

Molecular orbitals and bonding: What do unpaired electrons do?

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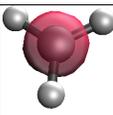
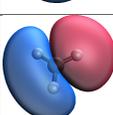
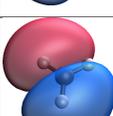
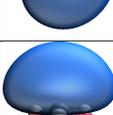
Description: Students learn how to compute and visualize molecular orbitals using *IQmol* and review the key concepts of the MO-LCAO picture of bonding. They also learn how to connect bond orders with experimentally observable properties (bond lengths and frequencies).

Suggested level: Beginning graduate. It is recommended to precede this activity by the “Bonding and Molecular Orbitals” lab.

Learning objectives: Learn how to interpret molecular orbitals in polyatomic molecules in terms of bonding patterns; understand the connection between bond orders and molecular properties.

I. BRIEF BACKGROUND

TABLE I: Molecular orbitals of the CH₃ radical, ordered by energy (1 is the lowest)

orbital	occupation	picture
1, core	2	
2, valence	2	
3, valence	2	
4, valence	2	
5, valence	1	

Lets us analyze molecular orbitals (MOs) of the CH₃ radical — this will be useful for understanding bonding patterns in other species studied in this lab (it is often convenient to analyze the character of complicated molecules in terms on the orbitals of the constituent fragments). CH₃ radical has 9 electrons. Table I shows occupied MOs, ordered by energy. In the ground state, CH₃ has four doubly occupied MOs and a one singly occupied MO. Important observations:

- The core orbital ($1s_C$) is very compact and it does not participate in bonding; only the valence orbitals contribute to bonding.
- As the orbitals' energies increase, the orbitals develop more and more nodes.
- The canonical MOs are always delocalized.

The bonding pattern in CH_3 can be understood by making the following observations. Orbital #2 is a linear combination of hydrogens' s -orbitals and carbon's $2s$ -orbital. This orbital contributes to bonding for all three C–H bonds. Orbitals #3 and #4 are linear combinations of hydrogens' s -orbitals and carbon's $2p$ -orbitals; they can be described as σ_{CH} bonds. Orbital #3 contributes to bonding of one C–H bond (the part, shown in red), and partly to the two other bonds. Orbital #4 does not contribute to C–H bonding of the right top hydrogen, but does contribute to bonding of two other C–H bonds. Orbital #5 is carbon's $2p$ orbital. It does not participate in bonding and is similar to a lone pair (only that it hosts only one electron, so there is no “pair”).

Delocalized nature of MOs complicates the determination of the bonding pattern. You may find helpful to consider linear combinations of the MOs with the same occupations. For example, $\phi_2 - \phi_3$ gives an orbital, localized on the C–H bond with the right top hydrogen. No other linear combinations, orthogonal to this orbital, give any significant contribution to this bond; therefore, its order is one. Similarly, $\phi_2 + \phi_4$ and $\phi_2 - \phi_4$ give orbitals, localized on two other C–H bonds. Therefore, the bond orders of the last two C–H bonds are also one.

II. EXERCISE DESCRIPTION

This is a group activity. The students divide in two groups. Within each group, students decide how to divide the calculations. Then they together analyze and discuss the results and prepare an executive summary. One member of the group presents the summary to the class; the results are discussed. The presentation and discussion from each group is approximately 20 minutes.

A. Group 1

Consider three molecules: CH_3Cl (closed-shell), CH_2Cl (a doublet radical with one unpaired electron), and CH_3 (also, a doublet). Begin by computing optimized structures. At the optimized geometry, analyze occupied molecular orbitals in terms of bonding patterns (focus on carbon and on C–Cl bond). Compute frequencies (at the optimized geometries). Use $\omega\text{B97X-D/6-31G}^*$ in all calculations.

Answer the following questions:

- What is C–Cl bond order in CH_3Cl ?
- On what type of molecular orbital resides the unpaired electron in CH_3 and in CH_2Cl ?
- What is bond order in CH_2Cl ?

- Compare the C-Cl bond lengths and the frequencies corresponding to the C-Cl stretch in CH_3Cl and CH_2Cl . Do the trends agree with the respective bond orders?

B. Group 2

The main goal is to understand the bonding in the allyl radical (CH_2CHCH_2 , a doublet radical with one unpaired electron). Begin by considering three closed-shell molecules: ethylene (C_2H_4), ethane (C_2H_6), and CH_2CHCH_3 . Begin by computing optimized structures. At the optimized geometries, analyze occupied molecular orbitals in terms of bonding patterns (focus on CC bonds). Compute the frequencies (at the optimized geometries). Use $\omega\text{B97X-D/6-31G}^*$ in all calculations.

Answer the following questions:

- What are C-C bond orders in these species?
- On what type of molecular orbital resides the allyl's unpaired electron?
- Analyze the C-C bond lengths and the frequencies corresponding to the C-C stretch in these species. Do the trends agree with the respective bond orders?

C. Useful tips

Varying isovalue might be helpful in deciphering dominant characters of MOs.