PQSMol

User's Manual

www.pqs-chem.com

Conventions used in this manual

Filenames, commands typed in at the command prompt are written in typewriter font:

```
pqsview aspirin.out
```

The term **mouse click** refers to the left mouse button being pressed.

The term **mouse drag** refers to holding down the left mouse button while moving the mouse.

The term **icon** refers to an object in the graphical user interface, which is a small image usually on top of a button.

The term **button** refers to an object in the graphical user interface, which triggers an action when activated.

The term **radio button** refers to an object in the graphical user interface, which is usually grouped with a set of other objects of the same type. These objects are mutually exclusive, i.e., only one of the objects can be active at a time.

The term **slider bar** refers to an object in the graphical user interface, which has an associated range of values and can be adjusted within this range.

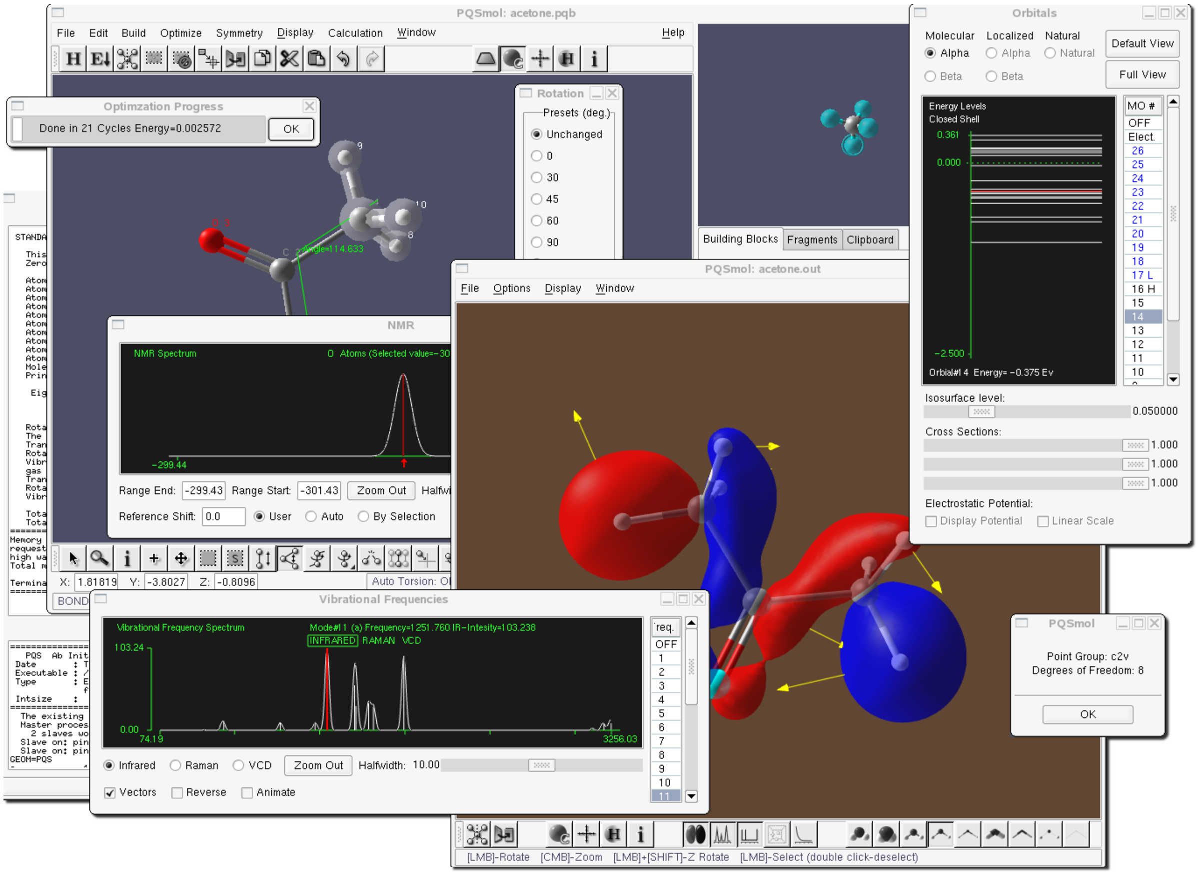
The term **entry** refers to an object in the graphical user interface, which accepts text input.

Contents

Chapter 1

Introduction

PQSMol is the graphical user interface that can be used in conjunction with the **PQS** *ab initio* program. It contains a model builder with two built-in molecular mechanics force fields together with options for job input preparation, job submission (serial or parallel), and post-job visualization and display. The latter includes visualization of molecular orbitals (canonical, localized and natural), electron densities and electrostatic potentials, optimization history (energy/geometry at each cycle of a geometry optimization), dynamics trajectories, animation of vibrational modes, and simulation of IR/Raman, VCD and NMR spectra.



Done in 21 Cycles Energy=0.002572

● Unchanged ○ 0 ○ 30 ○ 45 ○ 60 ○ 90

● Alpha ○ Alpha ○ Natural ○ Beta ○ Beta

Orbital# 14 Energy= −0.375 Ev

Isosurface level: 0.050000

Cross Sections: 1.000 1.000 1.000

Electrostatic Potential: ☐ Display Potential ☐ Linear Scale

Range End: -299.43 Range Start: -301.43

Reference Shift: 0.0 ● User ○ Auto ○ By Selection

X: 1.81819 Y: -3.8027 Z: -0.8096

Mode#11 (a) Frequency=1251.760 IR-Intensity=103.238

● Infrared ○ Raman ○ VCD Halfwidth: 10.00

☑ Vectors ☐ Reverse ☐ Animate

Point Group: c2v
Degrees of Freedom: 8

Figure 1.1: PQSMol in action

There are two modes of operation for **PQSMol**: **build mode** and **view mode**. **Build mode**, as the name implies, is for building a new molecule or modifying an existing one. **View mode** is for visualization of already computed quantities. Structures read into **PQSMol** in **view mode** cannot be modified.

In **view mode** there is one main *View window* and several additional windows for displaying various properties. In **build mode** there are two: the main *Build window* and the *Segment window*. The latter provides access to the various fragments and "building blocks" from which new molecular structures can be constructed. As well as using predefined fragments, you can build your own fragments and store them for future use.

Within **build mode**, you can choose either **restricted mode** (the default) or **unrestricted mode**. In **restricted mode**, molecules can be constructed only using well-defined building blocks that are recognized by either of the two available force fields; this ensures that any molecule that is built can be optimized using one or the other of these force fields. In **unrestricted mode**, *all* generic structural motifs are accessible for *any* atom in the periodic table. Additionally, one can add (and delete) valency ("bonding") to any atom, increasing (or decreasing) the number of bonds that can be made to other atoms. The nature of a bond (single, double, aromatic etc...) can also be changed. In other words you can build just about anything. *However*, the downside is that, once you have switched to **unrestricted mode**, there is no guarantee you will be able to optimize the geometry of your system, as many atom types may no longer be recognizable by the force fields.

The basic idea then is to build your system, using a combination of well-defined atom types (or building blocks) and predefined structural fragments, optimize the structure using either of the two available forcefields, possibly symmetrize the resulting geometry and then prepare the input for, and submit, a PQS job. The job can be submitted either in serial or parallel, in the background or to a job queue, depending on what options are available on the particular machine. When the job has finished, various results can be visualized.

If you are already familiar with existing model builders (such as SPARTAN, PCModel or MAESTRO) then you should have no difficulty in using **PQSMol** which is fairly intuitive. Build commands are accessed via drop-down menus and toolbars (you need a three-button mouse; right, left and center mouse buttons are all potentially active).

The plan from here on is to describe all of the build/visualize tools available in **PQSMol** and how to use them. The vast majority are accessed through various buttons in either the upper or lower toolbar in the main (*Build*/*View*) window. The icons have some pictorial relationship to the actual function they represent, and simply positioning the mouse pointer over a button will display a tooltip with a brief description of its functionality. Following a description of all the build/visualize tools, several tutorials will be presented covering all aspects of **PQSMol**, including building a molecule, input preparation, job submission and displaying the final results.

1.1 Starting PQSMol

To start **PQSMol** in **build mode** from the command line prompt, type the following command and press <Enter>:

```
pqsmol
```

To start **PQSMol** in **view mode** type:

```
pqsview
```

and press <Enter>.

You may also start **PQSMol** with a specific file name passed as a command line argument:

```
pqsmol filename
```

This command will launch **PQSMol** in **build mode** and open the file `filename`. The only valid file extension in **build mode** is `.pqb`. In **view mode** there are several input file types available:

```
pqsview filename
```

where the **filename** extension may be one of:

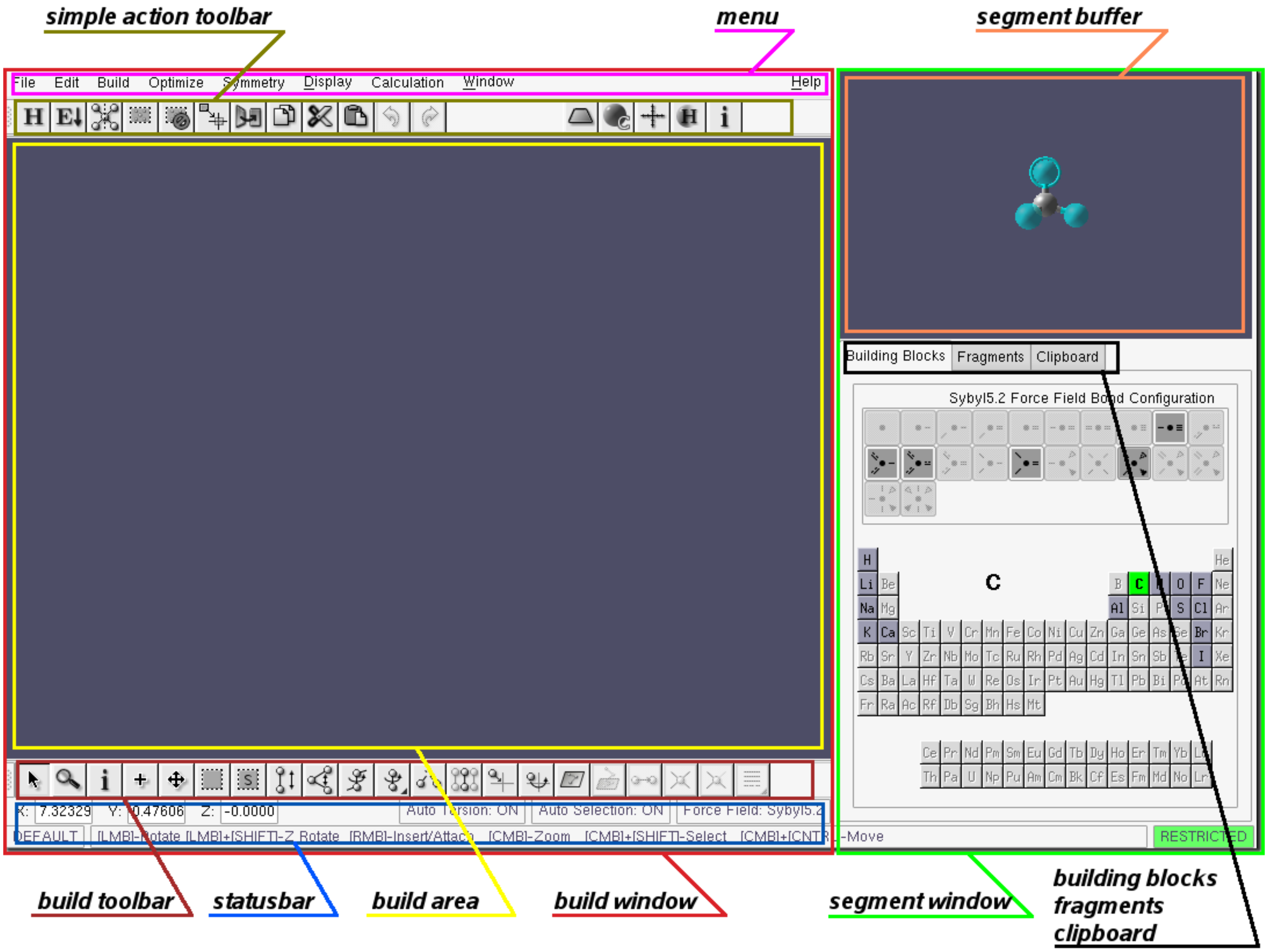
inp	standard PQS job input file.
coord	PQS coordinate file.
out	PQS job output file.
log	PQS job log file.
mop	MOPAC input file.
car	Biosym CAR file.
zmat	Z-Matrix input file.
hin	Hyperchem input file.
xyz	XYZ coordinate file.

Please report any problems with **PQSMOL** by email to *tech@pqs-chem.com*.

Chapter 2

Build mode

When **PQSMol** is started without command line arguments the application runs in **build mode**. In Figure 2.1 individual components of the interface are labeled and surrounded with colored rectangles.



X: 7.32329 Y: 0.47606 Z: -0.0000 Auto Torsion: ON Auto Selection: ON Force Field: Sybyl5.2

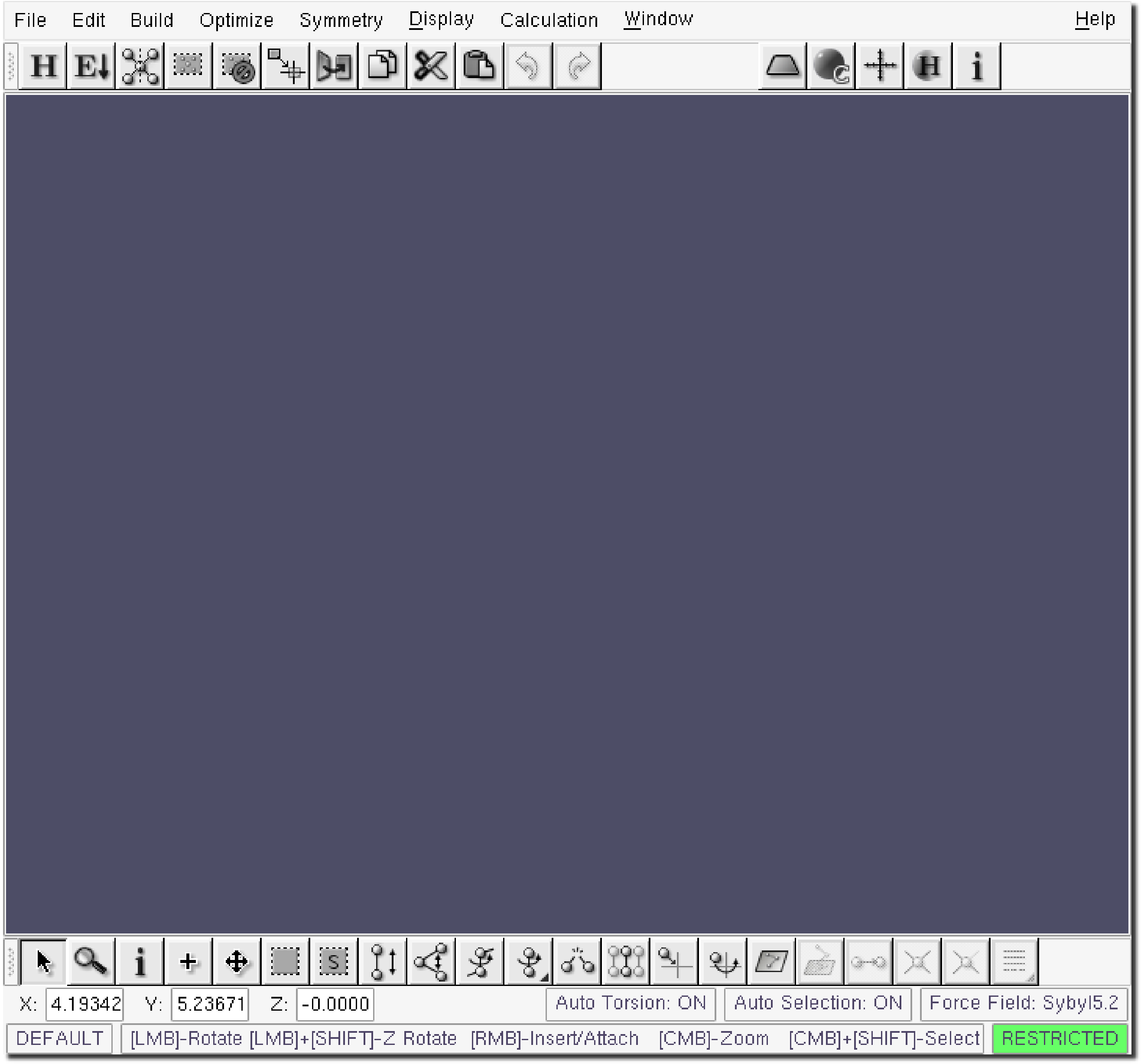
DEFAULT [LMB]-Rotate [LMB]+[SHIFT]-Z Rotate [RMB]-Insert/Attach [CMB]-Zoom [CMB]+[SHIFT]-Select [CMB]+[CNTR]-Move RESTRICTED

Figure 2.1: PQSMol executing in build mode

The main window is divided into two vertical frames. One frame contains the *Build window* labeled in red, and the other the *Segment window* labeled in green. The *Build window* contains a menubar - purple, simple action toolbar - olive, the build area - yellow, the build toolbar - brown, and the statusbar - blue.

The *Segment window* provides access to a set of basic building blocks, a library of fragments, and a clipboard. The *Building Blocks tab*, the *Fragments tab* and the *Clipboard tab* are labeled in black. The *Segment buffer* which displays segments to be inserted into the build area is labeled in orange.

2.1 Build window



X: 4.19342 Y: 5.23671 Z: -0.0000

Auto Torsion: ON

Auto Selection: ON

Force Field: Sybyl5.2

DEFAULT

[LMB]-Rotate [LMB]+[SHIFT]-Z Rotate [RMB]-Insert/Attach [CMB]-Zoom [CMB]+[SHIFT]-Select

RESTRICTED

Figure 2.2: The *Build window*

2.1.1 Toolbars

The majority of actions available in **PQSMol** are accessible through the two toolbars in the main window. Each toolbar button has an icon and a tooltip to identify its action. The top toolbar contains buttons for simple tools that require no interaction with the *Build window*. The bottom toolbar groups more complex tools, that often require multiple clicks in the *Build window* to complete their function. Information for each of these tools is displayed in the statusbar at the bottom of the *Build window*.

Buttons with a dark triangle in the lower right corner have options available through a drop down menu. To access the menu right-click on the button.

Tip: To show any button's tooltip move the mouse pointer over the button.

Simple action toolbar

Simple, single-click tools in **PQSMol** are grouped in the top toolbar.

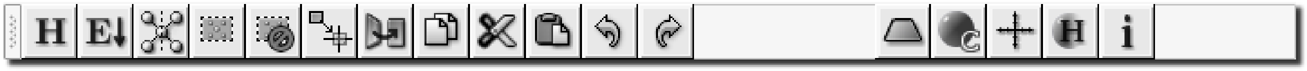


Figure 2.3: Simple action - top toolbar

Buttons from left to right are:

Hydrogen Fill
Fills all free single valencies (vacant single bonds capped with green translucent dummy atoms) with hydrogen atoms.

Optimize
Performs a geometry optimization on the current structure using the currently selected force field. See Section 2.4.

Check Symmetry
Determines the molecular point group symmetry. See Section 2.5.

Select All
Selects *everything* (all atoms and bonds) in the *Build window*. Subsequent build operations, such as *Cut*, *Paste*, are applied to the complete structure.

Select None
Deselects *all* atoms and bonds that are currently selected.

Center All
Positions the current structure in the center of the *Build window*.

Face Front

Rotates the current structure so that the XY plane is parallel with the screen.

Copy

Copies that part of the structure that is currently selected into the clipboard and displays it in the *Segment buffer*.

> **Note:** The *copy* operation automatically activates the *Clipboard tab* in the *Segment window*.

Cut

Copies that part of the molecule that is currently selected into the clipboard, displays it in the *Segment buffer*, and removes it from the *Build window*.

> **Note:** The *cut* operation automatically activates the *Clipboard tab* in the *Segment window*.

Paste

Pastes the contents of the clipboard into the *Build window*.

Undo

Undoes the effects of the last operation (i.e., the last change made to the current structure in the *Build window*).

Redo

Re-does the effect of the last operation before the undo (i.e., undoes the undo).

> **Note:** Multiple *undo* and *redo* operations are supported.

> **Note:** Actions performed in the *Build window* form a list of build events. Each item in the list stores a structure which is a result of all previous build events stored in the list. The *undo* operation moves backward through the list. The *redo* moves forward through the list. If the beginning of the list is reached, the *undo* operation becomes inactive. If the end of the list is reached then the *redo* operation is no longer available. In a situation where a new operation is inserted in the middle of the list, all subsequent list items are destroyed and the resulting geometry is stored as the last item in the list.

Drawing Plane

Toggles on/off the drawing plane.

> **Note:** The drawing plane is defined by three user-selected atoms in the molecule. If these are not defined, the **Define drawing plane** tool from the bottom toolbar is automatically selected.

Atom Labels
Toggles on/off atom labels.

Coordinate Axes
Toggles on/off the coordinate axes.

> **Note:** The spacing between the tic marks on each coordinate axis is one Angström.

Hydrogen Hide
Shows or hides hydrogen atoms.

Info Window
Toggles on/off the info window, see Section 2.32.

Build tools toolbar

The bottom toolbar groups complex tools. Use these tools to interact with the objects in the *Build window*.

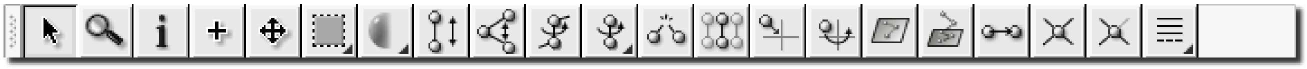


Figure 2.4: Build tools - bottom toolbar

The tools from left to right are:

Default tool
The primary action of the default tool is rotation of the molecule.

Usage: Drag the mouse vertically and horizontally to rotate the structure along the X and Y axes, respectively. Press the <SHIFT> key while dragging to rotate around the Z axis (i.e., out of the plane of the *Build window*).

To speed up the building process for advanced users, the **Default** tool is overloaded with additional actions.

1. **Add/Attach/Connect**
   Use the right mouse button to perform the same actions as described in the **Add/Attach/Connect** tool.

2. **Zoom**
   Drag vertically using the center mouse button.

3. **Select**
   Press the <SHIFT> key while clicking the center mouse button to perform actions described in the **Select** tool.

4. **Move**
   Press the <CONTROL> key while clicking the center mouse button to perform actions described in the **Move** tool.

> **Note:** Each of the overloaded actions is available through its own dedicated tool button. The **Default tool** is the only tool that uses buttons other than the left. The remainder of the **PQSMol** tools use only the left mouse button.

🔍

Zoom tool

Moves the viewpoint directly over the center of the selected area of interest and zooms in to show the atoms within.

Usage: Drag the mouse over the area of interest to zoom in. Double click to return to full view.

> **Note:** In the full view (zoom out) the origin of rotation is the center of the coordinate system (point {0.0, 0.0, 0.0}). The zoom operation effectively changes the origin of rotation for the molecule to be the center of the selected area of interest.

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Info tool

Displays information about atoms, bonds, distances, angles, torsions and out-of-plane bends. For each atom the information includes atom type, atom position in the input geometry, assigned symbols for Sybyl5.2 and Universal force fields and the Cartesian coordinates. This information is displayed in the info window at the bottom of the *Build window*. The info window is automatically opened when the **Info** tool is selected. It is not, however, automatically closed when a different tool is selected. Use the **Info Window** button in the simple action toolbar to close the info window.

Usage: Click on any atom to get its coordinates, click on two atoms to get the distance between them, click on three for the 1-2-3 angle and click on four to get the 1-2-3-4 torsion and out-of-plane bend. To clear the current info selection double-click over empty space in the window.

> **Tip:** This tool also works with bonds. Click on any bond to get its length, any two adjacent bonds to get the angle between them, or any three bonds sharing two atoms to get the torsion and out-of-plane bend.

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Add/Attach/Connect tool

The tool performs three distinct actions. The **Add** action inserts the current segment in the *Segment buffer* into the *Build window*. The **Attach** action attaches the current segment in the *Segment buffer* to a structure inside the *Build window*. The **Connect** action is used to connect two atoms which are already inside the *Build window*.

Usage:

1. **Add**
   Move the mouse pointer over empty space in the *Build window*. The mouse pointer changes to

   +|

   Click to insert the segment displayed in the *Segment buffer* into the *Build window* at the location of the mouse pointer.
2. **Attach**
   Move the mouse pointer over an atom. If the atom is a *compatible* attachment point the mouse pointer changes to

   +A

   and the atom under the pointer is highlighted. Click to attach the segment displayed in the *Segment buffer* to the molecule in the *Build window* at the selected attachment atom. If the atom under the mouse pointer is not a compatible attachment point the mouse pointer changes to

+x

3. **Connect**
   Move the mouse pointer over an atom, click and drag the mouse to a second atom. If the second atom is a valid connection point the cursor changes to

   +C

   Release the mouse button to create a bond between the two atoms. If the atom under the mouse pointer is not a compatible connection point the mouse pointer changes to

   +x

Tip: At all times, a single atom in the structure in the *Segment buffer* is highlighted. This atom is the **attachment point** for the segment. During the *attach* operation, this atom will be replaced with a bond connecting the newly inserted segment with the structure inside the build area. You can change the attachment point of the segment by clicking on any atom that has just one bond connecting it to the reset of the segment.

✥ Move tool

Repositions selected atoms and bonds inside the *Build window*. This tool's functionality depends on the state of the **Auto Selection mode**. With **Auto Selection mode** enabled, a selection is automatically applied to the entire segment containing an atom to be moved. The whole segment is then moved. With **Auto Selection mode** disabled, a manual selection is required before using the **Move** tool. Although an additional step is required, this mode offers more control over atom and bond movement.

Usage: Move the mouse pointer over an atom and click. If the **Auto Selection** option is on, the segment containing the atom is selected and highlighted with a gray translucent surface. Drag the segment to the desired location and release the mouse button.

If **Auto Selection mode** is off, first select the atoms to move using either the **Select** or the **Select Segment** tool. Then using the **Move** tool, drag the selection to the desired location.

Tip: To change the **Auto Selection** click on the **Auto Selection** area in the statusbar or use the **Build→Auto Selection** item in the main menu bar.

⬚ Select tool

The **Select** tool works in two ways. It either selects individual atoms and/or bonds or can be used to create rectangular selection areas selecting any objects they encompass. The selected atoms and bonds are surrounded by a translucent gray surface. Selection operations are cumulative.

Usage: Form a rectangular box (selection area) which selects all atoms in the box for a subsequent action (e.g., Cut, Move), by clicking anywhere in the build area (close to the atoms to be selected) and dragging the mouse horizontally and vertically to define the box dimensions. Releasing the mouse will complete the box definition. The selected atoms and bonds are surrounded by a translucent gray surface. To toggle the selection of an individual atom or bond, click on the atom or on the bond.

Note: The **Box Selection** mode is the default behavior of the **Select** tool. The alternative mode of operation is **Segment Selection**, in which a mouse click over any atom will select the entire segment (all connected atoms) containing the atom. To switch between the two modes, right click over the **Select** tool button and choose the desired mode from the drop down menu.

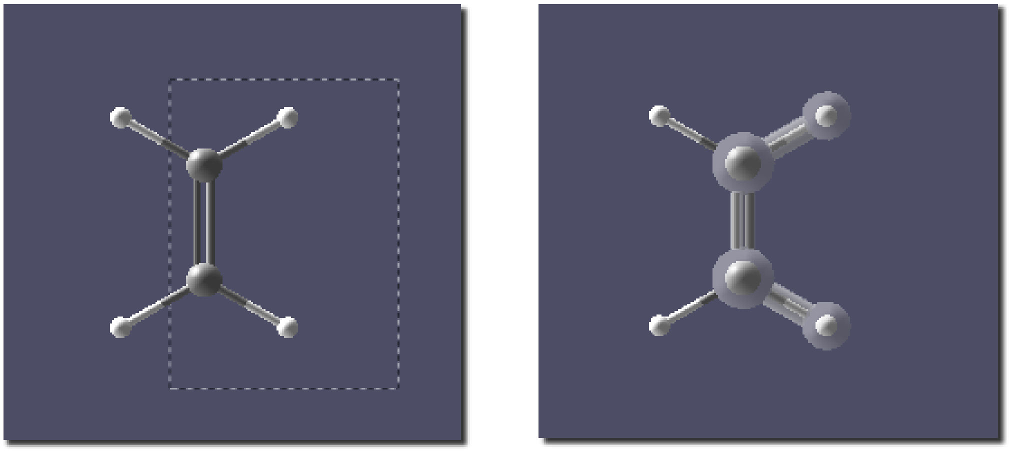


Figure 2.5: Selection

Selections can be cleared with the **Select None** button in the simple action toolbar.

Tip: Double-clicking in the build area will clear all selections, regardless of the current tool.

Hide Nonessential

Deemphasizes atoms which are not part of the area of interest.

Usage: Drag the mouse over the *a*rea of interest. The atoms inside the selected area are unchanged. Outside of this area all Hydrogen atoms become hidden and only the bond structure for the remainder of atoms is shown.

Tip: This tool is particularly useful while building large molecules (100's of atoms) to reduce the atom clutter on the screen. Use it in conjunction with the **Zoom** tool to easily locate attachment points in large molecules.

Bond Length tool

Adjusts the length of a bond.

Usage: Click on a bond to select it for length adjustment. The selected bond is highlighted and its length is displayed in Angströms.

The selected bond partitions the atoms in the system into two groups: stationary and active. The active group is surrounded by a gray translucent surface. The stationary group is unaffected by the bond length adjustment. All atoms in the active group will move when the bond length is adjusted. Dragging the mouse up/down will increase/decrease the bond length. Double-click to set the length. Double-click while pressing the <SHIFT> key to set the default length for that bond.

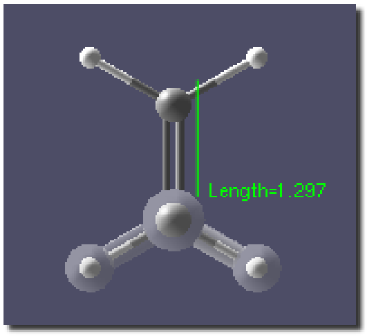


Figure 2.6: Bond length adjustment. The active group is surrounded by a gray translucent surface.

Tip: To modify the active group, switch to the **Select tool** and click on a stationary atom to add it to the active group or on an active atom to remove it from the group. Switch back to the **Bond Length tool** to adjust the bond length with the modified active group.

Tip: Press the <SHIFT> key while adjusting the length of the bond to slow down the rate of change and increase accuracy.

Bond Angle tool

Adjusts the angle between two bonds.

Usage: Click on two adjacent bonds to select the angle for adjustment. The selected bonds are highlighted and the angle between them is displayed in degrees. All atoms connected to the open end of the second selected bond are added to the active group and are surrounded by a gray translucent surface. Only the atoms and bonds in the active group are affected by the bond angle adjustment. Drag vertically to change the angle. Double-click to set the angle.

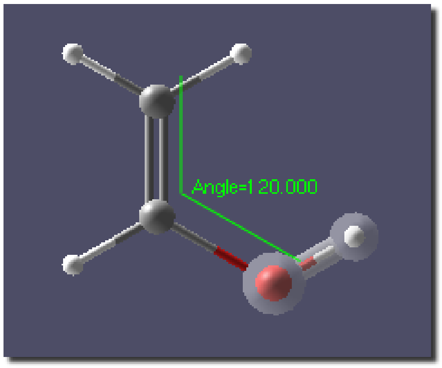


Figure 2.7: Bond angle adjustment

Tip: Press the <SHIFT> key while dragging the mouse for more accuracy in setting the angle.

Bond Torsion tool

Adjusts the torsion of three selected bonds. The active group in the **Bond Torsion** tool includes all atoms and bonds connected to the third selected bond not including the rotation bond, as shown in Figure 2.8.

Usage: Click on three adjacent bonds to select the torsion angle for adjustment. The selected bonds are highlighted and the torsion angle between them is displayed in degrees. All atoms connected to the open end of the third selected bond are added to the active group and are surrounded by a gray translucent surface. Only the atoms and bonds in the active group are affected by the torsion angle adjustment. Drag vertically to change the torsion angle. Double-click to set the torsion angle.

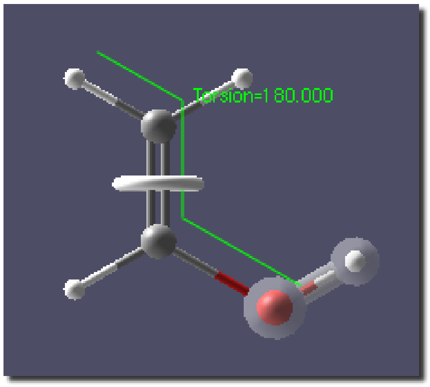


Figure 2.8: Bond torsion angle adjustment

Tip: Press the <SHIFT> key while dragging the mouse for more accuracy in setting the torsion.

Rotate About a Bond tool

Adjusts the torsion of three automatically selected bonds. The bond selection is based on the rotation bond you select. The active group in **Rotate About a Bond** tool includes all atoms and bonds on one side of the rotation bond, as shown in Figure 2.9. In essence, this tool twists one part of the molecule with respect to the other around the rotation bond.

Usage: Click on a bond to select the axis for rotation. The selected bond is highlighted. An adjacent bond is automatically selected on each side of the selected bond. The torsion and out-of-plane bend are displayed in degrees. All atoms connected to one end of the axis of rotation bond are added to the active group and are surrounded by a gray translucent surface. Drag vertically to change the torsion angle. Double-click to set the angle.

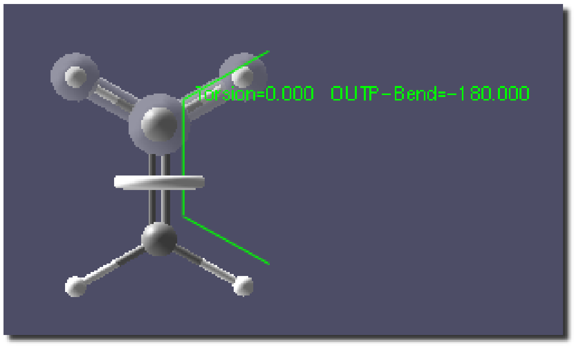
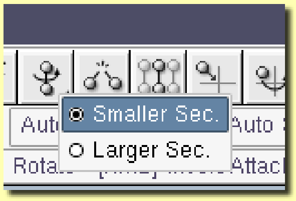


Figure 2.9: Rotation about a bond

Tip: Press the <SHIFT> key while dragging the mouse for more accuracy in setting the torsion.

> **Note:** The axis of rotation bond divides the molecule into two groups. By default the **active group** is composed of atoms in the group which contains the smaller number of atoms. To force the selection of the larger group of atoms right click on the **Rotate About a Bond** button and select **Larger Secion**.
>
> 
>

Bond Break tool

Breaks a bond.

Usage: Click on a bond to break it. To preserve the correct atomic valency, the broken bond is replaced by two bonds, one on each atom, each capped with a dummy atom. Dummy atoms are represented by semitransparent green spheres.

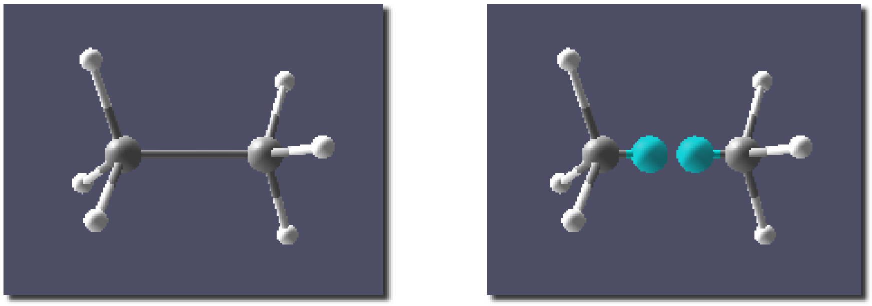


Figure 2.10: Bond break

Bond Fuse tool

The fuse bond tool allows two bonds in separate segments to be fused into a single bond, fusing the two segments together into a united whole. After fusion, the second of the formerly separate segments is selected and the fuse bond is set as the rotation bond, allowing the angle between the two sections to be adjusted.

> **Note:** Not all bonds are fusible. A fusible bond has:
>
> - exactly one closed bond on at least one end
> - if an end has a closed bond, that end also has at least one open bond
>
> An open bond is a bond that is connected to an atom with a valency of one, i.e., no other bonds are connected to the atom. A closed bond is one which is connected to atoms with valencies higher than one at both ends.

Usage: Move the mouse pointer over a bond. If the bond is fusible, it will be highlighted with a yellow translucent surface. The surrounding open and closed bonds will be highlighted with a green translucent surface. Click on the bond to select it as the fuse bond. Move the pointer over a matching fuse bond in a separate segment.

Note: A matching fuse bond has:

- the same number of open and closed bonds as the fuse bond, at both corresponding ends

If the bond is a matching fuse bond, it will be highlighted with a yellow translucent surface and the surrounding open and closed bonds will be highlighted with a gray translucent surface. Click to fuse the two bonds.

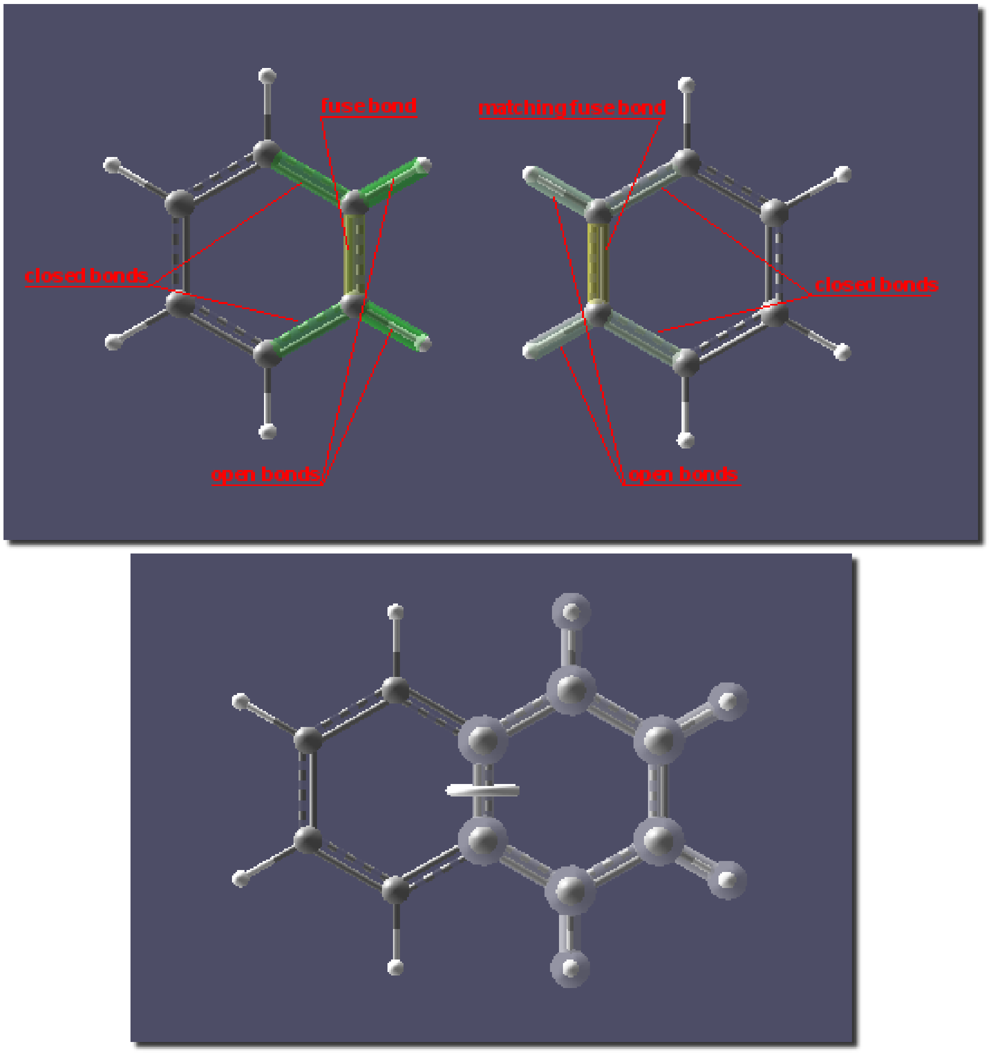


Figure 2.11: Bond fuse example #1

Note: Bond fusion involves moving one of the two segments so as to fuse onto the other segment at the position of the fuse bond. During this procedure, the segment containing the initially selected fuse bond will remain stationary, while the second segment will move. Bear this in mind if there are other segments in the *Build window* whose position relative to one or other of the segments to be fused you wish to remain unchanged.

When the segments are fused, the newly fused bond is automatically selected as the axis of rotation and all atoms and bonds in the matching fuse bond segment are added to the active group. Drag the mouse vertically to adjust the dihedral angle. Double-click to set.

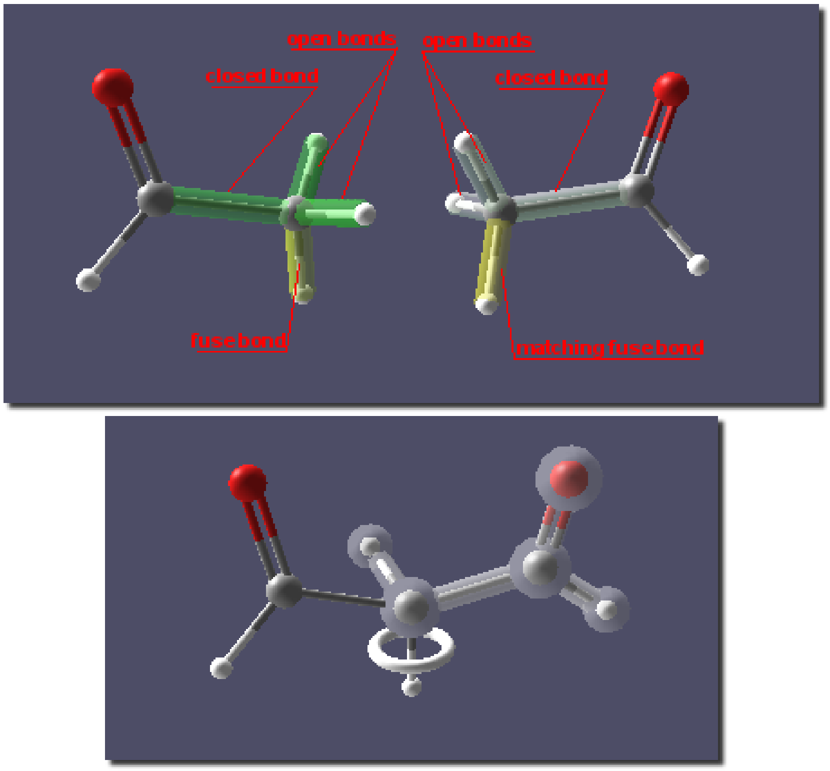


Figure 2.12: Bond fuse example #2

Center on Atom tool

Centers the structure with respect to a specific atom.

Usage: Click on an atom. All atoms and bonds are shifted so that the selected atom is at the origin of the coordinate system.

Reorient Selection tool

Repositions the current selection with respect to a selected reorient atom. It is useful for reorienting molecules relative to one another.

This tool's behavior depends on the state of the **Auto Selection mode**. With **Auto Selection mode** enabled, the entire segment containing the selected reorient atom is automatically selected for reorientation. With **Auto Selection mode** disabled, you must first manually select atoms and bonds to reorient, and then use the **Reorient Selection** tool to select the reorient atom and reorient the selection. Although an extra step is necessary with the **Auto Selection mode** disabled, this method allows segments, or individual unconnected atoms, to be repositioned about any given reorient atom, not necessarily contained in the segment itself.

Usage: Select an atom to be the reference point for reorientation. The atom is highlighted with a green translucent sphere. In the **Auto Selection mode** all atoms and bonds in the selected atom's segment are added to the active group. Drag the mouse vertically and horizontally to reposition the atoms and bonds in the active group. Drag the mouse while pressing the <SHIFT> key to rotate the active group around the Z axis (i.e. out of the plane of the *Build window*). Double-click to set.

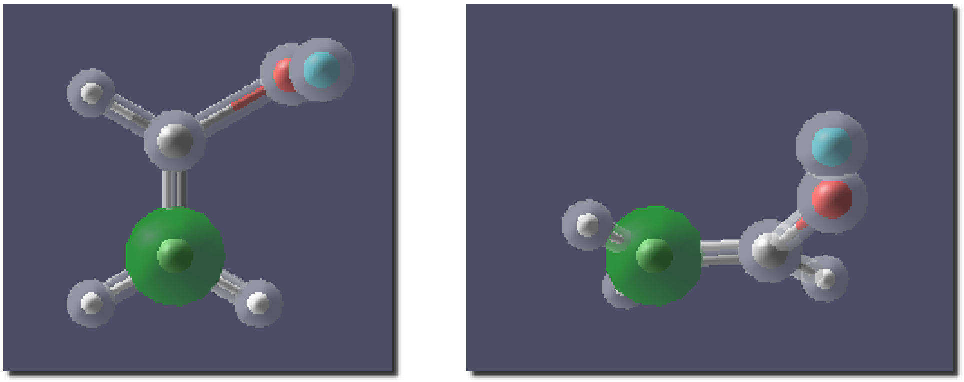


Figure 2.13: Reorient example

Note: If **Auto Selection mode** is off, then the atoms to be reoriented should be selected first via the **Select tool** and then the reference atom for the reorientation selected using the **Reorient Selection tool**.

Define Draw Plane tool

Defines a drawing plane by selecting three drawing plane atoms.

Usage: Click on three non-linear atoms to define a drawing plane. Each selected atom will be highlighted with a red translucent sphere. When the third atom is selected, the drawing plane intersecting the three atoms will be displayed.

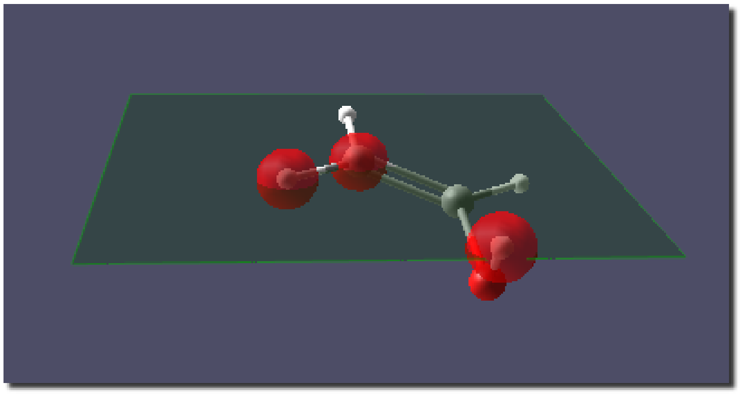


Figure 2.14: drawing plane

Simultaneously with the drawing plane, the **Plane Shift** window appears, Figure 2.15. This enables the plane to be shifted vertically (perpendicular) from its original location, by a specific distance in Angströms. To set the plane shift back to 0 Angströms press the **Reset** button.

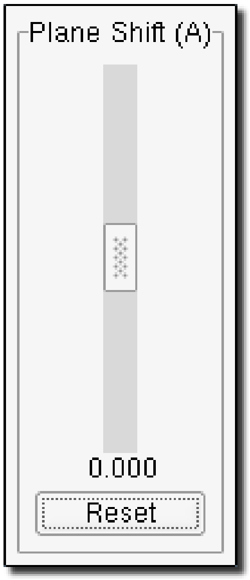


Figure 2.15: Plane Shift window

To toggle the drawing plane use the **drawing plane** button in the upper toolbar.

Snap to Plane tool

Positions structures in the drawing plane as defined by the **Define Draw Plane tool**. Up to three selected atoms can be position in the drawing plane. The segment (possibly segments) containing these atoms are moved accordingly. The drawing plane must be defined before the **Snap-to-Plane tool** can be used.

