

A Brief Introduction to Computational Chemistry with Spartan

This guide will serve two purposes. The first is to provide you with some very basic terminology relevant to computational chemistry, and the second is to help you learn how to make Spartan produce the results you want. The latter is fairly straightforward, since the program is run by a more-or-less friendly and intuitive graphical interface, but the former can be a bit daunting at first.

What Can Computational Chemistry Do?

Computational chemistry uses underlying laws of atomic physics to predict the chemical and physical behaviour and properties of molecules and molecular systems, by doing lots and lots of tedious mathematics.

Types of Calculation

There are three basic types of calculation that be performed, a *single-point calculation*, a *geometry optimization*, and a *frequency calculation*, each of which provides its own information about a system.

Single-point calculations determine the electronic energy of a specific arrangement of atoms, and require relatively little computational time. Depending on the method chosen for the calculation, this calculation can predict properties such as

- atomic charges
- ionization energy
- electronic energy levels
- dipole moment
- spectroscopy
- molecular orbitals

Comparisons of the energies of different structures can provide information such as bond strengths, or the energy changes and barriers associated with conformational changes or chemical reactions.

Geometry optimizations determine the *minimum* energy structure of a system, by performing an iterative series of single point calculations and adjusting the geometry at each step until a lowest-energy arrangement is found. For example, one could perform single-point calculations on any staggered or eclipsed conformation of butane and determine its energy, but no one such calculation would tell you whether your chosen conformation was an energy minimum or maximum. However, a correctly-performed optimization would result in the lowest-energy *anti* conformation, regardless of the initial structure provided. An optimization necessarily requires far more computational resources than just a single-point determination. The same properties can be predicted as with a single point calculation, as well as calculated bond lengths and angles of the most stable geometry. In addition, such calculations can be used to determine the energy and properties of energy *maxima* such as transition state structures.

Frequency calculations calculate the various modes of nuclear vibrational motion within a molecule. In addition to predicting the infrared spectrum of a compound, such a calculation is necessary to determine zero-point and thermal corrections to the internal energy, enthalpy, and free energies of a system. Only high-level methods are capable of performing frequency calculations, although they tend to require less computational time than a full optimization.

Computational Methods

There are different ways to approach any of the above problems, but the more accurate the approach the longer it will take. The two general methods are Molecular Mechanics

and Electronic Structure methods, the latter including Semi-Empirical and Ab Initio calculations. Molecular mechanics methods base calculations on simple classical descriptions of electrostatics, while electronic methods employ quantum mechanics to find approximate solutions to the Schrödinger Equation.

Molecular Mechanics uses laws of classical physics and some particular set of empirically-determined parameters for each atom to calculate the energy of a system. For example, a given MM method “knows” that sp^3 and sp^2 hybridized C atoms have different preferred geometries and bond lengths, and so attempts to position nearby nuclei accordingly. It does not treat electrons explicitly, and so can only provide information related to nuclear geometry. Examples: MM+, Amber, Charmm

- Advantages: exceedingly fast, very useful for large macromolecules (e.g. proteins)
- Disadvantages: only achieves good results for systems containing atoms for which it has parameters (e.g. most MM methods handle transition metals very poorly, if at all), no information about electron-based properties

Semi-Empirical methods use some empirical parameters derived from experimental data to simplify the calculation. Generally, the parameter sets include very approximate functions for various atomic orbitals, from which molecular orbitals are then constructed. These approximate AOs are generally invariant for a given atomic number, so that a semi-empirical calculation thinks that every carbon atom in every molecule has exactly the same atomic orbital functions. Examples: Extended Hückel, AM1, MINDO/3, PM3

- Advantages: very fast, good for qualitative understanding of MOs, reasonably quantitative predictions of energies/structures for systems with valid parameter sets
- Disadvantages: useful only for systems closely related to those from which parameters have been derived, no information about inter-electron interactions (e.g. high-spin vs low-spin, excited states)

Ab Initio methods use no empirical information. Instead, they are based solely on the “first principles” of quantum mechanics: the Schrödinger Equation and the values of some fundamental constants. (Ab initio is Latin for “from the beginning”, referring to these beginning principles.) However, these methods use some approximations (of varying rigour) in order to solve the equations. Ab initio can (potentially) provide meaningful results for any chemical system of any size, limited only by how long you are willing to wait for the results. An ab initio technique also requires a choice of *basis set*, a collection of mathematical functions that represent the atomic orbitals used in the calculation. Basis sets vary in complexity, with the larger sets involving both a greater number of atomic orbitals for each atom and a greater number of independent functions making up each orbital; again greater accuracy requires more computer time.

