Spartan Student User's Guide

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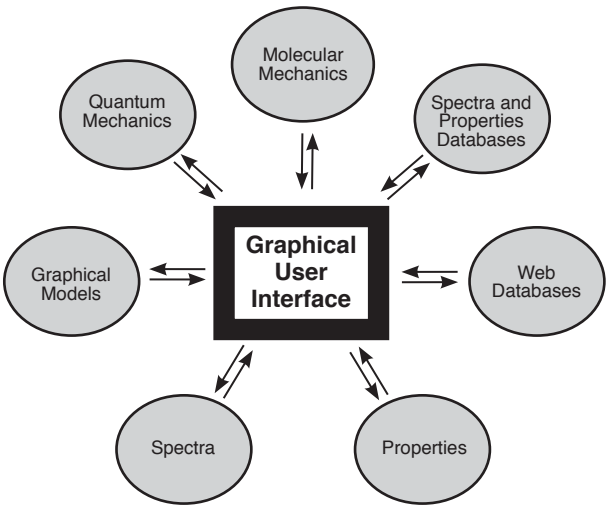
Chapter 1

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 molecular mechanics and quantum chemical calculation modules tightly connected via a graphical user interface that is highly functional, yet simple and uncluttered. It has been designed not only to greatly reduce the drudgery and possibility for human error associated with the preparation of input for calculations, but also to guide the interpretation of output from the calculations. 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 3D builders for organic, inorganic and organometallic molecules, polypeptides and polynucleotides, and a procedure for guessing transition states. 2D sketch capability for organic and organometallic molecules has been refined with this

version of ***Spartan Student***. Additionally, access to ChemDraw[1] is provided without having to exit the interface. A ≈6,000 molecule subset of the Spartan Spectra and Properties Database (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. On-line access to the Protein Data Bank (PDB)[2], a collection of >158,000 biological macromolecular structures, is provided. Experimental infrared spectra for ≈2,000 molecules are available from the NIST website[3] and experimental NMR spectra for ≈43,000 molecules are available from NMRShiftDB website.[4]

Spartan Student's interface provides the gateway to a range of modern computational methods[5]. The simplest of these is the MMFF molecular mechanics model, available to determine equilibrium geometries and equilibrium conformers of molecules comprising upwards of several thousand atoms. It is the only computational technique that is applicable to biopolymers.

Quantum chemical models are required to account for the geometries of transition states as well as for reaction and activation energies.[7] 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, EDF2, and new to version 8, ωB97X-D 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. Also new in ***Spartan Student version 8*** is the T1[6] thermochemical recipe, providing high accuracy heats of formation for uncharged, closed-shell systems containing H, C, N, O, F, Si, P, S, Cl and Br.

Spartan Student provides access to infrared spectra (MMFF, PM3, Hartree-Fock, B3LYP, EDF2, ωB97X-D and MP2 models) and NMR spectra[7] (Hartree-Fock, B3LYP, EDF2, ωB97X-D models only). These are available both as numerical data (vibrational frequencies, chemical shifts) as well as spectral plots. ***Spartan Student*** provides internet access to experimental IR and NMR databases[3,4], allowing direct comparison with calculated spectra. Infrared spectra from density functional models has been corrected using both a multiplicative scale of calculated frequencies and peak width at half height as parameters. Proton and ^{13}C chemical shifts obtained from B3LYP/6-31G* and ωB97X-D/6-31G* as well as proton, ^{13}C and ^{19}F chemical shifts obtained from the EDF2/6-31G* density functional model have been empirically corrected to account for local environment.

Also available are energy, equilibrium and transition state geometry, and frequency calculations using the C-PCM solvation model in conjunction with Hartree-Fock and density functional models only. The model depends only on the dielectric constant of the solvent and preset values are available for typical non-polar and polar solvents as well as water.

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.

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. PDB web reference: https://www.rcsb.org.
3. NIST web reference: https://webbook.nist.gov
4. NMRShiftDB web reference: https://nmrshiftdb.ice.mpg.de
5. 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).
6. W.S. Ohlinger, P.E. Klunzinger, B.J. Deppmeier, W.J. Hehre, ***J. Phys. Chem. A***, **103**, 10, 2165 (2009).
7. Chemical shifts only. HH coupling constants and splitting patterns are evaluated empirically.

Chapter 2
Operating *Spartan Student*

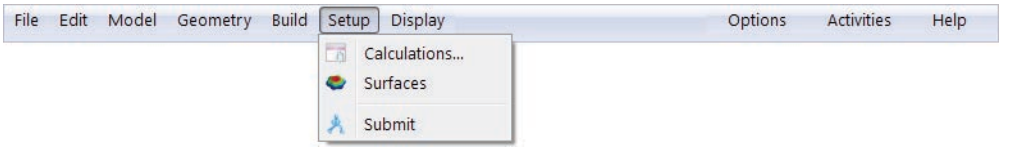
This chapter describes the general operating features of ***Spartan Student****.*

Opening and Quitting *Spartan Student*

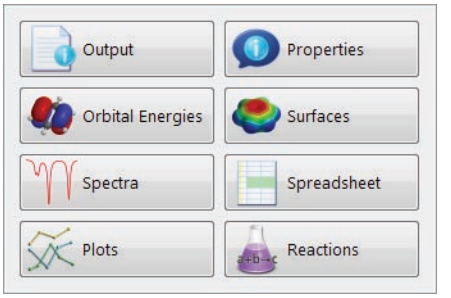
To open on Windows, *click* on the **Start** button, then *click* on **All Programs**, and finally *click* on ***Spartan Student*** (or *double click* on the ***Spartan Student*** icon on your desktop). To open on Macintosh, *double click* on the ***Spartan Student*** icon in the Applications Folder. 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 and Icons

Program functions may be accessed either from the menu bar or from icons in the toolbar which is directly underneath the menu bar. The menu bar may either be accessed as pull-down menus (**Classic List**), for example, the **Setup** menu:



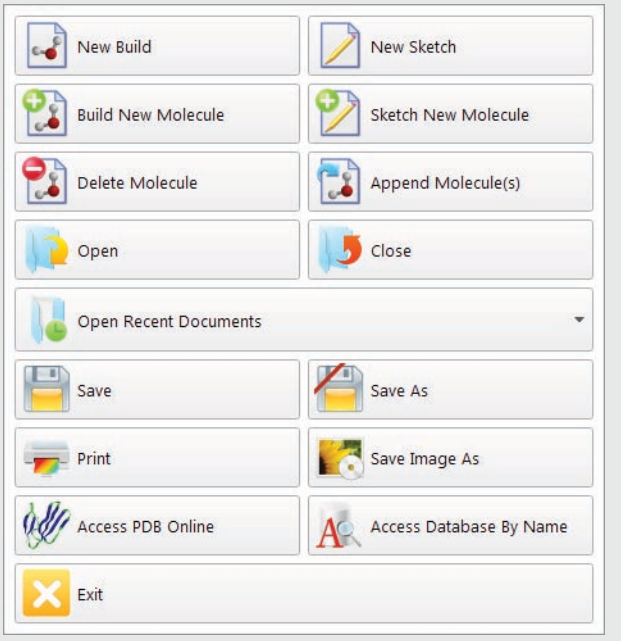
or under Windows (only) from a list of icons presented in a palette (**Button Pad**), for example, the **Display** menu:



Selection is made in the **Settings Preferences** dialog (**Preferences...** under the **Options** menu; **Chapter 10**).

Icons for all menu functions (as shown alongside text in both **Classic List** and **Button Pad** styles) are available. Display choice (beyond the default initially supplied with ***Spartan Student***) is made in the **Icons** tab (**Preferences...** under the **Options** menu; **Chapter 10**). Icon size is selected from the **Settings** tab (**Preferences...** under the **Options** menu; **Chapter 10**).

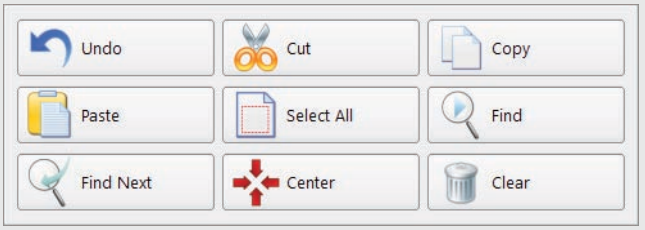
File



Allows you to build or sketch a new molecule or read in a molecule that you have previously saved, to retrieve the structure, properties and IR and NMR spectra from a molecule in ***Spartan Student***'s database from

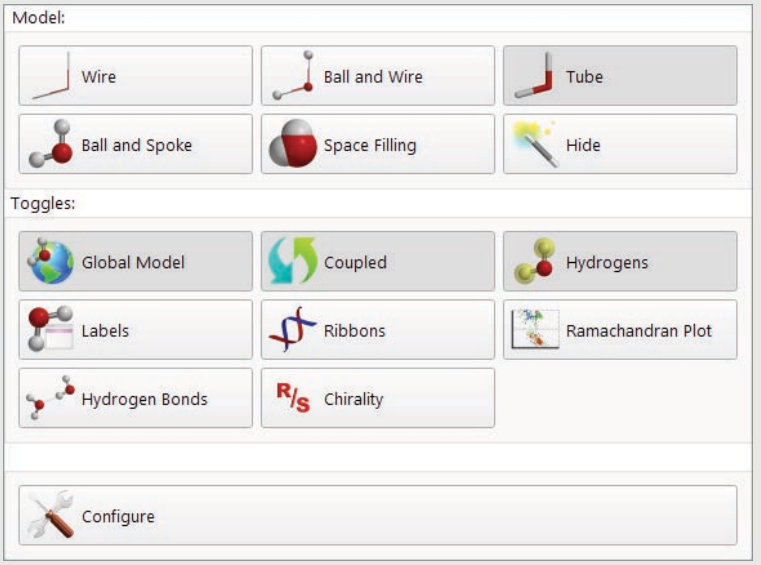
its name, to retrieve a protein structure from the Protein Data Bank, to print what is on screen or save it as an image file, and to make QuickTime movies (Macintosh only).

Edit



Allows you to transfer information to and from the clipboard, to undo the last operation, to find text strings and molecule fragments, to center molecules on screen, and to clear the active molecule by deleting it.

Model

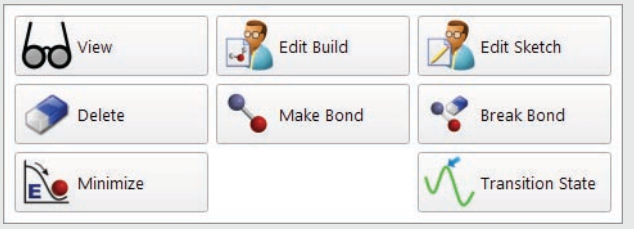


Allows you to control the style of your model, to display hydrogen bonds and to couple or decouple molecules in a multi-molecule document. Allows you to display of a Ramachandran plot for a protein structure brought in from PDB, toggle on/off display of hydrogen bonds and highlight R/S chiral centers.

Geometry

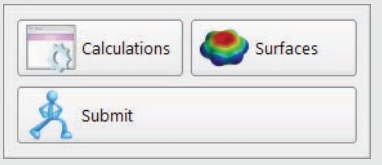
Allows you to measure and constrain bond lengths, angles and dihedrals, define points and planes, specify atoms to be "frozen" and align molecules.

Build



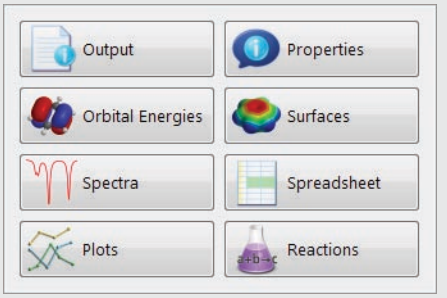
Allows you to build or sketch and edit molecules, and to estimate a transition state geometry based on a library of reactions (using arrow pushing markers).

Setup



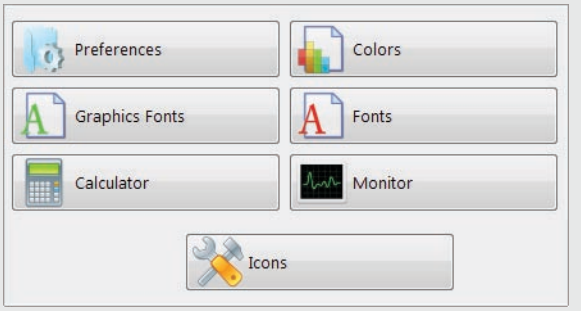
Allows you to specify the task to be performed and the theoretical model to be employed for this task, and specify graphical surfaces and property maps and to submit jobs for calculation.

Display



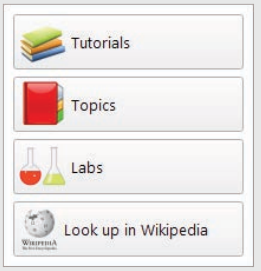
Allows you to display text output, molecular and atomic properties, orbital energy diagrams, surfaces and property maps and infrared and NMR spectra, as well as to access experimental IR and NMR over the internet. Allows you to present data in a spreadsheet and make plots from and perform regression analysis on these data, and to compute reaction energies based either on user data or from entries in the database associated with ***Spartan Student***.

Options



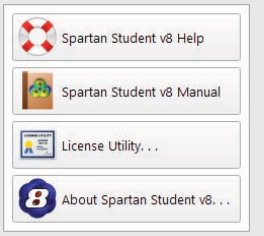
Allows you to set display standards, specify the location of the database, monitor executing jobs and customize colors, icons and other aspects of the graphical user interface.

Activities



Allows you to display tutorials, topics, and lab activities inside of ***Spartan Student*** and to search Wikipedia.

Help



Provides access to information on ***Spartan Student's*** general operation and a number of computational FAQ's, the ***Spartan Student*** **Manual**, and license information.

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

Additional Icons

A variety of other icons appear in ***Spartan Student***, both in individual dialogs and in the information bar at the bottom of the screen.

Post to Spreadsheet Search Transition State

Lock/Unlock Constraints Move Up/Down Dialog

Play Pause Step

Revert to Fullscreen Extend to Fullscreen Play

Look Up in Wikipedia

Tabs

Spartan Student assigns a tab to each open document. When more than a single document is open, these appear in a single row along the bottom of the screen in the order that the documents were created or read. Backward and forward step keys (and) at the far right provide access to tabs outside of those displayed. Documents are selected for display by *clicking* on its tab. To the left of each tab is a check box, if checked, this indicates that the document will be displayed on screen even if it is not the selected document. By default, tabs are not checked. Selecting **Pin New Documents** from the **Settings** tab (**Preferences...** under the **Options** menu; **Chapter 10**) changes the behavior and checks all tabs.

Mouse/Keyboard Operations

The following functions are associated with a standard mouse and keyboard.

	Button	
Keyboard	**Center (wheel)**	
No keys selected	Zooming, scroll up/down	
Keyboard	**Left**	**Right**
No keys selected	X/Y rotation, atom/fragment substitution[a], insertion[a]	X/Y translate
Shift	Range selection, Z rotate	Zooming (Z translate)
Ctrl (view mode) **Windows**	multiple selection, X/Y rotation for all visible molecules	X/Y translation for all visible molecules
Command (view mode) **Macintosh**	multiple selection	
Ctrl (build mode) **Windows**	selected fragment X/Y rotate, chiral center inversion[a]	selected fragment X/Y translate
Command (build mode) **Macintosh**	selected fragment X/Y rotate, chiral center inversion[a]	scaling[b]
Ctrl + **Shift** (view mode) **Windows**	Z rotation for all visible molecules	
Command + **Shift** (view mode) **Macintosh**	Z rotation for all visible molecules	
Ctrl + **Shift** (build mode) **Windows**	selected fragment Z rotate, absolute configuration inversion[a]	
Command + **Shift** (build mode) **Macintosh**	selected fragment Z rotate, absolute configuration inversion[a]	
Alt/Option (view mode)	group selection[b]	
Alt/Option (build mode)	bond rotation	bond stretching

a) Build mode only, requires *double clicking*.
b) With center wheel depressed or both left and right mouse buttons held down, dragging enables a selection box for supports group selection.

These broadly fall into two categories: selection (picking) and manipulation (translation/rotation/zooming).

Selection. *Clicking* (left button) selects objects on screen and/or menu items. Left and right buttons together are used to define a selection box for copying 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. Together with the **Alt** key (**option** key for Mac), the left button allows for selection of an entire group (detached molecular fragment).

In **Edit Build** mode (only), *double clicking* (left button) on an atom exchanges it with the atom or atomic fragment selected in the model kit. *Double clicking* on an atom while holding down the **Ctrl** key leads to inversion in chirality of the atom and *double clicking* on a molecule while holding down both the **Ctrl** and **Shift** keys inverts the absolute configuration of the molecule. These operations are not available in the 2D sketcher (**Edit Sketch** mode). Once an initial fragment, group or ring has been drawn, *double clicking* on the background will insert it alongside (but not bonded to) whatever fragments currently exist on screen.

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, moving the mouse while holding down the left button gives rise to rotation about the X and Y (screen) axes, while moving the mouse while holding down the right button gives rise to translation in the X and Y (screen) directions. Together with the **Shift** key, moving the mouse while holding down the left button gives rise to rotation about the *Z* direction, while moving the mouse while holding down the right 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 **Edit Build**/**Edit Sketch** 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 **Edit Build** mode (only), 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 (does not apply to **Edit Sketch** mode).

In **Edit Build** mode (only), moving the mouse while holding down the **Alt** key (**option** key for Mac) together with the left mouse button rotates about the selected bond and, with the right mouse button, changes the length of the selected bond. Bond rotation (only) may also be accomplished by moving the mouse up and down inside the demarked area at the left of the screen while holding down the left button (does not apply to **Edit Sketch** mode).

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 (**option** for Mac)	In **Edit Build**/**Edit Sketch** 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. 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** for Mac)	Required following text or data entry into spreadsheet or dialogs.

Touch-Screen Operations

Tapping is equivalent to *clicking* and *double tapping* is equivalent to *double clicking*. Touch commands for range and multiple selection have not been implemented. One finger motions on screen are equivalent to left button motions (object and bond rotation). Two finger motions are equivalent to right button motions (object translation). Two finger pinching is equivalent to scroll wheel operations (zooming).

Selecting Molecules

While two or more molecules may be simultaneously displayed in ***Spartan Student***'s window (see **Tabs** earlier in this chapter), only one molecule may be selected. Only the selected molecule has access to all capabilities. Molecule selection occurs by *clicking* on its structure model or on any of its associated graphical surfaces. The previously selected molecule is deselected.

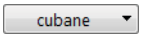
Where the molecule belongs to a document with more than a single molecule, selection from among the different molecules may be made using either the ◂ and ▸ buttons or the scroll bar at the bottom left of the screen. *Clicking* on ▶ at the bottom left of the screen animates the display of molecules in the document, that is, steps through them sequentially. Animation speed is controlled from the **Settings** tab (**Preferences...** under the **Options** menu; **Chapter 10**). *Clicking* on ⏸ (that replaces ▶) stops the animation. If the spreadsheet associated with the document is open (**Spreadsheet** under the **Display** menu; **Chapter 9**), selection can also be made by *clicking* on the molecule label at the left of the spreadsheet.

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.

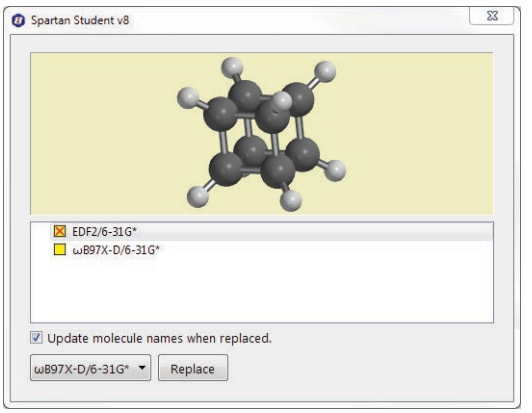
Database

Included with ***Spartan Student*** is a ≈6,000 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* or ωB97X-D/6-31G* density functional model. The database 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 allows a 3D model of the entry in the database to be rotated, translated and scaled using the usual mouse/keyboard commands (you need to position the cursor inside the viewing area). Model style may not be changed.



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**). If ***Update molecule names when replaced*** is checked, the name of the molecule in the database will replace the name previously associated with the molecule.

* The SSPD is a growing collection of >300,000 organic molecules along with associated properties and IR and NMR spectra data. Contact sales@wavefun.com for licensing options.

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 are available. In this case, *clicking* on **Replace** will give rise to a second dialog. *Clicking* on **All** will replace all the molecules in the document, while *clicking* on **Current** will replace only the selected molecule.

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, not applicable to the 2D sketcher.

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.

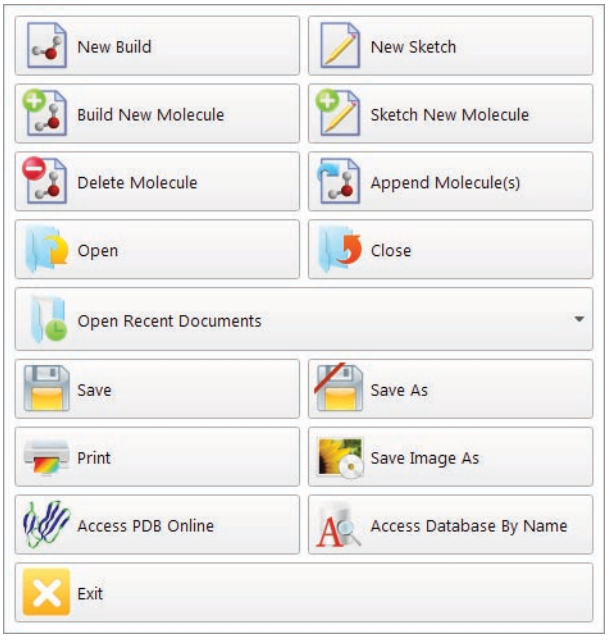
Monitoring and Terminating Jobs

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

Chapter 3

The File Menu

*The **File** menu accesses a 2D sketch pad, model kits to build, edit and substitute molecules in 3D, the file system to read and write both native and non-native files, print text and on-screen graphics, save on-screen graphics as image files, the database of quantum chemical results by name, the online PDB database of protein and nucleotide structures, and QuickTime movie creation (Macintosh only).*



New Build ()

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

New Sketch ()

Brings up the 2D sketch pane and clears the screen. The 2D sketch pane is discussed in **Chapter 7**.

Build New Molecule ()

Brings up a model kit and clears the screen. **Build New Molecule** differs from **New Build**, in that the resulting molecule is appended to the end of the document associated with the molecule (or sketch) that is presently selected.

Sketch New Molecule ()

Brings up the 2D sketch pane and clears the screen. The menu bar is still accessible, but only the **View** () and **Sketch New Molecule** () icons are available. **Sketch New Molecule** differs from **New Sketch** in that the resulting sketch is appended to the end of the document associated with the molecule (or sketch) that is presently selected.

Delete Molecule ()

Deletes the selected molecule(s) from a document. Deleting the last molecule 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.*

Open... ()

Opens a file that contains all information associated with a particular

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* 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.