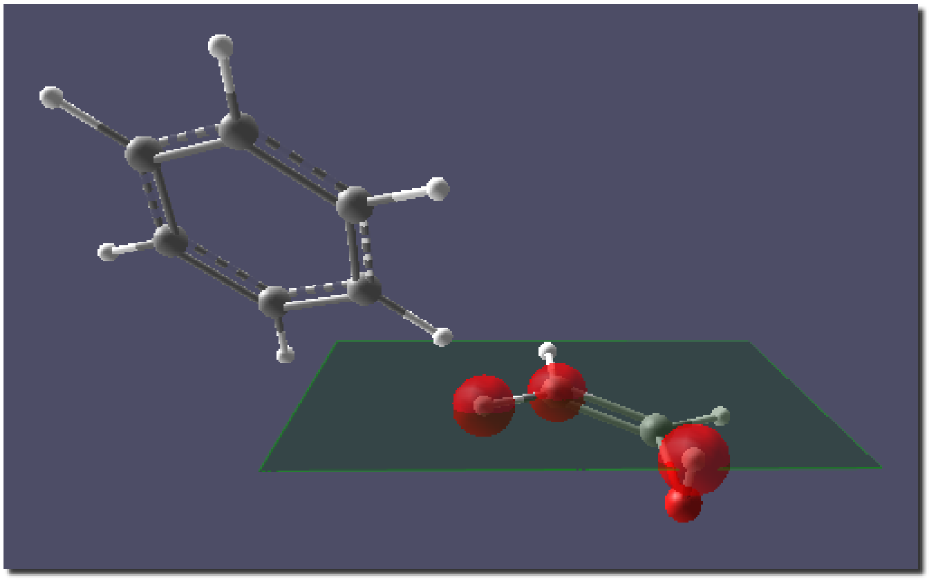


Figure 2.16: Snap to Plane example - starting configuration

Usage: Click on an atom in the structure to be reoriented. The selected atom is highlighted with a green translucent sphere. All remaining atoms in the segment are added to the active group and the segment moves so that the atom selected is in the drawing plane.

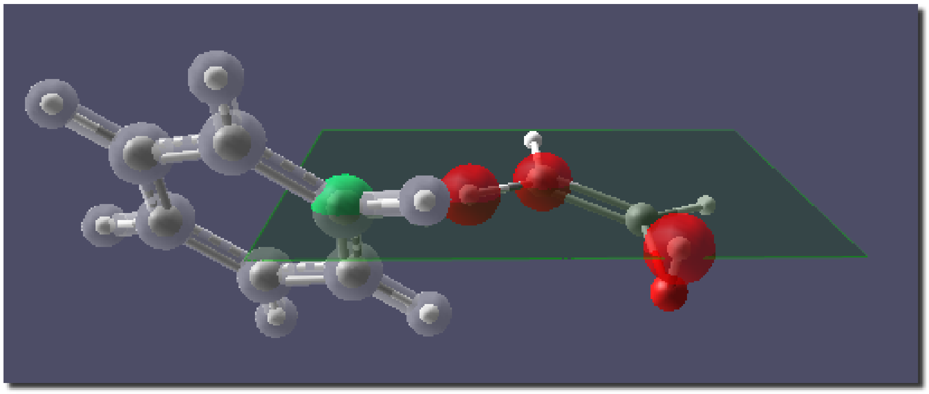


Figure 2.17: Snap to Plane example - first atom selected

Click on the second atom. The atom is highlighted with a green translucent sphere and all atoms in the active group are rotated so that the second atom is also positioned in the drawing plane.

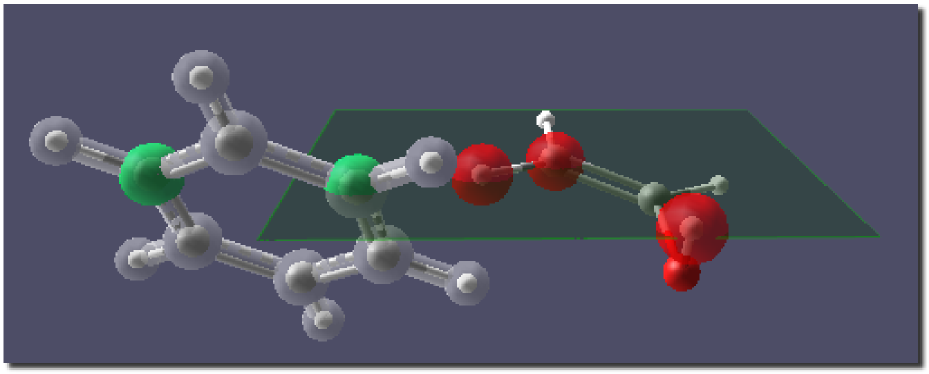


Figure 2.18: Snap to Plane example - second atom selected

Click on the third atom in the structure. This atom is also highlighted with a green translucent sphere and all atoms in the active group are rotated so that all three selected atoms are positioned in the drawing plane.

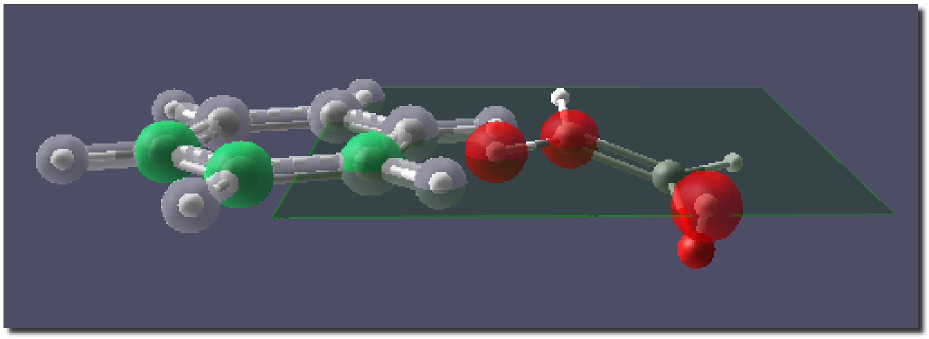


Figure 2.19: Snap to Plane example - third atom selected

Note: This tool is only available if the drawing plane is turned on.

Replace tool

Replaces any atom in the current structure in the *Build window* with any other atom in the periodic table.

Usage: Click on the atom in the periodic table you wish to substitute. Click on any atom in your current structure to replace that atom with an atom of selected element type. All bonds to that atom will remain as they were, both with respect to distance and angles.

> **Note:** This tool is only available in **unrestricted mode**.

Add Valence tool

Adds a free valence to an atom allowing another bond to be formed to that atom . The new bond will be automatically positioned as far away geometrically from any existing bonds (up to three) as possible. Once four or more bonds are already present, the new bond will be placed in the same location every time and will have to be moved into an appropriate position. When the free valence is in place, other building blocks can be added to it using the **Add/Attach/Connect tool**.

Usage: Click on an atom to add a valence. A new bond capped with a dummy atom is added to the selected atom. Drag the mouse horizontally and/or vertically to rotate the new bond along the X and Y axes, respectively. Press the <SHIFT> key while dragging the mouse to rotate the bond about the Z axis (i.e., out of the plane of the *Build window*).

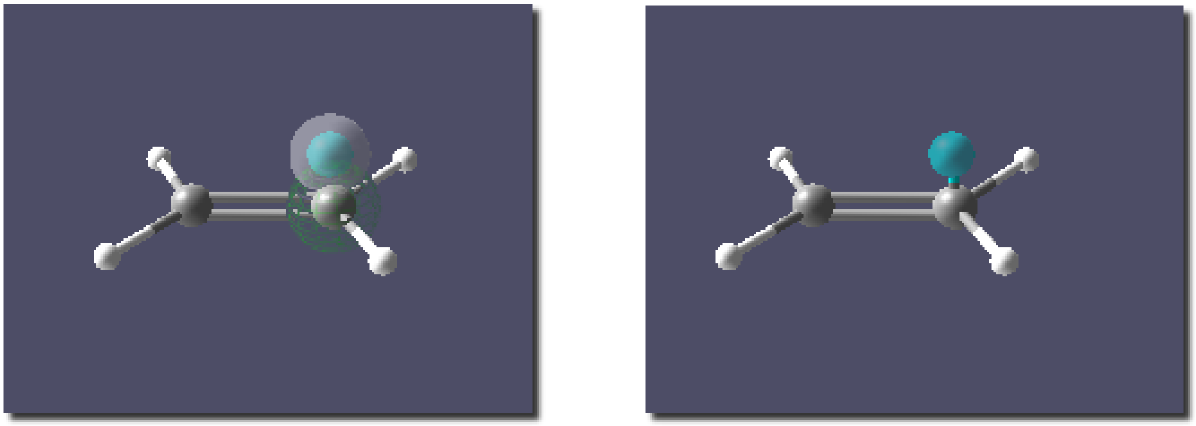


Figure 2.20: Add Valence example

> **Note:** This tool is only available in **unrestricted mode**.

Remove Valence tool

Removes monovalent atoms *and* their valencies.

Usage: Click on any monovalent atom to delete it from the current molecule.

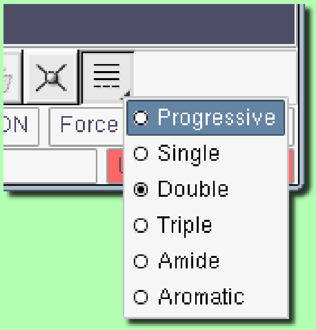
> **Note:** This tool is only available in **unrestricted mode**.

Bond Type tool

Changes the bond type for a bond.

Usage: Click on a bond to change its type. Each click will advance the bond type to the next element in the following list: **Single→Double →Triple →Amide →Aromatic**

Tip: To set a specific bond type on the first click, right click on the **Bond Type** button and select the desired bond type.



Note: This tool is only available in **unrestricted mode**.

2.1.2 Menu

At the top of the **PQSMol** main window is the menubar, Figure 2.21. Almost all of the functions of **PQSMol** are available by activating the appropriate menu item. The functions have been grouped according to their type.

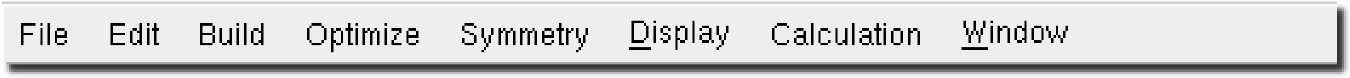
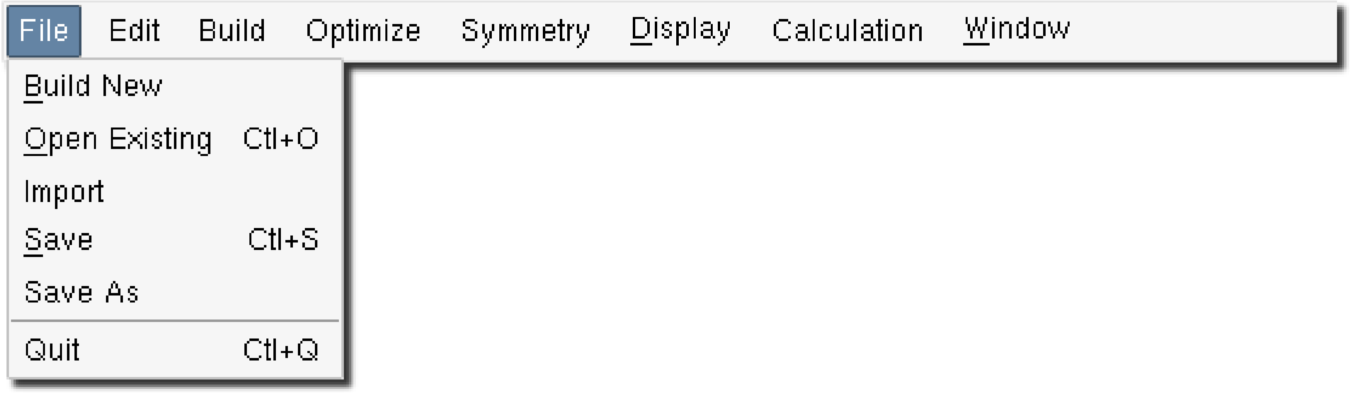


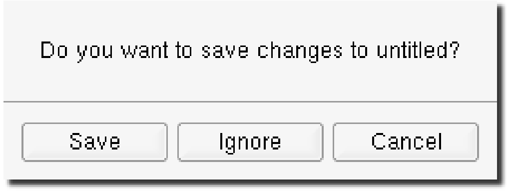
Figure 2.21: The PQSMol Menubar in build mode

The File menu

The file operations have been grouped into the **File** menu



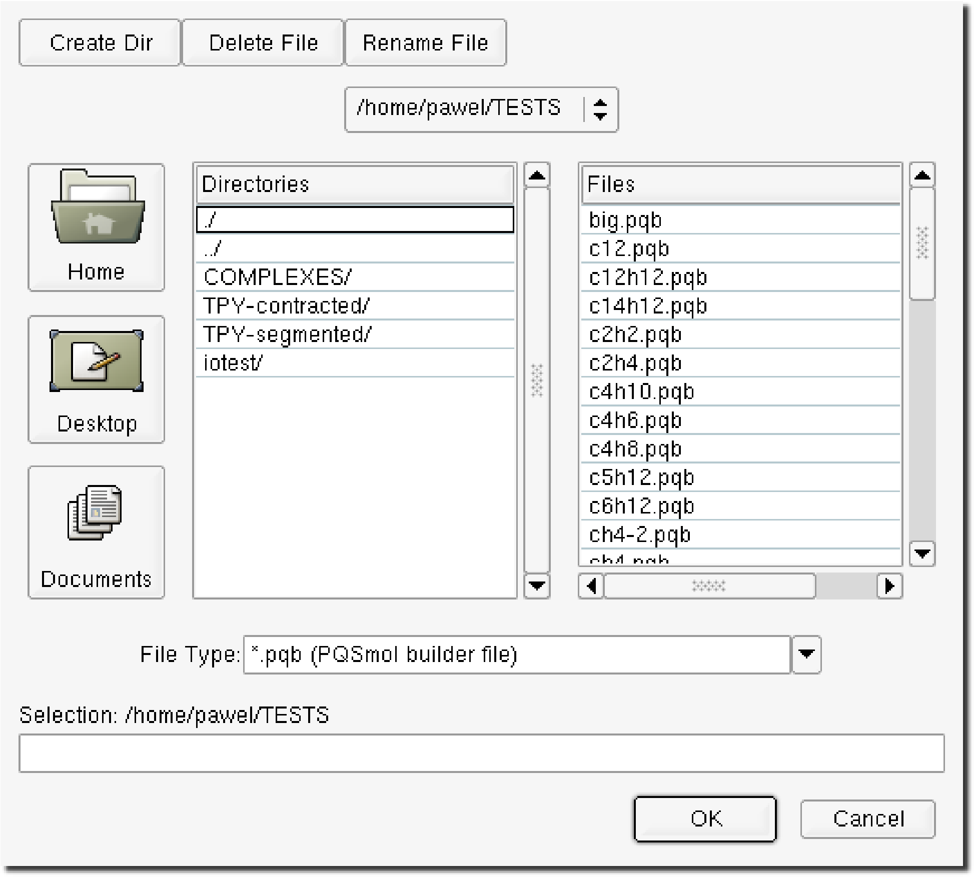
- **Build New** starts a new build project. If the currently edited structure has been modified since the last save operation, you are presented with the **Save Changes** dialog, Figure 2.22 . The **Save** button in the dialog saves the current molecule. If the project is untitled, the **Save As** dialog is displayed. The **Ignore** button in the dialog causes the last changes in the edited molecule to be lost. The **Cancel** dialog button cancels the operation.



Do you want to save changes to untitled?

Figure 2.22: Save Changes dialog

- **Open Existing** opens an existing build file. The File Open dialog, Figure 2.23, lets you browse directories for a specific file. The file list is filtered so that only the pqsmol build files, with the `.pqb` extension, are displayed. You can change the current browse directory by selecting entries in the *Directories* list on the left and a specific file can be selected from the **Files** list on the right side.



File Type: *.pqb (PQSmol builder file)

Selection: /home/pawel/TESTS

Figure 2.23: File Open dialog

- **Import** allows a range of different file types (other than `.pqb` files) to be imported. The *Import Geometry* dialog is shown in Figure 2.24.

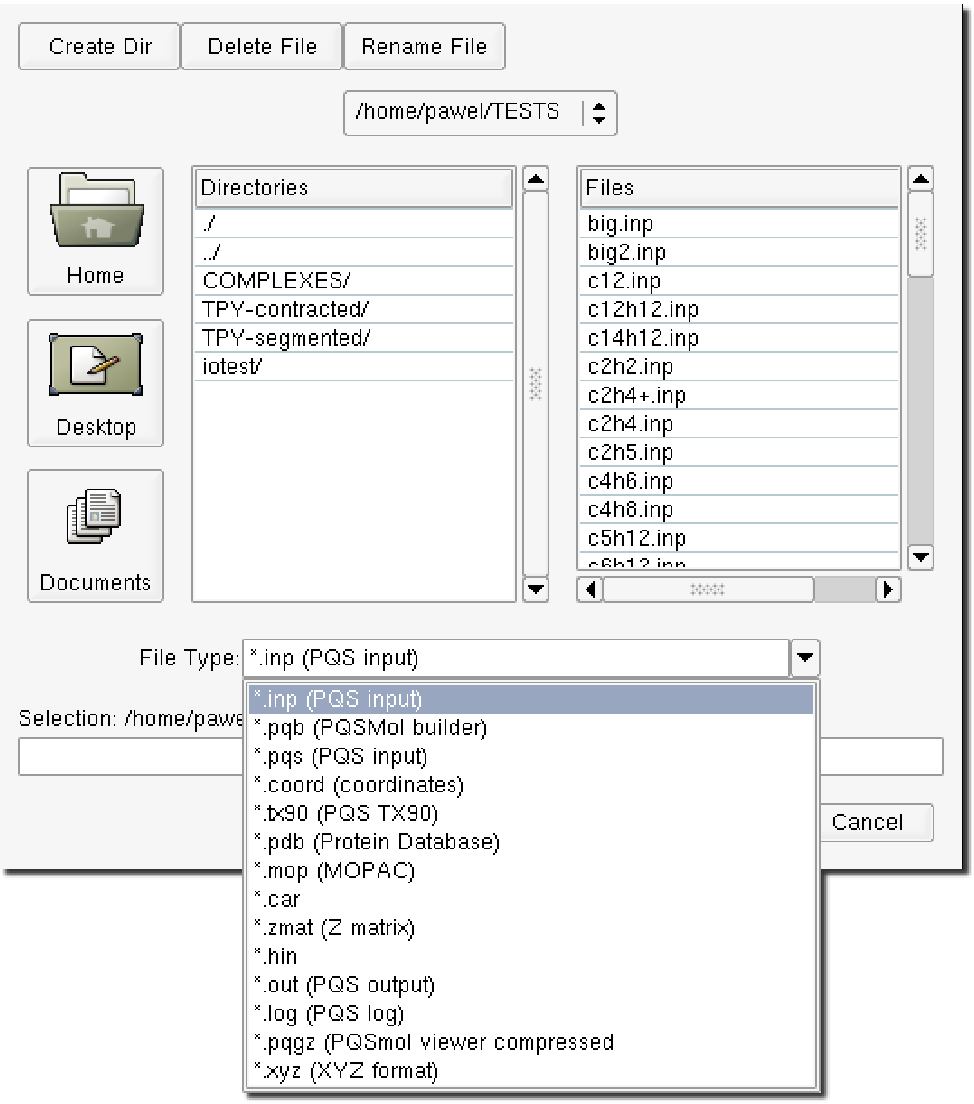


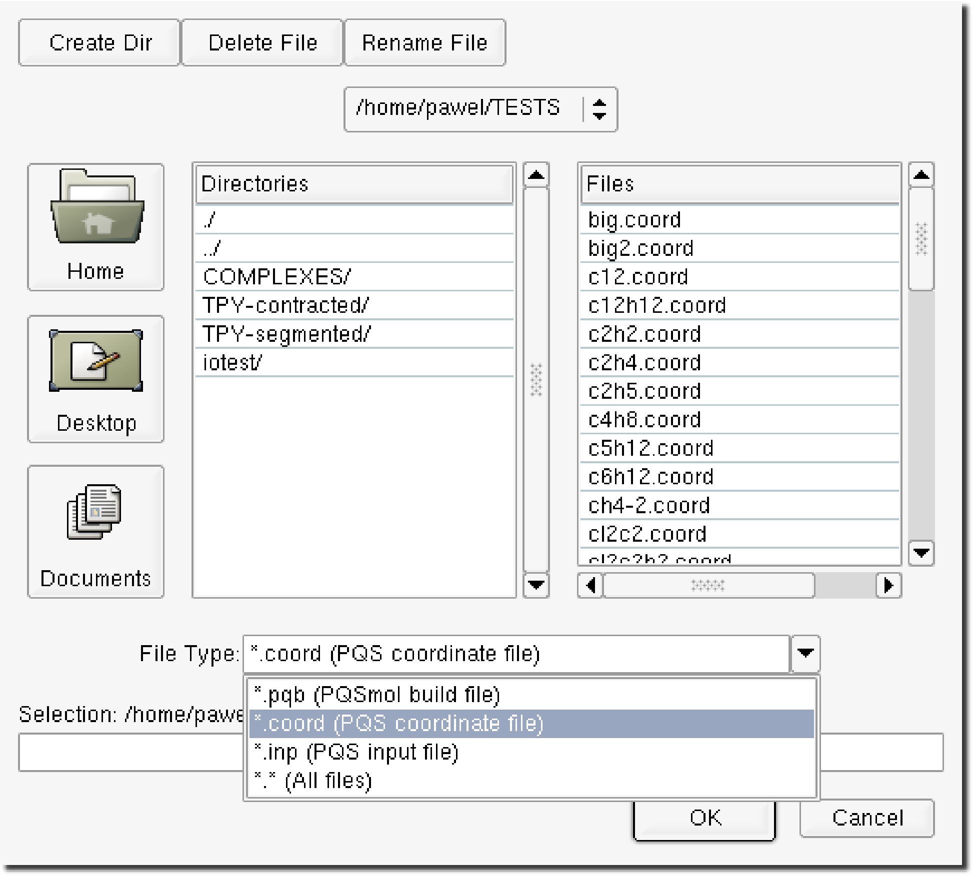
Figure 2.24: Import geometry dialog

Note: Imported structures are placed in the clipboard.

The type of file to be imported is selected via the *File Type* pulldown menu and the actual file is selected in the *Files* list.

- **Save** saves the current structure in the *Build window*. If the project is untitled then the **Save As** dialog is displayed.

- **Save As** saves the current structure in the *Build window* under an alternative name. The default file type is the **PQSMol** build file `.pqb`. Additionally, `.coord` and `.inp` formats are available.



/home/pawel/TESTS

File Type: *.coord (PQS coordinate file)

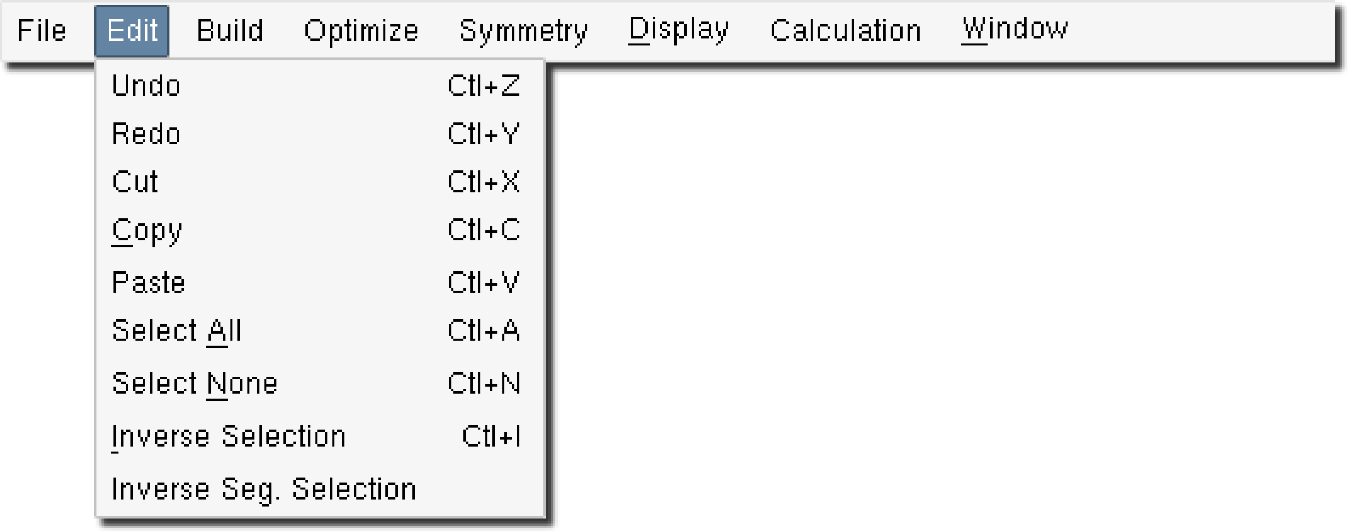
Selection: /home/pawe

Figure 2.25: File Save As dialog

Note: The `.coord` and `.inp` file formats do not store the connectivity information nor the force field symbols for each atom. When files of these types are imported into **PQSMol**, the connectivity information, which includes bond types and the Sybyl5.2 and Universal forcefield symbols, are autodetected.

- **Quit** exits **PQSMol**. If the currently edited molecule has been modified since the last save operation, you are presented with the **Save Changes** dialog, Figure 2.22.

The Edit menu



- **Undo** undoes the effects of the last operation (the last change made to the current structure in the build area).

Note: Multiple undo and redo operations are supported.

- **Redo** re-does the last undone operation (i.e., undoes the undo).

- **Cut** removes the current selection.

Tip: Structures *cut* or *copied* from the *Build window* are placed in the clipboard and may be reused.

- **Copy** copies the current selection into the clipboard.

- **Paste** pastes the contents of the clipboard into the *Build window*.

- **Select All** selects all atoms and bonds.

- **Select None** deselects all atoms and bonds.

- **Inverse Selection** toggles the selection state of all atoms and bonds. All selected atoms before the operation become deselected after the operation and vice versa as shown in Figure 2.26.

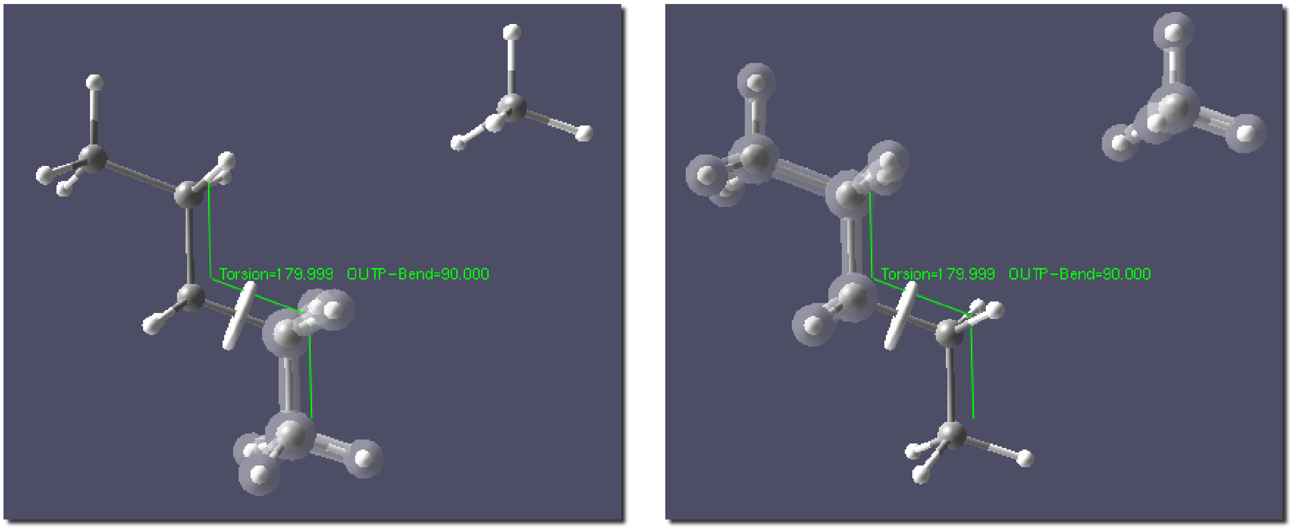


Figure 2.26: Inverse Selection example - before (left image), after (right image)

- **Inverse Seg. Selection** toggles the selection state of all atoms and bonds within segments which have some atoms or bonds selected. All selected atoms *within a given segment* before the operation become deselected after the operation and vice versa as shown in Figure 2.27

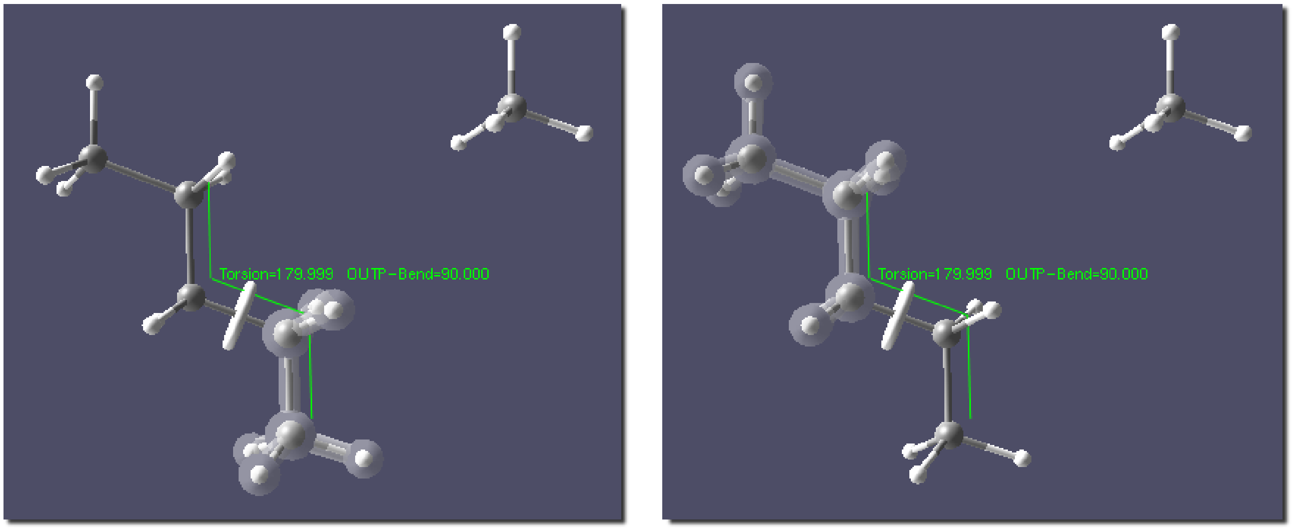
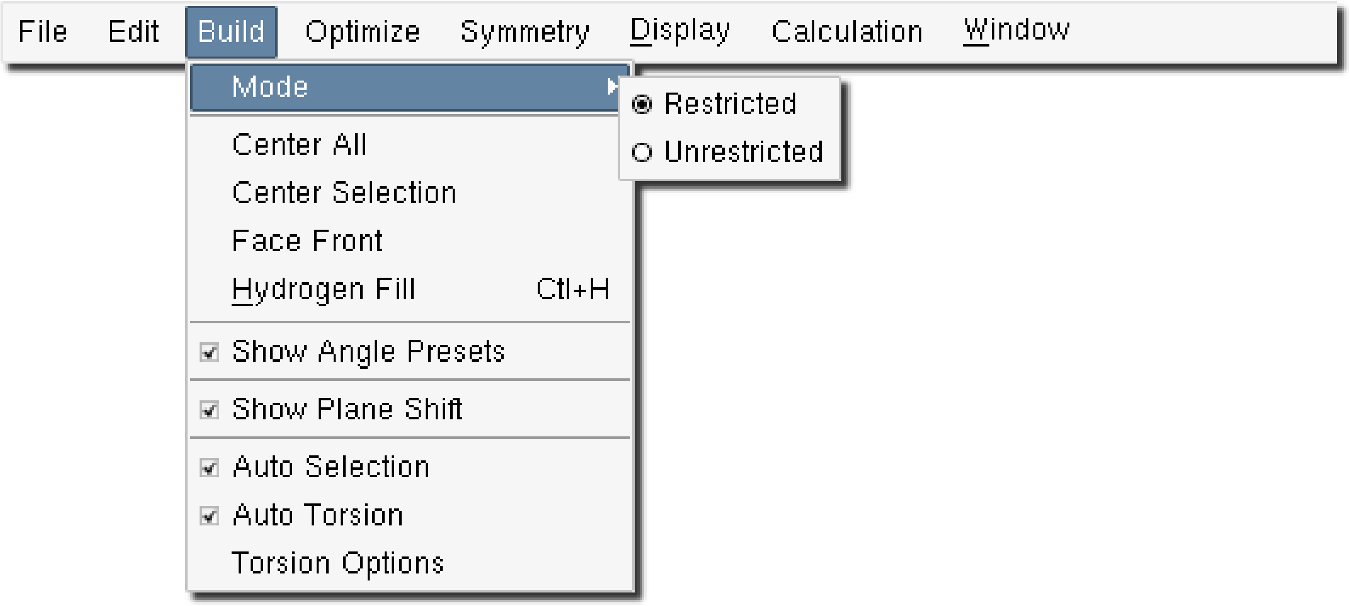


Figure 2.27: Inverse Segment Selection example - before (left image), after (right image)

The Build menu



- **Mode→restricted** sets the **restricted** building mode (Section 2.3.3).

- **Mode→unrestricted** sets the **unrestricted** building mode (Section 2.3.3).

- **Center All** centers the contents of the *Build window*.

- **Center Selection** centers the selection in the *Build window*.

- **Face Front** rotate the structure in the *Build window* so that XY plane is parallel with the screen.

- **Hydrogen Fill** replaces all single-bond, dummy atoms with Hydrogen.

- **Show Angle Presets** toggles the **Angle Presets** window, Figure 2.28. When enabled, the presets window will automatically appear whenever a rotation bond is selected or a second bond is selected with the bond angle tool. Activating any of the preset angles listed will set the torsion about the rotation bond or the bond angle to the selected preset.

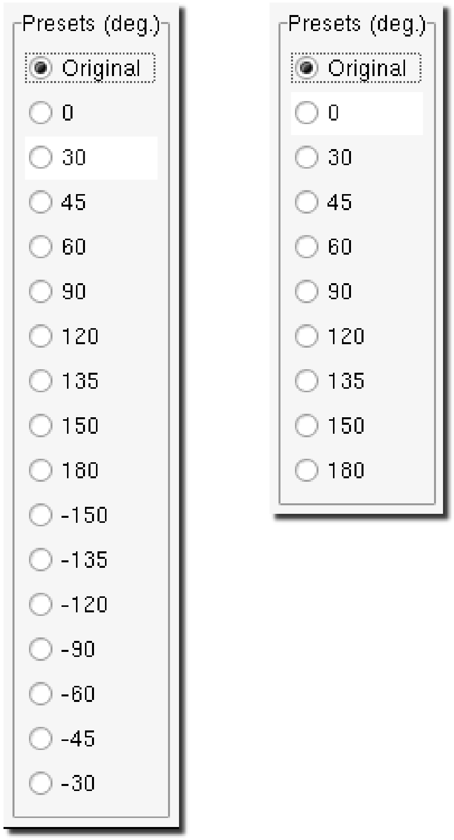


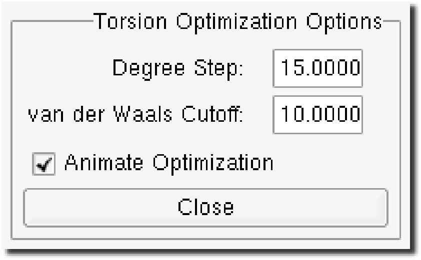
Figure 2.28: Angle Presets window, left image - torsion presets, right image - angle presets

- **Plane Shift** toggles the Plane Shift window, Figure 2.15. When enabled, the Plane Shift window will automatically appear whenever a drawing plane is activated. It is used to shift the drawing plane by a specific distance in Angströms. To set the plane shift back to 0 Angströms press the **Reset** button.

- **Auto Selection** toggles the building mode (Section 2.3.2).

- **Auto Torsion** toggles the torsion building mode (Section 2.3.1).

- **Torsion Options** shows the **Torsion Options** window, Figure 2.29. If the **Auto Torsion** building mode is active, **PQSMol** attempts to find the minimal energy configuration during an *attach* operation. When a new segment is attached to the existing structure inside the build area, it is rotated around the attachment bond starting at a torsion of 0 degrees. The torsion angle is repeatedly incremented by **Degree Step** degrees, until a full rotation is completed. At each point in the rotation the van der Waals energy is calculated using the **van der Waals Cutoff**, given in Angströms. The segment is attached at the torsion angle with the lowest van der Waals energy. The **Animate Optimization** check box toggles the animation of the torsion optimization process.



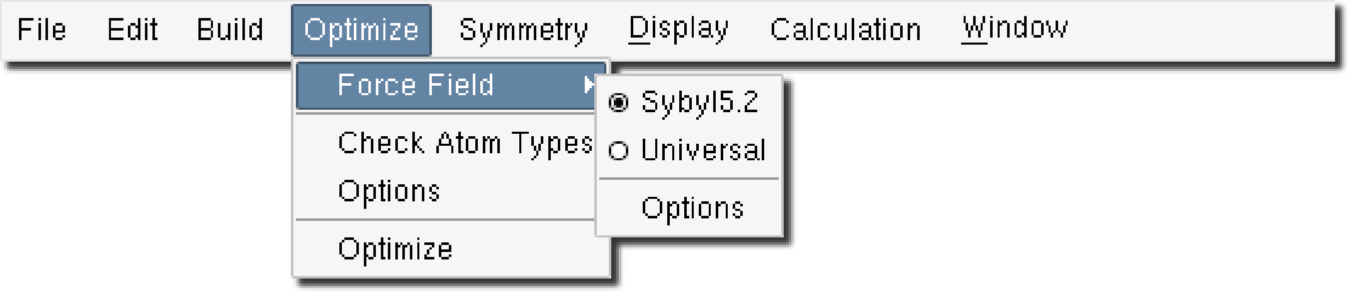
Degree Step: 15.0000

van der Waals Cutoff: 10.0000

☑ Animate Optimization

Figure 2.29: Torsion Options window

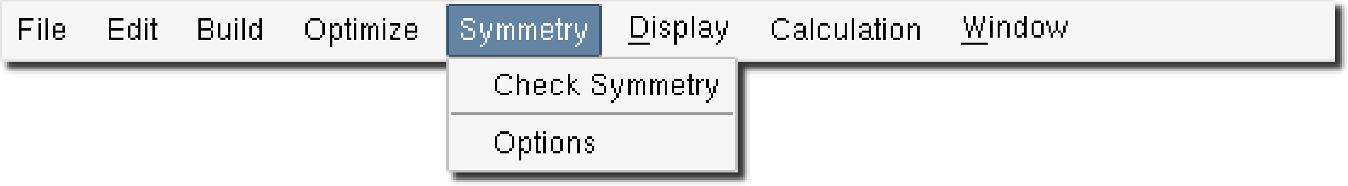
The Optimize menu



Refer to Section 2.4 for a detailed discussion of the optimization process.

- **Force Field→Sybyl5.2** sets **Sybyl5.2** as the current force field.
- **Force Field→UFF** sets **UFF** as the current force field.
- **Force Field→Options** shows the Force Field options window, see Section 2.4.1.
- **Check Atom Type** checks or modifies the Force Field atom types, see Section 2.4.3.
- **Options** shows the *Optimization options window*, see Section 2.4.2.
- **Optimize** executes the optimizer, see Section 2.4.

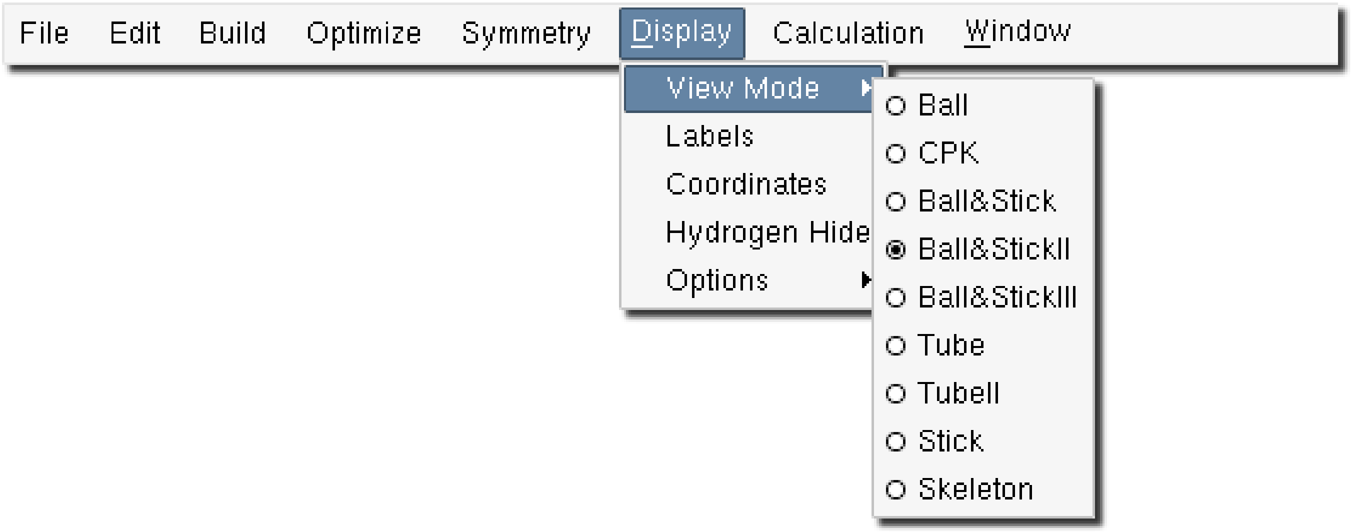
The Symmetry menu

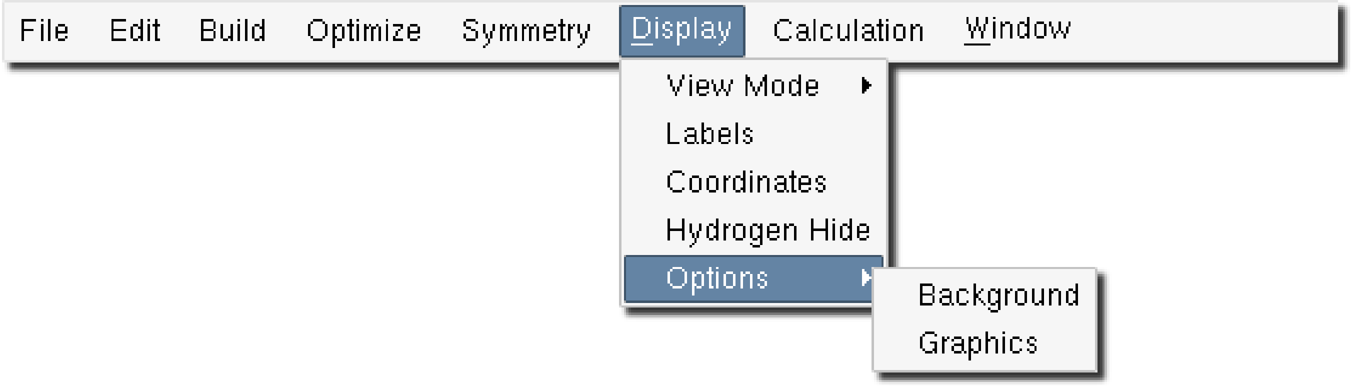


See Section 2.5 for a detailed discussion of the symmetry operation.

- **Check Symmetry** executes the symmetrizer, see Section 2.5.
- **Options** shows the *Symmetry options window*, see Section 2.5.1.

The Display menu





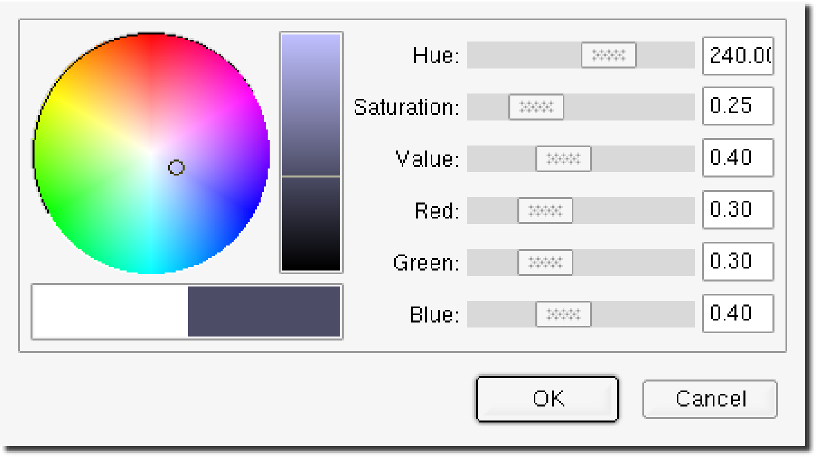
- **View Mode** offers nine viewing modes, which differ from each other primarily in the radii of the spheres representing atoms and the radii of the cylinders representing bonds. The **Skeleton** view mode is the fastest to render. It is recommended for large structures, i.e., containing hundreds of atoms, and slow graphics cards.

- **Labels** toggles atom labels.

- **Coordinates** toggles the coordinate axes.

- **Hydrogen Hide** shows/hides hydrogen atoms.

- **Options→Background** shows the Background Color window, Figure 2.30.



Hue: 240.0

Saturation: 0.25

Value: 0.40

Red: 0.30

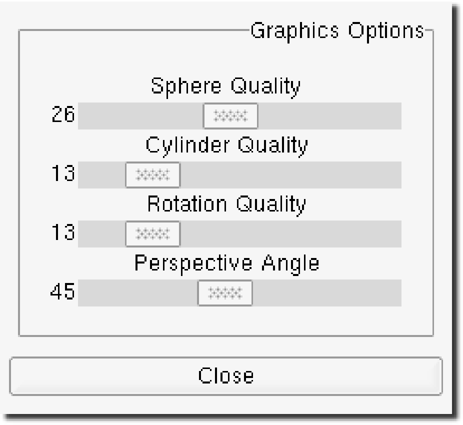
Green: 0.30

Blue: 0.40

Figure 2.30: Background Color window

This allows the background color of the *Build window* to be set via the slide bars. The background color can also be selected by positioning the mouse pointer on the small circle inside the large colored circle and dragging the mouse to the desired location; as the small circle moves, the slide bars will also shift, reflecting the new background color.

- **Options→Graphics** shows the Graphics Options window.



Sphere Quality 26

Cylinder Quality 13

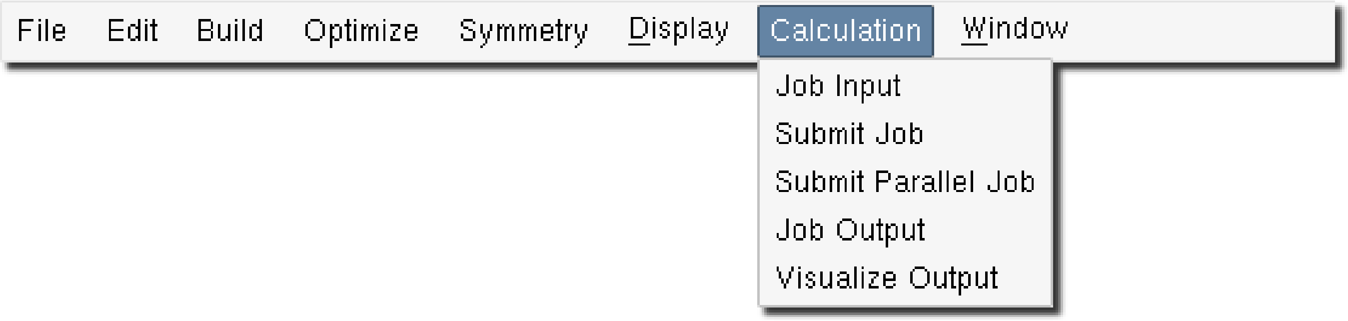
Rotation Quality 13

Perspective Angle 45

Figure 2.31: Graphics Options window

This window controls the quality of the graphics, again using slide bars. Moving the slide bars further to the right increases the corresponding value. High quality graphics will give crisp, clear pictures but will increase the time taken to display or manipulate any graphical image.

