

Exercise 2.4

Molecular Orbital Energy Level Diagrams: Homonuclear Diatomics

This exercise assumes that you are familiar with the “count and sort” algorithm described in Exercise 2.3. The table of atomic orbital energies is repeated below for easy reference.

Table of Atomic Orbital Energies. All Energies are in Ry.

	1s	2s	2p
H	-1.00		
He	-1.81		
Li	-4.77	-0.40	
Be	-8.9	-0.69	
B	-14.5	-1.03	-0.42
C	-21.6	-1.43	-0.79
N	-30.0	-1.88	-0.95
O	-39.9	-2.38	-1.17
F	-51.2	-2.95	-1.37
Ne	-64.0	-3.56	-1.59

All energies are from J.C. Slater Physical Review (1955) **98**, 1039-1045.

Molecular Orbital Energy Level Diagrams for O_2 , F_2 , and Ne_2

In oxygen, fluorine and neon atoms, the difference between the energies of the 2s and 2p orbitals is greater than 1 Ry. As such, we can assume that there is no significant interaction between the 2s and 2p orbitals. Thus, when we group the atomic orbitals (AOs) by symmetry and energy, there are four distinct groups:

- two pi-symmetric $2p_x$ orbitals, one from each atom,
- two pi-symmetric $2p_y$ orbitals, one from each atom,
- two sigma-symmetric 2s orbitals, one from each atom, and
- two sigma-symmetric $2p_z$ orbitals, one from each atom.

Each group makes two molecular orbitals (MOs) of the appropriate symmetry.

Molecular Orbital Energy Level Diagrams for B_2 , C_2 , and N_2

In boron, carbon and nitrogen atoms, the difference between the energies of the 2s and 2p orbitals is less than 1 Ry. As such, there is significant interaction between the 2s and 2p orbitals. Thus, when we group the AOs by symmetry and energy, there are only three groups:

- two pi-symmetric $2p_x$ orbitals, one from each atom,
- two pi-symmetric $2p_y$ orbitals, one from each atom, and
- four sigma-symmetric orbitals, both 2s and $2p_z$ from each atom.

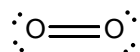
All four sigma-symmetric AOs (2s and $2p_z$ on both atoms) combine to make a set of four sigma-symmetric MOs. This lowers the energy of the 2σ orbital and raises the energy of the 3σ orbital (relative to where they would have been if the 2s and $2p_z$ orbitals did not interact). The most notable consequence of this interaction is that the energy of the 3σ orbital is raised enough that it becomes higher in energy than the 1π orbitals.

Molecular Orbital Energy Level Diagram for O_2

First, the electron configuration for each oxygen atom is written: $1s^2 2s^2 2p^4$

This tells us that the valence shell for each oxygen atom is $n = 2$, and that the valence AOs are the $2s$ and $2p$ orbitals. It also tells us that O_2 has twelve valence electrons.

A Lewis diagram for O_2 is shown below and, since there are only two atoms, it must be linear.



