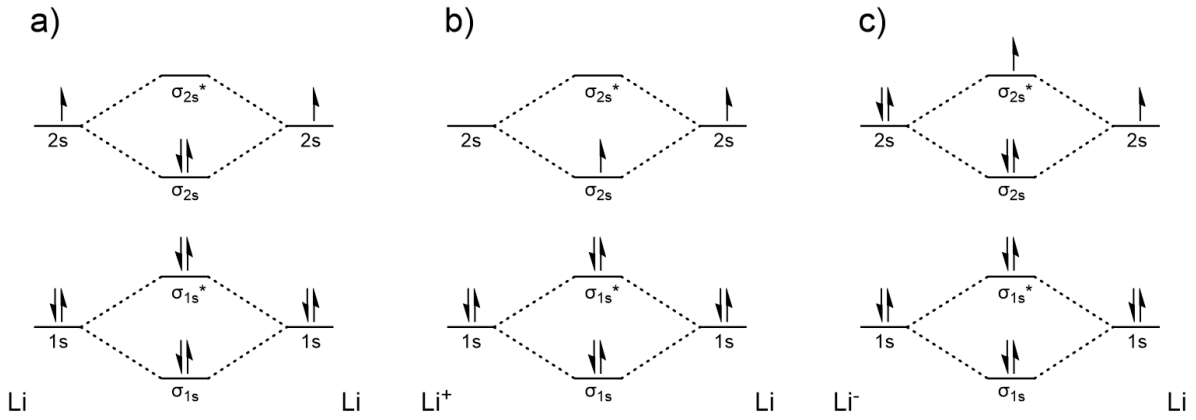
Exercises 9

Exercise 9.1

Draw a molecular orbital energy-level diagram and evaluate the bond order expected for each of the following diatomic species: a) Li_2 , b) Li_2^+ , c) Li_2^-

State whether each molecule or ion will be paramagnetic or diamagnetic. If it is paramagnetic, give the number of unpaired electrons.

The molecular orbital diagrams are as follows (only the valence electrons are shown):



Every electron in the bonding MOs contribute positively to the bond, and every electron in the antibonding(*) MOs contribute negatively to the bond. We can calculate the bond orders as follows:

a) Li_2 BO = ½ (2) = 1 ; diamagnetic, no unpaired electrons

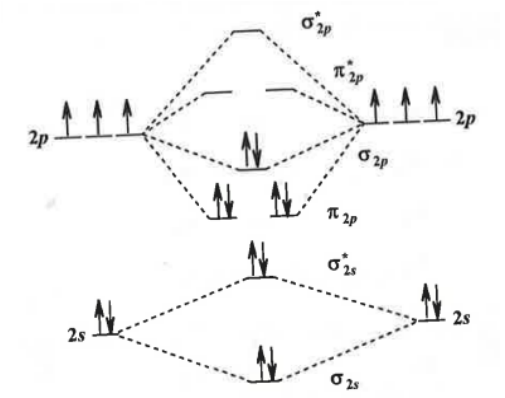
b) Li_2^+ BO = ½ (1) = 0.5 ; paramagnetic, one unpaired electron

c) Li_2^- BO = ½ (2-1) = 0.5 ; paramagnetic, one unpaired electron

Exercise 9.2

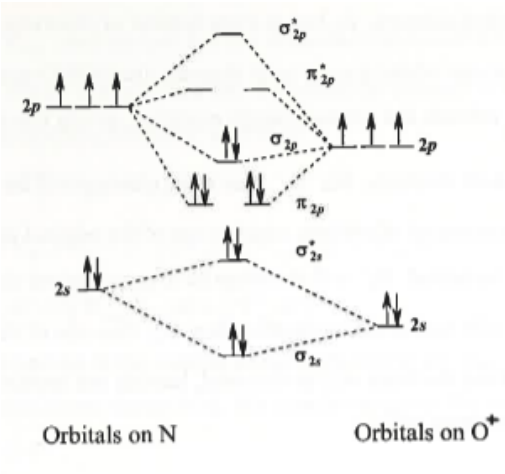
a) Draw the molecular orbital energy-level diagram for N_2 and label the energy levels according to the type of orbitals from which they are made, whether they are σ- or π-orbitals, and whether they are bonding or antibonding.