The Calculation menu

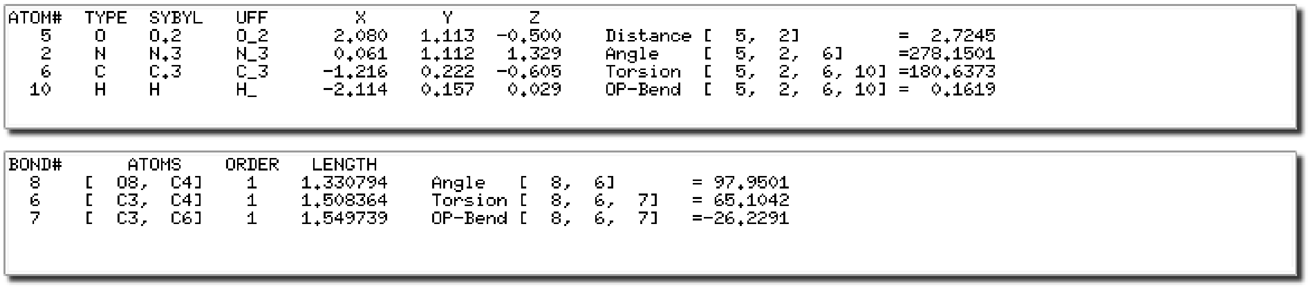


The Calculation menu provides an interface to the **PQS** program. It controls various aspects of job input preparation, job submission, job progress monitoring and post-job visualization and display. See Section 2.6 for a detailed discussion on running a PQS calculation.

- **Job Input** prepares a PQS input file containing the geometrical structure from the *Build window*, See Section 2.6.1.
- **Submit Job** runs a serial PQS calculation, see Section 2.6.2.
- **Submit Parallel Job** submits a parallel PQS calculation in the background or into a queue, see Section 2.6.2.
- **Job Output** monitors the PQS output and log files.
- **Visualize Output** launches **PQSMol** in view mode with the output file from the **PQS** calculation as an argument, see Chapter 3.

The Window menu

- **Segment** toggles on/off or repositions the *Segment window* frame. Selecting the appropriate option will either position the *Segment window* frame to the right of the *Build window*, position it to the left of the *Build window* or hide it entirely.
- **Info** toggles on/off the info window, Figure 2.32.



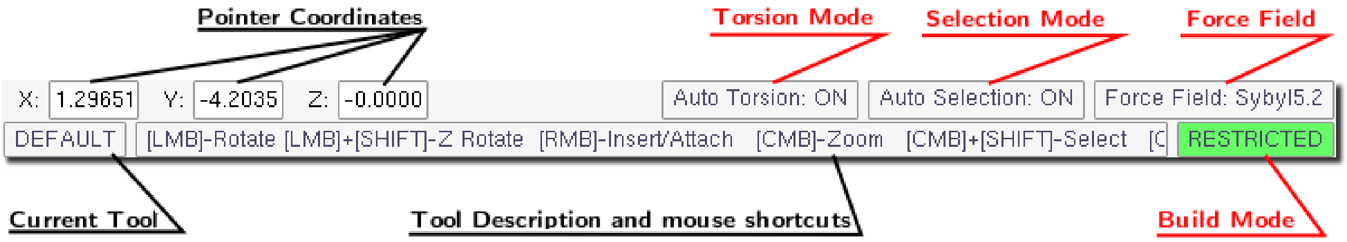
```
ATOM#  TYPE  SYBYL   UFF        X       Y       Z      Distance [  5,  2]        =  2.7245
  5     O    O.2     O_2      2.080   1.113  -0.500    Angle    [  5,  2,  6]     =278.1501
  2     N    N.3     N_3      0.061   1.112   1.329    Torsion  [  5,  2,  6, 10] =180.6373
  6     C    C.3     C_3     -1.216   0.222  -0.605    OP-Bend  [  5,  2,  6, 10] =  0.1619
 10     H    H       H_      -2.114   0.157   0.029
```

```
BOND#      ATOMS     ORDER   LENGTH
  8     [  O8,  C4]    1    1.330794    Angle   [  8,  6]      = 97.9501
  6     [  C3,  C4]    1    1.508364    Torsion [  8,  6,  7]  = 65.1042
  7     [  C3,  C6]    1    1.549739    OP-Bend [  8,  6,  7]  =-26.2291
```

Figure 2.32: Info window - atom info, top image; bond info - bottom image

The Info window displays information gathered by the info tool. The info tool can collect information about atoms, Figure 2.32 - top image, or bonds, Figure 2.32 - bottom image. If a single atom is selected by the info tool, the atom's number, atom's symbol, Sybyl5.2 and Universal atom types and coordinates are displayed. When a second atom is selected, the distance in Angströms, between the two atoms is displayed. Selection of a third atom shows the angle between the three atoms, and selection of a fourth gives the torsion and out-of-plane bend. If the info tool is used to select bonds, a single bond gives information about the bond number, the atoms it connects, bond type and bond length. Selection of a second bond gives the angle between the two bonds, and selection of a third shows the torsion and the out-of-plane bend.

2.1.3 Statusbar



X: 1.29651 Y: -4.2035 Z: -0.0000 Auto Torsion: ON Auto Selection: ON Force Field: Sybyl5.2

DEFAULT [LMB]-Rotate [LMB]+[SHIFT]-Z Rotate [RMB]-Insert/Attach [CMB]-Zoom [CMB]+[SHIFT]-Select [C RESTRICTED

Figure 2.33: Statusbar in build mode

The statusbar displays information about the current status of **PQSMol**, Figure 2.33. In the top left corner, the 3D coordinates of the mouse pointer in Angströms are shown. During the *add* operation, point (0,0,0) in the segment being inserted will be aligned with the mouse pointer coordinates. On the top right side of the statusbar the **Torsion Mode** and the **Selection Mode** are shown, as well as the current **Force Field**.

In the bottom left corner of the statusbar, the name of the **Current Tool** is displayed. The area to the right is the **Tool Description**, which displays information on how to use the tool. The acronyms *LMB*, *RMB* and *CMB* stand for *Left Mouse Button*, *Right Mouse Button* and *Center Mouse Button*, respectively. In the lower right corner the current **restriction mode** is displayed.

The **torsion mode**, **selection mode**, **force field** and the **restriction mode** can all be toggled via a mouse click in the corresponding entry in the statusbar.

2.1.4 Useful Shortcuts

- **Ctrl+O** Open File
- **Ctrl+S** Save File
- **Ctrl+Q** Quit
- **Ctrl+Z** Undo
- **Ctrl+Y** Redo
- **Ctrl+X** Cut
- **Ctrl+C** Copy
- **Ctrl+V** Paste
- **Ctrl+A** Select All
- **Ctrl+N** Select None
- **Ctrl+I** Inverse Selection
- **Ctrl+H** Hydrogen Fill

2.2 Segment window

The *Segment window* provides access to the various fragments and “building blocks” from which new molecular structures can be constructed. The top area of the *Segment window* is the *Segment buffer*. At any time, the *Segment buffer* stores and displays the segment which would be inserted into the *Build window*, if the user executes the *insert* operation. Immediately below the *Segment buffer* there are three tabs. These are labeled: **Building Blocks**, **Fragments** and **Clipboard**. The *Segment buffer* is used to display structures selected in all three tabs.

2.2.1 Building Blocks

The *Building Blocks tab* contains a periodic table of elements and a *Bond Configuration* frame. The availability of individual element buttons in the periodic table, as well as buttons in the *Bond Configuration* frame, depend on the current force field. Only elements that are defined in the current force field are available in the periodic table, and only the bond configurations known to the current force field are available in the *Bond Configuration* frame.

The currently selected basic "building block" appears in the *Segment buffer* and can be added to the build area; as shown, the default is an sp3-hybridized carbon. The force field type currently selected is shown in the statusbar of the *Build window*, see Figure 2.33; a click on this box will toggle between the Sybyl5.2 and Universal force fields. The current atom type is highlighted in the periodic table as a button with a green background; it is also displayed in large font above the periodic table.

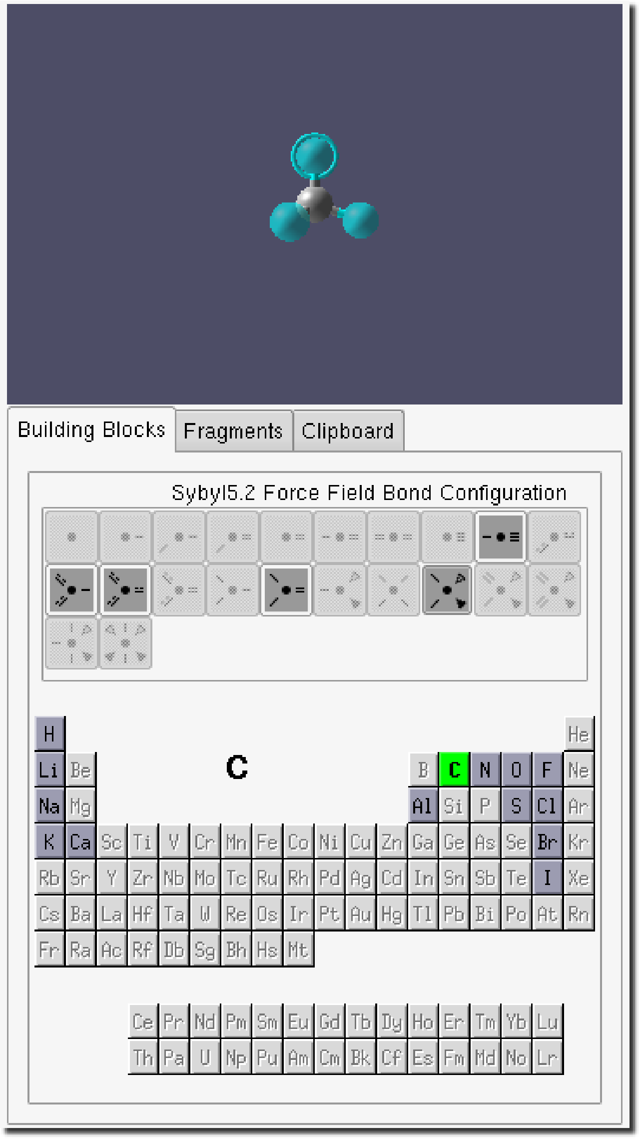


Figure 2.34: Segment window with the Sybyl5.2 force field selected

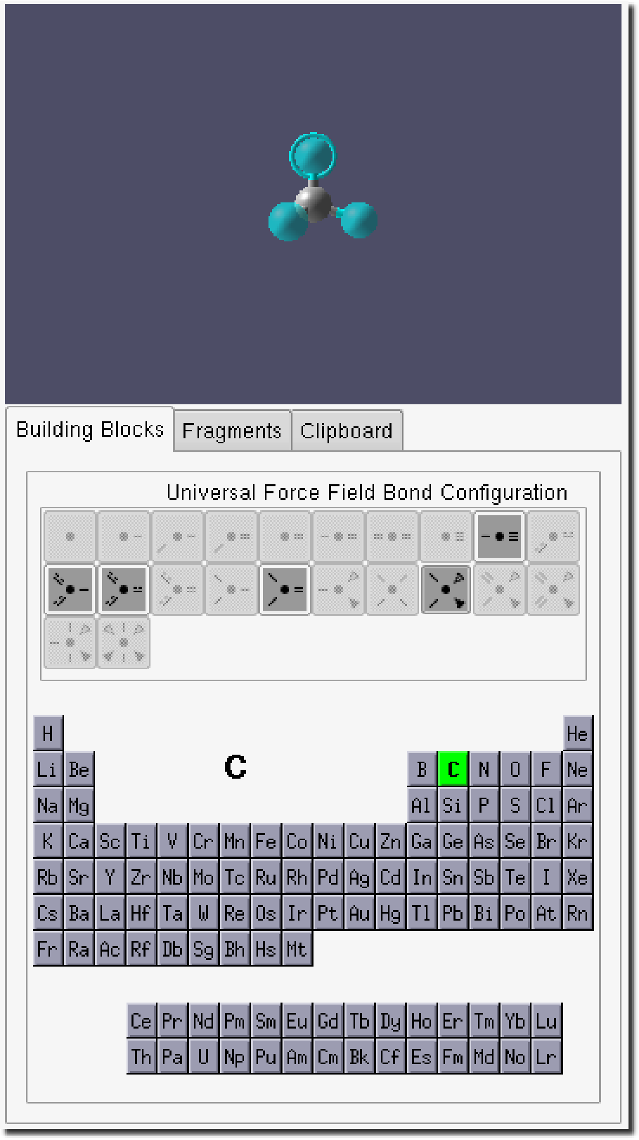


Figure 2.35: Segment window with the Universal force field selected

If the current force field is changed, the bond configuration list changes to contain all the building blocks for the current atom in the current force field. Also the periodic table changes, activating only the buttons for the elements defined in the current force field. Note the difference between Figures 2.35 (Sybyl5.2) and 2.35 (Universal). As the Universal force field covers essentially the entire periodic table, there are many more atom types (a total of 126) than for the Sybyl force field.

Note that, although all elements are covered in UFF, many metals must have a well-defined coordination (usually octahedral) or they will either not be properly recognized or distort significantly if a geometry optimization is attempted. In particular, UFF simply does not recognize a trigonal bipyramidal configuration around a central atom. On the other hand, although the Sybyl force field has far fewer atom types, there are default values for most parameters, and it can be used even for atoms for which it was not originally defined.

In these cases, "equilibrium" bond lengths and angles involving unknown atom types will be assumed to have values as derived from the original geometry. If you are building an organometallic system and have the geometry around the metal atom more-or-less correct, then you might be better off using the Sybyl force field to optimize the structure rather than UFF, even though the metal is recognized in UFF but not in Sybyl. Taking idealized geometrical parameters directly from the input geometry has a couple of side effects that the user needs to be aware of: (1) slightly different starting structures for the same system will optimize to different final geometries; and (2) if optimized structures are reoptimized, they will again change. For more details about the Sybyl 5.2 and Universal force fields, see the User's Guide to PQS.

2.2.2 Fragments

In addition to the building blocks, a large library of preconstructed molecular fragments can be accessed via the *Fragments tab* in the *Segment window*. The available fragments are the same for both the Sybyl5.2 and Universal force fields. Currently these are grouped under:

- AMINO ACIDS
- BICYCLIC
- CHAINS
- FUNCTIONAL GROUPS
- HETROCYLCIC
- LIGANDS
- MONOCYCLIC
- NUCLEOTIDES
- POLYCYCLIC
- SOLVENTS
- SUGARS
- ORGANOMETALLICS
- TS (Transition States)

All fragments except those in the last two categories have been preoptimized using the Sybyl force field. Fragments in the TS group are basically templates for common organic reaction transition states; they should not be optimized in the builder as neither force field is capable of handling transition structures.

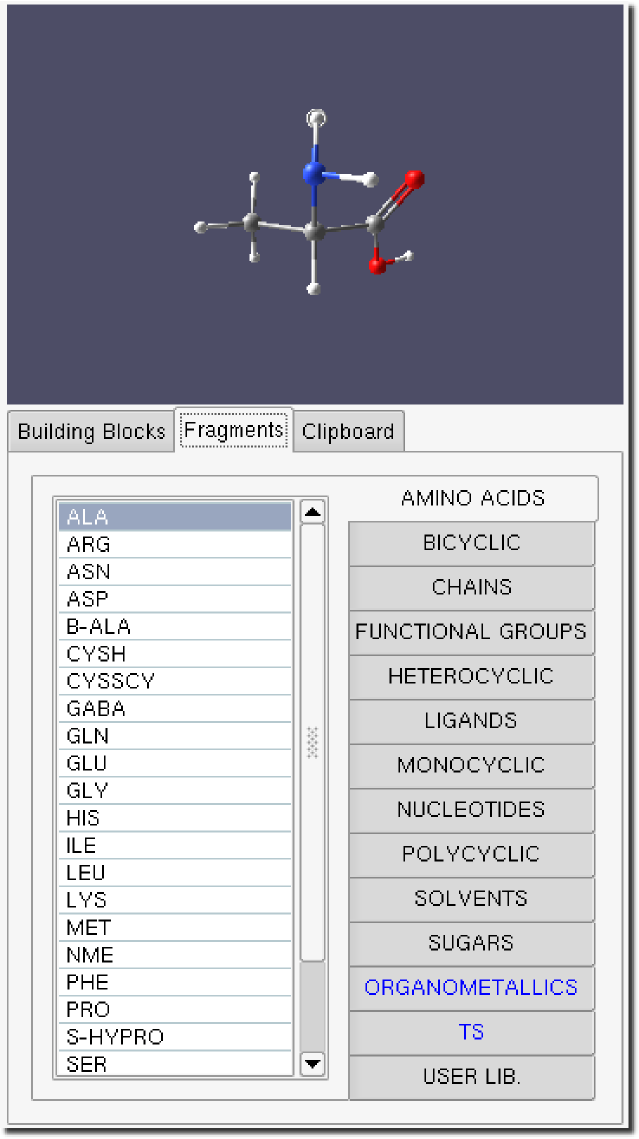
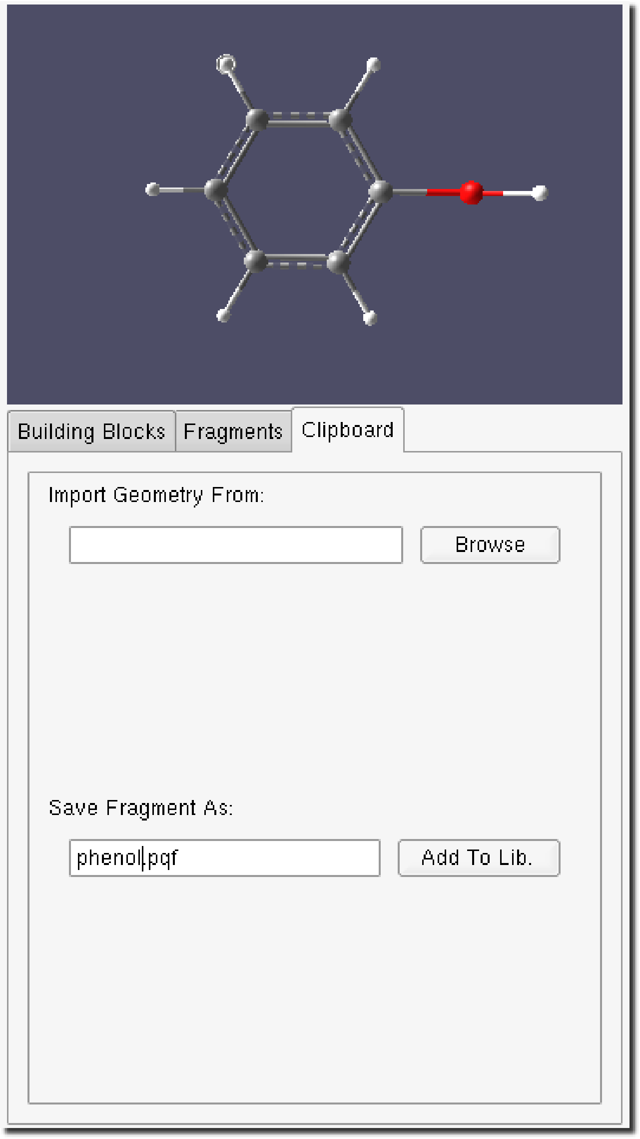


Figure 2.36: Segment buffer with the Fragments tab selected



Save Fragment As: phenol.pqf

Figure 2.37: Segment buffer with the Clipboard tab selected

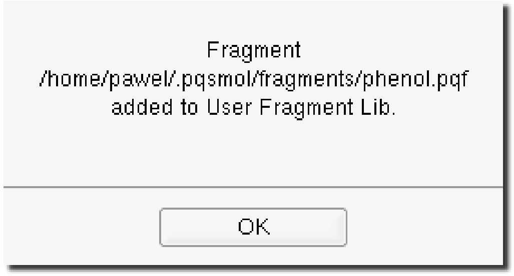
The actual fragments available under each category are accessible in a list on the left side of the window. Fragments selected from the list appear in the *Segment buffer*. As shown in Figure 2.36, when the *Fragments tab* is first selected, the first available AMINO-ACID (alanine) is displayed. Note the circle around one of the atoms (nominally a hydrogen atom). This is the attachment point for the fragment. It indicates where the new bond will form if the fragment is attached to an existing structure in the build area. The attachment point can be changed by clicking on another open atom in the current fragment.

2.2.3 Clipboard

The *Clipboard tab* allows you to manipulate segments copied or cut from the *Build window*. When a copy or cut operation takes place in the *Build window*, the *Clipboard tab* is automatically selected and the contents of the clipboard are updated and displayed in the *Segment buffer*. Once in the clipboard, a segment can be reused and pasted or attached back in the *Build window*, possibly multiple times.

The clipboard is also used for importing fragments into **PQSMol**. When a fragment is imported, it is first placed in the clipboard. This allows you to inspect the fragment and select its attachment point before using it in the *Build window*.

Additionally, the clipboard is an interface to the *USER LIB*rary. As well as using the predefined fragments, you can build your own fragments and store them in the *USER LIB*rary. The fragment can be constructed in the *Build window*, optimized and then selected in its entirety and copied into the clipboard. Once in the clipboard, Figure 2.37, it can be added to the user's own fragment library. The fragment has to be given a filename with a `.pqf` extension in the *Save Fragment As* text entry. The `.pqf` extension is the common extension for all stored fragments. The **Add To Lib.** button saves the file in the user's fragment library, producing the dialog shown in Figure 3.4. The fragment will now appear in the list under the *USER LIB* category.



Fragment
/home/pawel/.pqsmol/fragments/phenol.pqf
added to User Fragment Lib.

Figure 2.38: Addition to User Library confirmation dialog

Note: User Library fragments are stored by default in the user's home directory in `$HOME/.pqsmol/fragments/`. The default storage location can be changed by editing the line:

```
user_fragments $HOME/.pqsmol/fragments
```

in the system-wide `pqsmol.conf` configuration file.

2.3 Building Modes

There are three building modes in **PQSMol**:

- **Auto Torsion**
- **Auto Selection**
- **Restricted/Unrestricted mode**

The status of each mode is displayed in the statusbar, Figure 2.39

X: 2.87664 Y: 3.10961 Z: -0.0000 Auto Torsion: ON Auto Selection: ON Force Field: Sybyl5.2
ROTATE ABOUT A BOND [LMB] to select a rotation bond + [DRAG], double click to set, [SHIFT] + double c RESTRICTED

Figure 2.39: Statusbar with the Building Modes highlighted

All three modes may be toggled by either clicking in the appropriate area in the statusbar or activating the corresponding menu item: **Build→Auto Torsion**, **Build→Auto Selection**, and **Build→Mode**.

2.3.1 Auto Torsion

When the **Auto Torsion mode** is active, **PQSMol** attempts to find the minimal energy configuration for the resulting structure during the *attach* and *connect* operations. When a new segment is attached to the existing structure inside the build area, it is rotated around the attachment bond starting at a torsion of 0 degrees. The torsion angle is repeatedly incremented by a specified number of degrees (see Figure 2.29), until a full rotation is completed. At each point in the rotation the van der Waals energy is calculated using a specified **van der Waals Cutoff**, (see Figure 2.29). The segment is attached at the torsion angle with the lowest van der Waals energy.

Note: The **Auto Torsion** option affects the *attach* and *connect* operations only.

2.3.2 Auto Selection

When the **Auto Selection** building mode is active, **PQSMol** automatically selects the entire affected segment during the *move* and *reorient* operations, Figure 2.40 right image.

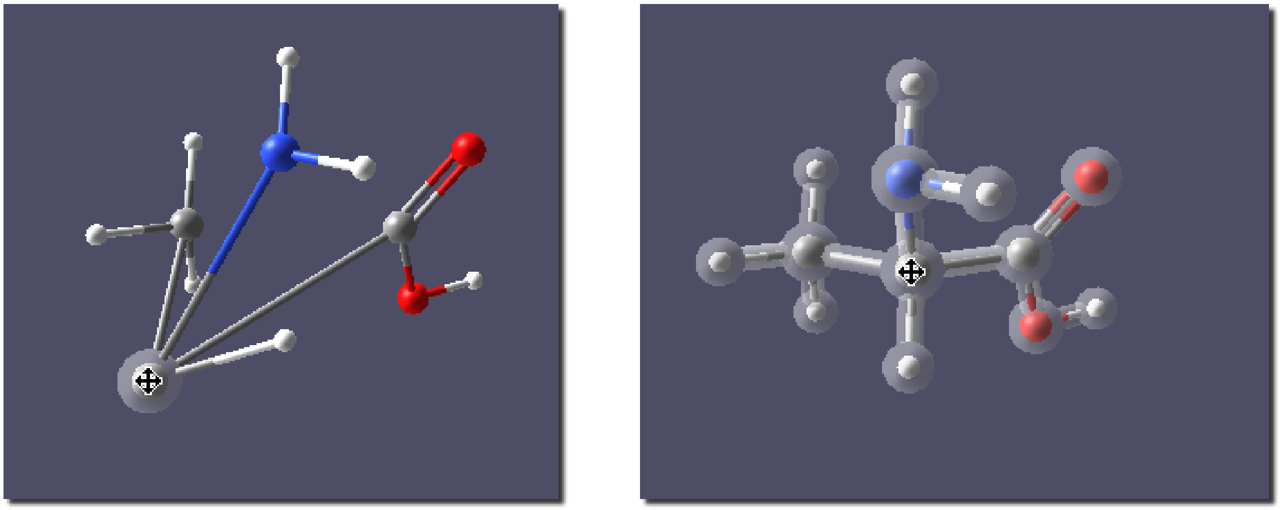


Figure 2.40: Move operation with Auto Selection off (left) and on (right)

The *move* operation will only modify atoms which are currently selected. If the **Auto Selection mode** is inactive and no selection is made, *move* will have no effect on the structure in the *Build window*. However, in this mode it is possible to make custom selections which do not involve all atoms in a given segment. This is illustrated in the left image of Figure 2.40, where only the center Carbon atom is selected and moved.

Note: The **Auto Selection** option affects the *move* and *reorient selection* operations only.

2.3.3 Restricted/Unrestricted

There are two restriction modes available in **PQSMol**: **restricted** and **unrestricted**. The two modes control the amount of freedom you have when constructing molecules. The **restricted mode** is the default mode of operation. In this mode, molecules can be constructed using only the well-defined building blocks that are recognized by either the **Sybyl5.2** or the **UFF** force field (see Figure 2.41, left image). This ensures that any molecule that is built can in fact be optimized using one or the other of these force fields.

You can select the restriction mode through the **Build→Mode** menu. A quicker way of changing the current restriction mode is to click on the area of the statusbar displaying the current restriction mode in the lower right corner, (see Figure 2.39).

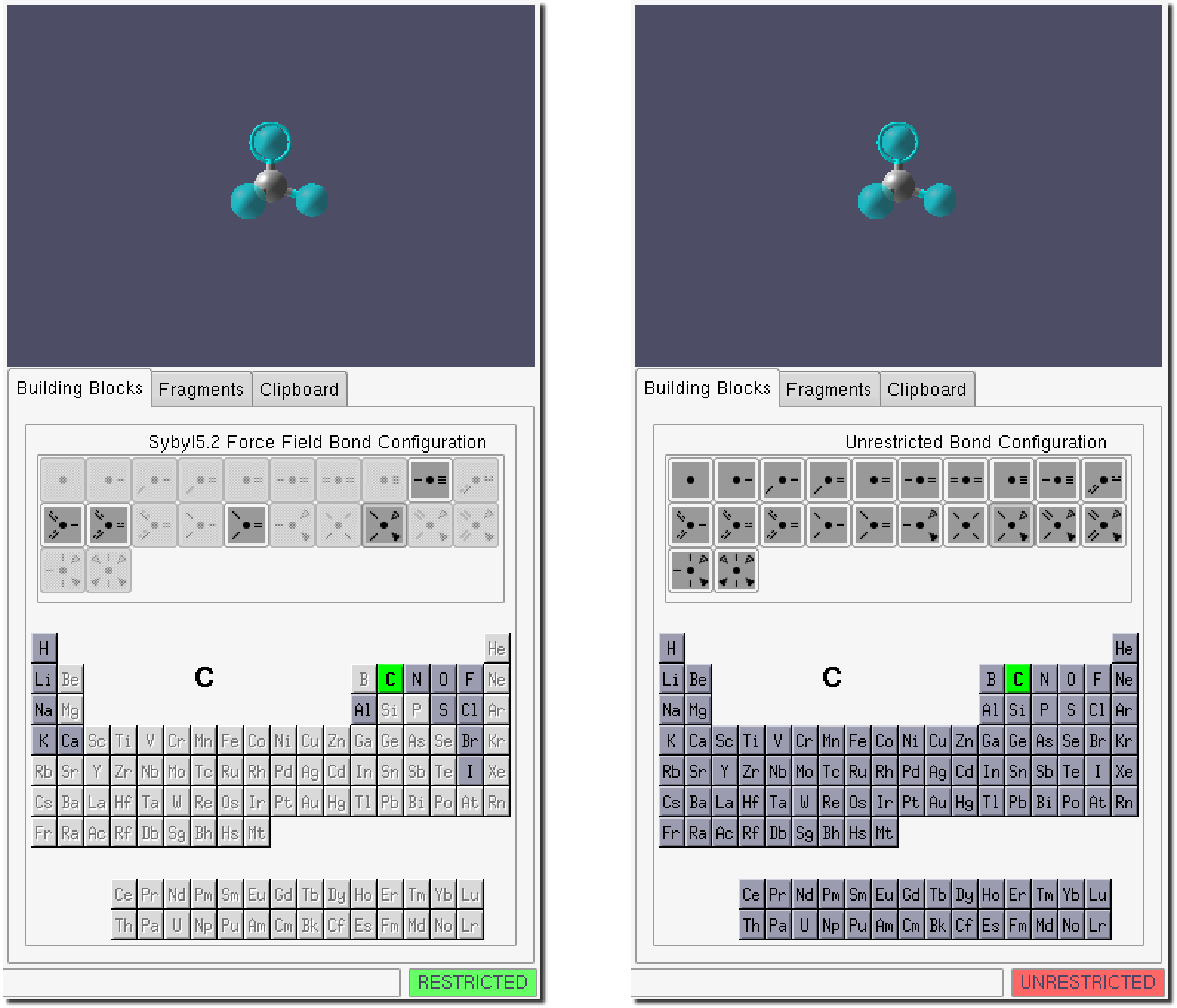


Figure 2.41: Segment window, in restricted mode (left) and in unrestricted mode (right).

In **unrestricted mode**, all generic structural motifs are accessible (see Figure 2.41, right image) and can be used with any atom in the periodic table. Thus you can construct a system containing, e.g., an octahedrally coordinated hydrogen atom. Additionally, you can add and delete valency "bonding") to any atom, increasing or decreasing the number of bonds that can be made to other atoms. The nature of a bond (single, double, aromatic etc...) can also be changed. The downside to being able to build almost anything is that, once you have switched to **unrestricted mode**, there is no guarantee that you will be able to optimize the geometry of your system, as many atom types may no longer be recognizable to the **Sybyl5.2** and the **UFF** force fields.

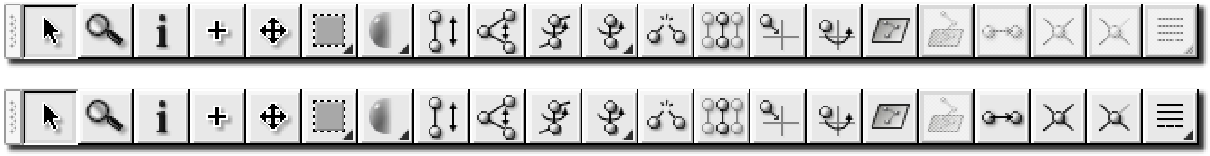


Figure 2.42: Lower toolbar, in restricted mode (top) and in unrestricted mode (bottom). Note the last four buttons in both images.

The **unrestricted mode** allows access to four additional tools, not available in the **restricted mode**: **Replace**, **Add Valence**, **Remove Valence** and **Bond Type**, (Figure 2.42).

2.4 Optimization

The optimizer in **PQSMol** is a bare-bones minimizer based on a direct BFGS-update of the (approximate) inverse Hessian matrix, with a preliminary energy-only line search if the starting structure has large residual forces. It cannot be used to optimize transition structures.

Geometry optimization is performed using the current force field. Available force fields are **Sybyl5.2** and **UFF**. The current force field is displayed in the upper left corner of the statusbar, Figure 2.43. You can select the current force field via **Optimize→Force Field** in the menubar, Figure 2.1.2

X: 2.87664 Y: 3.10961 Z: -0.0000 Auto Torsion: ON Auto Selection: ON Force Field: Sybyl5.2

ROTATE ABOUT A BOND [LMB] to select a rotation bond + [DRAG], double click to set, [SHIFT] + double c RESTRICTED

Figure 2.43: Statusbar with the current forcefield highlighted.

Tip: You can also change the current force field by clicking on the force field name in the statusbar.

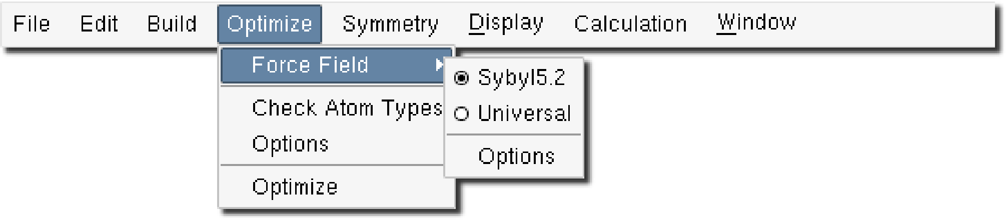


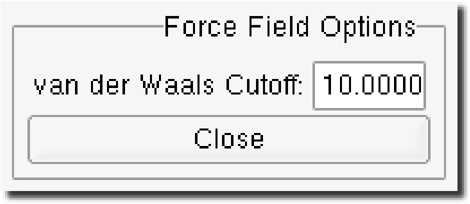
Figure 2.44: Optimize menu

The **Optimize** menu enables you to set the current force field, set the force field options, check and change the force field atom types, and set the optimization options.

Optimize→Optimize will start the optimization. This is equivalent to clicking the E↓ button in the upper toolbar.

2.4.1 Force Field Options

Force field options (currently just the van der Waals cutoff), are available in the menubar under **Optimize→Force Field→Options**, see Figure 2.45. The force fields in **PQSMol** do not have an Ewald summation (or equivalent) of all pair-wise van der Waals interactions; instead there is a simple cutoff (default 10 Angströms) beyond which the van der Waals terms are simply neglected. This value can be changed here.

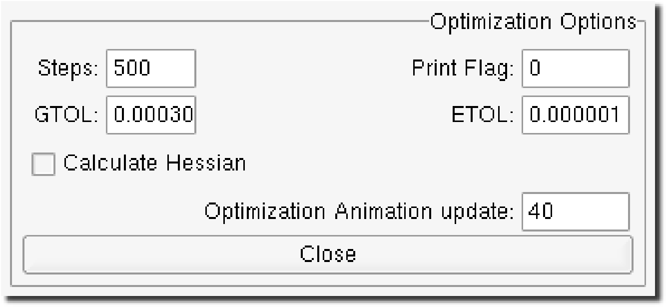


van der Waals Cutoff: 10.0000

Figure 2.45: Force Field Options window

2.4.2 Optimization Options

There are several optimization options available, Figure 2.46.



Steps: 500
Print Flag: 0
GTOL: 0.00030
ETOL: 0.000001
☐ Calculate Hessian
Optimization Animation update: 40

Figure 2.46: Optimization options

- **Steps** sets the number of optimization cycles (default 500)
- **GTOL** sets the convergence criterion for the root mean square gradient (default 0.0003)
- **ETOL** sets the convergence criterion on the change in energy from the previous cycle (default 10^{-6})
- **Print Flag** sets the verbose output level (for debugging only)
- **Calculate Hessian** calculates a starting Hessian matrix for the Sybyl5.2 force field *only* (there is no effect for the Universal force field)
- **Optimization Animation update** sets the number of cycles between geometry updates to the *Build window*. Setting this option to a value of 1 will cause a structure geometry update on every optimization cycle. A value of 0 will turn off optimization animation.

If both the **GTOL** and **ETOL** convergence criteria are satisfied or the maximum number of optimization cycles **Steps** has been exceeded, the optimization will stop. In line with similar criteria in the **PQS** program, **GTOL** and **ETOL** are measured in atomic units.

Checking the **Calculate Hessian** box will compute (by central-difference on the gradient) and invert the Hessian matrix before starting the optimization. This is rarely needed and is unlikely to speed up the optimization; it might be useful in cases where there appear to be convergence problems.

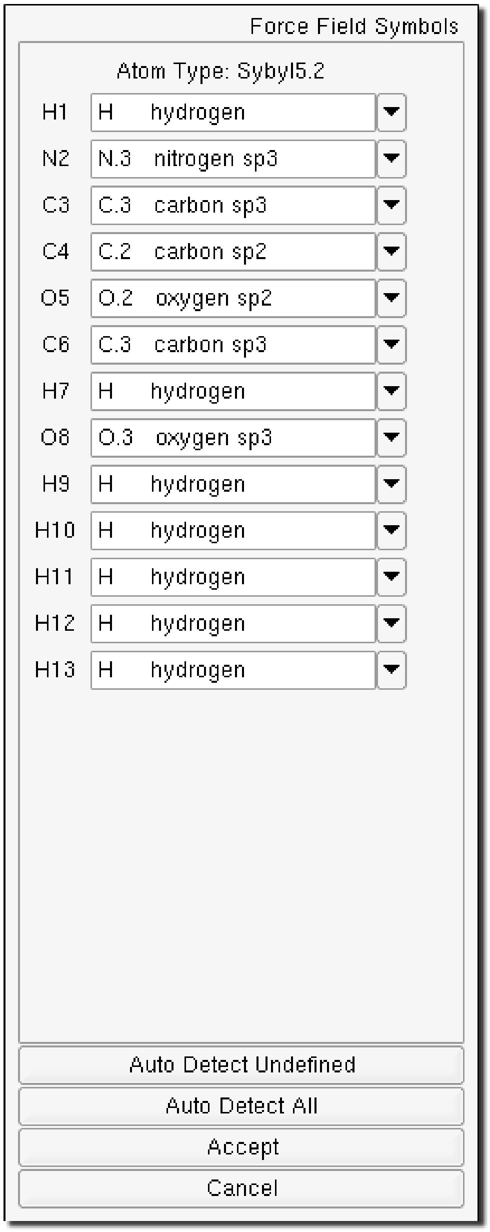
Normally the optimization will proceed "silently", i.e., with no print out. Setting the **Print Flag** (to a small integer value, the bigger the value the more print out) will write intermediate quantities such as the energy, RMS gradient and RMS displacement at each optimization cycle to filename `debug` in the current working directory. As the filename implies, this might help debug any apparent convergence problems.

Finally the **Optimization Animation update** gives the number of optimization cycles between each update of the geometry in the *Build window*. The default is to redisplay the geometry every 40 cycles. The final converged geometry is always displayed, in addition to intermediate geometries (depending on the number of cycles the optimization actually takes). Setting this to a smaller value increases the rate at which geometry changes are displayed. Note that redisplaying the geometry does take some time, especially for large systems, and too small a value will cause a noticeable slowdown in the apparent speed of the optimization.

2.4.3 Force Field Symbols

Geometry optimization is performed based on the force field atom type assigned to each atom. The Sybyl5.2 force field has 33 atom types defined for the following elements: Carbon, Nitrogen, Oxygen, Sulfur, Phosphorus, Hydrogen, Bromine, Chlorine, Fluorine, Iodine, Sodium, Lithium, Potassium, Calcium, Aluminum, and Silicon. Depending on the number of bonds and its environment, an atom of one type may be represented by multiple force field symbols. For example, available Carbon Sybyl force field types are: C.1, C.2, C.3, C.ar. The basic building blocks and the fragment library in **PQSMol** contain molecule segments with correct force field types defined for both Universal and Sybyl5.2 force field. However, when building molecules from fragments imported from foreign file formats, **PQSMol** will attempt to guess the force field types for the atoms in the imported geometries.

You can manually change the assigned force field symbol of each atom in the molecule by selecting **Optimize→Check Atom Types** in the main menu.



Atom Type: Sybyl5.2

H1	H	hydrogen
N2	N.3	nitrogen sp3
C3	C.3	carbon sp3
C4	C.2	carbon sp2
O5	O.2	oxygen sp2
C6	C.3	carbon sp3
H7	H	hydrogen
O8	O.3	oxygen sp3
H9	H	hydrogen
H10	H	hydrogen
H11	H	hydrogen
H12	H	hydrogen
H13	H	hydrogen

Figure 2.47: Force field symbols

The Force field symbol window, Figure 2.47, shows a list of all atoms and their assigned force field symbols. To manually change the force field symbol for a given atom, select a symbol from a drop down list on the right of the atom label. The list can include undefined atom types (which are acceptable in the Sybyl force field but not in Universal). Attempts can be made to automatically assign any atom types that are currently unknown by clicking on **Auto Detect Undefined**. In general this is only likely to occur if the structure was either imported or built in **unrestricted mode**. Clicking on **Auto Detect All** will force an automatic detection of *all* atoms in the system, whether defined or not.

Any changes to the existing atom types will only be implemented by pressing the the **Accept** button. The **Cancel** button restores the original force field atom types and cancels the operation.

> **Note:** Clicking inside the text entry area of any atom will highlight the corresponding atom in the *Build window*.

Tip: Turn on atom labels with the **Labels** button in the top menubar to visually identify all atoms.

2.5 Symmetry

The symmetrizer allows you to symmetrize a molecule whose geometry is not exactly symmetrical, and to determine the point group symmetry of the structure.

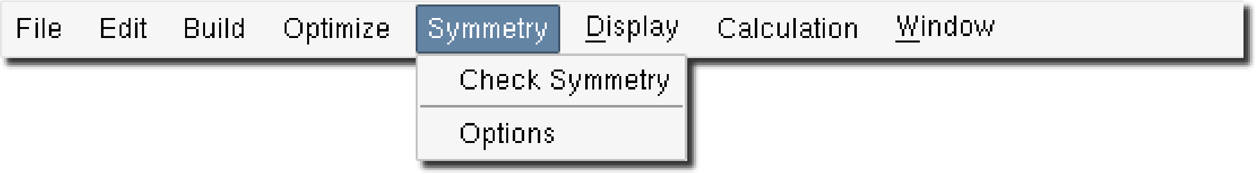
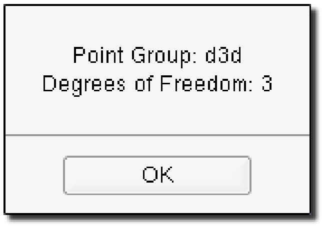


Figure 2.48: Symmetry menu

The **Symmetry→ Check Symmetry** will execute the symmetrizer. This is equivalent to clicking the button in the upper toolbar.



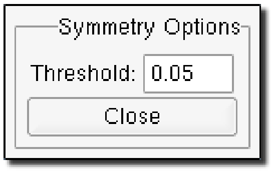
```
Point Group: d3d
Degrees of Freedom: 3
```

Figure 2.49: Symmetry output

If any symmetry is found, the geometry will be symmetrized so that the structure does indeed conform fully to the particular point group. If it seems as if the system should have symmetry, but check symmetry fails to find any (i.e., the point group is C1) even with a large threshold, then manipulating the structure by hand, e.g., ensuring that groups of atoms are in the same plane, or reoptimizing with tighter optimization thresholds, may help to locate the desired symmetry.

2.5.1 Symmetry Options

Symmetry options are available in the menubar under **Symmetry→Options**, see Figure 2.50.



Threshold: 0.05

Figure 2.50: Symmetry Options window

The only symmetry option is the symmetry **Threshold**. The code used to determine the point group symmetry is essentially a copy of the same code that is in the **PQS** program. This attempts to recognize symmetry planes and axes of symmetry relative to the center of mass of the system, and to locate atoms that are symmetry-equivalent within the given threshold. The higher the threshold, the more likely that symmetry will be found; however setting the threshold too high may find symmetry that is really not present. Setting the threshold to a value greater than 1.0 is not recommended.

2.6 PQS Calculation

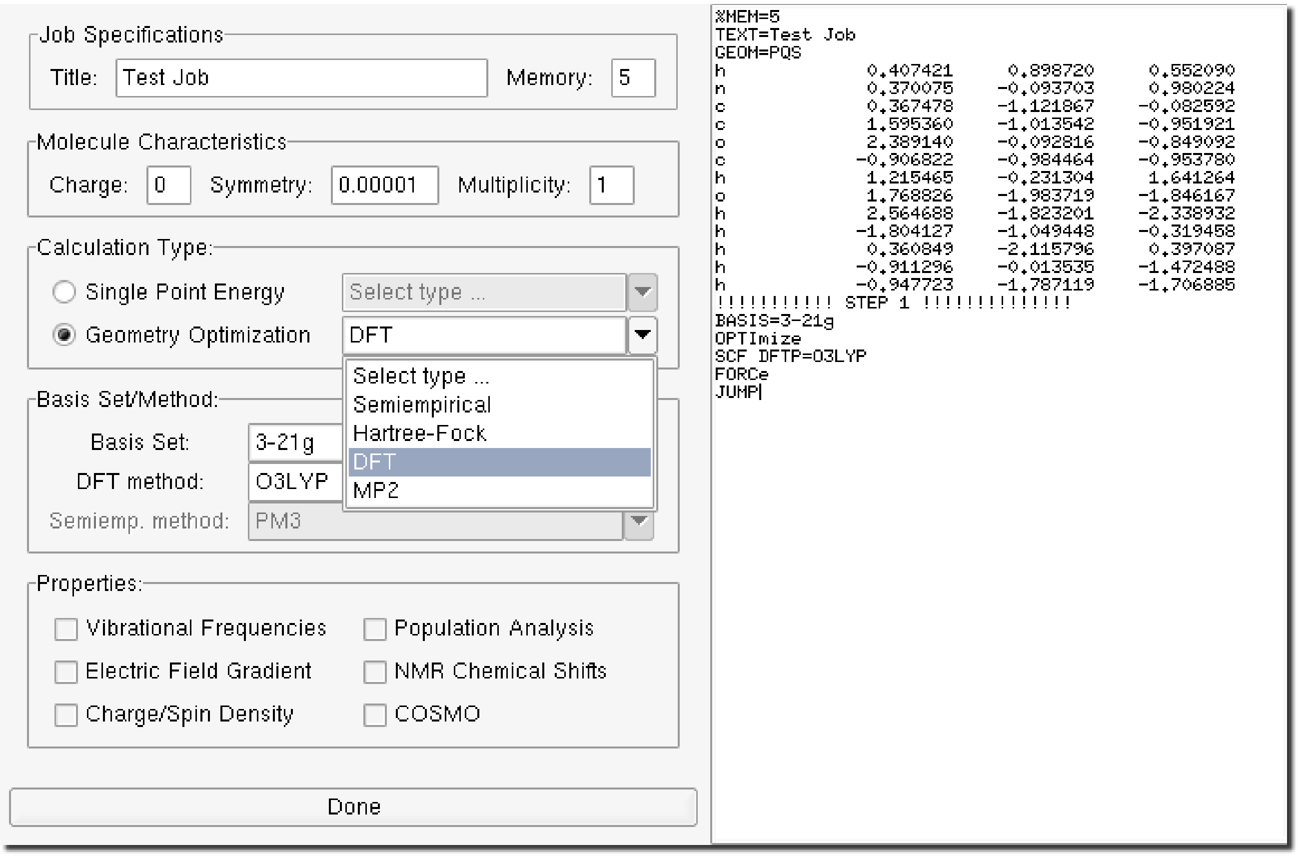
The procedure for running a PQS calculation involves the following steps:

- building a molecule
- creating a PQS input file
- submitting the PQS job
- displaying calculation results

2.6.1 PQS input file

The PQS input file contains the geometrical structure and a series of commands, instructing the program to perform calculations on the given structure. PQS input files use a set of specific keywords and a strict syntax. **PQSMol** assists in creating PQS input files through the **Job Parameters** window. The **Calculation→Job Input** menu item opens the **Job Parameters** window, Figure 2.51.

Note: If the structure in the *Build window* (the system you are about to do the calculation on) has not previously been saved as a *.pqb* file, you will be prompted to save it as such (with a default filename corresponding to the empirical formula).

