When does water become OH + H?

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Information

Molecular orbitals (MOs) 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.

MOs 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. Keep this in mind as you build the water molecule. When do we say there is a "bond?" When two atoms are sharing an orbital. When does the bond break? That's a bit more tricky. Typically, this occurs when the electrons no longer occupy their fully bonding orbital.

Part 1 Procedure

1. In the molecule editor, create a water molecule with the O-H bonds the same length. For instructions on creating the molecule, please see the Tutorial lab.

2. Optimize this geometry with PSI4 and B3LYP/cc-pVDZ

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

3. Record the bond lengths and bond angles.

4. Compute the Hartree-Fock (HF) cc-pVDZ molecular orbitals (MOs).

Job Name: "(yourinitials) H2O DZ MOs"
Calculation: Molecular Orbitals
Method: Hartree-Frock
Basis set: cc-pVDZ

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5. Click the magnifying glass icon to view the output of the file. Then, towards the bottom of the output page, click the magnifying glass icon beside the desired molecular orbital you wish to view.

6. Go back to your HF/cc-pVDZ output by clicking "Molecule Viewer" tab at the top of the molecule viewing window. Select "New Job Using this Geometry."

7. Now set **ONE** O-H bond distance to 1.5 Å, and plot the MOs as you have above with the title "(yourinitials) H2O DZ 1.5 MOs."

8. Do this again for 2.0 Å, 2.5 Å, and 3.0 Å. Note: Some answers may be found in the raw output and not solely on the WebMO output page.

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Name _____ Date _____

Lab Partner _____

Part 1 Questions

1. O-H bond length: _____

2. H-O bond angle: _____

3. Total # of occupied orbitals:_____ Total # of unoccupied orbitals:_____

4. What atomic orbitals (1s, 2s, $2p_x$, $2p_y$, $2p_z$) from each of the three atoms (H, H, & O) make up each of the MOs (remember that the H orbitals here come in H+H and H-H combinations) for:

MO #1: MO #2:

MO #3: MO #4:

MO #5: MO #6:

5. Draw MO #3.

6. Write the MO energies for each MO:

MO #1: _____ MO #2: _____ MO #3: _____

MO #3: _____ MO #4: _____ MO #5: _____

7. For each specified O-H bond stretched distance:

   a) Write each corresponding MO energy:

O-H Bond	MO #1	MO #2	MO #3	MO #4	MO #5	MO #6
1.5 Å						
2.0 Å						
2.5 Å						
3.0 Å						

   b) Look at the MOs and indicate which MO number(s) corresponds to MO #3 in the standard water molecule. (Hint: The MO orderings may change as some orbitals destabilize.)

1.5 Å:

2.0 Å:

2.5 Å:

3.0 Å:

   c) Thought question: At what bond length do you expect the H atom finally to dissociate and "destroy" the water molecule? (Hint: this is a roughly linear function) Explain your answer.

   d) Discuss why and how the orbital energies are changing.