

Molecular Orbitals of Diatomic Molecules in Their Lowest Singlet and Triplet States

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Description:

In this lab we will compute the geometries and molecular orbitals of three diatomic molecules: H_2 , N_2 , and O_2 . Using these molecular orbitals and their electron occupations, we will learn about how electronic structure determines the properties of molecules in different spin states.

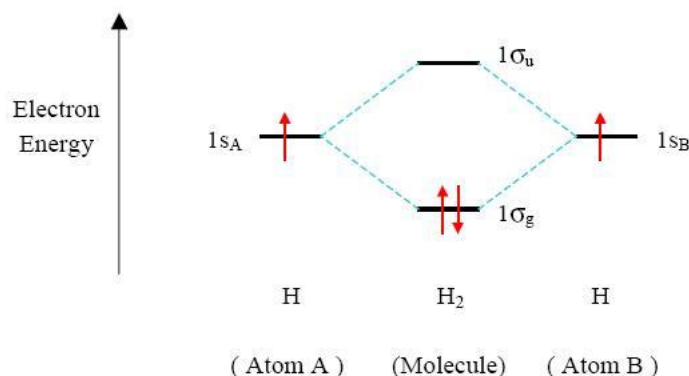
Suggested level: Advanced high school or undergraduate students.

Learning objectives: Learn how to compute molecular orbitals and to make predictions about molecular properties such as bond order from these orbitals and their occupations.

I. Background

Molecular Orbital (MO) theory explains how molecules are constructed from atoms. For a deeper background of MOs and how they are formed by in-phase and out-of-phase combinations of atomic orbitals, see this [general introduction about MOs](#) from LibreText.

Below is an example of how 1s atomic orbitals of two hydrogen atoms (A and B) combine in phase to form a bonding sigma MO (1σ) and out of phase to form an anti-bonding MO ($1\sigma^*$):



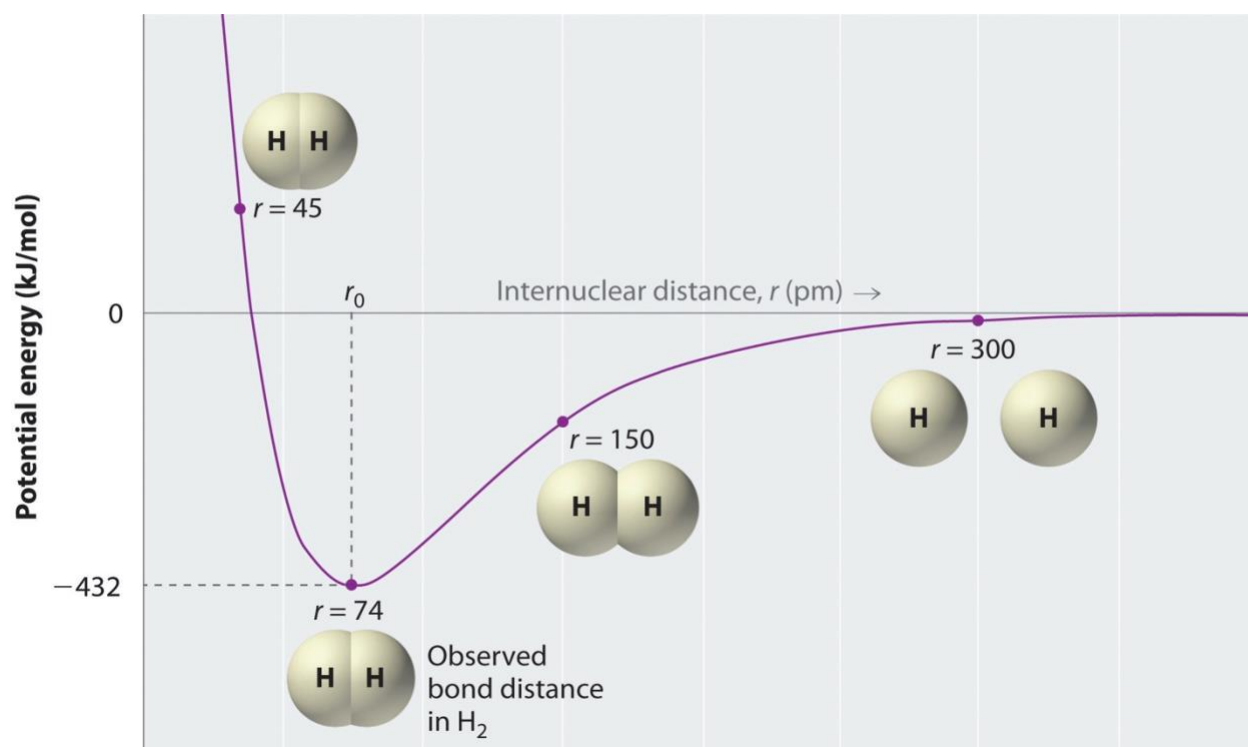
Adapted from [Molecular Orbital Theory \(Florida State University\)](#)