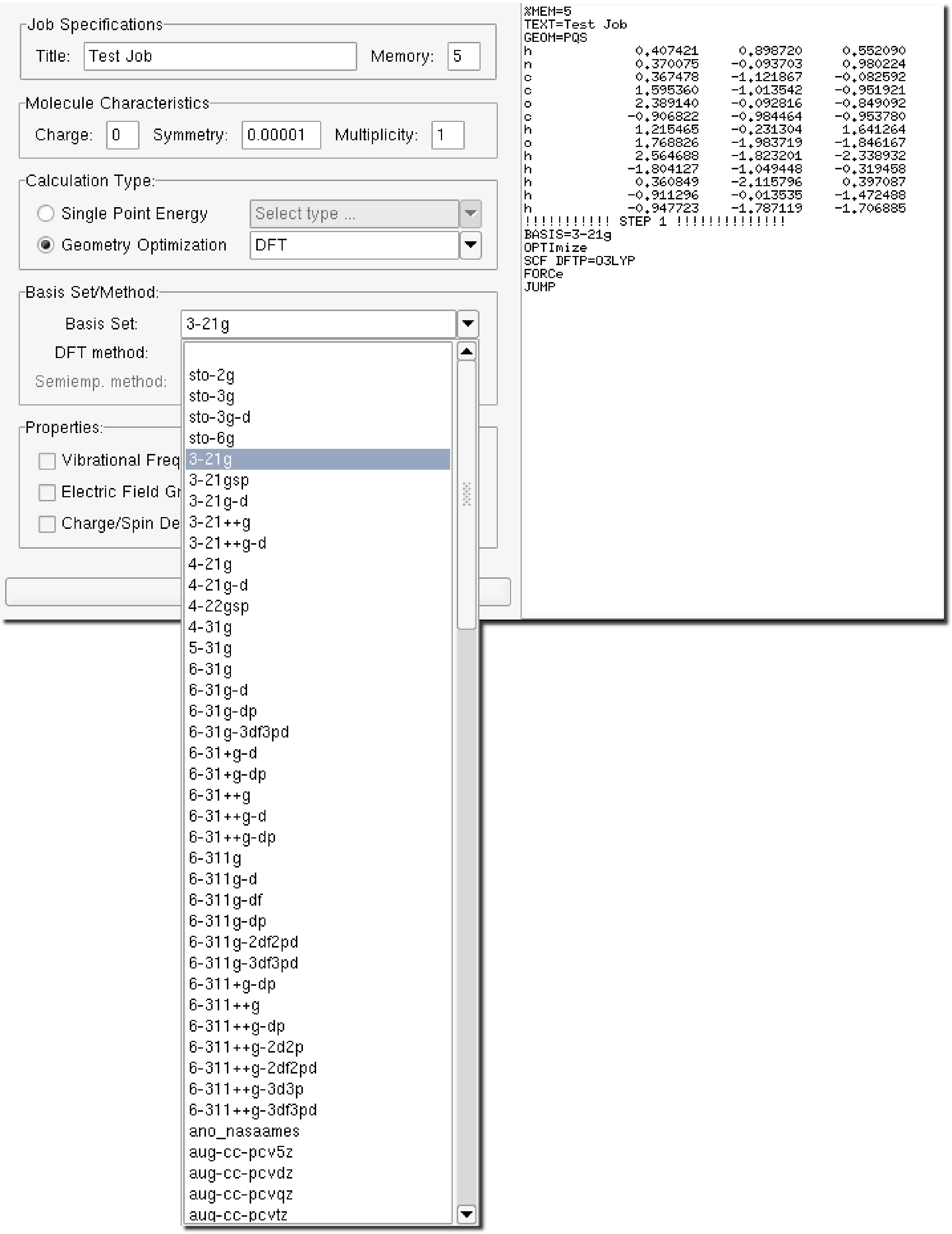


Title: Test Job
Memory: 5
Charge: 0
Symmetry: 0.00001
Multiplicity: 1
● Geometry Optimization: DFT
Basis Set: 3-21g
DFT method: O3LYP
Semiemp. method: PM3
☐ Vibrational Frequencies
☐ Electric Field Gradient
☐ Charge/Spin Density
☐ Population Analysis
☐ NMR Chemical Shifts
☐ COSMO

```
%MEM=5
TEXT=Test Job
GEOM=PQS
h             0.407421     0.898720     0.552090
n             0.370075    -0.093703     0.980224
c             0.367478    -1.121867    -0.082592
c             1.595360    -1.013542    -0.951921
o             2.389140    -0.092816    -0.849092
c            -0.906822    -0.984464    -0.953780
h             1.215465    -0.231304     1.641264
o             1.768826    -1.983719    -1.846167
h             2.564688    -1.823201    -2.338932
h            -1.804127    -1.049448    -0.319458
h             0.360849    -2.115796     0.397087
h            -0.911296    -0.013535    -1.472488
h            -0.947723    -1.787119    -1.706885
!!!!!!!!!!! STEP 1 !!!!!!!!!!!!!!
BASIS=3-21g
OPTImize
SCF DFTP=O3LYP
FORCe
JUMP
```

Figure 2.51: Job Parameters window - calculation type

Initially just the current geometry will be displayed in the input file in the text area on the right. Filling in various options in the window on the left will add lines and keywords into the input file; for example, whatever is typed in the Title box will appear just above the geometry in the input file on the right. The entries in *Job Specifications* and *Molecule Characteristics* require data to be typed in to make changes, those in *Calculation Type* and *Basis Set/Method* involve pulldown menus, and those in *Properties* are simple check boxes.


Job Specifications
Title: Test Job
Memory: 5

Molecule Characteristics
Charge: 0
Symmetry: 0.00001
Multiplicity: 1

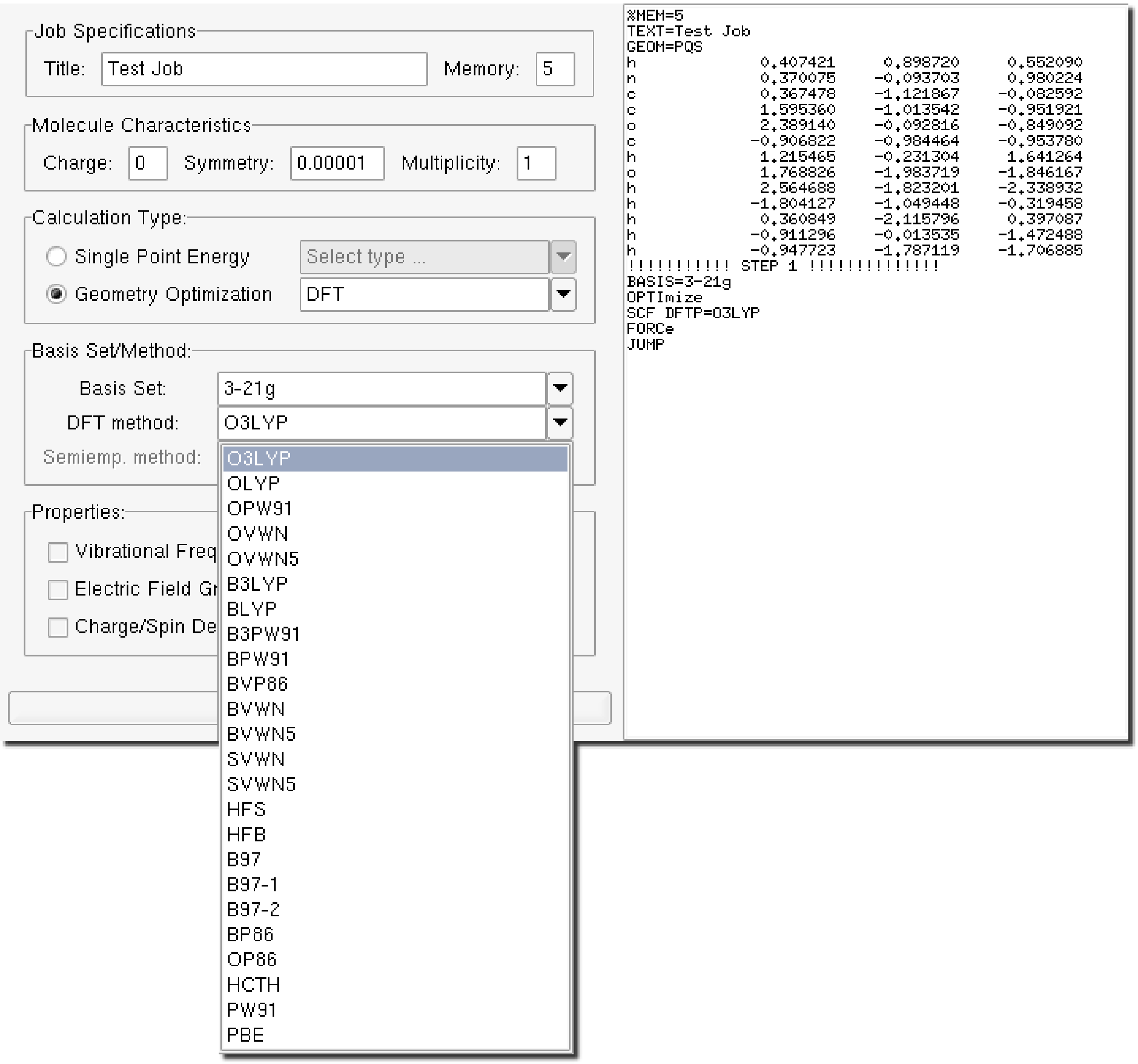
Calculation Type:
○ Single Point Energy
● Geometry Optimization
DFT

Basis Set/Method:
Basis Set: 3-21g

```
%MEM=5
TEXT=Test Job
GEOM=PQS
h               0.407421     0.898720     0.552090
n               0.370075    -0.093703     0.980224
c               0.367478    -1.121867    -0.082592
c               1.595360    -1.013542    -0.951921
o               2.389140    -0.092816    -0.849092
c              -0.906822    -0.984464    -0.953780
h               1.215465    -0.231304     1.641264
o               1.768826    -1.983719    -1.846167
h               2.564688    -1.823201    -2.338932
h              -1.804127    -1.049448    -0.319458
h               0.360849    -2.115796     0.397087
h              -0.911296    -0.013535    -1.472488
h              -0.947723    -1.787119    -1.706885
!!!!!!!!!!! STEP 1 !!!!!!!!!!!!!!
BASIS=3-21g
OPTImize
SCF DFTP=O3LYP
FORCe
JUMP
```

Figure 2.52: Job Parameters window - basis set

As shown above in Figure 2.52, a *Geometry Optimization* has been chosen and *DFT* has been selected from among the available calculation methods. The basis set can be selected from a pulldown menu. There are a large number of choices which cover all of the basis sets stored in the PQS basis library (in the *$PQS-ROOT/BASDIR* directory). The selected basis set will appear in the Basis Set box and will also be added to the input file on the right.



Job Specifications
Title: Test Job
Memory: 5

Molecule Characteristics
Charge: 0
Symmetry: 0.00001
Multiplicity: 1

Calculation Type:
○ Single Point Energy — Select type ...
● Geometry Optimization — DFT

Basis Set/Method:
Basis Set: 3-21g
DFT method: O3LYP
Semiemp. method:

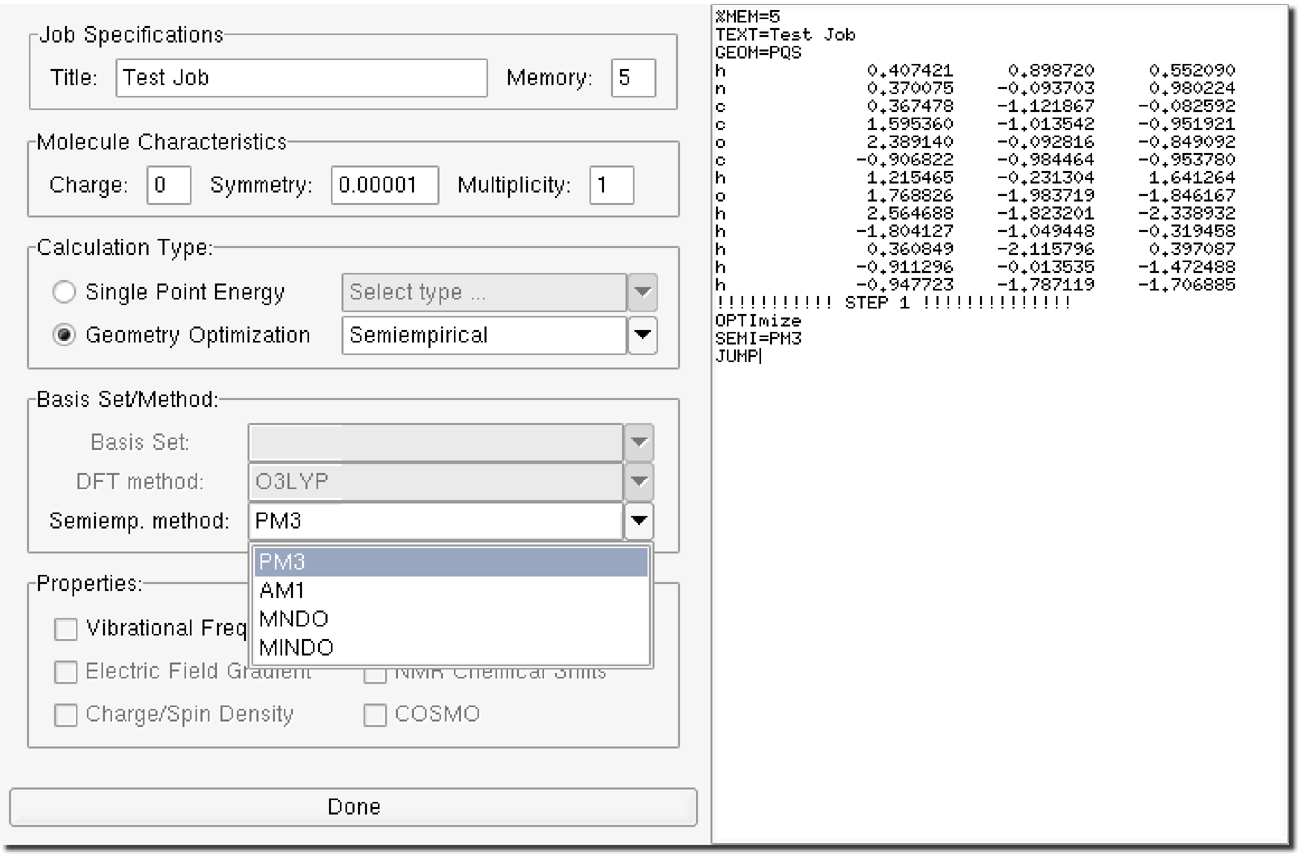
Properties:
☐ Vibrational Freq
☐ Electric Field Gr
☐ Charge/Spin De

```
%MEM=5
TEXT=Test Job
GEOM=PQS
h              0.407421     0.898720     0.552090
n              0.370075    -0.093703     0.980224
c              0.367478    -1.121867    -0.082592
c              1.595360    -1.013542    -0.951921
o              2.389140    -0.092816    -0.849092
c             -0.906822    -0.984464    -0.953780
h              1.215465    -0.231304     1.641264
o              1.768826    -1.983719    -1.846167
h              2.564688    -1.823201    -2.338932
h             -1.804127    -1.049448    -0.319458
h              0.360849    -2.115796     0.397087
h             -0.911296    -0.013535    -1.472488
h             -0.947723    -1.787119    -1.706885
!!!!!!!!!!! STEP 1 !!!!!!!!!!!!!!
BASIS=3-21g
OPTImize
SCF DFTP=O3LYP
FORCe
JUMP
```

Figure 2.53: Job Parameters window - density functional

After selecting the basis set, the density functional can be selected from a list of commonly available functionals, Figure 2.53. The default is `O3LYP`.

Whichever functional is finally selected will appear in the `DFT Method` box and also in the input file on the right.



Job Specifications

Title: Test Job

Memory: 5

Molecule Characteristics

Charge: 0

Symmetry: 0.00001

Multiplicity: 1

Calculation Type:

○ Single Point Energy — Select type ...

● Geometry Optimization — Semiempirical

Basis Set/Method:

Basis Set:

DFT method: O3LYP

Semiemp. method: PM3

Properties:

☐ Vibrational Freq

☐ Electric Field Gradient

☐ Charge/Spin Density

☐ COSMO

```
%MEM=5
TEXT=Test Job
GEOM=PQS
h           0.407421     0.898720     0.552090
n           0.370075    -0.093703     0.980224
c           0.367478    -1.121867    -0.082592
c           1.595360    -1.013542    -0.951921
o           2.389140    -0.092816    -0.849092
c          -0.906822    -0.984464    -0.953780
h           1.215465    -0.231304     1.641264
o           1.768826    -1.983719    -1.846167
h           2.564688    -1.823201    -2.338932
h          -1.804127    -1.049448    -0.319458
h           0.360849    -2.115796     0.397087
h          -0.911296    -0.013535    -1.472488
h          -0.947723    -1.787119    -1.706885
!!!!!!!!!!! STEP 1 !!!!!!!!!!!!!!
OPTImize
SEMI=PM3
JUMP
```

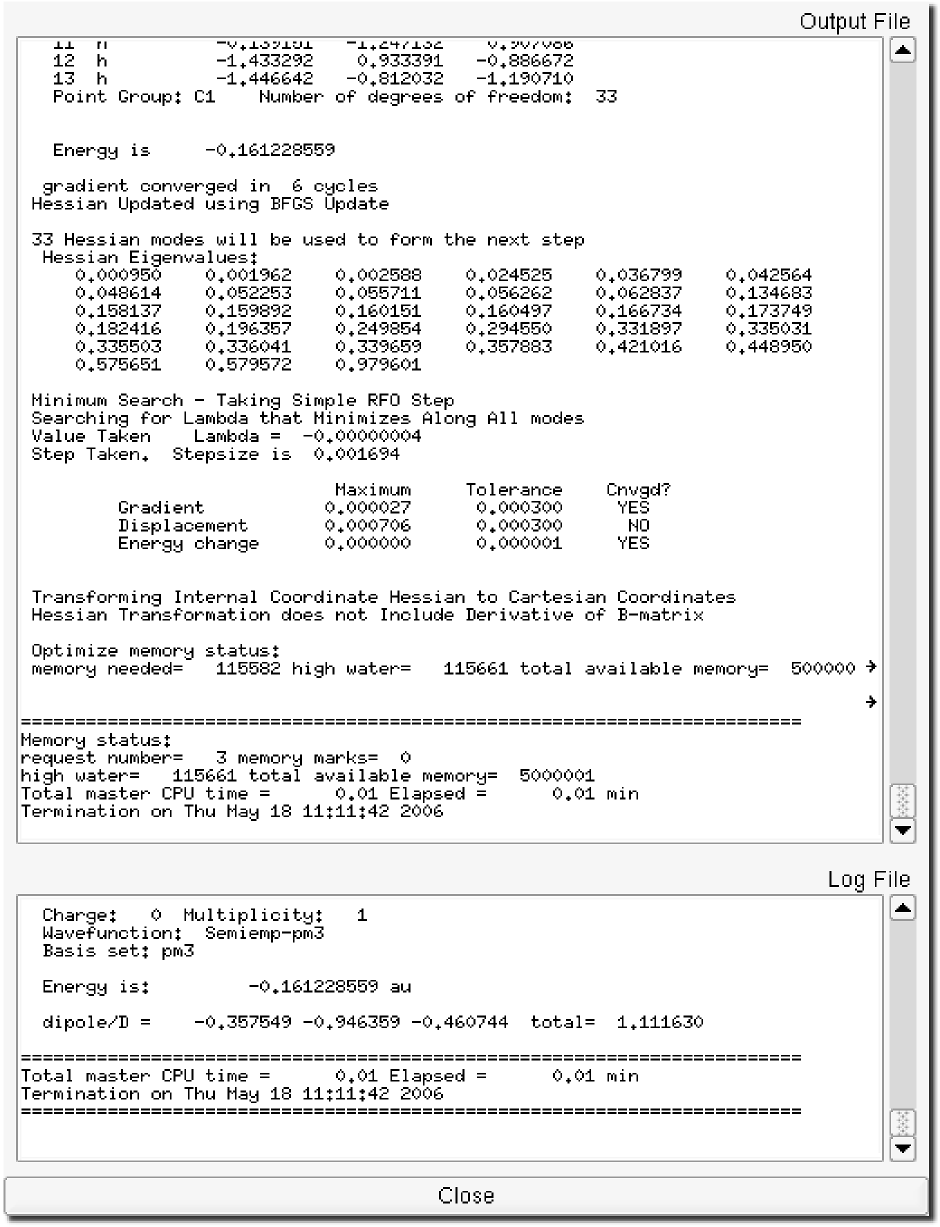
Figure 2.54: Job Parameters window - semiempirical

If `Semiempirical` had been selected instead of `DFT`, Figure 2.54, then no basis set selection is required and the desired semiempirical method can be selected from the corresponding pulldown menu. Note that the Properties that can be selected depend on the calculation type, and unavailable properties are grayed out. For semiempirical wavefunctions, most of the properties can no longer be selected.

The window containing what will become the input file can be edited by hand. Simply move the mouse pointer to the desired location in the window, click and start typing. Note that anything typed in may be deleted if further selections are made in the left hand window, so you should only edit the input file when you have made all the major job selections.

2.6.2 Job submission

Once the input file has been prepared, the **Calculation→Submit Job** menu item will submit the job. This will be serial only and will run in the background. If so configured, **PQSMOL** may also submit parallel jobs to run in the background or to a queuing system such as SGE, DQS or PBS (see following subsection).



```
   12  h          -1.433292    0.933391   -0.886672
   13  h          -1.446642   -0.812032   -1.190710
   Point Group: C1    Number of degrees of freedom:  33


   Energy is     -0.161228559

  gradient converged in  6 cycles
 Hessian Updated using BFGS Update

 33 Hessian modes will be used to form the next step
  Hessian Eigenvalues:
     0.000950    0.001962    0.002588    0.024525    0.036799    0.042564
     0.048614    0.052253    0.055711    0.056262    0.062837    0.134683
     0.158137    0.159892    0.160151    0.160497    0.166734    0.173749
     0.182416    0.196357    0.249854    0.294550    0.331897    0.335031
     0.335503    0.336041    0.339659    0.357883    0.421016    0.448950
     0.575651    0.579572    0.979601

 Minimum Search - Taking Simple RFO Step
 Searching for Lambda that Minimizes Along All modes
 Value Taken    Lambda =  -0.00000004
 Step Taken.  Stepsize is  0.001694

                          Maximum     Tolerance    Cnvgd?
         Gradient        0.000027      0.000300     YES
         Displacement    0.000706      0.000300      NO
         Energy change   0.000000      0.000001     YES


 Transforming Internal Coordinate Hessian to Cartesian Coordinates
 Hessian Transformation does not Include Derivative of B-matrix

 Optimize memory status:
 memory needed=   115582 high water=   115661 total available memory=  500000


========================================================================
Memory status:
request number=   3 memory marks=  0
high water=   115661 total available memory=  5000001
Total master CPU time =      0.01 Elapsed =      0.01 min
Termination on Thu May 18 11:11:42 2006
```

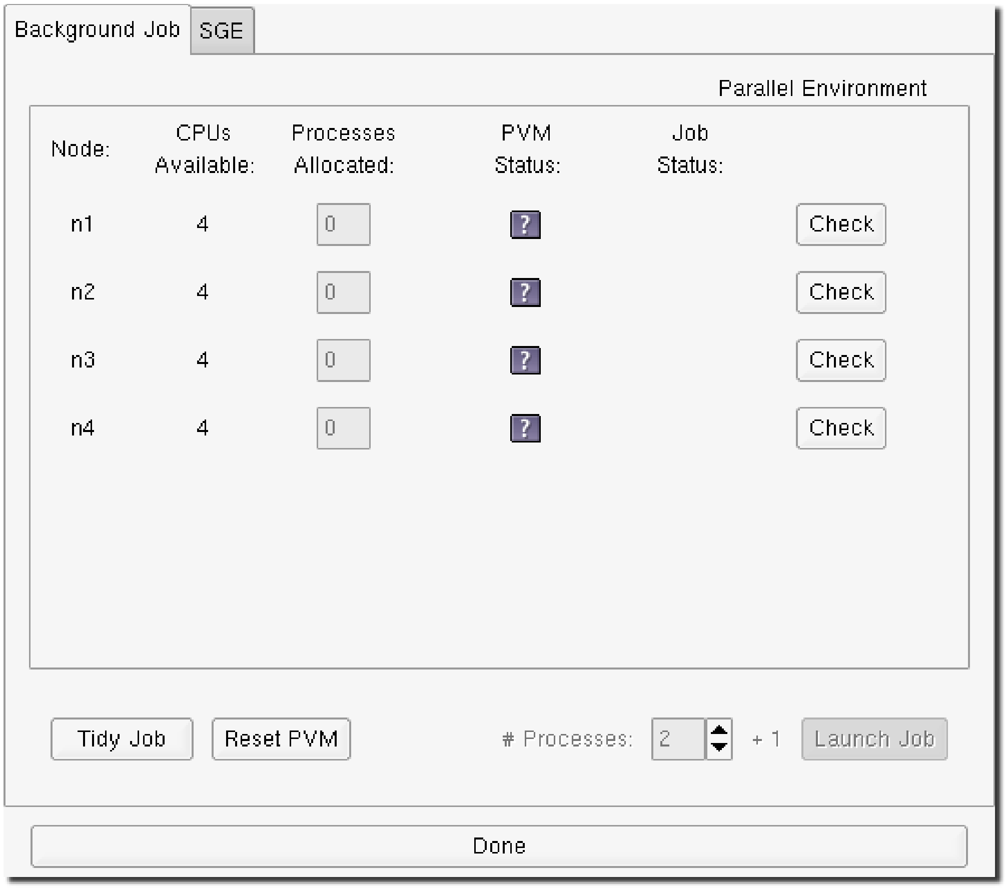
```
  Charge:   0  Multiplicity:   1
  Wavefunction:  Semiemp-pm3
  Basis set: pm3

  Energy is:         -0.161228559 au

  dipole/D =    -0.357549 -0.946359 -0.460744  total=  1.111630

========================================================================
Total master CPU time =      0.01 Elapsed =      0.01 min
Termination on Thu May 18 11:11:42 2006
========================================================================
```

Figure 2.55: Job Output window

Following job submission, the **Job Output** window (Figure 2.55) will automatically open, displaying both the output file (upper window) and the summary log file (lower window). Both of these windows will be updated in real time. When the job completes successfully, the Visualize Output window automatically opens, allowing post-job visualization.

Parallel Job submission

This feature allows a job to be submitted in parallel to the background or to the SGE job queue (assuming it is configured and is available on your system) using the Parallel Virtual Machine (PVM) software. A window similar to the one in Figure 2.56 appears (the exact details are system-dependent).



Node:	CPUs Available:	Processes Allocated:	PVM Status:	Job Status:	
n1	4	0	?		Check
n2	4	0	?		Check
n3	4	0	?		Check
n4	4	0	?		Check

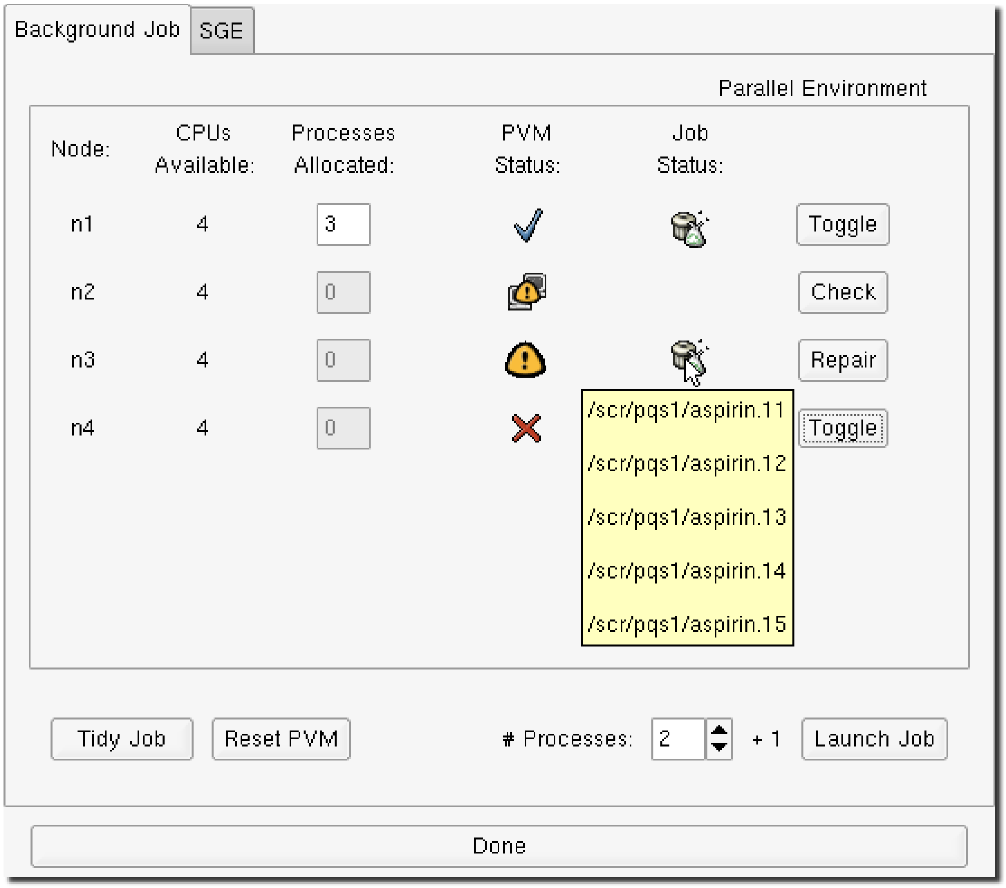
\# Processes: 2 + 1

Figure 2.56: Parallel Job Submission window - background job, initial view

All configured nodes are listed in the **Background Job** tab, Figure 2.56. Each row in the list contains the node name, the number of available CPUs on the node, an entry containing the number of processes allocated to your job (you can allocate more processes than there are CPUs, but this is not advisable), an icon representing the state of the PVM, an icon representing the state of the current job and a status button. Initially, the PVM status of each node is represented with a question mark icon and the status button is labeled **Check**. This indicates that the state of each node is unknown. To check the status of a given node click on the **Check** button in the corresponding row.

? status unknown
⚠ no connection
⚠ PVM error
✗ PVM off
✓ PVM on
⚙ PQS job executing
🗑 PQS scratch files present
🗐 PQS output present
🗐 PQS output and scratch files present

Figure 2.57: Background Job icon legend



Node:	CPUs Available:	Processes Allocated:	PVM Status:	Job Status:	
n1	4	3	✓		Toggle
n2	4	0	⚠		Check
n3	4	0	⚠		Repair
n4	4	0	✗		Toggle

/scr/pqs1/aspirin.11
/scr/pqs1/aspirin.12
/scr/pqs1/aspirin.13
/scr/pqs1/aspirin.14
/scr/pqs1/aspirin.15

Processes: 2 + 1

Figure 2.58: Parallel Job Submission window - background job, nodes checked

Figure 2.58 shows the status of the cluster after the **Check** button has been clicked for each node. In this example node `n1` has a check mark icon, indicating that a PVM daemon is running on that node. The additional icon of a garbage can in the *Job Status* column, indicates that there are *scratch* files (temporary files left over from a previous PQS calculation) on that node. The label of the status button for node `n1` changes to **Toggle**. This means that there is a connection to that node and the state of the PVM on node `n1` can be toggled (i.e., switched on and off) by clicking on the **Toggle** button.

The icon shown for node `n2` indicates no connection to that node (the “ping” command did not receive a response from that node). Notice that the label on the status button remains unchanged. Clicking on the **Check** button will cause another attempt to “ping” the node.

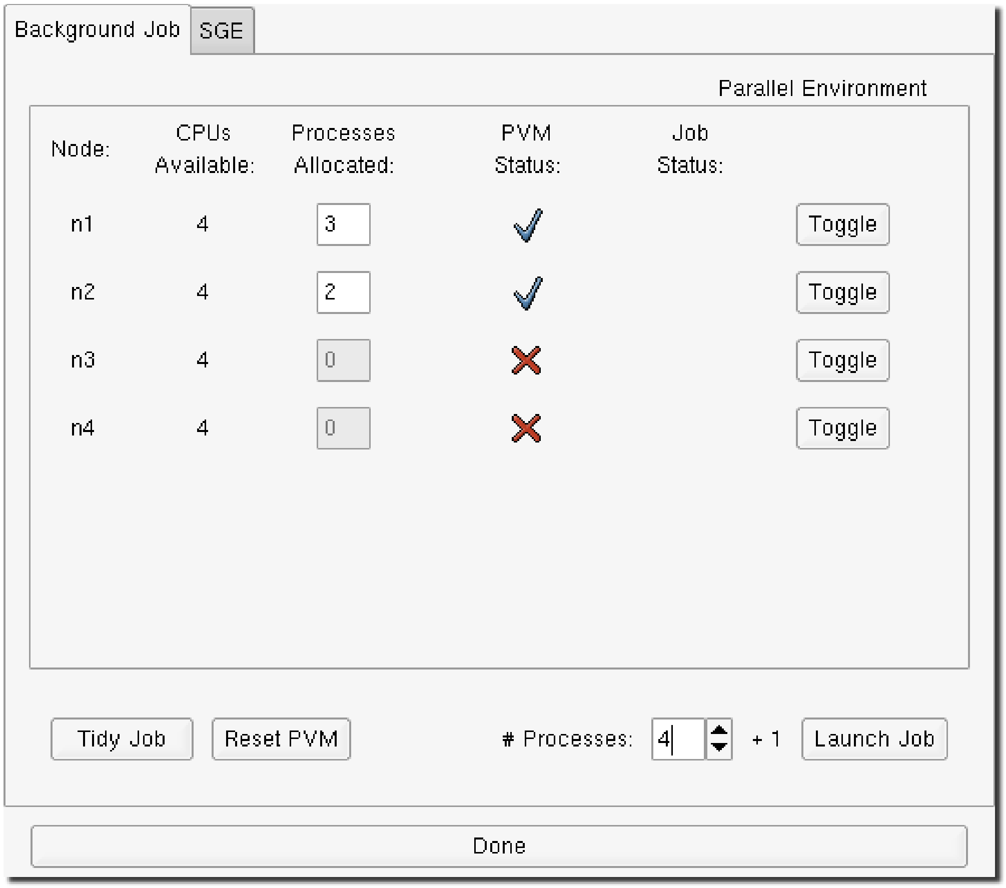
The icon shown for node `n3` indicates a problem with PVM on that node. This is a result of more than one PVM daemon executing on the node. The status button for this node is labeled **Repair**. If clicked, it will execute a command which will kill all running PVM daemons on that node and clean the temporary PVM directory.

The icons for node `n4` show that the PVM daemon is not running and that there are *scratch* files present on that node. The status button is labeled **Toggle** and if clicked will add this node to the PVM. Refer to Figure 2.57 for a complete list of icons and their meanings.

Tip: You can move the mouse pointer over the garbage icon to display a list of scratch files, as shown in Figure 2.58 for node `n4`.

Since at least one node is now a part of the PVM (node `n1`), the **Launch Job** button and the *# Processes* entry box become active; compare Figures 2.56 and 2.58. All PVM processes, in our example three (two computation processes + the master process), are scheduled to run on the only available node in the PVM – node `n1`.

Note: A parallel PQS job is composed of multiple computing processes and one master process. The master process performs little or no computation. It simply distributes the workload among the computing processes and gathers the results. It is necessary to schedule this additional job in PVM. This means that a two process parallel PQS job is in fact a *three* process PVM job. The number entered in the # *Processes* entry box in the job submission window refers to the number of computing (slave) processes only.



Node:	CPUs Available:	Processes Allocated:	PVM Status:	Job Status:	
n1	4	3	✓		Toggle
n2	4	2	✓		Toggle
n3	4	0	✗		Toggle
n4	4	0	✗		Toggle

Processes: 4 + 1

Figure 2.59: Parallel Job Submission window - background job, nodes ready

Figure 2.59 shows the status of a cluster with all nodes up, connected and ready to run a parallel job. You may select a number of computing processes in the # *Processes* entry box. The processes will be allocated to the nodes according to the order in which the nodes were added to the PVM (round-robin). In our example we have a total of five PVM processes with node `n1` added first and `n2` added second to the PVM. So the first PVM process (p1 – PQS master process) is assigned to node `n1`, the second to `n2`, and so on, resulting in three processes on `n1` (p1, p3, p5) and two processes on `n2` (p2, p4).

In our example cluster, we have a 16-CPU system comprising four dual-processor, dual-core nodes, with four CPUs from nodes `n1` and `n2` in the PVM. The **Launch Job** button will submit a 4-processor parallel job. The existing PVM can be deleted by clicking the **Reset PVM** button. Old *scratch* files for the current, named job can be removed on all nodes in the cluster by clicking the **Tidy Job** button (see the **PQS** Manual for more details).

To prevent accidental interruption of an executing job several checks are performed before stopping PVM daemons. Figure 2.60 shows the dialog window displayed when the **Reset PVM** button is clicked while PQS jobs are executing on any of the nodes in the cluster. The dialog window in Figure 2.61 is displayed when the **Tidy** button is clicked while PQS jobs are executing.

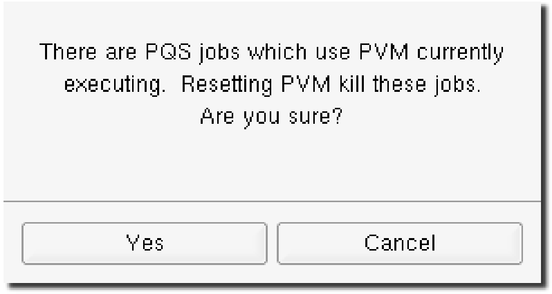

There are PQS jobs which use PVM currently executing. Resetting PVM kill these jobs. Are you sure?

Figure 2.60: PVM reset warning dialog

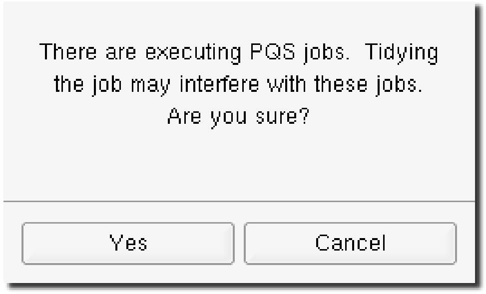

There are executing PQS jobs. Tidying the job may interfere with these jobs. Are you sure?

Figure 2.61: Tidy job warning dialog

Removing a node from the PVM (by clicking on the **Toggle** button of an active PVM node) while a PQS job is running produces the dialog window shown in Figure 2.62. Also, if a PQS job is scheduled to run in the queue and the nodes are removed from the PVM (either by resetting the PVM with the **Reset PVM** button or by stopping a PVM daemon with a **Toggle** button) the dialog window in Figure 2.63 is displayed.

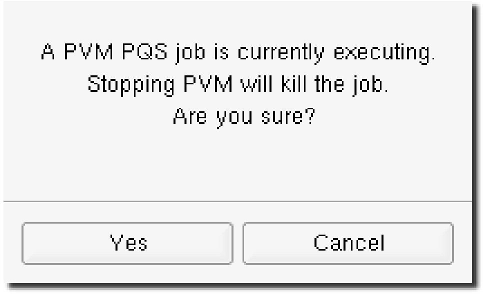

A PVM PQS job is currently executing. Stopping PVM will kill the job. Are you sure?

Figure 2.62: Removing nodes from PVM warning dialog

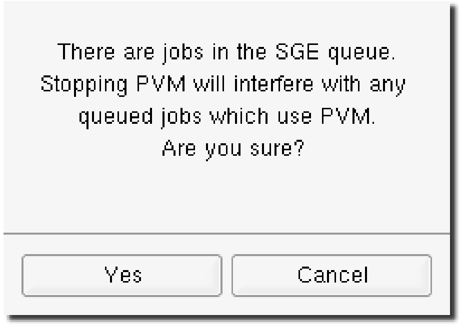
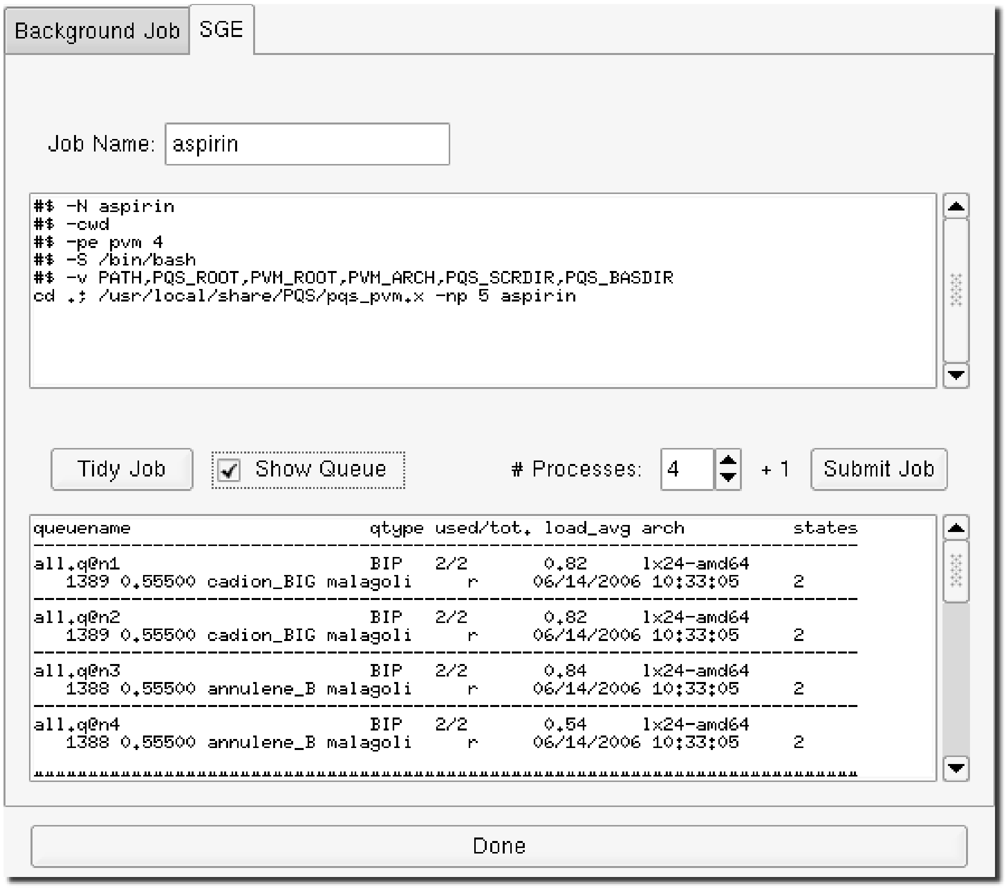

There are jobs in the SGE queue. Stopping PVM will interfere with any queued jobs which use PVM. Are you sure?

Figure 2.63: Removing nodes from PVM while jobs are scheduled in the queue



Job Name: aspirin

```
##$ -N aspirin
##$ -cwd
##$ -pe pvm 4
##$ -S /bin/bash
##$ -v PATH,PQS_ROOT,PVM_ROOT,PVM_ARCH,PQS_SCRDIR,PQS_BASDIR
cd .; /usr/local/share/PQS/pqs_pvm.x -np 5 aspirin
```

Processes: 4

```
queuename                      qtype used/tot. load_avg arch          states
----------------------------------------------------------------------------
all.q@n1                       BIP   2/2       0.82     lx24-amd64
   1389 0.55500 cadion_BIG malagoli     r     06/14/2006 10:33:05     2
----------------------------------------------------------------------------
all.q@n2                       BIP   2/2       0.82     lx24-amd64
   1389 0.55500 cadion_BIG malagoli     r     06/14/2006 10:33:05     2
----------------------------------------------------------------------------
all.q@n3                       BIP   2/2       0.84     lx24-amd64
   1388 0.55500 annulene_B malagoli     r     06/14/2006 10:33:05     2
----------------------------------------------------------------------------
all.q@n4                       BIP   2/2       0.54     lx24-amd64
   1388 0.55500 annulene_B malagoli     r     06/14/2006 10:33:05     2
```

Figure 2.64: Parallel Job Submission window - queue

The **SGE** tab allows jobs to be submitted into the SGE job queue, Figure 2.64. In this example, a job with the name aspirin is being set up for submission on four CPUs. Normally the only information the user needs to supply is the job name (this should already be available in the Job Name box corresponding to the name given in the Job Input section, above) and the number of CPUs to run on (selected by clicking the up and down arrows next to the *# Processes* entry box; alternatively the number can be typed directly into the box). This information will automatically be used in the SGE script shown in the text area at the top of the window.

The current status of the SGE parallel job queue is displayed in the text area at the bottom of the window. The *Show Queue* checkbox is automatically activated when SGE job submission is invoked, so the status of the job queue will be immediately displayed. In this example two 4-processor jobs (`cadion_BIG` and `annulene_B`) are already running in the queue, submitted by user "malagoli".

> **Tip:** To hide the queue deselect the *Show Queue* checkbox.

Clicking the **Submit Job** button will submit the SGE script. If all CPUs are currently running other jobs, the job will be placed in the queue in a "wait" state until CPUs are freed up.

Note: The configuration for the Job Submission module is stored in the file:

```
/usr/local/share/PQS/PQSMOL/data/pqssubmit.conf
```

This is a typical configuration file:

```
$nodes
n1=4 n2=4 n3=4 n4=4
$paths
PQS: /usr/local/share/PQS/pqs_pvm.x
PQS_SCR: /scr/$USER
PVM: /usr/bin/pvm
PVM_TMP: /tmp
RSH: /usr/bin/rsh
QUEUE_STAT_CMD: qstat -f
QUEUE_SUB_CMD: qsub
SGE_SCRIPT: /usr/local/share/PQS/PQSMOL/data/sge_script
#PBS_SCRIPT: /usr/local/share/PQS/PQSMOL/data/pbs_script
#DQS_SCRIPT: /usr/local/share/PQS/PQSMOL/data/dqs_script
```

Clicking on the **Done** button will close the Submit window.

2.6.3 Job Results

The **Calculation→Job Results** menu item invokes the PQS view mode which opens a separate window allowing post-job visualization and display.

Display options include visualization of molecular orbitals (canonical, localized and natural), electron densities and electrostatic potentials, optimization history (energy/geometry at each cycle of a geometry optimization), dynamics trajectories, animation of vibrational modes, and simulation of IR/Raman, VCD and NMR spectra.

All of these will be discussed further in Chapter 3.

