9.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule

> 🧠 **Learning Objectives**
>
> - Using bond order as a metric for the existance of molecules

Bond Order

In the Lewis electron structures, the number of electron pairs holding two atoms together was called the *bond order*. Within the molecular orbital approach, *bond order* is defined as one-half the *net* number of bonding electrons:

$$\text{bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2} \tag{9.8.1}$$

To calculate the bond order of H_2, we know that the σ_{1s} (bonding) molecular orbital contains two electrons, while the $\sigma_{1s}^\star$ (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\text{bond order} = \frac{2-0}{2} = 1 \tag{9.8.2}$$

This result corresponds to the single covalent bond; double and triple bonds contain four or six electrons, respectively, and correspond to bond orders of 2 and 3.

We can use energy-level diagrams to describe the bonding in other pairs of atoms and ions where $n = 1$, such as the H_2^+ ion, the He_2^+ ion, and the He_2 molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund's Rules.
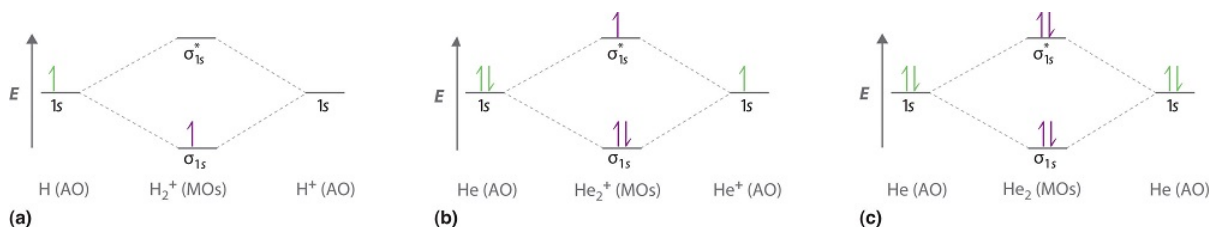

Figure 9.8.1 : Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1s Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here. (CC BY-SA-NC; anonymous)

Figure $9.8.1a$ shows the energy-level diagram for the H_2^+ ion, which contains two protons and only one electron. The single electron occupies the σ_{1s} bonding molecular orbital, giving a $(\sigma_{1s})^1$ electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is (via Equation 9.8.1)

$$\text{bond order} = \frac{1-0}{2} = 1/2$$

Because the bond order is greater than zero, the H_2^+ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and the calculated bond order to predict the relative stability of species such as H_2^+. With a bond order of only 1/2 the bond in H_2^+ should be weaker than in the H_2 molecule, and the H–H bond should be longer. As shown in Table 9.8.1 , these predictions agree with the experimental data.

Table 9.8.1 : Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

Species	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$	1/2	106	269
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2(\sigma_{1s}^\star)^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma_{1s}^\star)^2$	0	5,500	4.6×10^{-5}

Figure $9.8.1b$ is the molecular orbital energy-level diagram for He_2^{2+}. This ion has a total of three valence electrons. Because the first two electrons completely fill the σ_{1s} molecular orbital, the Pauli principle states that the third electron must be in the $\sigma_{1s}^{\star}$ antibonding orbital, giving a $(\sigma_{1s})^2(\sigma_{1s}^{\star})^1$ electron configuration. This electron configuration gives a bond order (via Equation 9.8.1) of

$$\text{bond order} = \frac{2-1}{2} = 1/2$$

As with H_2^+, the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2. In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (Table 9.8.1).

✔ Example 9.8.1 : The ion

Use a molecular orbital energy-level diagrams to predict the bond order and stability of the He_2^{2+} ion.

**Given:** chemical species

Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

  A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.
  B. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
  C. Calculate the bond order and predict whether the species is stable.

Solution:

A Two He $1s$ atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a $\sigma_{1s}^{\star}$ antibonding orbital at higher energy. The bonding in any diatomic molecule with two He atoms can be described using the following molecular orbital diagram:
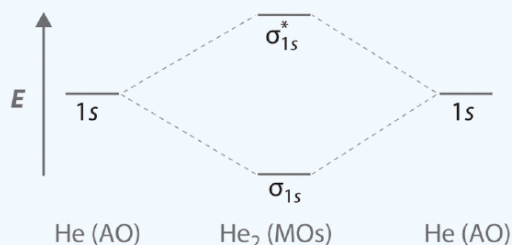
B The He_2^{2+} ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view He_2^{2+} as being formed from two He^+ ions, each of which has a single valence electron in the $1s$ atomic orbital. We can now fill the molecular orbital diagram:
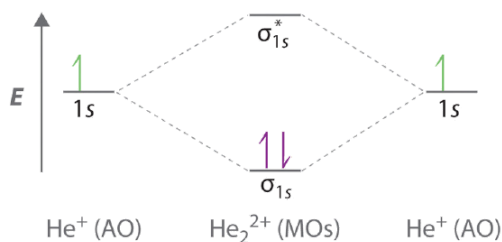
The two electrons occupy the lowest-energy molecular orbital, which is the bonding (σ_{1s}) orbital, giving a $(\sigma_{1s})^2$ electron configuration. To avoid violating the Pauli principle, the electron spins must be paired.