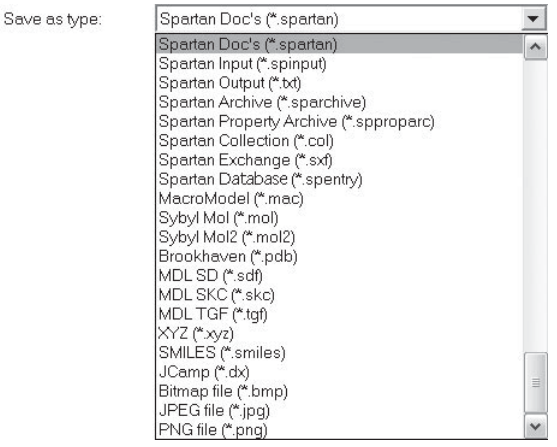
molecule (or list of molecules). In addition to native (.spartan) files (documents) including 2D sketch files, supported are files containing 2D drawings, 3D structures and 1D strings. Also supported are file formats for experimental IR and NMR spectra. Non-native files are normally hidden from view, but may be seen by selecting **All Files** from the **Files of type** menu at the bottom of the dialog.

Open Recent Documents ( )

Brings up a list of (at most) ten recent documents. *Clicking* on one opens the document.

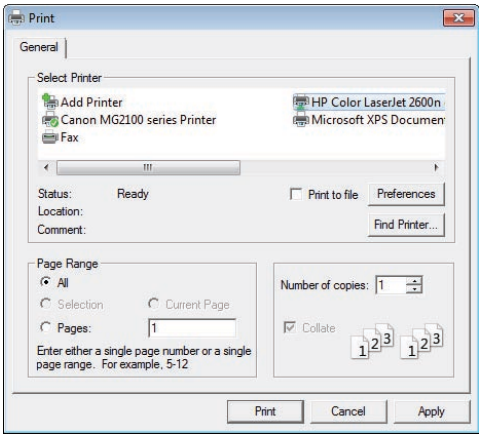
Save ( )
Save As... ( )
Save Image As... ( )

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 the formats listed under **Open**. In addition, Bitmap (.bmp), JPEG (.jpg) and PNG (.png) graphics file formats are supported. Support is also provided for writing QuickTime (movie) files for Macintosh only (see discussion later in this chapter). Selection is made under the **Save as type** menu in the **Save As** dialog. **Save Image As...** allows for saving molecules as high resolution PNG files.



Print ( )

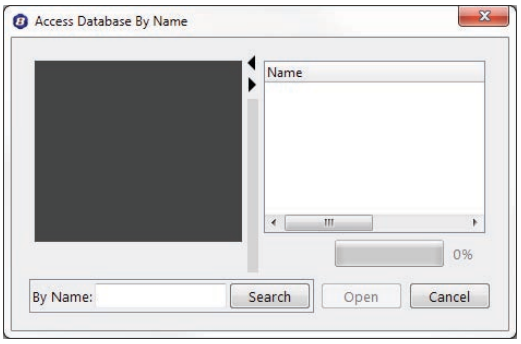
Selection leads to a dialog in order to designate a printer, specify print layout and number of copies. It also allows printing to a file.



The contents of the spreadsheet (**Spreadsheet** under the **Display** menu; **Chapter 9**) may be printed using **Print** from the contextual menu. The results of a reaction energy calculation (**Reactions...** under the **Display** menu; **Chapter 9**), may be printed using **Print** from the contextual menu.

Access Database By Name... ( )

Included with ***Spartan Student*** is a ≈6,000 molecule subset of the Spartan Spectra and Properties Database (SSPD). The individual entries correspond to calculations from the EDF2/6-31G* and ωB97X-D/6-31G* density functional model and each includes the structure, energy, infrared and NMR spectra, as well as a variety of molecular and atomic properties. The wave function is available allowing graphical surfaces and property maps to be computed on-the-fly. Selection brings up a dialog:

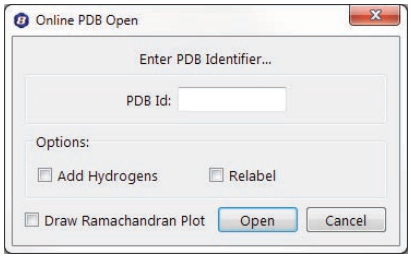


A name search is initiated by entering a name (or partial name) in the box to the right of **By Name:** at the bottom of the **Access Database by Name** dialog. The search will return all entries that include whatever text string is entered into this box. For example, typing in ***toluene*** will not 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.

Access PDB Online... ( )

Provides access to the online **P**rotein **D**ata **B**ank (**PDB**)* comprising more than 158,000 protein and nucleotide structures. Selection results in a dialog.



To access a PDB structure, enter the four character identification code in the box to the right of **PDB ID** and *click* on **Open**. If the PDB entry contains more than one structure and/or the PDB ID yields more than one entry, all structures will be returned in a single document.

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* The web address is https://www.rcsb.org.

PDB access will typically require a few seconds. The PDB ID will appear at the right and a ribbon model of the protein or nucleotide will appear on screen. A Ramachandran plot associated with a protein structure may either be drawn upon initial retrieval of the PDB file by *checking* the box to the left of **Draw Ramachandran Plot** or later from **Ramachandran Plot** under the **Model** menu (**Chapter 5**).

Start/Stop QuickTime Recording () (Macintosh only)

This allows QuickTime movies to be created. To start making a movie, select **Start QuickTime Recording**. Any motions of all molecules in ***Spartan Student***'s 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 recording, select **Stop QuickTime Recording** (which has replaced **Start QuickTime Recording** in the **File** menu) and supply the requested file name. Starting and stopping the recording can also be controlled with the ⌘ + **R** key.

Note that the QuickTime entry in the **File** menu will only appear if QuickTime is actually installed on your machine.

Close ()

Closes the document containing the selected molecule, as well as any 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.

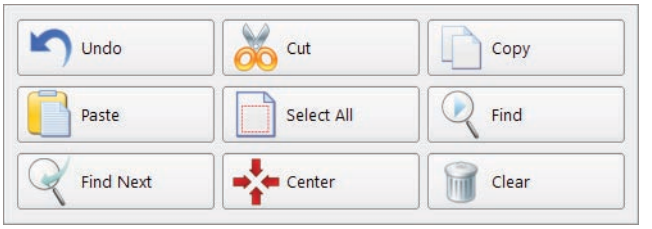
Exit ()

Exits ***Spartan Student***, that is, 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. Undoes transition-state formation (see **Transition State** in **Chapter 7**).

Cut ( ), Copy ( ), Paste ( )

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. Among the important uses of the clipboard are:

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

(ii) Temporary storage of a 3D molecular structure for use in molecule building. Temporary storage of a 2D sketch is accomplished using **Copy/Paste** under a contextual menu (see **Chapter 7**).

(iii) Transferring data between ***Spartan Student*** spreadsheets and 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. Position the cursor slightly above and slightly to the left of the item to be transferred, hold down both buttons and *drag* the mouse to a location slightly below and slightly to the right of the item to be transferred and 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 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 discussion relating to use of the clipboard in molecule building is provided in **Chapter 7** and for moving data in and out of the spreadsheet in **Chapter 9**.

Select All ()

Selects all atoms in the selected molecule.

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).

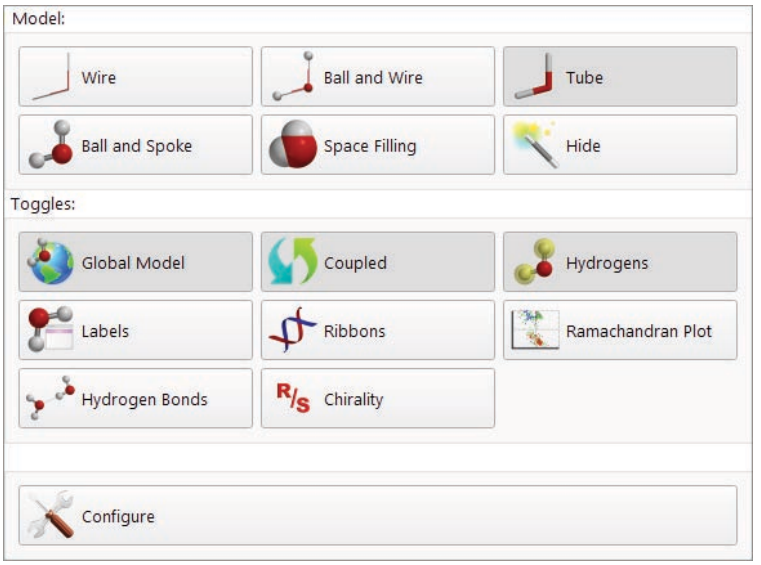
Clear ()

Clears (deletes) the structure and other information for the selected molecule, and brings up a model kit. Information is not 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, with or without atom labels, and with or without R/S chirality labels, as well as ribbon displays for polypeptides and polynucleotides, with or without labels and with or without hydrogen bonds indicated. It allows drawing a Ramachandran plot for a protein structure retrieved from the Protein Data Bank (PDB). The menu also provides for configuring atom labels to display element name, 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 a check mark ✔ in front of its entry in the menu or

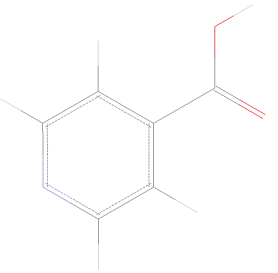
by a highlighted button in the case of the button pad option. **Global Model**, **Coupled**, **Hydrogens**, **Labels**, **Ribbons** and **Hydrogen Bonds** operate as toggle switches. A ✔ in front of the entry in the menu indicates that it is selected.

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 (**Preferences...** under the **Options** menu; **Chapter 10**). Both structure models and graphics may be presented in 3D stereo. This is also controlled from the **Settings** tab as well as from the **3** key. Stereographic displays require perspective projections.

Wire ( )

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

Wire Model



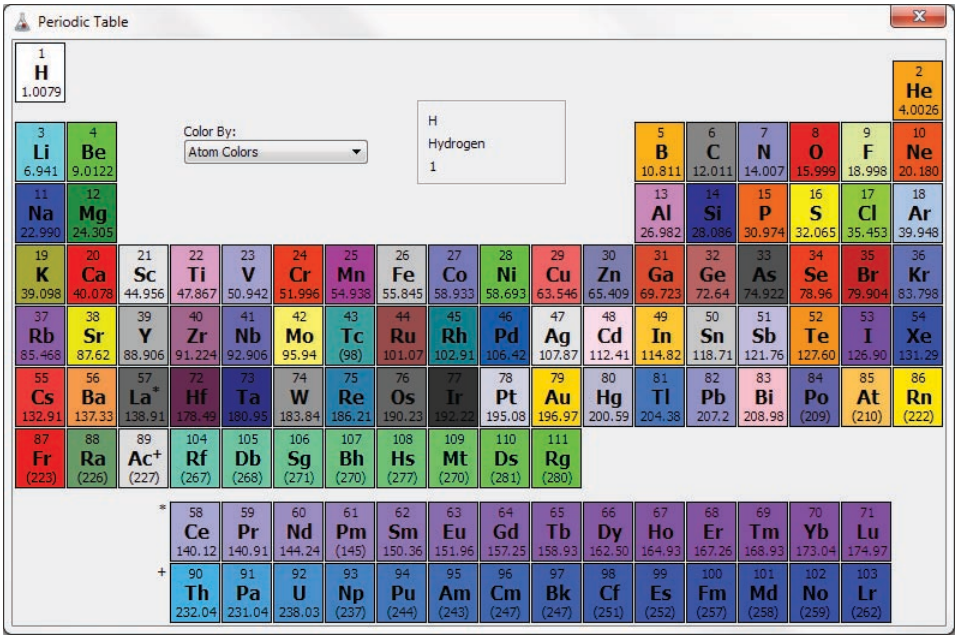
The bonds are drawn in two colors, one for each of the atoms making up the bond. Default atom colors are given in **Figure 5-1**.

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 globally or individually.

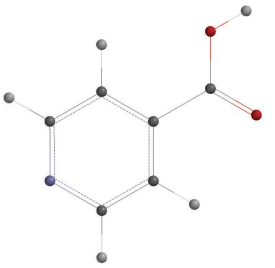
Ball and Wire( )

This represents atoms by small balls and bonds by wires.

Figure 5-1: Default Atom Colors



Ball-and-Wire Model

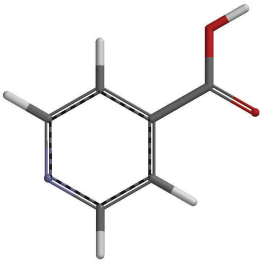


The balls are color coded according to atom type, and the wires representing bonds are drawn in two colors (as in wire models).

Tube ( )

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

Tube Model

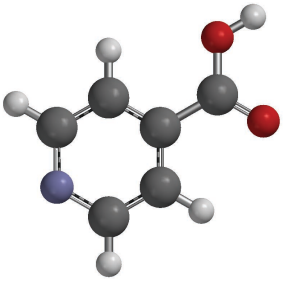


Tubes may either be solid cylinders or be split to represent multiple bonds. As with wire models, bonds are drawn in two colors.

Ball and Spoke ( )

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

Ball-and-Spoke Model

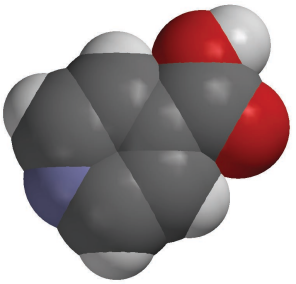


Spokes may either be cylinders or be split to represent multiple bonds. Bond (spoke) color is gray by default but it may be changed using the **Color** dialog (**Colors** under the **Options** menu; **Chapter 10**).

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.

Space-Filling Model



Volume, surface area and polar surface area (PSA)** are displayed in the **Molecule Properties** dialog (**Properties** under the **Display** menu; **Chapter 9**) and 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.

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* Default values for van der Waals radii may be changed from the **VDW Radii** tab accessible from **Preferences** under the **Options** menu (**Chapter 10**). Settings apply to all atoms of given atomic number.

** Polar surface area is defined as the area due to nitrogen and oxygen and any hydrogens attached to nitrogen and oxygen.

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.

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. (If only ribbons are desired, for example, in proteins, select **Hide** for the model.) **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 Online** 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.

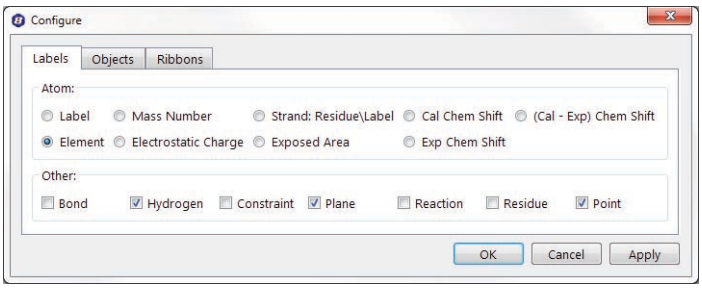
R/S Chirality ( )

If selected, this adds R/S chirality labels to the model. **R/S Chirality** acts in a toggle manner, that is, repeated selection turns R/S labels on and off.

Configure... ( )

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

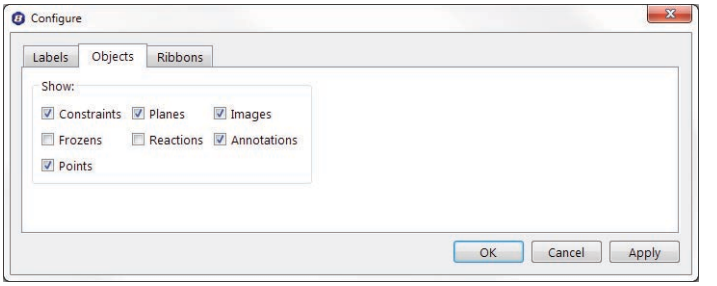
Configure Labels



Atom labels may be selected from among the following: **Labels**, a unique element/number combination that may be changed from the **Atom Properties** dialog (accessible from **Properties** under the **Display** menu; **Chapter 9**), **Element**, **Mass Number**, **Electrostatic Charge**, **Strand: Residue\Label** (polypeptides and polynucleotides), and **Exposed Area** (of an atom in a space-filling model) and **Chem Shift** (Calculated, Experimental, and Calculated-Experimental). 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

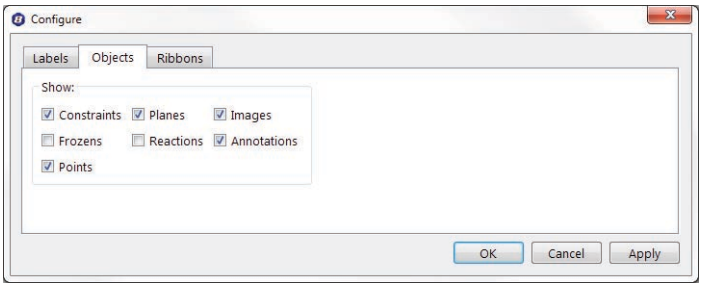
Clicking on the **Objects** tab leads to the **Configure Objects** dialog.



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.



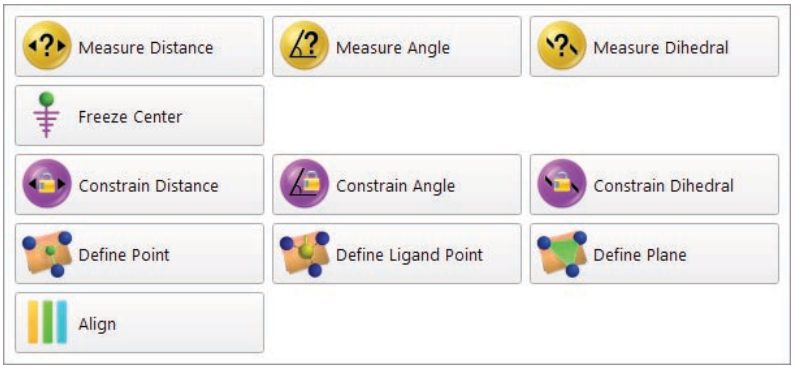
Ribbon coloring may be selected from among the following: **Monochrome**, **By Secondary Structure**, **By Strand** or **By Residue**. Ribbon style may be selected from among the following: **Ribbons**, **Extended Ribbons**, **Beads**, or **Lines**.

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

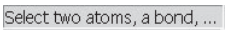
The Geometry Menu

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



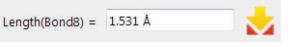
Measure Distance ()
Measure Angle ()
Measure Dihedral ()

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

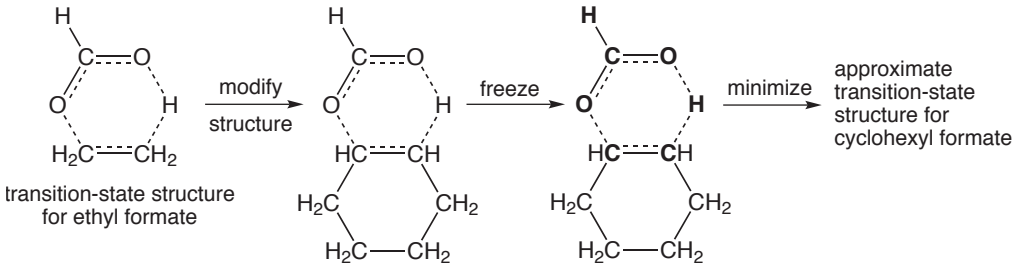
altering the contents of the box to the right of **Distance (A,B)** = or **Length (A)=**, and then *pressing* the **Enter** key (**return** key on Mac). The distance (length) may be entered into the spreadsheet by *clicking* on  to the right of its display (see **Spreadsheet** under the **Display** menu; **Chapter 9**). Alternatively, the label "**Distance (A,B)=**" or "**Length (A)=**" may be *dragged* into the spreadsheet.

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.

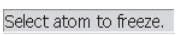
Freeze Center ()

This forces atoms to be held in place during minimization (in the 3D builder) or during equilibrium or transition-state geometry optimization, conformational searching, or energy profile generation using methods specified in the **Calculations** dialog (**Calculations...** from the **Setup** menu; **Chapter 8**).

Atom freezing may be useful in a number of situations, among them guessing a transition-state geometry 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 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 ( ). Whether or not these are included with the model (outside of freeze center mode) is controlled from the **Molecule Preferences** dialog under **Preferences...** in the **Options** menu (**Chapter 10**).

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

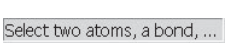
These introduce one or more geometrical constraints during structure minimization (in build mode), and during equilibrium or transition-state geometry optimization or conformational searching using methods specified in the **Calculations** dialog (**Calculations...** from the **Setup** menu; **Chapter 8**). They also allow for setting a range of constraints needed for generation of energy profiles. 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.



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

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  to its right. Alternatively, the label ***Constraint (A,B)=*** may be *dragged* into the spreadsheet.

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.

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

Checking the  leads to additional options 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 **Calculations...** under the **Setup** menu; **Chapter 8**).

The leftmost box sets the initial value of the constraint, the middle

* Note, however, that you should not start a constrained geometry optimization from a structure that is very different from that satisfying one or more constraints.

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, (see **Properties** under the **Display** menu; **Chapter 9**) and the value of the constraint posted to the spreadsheet.

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 Preferences** dialog (**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.

Whether or not points and ligand points are shown as part of the model is controlled from the **Molecule Preferences** dialog (**Preferences...** under the **Options** menu; **Chapter 10**).

Define Ligand Point ()

This defines 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). *Clicking* on atoms (or points) in any order, and *clicking* a second time on any one of the atoms (or points) defines a ligand point (depicted as a small sphere). As many ligand points as desired can be defined. 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.

Whether or not points and ligand points are shown as part of the model is controlled from the **Molecule Preferences** dialog (**Preferences...** under the **Options** menu; **Chapter 10**).

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.

Whether or not planes are included as part of the model is controlled from the **Molecule Preferences** dialog (**Preferences...** under the **Options** menu; **Chapter 10**).

Align ( )

This aligns the selected molecule to all other molecules in the same document. Note: the **Align** icon or menu entry will only be available if you access it with focus on a multi-molecule document. If your document has a single molecule the icon is grayed out. Selection of **Align** from the **Geometry** menu 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 **Molecule List** tab (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 a sketch palette for drawing molecules in 2D, model kits and associated tools for building and editing organic, inorganic and organometallic molecules as well as polypeptides and polynucleotides in 3D, 2D to 3D conversion and 3D structure refinement using molecular mechanics.*

Spartan Student provides a variety of tools for specification of 3D molecular structure, a necessary first step to any molecular mechanics or quantum chemical calculation. Molecules can either be rendered as 2D sketches and later brought into 3D*, or directly constructed from 3D fragments. Polypeptides and polynucleotides need to be built in 3D.

2D Sketch Palette

The 2D sketch palette contains tools for making and manipulating drawings. There are also tools for specifying charges and radical sites and for adding cues to designate stereochemistry.

Defined Atoms. H, B, C, N, O, F, Si, P, Cl, Br and I only.

* The Windows version of ***Spartan Student*** also allows seamless access to ChemDraw installed and licensed on the same computer. 2D drawings are automatically brought into 3D. Both Windows and Mac versions of ***Spartan Student*** are able to read ChemDraw files. Information is provided in **Appendix E**.

Periodic Table, Groups, Ligands. A "More" icon which appears below the H and B icons allows any atom as well as a variety of common functional groups and a selection of common ligands to be specified.

Common Rings. Three icons facilitate the rapid addition of benzene (), cyclohexane () and cyclopropane (), cyclobutane (), cyclopentane () and cycloheptane ().

Common Carbonyl Groups. Three icons facilitate the rapid addition of carbonyl (), carboxylic acid/ester () and amide () groups to drawings.

Stereochemical Markers. Wedges and dashes, represented by  and  , can be used to designate in-out stereochemistry. Once a stereochemical marker has been added to a drawing, it is possible to designate the orientation of hydrogen atoms and/or substituents bonded to six-member rings as **ax(ial)** or **eq(uatorial)** (*ax* and *eq* labels appear only on the drawing, not in the palette).

