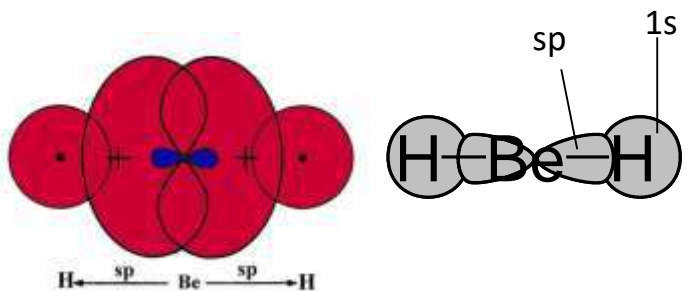


The Delocalized Approach to Bonding: Molecular Orbital Theory

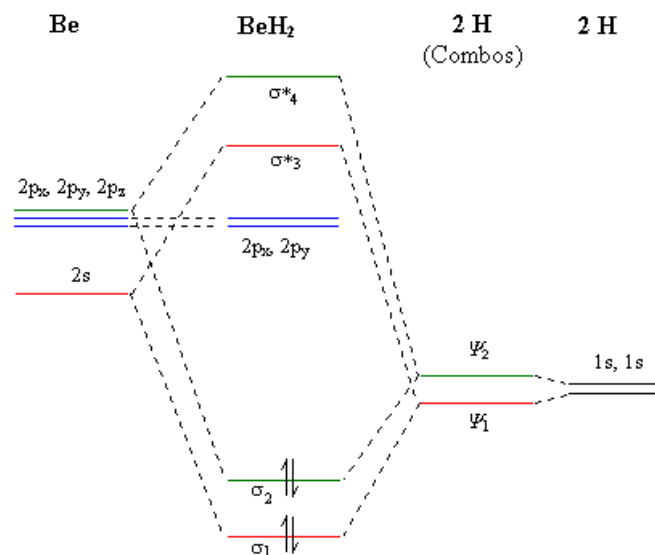
The localized models for bonding we have examined (Lewis and VBT) assume that all electrons are restricted to specific bonds between atoms or in “lone pairs”. In contrast, the delocalized approach to bonding places the electrons in Molecular Orbitals (MO's) - orbitals that encompass the entire molecule 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

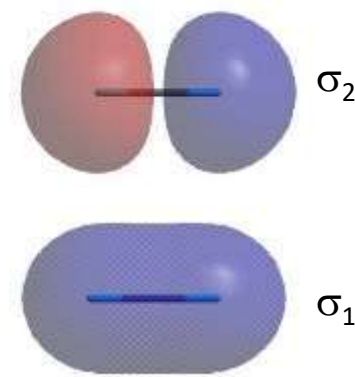


Two (sp-1s) Be-H σ bonds.

Delocalized Bonding



MO diagram for BeH₂



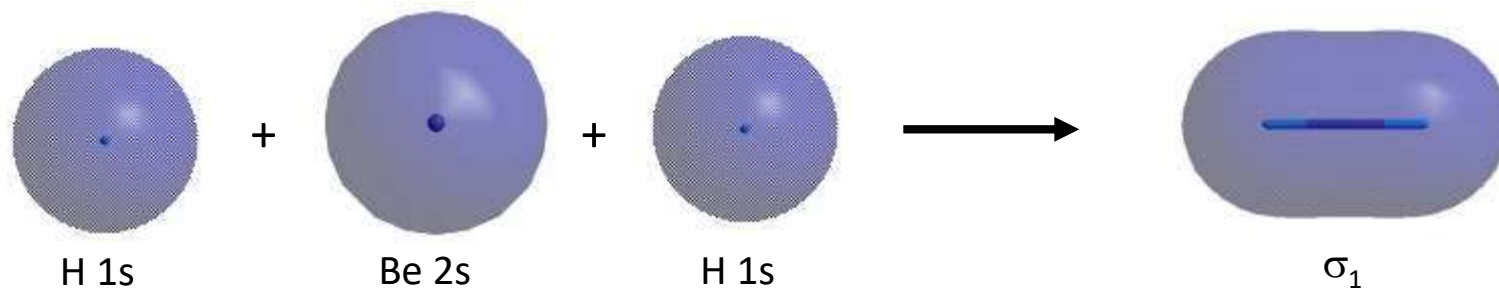
The two σ bonding MO's in BeH₂

Molecular Orbital Theory

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.

