

Physical Chemistry II Introduction to *Spartan* quantum-chemistry software

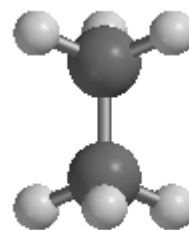
The instructions in this tutorial were tested on *Spartan06*, which is installed in room 318 of the UMD Chemistry building. Although the instructions are expected to work on the *Student Edition*, there may be some discrepancies regarding the graphical user interface. For more information at any point, please consult the *Spartan Student Edition Spartan Student Overview*, <http://downloads.wavefun.com/SpartanStudentOverview.pdf>.

Viewing and manipulating molecules

Start Spartan.

Download the Spartan ethane file, [ethane.spartan](#).

Use the File/Open menu in Spartan to open the ethane molecule.



Mouse control of a selected molecule:

select molecule click on the molecule (left mouse button)

rotate molecule press the left button and move the mouse

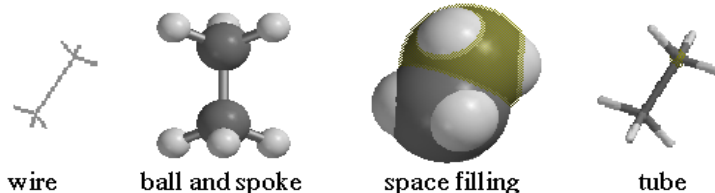
translate molecule press the right button and move the mouse

scale molecule press both the Shift key (mac: apple and option keys) and the right button and move the mouse vertically

Try translating, rotating and scaling the ethane molecule.


Spartan offers several “models” with which to view molecules.

Click on “Model” on the menu bar. Try a few of the renderings offered.



Distances, angles and dihedral angles can be measured.



To measure distance, either choose “measure distance” from the Geometry menu, or click on the  icon. Then select two atoms. The distance between the two atoms selected will

appear in the lower right-hand corner of the Spartan window. The C-C distance is 1.53 Angstroms.

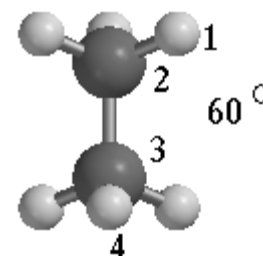


To measure an angle, either choose “measure angle” from the Geometry menu, or click on the angle button. Then select three atoms. The angle (first atom to second atom to third atom) will appear. Note that the order in which the atoms are selected matters.

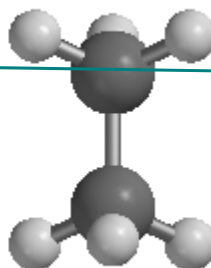
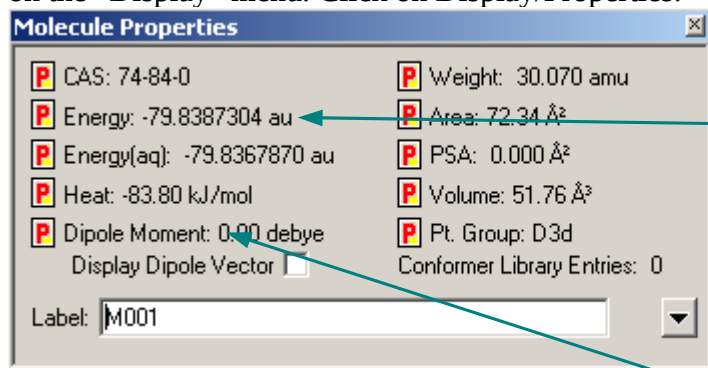
The H-C-H angle is 107.5°.



The dihedral angle formed by four atoms can be measured using either the Geometry menu or the dihedral-angle button, then selecting four atoms. The H-C-C-H dihedral angle shown at right is 60°.