Charge/Radical Markers. Conventional bonding rules (neutral C makes 4 bonds, neutral N makes 3 bonds, and so on) are enforced when 2D perspective drawings are converted into 3D models. This is accomplished by adding hydrogen atoms to the drawing. For example, a single carbon on screen will give methane, a single line, ethane, and a double line, ethylene. (Hydrogen atoms are added to nitrogen, oxygen, phosphorous and sulfur in the 2D drawings.) When another outcome is desired, for example, for an ion or free radical, charge or radical markers must be added to the drawing.

Two icons,  and  , are used to label atoms that bear formal charges.  is used to label atoms that are neutral, open-shell radicals. Each of these markers affects the number of electrons and the number of hydrogen atoms added to the 3D model. For example, **O** will produce a 3D model of water, H_2O. However, adding the appropriate marker will result in 3D models of H_3O^+ (), HO^- (), or HO radical (), respectively. Only one charge/radical marker can be assigned to an atom.

Only one charge/radical marker is displayed on the palette, but *clicking* on the icon will cause each marker to appear in turn.

Reaction Arrows. designates one ore more curved arrows allowing access to ***Spartan's*** automated search transition state procedure. 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. *Clicking* again on the same atom (or same bond) removes the highlighting. 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 by *clicking* on it two times. If the destination is an existing bond (leading to an increase in bond order from single → double or double → triple), then select (*click* on) the bond. If no bond presently exists, select (*click* on) 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.

Note that the head and tail do not need to reside on atoms or bonds on the same fragment. Also the tail may involve atoms of two detached fragments.

The process (tail selection followed by head selection) is repeated as necessary to fully define the reaction. Incorrect reaction arrows may be removed by *clicking* on from the palette and *clicking* on the arrow. You then need to select to continue arrow specification.

Once defined, reaction queries can be used to provide a guess at a transition state based on its similarity to an entry in an internal database* of transition states for a variety of common reactions.

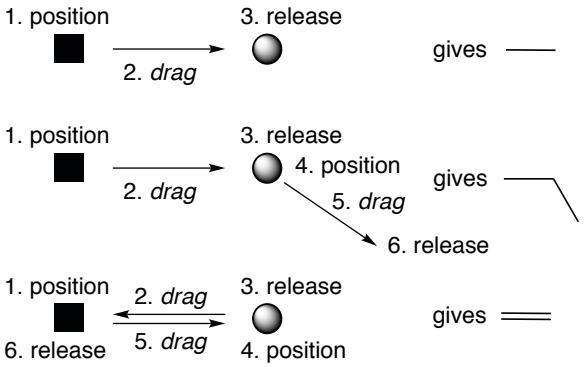
Drawing Tools. Undoes the most recent drawing operation. Removes or modifies parts of a drawing. Deletes an entire

* This collection presently consists of more than 2000 named reactions.

drawing (a warning is provided). Improve the readability of a drawing by applying various "clean up" procedures.

Making a Sketch

To start a sketch, first select (*click* on) an atom, group, ring or the **More** icon in the sketch palette and then *double click* in the white portion of the screen (the drawing area). To draw a bond, first *click* on an atom, group, ring or **More** icon in the sketch palette to designate what is at the end of the bond, then position the cursor over the atom in the drawing area where you want the bond to start, move the cursor while holding down the left button (*drag* the cursor) to the place in the drawing area where you want the bond to end and release the button. Multiple bonds are made by dragging over existing bonds.



To make a bond touch the screen where you want it to start, move one finger to where you want it to end and lift. Replace position by touch, drag by move and release by lift in the diagram above.

Manipulating a Sketch

To translate the sketch, move the mouse over the screen while holding down the right button. To rotate the sketch (in the plane of the screen), move the mouse up and down while holding down both the left button and **Shift** key. Use the scroll wheel to resize the sketch.

To translate the sketch, move two fingers over the screen. To rotate the sketch in the plane of the screen, *twist* two fingers on the screen. To resize the sketch, pinch (or spread) two fingers on the screen.

Sketch Operations

Add an Atom, Ring, or Carbonyl Group. To add an atom, *click* on that atom's icon. Position the cursor over the atom in the drawing that will connect to the new atom, *drag* it away and release the button. To add a common ring or carbonyl group, *click* on that ring's (group's) icon, position the cursor over the atom in the drawing that will connect to the new ring (group) and *drag* it away and release the button. The carboxylic acid/ester  and amide  icons contain an arrow that shows which atom in these groups will be connected to the existing drawing. To change the location of this connection point (arrow), *click* on the group's icon until the arrow reaches the desired location.

Add Multiple Bonds. To add a multiple bond, first draw a single bond at the location where the multiple bond is needed, then redraw this line once to make a double bond, and redraw it again to make a triple bond (in other words, position the cursor over one end of the bond, drag to the other end, and release the button).

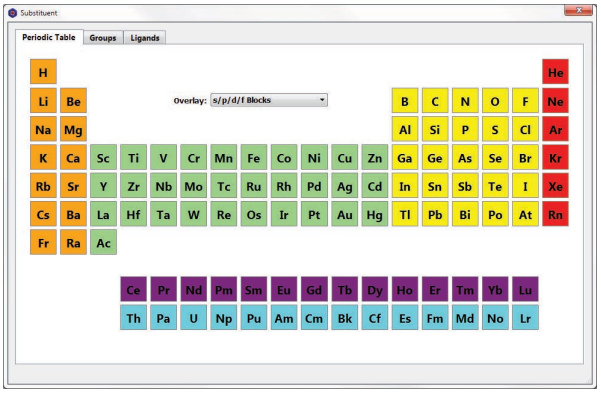
Fuse Rings. *Click* on an icon for the first ring and *double click* on the screen. Next, *click* on the icon for the second ring and double tap the bond that the rings will share. This will create a drawing with a fused bicyclic ring system. Note that the (*cis* or *trans*) stereochemistry of the ring juncture is ill-defined. This will be addressed later (**Add Stereochemical Markers**).

This technique can also be used to add rings to an existing bond in any drawing. *Click* on the icon for the ring to be added and *double click* on the bond that will become part of the ring.

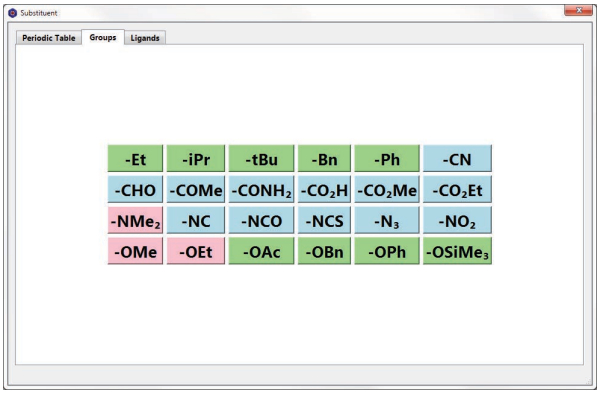
Replace an Atom with Another. If a drawing contains atom A where atom B is needed, *click* on the icon for B, then *double click* on A in the drawing. This allows the drawing of heterocycles. First, draw an all-carbon ring and then replace specific carbons with heteroatoms.

Access an Element, Functional Group, or Ligand. *Click* on the icon underneath H and B (this icon will initially be labeled with the name of the group that was previously selected (or with

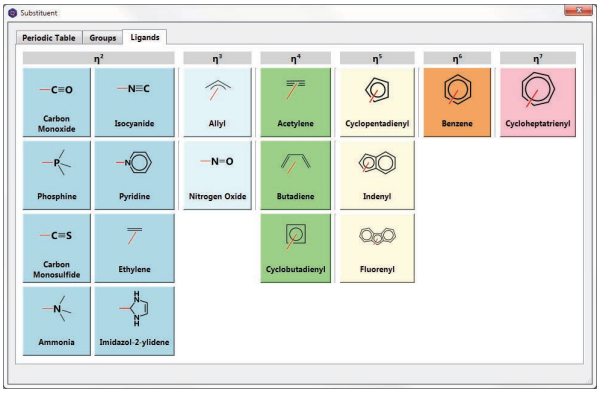
More if no previous selection was made) and will change each time you select a new moiety. A tabbed dialog initially displaying a ***Periodic Table*** *results*.



If instead of an element, a functional group is desired, *click* on the **Groups** tab, and then on a group from the dialog that results.



Finally, if a ligand is desired, *click* on the **Ligands** tab, and then a ligand from the dialog that results.



An element, group or ligand defined in this way can be added to a drawing, replaced, or removed using the same drawing techniques used for standard atoms.

Add a Stereochemical Marker (Dash or Wedge). 3D information can be added to a drawing by replacing **single** bonds with stereochemical markers: dashes or wedges. The single bond must be drawn before a marker can be added.

To replace a single bond with a marker, *click* either  or  , then *re-draw* the single bond. To reverse the orientation of the marker, *re-draw* the bond or marker in the opposite direction. One type of marker can be replaced directly by the other. *Click* on the desired marker and then *re-draw* the existing marker. Markers can also be converted back into single bonds. *Click* on  , then *double click* on the marker.

For best results during 2D-to-3D conversion, all substituent bonds to rings should be drawn with stereochemical markers.

Add an *Axial* or *Equatorial* Marker (6-member rings only). The orientation of a hydrogen/substituent on a 6-member ring can be specified by marking **one** ring substituent as either **ax(ial)** or **eq(uatorial)**. If the molecule contains multiple rings, the conformation of each ring can be specified by marking **one** substituent per ring. *Axial* or *equatorial* markers can only be added to stereochemical markers (dashes, wedge) so the bond connecting the substituent to the ring must be drawn with a stereochemical marker first.

To add an *axial* or *equatorial* marker to a stereochemical marker, *click* on either  or  , then *double click* on the stereochemical marker. ax will appear on top of the stereochemical marker. To replace ax with eq, *double click* on the stereochemical marker again. To remove the marker, *double click* on the marker again.

Although it is possible to produce a drawing in which several bonds are marked as *axial* or *equatorial*, **only one** marker is used when converting a 2D ring drawing into a 3D model.

Assign Charges and Radical Sites. Formal charges and unpaired electrons can be assigned to individual atoms using charge/unpaired electron markers. To assign a **positive** formal charge to an atom, *click* on  and *double click* on the atom in the drawing. To assign a **negative** formal charge or **unpaired electron**, *click* on the charge/unpaired electron marker until the desired icon appears (tapping the marker rotates it through three possibilities:  ,  , and ) and double tap the atom in the drawing.

To replace a charge/unpaired electron marker on an atom with a different marker, *click* on the desired charge/unpaired electron icon and *double click* the marked atom. To remove a marker, *click* on  and *double click* on the marker.

Charge/unpaired electron markers play an important role during the conversion of 2D drawings into 3D models in that they determine the number of hydrogens that need to be added to the model (it is usually unnecessary to draw hydrogens unless they are needed to mark stereochemistry).

Hydrogens are not shown in 2D perspective drawings unless they have been drawn explicitly (exceptions: hydrogens attached to neutral N, O, P, and S are shown). When a drawing is converted into a 3D model, hydrogens are added to the model according to conventional bonding rules. A neutral carbon atom is assumed to form four bonds, nitrogen three bonds, oxygen two bonds, and so on. Analogous logic is used for atoms that carry a formal charge or unpaired electron marker.

Charge and unpaired electron markers are carried over into specification of quantum chemical calculations (**Calculations...** from the **Setup** menu; **Chapter 8**). The total charge is set equal to the sum of the formal charges in the 2D drawing. A model with one unpaired electron is treated as a free radical (drawings that contain more than one unpaired electron may give unanticipated results).

Undo the Last Action. *Click* on  to return to the drawing as it existed before the last action.

Clean Up a Drawing. *Click* on  to clean up a drawing, that is, to equalize bond lengths, bond angles, and so on. Clean up can improve the appearance of a 2D drawing, but not every clean up will produce a desirable result. To undo an unsatisfactory clean up operation, *click* on  .

Remove an Atom or Bond. *Click* on  and then *double click* on the atom or bond. If you *click* an atom, all bonds to that atom will also be removed. Removing a bond, either by *clicking* on an atom or by *clicking* on the bond itself, will also remove terminal atoms, that is, atoms not connected to any other atoms in the drawing will be removed along with the bond.

Remove a Multiple Bond. To remove a multiple bond, *click* on  then *double click* on the multiple bond. This reduces the bond order by one. Repeated *double clicks* on a triple bond will reduce the bond order: triple → double → single → no bond.

Remove a Reaction Arrow. To remove a reaction arrow, *click* on  and *double click* on the reaction arrow.

Remove a Stereochemical Marker. *Click* on  , then *double click* the marker. This replaces the marker with a single bond.

Change or Remove an *Axial* or *Equatorial* Label from a Stereochemical Marker. Tap either  or  , then *double click* on the stereochemical marker where an *axial* or *equatorial* label appears. This cycles the label (in order) among **ax** (*axial*), **eq** (*equatorial*) and nothing. The stereochemical marker itself will not be affected.

Remove a Charge or Radical Marker. *Click* on  and *double click* on the marker.

Clear the Screen. *Click* on  . A warning message will ask you to confirm this operation.

A 3D structure is obtained from the 2D sketch by *clicking* on  .

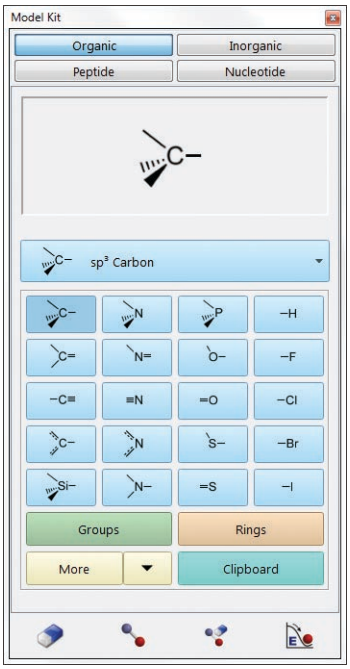
3D Model Kits

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 well represented in terms of an uncharged (non-zwitterionic) valence structure, 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.

3D 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:

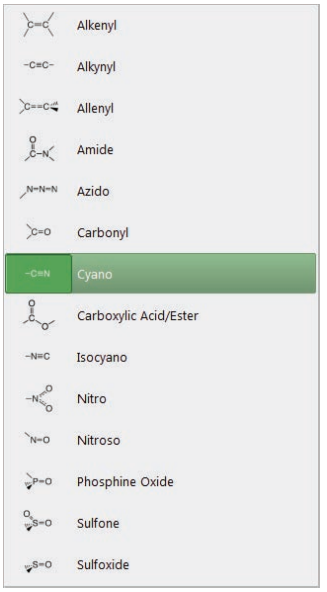
$C(sp^3)$	$N(sp^3)$	$P(sp^3)$	H
$C(sp^2)$	$N(sp^2)$	$O(sp^3)$	F
C(sp)	N(sp)	$O(sp^2)$	Cl
C(aromatic)	N(aromatic)	$S(sp^3)$	Br
$Si(sp^3)$	N(planar)	$S(sp^2)$	I

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 appended onto an existing structure. To initiate building, *double-click* anywhere on screen. To add alongside of an existing structure, 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, Si, 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 (accessible from **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 ***Spartan***'s file system (**More**). The model kit also accesses the clipboard (**Clipboard**).

Groups

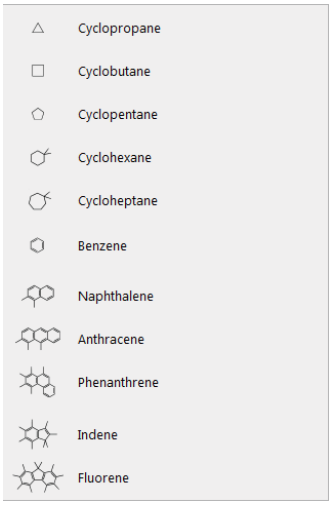


Clicking on **Groups** brings up a menu of groups, and displays an icon of one group in a box at the top of the model kit.

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 circulates 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 in a box 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. A ring may be "fused" by *double clicking* on a bond in an existing ring. Note that the (*cis* or *trans*) stereochemistry of the ring juncture may need to be adjusted by inverting chirality (see discussion later in the chapter).

Cyclohexane, cycloheptane, naphthalene, anthracene, phenanthrene, indene and fluorene 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 circulates among the available positions with repeated *clicking* on the icon. Selection of an *axial* or *equatorial* free valence in cyclohexane and cycloheptane 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 access user-defined entities (rings, groups, ligands, etc.). 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 **Library** directory containing documents of common rings.

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

Clicking on a document followed by *clicking* on **Open** or *double clicking* on a document 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 in a box 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) or with the usual one and two-finger touch commands. 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.

Documents containing ligands, chelates and high-coordination fragments intended for use with the inorganic model kit (discussed in the next section) are also available. In addition,

any ***Spartan Student*** document may also be accessed.

Clipboard

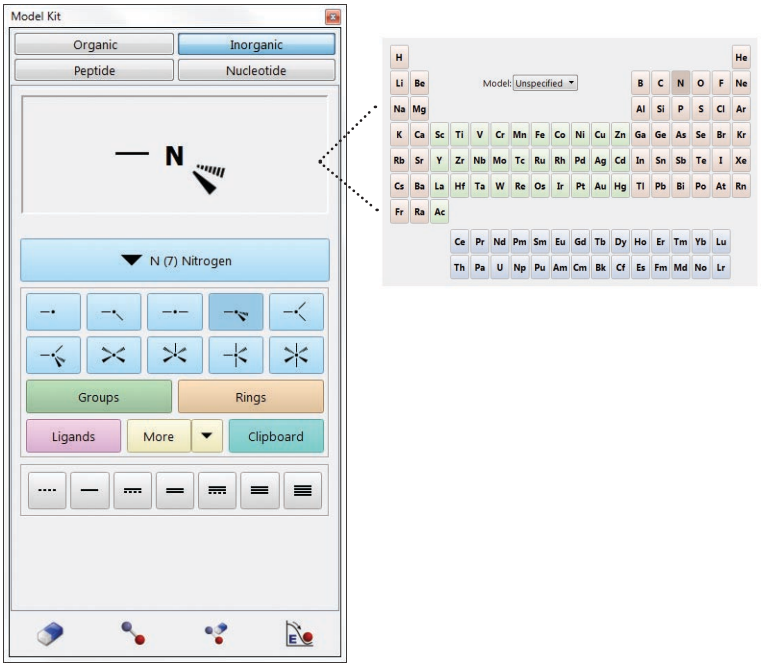
Clicking on **Clipboard** accesses the clipboard. A ball-and-wire model of whatever is on the clipboard is displayed in a box at the top of the model kit. This may be manipulated using the usual mouse/keyboard commands (you need to position the cursor inside the box or with the usual one and two-finger touch commands). Once selected, the contents of the clipboard 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.

An empty clipboard will be signaled by:

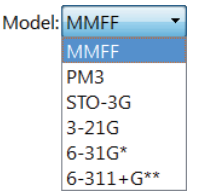
Inorganic Model Kit

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 bonding rule enforcement. The inorganic model kit is reached by selecting **Inorganic** from among the tabs at the top of the model kit.*

* Tabs may require too much vertical space on computers or tablets with very small screens. Alternative **Builder Selection Methods** are available in the **Miscellaneous** tab (**Preferences** from the **Options** menu; **Chapter 10**).



Atoms may be selected by *clicking* on the selection bar near the center of the model kit. This brings up a full *Periodic Table*. Main-group elements are colored red, transition metals are colored green and lanthanides and actinides are colored blue. The **Model** menu inside the *Periodic Table* highlights elements for which the selected model is available.



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.

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, *double click* anywhere on screen. To add alongside of an existing structure, hold down the **Insert** key (**option** key on Mac) and *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 from a menu near the bottom of 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 which reference a Lewis structure (including minimization in the builder; see discussion later in this chapter).

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

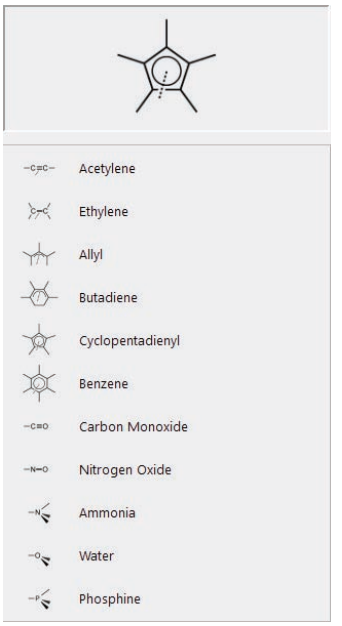
Menus under **Groups**, **Rings** and **More** are the same as those described for the organic model kit as is **Clipboard**. One additional fragment collection is provided:

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

* Hybrids for a number of high-coordination centers are available as a library reachable from **More** (see discussion under **Organic Model Kit**).

being displayed in a box at the top of the model kit.

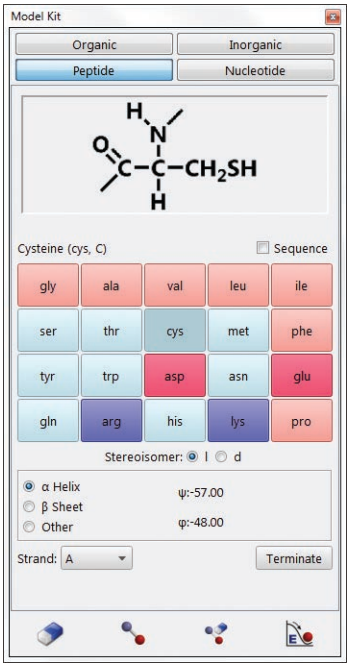


A ligand may be used to initiate building or to add alongside or to an existing structure. Additional ligands are accessible from **More** (see previous discussion). Ligands may also be built with the aid of ligand points (**Define Ligand Point** in the **Geometry** menu; **Chapter 6**).

To toggle the selection bar back to atom selection from the *Periodic Table*, *click* on one of the atomic hybrid icons.

Peptide Model Kit

The peptide model kit available in ***Spartan Student*** is not intended to be used for constructing proteins (although this is actually possible). Rather, it is primarily intended to build idealized helix and sheet structures. Protein structures are best entered from the Protein Data Bank (see **Access PDB Online...** under the **File** menu; **Chapter 3**). A model kit for construction of polypeptides is reached by selecting **Peptide** from among the tabs at the top of the model kit.



At the middle of the peptide model kit are icons designating the amino acids (specified by their three-letter codes). An amino acid is selected by *clicking* on its three-letter code, the icon of the amino acid is displayed in the box at the top of the model kit. If the **Sequence** check box is selected, the three-letter code for the amino acid is appended to the sequence of codes in the box at the top of the model kit. 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:

Specify 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**.

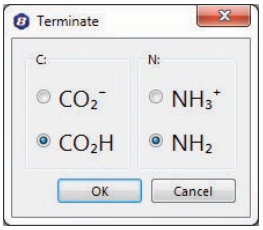
Specify Macroscopic Structure

Once sequencing is complete, macroscopic structure (ψ and ϕ angles), is specified by *clicking* on one of 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.