The bond order between the two atoms in a diatomic molecule is determined by the occupation number of bonding and anti-bonding orbitals as follows:

$$\text{Bond Order} = \frac{1}{2} ((\text{Number of bonding electrons}) - (\text{Number of antibonding electrons}))$$

In the H₂ example, for instance, both electrons occupy the bonding orbital (1σ) and, therefore, the bond order $\frac{1}{2} * (2 - 0) = 1$. H₂ has a single bond in its most favorable (i.e., lowest in energy) state.

Bonding leads to a potential energy interaction between the two atoms that draws them together to some optimal bond length (referred to as the equilibrium length). The potential energy plotted as a function of H-H distance resembles a Morse potential that increases exponentially at small distances (due to strong nuclear-nuclear and Pauli repulsion) and approaches zero at long distances (where the bond is broken and there is no interaction energy):



Adapted from [LibreTexts](#)

The bond dissociation energy is the energy difference between the energy of the molecule at its equilibrium geometry and when there is an infinite distance between its atoms. In the example above, for instance, the bond dissociation energy of H₂ is shown as -432 kJ/mol.

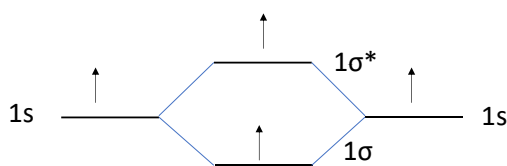
The shape of the bonding potential, and the associated equilibrium bond distance and bond dissociation energy, are affected by the bond order.

MO diagrams are filled up with electrons following similar rules to atomic orbitals. Namely, the electrons are first placed on the lowest available orbital (Aufbau or building-up principle); the Pauli exclusion principle ensures that a maximum of two spin-paired electrons are allowed in the same MO; and Hund's maximum multiplicity rule means that if two or more orbitals of equal energy are available, electrons will preferentially occupy them singly before filling them

in pairs, in such a way to maximize multiplicity. Note that the multiplicity is a function of a molecule's total spin (\mathbf{S}). \mathbf{S} is calculated as the sum of the spins of all electrons in the system ($\mathbf{S} = \sum_i \mathbf{m}_{s_i}$; where $\mathbf{m}_s = \pm 1/2$). The multiplicity is then given by $2\mathbf{S}+1$ and is the number of possible total spatial spin orientations the molecule can take with equal energy (degeneracy).

The rules above apply for determining a molecule's lowest energy state (the ground state). While the Pauli exclusion principle always holds, molecules may exist in other states (excited states— states that are higher in energy than the ground state). In excited states, electrons can occupy higher energy orbitals and do not necessarily obey Hund's rule. Such states can be accessed, for instance, by light.

Below is one example of an excited state configuration of H_2 .