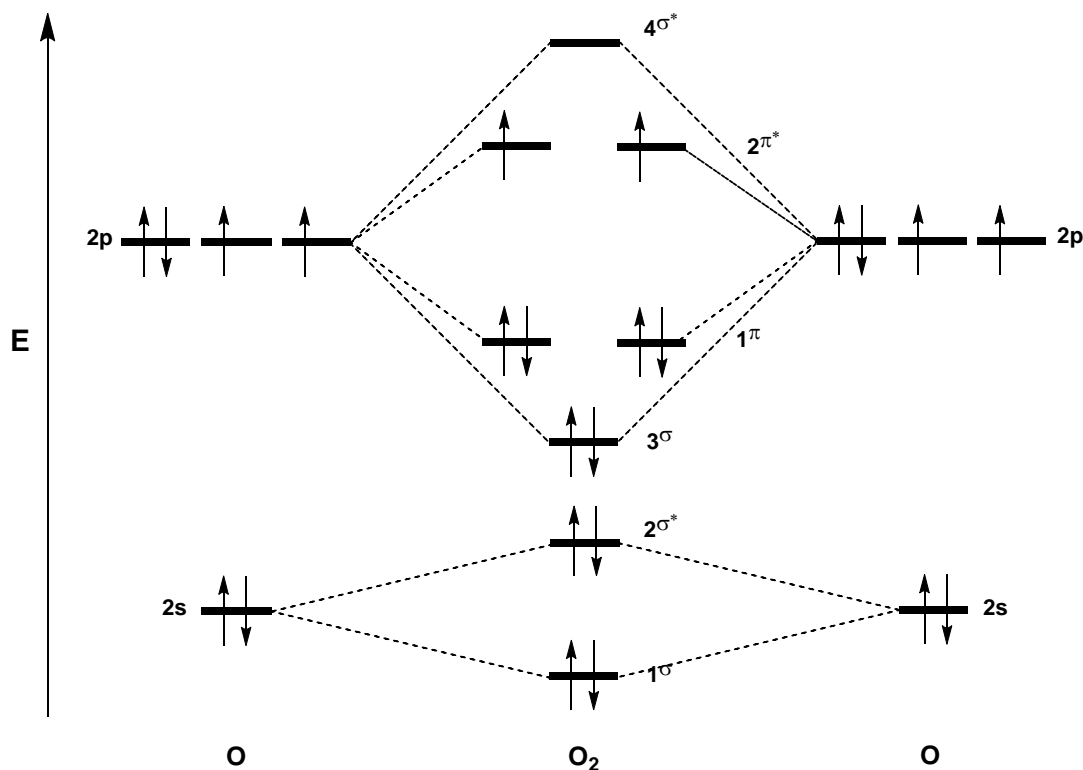
Grouping the AOs by symmetry and energy gives:

- two pi-symmetric $2p_x$ orbitals, one from each atom,
- two pi-symmetric $2p_y$ orbitals, one from each atom,
- two sigma-symmetric $2s$ orbitals, one from each atom, and
- two sigma-symmetric $2p_z$ orbitals, one from each atom.

Each group makes two MOs, one bonding and one antibonding.

- The bonding MO is lower in energy than the AOs from which it was made, and the antibonding MO is higher in energy than the AOs from which it was made.
- The MOs made from $2p$ orbitals are higher in energy than the MOs made from $2s$ orbitals.
- Because the electron density in 3σ is concentrated along the line between the nuclei, 3σ is lower in energy than the 1π MOs. For similar reasons, $4\sigma^*$ is higher in energy than $2\pi^*$.

Following the remaining steps of the algorithm gives this MO energy level diagram:



Bond order for O_2 can be calculated: $\frac{8-4}{2} = \frac{4}{2} = 2$ and is consistent with the double bond observed on the Lewis diagram. Where this diagram differs from the Lewis diagram is that it shows that O_2 has two unpaired electrons. This explains why O_2 behaves as a paramagnetic substance.

All reactions of O_2 are expected to involve the $2\pi^*$ MOs; they contain the highest energy electrons *and* the lowest unoccupied spaces for new electrons to be added. So, $2\pi^*$ is functioning as both HOMO and LUMO. Alternatively, it can be labeled SOMO (Singly Occupied Molecular Orbital).

Molecular Orbital Energy Level Diagram for N_2

First, the electron configuration for each nitrogen atom is written: $1s^2 2s^2 2p^3$

This tells us that the valence shell for each oxygen atom is $n = 2$, and that the valence AOs are the $2s$ and $2p$ orbitals. It also tells us that N_2 has ten valence electrons.

A Lewis diagram for N_2 is shown below and, since there are only two atoms, it must be linear.