Terminate

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

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

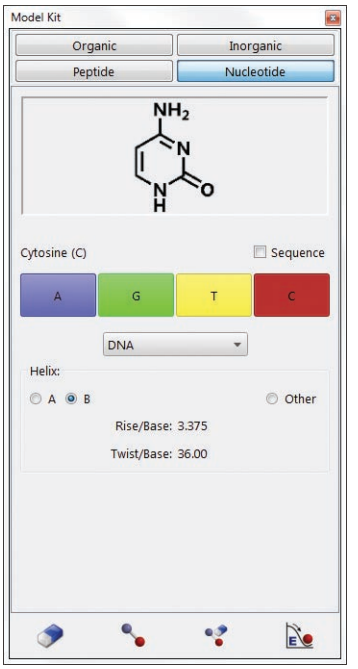


C and N terminating groups may be selected by repeated *clicking* on the C and N icons, respectively. Selection will rotate among the available terminating groups. *Clicking* on **OK** removes the dialog and terminates the polypeptide. *Clicking* on **Cancel** or  removes the dialog but does not terminate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

The peptide (or single amino acid) may now be used either to initiate building, by *double-clicking* anywhere on screen or added alongside of an existing structure, by holding down the **Insert** key (**option** key on Mac) and *clicking* anywhere on screen, or by *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

Finally, ***Spartan Student*** provides a model kit for construction of polynucleotides. It is reached by selecting **Nucleotide** from among the tabs at the top of the 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 above 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) has been 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:

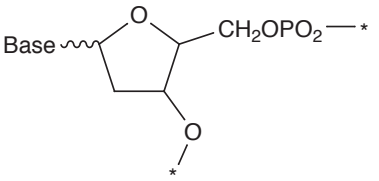
Specify Base Sequence

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**.

Specify 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 *double-clicking* anywhere on screen, Add alongside an existing structure, by first holding down the **Insert** key (**option** key on Mac) and *clicking* anywhere on screen, or *double clicking* on a blank area on screen. Join onto an existing structure by *clicking* on a free valence. In the latter case, attachment is made from the phosphate end.

General Molecule Building Functionality

Additional capabilities are available with **Edit Build** selected:

Multiple Fragments

Multiple fragments may result either from bond breakage (see **Break Bond** later in this chapter) or from use of the **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 yellow (free valences for any non-selected fragments are colored white). Rotation and translation apply to the entire set of fragments, but may be made to apply to the selected fragment (only) by holding down the **Ctrl** key while carrying out these operations.

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

Rotate/Stretch Bonds

In addition to molecule rotation, translation and scaling, the mouse is used to rotate about and stretch bonds not incorporated into 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, ring or substituent 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. Bond rotation (only) also follows from moving the cursor up and down inside the demarked area at the left of the screen while holding down the left button.

Replace Atom/Fragment

Another function of the mouse is atom replacement. This behaves differently in the organic and inorganic model kits. *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 or that would disrupt substituents 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, that is, 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 applicable to the peptide or nucleotide model kits.

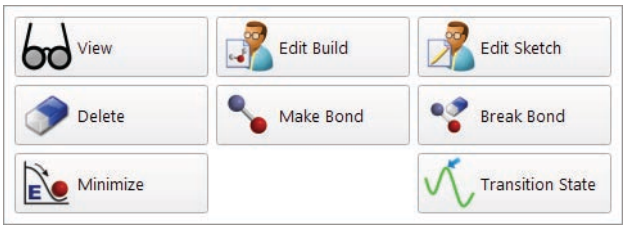
Invert Chirality

In the **Edit Build** mode, *double clicking* on a chiral atom with the **Ctrl** key (**Command** key on Mac) depressed inverts the chirality of the atom (R→S or S→R). *Double clicking* on any atom with both **Ctrl** (**Command** key on Mac) and **Shift** keys depressed inverts the absolute configuration of the molecule.

Replace *click* with *tap* and *double click* with *double tap* for multiple fragment, fragment replacement and chirality inversion. One finger movement up and down the shaded area at the left of the screen results in rotation about the marked bond.

Building/Editing Menu Functions

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



Icons for **Delete**, **Make Bond**, **Break Bond** and **Minimize** are also found at the bottom of the model kit. They may also be included in the icon toolbar at the top of the screen.

View ( )

This exits build mode, and removes the model kit from the screen and also adds hydrogens to any open valences (one does ***not*** need to explicitly add hydrogens).

Initial entry into the 3D builder is by way of **New Build** or **Build New Molecule** under the **File** menu (**Chapter 3**). **Edit Build**, **Delete**, **Make Bond**, **Break Bond** and **Minimize** are for modifying existing structures.

Edit Build ( )

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

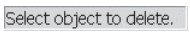
fragment may be used to initiate building by *double-clicking* anywhere on screen, to add alongside an existing structure on screen by holding down the **Insert** key (**option** key on Mac) and by *clicking* anywhere on screen, or by *double clicking* in a blank area on screen, or be added to an existing structure by *clicking* on the appropriate free valence. Fragment addition can be terminated by selection of any other function.

Edit Sketch ()

This allows a 2D sketch to be modified in the 2D sketcher after it has been converted to a 3D structure. **Edit Sketch** is unavailable when the existing 3D molecule contains more than 250 atoms.

Delete ()

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



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. Selection of **Delete** does not bring up a model kit nor does it remove a model kit that is present on screen. **Delete** is (by default) a one-time operation. *Double-clicking* on the **Delete** icon will hold the delete mode open until the user selects another mode (for example  to **View**, or  to return to **Edit Build)**.

> **Delete** is also used to delete points and planes.

Deletion may also be accomplished by holding down on the **Delete** key (on the keyboard) while *clicking* on the item to be deleted. This mode (also) allows multiple deletions.

Make Bond ()

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

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.

Replace *click* with *tap* and *double click* with *double tap* for delete, make bond and break bond operations.

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

Minimize ( )

This uses molecular mechanics to refine the geometry. 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 icon at the bottom right of the screen. Any geometrical constraints imposed on the structure (see **Constrain Distance**, **Constrain Angle**, **Constrain Dihedral** under the **Geometry** menu; **Chapter 6**) are enforced during minimization. Also, any frozen atoms in the structure (see **Freeze Center** under the **Geometry** menu; **Chapter 6**) remain frozen.

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 (the linear synchronous transit method) is automatically invoked.

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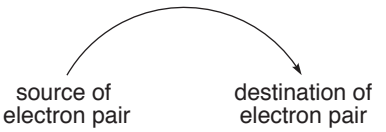
* The mechanics energy is a combination of the strain energy which is either zero or positive and the non-bonded or intramolecular interaction energy which can be either positive or negative. It will most commonly be a positive quantity, although it can be slightly negative.

Input to ***Spartan Student's*** transition-state guessing procedure will be familiar to organic chemistry students (and organic chemists), in that it is based on reaction arrows. 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:

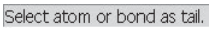


There are two possible sources of an electron pair and three possible destinations, leading to six combinations:

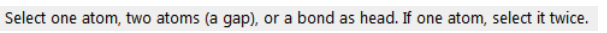
lone pair → lone pair	move lone pair
lone pair → bond	use lone pair to increase bond order
lone pair → space between atoms	use lone pair to make a new (single) bond
bond → lone pair	decrease bond order to make lone pair
bond → bond	decrease bond order of one bond to increase bond order of another bond
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 **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 (*click* on) the atom that holds the lone pair. If the source is a bond, then select (*click* on) 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. *Clicking* again on the same atom or bond deselects (de-highlights) it and leads back to the first message.



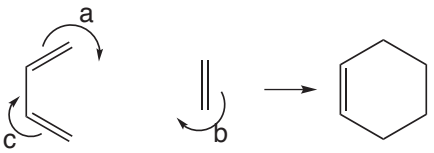
The head of the arrow corresponds to the destination of the electron pair. If the destination is an atom (leading to a lone pair), then select (*click* on) the atom that will hold the lone pair two times. If the destination is an existing bond (leading to an increase in bond order from single → double → or double → triple), then select (*click* on) the bond. If no bond presently exists, then select (*click* on) 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. You can also use the **Undo** feature ( ). Alternatively, *click* on the arrow(s) to be deleted while holding down the **Delete** key on your keyboard.

After all reaction arrows have been properly designated, *click* on the **Search Transition State** icon ( ) 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

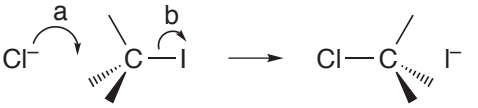
Diels-Alder reaction of 1,3-butadiene and ethylene



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

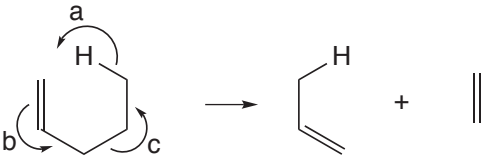
S_N2 reaction of chloride and methyl iodide



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

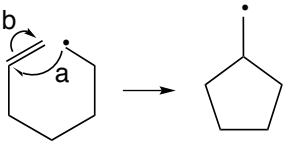


a. single bond to empty space leading to loss of the single bond and to a new single bond

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

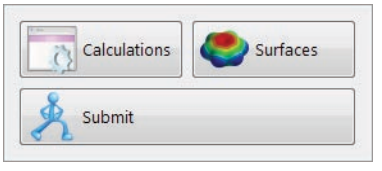
Chapter 8

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, EDF2, and ωB97X-D density functional calculations, MP2 and T1 thermochemical recipe calculations. Tasks include calculating energy, equilibrium geometry, equilibrium conformation, conformer distribution, and transition-state geometry, enumerating accessible conformers 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, ωB97X-D and MP2 calculations. Hartree-Fock and density functional calculations may be carried out in solvent as well as in the gas. Not all methods are applicable to all tasks.* ***Calculations...*** *also optionally requests IR and NMR spectra, QSAR properties.*

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.*



Calculations... ()

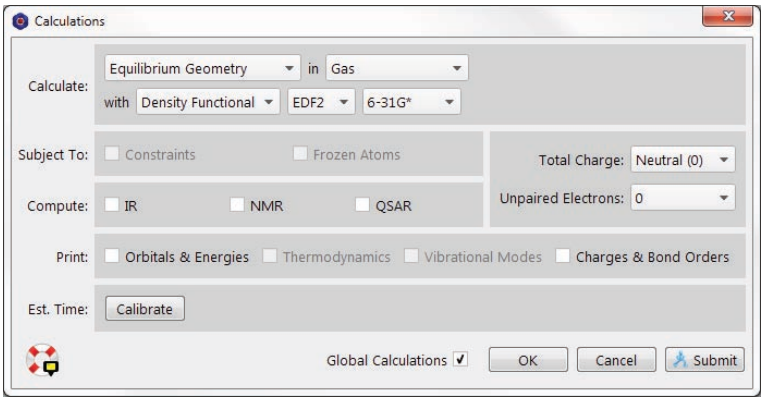
The MMFF molecular mechanics model, the PM3 semi-empirical molecular orbital model, Hartree-Fock molecular orbital models, B3LYP. EDF2 and ωB97X-D density functional models and MP2

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. The MMFF molecular mechanics model is also available to calculate equilibrium conformation or conformer distribution. 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, ωB97X-D and MP2 calculations. The T1 recipe (although including an equilibrium geometry task) is only available when the task specified is an energy calculation.

Hartree-Fock and density functional calculations, aside from NMR calculations, may be carried out in solvent according to the C-PCM model.

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 Hartree-Fock or density functional models.

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

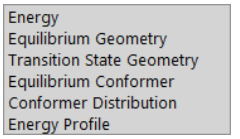


This contains pull-down menus, buttons and check boxes:

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 wave function) 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, ωB97X-D 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 be either 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).

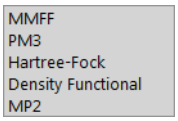
1 atomic unit = 2625 kJ/mol

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.

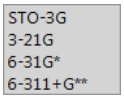
To summarize, the heat of formation differs from the total energy both with regard to the standard reaction and with regard to units. Either provides a suitable basis for thermochemical calculations.

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.

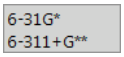
Except for **Equilibrium Conformer** and **Conformer Distribution**, a theoretical model needs to be specified by way of pull-down menus. (**Equilibrium Conformer** and **Conformer Distribution** are limited to MMFF Molecular Mechanics.) The first provides a choice among different classes of models.



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, ωB97X-D** or **MP2** leads to an abbreviated menu of available basis sets.



Transition State Geometry is not available for **Molecular Mechanics**. Use of solvent is available for **Hartree-Fock** and **Density Functional** models.

Spectra

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). 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*, EDF2/6-31G*, and ωB97X-D/6-31G* calculations have been uniformly scaled to account for known systematic errors. Calculated frequencies from all other models have not been scaled. 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.

If *checked*, **NMR Spectra** specifies that NMR chemical shifts 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** pane accessible from **Spectra** under the **Display** menu (**Chapter 9**)*. For density functional calculations with the 6-31G* basis set, ^{13}C, chemical

* 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**).

shifts have been empirically corrected for local environment. Line intensities are 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 these have been used to simulate splitting patterns.

QSAR

If *checked*, calculates a number of wave function-based properties accessible from the **QSAR** tab in the **Molecular Properties** dialog (**Chapter 9**).

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.

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.

Calibrate/Est. Time

The **Calibrate** feature runs a single back-end calculation that should take no more than 30 seconds. This is compared against a reference calculation and is used to provide an estimate of how long a specified calculation will take. Once calibrated, all future specified calculations will include an **Est. Time**.

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.

The ***electron density*** is the number of electrons found at a point in space. It is the quantity measured in an X-ray diffraction experiment that is then used to locate atomic positions, that is, most electrons are closely associated with atoms. While the electron density is non-zero everywhere, it is possible to define surfaces of constant density. The most important of these contains most of a molecule's electrons and that roughly corresponds to a space-filling model, that is, a van der Waals surface. We will refer to this as the ***electron density***. It is interesting because it reveals overall molecular size and shape and demarks the steric barrier seen by encroaching molecules. Another important surface, that we will refer to as the ***bond density***, contains fewer electrons in total and demarks atomic connectivity.

The ***spin density*** is the difference in the number of electrons of α and β spin at a point in space. It indicates the location of the unpaired electron in a radical or unpaired electrons in a triplet.

The ***electrostatic potential*** is the energy of interaction of a positive charge with a molecule. This assumes a fixed electron distribution for the molecule. It represents a balance between repulsive interactions involving the positively-charged nuclei and attractive interactions involving the negatively-charged electrons. Regions where the balance tips toward attraction are said to be electron rich (basic) and subject to attack by electrophiles, while regions where the balance tips toward repulsion are said to be electron poor (acidic) and subject to attack by nucleophiles. Electron-rich regions such as lone pairs are typically located outside the van der Waals surface. As such, they may be easily identified by

constructing a surface of negative (attractive) electrostatic potential. While interesting electron-poor areas such as acidic hydrogens also lie outside the van der Waals surface, the electrostatic potential is also positive (repulsive) throughout the region inside this surface.

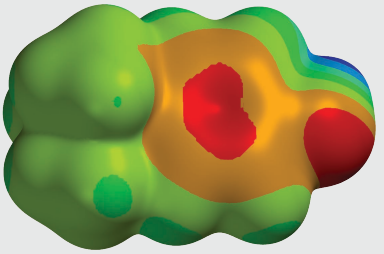
The ***local ionization potential*** indicates the ease or difficulty of electron removal (ionization). Like the negative regions of the electrostatic potential, regions of low local ionization potential are likely to be subject to attack by electrophiles.

Note that neither electrostatic potential nor the local ionization potential are experimental observables, although they relate to quantities that can be given clear chemical interpretation.

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.*

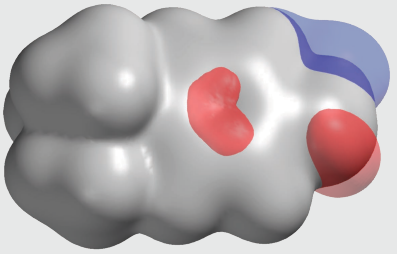
The ***electrostatic potential map*** paints the value of the electrostatic potential onto an electron density surface. By convention, colors toward red depict negative potential, while colors toward blue depict positive potential, and colors in between (orange, yellow, green) depict intermediate values of the potential. Thus, an electrostatic potential map for *p*-*tert*-butylphenol will show oxygen to be red, its attached (acidic) hydrogen to be blue, the π faces of benzene to be orange or yellow and the *tert*-butyl group to be green.

* 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** tab (**Preferences** under the **Options** menu; **Chapter 10**).



The main advantages of this presentation relative to separate electron density and electrostatic potential surfaces are its clarity and its compactness. A disadvantage is that it provides information only about the contact surface and does not reveal how far electron-rich and electron-poor areas extend beyond the surface.

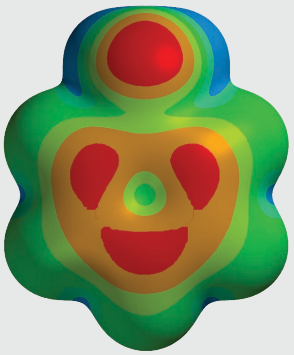
An alternative to an electrostatic potential map, referred to as an ***exposed electrostatic potential surface***, is a composite of three different surfaces: an electron density surface depicting overall molecular size and shape, a negative electrostatic potential surface identifying electron-rich regions and a positive electrostatic potential surface identifying electron-poor regions. These surfaces need to be generated and then displayed simultaneously. The electron density may either be displayed as an opaque solid or as a transparent solid (in order that the molecular skeleton may be seen inside). The two potential surfaces are best represented as transparent solids, the negative surface colored red and the positive surface colored blue. The exposed electrostatic potential surface for *p-tert*-butyl phenol is shown below.



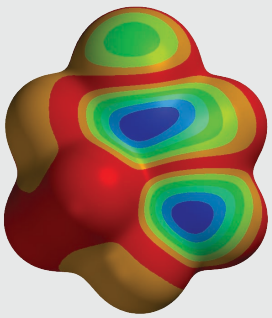
Note that the exposed electrostatic potential surface provides the same information as the electrostatic potential map. Red areas in the map correspond to regions when the negative electrostatic potential surface is likely to protrude from the electron density while blue areas correspond to regions where the positive electrostatic potential surface is likely to stick out.

The ***local ionization potential map*** paints the value of the local ionization potential onto an electron density surface. By convention, colors toward

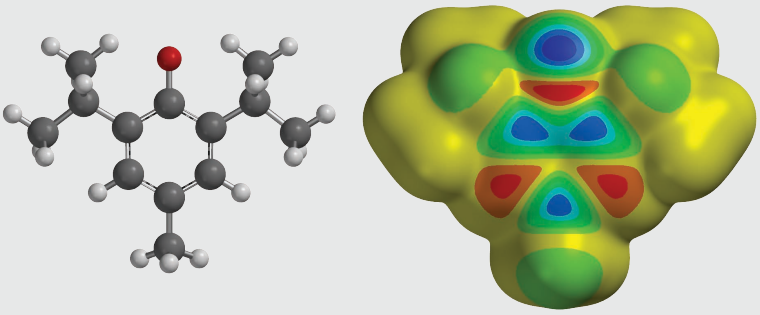
red indicate low ionization potential, while colors toward blue indicate high ionization potential. Thus, the local ionization potential map for aniline shows that the *ortho* and *para* ring positions have a lower ionization potential than the *meta* positions, consistent with the known directing ability of an amino group in electrophilic aromatic substitution.



The ***|LUMO| map*** paints the absolute value of the lowest-unoccupied molecular orbital (the LUMO) onto an electron density surface. By convention, colors near blue indicate high concentration of the LUMO, while colors near red indicate low concentration. Given that the LUMO designates space available for a pair of electrons, a |LUMO| map indicates where nucleophilic attack would likely occur. For example, a |LUMO| map for cyclohexenone shows concentration in two regions, one over the carbonyl carbon and the other over the β carbon, consistent with both carbonyl addition and Michael (conjugate) addition.



The ***spin density map*** paints the value of the spin density onto an electron density surface. By convention, colors near blue indicate high concentration of spin density, while colors near red indicate low concentration. For example, a spin density map for the radical resulting from loss of hydrogen from 3,5-di-*tert*-butylhydroxytoluene (BHT) shows that the spin has delocalized from oxygen onto the *ortho* and *para* ring positions.



This radical would be expected to be particularly stable, which explains why BHT acts as an antioxidant (scavenging less favorable localized radicals).

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**).

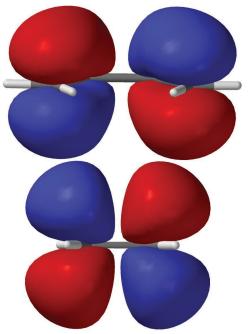
Calculated quantities may also be displayed as two dimensional contour plots (slices). Unlike surfaces and maps, these can be translated, rotated and zoomed independently of the molecular skeleton. An example of a slice display is provided in **Figure 8-1**.

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 improved visualization.

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

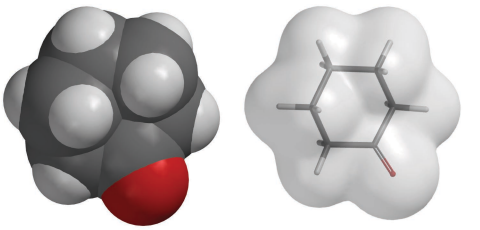
Figure 8-1: Examples of Graphical Displays Available in *Spartan Student*

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



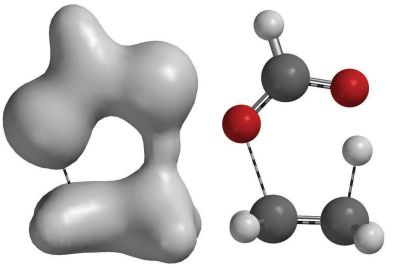
showing interaction of the HOMO of 1,3-butadiene and the LUMO of ethylene.

Space-filling model and electron density surface of cyclohexanone,



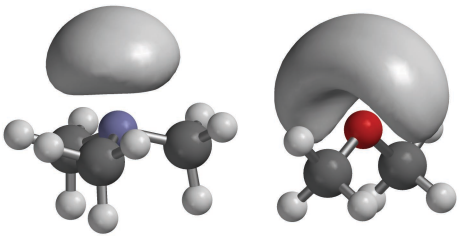
showing overall molecular size and shape.

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



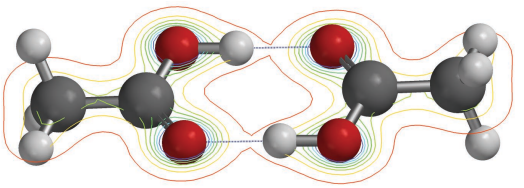
showing bonding in the transition state.

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



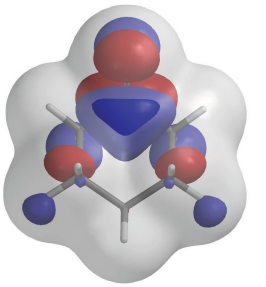
showing the lone pairs on nitrogen and oxygen, respectively.

Electron density slice for acetic acid dimer,

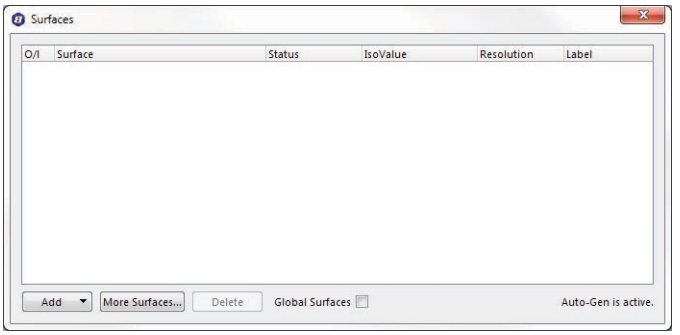


showing hydrogen bonding.

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



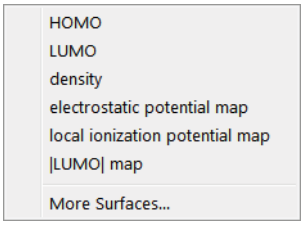
showing accessibility for nucleophilic attack.



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.