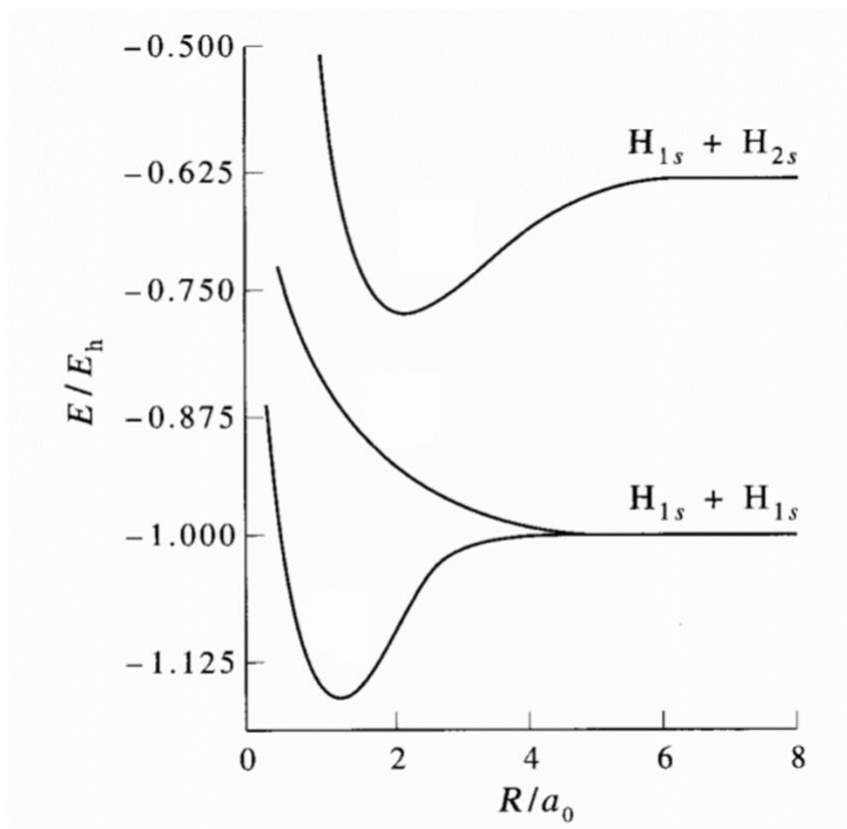


An excited state configuration of H_2 having triplet multiplicity

Note that the above configuration represents a triplet state of H_2 because the total electronic spin ($S = \frac{1}{2} + \frac{1}{2} = 1$) gives a multiplicity of $2(1) + 1 = 3$. While this is the lowest energy triplet state configuration of H_2 (because the Pauli exclusion principle prevents two electrons with the same spin to exist in the same orbital), it is still an excited state of H_2 because the electrons prefer to occupy the singlet state with both electrons in the bonding 1σ orbital.

Since excited states have different electronic configurations than the ground state, molecules usually have different bonding properties in their excited state compared to the ground state. For instance, In the triplet state electronic configuration shown above, the overall bond order is $\frac{1}{2}(1 - 1) = 0$. This means that H_2 is not bonded in its lowest triplet state and prefers to dissociate. This is demonstrated in the figure on the following page where the lowest energy state belongs to the ground state, and the first excited state immediately above it represents a dissociative excited state with electronic configuration $(1\sigma)^1(1\sigma^*)^1$. As indicated in that figure, there are other excited states of H_2 . The second one shown there (labeled as H_{1s+2s}) is an excitation arising from the excitation of one of H_2 's 1σ bonding orbital to its 2σ bonding orbital formed by $2s$ orbitals of the hydrogens.

To avoid the calculation of excited states in this lab (of which there are many), we will focus instead on the lowest singlet and triplet states of H_2 , O_2 , and N_2 . First, we will fill out MO diagrams for those states and use them to predict the properties of the states. Then, we will perform quantum chemical calculations using IQmol/Q-Chem to optimize these diatomic molecules' geometries and visualize their frontier MOs in different states.