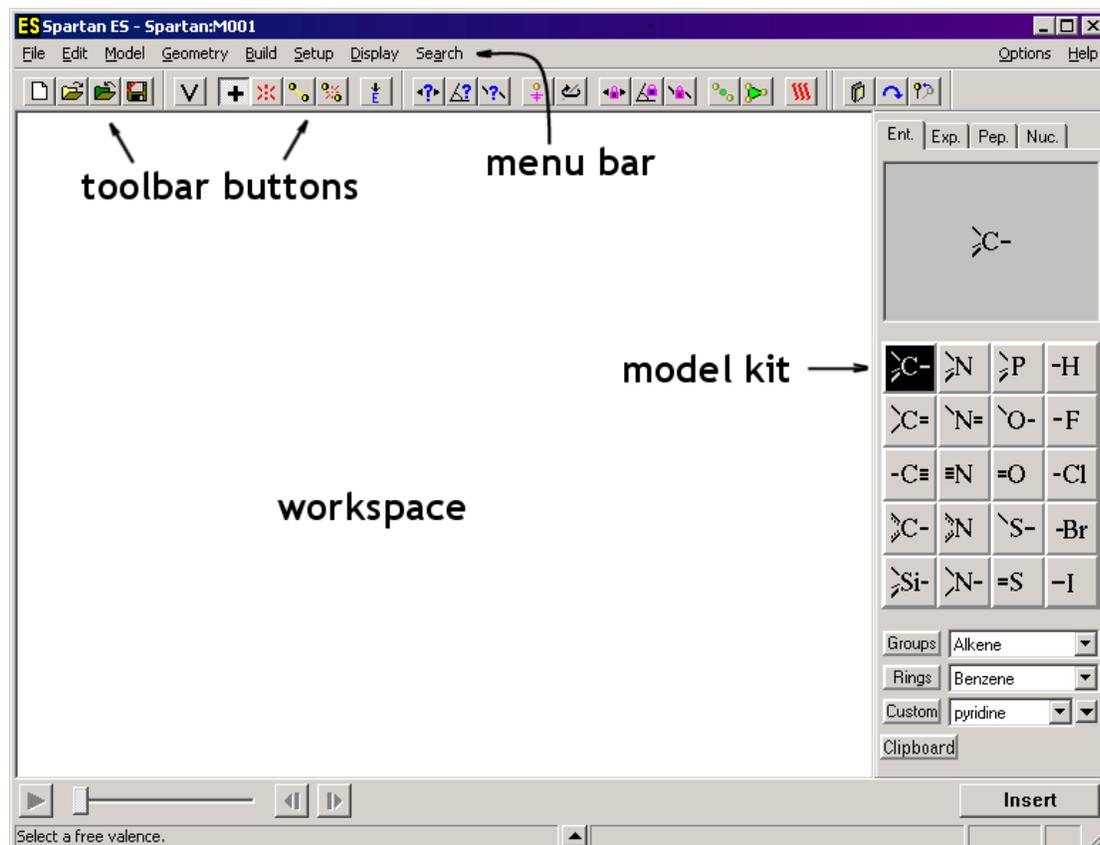
Examples: Hartree-Fock

- Advantages: far more rigorous than semi-empirical, computes many properties beyond energies, structures, and simple orbital densities
- Disadvantages: computational time and expense

An Introduction to Spartan

Remember, when in doubt, there's always Help, which gives you access not only to some quick links, but also to the entire Tutorial and User's Guide. If you prefer your help in a hardcopy, you can sign out a copy of that Guide from Steve.

Screen Features



General Mouse / Keyboard Use

The toolbar buttons provide access to selected functions also found under the **File**, **Build**, **Geometry** and **Search** menus. If they don't have text and you forget what they do, just hover the mouse over one for a second.

New	Break Bond	Constrain Angle
Open	Minimize	Constrain Dihedral
Close	Measure Distance	Define Point
Save As	Measure Angle	Define Plane
View	Measure Dihedral	Align Molecules
Add Fragment	Freeze Center	CSD
Delete	Set Torsions	Transition States
Make Bond	Constrain Distance	Tautomers

Mouse/Keyboard combinations to select and manipulate structures		
keyboard	left button ^a	right button ^a
–	select, X/Y rotate	X/Y translate
Shift	range selection, Z rotate	zoom ^b
Control	multiple selection, global X/Y rotate ^b	global X/Y translate
Control + Shift	global Z rotate ^c	zoom ^b
Alt	group selection, bond rotation	bond stretching
Control ("Build" mode)	fragment X/Y rotate	fragment X/Y translate
Control + Shift ("Build" mode)	fragment Z rotate	zoom ^b

a) Left and right buttons together with no modifier keys are used for defining a section box.

b) Zoom is always applied to all open molecules and fragments.

c) Global rotations can be either molecule or screen centered. This is controlled by **Global Rotate** in the **Preferences** dialog (**Options** menu).

