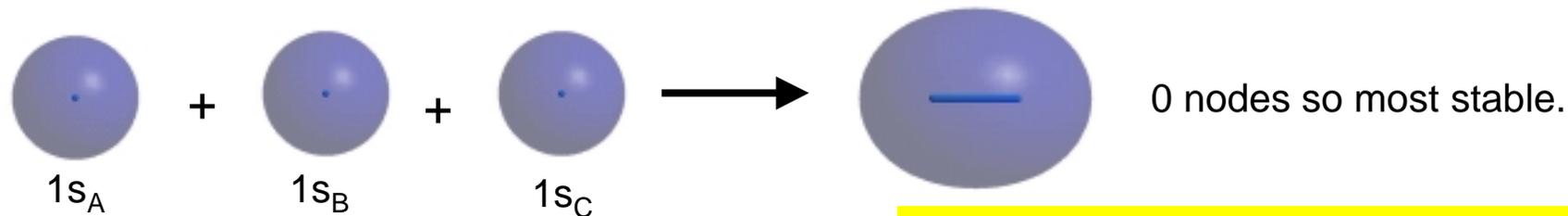
The relative energies of the AO's can be estimated based on the electronegativity of the atoms. More electronegative atoms will have more stable (lower) orbitals.

Chem 59-651 Molecular Orbital Theory

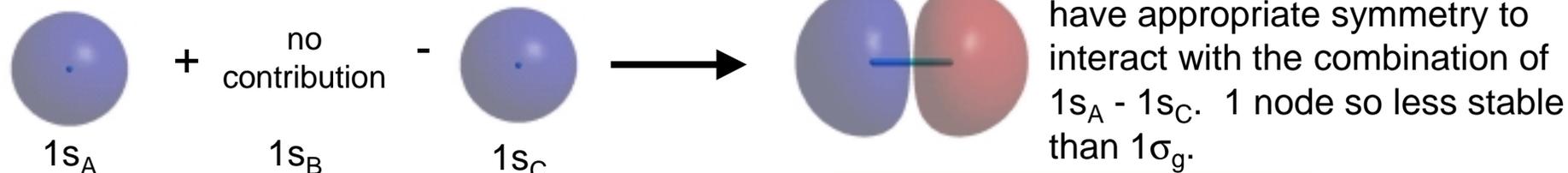
Polyatomic molecules: The bonding in H_3^+

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.

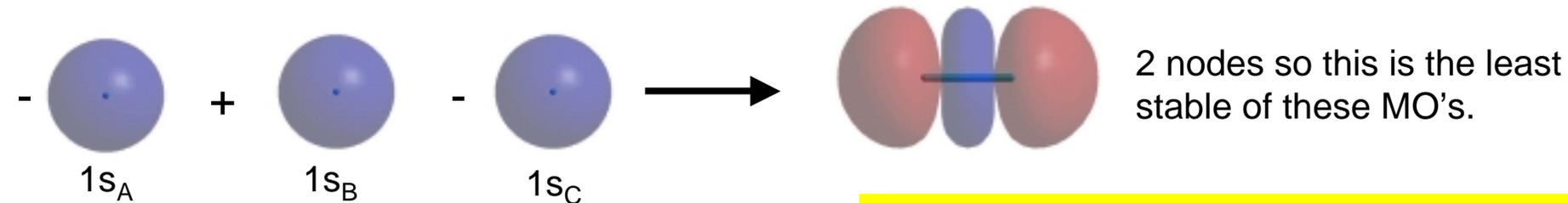
Consider the situation where the H atoms arranged to make a linear geometry. Note that atoms that are related by symmetry must be treated together.