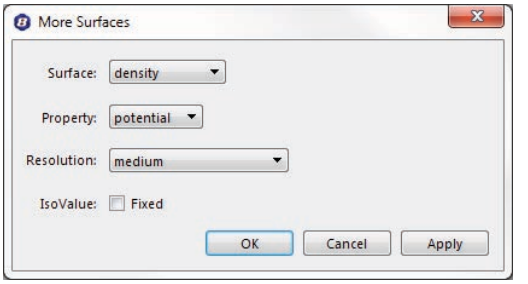


Selection of all but the last entry in the menu leads to a request for the analogous surface or map. A surface and property map specified from this menu will be calculated at medium resolution and will assume a fixed isovalue unless a different resolution has been selected and/or an adjustable isovalue has been requested.

More Surfaces

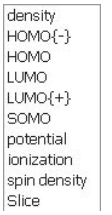
Additional surfaces and maps or the same surfaces or maps at different resolution and with adjustable isosurfaces may be requested by selecting **More Surfaces...** from the menu (or by *clicking* on **More Surfaces...** at the bottom of the **Surfaces** dialog). This leads to the **Add Surfaces** dialog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

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



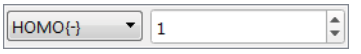
Surface

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 density**** 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 any molecular orbital to be specified..

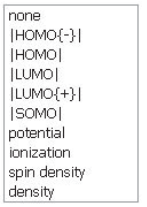


Slice designates that a plane will cut through the graphic defined by **Property**.

Property

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

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

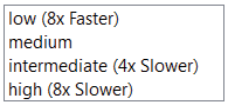


Available properties are the molecular orbitals (**HOMO{-}**, **HOMO**, **LUMO**, **LUMO{+}**, **SOMO**[*]), the electrostatic potential (**potential**), the local ionization potential (**ionization**) and the spin density (**spin density**)[*]. **none** indicates that no property is to be mapped onto 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 desirable for surfaces based on percentage enclosure. Both calculation time and disk storage increase significantly in moving from medium to high resolution.

Isovalue

Checking the box to the left of **Fixed** specifies 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 surface 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 surface may be deleted from the list by first highlighting (*clicking* on) it and then *clicking* on **Delete**.

Global Surfaces

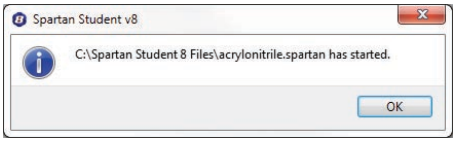
If *checked*, signifies that the requested surfaces will be calculated for all members of the list.

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 ()

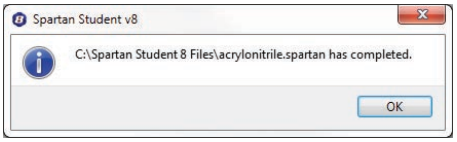
Following setup of a molecular mechanics or quantum chemical calculation, including any requests for spectra and/or graphical displays, the required calculations will begin when **Submit** is selected. If the job has not previously been saved or submitted, selection of **Submit** triggers a request for 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*** (where x is an integer starting with 1) for all successive jobs. After a name has been provided (or the document is saved) a dialog appears indicating that the job has actually been submitted.*

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



The message will close after 5 seconds, or you may *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.

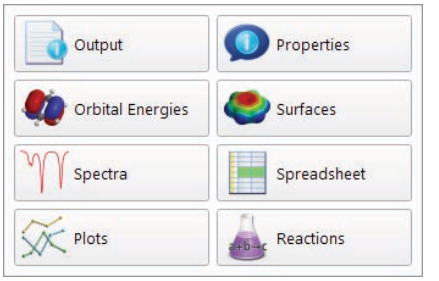


Click on **OK** to remove it.

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.spartan*** where ***document*** is the name given to the original document . A query dialog is provided asking whether the resulting document is to be opened. Similarly, upon completion of a conformer distribution calculation, a new document named ***document.Conf.spartan*** is created, and a prompt to open is provided.

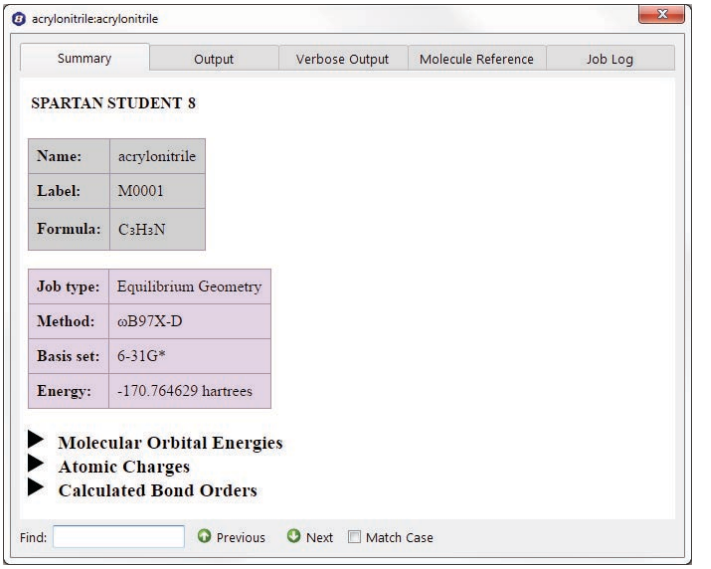
Chapter 9
The Display Menu

*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:



Tabs at the top left of the window select the type of output.

Summary provides a brief summary of the calculated data, in particular, the energy and any spectral quantities. **Output** provides standard text output. **Verbose Output** contains more detailed output, but is eliminated upon normal completion unless **Keep Verbose** is checked in the **Settings** tab (**Preferences** under the **Options** menu; **Chapter 10**). **Molecule Reference** provides the literature reference for data retrieved from the PDB. **Job Log** contains diagnostic information.

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. 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.

Only one 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 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, surfaces and constraints. For plots brought into the main ***Spartan Student*** window from the spectra and plot panes, **Properties** may be used to change default plot styles, limits and fitting functions. Only one **Properties** dialog may be open, and this refers either to the selected molecule (**Molecule Properties**), or to the selected component (atom, bond, etc.) or attribute (spectra, graphical surface, constraint, etc.) of the selected molecule (**Atom Properties**, **Bond Properties**, **Surface Properties**, etc.), or to a plot (**Plot Properties**, **Curve Properties**, etc.), or fitting function (**Regression Properties**).

Selection of a different molecule leads to the **Molecule Properties** dialog for that molecule. Dialogs that refer to components/attributes of the (newly selected) molecule follow by *clicking* on the component/attribute.

With the **Molecule Properties** dialog on screen, *clicking* on a component/attribute brings up the appropriate **Properties** dialog. For example, *clicking* on an atom brings up the **Atom Properties** dialog. *Clicking* on a different component/attribute brings up the appropriate **Properties** dialog. *Clicking* a second time on the same component reverts back to the **Molecule Properties** dialog.*

Most **Properties** dialogs have an associated **Utilities** or **Style** toggle. 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 de-emphasize) a particular molecule, component or attribute. **Utilities**/**Style** dialogs are reached 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.

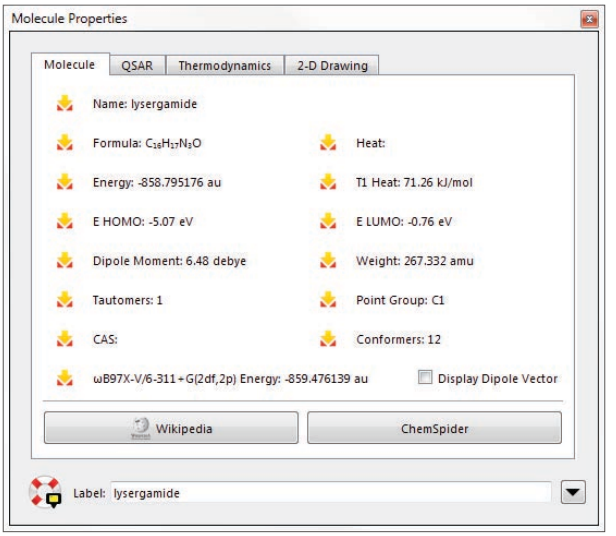
The **Properties** (or **Utilities**/**Style**) dialog may be removed from the screen by *clicking* on  .

Molecule Properties

The **Molecular Properties** dialog comprises four parts: **Molecule**, **QSAR**, **Thermodynamics** and **2D Drawing**, controlled by tabs at the top. Entries under the **Molecule** tab relate to common molecular properties, only some of which depend on the selected level of calculation.

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

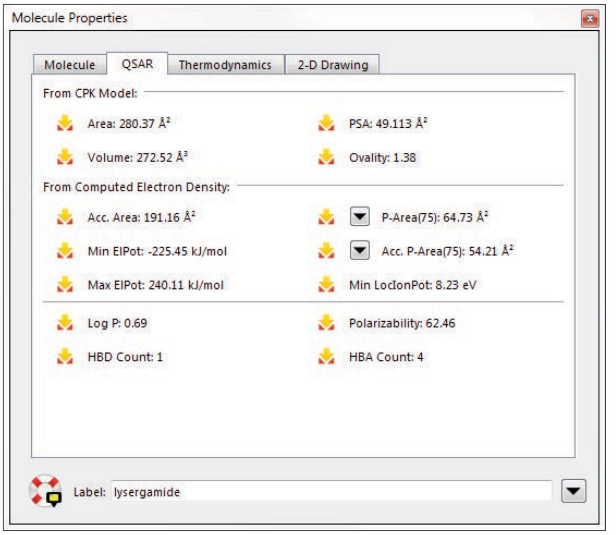
Molecule



Molecule properties include the name and molecular formula, the energy (the specifics of the type of energy and the units it is reported in depend on the theoretical model), the HOMO and LUMO energies (in eV), the dipole moment (in Debye), the molecular weight (in amu), the point group, the predicted number of (non-carbon) tautomers and the predicted number of conformers, and (if available) the experimental heat of formation (in kJ/mol), the heat of formation from the T1 thermochemical recipe (in kJ/mol) and the CAS number. These may be posted to the spreadsheet using the buttons, or *dragged* into the spreadsheet. The dipole moment vector may be added to the model by *checking* the box to the left of **Display Dipole Vector**. Buttons at the bottom right of the dialog access appropriate Wikipedia and ChemSpider pages based on InChi string. **Label** identifies the molecule in a document and appears in the first column of the spreadsheet (see **Spreadsheet**, later in this chapter).

QSAR

Entries under the **QSAR** tab provide additional properties, some of which may be particularly valuable in qualitative structure-activity relationship type analyses.



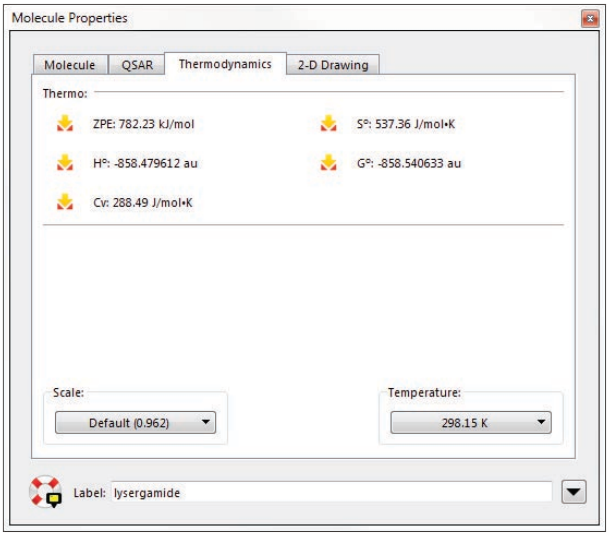
These include: the area, volume, polar surface area (PSA)* and ovality obtained from a space-filling model, and other structure-dependent indicators: LogP, polarizability and the number of hydrogen-bond donor (HBD) and acceptor sites (HBA).** All of these are independent of the level of calculation. Additional quantities which depend on the level of calculation and are based on the electron density surfaces as well as on electrostatic potential maps are also available: the accessible area, the polar area and accessible polar area corresponding to absolute values of the electrostatic potential greater than 75, 100 and 125 kJ/mol (selection is made by repeated *clicking* on ▼), the minimum and maximum values of the electrostatic potential (as mapped onto an electron density surface) and the minimum value of the local ionization potential (as mapped onto an electron density surface). These quantities are not calculated unless explicitly requested by checking **QSAR** inside the **Calculations** dialog (**Calculations...** under the **Setup** menu; **Chapter 8**).

* Polar surface area is defined as the area due to nitrogen and oxygen and any attached hydrogens. Polar surface areas corresponding to arbitrary alternative definitions are available for posting into the spreadsheet using the **PAREA** function. See **Table 22-3**.

** Counts of hydrogen-bond donors and acceptors.

Thermodynamics

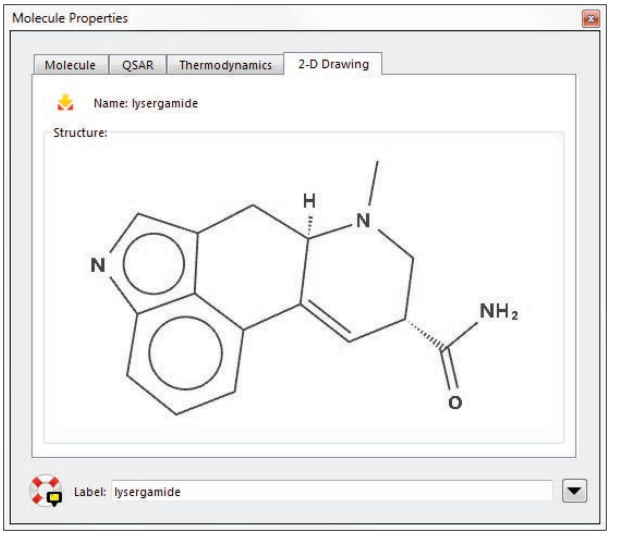
Entries under the **Thermodynamics** tab provide the zero-point energy, the enthalpy, the constant volume heat capacity, the entropy and the Gibbs energy. Except for the zero-point energy, all depend on temperature. The default setting (298.15 K) may be changed. All require vibrational frequencies. Density functional frequency calculations scaled by a number that is slightly smaller than 1 to account for systematic errors.



As discussed under **Properties and Spectra** in **Appendix A**, the entropy and Gibbs energy are subject to considerable uncertainty due to the underlying harmonic approximation.

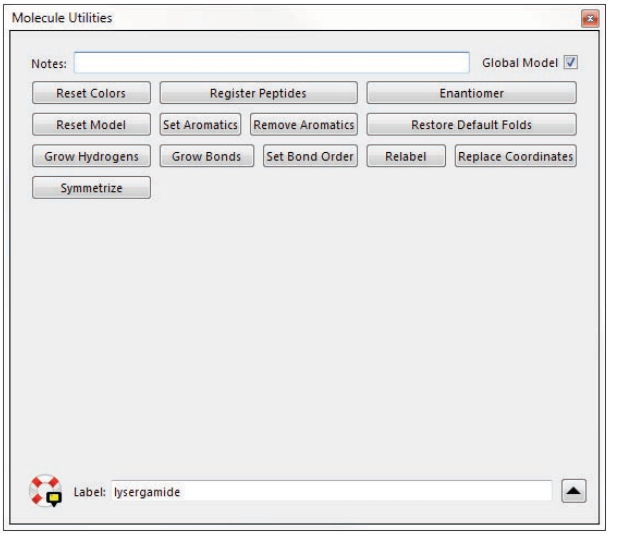
2D Drawing

Displays a 2D drawing for molecules up to 250 atoms.



Molecule Utilities

Clicking on ▼ at the bottom right of the **Molecule Properties** dialog brings up the **Molecule Utilities** dialog (*clicking* on ▲ returns to the **Molecule Properties** dialog).

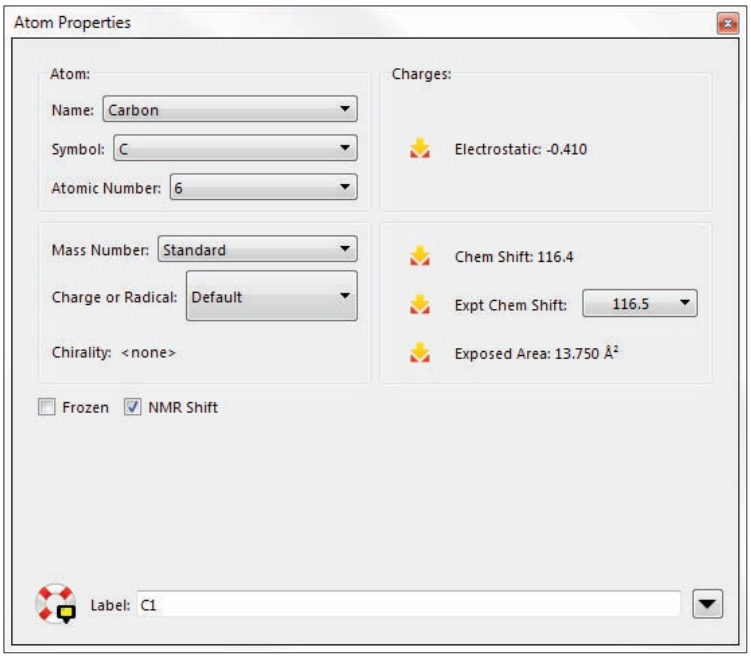


Notes is a user-supplied text string that is reproduced in the output. Controls reset model color and style, add missing hydrogens and

bonds, provide information about amino acids in polypeptides and replace coordinates by standards based only on atomic connectivity, change enantiomers, reset default conformer selections, relabel atoms, and attempt to find local symmetry.

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.



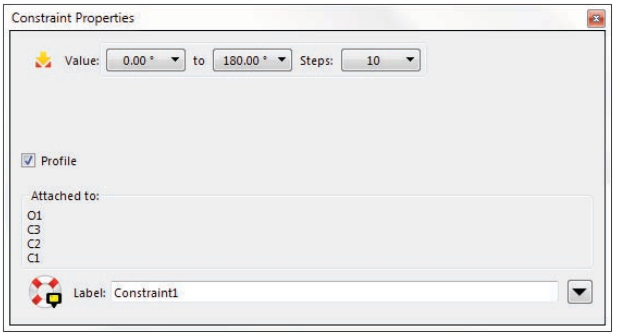
This displays the element name (and allows changing the element), R/S chirality, electrostatic-fit charges (in electrons), calculated NMR chemical shift (in ppm relative to the appropriate standard; tetramethylsilane for both proton and ^{13}C) and exposed surface area of a space-filling model (in $Å^2$). It also allows freezing the atom (see **Freeze Center** in **Chapter 6**), changing its mass number and the default label, setting an atom's charge or number of unpaired electrons, 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), Löwdin or 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).



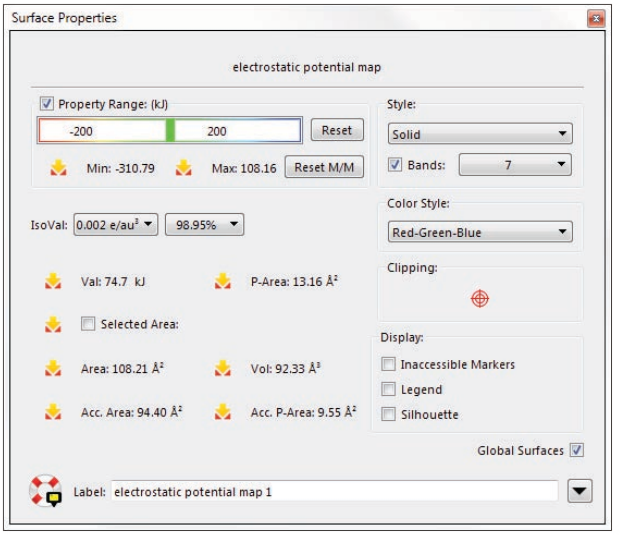
This allows setting the value of a constraint, posting it to the spreadsheet and changing the default constraint label. This also allows specifying a sequence of constraints for an energy profile (see **Calculations...** under the **Setup** menu; **Chapter 8**). The value of the starting constraint is 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 **10**. 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 6**).

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 and colors.

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.

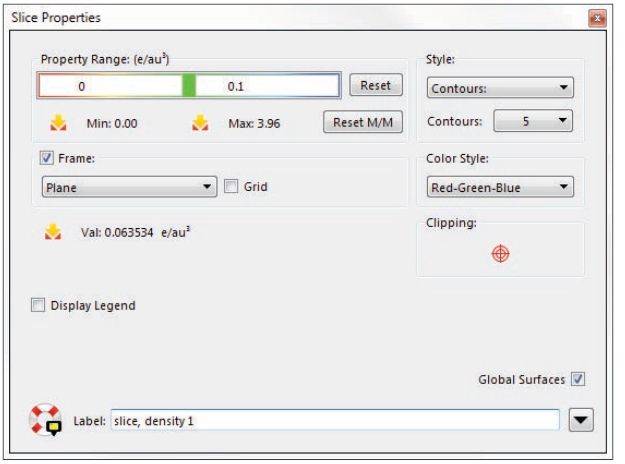


This allows changing display style, isovalue (and in the case of electron density surfaces), percentage of the electrons contained inside the surface, turning on mapped properties, selecting between continuous and banded displays and setting the range of the property, displaying accessible area of surfaces and maps and changing the default labels. A clipping plane may be invoked to allow part of the structural model to be exposed. 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

* 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

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.

Regression Properties

Following a linear regression analysis, a new row, labeled **Fit1***, appears near the bottom of the spreadsheet. This contains information about the fit. *Clicking* on this line with a **Properties** dialog on screen, or selecting **Properties** from the **Display** menu () after *clicking* on the line, leads to the **Regression Properties** dialog.

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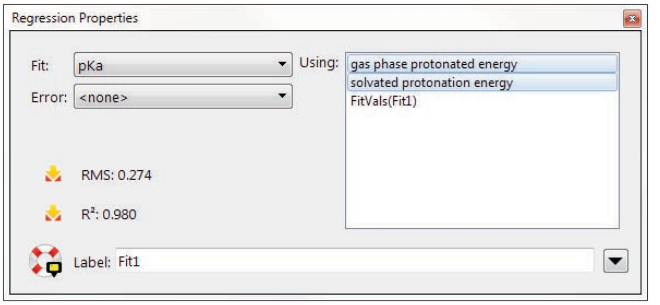
in the **Settings Preferences** dialog (**Preferences** under the **Options** menu; **Chapter 10**).

* 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.

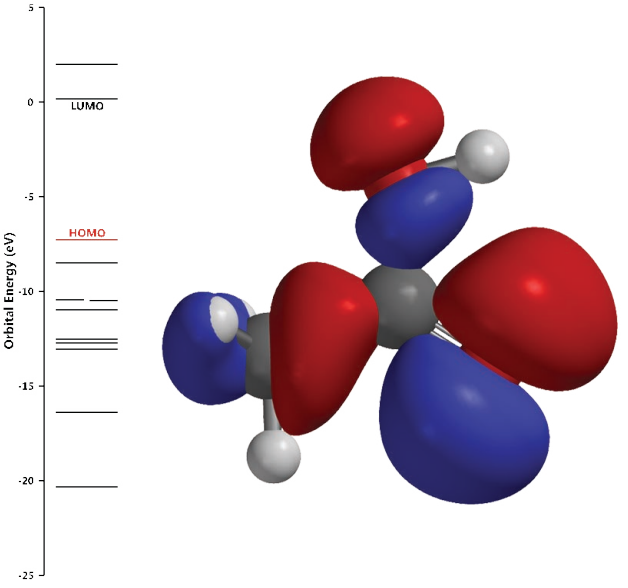
*** More precisely, a row will be written for each fit, and labelled **Fit1**, **Fit2**, ...



