

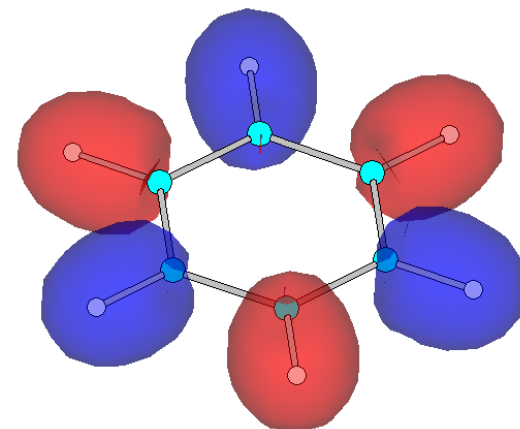
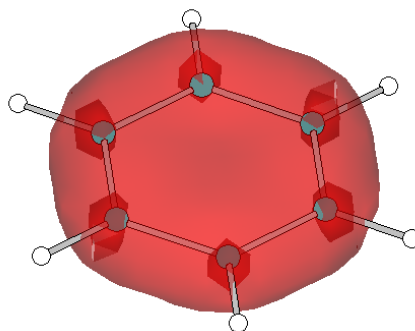
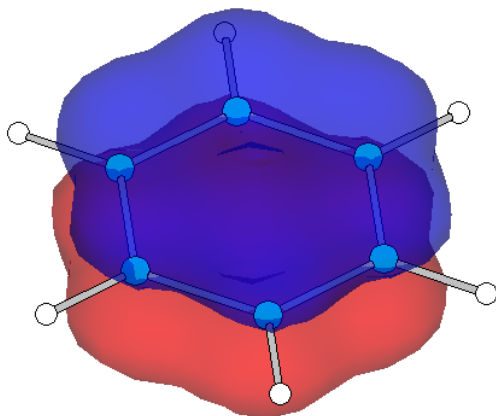
CHEMISTRY 2000

Topic #1: Bonding – What Holds Atoms Together?