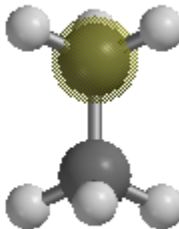
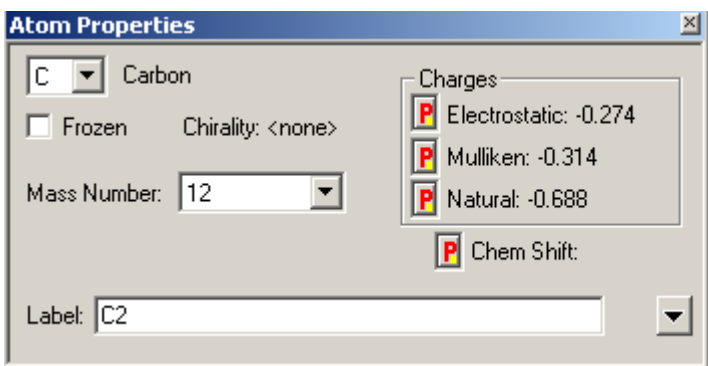
Energy, symmetry, dipole moment, and atomic charge are available in the Properties window found on the “Display” menu. Click on Display/Properties.



The energy of this molecule (within the method used to calculate it) is -79.8387304 Hartree. (The “au,” atomic unit, of energy is Hartree. 1 Hartree = 2625.5 kJ/mol.) Spartan recognizes the molecule as belong to the D_{3d} point

group. Note that Spartan, as other quantum-chemical codes, is not always able to recognize a molecule's full symmetry. The dipole moment is stated to be 0.0 Debye, which is correct for nonpolar ethane.


To see an atomic charge (or other atomic property) click on one of the atoms. Then Display/Properties will display properties of the atom rather than of the entire molecule. A carbon



atom in ethane, for example, has electrostatic charge -0.274 (in units of e, the electron charge).

Assignment 1: Download and open the file [HOOH.spartan](#), which contains hydrogen peroxide. Measure the O-O bond length and the H-O-O-H dihedral angle. Copy an image of the molecule to the windows clipboard simply by choosing “Copy” from Spartan's “Edit” menu, and then pasting the image into other software (e.g., Word, Excel, or Paint). Use Display/Properties to find the dipole moment of HOOH. Turn in an image of the molecule along with the O-O bond length, the H-O-O-H dihedral angle, and the dipole moment. (These are calculated values, not necessarily the same as experimental values.)

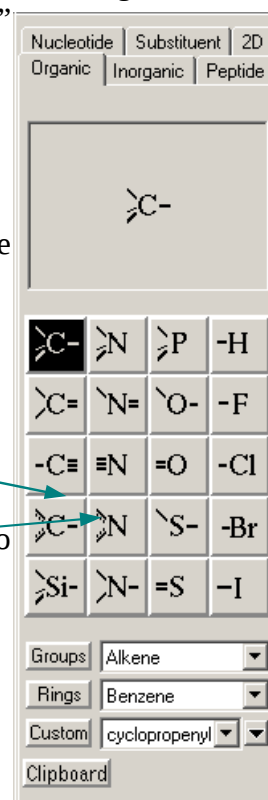
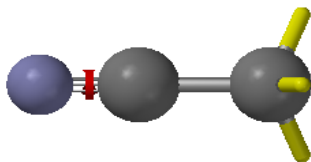
Building an organic molecule, acetonitrile (CH₃CN).

 Click on the “new file” button, or choose “New” on the File menu. A blank drawing area will appear, with molecule-building tools at the right. By default, the “organic” template opens. The “inorganic” tab will be described below.

Click on tetrahedral sp³ hybridized carbon from the library of atomic fragments. The fragment icon is highlighted, and a model of the fragment appears at the top of the model kit. Bring the cursor anywhere on Spartan's drawing window and click. An sp³ carbon with four free valences, which are represented by yellow lines attached to the atom, will appear.

Return to the build tools. Click on sp carbon. Then move the mouse to the drawing area and click on any one of the sp³ carbon's free valences. The sp carbon will bond to that free valence.

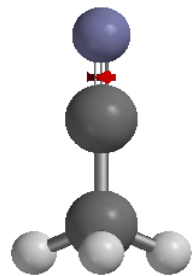
Finally, select a triple-bonding nitrogen atom from the build menu and add it to the triple-bonding free valence on the recently-added carbon atom.