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



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

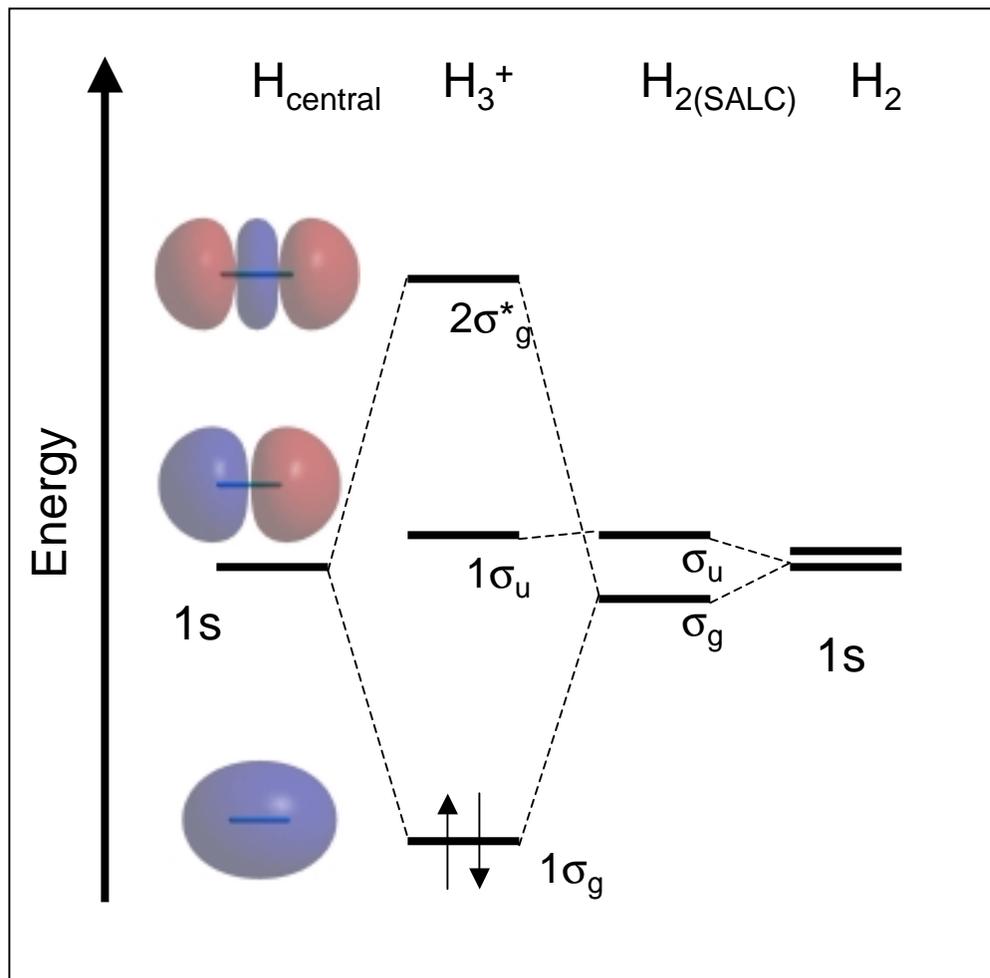


$$2\sigma_g^* = (-\sqrt{0.25} 1s_A + \sqrt{0.5} 1s_B - \sqrt{0.25} 1s_C)$$

Chem 59-651 Molecular Orbital Theory

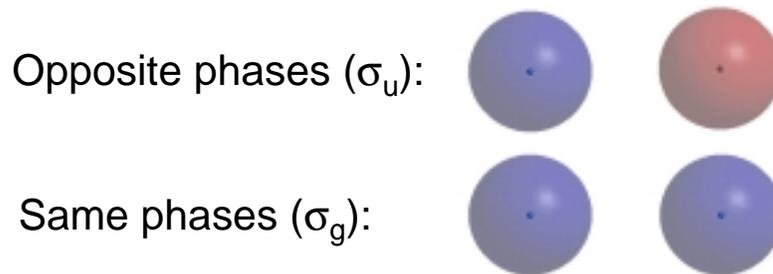
Polyatomic molecules: The bonding in H_3^+

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.

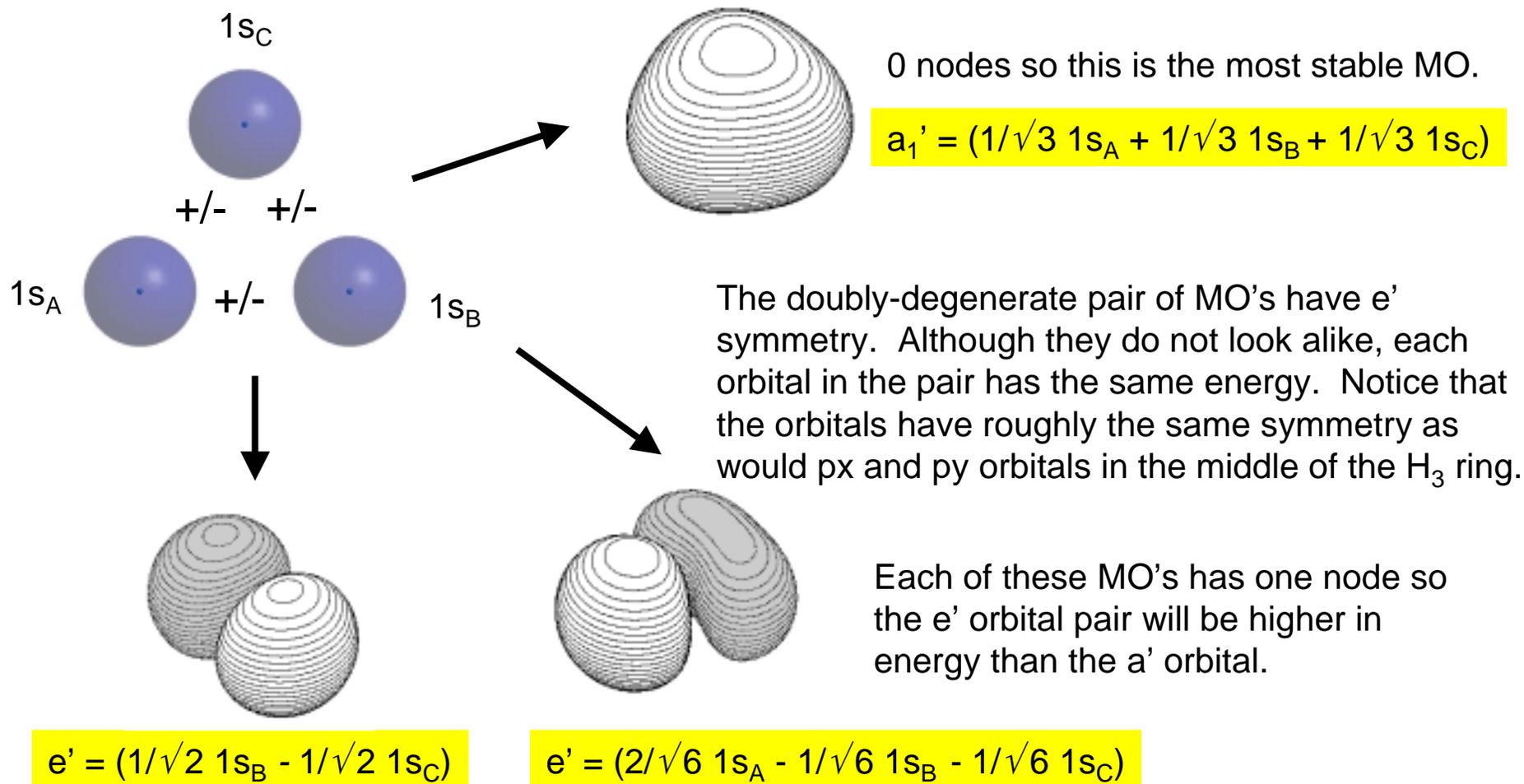
Note that the σ_u combination will be a little bit higher in energy than the σ_g so the non-bonding LUMO is a bit higher in energy than the AO in a free H atom.

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

Chem 59-651 Molecular Orbital Theory

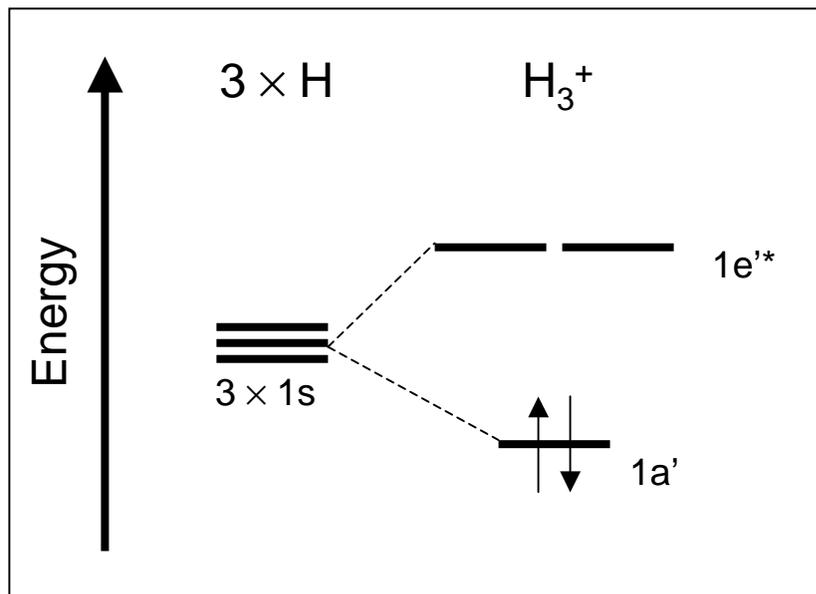
Polyatomic molecules: The bonding in H_3^+

