

9.5.1: The Predictive Power of MO Theory - The Case of Oxygen

Learning Objectives

- To describe the connection between bond order, bond length and bond energy in diatomic molecules
- To explain the observed paramagnetic properties of molecular oxygen with Molecular Orbital theory

In general chemistry courses, students learn that covalent bonds can come as either single, double or triple bonds, which are identified by their bond order. Both bond length and bond energy changes as the bond order increases and as the number of electrons shared between two atoms in a molecule increases, the bond order of a bond increases, the strength of the bond increases and the distance between nuclei decreases (Table 9.10.1).

Table 9.10.1 : General Correlation between Bond Strength, length and order in Covalent bonds

Bond	Bond Order	Bond Enthalpy (kJ/mol)	Bond Length (Å)
C–C	1	348	1.54
C=C	2	614	1.34
C≡C	3	839	1.20
N–N	1	163	1.47
N=N	2	418	1.24
N≡N	3	941	1.10

The above trend can be observed in the first row diatomics in Figure 9.10.1 . The bond order can be determined directly from the molecular orbital electron configurations. For diatomics, the occupations can correlate to bond length, bond energies (Figure 9.10.1).

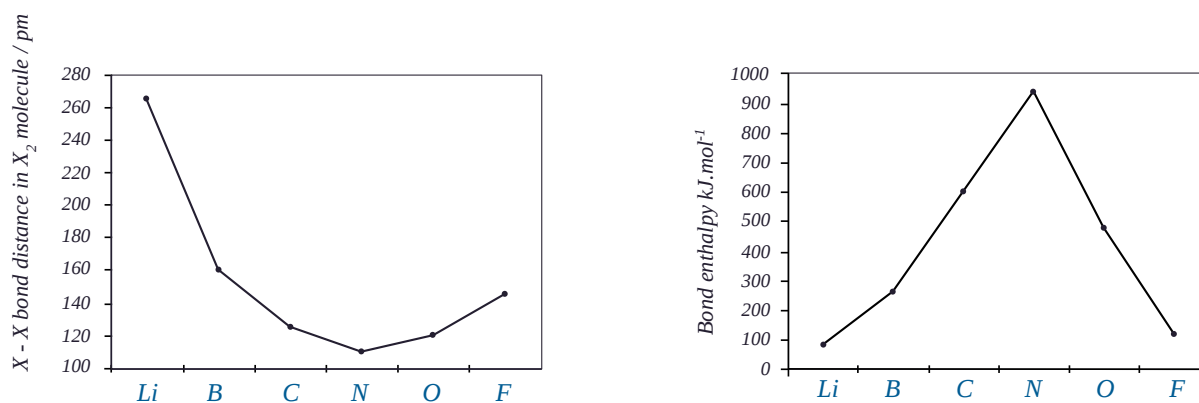


Figure 9.10.1 : Plot of bond length (left) and bond energy (right) for first row diatomics. (CC BY-NC; Ümit Kaya via LibreTexts)

The trends in Figure 9.10.1 and Table 9.10.1 extend to molecular ions.

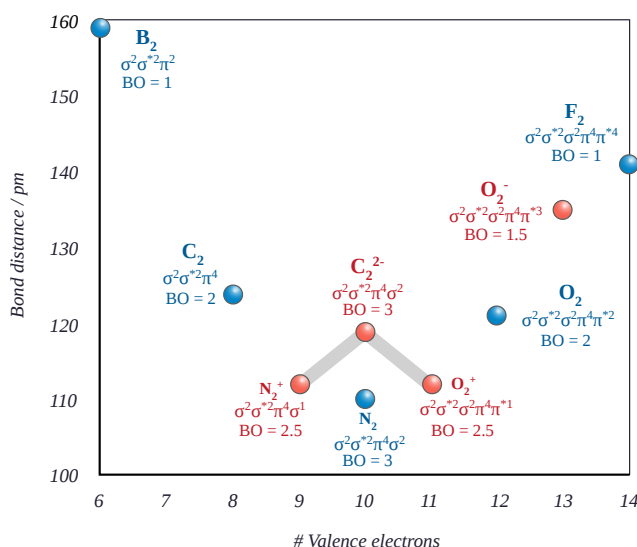


Figure 9.10.2 : Plot of bond length (left) and bond energy (right) for first row diatomics. (CC BY-NC; Ümit Kaya via LibreTexts)

✓ Example 9.10.1 : Molecular Oxygen

Arrange the following four molecular oxygen species in order of increasing bond length: O_2^+ , O_2 , O_2^- , and O_2^{2-} .