Fall 2020

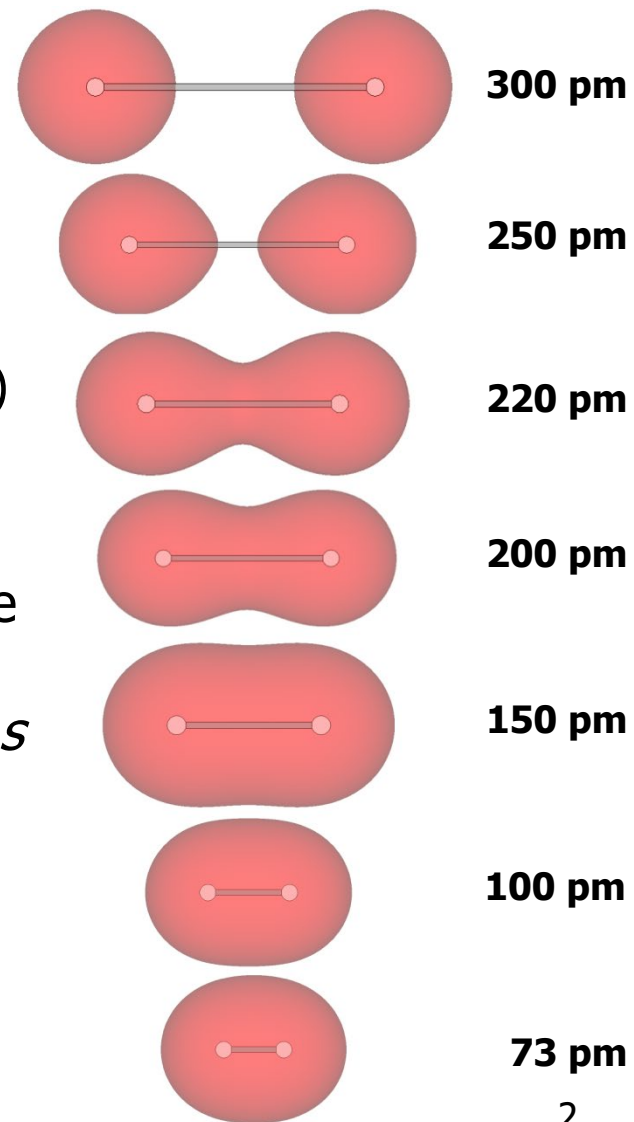
Dr. Susan Findlay

See Exercises 2.1, 2.2 and 2.4



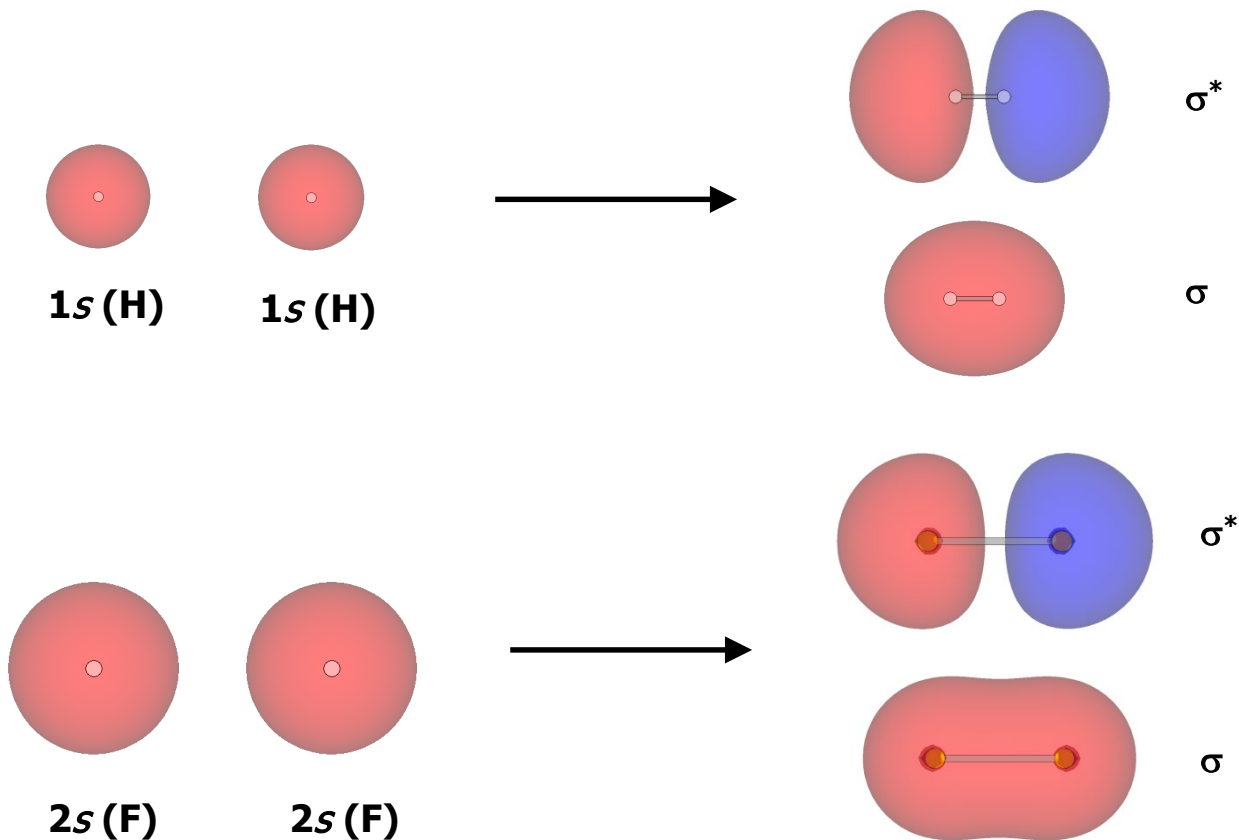
Molecular Orbitals of Homonuclear Diatomics

- Last class, we looked at the molecular orbitals obtained when two $1s$ orbitals are combined, as in H_2 . As the two hydrogen atoms approach, we can see that the orbitals change from looking like two separate $1s$ orbitals (one per H) to looking like a σ molecular orbital:
- The picture for the “development” of the antibonding σ^* molecular orbital is similar except that, instead of the two $1s$ orbitals appearing to “reach in toward” each other, they appear to “push away from” each other.



