A QUANTUM LEAP INTO THE FUTURE OF CHEMISTRY

Calculating Walsh Diagrams

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Description: In this lab you will calculate Walsh diagrams for several first row hydrides, and use these to predict their equilibrium structures.

Suggested level: Advanced graduate/advanced undergraduate; introductory organic chemistry is required.

Learning objectives: Learn how to use molecular-orbital diagrams to predict trends on molecular structure.

I. BACKGROUND

In methane, the $2s$ and $2p$ orbitals of the carbon atom hybridize to yield 4 sp^3 orbitals that are arranged tetrahedrally around the nucleus giving rise to T_d symmetry. In water a similar hybridization can occur, only this time two of the orbitals are non-bonding lone-pairs of electrons. In Valence Shell Electron Pair Repulsion (VSEPR) theory, these lone-pairs repel each other more than the bonding pairs, and so the H-O-H bond angle is predicted to be smaller than the ideal tetrahedral angle. Indeed, we find the bond angle in water is about 104°, just less then the tetrahedral angle of 109.5°.

The problem with this simplistic picture is that it predicts the same bond angle for other group 16 hydrides such as H_2S, where the bond angles are closer to 90°. In this lab we will use correlation diagrams to better understand the electronic effects that determine the equilibrium geometries of molecules.

Correlation diagrams (not to be confused with the correlation energy!) show the variation of orbital energies as some parameter changes. In the case of changing a bond angle, these diagrams are called Walsh diagrams. Tanabe-Sugano diagrams, which consider the field-splitting parameter, are another type of correlation diagram that you may have encountered before.

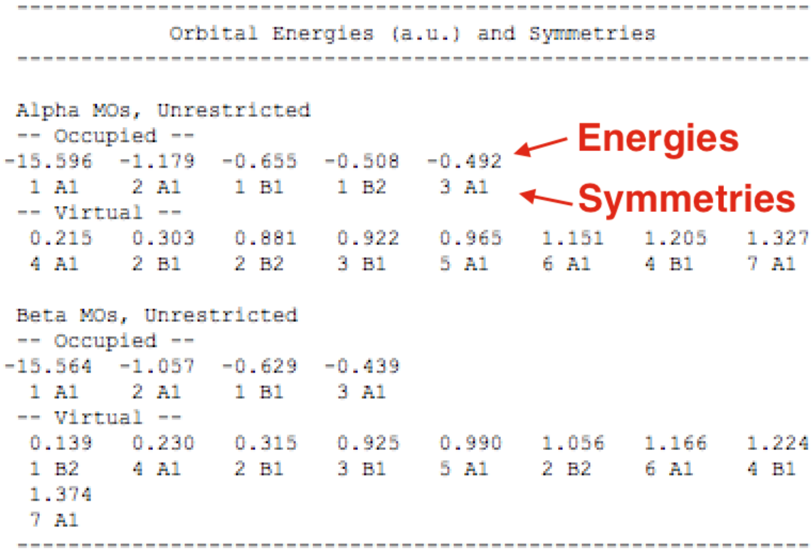
In this lab you will need to fix the geometric parameters of your molecules to particular values. To fix a bond length in IQmol select 2 atoms and use the Build ▶ Set Geometric Constraint menu option. A dialog will appear that allows you to set the length precisely. Bond angles can be fixed similarly, except you will need to select 3 atoms.

To view the molecular orbitals of a molecule, you need to first run a single point energy calculation and copy the results back from the server. Double-click the MO Surfaces item in the Model View to bring up the Add Surface dialog box. Select the orbitals you wish to view, and click the Calculate button.

II. METHOD

1. Draw a BeH_2 molecule and set the bond length to 1.325 Å and bond angle to 90°.

2. Perform an energy calculation using HF/6-31G**, *i.e.* set **Method** to HF and **Basis** to 6-31G**.
3. When the results have transferred from the server, open the Q-CHEM output file by double-clicking on the .out file under the Files item in the Model View. Record the *occupied* orbital energies and symmetries.