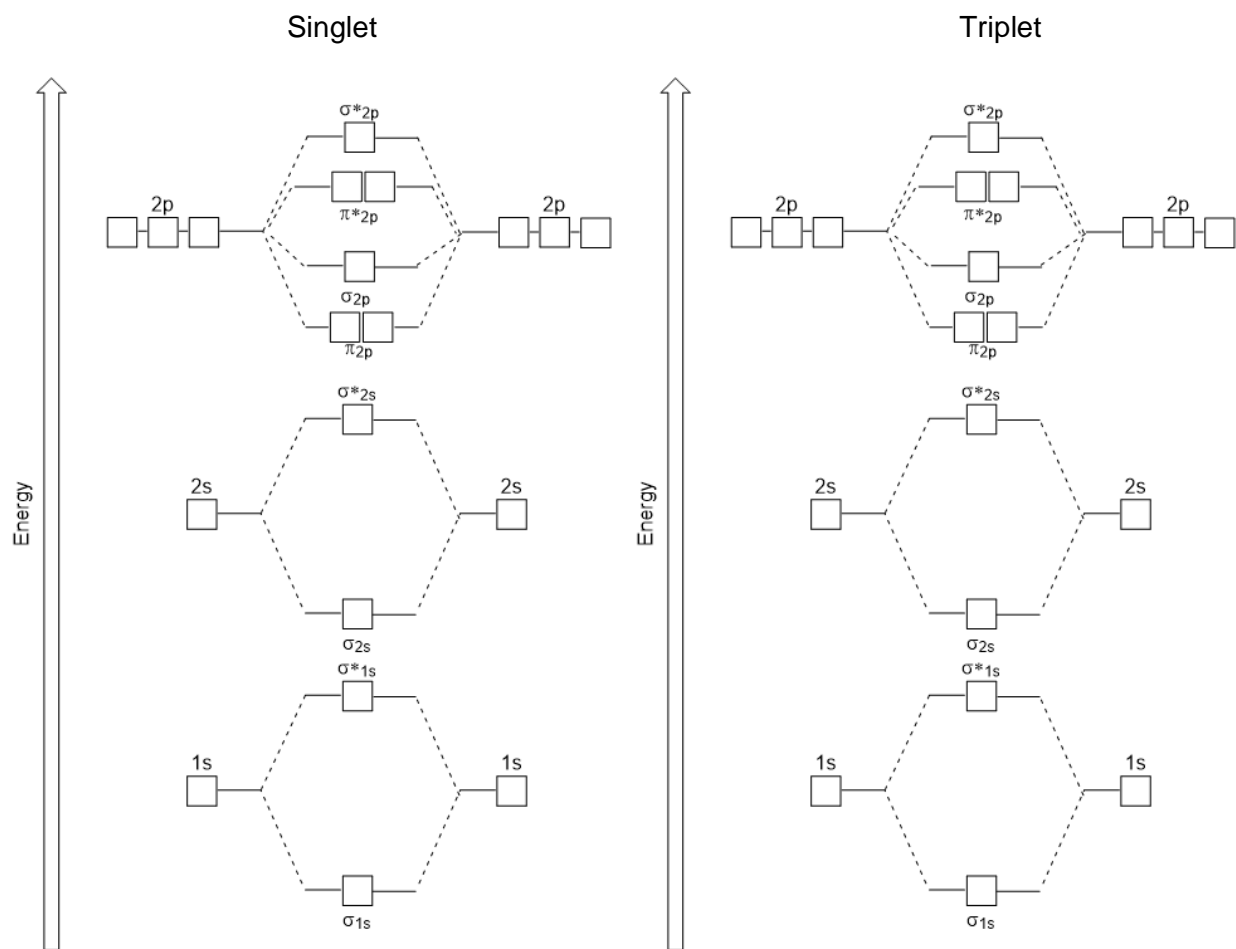


Adapted from McQuarrie, D.; Simon, J. *Physical Chemistry A Molecular Approach*; University Science Books, 1997; pp. 662.