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:

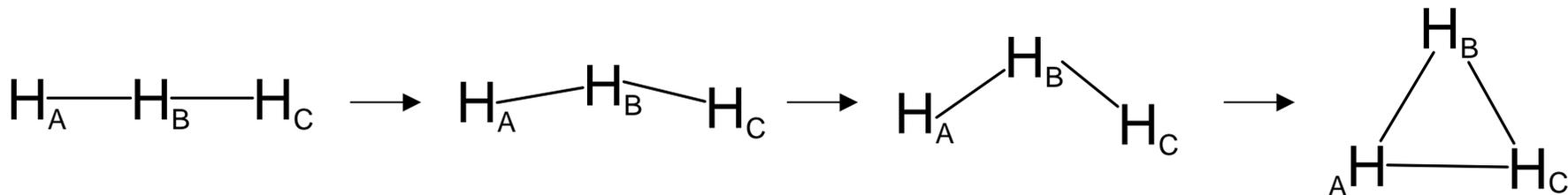


Notice that the e' pair must have identical energies and that the pair is less stable than either the free atoms or the a' MO so it can be called anti-bonding.

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.

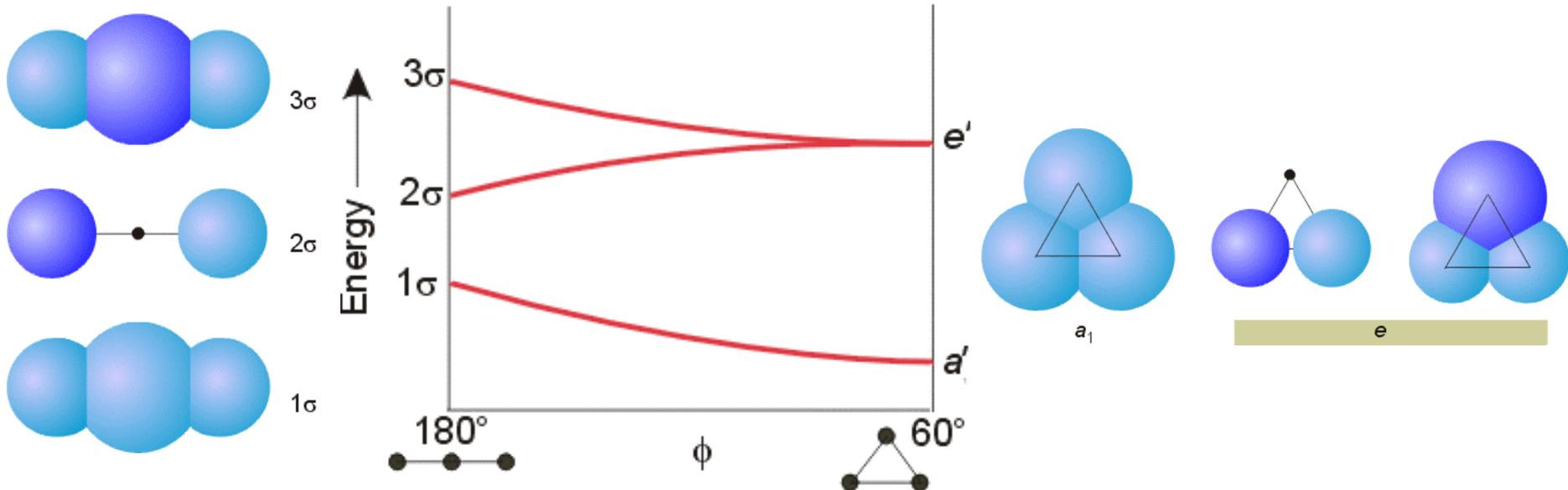
BUT...in theory, we could have any arrangement in between the linear and the triangular, so how do we find out which geometry is the most stable?



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}



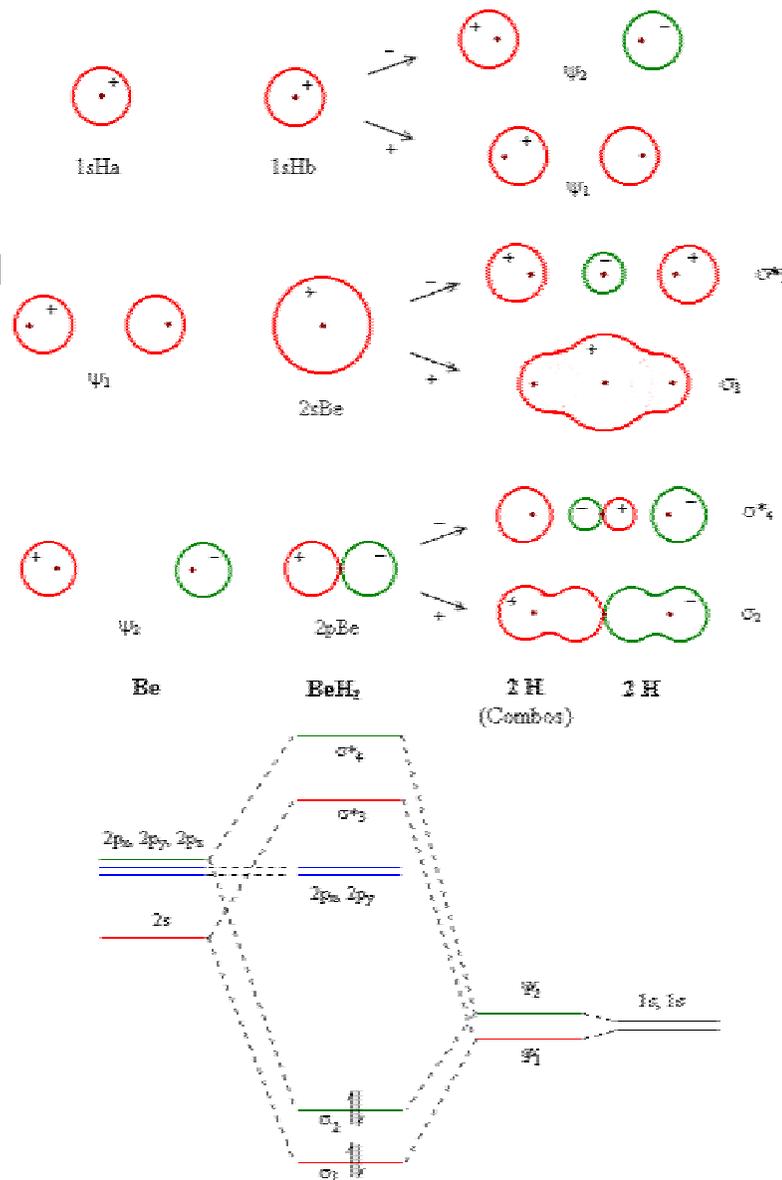
In the example of H_3^+ there are only two electrons, thus we only have to examine how the energy of the lowest orbital (1σ to a_1') varies with the change in angle. From the diagram we can see that the energy decreases from $D_{\infty h}$ to D_{3h} so the electronic energy of the triangular arrangement 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.

