Finding the Best Bond Angle and Bond Length of Water

In chemistry, we need to know about the structure of molecules. For example, are they straight molecules, bent molecules, planar (flat) molecules? All of these things make a difference. The structure of a molecule determines whether or not the molecule will react with another molecule, how it will behave, and what characteristics or properties it might have.

A molecule that everyone knows well is water. Water has two hydrogens and one oxygen, with the formula $\text{H}_2\text{O}$. In computational chemistry, we use a red sphere to represent oxygen, and white spheres to represent hydrogen. Figure 1 shows a representation of water. The "sticks" between the spheres represent bonds, which are actually electrons holding the atoms together.

You might notice that this molecule is bent. There is a bond angle between the three atoms (H-O-H), and that angle is typically reported at 109.5° (degrees). There is also a distance between the hydrogens and the oxygen, and these are typically reported in units of Angstroms (Å), which is very small – 0.0000000001 meters – or $1.0\times10^{-10}$m. A human hair has a thickness of about 300 Å, so this is pretty small. The bond length between hydrogen and oxygen is about 1.05 Å.

When the bond angle is 109.5° and the bond length is 1.05 Å the molecule has a very specific amount of energy. In computational chemistry, we use a unit of energy known as the hartree, named after a famous scientist. We use the abbreviation $E_h$ to represent this energy.

The amount of energy that a molecule has determines how stable the molecule is, and the lower the energy, the more stable the molecule is. Lower energy is better. And that’s the research question in this lab: what geometry configuration (bond angle and bond length) produces the lowest energy value. It’s your job to find out. The textbooks all say 109.5° and 1.05 Å. Are they right?
Procedure:
1. Log into http://chemistry.ncssm.edu using the username “guest” and the password “guest”.
2. From the Build menu, select the oxygen atom. Click in the window to get a red ball.
3. From the Cleanup menu, do a comprehensive (idealized) cleanup. You should now have the hydrogen atoms and a bent structure!
4. From the Symmetry menu, click on Symmetrize Molecule, symmetrize it, and then click on OK.
5. Go to the next menu by clicking on the blue arrow in the bottom right corner. Choose “Gaussian” as your computational engine.
6. In the new menu, you can give your name a job, such as “Energy Scan of Water”, or just leave it as H2O.
7. Under the Calculation menu, choose “Coordinate Scan”. Everything else in the menu can stay as it is.
8. Click on the Advanced tab, turn off (uncheck) “Include Connectivity”.
9. Click on the Preview tab, then hit “Generate”. You should get a window that looks like the one in Figure 2.
10. You now want to change the code generated to look like the code in Figure 3. This is what this means:
   - The keyword “Scan” at the top says that we want to scan the coordinates. In our case, we are scanning the bond angle and the bond length.
   - Since the bonds between the two hydrogens and the oxygen are the same, we call both of them “B1”. “A1” is the angle, and it’s the only angle we have.
   - We want to scan B1 (the bond length starting at 0.88 Å in 10 steps, each step being 0.04 Å (0.88, 0.92, 0.96, etc.). Notice that the 10 steps is an INTEGER number, and the other two are decimals.
   - Likewise, we are going to scan the bond angle (A1), starting at 60 degrees and going to 150 degrees, so this will be 10 steps at 10.0 degrees per step (60.0, 70.0, 80.0, etc.).

   ![Configure Gaussian Job Options](image)

   Figure 2: Configure window

   - Make sure there is a blank line at the very end. If you hit the return key a couple of times, you will be safe.

11. Now click on the next window arrow, bottom right. It will ask you if you want to submit the edited file, and you do.
12. Now wait for a while, probably 15-20 minutes. You might get stuck in the queue! You can click on the word “Refresh” at the top of the menu items to update your
13. Once your job is done, scroll down to the bottom, and find the results of your coordinate scan. You should see all of your bond angles and bond lengths and the associated energy value.

14. Click on the magnifying glass. You should get a 2D color graphic. Red color means lower energy. You can mouse over that, see if you can find the lowest energy value.

15. If you click on the disk icon, it will download a CSV (comma separated value) dataset to your computer.

16. In Mathematica, use the Import command to import the CSV dataset into MMA (making sure you give your dataset a variable name).

17. Show your data as a nice table, using the \( // \) TableForm command or the Grid command!

18. Plot your 3D surface using the ListPlot3D command. Label your axes (you will have to figure out which axes is which!)

19. Find the coordinates (bond length and bond angle) that correlate to the lowest energy value.

**Deliverable**

Create a Mathematica notebook that has these components:

1. Your downloaded dataset that you imported into Mathematica
2. Your 3D plot, with axes labeled appropriately
3. The coordinates you found for the lowest energy value

Now, do the scan TWO MORE times. From the lowest energy value of the first run that you did, do 10 runs for both bond length and bond length. Set your intervals so that you have 5 scans below and 5 above at HALF of the interval you used for the first run.

- For example, if your optimal length is 0.98, then you want 10 scans at an interval of 0.02, starting at something like 0.92 Å. At the same time, cut your bond angle interval in half (5 degrees instead of 10), and start 5 steps below your best angle (so, if your best angle is 105 degrees, start at something like 80 degrees).

Then do the same thing, cutting your intervals in half again (0.01 Å and 2.5 degrees), again starting at the appropriate place. What you are trying to do here is to zoom in on the lowest energy level. By cutting the interval, we are able to find the most optimal bond
length and bond angle.

For EACH of these two additional runs, download the CSV scan file, do a 3D plot, and use your modified code to find the coordinates where the energy is at a minimum. The THIRD run should be your final results!

A standard student results is shown below. We have not included the student-generated Mathematica code, but a plot of this type can easily be generated in Microsoft Excel or some other type of tool. The student has determined that the hydrogen-oxygen bond lengths are 0.95 angstroms and the bond angle is 105.0 degrees, which correlates to an energy value of -76.0107 hartrees. If the student uses a tool, such as Mathematica or Microsoft Excel, the student can rotate the 3D graphic to see the “minima” that correlates to these specifications.

![Plot of Coordinate Scan of H2O](image)

<table>
<thead>
<tr>
<th>Bond Length</th>
<th>Bond Angle</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.95</td>
<td>105.0</td>
<td>-76.0107</td>
</tr>
</tbody>
</table>