II. Instructions and lab questions

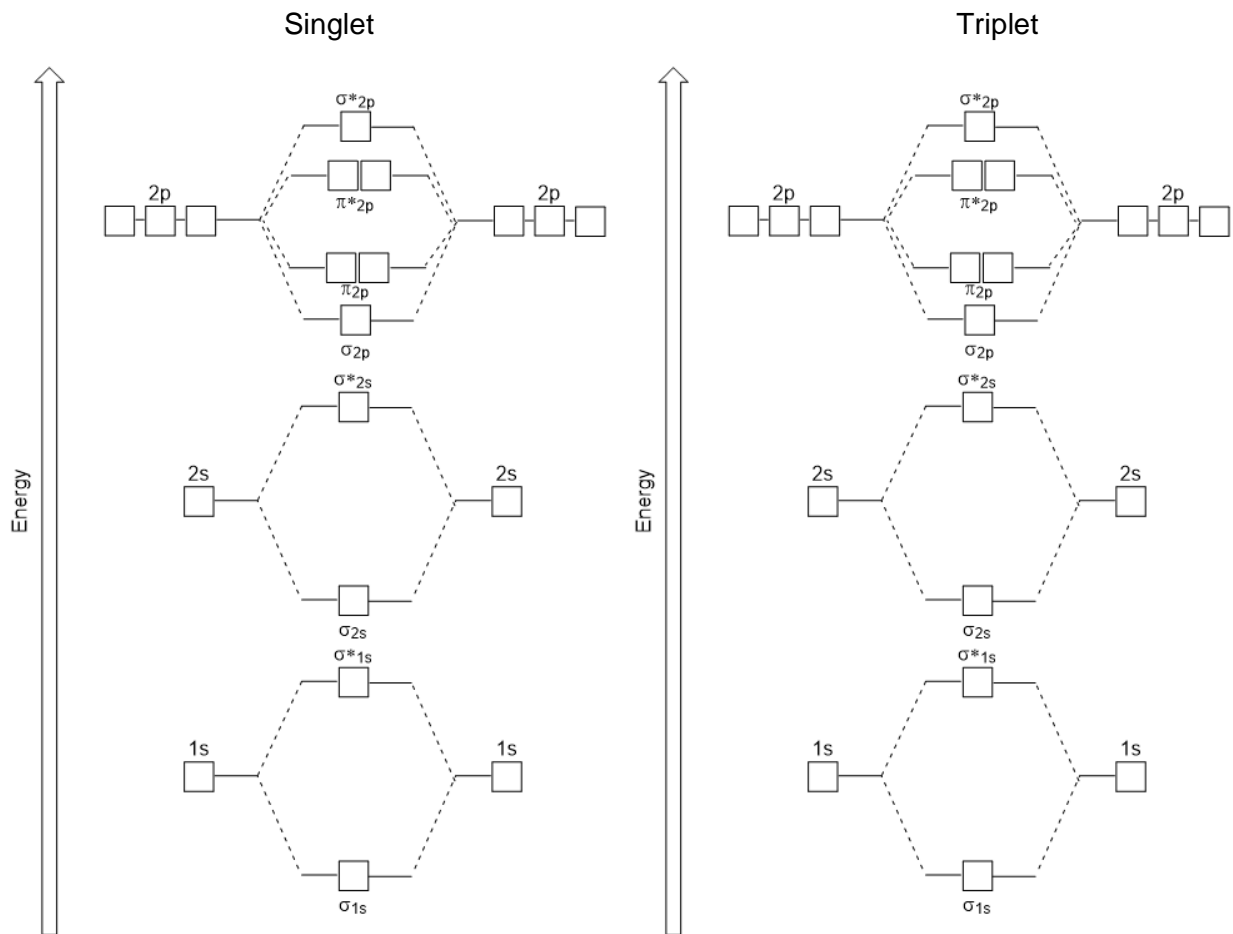
In this lab we will focus on three diatomic molecules (which at standard conditions exist as well-known gases—hydrogen, nitrogen, and oxygen): H_2 , N_2 , and O_2 . The singlet and triplet electronic configurations of H_2 were already presented in the introduction.

