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Molecular orbitals of Li_2 , Be_2 , ... to F_2

Skills to develop

- Explain how the energy levels of atomic orbitals vary for H, Li, Be, B, C, N, and O.
- Draw relative energy levels diagrams for homonuclear diatomic molecules of period 2 elements.
- Explain why the relative energy levels diagrams for Li_2 , Be_2 , B_2 , C_2 , N_2 are different from those of O_2 and F_2 .
- Point out relevant data to support the energy level diagrams of diatomic molecules of period 2 elements.

Underconstruction - Red Alert:

This page is made up on Dec. 5, 1999, yet to be proof read....

The molecular orbital theory of Li_2 to F_2 gives a graphical explanation. The following is more verbal.

Molecular orbitals of Li_2 , Be_2 , ... to F_2

The molecular orbital theory (MO) has been introduced for the diatomic hydrogen molecules. The same method can be applied to for other diatomic molecules, but involving more than the 1s atomic orbitals. For the second period elements, the 2s and 2p orbitals are important for MO considerations.

A linear combination of properly oriented atomic orbitals for the formation of sigma σ and pi π bonds. The formation of bonds from the linear combination of atomic orbitals is the same as that of the valence bond theory. For simplicity, we are not going into the details of the theory, but simply show you how to construct the MO energy level diagram.

Relative energy levels of atomic orbitals from hydrogen to fluorine

In the discussion of electronic configurations of many-electron atoms, the variation of energy levels of the atomic orbitals was given. The all corresponding levels become more negative as the atomic number increases. The energy levels E_{2s} and E_{2p} of the second period is given in the table on the right.

The energy level E_{2s} range from -521 to -4680 kJ mol^{-1} for these elements. The E_{2p} energy levels also become more negative, but the decrease (because they are negative) is not as rapid as that of the E_{2s} levels. Thus, the differences $E_{2p} - E_{2s}$ increase as the atomic numbers increase.

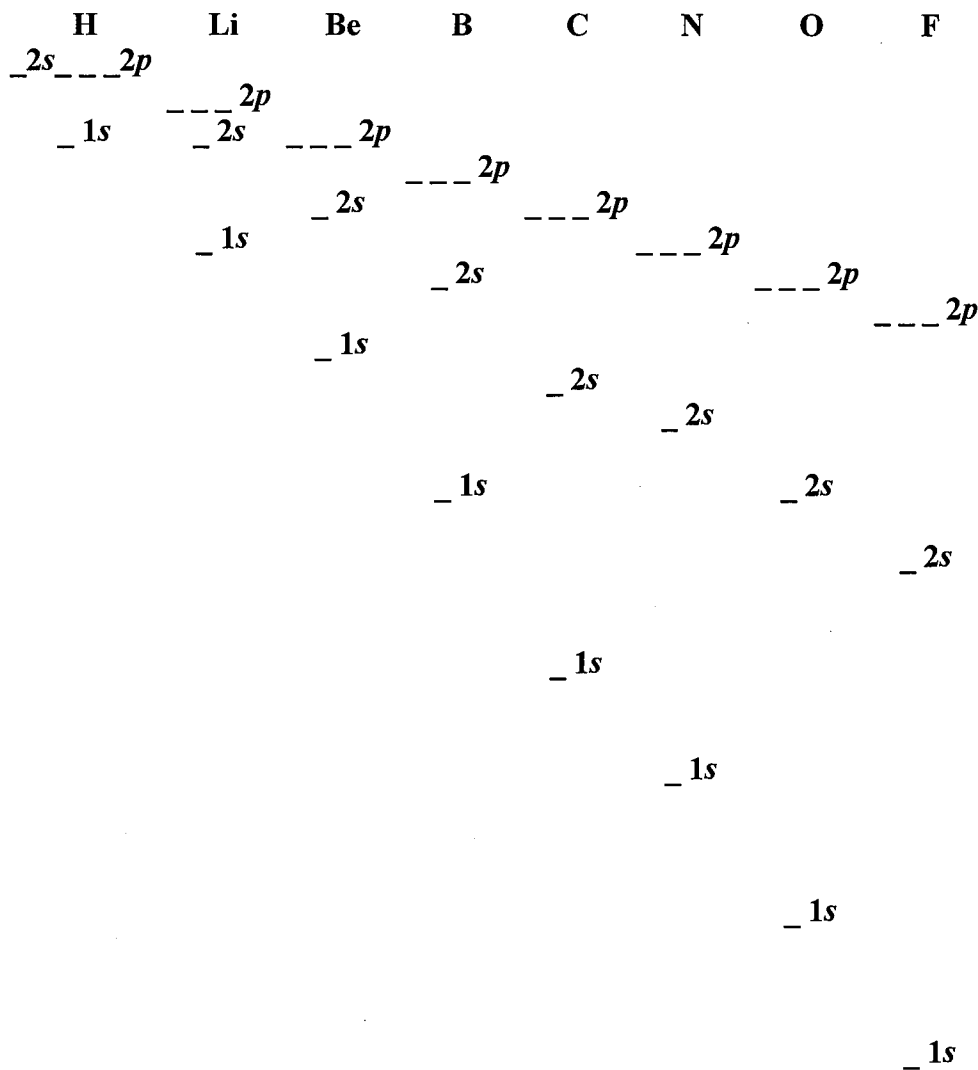
Atomic energy levels E in kJ mol^{-1}
of second group elements