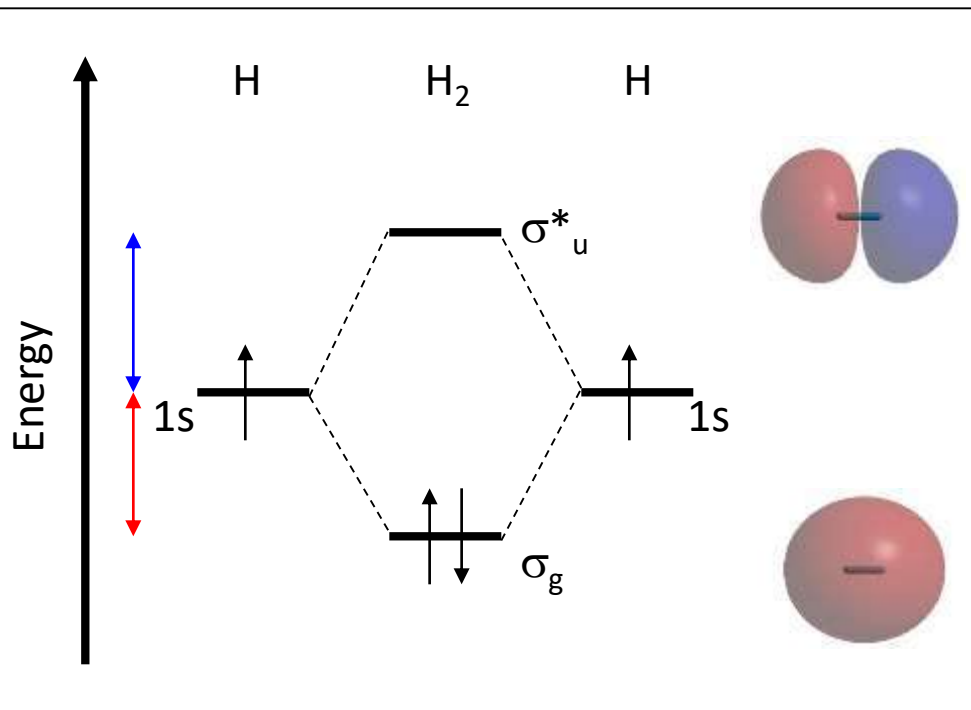


Molecular Orbital Theory



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:

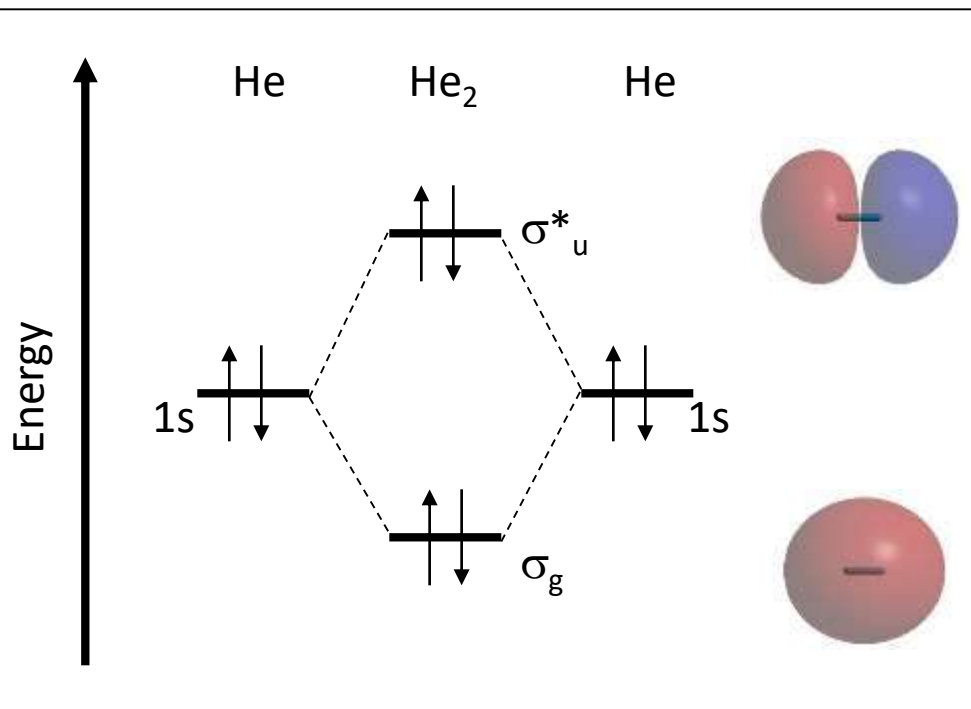
The amount of stabilization of the σ MO (indicated by the red arrow) is slightly less than the amount of destabilization of the σ^* MO (indicated by the blue arrow) because of the pairing of the electrons. For H_2 , the stabilization energy is 432 kJ/mol and the bond order is 1.