Chapter 3

View Mode

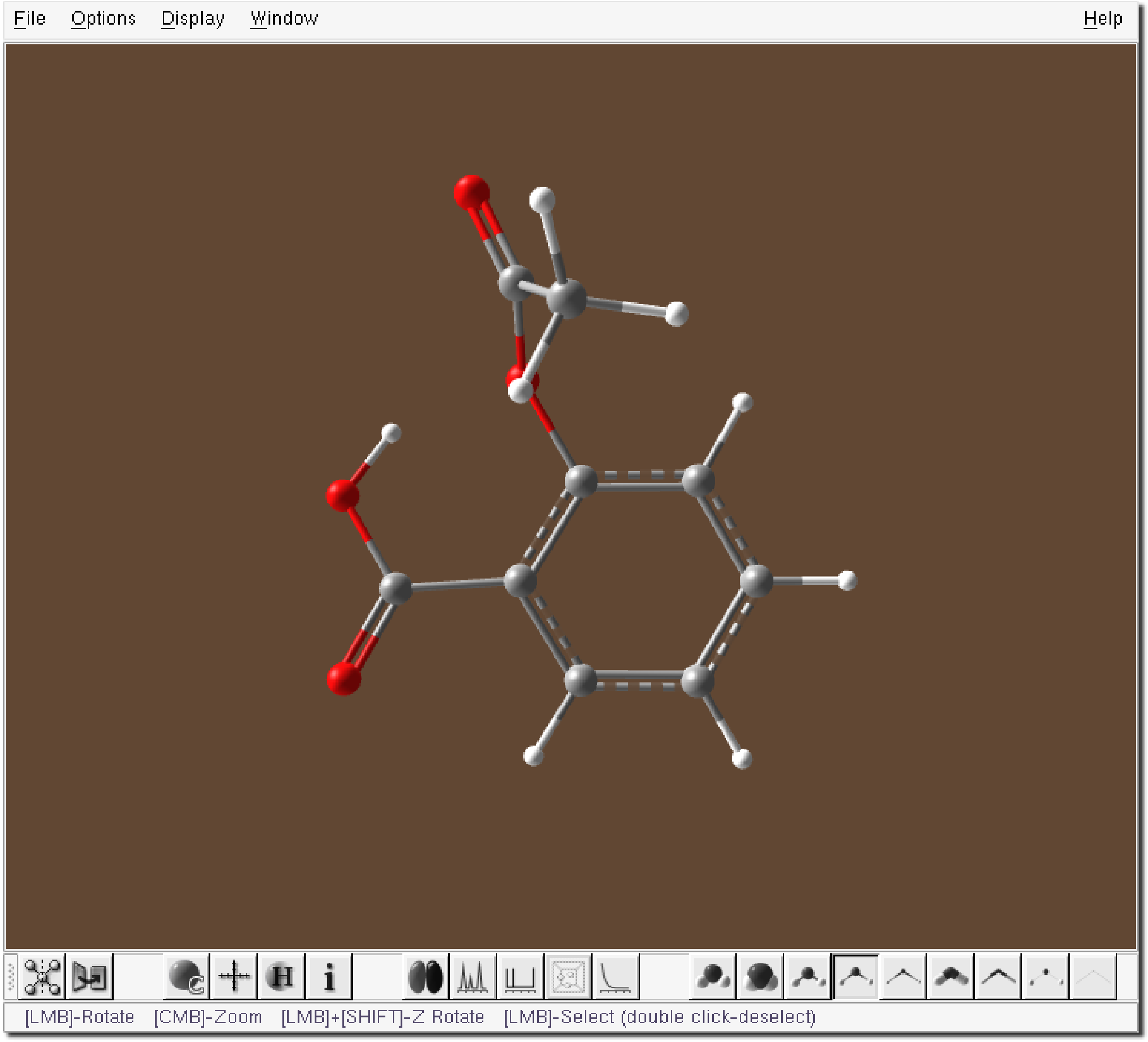


Figure 3.1: PQSMol running in view mode

Typing `pqsview` from the command prompt starts **PQSMol** in **view mode**. Without command line arguments **PQSMol** opens a file browser to choose a file to visualize. If `pqsview` is followed by a **PQS** job name (with the extension `.out`), providing the job has completed successfully and all relevant job files are available, the job is opened for visualization.

It is also possible to start job visualization in **build mode** using the **Calculation→Job Results** menu item.

Figure 3.1 shows **PQSMol** running in **view mode**, visualizing the results of a calculation on aspirin. A successful **PQS** job generates several files with various extensions. From among these **PQSMol** running in **view mode** can open files with extensions `.coord`, `.log`, `.out` and the input file itself `.inp`. From the `.coord`, `.log` and `.inp` files only the molecular geometry is extracted. To display the properties calculated in the **PQS** job, **PQSMol** must open the `.out` file.

Visualization options are available via the buttons in the toolbar at the bottom of the *View window* or in the menu at the top.

3.1 View window

3.1.1 Toolbar

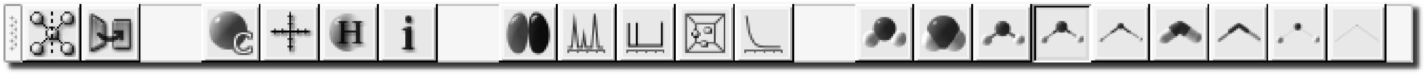


Figure 3.2: Toolbar in view mode

The first six icons in Figure 3.2 provide the same functionality that is available in **build mode**, Figure 2.1.1.

Check Symmetry
Determines the molecular point group symmetry. Unlike in **build mode** (Figure 2.5), there is no option for varying the symmetry threshold. Point group symmetry is determined using the same default threshold as in the **PQS** program itself.

Face Front
Rotates the molecule so that the X-Y plane is parallel with the screen.

Labels
Toggles atom labels.

Coordinates
Toggles the coordinate axes.

Hydrogen Hide
Shows/hides hydrogen atoms.

Info Window

Toggles the info window.

The next five icons activate the visualization windows: molecular orbitals, vibrational frequencies, NMR, dynamics trajectory and optimization history. If any of these features are unavailable for the current **PQS** job, i.e., were not calculated, the corresponding button will be greyed out and the feature will not be accessible.

Molecular Orbitals
Activates the *Orbitals window*. **PQSMol** can display canonical, localized and natural orbitals, the electron density and the electrostatic potential, Section 3.2.

IR/Raman/VCD Spectra
Activates the vibrational spectrum window. This allows a simulation of the IR, Raman or VCD spectra and animation and display of individual vibrational modes, Section 3.3.

NMR Spectra
Activates the *NMR window*. This shows a simulation of the NMR spectrum for each active nucleus, Section 3.4.

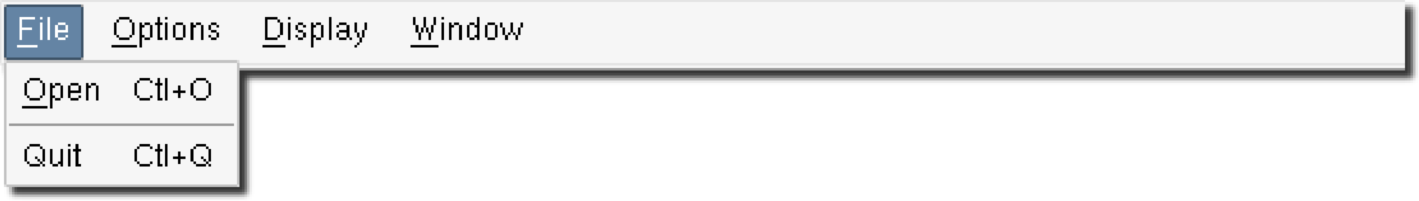
Dynamics Trajectory
Activates the *Dynamics Trajectory window*. This provides an interface for displaying a complete (or partial) dynamics trajectory, displaying the geometry at each cycle, Section 3.5.

Optimization History
Activates the *Optimization History window* (shown below). This window provides an energy vs. cycle number plot, Section 3.6

View Modes
Change the molecule drawing scheme. Options are: Ball, CPK, Ball&Stick, Ball&StickII, Ball&StickIII, Tube, TubeII, Stick and Skeleton.

3.1.2 Menu

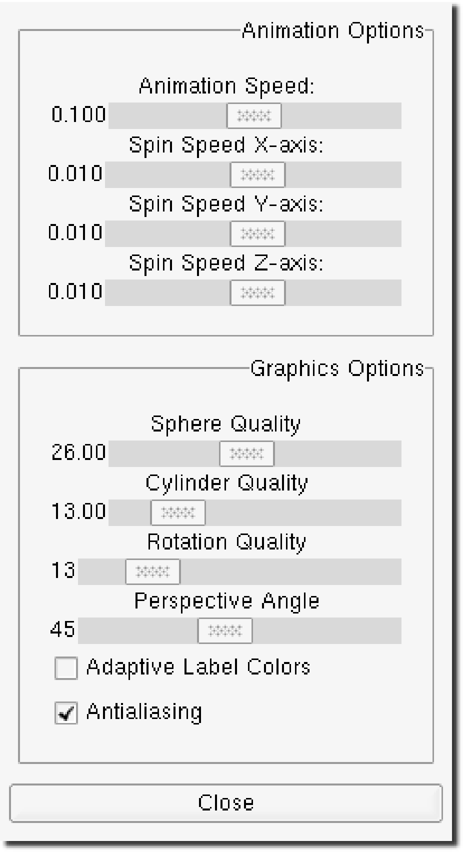
The File menu



- **Open** opens a new file.
- **Quit** exits **PQSMol**.

The Options menu

- **Background** displays a color chooser dialog for the *View window* background, see Figure 2.30.
- **Graph Background** displays a color chooser dialog for the graph background color, see Figure 2.30. The color selected in this window will be used as a background color in the *Orbitals*, *Vibrational Frequencies*, *NMR* and *Optimization History* windows.
- **Graph Plot** displays a color chooser dialog for the graph foreground color, see Figure 2.30. The color selected in this window will be used as the plot color in the *Orbitals*, *Vibrational Frequencies*, *NMR* and *Optimization History* windows.
- **Graphics** opens the *Graphics Options window*, Figure 3.3.


Animation Options

Animation Speed: 0.100
Spin Speed X-axis: 0.010
Spin Speed Y-axis: 0.010
Spin Speed Z-axis: 0.010

Graphics Options

Sphere Quality 26.00
Cylinder Quality 13.00
Rotation Quality 13
Perspective Angle 45
☐ Adaptive Label Colors
☑ Antialiasing

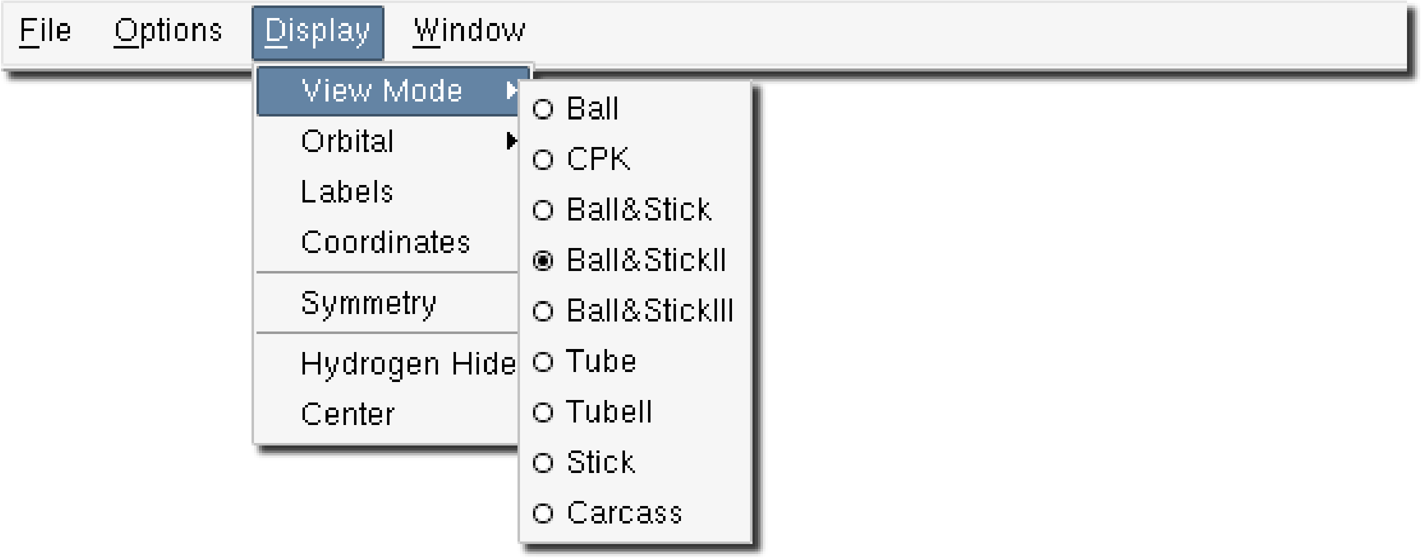
Figure 3.3: Graphics options window

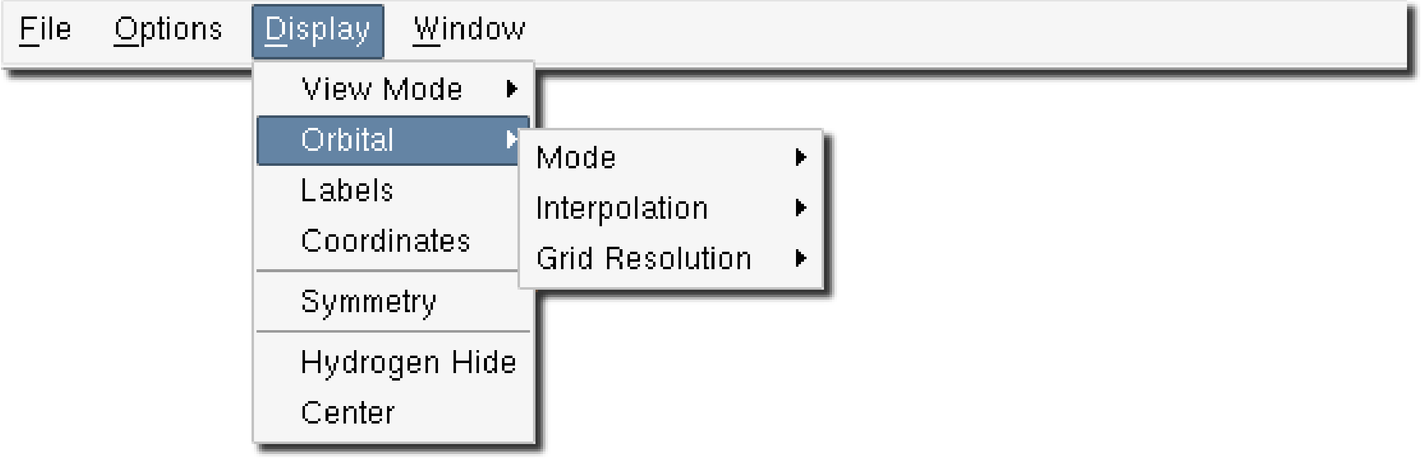
The **Animation Speed** slider adjusts the speed of the vibrational frequencies animation. The **Spin Speed X-axis**, **Spin Speed Y-axis** and **Spin Speed Z-axis** control the rotation speed of the displayed structure, providing the spin is enabled in the **Popup menu**, see Figure 3.5.

The **Sphere Quality** and the **Cylinder Quality** sliders control the number of polygons used to draw atoms (spheres) and bonds (cylinders). **Rotation Quality** controls the number of polygons used to draw atoms during a rotation. **Perspective Angle** adjusts the angle of view. Changes to this value produce a similar effect as changing a lens in a photographic camera, i.e., setting this value to the maximum of 100° will produce a fish-eye effect. The *Adaptive Label Colors* checkbox, when selected, causes all atom labels to be drawn with a color that is clearly visible against the current background color of the *View window.* When this option is turned off, the labels are drawn with the same color as the color of their respective atoms. The *Antialiasing* checkbox turns on antialiasing.

Tip: Turn off antialiasing to speed up image rendering.

The Display menu





- **View Mode** chooses one of the nine display schemes
- **Orbital→Mode** chooses one of four surface display schemes: *Wire*, *Points*, *Transparent*, *Solid.*
- **Orbital→Interpolation** chooses one of three grid point interpolation schemes: *None*, *Logarithmic*, *Linear.*
- **Orbital→Grid Resolution** selects the number of points along one axis of the cubic grid. I.e., a resolution of 10 gives a cubic grid of 10^3=1000 points, a resolution of 30 gives a cubic grid of 30^3=27000 points.
- **Labels** toggles atom labels.

- **Coordinates** toggles coordinate axes.
- **Symmetry** checks if the structure in the *View window* has any symmetry.
- **Hydrogen Hide** hides hydrogen atoms.
- **Center** shifts the structure so that it is centered in the *View window*.

The Window menu

Figure 3.4: Addition to User Library confirmation dialog

- **Info** toggles the Info window.
- **Orbitals** toggles the *Orbitals window*, Section 3.2.
- **Vib. Frequencies** toggles the *Vibrational Frequencies window*, Section 3.3.
- **NMR** toggles the *NMR window*, Section 3.4.
- **Dynamics Trajectory** toggles the *Dynamics Trajectory window*, Section 3.5.
- **Optimization Hist.** toggles the *Optimization History window*, Section 3.6.

The Popup menu

The popup menu is activated by pressing the right mouse button inside the view area.

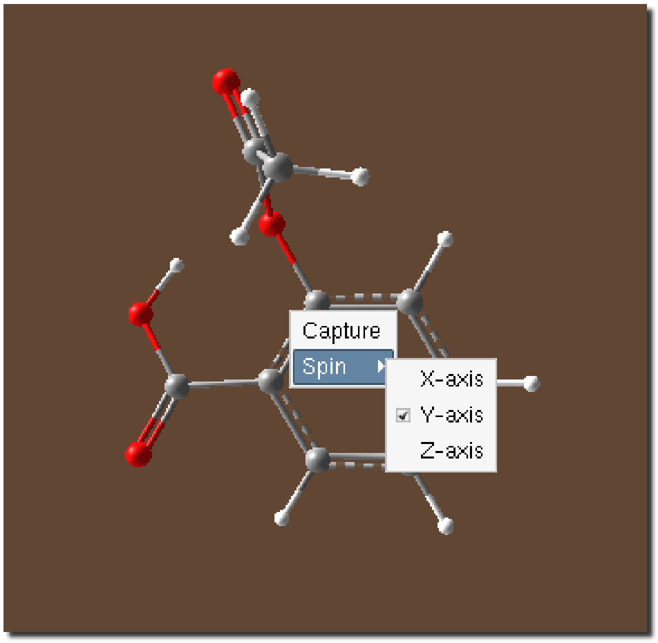


Figure 3.5: View window - popup menu activated via the right mouse button

- **Capture** saves the current image in the *View window*, as a *JPEG* file. A file save dialog, similar to Figure 2.25, is displayed to specify a file name.

- **Spin** animates the rotation of the molecule around the X, Y, and/or Z axes. See Figure 3.3 for rotation speed controls.

3.1.3 Statusbar

[LMB]-Rotate [CMB]-Zoom [LMB]+[SHIFT]-Z Rotate [LMB]-Select (double click-deselect)

Figure 3.6: Statusbar in view mode

The statusbar displays help information about mouse function. The acronyms *LMB*, *RMB* and *CMB* denote *Left Mouse Button*, *Right Mouse Button* and *Center Mouse Button*, respectively.

3.2 Orbitals window

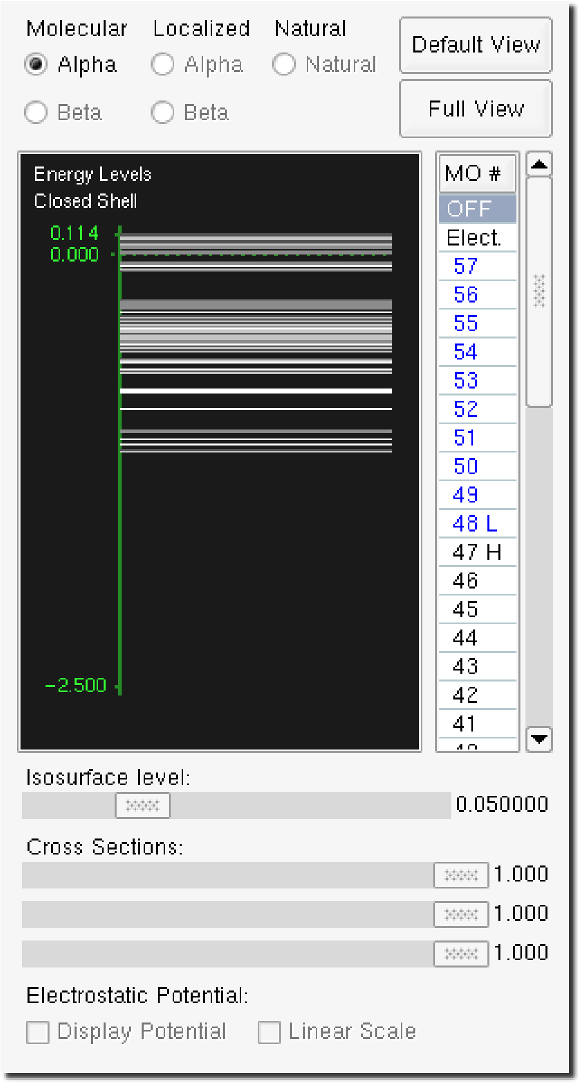


Figure 3.7: Orbitals window - initial display

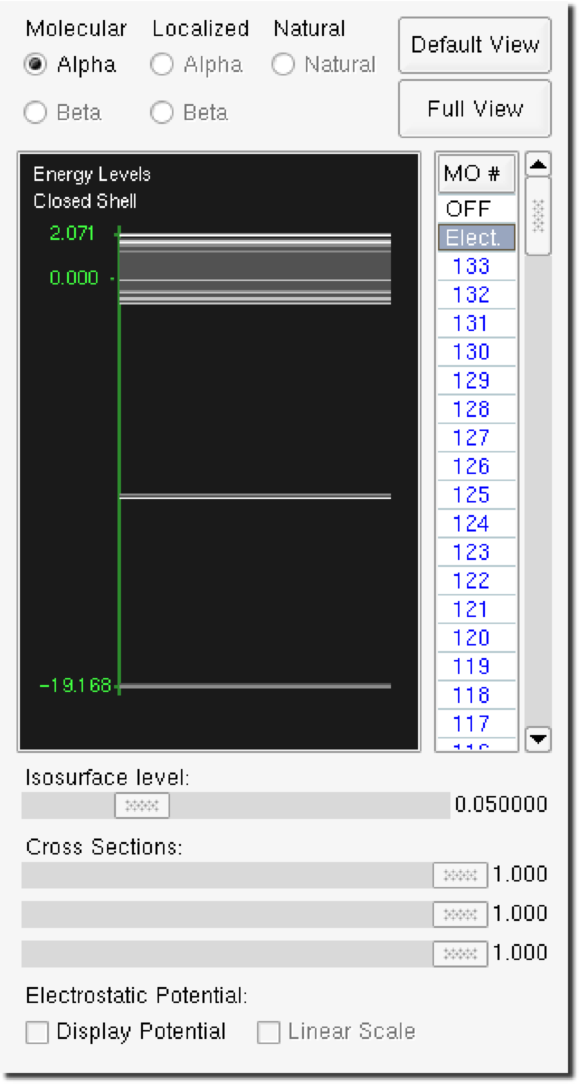


Figure 3.8: Orbitals window - electron density selected, full view

When first invoked, the *Orbitals window* presents the default view which shows all valence occupied MOs (above an energy of -2.500 E_h) and the first ten virtual (unoccupied) MOs. Orbital energy levels are displayed in a graph on the left and the orbital numbers are given in the list on the right side of of the window. The highest occupied orbital (HOMO) and the lowest unoccupied orbital (LUMO) are indicated (with an "H" and an "L", respectively) next to the corresponding orbital numbers in the list. The energy levels and the energy range are displayed in the large central window.

The type of orbitals to be displayed can be selected using radio buttons at the top of the window: *Alpha* or *Beta* spin canonical orbitals, *Alpha* or *Beta* spin localized orbitals, or *Natural* orbitals. The default is alpha spin canonical orbitals. In the example shown in Figures 3.7 and 3.8, the system (aspirin) is closed-shell, and so there is only one possibility and the other orbital types are greyed out.

The actual orbital to be visualized can be chosen either by selecting the orbital number in the list (probably the easiest) or by clicking on the desired energy level in the graph. Due to the fact that, in the default energy scale, many orbitals are close together, it is often difficult to select an orbital for display from the energy level graph. There is a zoom option that expands the energy scale in a selected region, allowing individual orbitals to be separated and selected.

For example, selecting the HOMO for display produces the image in Figure 3.9 in the *View window*.

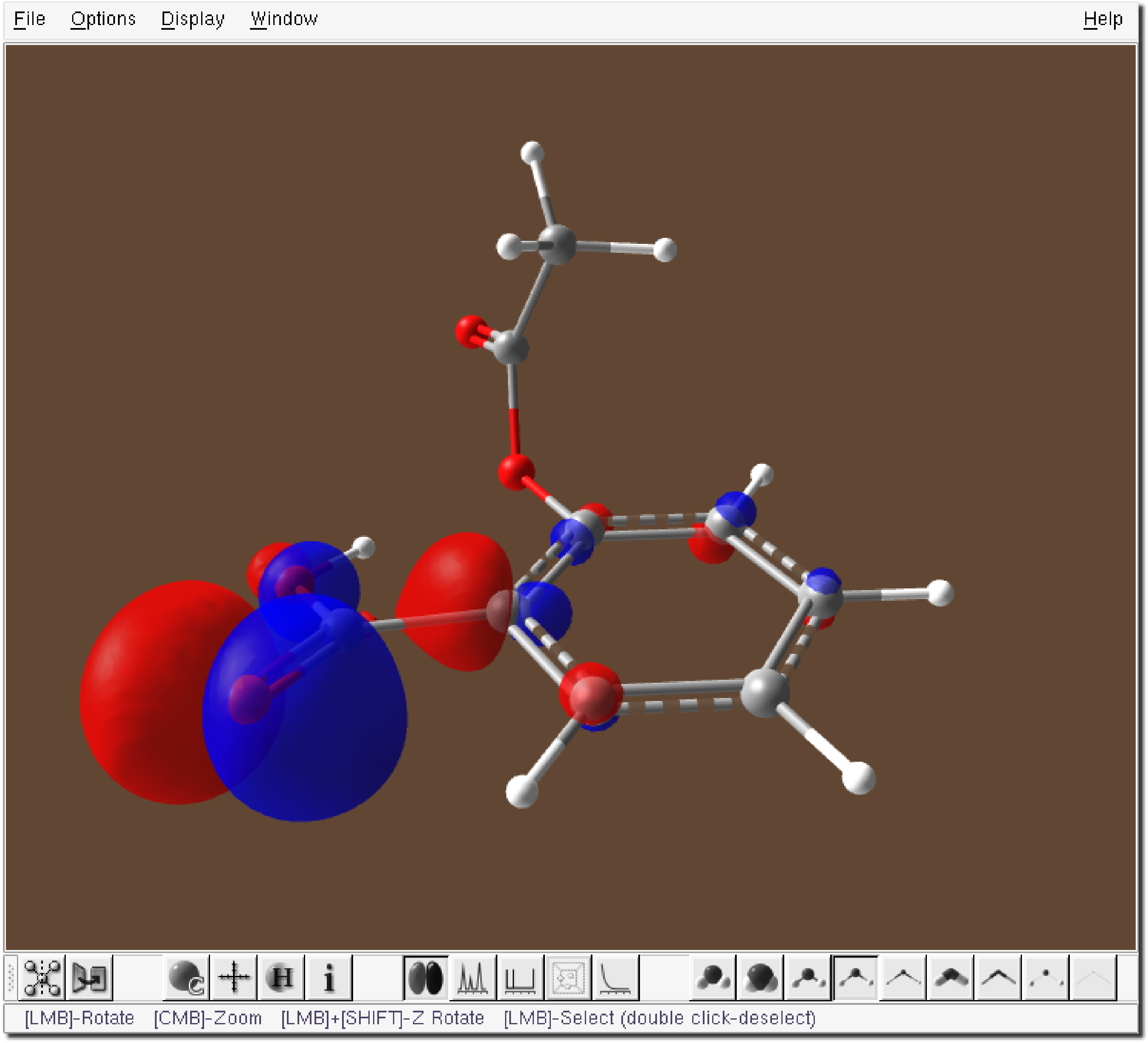
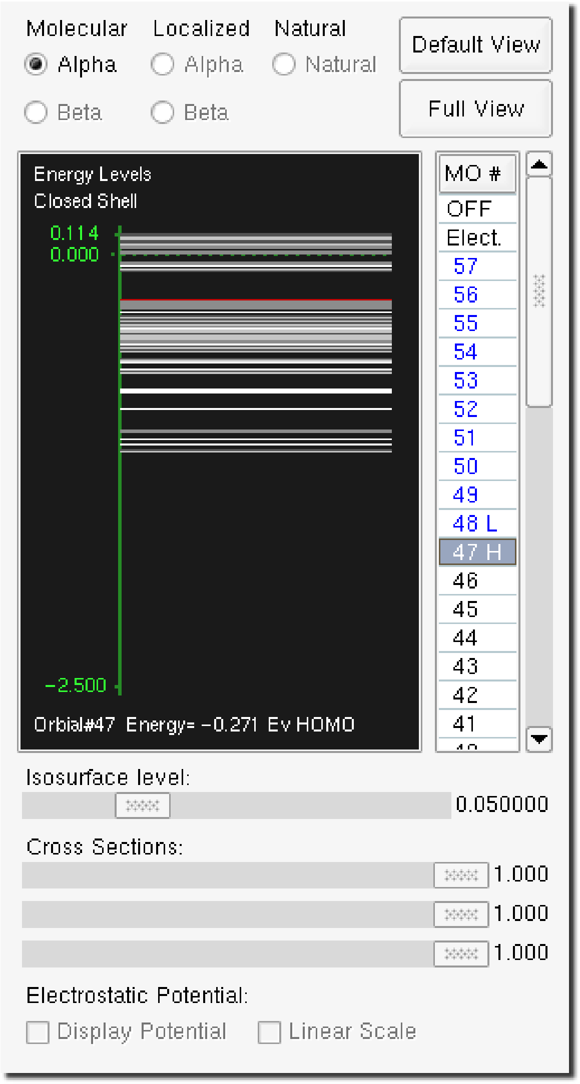


Figure 3.9: View window - HOMO orbital displayed

The size of the orbital lobes can be changed using the *Isosurface level* slider bar in the *Orbitals window*. Using the *Cross Sections* slider bars (in the X, Y and Z directions in that order) cuts off the orbitals in those directions, enabling the internal structure to be more easily seen.

Just as in **build mode**, the entire structure can be rotated, along with the displayed orbital, by dragging the mouse inside the *View window*. This allows the current display orbital to be examined from different perspectives.

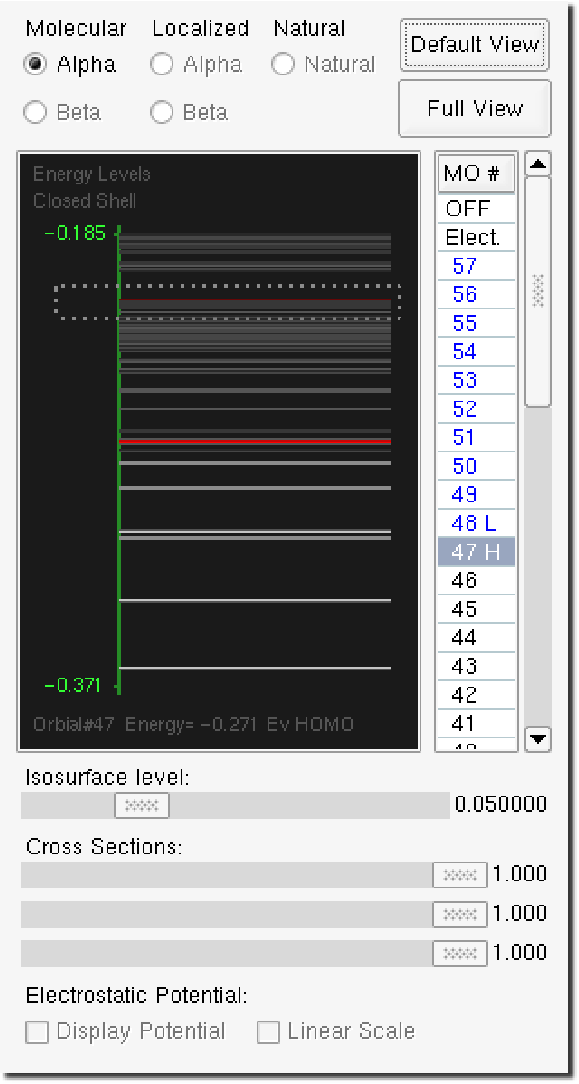


Orbial#47 Energy= −0.271 Ev HOMO

Isosurface level: 0.050000

Cross Sections: 1.000 1.000 1.000

Figure 3.10: Orbitals window - HOMO orbital selected



Orbial#47 Energy= −0.271 Ev HOMO

Isosurface level: 0.050000

Cross Sections: 1.000 1.000 1.000

Figure 3.11: Orbitals window - HOMO orbital zoom

Figure 3.10 shows the corresponding *Orbitals window* to the *View window* in Figure 3.9. The displayed orbital is highlighted with a red line in the energy level graph and the orbital number is highlighted in the orbital list.

An orbital zoom in the energy level graph can be accomplished by positioning the mouse pointer just below or just above the energy levels to be zoomed and dragging the mouse with the center mouse button vertically. A zoom about the HOMO energy level is shown in Figure 3.11.

Pressing the **Full View** button displays all orbital energy levels in the energy level graph and allows access to all orbitals via the list. Because of the extended energy scale (from deep core to the highest virtuals), the energy levels are compressed and the zoom feature would definitely be required to select orbitals for display from the energy level graph.

The expanded full range energy level graph and orbital list are shown in the *Orbitals window* in Figure 3.8. Note the difference in the starting and ending energy levels in the graph and the top orbital number as compared to Figure 3.7. In Figure 3.8 the electron density has been selected, which forms and displays the density from all the occupied orbitals. The corresponding *View window*, displaying the electron density isosurface, is shown in Figure 3.12.

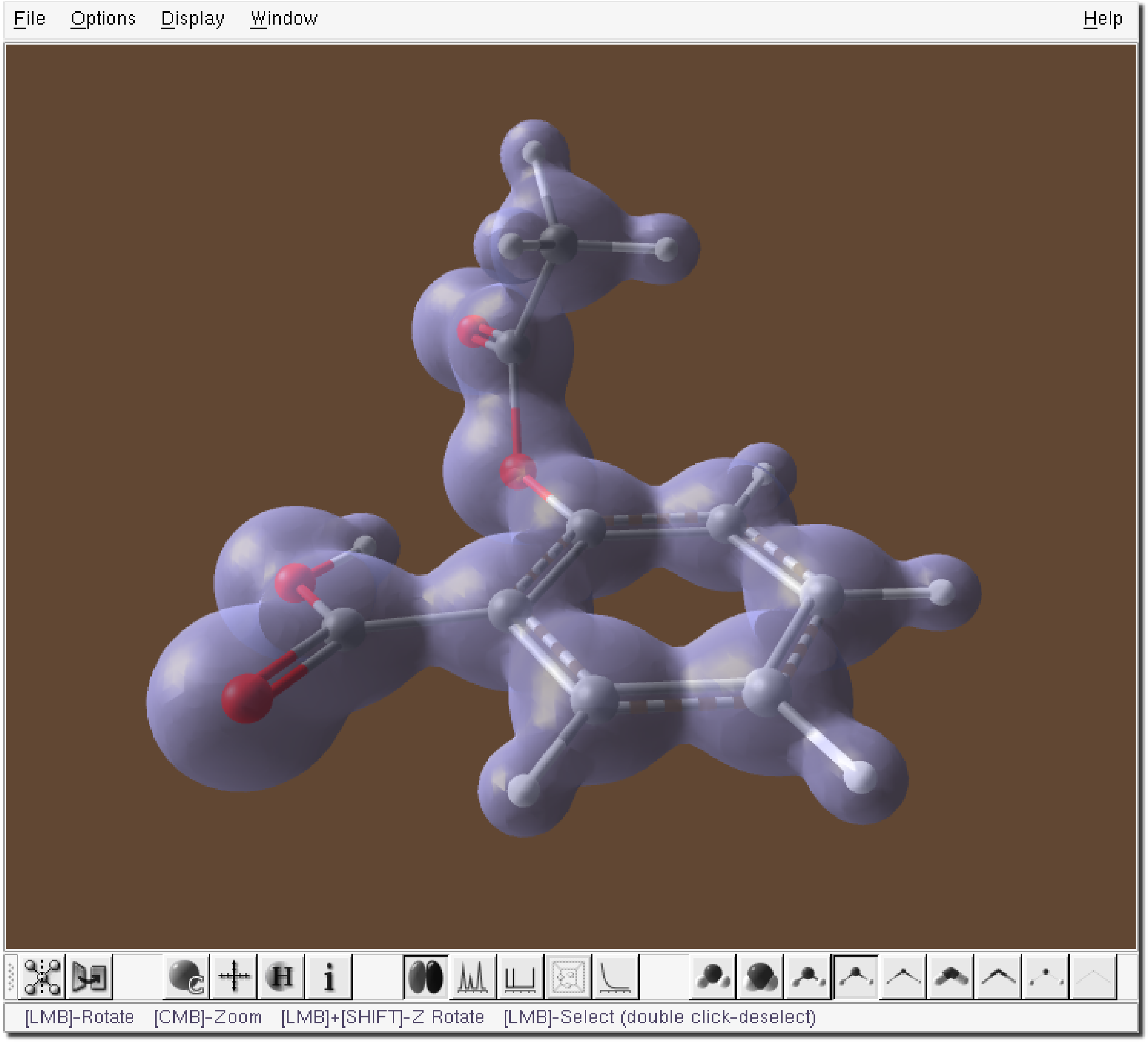


Figure 3.12: View window - electron density

As in the case of the orbitals, the density surface can be expanded and/or contracted via the *Isosurface level* slide bar in the *Orbitals window*. The electrostatic potential overlaid and color-coded on the density surface is shown in Figure 3.13.

Once the electron density has been displayed, the *Electrostatic Potential* checkbox in the lower left corner of the *Orbitals window* becomes sensitive (this was formerly greyed out - compare Figure 3.7 and Figure 3.10).

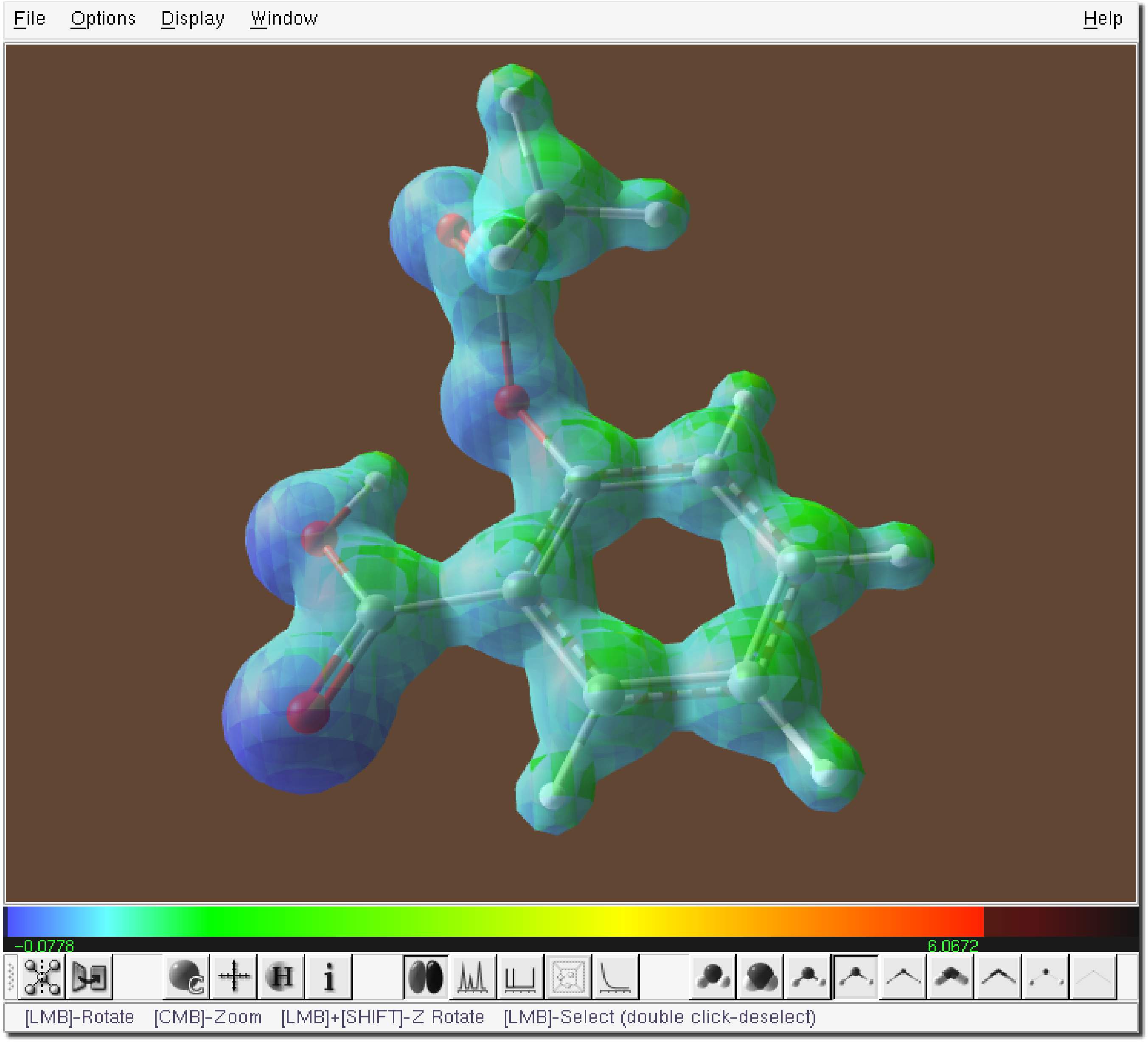


Figure 3.13: View window - electrostatic potential

The electrostatic potential in Figure 3.13 is overlaid on the electron density surface by activating the *Display Potential* checkbox. The electrostatic potential is calculated over a grid and smoothly interpolated onto the density surface. In the default view, the highest potential computed is colored red and the lowest blue, with a graduation in color for all values in between. If the *Linear Scale* checkbox is activated, then the potential is colored with respect to an absolute scale and there will likely be less graduation of color between high and low relative regions of the potential.

3.3 Vibrational Frequencies window

The *Vibrational Frequencies window* shows a simulation of the IR, Raman or VCD spectra and allows animation and display of individual vibrational modes.

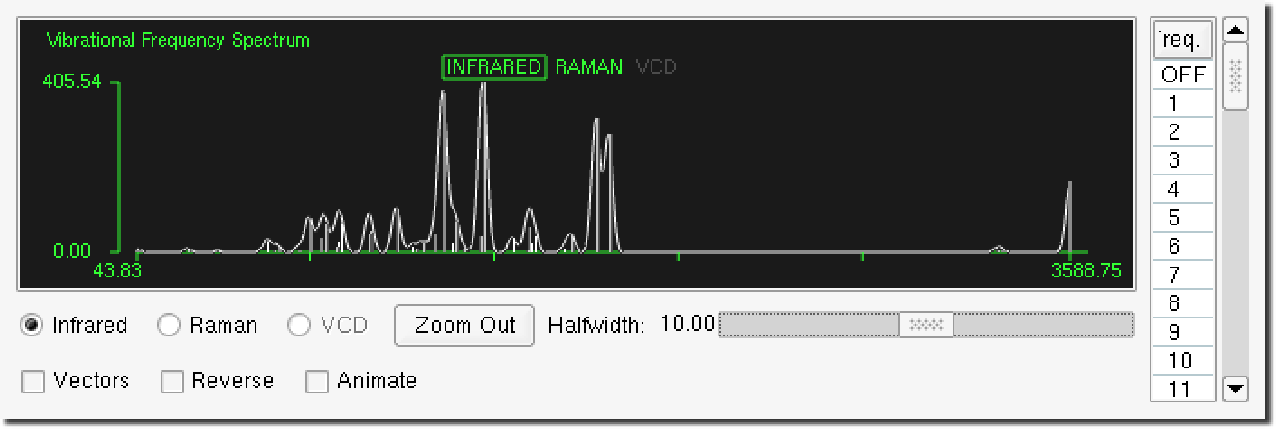


Figure 3.14: Vibrational Frequencies window

The default view, shown in Figure 3.14, is the simulated IR spectrum with peak height obtained from the computed IR intensities. The peaks are fit using a Lorentzian function with half width controlled via the sliding bar (bottom right). The lowest and highest frequencies have their wavenumbers displayed (in green) at either end of the wavenumber axis.

Individual vibrational modes can be displayed and/or animated either by selecting a specific frequency from the list to the right or clicking on the actual signal (line) in the simulated spectrum. The most intense signal in the spectrum selected in this way is shown below Figure 3.15. The mode being displayed is highlighted in red or indicated by a small red arrow in the frequency window, if the mode has a relatively low intensity.

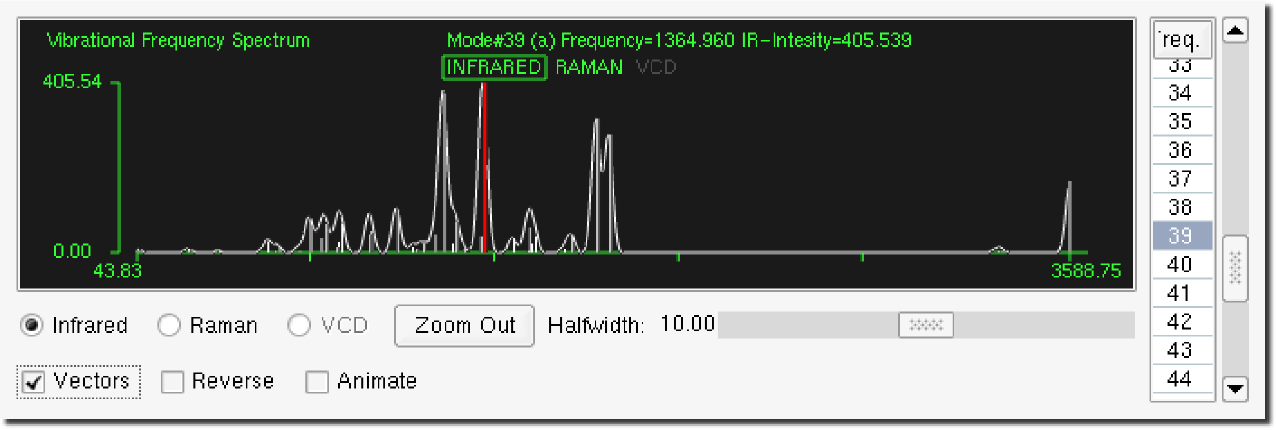
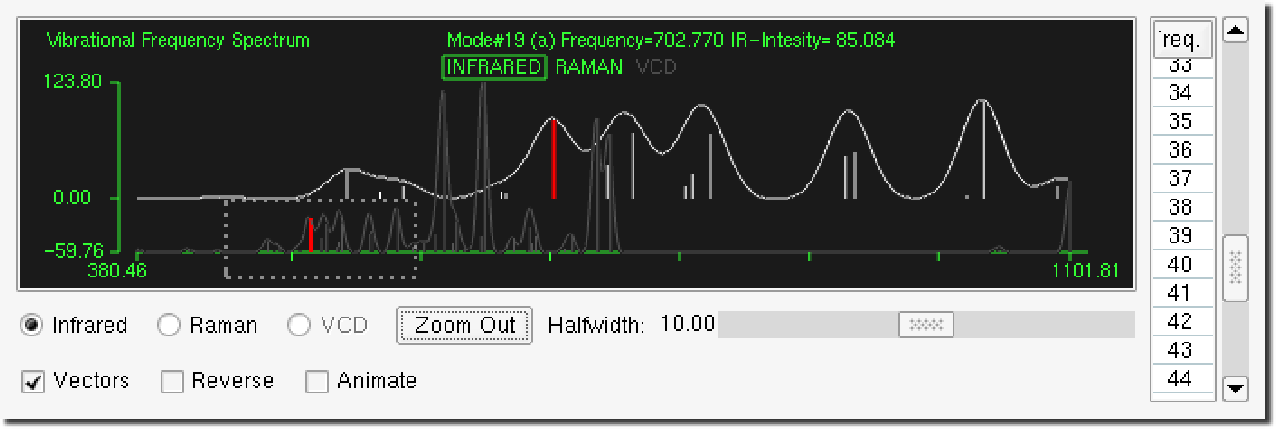

Mode#39 (a) Frequency=1364.960 IR-Intesity=405.539

Figure 3.15: Vibrational Frequencies window - mode #39 selected

The *Vectors* checkbox turns on the displacement vectors which are displayed in yellow in the *View window* Figure 3.17. The entire structure (including the vectors) can be rotated as usual by dragging the mouse in the *View window*. The direction of the arrows can be reversed by selecting the *Reverse* checkbox in the vibrational spectra visualization window and the vibration can be animated by selecting the *Animate* checkbox.



● Infrared ○ Raman ○ VCD

Halfwidth: 10.00

☑ Vectors ☐ Reverse ☐ Animate

Figure 3.16: Vibrational Frequencies window - zoom around the selected mode #19

To zoom in on a specific frequency region, position the mouse pointer ins the graph of the vibrational spectrum and drag the mouse the center mouse button over the region. Dragging the mouse horizontally changes the frequency range and vertically changes the intensity scale. An expansion about the group of low intensity signals in the left part of the IR spectrum is shown above, Figure 3.16. To return to the full frequency and intensity ranges spectrum, press the **Zoom Out** button.

To change the currently displayed spectrum select one of the three radio buttons labeled *Infrared*, *Raman* and *VCD* in the bottom left corner of the *Vibrational Frequencies window*. Note that, if polarizability derivatives have not been computed (i.e. there are no Raman intensities available), then *all* Raman active modes are given the *same* intensity in the simulated Raman spectrum.

