Spartan Student Overview

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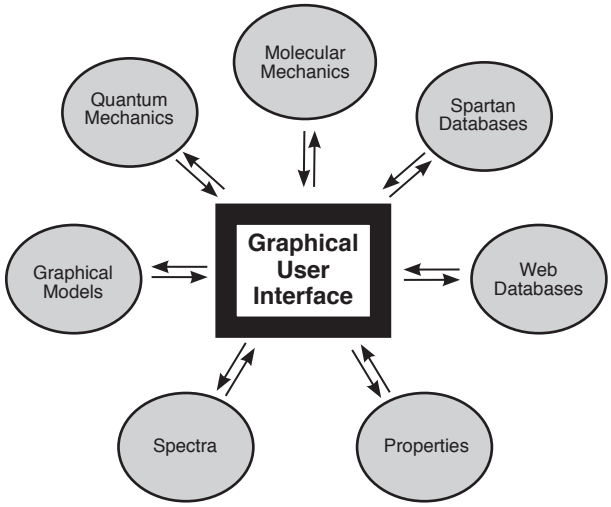
Chapter 1

Spartan Student

This chapter describes the architecture of ***Spartan Student****, focusing on the connectivity of computational, graphical and database components to the user interface. Available molecular mechanics and quantum chemical methods are enumerated and their utility and applicability assessed.*

Spartan Student comprises a series of independent modules tightly connected via a graphical user interface that is highly functional, yet elementary and uncluttered. It has been designed not only to greatly reduce the drudgery and possibility for human error associated with the preparation of input, but also to guide the interpretation of output. The interface is perhaps best viewed as an interactive and intuitive window into modern molecular mechanics and quantum chemical techniques.



Included in the interface are builders for organic, inorganic and organometallic molecules, polypeptides and polynucleotides, and a procedure for guessing transition states. Access to ChemDraw[1] is provided without having to exit the interface. Also accessible is a small (~5,000 molecule) subset of the Spartan Spectra and Properties Database (SSPD)[2] and (if desired) an equally small subset of the Spartan

Molecular Database (SMD)[3]. SSPD contains structures, infrared and NMR spectra as well as a wide variety of molecular properties obtained from the EDF2/6-31G* density functional model. The wavefunction is included, allowing quick access to a variety of graphical surfaces and property maps. SMD contains calculated structures and associated properties of molecules, each obtained from one or more of the theoretical models supported in ***Spartan Student***. On-line access to the Protein Data Bank (PDB)[4], a collection of >75,000 biological macromolecular structures, is provided. Experimental infrared spectra are available from the NIST website[5] and experimental NMR spectra from NMRShiftDB website.[6] Finally, compounds contained in the National Cancer Institute collection of molecules (CACTUS)[7] may be accessed via name search. Unlike SSPD, SMD and PDB, CACTUS contains no actual structure data, only connectivity information (allowing construction of an approximate structure).

Spartan Student's interface provides the gateway to a range of modern computational methods, the simplest of which is the MMFF molecular mechanics model. It is available to determine equilibrium geometries of molecules comprising upwards of several thousand atoms, and is the only computational technique that is applicable to biopolymers. It may also be employed to establish the best (lowest-energy) conformer of organic molecules.

Quantum chemical models are required to account for the geometries of transition states as well as for reaction and activation energies.[8] The simplest of these are semi-empirical molecular orbital models. The PM3 model, supported in ***Spartan Student***, has proven successful for determining equilibrium geometries including the geometries of transition-metal compounds, but it is not reliable for the calculation of the reaction or activation energies.

Hartree-Fock molecular orbital models are a mainstay of quantum chemical techniques, in particular, for determining equilibrium and transition-state geometries and reaction energies, and are supported in ***Spartan Student*** with the STO-3G, 3-21G, 6-31G* and 6-311+G** basis sets. Hartree-Fock models generally provide suitable descriptions of many types of reactions, but are ***not adequate*** for thermochemical

comparisons where bonds are broken or formed. In addition, they do not provide a proper account of the geometries of molecules incorporating transition metals. Supported in ***Spartan Student*** are the B3LYP and EDF2 density functional models and the MP2 Møller-Plesset model. All properly account for the energies of reactions that involve bond making and breaking and both density functional models (but not the MP2 model) properly account for the geometries of molecules incorporating transition metals. B3LYP, EDF2 and MP2 models are supported with the 6-31G* and 6-311+G** basis sets.

Spartan Student provides access to infrared spectra (MMFF, PM3, Hartree-Fock, B3LYP, EDF2 and MP2 models) and NMR spectra[9] (B3LYP/6-31G* and EDF2/6-31G* models only). These are available both as numerical data (vibrational frequencies, chemical shifts) as well as spectral plots. Experimental spectra may be read into ***Spartan Student***. In addition, internet access to experimental IR and NMR databases[5,6] is available allowing direct comparison with calculated spectra. ***Spartan Student*** allows a calculated infrared spectrum to be fit on-the-fly to an experimental spectrum, using both a multiplicative scale of calculated frequencies and peak width at half height as parameters. Also provided is an empirical correction to ^{13}C NMR chemical shifts.

Spartan Student provides a variety of graphical tools to assist in interpreting the results of calculations. These include molecular orbitals, electron and spin densities, local ionization potentials and electrostatic potentials that can be displayed as surfaces, slices and property maps. ***Spartan Student*** provides the ability to distinguish accessible and inaccessible regions on a density surface and on property maps based on this surface. Animations can be created and used to depict conformational changes or the progress of chemical reactions. Animations can be saved as QuickTime files.[10]

1. ChemDraw is not included with ***Spartan Student***, but may be obtained from CambridgeSoft (www.cambridgesoft.com). Seamless access to ChemDraw is not available in the Macintosh version although both Windows and Macintosh versions are able to read ChemDraw files.
2. The full Spartan Spectra and Properties Database contains ~110,000 entries from the EDF2/6-31G* density functional model and is available to license. Contact info@wavefun.com for more information.
3. The full Spartan Molecular Database contains ~150,000 molecules, each with up to 10 theoretical models and is available to license. Contact info@wavefun.com for more information.
4. PDB web reference: http://www.rcsb.org.
5. NIST web reference: http://webbook.nist.gov
6. NMRShiftDB web reference: http://nmrshiftdb.ice.mpg.de
7. CACTUS web reference: http://cactus.nci.nih.gov
8. Full discussion and assessment of the specific molecular mechanics and quantum chemical models available in ***Spartan Student*** is provided in: W.J. Hehre, ***A Guide to Molecular Mechanics and Quantum Chemical Calculations***, Wavefunction, Irvine, 2003. This is available as a PDF on Wavefunction's website (www.wavefun.com). See also: W.J. Hehre, L. Radom, P.v.R. Schleyer and J.A. Pople, ***Ab Initio Molecular Orbital Theory***, Wiley, New York, 1986; Y. Shao, L.F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S.T. Brown, A.T.B. Gilbert, L.V. Slipchenko, S.V. Levchenko, D.P. O'Neill, R.A. DiStasio Jr., R.C. Lochan, T. Wang, G.J.O. Beran, N.A. Besley, J.M. Herbert, C.Y. Lin, T. Van Voorhis, S.H. Chien, A. Sodt, R.P. Steele, V.A. Rassolov, P.E. Maslen, P.P. Korambath, R.D. Adamson, B. Austin, J. Baker, E.F.C. Byrd, H. Dachsel, R.J. Doerksen, A. Dreuw, B.D., Dunietz, A.D. Dutoi, T.R. Furlani, S.R. Gwaltney, A. Heyden, S. Hirata, C-P. Hsu, G. Kedziora, R.Z. Khalliulin, P. Klunzinger, A.M. Lee, M.S. Lee, W.Z. Liang, I. Lotan, N. Nair, B. Peters, E.I. Proynov, P.A. Pieniazek, Y.M. Rhee, J. Ritchie, E. Rosta, C.D. Sherrill, A.C. Simmonett, J.E. Subotnik, H.L. Woodcock III, W. Zhang, A.T. Bell, A.K. Chakraborty, D.M. Chipman, F.J. Keil, A.Warshel, W.J. Hehre, H.F. Schaefer, J. Kong, A.I. Krylov, P.M.W. Gill and M. Head-Gordon, ***Phys. Chem. Chem. Phys.,*** **8**, 3172 (2006).
9. Chemical shifts only. HH coupling constants may be evaluated empirically.
10. QuickTime is a multimedia framework developed by Apple, Inc.

Chapter 2
Operating *Spartan Student*

This chapter describes the general operating features of ***Spartan Student****.*

Opening and Exiting *Spartan Student*

To open on Windows, *click* on the **Start** button, then *click* on **All Programs**, and finally *click* on ***Spartan Student*** (or *double click* on the ***Spartan Student*** icon on your desktop). To open on Macintosh, *double click* on the ***Spartan Student*** icon in the Applications Folder. To exit, select **Exit** from the **File** menu (select **Quit Spartan Student** from the **Spartan Student** menu on Mac), or *click* the **Close** button ( ) at the top right (top left on Mac) of the ***Spartan Student*** interface.

Menus

Program functions may be accessed using pull-down menus under the headings in the menu bar, for example, the **Setup** menu.

File	Allows you to create a new molecule or read in a molecule that you have previously saved, to read in an experimental IR or NMR spectrum, to retrieve the structure, properties and IR and NMR spectra from a molecule in ***Spartan Student's*** database from its name, to retrieve a molecular structure from the National Cancer Institute (CACTUS) Database, to retreive a protein structure from the Protein Data Bank, to print, and to make QuickTime movies.
Edit	Allows you to transfer information to and from the clipboard, to undo the last operation, to find text strings, to center molecules on screen, and to delete the active molecule.

Model	Allows you to control the style of your model, to display labels on atoms, to display hydrogen bonds, to couple or decouple molecules in a multi-molecule file, and to display a Ramachandran plot for a protein structure input from PDB.
Geometry	Allows you to measure and constrain bond lengths, angles and dihedrals, define points and planes, designate atoms to be frozen, align molecules, and define points and planes.
Build	Allows you to build and edit organic, inorganic and organometallic molecules, polypeptides and polynucleotides, provides access to ChemDraw™ (Windows only), and to estimate a transition-state geometry based on a library of reactions.
Setup	Allows you to specify the task to be performed and the theoretical model to be employed, to request IR and NMR spectra, to specify graphical surfaces and property maps and to submit jobs for calculation.
Display	Allows you to display text output, molecular and atomic properties, surfaces and property maps and IR and NMR spectra, as well as to access experimental IR, and NMR spectra over the internet. Allows you to present data in a spreadsheet and make plots from these data, and to compute reaction energies based either on your data or from entries in the database associated with ***Spartan Student***.
Options	Allows you to set display standards, specify the location of the database and monitor executing jobs.
Help	Provides access to on-line information about ***Spartan Student***.

A complete listing of menu functions is provided in **Appendix B**.

Icons

Icons access selected functions under the **File**, **Build,** and **Geometry** and **Display** menus, as well as other specialized functions.

File

 New
 Open
 Close
 Save
 Save As
 Access Database By Name

Build

 View
 Make Bond
 Minimize
 Add Fragment
 Break Bond
 Guess Transition State
 Delete

Geometry

 Measure Distance
 Constrain Distance
 Define Point
 Measure Angle
 Constrain Angle
 Define Plane
 Measure Dihedral
 Constrain Dihedral
 Align
 Freeze Center

Display

 Orbital Energies
 Spectra
 Plots

Additional Icons

 Post to Spreadsheet
 Guess Transition State
  Lock/Unlock Constraints
  Move Up/Down Dialog
 Play
 Pause
  Step

Mouse and Keyboard Operations

The following functions are associated with the mouse.

	button	
keyboard	**left**	**right**
–	selection, X/Y rotate, atom/ fragment exchange[a], fragment insertion[a]	X/Y translate
Shift	range selection, Z rotate	scaling[b]
Ctrl	global X/Y rotate[c]	global X/Y translate
Ctrl + **Shift**	multiple selection, global Z rotate[c]	scaling[b]
Ctrl (add fragment mode)	fragment X/Y rotate chirality invert[a,e]	fragment X/Y translate
Ctrl + **Shift** (add fragment mode)	fragment Z rotate absolute configuration invert[a,e]	scaling[b]

Ctrl + **Shift**[d] (Mac)	bond rotation	bond stretching
Alt (Windows)	bond rotation[d]	bond stretching

a) Requires *double clicking*.
b) Scaling is always applied to all open molecules and all fragments. The center mouse wheel may also be used to scale molecules.
c) Global rotations can be either molecule or screen centered. This is controlled by **Global Rotate** in the **Miscellaneous Preferences** dialog (**Preferences...** under **Options** menu; **Chapter 10**).
d) In **Add Fragment** mode with bond selected (red arrow visible).
e) For Macintosh, **Apple** (⌘) key replaces **Ctrl** key for chirality inversion.

Mouse/keyboard operations may be broadly separated into two categories: selection (picking) and manipulation (translation/ rotation).

Selection. The left button is used for selection of objects on screen and/or of menu items. Left and right buttons together are used to define a selection box for copying/cutting to the clipboard, as well as for multiple model selection. Together with the **Shift** key, the left button allows for selection over a range. Together with the **Ctrl** (**Control**) key, the left button allows for multiple selection. Both range and multiple selection apply not only to text items in lists, but to atoms and bonds in molecules as well. In add fragment mode (+), *double clicking* the left button on an atom leads to atom or fragment exchange. *Double clicking* on an atom with the **Ctrl** key depressed leads to inversion in chirality of the atom and *double clicking* anywhere on a molecule with both **Ctrl** and **Shift** keys depressed inverts the absolute configuration of the molecule. Given a structure on screen, *double clicking* on the background with a fragment, group, ring or ligand selected inserts it alongside (not bonded to) the current structure.

Manipulation. The left button is used for rotation and the right button is used for translation and scaling of objects on screen. With no keys depressed, the left mouse button gives rise to rotation about the X and Y (screen) axes, while the right mouse button gives rise to translation in the X and Y (screen) directions. Together with the **Shift** key, the left mouse button gives rise to rotation about the Z direction and the right mouse button gives rise to scaling. The center (scroll) wheel on the mouse may also be used for scaling.

The **Ctrl** key in conjunction with the left or right mouse buttons and (optionally) the **Shift** key, signifies a change in focus away from the default for the purpose of rotations and translations. Outside of add fragment mode, the default is focus on a single molecule (the selected molecule). Use of the **Ctrl** key changes focus to the entire set of molecules on screen, meaning that rotations and translations are carried out globally. In add fragment mode, the default is focus on the full set of fragments that make up the molecule being constructed, and rotations and translations refer to this set of fragments as a whole. Use of the **Ctrl** key changes focus to a single fragment (the selected fragment), and rotations and translations now refer only to this fragment.

In add fragment mode, use of the **Alt** key (Windows) or **option** key (Mac) with the left mouse button allows for rotation about a selected bond and, with the right mouse button, for changing the length of the selected bond.

Additional keys control various ***Spartan Student*** functions.

3	**3** selects red-cyan stereo display. Pressing again returns to non-stereo display.
Page Up, Page Down Home, End	Moves up (**Page Up**), down (**Page Down**), to the top (**Home**) and to the bottom (**End**) of the set of open molecules. Also, moves up and down pages in the **Output** dialog.
Insert	In add fragment mode only, inserts a new fragment on screen. This is accomplished by selecting the fragment from the model kit, holding down the **Insert** key and *clicking* on screen (**option** key on Mac). Insertion may also be accomplished by *double clicking* on the background following selection of a fragment.
Delete	Deletes a fragment, free valence, reaction arrow or the contents of a selection box. This is accomplished by holding down the **Delete** key and *clicking* on the fragment, etc.

Enter (**return** on Mac)	Required following text or data entry into spreadsheet or dialogs.

Selecting Molecules, etc.

Two or more molecules may be simultaneously displayed in ***Spartan Student's*** window. However, only one molecule may be selected. The selected molecule has access to all capabilities (molecule building, job setup and submission and text and graphical display and manipulation), while non-selected molecules may only be displayed as static images. The exceptions involve scaling and the use of the **Ctrl** key.

Selection of a molecule occurs by *clicking* on its structure model or on any of its associated graphical surfaces. This will also result in deselection of any previously selected molecule. The name of the document and the selected molecule's label appear at the top of the screen. Molecular properties for the selected molecule are available in the **Properties** dialog (**Display** menu). Atom, bond and surface display properties, and information about geometrical constraints may be accessed by subsequent *clicking* on an atom, bond, etc., associated with the selected molecule, following which it will be highlighted (colored gold). *Clicking* a second time on the selected atom, bond etc., resets the display to molecular properties. *Clicking* on another molecule results in display of molecular properties for that molecule.

Where the molecule belongs to a document with more than a single member, selection from among the different members in the document may be made using either the ◀| and |▶ buttons or the scroll bar at the bottom left of the screen. Alternatively, if the spreadsheet for the document is open on screen (see **Chapter 9**), selection can be made by *clicking* on the molecule label at the left of the spreadsheet. *Clicking* on ▶ at the bottom left of the screen animates the display of molecules in the document, that is, steps through them sequentially. This is useful for displaying a progression of graphical surfaces along a reaction coordinate. *Clicking* on ⏸ (that replaces ▶) stops

the animation. Animation speed is controlled from the **Settings Preferences** dialog (see **Chapter 10**).

Two or more molecules from the same document may be displayed at once (although only one may be selected). Molecules are marked for display by *checking* the box immediately to the left of the molecule label in the spreadsheet (**Chapter 9**).

Dialogs

Dialogs indicated by **...** following their reference in a menu are modal and must be dismissed before program operation can continue. All other dialogs may be kept open on screen, and different dialogs and/or several copies of the same dialog (each copy referring to a different molecule in a document or different documents) may be simultaneously open on screen.

Database

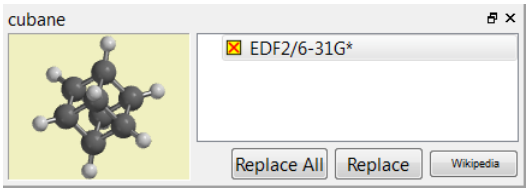
Included with ***Spartan Student*** is a small (~5,000 molecule) subset of the Spartan Spectra and Properties Database (SSPD).* This provides infrared and NMR spectra in addition to a variety of molecular properties obtained from the EDF2/6-31G* density functional model. More limited results for a wider range of quantum chemical models may be retrieved from an equally small subset of the Spartan Molecular Database (SMD). The SSPD and (optionally) SMD subsets may be accessed either by molecule name (see **Chapter 3**) or by molecule structure (see below).

The existence of the selected molecule in the database is signaled by its name being displayed at the bottom of the screen.

Details are provided by *clicking* on ▲ to the immediate left of the molecule name (it then changes to ▼). This brings up a dialog that comprises a viewing window on the left and the quantum chemical model(s) for which database entries exist on the left (only the EDF2/

* The SSPD is a growing collection of >110,000 organic molecules along with associated properties and 1R and NMR spectra data. Contact sales@wavefun.com for licensing options.

6-31G* model will appear unless the SMD subset is installed).



The 3D model may be rotated, translated and scaled using the usual mouse/keyboard commands (you need to position the cursor inside the viewing area). The model may be made to tumble automatically by *checking* the box to the left of **Replace All** at the bottom of the dialog. Model style may not be changed. Where the SMD subset is installed, a different database entry (corresponding to a different quantum chemical model) may be selected by *checking* the box to the left of the name of the quantum chemical model in the dialog.

The selected (on-screen) molecule may be replaced by the selected database entry by *clicking* on **Replace** at the bottom of the dialog. (Replacement can be undone by selecting **Undo** from the **Edit** menu; **Chapter 4**). Note that replacement overwrites all information except the molecule identifier (leftmost column of the spreadsheet) associated with the molecule being replaced. If desired, the molecule identifier can be changed to the molecule name by bringing up a spreadsheet (**Spreadsheet** under the **Display** menu; **Chapter 9**), and first *left clicking* to select, then *right clicking* inside the cell corresponding to the leftmost column and selecting **Rename Selected Using SSPD** from the menu that results.

In the event that the selected (on-screen) molecule belongs to a multi-molecule document, it is possible to replace all molecules in the document for which database entries for the specified level of calculation are available. This is accomplished by *clicking* on **Replace All** instead of **Replace**. A warning message is provided prior to replacement. Molecules in the document for which there are no database entries at the specified level of calculation are not affected. As with single molecule replacement, all information except the molecule identifier is replaced by that in the database. Molecule names from SSPD for all molecules in a document may be

substituted for the original molecule identifiers by first *left clicking* to select, then *right clicking* on the header cell of the leftmost column in the spreadsheet and selecting **Replaced Selected Using SSPD** from the menu that results.

Stereo Displays

Spartan Student supports red-cyan stereo. Red/blue glasses must be worn. To enter stereo mode, *press* the **3** key. *Press* again to return to non-stereo mode.

Changing Colors and Setting Preferences

Colors and **Preferences...** under the **Options** menu (**Chapter 10**) allow for changing default background and graphical object colors, and for setting (and resetting) program defaults, respectively.

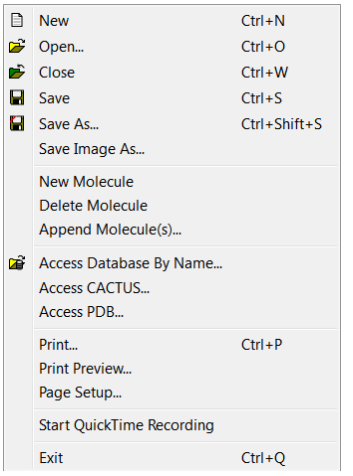
Monitoring and Terminating Jobs

Monitor under the **Options** menu (**Chapter 10**) allows for monitoring of executing jobs as well as for terminating jobs.

Chapter 3

The File Menu

*Operations under the **File** menu access model kits to build and edit molecules, and the file system to read and write both native and non-native files, import structures according to names contained in **Spartan's** internal database and the on-line National Cancer Institute CACTUS database, import protein structures from the on-line Protein Data Bank, print text and on-screen graphics, and create QuickTime movies.*



New (**)**

Brings up a model kit and clears the screen. Model kits are discussed in **Chapter 7**.

Open... (**)**

Opens a file that contains all information associated with a particular molecule (or list of molecules). In addition to native (.spartan and .spardir) files (documents), supported are files containing 2D drawings, 3D structures and 1D strings. Also supported are formats for experimental IR and NMR spectra. Non-native files are normally hidden from view, but may be seen by selecting **All Files** from the

Files of type (**All TEXT Files** from the **Enable** menu for Mac) menu at the bottom of the dialog.

Close ()

Closes the document containing the selected molecule, as well as the spreadsheet, graphics, plots, spectra and document specific dialogs. If the document has not previously been saved, a name is requested. If a previously-saved document has been altered, verification that the changes are to be saved is requested.

Save ()/ Save As... ()/Save Image As...

Saves the document containing the selected molecule ***exactly as it appears on screen***. Opening the document will bring it on screen exactly as it was last saved. If the document has not previously been named, **Save** behaves as **Save As...**. Documents may be either be saved in native format or in one of several alternative formats. Support is also provided for writing QuickTime (movie) files (see discussion later in this chapter). Selection is made under the **Save as type** (**Format** for Mac) menu in the **Save As** dialog. **Save Image As...** Allows for saving molecules as JPG, PNG, or BMP files as well as specifying resolution.

New Molecule

Brings up a model kit and clears the screen. This differs from **New**, in that the resulting molecule is appended to the end of the list associated with the molecule that is presently selected. Model kits are discussed in **Chapter 7**.

Delete Molecule

Deletes the selected molecule(s) from a document. Deleting of the last molecule in the document leads to an empty document.

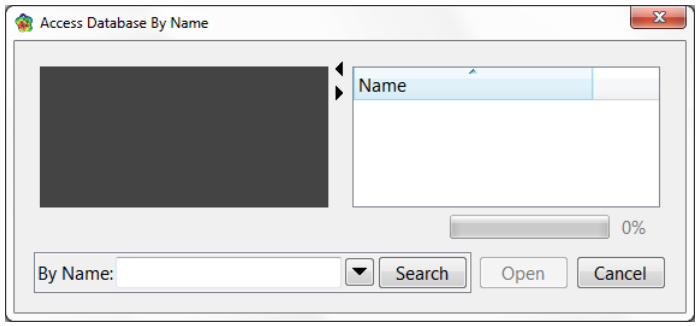
Append Molecule(s)...

Appends one or more documents onto the end of the document that contains the selected molecule. **Append Molecule(s)...** leads to a file

browser from which one or more documents need to be selected.*

Access Database By Name...

Included with ***Spartan Student*** is an ~5,000 molecule subset of the Spartan Spectra and Properties Database (SSPD).** The individual entries correspond to calculations from the EDF2/6-31G* density model and each includes the structure, gas and (estimated) aqueous phase energies, infrared and NMR spectra, as well as a variety of molecular, atomic and thermodynamic properties. The wavefunction is available allowing graphical surfaces and property maps to be computed on-the-fly. Selection brings up a dialog.



A name search is initiated by entering a name (or partial name) in the box to the right of **By Name:** at the bottom of the **Access Database by Name** dialog. The search will return all entries that

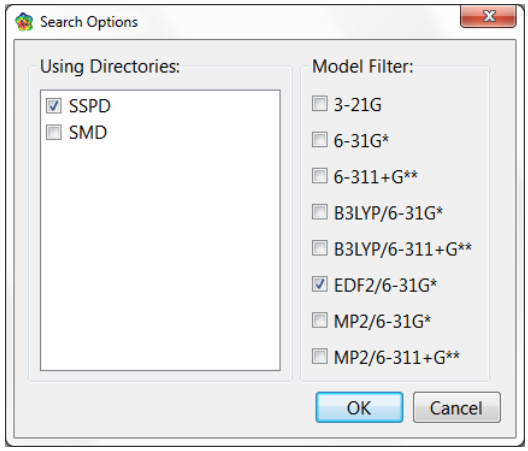
* Alternatively, molecules may be appended onto an existing document either by copy/paste operations using the clipboard or by *dragging* from an external window. Both require that the spreadsheet associated with the destination document be open on screen.
To copy a molecule open on screen onto the clipboard, first select (*click* on) it, and then select **Copy** from the **Edit** menu. Alternatively, *click* on its label in its spreadsheet (in the leftmost column), and then select **Copy** from the **Edit** menu. The latter permits several molecules to be selected (and copied) at once using the **Shift** and **Ctrl** keys in the usual manner. Once on the clipboard, the molecule or molecules may be moved to the destination list by *clicking* on an empty row header in the spreadsheet (for the destination document), and then selecting **Paste** from the **Edit** menu.
To copy a document from an external window, *drag* it onto the open spreadsheet (associated with the destination document) inside of ***Spartan Student***. Several documents can be *dragged* at once using the **Shift** and **Ctrl** keys in the usual manner.

** Available, but not installed in ***Spartan Student*** is an ~5,000 molecule subset of the Spartan Molecular Database (SMD). This provides less information about the individual molecules (spectra and thermodynamic properties are absent) but for most molecules at more than one theoretical model. This may be installed alongside of the SSPD subset, using the **Paths Preferences** dialog (see **Preferences** under the **Options** menu in **Chapter 10**). Contact info@wavefun.com to obtain the SMD (Student subset).

include whatever text string is entered into this box. For example, typing in ***toluene*** will not only result in toluene, but also molecules like para-toluenesulfonic acid and 4-chloro-2-fluorotoluene.

