What is Symmetry in Chemistry?

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Information

The role of symmetry and group theory in spectroscopy is unmistakable. It is also necessary in many stages of chemical synthesis and for a general understanding of the chemical environment. However, sometimes symmetry is hard to handle. The following lab demonstrates how modern computational chemistry interfaces can assist in the determination of point group symmetries and operator elements.

Part 1 H_2O & H_2O_2

1. Login to WebMO and create a water molecule.

2. Optimize the geometry B3LYP/cc-pVDZ.

Job Name: "(yourinitials) H2O B3LYP/cc-pVDZ Opt"
Calculation: Geometry Optimization
Method: DFT
Functional: B3LYP **Basis set**: cc-pVDZ
Reference: Restricted

3. Open the output file and select the icon to display the symmetry elements. If nothing shows up, you need to make sure that your molecule is actually symmetric.

4. Record the total energy, point group, and the symmetry elements (don't forget the identity) on the worksheet below. The WebMO symmetry tolerances are not tight enough for PSI4 to get a purely symmetric molecule all of the time. Note that the point group displayed may not be accurate. Be careful about your attribution of the point group. WebMO can show this after the next step.

5. Select "New Job Using This Geometry."

6. Stretch one of the bond lengths to 1.5 Å and run a B3LYP/cc-pVDZ "Molecular Energy" computation with "(yourinitials) H2O 1.5 DZ" as the job name.

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7. Record the total energy, point group, and symmetry elements.

8. Create hydrogen peroxide, but keep it planar. (Select all four atoms, starting with one of the hydrogens, click the dihedral button, and set to 180.0°.)

9. Optimize the geometry with B3LYP/cc-pVDZ with the job name "(yourinitials) H2O2 DZ Planar Opt."

10. Record the total energy, point group, and symmetry elements.

11. Since, H_2O_2 has four atoms, it does not have to be planar. Select "New Job Using This Geometry."

12. Select all four atoms and click on the dihedral button on the left hand side of the editor. Make the dihedral angle 160.0°.

13. Optimize the geometry B3LYP/cc-pVDZ with the job name "(yourinitials) H2O2 DZ Bent Opt."

14. Record the total energy, point group, and symmetry elements.

Part 2 Choose a molecule

Now that you have created two molecules and two conformers each giving you a few different point groups, it's your turn to show that you can utilize WebMO to help understand symmetry. You will be computing molecules of various point group symmetries. You WILL NOT receive any credit for molecules used from the "symmetry examples" list from WebMO. Follow the procedure below for each molecule.

15. Create your molecule in the WebMO viewer.

16. Run an "Optimize & Vib Freq" computation with B3LYP/cc-pVDZ with a proper job name. Once the job has finished running, open the output.

17. Verify that all of the frequencies are non-negative. In reality, these frequencies are imaginary, but Gaussian chooses to represent these with negative numbers. If you have any "negative" frequencies, you are not at the bottom of the well. Don't worry about the science behind this, yet. Just know that all frequencies must be real ("positive") in order for the molecule to be at the minimum.

18. Select “New job using this geometry.” Modify your molecular geometry some, and try again.

19. Verify that your molecule is of the proper point group symmetry in your output file. You may also be close. In which case, you will need to “symmetrize” your molecule.

20. Click the “Symmetry” tab above the editor followed by “Symmetrize Molecule...” The dialogue box requires you to click the “Symmetrize” button to get the geometry close to what it needs to be.

21. Once you have a molecule that satisfies the proper symmetry, draw a Lewis structure of the molecule and record the total energy.

22. Report one molecule for three of the following symmetries. Hence, you will have three molecules total, and each must be for a different symmetry. Use your creativity and chemical intuition **not** a google search for this. There are hundreds of correct answers. You may not use a molecule already studied in this lab or any previous labs, and your answer must be a “real” molecule.

a) C_s

b) C_2

c) C_{2v}

d) $C_{\infty v}$

e) $C_{\infty h}$

f) C_{2h}

g) C_{3h}

h) C_{3v}

i) D_{2h}

Part 3 Carbon based molecules

23. In “Job Manager,” select “New Job.”

24. On the left, beside the tool bar, click on “import.”

25. Select “XYZ Format” in the “Format” drop-down menu; click “Generate Bonds”, as well.

26. Copy and paste the coordinates of Molecule 1 (see text file) in the white area to the right of option 2.

27. Run a Hartree-Fock (HF) STO-3G Molecular Energy computation with an appropriate job name. What molecule is this? What is its point group symmetry? What is its total energy?

28. Again, in “Job Manager,” select “New Job.”

29. On the left, beside the tool bar, click on “import.”

30. Select “*XYZ* Format” in the “Format” drop-down menu. Also, click “Generate Bonds.”

31. Copy and paste the coordinates of Molecule 2 (see text file) in the white area to the right of option 2.

32. This is a fairly large molecule. As a result, we are going to use WebMO itself to get us a structure for this molecule. In the “Clean-Up” tab above the molecule viewer, select “Comprehensive-Mechanics”. This process may take around 5-10 minutes, but it will complete. During this time the “Clean-Up” button will be highlighted blue.

33. Record the “Strain Energy” that will show up at the bottom of the molecule viewer window. What molecule is this? What is its point group symmetry?

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Name _____ Date _____

Lab Partner _____

Part 1 H_2O & H_2O_2

1. H_2O Job number: _____

Total Energy: _____ Point Group: _____

List the symmetry elements:

2. 1.5 Å Stretched H_2O Job number: _____

Total Energy _____ Point Group _____

List the symmetry elements:

3. Planar H_2O_2 Job number: _____

Total Energy: _____ Point Group: _____

List the symmetry elements:

4. Optimized H_2O_2 Job number: _____

Total Energy: _____ Point Group: _____

List the symmetry elements:

5. Why does the point group symmetry change when one of the O-H bond lengths in water is longer than the other and when hydrogen peroxide is not planar?

Part 2 Choose a molecule

6. C_s Job number: _____

Total Energy: _____ Lewis Structure:

7. C_2 Job number: _____

Total Energy: _____ Lewis Structure:

8. C_{2v} Job number: _____

Total Energy: _____ Lewis Structure:

9. $C_{\infty v}$ Job number: _____

Total Energy: _____ Lewis Structure:

10. $D_{\infty h}$ Job number: _____

Total Energy: _____ Lewis Structure:

11. C_{2h} Job number: _____

Total Energy: _____ Lewis Structure:

12. C_{3h} Job number: _____

Total Energy: _____ Lewis Structure:

13. C_{3v} Job number: _____

Total Energy: _____ Lewis Structure:

14. D_{2h} Job number: _____

Total Energy: _____ Lewis Structure:

Part 3 Carbon based molecules

15. Molecule 1 Job number: _____

Molecule Name: _____

Total Energy _____ Point Group _____

16. Molecule 2 Job number: _____

Molecule Name: _____

Strain Energy (kcal/mol): _____ Point Group _____

17. What point group was the most difficult to find an example in Part B? Explain in complete and correct sentences.

18. Why did the computation of molecule 2 take so much longer than molecule 1? How does this change if just one atom is not aligned with proper symmetry? (You need to do these computations!) Discuss in complete and correct sentences.