ENERGY LEVELS FOR HOMONUCLEAR DIATOMIC MOLECULES

What do I have to know?

You will be responsible for being able to write or identify ground and excited state configurations for homonuclear diatomic molecules and their ions and be able to:

I. ***Determine whether the molecule is paramagnetic or diamagnetic***
II. ***Calculate the bond order***
III. ***From the bond order determine their relative bond length and bond strength***

To do this you will need to remember the energy ordering schemes for diatomic molecules.

For the lighter (B_2, C_2, N_2) and heavier (O_2, F_2, Ne_2) there are two different energy orderings for the molecular orbitals arising from the bonding (constructive interference) and antibonding (destructive interference) combinations of 2p atomic orbitals:

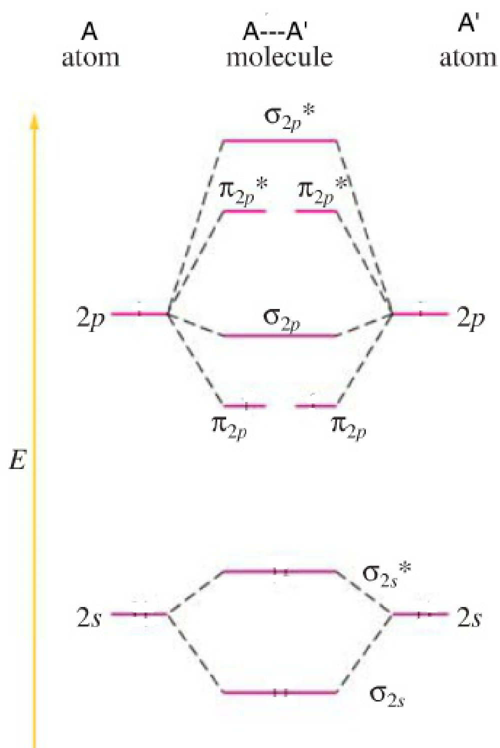


FIGURE 14.40 ***(with 2s-2p mixing)***

Applies to B_2, C_2, N_2

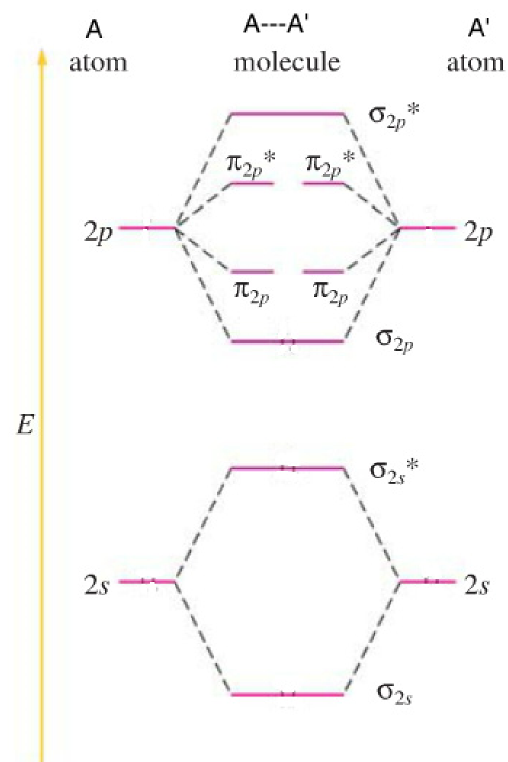


FIGURE 14.38 ***('simple')***

The *expected* MO energy-level diagram

Applies to O_2, F_2, Ne_2

Remember the two principles that determine whether a.o.'s on two atoms will interact to form bonding and antibonding m.o.'s:

A. The a.o.'s must have similar energies

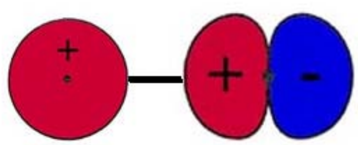
B. The two a.o.'s must 'overlap' and interact to have net constructive and destructive interference. The degree of stabilization by constructive interference (and destabilization by destructive) is determined by the extent of this interaction.

We can ask the following relevant questions:

1. **Why are there a pair of degenerate levels for each of the π_{2p} and π_{2p}* m.o.'s?**
   the two side-on interactions $(2p_y)_A \Leftrightarrow (2p_y)_{A'}$ and $(2p_z)_A \Leftrightarrow (2p_z)_{A'}$ are equivalent with the only difference being their directions in space; constructive interference leads to two π_{2p} m.o.'s of equal (lower) energy and destructive interference leads to two π_{2p}* of equal (higher) energy.