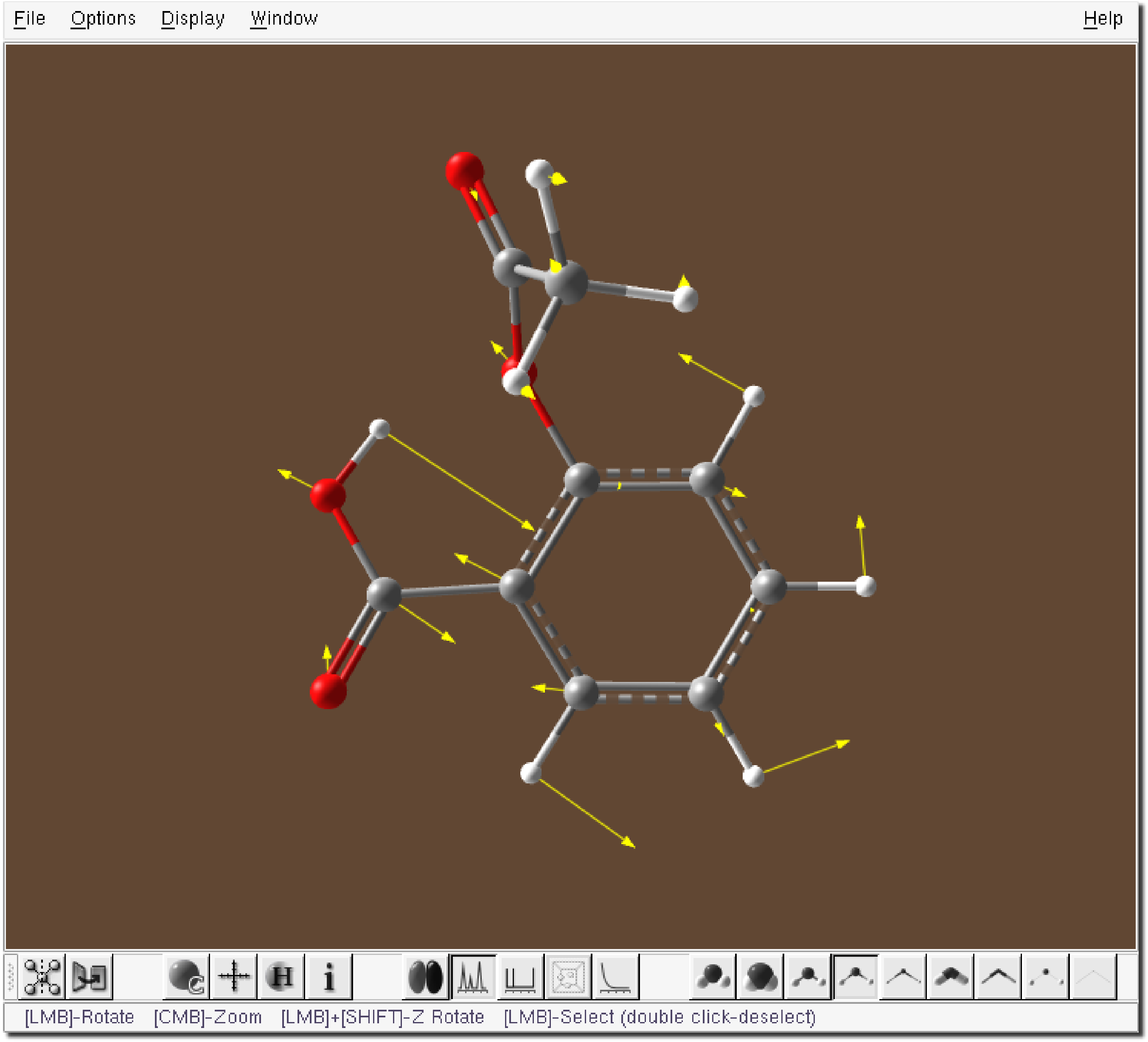
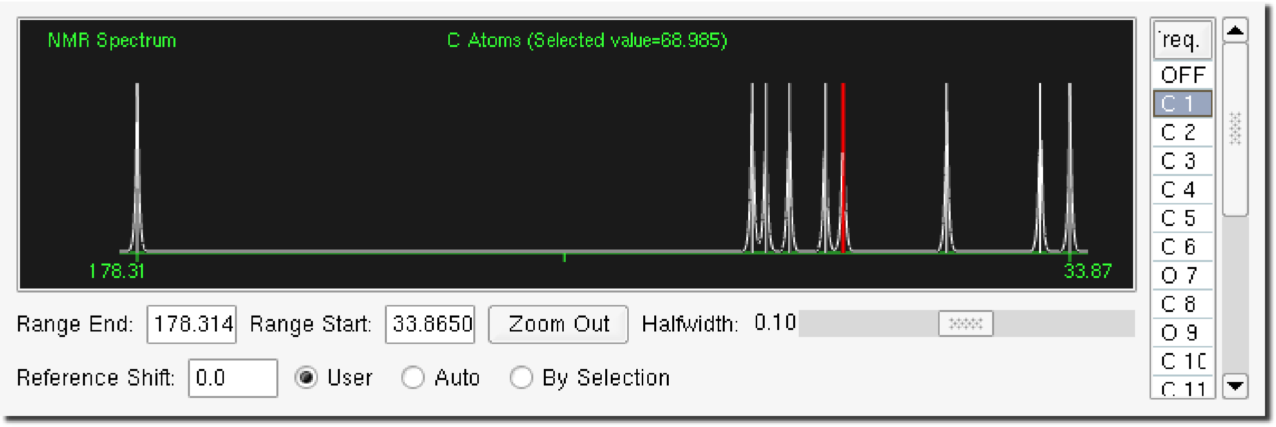


Figure 3.17: View window - motion in the most IR-active mode of aspirin

3.4 NMR window

The *NMR window*, Figure 3.18, allows visualization of the simulated NMR spectrum for each active nucleus.



Range End: 178.314 Range Start: 33.8650

Halfwidth: 0.10

Reference Shift: 0.0 ● User ○ Auto ○ By Selection

Figure 3.18: NMR window - C1 selected

The default is to display the NMR spectrum for all atoms of the same atom type as the first listed atom in the input geometry (in this case carbon). This particular atom is highlighted in the list to the right *C1*, and is also highlighted in red in the simulated spectrum. The atom is also highlighted in blue in the *View window* as shown in Figure 3.19.

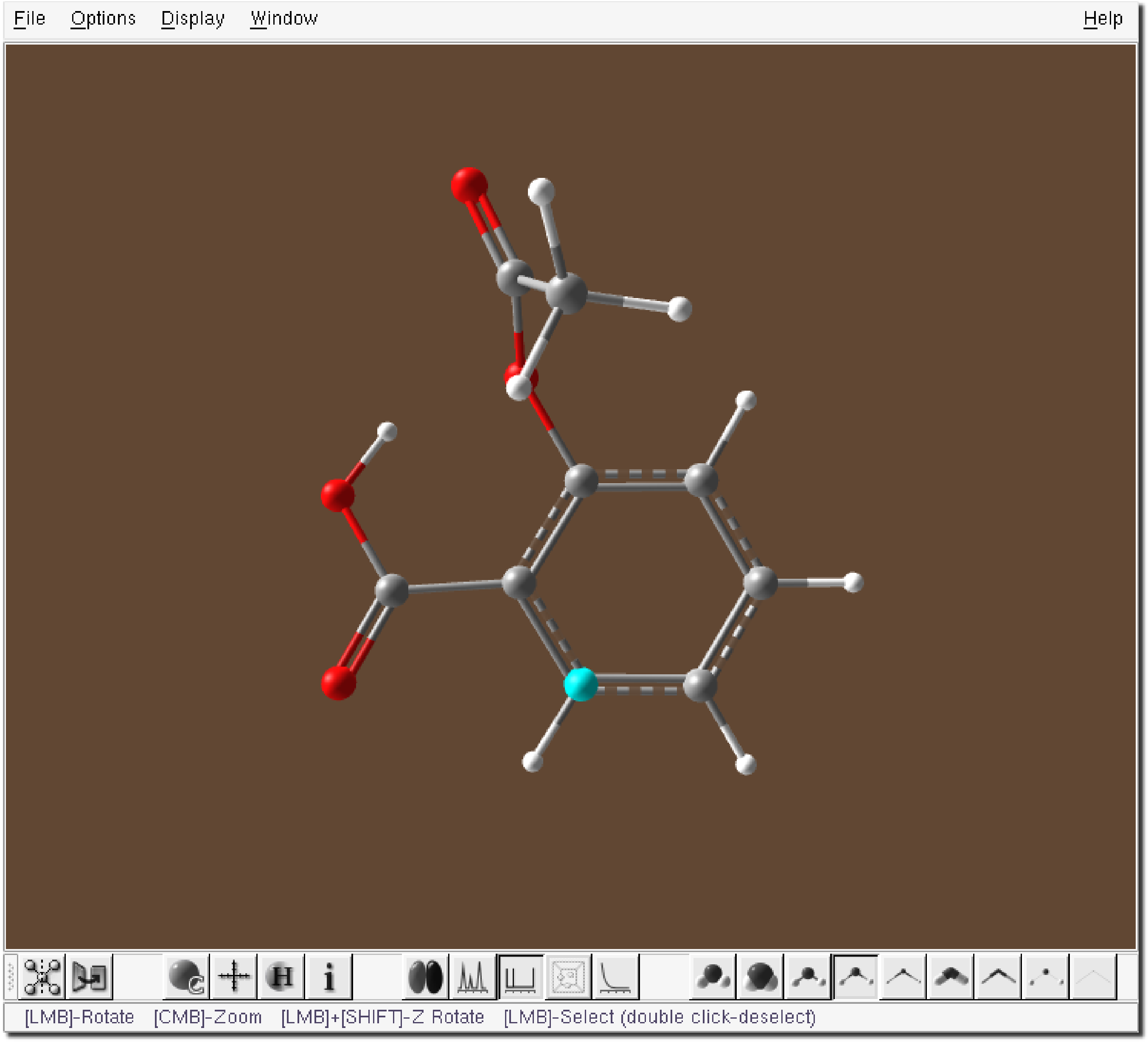
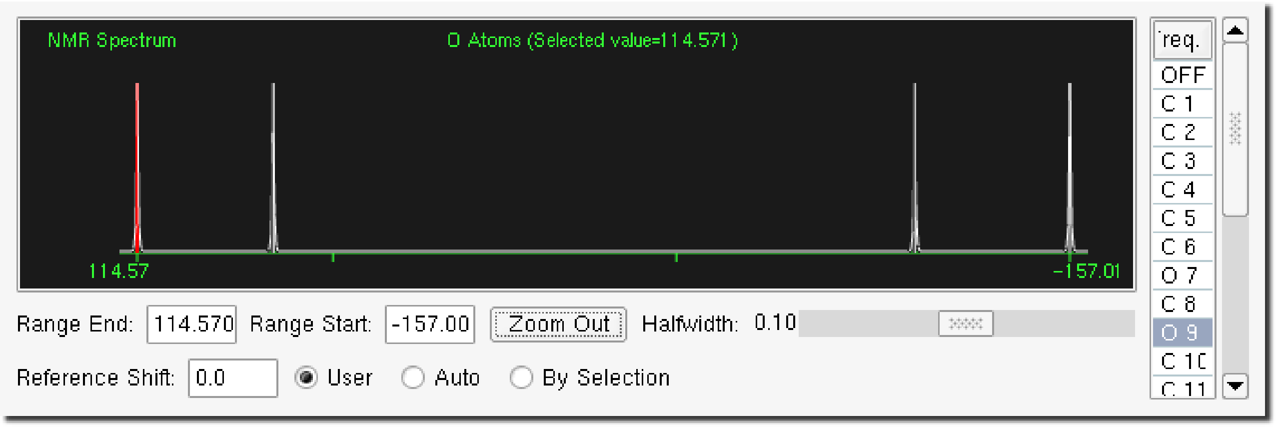


Figure 3.19: View window - C1 selected

The selected atom can be changed by clicking either on the desired atom in the *View window* or by selecting the atom in the list in the *NMR window*. For example, clicking on atom *O9* in the list will display the ^{17}O NMR spectrum, with the peak for atom *O9* highlighted in red in the spectrum, Figure 3.20.



Range End: 114.570 Range Start: -157.00 Halfwidth: 0.10

Reference Shift: 0.0 ● User ○ Auto ○ By Selection

Figure 3.20: NMR window - O9 selected

In the main visualize window, atom *O9* will be highlighted in green.

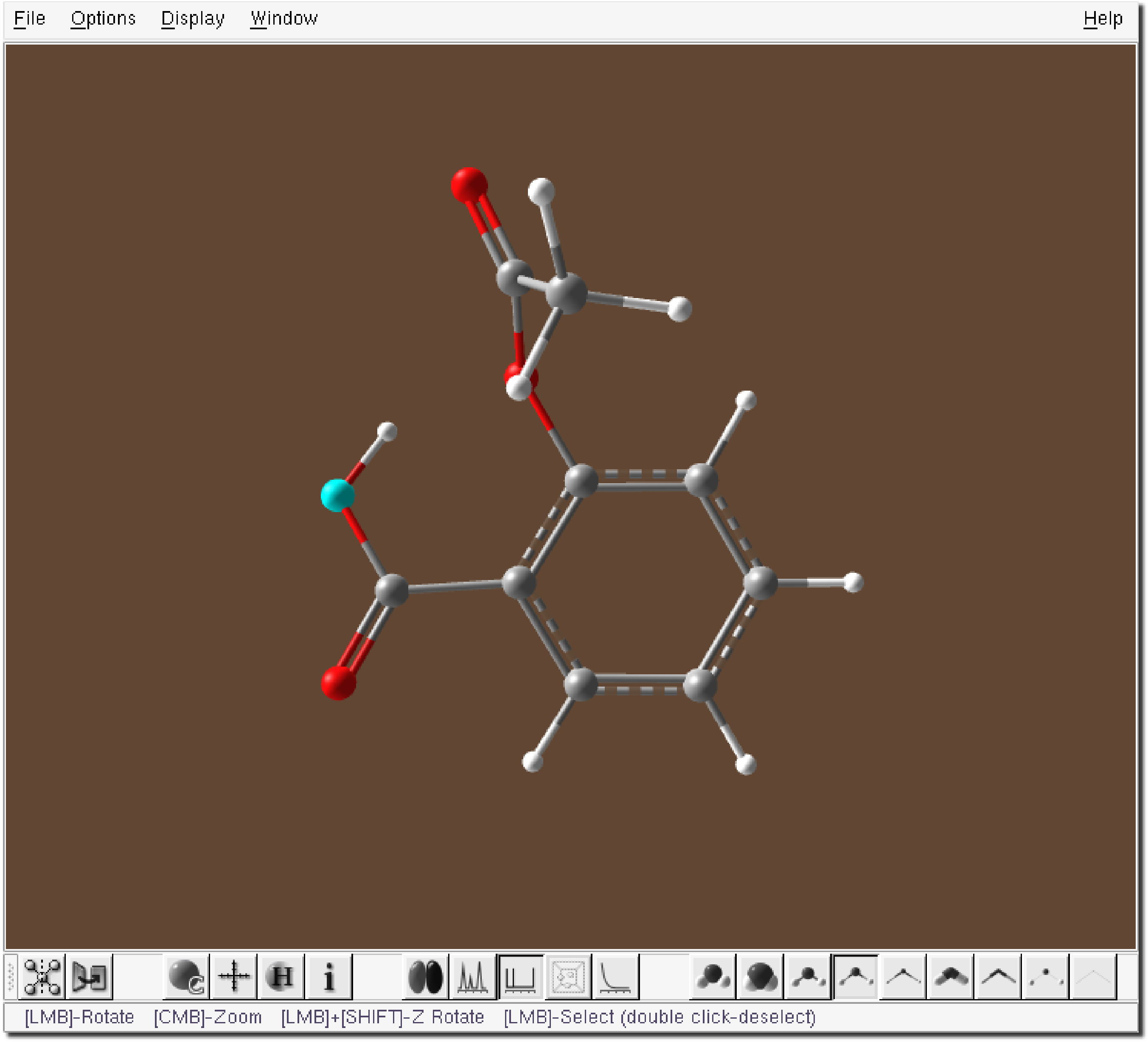
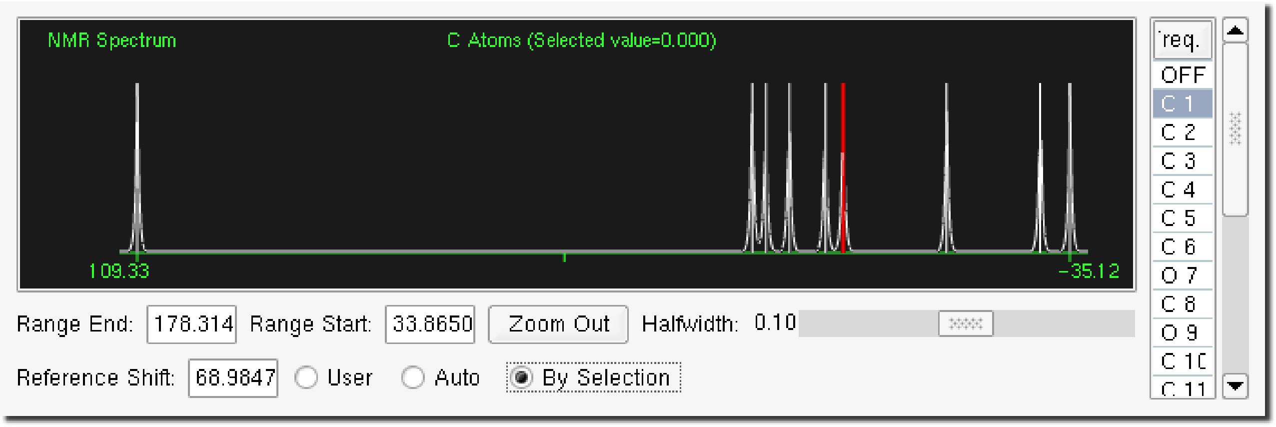


Figure 3.21: View window - O9 selected

The **Reference Shift** value is set to 0 by default. This value indicates no shift from the computed values. There are three modes for setting the value of the reference shift, selected by the three radio buttons at the bottom of the *NMR window* labeled *User*, *Auto* and *By Selection*. In *User* mode, you may type in the desired value directly into the *Reference Shift* entry. In *Auto* mode, the reference shift value is set so as to make the smallest calculated shift equal to 0 (the starting value on the right side of the graph is 0). Finally, *By Selection* mode adjusts the reference shift value so that the currently selected peak is at the point 0. The *NMR window* in all three modes is shown in Figures 3.22, 3.23 and 3.24 for the simulated ^{13}C NMR spectrum.

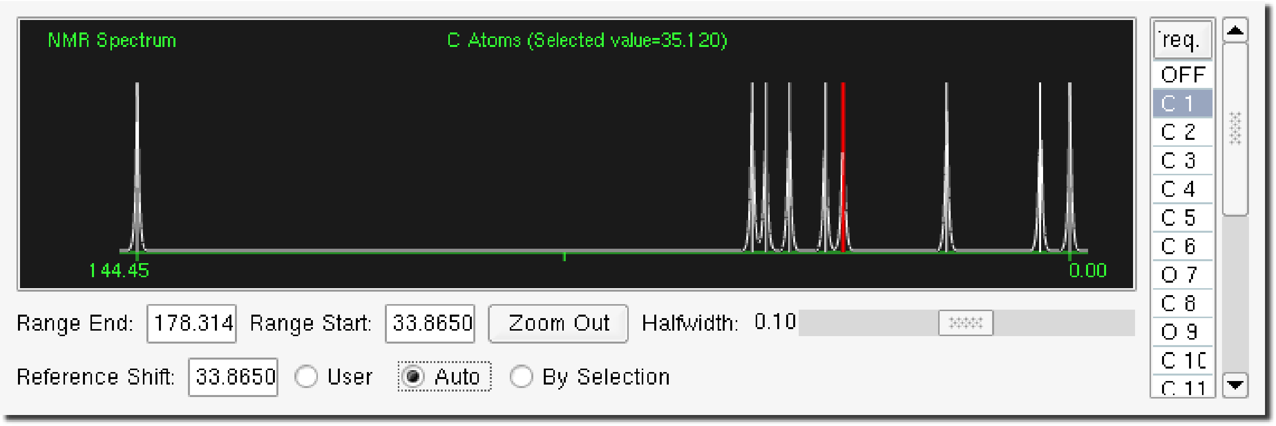


NMR Spectrum C Atoms (Selected value=0.000)

Range End: 178.314 Range Start: 33.8650 Halfwidth: 0.10

Reference Shift: 68.9847 ○ User ○ Auto ● By Selection

Figure 3.22: ^{13}C NMR Spectrum –by selection reference shift

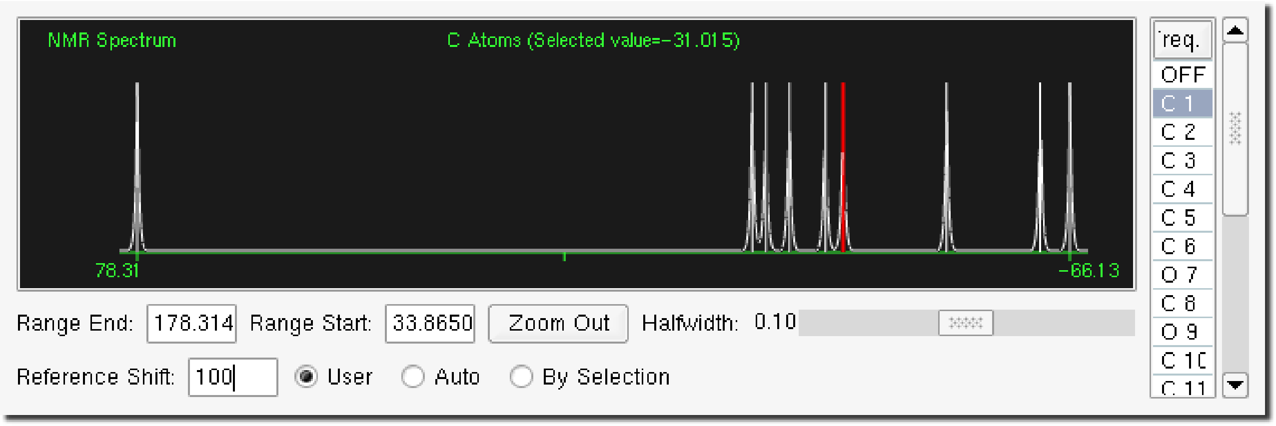


NMR Spectrum C Atoms (Selected value=35.120)

Range End: 178.314 Range Start: 33.8650 Halfwidth: 0.10

Reference Shift: 33.8650 ○ User ● Auto ○ By Selection

Figure 3.23: ^{13}C NMR Spectrum – auto reference shift



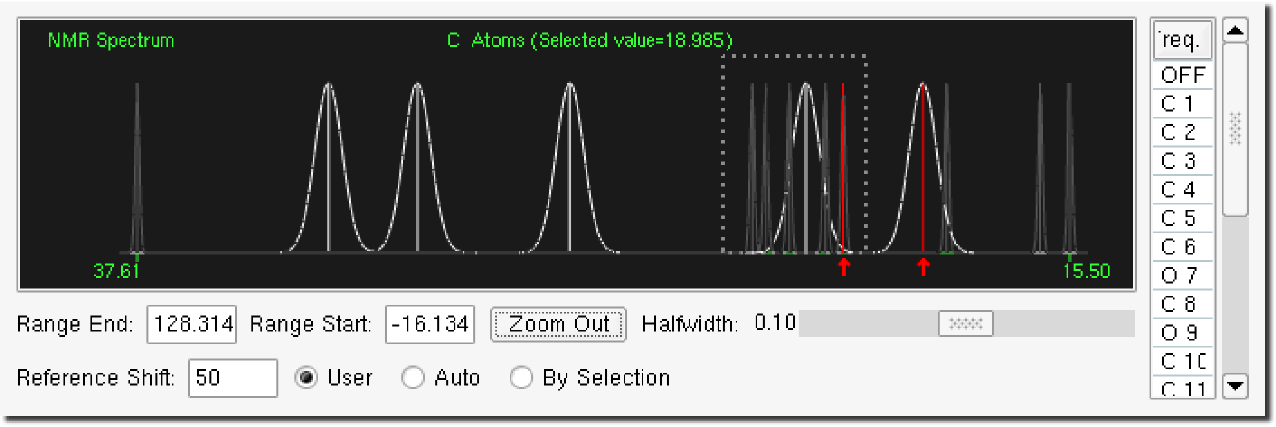
NMR Spectrum C Atoms (Selected value=-31.015)

Range End: 178.314 Range Start: 33.8650 Halfwidth: 0.10

Reference Shift: 100 ● User ○ Auto ○ By Selection

Figure 3.24: ^{13}C NMR Spectrum – user selected (100) reference shift

The zoom option works in a similar way to the zoom in the simulated vibrational spectrum. Position the mouse pointer in the *NMR window* just before the region to be expanded and drag the mouse with the center mouse button over the region. A zoom around the five right-of-center signals in the ^{13}C simulated NMR spectrum is shown below, Figure 3.25.



Range End: 128.314 Range Start: -16.134 Halfwidth: 0.10

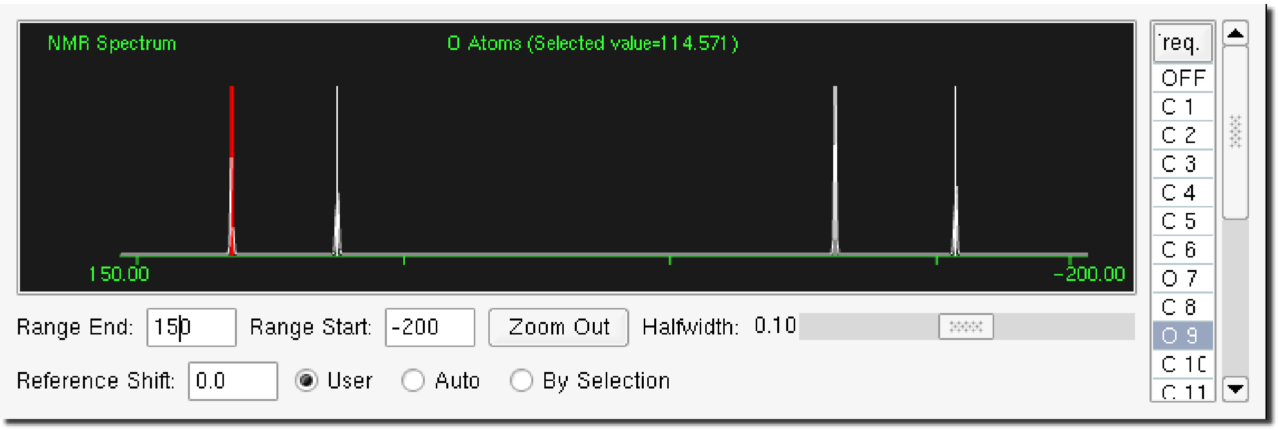
Reference Shift: 50 ● User ○ Auto ○ By Selection

Figure 3.25: ^{13}C NMR Spectrum – zoom

Press the **Zoom Out** button to return to the default NMR spectrum view.

The default values displayed in the *Range End* and *Range Start* entries in the *NMR window* are taken directly from the **PQS** job output, and represent the largest and smallest isotropic shieldings for that atom reported in the output file. The starting and ending ranges can be adjusted by explicitly setting values in the **Range End** and **Range Start** boxes. These should be greater than the highest value currently shown, and smaller than the lowest, if you want to ensure that the whole spectrum is displayed.

Adjusting the range from 150 to -200 ppm (normally 140.57 to -157) for the simulated ^{17}O NMR spectrum is shown below, Figure 3.26. This has the effect of slightly compressing the spectrum.



Range End: 150 Range Start: -200 Halfwidth: 0.10

Reference Shift: 0.0 ● User ○ Auto ○ By Selection

Figure 3.26: ^{17}O NMR Spectrum – user defined range

The point of doing this is that spectra of related compounds, e.g., isomers, can be individually simulated and adjusted so they are on the same scale, i.e., the starting and ending ranges for all spectra are identical. This allows a much clearer comparison between different simulated spectra in reports or publications.

Tip: Right-mouse clicking with the mouse pointer in a given window, e.g., the *NMR window*, enables a JPEG image of the graph to be captured.

3.5 Dynamics Trajectory window

The *Dynamics Trajectory window*, Figure 3.27, provides an interface to visualize a dynamics trajectory.

Figure 3.27: Dynamics Trajectory window

When first invoked the trajectory is loaded, starting at the initial geometry (step 1). This geometry is displayed in the *View window.* Selecting the **Play** button will run through the entire trajectory, displaying each geometry sequentially in the *View window.* Selecting the *Loop* checkbox will play the trajectory repeatedly.

The trajectory can also be played, in either direction (forward on back) via the slider bar, and stepped forward or back via the **Next** and **Prev** buttons, respectively.

3.6 Optimization History window

The *Optimization History window*, Figure 3.28, provides an energy with cycle number plot.

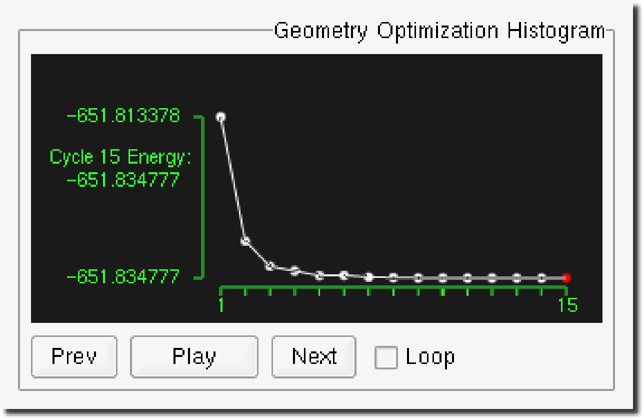


Figure 3.28: Optimization History window

As can be seen in Figure 3.28, the starting and final energies are given as well as the total number of optimization cycles (15 in this case). Clicking on any of the "points" (cycles) in the graph will display the geometry on that optimization cycle in the *View window.* Clicking on **Prev.** or **Next** button will display the previous or next geometry relative to the currently selected point, respectively. Pressing the **Play** button will run through the complete optimization history, displaying all geometries at all optimization cycles. Selecting the *Loop* checkbox will repeatedly loop through the entire history, i.e., will play continuously. This can be stopped by either deselecting the *Loop* checkbox or by closing the entire *Optimization History window.*

Chapter 4

Tutorials

4.1 Example 1 - Lactic Acid

To get you started using **PQSMol** and **PQS** , we will begin the tutorials with a simple example molecule – Lactic Acid.

Lactic acid, also known as milk acid or 2-hydroxypropanoic acid, is used in several biochemical processes in the human body. Its chemical formula is $C_3H_6O_3$. It is schematically shown in Figures 4.1 and 4.2.

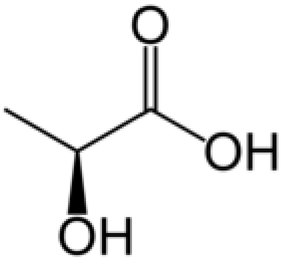


Figure 4.1: Lactic acid structure diagram

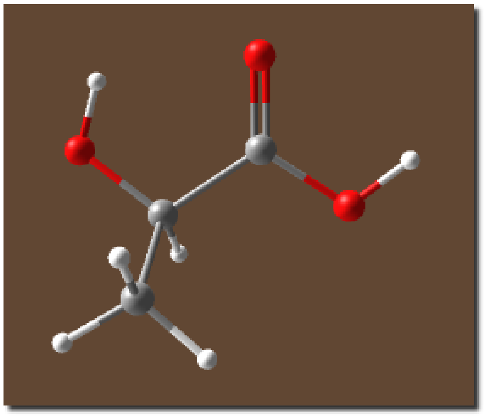


Figure 4.2: Lactic acid structure

In this example we will:

- build the molecule
- perform an initial optimization, using the *Sybyl5.2* force field
- create a **PQS** input file
- run a **PQS** calculation
- examine the molecular orbitals and display the vibrational frequencies

4.1.1 Building the Lactic Acid molecule

Step 1 Start the builder by typing `pqsmol` at the command prompt.

We will begin constructing the molecule by first connecting two tetrahedral carbon building blocks. Then we will attach the carboxyl functional group from the fragment library. The bent oxygen building block for the remaining O-H group will be attached next, and we will finish by filling all dummy atoms with hydrogens.

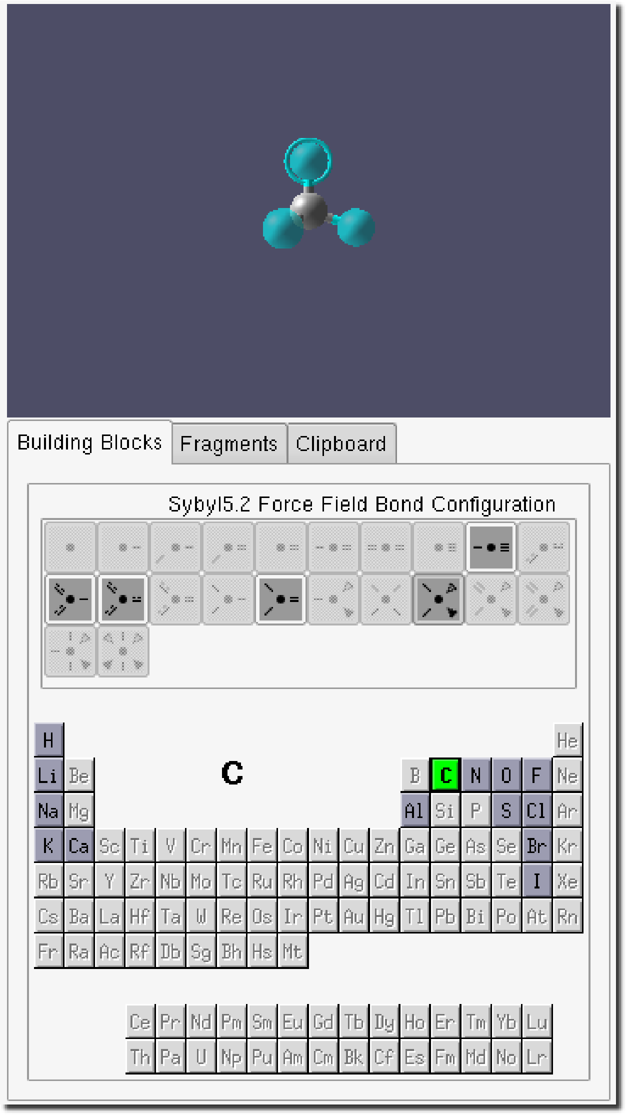


Figure 4.3: Segment window with tetrahedral carbon building block selected

Step 2 Insert the first tetrahedral carbon building block.

In the *Segment window*, Figure 4.3, press the carbon button in the periodic table of elements. The current element is displayed in large font above the periodic table. Also, all of the available building blocks for the current element are enabled in the *Bond Configuration* frame, directly above the periodic table.

The tetrahedral building block is the default building block for carbon, and should already be selected. It is activated by the last available button in the second row in the *Bond Configuration frame*, Figure 4.3.

When selected the building block will appear in the *Segment buffer*, above the *Bond Configuration* frame. At this point your *Segment window* should look like the one in Figure 4.3.

Note: The green semi-transparent atoms are dummy atoms. These only indicate a place for attaching other structures.

To insert the block into the build area, select the **Add/Attach/Connect** tool in the lower toolbar and click the left mouse button anywhere inside the build area.

Tip: You may also insert into the *Build window* using the **Default** tool by right-clicking in the *Build window*.

At this point your *Build window* should contain a single building block shown in Figure 4.4

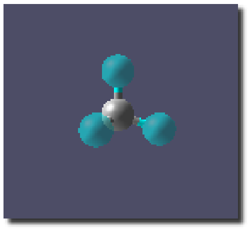


Figure 4.4: Build window with the tetrahedral carbon building block inserted

Step 3 Attach the second tetrahedral carbon building block.

Confirm that the tetrahedral carbon building block in the *Bond Configuration* frame is still selected. Attach the building block to the structure in the build area by moving the mouse over the lower right dummy atom of the structure. The atom will be highlighted with a circle surrounding it and the cursor will change to +A, indicating that this atom is a valid attachment point (Figure 4.5 left image). Press the left mouse button over the the atom to attach the building block, (Figure 4.5 right image).

Tip: You may also attach the contents of the *Segment buffer* to the structures in the *Build window* using the **Default** tool by right-clicking over a compatible attachment point in the *Build window*.

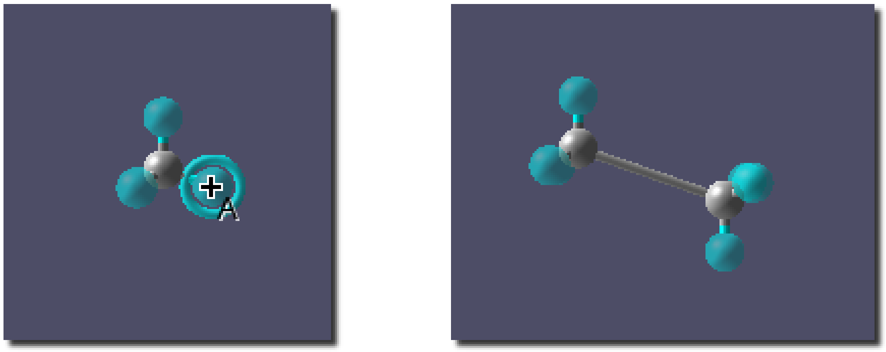


Figure 4.5: Build window - attaching the second tetrahedral carbon building block

Step 4 Attach the Carboxyl functional group.

Click on the *Fragments tab* in the *Segment window*, and then on the *FUNCTIONAL GROUPS* tab. Select the `carboxyl` fragment in the list on the left side of the window. The carboxyl functional group appears in the *Segment buffer*. Click on the left-most hydrogen atom in the group to set it as the attachment point for the fragment. The *Segment window* should now look like the one in Figure 4.6.

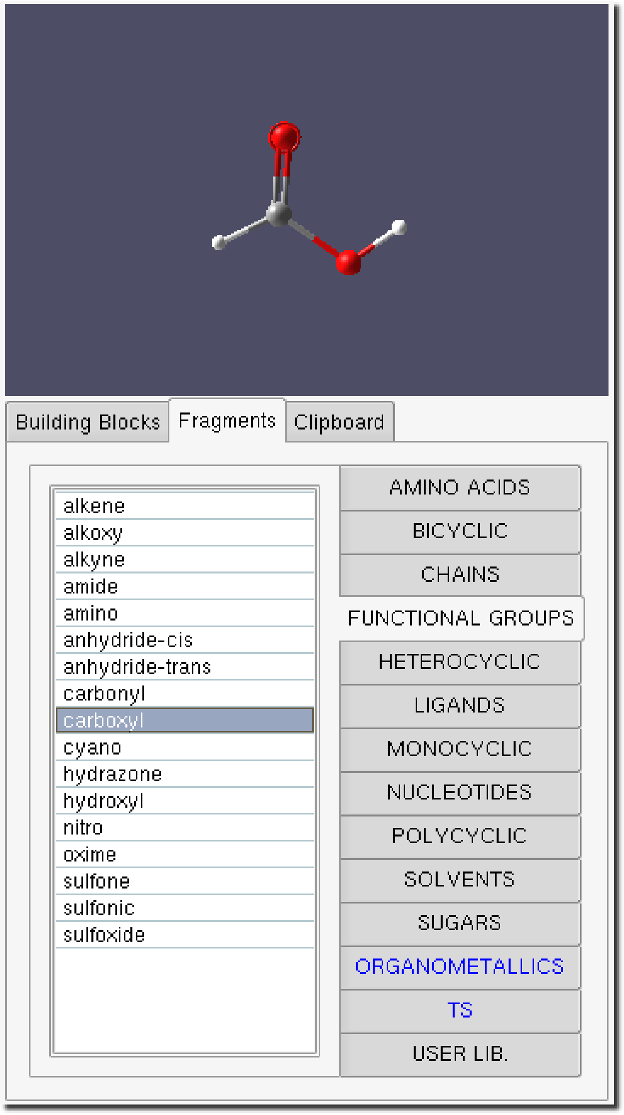


Figure 4.6: Segment window - Carboxyl functional group selected

Attach the Carboxyl group to the right-most upper dummy atom in the build area, by positioning the cursor over the atom until it is highlighted and clicking. The operation is shown in Figure 4.7.

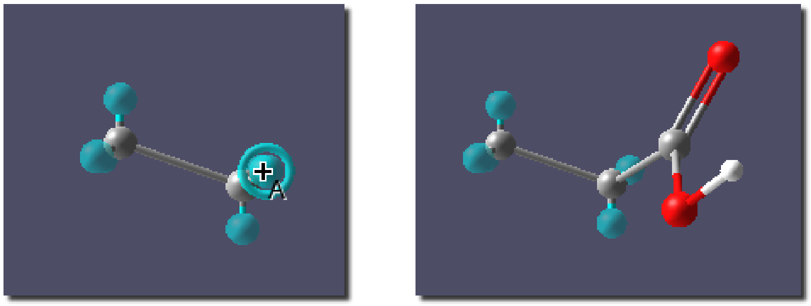


Figure 4.7: Build window - attaching the Carboxyl group

Step 5 Attach the bent oxygen building block.

In the *Segment window* select *Building Blocks tab* and then select oxygen in the periodic table. The list of available bond configurations changes. The default bent configuration for oxygen is automatically selected and the corresponding building block appears in the *Segment buffer*. We will use this block for the remaining O-H group needed.

In the *Build window*, attach the building block at the dummy atom on the center carbon closest to the double bonded oxygen, as shown in Figure 4.8.

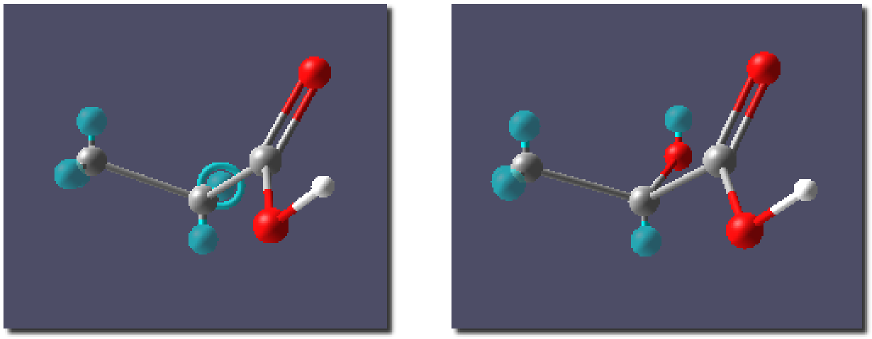


Figure 4.8: Build window - attaching the bent oxygen building block

Step 6 Fill with hydrogens.

The **Hydrogen Fill** tool is activated by the first button in the upper toolbar **H**. It replaces all the green, semi-transparent dummy atoms with real hydrogen atoms, right image in Figure .

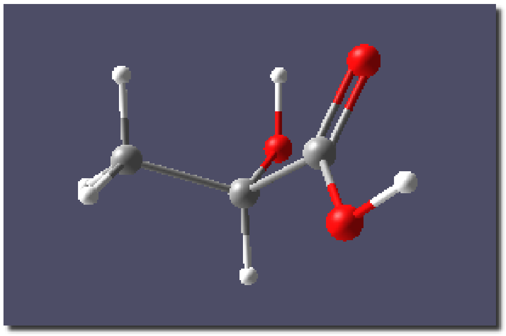
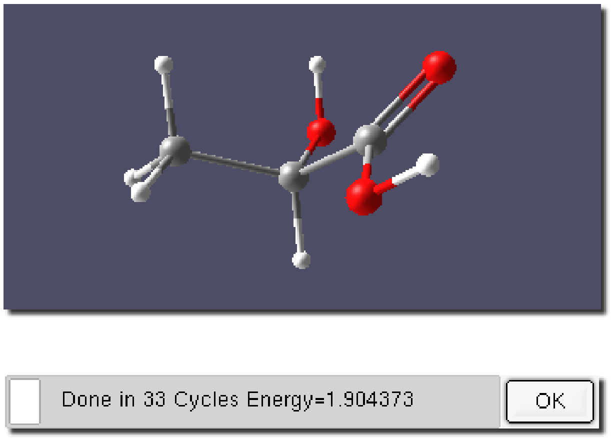


Figure 4.9: Build window - after Hydrogen Fill

Step 7 Preoptimize.

Finally, we finish building Lactic Acid by performing an initial energy . The second button in the top toolbar **E↓** executes the optimization. The result of the optimization is shown in Figure 4.10.



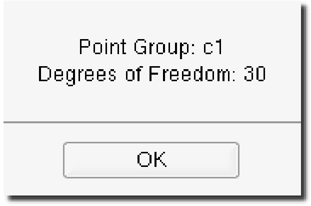
Done in 33 Cycles Energy=1.904373

Figure 4.10: Build window - optimization results

Press the **OK** button to close the Optimization Progress dialog.

Step 8 Check for symmetry

Use the **Check Symmetry** tool , the third button in the top toolbar, to check for any point group symmetry. There is no symmetry in lactic acid and so the point group is `C1`, Figure 4.11.



Point Group: c1
Degrees of Freedom: 30

Figure 4.11: Symmetry dialog

Press the **OK** button to close the Symmetry dialog.

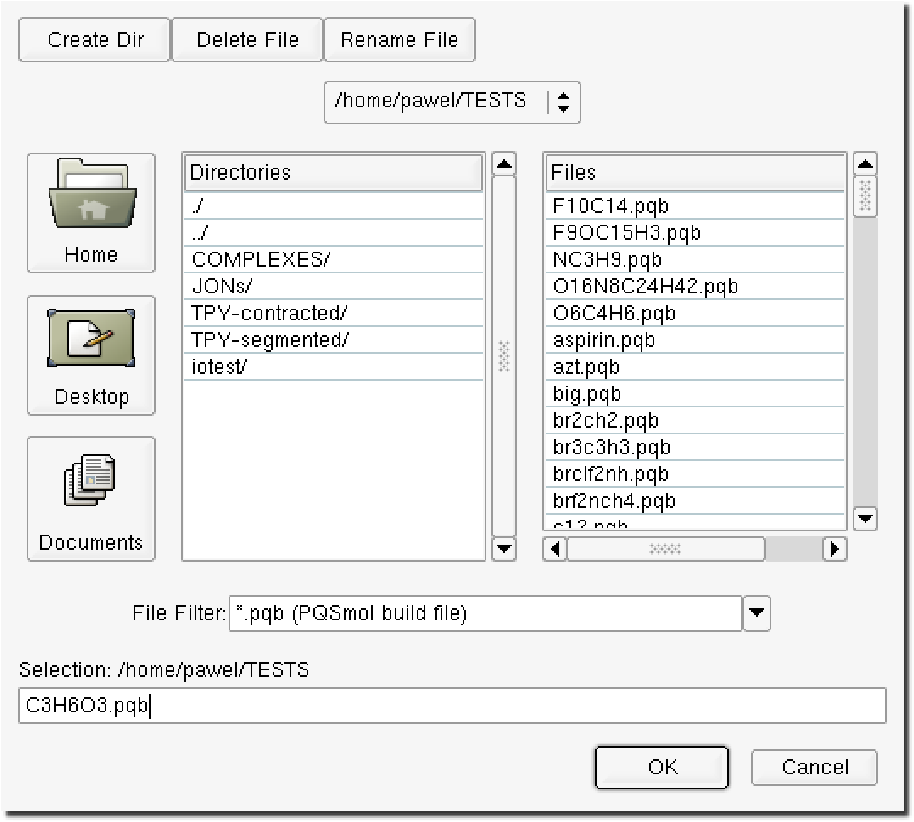
4.1.2 Creating a PQS input file

PQS package requires an input file to specify the type of calculations to be carried out. Because of the various capabilities and options available in PQS, there are a large number of keywords and options available in the input syntax. Refer to the **PQS** manual for a detailed description.

PQSMol has a built-in **PQS** input file generator, that provides a simple point and click interface for creating input files with the most common options.

Step 9 Create a **PQS** input file.

Select the **Calculation→Job Input** menu item to start the input generator. Since we have not named the structure in the *Build window*, before proceeding with input creation a **Save As** dialog is presented, Figure 4.12. The name of the file is automatically set to the empirical formula with a `.pqb` extension.