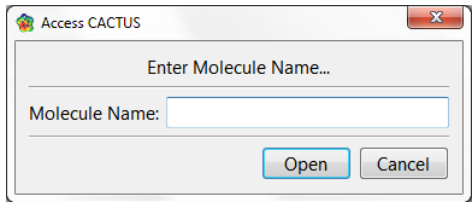
Following the search, one or more hits may be retrieved by selecting them from the hit list and then *clicking* on **Retrieve**. **Shift** and **Ctrl** keys are used in the usual way to select multiple entries from the hit list.

If (and only if) the SMD subset has been installed, it is necessary to specify which theoretical models are to be searched. This is done by *clicking* on ▼ to the right of the **Search** button and *checking* one or more entries in the dialog that results. *Click* on ✕ to close the dialog.



Access CACTUS...

Spartan Student provides on-line access to molecules contained in the National Cancer Institute CACTUS database. Selection gives rise to a dialog and request for a name.



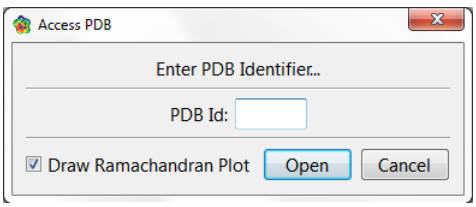
If the named molecule exists in CACTUS and if information is available regarding its structure, *clicking* on **Open** will return the structure resulting in display of a ball-and-spoke model. This will typically require a few seconds. If the named molecule does not exist

in CACTUS (an exact match is required) or if structural information is not available, a message will be displayed. Try again with another name or *click* on **Cancel** to remove the dialog.

Note that structures retrieved from CACTUS have been minimized using molecular mechanics, but have not been searched for best conformer.

Access PDB...

Spartan Student provides on-line access to the **P**rotein **D**ata **B**ank (**PDB**)* comprising upwards of 75,000 protein and nucleotide structures. Selection gives rise to a dialog and request for a four character identification code (**PDB Id**).

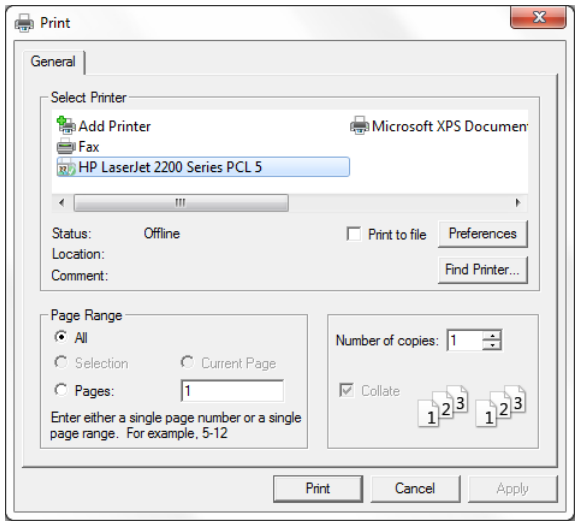


Clicking on **Open** accesses PDB and returns a structure. In the event that the PDB entry contains more than one structure, all will be returned. PDB access will typically require a few seconds, after which a ribbon model of the biomolecule will appear on screen. Any small molecules (ligands) associated with the protein will appear as a series of transparent spheres (much like a space-filling model) inside the biomolecule. *Checking* **Draw Ramachandran Plot** provides a Ramachandran (ϕ, ψ) plot for the protein. This may also be accessed from the **Model** menu (**Chapter 5**).

Print/Print Output/Print Spreadsheet

Selection leads to a dialog in order to designate a printer, specify print layout and number of copies. It also allows printing to a file.

* The web address is http://www.pdb.org.



Spartan Student prints whatever is displayed on screen. Note that it may be desirable to change the background color to white (**Colors** under the **Options** menu; **Chapter 10**). To print text output, bring up and select an output window (**Output** under the **Display** menu), *right click* in the **Output** window and choose **Print**. To print the contents of the spreadsheet, bring up a spreadsheet (**Spreadsheet** under the **Display** menu), *right click* in the spreadsheet and choose **Print**. Spectra and plots may be printed from within the **Spectra** or **Plot** dialogs, respectively, once spectra or plots have been displayed. **Print Preview** and **Page Setup** are also available.

Start/Stop QuickTime Recording

This allows QuickTime movies to be created. To start making a movie, select **Start QuickTime Recording**. Any motions of molecules in the main screen will be captured. Dialogs (including the builders) will not be captured. Note the use of tumbling (see **Settings Preferences** under **Preferences** in the **Options** menu; **Chapter 10**) in making QuickTime movies. To stop making a movie, select **Stop QuickTime Recording** (which has replaced **Start QuickTime Recording**) and supply a name.

Exit

Clears the screen and closes all open documents. A prompt for a name is provided for each document that has not previously been saved.

Chapter 4

The Edit Menu

*Operations under the **Edit** menu provide for undoing commands, copying items to and from the clipboard, finding text and graphics, centering molecules on screen and clearing the selected molecule.*

Undo

Undoes the last operation from the **Build** and **Edit** menus.

Cut, Copy, Paste, Select All

Cut moves the selected item to the clipboard and removes it from the document. **Copy** copies the item to the clipboard. The item is unaffected. **Paste** transfers the contents of the clipboard to the selected location. The contents of the clipboard are unaffected. **Select All** selects the entire contents of the output window or spreadsheet.

The following are among the important uses of the clipboard:

(i) Transferring on-screen graphics into other applications such as Microsoft Word® and PowerPoint®.

(ii) Temporary storage of a molecular structure for use in molecule building.

(iii) Transferring data between a ***Spartan Student*** spreadsheet and other applications such as Microsoft Excel®.

(iv) Making multi-molecule documents and/or transferring molecules between documents.

Cut operations for (i) and (ii) require drawing a selection box. First position the cursor slightly above and slightly to the left of the item to be transferred. Then, while holding down both buttons, *drag* the mouse to a location slightly below and slightly to the right of the item to be transferred. Finally, release both buttons. **Copy** operations for (i) and (ii) also refer to the contents of a selection box ***if one has been drawn***, but to the selected molecule if a box has not been drawn. **Copy** operations from a ***Spartan Student*** spreadsheet refer to all information associated with a molecule if selection is made on the header cell of the leftmost column, but only to the selected (text) information if selection is made on any other column. Further discussions relating to use of the clipboard in molecule building is provided in **Chapter 7** and for spreadsheet operations involving multi-molecule documents in **Chapter 9**.

Find..., Find Next

Find locates a text string defined in the **Find** dialog if an output window or a spreadsheet is selected, or a structure sequence defined on the clipboard if an on-screen model is selected. **Find Next** locates the next occurrence of a text string or a structure sequence.

Center

Centers on screen all molecules in the document for which the selected molecule is a member (only the selected molecule is displayed).

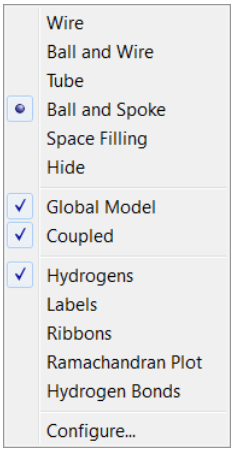
Clear

Clears (deletes) the structure and other information for the selected molecule, and brings up a model kit. No information is actually removed from the file system until the document is saved.

Chapter 5

The Model Menu

*Structure models available under the **Model** menu include wire, ball-and-wire, tube, ball-and-spoke and space-filling (CPK) models, with or without hydrogens, with or without hydrogen bonds indicated, and with or without atom labels, as well as ribbon displays for polypeptides and polynucleotides, with or without labels and with or without hydrogen bonds indicated. The menu provides for drawing a Ramachandran (ϕ,ψ) plot from a PDB file of a protein, for configuring atom labels to display element name, R/S chirality, mass number, charge or chemical shift, and for specifying color coding and display style for ribbon labels, as well as turning a variety of other labels on and off. Finally, it allows model style to be applied globally (to all molecules in a document) and models to be manipulated in concert.*



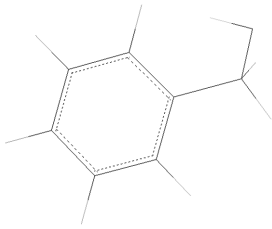
Only one model style **Wire**, **Ball and Wire**, **Tube**, **Ball and Spoke**, **Space Filling** or **Hide**) may be selected. The selected model is designated by ◉ in front of its entry in the menu. **Global Model**, **Coupled**, **Hydrogens**, **Labels**, **Ribbons** and **Hydrogen Bonds** operate as toggle switches. A ☑ in front of the entry in the menu indicates that it is turned on.

All structure models, and graphics may be displayed either in orthogonal or perspective projections. The latter may be valuable in helping to visualize large molecules. Selection is done in the **Settings** tab of the **Preferences** dialog (**Preferences...** under the **Options** menu; **Chapter 10**). Both structure models and graphics may be presented in 3D stereo. This is also controlled from the **Preferences** dialog as well as by *toggling* on or off the **3** key on the keyboard. Stereographic displays require perspective projections.

Wire

This represents the molecule as a wire model where the vertices represent the atoms.

Wire Model



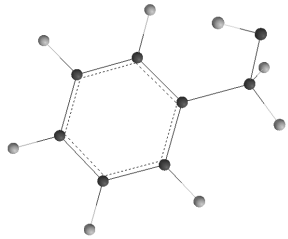
The bonds are drawn in two colors, one for each of the atoms making up the bond. Default atom colors are given in **Table 5-1**.

Atom colors apply globally (to all atoms of given type), and may be changed using the **Set Colors** dialog (**Colors** under the **Options** menu; **Chapter 10**). All models use the same color scheme for atoms, and provide for the same mechanism of changing colors.

Ball and Wire

This represents atoms by small balls and bonds by wires.

Ball-and-Wire Model



The balls are color coded according to atom type, and the wires representing bonds are drawn in two colors (as in wire models).

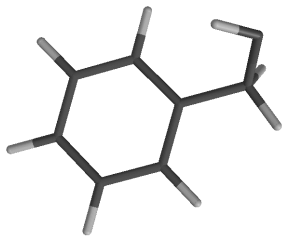
Table 5-1: Default Atom Colors

main group		main group (con't)	
Hydrogen	white	Indium	orange
Lithium	orange	Tin	gray
Beryllium	green	Antimony	orange
Boron	orange	Tellurium	orange
Carbon	gray	Iodine	violet
Nitrogen	blue-gray	**transition metals**	
Oxygen	red	Scandium-Zinc	green
Fluorine	pale yellow	Yttrium-Cadnium	green
Sodium	yellow	Lanthanum-Mercury	green
Magnesium	purple	**lanthanides**	
Aluminum	magenta	Cerium-Lutetium	violet
Silicon	gray	**actinides**	
Phosphorus	orange	Thorium-Lawrencium	dark blue
Sulfur	yellow	**noble gases**	
Chlorine	green	Helium	dark orange
Potassium	red	Neon	dark orange
Calcium	red	Argon	dark orange
Gallium	orange	Krypton	dark orange
Germanium	gray	Xenon	orange
Arsenic	dark orange		
Selenium	red orange		
Bromine	dark red		
Rubidium	red		
Strontium	red		

Tube

This is similar to the wire model, except that tubes instead of wires are used to represent bonds.

Tube Model

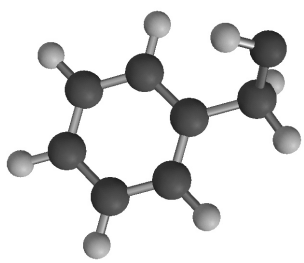


Tubes are split to represent multiple bonds. As with wire models, bonds are drawn in two colors.

Ball and Spoke

This represents atoms by balls (the size and color of which depend on atom type), and bonds by spokes.

Ball-and-Spoke Model



Spokes are split to represent multiple bonds. Bond (spoke) color is gray by default but it may be changed from **Colors** under the **Options** menu (**Chapter 10**).

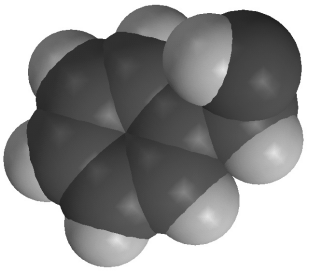
Space Filling

This represents the molecule as a composite of spheres, the radii of which have been chosen to approximate van der Waals contact distances.* Also known as CPK models, space-filling models are intended to portray overall molecular size and shape.

---

* van der Waals radii may be changed from the **VDW Radii** tab (**Preferences** under the **Options** menu; **Chapter 10**).

Space-Filling Model



Volume, surface area and polar surface area* displayed in the **Molecule Properties** dialog (**Properties** under the **Display** menu; **Chapter 9**) correspond to a space-filling model.

Hide

This removes the structure model from the screen. This may be desirable where its display may lead to unnecessary crowding, for example, in proteins where ribbon displays are more appropriate. A structure model may be restored by selecting it from the **Model** menu.

Global Model

If *checked* (turned on), this signifies that all molecules in a document will share attributes. These include presentation of hydrogens, atom and other labels, hydrogen bonds and ribbon displays. Global model style is controlled from the **Molecule** tab (**Preferences...** under the **Options** menu; **Chapter 10**). **Global Model** acts in a toggle manner, switching between global and local display. **Global Model** is normally on.

Coupled

If *checked* (turned on), this signifies that all molecules in a document selected for simultaneous display will be moved together. **Coupled** is turned on following molecule alignment (see **Align** under the **Geometry** menu; **Chapter 6**). **Coupled** acts in a toggle manner, that is, repeated selection couples and decouples the molecules.

---

* Polar surface area (PSA) is defined as the area due to nitrogen and oxygen and any hydrogens attached to nitrogen and oxygen. Small PSA typically indicates low solubility in polar media and large PSA indicates high solubility.

Hydrogens

If *checked*, this signifies that hydrogens are to be included in the model. **Hydrogens** acts in a toggle manner, that is, repeated selection turns the display of hydrogens on and off.

Labels

If *checked*, this signifies that labels associated with atoms, ribbons and bonds as well as with other attributes specified in **Configure...** (see discussion later in this chapter) are to be displayed in the model. **Labels** acts in a toggle manner, that is, repeated selection turns display of labels on and off. **Labels** is automatically turned on following selection of **Apply** or **OK** in the **Configure...** dialog.

Ribbons

If *checked*, this signifies that ribbons are to be displayed along with the selected model. For proteins, it will generally be advisable to remove the structure model from view (**Hide** from the **Model** menu). **Ribbons** acts in a toggle manner, that is, repeated selection turns display of ribbons on and off.

Ramachandran Plot

If *checked*, this draws a Ramachandran plot for a protein input from the Protein Data Bank (see **Access PDB...** under the **File** menu; **Chapter 3**). **Ramachandran Plot** acts in a toggle manner, that is, repeated selection turns the plot on and off. Note that coloring of the points on the plot (red for α-helices, blue for β-sheets, green otherwise) is not based on the actual 3D geometry but rather on assignments in the PDB file.

Hydrogen Bonds*

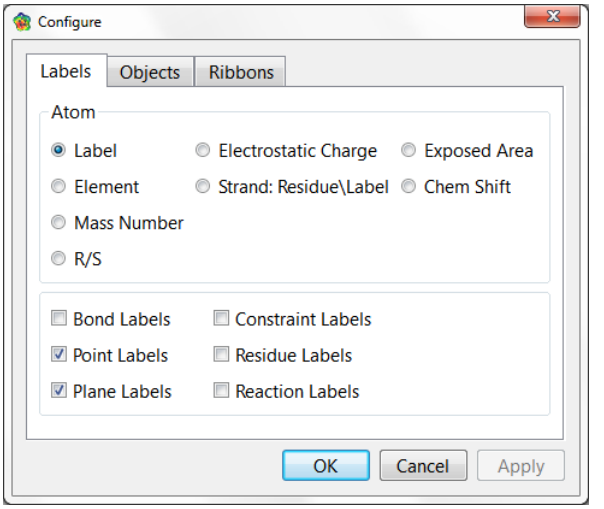
If *checked*, this signifies that hydrogen bonds are to be drawn as part of the model. **Hydrogen Bonds** acts in a toggle manner, that is, repeated selection turns display of hydrogen bonds on and off.

* Hydrogen bonds are defined as non-bonded contacts between a nitrogen, oxygen, or fluorine and a hydrogen attached to nitrogen, oxygen, or fluorine separated by a distance ranging from 1.6 to 2.1Å and making an X–H--Y (X, Y = N, O, F) angle of >120°.

Configure...

This selects the types of labels attached to atoms and ribbons.

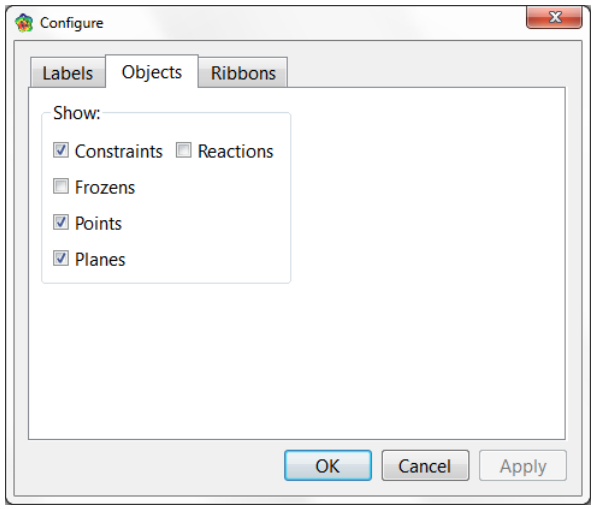
Configure Labels



Atom labels may be selected from among the following: **Labels**, a unique element/number combination that may be changed from the **Atom Properties** dialog (**Properties** under the **Display** menu; **Chapter 9**), **Element**, **Mass Number**, **R/S** (chirality), **Electrostatic Charge**, **Strand: Residue\Label** (polypeptides and polynucleotides), **Exposed Area** (of an atom in a space-filling model) or **Chem Shift**. In addition, **Bond Labels**, **Point Labels**, **Plane Labels**, **Constraint Labels**, **Residue Labels**, and/or **Reaction Labels** may be provided. Default settings (for a new molecule) are made in the **Molecule Preferences** dialog (**Preferences** under the **Options** menu; **Chapter 10**).

Configure Objects

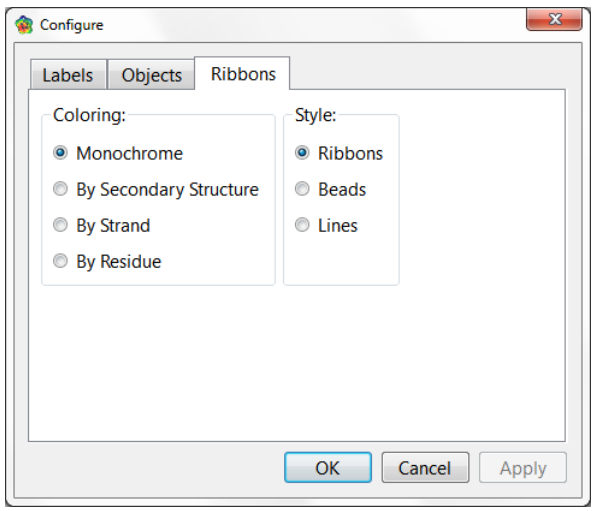
Clicking on the **Objects** tab leads to the **Configure Objects** dialog.



If checked, **Constraint** and **Frozen** markers, **Points** and **Planes**, and **Reaction** arrows attach to the model. If not checked, these are shown only in the respective modes, for example, **Frozen** markers are shown only if **Freeze Center** is selected.

Configure Ribbons

Clicking on the **Ribbons** tab leads to the **Configure Ribbons** dialog.

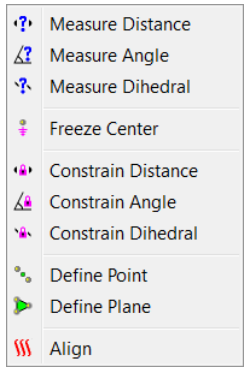


Ribbon coloring may be selected from among the following: **Monochrome**, **By Secondary Structure**, **By Strand** or **By Residue**. Ribbon style may be selected from among the following: **Ribbons**, **Beads** or **Lines**.

The **Configure** dialog is removed from the screen with all selections maintained by *clicking* on **OK**. *Clicking* on **Cancel** or on ☒ removes the dialog but selections are lost. *Clicking* on **Apply** maintains the selections but leaves the **Configure** dialog on screen. Note, that **Labels** (from the **Model** menu) will be turned on following either *clicking* on **OK** or on **Apply**.

Chapter 6
The Geometry Menu

*Functions available under the **Geometry** menu allow querying and changing bond lengths, angles and dihedral angles, defining points and ligand points and planes, setting geometrical constraints, freezing atomic centers and aligning molecules in a list.*



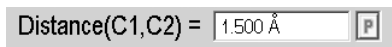
Measure Distance (**)**

Measure Angle (**)**

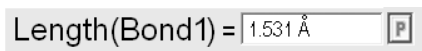
Measure Dihedral (**)**

Measure Distance displays the distance (in Ångstroms) between two atoms, whether or not they are bonded. Selection results in a message at the bottom left of the screen.

Clicking on two atoms displays the distance at the bottom right of the screen.



Alternatively, *clicking* on a bond displays its length.



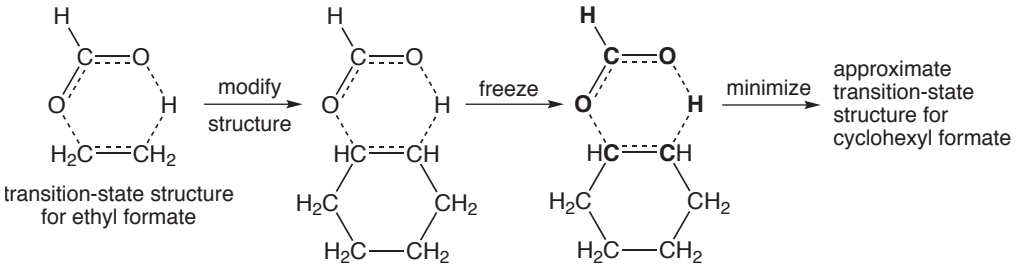
Measure Distance may also be used to alter the distance between atoms (as long as both are not incorporated into the same ring), by altering the contents of the box to the right of **Distance (A,B)** = or **Length (A)=**, and then *pressing* the **Enter** key (**return** key on Mac). The distance (length) may be entered into the spreadsheet by *clicking* on P to the right of its display (see **Spreadsheet** under the **Display** menu; **Chapter 9**).

Angle and dihedral angle queries are handled in a similar manner. Angles require that three atoms or two bonds be identified in the proper order while dihedral angles require that four atoms or three bonds be identified in the proper order.

Freeze Center ( )

This allows one or more atoms to be held in place during minimization (in the builder) and during equilibrium or transition-state geometry optimization or energy profile generation (for submitted jobs).

Atom freezing may be useful in a number of situations, among them building a guess for a transition state for a reaction that is closely related to one for which a transition state is available. For example, a good guess at the transition state for pyrolysis of cyclohexyl formate will be obtained by modifying the transition state for pyrolysis of ethyl formate, freezing all but the modified sections (designated in bold in the figure below) and then minimizing.



Selection of **Freeze Center** leads to a message at the bottom left of the screen.

Clicking on an atom or free valence*, freezes it; *clicking* again thaws

* The bond distance in this case is that appropriate for hydrogen being added to the free valence.

it. Buttons at the bottom right of the screen allow for freezing all atoms (**Freeze All**), freezing all heavy (non-hydrogen) atoms (**Freeze Heavy**) and for thawing all atoms (**Thaw All**).

Frozen atoms are indicated by magenta colored markers ( ).

Constrain Distance ( )
Constrain Angle ( )
Constrain Dihedral ( )

These introduce of one or more geometrical constraints during structure minimization (in the builder), and during equilibrium or transition-state geometry optimization or energy profile generation. Constraints may be useful in a number of situations, among them:

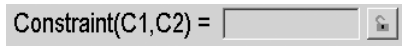
(i) constructing conformational energy profiles where one or more dihedral angles need to be fixed while other geometrical variables are optimized,

(ii) optimizing molecular structures where the values of certain key parameters are known, for example, optimizing the geometry of a molecule with an intramolecular hydrogen bond or a disulfide linkage, and

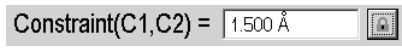
(iii) building molecules with unusual geometries, for example, molecules with very long bonds, as might be required in the construction of transition states and intermolecular complexes.

Selecting **Constrain Distance** results in a message at the bottom left of the screen.

Clicking on two atoms, or a bond results in a message at the bottom right of the screen.



Clicking on changes it to and shows the current distance.



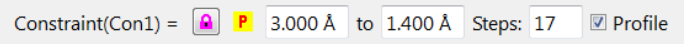
This (constraint) distance can now be changed by altering the contents

of the box and then *pressing* the **Enter** key (**return** key on Mac). Alternatively, the existing distance may be used as the constraint distance. If the selected distance had previously been constrained, the icon would have been initially displayed. In this case, *clicking* on turns the constraint off and returns the icon to . Finally, the value of the constraint, that may be different from the value of the current distance*, may be entered into the spreadsheet by *clicking* on P to its right.

This sequence of operations (bond identification followed by turning the constraint on and off) may be repeated as many times as necessary. Any bonds or non-bonded distances on which constraints are to be imposed are indicated by magenta colored markers. Any constraints introduced are automatically enforced only upon energy minimization in add fragment mode ( ), but need to be requested for methods under the **Calculations** dialog (**Chapter 8**).

Angle and dihedral angle constraints are handled in a similar manner. Note that ***points and planes may not be used to define constraints***.

Locking in a constraint leads to two additional text boxes at the bottom right of the screen. This allows a sequence of constraints to be defined (from some initial value to some final value in a given number of steps) for the purpose of constructing an energy profile along a predefined set of coordinates (see discussion under **Calculations** from the **Setup** menu; **Chapter 8**).



The leftmost box sets the initial value of the constraint, the middle box to the right of **to** sets the final value, and the rightmost box to the right of **Steps:** sets the number of steps. For example, were the initial value set to 0°, the final value to 180° and the number of steps to 10, then a series of ten constraints (0°, 20°, 40°, ... 180°) would be specified. This can also be accomplished using the **Constraint Properties** dialog, and the value of the constraint posted to the spreadsheet.

---

* Note, however, that it may be problematic to carry out a constrained geometry optimization starting from a structure that is very different from that satisfying one or more constraints.

Whether or not constraint markers are included as part of the model (outside of constrain distance, constrain angle or constrain dihedral mode) is controlled from the **Molecule** tab (**Preferences...** under the **Options** menu; **Chapter 10**).

Define Point ( )

This defines a point as the geometric (unweighted) center of selected atoms (or points) previously defined. Selection results in display of a message at the bottom left of the screen.

Clicking on atoms (or points) in any order, and *clicking* a second time on any one of the atoms (or points) defines a point (depicted as a small sphere). As many points as desired can be defined and these are treated in the same way as an atom in defining distances, angles, etc. Points move with the molecule as its geometry is altered.

Selecting **Define Point** (or *clicking* on) while holding down on the **Shift** key, followed by *clicking* on the appropriate atoms, leads to a ***ligand point***. This is a point of attachment directed perpendicular to the geometric center of the plane defined by three atoms (or best plane in the case of four or more atoms). A ligand point shares all the characteristics of a normal point, but may also be used to bond to atomic fragments, functional groups, etc. See **Make Bond** under the **Build** menu (**Chapter 7**) for a discussion. Ligand points move with the molecule as geometry is altered.

> **Delete** from the **Build** menu ( ) or the **Delete** key may be used to remove a point or ligand point.

Define Plane ( )

This defines and displays a reference plane. Selection results in display of a message at the bottom left of the screen.