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.

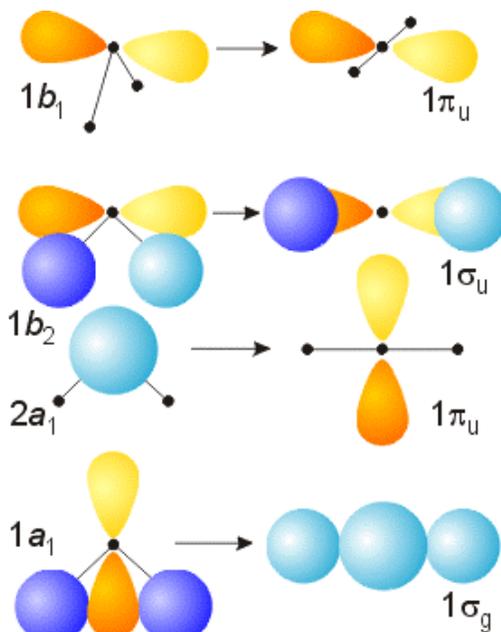
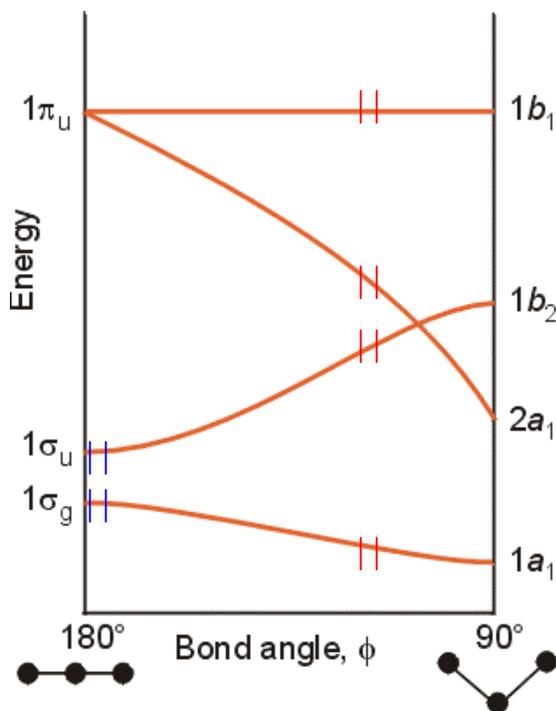
e.g. BeH_2



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 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° .

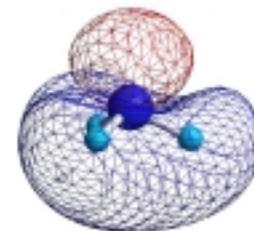
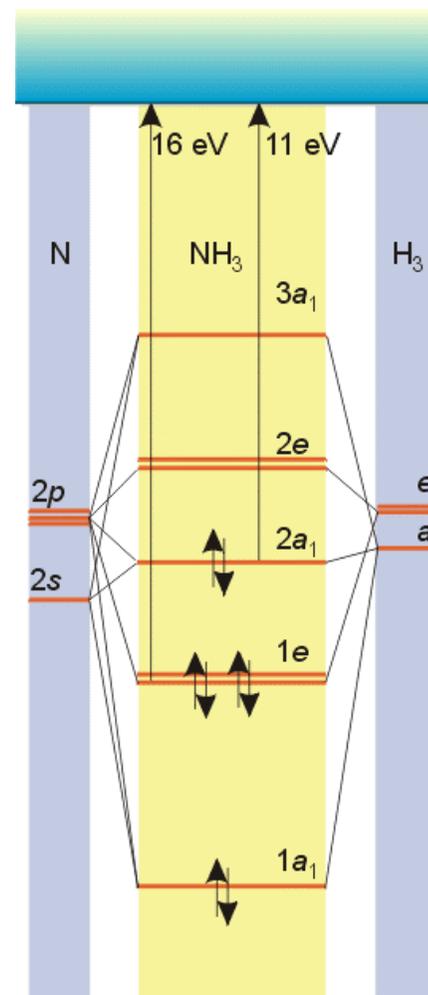
In H_2O , there are 8 valence electrons which will fill up all four orbitals in the diagram. Since the energy of the $1b_1$ orbital doesn't change as the angle is changed, the overall energy is mostly determined by the relative energies of the $2a_1$ and the $1b_2$. A reasonable guess is shown in red.

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.

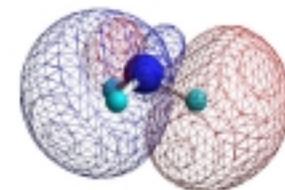
E.g. Building a MO diagram for NH_3 :

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 H_3^+ , but the point group that must be used for NH_3 is C_{3v}).
3. $X_N \approx 3$ and $X_H \approx 2.2$ 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 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 NH_3 can also act as a Lewis acid through the H atoms.



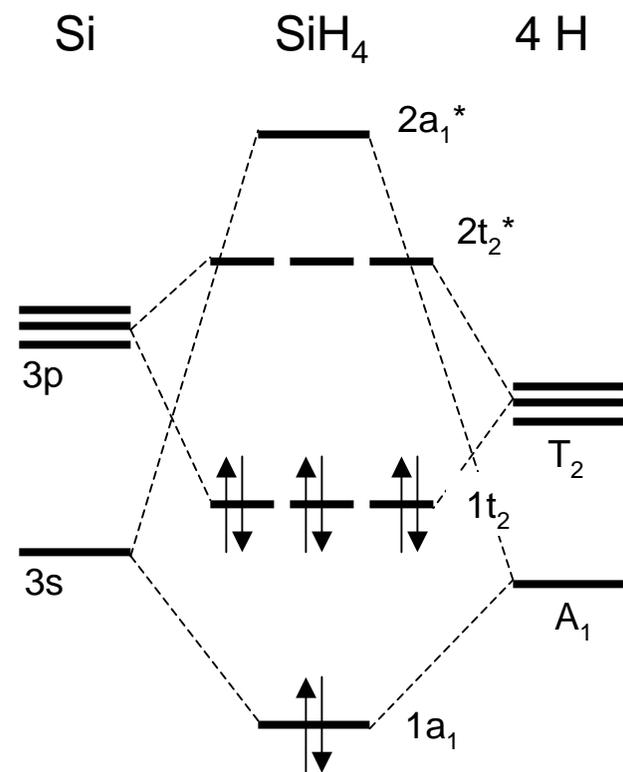
HOMO



LUMO

E.g. Building a MO diagram for 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. $X_{\text{Si}} \approx 1.9$ and $X_{\text{H}} \approx 2.2$ 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.