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           Orbital Energies (a.u.) and Symmetries
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 Alpha MOs, Unrestricted
 -- Occupied --
-15.596  -1.179  -0.655  -0.508  -0.492
  1 A1     2 A1    1 B1    1 B2    3 A1
 -- Virtual --
  0.215   0.303   0.881   0.922   0.965   1.151   1.205   1.327
  4 A1    2 B1    2 B2    3 B1    5 A1    6 A1    4 B1    7 A1

 Beta MOs, Unrestricted
 -- Occupied --
-15.564  -1.057  -0.629  -0.439
  1 A1     2 A1    1 B1    3 A1
 -- Virtual --
  0.139   0.230   0.315   0.925   0.990   1.056   1.166   1.224
  1 B2    4 A1    2 B1    3 B1    5 A1    2 B2    6 A1    4 B1
  1.374
  7 A1
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4. Repeat the calculation for bond angles between 90-180° in steps of 15°. Keep the same bond length for each angle.
5. Generate a Walsh diagram by plotting the variation of the orbital energies with respect to the changing bond angle. Plot all energies on a single plot, but be sure to clearly label your data. Don't worry about the core orbitals which are at a much lower energy.

Repeat the steps 1–5 above for the BH_2, CH_2, NH_2, and OH_2 molecules using the following bond lengths and multiplicities:

Molecule	Bond	Multiplicity
BeH_2	1.325	singlet
BH_2	1.182	doublet
CH_2	1.073	triplet
NH_2	1.023	doublet
OH_2	0.961	singlet

For singlet systems, the α and β orbitals have the same energy, so only one set needs to be considered. For doublet and triplet systems, the spin orbital energies will be different and both sets of energies need to be considered.

The Hartree-Fock energy for a closed-shell N-electron system is given by

$$E_0 = 2\sum_{i}^{N/2} \epsilon_i - \sum_{i}^{N/2}\sum_{j}^{N/2}(2J_{ij} - K_{ij}) \tag{1}$$

where ϵ_i are the orbital energies and J_{ij} and K_{ij} are the Coulomb and exchange contributions. From this it is clear that the total HF energy is *not* just the sum of orbital energies, however, if we approximate it as such, *i.e.*

$$E_0 \approx \sum_i^N \epsilon_i \tag{2}$$

we get a very crude approximation to the total energy. This approximation double counts the Coulomb and exchange contributions to the energy, and therefore overestimates the repulsion between electrons. Use this approximation, and your Walsh diagrams, to predict what the most stable bond angle is for each molecule.

Use Q-CHEM to calculate the equilibrium geometry for each molecule at the HF/6-31G** level of theory. You will need these data to to answer the questions.

For your optimized water structure, plot each of the occupied MOs and save images of each, you will need these to answer the questions.

Note: There are different conventions for the orientation of a C_{2v} molecule. Q-CHEM places them in the *xz*-plane whereas many point-group tables place them in the *yz*-plane. This has the effect of swapping the two reflection planes and therefore inter-converting the B_1 and B_2 irreducible representations. See https://iopenshell.usc.edu/resources/howto/symmetry/ for more details.

III. EXERCISES

You report should include your Walsh diagrams for each of the 5 molecules, along with a table of calculated and predicted bond angles. Use these to answer the following questions:

1. Describe the method you took to determine the bond angles from your Walsh diagrams?
2. The core orbitals do not participate in bonding; do your predictions change if you include/exclude the core orbital energies?
3. Explain any discrepancies between your predicted and calculated bond angles. (Hint: consider any approximations made.)
4. For each of the molecular orbitals you plotted for water:
   (a) Label the MO with its symmetry, energy and a description of the orbital (bonding/anti-bonding lone pair etc).
   (b) Describe what happens to the orbital as the bond angle is increased.
   (c) Use this to explain the trends observed in the orbital energies.