/home/pawel/TESTS

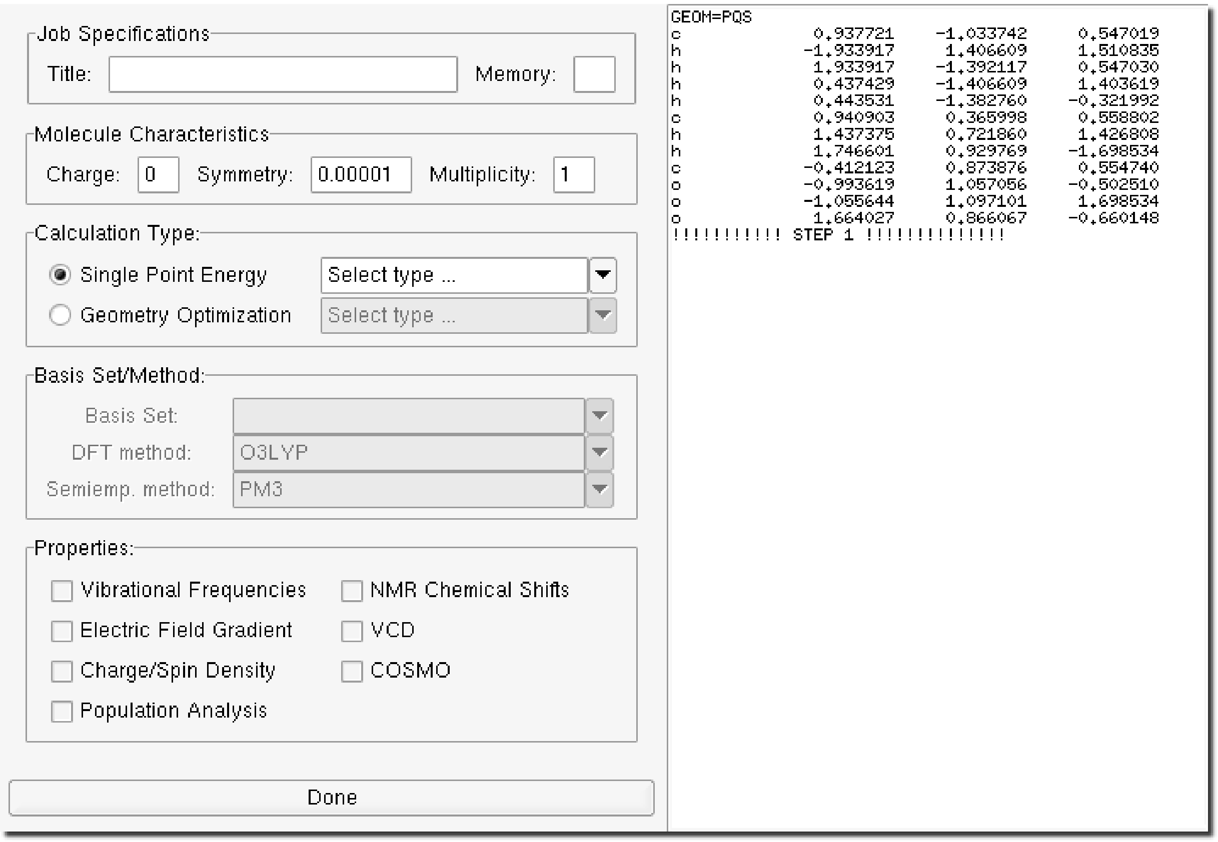
File Filter: *.pqb (PQSmol build file)

Selection: /home/pawel/TESTS

C3H6O3.pqb

Figure 4.12: Save As dialog

You may keep this name or overwrite it with another. In either case, as soon as the file name is accepted and the file is saved (by pressing the **OK** button), the input generator window appears, Figure 4.13.



Job Specifications

Title:

Memory:

Molecule Characteristics

Charge: 0

Symmetry: 0.00001

Multiplicity: 1

Calculation Type:

● Single Point Energy — Select type ...

○ Geometry Optimization — Select type ...

Basis Set/Method:

Basis Set:

DFT method: O3LYP

Semiemp. method: PM3

Properties:

☐ Vibrational Frequencies

☐ NMR Chemical Shifts

☐ Electric Field Gradient

☐ VCD

☐ Charge/Spin Density

☐ COSMO

☐ Population Analysis

```
GEOM=PQS
c          0.937721   -1.033742    0.547019
h         -1.933917    1.406609    1.510835
h          1.933917   -1.392117    0.547030
h          0.437429   -1.406609    1.403619
h          0.443531   -1.382760   -0.321992
c          0.940903    0.365998    0.558802
h          1.437375    0.721860    1.426808
h          1.746601    0.929769   -1.698534
c         -0.412123    0.873876    0.554740
o         -0.993619    1.057056   -0.502510
o         -1.055644    1.097101    1.698534
o          1.664027    0.866067   -0.660148
!!!!!!!!!!! STEP 1 !!!!!!!!!!!!!!
```

Figure 4.13: Input generation window

The left frame of the window contains the input fields, which are used to generate the input file. In the right frame the input file itself is displayed. Initially, the source of the pqs input file contains only the geometry of the molecule we just created. As values are entered on the left, the input file is updated in real time. This way you can see how the specific options appear in the input file.

Enter the title ”`Lactic Acid - vibrational frequencies`” into the *Title:* field. This option is used only as a descriptive title. In the *Memory:* field enter a value of 20. This option controls the amount of memory the program will request from the operating system to execute the job.

Note: The unit of memory usage in the *Memory:* field is a MegaWord (MW).

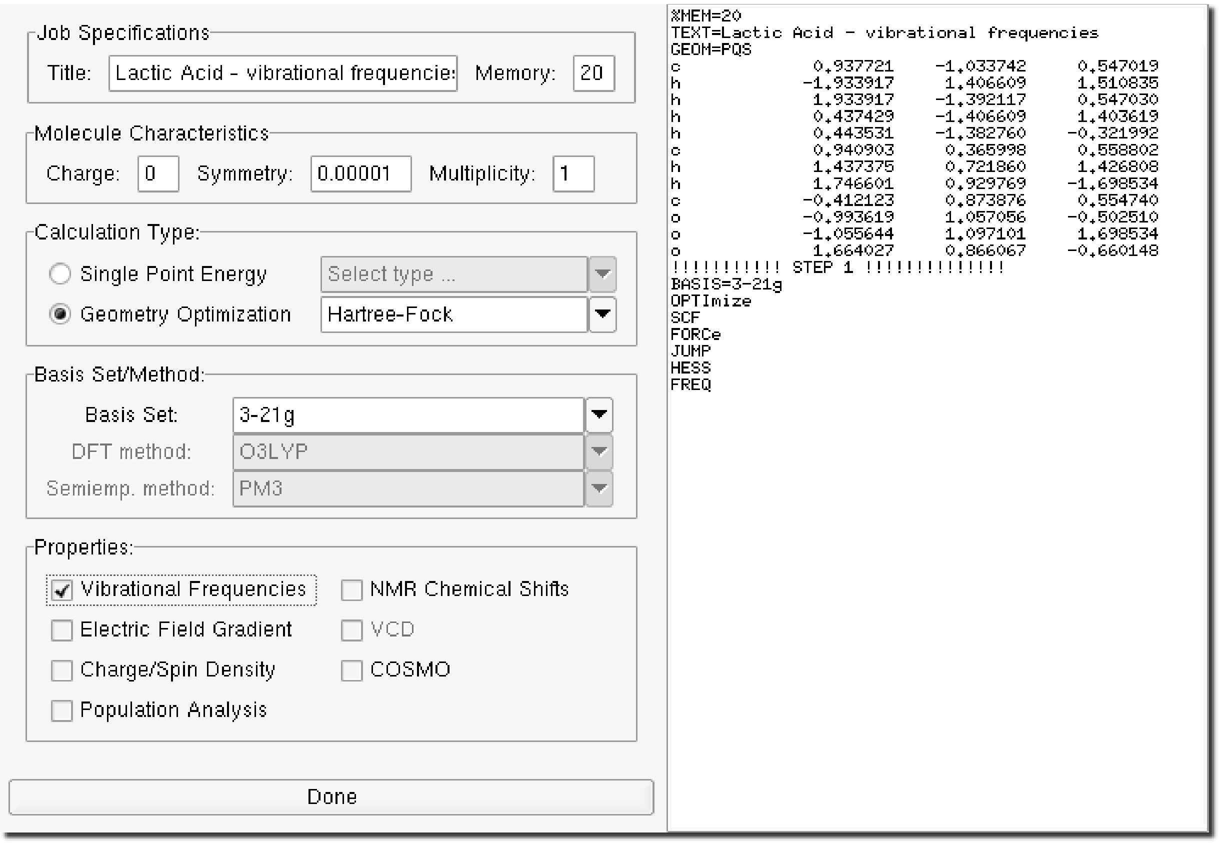
1 MW = 8,000,000 Bytes ≈ 7.3 MBytes

If, however, the entered value is > 2000 then it is interpreted as words (W)

1 W = 8 Bytes

Lactic acid is a neutral, closed-shell system and we have already determined the point group symmetry (`C1`) so none of the molecular characteristics need to be changed.

Select the *Geometry Optimization* radio button in the *Calculation Type* and choose `Hartree-Fock` from the dropdown menu. Choose the `3-21g` basis set in the *Basis Set* dropdown menu. In the *Properties* frame activate the *Vibrational Frequencies* checkbox. Figure 4.14 shows the final input file.


Job Specifications

Title: Lactic Acid - vibrational frequencie:

Memory: 20

Molecule Characteristics

Charge: 0

Symmetry: 0.00001

Multiplicity: 1

Calculation Type:

○ Single Point Energy — Select type ...

● Geometry Optimization — Hartree-Fock

Basis Set/Method:

Basis Set: 3-21g

DFT method: O3LYP

Semiemp. method: PM3

Properties:

☑ Vibrational Frequencies

☐ Electric Field Gradient

☐ Charge/Spin Density

☐ Population Analysis

☐ NMR Chemical Shifts

☐ VCD

☐ COSMO

```
%MEM=20
TEXT=Lactic Acid - vibrational frequencies
GEOM=PQS
c          0.937721    -1.033742     0.547019
h         -1.933917     1.406609     1.510835
h          1.933917    -1.392117     0.547030
h          0.437429    -1.406609     1.403619
h          0.443531    -1.382760    -0.321992
c          0.940903     0.365998     0.558802
h          1.437375     0.721860     1.426808
h          1.746601     0.929769    -1.698534
c         -0.412123     0.873876     0.554740
o         -0.993619     1.057056    -0.502510
o         -1.055644     1.097101     1.698534
o          1.664027     0.866067    -0.660148
!!!!!!!!!!! STEP 1 !!!!!!!!!!!!!!
BASIS=3-21g
OPTImize
SCF
FORCe
JUMP
HESS
FREQ
```

Figure 4.14: Input generation window - finished input

Press the **Done** button at the bottom of the window to save the input file. The input file is saved under the same name as the build file with a `.inp` extension, `O3C3H6.inp` in our example.

4.1.3 Submitting the PQS job

Step 10 Submit the job.

With a completed input file we are ready to submit the job. Use the **Calculation→Submit Job** menu item to run the calculation. The job is submitted and you should see a confirmation dialog in Figure 4.15.

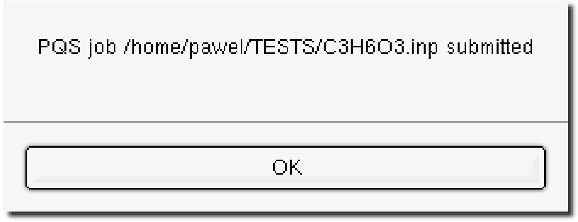
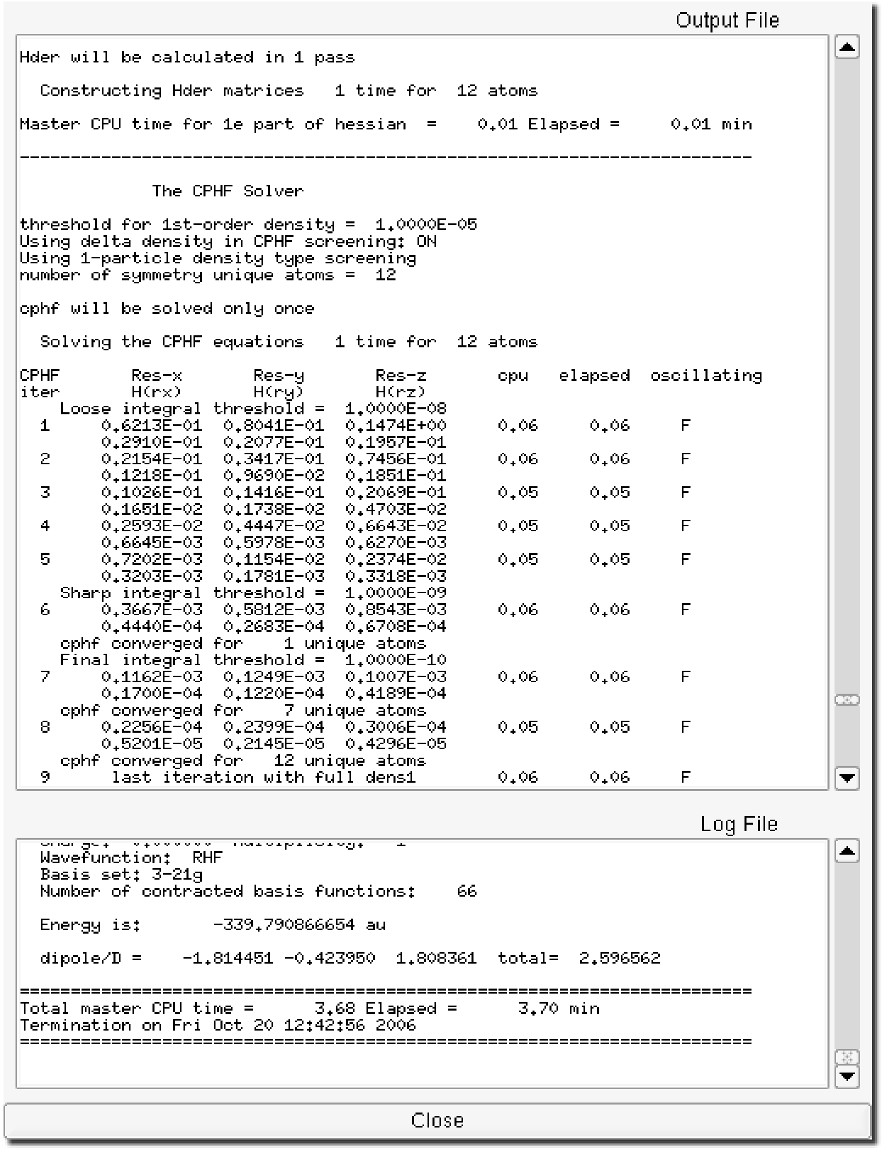

PQS job /home/pawel/TESTS/C3H6O3.inp submitted

Figure 4.15: Job Submission - confirmation

At this point **PQSMol** begins to monitor the output of the **PQS** calculation. As soon as output is produced it is displayed in the `PQS Output` window, shown in Figure 4.16.



```
Hder will be calculated in 1 pass

  Constructing Hder matrices   1 time for  12 atoms

Master CPU time for 1e part of hessian  =    0.01 Elapsed =     0.01 min

------------------------------------------------------------------------

             The CPHF Solver

threshold for 1st-order density =  1.0000E-05
Using delta density in CPHF screening: ON
Using 1-particle density type screening
number of symmetry unique atoms =  12

cphf will be solved only once

  Solving the CPHF equations   1 time for  12 atoms

CPHF       Res-x       Res-y       Res-z       cpu   elapsed  oscillating
iter       H(rx)       H(ry)       H(rz)
    Loose integral threshold =  1.0000E-08
  1     0.6213E-01  0.8041E-01  0.1474E+00     0.06     0.06     F
        0.2910E-01  0.2077E-01  0.1957E-01
  2     0.2154E-01  0.3417E-01  0.7456E-01     0.06     0.06     F
        0.1218E-01  0.9690E-02  0.1851E-01
  3     0.1026E-01  0.1416E-01  0.2069E-01     0.05     0.05     F
        0.1651E-02  0.1738E-02  0.4703E-02
  4     0.2593E-02  0.4447E-02  0.6643E-02     0.05     0.05     F
        0.6645E-03  0.5978E-03  0.6270E-03
  5     0.7202E-03  0.1154E-02  0.2374E-02     0.05     0.05     F
        0.3203E-03  0.1781E-03  0.3318E-03
    Sharp integral threshold =  1.0000E-09
  6     0.3667E-03  0.5812E-03  0.8543E-03     0.06     0.06     F
        0.4440E-04  0.2683E-04  0.6708E-04
    cphf converged for    1 unique atoms
    Final integral threshold =  1.0000E-10
  7     0.1162E-03  0.1249E-03  0.1007E-03     0.06     0.06     F
        0.1700E-04  0.1220E-04  0.4189E-04
    cphf converged for    7 unique atoms
  8     0.2256E-04  0.2399E-04  0.3006E-04     0.05     0.05     F
        0.5201E-05  0.2145E-05  0.4296E-05
    cphf converged for   12 unique atoms
  9      last iteration with full dens1        0.06     0.06     F
```

```
  Wavefunction:  RHF
  Basis set: 3-21g
  Number of contracted basis functions:    66

  Energy is:       -339.790866654 au

  dipole/D =    -1.814451 -0.423950  1.808361  total=  2.596562

========================================================================
Total master CPU time =      3.68 Elapsed =      3.70 min
Termination on Fri Oct 20 12:42:56 2006
========================================================================
```

Figure 4.16: PQS Output window

Two files produced by PQS are monitored. In the top frame, the contents of the `.out` file (in our example `C3H6O3.out`) and in the bottom frame the `.log` file (in our example `C3H6O3.log`) are displayed.

4.1.4 Visualizing the PQS job output

Step 11 Visualize the output.

As soon as the job finishes **PQSMol** is launched in **View mode** in a separate window with the current job output file as an argument producing the window in Figure 4.17.

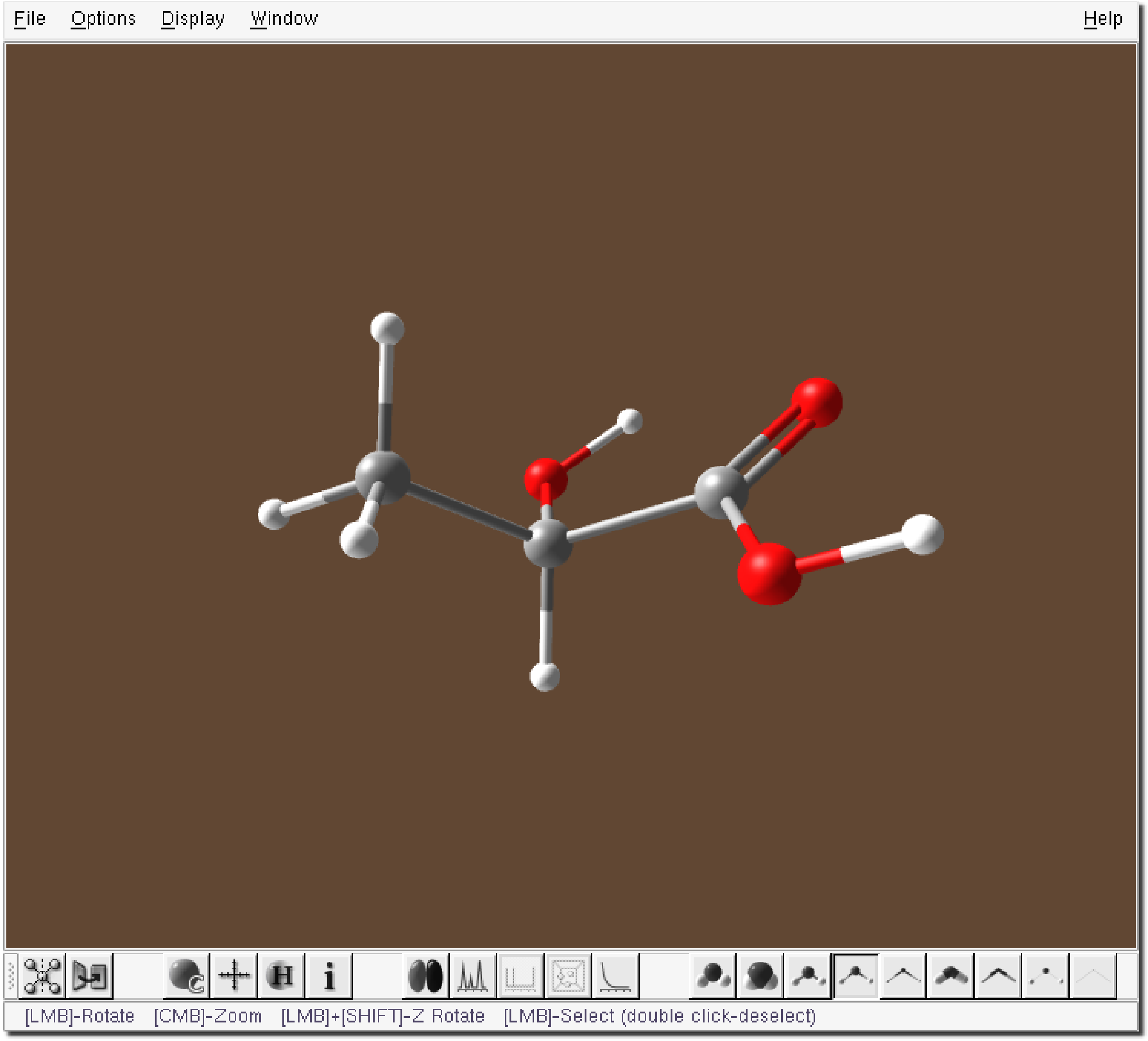
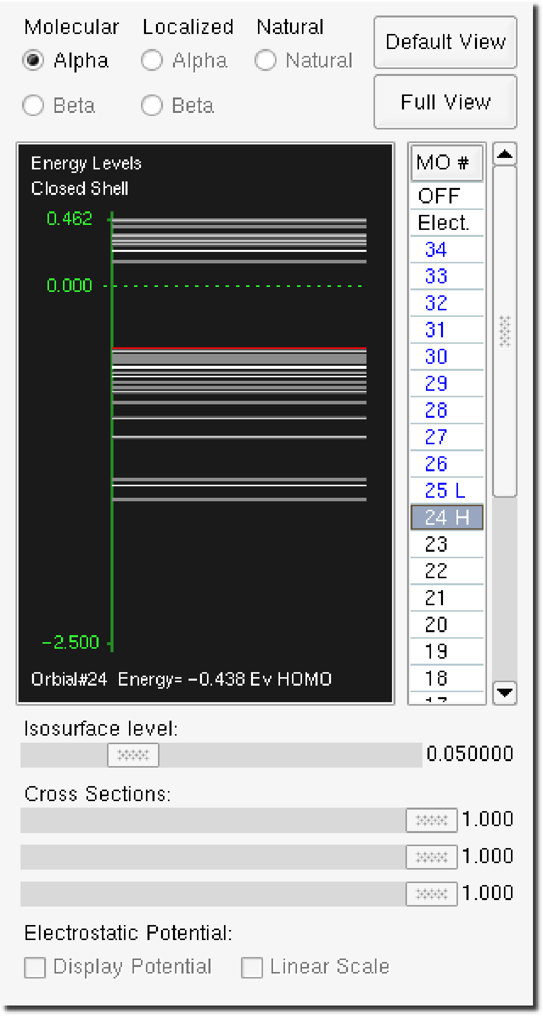


Figure 4.17: View window - initial display

Step 12 Examine the calculated molecular orbitals.

Press the **Orbitals** button the toolbar at the bottom of the *View window*. Select the HOMO (#24) in the list on the right side of the window. A line representing the energy level of the 24^{th} orbital is highlighted in red, see Figure 4.18.



Orbial#24 Energy= −0.438 Ev HOMO

Isosurface level: 0.050000

Cross Sections: 1.000 1.000 1.000

Figure 4.18: Orbitals window - HOMO selected

The corresponding *view window*, displaying the HOMO is shown in Figure 4.19. Move the *Isosurface level* slider to change the isosurface displayed in the *View window*. Also, experiment with the *Cross Sections* sliders to produce various display results.

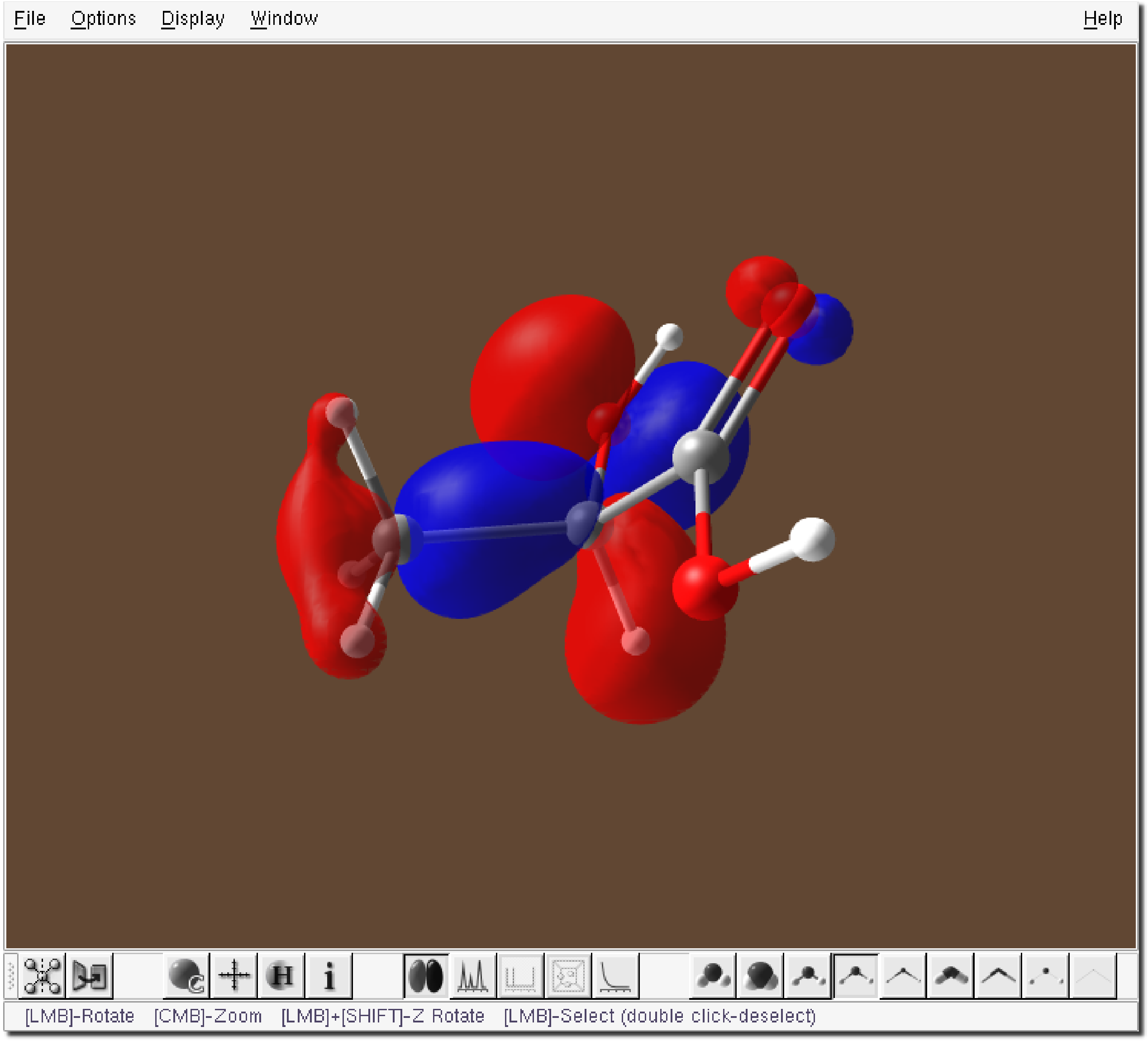
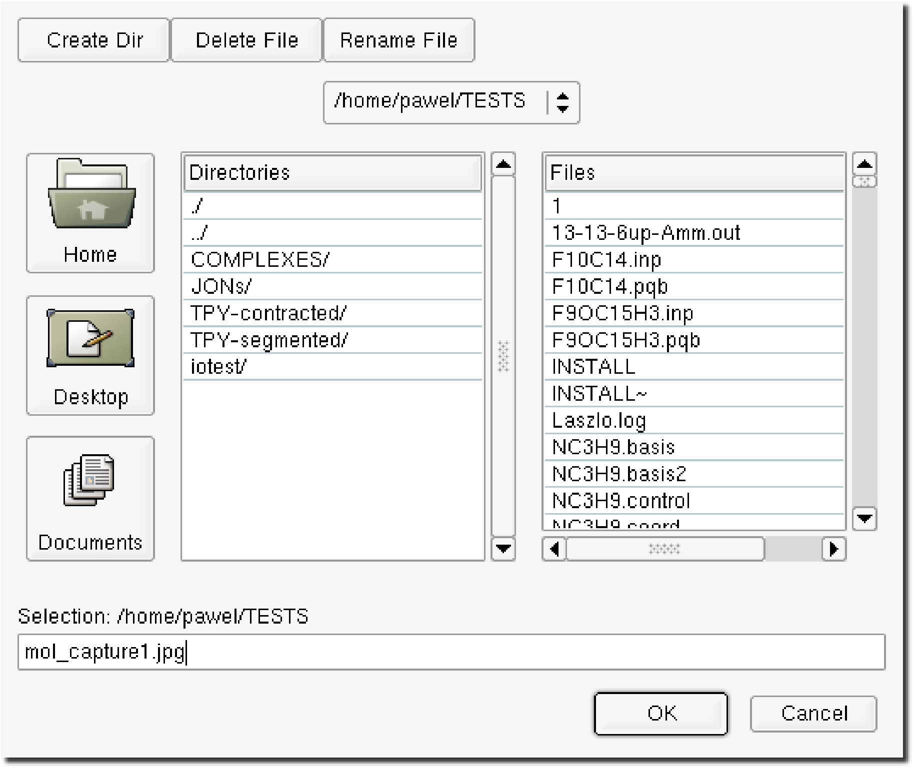


Figure 4.19: View window - HOMO displayed

Select other molecular orbitals in the list to see their display in the *View window*. Try changing the default settings in the **Display→Orbital** submenu in the menu at the top of the *View window*, including changing the grid resolution under **Display→Orbital→Grid Resolution**.

Step 13 Save a screen shot from the *View window*.

Once you have produced a "publication-quality" image in the *View window*, you can save it in JPEG format via the popup menu. Right-click anywhere within the *View window* and select the **Capture** menu item. A dialog prompting for a filename appears, Figure 4.20.



Selection: /home/pawel/TESTS

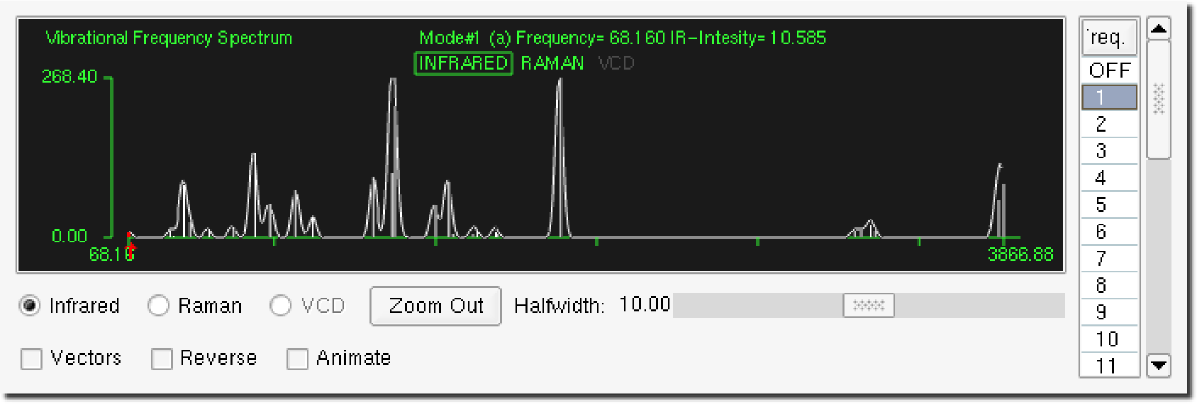
mol_capture1.jpg

Figure 4.20: Save Image dialog

You may save the image under the suggested name `mol_capture1.jpg` in the current working directory by simply pressing the **OK** button. To turn off the MO display either toggle the state of the **Orbitals** button in the toolbar or close the *Orbitals window*.

Step 14 Examine the Vibrational spectrum.

To display the simulated IR spectrum click on the **Vibrational Frequencies** button in the toolbar at the bottom of the *View window*. The simulated IR spectrum is shown in Figure 4.21.



Mode#1 (a) Frequency= 68.160 IR-Intesity= 10.585

● Infrared

Halfwidth: 10.00

Figure 4.21: Vibrational Frequencies window - IR spectrum, mode #1 selected

The list on the right side of the *Vibrational Frequencies window* allows access to all of the vibrational frequencies of the molecule (30 in this example). Select the first frequency. A small red arrow appears under the corresponding frequency in the vibrational spectrum and details for that mode appear in green font at the top of the window (mode number, symmetry, frequency and intensity). This mode is primarily a twisting about the C-O bond and has a low intensity that does not show up in the simulated IR spectrum.

Now, activate the *Vectors* checkbox in the bottom left corner of the window, as shown in Figure 4.21. This will show the atomic displacements in the vibrational mode #1 as yellow vectors at each atom of the structure in the *View window*, Figure 4.22. Activate the *Animate* checkbox to animate the structure by showing the motion in the vibrational mode #1.

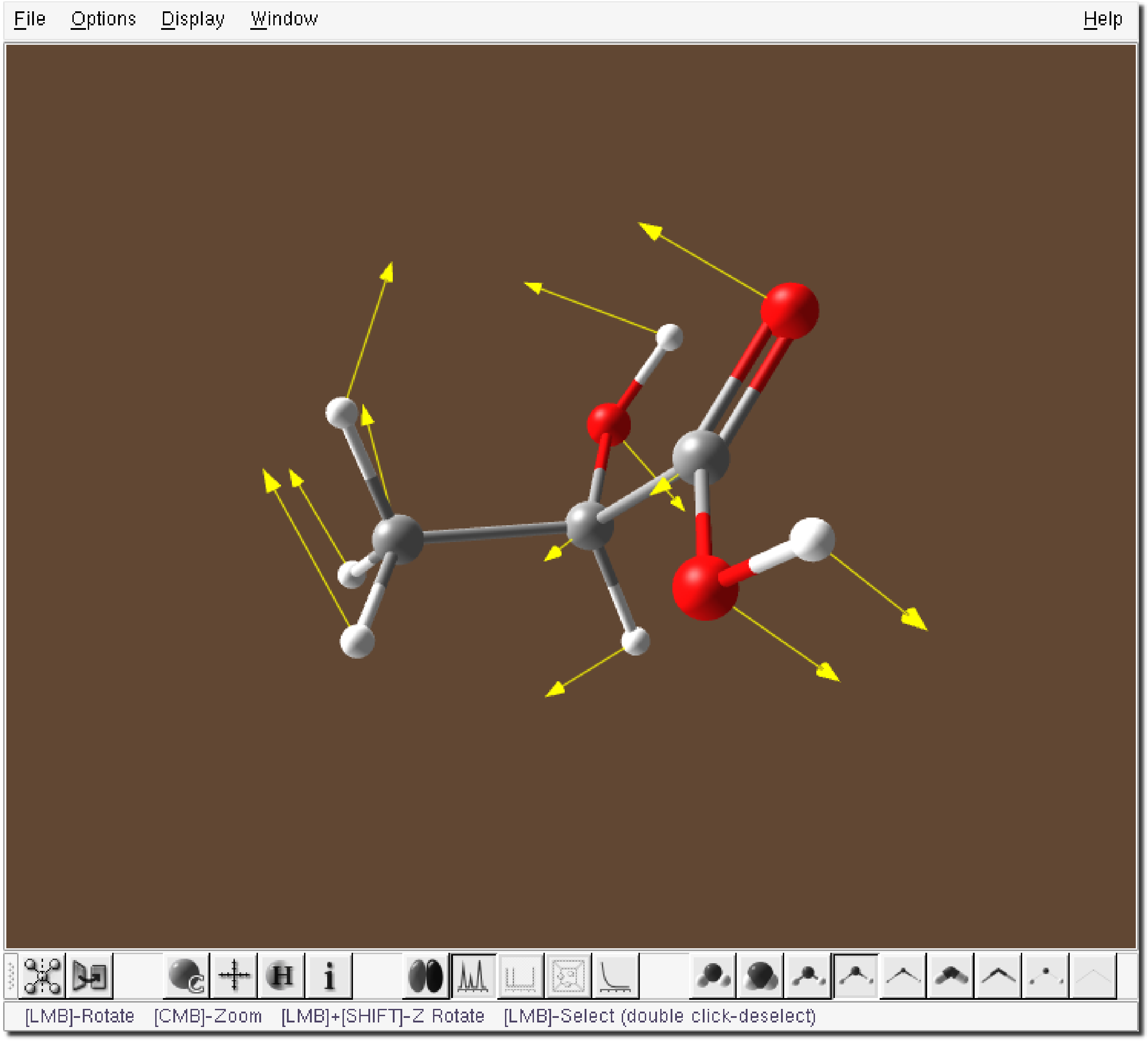
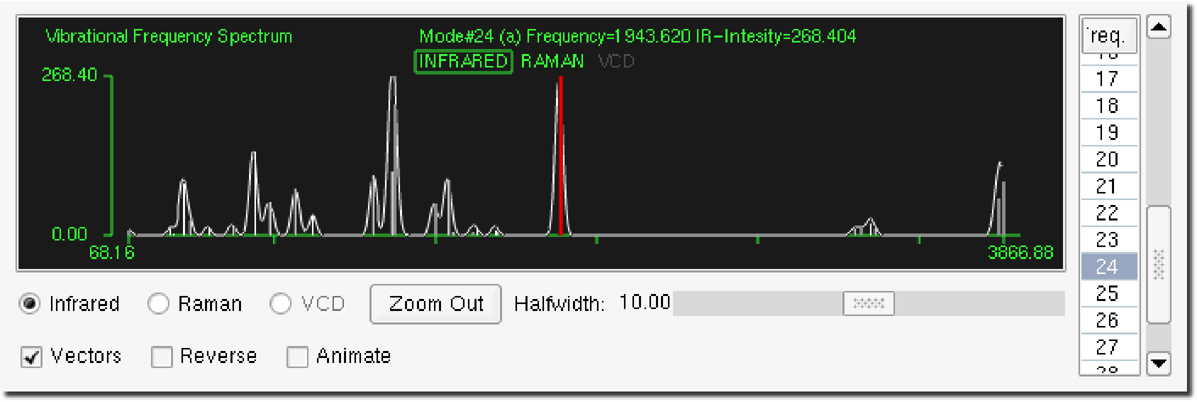


Figure 4.22: View window - vibrational mode #1 displacement vectors

Other vibrational modes can be selected from the list at the right side of the *Vibrational Frequencies window* or by directly selecting the peak in the simulated spectrum.



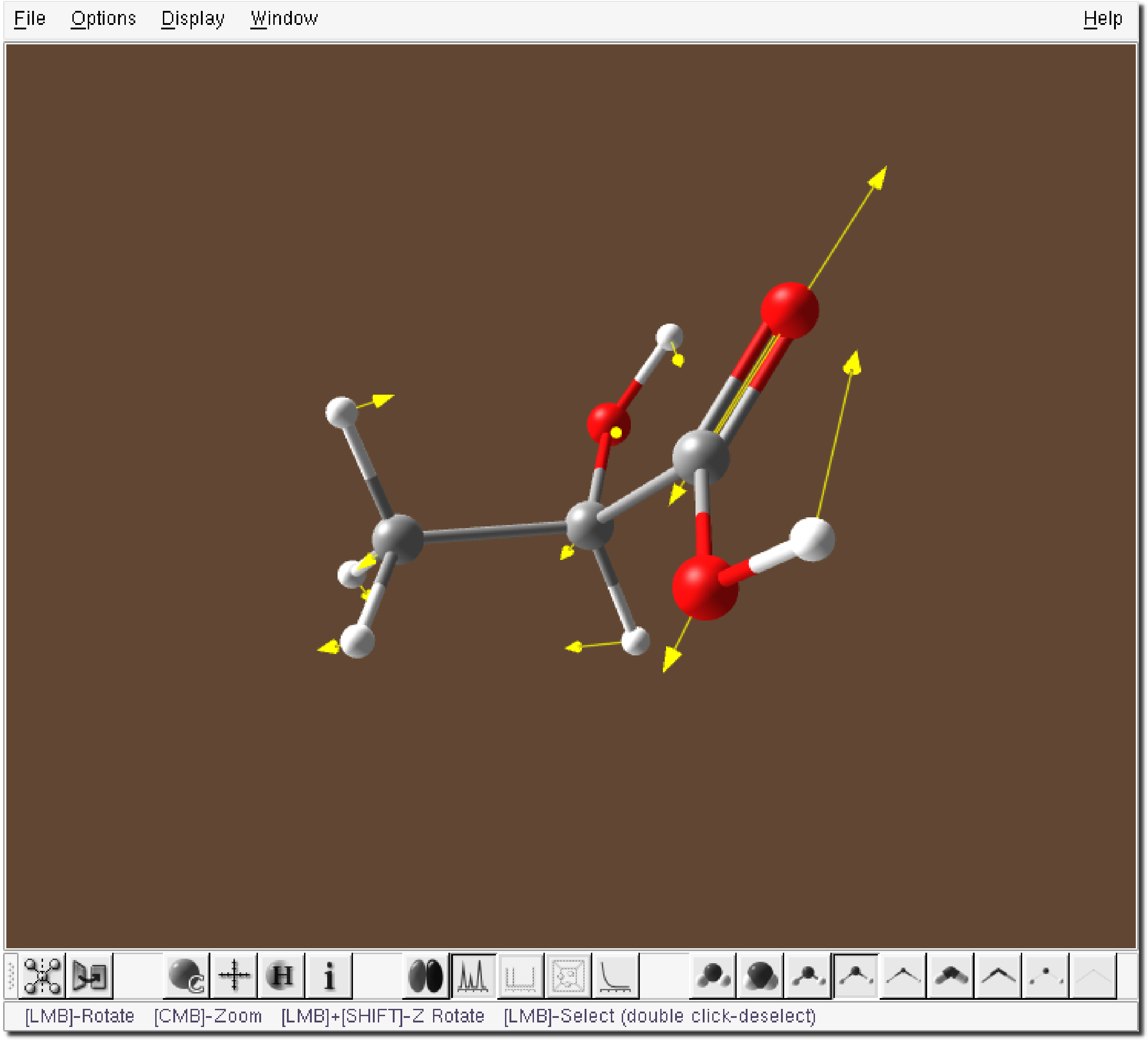
Mode#24 (a) Frequency=1943.620 IR-Intesity=268.404

● Infrared ○ Raman ○ VCD

Halfwidth: 10.00

☑ Vectors ☐ Reverse ☐ Animate

Figure 4.23: Vibrational Frequencies window - IR spectrum, mode #24 selected



[LMB]-Rotate [CMB]-Zoom [LMB]+[SHIFT]-Z Rotate [LMB]-Select (double click-deselect)

Figure 4.24: View window - highest intensity vibrational mode #24 displacement vectors

Figure 4.24 shows the displacement in the most intense IR mode #24 and Figure 4.23 shows the corresponding *Vibrational*

Frequencies window, with the peak highlighted in red.

4.2 Example 2 - CHFClBr

Our next example is simple to build. The molecule is CHFClBr, Figure 4.25.

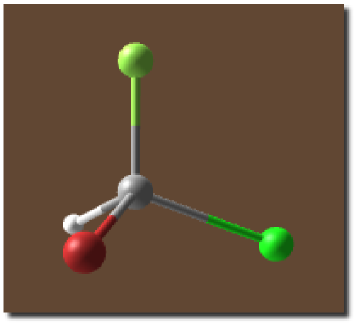


Figure 4.25: CHFClBr

This system is chiral and we are going to calculate and examine its VCD spectrum. This involves both an NMR and a standard Hessian computation enabling both the IR and NMR spectra to be simulated as well.

4.2.1 Building CHFClBr

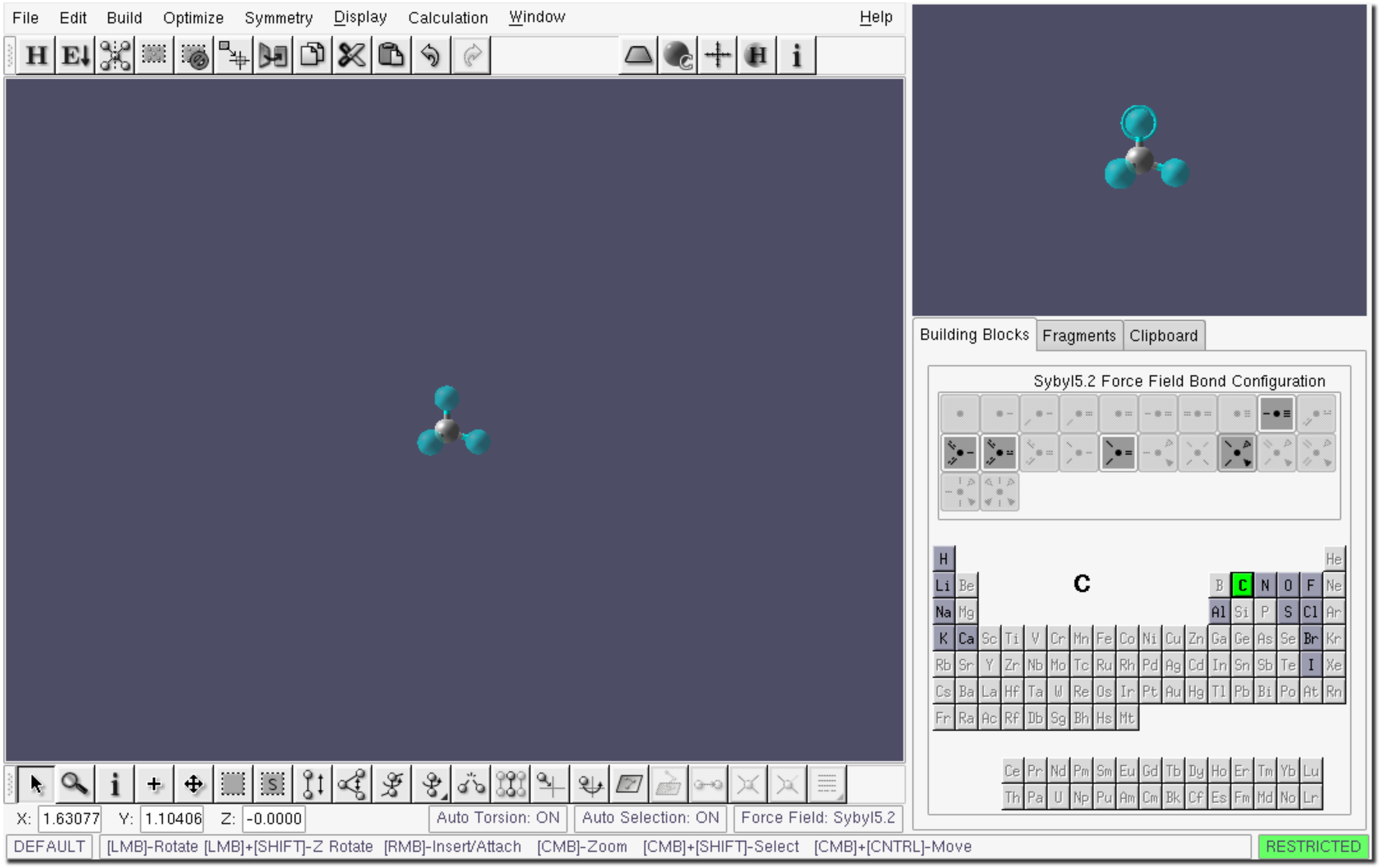
Step 1 Start the builder by typing `pqsmol` at the command prompt.