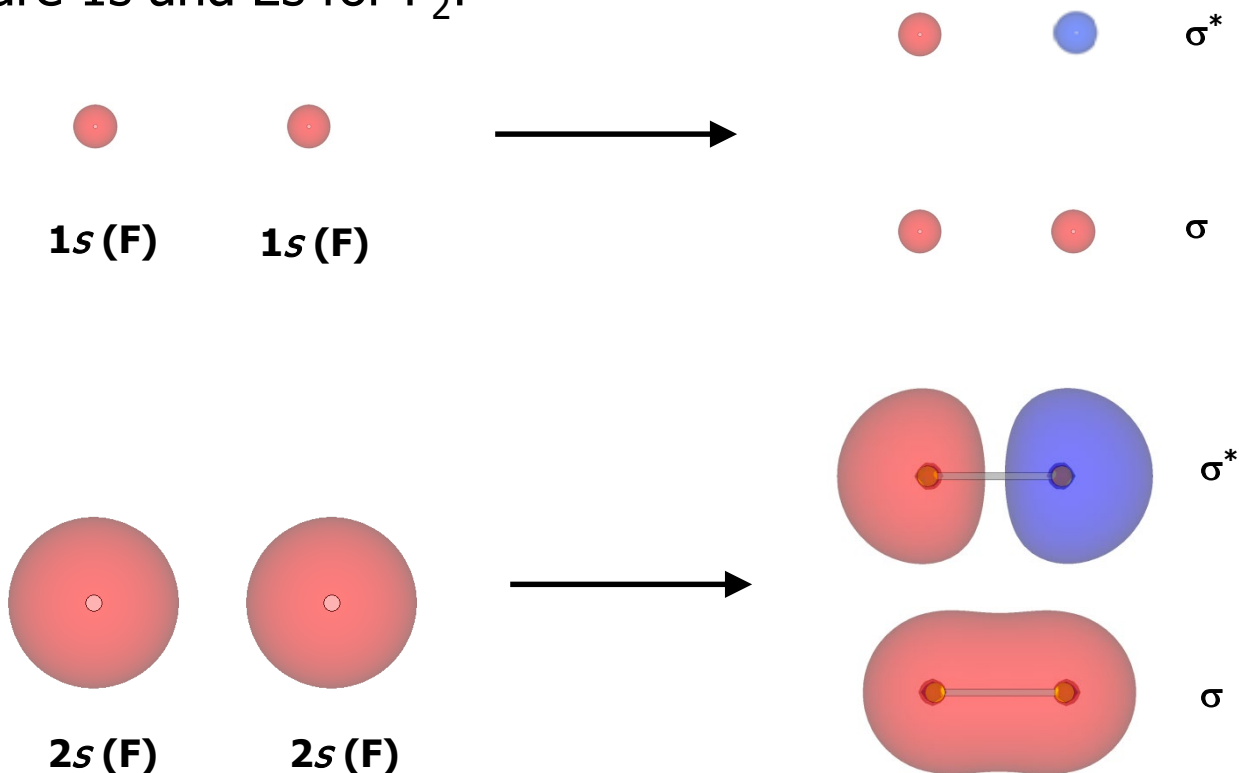
Molecular Orbitals of Homonuclear Diatomics

- We can combine higher energy atomic orbitals in the same way. Compare the σ and σ^* orbitals made from the 2s orbitals in F_2 to the σ and σ^* orbitals made from the 1s orbitals in H_2 :



Molecular Orbitals of Homonuclear Diatomics

- Note that as the distance between nuclei increases, the overlap between the 1s orbitals decreases. That's why we can't just compare 1s and 2s for F_2 !