Nucleotide	Substituent	2D
Organic	Inorganic	Peptide

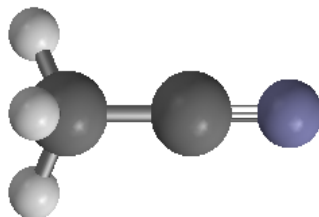
Groups: Alkene
Rings: Benzene
Custom: cyclopropenyl
Clipboard

All atoms except hydrogens have been added to the molecule.



Now click the “minimize” button, . That will add hydrogen atoms to satisfy free valences. It also adjusts bond angles and distances based on approximate molecular mechanics. The result is a good representation of acetonitrile. It can be refined with quantum-chemical calculations.

Close the drawing window by clicking on the “V” (view) button. (One can return to the build window by clicking on the “+” button.)



Set up a quantum-chemical calculation for acetonitrile, as follows. Click on Calculations on the “Setup” menu. A dialog box similar to that shown at right, which is from *Spartan06*, should appear.

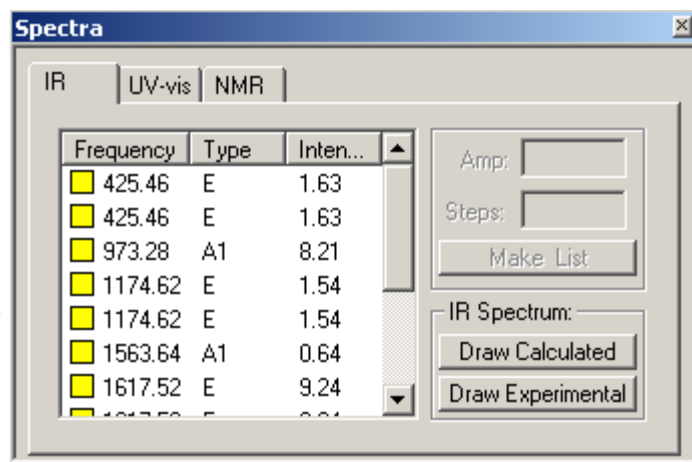
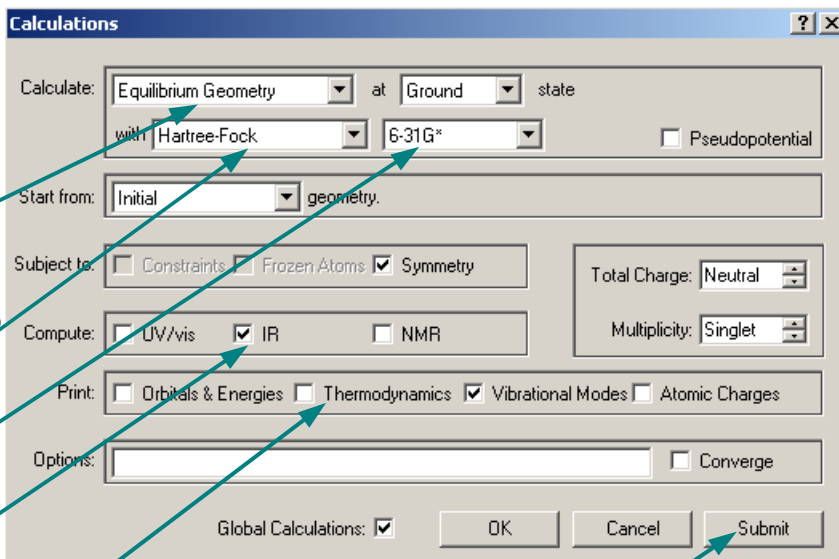
“Equilibrium geometry” is used to optimize bond angles, bond lengths, and dihedral angles so as to achieve the lowest energy possible with the selected method.

The Hartree-Fock method is a basic ab initio quantum-mechanical method. It is often used as a first approach to refining molecular properties. The basis set 6-31G* is a medium-size basis set suitable for initial work. If we want to calculate vibration frequencies, IR must be checked. To calculate thermodynamic functions (enthalpy, entropy, etc.) both IR and Thermodynamics must be checked. For this calculation, select the Hartree-Fock method with the 6-31G* basis set and IR frequencies.