C So the bond order is (via Equation 9.8.1)

$$\frac{2-0}{2} = 1$$

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

❓ Exercise 9.8.1 : The Ion

Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the H_2^{2-} ion. Is this a stable species?

Answer

H_2^{2-} has a valence electron configuration of $(\sigma_{1s})^2 (\sigma_{1s}^\star)^2$ with a bond order of 0. It is therefore predicted to be unstable.

The Helium Dimer

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Figure 9.8.1c is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and $\sigma_{1s}^\star$ antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2 (\sigma_{1s}^\star)^1$ electron configuration, with a predicted bond order (via Equation 9.8.1) of

$$\text{bond order} = \frac{2-2}{2} = 0 \tag{9.8.3}$$

which indicates that the He_2 molecule has no net covalent bond and is not a stable species.

The ability to track bond order to bond strength is due to the fact that the energy difference between the anti-bonding $\sigma_{1s}^\star$ molecular orbital and the original $1s$ atomic orbital is *larger* than the energy difference between the bonding σ_{1s} molecular orbital and the $1s$ atomic orbitals. This was derived previously where the stabilization energy (ΔE_+) of the σ_{1s} molecular orbital is less than the destabilization energy (ΔE_-) of the anti-bonding $\sigma_{1s}^\star$ molecular orbital:

$$\Delta E_\pm = E_\pm - E_H \tag{9.8.4}$$

$$= \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \tag{9.8.5}$$

Hence, the anti-bonding $\sigma_{1s}^\star$ molecular orbital is more destabilized relative to the atomic orbitals than the bonding σ_{1s} molecular orbital is stabilized relative to the $1s$ atomic orbitals (E_H.

The fact that the anti-bonding MO energy difference is larger than the bonding σ_{1s} molecular orbital energy difference is the true reason that helium dimer is not predicted to exist with a covalent bond. Of the four valence electrons in helium dimer, two will fill the bonding σ_{1s} molecular orbital, and the other two will fill the anti-bonding $\sigma_{1s}^\star$ molecular orbital. The two electrons in the bonding σ_{1s} molecular orbital will achieve some stabilization relative to the $1s$ atomic orbitals, but the two electrons in the anti-bonding $\sigma_{1s}^\star$ molecular orbital will achieve *greater* de-stabilization relative to their position in the atomic orbitals. The net result is a less stable molecule than if the electrons remained in their respective $1s$ atomic orbitals.

> *The electrons in antibonding orbitals cancel (and exceed) the stabilization resulting from electrons in bonding orbitals. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature (at least as a covalently bonding complex).*

📌 However, Van der Waals Helium Dimers do exist

Based on molecular orbital theory discussed above, the He_2 molecule should not exist since no covalent bond formed between the helium atoms (Equation 9.8.3). However, the molecular orbital description above neglects the van der Waals force that exists between the atoms as demonstrated by the existence of liquid helium (at 4 K). So a "molecule" composed of two helium atoms bound by the van der Waals force may exist by this attractive force instead - and it does.

A helium dimer molecule bound by Van der Waals forces was first proposed by John Clarke Slater in 1928 and observed in 1993 by Gentry and coworkers. Interestingly, He_2 is the largest known molecule of two atoms when in its ground state with an extremely long bond length with a separation of about 5,200 pm. The binding energy is only $4.6 \times 10^{-5} \, kJ/mol$, so the $He-He$ bond is 5,000 times weaker than the covalent bond in the hydrogen molecule (Table 9.8.1).
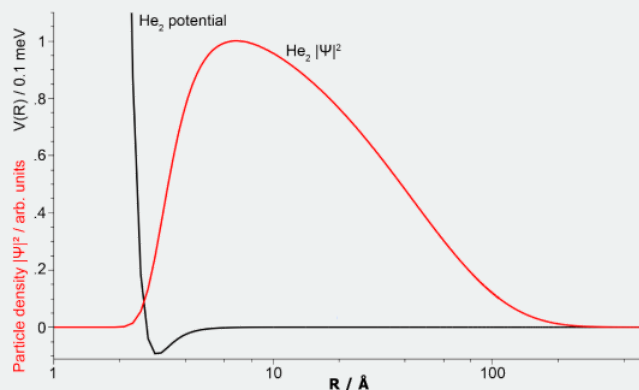
Figure 9.8.2 : The weak helium-helium Van der Waals potential decrease leads to the particle probability density distribution leaking more into the classically forbidden region (i..e, tunneling). This effect allows the wavefunction to extend to sizes of fullerenes, the diameter of DNA and even small viruses (He_2 potential and wavefunction taken from Przybytek 2010), while the classical turning point is located at 13.6 Å, the overall wavefunction extends to more than 200 Å. (Inspire; http://inspirehep.net/record/1415151/plots)

Conclusion

The decrease in energy caused by the bonding orbital (constructive interference of the atomic orbitals) is canceled by the increase in energy caused by the antibonding orbital (destructive interference of the atomic orbitals), so it is not energetically favorable for the helium atoms to be in such proximity, so if that situation arises, they'll separate quickly since there's no force keeping them there.

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