Clicking on three atoms or points defines a plane. As many planes as desired may be defined, and these may be used in defining distances,

angles, etc. Planes move with the molecule as its geometry changes.

> **Delete** from the **Build** menu ( ) or the **Delete** key may be used to remove a plane.

Align ( )

This aligns the selected molecule to all other molecules in the same document based on structure. Selection of **Align** results in a message at the bottom left of the screen.

Clicking on an atom designates it as an alignment center, and marks it with a red circle. *Clicking* on the circle removes the designation (and the circle). Following selection of alignment centers, *clicking* on the **Align** button at the bottom right of the screen aligns the molecules. If no atoms are selected prior to *clicking* on **Align**, then alignment is based on all (non-hydrogen) atoms.

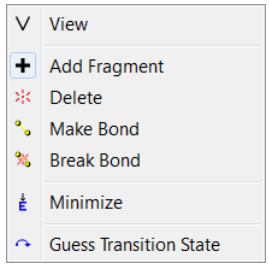
Following alignment, two or more molecules may be displayed at once using spreadsheet functions (see **Spreadsheet** under the **Display** menu; **Chapter 9**). Their motions (coordinates) will be coupled following alignment, but may be uncoupled allowing the aligned molecules to move independently (see **Coupled** under the **Model** menu; **Chapter 5**). Note that alignment center selections are kept and molecules can be realigned by again selecting **Align** from the **Geometry** menu (or *clicking* on) followed by *clicking* on the **Align** button.

The alignment score from 0 to 1 (where 1 designates perfect alignment), is available in the spreadsheet. This is accessed by *clicking* on the **Add** button at the bottom of the spreadsheet, and selecting **Alignment Score** from the list of available properties (see **Spreadsheet** under the **Display** menu; **Chapter 9**). A score of 0 is assigned to molecules that cannot be aligned to the selected molecule.

Chapter 7

The Build Menu

*The **Build** menu provides model kits and tools for building and editing organic, inorganic and organometallic molecules, as well as polypeptides and polynucleotides, and a molecular mechanics procedure for structure refinement. This menu also provides seamless access to ChemDraw (Windows only) and a facility for guessing transition states for reactions based on their similarity to transition states in a database of reactions.*



Model Kits

Spartan Student provides four different model kits for assembling a variety of molecular systems: an organic model kit for most organic molecules, an inorganic model kit for organic molecules not easily represented in terms of classical valence structures, as well as inorganic and organometallic molecules, and model kits for polypeptides and polynucleotides. The organic and inorganic model kits utilize atomic fragments, functional groups and rings (and ligands in the inorganic model kit), while the peptide model kit uses the set of natural amino acids as building blocks, and the nucleotide model kit the set of nucleotide bases.

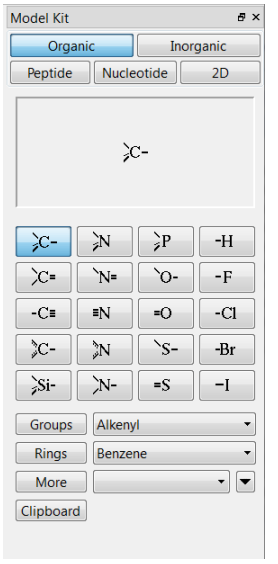
Two-dimensional molecular structures (drawings) produced using ChemDraw* can also be brought into ***Spartan Student*** and converted to three-dimensional structures.

* Seamless access to ChemDraw is provided in the Windows version only (via the 2D tab). Both Windows and Macintosh versions are able to read ChemDraw files. ChemDraw is not included with ***Spartan Student*** but is available from CambridgeSoft at http://www.cambridgesoft.com.

Molecule construction in ***Spartan Student*** proceeds much in the same manner as a chemist would assemble a structure from a plastic model kit, that is, pieces are taken from the kit one at a time and added sequentially to the molecule under construction.

Organic Model Kit

The organic model kit contains a suite of molecule building/editing tools specifically designed to construct organic molecules.



In the center of the model kit are a selection of atomic fragments, which from left to right and then top to bottom, correspond to:

$C(sp^3)$	$N(sp^3)$	$P(sp^3)$	H
$C(sp^2)$	$N(sp^2)$	$O(sp^3)$	F
C(sp)	N(sp)	$O(sp^2)$	Cl
C(aromatic)	N(aromatic)	$S(sp^3)$	Br
$Si(sp^3)$	N(planar)	$S(sp^2)$	I

A fragment is chosen by *clicking* on its icon, which is then displayed at the top of the model kit. Once selected, the fragment may be used to initiate building, to add alongside of an existing structure or to bond to an existing structure. To initiate building, *click* anywhere on screen. To add alongside of an existing structure, first *click* on the **Insert**

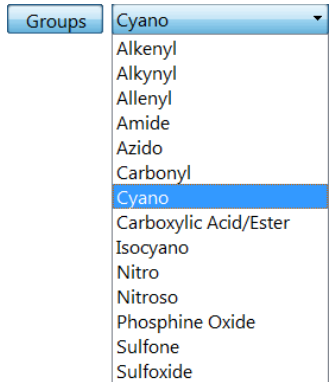
button at the bottom right of the screen or hold down the **Insert** key (**option** key on Mac) and then *click* anywhere on screen, or *double click* in a blank area on screen. To bond to an existing structure, *click* on a free valence (***not an atom***). (Free valences are colored yellow on the selected molecule.) Bond type in the case of atomic fragments with multiple bond types, for example, sp^2 carbon, depends on the nature of the free valence selected.

> While only H, C, N, O, F, P, S, Cl, Br and I are available from the organic model kit, other elements may be substituted using atom replacement feature available in the inorganic model kit (see **General Molecule Building Functionality** later in this chapter). Similarly, bond types may be altered in the inorganic model kit. Atom and bond types may also be altered using the **Atom** and **Bond Properties** dialogs, respectively (**Properties** under the **Display** menu; **Chapter 9**).

Menus inside the model kit provide access to a number of pre-built fragments corresponding to functional groups (**Groups**) and rings (**Rings**), and to additional libraries of rings (as well as any user-defined structures) stored in the file system (**More**). The model kit also accesses the clipboard (**Clipboard**).

Groups

Clicking on **Groups** brings up a menu of groups, and displays an icon of one group at the top of the model kit.

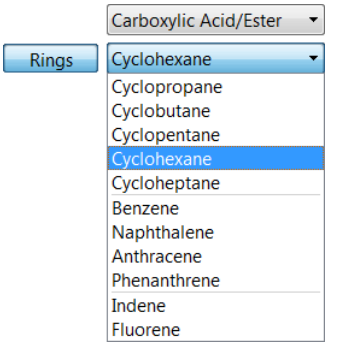


Once selected from the menu, a group may be used to initiate building, to add alongside of an existing structure on screen, or to add to an existing structure.

The amide and carboxylic acid/ester groups have more than one different free valence. The free valence that is to be used is marked with a gold • (in the icon at the top of the model kit). The marked position rotates among the possible positions with repeated *clicking* on the icon.

Rings

Clicking on **Rings** brings up a menu of hydrocarbon rings, and displays an icon of one ring at the top of the model kit.



Once selected from the menu, a ring may be used to initiate building, to add alongside of an existing structure on screen, or to add to an existing structure.

Cyclohexane, napthalene, anthracene and phenanthrene have more than one different free valence. The one that is to be used is marked with a gold • (in the icon). The marked position rotates among the available positions with repeated *clicking* on the icon. Selection of an *axial* or *equatorial* free valence in cyclohexane is indicated by the label **ax** or **eq** appearing alongside the icon. All rings in this menu are hydrocarbons, but heteroatoms may be substituted (see **General Molecule Building Functionality** later in this chapter).

More

This provides access to a broader selection of rings as well as to user-defined entities (normal .spartan files). Upon initial entry, the menu to the right of **More** will be empty. It can be populated, by *clicking* on ▾ to the far right. This brings up a file browser that

has been set to point toward a directory containing (among other entries) several ***Spartan Student*** files of common rings.

nitrogen heterocycles	saturated nitrogen rings
oxygen heterocycles	saturated oxygen rings
sulfur heterocycles	saturated sulfur rings
	saturated mixed rings

Clicking on a file followed by *clicking* on **Open** or *double clicking* on a file fills the menu to the right of **More**. Menu entries are selected in the usual way. In response, a ball-and-wire model of the selected ring will appear at the top of the model kit. This may be manipulated (rotated, translated, zoomed) using the usual mouse/keyboard commands (you need to position the cursor inside the box). The ring may be used to initiate building, to add alongside of an existing structure, or to add to an existing structure. In the latter case, the attachment point (on the ring in the window) needs to be identified by *clicking* on the appropriate free valence.

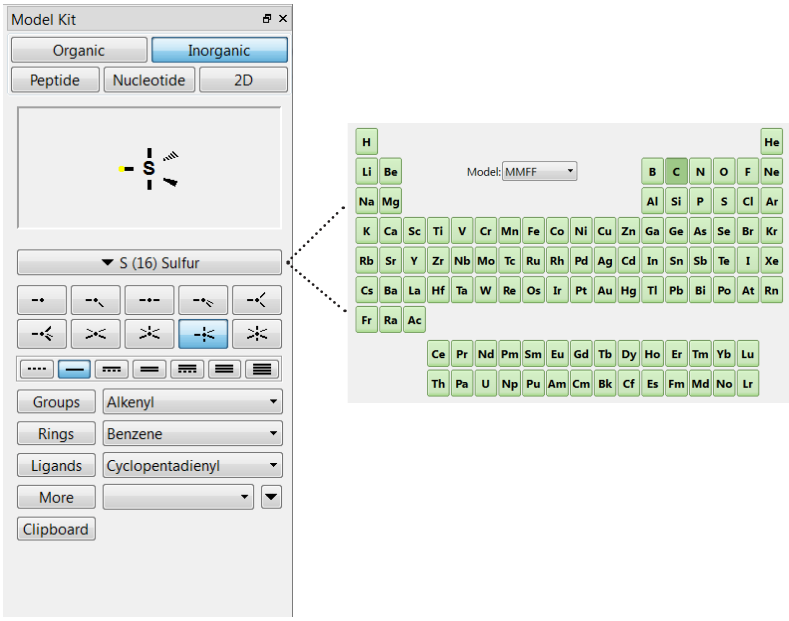
Clipboard

Clicking on **Clipboard** accesses the clipboard. A ball-and-wire model of whatever is on the clipboard is displayed at the top of the model kit. This may be manipulated using the usual mouse/keyboard commands (you need to position the cursor inside the box). Once selected, the molecule may be used to initiate building, to add alongside of an existing structure, or to add to an existing structure. In the latter case, the attachment point needs to be identified by *clicking* on the appropriate free valence in the clipboard.

An empty clipboard will be signaled by:

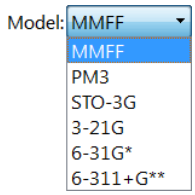
Inorganic Model Kit

Spartan Student's inorganic model kit allows construction of a much wider class of molecules (including inorganic and organometallic species) than possible with the organic model kit. Structures that violate conventional bonding rules may be constructed, as this model kit purposefully provides no checking. The inorganic model kit is reached by *clicking* on the **Inorganic** tab, located at the top of the organic (peptide, nucleotide or 2D) model kit. (Return to the organic, peptide or nucleotide model kit, or to ChemDraw is accomplished by *clicking* on the **Organic**, **Peptide**, **Nucleotide**, or **2D** (Windows only) tab, respectively, from the inorganic model kit).



Atoms may be selected by *clicking* on the center atom button. This leads to a full *Periodic Table*. Main-group elements are colored orange, transition metals are colored green and lanthanides and actinides are colored blue. The **Model** menu inside the *Periodic Table* contains the theoretical models supported in ***Spartan Student***.*

* More precisely, except for MMFF and PM3, it lists the elements that are supported with the basis sets used by the Hartree-Fock, B3LYP, EDF2 and MP2 models.



Selecting an entry from this menu leads to recoloring of the *Periodic Table*. A light green color is used to indicate elements for which the selected model may be used.* Immediately below is a selection of atomic hybrids. Following this is a selection of bond types. **Groups**, **Rings**, **More** and **Clipboard** are the same as in the organic model kit; **Ligands** is new to the inorganic model kit.

Selection of atom type is effected by *clicking* on the appropriate element in the *Periodic Table*. The entry will be highlighted. Selection of an atomic hybrid follows by *clicking* on the appropriate icon which will then be highlighted.** This combination (atom type + atomic hybrid) may be used to initiate building, to add alongside of an existing structure or to append onto an existing molecular fragment. To initiate building, *click* anywhere on screen. To add alongside of an existing structure, first *click* on **Insert** at the bottom right of the screen or *press* the **Insert** key (**option** key on Mac), and then *click* anywhere on screen, or *double click* in a blank area on screen. To bond to an existing fragment, *click* on the appropriate free valence.

Two of the hybrids (trigonal bipyramidal and square-based pyramidal) may bond either *axially* or *equatorially*. Selection of the appropriate bonding point, marked by a •, is effected by repeatedly *clicking* on the icon; the bonding point alternates between the two sites.

Atoms are connected with whatever bond type (partial single, single, aromatic, double, triple or quadruple) is selected in the model kit. A bond type may be changed by first selecting a type and then *double clicking* on the bond. Bond types have no impact on quantum chemical calculations, but do affect molecular mechanics calculations (including energy minimization in the builder; see discussion later in this chapter).

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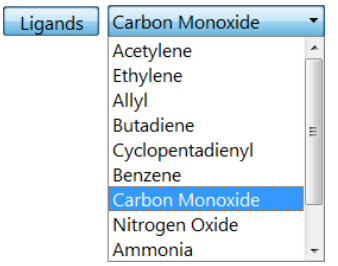
* While molecular mechanics models are available for all elements, they have been carefully parameterized for only a relatively few of these.

** Additional hybrids for high-coordination centers are available as a library accessible from **More** (see discussion under organic model kit).

No valence checking is performed in the inorganic model kit, and the user is free to construct any arrangement of atoms.

Ligands

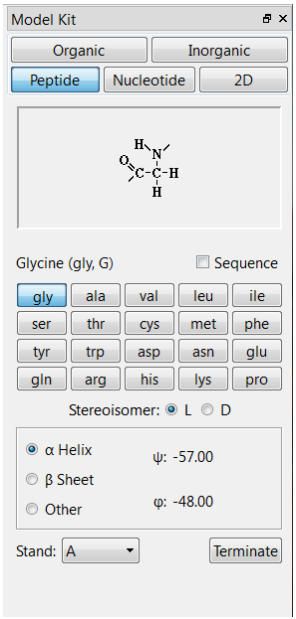
This provides access to a number of pre-built ligands, useful in the construction of inorganic and organometallic molecules. Its operation is analogous to that for the **Groups** and **Rings** menus. *Clicking* on **Ligands** brings up a menu of available ligands, and results in an icon of one ligand from this menu being displayed at the top of the model kit.



A ligand may be used to initiate building or to add alongside or to an existing structure. Additional ligands are accessible from **More** (see previous discussion). Ligands may also be built with the aid of ligand points (**Define Point** in the **Geometry** menu; **Chapter 6**).

Peptide Model Kit

A model kit for construction of polypeptides is reached by *clicking* on the **Peptide** tab located at the top of the organic, inorganic, nucleotide and 2D model kits. (Return to the organic, inorganic or nucleotide model kit, or to ChemDraw is accomplished by *clicking* on the **Organic**, **Inorganic**, **Nucleotide**, or **2D** (Windows only) tab, respectively, from the peptide model kit.)



At the middle of the peptide model kit are icons designating the amino acids (specified by their usual three-letter codes). An amino acid is selected by *clicking* on its three-letter code, following which either an icon of the amino acid is displayed in the box at the top of the model kit, or the three-letter code for the amino acid is appended to the sequence of codes in the box. Amino acids replace atoms, functional groups, rings and ligands as the building blocks in the peptide model kit. Because these other building blocks are missing, modifications of peptides, aside from modifications in sequence and in overall conformation, need to be carried out using the organic or inorganic model kits.

There are two different modes of operation: single amino acid mode and polypeptide mode. The former is used to initiate building with a single amino acid, to add a single amino acid alongside of an existing structure or to add a single amino acid to an existing structure, while the latter is used to construct amino acid sequences (polypeptides). **Sequence** off (unchecked) corresponds to single amino acid mode, and on (checked) corresponds to polypeptide mode.

Peptide construction (**Sequence** on) is accomplished in three steps:

Specification of Amino Acid Sequence

This is accomplished by *clicking* in the desired order on the amino acid codes. Building occurs from the N end to the C end of the peptide. In response to each selection, the three-letter code is appended to the sequence of codes in the box at the top of the model kit. The stereochemical configuration of the amino acid is by default the L configuration; this may be changed to the D configuration prior to selection of the amino acid, by *checking* **D** to the right of **stereoisomer** in the model kit. (It may be changed back to L by *checking* **L**). D amino acids are indicated by **.d** following the code in the box.

The sequence may be altered by changing the text in the box. Existing amino acid codes may be deleted or changed or new codes can be added. The entire sequence may be specified in this way if desired. Specification of a non-existent code will result in an error message. The sequence can be cleared by *clicking* on **Clear**.

Specification of Macroscopic Structure

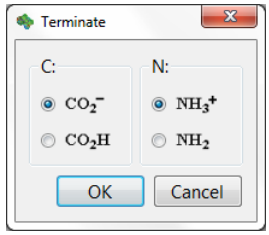
Once sequencing is complete, macroscopic structure (ψ and ϕ angles), is specified by *clicking* on α **Helix**, β **Sheet** or **Other**. In the case of the first two, preset angle values are displayed on the right. In the case of specification of **Other**, boxes appear, into which the desired dihedral angles need to be entered.

Termination

The peptide is not yet terminated, and the two ends are still set up for addition of further amino acids.

C end N end

where the * indicates a free valence. *Clicking* on **Terminate** at the bottom of the model kit leads to the **Terminate** dialog.

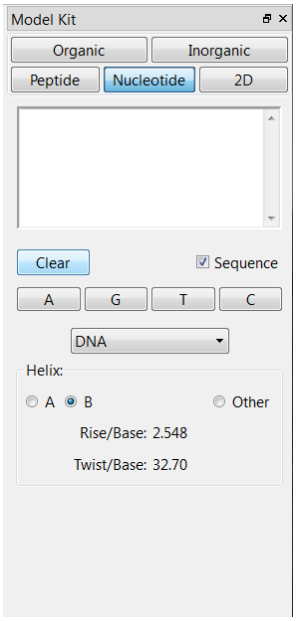


C and N terminating groups may be selected by repeated *clicking* on the C and N icons, respectively. Selection will toggle between neutral and charged terminating groups. *Clicking* on **OK** removes the dialog and terminates the polypeptide. *Clicking* on **Cancel** or  removes the dialog but does not terminate the polypeptide.

The peptide (or single amino acid) may now be used either to initiate building, by *clicking* anywhere on screen or added alongside of an existing structure, by first *clicking* on **Insert** at the bottom right of the screen or *pressing* the **Insert** key (**option** key on Mac), followed by *clicking* anywhere on screen, or *double clicking* in a blank area on screen. If unterminated, it may also be joined onto an existing structure by *clicking* on a free valence. In the latter case, attachment is made from the N end, unless the free valence corresponds to an unterminated peptide fragment, in which case the appropriate end required to make an amide bond is used.

Nucleotide Model Kit

Spartan Student provides a model kit for construction of polynucleotides. It is reached by *clicking* on the **Nucleotide** tab which is located at the top of the organic, inorganic, peptide and 2D model kits. (Return to the organic, inorganic or peptide model kit, or to ChemDraw is accomplished by *clicking* on the **Organic**, **Inorganic**, **Peptide**, or **2D** (Windows only) tab, respectively, from the nucleotide model kit.)



At the middle of the model kit is a menu designating the type of polynucleotide.

DNA
DNA (single strand)
DNA-RNA
RNA
RNA (double strand)
RNA-DNA

Immediately below this menu are icons, designating the nucleotide bases. Selection of DNA, DNA (single strand) or DNA-RNA from the menu leads to one set of icons.

Selection of RNA, RNA (double strand) or RNA-DNA leads to a second set, the only difference is that uracil (U) is substituted for thymine (T).

A nucleotide base is selected by *clicking* on its letter, following which either an icon of the base is displayed in the box at the top of the model kit, or the letter for the base is appended to the sequence of letters in the box. Nucleotide bases replace atomic fragments,

functional groups, rings and ligands as the building blocks in the nucleotide model kit. Because these other building blocks are missing, modifications of nucleotides, aside from modifications in sequence and helical structure, need to be carried out using either the organic or inorganic model kits.

There are two different modes of operation: single base mode and polynucleotide mode. The former is used to place a single base or base pair on screen, to add a single base or base pair alongside of an existing structure, or to add a single base or base pair to an existing structure, while the latter is used to construct strands of DNA or RNA (or mixed strands). **Sequence** off (unchecked) corresponds to single base (base pair) mode and on (checked) corresponds to polynucleotide mode.

Polynucleotide construction (**Sequence** on) is accomplished in two steps:

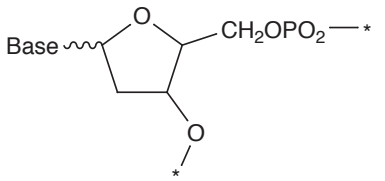
Specification of Base Sequence

This is accomplished by *clicking* in order on the base codes. In response to each selection, the letter code is appended to the sequence of codes in the box at the top of the model kit. The sequence may be altered by editing the contents of the box. Existing base codes may be deleted or changed or new codes added. The entire sequence can be specified in this way if desired. The sequence may be cleared by *clicking* on **Clear**.

Specification of Helical Structure

Once sequencing is complete, a helical structure may be specified by *clicking* on **A** or **B**. These correspond to A and B helices, respectively. Selecting **Other** allows user modification of the rise (in Å) per base (**Rise/Base**) and twist (in degrees) per base (**Twist/Base**).

Note that the polynucleotide is not yet terminated, and the two ends are still set up for addition of further bases or base pairs.



* indicates a free valence. Hydrogens occupy all free valences (except the *'ed positions at the two ends of the chain).

The polynucleotide (or single base pair) may now be used to either initiate building, by *clicking* anywhere on screen, added alongside of an existing structure, by first *clicking* on **Insert** at the bottom right of the screen or *pressing* the **Insert** key (**option** key on Mac) followed by *clicking* on screen, or *double clicking* on a blank area on screen, or joined onto an existing structure by *clicking* on a free valence. In the latter case, attachment is made from the phosphate end.

Accessing ChemDraw (Windows only)*

The ChemDraw program may be seamlessly accessed from inside ***Spartan Student***** allowing chemical drawings to be produced in a familiar environment and then brought over as 3D structures***. The conversion is unambiguous as long as all stereochemical cues are in place in the 2D drawing. Note that the conformation implied by the 2D drawing may be ambiguous and may need to be altered.

To access ChemDraw, enter the builder, *click* on the **2D** tab and *click* on **Edit** at the bottom of the panel that results. ChemDraw will appear. To return to ***Spartan Student***, close ChemDraw. The 2D drawing will appear at the center of the panel and manipulatable 3D structure will appear at the top of the panel. *Clicking* on screen will move the 3D structure into ***Spartan Student's*** main window.

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* ChemDraw files (.cdx) may be read with both Windows and Macintosh versions of ***Spartan Student***.

** ChemDraw is not provided with ***Spartan Student*** but is available from CambridgeSoft at http://www.cambridgesoft.com.

*** Transfer is one directional only. 3D structures that have been altered may not be transferred back to ChemDraw.

General Molecule Building Functionality

Additional capabilities are available with **Add Fragment** selected:

Multiple Fragments

Multiple fragments may result either from bond breakage (see **Break Bond** later in this chapter) or from use of the **Insert** button or **Insert** key (**option** key on Mac), or *double clicking* in a blank area on screen. A fragment is selected by *clicking* on it, following which the associated free valences are colored gold (free valences for any non-selected fragments are colored white). All builder functions apply to the selected fragment only. Rotation and translation also apply to the entire set of fragment, but may be made to apply to the selected fragment by holding down the **Ctrl** key while carrying out these operations.

Fragments may be attached using **Make Bond** (see discussion later in this chapter).

Bond Rotation/Bond Stretching

In addition to molecule rotation, translation and scaling, the mouse is used to rotate about and stretch bonds not incorporated in rings. This is accomplished via the following sequence of operations:

(i) *Clicking* on the bond, which is then marked by a red cylindrical arrow. (The bond connecting the last atom, group or ring added to the molecule is automatically selected.)

(ii) Simultaneously holding down the **Alt** key (**option** key on Mac) and the left mouse button while *dragging* the mouse up and down, for bond rotation, or the **Alt** (**option**) key and the right mouse button for bond stretching.

Atom/Fragment Replacement

Another function of the mouse is atom replacement. *Double clicking* on an atom (not a free valence) while an atomic fragment in the organic model is highlighted, replaces the atom by selected fragment. Free valences are adjusted to accommodate the

replacement, for example, replacement of sp^3 carbon by sp^3 oxygen results in two free valences being removed. Atom replacements that violate valence rules are not permitted. *Double clicking* on an atom (not a free valence) while an element in the *Periodic Table* from the inorganic model kit is selected, replaces the atom by the selected element. The latter merely changes the atomic number. No changes in the number or arrangement of free valences is made, and no checking is done. Atom replacement is not available in the peptide and nucleotide model kits.

Chirality Inversion

In the **Add Fragment** mode, *double clicking* on a chiral atom while *pressing* the **Ctrl** key (key on Mac) inverts the chirality of the atom (R→S or S→R). This is not available in fused ring systems. *Double clicking* on any atom while *pressing* both **Ctrl** (key on Mac) and **Shift** keys inverts the absolute configuration of the molecule.

Building/Editing Menu Functions

Molecule building/editing functions are found under the **Build** menu.

View (V)

This exits build mode, and removes the model kit from the screen.

> Initial entry into build mode is by way of **New** or **New Molecule** under the **File** menu (**Chapter 3**). **Add Fragment**, **Delete**, **Make Bond**, **Break Bond** and **Minimize** are for modifying existing structures.

Add Fragment (+)

In addition to the capabilities discussed under **General Molecule Building Functionality**, this allows access to the libraries of atomic fragments, groups, rings and ligands, as well as the file system and the clipboard. *Clicking* on any buttons or menus in the organic, inorganic, peptide or nucleotide model kits, leads to **Add Fragment**. (If a model kit is not on screen, selection brings

up the last-accessed model kit.) A fragment may be used to initiate building by *clicking* anywhere on screen, to add alongside an existing structure on screen by *clicking* on the **Insert** button at the bottom right of the screen or *pressing* the **Insert** key (**option** key on Mac) followed by *clicking* anywhere on screen, or by *double clicking* in a blank area on screen, or be added to an existing structure by *clicking* on the appropriate free valence. Fragment addition can be terminated by selection of any other function.

Delete ( )

This allows atom or free valence removal from a structure. Selection leads to a message at the bottom left of the screen.

Select object to delete.

Subsequent *clicking* on an atom or free valence results in its deletion. Deletion of an atom results in deletion of all of its associated free valences. Free valences for any atoms to which the deleted atom was previously connected are restored. Note that atom deletion may result in one or more detached fragments. *Clicking* inside a selection box results in deletion of everything inside the box. Selection of **Delete** does not bring up a model kit nor does it remove a model kit that is present on screen. **Delete** may be terminated by selection of any other function.

> **Delete** may also be used to delete points, planes, constraints, and frozen atom markers.

Deletion may also be accomplished by holding down on the **Delete** key while *clicking* on the item to be deleted.