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

Molecular Orbital Theory

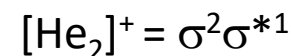
Diatomic molecules: The bonding in He₂

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**.

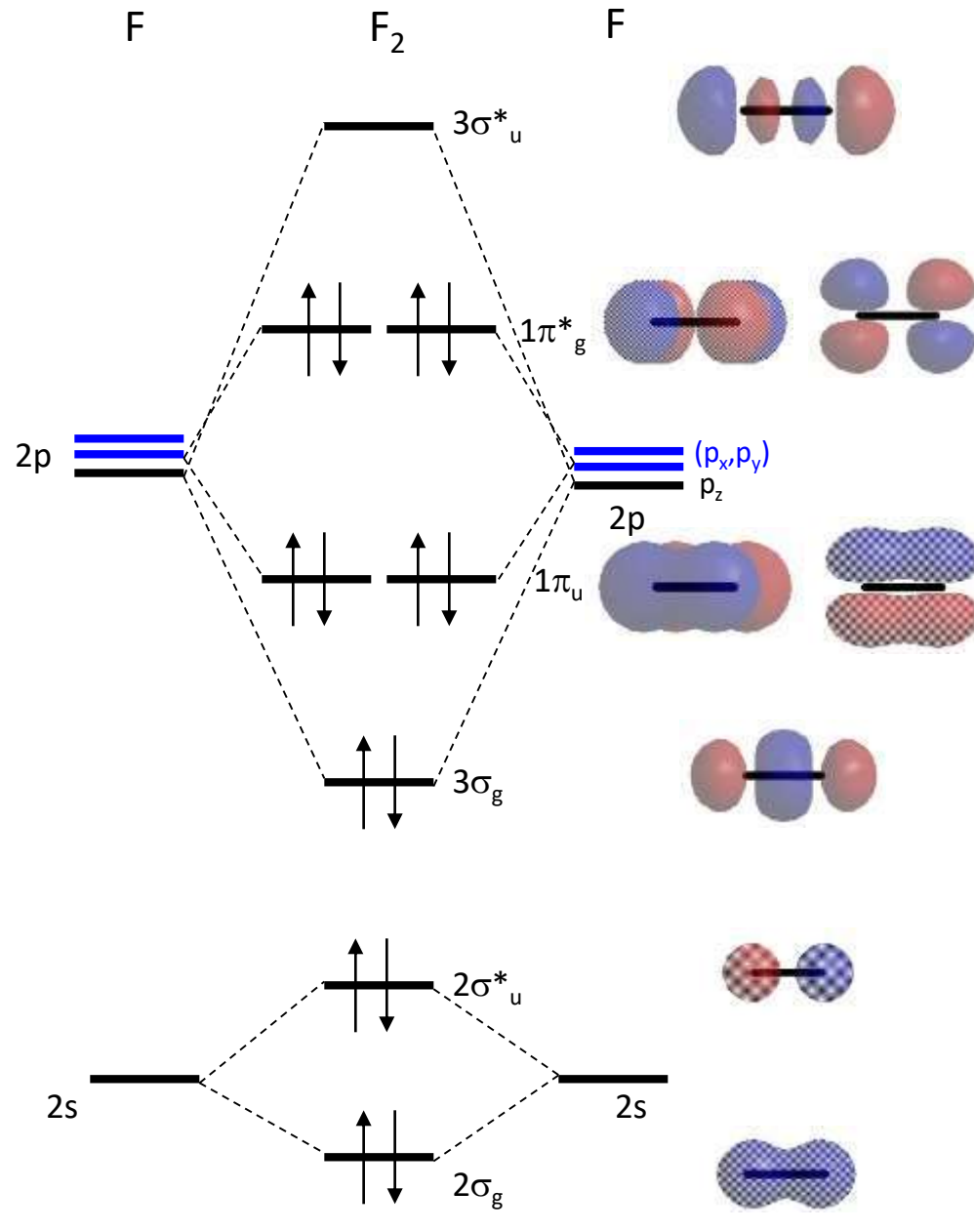
However the cation [He₂]⁺, in which one of the electrons in the σ* MO is removed, would have a bond order of $(2-1)/2 = \frac{1}{2}$, so such a cation might be predicted to exist. The electron configuration for this cation can be written in the same way as we write those for atoms except with the MO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