Selection

Clicking the **left** button selects objects (e.g. an atom or bond). Using the left and right buttons together can define a selection box for copying/cutting, or to select designated parts of a molecule. **Shift + left** button allows for selection of multiple objects (such as atoms and bonds) over a continuous range, while **Ctrl + left** button allows for selection of multiple discrete objects. **Alt + left** selects and entire molecular fragment.

Manipulation

Dragging the mouse in the screen manipulates objects. **Left** and **Shift + Left** rotate a selected object. **Right** moves the object side to side, **Shift + Right** zooms in and out. These manipulations usually apply to one object at a time, or to the full set of fragments which make up the molecule being constructed when in "Build" mode. If the **Ctrl** key is depressed, then the manipulations apply to *all* molecules on the screen ("globally"), or to a *single* selected fragment in "Build" mode.

Building Structures

- 1) Click on the *New* button or select *File, New*. The Model Kit appears on the right, with the Entry Tab selected. You can select from various common atomic fragments on the table, or select common functional groups or ring systems from the popup menus below. If you're really adventurous, you can select the Expert Tab, which affords you a periodic table and higher coordination numbers. Clicking in the workspace builds your selected fragment, with unused valences (uncapped bond positions) shown in yellow. Clicking on a free valence will build the new fragment at that position. If you make a mistake, *Edit, Undo* or Ctrl-Z will undo it. *Edit, Clear* will make the whole molecule go away.
- 2) Build the C and O skeleton of ethylphenylketone, CH₃CH₂COC₆H₅. You can do that one atom at a time, but it's faster to make use of the Groups and Rings popup menus. You do not need to draw each individual H atom. Once done, select *Build, Minimize* (or click  in the toolbar) to find a crude minimum-energy configuration. In the lower right are displayed a name and point group for the compound.

- 3) Select *Build, View* (or click  in the toolbar) to see the completed structure. The unused valences are replaced automatically with H atoms. (The Model Kit disappears. If you want it back, select *Build, Add Fragment* or click .) One after the other, look at different representations of the compound by selecting various options in the *Model* menu: *Wire, Ball and Wire, Tube, Ball and Spoke, Spacefilling*.
- 4) To calculate a minimum energy geometry for the complex, select *Setup, Calculations...* and choose the following items from the popup menus: Calculate: **Equilibrium Geometry with Hartree-Fock, 3-21G(*)**. Then click *Submit*.
- 5) Choose a filename and location to store the calculation results. If in doubt, the desktop is a good place. Click *Save*. You should get a notification that the calculation has started.
- 6) This might take minute or two. If you're bored, you can select *Options, Monitor*, and then select your calculation in the upper window. The lower window shows you what the computer is thinking about, but it's pretty cryptic. Eventually, you get a notification that the calculation is finished. Click *OK*.
- 7) Select *Geometry, Measure Distance* (or click ). At the bottom left, you are asked to select two atoms; once done, the distance between them is displayed at bottom right. You can select two bonded atoms with one click by selecting the connecting bond. You can measure angles and dihedral angles in a similar manner.
- 8) Select *Display, Properties*. A box pops up telling you the calculated total energy,* the HOMO and LUMO energies, the dipole moment, etc. If you select the dipole moment box, an arrow appears on screen displaying the direction of the dipole.
- 9) Select *Setup, Surfaces* and click *Add...* to display the *Add Surface* dialog. Choose the following surfaces, hitting *OK* after each one.
 Surface: *density*, Property: *potential* (an electrostatic potential map)
 Surface: HOMO (Property is dimmed out)
 Surface: LUMO (Property is dimmed out)
- 10) Select *Setup, Submit* to generate the surfaces. When complete, you can click the yellow box by each surface in the Surfaces box. On the electrostatic surface, red indicates strongly δ^- and blue is strongly δ^+ . Click on the surface to select it, and in the lower right you can control its appearance – Transparent is very cool. Note that the LUMO is π^* on the CO group, and also π^* through the aromatic ring.

There are lots of other cool things Spartan can do, most of which are pretty intuitive once you get used to the interface. The Chem 220 lab manual will walk you through the basics of what you need to do for those labs, and the online version of the Tutorial and User's Guide available under the *Help* menu. When in doubt, you can always bug Steve. He's probably by his phone at 807-8751.

* Depending on the property and method you're looking at, there are a number of energy units you might be exposed to in Spartan. The convert as follows:

$$1 \text{ Hartree} = 1 \text{ Atomic Unit (au)} = e^2/a_0 = 27.2166 \text{ eV} = 627.510 \text{ kcal/mol} = 2625.5 \text{ kJ/mol}$$