- This is also why, for the most part, we focus on **valence** molecular orbitals. The core MOs look just like core AOs.



Molecular Orbitals of Homonuclear Diatomics

- p orbitals can also be combined to make molecular orbitals. The type of molecular orbital formed will depend on the orientation of the p orbitals.
- p orbitals that overlap head-on (usually defined as the p_z orbitals) give σ molecular orbitals:

Recall: σ orbitals have electron density along the axis connecting the nuclei



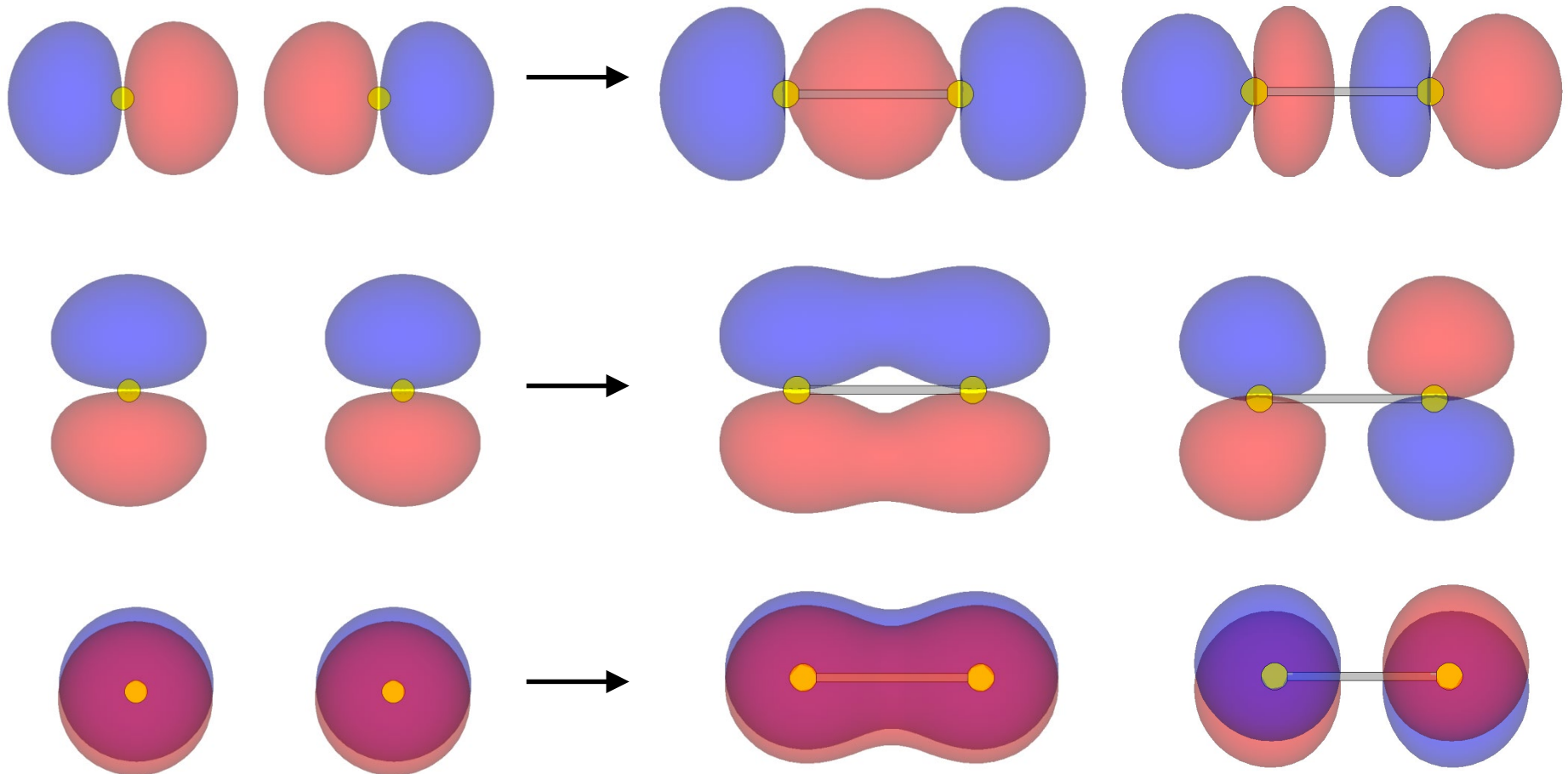
Molecular Orbitals of Homonuclear Diatomics