When the calculations dialog box is ready, click on Submit (*not* “OK”). Unless you have already saved the molecule, Spartan will prompt for a file name. A name such as “acetonitrile” will work. Spartan will state that calculations have started. When calculations are done, Spartan will say so.

Display/properties will show Energy = -131.9275 Hartree.

Choosing Spectra from the “Display” menu will display a list of vibration frequencies, their symmetries (“Type”) and calculated infrared intensities. Frequencies are given in wavenumbers, cm^{-1} . The lowest-frequency vibration of acetonitrile is 425 cm^{-1} and is doubly degenerate. By clicking on the yellow box next to that frequency, you will see that it is a C-C-N bending mode. (To stop the animation, uncheck the yellow box.)



Assignment 2: Create acetonitrile. Optimize the geometry (“equilibrium geometry” calculation) using density functional theory (DFT) with the B3LYP functional and the 6-31G* basis set. Turn in two results: the charge on the nitrogen atom, and the highest vibration frequency (in cm^{-1}).

Building an Inorganic Molecule, OCS

Use File/New or the new-page icon to open a new drawing area. Choose the “inorganic” tab on the molecule-building toolbox.

When using the inorganic tools, first choose an atom (e.g., C) and then choose bonding valence and geometry. For example, to enter a carbon that will be bonded linearly to two substituents, choose “C” and the linear divalent pattern. Click in the drawing area. A divalent carbon atom will appear.

Choose singly-bonded oxygen. Bond it to one of the free valences on the carbon atom.

Lastly, choose singly-bonded sulfur and attach it to the remaining free valence on carbon.

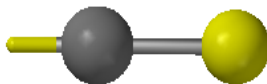
Clicking on the “Minimize” button will cause Spartan to attempt to improve the bond lengths and angle.

Should a molecule need alteration, there are three handy buttons.



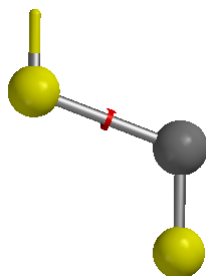
erase, make bond, break bond

The left button is to erase a free valence or an atom. To erase the oxygen, for example, first click on the erase button, then on the oxygen atom. That leaves a -C-S fragment.



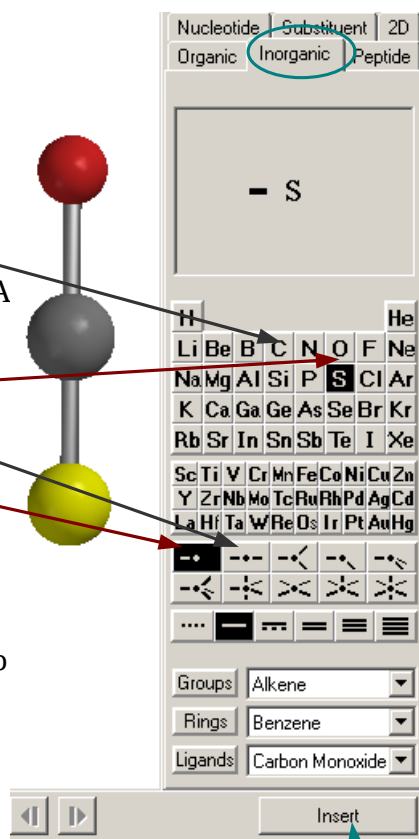
Now add a sulfur atom anywhere in the free drawing area. To do this, first select a sulfur atom and a bonding type. For practice, choose divalent sulfur, an intentional mistake. Then click on the “Insert” button. Then move the mouse to an open area and click to insert a sulfur atom. The result is shown at right, below.

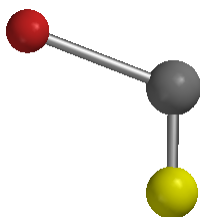
We can form a C-S sulfur bond. First click on the “make bond” icon, which is shown above. Then click on one of the free valences on the lone sulfur atom, and then click on the free valence on carbon. A bond will be drawn.