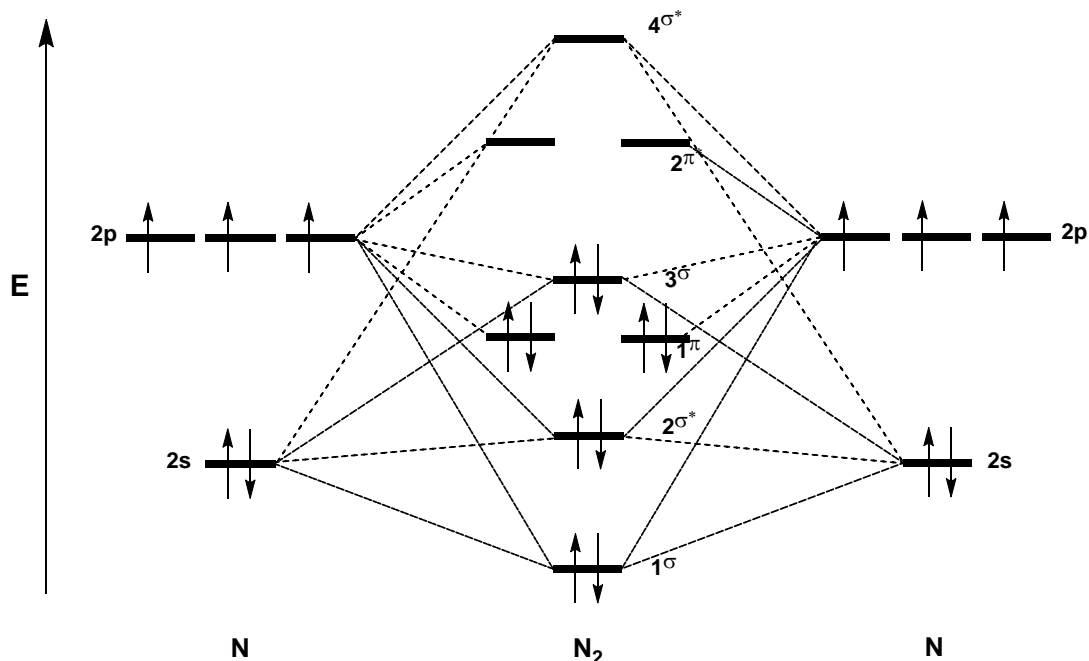
Grouping the AOs by symmetry and energy gives:

- two pi-symmetric $2p_x$ orbitals, one from each atom,
- two pi-symmetric $2p_y$ orbitals, one from each atom, and
- four sigma-symmetric orbitals, both $2s$ and $2p_z$ from each atom.

This first two groups each make two MOs, one bonding and one antibonding. There is no energy difference between the π_x and π_y orbitals.

The last group makes four MOs, two bonding and two antibonding. The lowest energy MO is lower in energy than all four AOs. The highest energy MO is higher in energy than all four AOs. As noted on the first page of this exercise, the 3σ orbital is higher in energy than the 1π orbitals.

Following the remaining steps of the algorithm gives this molecular orbital energy level diagram:



As you can see, the diagram is starting to look cluttered due to the large number of tie lines. As molecules get larger, this problem gets worse, so they're typically only used for small molecules.

Bond order for N_2 can be calculated: $\frac{8-2}{2} = \frac{6}{2} = 3$ and is consistent with the triple bond observed on the Lewis diagram.

The HOMO is 3σ , so those are the electrons donated in reactions where N_2 is an electron donor. The LUMO is $2\pi^*$, so that is where electrons will be added in reactions where N_2 is an electron acceptor. Since electrons would either be donated from a bonding orbital or added to an antibonding orbital, any reaction of N_2 will reduce the N-N bond order.

1. Add pictures of the atomic orbitals and molecular orbitals to the molecular orbital energy level diagrams of O_2 and N_2 provided in the preceding text.
2. Write valence orbital occupancies for O_2 and N_2 based on the molecular orbital energy level diagrams provided in the preceding text.
 - (a) O_2
 - (b) N_2
3.
 - (a) Construct a molecular orbital energy level diagram for F_2 .

- (b) How does the diagram change if two electrons are added? What does this tell you about what happens when two electrons are added to F_2 ?

4.

(a) Construct a molecular orbital energy level diagram for C_2 .

(b) How does the diagram change if two electrons are added? What does this tell you about what happens when two electrons are added to C_2 ?

5. In Cl_2 , there is **not** enough interaction between the 3s and 3p orbitals to raise the energy of the 3σ MO higher than that of the 1π MOs.

Knowing this, construct a molecular orbital energy level diagram for Cl_2 .

Draw pictures of each molecular orbital on or next to your diagram. It must be clear which picture corresponds to each labeled energy level.

How does this diagram compare to the diagram you drew for F_2 in question 2?