Make Bond ( )

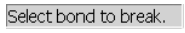
This allows bonds to be drawn between free valences and/or atoms on different centers. Selection leads to a message at the bottom left of the screen.

Select two free valences.

Clicking on two free valences (on different atoms) will cause these atoms to be linked by a single bond. Alternatively, *double clicking* on each of two atoms will bond them, and *clicking* on a free valence on one atom and *double clicking* on a different atom will bond the two atoms. Note that available free valences are consumed as a result of bond formation, irrespective of whether free valences or atoms are selected.* If the selected atoms are already bonded, this will result in the bond order being increased by one, that is, single → double, double → triple. Selection of **Make Bond** does not bring up a model kit nor does it remove a model kit that is already present on screen. **Make Bond** may be terminated by selection of any other function.

Break Bond ( )

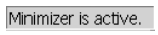
This allows breaking an existing bond resulting in free valences. Selection leads to a message at the bottom left of the screen.



Clicking on a bond breaks it and restores free valences. Note that bond breaking may result in detached fragments. Selection of **Break Bond** does not bring up a model kit nor does it remove a model kit that is present on screen. **Break Bond** may be terminated by selection of any other function.

Minimize ( )

This uses the molecular mechanics model to refine the geometry of a molecule or system. Selection leads to a message at the bottom left of the screen.



The molecular mechanics energy in kJ/mol, displayed at the bottom right of the screen, is continually updated during the minimization process. Minimization may be stopped at any time by *clicking* on the STOP icon at the bottom right of the screen. Any

* Free valences can be protected without altering the geometry of the molecule by adding hydrogens to them (-H from the organic model kit).

geometrical constraints imposed on the structure (see **Constrain Distance**, **Constrain Angle**, **Constrain Dihedral** in **Chapter 6**) are enforced during minimization. Also, any frozen atoms in the structure (see **Freeze Center** under the **Geometry** menu; **Chapter 6**) remain frozen.

Following completion, **Minimize** reverts back to **Add Fragment** only if a model kit is on screen.

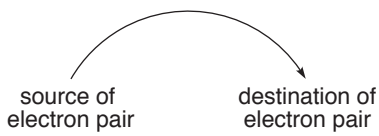
Guess Transition State ( )

Spartan Student provides a facility for automatically guessing the geometries of transition states based on the similarity of the reaction of interest with one or more entries in ***Spartan Student's*** reaction database. Where an exact match is not available, ***Spartan Student*** will attempt to provide as close a match as possible. This will generally involve a less substituted system or one in which substituents differ. Here, the procedure is to use those parts of the structure of the transition state in the database that are common, and to optimize the remaining parts (using molecular mechanics).

It may be essential for the reactants to be properly oriented to reflect the desired stereochemical outcome of the reaction.

Where a reaction is completely unknown to the database, a fallback technique similar to the linear synchronous transit method is automatically invoked.

Input to ***Spartan Student's*** transition-state guessing procedure will be very familiar to (organic) chemists, in that it is based on reaction arrows. The difference is that arrows are superimposed onto a three-dimensional structure rather than a two-dimensional drawing. The reaction is specified using curved arrows, where each arrow identifies the movement of one electron pair. The direction of electron flow follows customary practice:

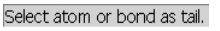


There are two possible sources of an electron pair and three possible destinations, leading to six combinations:

lone pair → lone pair	move lone pair
lone pair → bond	use lone pair to increase bond order
lone pair → space between atoms	use lone pair to make a new (single) bond
bond → lone pair	decrease bond order to make lone pair
bond → bond	decrease bond order of one bond to increase bond order of another bond
bond → space between atoms	decrease bond order to make a new (single) bond

The first of these is a null operation, and its inclusion has no effect.

Selecting **Guess Transition State** results in a message at the bottom left of the screen.



The tail of the arrow corresponds to the source of the electron pair. If the source is a lone pair, then select the atom that holds the lone pair. If the source is a bond, then select the bond. *Clicking* on an atom or bond highlights (colors gold) the atom or bond and leads to a new message at the bottom left of the screen.

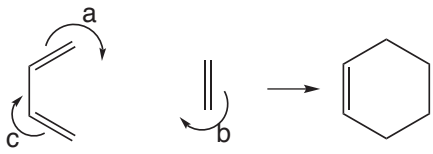
The head of the arrow corresponds to the destination of the electron pair. If the destination is an atom (leading to a lone pair), then select the atom that will hold the lone pair. If the destination is an existing bond (leading to an increase in bond order from single → double → or double → triple), then select the bond. If no bond presently exists, *press* the **Shift** key and select the two atoms that will become bonded upon reaction. These operations result in a curved arrow being drawn on the reactant structure. This extends from an atom, or the center of a bond to an atom, or the center of a bond, or the center of a dotted line that has been drawn between atoms that are to be bonded. The original message returns to the bottom left of the screen.

The process (tail selection followed by head selection) is repeated as necessary to fully define the reaction. Incorrect reaction arrows may be removed by selecting **Delete** from the **Build** menu ( ) followed by *clicking* on the arrow to be deleted. It is necessary to again select **Guess Transition State** ( ) in order to continue arrow specification. Alternatively, *click* on the arrow(s) to be deleted while holding down the **Delete** key on the keyboard.

After all reaction arrows have been properly designated, *click* on at the bottom right of the screen to replace the reactant with a guess at the transition state. In the event that the guess is unreasonable, this operation may be undone (select **Undo** from the **Edit** menu). This allows you to review your assignment of arrows and make changes as needed.

Examples

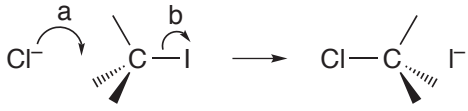
Diels-Alder reaction of 1,3-butadiene and ethylene



a, b. double bond to empty space leading to a single bond and to a new single bond

c. double bond to single bond leading to a single bond and a double bond

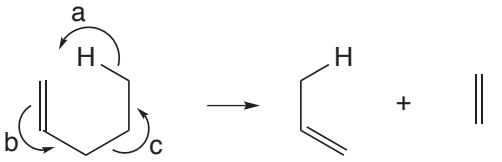
S_N2 reaction of chloride and methyl iodide



a. atom to empty space leading to a new single bond

b. single bond to an atom leading to the loss of the single bond

Ene reaction of 1-pentene

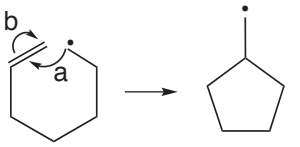


a. single bond to empty space leading to loss of the single bond and to a new single bond

b. double bond to single bond leading to a single bond and a double bond

c. single bond to single bond leading to loss of the single bond and to a double bond

Ring closure of 1-hexenyl radical to methylcyclopentyl radical



a. atom to empty space leading to a new single bond

b. double bond to an atom leading to a single bond

Chapter 8

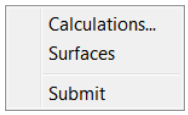
The Setup Menu

*This chapter describes functions available under the **Setup** menu. **Calculations** is used to specify MMFF molecular mechanics calculations, PM3 semi-empirical molecular orbital calculations, Hartree-Fock molecular orbital calculations, B3LYP and EDF2 density functional calculations and MP2 calculations. Tasks include calculation of energy, equilibrium geometry, equilibrium conformation and transition-state geometry and constructing energy profiles. STO-3G, 3-21G, 6-31G* and 6-311+G** basis sets are provided for Hartree-Fock calculations and 6-31G* and 6-311+G** basis sets for B3LYP, EDF2 and MP2 calculations. **Calculations** also requests IR and NMR spectra, and extended printing.*

***Surfaces** is used to designate graphical surfaces, including electron and spin densities, electrostatic potentials, local ionization potentials and molecular orbitals, for later display as surfaces, property maps and contour plots. Inaccessible regions on electron density surfaces and property maps based on these surfaces may be demarked.*

***Submit** is used to initiate calculation.*

The **Setup** menu provides access to dialogs for specifying molecular mechanics and quantum chemical calculations, for specifying surfaces and property maps and for submitting jobs for calculation.



Calculations...

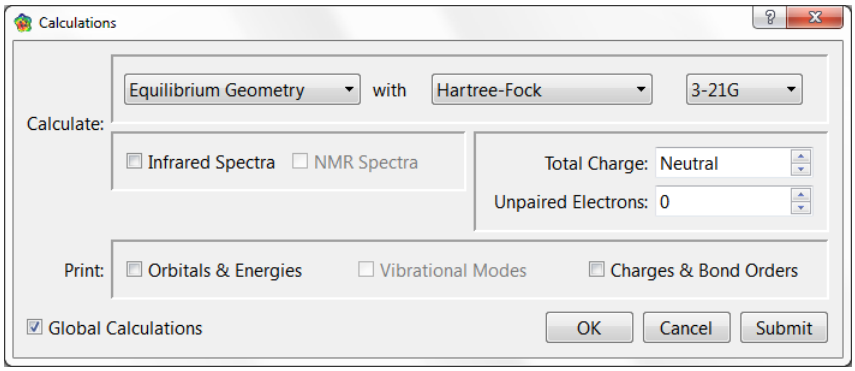
The MMFF molecular mechanics model, the PM3 semi-empirical molecular orbital models, Hartree-Fock molecular orbital models, B3LYP and EDF2 density functional models and the MP2 Møller-Plesset models are available to calculate energy, equilibrium geometry

and make energy profiles. All models except MMFF are available for calculating transition state geometry. Only the MMFF molecular mechanics model is available to calculate equilibrium conformation. STO-3G, 3-21G, 6-31G* and 6-311+G** basis sets are available for Hartree-Fock calculations and 6-31G* and 6-311+G** basis sets for B3LYP, EDF2 and MP2 calculations.

The aqueous solvation energy obtained by the SM5.4 model is added to the energy of any molecular mechanics or quantum chemical calculation and provided in the **Molecule Properties** dialog (**Properties** under the **Display** menu; **Chapter 9**).

Quantum chemical calculations also provide atomic charges, IR and NMR spectra. IR spectra are available for all models but NMR spectra are only available for the B3LYP/6-31G* and EDF2/6-31G* models.

Selection of **Calculations...** results in the **Calculations** dialog.

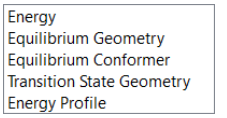


This contains pull-down menus, buttons and check boxes:

Calculate

This section is used to specify the task to be accomplished, theoretical model to be employed and spectra to be supplied.

Specification of a task is by way of a pull-down menu:



Energy specifies calculation of energy (and in the case of quantum chemical methods, a wavefunction) at a single geometry.

Spartan Student reports energies from molecular mechanics calculations in kJ/mol, from semi-empirical calculations as heats of formation in kJ/mol, and from Hartree-Fock, B3LYP, EDF2 and MP2 calculations as total energies in atomic units (hartrees).

The molecular mechanics energy comprises two parts: the strain energy and the non-bonded energy. The strain energy is the difference in energy between a molecule and its "strain free" analog. It is nearly always positive and less than a few hundred kJ/mols in magnitude. The non-bonded energy accounts for attraction or repulsion between atomic centers that are not connected due to van der Waals and Coulombic interactions. Because the strain energy of every molecule relates to a different standard, molecular mechanics energies cannot be used to obtain reaction energies (unless there are no changes in bonding between reactants and products).

The heat of formation is to the enthalpy at 298K of a balanced chemical reaction in which a molecule is converted to a set of standard products. For example, the heat of formation of ethylene is given by reaction,

$$C_2H_4 + \rightarrow 2C\ (\text{graphite}) + 2H_2\ (\text{gas})$$

where graphite and hydrogen molecule are the carbon and hydrogen standards, respectively. In practice, the actual measurement is typically carried out for a combustion reaction, for example, for ethylene:

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

Heats of formation may either be positive or negative quantities and generally span a range of only a few hundred kJ/mol.

Heats of formation are not suitable for presenting energy data from quantum chemical calculations, simply because the standards for several important elements (most notably, carbon) are not well-defined isolated species. In its place is the energy of a reaction that splits a molecule into isolated nuclei and electrons, for example, for ethylene:

$$C_2H_4 \rightarrow 2C^{+6} + 4H^{+} + 16e^{-}$$

Total energies, as the energies of such reactions are termed, are always negative and may be very large (tens of thousands of kJ/mol). They are most commonly given in atomic units (hartrees).

$$1\ \text{atomic unit} = 2625\ \text{kJ/mol}$$

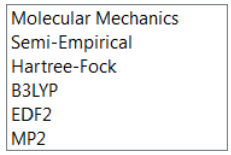
It is possible to relate total energies to heats of formation by incorporating data on atomic species. Heats of formation reported from T1 calculations

(part of the information provided in ***Spartan Student's*** database) relate directly to experimental heats and are given in kJ/mol.

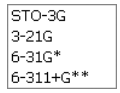
To summarize, the heat of formation differs from the total energy both with regard to the standard reaction and with regard to units. Either provides a suitable basis for thermochemical calculations.

Equilibrium Geometry specifies that the nearest energy minimum will be located, **Equilibrium Conformer** specifies that the lowest energy conformer will be located and **Transition State Geometry** specifies that the nearest transition state (energy maximum in one dimension and energy minima in all other dimensions) will be located. **Energy Profile** steps along user-defined coordinates.

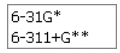
Except for **Equilibrium Conformer**, a theoretical model needs to be specified by way of pull-down menus. The first provides a choice among different classes of models.



Selection of **Molecular Mechanics** leads to a single method, MMFF. Selection of **Semi-Empirical** leads to a single method, PM3. Selection of **Hartree-Fock** leads to a second menu of available basis sets.



Selection of either **B3LYP, EDF2** or **MP2** leads to an abbreviated menu of available basis sets.



Transition State Geometry is not available for **Molecular Mechanics** and **Equilibrium Conformer** is only available for **Molecular Mechanics**.

If *checked*, **Infrared Spectra** calculates vibrational frequencies

and intensities together with the corresponding vibrational modes. These are available in the output (**Output** under the **Display** menu; **Chapter 9**) along with zero-point energies and thermodynamic properties (enthalpies, entropies, heat capacities and Gibbs energies). The thermodynamic properties are also available from the **Thermodynamics Properties** dialog (**Properties** under the **Display** menu; **Chapter 9**) as a function of temperature. Vibrational motions (***normal modes***) may be animated and an IR spectrum displayed from the **IR** dialog accessible from **Spectra** under the **Display** menu (**Chapter 9**). Frequency calculations involving MP2 models are very costly in terms of computation and are not recommended.

Infrared frequencies from B3LYP/6-31G* and EDF2/6-31G* calculations (only) have been uniformly scaled to account for known systematic errors. Calculated frequencies from the other available models have been left unscaled. In addition, the lines in the calculated infrared spectrum obtained from all models have been broadened to account for the fact that the calculations correspond to 0K, whereas experimental measurements are carried out at finite temperature. Scale and line width parameters may be adjusted following display of the spectrum (**Spectra** under the **Display** menu; **Chapter 9**).

If *checked*, **NMR Spectra** specifies that NMR chemical shifts from the B3LYP/6-31G* and EDF2/6-31G* models (only) will be calculated. These are then available in the output (**Output** under the **Display** menu; **Chapter 9**) as well as from the **Atom Properties** dialog (**Display** menu) and as atom labels (**Configure...** under the **Model** menu; **Chapter 5**). ^{13}C (proton decoupled) and ^{1}H spectra may be displayed from the **NMR Spectra** dialog accessible from **Spectra** under the **Display** menu (**Chapter 9**)*. ^{13}C chemical shifts (only) that have been empirically corrected for local environment are also available in the printed output, as atom labels, from the **Atom Properties** dialog and in spectral plots. Line intensities are

* Chemical shifts for other nuclei are available in the **Output** dialog (**Output** under the **Display** menu) and may also be attached as labels (**Configure...** under the **Model** menu; **Chapter 5**).

assumed to be proportional to the number of equivalent carbons or hydrogens. Three-bond HH coupling constants for ^{1}H spectra are estimated empirically and may be displayed in terms of spectral splittings.

Total Charge

Total charge. The default setting (**Neutral**) may be changed either by *clicking* on , and selecting **Anion**, **Dianion**, **-3**, etc. from the menu, or by typing a number in the. **Total Charge** is ignored for molecular mechanics calculations.

Unpaired Electrons

The number of unpaired electrons. The default setting (**0**) may be changed either by *clicking* on , and selecting **1** or **2** from the menu, or by typing in the menu. **Unpaired Electrons** is ignored for molecular mechanics calculations.

Print

If *checked*, writes the quantity to the output window. Text output may be seen by selecting **Output** from the **Display** menu (**Chapter 9**) and printed by first selecting the output dialog and then selecting **Print Output** from the **File** menu (**Chapter 3**).

If *checked*, **Orbitals & Energies** writes the orbitals and energies to the output. An orbital energy diagram may also be displayed (**Orbital Energies** under the **Display** menu; **Chapter 9**) and HOMO and LUMO energies are also available in the spreadsheet (**Spreadsheet** under the **Display** menu; **Chapter 9**).

If *checked*, **Vibrational Modes** writes vibrational frequencies and modes to the output. This requires that the infrared spectrum has been calculated.

If *checked*, **Charges and Bond Orders** writes atomic charges and bond orders to the output.

Global Calculations

If *checked*, signifies that settings in the **Calculations** dialog are to be applied to all molecules in the document.

The **Calculations** dialog may be exited by clicking on **Submit**, **Cancel** or **OK** at the bottom right of the dialog, or on  at the top. (**Submit** and **OK** are not available if the job is already executing.) Clicking on **OK** or on **Submit** overwrites any previous information. Additionally, **Submit** enters the job in the execution queue (see discussion later this chapter). Clicking on **Cancel** or on  exits the **Calculations** dialog without saving any changes.

Surfaces

Spartan Student allows graphical display of the HOMO and LUMO among other molecular orbitals, the electron density, the spin density for molecules with unpaired electrons, the electrostatic potential and the local ionization potential.

Additionally, any one of the quantities listed above (except the electron density) may be mapped onto any surface (except a molecular orbital surface). In practice, the only maps to have received widespread attention are those based on the electron density surface (depicting overall molecular size and shape). Most common are the electrostatic potential map, the local ionization potential map and the LUMO map. Some regions of an electron density surface are inaccessible and are not available for interaction with their environment (or with an incoming reagent). ***Spartan Student*** allows these regions to be identified.*

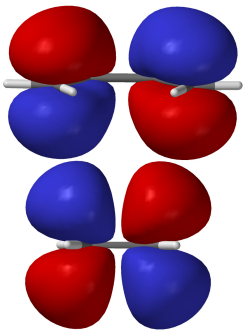
Surfaces (including those underlying maps) connect points of equal value (they are isosurfaces), and may be displayed as an arrangement of dots, a mesh, or an opaque or translucent solid. Examples of graphical output in orthogonal projection are provided in **Figure 8-1**. Surfaces (and maps) may also be rendered in perspective (see **Chapter 5**) and in stereo (see **Chapter 2**).

---

* A region on a density surface is designated as inaccessible if a sphere of radius 1.0 Å centered on a line normal to the surface and touching a point in the middle of the region, impinges on any other regions of the density surface. The sphere radius may be changed in the **Settings Preferences** dialog (**Preferences** under the **Options** menu; **Chapter 10**).

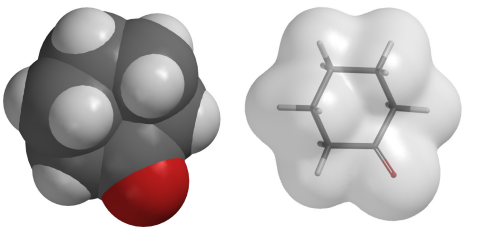
Figure 8-1: Examples of Graphical Displays Available in *Spartan Student*

Frontier orbitals for a symmetry-allowed Diels-Alder reaction,



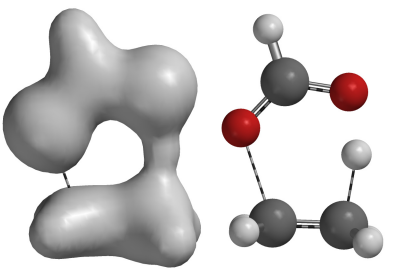
showing interaction of the HOMO of 1,3-butadiene and the LUMO of ethylene.

Space-filling model and electron density surface of cyclohexanone,



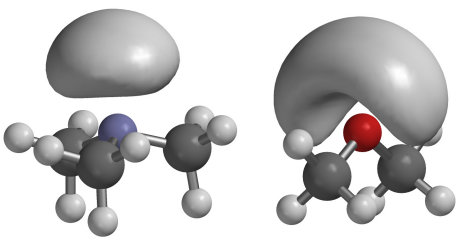
showing overall molecular size and shape.

Electron density surface (0.08 electrons/au^3) of transition structure for pyrolysis of ethyl formate,



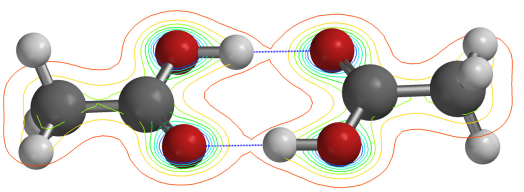
showing bonding in the transition state.

Electrostatic potential surfaces (-40 kJ/mol) of trimethylamine (left) and dimethyl ether (right),



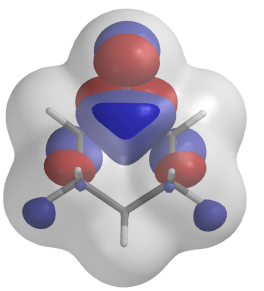
showing the lone pairs on nitrogen and oxygen, respectively.

Electron density slice for acetic acid dimer,



showing hydrogen bonding.

Simultaneous display of the LUMO and the electron density surfaces of cyclohexanone,

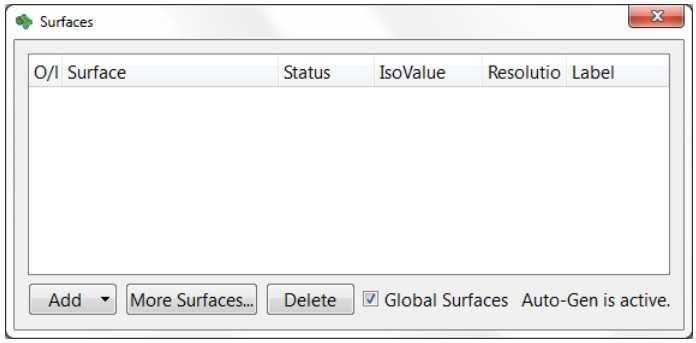


showing accessibility for nucleophilic attack.

Calculated quantities may also be displayed as two dimensional contour plots (slices). Unlike surfaces and maps, these can be translated, rotated and zoomed independently of the molecular skeleton. An example of a slice display is provided in **Figure 8-1**.

Several different surfaces, maps and slices may be simultaneously displayed. In addition, any of the usual structure models may be displayed along with the graphic. The total display can become very complex, and selective use of meshes and/or translucent solids (as opposed to opaque solids) may facilitate visualization.

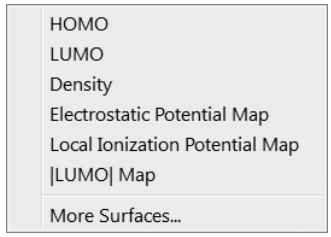
Selection of **Surfaces** leads to the **Surfaces** dialog.



This contains a box at the top for listing requested surfaces and property maps.

Common Surfaces and Property Maps

Add at the bottom of the dialog is used to specify a number of commonly-used graphical surfaces and property maps*. *Clicking* on it leads to a menu.



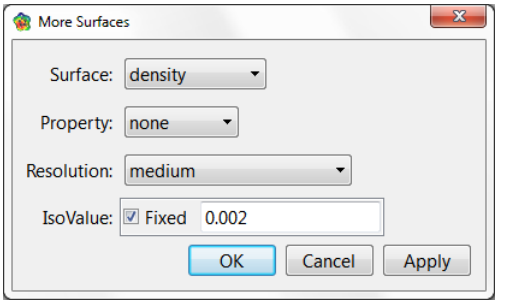
Selection of all but the last entry in the menu leads to a request for the analogous surface or map. A surface and property map

* Additional selections are provided if the molecule has unpaired electrons.

specified from this menu will be calculated at medium resolution and will assume a fixed isovalue unless a different resolution has been selected and/or an adjustable isovalue has been requested.

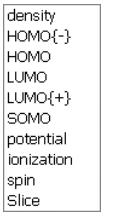
More Surfaces

Additional surfaces and maps or the same surfaces or maps at different resolution and with adjustable isosurfaces may be requested by selecting **More Surfaces...** from the menu (or by *clicking* on **More Surfaces...** at the bottom of the **Surfaces** dialog). This leads to the **Add Surfaces** dialog that contains three menus and a check box:



Surface

Available surface types appear under the **Surface** menu.



Density is the total electron density which may be used to reveal bonding as well as overall molecular size and shape, ***HOMO{-}, HOMO, LUMO, LUMO{+}, SOMO**** are molecular orbitals, ***potential*** is the electrostatic potential, ***ionization*** is the local ionization potential and ***spin**** is the spin density.

Selection of **HOMO{-}** and **LUMO{+}** results in display of a box to decrement the HOMO and increment the LUMO. This allows

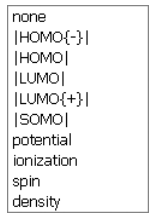
* These menu entries appear only for molecules with one or more unpaired electrons.

any molecular orbital to be specified..

Slice designates that a plane will cut through the graphic defined by **Property**.

Property

Properties for maps appear in the **Property** menu.

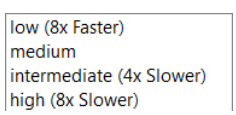


Available properties are the molecular orbitals (**HOMO{-}**, **HOMO**, **LUMO**, **LUMO{+}**, **SOMO**[*]), the electrostatic potential (**potential**), the local ionization potential (**ionization**) and the spin density (**spin**)[*]. **none** indicates that no property is to be mapped onto the surface). As with **Surface** above, selection of **HOMO{-}** and **LUMO{+}** leads to a decrement (increment) box.

A **Spin** button will be displayed if **Unpaired Electrons** (in the **Calculations** dialog) is set to a value other than **0**, and if **HOMO{-}**, **HOMO**, **LUMO** or **LUMO{+}** has been selected for **Surface** or for **Property**. *Clicking* on **Spin** toggles it between **Alpha** and **Beta**. **Alpha** designates that the molecular orbital either to be displayed as a surface or mapped as a property corresponds to α spin; **Beta** designates that the molecular orbital corresponds to β spin.

Resolution

Selection of surface resolution is from the **Resolution** menu.



High resolution is necessary for surfaces based on percentage enclosure. Both calculation time and disk storage increase significantly in moving from medium to high resolution.

Isovalue

Allows calculation of a surface with fixed isovalue. In the case of a density surface, the default value of 0.002 electrons/bohr^3 corresponds roughly to enclosure of 99% of the total number of electrons and closely resembles a space-filling model. Fixed surfaces take less time to compute and require less storage.

Following **Surface**, **Property**, **Resolution**, **Isovalue** and (optionally) spin selection, *clicking* on **OK** adds the requested graphic to the list and removes the (**Add Surfaces**) dialog. *Clicking* on **Apply** adds the requested graphic to the list but leaves the dialog on screen. *Clicking* on **Cancel** does not add a graphic to the list but removes the (**Add Surfaces**) dialog.

The process (*clicking* on **Add...**, followed by selection from the menu or *clicking* on **More Surfaces...** followed by selection of surface, property, resolution and isovalue and *clicking* on **OK** or **Apply**) may be repeated as required.

An existing graphic may be deleted from the list by first highlighting (*clicking* on) it and then *clicking* on **Delete**.