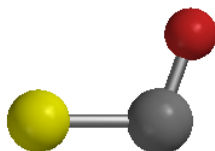
Click on the “erase” button, and then on the extra free valence on the sulfur atom. That will remove the dangling free valence.

It remains to change one of the sulfur atoms to oxygen. One way to do this is to choose an O atom from the inorganic build toolbox. Then double-click on one of the two sulfur atoms. That atom will be changed to an oxygen atom.



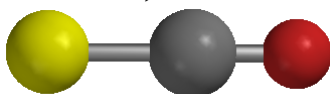


Finally, improve the geometry by using the “minimize” button.  Energy-minimizing the structure above improved bond lengths but the molecule remained bent.



Use the “V” (view) button to return to the general viewing screen. Open the Setup/Calculation dialog box. Set up a calculation: “Equilibrium geometry” using Hartree-Fock theory and the 6-31G* basis set.. Choose IR as well, so that vibration frequencies will be calculated. Submit the calculation.

At the end of the calculation, SCO will be linear, which is its equilibrium geometry.



View the vibration frequencies by using Display/Spectra. Note that all four frequencies are real numbers. If the linear geometry were unstable (i.e., if bending lowered the energy) at least one of the frequencies would be imaginary. In the list of frequencies, an imaginary frequency would be labeled with a lower-case “i.”

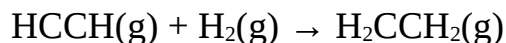
Spectra		
IR		
Frequency	Type	Intensity
566.52	A	19.77
566.52	A	19.77
889.18	A	46.77
2306.04	A	1181.69

Assignment 3: Build MgOH^+ . This cation is linear. To build a cation, proceed as for a neutral species. In the Setup/Calculations dialog box, specify the total charge on the species, “cation” in this case.

Use the Hartree-Fock theory with the 6-31G* basis set to calculate the equilibrium geometry and the vibration frequencies.

Turn in the following: An image of your MgOH^+ , the Mg-O bond length, and the lowest vibration frequency (in cm^{-1}).

Reaction thermodynamics, partial hydrogenation of acetylene.

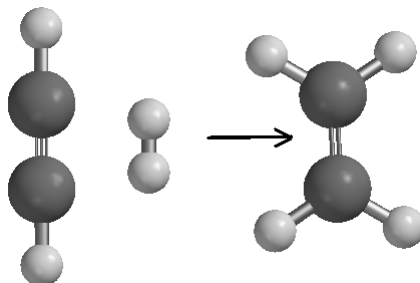


To calculate ΔE for a reaction, calculate the energy of each species individually. Each molecule's geometry must be optimized (i.e., "equilibrium geometry" calculated). The zero-point vibrational energy should be added to each molecule's electronic energy. It is essential that calculations for all molecules use the same theory and the same basis set. Then take the energy difference, products minus reactants. The resulting ΔE is the energy change at absolute zero temperature, $\Delta E(0)$. Let $E_i(0) = E_i + (\text{ZPE})_i$, the sum of the total electronic energy, E_i , and the vibrational zero-point energy of species i . The electronic energy E_i is the energy that is shown in the Display/Properties box. The zero-Kelvin reaction energy, $\Delta E(0) = \sum (v_i E_i(0))$, where v_i is the stoichiometric coefficient of species i .

The reaction enthalpy can be calculated at 298K. One first calculates the enthalpy correction $\delta H_i = H_i - E_i$, for each species. The correction δH_i includes zero-point vibrational energy. Then ΔH equals the sum, products minus reactants, of $E_i + \delta H_i$. $\Delta H_{298} = \sum [v_i (E_i + \delta H_i)]$.

Use this tutorial as an opportunity to calculate $\Delta E(0)$ and ΔH_{298} .

Begin by constructing acetylene, hydrogen and ethene. Having all three molecules on the Spartan screen at once works. Each is saved in its own file. Spartan will not confuse them. For each molecule, do an equilibrium geometry calculation using density functional theory with the B3LYP functional and the 6-31G* basis set. Check the IR and Thermodynamics boxes on the Calculations dialog box.