Molecular Orbital Theory

MO diagram for F₂



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.

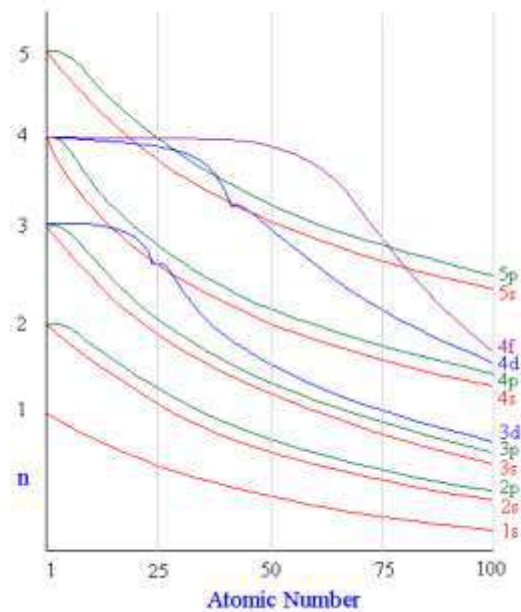
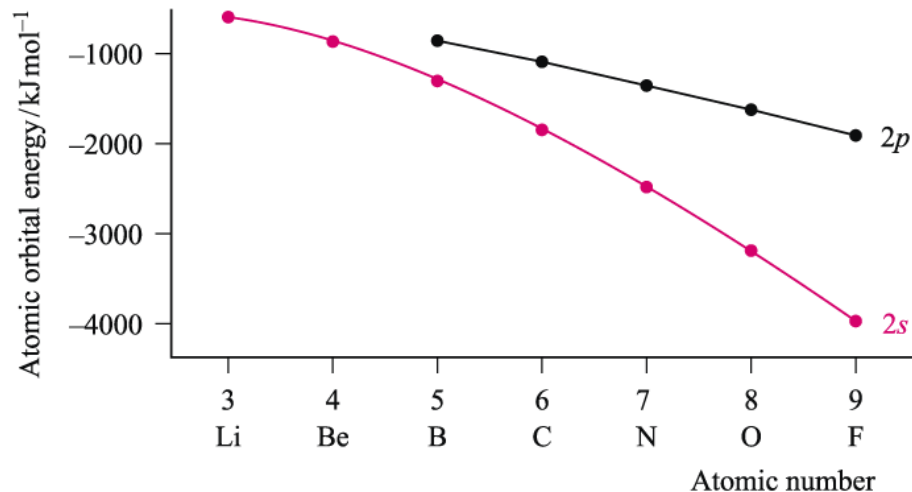
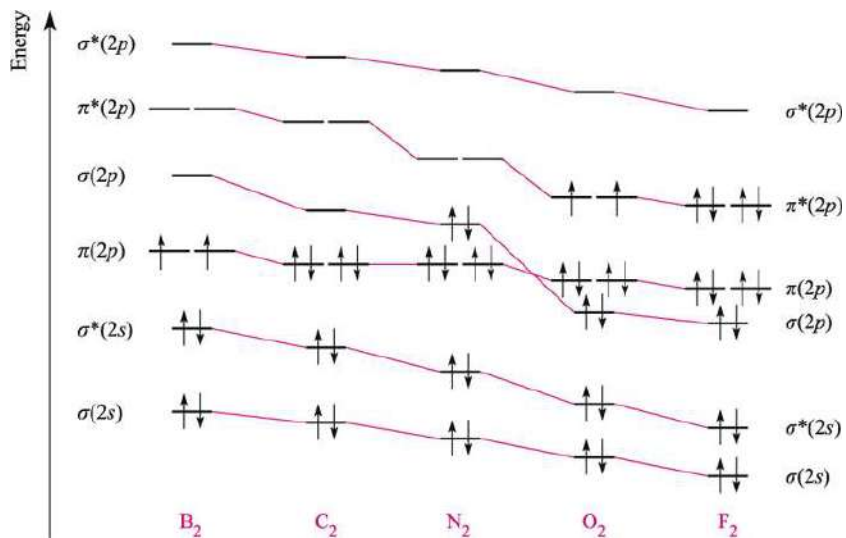
Notice that there is no mixing of AO's of the same symmetry from a single F atom because there is a sufficient difference in energy between the 2s and 2p orbitals in F.