This reports RMSD and R^2, as well as allows for changing what is to be fit (**Fit**) and what it is to be fit to (**Using**). The error statistics will immediately update.

Orbital Energies ( )

Selecting **Orbital Energies** leads to the display of an orbital energy diagram (accessible when the wave function is available). This comprises up to ten occupied molecular orbitals and two unoccupied molecular orbitals, the highest-occupied (HOMO) and lowest-unoccupied (LUMO) being explicitly designated.



Clicking on an energy level in the diagram leads to display of the corresponding molecular orbital. This may be manipulated in the usual way; the energy can be posted to the spreadsheet and the display style altered (from the menu at the bottom right of the

screen). After one energy level has been selected and the associated orbital displayed, moving the mouse up or down over the diagram while holding down the left button ("swiping") then releasing the button selects the next higher or lower energy level.

Moving a finger up or down over the diagram then lifting selects the next higher or lower energy level.

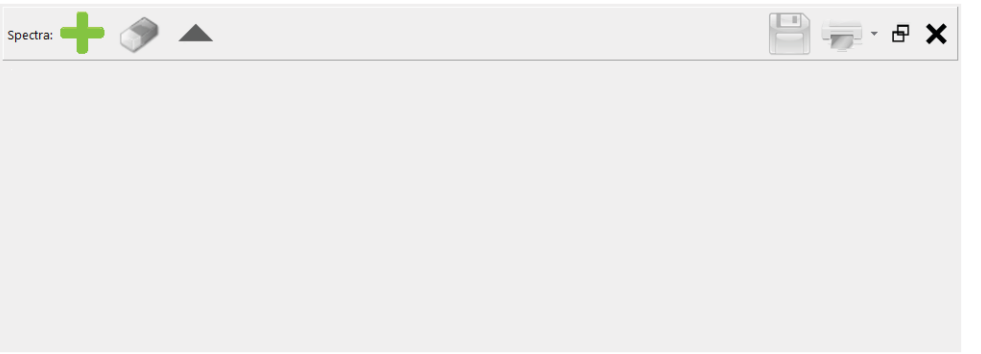
Surfaces ()

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

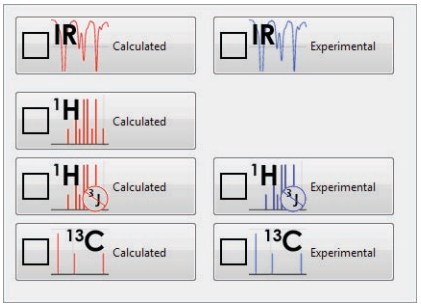
Spectra ()

Spartan Student displays calculated IR and NMR spectra. Spectra need to have been previously requested from the **Calculations** dialog (**Calculations...** under the **Setup** menu; **Chapter 8**). In addition, it provides on-line access and display of experimental IR and NMR spectra from public databases, allowing comparison with calculated spectra.

Selecting **Spectra** from the **Display** menu leads to an empty display pane at the bottom of the screen.

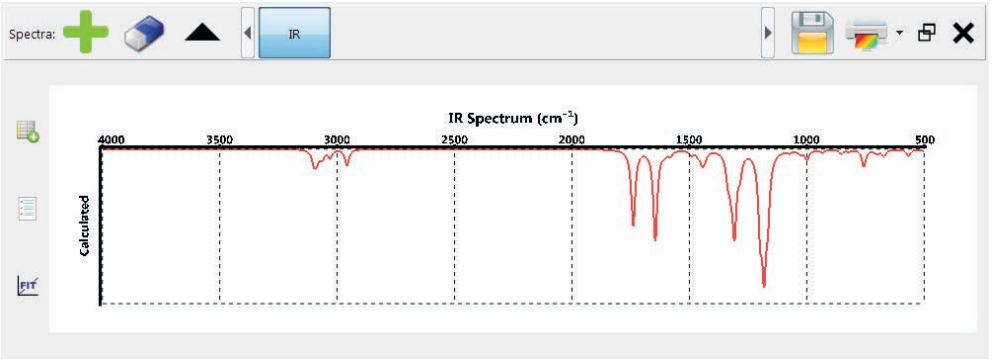


The only accessible control (in a bar at the top of the pane) is  (add a spectrum). *Clicking* on this leads to a palette.



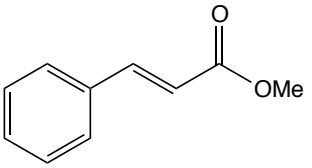
The left hand column lists the types of spectra for which calculations are available: IR, proton NMR with and without three-bond HH coupling, and ^{13}C NMR. The entry is "red" if a calculation has actually been performed and the corresponding spectrum is available. The right hand column lists the types of spectra for which experimental spectra ***may be available*** (from on-line public databases): IR, proton NMR, and ^{13}C NMR. These are shown in blue.

The procedure for displaying either a calculated or experimental spectrum (or both) is independent of the type of spectrum. For the purpose of illustration, we use the IR spectrum of methyl *trans*-cinnamate. A calculated spectrum is displayed by *clicking* on the appropriated (red highlighted) entry, following which the palette is dismissed.



Clicking on IR results in an IR spectrum. Moving the mouse while holding down the left button moves the cursor (unfilled markers at the top and bottom of the spectrum) over the spectrum. When positioned directly over a special line, the markers are darkened and connected by a vertical green line, and a numerical value for the line is provided at the bottom of the spectrum. In the case of an IR spectrum, this is a frequency in cm^{-1} and corresponds to a particular vibration of the

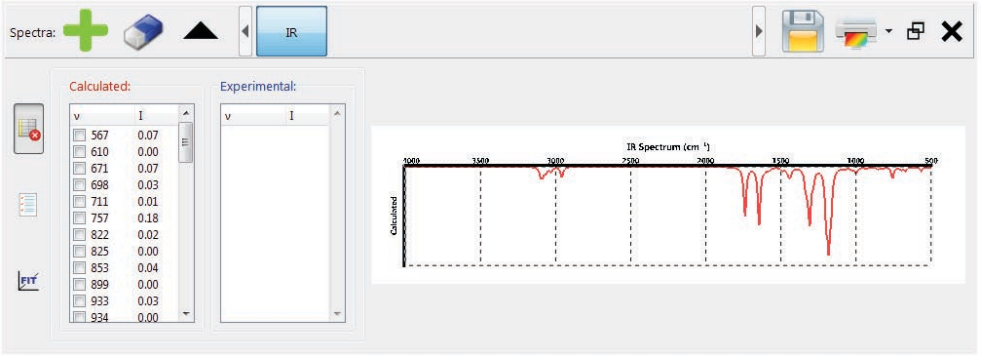
atoms in the molecule. The molecular model (above the spectrum) vibrates to show this motion. For methyl *trans*-cinnamate, the line at 1645 cm^{-1} corresponds to the C=C stretch while the line at 1739 cm^{-1} corresponds to the C=O stretch.



Moving the mouse while holding down the right button slides the viewable scale from 4000 cm^{-1} to 500 cm^{-1} but does not change the overall range (of 3500 cm^{-1}). The range is changed by using the scroll wheel. The original settings may be restored by *clicking* on  in the bar at the top of the spectra pane.

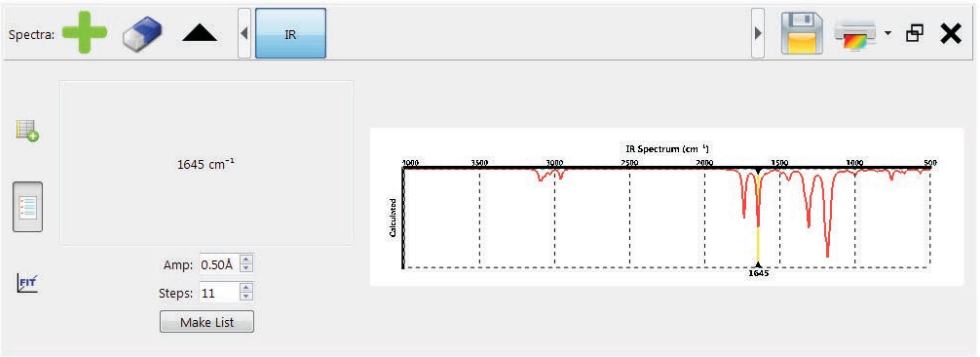

Move one finger over the spectrum to position the cursor, move two fingers to slide the viewable scale and pinch two fingers to change the range.

In the case of IR (only) three buttons appear at the left of the spectrum,  (Tables),  (Make List), and  (Fit). *Clicking* on () leads to a scrollable panel at the left of the spectrum.



This contains a listing of calculated infrared frequencies and intensities. *Checking* the box to the left of an individual frequency moves the cursor on the spectrum over this line and animates the vibrational motion.

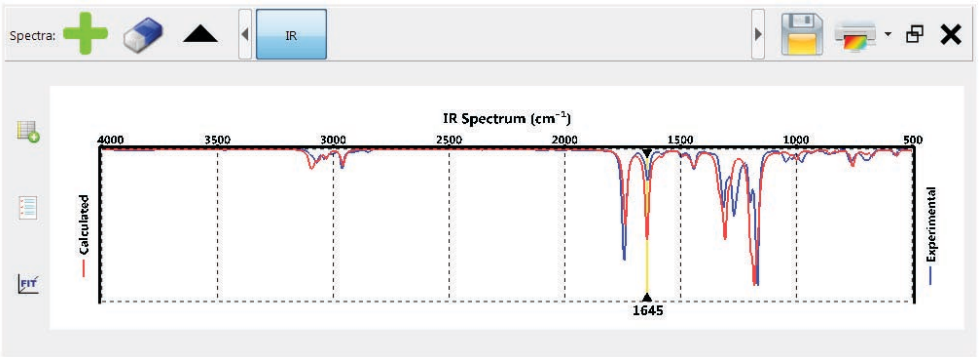
With a frequency selected, clicking on  (Make List) leads to a new panel.



This is used to make a list of structures centering around the minimum (or maximum in the case of a transition state) with control over the amplitude of vibration (maximum displacement in Å) and number of steps. *Clicking* on **Make List** leads to a separate document.

If available, an experimental spectrum from one of the public on-line databases may be superimposed on top of the calculated spectrum. The IR spectrum of methyl *trans*-cinnamate is available. *Click* on  and select 

from the palette.



You can if you wish **only** display the experimental spectrum. If a calculated is already displayed, *click* on  and re-select 

(the control operates in toggle mode).

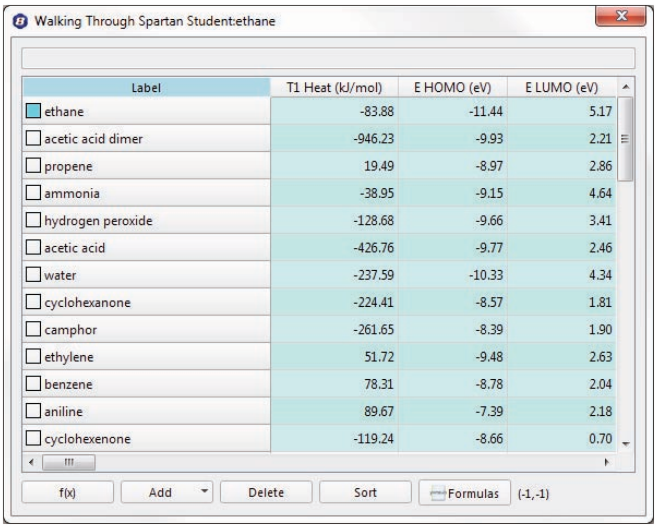
Additional spectra may be requested by *clicking* on  in the bar above the spectra pane and then *clicking* on the appropriate entry in the resulting palette. Each new spectrum adds a tab to the bar, although calculated and experimental spectra share the tab. Switching between tabs changes the display. A spectrum can be deleted by *clicking* on  in the bar above the spectra pane. If both calculated and experimental

spectra were displayed, both will be deleted.

Controls at the top right of the spectra pane allow saving the spectrum as a PNG, JPEG or Bitmap image file ( ), printing the file ( ), detaching the spectrum pane from the main window ( ) and closing the pane ( ).

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.

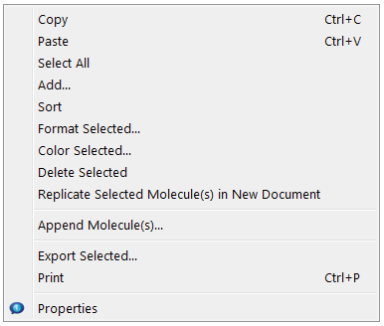


The spreadsheet comprises a series of rows (corresponding to different molecules in the document) and columns (corresponding to different properties). Together, a row and column define a "cell". The spreadsheet may be expanded or contracted by positioning the cursor at one of the corners, *pressing* 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, ...***) can be replaced by chemical names if the molecule has been retrieved from the Spartan Spectra and Properties Database (SSPD).



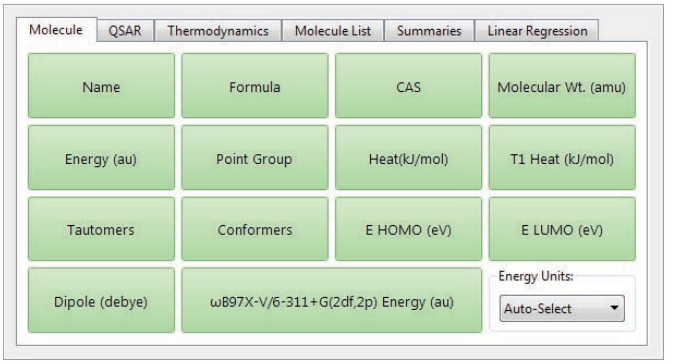
Right-clicking on a column leads to contextual menu with addition spreadsheet controls including copy/paste, selection, sorting, and formatting (to name a few).

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 to select **Add...** from the menu that results.

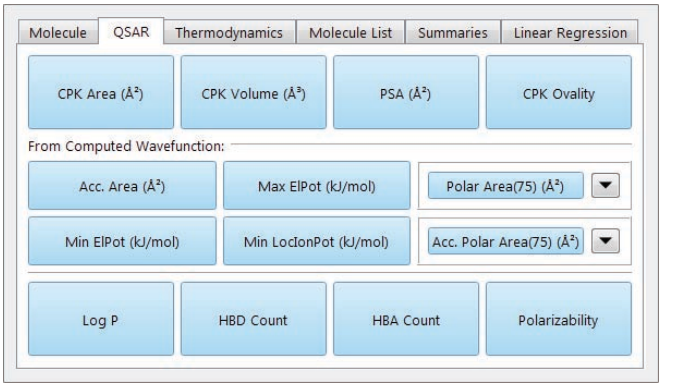
This leads to a multi-tab dialog with **Molecule** selected.



Name	molecule name as it appears in SSPD or SMD
Formula	molecular formula
CAS	Chemical Abstracts designator (if available)
Molecular Weight	molecular weight (in amu)
E	energy (heat of formation, strain energy)
Pt Group	symmetry point group
Heat (kJ/mol)	experimental heat of formation in kJ/mol (if available)
T1 Heat (kJ/mol)	T1 heat of formation in kJ/mol
Tautomers	number of tautomers (proton-transfer isomers)
Conformers	number of conformers
E HOMO	energy of highest-occupied molecular orbital
E LUMO	energy of lowest-occupied molecular orbital
Dipole	dipole moment (in debye)

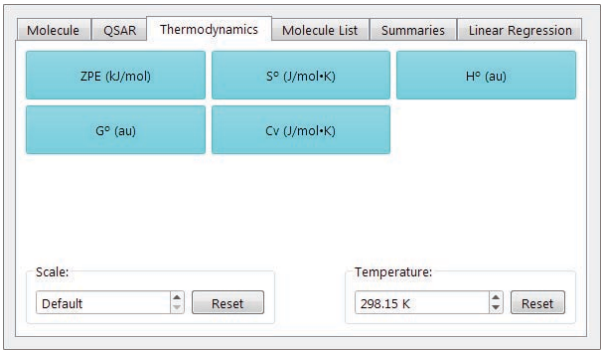
One or more properties may be added to the spreadsheet by *clicking* on their entries.

Clicking on the **QSAR** tab leads to another panel.



CPK Area (Å^2)	surface area of a space-filling (CPK) model (in Å^2)
CPK Volume (Å^3)	volume of a space-filling (CPK) model (in Å^3)
PSA (Å^2)	polar surface area of a space-filling (CPK) model (in Å^2). Defined as the area due to electronegative atoms (N, O) and hydrogens attached to the atoms
CPK Ovality	measure of deviation from a spherical shape, where 1.0 = a sphere and values > 1.0 indicate deviation
Acc. Area (Å^2)	accessible surface area of an electron density surface (in Å^2). Surface is defined by electron density of 0.002 electrons/au^3 and accessible corresponds to a probe with a 1Å radius. Probe radius may be changed in the **Settings** tab of the **Preferences** dialog (**Options** menu)
Max ElPot (kJ/mol)	maximum value of the electrostatic potential on an electron density surface (in kJ/mol)
Min ElPot (kJ/mol)	minimum value of the electrostatic potential on an electron density surface (in kJ/mol)
Min LocIonPot (kJ/mol)	minimum value of the local ionization potential on an electron density surface (kJ/mol)
Polar Area(75) (Å^2)	area of the region on an electrostatic potential map where the absolute value of the electrostatic potential is > 75 kJ/mol (in Å^2). The value of the potential may be changed to 100 and 125 kJ/mol.
Acc. Polar Area(75) (Å^2)	accessible area of the region on an electrostatic potential map where the absolute value of the electrostatic potential is >75 kJ/mol (in Å^2). The value of the potential may be changed to 100 and 125 kJ/mol. Probe radius may be changed from the default of 1Å^2 in the **Settings** tab of the **Preferences** dialog (**Options** menu).
Log P	octanol water partition coefficient
HBD Count	number of hydrogen-bond donor sites
HBA Count	numner of hydrogen-bond acceptor sites
Polarizability	polarizability

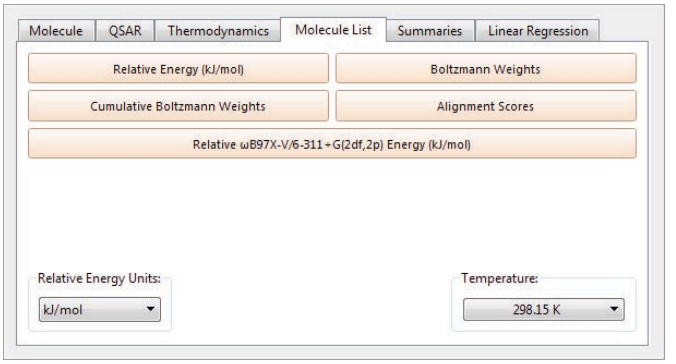
Clicking on the **Thermodynamics** tab leads to another panel:



ZPE (kJ/mol)	zero-point energy (in kJ/mol)
S° (J/mol•K)	entropy (in J/mol•K)
H° (au)	enthalpy (in au). Sum of electronic energy and zero-point energy adjusted for finite temperature
G° (au)	Gibbs energy (in au). Sum of enthalpy and entropy.
Cv (J/mol•K)	heat capacity at constant volume (in J/mol•K)

Scale is used to scale calculated frequencies, where default applies to B3LYP/6-31G* and EDF2/6-31G*, and **Temperature** is used to set temperature. Note that vibrational frequencies need to be available.

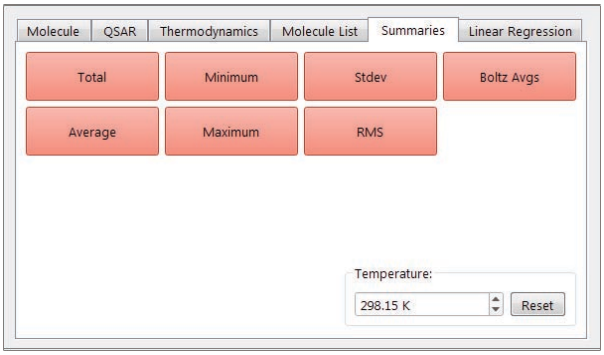
Clicking on the **Molecule List** tab leads to another panel. This allows quantities for different molecules (or different conformers of the same molecule) in a list to be related:



rel. E (kJ/mol)	energy (heat of formation, strain energy) relative to selected molecule
Boltzmann Weights	Boltzmann weight
Cumulative Boltzmann Weights	Sum of the Boltzmann weights for the selected molecule and all molecules with lower energy than the selected molecule
Alignment Scores	$1\text{-}R^2/N$, where R^2 is the root mean square distance and N is the number of alignment centers. 1 is a perfect score

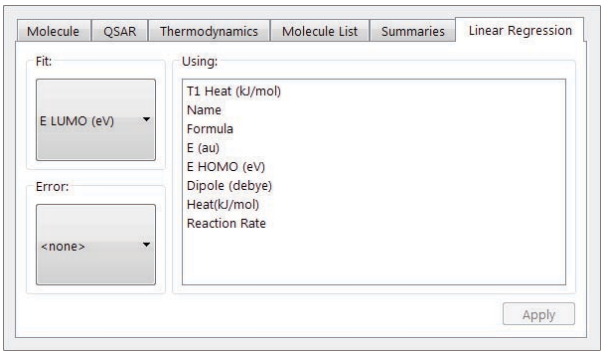
Units for relative energies and temperature for Boltzmann weights and cumulative Boltzmann weights may be selected from menus at the bottom.

Clicking on the **Summaries** tab leads to another panel:



Total	sum of column values
Minimum	minimum of column values
Stdev	standard deviation of column values
Boltz Avgs	Boltzmann weighted average of column values
Average	average of column values
Maximum	maximum of column values
RMS	rms of column values

Linear regression analysis may be performed on data in the spreadsheet. *Clicking* on the **Linear Regression** tab leads to another panel:



Select one entry from the **Fit** menu and one or more entries from the list under **Using**. *Clicking* on **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. Additional information about the regression analyses is available from the **Regression Properties** dialog (see discussion earlier in this chapter).

From Post ( ) Buttons

Post buttons ( ) 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; **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 and accessible polar area of an electrostatic potential map, the area of a selected region (band) of a banded property 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 and the area of a selected band, 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, for example, molecules resulting from a conformational search, or where labels have been explicitly reassigned*. The property value and the area of a selected band on a map is posted only for the selected molecule. Post buttons are also available for CAS numbers, experimental heats of formation and for T1 heats of formation contained in SSPD.

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 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.

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*

* Label reassignment is accomplished using the **Atom Properties** dialog (see discussion earlier in this chapter).

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)
ZPE	zero point energy
HØ	absolute enthalpy at 298K
CV	constant volume heat capacity at 298K
SØ	absolute entropy at 298K
GO	Gibbs energy at 298K

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

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 formatted 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 formatted 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**.

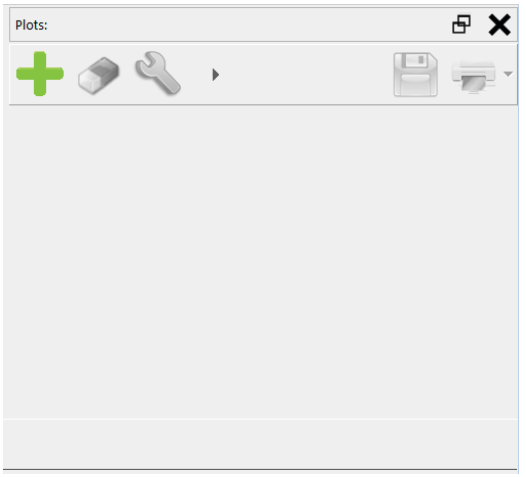
As many spreadsheets as desired (corresponding to the same or to different documents) may be open on screen. A spreadsheet is removed when the associated document is closed and may also be removed by *clicking* on  .