2. **Why in the "expected" is the energy of the σ_{2p} is lower than that of the π_{2p} in the 'simple' energy level scheme (Fig 14.38)?**
   the end-on interactions of the $(2p_x)_A \Leftrightarrow (2p_x)_{A'}$ are stronger than the side-on interactions of $(2p_y)_A \Leftrightarrow (2p_y)_{A'}$ or $(2p_z)_A \Leftrightarrow (2p_z)_{A'}$ **(principle B).**

3. **What is meaning of 2s-2p mixing and why is it more important for B_2, C_2, N_2 than for O_2, F_2, Ne_2?**
   A 2s orbital on atom A will have net interference ('overlap') with a $2p_x$ on atom A'.



2s on A ***2px on A'***

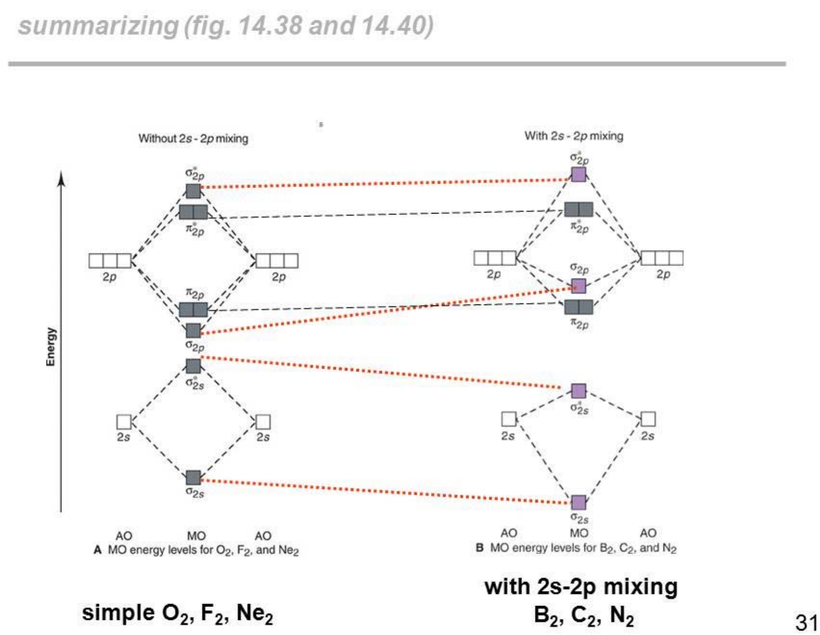
yes for 2s-$2p_x$ we can have net constructive or destructive interference

and thus they could contribute to the same m.o. **(principle B)** ***if they had similar energies*** **(principle A).**

In O_2, F_2, Ne_2 the larger Z (nuclear charge) makes the energy of the 2s atomic orbital much lower than the 2p atomic orbital and thus the 2s and 2p on A and A' DO NOT mix when forming m.o.'s (simple scheme no 2s-2p mixing).

However in B_2, C_2, N_2 the energies of the 2s and 2p atomic orbitals are much closer and thus the σ_{2s} and σ_{2s}* m.o.'s contain some contribution from $2p_x$ a.o.s and the σ_{2p} and σ_{2p}* m.o.'s contain some contribution from 2s a.o.'s.; i.e. THERE IS 2s-2p mixing for B_2, C_2, N_2

4. ***What is the effect of 2s-2p mixing on the energy level diagram?***
The $2p_x$ provides bonding (constructive) interactions in the σ_{2s} and σ_{2s} m.o.'s LOWERING their energies.*
The 2s participates in the σ_{2p} and σ_{2p} m.o.'s with antibonding (destructive) interactions and thus RAISES the energies of the σ_{2p} and σ_{2p}* m.o.'s.*
The energies of the π_{2p} and π_{2p} m.o.'s are unaffected since there is no 2s mixing with the $2p_y$ or $2p_z$.*
The result TO REMEMBER is that <u>for B_2, C_2, N_2 the π_{2p} has a lower energy than the σ_{2p}.</u>



5. **How can one experimentally verify that the 2s-2p scheme mixing applies to B_2 and C_2?**
One can ask "what would be the predictions for the ground state electronic configurations of B_2 and C_2 in the two energy level schemes"?

B_2: simple: $(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2$ ⟹ DIAMAGNETIC
2s-2p mixing: $(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^2$ ↑ ↑ ⟹ PARAMAGNETIC ☑
and B_2 is observed to be PARAMAGNETIC !!

C_2: simple: $(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^2$ ↑ ↑ ⟹ PARAMAGNETIC
2s-2p mixing: $(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4$ ↑↓ ↑↓ ⟹ DIAMAGNETIC ☑
and C_2 is observed to be DIAMAGNETIC !!

6. **How can one experimentally verify that the simple scheme applies to O_2 and F_2?**
The configurations for these molecules are the same for the two schemes (except for reversal of the inner σ_{2p} and π_{2p} levels) and thus would not predict differing numbers of unpaired electrons. Experimental verification requires analysis of the electronic excitation spectra of these molecules. THE ENERGY LEVELS DO CORRESPND TO THE SIMPLE SCHEME!!