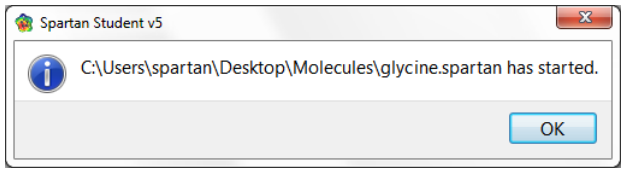
Global Surfaces, if *checked*, signifies that the requested surfaces will be calculated for all members of the list.

Only one copy of the **Surfaces** dialog may appear on screen, and any actions relate to the currently selected molecule. The dialog may be removed by *clicking* on  .

Submit

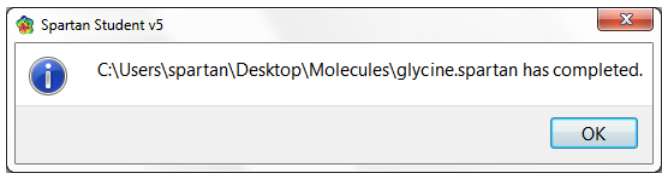
Following setup of a molecular mechanics or quantum chemical calculation, as well as any requests for properties, spectra and/or graphical displays, the required calculations will begin when **Submit** is selected. If the job has not previously been saved or submitted, selection of **Submit** triggers a request for a name. If the document

contains only a single molecule and that molecule exists in the Spartan Spectra and Properties Database, the name in the database will be presented as a default name. Otherwise, the default name presented will be ***spartan*** for the first job and ***spartanx*** (x an integer starting with 1 for all successive jobs). After a name has been provided (or if a name already exists or if the default name is accepted) a dialog appears indicating that the job has actually been submitted.*



Click on **OK** to remove it. After a job has started, and until it has completed, all associated files will be designated read only.

Another dialog appears following completion of a calculation.



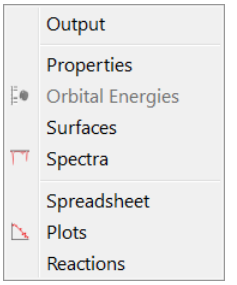
Click on **OK** to remove it.

Upon completion, an energy profile calculation leads to an additional document being created for each molecule in the original document. These new documents are named ***document.Prof.identifier*** where ***document*** is the name given to the original document and ***identifier*** identifies the molecule inside the original document. A query dialog is provided asking whether the resulting ***Spartan*** document is to be opened.

* The job is submitted to a job queue and will be submitted for execution only when released from this queue. See **Monitor** under the **Options** menu (**Chapter 10**) for discussion.

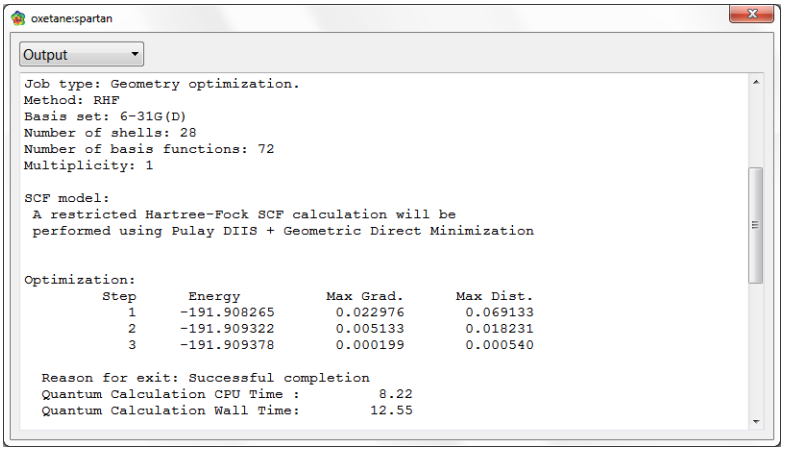
Chapter 9
The Display Menu

*Functions available under the **Display** menu provide for text, dialog, spreadsheet and graphical displays. Functions are also available to query a variety of on-screen objects, display both calculated and (if available) experimental IR and NMR spectra, animate vibrational motions, prepare plots from spreadsheet data and calculate reaction energies.*



Output

Selection of **Output** opens a window.



The contents of the output window may be scrolled and may be paged up or down by *clicking* above or below the scroll bar. The contents may be printed or copied by *right clicking* inside the **Output** window and selecting **Print** or **Copy** from the menu that results. Alternatively,

if **Confined** has been selected for **Output/Spreadsheet Windows** (from the **Preferences** menu, **Chapter 10**), printing is accomplished by selecting **Print Output...** from the **File** menu (this replaces **Print...** when an output window is selected). Similarly, copying is accomplished by selecting **Copy** from the **Edit** menu when an output is selected. **Find...** and **Find Next** functions from the **Edit** menu are also available.

A single output window is associated with each document, and changes focus as different molecules from the document are selected. Output windows for different documents may be simultaneously open on screen. An output window may be closed by *clicking* on  .

> Output from jobs that are currently executing or are in the execution queue, is unavailable. Output for jobs that are executing may be viewed using the **Monitor** under the **Options** menu (**Chapter 10**).

Properties

Spartan Student provides specialized dialogs for reporting and (in some cases) changing the properties of molecules, atoms, bonds, graphical surfaces and geometrical constraints. Only one **Properties** dialog may be opened at a time. Dialog selection operates in a toggle mode. The default **Properties** dialog is **Molecule Properties**. Other **Properties** dialogs may be accessed by *clicking* on an atom, bond, surface, or constraint. For example, *clicking* a second time on an atom, bond, or constraint reverts the currently displayed **Properties** dialog back to **Molecule Properties**.*

Most **Properties** dialogs have an associated **Utilities** or **Style** dialog. For example, associated with the **Molecule Properties** dialog is a **Molecule Utilities** dialog. These access additional information about the molecule and its components/attributes, or provide style and color controls. This is useful for highlighting (or deemphasizing) a particular molecule, component or attribute. **Utilities**/**Style** dialogs are reached

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* The exception to this involves *clicking* on a property map to obtain the value of the property at a particular surface location. *Clicking* a second time on a new location will report a new value of the property. *Clicking* on the background leads to the **Molecule Properties** dialog.

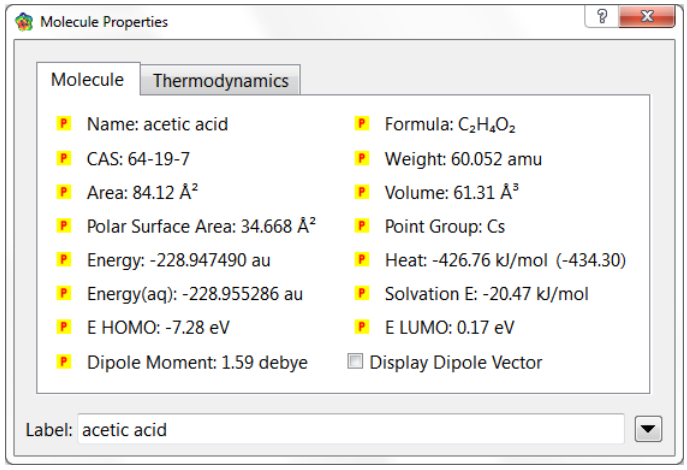
by *clicking* on ▼ at the bottom right of the appropriate **Properties** dialog. Return to the **Properties** dialog follows from *clicking* on ▲ at the bottom right of the associated **Utilities**/**Style** dialog.

The **Properties** (or **Utilities**/**Style**) dialog may be removed from the screen by *clicking* on x.

Molecule Properties and Thermodynamics

The **Molecular Properties** dialog is divided into two displays **Molecule** and **Thermodynamics**, controlled by tabs at the top left. Entries under the **Molecule** tab relate to common molecular properties that (if applicable to the selected level of calculation) are automatically calculated.

Molecule Properties

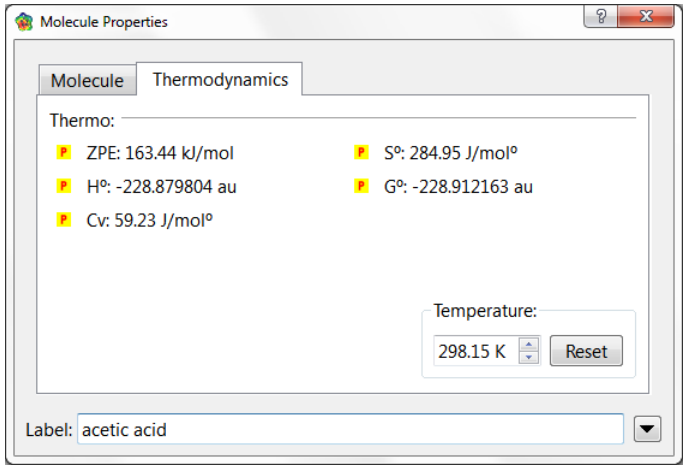


The dialog under this tab includes the name, formula, CAS number, molecular weight (in amu), surface area and polar surface area (PSA) of a space-filling model (in $Å^2$), volume of a space-filling model (in $Å^3$) and the point group. It provides the energy (in au) of a Hartree-Fock, B3LYP, EDF2 or MP2 calculation, the heat of formation (in kJ/mol) of a PM3 calculation, or the sum of the strain energy and non-bonded energy (in kJ/mol) of an MMFF calculation, the energy (heat of formation, strain energy) corrected for an aqueous environment (in the same units as the non-corrected quantity), the solvation

energy (in kJ/mol) as the difference between aqueous and gas-phase energies, (if available) the heat of formation from the T1 model (in kJ/mol), (if available and in parenthesis) the experimental heat of formation (in kJ/mol) and the dipole moment (in debyes). With the exception of experimental heat of formation, any or all of these may be posted to the spreadsheet using the P buttons to the left of their values. **Label** (also referred to as identifier) identifies the molecule in a document. It appears in the first column of the spreadsheet (see **Spreadsheet** later in this chapter) and can be changed to the molecule's name from the Spartan Spectra and Properties Database.* Finally, the dialog permits display of the dipole moment vector by *checking* the box to the right of **Display Dipole Vector**.

Thermodynamics

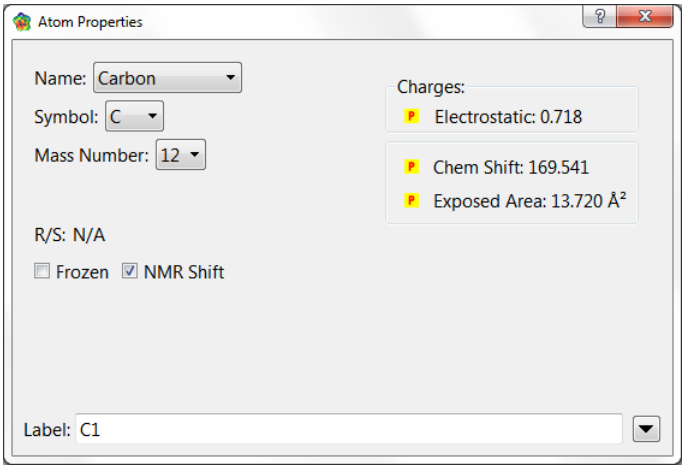
Entries under the **Thermodynamics** tab provide the zero-point energy, the enthalpy, the constant volume heat capacity, the entropy and the Gibbs energy. Except for the zero-point energy, all depend on temperature which can be specified. All require vibrational frequencies.



* If the molecule does not appear in the Spartan Spectra and Properties Database, the name will be ***M000X*** (X=1,2,...) unless altered by the user.

Atom Properties

Selection of an atom with a **Properties** dialog on screen, or selection of **Properties** following selection of an atom, leads to the **Atom Properties** dialog.



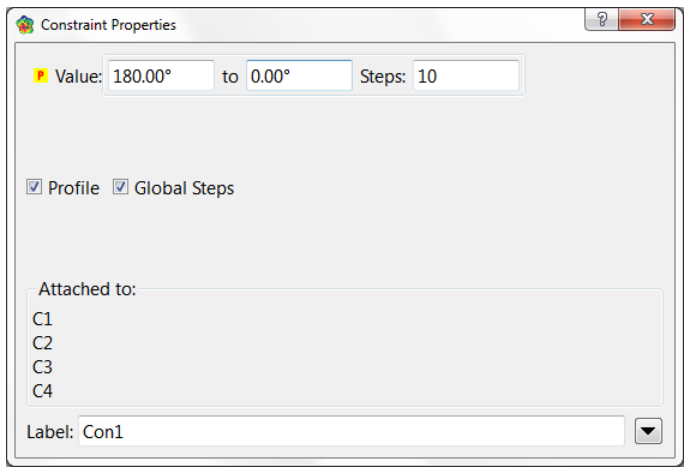
This displays the element name (and allows changing the element), R/S chirality, electrostatic-fit charges (in electrons), calculated NMR chemical shift (in ppm relative to the appropriate standard; tetramethylsilane for both proton and ^{13}C) and exposed surface area of a space-filling model (in $Å^2$). It also allows freezing the atom (see **Freeze Center** in **Chapter 6**), eliminating the line from the displayed NMR spectrum, changing its mass number and the default label, and posting atomic charges, chemical shifts and exposed areas to the spreadsheet.

Bond Properties

Selection of a bond with a **Properties** dialog on screen, or selection of **Properties** following selection of a bond leads to the **Bond Properties** dialog (not shown). This displays the bond length (in Å), Mulliken bond order (in electrons) and bond type (and allows changing the bond type). Note that the results of quantum chemical calculations do not depend on bond types.

Constraint Properties

Selection of a constraint marker with a **Properties** dialog on screen, or selection of **Properties** following selection of a constraint marker, leads to the **Constraint Properties** dialog (expanded form shown).



This allows setting the value of a constraint, posting it to the spreadsheet and changing the default constraint label. *Checking* **Dynamic** leads to the expanded dialog shown above. This allows specifying a sequence of constraints for an energy profile (see **Calculations...** under the **Setup** menu; **Chapter 8**). The value of the starting constraint is given in the box to the right of **Value**, and the value of the ending constraint is given in the box to the right of **to**. The number of steps in the profile is given in the box to the right of **Steps**. Initially, the numbers in both boxes to the right of **Value** will be the same, and **Steps** will be set to **1**. These may be altered by typing the desired numbers into the appropriate boxes and then *pressing* the **Enter** key (**return** key on Mac). This functionality may also be accessed from **Constrain Distance** (**Angle**, **Dihedral**) under the **Geometry** menu (**Chapter 16**). If **Global Steps** is *checked*, the independent variables are moved in concert, meaning that the number of steps must be the same for each variable (the constraint ranges may be different). If *unchecked*, the variables are moved independently and the number of steps may differ from one to another. In this case, the total number of

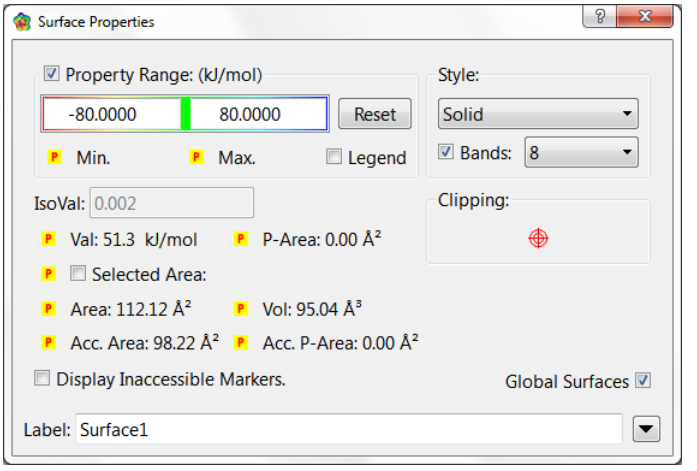
steps in the profile is the product of the number of steps for each variable. An energy profile may involve constraints on more than one geometrical variable.

Point and Plane Properties

Selection of a user-defined point or plane with a **Properties** dialog on screen, or selection of **Properties** from the **Display** menu following selection of a point or plane, leads to the **Point Properties** or **Plane Properties** dialog (not shown). These allow changing point or plane labels.

Surface Properties

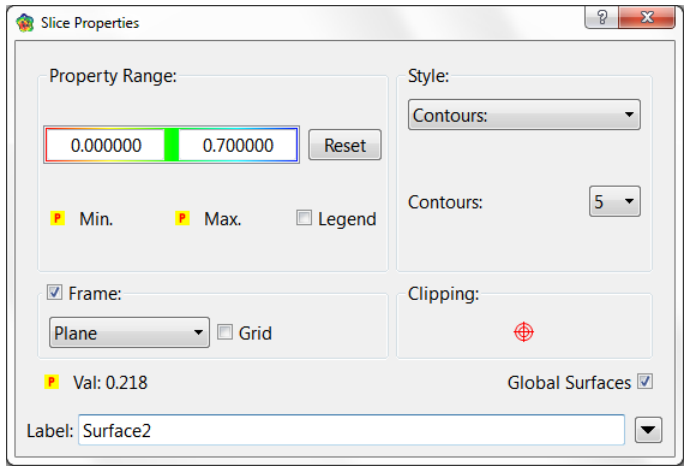
Selection of a graphical display with a **Properties** dialog on screen, or selection of **Properties** following selection of a graphical display, leads to the **Surface Properties** dialog.



This allows changing display style, isovalue (and in the case of electron density surfaces), percentage of the electrons contained inside the surface, turning on mapped properties, selecting between continuous and banded displays and setting the range of the property, displaying accessible area of surfaces and maps and changing the default labels. The dialog also reports (and optionally posts to the spreadsheet) the area and volume of the graphic, the

accessible area*, the polar area of an electrostatic potential map**, maximum and minimum value of the mapped property and its value at the cursor position***. If *checked*, **Legend** displays a scale. If *checked*, **Global Surfaces** designates that the settings apply to all molecules in the document.

If the selected graphical surface is a slice, the **Slice Properties** dialog replaces the **Surface Properties** dialog.



This contains similar controls to that found in the previous dialog. Specification of isovalue has been replaced by specification of the number of contours to be displayed. A sphere or a cylinder may be selected instead of a plane, and check boxes allow for a frame around the slice and for a grid.

Surfaces

This accesses the same dialog previously described in **Chapter 8**.

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* A region on a density surface is designated as inaccessible if a sphere of radius 1.0 Å centered on a line normal to the surface and touching a point in the middle of the region, impinges on any other regions of the density surface. The default radius (**Accessible Area Radius**) may be changed in the **Settings Preferences** dialog (**Preferences** under the **Options** menu; **Chapter 10**).

** This is defined as that part of the surface area for which the absolute value of the electrostatic potential is > 100 kJ/mol. The cutoff (**Polar Area Range**) may be changed in the **Settings Preferences** dialog (**Preferences** under the **Options** menu; **Chapter 10**).

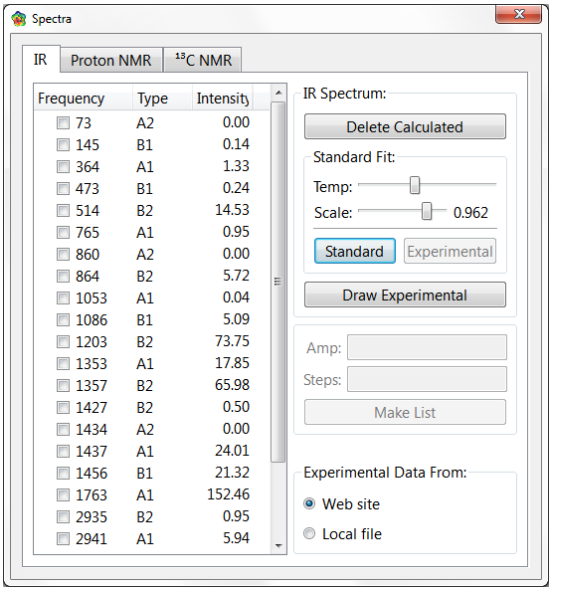
*** To determine property value at another position *click* on it. To bring up the **Molecule Properties** dialog, *click* on the background.

Spectra ( )

Spartan Student provides for display of calculated IR and NMR spectra. (These need to have been previously requested from the **Calculations** dialog under the **Setup** menu; **Chapter 8**.) In addition, it allows on-line access and display of experimental spectra from publicly available collections. This allows direct visual comparison of calculated and experimental spectra. Finally, the **IR Spectra** dialog allows fitting of calculated and experimental spectra, using a linear scaling parameter and a peak width parameter to adjust the calculated spectrum. Access to spectra display is via tabbed dialogs (**IR**, **Proton NMR** and **^{13}C NMR**).

IR

The **IR Spectra** dialog not only provides for display of a calculated and (if available) experimental infrared spectra, but also allows for animated display of the vibrational modes as well as for generation of a sequence of structures along a vibrational coordinate.



At the left-hand side of the dialog is an ascending list of frequencies (in cm^{-1})* together with (infrared) intensities and symmetry labels.

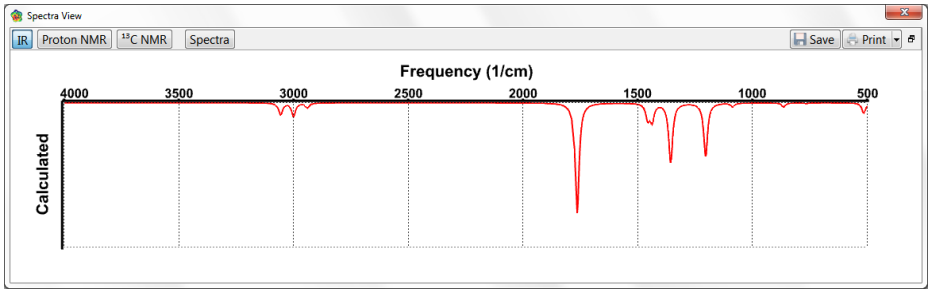
* Imaginary frequencies, for example, corresponding to the reaction coordinate for a transition state, will appear first in the list with the letter **i** in front of the frequency value.

A frequency is selected for display by *clicking* on it. This results in display (animation) of the vibrational motion. *Clicking* again deselects it (stops the animation).

The amplitude of vibrational motion (the maximum displacement away from equilibrium of any pair of atoms) may be changed from the default amplitude (0.5Å, which is much larger than the actual amplitude of vibrational motion at room temperature) by altering the contents of the box to the right of **Amp** at the lower right of the dialog. The default number of steps that make up the display (11) may be changed by altering the contents of the box to the right of **Steps*** at the lower right of the dialog.

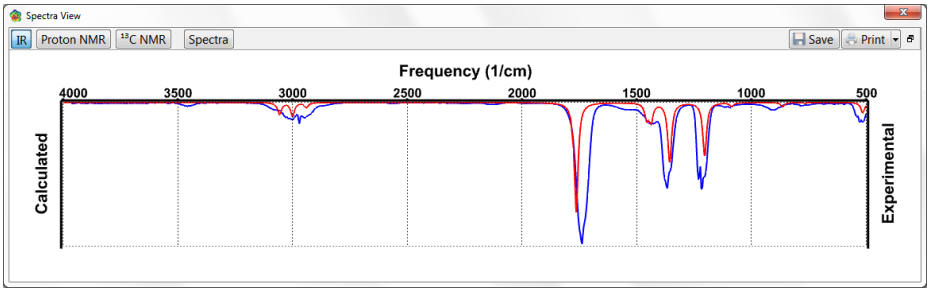
Clicking on **Make List** creates an unnamed ***Spartan Student*** document containing a sequence of structures corresponding to motion along the selected vibrational mode. Sequences (corresponding to different vibrations) can be created.

The calculated spectrum may be drawn by *clicking* on **Draw Calculated** at the top right of the dialog.



The experimental spectrum may be drawn with or without the calculated spectrum by *clicking* on **Draw Experimental** at the center right of the dialog.

* It is recommended that the number of steps be odd ensuring that the center point corresponds to the actual equilibrium or transition-state structure.



Experimental IR spectra are accessed from the NIST (National Institute of Standards and Technology) website (http://webbook.nist.gov/chemistry). This comprises approximately 7,000 IR spectra, primarily for organic molecules.

Draw operations for both calculated and experimental IR spectra, apply to all molecules in the document (not just the selected molecule). The range for calculated and experimental IR spectra is from 4000 cm^{-1} to 500 cm^{-1}, corresponding to the range commonly measured and reported.

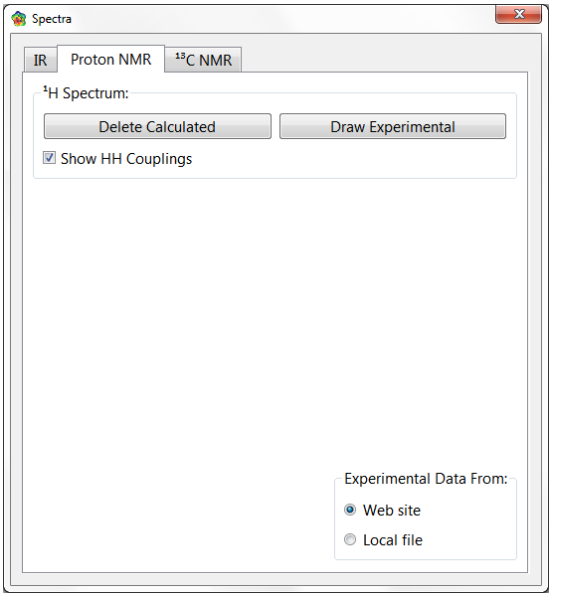
Calculated IR frequencies exhibit systematic errors. Stretching frequencies obtained from Hartree-Fock models are typically 10-12% larger than measured frequencies, while stretching frequencies obtained from B3LYP, EDF2 and MP2 models are typically 5-6% larger than measured frequencies. Systematic errors may be revealed (and quantified) by first simultaneously displaying calculated and experimental spectra and then scaling one of the spectra to provide a best visual fit. To scale the calculated spectrum, use the slider bar to the right of **Scale** near the top right of the dialog. Scaling applies uniformly to all molecules in a list (not just the selected molecule).

A second slider bar marked **Temp** controls peak width. (This is loosely connected with the temperature at which the experimental measurement is carried out.) Low "temperature" (slider to the left) will produce sharp spikes, whereas high "temperature" (slider to the right) will produce broad bands. The default setting gives spectra that resemble experimental spectra.

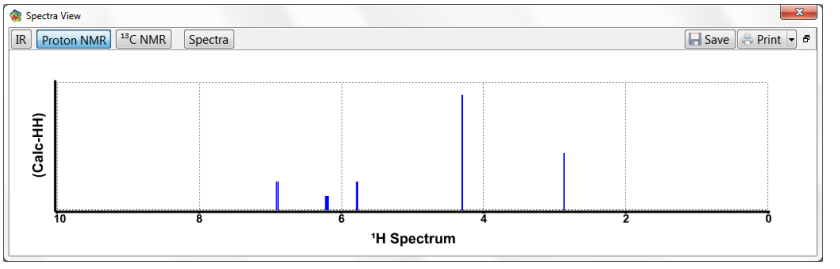
A best fit of calculated to experimental infrared spectra is obtained by *clicking* on **Experimental**.