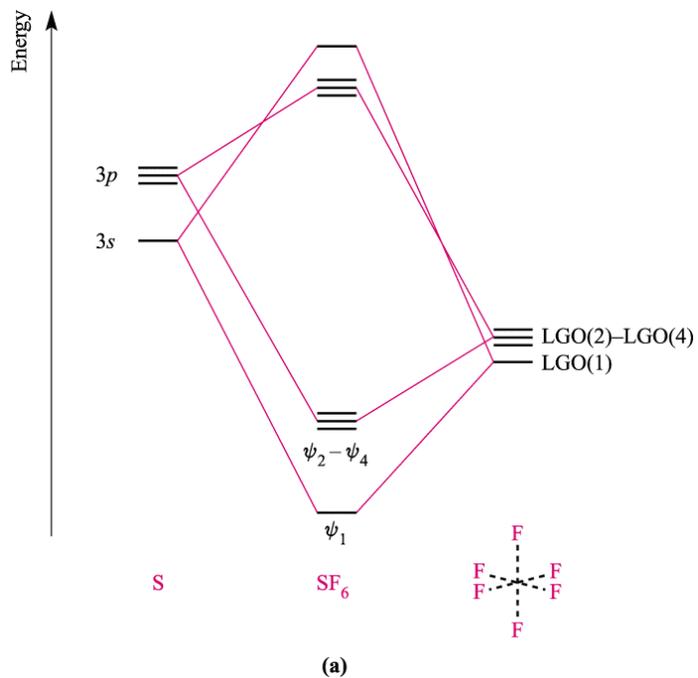
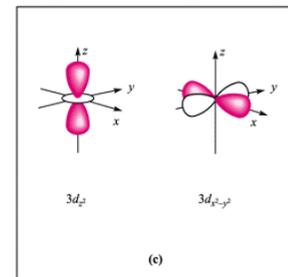
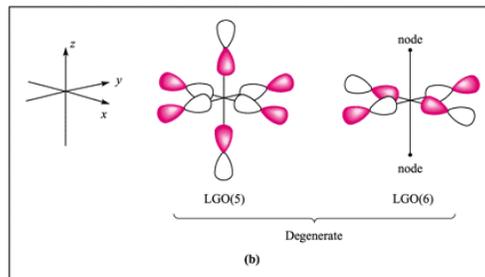
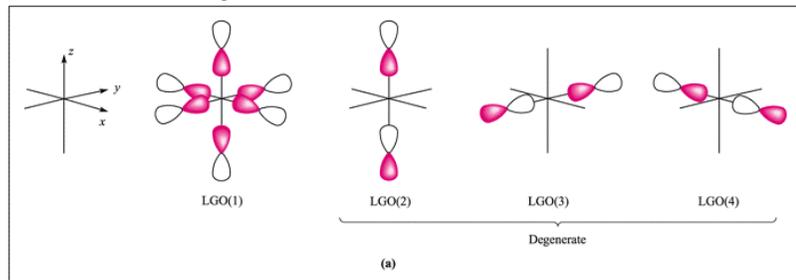


In SiH_4 , the HOMO is a mostly based on the peripheral hydrogen atoms and the LUMO is dominated by Si so SiH_4 will act as an electron donor through the H atoms and an electron acceptor at Si.

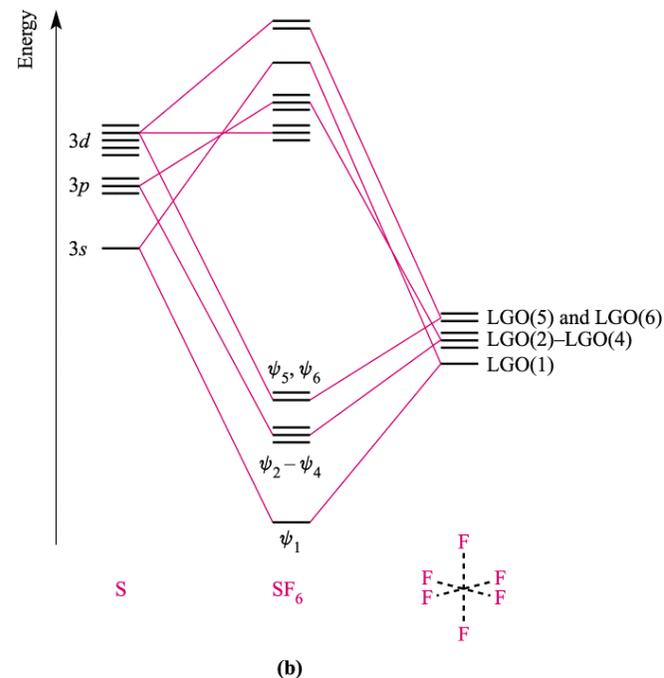
Molecular Orbital Theory

Polyatomic molecules: SF₆

The same principles can be applied to make MO diagrams for octahedral complexes using SALCs made from either s or p atomic orbitals on the ligands.