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.

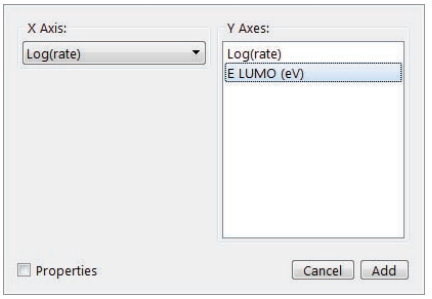
The contents of an Excel spreadsheet may be brought into ***Spartan Student***. Copy whatever information is to be transferred from Excel, move into ***Spartan Student***, *click* on the appropriate cell and select **Paste** from the **Edit** menu (or *right click* on the appropriate cell and select **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 ()

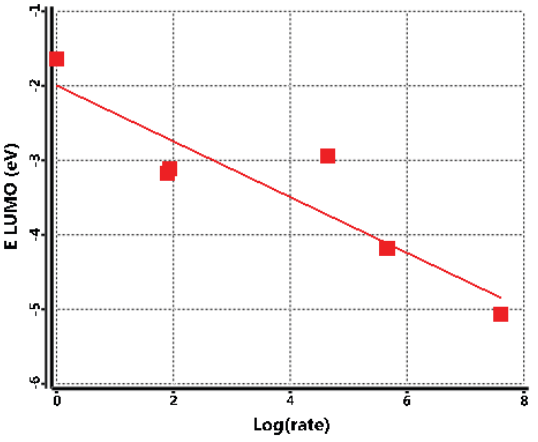
Plots may be constructed from data in a spreadsheet and a variety of simple curves fit to these data. Selecting **Plots** from the **Display** menu leads to an empty display pane at the right of the screen.



Clicking on (add plot) in the bar at the top of the plots pane leads to a dialog.



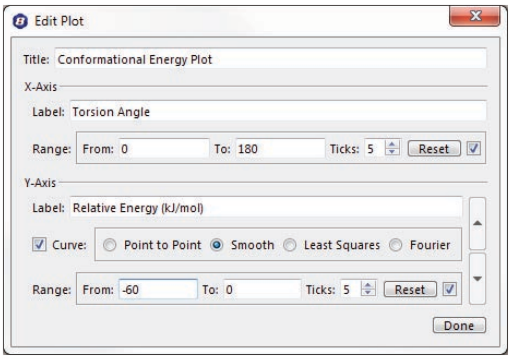
You need to select an item from the **X Axis** menu and one or more items from the **Y Axes** list, and then *click* on the **Create** button at the bottom of the dialog. A plot appears in the plot pane and the **Add Plot** dialog is dismissed.



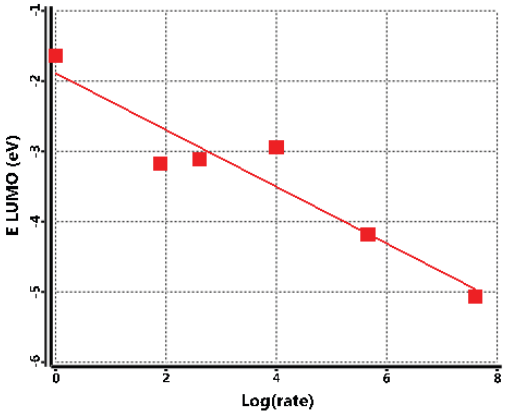
By default, the scales for both horizontal and vertical axes are set to bound the data trying to provide limits and increments that are "rounded". Moving the mouse left and right while holding down the right button slides the horizontal scale but does not change the range. Similarly, moving the mouse up and down while holding down the right button slides the vertical scale. The horizontal range may be changed by moving the mouse left and right while holding down both the right button and shift key, and the vertical range changed by moving the mouse up and down while holding down both the right button and the shift key. The scroll wheel may be used to simultaneously change both horizontal and vertical ranges. The original settings may be restored by *clicking* on  in the bar at the top of the plots pane.


Move two fingers left and right and up and down to slide the viewable horizontal and vertical scales, respectively. Pinch two fingers left and right and up and down to change the horizontal and vertical scales, respectively.

The plot ranges may also be changed by *clicking* on  in the bar at the top of the plots pane.



The resulting dialog also allows axis labels to be altered (from their initial values designated in the spreadsheet) the number of "tics" of horizontal and vertical axes to be changed and a plot title to be added. Finally, the "curve" can be changed, the default is set to display data points only (no curve selected).



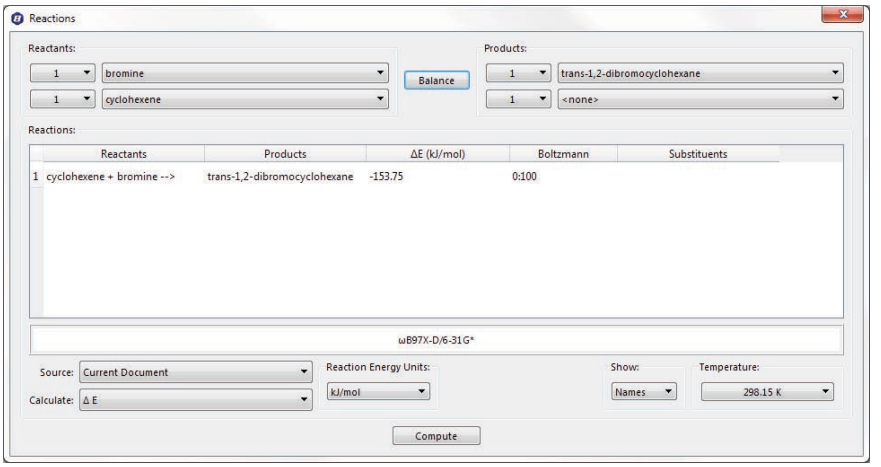
Additional plots may be added by *clicking* on  in the bar at the top of the plots pane. Each plot is given a tab. Only one plot may be displayed at a time as controlled by which tab is selected. The selected (and displayed) plot may be deleted by *clicking* on  .

Reactions... ()

Data in a ***Spartan Student*** document or in SSPD may be used to calculate 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.



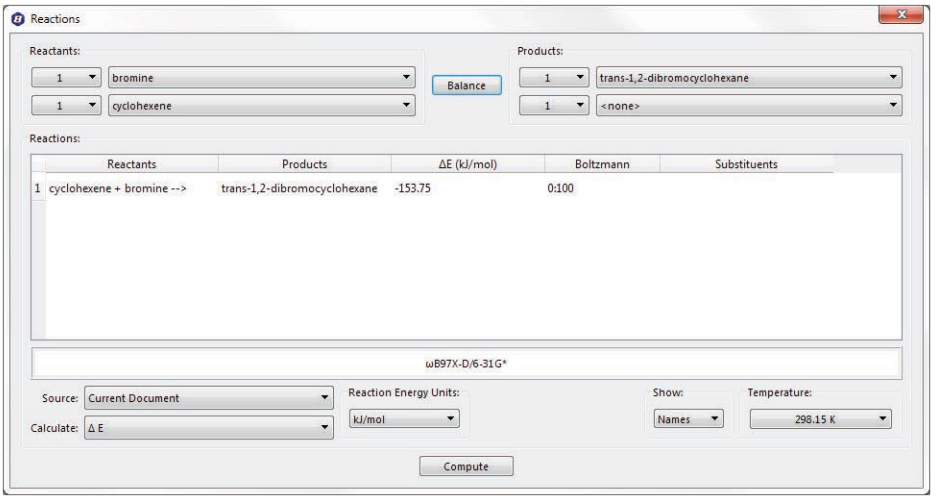
Two sets of menus under **Reactants:** and two sets of menus under **Products:** specify the number of each reactant and product and

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 **Source** menu identifies the source of the energies to be used in the reaction energy calculation. Either the **Current Document** or **SSPD** may be chosen. If the **SSPD** is selected, there will also be a choice of **Theoretical Model**.

Under **Source** is the **Calculate** drop down menu. This allows for selection of ΔE, ΔH°, or ΔG°. Note that if the **Source** is set to **Current Document**, an IR calculation is required to obtain ΔH° and ΔG° values.

A reaction energy is computed by *clicking* on **Compute** at the bottom right of the dialog.

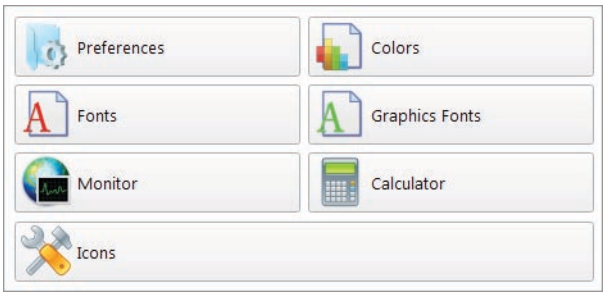


The results of a reaction energy calculation may be printed by *right clicking* inside the display area of the **Reactions** dialog and selecting **Print** from the menu that results.

The **Reactions** dialog is closed by *clicking* on .

Chapter 10
The Options Menu

*Functions under the **Options** menu* set default colors, fonts, user preferences and van der Waals radii, provide addresses for on-line databases, set icon displays and identify/change URL's for on-line accesses. They also allow for changing default colors and fonts and for monitoring executing jobs.*

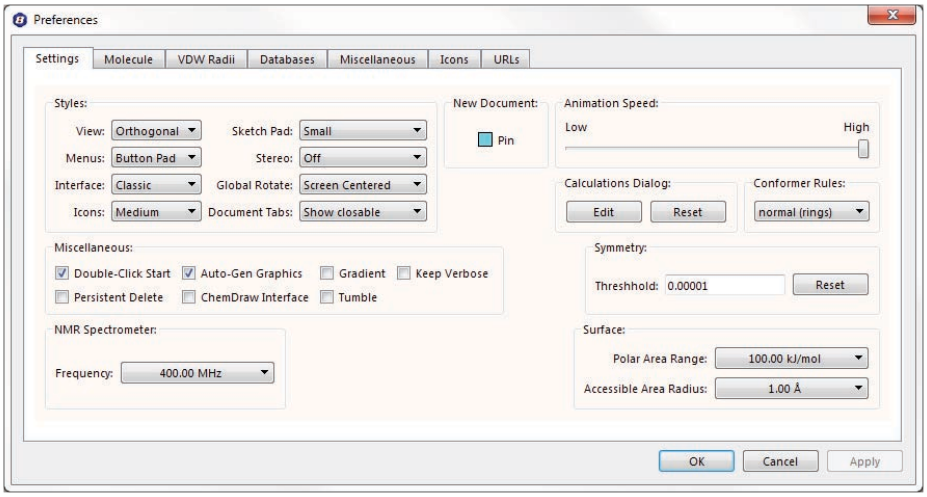


Preferences...(**)**

This sets up preferences relating to the graphical user interface (**Settings**), and to molecule displays (**Molecule**). 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 local databases (**Databases**), specifies miscellaneous features (**Miscellaneous**), specifies which icons are to be displayed (**Icons**) and specifies URLs (**URLs**) for on-line connections. Selection results in one of seven tabs. *Clicking* on a tab brings up the associated preference options. To exit a **Preferences** dialog *click* on **OK**. *Clicking* on **Cancel** or exits the dialog without instituting any changes.

* **Preferences** is found under the ***Spartan Student*** menu in the Macintosh version.

Settings Tab



Style

(i) **View: Orthogonal/Perspective**
Controls the view of structural models and graphics.

(ii) **Menus: Classic List/Button Pad**
Controls presentation of menus either as lists (Classic List) or as icon palettes (Button Pad). The latter is likely to be better suited to touch screen computers and tablets.

(iii) **Interface: Classic/Touch**
Under the **Touch** setting, some menu/dialog items (including up/down arrows) are displayed in a larger size to better support touch screen computers and tablets.

(iv) **Icons: Small/Medium/Large/Extra Large/Jumbo**
Controls size of program icons in the tool bar.

(v) **Sketch Pad: Small/Medium/Large**
Controls the size of the sketch pad (palette of sketch tools) for ***Spartan***'s 2D builder.

(vi) **Stereo: Off/Red-Cyan**
Turns stereographic display on and off. This can also be controlled by toggling the "**3**" key on the keyboard.

(vii) **Global Rotate: Screen Centered/Molecule Centered**
Screen Centered rotates all molecules about a common center. **Molecule Centered** rotates each molecule about its own center.

(viii) **Document Tabs**
Hide will revert display style to that of versions of ***Spartan*** prior to ***Spartan'14***, that is, all open documents will be visible when in **View** mode. If **Show** is *checked*, this displays a tab at the bottom of the screen for each open document. This allows for displaying molecules from documents other than the currently selected document by *checking* the box to the left of the tab. **Show closable** is the same as **Show** but includes the ability to close the document by *clicking* on the  button at the right of the tab

(ix) **New Document: Pin**
If *checked*, defaults to display of any new documents (from building or brought in from the **File** menu) irrespective of whether or no they have been explicitly selected. Does not affect the status of existing open documents. **Pin** setting is only applicable if either **Show** or **Show closable** is selected (see **Documents Tabs** above).

(x) **Animation Speed**
Slider bar controls the speed for animations.

(xi) **Conformer Rules: Normal/Skeletal/Thorough**
Chooses between rule sets for conformational searching. **Normal** is the default and should be used for **Equilibrium Conformer** and **Conformer Distribution** calculations where the Monte Carlo approach is involved. **Skeletal** (in prior versions this was called **Trimmed**) eliminates degrees of freedom and should be used for **Similarity Library** calculations where a systematic approach is carried out. **Thorough** considers twist-boat conformers of six-membered rings (in addition to chair conformers).

(xii) **Calculations Dialog**
Controls the default task that is displayed upon entering **Calculations...** () from the **Setup** menu. The default is Equilibrium Geometry with the ωB97X-D/6-31G* model, this can be modified by clicking the **Edit** button, which leads to a sample **Calculations** dialog. *Clicking* on **Reset** restores the default task.

Miscellaneous

(xiii) **Double-Click Start**
If *checked*, *double-click* as opposed to *single-click* is required to place the initial atom, group, ring, ligand, etc. on screen when using the 3D builder (consistent with the 2D Sketch builder behavior).

(xiv) **Persistent Delete**
If *checked*, delete function is persistent. If not *checked*, delete will revert to the previously selected function after a single delete operation.

(xv) **Auto-Gen Graphics**
If *checked*, graphics calculations will be performed by the graphical interface (without having to submit a calculation) as long as the information necessary to generate the surface is available (a previous calculation has been run, or the molecule has been retrieved from the SSPD). Note, however, that graphics calculations will not be auto-generated on documents containing more than 25 molecules. These will need to be submitted as a calculation.

(xvi) **ChemDraw Interface** (Windows only)
If *checked*, adds **ChemDraw** as a tab at the top of the model kit. This allows for use of the ChemDraw program (version 10 or newer) as an alternative for sketching molecules

(xvii) **Gradient**
If *checked*, this replaces the single color background by a color gradient background.

(xviii) **Tumble**

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

To start tumbling, swipe one finger over the screen. To stop, tap anywhere on screen.

(xix) **Keep Verbose**

If *checked*, keeps extended Q-Chem output. Normally discarded upon successful completion of submitted calculations, this may be useful for identifying the source of problems for calculations that have not successfully completed or have led to suspicious results. (The last 100 lines of the verbose output is automatically kept for a job that has abnormally terminated). Verbose output significantly increases the size of the ***Spartan*** document.

NMR Spectrometer

(xx) **Frequency**

The frequency of the spectrometer, used in coupling constant calculations.

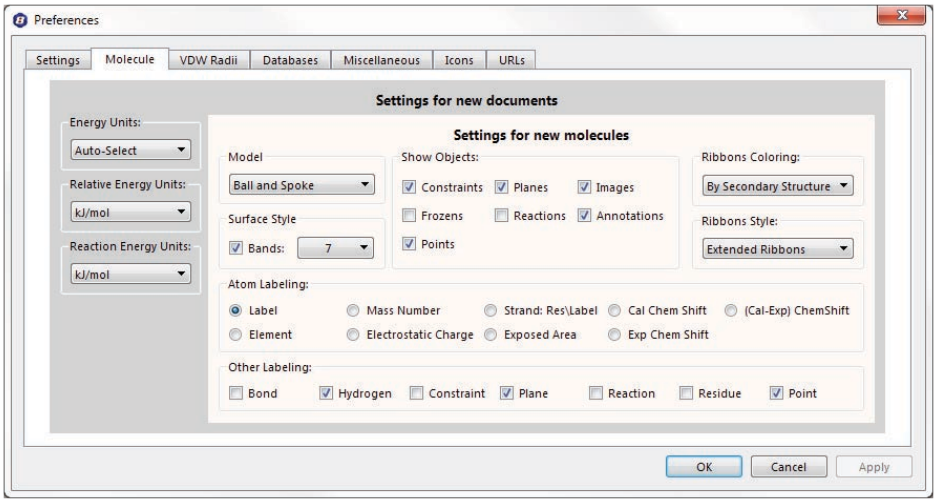
Surface

(xxi) **Polar Area Range (kJ/mol)**

Sets the potential (in kJ/mol) for calculating polar area from the electrostatic potential map. The range is given as a single number but represents the range between –value to +value, for example, the default range of 100 kJ/mol means a range from -100 to +100 kJ/mol. Values above and below the range are considered when determining polar area. *Click* inside the box and use the number pad that appears.

(xxii) **Accessible Area Radius (Å)**
Sets sphere radius (in Å) for determining accessible area, the default is 1.0Å. *Click* inside the box and use the number pad that appears.

Molecule Tab



This specifies default settings for model appearance. These settings may be overridden for individual molecules in a document using entries under the **Model** menu and for specific portions of a molecule using **Utilities/Style** dialogs associated with **Properties** dialogs (**Properties** under the **Display** menu; **Chapter 9**).

(i) **Energy Units**
Auto Select, where units depend on the model and on whether they refer to absolute or relative quantities, ***au*** (atomic units), ***kJ/mol*** and ***kcal/mol***

(ii) **Relative Energy Units**
au (atomic units), ***kJ/mol*** and ***kcal/mol***

(iii) **Reaction Energy Units**
au (atomic units), ***kJ/mol*** and ***kcal/mol***

(iv) **Model: Wire/Ball and Wire/Tube/Ball/Spoke/Space Filling/Line**
Controls default model style.

(v) **Surface Style**
If **Bands** is *checked*, this specifies that graphical surfaces, for example electrostatic potential maps, are to be displayed in terms of a series of color bands, rather than as a continuous spectrum. The number of bands is selected from the menu to the right. This setting can be changed at the document level and individual surface level as well (**Surface Properties** under the **Display** menu; **Chapter 9**).

(vi) **Show: Constraints/Frozens/Points/Planes/Reactions/ CFD's/Images/Annotations**
If *checked*, constraints and frozen markers, points and planes, reaction arrows, and attached images and text will always be shown as part of the model. Otherwise, they will be shown only in the appropriate mode.

(vii) **Atom Labeling: Label/Element/Mass Number/Mulliken Charge/Electrostatic Charge/Natural Charge/Strand: Residue/Label/R/S/Exposed Area/Cal Chem Shift/Exp Chem Shift/Cal-Exp Chem Shift**
Controls default label type.

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

(ix) **Hydrogen Labels**
If *checked*, displays labels on hydrogen atoms.

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

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

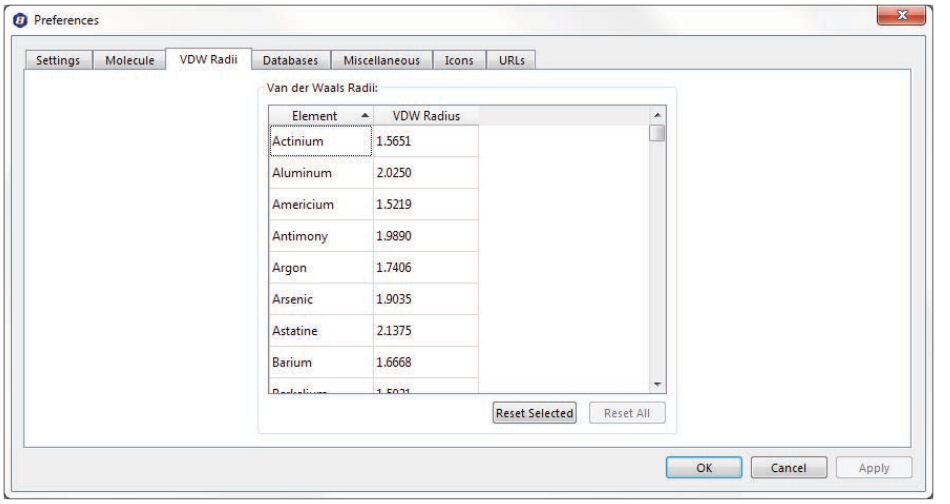
(xii) **Reaction Labels**
If *checked*, reaction arrow labels will be shown.

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

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

vdW Radii Tab

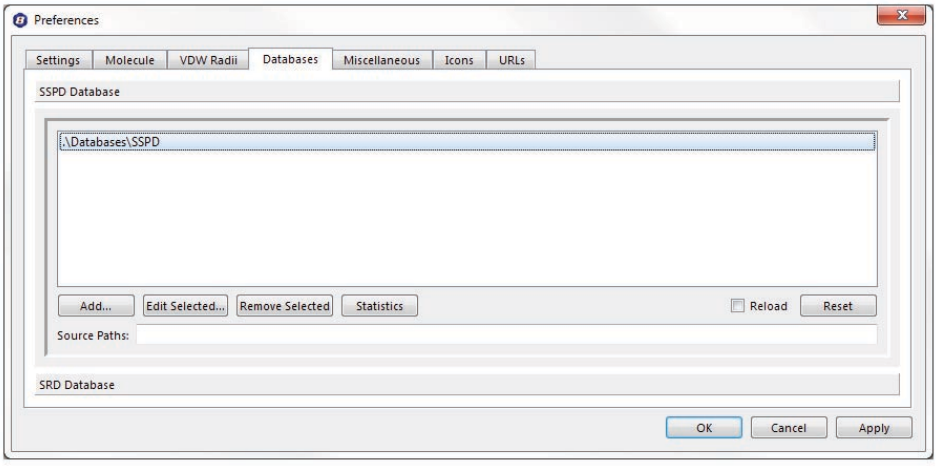
This provides a list of van der Waals radii



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.

Databases

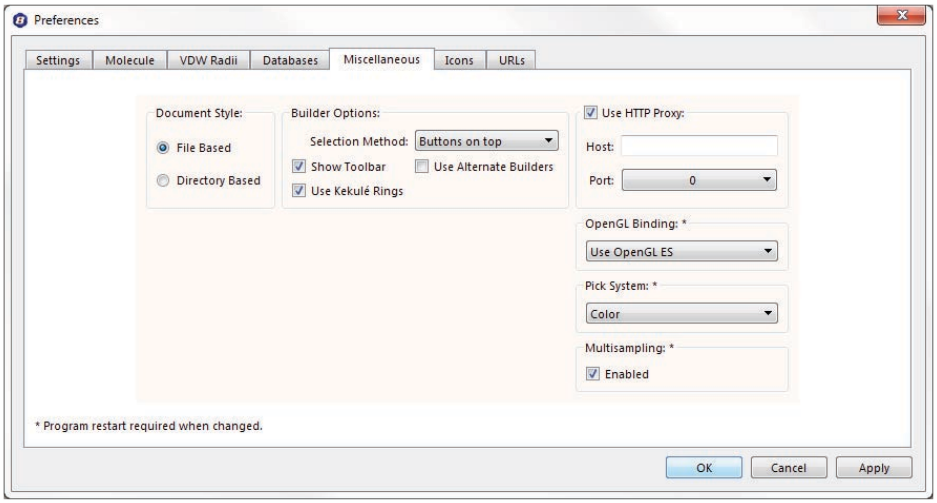
This allows setting up of paths for installed database associated with ***Spartan Student***.