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.

Molecular Orbital Theory

Diatomic molecules: MO diagrams for B₂ to F₂ and beyond

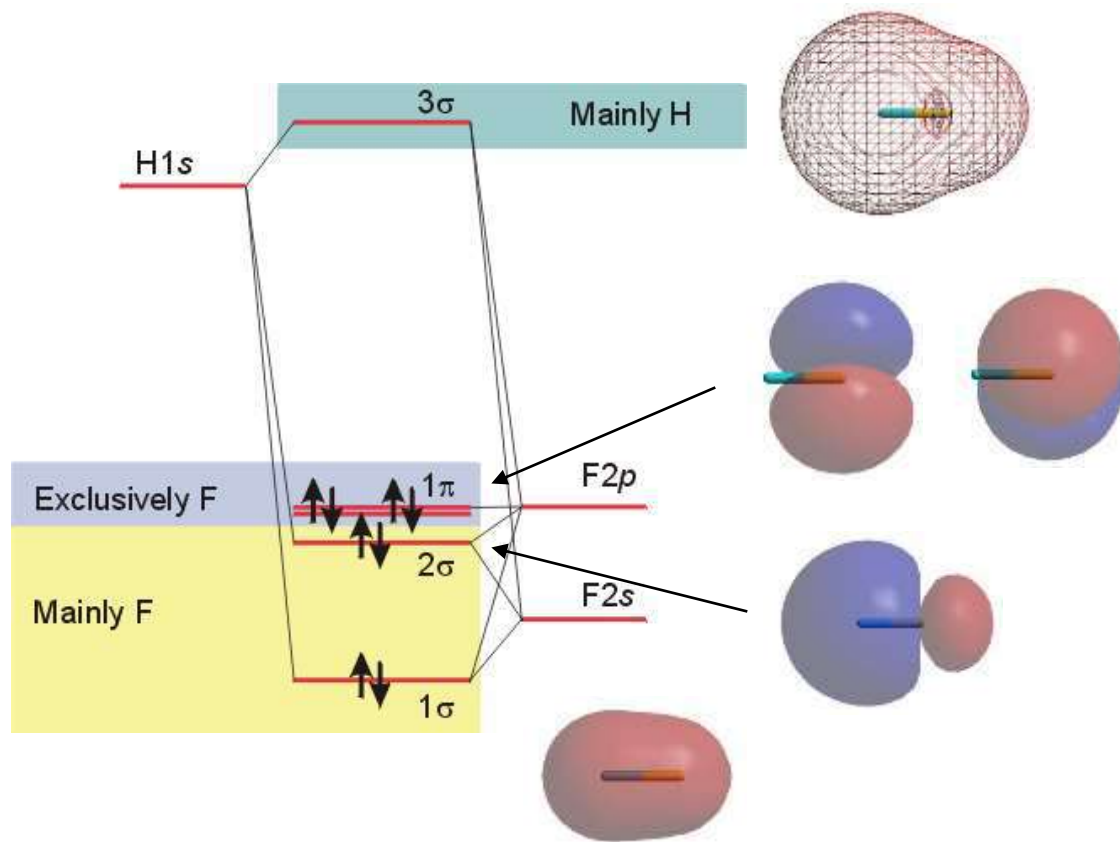


Remember that the separation between the *ns* and *np* orbitals increases with increasing atomic number. This means that as we go from the 2nd row of the periodic table to the 3rd row and below, there is no longer much mixing and all of the heavier homonuclear diatomic molecules (if they exist) should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

Molecular Orbital Theory

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.