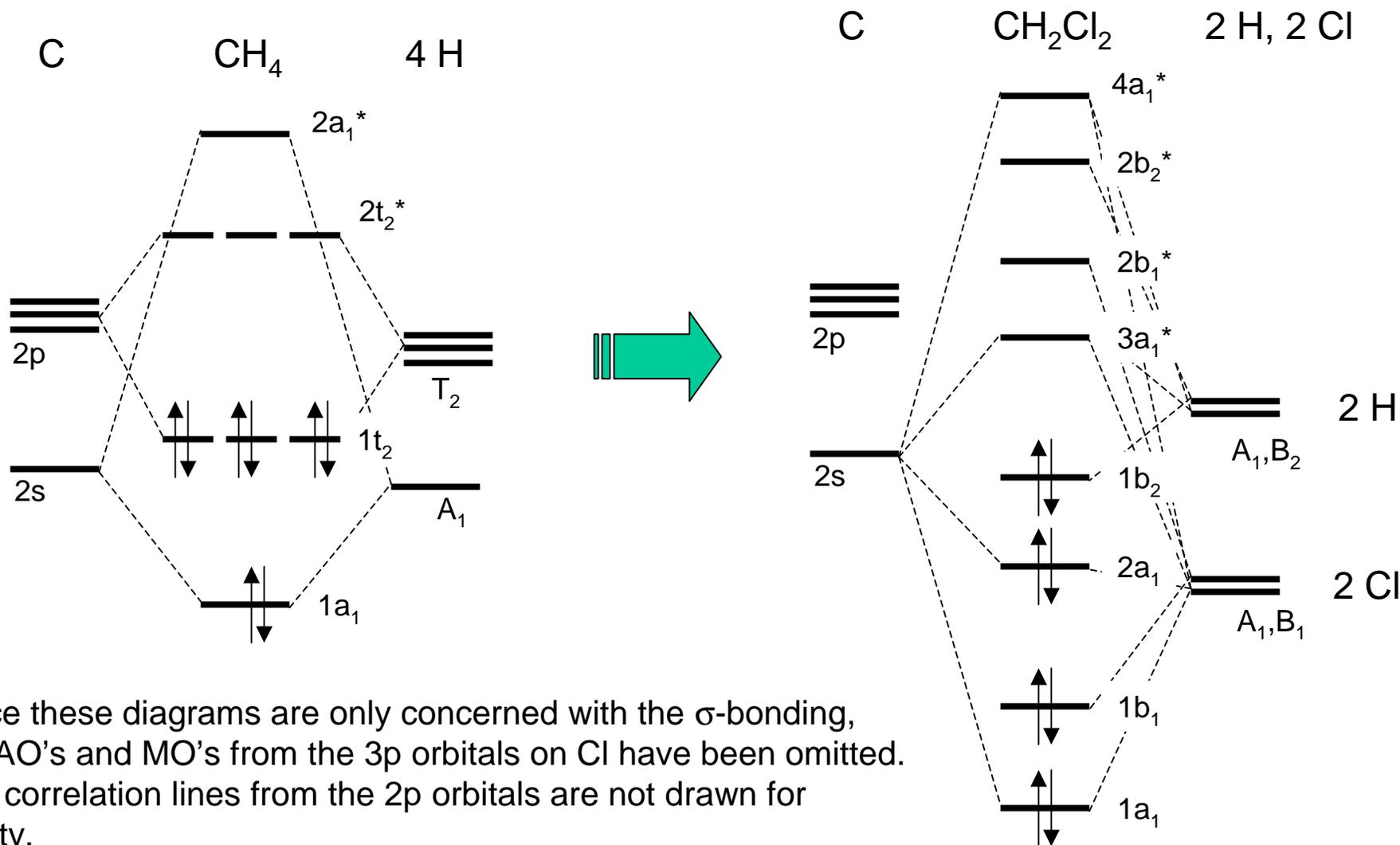
The MO diagrams for octahedral complexes can be made to ignore (a) or include (b) d-orbital contributions. In diagram (a), the e_g set is considered to be non-bonding, thus there would only be 8 electrons binding the 6 F ligands to the S atom.



Molecular Orbital Theory

Polyatomic molecules

Consider what happens to the σ -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).

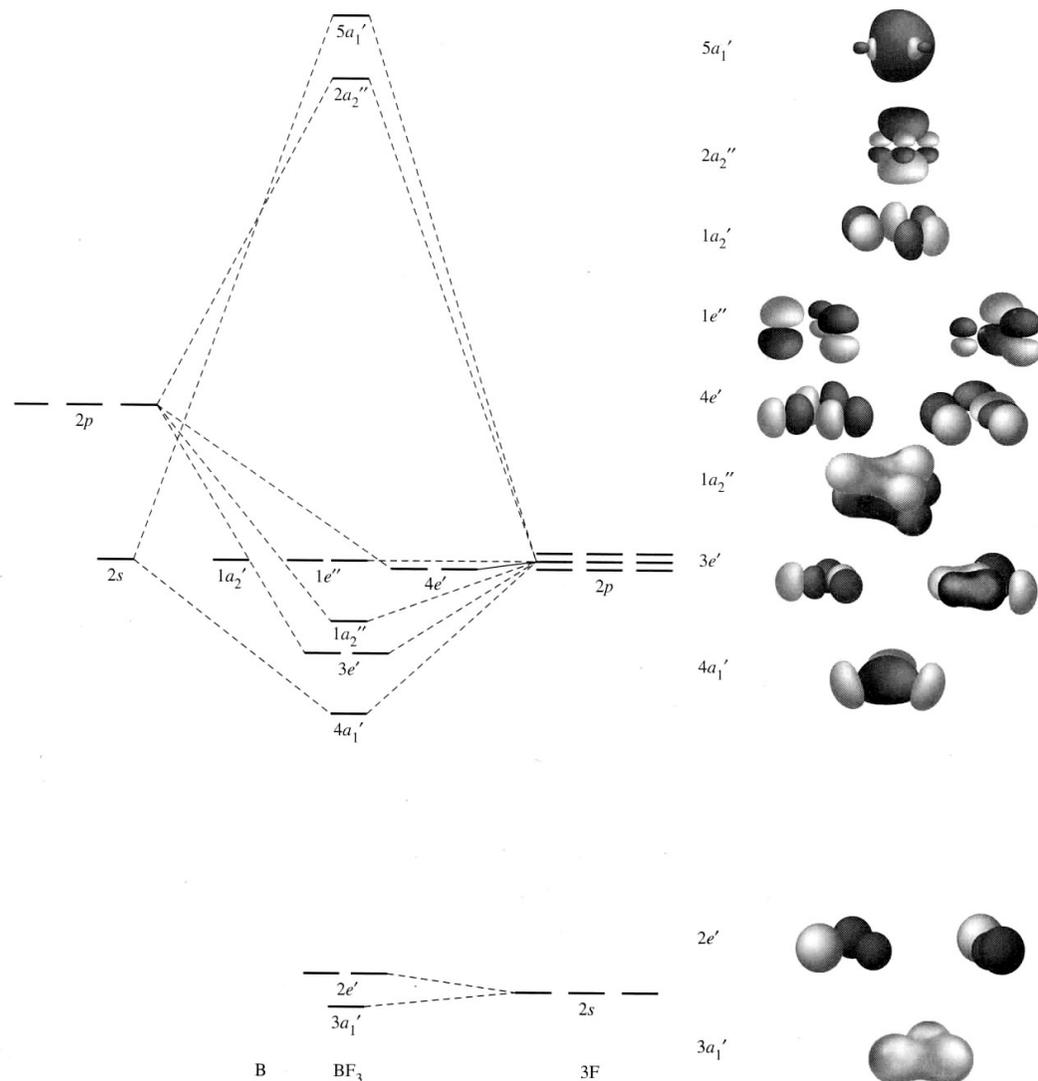


E.g. Building a MO diagram for BF_3 :

1. The point group is D_{3h} .
2. All F's are related so the orbitals on these must be split into appropriate SALC's of a-type and e-type symmetry.
3. $X_F \approx 4$ and $X_B \approx 2.0$ so the energy levels of the AO's on F will be lower than those on the B atoms.
4. From the D_{3h} character table, the symmetry of the AO's on B are: A_1' (2s), A_2'' ($2p_z$), and E' ($2p_x, 2p_y$). Each of these orbitals can interact with the SALC's from the F atoms.