The energy level diagram for N_2 is as follows:



b) The orbital structure of the heteronuclear diatomic ion NO^+ is similar to that of N_2. How will the fact that the electronegativity of N differs from that of O affect the molecular orbital energy-level diagram of NO^+ compared with that of N_2? Use this information to draw the energy-level diagram for NO^+.

As we have seen in the first part of the question, because the orbitals of homonuclear (consisting of one type of atom) molecules all have the same energy, the molecular orbitals are symmetrical. It is clearly not the case here, as the orbitals of more electronegative oxygen have less energy than their nitrogen counterparts. This will make all of the bonding orbitals closer to oxygen than to nitrogen in energy and will make all the antibonding orbitals closer to nitrogen than to oxygen in energy. This is the reason for the unsymmetrical distribution of the molecular orbitals seen below:



c) In the highest occupied molecular orbital, will the electrons have a higher probability of being at N or at O? Why?

The electrons in the bonding orbitals will have a higher probability of being at O because O is more electronegative and its orbitals are lower in energy.

Exercise 9.3

Write the valence-shell electron configurations and bond orders of a) O_2^{2-} , b) N_2^- , c) C_2^-

O_2^{2-} : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi_{2p}^*)^4$ BO = ½ (8-6) = 1

N_2^- : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^2 (\pi_{2p}^*)^1$ BO = ½ (8-3) = 2.5

C_2^- : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^1$ BO = ½ (7-2) = 2.5

We have to keep in mind that the MO order for Z≤7 is (π_{2p}) (σ_{2p}) and for Z>7 it is (σ_{2p}) (π_{2p}). (As a general rule, if a molecule has one Z≤7 atom, the order is (π_{2p}) (σ_{2p}), no matter the second atom.)

Exercise 9.4

Give the valence-shell electron configurations and bond orders for NO and NO^+. Use that information to predict which species has stronger bonds.

NO : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^2 (\pi_{2p}^*)^1$ BO = ½ (8-3) = 2.5
NO^+ : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^2$ BO = ½ (8-2) = 3

Because bond strength is directly proportional to the bond order, $NO^+ > NO$

Exercise 9.5

Calculate the bond orders and use them to predict which species of each of the following pairs has the stronger bond: a) C_2 or C_2^- , B) N_2 or N_2^-

C_2^- : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^1$ BO = ½ (7-2) = 2.5
C_2 : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4$ BO = ½ (6-2) = 2

$C_2^- > C_2$

N_2^- : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^2 (\pi_{2p}^*)^1$ BO = ½ (8-3) = 2.5
N_2 : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^2$ BO = ½ (8-2) = 3

$N_2 > N_2^-$

Exercise 9.6

Based on their valence-shell electron configurations, which of the following species would you expect to have the least electron affinity: a) Be_2 , b) F_2 , c) B_2^+ , d) C_2^+

Electron affinity is essentially how willing a species is to get an electron. An addition to a bonding MO increases the bond order, which directly translates to a stronger bond and an increase in the stability. The opposite is true for an addition to an antibonding MO, every addition decreases the bond order by 0.5 and reduces the stability.

Electron affinity is higher when the bond order increases, as transition to a more stable state is favourable.

Bond orders before the addition of an electron:

Be_2 : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2$ BO = ½ (2-2) = 0
F_2 : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi_{2p}^*)^4$ BO = ½ (8-6) = 1
B_2^+ : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^1$ BO = ½ (3-2) = 0.5
C_2^+ : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^3$ BO = ½ (5-2) = 1.5

Bond orders after the addition of an electron:

Be_2^- : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^1$ BO = ½ (3-2) = 0.5

F_2^- : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi_{2p}^*)^4 (\sigma_{2p}^*)^1$ BO = ½ (8-7) = 0.5

B_2 : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^2$ BO = ½ (4-2) = 1

C_2 : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4$ BO = ½ (6-2) = 2

We can see that apart from F_2, every molecule increases their bond order. We can thus conclude that F_2 has the least electron affinity.