After a calculation finishes, choose “Output” on the “Display” menu. A text file that summarizes the calculation will be displayed. The output file for the hydrogen calculation is below.

```
SPARTAN '06 MECHANICS PROGRAM: PC/x86          129
Frequency Calculation
Reason for exit: Successful completion
----- lines deleted -----
Job type: Geometry optimization.
Method: RB3LYP          confirming that the DFT B3LYP method was used
Basis set: 6-31G(D)    which is the same as 6-31G*
---- lines deleted ----
```

```
Optimization:
Step      Energy          Max Grad.      Max Dist.
  1      -1.1754839      0.000557      0.001080
  2      -1.1754842      0.000148      0.000389
```

The last energy in the “Optimization” list is the final total electronic energy of the molecule, **in au.**

```
----- more lines deleted -----
Standard Thermodynamic quantities at 298.15 K and 1.00 atm
      Term          ZPE          Enthalpy      Entropy       Cv
      kJ/mol        kJ/mol        J/mol.K       J/mol.K
--  -----
Total Vibrations    26.6576      0.0000      0.0000      0.0000
Ideal Gas
Translation         3.7184      117.4876     12.4716
Rotation            2.4789      12.7643      8.3144
-----
Totals              35.3339     130.2519     20.7860
```

Zero-point vibration energy (ZPE)

Enthalpy correction, including ZPE

-----more lines were deleted -----

Below are data copied from the output files for hydrogen, acetylene, and ethene.

Note that the atomic unit of Hartree, multiplied by 2625.50, equals kJ/mol.

	energy (au)	E (kJ/mol)	ZPE (kJ/mol)	E+ZPE (kJ/mol)	$\delta H_i = H_{\text{corr}}$ (kJ/mol)	$H = E + \delta H_{\text{corr}}$ (kJ/mol)
hydrogen	-1.175484	-3086.24	26.66	-3059.58	35.33	-3050.91
acetylene	-77.325652	-203018.50	69.97	-202948.53	80.13	-202938.37
ethene	-78.587448	-206331.34	134.46	-206196.88	144.93	-206186.41
products- reactants		-226.60	37.83	$\Delta E(0) = -188.77$	29.47	$\Delta H = -197.13$

The $\Delta E(0)$ value calculated above is for zero temperature – for all molecules and their vibrations in their ground states. The ΔH value calculated above is for 298K. It includes (through statistical thermodynamics) vibrational, rotational and translational energy.

For comparison, ΔH_{298}° from tabulated enthalpies of formation at 298K is

$$\Delta H_{298}^{\circ} = 52.5 - 228.2 - 0.0 = -175.7 \text{ kJ/mol (CRC Handbook, 71st ed., page 5-10.)}$$

Some molecules have unpaired electron spins. A famous case is molecular oxygen, O_2 , which has two unpaired electron spins in its ground state. That is, the ground state of O_2 is a triplet state. Spin

multiplicity (singlet, doublet, triplet, and so on) is specified in *Spartan* in the Setup/Calculations dialog box.

In most molecules having an even number of electrons, the electron spins are paired and the spin multiplicity is singlet. Singlet multiplicity is *Spartan*'s default.

Any molecule that has an odd number of electrons (e.g., ClO_2) cannot have singlet multiplicity.

For a single unpaired electron, set the multiplicity to “doublet.”

Calculating reaction energy requires a method that includes electron correlation. The two commonly available methods are Moller-Plesset Perturbation theory (MP2) and density functional theory (DFT). MP2 theory is a post-Hartree-Fock theory comparable to DFT/B3LYP theory. MP2 may be slightly more robust. It is often less accurate.

Assignment 4: Calculate $\Delta E(0)$ for dichlorine monoxide reacting with molecular oxygen to form chlorine dioxide in the gas phase: $2 Cl_2O + 3 O_2 \rightarrow 4 ClO_2$. The spin multiplicity of dichlorine monoxide is singlet. Use second-order Moller-Plesset perturbation theory (MP2) with the 6-31G* basis set for all three molecules. Turn in images of the geometry-optimized molecules, their energies and zero-point energies, and the overall $\Delta E(0)$ for the reaction. Give all energies in kJ/mol.