Use the MO diagram below to fill out the electronic configuration of N_2 in its lowest singlet and triplet state. Follow Hund's rule and the "building-up" principle when possible but make sure that the Pauli exclusion principle is always enforced.



MO diagrams for N_2

Similarly, do the same for O_2 using the MO diagram on the following page. Note that in O_2 (as well as F_2 , etc.), there is a reordering of the σ_{2p} and π_{2p} orbitals compared to N_2 and smaller diatomics. The reason for this is mixing between the 2s and 2p molecular orbitals in the smaller diatomics which causes the σ_{2p} MO to increase in energy.



MO diagrams for O₂

For each of H₂, N₂, and O₂, determine:

- The identity of the **HOMO** (or **SOMO**, if singly occupied) and **LUMO** orbitals, and indicate their shape (σ , π , σ^* , or π^*). Sketch an image of what you expect these MOs to look like.

HOMO = Highest Occupied Molecular Orbital

SOMO = Highest Singly Occupied Molecular Orbital

LUMO = Lowest Unoccupied Molecular Orbital

- The formal **bond order** of each molecule in its lowest singlet and triplet states.

- Which state (the singlet or the triplet) has a more energetically favorable configuration based on the rules discussed in the introduction?

Next, we will carry out computations to support the predictions above.

- Using IQMol, construct these molecules and minimize their energy.
- Optimize their geometries using HF/6-31G* followed by a frequency calculation. See below how to set up the calculations:
 - i. Set 'Basis' to 6-31G* and 'Method' to HF.
 - ii. Select Geometry for the 'Calculate' option.
 - iii. For the charge and multiplicity, use the data in the table below. You should run a total of six calculations since you will need to run the singlet and triplet state for each molecule.

Molecule	Charge	Multiplicity
H ₂	0	1 and 3
N ₂	0	1 and 3
O ₂	0	1 and 3

- Once each calculation is done, store the outputs in a working directory on your device. Make sure you know where you placed each of the six calculations and give these files descriptive names to identify them.
- To visualize the information for the calculations, you need to load the .fchk file into IQmol. Then you can use this graphic tool to extract different properties produced by the calculation. First, use IQmol's select tool to select the two atoms, which will give the distance between them. Record those distances for each molecule in each multiplicity. Next, expand the "Geometries" tab in the left panel by clicking on the ">" sign next to it. You should see a list of numbers there. Record the last number. This is the total energy of your system (from approximate quantum chemical calculations). Finally, expand the 'Surfaces' tab, double-click on the first 'Canonical Orbitals' and click on 'Calculate' to generate the HOMO and LUMO of each molecule. You should then be able to expand the "Canonical orbitals" tab to select the HOMO or LUMO to visualize. Export images or take screenshots of the HOMO and LUMO of each molecule in each of state singlet and triplet state.

Questions:

- Is there a relation between the bond distances computed in IQmol and your bond orders predicted from MO theory for each molecule in each state? Explain your answer.
- Compare the singlet and triplet state energies for each molecule. Which state is lower in energy, the singlet or the triplet? Note that lower in energy means more negative. Is this consistent with your expectations from your MO diagram? Explain which rule plays the main role in determining the ground state multiplicity of O₂.
- Compare your computed HOMO and LUMO orbitals with the sketches you drew after constructing the MO diagrams. Are they consistent with what you expected? Explain.
- How many nodes does the HOMO have in H₂, N₂, and O₂? Does the number of nodes change when changing states for each molecule? Explain your answer.

Bonus questions:

- Repeat this exercise for the molecular cations H_2^+ , N_2^+ , and O_2^+ . First, using the MO diagrams, predict the bond order and multiplicity of those systems. Then, calculate the geometries, energies, and molecular orbitals of those systems and explain whether they are consistent with your predictions from the MO diagrams.
- Repeat this exercise for the molecular anions H_2^- and O_2^- . Note that H_2^- is an unstable anion that rapidly undergoes detachment to give H_2 and e^- . Such short-lived states are referred to as metastable states.