Molecular Geometry

In order to understand the specific geometry of even the simplest molecules experimentation is necessary as well as some detailed knowledge of quantum mechanics. One can, however, make some reasonable predictions based on some simple rules:

- Electrons within each shell come in pairs with opposite spin (note that *not* all pairs within a given shell have the same energy).
- The pairs of electrons within a given shell will naturally repel one another and thus seek to be as far away as possible from one another.
- Electrons which form covalent bonds will tend to be found between the atoms which they are bonding.

Because there are surprises hiding everywhere, those who do not have a good familiarity with chemistry should focus on the symmetry aspects and perhaps those with more background in chemistry can explain some of the theories of how the constituent atoms bond with one another in the different substances: questions involving bonding issues are marked with stars. Of particular interest here is the "hybridization" phenomenon where normally distinct orbitals "mix" to form "hybrid orbitals" of different kinds.

For the symmetry addressed in these questions, consider the nucleii of the different atoms in each molecules– in other words, for water in making a model you would plot three points, the oxygen nucleus and the two hydrogen nucleii. Of course one cannot ignore the electrons in trying to determine what structure the nucleii will form!

1. Returning to the molecules considered in the previous problem set, we would like to describe the geometry and symmetry of some well known molecules. We will start with carbon dioxide

***a*.** Which electrons (that is which orbitals) of the carbon atom bond with each oxygen atom? Be precise since the four electrons in the second shell of the carbon atom are *not* in principle interchangeable. What is the most "symmetric" way of dealing with this problem?

b. Draw a picture or make a model of the carbon dioxide molecule.

c. What are the symmetries of the carbon dioxide molecule?

2. Here we consider ammonia, NH_3, and methane, CH_4.

***a*.** How does the nitrogen atom bond with the hydrogen atoms in ammonia?

b. Do you expect to see a true tetrahedron in ammonia, with the four vertices given by the nucleii of the constituent atoms? How would you expect the shape of ammonia to compare to that of phosphine, PH_3? Why? What are the symmetries of these molecules?

c. For methane, how does the carbon atom bond with the four hydrogen atoms? Would you expect to see a true tetrahedron (with vertices given by the hydrogen nuclei)? Why? What are the symmetries of methane?

3. Benzene has chemical formula C_6H_6.

a. Are there different ways in which this chemical formula can be realized as a stable molecule (remember that with this formula the carbon atoms should be interchangeable with one another and similarly for the hydrogen atoms)?

b. What are the symmetries of benzene?

c. What happens to the symmetry if you replace one of the hydrogen atoms with a Fluorine atom? What if you replace two of the hydrogen atoms with Fluorine atoms? Explain how studying the corresponding molecules can be used to *confirm* your hypothesis about the structure of benzene.

4. One very important concept in chemistry is that of *chirality*. Chiral molecules have no planes of symmetry, that is they are not superimposable with any mirror image of themselves.

a. Find all planes of symmetry of methane, CH_4.

b. Find all planes of symmetry of chloromethane, CH_3Cl.

c. Find all planes of symmetry of dichloromethane, CH_2Cl_2.

d. Can you turn the methane molecule into a chiral molecule by substituting different atoms for the four hydrogen atoms in methane?