

# What Happens to the Orbitals as a One-Dimensional Box Gets Longer?

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## Information

Molecular orbitals are the basic building block of molecular modeling and quantum chemical computation. In this lab you will compute the molecular orbitals for various molecules in order to gain an appreciation for how computational chemical models are used to help elucidate issues that often crop up in chemical research.

Molecular orbitals are composed of linear combinations of atomic orbitals. The atomic orbitals for those “off the axis of symmetry” are often treated as symmetry pairs. As a result, the orbitals for atoms not on the axis of symmetry are not treated independently. They come in various + and – combinations for small atoms. Can you think of why this is? Consider the particle-in-a-box wavefunction at higher  $n$  values. The change in sign as the function crosses the axis creates a node. The addition of off-axis orbitals also creates nodes that must be considered since MOs are wavefunctions unto themselves.

For linear molecules, the computations don’t actually create true  $\pi$  orbitals that encompass the entire exterior of the molecule. Due to some limits in the computation, these are treated as degenerate pairs (hence, two orbitals with the same energy) which have one item in the on-linear (xz-plane) and another in the off-linear (yz-plane) Cartesian directions. If the linear molecule has the main axis of the molecule along the z-axis, for instance, this pair of degenerate  $\pi$  orbitals will be found in the xz and yz-planes. This and the other points should become clear in the below exercise. Remember to answer all questions in complete and correct sentences.

## Part 1 Procedure

1. Login to WebMO and build the acetylene molecule ( $\text{C}_2\text{H}_2$ ). For information on building molecules, please see the tutorial.
2. Optimize the geometry of this molecule (HF/cc-pVDZ) keeping in mind that it should be perfectly linear.

**Job Name:** “(yourinitials) C2H2 HF Opt”

**Calculation:** Geometry Optimization

**Theory:** Hartree-Fock

**Basis set:** cc-pVDZ

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3. Submit the job by clicking on the right arrow at the bottom-right of the box.
4. Once the job has finished running, click on the completed file.
5. Record the bond lengths.
6. Click "New Job Using this Geometry." You do not need to edit this geometry any more since it has been optimized. Click the right arrow.
7. Now you will submit a Hartree Fock molecular orbital computation.

**Job Name:** "(yourinitials) C<sub>2</sub>H<sub>2</sub> HF MOs"

**Calculation:** Molecular Orbitals

**Theory:** Hartree-Fock

**Basis set:** cc-pVDZ

8. Submit the job to run. It will show its progress in the "Job Manager." When "Status" says "Complete" and turns green, click the magnifying glass icon to view the output of the file.
9. Record the number of occupied molecular orbitals. How many  $\pi$  and  $\sigma$  orbitals are present?
10. Repeat steps 1-9 for diacetylene and triacetylene making changes in the job name. The carbon atoms are numbered from one side to the other sequentially. When you need to view the MOs to answer the discussion questions, click on the magnifying glass icon to the right of each orbital at the bottom of the "View Job" page.

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Name \_\_\_\_\_ Date \_\_\_\_\_

Lab Partner \_\_\_\_\_

## Part 1 Questions

1. C<sub>2</sub>H<sub>2</sub> Job number: \_\_\_\_\_

(a) Bond lengths (in Å)

C <sub>1</sub> –H	
C <sub>1</sub> –C <sub>2</sub>	
C <sub>2</sub> –H	

(b) Energy (in E<sub>h</sub>)

$\pi$ occupied	1 <sup>st</sup> $\pi$ unoccupied

(c) # of occupied

$\sigma$ orbital	$\pi$ orbital

2. C<sub>4</sub>H<sub>2</sub> Job number: \_\_\_\_\_

(a) Bond lengths (in Å)

C <sub>1</sub> –H	
C <sub>1</sub> –C <sub>2</sub>	
C <sub>2</sub> –C <sub>3</sub>	
C <sub>3</sub> –C <sub>4</sub>	
C <sub>4</sub> –H	

(b) Energy (in E<sub>h</sub>)

$\pi$ occupied	1 <sup>st</sup> $\pi$ unoccupied

(c) # of occupied

$\sigma$ orbital	$\pi$ orbital

3.  $C_6H_2$  Job number: \_\_\_\_\_

(a) Bond lengths (in Å)

$C_1-H$	
$C_1-C_2$	
$C_2-C_3$	
$C_3-C_4$	
$C_4-C_5$	
$C_5-C_6$	
$C_6-H$	

(b) Energy (in  $E_h$ )

$\pi$ occupied	1 <sup>st</sup> $\pi$ unoccupied

(c) # of occupied

$\sigma$ orbital	$\pi$ orbital

4.  $C_8H_2$  Job number: \_\_\_\_\_

(a) Bond lengths (in Å)

$C_1-H$	
$C_1-C_2$	
$C_2-C_3$	
$C_3-C_4$	
$C_4-C_5$	
$C_5-C_6$	
$C_6-C_7$	
$C_7-C_8$	
$C_8-H$	

(b) Energy (in  $E_h$ )

$\pi$ occupied	1 <sup>st</sup> $\pi$ unoccupied

(c) # of occupied

$\sigma$ orbital	$\pi$ orbital

5. What is the visual difference in the  $\pi$  orbitals for each successive level for each molecule?
6. What happens to the energy of the  $\pi$  highest occupied molecular orbital (HOMO) for each successively longer for molecule?
7. How does this relate to the particle-in-a-box model and to the pattern of bond lengths (Hint: think nodes)? To properly view the MOs, you may need to change the opacity in the settings.