Proton NMR

The **Proton NMR Spectra** dialog provides for display of both calculated and (if available) experimental ^{1}H spectra.*



The calculated proton NMR spectrum may be drawn by *clicking* on **Draw Calculated** and line splittings due to three-bond HH coupling shown by *checking* **Show HH Couplings**.**



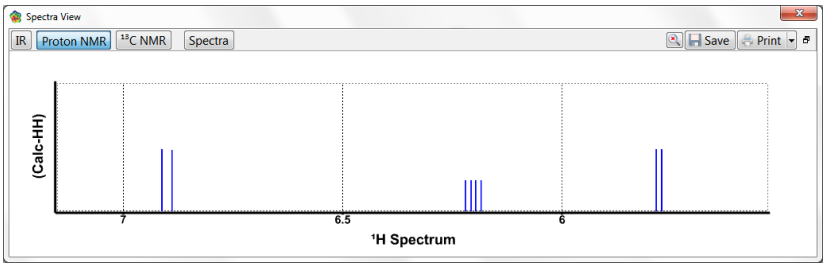
An experimental proton spectrum may be added to the plot by *clicking* on **Draw Experimental**. Draw operations apply to all

* Chemical shifts are available only from B3LYP/6-31G* and EDF2/6-31G* calculations. Chemical shifts for nuclei other than hydrogen and carbon may be displayed as labels (see **Configure...** under the **Model** menu; **Chapter 5**).

** Coupling constants are not calculated models but rather are estimated empirically.

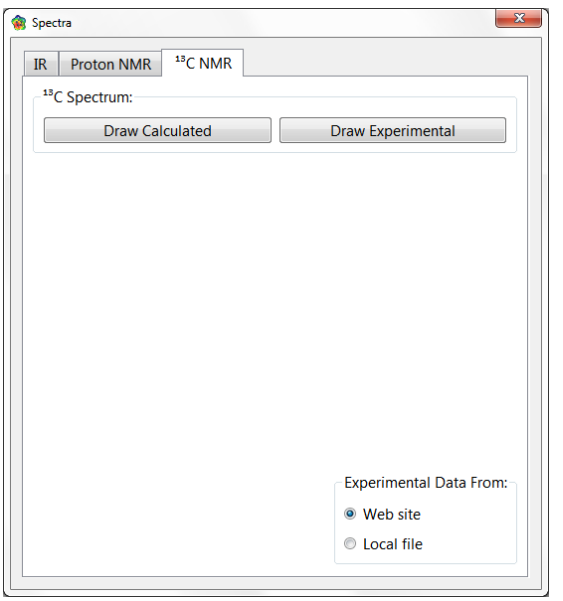
molecules in a list. Spectra may be removed by *clicking* on **Delete Calculated** and **Delete Experimental** (that have replaced the cooresponding draw buttons). The range for both calculated and experimental proton spectra is from 0 ppm to 10 ppm (relative to TMS). This corresponds to the range typically measured and reported.

To magnify a region on a plot, position the cursor at one corner of the region, *drag* the mouse to the opposite corner while holding down the left button and release the button.

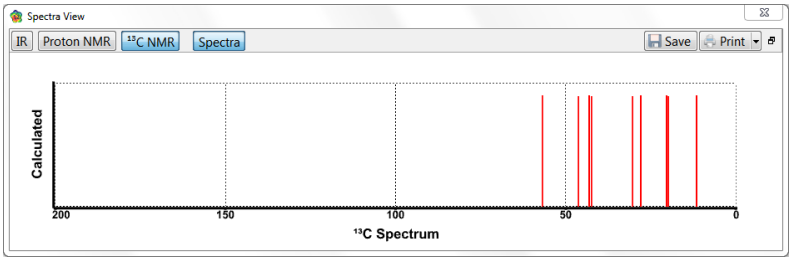


^{13}C NMR

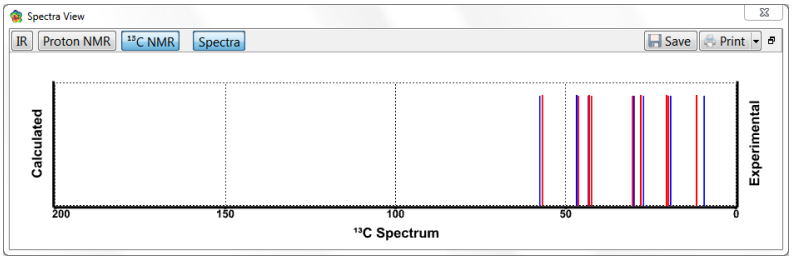
The **^{13}C NMR** dialog provides for display of both calculated and (if available) experimental ^{13}C spectra.



The calculated ^{13}C spectrum may be drawn by *clicking* on **Draw Calculated**. ^{13}C NMR spectra will be based on chemical shifts that have been empirically corrected to account for local environment.



The corresponding experimental ^{13}C spectrum (if available) may be displayed together with or independently of the calculated spectra by *clicking* on **Draw Experimental**.

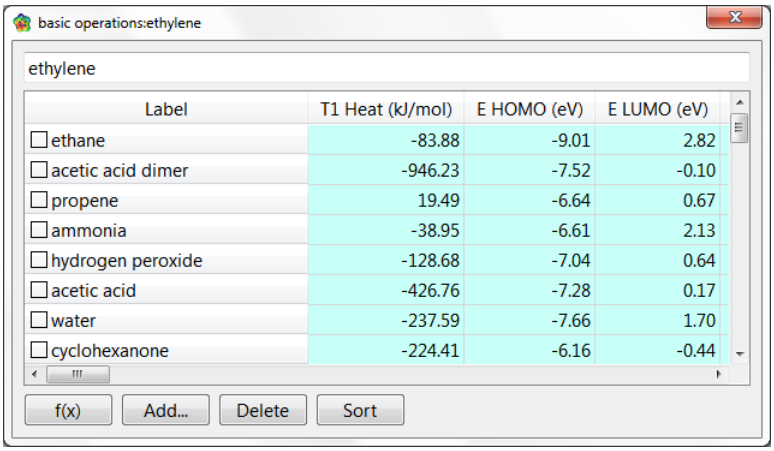


Draw operations for both calculated and experimental NMR spectra apply to all molecules in a list. The calculated spectrum may be removed by *clicking* on **Delete Calculated** (that has replaced **Draw Calculated**) in the appropriate section of the dialog. Similarly, the experimental spectrum may be removed by *clicking* on **Delete Experimental**). The range for both calculated and experimental ^{13}C spectra is 0 ppm to 200 ppm (relative to TMS). This corresponds to the range typically measured and reported.

Only a single copy of one of the dialogs under **Spectra** may appear on screen; scaling will relate to the currently selected molecule. The dialog may be removed by *clicking* on  .

Spreadsheet

Associated with each ***Spartan Student*** document (including documents with only a single molecule) is a spreadsheet. This may be displayed by selecting **Spreadsheet** from the **Display** menu.



The spreadsheet comprises a series of rows (corresponding to different molecules in the document) and columns (corresponding to different properties). This gives rise to cells, the number of which is the product of the number of rows (molecules) and the number of columns (properties). The spreadsheet may be expanded or contracted by positioning the cursor at one of the corners, *pressing* the left mouse button and *dragging* the mouse.

Only one molecule from one document may be selected (although several molecules may be simultaneously displayed). Molecule selection follows either by *clicking* on the spreadsheet cell containing the molecule label or identifier (leftmost column), or by using the ◂ and ▸ buttons or the scroll bar at the bottom left of the screen. Molecules may be ***animated*** (stepped through in succession) using the ▸ button at the bottom left of the screen. Animation speed may be adjusted from the **Settings** tab (**Preferences** under the **Options** menu; **Chapter 10**). Selection of a new molecule in the document results in deselection of the previously selected molecule. A molecule may be designated for permanent display by *checking* the box to the left of its identifier (**Label**) in the spreadsheet. The molecules in a document may either be translated and rotated in concert or

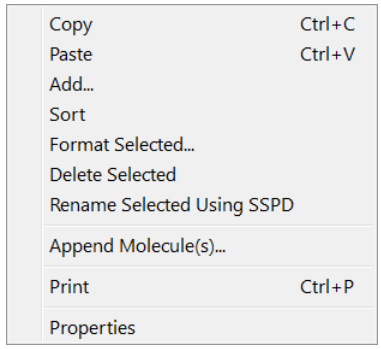
manipulated independently. This is controlled by **Coupled** under the **Model** menu (**Chapter 5**). By default (**Coupled** checked) molecules move in concert. *Uncheck* **Coupled** to move them independently.

Upon initial entry, all columns of the spreadsheet except the leftmost column, are blank. The leftmost column contains a label that may be changed either by directly typing a new label into the spreadsheet or into the **Label** box in the **Molecule Properties** dialog (see discussion earlier in this chapter). Additionally, default identifiers (***M0001,*** **...**) may be replaced by chemical names if the molecule exists in the subset of the Spartan Spectra and Properties Database (SSPD) included with ***Spartan Student*** by *right clicking* inside the cell that contains the identifier and selecting **Rename Selected Using SSPD** from the menu that results. To replace all identifiers, *left click* on the header cell and then *right click* and select **Rename Selected Using SSPD**.

Information may be added to the spreadsheet in several ways:

From the Add Dialog

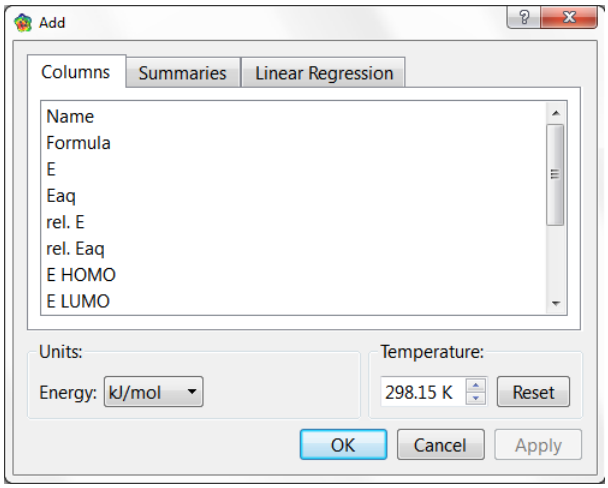
A selection of molecular properties may be entered into the spreadsheet by first *clicking* on the header cell of an empty column, and then *clicking* on **Add...** at the bottom of the spreadsheet. Alternatively, *right click* inside the header cell and then select **Add...** from the menu that results.



This leads to the **Add** dialog (comprised of three tabs). The **Columns** tab requests information about the properties of individual molecules, the **Summaries** tab provides summaries

of the properties for all molecules and the **Linear Regression** tab attempts to find relationships among properties of the molecules.

With the **Columns** tab selected, the following data are available.

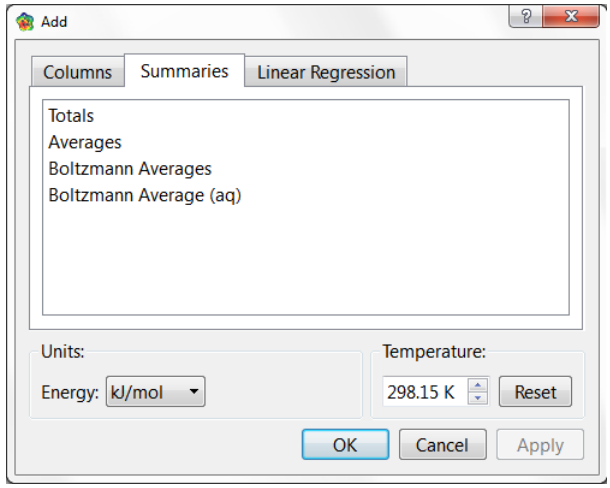


Name	molecule name as it appears in SSPD
Formula	molecular formula
E	energy (heat of formation, strain energy)
E_{aq}	aqueous energy (heat of formation, strain energy) based on the SM5.4 model
rel. E	energy (heat of formation, strain energy) relative to selected molecule
rel. E_{aq}	aqueous energy (heat of formation, strain energy) relative to selected molecule based on the SM5.4 model
E HOMO	energy of highest-occupied molecular orbital
E LUMO	energy of lowest-occupied molecular orbital
Dipole	dipole moment (in debyes)
Boltzmann Distribution	Boltzmann distribution based on energy
Boltzmann Distribution (aq)	Boltzmann distribution based on aqueous energy as estimated from SM5.4 model
Alignment Score	$1\text{-}R^2/N$, where R^2 is the root mean square distance and N is the number of alignment centers. 1 is a perfect score

One or more properties may be added to the spreadsheet by *clicking* on their entries, and where appropriate specifying units

from the **Energy** menu, varying temperature from the **Temp** menu (as applied to thermodynamic quantities and to the Boltzmann distributions), and finally *clicking* on **OK** or **Apply**. In the former case, the dialog is dismissed and in the latter it is left on screen. *Clicking* on **Cancel** or  removes the dialog.

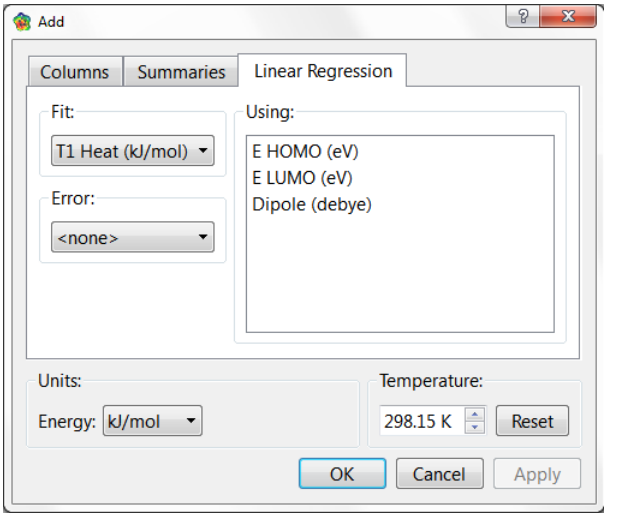
Column totals, averages and Boltzmann-weighted averages may be accessed by *clicking* on the **Summaries** tab. Alternatively, *click* on an empty row header (instead of an empty column header) inside the spreadsheet prior to *clicking* on **Add...**. This leads to **Summaries** tab.



Totals	sum of column values
Averages	average of column values
Boltzmann Averages	Boltzmann weighted average of column values
Boltzmann Averages (aq)	Boltzmann weighted average of column values using energies corrected for aqueous environment based on the SM5.4 model

Clicking on one or more of these followed by *clicking* on **OK** or **Apply**, leads to the requested summaries as rows at the bottom of the spreadsheet, identified as **Totals**, **Averages**, etc. (one row for each).

Finally, a linear regression analysis may be performed on the data in the spreadsheet. First *click* on the **Linear Regression** tab.



Select one entry from the **Fit** menu and one or more entries from the list under **Using**. *Clicking* on **OK** or **Apply** performs the linear regression analysis and places the results in a row at the bottom of the spreadsheet identified by **Fit**. As many regression analyses as desired may be performed on the data in the spreadsheet. The individual results will be entered as separate rows in the spreadsheet, with names **Fit1**, **Fit2**, etc.

Numerical Data

Numerical data may be entered by typing directly into the spreadsheet. A column header first needs to be specified. *Double click* on an empty column header cell, type in a name and *press* the **Enter** key (**return** key on Mac). Then, type the data into individual cells of the new column (*press* the **Enter** or **return** key following each data entry).

User-Defined Expressions

An expression may be entered either into a header cell (in which case it refers to all entries in a column) or into an individual cell (in which case it refers only to a single entry). Expressions in the column header take the form ***name=formula***, where ***formula*** may involve arithmetic operations, specialty functions, calculated quantities, conversion factors and constants in addition to numerical values. References to specialty functions, molecular mechanics and quantum chemical quantities and conversion factors and constants must be preceded by **@**. For example, ***mu = @DIPOLE*** typed into a header cell gives the dipole moment. Some functions have arguments, for example, ***c1*** and ***c2*** in the expression ***c12= @DISTANCE (c1,c2)*** refer to atoms c1 and c2, while ***3*** in the expression ***orbitalE=@HOMO (-3)*** designates the energy of the molecular orbital three orbitals below the HOMO. It is necessary to *press* the **Enter** key (**return** key on Mac) following entry of the expression into a cell. The leading ***name=*** is optional for entries in an individual (non-header) cell.

Arithmetic Operations		**Boolean Operations**	
+	addition	>	greater than
_	subtraction	>=	greater than or equal to
*	multiplication	<	less than
/	division	<=	less than or equal to
^	raise to a power	==	equal to
		!=	not equal to
		|	or
		&	and

Mathematical Functions

ABS(x)	absolute value	LN(x)	natural logarithm
ACOS(x)	inverse cosine	LOG(x)	log (base 10)
ASIN(x)	inverse sine	SIN(x)	sine
ATAN(x)	inverse tangent	SQRT(x)	square root
COS(x)	cosine	TAN(x)	tangent
EXP(x)	exponential		

Specialty Functions

AVG (column name)	average of values in column
FITVAL (fit name)	column of fit values from regression analysis
MIN (column name)	minimum of values in column
MAX (column name)	maximum of values in column
NUM (column name)	number of defined entries in column
ROW	the number of the row in the spreadsheet
ROW(molecule name)	the number of the row of molecule
REF(i, x)	the value of the x referenced to row i
STDEV (column name)	standard deviation of values in column
SUM (column name)	sum of values in column

Calculated Quantities

ANGLE(i, j, k)	angle involving atoms i, j, k (degrees)
AREA	area of a user-defined plane ($Å^2$)
DIHEDRAL(i, j, k, l)	dihedral angle involving atoms i, j, k, l (degrees)
DISTANCE(i, j)	distance involving atoms i, j (Å)
ELECTROSTATIC (i)	electrostatic charge on atom i (electrons)
HOMOev(-n)	energy of n^{th} orbital below the HOMO (eV)
HOMOBETAev(-n)	energy of the n^{th} orbital below the β HOMO (eV)
INTERTIA(i)	principle movements of inertia from largest (i=1) to smallest (i=3)
ISOTOPE(i)	mass number of atom i
LENGTH (i)	length of bond i (Å)
LUMOev(+n)	energy of the n^{th} orbital above the LUMO (eV)
LUMOBETAev(+n)	energy of the n^{th} orbital above the β LUMO (eV)

Conversion Factors and Constants

ANGS2AU	Ångstroms to atomic units
AU2ANGS	atomic units to Ångstroms
EV2HART	eV to atomic units (hartrees)
EV2KCAL	eV to kcal/mol
EV2KJ	eV to kJ/mol
HART2KCAL	atomic units (hartrees) to kcal/mol
HART2EV	atomic units (hartrees) to eV
HART2KJ	atomic units (hartrees) to kJ/mol
KCAL2EV	kcal/mol to eV
KCAL2HART	kcal/mol to atomic units (hartrees)
KCAL2KJ	kcal/mol to kJ/mol
KJ2EV	kJ/mol to eV
KJ2HART	kJ/mol to atomic units (hartrees)
KJ2KCAL	kJ/mol to kcal/mol
PI	π

Table 9-5: Examples of User Defined Expressions

E/area = @ENERGY/@AREA	energy divided by surface area
RelE = @ENERGY-@REF (6,@ENERGY)	energy relative to energy of molecule in row 6
Eq = @EXP (-@ENERGY/592.1)	equilibrium constant at room temperature
EnergyFilter = @ENERGY<-99.43	"true" (≠0) for all energies <-99.43
RowFilter = @ROW>10	"true" (≠0) all entries past row 10

From Post (P) Buttons

Post buttons **(P)** found in a number of properties dialogs provide an alternative method to the **Add** dialog for entering calculated properties into the spreadsheet. Note that some properties may require user specification. These include individual bond distances, angles and dihedral angles (available from **Measure**

Distance, **Measure Angle** and **Measure Dihedral** under the **Geometry** menu; **Chapter 6**), bond distance, angle and dihedral angle constraints (available from **Constrain Distance**, **Constrain Angle** and **Constrain Dihedral** under the **Geometry** menu; see discussion in **Chapter 6**), atomic charges, chemical shifts (available from the **Atom Properties** dialog; this chapter), the accessible area of an electron density surface, the polar area of an electrostatic potential map, minimum and maximum property values on a map and the value of the property at a specific location on a property map (available from the **Surfaces Properties** dialog; this chapter). With the exception of the property value on a map, post generates an entire column. Where atom labels are involved, for example, in defining a specific distance, post can be expected to yield consistent results for all molecules in a document only where the molecules are closely related, or where labels have been explicitly reassigned*. The property value on a map is posted only for the selected molecule. Post buttons are also available for CAS numbers, for heats of formation from the T1 thermochemical recipe and (where available) for experimental heats of formation contained in ***Spartan Student's*** internal database.

Copy/Paste

Properties of one or more molecules in a document may be copied and then pasted into individual or multiple spreadsheet cells. These include (but are not restricted to) bond distances, angles and dihedral angles (**Measure Distance**, **Measure Angle** and **Measure Dihedral** under the **Geometry** menu), bond distance, angle and dihedral angle constraints (**Constrain Distance**, **Constrain Angle** and **Constrain Dihedral** under the **Geometry** menu), atomic charges and chemical shifts (**Atom Properties** dialog), infrared frequencies and chemical shifts (**IR Spectra** and **NMR Spectra** dialogs, respectively) and the value of a property on a property map (**Surface Properties** dialog). To copy the spreadsheet, first highlight the numerical value of the

* This may be done using the **Atom Properties** dialog (see discussion earlier in this chapter).

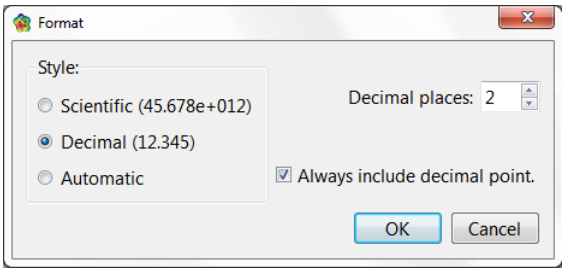
property in the appropriate screen location (distances, etc.) or dialog (charges, etc.), then select **Copy** from the **Edit** menu, then *click* on the appropriate (destination) cell in the spreadsheet, and finally select **Paste** from the **Edit** menu.

Each row in a spreadsheet corresponds to a molecule in a document, and new rows are automatically added in response to adding new molecules to the document. New molecules are added by building (**New Molecule** under the **File** menu; **Chapter 3**), by appending one or more existing documents each containing one or more molecules using either **Append Molecule(s)...** under the **File** menu (**Chapter 3**), or by *right clicking* inside the header cell of the first available row and selecting **Append** from the menu that appears, by pasting from the clipboard, or by *dragging* from the file system. To copy a molecule into the clipboard, first select (*click* on) it, and then select **Copy** from the **Edit** menu, or *click* on its identifier (left most column) in its spreadsheet, and then select **Copy** from the **Edit** menu. Alternatively *right click* either on the molecule or on its identifier in the spreadsheet and select **Copy** from the menu that appears. Use of the clipboard permits several molecules to be selected (and copied) at once using the **Shift** and **Ctrl** keys in the usual manner. To copy the contents of the clipboard to its destination, *click* on an empty row header in the spreadsheet (for the destination document), and then select **Paste** from the **Edit** menu. An alternative to the two-step **Copy-Paste** procedure is to *drag* the molecule or set of molecules from one spreadsheet to another.

A row (molecule) may be deleted from a spreadsheet, either by first selecting the molecule and then selecting **Delete Molecule** from the **File** menu, or by first *clicking* on its identifier in the spreadsheet (leftmost column) and then either *clicking* on the **Delete** button at the bottom of the spreadsheet, or by *right clicking* on its identifier in the spreadsheet and then selecting **Delete Selected** from the menu that appears. In all cases, a warning is provided prior to deletion. An entire column in the spreadsheet may be deleted by first *clicking* inside its header cell and then *clicking* on the **Delete** button (or **Delete Selected** from the menu).

Rows in the spreadsheet may be sorted according to the numerical values in any column either by first *clicking* inside the header cell and then *clicking* on the **Sort** button at the bottom of the spreadsheet or by *right clicking* inside the header cell and selecting **Sort** from the menu that appears. The rows are placed in ascending order, the smallest (least positive) value of the selected property at the top, largest (most positive) value at the bottom. To sort in descending order, hold down the **Shift** key before *clicking* on the **Sort** button or selecting **Sort** from the menu.

Information in one or more columns of the spreadsheet may be formated by *right clicking* inside the header cell(s) and selecting **Format Selected** from the menu that appears.



Format as desired and *click* on **OK** to remove the dialog. The full contents of the spreadsheet may be formated by *right clicking* inside the header cell for the left most column and then selecting **Format Selected** from the menu.

A button at the bottom right of the spreadsheet toggles between numerical representation of data, **f(x)**, and formula presentation, **=?**.

The spreadsheet may be printed by *right clicking* in the spreadsheet and selecting **Print**.

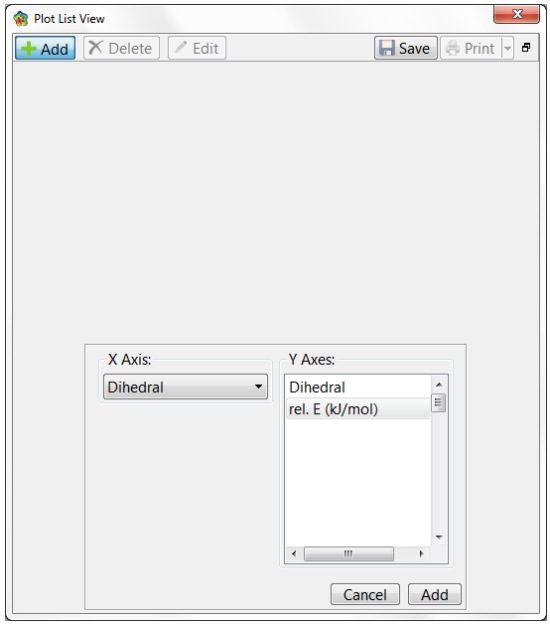
As many spreadsheets as desired (corresponding to the same or to different documents) may be open on screen. A spreadsheet is removed when the associated document is closed and may also be removed by *clicking* on .

The contents of the spreadsheet may be brought into Excel™ using the clipboard. Select whatever cells are to be copied, select **Copy** from the **Edit** menu. Alternatively, *right click* with the proper cells selected and select **Copy** from the menu that appears. **Paste** into Excel.

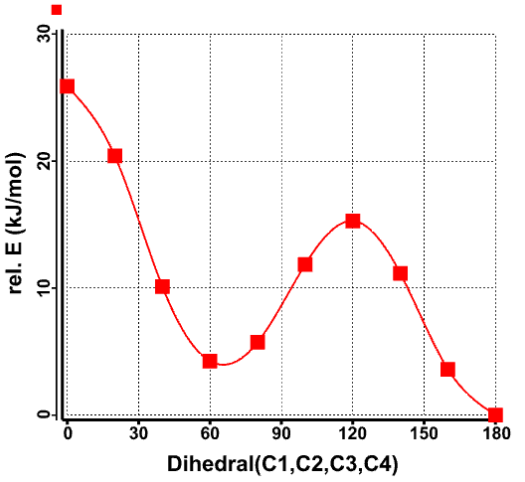
The contents of an Excel spreadsheet may be brought into ***Spartan Student***. Copy whatever information is to be transferred from Excel, move into ***Spartan Student***, *click* on the appropriate cell and select **Paste** from the **Edit** menu (or *right click* on the appropriate cell and select **Paste** from the menu that appears). Note, that information on the clipboard that goes beyond the number of rows in ***Spartan Student's*** spreadsheet will be ignored.

