

Practical quantum chemistry today involves using complicated computer programs. Some very sophisticated commercial molecular modeling packages have been developed which, among other options, use quantum mechanics to determine a range of molecular properties. Some require large computers, but much can be done on PC's. Although most of this course focuses on the theories and formal mathematical tools of quantum chemistry as applied to molecular spectroscopy, it is important to see some of these modern computational tools.

The department owns a number of copies of the molecular modeling package **PC-Spartan (ES)**. Spartan starts with a graphical molecule building unit, where you to construct a molecule, specifying the connectivity. Quite large and complicated molecules can be built. Then you can do a quick calculation to minimize the structure: finding the equilibrium geometry. Different kinds of structural calculations may then be performed: empirical, semi-empirical, or *ab initio*.

**Molecular Mechanics** (empirical) methods calculate energies and other molecular properties from **force fields**: sums of relatively simple terms for stretches, bends, and other interactions. Parameters in these force fields have been carefully chosen to do a good job of fitting large sets of experimental data. Force field calculations involve no quantum mechanics. Details of the force fields differ from package to package. Calculations using empirical force fields are important tools in the pharmaceutical industry. Spartan's initial energy minimization uses an empirical force field. Our version of Spartan has **MMFF** and **SYBYL** force fields.

**Semiempirical calculations** use approximate quantum mechanical methods to solve the Schrodinger equation, avoiding some problems associated with a large number of electrons by making empirical approximations for certain terms in the quantum equations. PC-Spartan includes three semiempirical methods: **AM1**, **PM3** and **MNDO**. We will not work with these.

**Ab initio** ("from the beginning") calculations make no empirical approximations to the quantum mechanical equations, solving the Schrodinger equation directly. Approximations are made; we will learn about these in class. These calculations are computationally intensive, and are practical on small computers for fairly small molecules only. The PC version of Spartan we have does just one kinds of *ab initio* calculations: **SCF**. Geometries and forces are often reasonably accurate, but energies may be less reliable. Seven basis sets of increasing complexity are in this version of Spartan: from **STO-3G** to **6-311+G\*\***.

### YOUR PROJECT

Each of you will choose three molecules: one diatomic, one small polyatomic, and one somewhat larger polyatomic. A list of possibilities is below; no two people should work on the same molecule. Tell me your choice soon: first come, first served (sign up sheet on my office door). You may make suggestions not listed below. You may change later, if something more interesting develops, or if your molecule is giving you special problems. Note that I have not studied all of these, so I do not know what challenges may present themselves. You may also find that you will want to look at and compare with related molecules to gain more understanding.

Early in the term, in order to become familiar with the program, use PC-Spartan's molecule builder to build each molecule. Examine the molecule using various representations, and move it around and rotate it so you can see it from various angles. Minimize the structures, and report the geometries. You are encouraged to collaborate and help each other. Print a picture of each molecule and **hand them in by November 2**. Save the files.

Later in the semester, after we have studied a bit more about quantum chemistry, orbitals, SCF, and basis sets, you will carry out various full *ab initio* calculations on your molecules.

**Choosing your molecules.** Ions and radicals as well as atoms with odd numbers of electrons are sometimes more challenging than neutral molecules with an even number of electrons. Double bonds and conjugation often make molecules more interesting. Listed below are some suggestions. Include only elements with  $Z < 18$ : every electron adds to the size of a calculation.

**Diatomics:**  $\text{Li}_2$ ,  $\text{Be}_2$ ,  $\text{B}_2$ ,  $\text{C}_2$ ,  $\text{N}_2$ ,  $\text{LiH}$ ,  $\text{LiF}$ ,  $\text{HF}$ ,  $\text{CO}$ ,  $\text{CN}^-$ ,  $\text{BeO}$ ,  $\text{BeH}^+$ ,  $\text{CO}^+$ ,  $\text{N}_2^+$ ,  $\text{OH}^-$ ,  $\text{OH}$  (radical),  $\text{NO}$ ,  $\text{NO}^+$ ,  $\text{NaH}$ ,  $\text{NaF}$ ,  $\text{HCl}$ ,  $\text{LiCl}$ ,  $\text{MgO}$ , etc.

**Smaller molecules (three to five atoms):** nitrous acid, nitrite ion, nitrate ion, nitrous oxide, ammonia, the ammonium ion, formaldehyde, formyl fluoride, water, methyl radical, methane, hydrosulfuric acid, acetylene, hydrogen peroxide, etc.

**Intermediate sized molecules (five to 10 atoms):** methanol, silane, ethylene, ethane, propane, propene, cyclopropane, nitric acid, glycine, sulfuric acid, the sulfate anion, phosphoric acid, the phosphate ion, acetone, various boranes, and many more!

For your own interest and amusement, feel free to build and look at larger molecules.

### Scope of the Project

Everyone will ultimately carry out SCF calculations on the diatomic and the small molecule, looking at the resulting orbitals and energies. Try to relate these to what you know about the molecule. With your intermediate-sized molecule, you may choose to focus on one or two of the avenues below, or to explore something else of your own design.

What do the orbitals look like? What is the best way to represent them (isosurfaces, contour maps, solid vs. frame etc.)? What can you learn from looking at orbitals?

Electron density maps: what do they tell you? Can they explain how and where molecules react? How are they best represented? What about displaying electronic potential as a property superimposed on an electron density map?

Reliability of calculated values: geometries, energies, dipole moments. (You can calculate the bond energy of a diatomic by forcing the bond length to become very large, comparing that energy with the equilibrium value.) Ring strain energy. Conformational energy changes. Comparing energies of tautomers.

Constructing a *quantitative* MO energy level diagram.

Comparing basis sets in SCF calculations.

Vibrational spectra (smaller and intermediate molecules): what are the frequencies? Are they accurate? What do the corresponding motions look like? How do they change upon isotope substitution?

A written report of your results is due on the last day of class. The report should be typed with no more than ten double spaced pages of text. You are encouraged to include tables and a modest number of figures. You will also be asked to give a 5 minute oral report on some interesting aspect of one of your molecules. While you are each looking at different molecules, I encourage you to help each other out, with running the program, framing the questions, and interpreting the results.

**Logistics.** PC-Spartan is found on all computers in the chemistry computer lab, 613 Altschul. Running this expensive program requires a hardware key, so it cannot be used elsewhere. We will try to facilitate off-hours access later in the semester.

While the project reports are due at the end of the term, it is essential to start early to become familiar with the program. Please note that these computers may be unavailable some afternoons, when laboratories in session in 615 may need them.

### **References (available in computer room)**

*PC Spartan Tutorial and User's Guide* (Wavefunction, Inc. 1996).

W.J. Hehre and J.E. Nelson, *Introducing Molecular Modeling into the Undergraduate Chemistry Curriculum* (Wavefunction, Inc., 1997).