Solution

The bond length in the oxygen species can be explained by the positions of the electrons in molecular orbital theory. To obtain the molecular orbital energy-level diagram for O_2 , we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in Figure 9.10.1 . We again fill the orbitals according to Hund's rules and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and σ_{2s}^* orbitals, two more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate $\pi_{2p_x}^*$ and $\pi_{2p_y}^*$ orbitals. According to Hund's first rule, the last 2 electrons must be placed in separate π^* orbitals with their spins parallel, giving a multiplicity of 3 (a triplet state) with two unpaired electrons. This leads to a predicted bond order of

$$\frac{8 - 4}{2} = 2$$

which corresponds to a double bond, in agreement with experimental data: the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

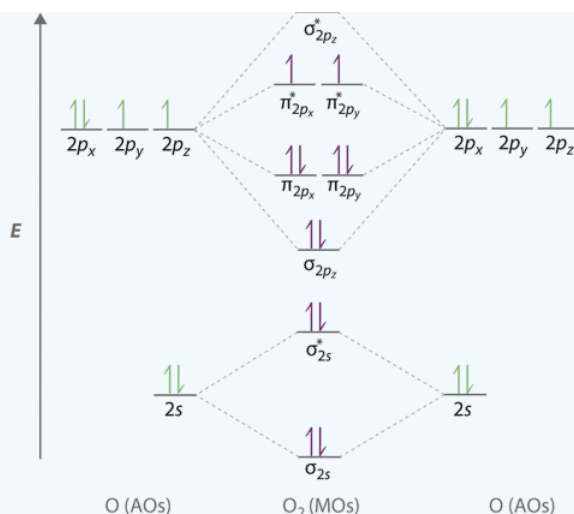


Figure 9.10.3 : Molecular Orbital Energy-Level Diagrams for O_2 . With 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $(\pi_{2p_x}^*, \pi_{2p_y}^*)$ pair of orbitals. Hund's first rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2. (CC BY-SA-NC; Anonymous by request).

The bond order is determined from the the electron configurations. The electron configurations for the four species are contrasted below.

- O_2 :

$$\sigma_{1s}^2 \sigma_{1s}^*{}^2 \sigma_{2s}^2 \sigma_{2s}^*{}^2 \sigma_{2p}^2 \pi_{2p_y}^2 \pi_{2p_x}^2 \pi_{2p_y}^*{}^1 \pi_{2p_x}^*{}^1$$

From Equation ???, the bond order for O_2 is 2 (i.e., a double bond).

- O_2^+ :

$$\sigma_{1s}^2 \sigma_{1s}^*{}^2 \sigma_{2s}^2 \sigma_{2s}^*{}^2 \sigma_{2p}^2 \pi_{2p_y}^2 \pi_{2p_x}^2 \pi_{2p_y}^*{}^0 \pi_{2p_x}^*{}^0$$

From Equation ???, the bond order for O_2^+ is 2.5. An alternative and equally valid configuration is

$$\sigma_{1s}^2 \sigma_{1s}^*{}^2 \sigma_{2s}^2 \sigma_{2s}^*{}^2 \sigma_{2p}^2 \pi_{2p_y}^2 \pi_{2p_x}^2 \pi_{2p_y}^*{}^0 \pi_{2p_x}^*{}^1$$

- O_2^- :

$$\sigma_{1s}^2 \sigma_{1s}^*{}^2 \sigma_{2s}^2 \sigma_{2s}^*{}^2 \sigma_{2p}^2 \pi_{2p_y}^2 \pi_{2p_x}^2 \pi_{2p_y}^*{}^2 \pi_{2p_x}^*{}^1$$

From Equation ???, the bond order for O_2^- is 1.5. An alternative and equally valid configuration is

$$\sigma_{1s}^2 \sigma_{1s}^*{}^2 \sigma_{2s}^2 \sigma_{2s}^*{}^2 \sigma_{2p}^2 \pi_{2p_y}^2 \pi_{2p_x}^2 \pi_{2p_y}^*{}^1 \pi_{2p_x}^*{}^2$$

- O_2^{2-} :

$$\sigma_{1s}^2 \sigma_{1s}^*{}^2 \sigma_{2s}^2 \sigma_{2s}^*{}^2 \sigma_{2p}^2 \pi_{2p_y}^2 \pi_{2p_x}^2 \pi_{2p_y}^*{}^2 \pi_{2p_x}^*{}^2$$

From Equation ???, the bond order for O_2^{2-} is 1.

The bond order decreases and the bond length increases in the order. The predicted order of increasing bondlength then is $O_2^+ < O_2 < O_2^- < O_2^{2-}$. This trend is confirmed experimentally with O_2^+ (112.2 pm), O_2 (121 pm), O_2^- (128 pm) and O_2^{2-} (149 pm).

9.5.1.1: Molecular Oxygen is Paramagnetic

We now turn to a molecular orbital description of the bonding in O_2 . It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. None of the other bonding models (e.g., Valence Bond theory or Lewis bonding) can predict the presence of two unpaired electrons in O_2 .

Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in Video 9.10.1, it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches.



Video 9.10.1 : Liquid O_2 Suspended between the Poles of a Magnet. Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates.

Advanced: Spin Barriers

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O , CO_2 , and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O , CO_2 , and N_2 , have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O , CO_2 , and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*.

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