- p orbitals that overlap side-on (usually defined as the p_x or p_y orbitals) give π molecular orbitals:

π orbitals have a node along the axis connecting the nuclei

Molecular Orbitals of Homonuclear Diatomics

- ...and here are the pretty computer-generated pictures of those orbitals:





General Rules for LCAO-MOs

- Linear Combination of Atomic Orbitals (LCAO) can only be used to generate molecular orbitals when the atomic orbitals have compatible symmetry.
e.g. Combination of an s orbital and a p orbital

allowed

disallowed

- When atomic orbitals are added in phase (constructive interference), a bonding orbital is made. When added out of phase (destructive interference), an antibonding orbital is made.

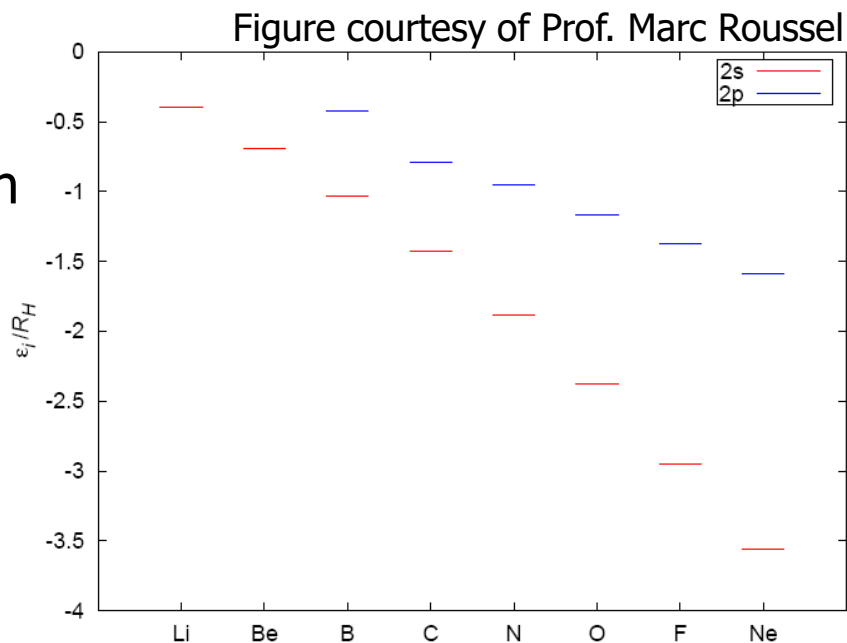
bonding

antibonding

THE NUMBER OF MOLECULAR ORBITALS IS **ALWAYS** EQUAL TO THE NUMBER OF ATOMIC ORBITALS USED TO MAKE THEM!!!