Plots ( )

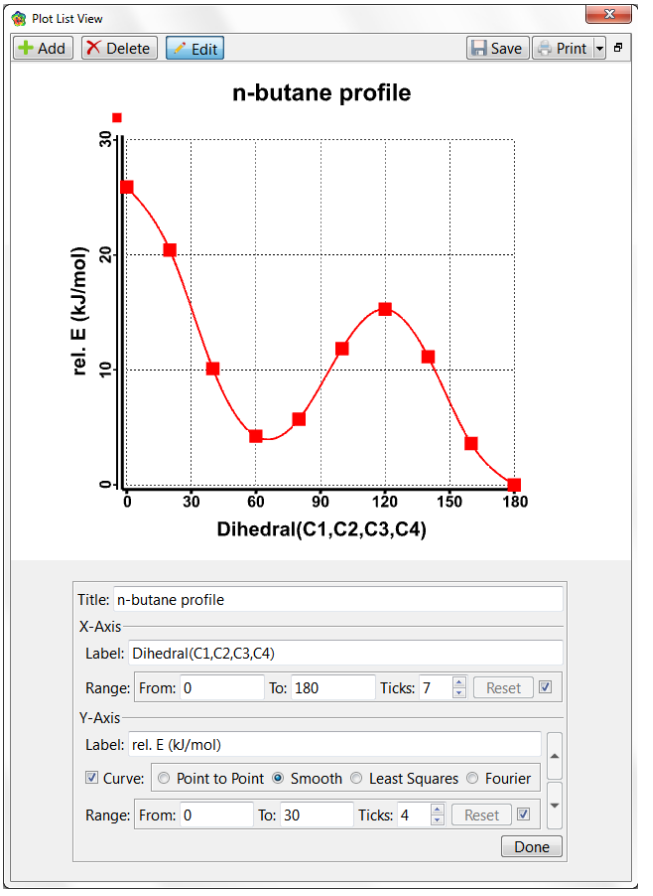
Plots may be constructed from data in a spreadsheet and a variety of simple curves fit to these data. Selection of **Plots...** from the **Display** menu leads to the **Plots** dialog.



To construct a plot, select an item from the **X Axis** menu to designate the molecular property to be displayed on the X axis, then *click* on one or more items from the **Y Axes** list to designate properties to be displayed along the Y axis and finally *click* on **Add**. (Repeated *clicking* on a property in the **Y Axes** list turns it on and off.) The dialog is removed from the screen and a plot appears.



The plot window can be detached from the screen by *clicking* on . It can be edited (a title and axis label supplied and axis ranges changed) by *clicking* on Edit.



The data points on a plot initially presented are connected by a smooth curve. They may be fit to a straight line (**Least Square**) or to a periodic function (**Fourier**).

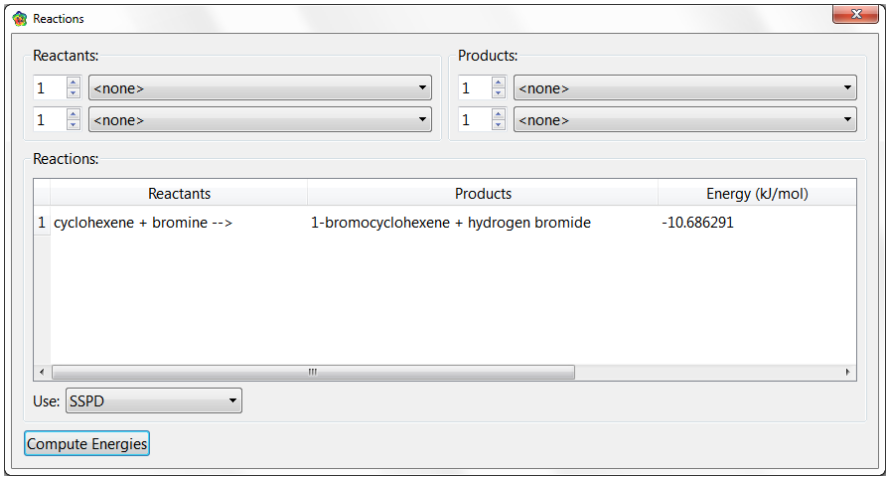
Additional plots may be added by *clicking* on Add. This will lead to a set of tabs at the top of the dialog. Only one plot may be displayed at a time. A plot may be deleted by *clicking* on its tab and then *clicking* on Delete.

Reactions...

Data in a ***Spartan Student*** document may be used to caculate reaction energies including activation energies.

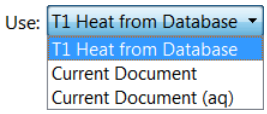
$$\Delta E = NP_1 E_{product1} + NP_2 E_{product2} - NR_1 E_{reactant1} + NR_2 E_{reactant2}$$

NP_1 and NP_2 are the numbers of product molecules 1 and 2 and NR_1 and NR_2 are the numbers of reactant molecules 1 and 2. Selection of **Reactions...** from the **Display** menu leads to the **Reactions...** dialog.



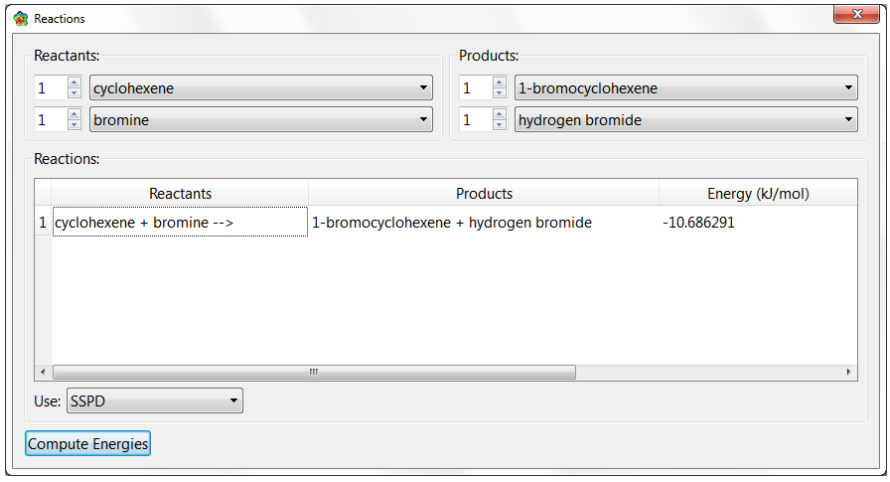
Two sets of menus under **Reactants:** and two sets of menus under **Products:** specify the number of each reactant and product and identify them. The latter correspond to the labels (identifiers) of the molecules in the document, plus a null entry **<none>**. The overall reaction needs to be mass balanced.

The **Use** menu identifies the source of the energies to be used in the reaction energy calculation.



SSPD refers to heats of formation drawn from the T1 data provided in the Spartan Spectra and Properties Database (SSPD), **Current Document** refers to energies in document and **Current Document (aq)** refers to energies in the document that have been empirically corrected for aqueous solvent using the SM5.4 model.

A reaction energy (in kJ/mol) is computed by *clicking* on **Compute Energies** at the bottom left of the dialog.

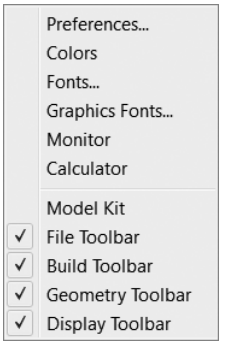


The results of a reaction energy calculation may be printed by *right clicking* inside the display area of the **Reactions** dialog and selecting **Print** from the menu that results.

The **Reactions** dialog is closed by either *clicking* on **OK** or .

Chapter 10
The Options Menu

*Functions under the **Options** menu* set default colors, fonts, user preferences and van der Waals radii, locate databases, set icon displays, identify/change URL's for on-line accesses, and monitor executing jobs.*

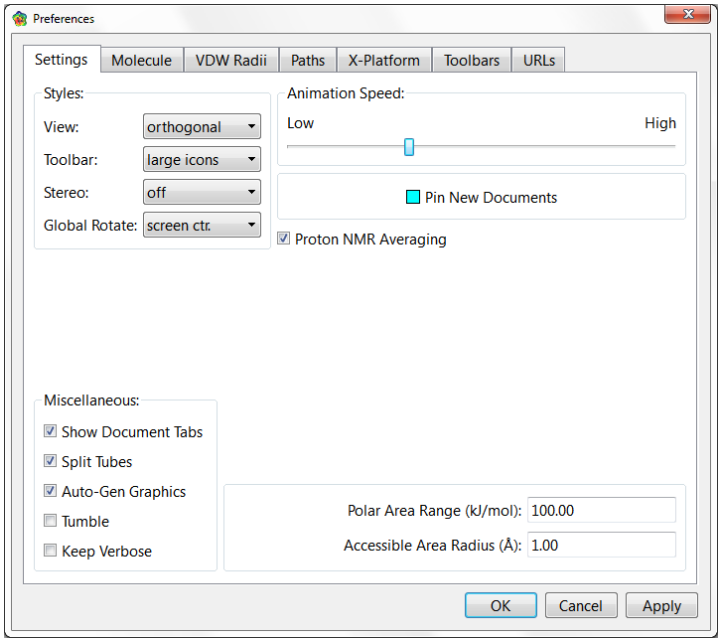


Preferences...

This sets up preferences relating to the graphical user interface (**Settings**), and to molecule displays (**Molecules**). It permits changes to default van der Waals radii used for space-filling models as well as for calculating molecular surface areas and volumes (**VDW Radii**). It also specifies the locations of databases (**Paths**), specifies platform dependent features (**X-Platform**), specifies which icons are to be displayed (**Toolbars**) and specifies URLs (**URLs**) for on-line connections. Selection results in one of seven dialogs, depending on which tab has been selected in the previous entry. *Clicking* on a tab brings up the associated dialog. To exit a **Preferences** dialog *click* on **OK**. *Clicking* on **Cancel** or  exits the dialog without instituting any changes.

* **Preferences** are also under the ***Spartan Student*** menu on the Macintosh version.

Settings



(i) **View: orthogonal, perspective**
Controls the view of structural models and graphics.

(ii) **Toolbar Style: text, small icons, medium icons, large icons**
Controls presentation style (text vs. icons) and size of the icons.

(iii) **Stereo: off, red-cyan**
Turns **red-cyan** stereographic display on and off.

(iv) **Global Rotate: screen ctr., molecule ctr**.
Screen ctr. rotates all molecules about a common center, while **molecule ctr.** rotates each molecule about its own center.

(v) **Animation Speed**
A slider bar controls the maximum speed for animations. This has become an important control as the performance of graphics cards has increased.

(vi) **Pin New Documents**
If *checked*, defaults to display of any new documents (from

building or brought in from the **File** menu) irrespective of whether or not they are selected. Does not affect the status of existing documents. **Pin New Documents** has no meaning unless **Show Document Tabs** (see discussion following) is *checked*.

(vii) **Show Document Tabs**
If *checked*, this displays a tab at the bottom of the screen for each open document. Only if the box to the left of the tab is *checked* will the molecule display (if it is not the selected document). If **Show Document Tabs** is not *checked*, the display corresponds to previous versions of ***Spartan Student***.

(viii) **Split-Tubes**
If *checked*, the tubes in tube and ball-and-spoke models are split to designate multiple bonds.

(ix) **Auto-Gen Graphics**
If *checked*, graphics calculations will be performed in the interface (without having to submit the job). Does not pertain to orbital displays initiated from **Orbital Energies** under the **Display** menu. Note, however, that graphics calculations on documents containing more than 25 molecules will not be performed in the interface irrespective of this setting.

(x) **Tumble**
If *checked*, allows automatic tumbling of molecule. To tumble a molecule, select it, *press* the left mouse button, move the mouse and release the button. To stop tumbling, *left click*.

(xi) **Keep Verbose**
If *checked*, keeps extended (verbose) output. Verbose output is normally discarded upon successful completion, but may be useful for identifying the source of problems for calculations that have not successfully completed or have led to suspicious results. (Verbose output is automatically kept for a job that has abnormally terminated.) Note that

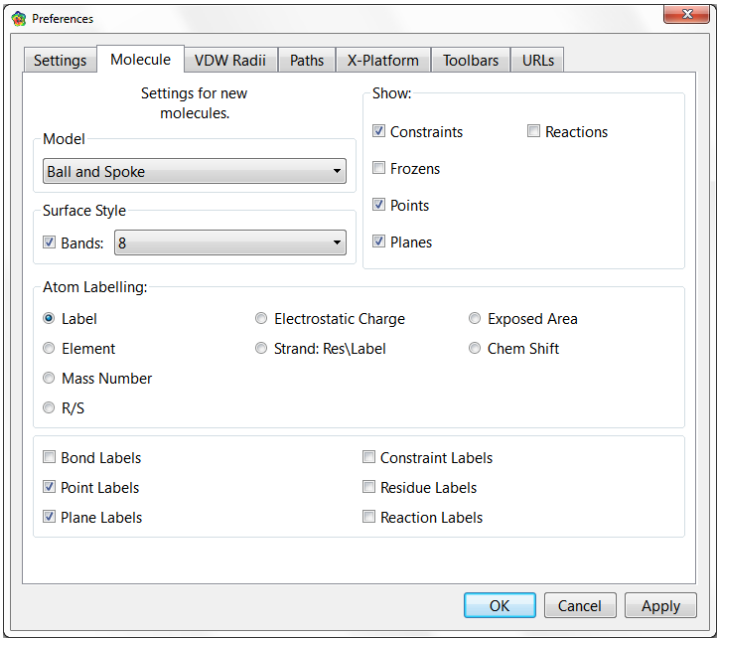
keeping verbose output significantly increases the size of the ***Spartan Student*** document.

(xii) **Proton NMR Averaging**
If *checked*, averages protons that are likely to be equivalent by conformational equilibrium.

(xiii) **Polar Area Range**
Set potential (in kJ/mol) for calculating polar area from elecrostatic potential map. Values > | range | contribute to polar area. Default is 100 kJ/mol.

(xiv) **Accessible Area Radius**
Set sphere radius (in Å) for determining accessible area. Default is 1.0.

Molecule



This specifies default settings for model appearance. These settings may be overridden for a specific molecule (or list of molecules) using entries under the **Model** menu.

(i) **Model: Wire, Ball and Wire, Tube, Ball and Spoke, Space Filling**
Controls default model style.

(ii) **Surface Style: Bands**
If *checked*, property maps will be shown in terms of discrete color bands, the number of which is set in the menu to the right. Otherwise, property maps will be shown as continuous displays.

(iii) **Show: Constraints, Frozens, Points, Planes, Reactions**
If *checked*, constraints and frozen markers, points and planes, and reaction arrows will always be shown as part of the model. Otherwise, they will be shown only in the appropriate mode.

(iv) **Atom Labeling: Label, Element, Mass Number, R/S, Electrostatic Charge, Strand: Res\Label, Exposed Area, Chem Shift**

(v) **Bond Labels**
If *checked*, bond labels will be shown.

(vi) **Point Labels**
If *checked*, point labels will be shown.

(vii) **Plane Labels**
If *checked*, plane labels will be shown.

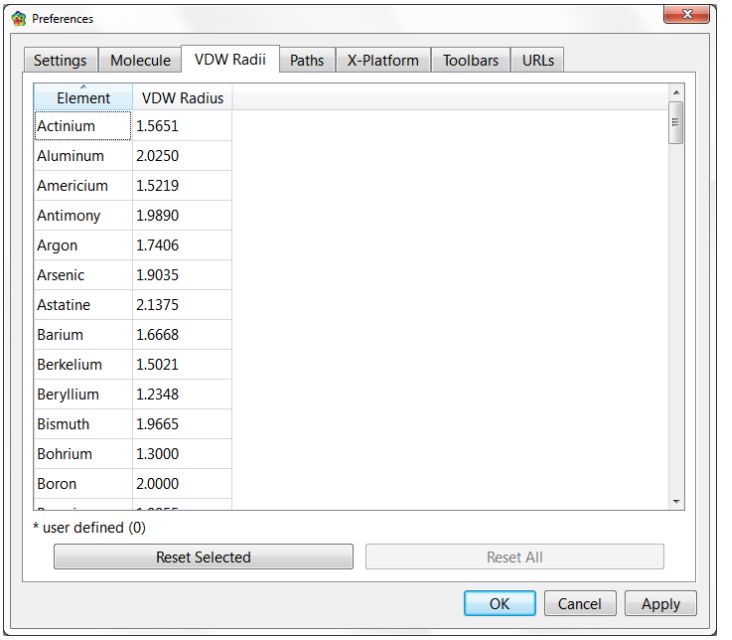
(viii) **Constraint Labels**
If *checked*, constraint labels will be shown.

(ix) **Residue Labels**
If *checked*, residue labels will be shown.

(x) **Reaction Labels**
If *checked*, reaction arrow labels will be shown.

VDW Radii

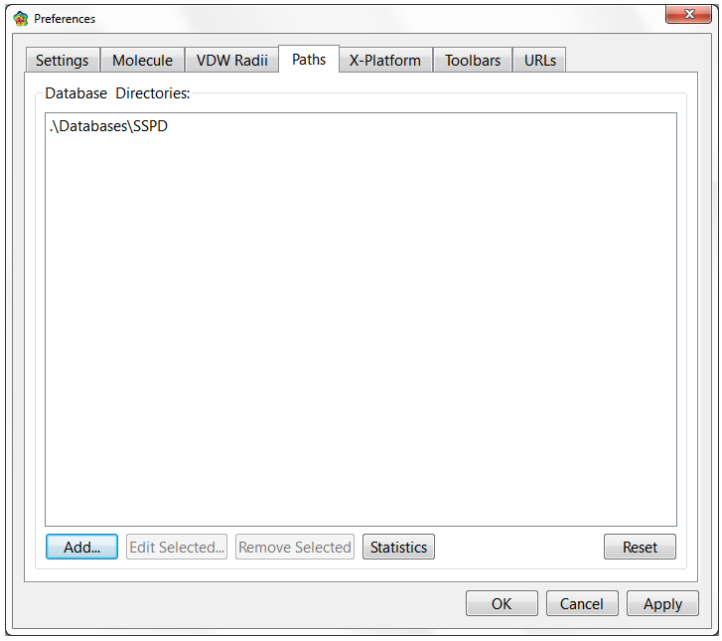
This provides a list of van der Waals radii



To order the list by element name *click* on **Element**, and by atomic radius *click* on **VDW Radius**. Individual entries may be changed from default values by first *clicking* on the entry and then entering a new value. The currently selected entry may be returned to its default radius by *clicking* on **Reset Selected** at the bottom of the dialog, and the full set of radii may be returned to their default values by *clicking* on **Reset All** at the bottom of the dialog.

Paths

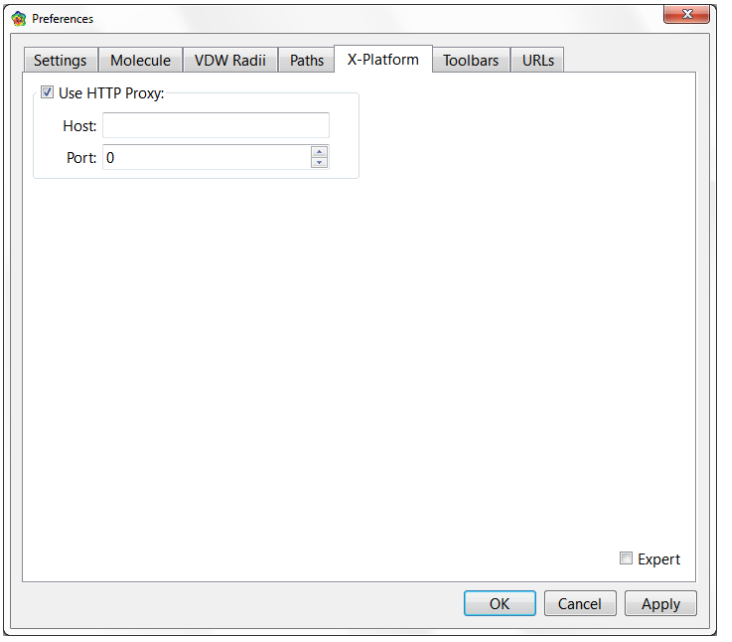
This allows setting up of paths for the SSPD included with ***Spartan Student***.

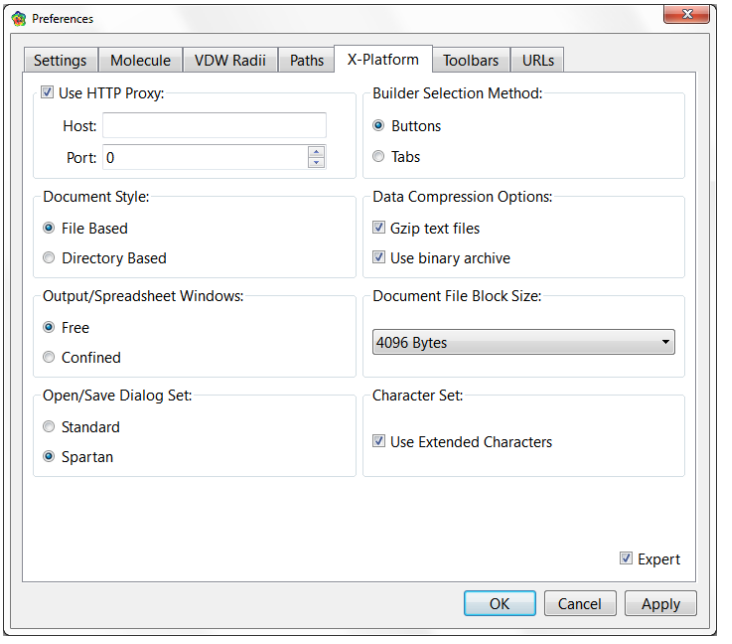


Other databases may be added, in particular, the subset of the Spartan Molecular Database (SMD).

X-Platform

This controls platform (computer) dependent features.



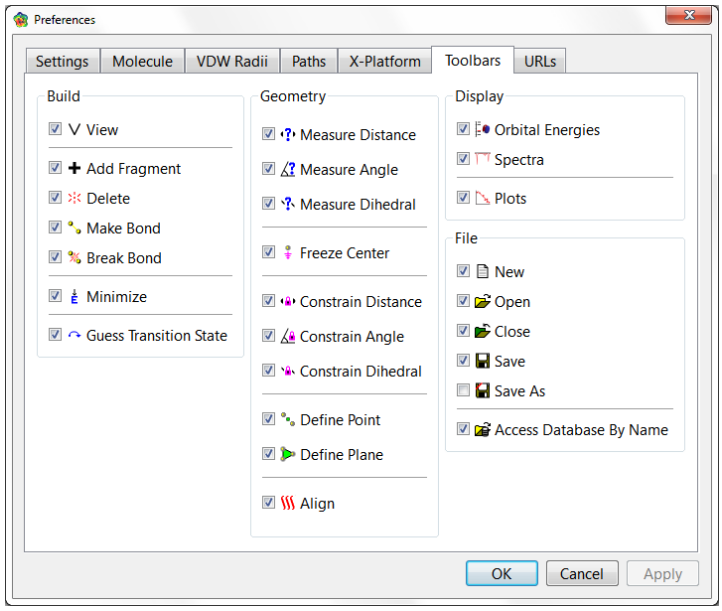


Output/Spreadsheet Windows controls whether these are **Free**, that is, able to move outside **Spartan Student's** main window or **Confined** inside this window. **Free** is only appropriate for large monitors.

Builder Selection Method controls whether selection of model kit is from two rows of **Buttons** or from a vertical **Tab**. The latter is needed for very small screens as for example found on netbook computers.

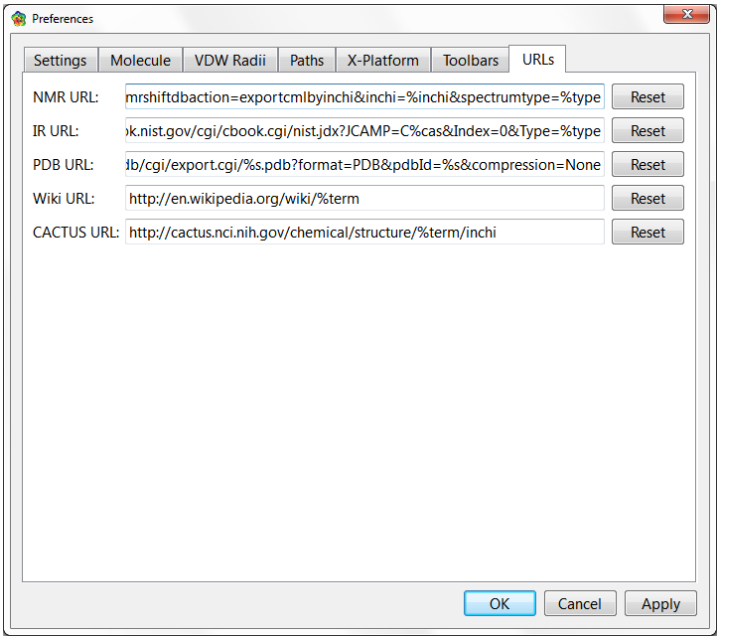
Toolbars

A listing of all icons available for entries in the **File**, **Geometry**, **Build** and **Display** menus is provided. If *checked*, the icon will appear at the top of the ***Spartan Student*** screen.



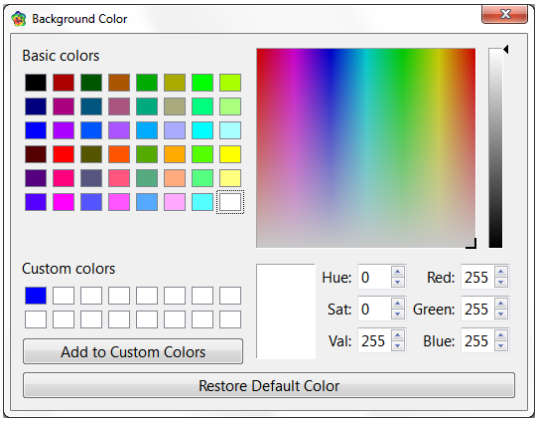
URL's

Lists URL's for access to experimental structural and spectral databases and to Wikipedia.



Colors

This alters default colors. Selection leads to the **Colors** dialog.

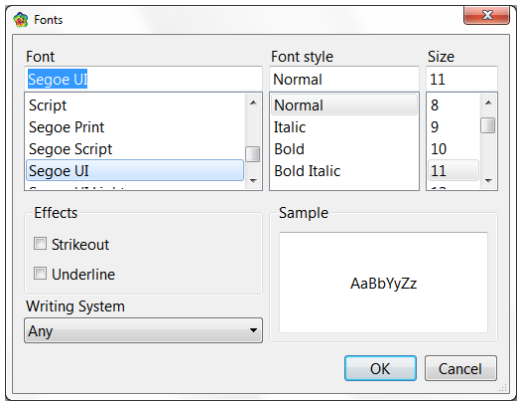


After selecting an object, its color may be set by choosing from the palette, moving the cursor inside the window of colors, or by selecting either a set of hue, saturation and values, or red, green and

blue settings. The default color may be reset by *clicking* on **Restore Default Color**. Color selection applies to all objects of the same type, for example, all carbon atoms, and not just to the selected carbon. Further control of colors is available from **Utilities/Style** dialogs associated with **Properties** dialogs (**Properties** under the **Display** menu; **Chapter 9**). *Clicking* on  removes the dialog.

