

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 π 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 π 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. Go to the [Psi4 submit page](#). Enter C2H2 in the Search for a molecule box and hit enter. You should see an acetylene molecule in the 3D Panel.
2. Scroll down to "Set Parameters for Quantum Mechanical Calculation and click "Reset Settings to Default"
3. Select these options for the computation:

Select your package: PSI4

Name for input file: “C2H2_your name”

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Type: Geometry Optimization

Add-Ons: None

Basis Set: aug-cc-pVDZ

DFT Functional: None

The other options should be left at the default values they were set to when you clicked "Reset Settings"

4. Click Submit Job. This will take you to the Status page where you can view the results of your job. You should see the output from the job scroll by.
5. After the calculation is complete, scroll down to the 3D picture of the molecule. The electronic energy is located at the top of the 3D window. Record the Electronic Energy in Hartrees (a.u.). You can change the Energy Units with the dropdown.
6. Record the bond lengths. Double click on one atom then double click on another.
7. The molecular orbitals are listed under "Visualizations (Orbitals)". Lowest energy orbitals are at the bottom. Psi4 calculates how many electrons occupy the orbital and this is shown as 1e or 2e if occupied. You may need to change the MO Cutoff value to see the orbital, e.g. try 0.03 if 0.05 doesn't show any orbital. Take screenshots and note any nodes.
8. Record the number of occupied molecular orbitals. Click on each orbital and observe the shape of the MO. How many π and σ orbitals are present?
9. Repeat steps 1-9 for diacetylene, triacetylene, and tetraacetylene making changes in the job name. When noting bond lengths number the carbon atoms sequentially from one end to the other.
10. Note: It may be necessary to force linearity on triacetylene. Click "Advanced Options" and "Manually alter coordinates". Set all the z-coordinates to 0. Click Resymmetrize after changing the atom coordinates. A linear molecule should have Dih symmetry ($D_{\infty h}$). Or you can disable optimization (uncheck Automatically Optimize Molecule before searching for triacetylene in the database)

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Name _____ Date _____

Lab Partner _____

Part 1 Questions

1. C₂H₂ Job number: _____

(a) Bond lengths (in Å)

C ₁ –H	
C ₁ –C ₂	
C ₂ –H	

(b) Energy (in E_h)

π occupied	1 st π unoccupied

(c) # of occupied

σ orbital	π orbital

2. C₄H₂ Job number: _____

(a) Bond lengths (in Å)

C ₁ –H	
C ₁ –C ₂	
C ₂ –C ₃	
C ₃ –C ₄	
C ₄ –H	

(b) Energy (in E_h)

π occupied	1 st π unoccupied

(c) # of occupied

σ orbital	π 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)

π occupied	1 st π unoccupied

(c) # of occupied

σ orbital	π 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)

π occupied	1 st π unoccupied

(c) # of occupied

σ orbital	π orbital

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5. What is the visual difference in the π orbitals for each successive level for each molecule?
6. What happens to the energy of the π 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.