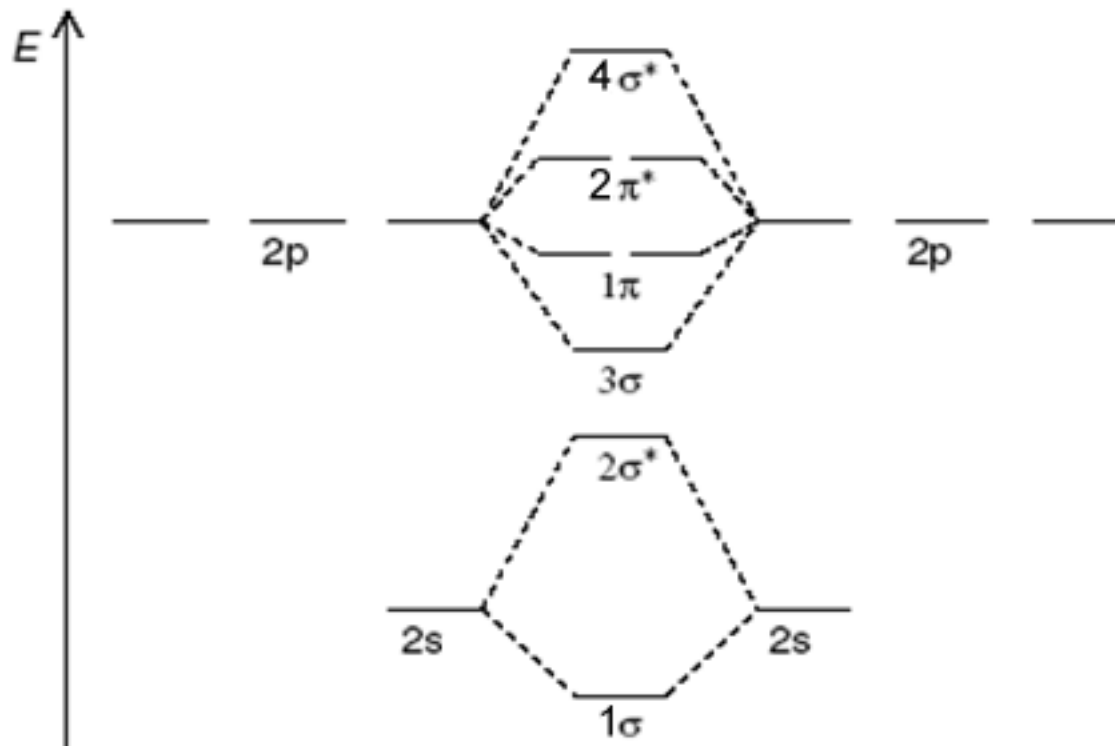
Molecular Orbitals of Homonuclear Diatomics

- Which p orbital combines with which other p orbital is symmetry-determined. Since orthogonal orbitals on different atoms don't combine, you won't see combination of a p_x orbital on one atom and a p_y orbital on its neighbour, for example.
- s orbitals *can* combine with p orbitals when making σ MOs *if* the orbitals are close enough in energy (within $1 \text{ Ry} = 2.179 \times 10^{-18} \text{ J} = R_H$).
- The figure at the right shows $2s$ and $2p$ atomic orbital energies for the elements in period 2. We can see that there will be little mixing between $2s$ and $2p$ orbitals for the heavier elements in period 2.



Molecular Orbitals of Homonuclear Diatomics

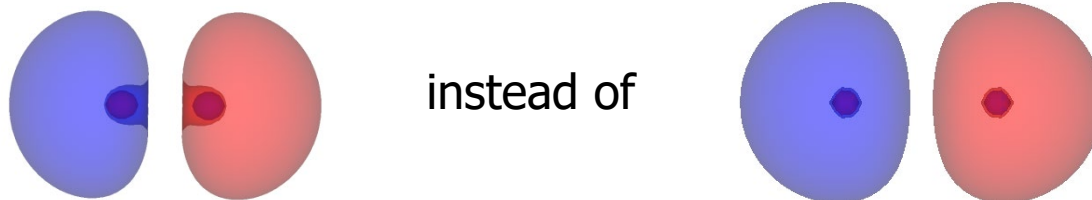
- O, F and Ne have large enough energy gaps between their $2s$ and $2p$ orbitals that they give the "normal" MO diagram:



Molecular Orbitals of Homonuclear Diatomics

- Because Li, Be, B, C and N have smaller energy gaps between their $2s$ and $2p$ orbitals, some mixing is observed when forming the σ and σ^* orbitals, primarily $2\sigma^*$ and 3σ :

- Mixing in some " p character" lowers the energy of the $2\sigma^*$ MO

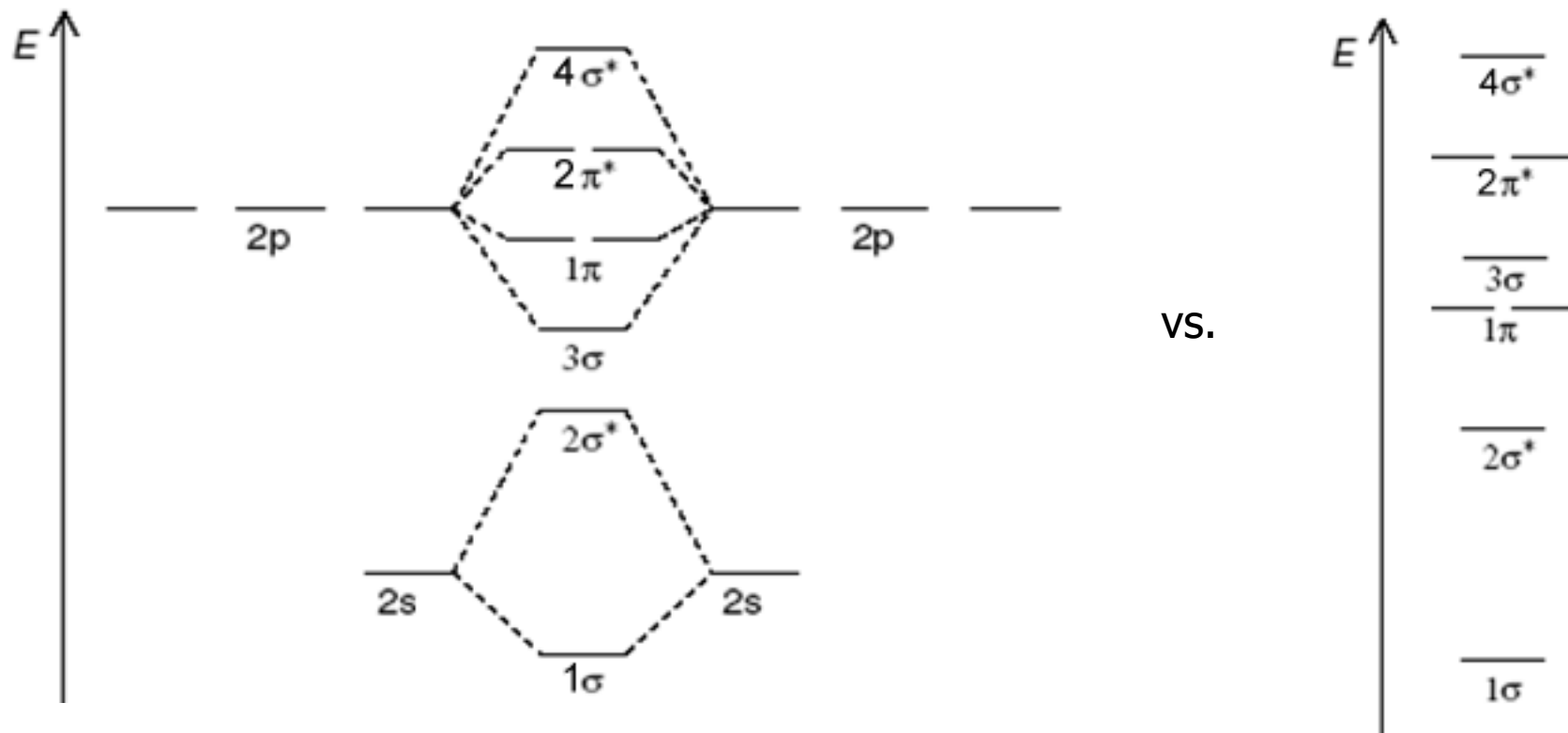


- Mixing in some " s character" raises the energy of the 3σ MO



- If this effect is strong enough, the 3σ orbital can end up higher in energy than the 1π orbital, giving the MO diagram on the next page. This is the case in Li_2 , Be_2 , B_2 , C_2 and N_2 .

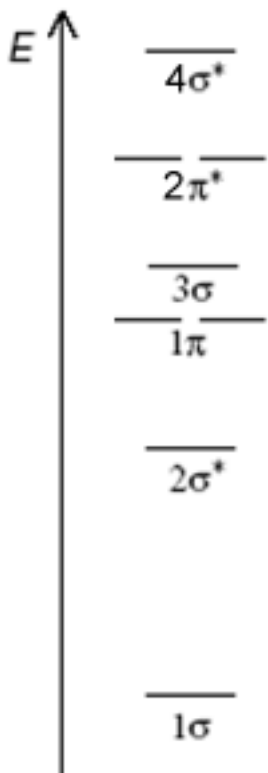
Molecular Orbitals of Homonuclear Diatomics



Molecular Orbitals of Homonuclear Diatomics