Element	E_{2s}	E_{2p}	$E_{2p} - E_{2s}$
Li	-521		
Be	-897		
B	-1350	-801	549
C	-1871	-1022	849
N	-2470	-1274	1196
O	-3116	-1524	1592
F	-3879	-1795	2084

A qualitative diagram showing the changes of energy levels of atomic orbitals is given below:

Ne -4680 -2084 2596

Variation of energy levels for atomic orbitals of some elements

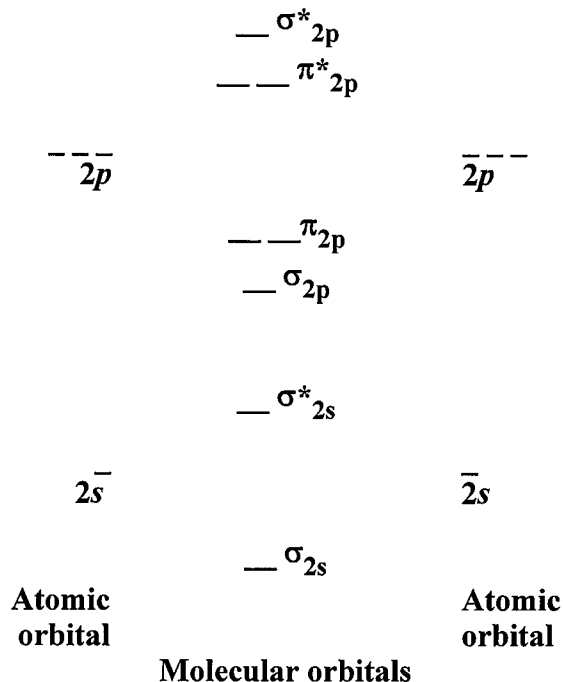


Relative energy levels of molecular orbitals of O_2 and F_2 .

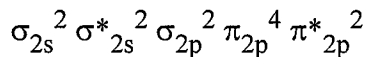
The $2s$ and $2p$ energy levels of O and F are very far apart. The combination of the $2s$ orbitals from the two atoms form a sigma bonding and sigma antibonding orbitals in a way very similar to the case of the hydrogen molecules, because the $2p$ orbitals have little to do with the $2s$ orbitals.

On the other hand, the three $2p$ orbitals of each O (or F) atom can form one sigma and two pi bonds and their corresponding antibonding molecular orbitals. The interaction of the $2p$ orbitals for the sigma bond is stronger, and the levels of sigma and anti sigma bonds are farther apart than those of pi and anti pi bonds. Thus, the relative energy level diagram of O_2 and F_2 has the following arrangement:

Relative energy levels of O_2 and F_2 molecules



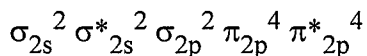
The electronic configuration for O_2 is:



This electronic configuration indicates a bond order of 2, and the bond can be represented by $O=O$. There is no net bonding from the σ_{2s} orbitals, because the number of bonding electrons equals the number of antibonding electrons. The two electrons in π_{2p}^2 cancel two of the 6 bonding electrons ($\sigma_{2p}^2 \pi_{2p}^4$). Therefore, there are 4 total bonding electrons. The two electrons in the π_{2p}^{*2} orbitals have the same spin, and they are responsible for the paramagnetism of oxygen.