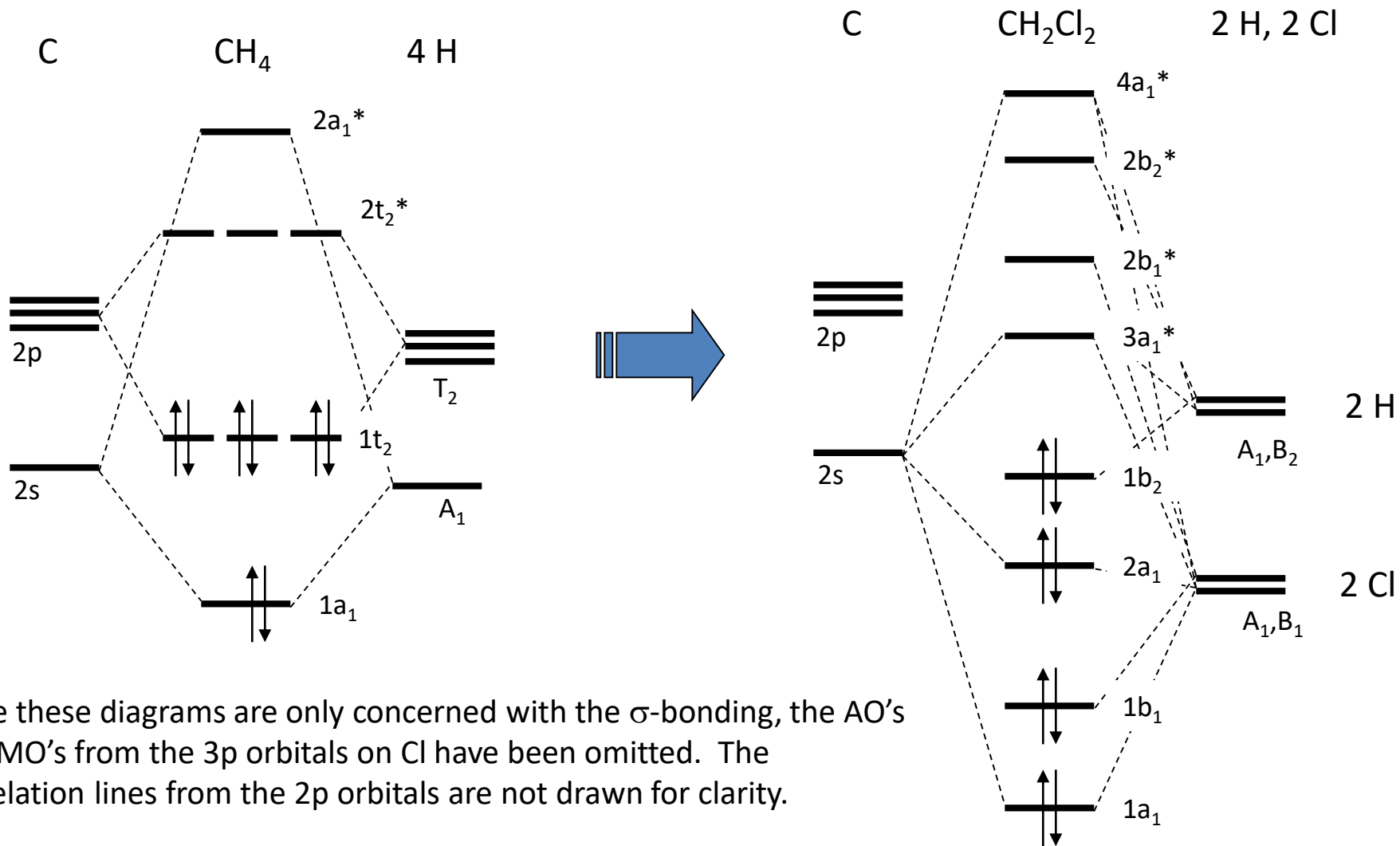
F also has the 2p_x and 2p_y orbitals that cannot interact with the H 1s orbital because they have the wrong symmetry! If you try to combine these orbitals with the 1s on H, you will find that the overlap integral, S , is equal to 0. Thus these orbitals are exclusively found on the F atom and are called *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.

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).



Since these diagrams are only concerned with the σ -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.