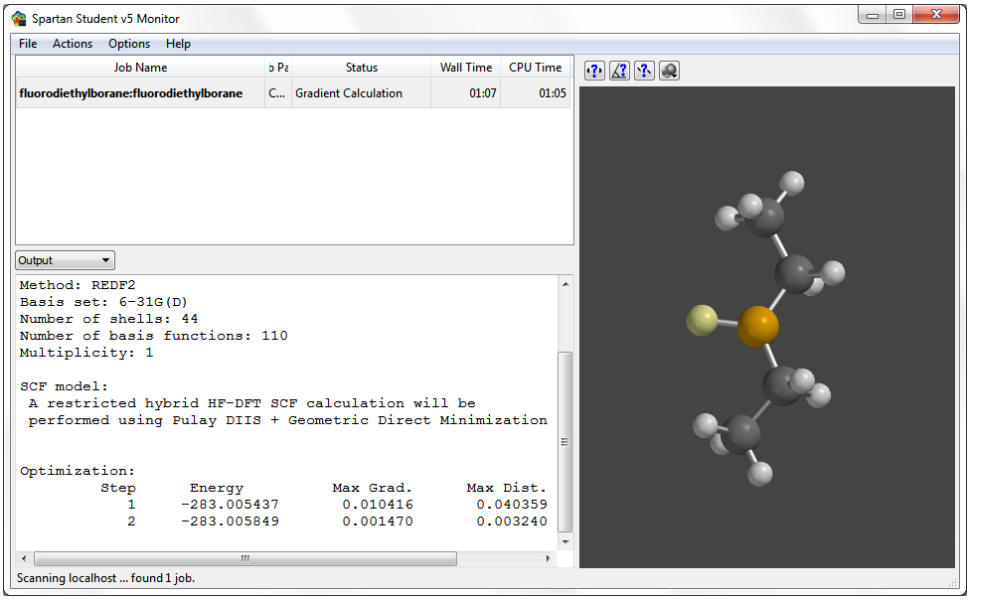
Fonts/Graphic Fonts

This selects fonts, style and size for menus and labels attached to molecules (**Labels** and **Configure...** under the **Model** menu; **Chapter 5**), and plots (**Plots...** under the **Display** menu; **Chapter 9**). Selection leads to the **Fonts** dialog.



Selections are made from the **Font**, **Font Style** and **Size** menus. *Clicking* on **OK** dismisses the dialog with selections kept. *Clicking* on **Cancel** or on  dismisses the dialog but selections are lost.

Monitor



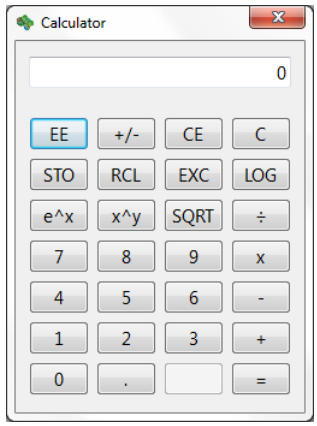
This provides a listing of all executing/queued jobs and their status. To see accumulated output for an executing job, *click* on its name. A ball-and-spoke model of the selected (executing) job will be displayed in a window to the right of the dialog. It can be manipulated using the usual mouse commands (you need to position the cursor inside the window). Model style cannot be changed. Note that (except for molecular mechanics and semi-empirical calculations) the structure is updated throughout an equilibrium geometry of transition state optimization, and bond lengths, angles and dihedral angles can be queried.

To kill a job, *click* on its name, and then select **Terminate** from the **Actions** menu at the top of the dialog (or *right click* on its name and select **Terminate** from the menu that appears). To start a queued job (irrespective of the imposed queue limits; see previous discussions under **Jobs**), *click* on its name and select **Start** from the **Actions** menu (or *right click* on its name and select **Start** from the menu that appears).

The **Monitor** may be removed either by selecting **Exit** from the **File** menu or by *clicking* on  at the top of the dialog.

Calculator

Selection brings up a **Calculator**.



This functions the same way as a normal pocket calculator. The **Calculator** is removed by *clicking* on .

Model Kit

If *checked*, this signifies that a model kit (organic, inorganic, peptide, nucleotide or substituent) is to remain on screen. Does not apply to ChemDraw.

File Toolbar, Geometry Toolbar, Build Toolbar, Display Toolbar

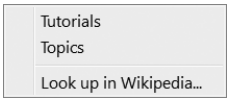
If *checked*, this provides display of toolbars that access functions contained in the **File**, **Build**, **Geometry** and **Display** menus, respectively.

Cascade, Tile

Arranges open windows in a cascade or as tiles on top of ***Spartan Student's*** main window (Windows only).

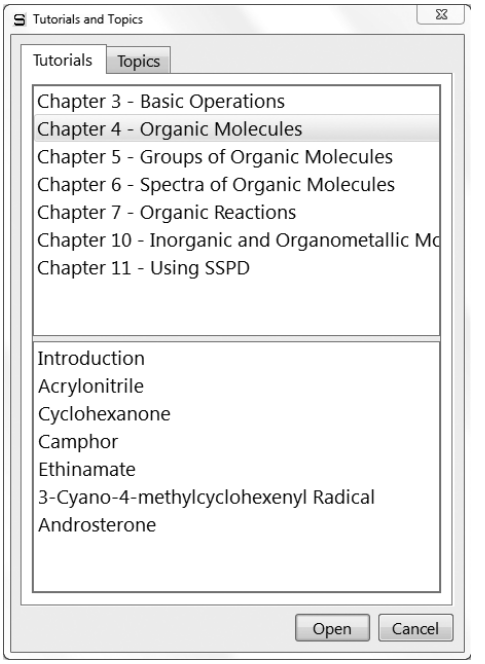
Chapter 11
The Activities Menu

*The **Activities** menu permits on-screen display of the full set of **Spartan Student** tutorials and a series of topics of practical relevance to molecular modeling. It also allows a Wikipedia page to be brought up (external to **Spartan**).*

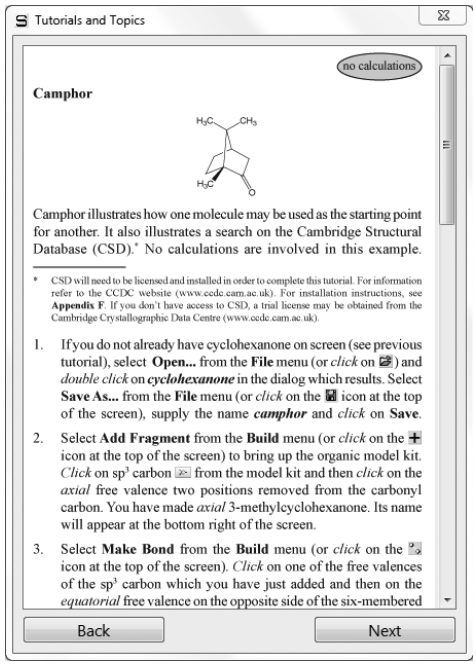


Tutorials/Topics

Selection of **Tutorials** or **Topics** brings up a dialog with either the **Tutorials** or **Topics** tab selected (**Tutorials** tab shown).



Tutorials are specified by a chapter number (in the **Spartan Student Tutorials**) and by name. Selection followed by *clicking* on **Open** leads to a scrollable window containing the appropriate text. This may be moved about the screen but may not be sized.

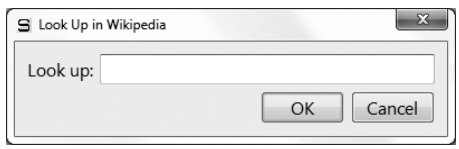


Topics are specified by name only (in the upper half of the dialog).

Note that the full User's Guide is available as a PDF under the **Help** menu (see next chapter).

Look Up in Wikipedia...

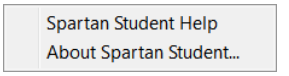
Selection results in a dialog.



Entering a query followed by *clicking* on **OK** leads to a Wikipedia page. This occupies a window that is external to ***Spartan Student***.

Chapter 12
The Help Menu

This chapter describes help.



Help

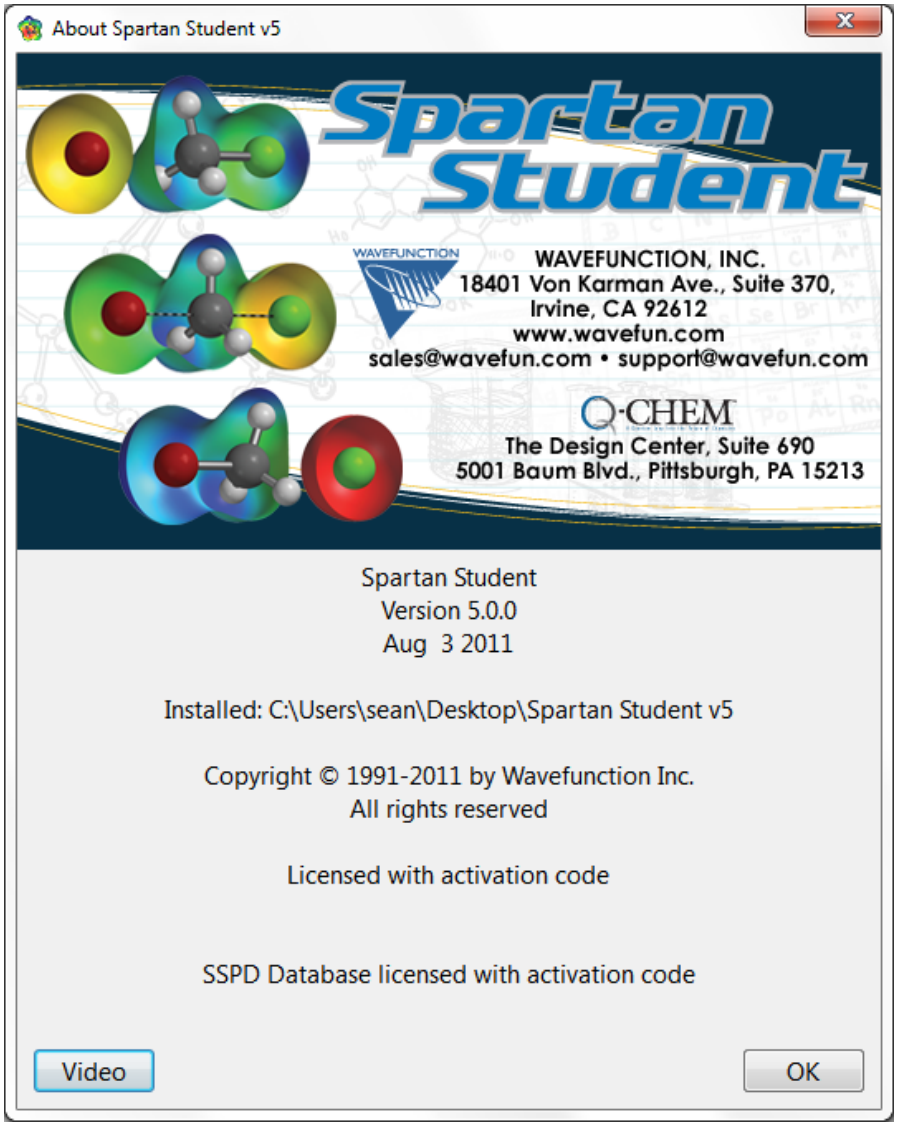
This provides information relating to application of computational methods available in ***Spartan Student***, as well as technical details regarding the program's operation. **Help** also provides a link to Wavefunction's website. Help files are HTML documents and require that Internet Explorer is installed to access them.

Spartan Student Tutorials, ***Spartan Student Overview*** (this document) and ***A Guide to Molecular Mechanics and Quantum Chemical Calculations*** are also available (as PDF files) under **Help**.

Finally, note that several dialogs, in particular, the **Calculations** dialog incorporate imbedded help messages. *Clicking* on  at the upper right, followed by *clicking* on a menu, button, etc. in the dialog gives rise to a brief informative message about the object queried.

About...*

Provides information about the user's release of ***Spartan Student***.



* About is located under the **Spartan Student** menu on the Macintosh version.

Appendix A
Capabilities and Limitations

Molecular Mechanics Models[1]

The MMFF molecular mechanics model is available for the calculation of energy (a combination of strain energy and intramolecular interaction energy), equilibrium geometries, equilibrium conformers and vibrational frequencies. Energies may be corrected for the effects of aqueous solvent. There are no atom limits for molecular mechanics calculations.

Semi-Empirical Models[1]

The PM3 semi-empirical model is available for calculation of heats of formation, wavefunctions, equilibrium and transition-state geometries and vibrational frequencies. The elements H-Ne, Mg-Ar, Ca, Ti-Br, Zr, Mo-Pd, Cd-I, Hf-Pt and Hg-Bi and Gd are supported. PM3 calculations are limited to 75 atoms.

Hartree-Fock Models[1-3]

Hartree-Fock models are available for calculation of energies and wavefunctions, equilibrium and transition-state geometries and vibrational frequencies with STO-3G, 3-21G, 6-31G* and 6-311+G** basis sets. Hartree-Fock calculations are limited to 30 atoms.

Density Functional Models[1,]

B3LYP and EDF2 density functional models are available for calculation of energies and wavefunctions, equilibrium and transition-state geometries and vibrational frequencies with both 6-31G* and 6-311+G** basis sets. NMR chemical shifts are available for the B3LYP/6-31G* and EDF2/6-31G* models only. Density functional calculations are limited to 30 atoms.

MP2 Møller-Plesset Models[1]

The MP2 Møller-Plesset model is available for calculation of energies and wavefunctions and equilibrium and transition-state geometries with 6-31G* and 6-311+G** basis sets. Vibrational frequencies are also available, but are very costly in terms of computation. MP2 calculations are limited to 20 atoms.

Solvent Models

Spartan Student supports the SM5.0R[4] (for molecular mechanics calculations) and SM5.4[5] (for quantum chemical calculations) empirical solvation models to estimate the aqueous solvation energy. Both methods are parameterized for H, C–F, S–Cl, Br and I. Solvation energies are added to gas phase energy calculations to provide an aqueous energy (Eaq).

Properties and Spectra

The properties module (that is automatically called from the molecular mechanics module or one of the quantum chemical modules) provides for text output printing, population analyses based on fits to electrostatic potentials), evaluation of thermodynamic quantities (enthalpy, entropy, free energy and heat capacity), and calculation of the dipole moment.

The properties module is also responsible for calculating quantities related to infrared spectra (vibrational frequencies and intensities), and NMR chemical shifts (^{13}C chemical shifts are correlated for local environment). IR spectra calculations may be carried out with molecular mechanics models, semi-empirical models, Hartree-Fock models, B3LYP, EDF2 and MP2 models. NMR spectra calculations may be carried out only with the B3LYP/6-31G* and EDF2/6-31G* models.

Graphical Models

The graphics module provides for data preparation associated with the display as surfaces, property maps and slices of molecular orbitals, electron densities, spin densities, electrostatic potentials and local ionization potentials. The sizes of electron density surfaces (and of

property maps based on electron density surfaces) may be chosen either using a specific value of the density or a value that encloses a specific percentage of the total number of electrons. Accessible and inaccessible regions may be distinguished for electron density surfaces and all property maps based on electron density surfaces.

Database

The database supported with ***Spartan Student*** is a subset of the Spartan Spectra and Properties Database (SSPD). It contains structures, energies, T1[6] heats of formation, IR and NMR spectra and diverse molecular properties for ~5,000 molecules obtained from EDF2/6-31G* calculations. In addition, it contains the wavefunction allowed on-the-fly calculation and display of the full variety of graphical surfaces and property maps. The full version of SSPD (currently 105,000 molecules) may be licensed separately. Also available is an ~5,000 molecule subset of the Spartan Molecular Database. This does not contain spectra, nor does it include the wavefunction. However, the SMD subset includes calculations from multiple theoretical models. The full version of SMD (currently 600,000 records and 150,000 molecules) is also available.

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1. For a general discussion and assessment of the techniques and methods available in ***Spartan Student***, see: W.J. Hehre, ***A Guide to Molecular Mechanics and Quantum Chemical Calculations***, Wavefunction, Inc., Irvine, CA 2003. This is available from Wavefunction's website (www.wavefun.com).
2. For a review of the quantum chemical methods utilized in ***Spartan Student*** (except for the PM3 semi-empirical method) with emphasis on recent developments, see: Y. Shao, L.F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S.T. Brown, A.T.B. Gilbert, L.V. Slipchenko, S.V. Levchenko, D.P. O'Neill, R.A. DiStasio Jr., R.C. Lochan, T. Wang, G.J.O. Beran, N.A. Besley, J.M. Herbert, C.Y. Lin, T. Van Voorhis, S.H. Chien, A. Sodt, R.P. Steele, V.A. Rassolov, P.E. Maslen, P.P. Korambath, R.D. Adamson, B. Austin, J. Baker, E.F.C. Byrd, H. Dachsel, R.J. Doerksen, A. Dreuw, B.D. Dunietz, A.D. Dutoi, T.R. Furlani, S.R. Gwaltney, A. Heyden, S. Hirata, C-P. Hsu, G. Kedziora, R.Z. Khalliulin, P. Klunzinger, A.M. Lee, M.S. Lee, W.Z. Liang, I. Lotan, N. Nair, B. Peters, E.I. Proynov, P.A. Pieniazek, Y.M. Rhee, J. Ritchie, E. Rosta, C.D. Sherrill, A.C. Simmonett, J.E. Subotnik, H.L. Woodcock III, W. Zhang, A.T. Bell, A.K. Chakraborty, D.M. Chipman, F.J. Keil, A.Warshel, W.J. Hehre, H.F. Schaefer, J. Kong, A.I. Krylov, P.M.W. Gill and M. Head-Gordon, *Phys. Chem. Chem. Phys.,* **8**, 3172 (2006).
3. For an older account see: W.J. Hehre, L. Radom, P.v.R. Schleyer and J.A. Pople, ***Ab Initio* Molecular Orbital Theory**, Wiley, New York, 1986.
4. G.D. Hawkins, C.J. Cramer and D.G. Truhlar, *J. Phys. Chem. B.*, **101**, 7147 (1997).
5. C.C. Chambers, C.J. Hawkins, C.J. Cramer, D.G. Truhlar, *J. Phys. Chem.*, **100**, 16385 (1996).
6. W.S. Ohlinger, P.E. Klunzinger, B.J. Deppmeier, W.J. Hehre; *J. Phys. Chem. A.*, **113**, 10, 2165 (2009).

Appendix B

Menus

Spartan Student Screen

File

New	Brings up a model kit for molecule building; accesses ChemDraw (Windows only)
Open...	Opens (imports) a molecule
Close	Closes a molecule
Save	Saves (exports) a molecule
Save As...	Saves a molecule as a ***Spartan Student*** document under a user-specified name
New Molecule	Adds a molecule to an existing list; brings up a model kit for molecule building; accesses ChemDraw (Windows only)
Delete Molecule	Deletes a molecule (or molecules) from a list
Append Molecule(s)...	Appends molecules to an existing list
Search Database by Name	Searches the ***Spartan Student*** database by name or partial name
Access CACTUS	On-line access to the National Cancer Institute CACTUS Database
Access PDB	On-line access to the Protein Data Bank by PDBid
Print...	Prints on-screen display; also prints contents of output window and the Spreadsheet
Start/Stop QuickTime Recording	Starts and stops QuickTime recording of contents of main ***Spartan Student*** screen
Exit	Exits ***Spartan Student***

Edit

Undo	Undoes previous operations
Cut	Moves the current molecule or contents of the selection box to the clipboard
Copy	Copies the current molecule or contents of the selection box to the clipboard
Paste	Pastes contents of the clipboard to the screen
Select All	Selects the entire contents of output dialog or spreadsheet
Find...	Locates a text string in the output dialog or an on-screen molecular fragment
Find Next	Locates next occurrence of a text string or molecular fragment
Center	Centers the molecule on screen; applies to all molecules in a document
Clear	Clears the selected molecule

Model

Wire	Displays structure as wire-frame model
Ball and Wire	Displays structure as ball-and-wire model
Tube	Displays structure as tube model
Ball and Spoke	Displays structure as ball-and-spoke model
Space Filling	Displays structure as space-filling model
Hide	Hides structure model from view
Global Model	Applies model type and labels of current molecule to all molecules in the document
Coupled	Couples motions of all molecules in the document
Hydrogens	Toggles hydrogens on and off
Labels	Toggles labels on and off
Ribbons	Toggles ribbons on and off
Ramachandran Plot	Creates a Ramachandran plot based on a proton structure input from PDB

Hydrogen Bonds	Toggles hydrogen bonds on and off
Configure...	Labels atoms, bonds, etc., provides information about polypeptides/polynucleotides residues and designates ribbon displays

Geometry

Measure Distance	Displays and/or sets bond distance
Measure Angle	Displays and/or sets bond angle
Measure Dihedral	Displays and/or sets dihedral angle
Freeze Center	Freezes selected atomic positions
Constrain Distance	Constrains bond distance
Constrain Angle	Constrains bond angle
Constrain Dihedral	Constrains dihedral angle
Define Point	Defines a point as a geometric mean of a set of atoms; defines ligand point as a position that is perpendicular to the centroid of a plane made by three or more atoms
Define Plane	Defines a plane made by three or more atoms
Align	Aligns molecules in a document according to selected atoms

Build

View	Removes the model kit
Add Fragment	Brings up a model kit that contains libraries of atomic fragments, functional groups, rings and ligands; accesses user-defined libraries; provides access to ChemDraw (Windows only)
Delete	Deletes atoms, bonds, points, planes, etc.
Make Bond	Makes bonds between free valences or atoms
Break Bond	Breaks a bond
Minimize	Performs energy minimization using molecular mechanics
Guess Transition State	Provides transition-state guess based on reaction database or, lacking a database entry,

	based on linear synchronous transit

Setup

Calculations...	Sets up molecular mechanics and quantum chemical calculations; specifies calculation of IR and NMR spectra
Surfaces	Sets up generation of and displays graphical surfaces
Submit	Submits job to the execution queue

Display

Output	Displays text output
Properties	Displays molecule, bond and atom properties as well as information about geometrical constraints and graphical surfaces
Surfaces	Sets up generation of and displays graphical surfaces (same as entry in **Setup** menu)
Spectra	Displays IR and NMR spectra, animates vibrational modes, and accesses on-line experimental spectral databases; fits calculated infrared spectra to experimental spectra
Spreadsheet	Displays spreadsheet
Plots...	Creates plots from the data in the spreadsheet
Reactions	Calculates reaction energies using data either from current document or from the Spartan Spectra and Properties Database

Options

Preferences...	Sets various run-time and labeling preferences
Colors	Sets screen and model colors
Fonts..., Graphics Fonts...	Sets fonts for labels and plot displays
Monitor	Monitors and allows for killing executing jobs and bypassing queue to start jobs

Calculator	Pocket calculator

Help

Help	Provides information about the performance and timing of computational methods in ***Spartan Student***; provides information about using graphical models in ***Spartan Student***
About...	Provides program version information for citation and support

Contextual (Right Click to Access)

Main Screen

Copy	Copies selected molecule to the clipboard
Paste	Pastes the contents of the clipboard into the selected document
Delete Selected	Deletes selected molecule from document
Properties	Brings up the **Molecular Properties** dialog

Spreadsheet

Copy	Copies text of selected cell or cells to the clipboard. If leftmost cell (or cells) selected, copies molecule(s) to the clipboard
Paste	Pastes the contents of the clipboard into selected cells. If leftmost cell (or cells) selected, either pastes text or molecule(s) depending on menu choice
Add	Brings up the **Add** dialog (spreadsheet) for adding calculated quantities into the spreadsheet
Sort	Sorts the column from low to high. *Pressing* the **Shift** key prior to menu selection sorts from high to low

Format Selected	Formats selected cell(s), selected column(s) if selection is in a header cell, or entire spreadsheet if selection is header cell of leftmost column
Delete Selected	Deletes selected molecule(s) from document
Append	Appends the contents of ***Spartan Student*** document(s) to the spreadsheet (corresponding to the selected document)
Rename Selected Using SSPD	Rename selected molecule(s) with names in the Spartan Spectra and Properties Database; appears only when leftmost cell(s) selected
Properties	Brings up the **Molecular Properties** dialog

Reactions

Copy	Copies selected text to the clipboard
Print	Prints selected text

Output Window

Copy	Copies selected text to the clipboard
Print	Prints selected text

Appendix C

Units

Geometries

Cartesian coordinates are given in Ångstroms (Å), and in atomic units (au).

Bond distances are given in Å and in au. Bond angles and dihedral angles are given in degrees (°).

Surface areas, accessible surface areas and polar surface areas are available in $Å^2$ and volumes in $Å^3$, and in au^2 (au^3).

1 Å = 0.1 nm=1.889762 au

Energies, Heats of Formation and Strain Energies, Zero-Point Energies, Enthalpies and Gibbs Energies and Entropies

Total energies from Hartree-Fock calculations are available in au, kcal/mol, kJ/mol and electron volts (eV).

Experimental heats of formation as well as those from semi-empirical calculations and from thermochemical recipes are available in kJ/mol, au, kcal/mol and eV.

Strain energies from molecular mechanics calculations are available in kJ/mol, au, kcal/mol and eV.

Energies, heats of formation and strain energies corrected empirically for the effects of aqueous media are given in the same units as the corresponding gas-phase quantities.

Zero-point energies, enthalpies and Gibbs energies available in kJ/mol, kcal/mol and au/mol. Entropies are available in kJ/mol•degree, kcal/mol•degree and au/mol•degree.

Orbital Energies

Orbital energies are available in eV, kcal/mol, kJ/mol and au.

Energy Conversions

	au	kcal/mol	kJ/mol	eV
1 au	-	627.5	2625	27.21
1 kcal/mol	1.593 (-3)	-	4.184	4.337 (-2)
1 kJ/mol	3.809 (-4)	2.390 (-1)	-	1.036 (-2)
1 eV	3.675 (-2)	23.06	96.49	-

a) exponent follows in parenthesis, e.g., 1.593 (-3) = 1.593×10^{-3}

Electron Densities, Spin Densities, Dipole Moments, Charges, Electrostatic Potentials and Local Ionization Potentials

Electron densities and spin densities are given in electrons/au^3.

Dipole moments are given in debyes.

Atomic charges are given in electrons.

Electrostatic potentials are given in kJ/mol.

Local ionization potentials are given in eV.

Vibrational Frequencies

Vibrational frequencies are given in wavenumbers (cm^{-1}).

Chemical Shifts, Coupling Constants

Chemical shifts are given in parts-per-million (ppm) relative to the following standards: hydrogen, tetramethylsilane; carbon, tetramethylsilane; nitrogen, nitromethane; fluorine, fluorotrichloromethane; silicon, tetramethylsilane, phosphorous, phosphoric acid.

Coupling constants are in ppm.

Appendix D

Citation

The proper citation for ***Spartan Student*** is as follows:

Spartan Student
Wavefunction, Inc.
Irvine, CA

Except for molecular mechanics and semi-empirical models, the calculation methods used in ***Spartan Student*** have been documented in: Y. Shao, L.F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S.T. Brown, A.T.B. Gilbert, L.V. Slipchenko, S.V. Levchenko, D.P. O'Neill, R.A. DiStasio Jr., R.C. Lochan, T. Wang, G.J.O. Beran, N.A. Besley, J.M. Herbert, C.Y. Lin, T. Van Voorhis, S.H. Chien, A. Sodt, R.P. Steele, V.A. Rassolov, P.E. Maslen, P.P. Korambath, R.D. Adamson, B. Austin, J. Baker, E.F.C. Byrd, H. Dachsel, R.J. Doerksen, A. Dreuw, B.D. Dunietz, A.D. Dutoi, T.R. Furlani, S.R. Gwaltney, A. Heyden, S. Hirata, C-P. Hsu, G. Kedziora, R.Z. Khalliulin, P. Klunzinger, A.M. Lee, M.S. Lee, W.Z. Liang, I. Lotan, N. Nair, B. Peters, E.I. Proynov, P.A. Pieniazek, Y.M. Rhee, J. Ritchie, E. Rosta, C.D. Sherrill, A.C. Simmonett, J.E. Subotnik, H.L. Woodcock III, W. Zhang, A.T. Bell, A.K. Chakraborty, D.M. Chipman, F.J. Keil, A.Warshel, W.J. Hehre, H.F. Schaefer, J. Kong, A.I. Krylov, P.M.W. Gill and M. Head-Gordon, *Phys. Chem. Chem. Phys.,* **8**, 3172 (2006).