5. Fill the MO's with the valence electrons.

This diagram is more complicated than it has to be - we can split it into a σ -bonding diagram and a π -bonding diagram.



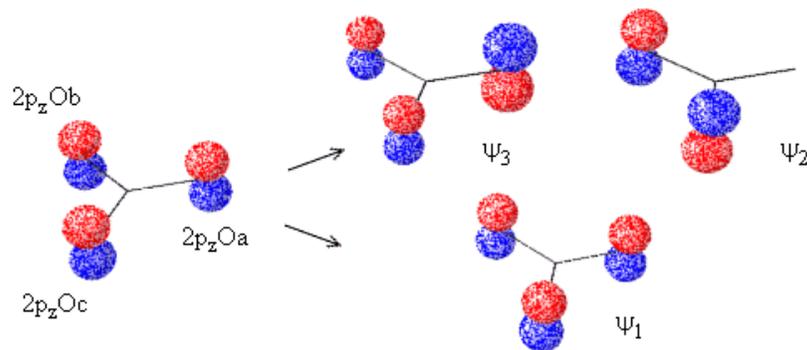
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Pi-bonding in polyatomic molecules

Molecular orbital theory considers π -bonding in exactly the same way as σ -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 π -bonding because the MO's are spread equally over the π -system of the entire molecule. Not surprisingly, the delocalized model of bonding provides a much better picture of the *delocalized* π -system.

E.g. the π -bonding in CO_3^{2-}

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



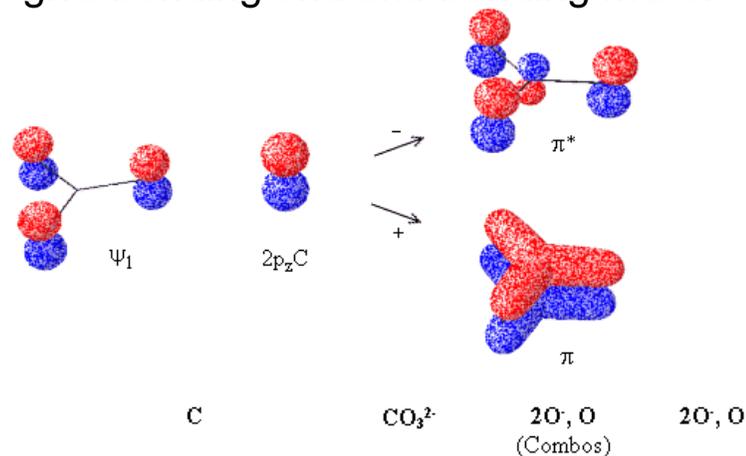
These are analogous to the SALC's we built for H_3^+ and so the normalization coefficients are identical:

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

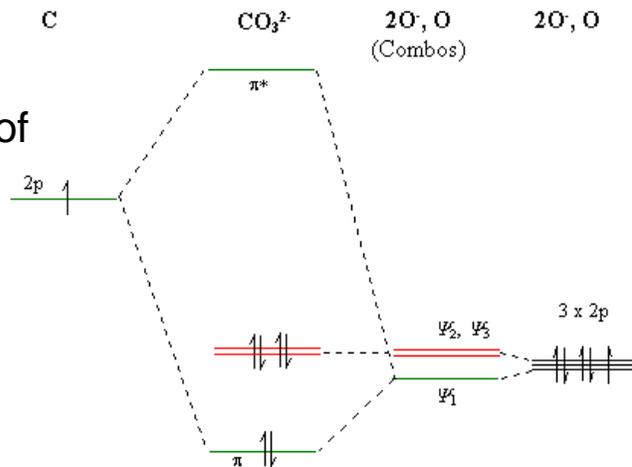
$$e'' = (1/\sqrt{2} 2p_{zB} - 1/\sqrt{2} 2p_{zC})$$

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

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 π -bonding:

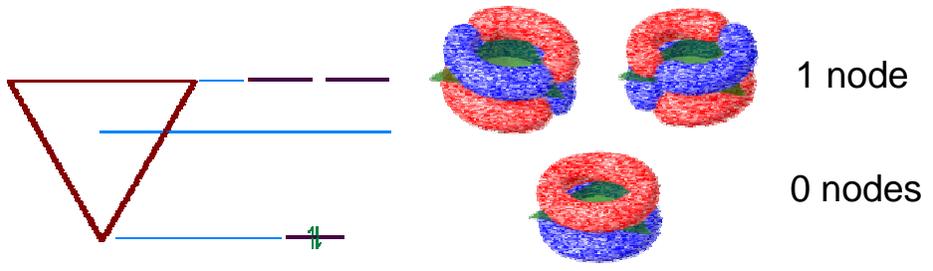


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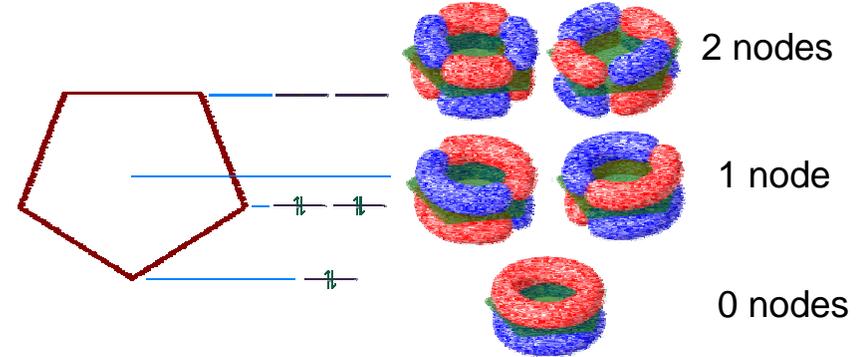
Pi-bonding in aromatic molecules

