The Study of Hydrogen Bonds in Water and Urea

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Introduction

Water is a special molecule; life originates in water and relies on water. It is very important to understand why water is unique, especially as regards understanding the chemistry of life.
One special physical characteristic of water is the Hydrogen Bond (H-bond) that water can form. This research investigates the energetic properties and consequences of the H-bond.

Methods

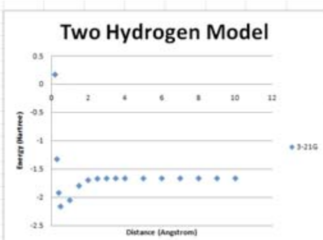
The general method used in this research is computational quantum chemistry. Software called Ecce, can read in the molecules orientation and calculate quantum mechanical energy values, by solving the Schrodinger Equation with NWChem.
To get the H-bond energy, I used the whole system energy subtracted by internal energy of each molecule. Finally, a graph of ENERGY vs. DISTANCE was made for each system. I tested $2H_2$ before considering $2H_2O$ and H_2O-Urea.

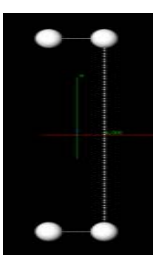
Results and Analysis

The Two Hydrogen Molecule Model, $2H_2$

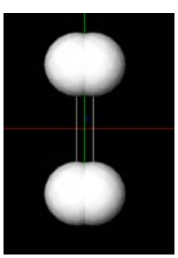
This model was designed for me to check the methods with the software.

Distance (Angstrom)	Energy (Hartree)
0.02	47.521692
0.1	5.260925
0.2	0.168443
0.3	-1.331654
0.4	-1.927276
0.5	-2.168803
1	-2.058976
1.5	-1.802579
2	-1.702488
2.5	-1.676397
3	-1.671451
3.5	-1.67070741
4	-1.670664
5	-1.6707657
6	-1.670657
7	-1.670657
8	-1.670657
9	-1.670657
10	-1.670657





4.0 angstrom



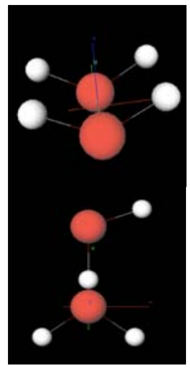
0.4 Angstrom

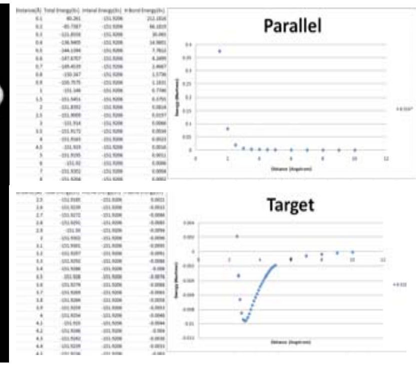
The program naturally uses the energy unit of Hartrees. Since 1 Hartree = 627 kcal/mol great precision is required to subtract the isolated atom or molecule results from the answer to obtain the interaction between two molecules.

In addition there is no need to start the calculation near zero distance. When the distance is only 0.1 angstrom, we are in the realm of high energy physics, and no longer chemistry. I started my following calculations at 2 angstroms.

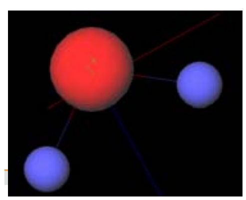
The Two Water Model, 2H2O

The problem with this model is there are too many orientations for the two water system. I choose two special cases for study, which I called the "parallel" and the "target" or H-bond geometry.





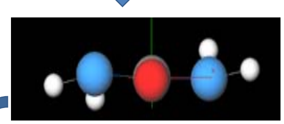
The result from the graphs show totally different trends.
To explain this phenomenon, I thought from the perspective of partial charges on each atom: negative for O, positive for H.
In "**PARALLEL**", Oxygen is close to Oxygen and Hydrogen is close to Hydrogen. The same partial charges repel each other. In "**TARGET**", or H-bonding geometry, it is the opposite charges which are close, so that they attract each other. That is what caused the difference.

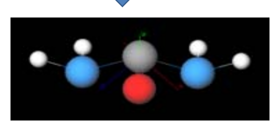


The Urea-Water Model

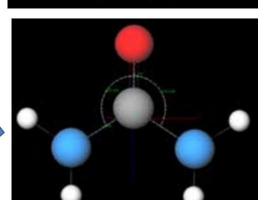
First I built urea. Specifically, its geometry is caused by its electron pair arrangements on carbon. Should it be trigonal planar or slightly trigonal pyramidal?

Planar or Pyramidal?



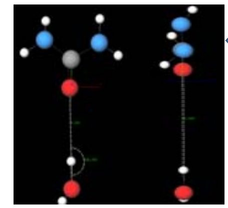


Optimized



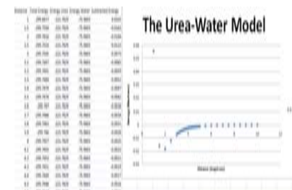
After considerable calculation the geometry optimization function found that the answer was trigonal PLANAR.

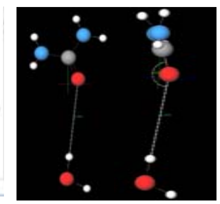
The calculation between water and urea was difficult because the complex's geometry was sensitive to the level of calculation I found that the system was not in a minimum energy configuration when 6 atoms were in the same plane.



In Same Plane

In Different Planes





The general quantum mechanical energy of the H-bond in Water-Urea is actually much lower than the H-bond in the Water-Water system. This is probably because the other atoms in the urea affect the interaction between the oxygen atom and hydrogen atom.

Conclusion

The hydrogen bond between waters is best formed when the orbital overlap (S_{ij}) of the hydrogen atom and oxygen atom is negative. There is a minimum at a distance between heavy atoms (non hydrogen) of about 3 angstrom, where the molecule system is in the most stable situation. The urea-water H-bond is stronger than water-water which may help to explain some of its properties such as having a high solubility

Reference

Northwest Computational Chemistry Package (NWCHEM 5.1.1)
Extensible Computational Chemistry Environment (ECCE)

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