- Just as we could use MO diagrams to calculate bond order for H_2 and He_2 (thereby demonstrating why He_2 doesn't form), we can use these new MO diagrams to predict properties of the period 2 diatomics.

e.g. Predict the bond order for Li_2 .



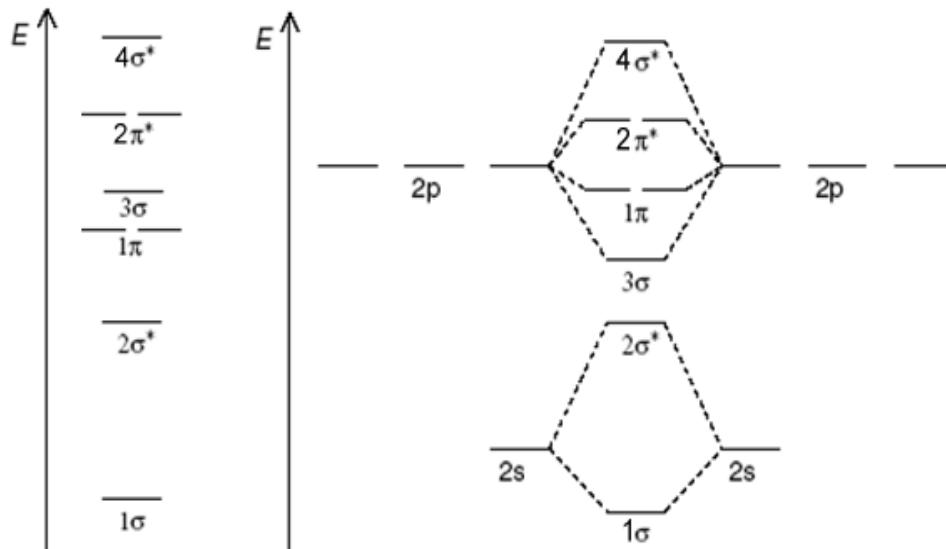
Is Li_2 diamagnetic or paramagnetic?

Do these answers agree with a Lewis diagram for Li_2 ?

Molecular Orbitals of Homonuclear Diatomics

- Determine the bond order for each of the remaining period 2 homonuclear diatomics.

- Be₂
- B₂
- C₂
- N₂
- O₂
- F₂
- Ne₂



- Do any of these bond orders disagree with what you'd expect based on the Lewis structures?
- Which of the period 2 homonuclear diatomics are paramagnetic? What does that tell us about those molecules?