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

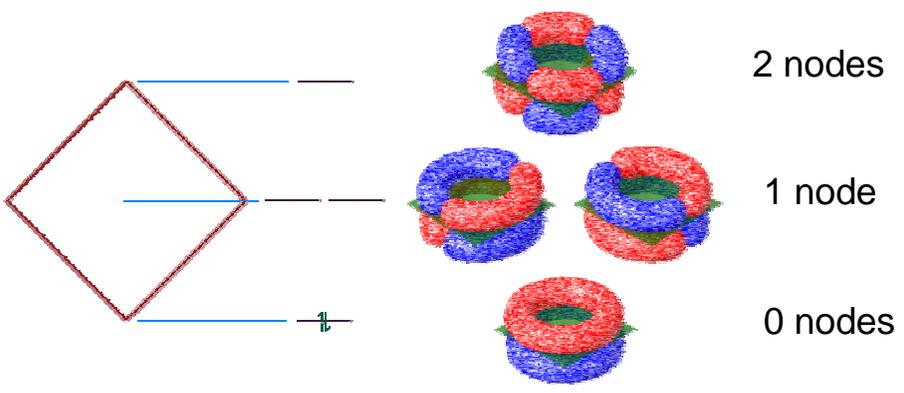
The π -bonding in $C_3H_3^{+1}$ (aromatic)



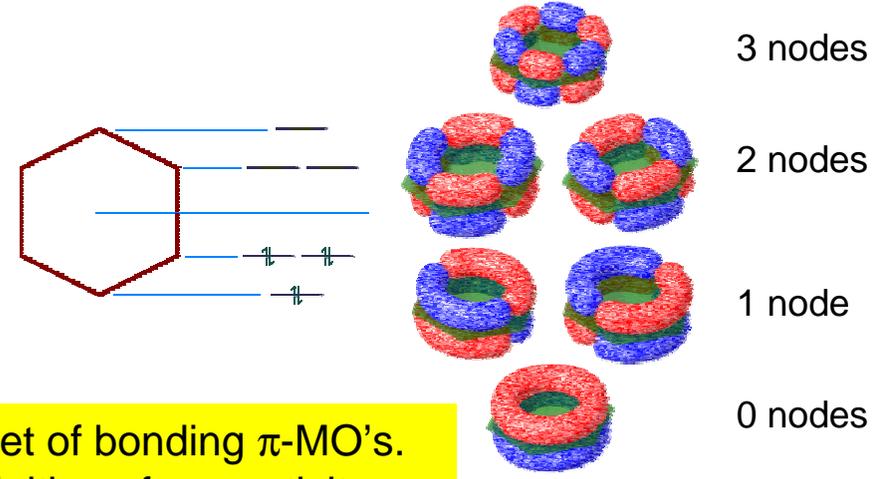
The π -bonding in $C_5H_5^{-1}$ (aromatic)



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



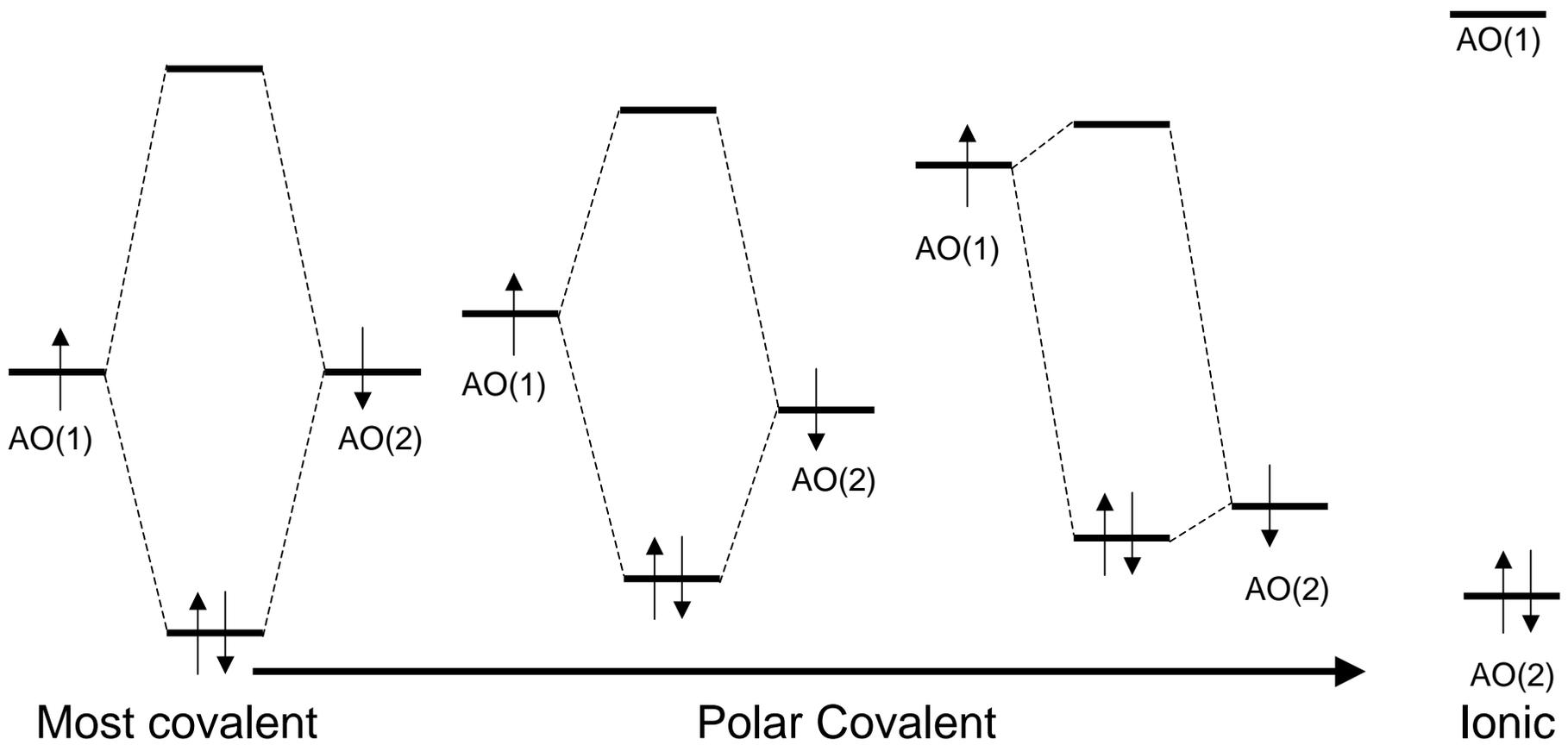
The π -bonding in C_6H_6 (aromatic)



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

Chem 59-651 Molecular Orbital Theory

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.



$\Delta X < 0.5$: covalent $2 > \Delta X > 0.5$: polar $\Delta X > 2$: ionic