As an exercise, *please fill electrons in the molecular orbitals of relative energy levels diagram to derive and confirm the above conclusion* as well as the conclusion regarding the F_2 molecule.

The electronic configuration for F_2 is:



This electronic configuration shows a single F-F bond in the molecule for the reasons given for the O_2 molecule. The bondlengths and bond energies of O_2 and F_2 shown on the right, correspond to $O=O$ and F-F respectively. The bond energy is higher for $O=O$ than for F-F due to the double $O=O$ bond, and its $O=O$ bondlength is shorter than that of F-F.

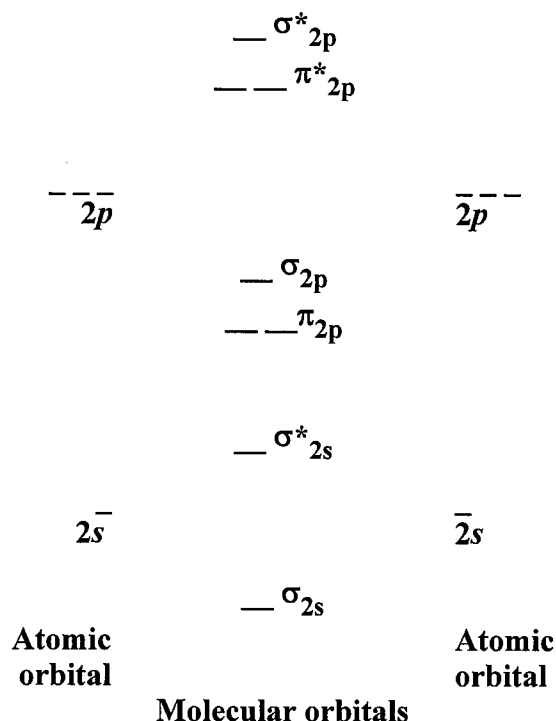
	Bondlength (pm) and bond energy (kJ mol^{-1}) of O_2 and F_2	
	Bondlength	Bond energy
O=O	121	494
F-F	142	155

Relative energy levels of molecular orbitals for Li_2 to N_2 .

Recently, the study of the energies of electrons in molecules revealed that the relative energy levels of molecular orbitals of Li_2 to N_2 are different from those of O_2 and F_2 . The explanation for the difference comes from the consideration of hybrid atomic orbitals. Because the $2s$ energy levels and $2p$ energy levels for Li to N are relatively close, the $2s$ orbitals are influenced by the $2p$ orbitals. This influence makes the bonding orbitals stronger than, and the antibonding orbitals weaker than those formed by pure $2s$ orbitals. This process is called ***sp* mixing**

Due to *sp* mixing, the σ_{2p} orbital is weakened, and the σ_{2p}^* is also affected. These effects cause the relative order to change, and a typical relative energy levels for Li_2 , Be_2 , B_2 , C_2 and N_2 to have the following diagram:

Relative energy levels of Li_2 to N_2 molecules



The electronic configurations agrees with the experimental bondlengths, and bond energies of homonuclear diatomic molecules of second-period elements. They are given in a table below. The argument regarding bondlengths, bond orders, and bond energies given for O_2 and F_2 above applies to all these molecules. Note also that B_2 and O_2 are paramagnetic due to the unpaired electrons in the molecular orbitals. Other molecules in this group are diamagnetic.

Electronic configuration, bondlength (pm) and bond energy (kJ mol^{-1}) of Li_2 to F_2

	Electronic configuration	Bondlength	Bond energy
Li-Li	σ_{2s}^2	267	110
Be..Be	$\sigma_{2s}^2 \sigma_{2s}^{*2}$	exist?	exist?
B-B	$\sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^2$	159	290
C=C	$\sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4$	124	602
N≡N	$\sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4 \sigma_{2p}^2$	110	942
O=O	$\sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^4 \pi_{2p}^{*2}$	121	494
F-F	$\sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^4 \pi_{2p}^{*4}$	142	155

The molecular orbital theory of Li_2 to F_2 has given a diagramatic explanation of $s p$ mixing leading to the difference in relative orbital energy levels. This link is from the University of Florida.

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