Spartan Student includes a ≈6,000 molecule subset of SSPD. The full database of >300,000 molecules is available for license with the ***Spartan Parallel Suite***.

Miscellaneous

A number of miscellaneous preferences are accessible from this tab.



(i) **Document Style**
Toggles between **File Based** and **Directory Based**. The former is the default and the latter is for compatibility with older ***Spartan*** Linux and Macintosh versions.

(ii) **Builder Selection Method**
Toggles among **Buttons on top**, **Tabs on side** and **Menu** to control selection of the model kits in the 3D builder. The second and third choices conserve vertical space on small screen laptops and tablets.

(iii) **Show Toolbar**
Turns on/off the delete, make bond, break bond, and minimize icons at the bottom of the 3D model kit.

(iv) **Use Kekulé Rings**
Displays aromatic rings with the alternating single and double bonds or an aromatic (1.5) bond style.

(v) **Use Alternate Builders**
Provides a different presentation of the model kits in the 3D builder. Try both and see which one you like.

(vi) **Use HTTP Proxy**
Allows setting up of an alternative path for access to external websites, for example, experimental spectra databases. Rarely needed.

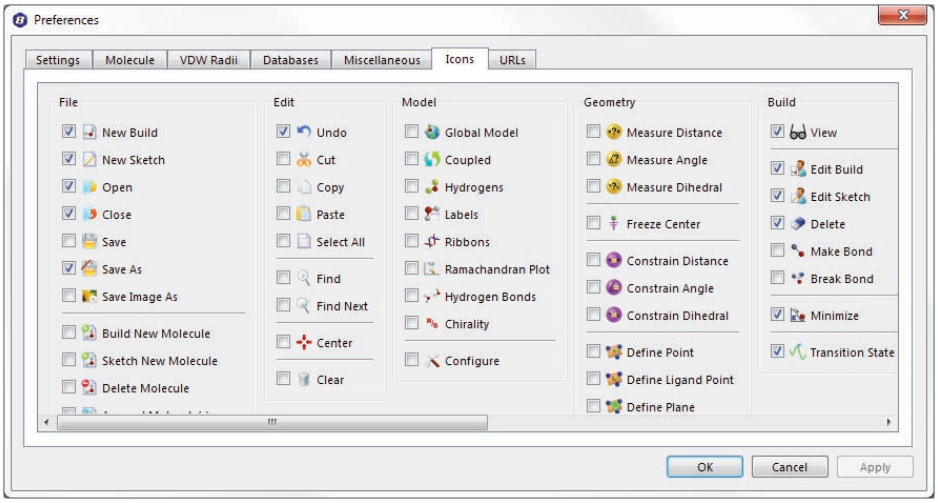
(vii) **Open GL Binding**
Allows for use of the OpenGL (3D visualization) libraries associated with your video card (**Use Desktop OpenGL**) or the option of using software-based libraries (**Use Software OpenGL**), or the three-dimensional viewing libraries developed to support web-based visualization (**Use OpenGL ES**).

(viii) **Pick System**
Toggles between **OpenGL**, **Color** and **Color + Geometric** picking models. **OpenGL** is the standard but causes problems for Intel HD4000 and HD5000 series graphics (very common), where either **Color** or **Color + Geometric** should be used. Graphics chip is automatically detected at installation and this control should be properly set.

(ix) **Multisampling**
Improves visualization using anti-aliasing.

Icons

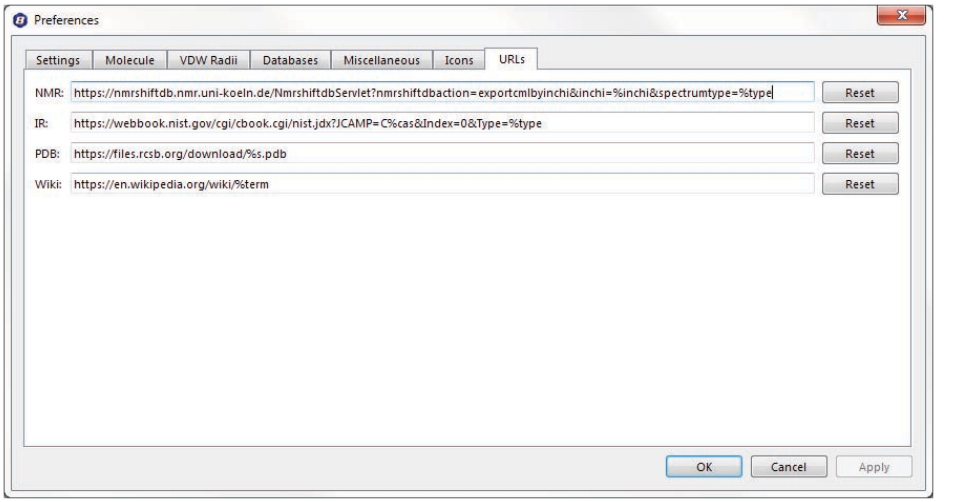
Icons for all menu entries are listed (you will need to use the horizontal slider bar to see them all). If *checked*, the icon will appear above the menu bar at the top of the ***Spartan Student*** screen.



Icon display is limited to one "permanent" row. Approximately 20 medium size icons will fit on screen. All icon choices may be accessed via menu, irrespective of their selection preferences for permanent display.

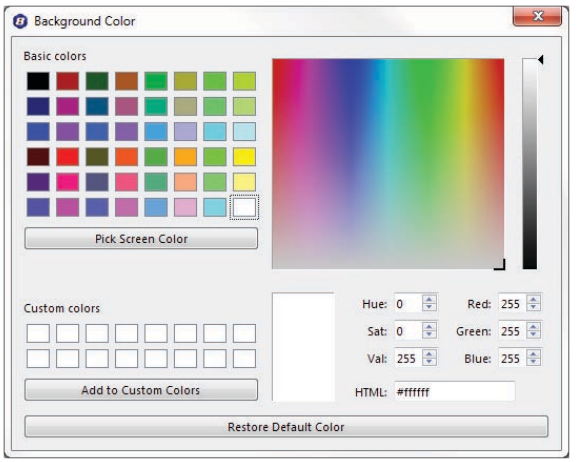
URLs

Lists URLs for access to experimental structural and spectral databases and to Wikipedia.



Colors ( )

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

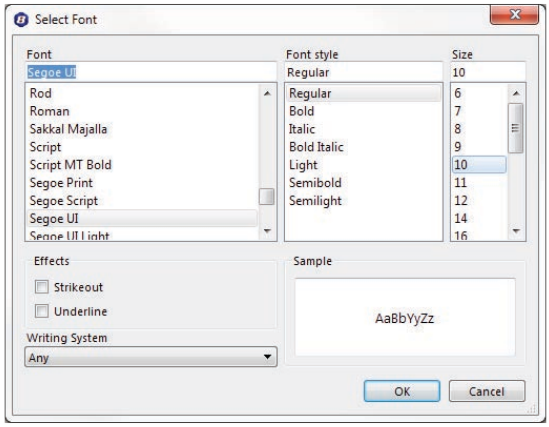


After selecting an object, its color may be set by choosing from the palette, moving the cursor inside the window of colors, or by selecting either a set of hue, saturation and values, or red, green and blue settings. The default color may be reset by *clicking* on **Restore Default Color**. Color selection applies to all objects of the same type, for example, all carbon atoms, and not just to the selected carbon.

To change the default Label Color, hold the shift key down and *click* on the **Colors** entry in the **Options** menu. 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.

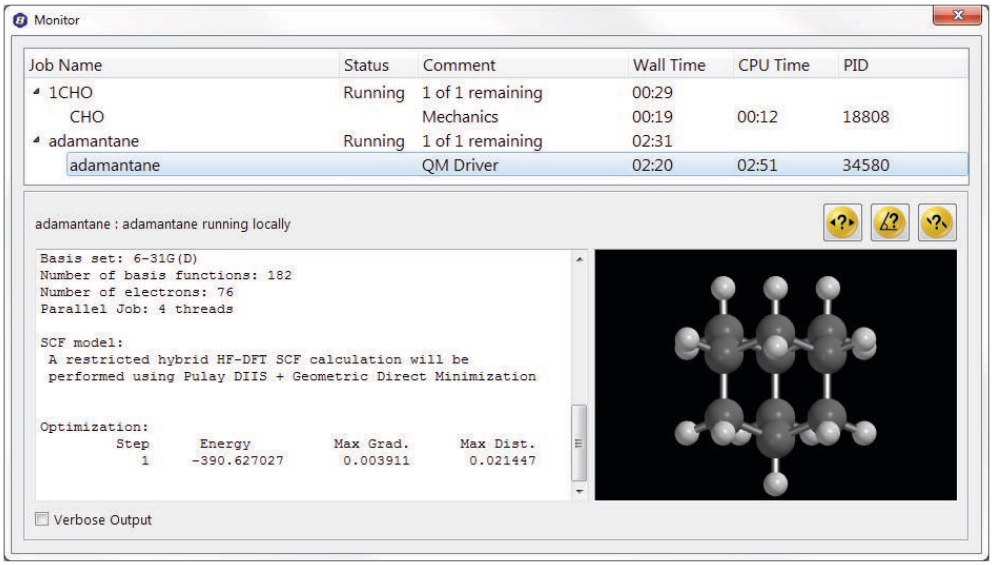
Fonts/Graphics Fonts ( / )

This selects fonts, style and size of 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 and does not apply new selections.

Monitor ( )



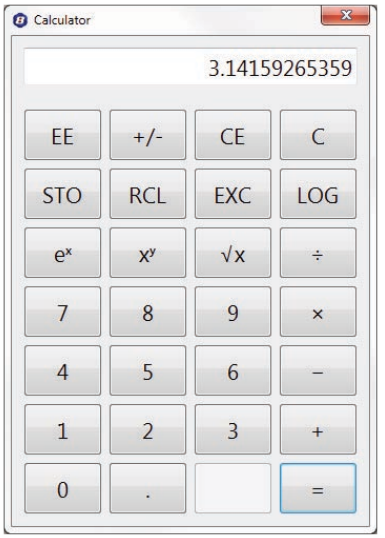
This provides a listing of all executing/queued jobs and their status. To see accumulated output for an executing job, *click* on its name. A ball-and-spoke model of the selected (executing) job will be displayed in a window to the right of the dialog. It can be manipulated using the usual mouse commands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

To terminate a job, *right click* on its name, and then select **Terminate**. To start a queued job, *right click* on its name and select **Start**.

The **Monitor** may be removed 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 .

Icons ( )

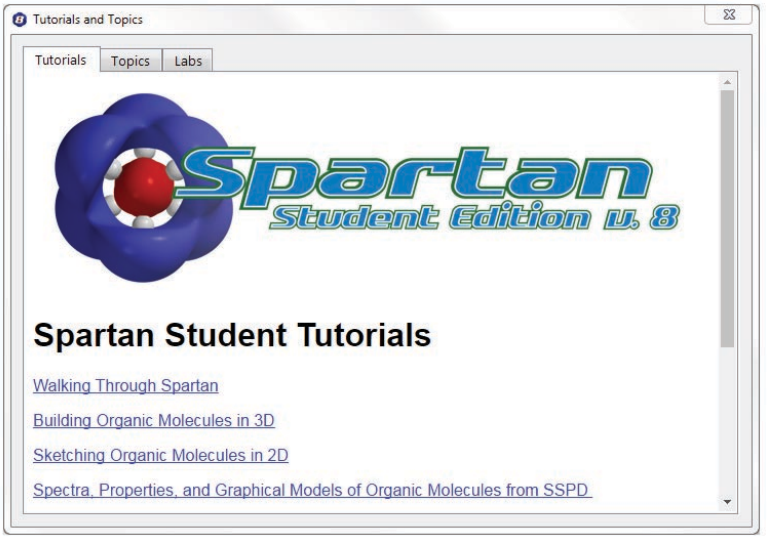
Toggles the display of icons above the menu bar on and off.

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 Student**).*

Tutorials, Topics, and Labs

Selection of **Tutorials and Topics** brings up an HTML page (**Tutorials** shown).

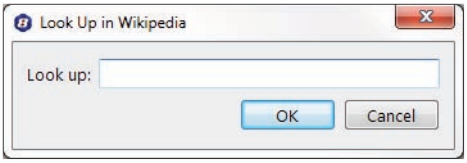


Clicking on an entry (link) brings up the computer's PDF reader alongside of ***Spartan Student***. This allows you to access the materials while working with the program.

Note that the full Manual is available as a PDF under the **Help** menu (see next chapter).

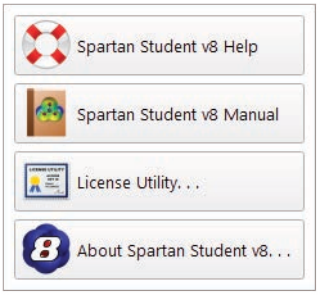
Look Up in Wikipedia...

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



Spartan Student v8 Help

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

Spartan Student v8 Manual

Opens a PDF file providing documentation on ***Spartan Student Edition*** menus and features (this document).

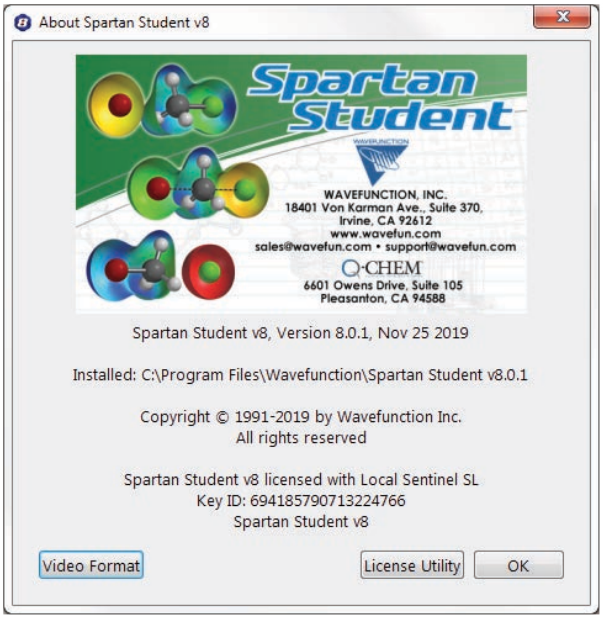
License Utility . . .

Provides access to the **License Utility** dialog. From here you can access your license **activation code** or **KeyID**, **Maintenance Status** and academic licenses can request a **Transfer**.*

* Transfers are not available for student-purchased licenses that utilize an activation code.

About *Spartan Student* v8. . .*

Provides information about the user's release of ***Spartan Student***, and their license type. It also contains information on the machines video format and a button to access the license utility dialog.



* About is located under the **Spartan Student** menu in 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, conformer energy distributions and vibrational frequencies. 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, wave functions, equilibrium and transition-state geometries and vibrational frequencies. The elements H, Li-F, Mg-Cl, 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 wave functions, 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, EDF2, and ωB97X-D density functional models are available for calculation of energies and wave functions, equilibrium and transition-state geometries and vibrational frequencies with both 6-31G* and 6-311+G** basis sets. 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 wave functions 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 time. MP2 calculations are limited to 20 atoms.

T1[4] Thermochemical Recipe

The T1 recipe has been developed to closely reproduce G3(MP2) heats of formation. It makes use of an HF/6-31G* geometry, instead of the MP2/6-31G* geometry, replaces the large basis set MP2 calculation in G3(MP2) by a dual-basis set RI-MP2 calculation, eliminates both the QCISD(T) calculation and the vibrational frequency calculation (needed to obtain zero-point energy and to correct the energy for finite temperature) and introduces an empirical correction based on the atom counts and Mulliken bond orders. The result is that T1 requires 2-3 orders of magnitude less computation time than G3(MP2).

T1 is limited to closed-shell, uncharged molecules comprising H, C, N, O, F, Si, P, S, Cl and Br only and, because it incorporates parameters which depend explicitly on molecular geometry, is in practice limited to molecules that can be properly described in terms of a conventional valence structure. T1 is likely to be unsatisfactory for transition states. T1 calculations are limited to 20 atoms.

Solvent Models

Spartan Student supports SM5.0R[5] for molecular mechanics calculations this estimates the aqueous solvation energy. For systems with H, C–F, S–Cl, Br and I. Hartree-Fock and density functional models support the C-PCM[6,7] solvent model, allowing for calculations in water and both polar and non-polar solvents.

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 corrected for local environment). IR spectra calculations may be carried out with molecular mechanics models, semi-empirical models, Hartree-Fock models, B3LYP, EDF2, ωB97X-D and MP2 models. NMR spectra calculations may only be carried out with Hartree-Fock, B3LYP, EDF2, and ωB97X-D 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 heats of formation, IR and NMR spectra and diverse molecular properties for ≈6,000 molecules obtained from EDF2/6-31G* and ωB97X-D/6-31G* calculations. In addition, it contains the wave allowing for function on-the-fly calculation and display of the full variety of graphical surfaces and property maps. The full version of SSPD (currently 300,000 molecules) may be licensed separately with the ***Spartan Parallel Suite*** (the research version of ***Spartan***).

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. W.S. Ohlinger, P.E. Klunzinger, B.J. Deppmeier, W.J. Hehre; *J. Phys. Chem. A*., **113**, 10, 2165 (2009).
5. G.D. Hawkins, C.J. Cramer and D.G. Truhlar, *J. Phys. Chem. B*., **101**, 7147 (1997).
6. A.W. Lange, J.M. Herbert, *Chem. Phys. Lett.,* **509**, 77 (2011).
7. V. Barone and M. Cossi, *J. Phys. Chem. A*., **102**, 11,1995 (1998).

Appendix B

Menus

Spartan Student Screen

File

New Build 	Brings up a model kit for 3D molecule building or substitution
New Sketch 	Brings up the sketch pad for molecule sketching in 2D
Delete Molecule 	Deletes a molecule (or molecules) from a document
Build New Molecule 	Adds a molecule to an existing document; brings up a model kit for molecule building
Sketch New Molecule 	Adds a molecule to an existing document; brings up the sketch pad for molecule sketching in 2D
Append Molecule(s)... 	Appends molecules to an existing document
Open... 	Opens (imports) a molecule or multi-molecule document
Open Recent Documents 	Brings up a list of recent documents, allowing one of which to be opened
Save 	Saves (exports) a molecule or multi-molecule document
Save As... 	Saves a document as one of a number of file formats under a user-specified name
Save Image As 	Saves molecule or graphical model as a high-resolution PNG file

Print...	Prints on-screen display; also prints contents of output window and the **Spreadsheet**
Access Database by Name	Searches the ***Spartan Student*** database by name or partial name
Access PDB Online...	Accesses the online Protein Data Bank (PDB)
Start/Stop QuickTime Recording	Starts and stops QuickTime recording of contents of main ***Spartan Student*** screen (Macintosh only)
Close	Closes a molecule or multi-molecule document
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 all atoms in the selected molecule
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	Display a Ramachandran plot for a protein that has been brought in from the Protein Data Bank (PDB)
Hydrogen Bonds	Toggles hydrogen bonds on and off
R/S Chirality	Toggles R/S chirality labels 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
Constrain Distance	Constrains bond distance
Constrain Angle	Constrains bond angle
Constrain Dihedral	Constrains dihedral angle
Freeze Center	Freezes selected atomic positions
Align	Aligns molecules in a document
Define Point	Defines a point as a geometric mean of a set of atoms
Define Ligand Point	Defines a 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

Build

View	Removes the model kit
Edit Build	Brings up a 3D model kit (organic, inorganic, peptide, nucleotide, or ChemDraw) with the presently selected molecule
Edit Sketch	Brings up the sketch pad with the presently selected molecule. This function is only available if the sketch has not been altered using any of the 3D model kits or has not been replaced by an entry in SSPD.
Delete	Deletes atoms, bonds, points, planes, etc. Also available at the bottom of the 3D model kits
Make Bond	Makes bonds between free valences or atoms. Also available at the bottom of the 3D model kits
Break Bond	Breaks a bond. Also available at the bottom of the 3D model kits

Minimize	Performs energy minimization using MMFF molecular mechanics. Also available at the bottom of the 3D model kits
Transition State	Provides transition-state guess based on reaction database or, lacking a database entry, based on a linear synchronous transit procedure

Setup

Calculations...	Sets up molecular mechanics and quantum chemical calculations; specifies calculation of IR and NMR spectra and QSAR properties
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, graphical surfaces and statistical analyses
Orbital Energies	Displays an orbital energy diagram and allows on-the-fly generation and display of molecular orbitals
Surfaces	Sets up generation of and displays graphical surfaces (same as entry in **Setup** menu)
Spectra	Displays IR and NMR spectra, animates vibrational modes (IR), and accesses on-line experimental spectral databases

Spreadsheet	Displays spreadsheet
Plots...	Creates 2D plots from the data in the spreadsheet
Reactions	Calculates reaction (and activation) energies using data either from current document or from the Spartan Spectra and Properties Database (SSPD)

Options

Preferences...	Sets various run-time and labeling preferences, icon displays, establishes URL's for on-line access
Colors	Sets screen and model colors
Fonts...	Sets fonts for menus
Graphics Fonts...	Sets fonts for graphical displays
Monitor	Monitors and allows for killing jobs
Calculator	Pocket calculator
Icons	Toggles display of icons on and off

Activities

Tutorials	Brings up ***Spartan Student*** tutorials as PDF documents
Topics	Brings up selection of topics relevant to calculations performed in ***Spartan Student*** as PDF documents
Labs	Brings up a sample set of student lab activities
Look up in Wikipedia	Brings up a Wikipedia page

Help

Spartan Student v8 Help 	Provides information about the performance and timing of computational methods in ***Spartan Student***; provides information about using graphical models in ***Spartan Student***; bulletin board for FAQs about ***Spartan Student***
Spartan Student v8 Manual 	Opens a PDF file providing a guided tour through ***Spartan Student Edition*** menus
License Utility . . .	Accesses information about your ***Spartan Student*** license
About Spartan Student v8. . . 	Provides program version information for citation and support

Contextual

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 a wide selection of calculated quantities for adding to 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 or group of molecules
Append	Appends the contents of ***Spartan Student*** document(s) to the spreadsheet (corresponding to the selected document)
Rename Selected Using SSPD	Renames selected molecule(s) with names in the Spartan Spectra and Properties Database (SSPD)
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
Find/Find Next	Performs text search of Output
Print	Prints selected text
Save As PDF	Saves output as .pdf file

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.

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 debye.

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).

Appendix E
Accessing ChemDraw (Windows Only)*

The ChemDraw program may be seamlessly accessed inside of ***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 need to be altered.

You need to check the box next to **ChemDraw Interface** in the Settings Preferences dialog under the **Options** menu (**Chapter 10**). This will add a **ChemDraw** button, tab or menu entry to the 3D builder.

To access ChemDraw, select **ChemDraw** from the buttons or menu at the top of the model kit, 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 manipulable 3D structure will appear at the top of the panel. *Clicking* on screen will move the 3D structure into ***Spartan Student***'s main window.

* ChemDraw files (.cdx) may be read with all versions of ***Spartan***.

** ChemDraw is not provided with ***Spartan*** but must be obtained from Perkin Elmer.

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