As shown in Figure 4.25, the whole molecule consists of 4 atoms, with the tetrahedral carbon in the center. We will start with this carbon.

Step 2 Insert the tetrahedral carbon building block.

When **PQSMol** is first started, the default current element is carbon. The current element is displayed in large font above the periodic table in the *Segment window* and the current element's button is highlighted with a green background. There may be multiple building blocks available for a given element. These are listed in the *Bond Configuration* frame. The default building block for carbon is the tetrahedral block. The current building block is displayed in the *Segment buffer*.

At this point we should have the correct building block ready to insert into the *Build window*. The *Segment window* should look like the one in Figure 4.26. To insert the building block, first select the **Add/Attach/Connect** tool from the toolbar at the bottom of the window and click anywhere inside the build area.



X: 1.63077 Y: 1.10406 Z: -0.0000 Auto Torsion: ON Auto Selection: ON Force Field: Sybyl5.2

[LMB]-Rotate [LMB]+[SHIFT]-Z Rotate [RMB]-Insert/Attach [CMB]-Zoom [CMB]+[SHIFT]-Select [CMB]+[CNTRL]-Move

Figure 4.26: Build and segment windows - inserting the tetrahedral carbon building block

Tip: You may also insert into the *Build window* using the **Default** tool by right-clicking in the *Build window*.

Note: If for some reason the building block in your *Segment window* is different than the one in Figure 4.26, you can select the tetrahedral carbon building block by clicking on the carbon button in the periodic table.

Figure 4.26 shows the *Build window* with the tetrahedral carbon inserted.

Step 3 Connect the fluorine building block.

In the *Segment window* press the fluorine button in the periodic table. There is only one building block available for fluorine. Your *Segment window* should now be identical to the one in Figure 4.27.

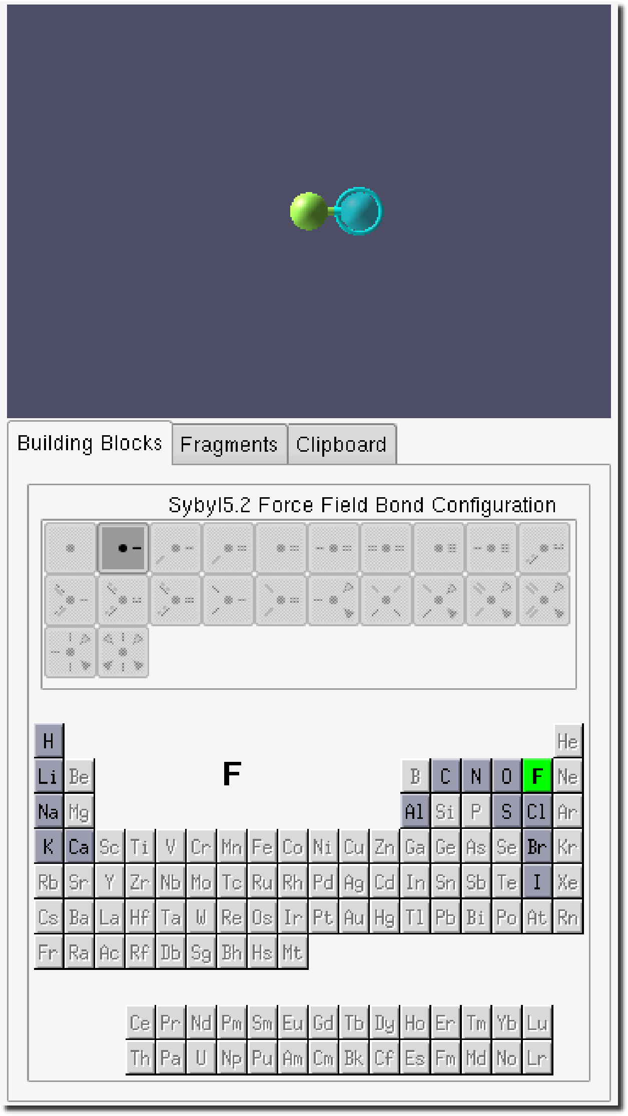


Figure 4.27: Segment window - fluorine building block selected

Using the same **Add/Attach/Connect** tool move the mouse over the top-most dummy atom in the build area. The dummy atom will be highlighted with a circle around it. The mouse pointer will change to a plus sign with a letter "A", as shown in the left image of Figure 4.28. This indicates that the dummy atom is a valid attachment point for the segment in the *Segment buffer*.

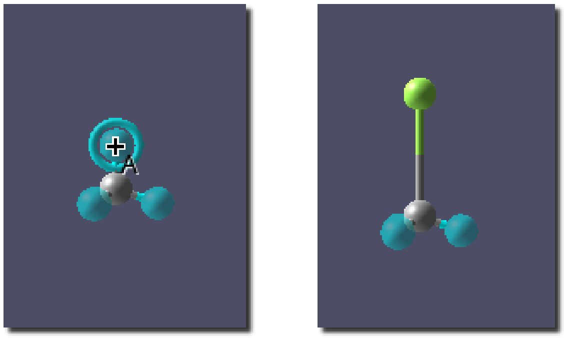
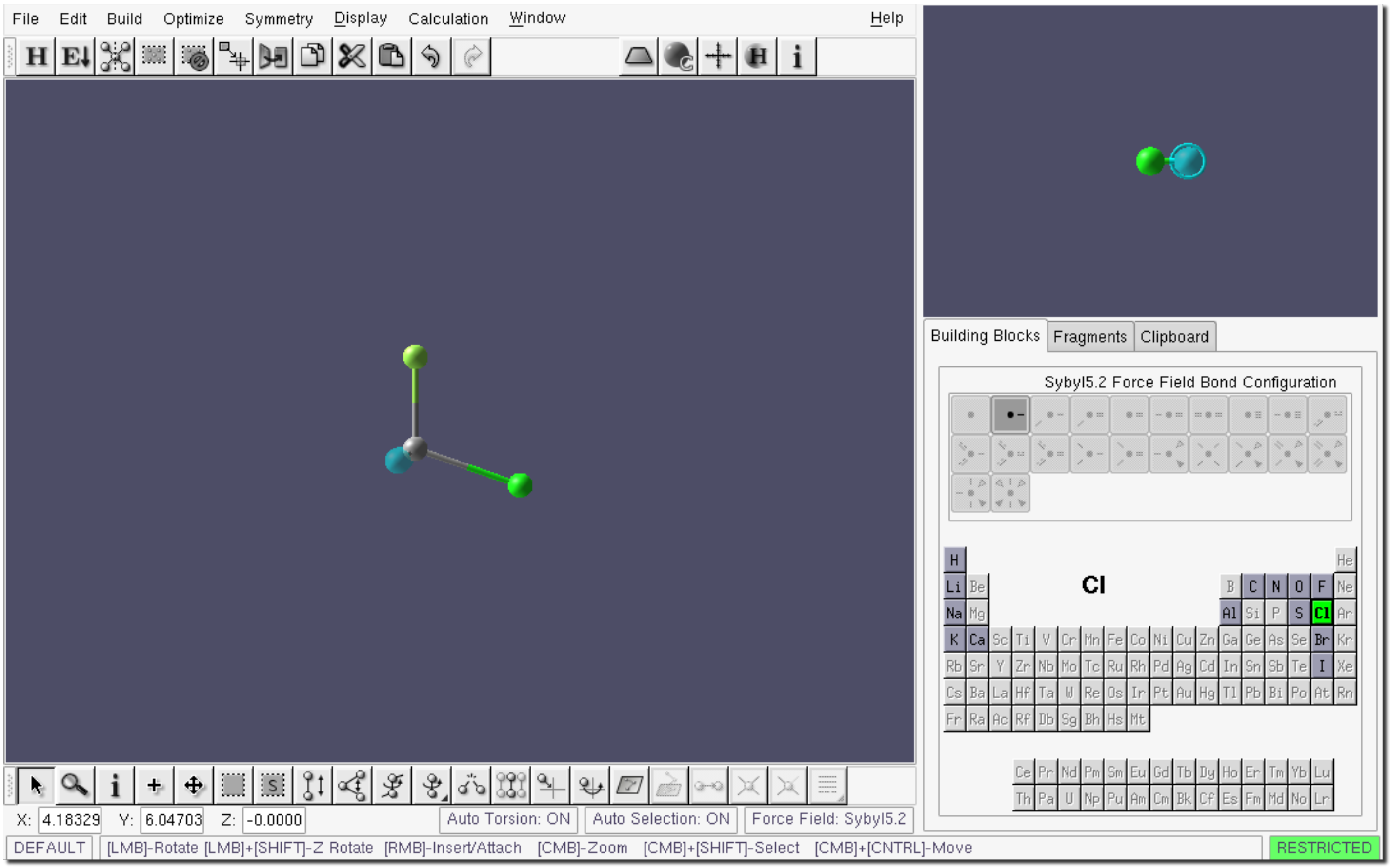


Figure 4.28: Build area - attaching the fluorine building block

Click the mouse button over the atom. The result is shown in the right image of Figure 4.28.

Step 4 Connect the Chlorine building block.

Select Chlorine in the periodic table. Again for Chlorine only one building block is available. Using the **Add/Attach/Connect** tool attach the Chlorine building block to the right-most dummy atom, as shown in Figure 4.29.



X: 4.18329 Y: 6.04703 Z: -0.0000

Auto Torsion: ON

Auto Selection: ON

Force Field: Sybyl5.2

DEFAULT [LMB]-Rotate [LMB]+[SHIFT]-Z Rotate [RMB]-Insert/Attach [CMB]-Zoom [CMB]+[SHIFT]-Select [CMB]+[CNTRL]-Move

RESTRICTED

Figure 4.29: Build and segment windows - attaching the Chlorine building block

Step 5 Connect the Bromine building block.

Select Bromine in the periodic table. Again for Bromine only one building block is available. Using the **Add/Attach/Connect** tool attach the Bromine building block to the left-front dummy atom.

Step 6 Fill dummy atoms with hydrogen.

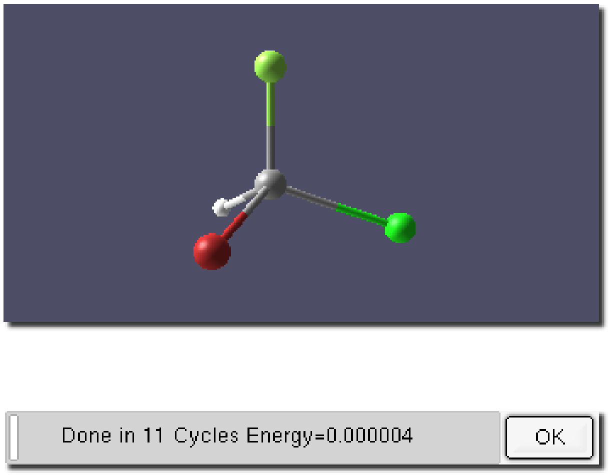
Press the **Hydrogen Fill** button H to replace all remaining single-bond dummy atoms with hydrogen. In our case, we only have one such dummy atom.

Step 7 Preoptimize.

PQSMol has the capability to perform an initial geometry optimization using one of two built-in force fields. The default force field is Sybyl5.2 (this can be seen in the status bar at the bottom of the *Build window* in Figure 4.30) which is perfectly adequate for this example.

To run the optimizer press the **Optimize** button E↓ in the top toolbar. Figure 4.30 shows the result.

Press the **OK** button to close the geometry optimization dialog.

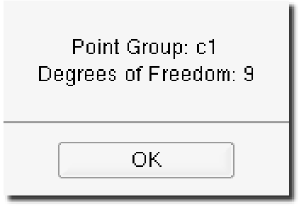


Done in 11 Cycles Energy=0.000004

Figure 4.30: Geometry optimization results

Step 8 Check for symmetry.

The symmetrizer in **PQSMol** is initiated via the **Check Symmetry** button in the top toolbar. This operation attempts to find any axes of symmetry in the built structure, within a specified threshold. If any symmetry is found, the atoms are repositioned to conform exactly with the found symmetry. Our example molecule has ”c1” symmetry i.e., no detected symmetry, as shown in Figure 4.31.



Point Group: c1
Degrees of Freedom: 9

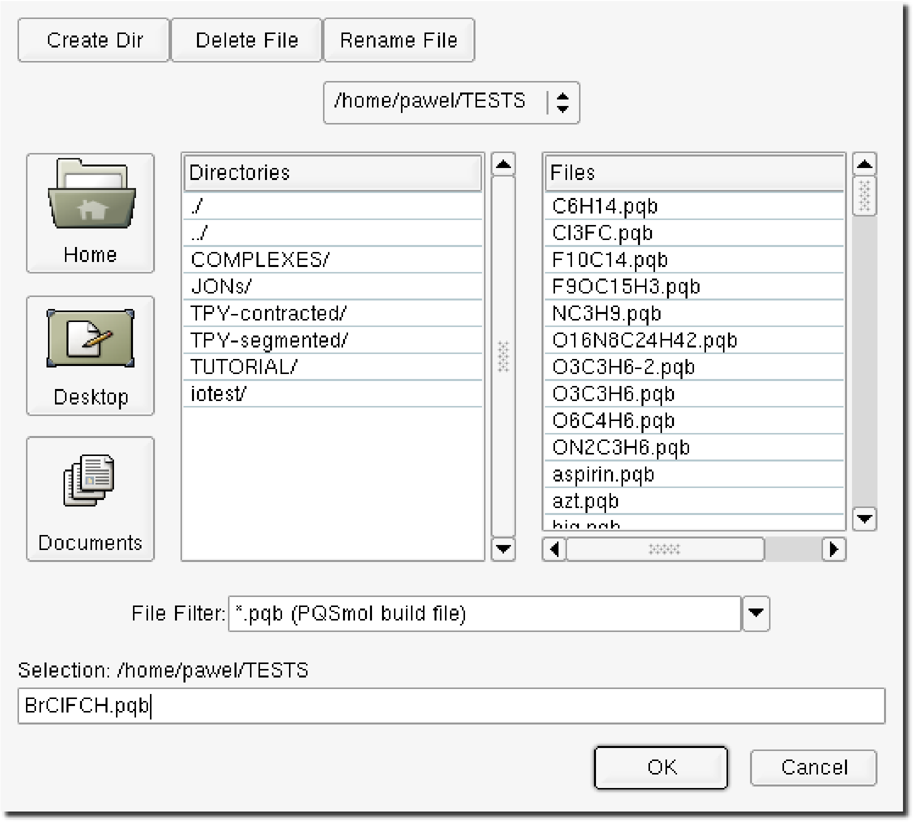
Figure 4.31: Symmetry results dialog

4.2.2 Creating a PQS input file

PQSMol includes a built-in **PQS** input generator, which lets you create **PQS** input files in a graphical environment using text entries, radio buttons, checkboxes and dropdown menus. The result is a text file containing the proper keywords, formating and syntax required by the **PQS** program.

Step 9 Save the build file.

Before proceeding with input file creation, we need to name our build file. Use the **File→Save** menu item to name our example file. You should now see the dialog in Figure 4.32.



/home/pawel/TESTS

Directories
- ./
- ../
- COMPLEXES/
- JONs/
- TPY-contracted/
- TPY-segmented/
- TUTORIAL/
- iotest/

Files
- C6H14.pqb
- Cl3FC.pqb
- F10C14.pqb
- F9OC15H3.pqb
- NC3H9.pqb
- O16N8C24H42.pqb
- O3C3H6-2.pqb
- O3C3H6.pqb
- O6C4H6.pqb
- ON2C3H6.pqb
- aspirin.pqb
- azt.pqb

File Filter: *.pqb (PQSmol build file)

Selection: /home/pawel/TESTS

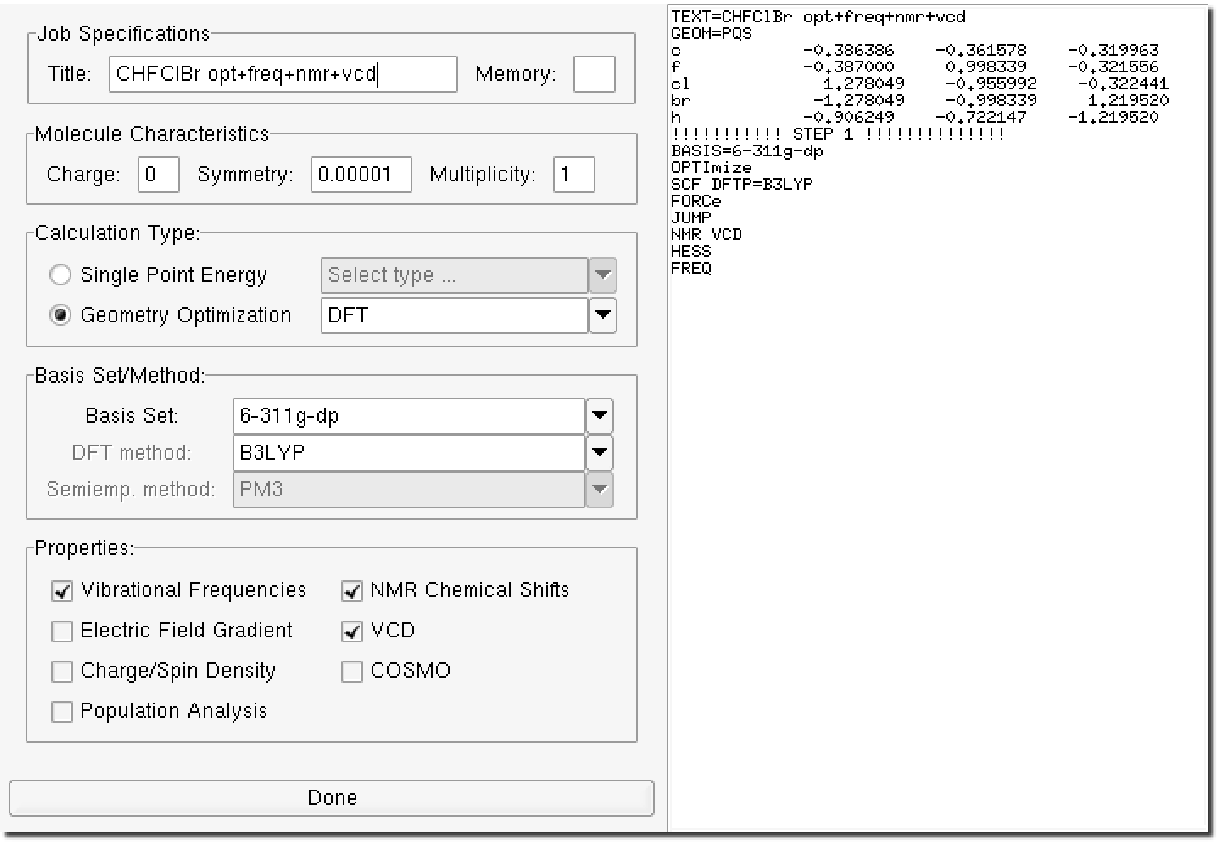
BrClFCH.pqb

Figure 4.32: Save dialog

The empirical formula is automatically set as the filename with the `.pqb` extension. You may change the filename, however it has to end with `.pqb`. Click the **OK** button to save the file under the selected name.

Step 10 Start the input generator.

Use the **Calculation→Job Input** menu item to start the input generator. The job parameters window is shown in Figure 4.33.



Title: CHFClBr opt+freq+nmr+vcd

Memory:

Charge: 0

Symmetry: 0.00001

Multiplicity: 1

○ Single Point Energy Select type ...

● Geometry Optimization DFT

Basis Set: 6-311g-dp

DFT method: B3LYP

Semiemp. method: PM3

☑ Vibrational Frequencies

☑ NMR Chemical Shifts

☐ Electric Field Gradient

☑ VCD

☐ Charge/Spin Density

☐ COSMO

☐ Population Analysis

```
TEXT=CHFClBr opt+freq+nmr+vcd
GEOM=PQS
c            -0.386386    -0.361578    -0.319963
f            -0.387000     0.998339    -0.321556
cl            1.278049    -0.955992    -0.322441
br           -1.278049    -0.998339     1.219520
h            -0.906249    -0.722147    -1.219520
!!!!!!!!!!! STEP 1 !!!!!!!!!!!!!!
BASIS=6-311g-dp
OPTImize
SCF DFTP=B3LYP
FORCe
JUMP
NMR VCD
HESS
FREQ
```

Figure 4.33: Job parameters window - complete input file

The left frame of the job parameters window contains the user interface objects to create the input file. The left frame shows the actual source of the input file generated. It is updated in real time, as options are selected in the left frame.

Fill in the options as follows. In the **Job Specification** frame enter the optional title `CHFClBr opt + freq + nmr + vcd`. In the *Calculation Type* frame select the *Geometry Optimization* radio button and the `DFT` item in the dropdown menu. In the *Basis Set/Method* frame, select the `6-311g-dp` basis set, and `B3LYP` for the DFT method. In the *Properties* frame, check the *Vibrational Frequencies*, *NMR Chemical Shifts* and *VCD* checkboxes. The resulting input file source is shown in the right frame in Figure 4.33. Press the **Done** button at the bottom of the window to save the input file.

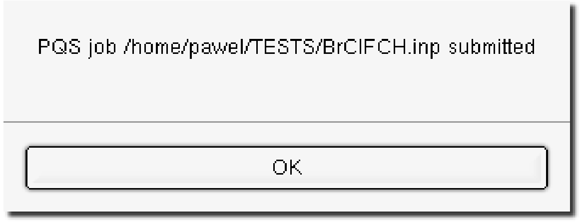
Note: The input file is saved under the same filename as the build file but with the extension `.inp`.

Note: If you attempt to start the input generator with an untitled build file, the Save dialog will be automatically open. The input generator will not execute until a valid filename is assigned to the build file.

4.2.3 Submitting a PQS job

Step 9 Submit the **PQS** job.

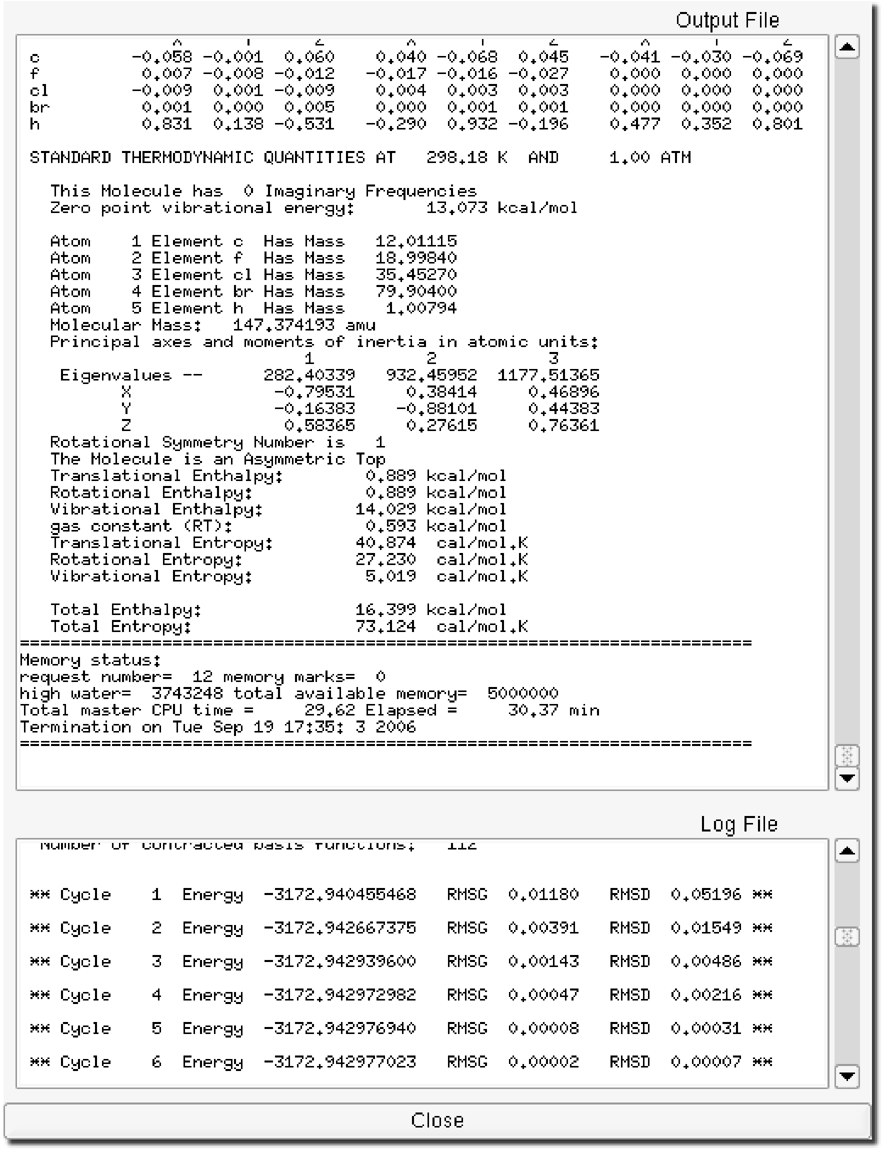
We are now ready to run the **PQS** calculation. Use the **Calculation→Submit Job** menu item to submit the job. You should now see the confirmation dialog in Figure 4.34.



PQS job /home/pawel/TESTS/BrClFCH.inp submitted

Figure 4.34: Job submission confirmation dialog

Press the **OK** button to close the Job Submission confirmation dialog. As soon as any output is generated by **PQS** job, it is displayed and updated in real time in the output window, Figure 4.35.



```
 c         -0.058 -0.001  0.060    0.040 -0.068  0.045   -0.041 -0.030 -0.069
 f          0.007 -0.008 -0.012   -0.017 -0.016 -0.027    0.000  0.000  0.000
 cl        -0.009  0.001 -0.009    0.004  0.003  0.003    0.000  0.000  0.000
 br         0.001  0.000  0.005    0.000  0.001  0.001    0.000  0.000  0.000
 h          0.831  0.138 -0.531   -0.290  0.932 -0.196    0.477  0.352  0.801

 STANDARD THERMODYNAMIC QUANTITIES AT   298.18 K  AND     1.00 ATM

   This Molecule has  0 Imaginary Frequencies
   Zero point vibrational energy:       13.073 kcal/mol

   Atom    1 Element c  Has Mass   12.01115
   Atom    2 Element f  Has Mass   18.99840
   Atom    3 Element cl Has Mass   35.45270
   Atom    4 Element br Has Mass   79.90400
   Atom    5 Element h  Has Mass    1.00794
   Molecular Mass:   147.374193 amu
   Principal axes and moments of inertia in atomic units:
                            1            2            3
    Eigenvalues --      282.40339   932.45952  1177.51365
          X              -0.79531     0.38414     0.46896
          Y              -0.16383    -0.88101     0.44383
          Z               0.58365     0.27615     0.76361
   Rotational Symmetry Number is   1
   The Molecule is an Asymmetric Top
   Translational Enthalpy:        0.889 kcal/mol
   Rotational Enthalpy:           0.889 kcal/mol
   Vibrational Enthalpy:         14.029 kcal/mol
   gas constant (RT):             0.593 kcal/mol
   Translational Entropy:        40.874  cal/mol.K
   Rotational Entropy:           27.230  cal/mol.K
   Vibrational Entropy:           5.019  cal/mol.K

   Total Enthalpy:               16.399 kcal/mol
   Total Entropy:                73.124  cal/mol.K
========================================================================
Memory status:
request number=  12 memory marks=  0
high water=  3743248 total available memory=  5000000
Total master CPU time =     29.62 Elapsed =     30.37 min
Termination on Tue Sep 19 17:35: 3 2006
========================================================================
```

```
  Number of contracted basis functions:   112


 ** Cycle    1  Energy  -3172.940455468   RMSG  0.01180   RMSD  0.05196 **

 ** Cycle    2  Energy  -3172.942667375   RMSG  0.00391   RMSD  0.01549 **

 ** Cycle    3  Energy  -3172.942939600   RMSG  0.00143   RMSD  0.00486 **

 ** Cycle    4  Energy  -3172.942972982   RMSG  0.00047   RMSD  0.00216 **

 ** Cycle    5  Energy  -3172.942976940   RMSG  0.00008   RMSD  0.00031 **

 ** Cycle    6  Energy  -3172.942977023   RMSG  0.00002   RMSD  0.00007 **
```

Figure 4.35: Job output window

Two files are monitored in the job output window: the `.out` file in the text area at the top of the window, and the `.log` file in the bottom. As output is produced it is added to the end of the file and the display scrolls down. Use the scrollbars on the left side of the windows to scroll up and down through the file.

4.2.4 Visualizing the PQS job output

When the job is finished, **PQSMol** is automatically started in **View mode** with the job's output file as an argument, Figure 4.36.

Note: You can also start the job visualization via **Calculation→Visualize Output** menu item in the *Build window* menubar.

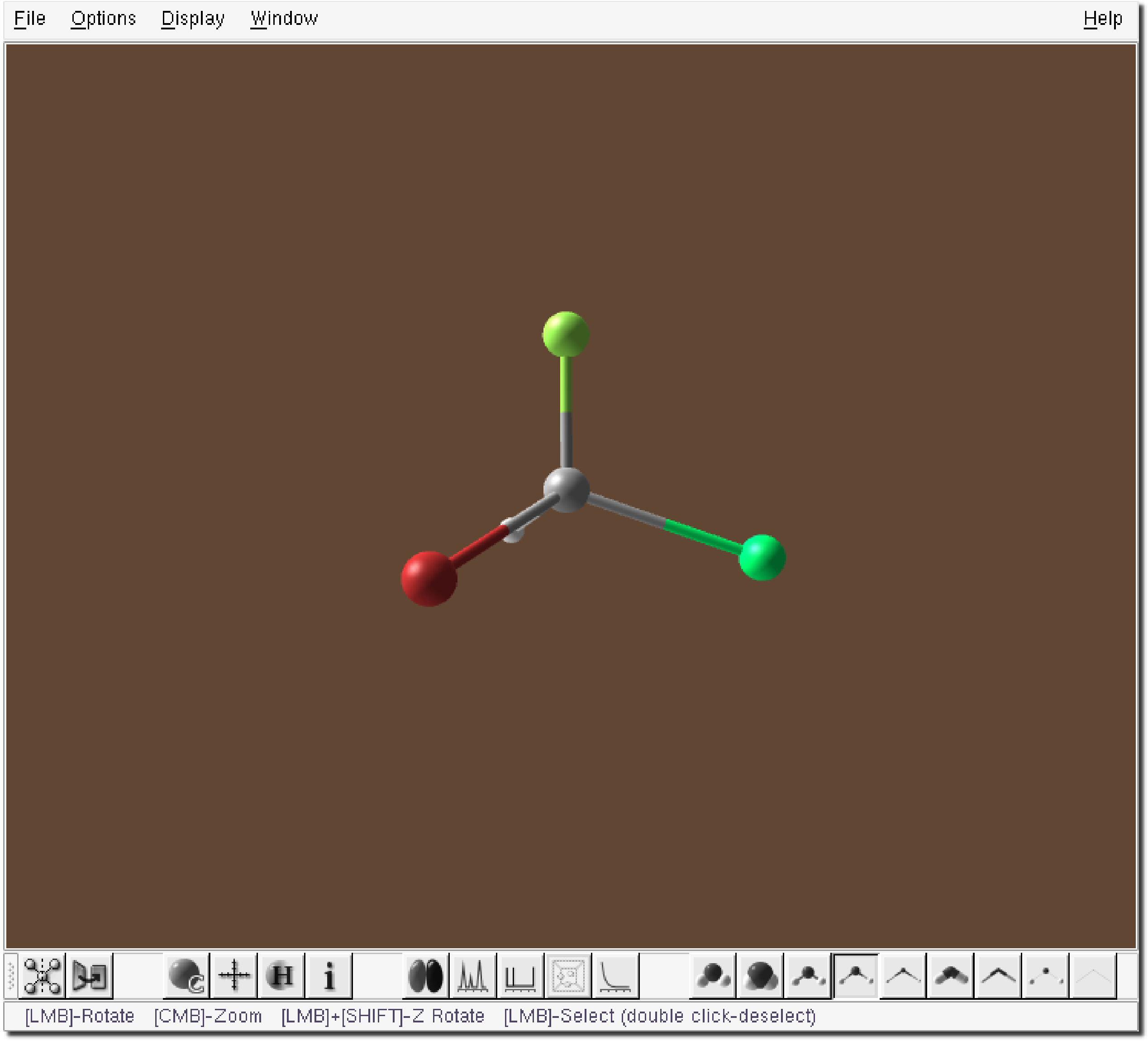
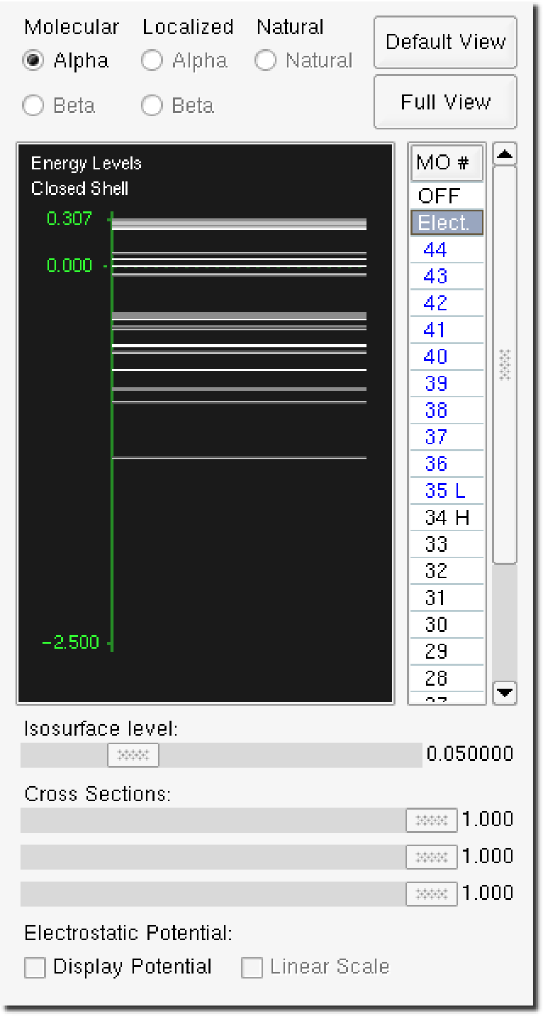


Figure 4.36: View window - initial display

Step 10 Examine the electron density

Press the **Orbitals** button  in the toolbar at the bottom of the *view window*, to open the *Orbitals window*, Figure 4.37. The graph on the left side of the window shows the the energy levels for the individual orbitals. The orbital list on the right contains the calculated orbitals. By default, the list and the graph are limited to displaying orbitals from an energy level of -2.5Ev and no more than the first 10 virtual orbitals. To display all calculated orbitals press the **Full View** button. The **Default View** button toggles back the default orbital range.

In the list on the right select *Elect.*ron density item, as shown in Figure 4.37.



Molecular: ● Alpha ○ Beta Localized: ○ Alpha ○ Beta Natural: ○ Natural

Isosurface level: 0.050000

Cross Sections: 1.000 1.000 1.000

☐ Display Potential ☐ Linear Scale

Figure 4.37: Orbitals window - electron density selected

The corresponding *View window* is shown in Figure 4.38.

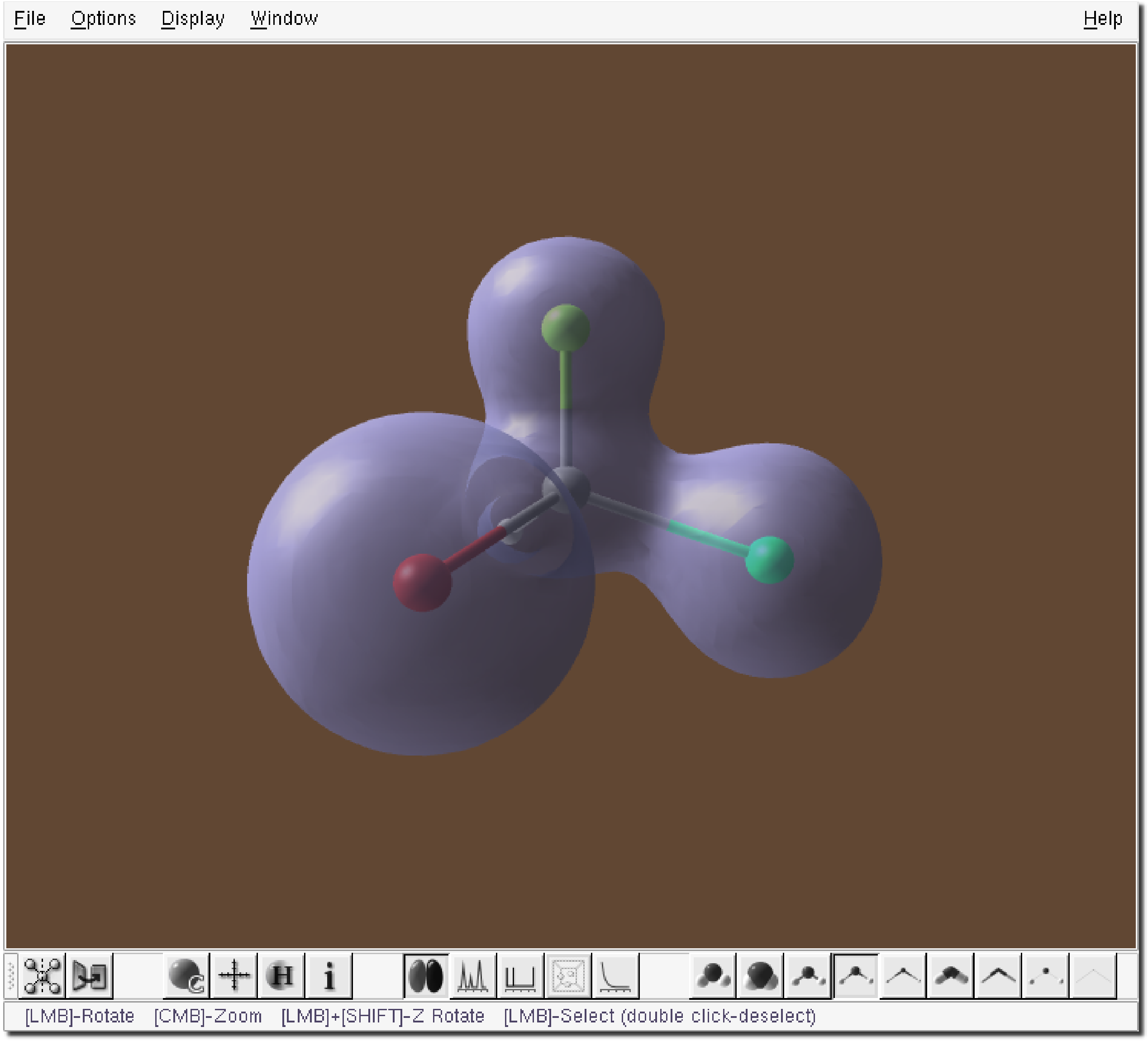
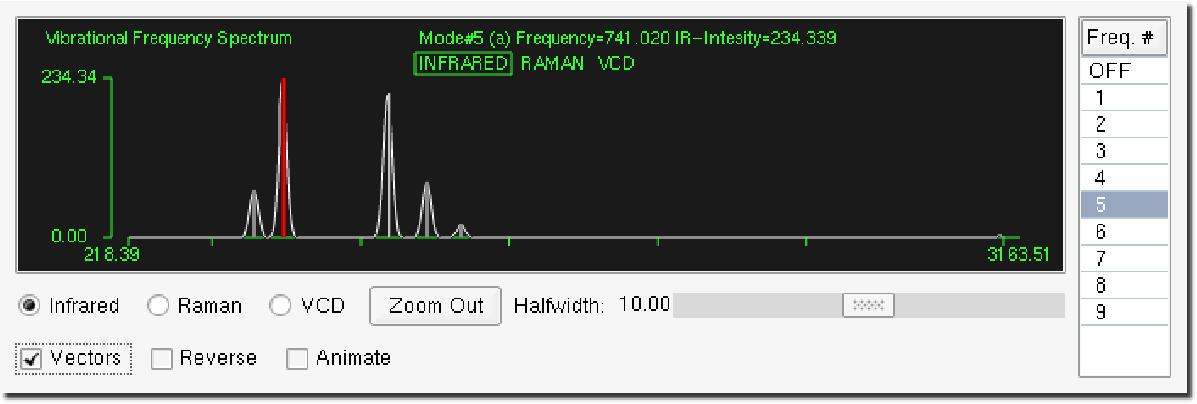


Figure 4.38: View window - electron density displayed

Use the *Isosurface level* slider in the *Orbitals window* to change the displayed isosurface.

Step 11 Examine the IR Spectrum

Press the **Vibrational Frequencies** button in the toolbar at the bottom of the *view window*. The *Vibrational Frequencies window* appears, Figure 4.39, displaying the simulated IR spectrum. Select the most intensive signal in the IR spectrum by clicking on highest peak in the graph or select #5 in the Frequencies list on the right.After activating the *Vectors* checkbox, the atomic displacements in this mode will be displayed as yellow arrows at each atom in the structure in the *View window*, Figure 4.40.



Mode#5 (a) Frequency=741.020 IR-Intesity=234.339

● Infrared ○ Raman ○ VCD

Halfwidth: 10.00

☑ Vectors ☐ Reverse ☐ Animate

Figure 4.39: Vibrational Frequencies window - most intense IR mode in CHFCLBr

The corresponding *View window* is shown in Figure 4.40.

Activating the *Reverse* checkbox will reverse the directions of the arrows. To show an animation of the vibrational mode in the *View window* activate the *Animate* checkbox in the Vibrational Frequencies window. To view other modes either select another peak in the simulated spectrum or select another mode number in the Frequencies list.

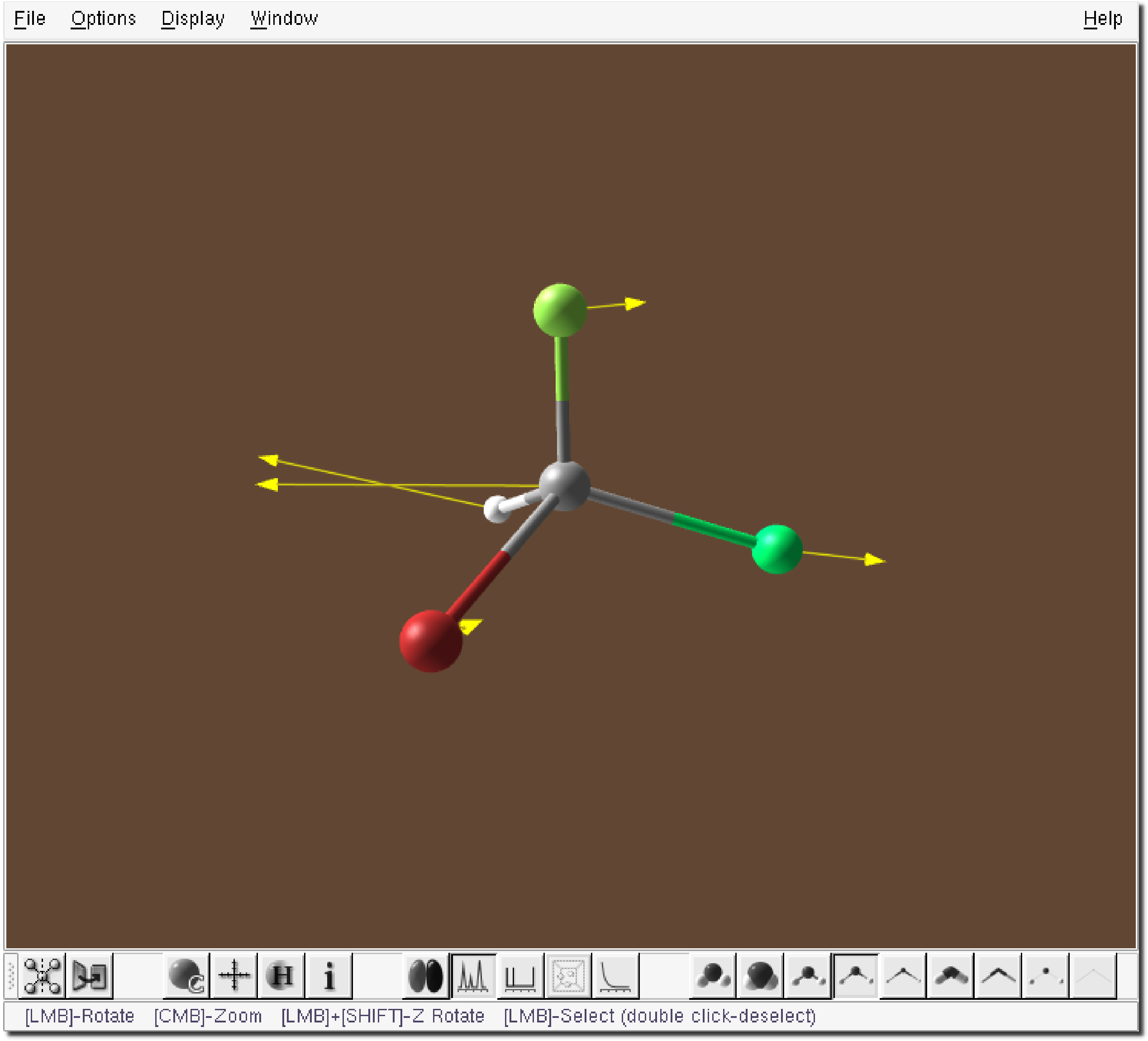
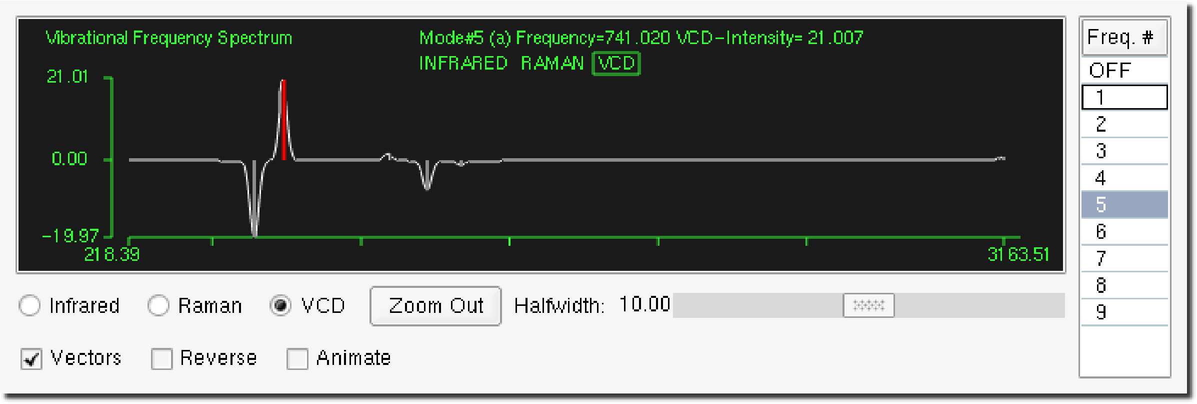


Figure 4.40: View window - displacements in the most intense IR mode in CHFClBr

Step 12 Examine the Vibrational Circular Dichroism Spectrum

Select the *VCD* radio button at the bottom of the *Vibrational Frequencies window.* This will display the simulated VCD spectrum, Figure 4.41.



Vibrational Frequency Spectrum

Mode#5 (a) Frequency=741.020 VCD-Intensity= 21.007

○ Infrared ○ Raman ● VCD

Halfwidth: 10.00

☑ Vectors ☐ Reverse ☐ Animate

Figure 4.41: Vibrational Frequencies window - VCD spectrum, Frequency no. 5 selected

The corresponding vibrational modes can be displayed and/or animated in exactly the same way as for the simulated IR spectrum. Selecting the peak with positive rotational strength (signal pointing up) with the *Vectors* checkbox activated will show the corresponding atomic displacements in the *View window*, Figure 4.40. At the same time the frequency number will be highlighted in the Frequencies list on the right.

4.3 Example 3 - Methoxy Substitution in Perfluoroanthracene

In this example we look at nucleophilic substitution in aromatic perfluorocarbons; specifically methoxy (-OCH_3) substitution in perfluoroanthracene.

Perfluoroanthracene is shown schematically in Figure 4.42 and its structure in Figure 4.43. The ring carbon substitution sites are labeled in red and there are effectively three different single-substitution sites: 1, 2 and 9. (Other sites are equivalent by symmetry.)

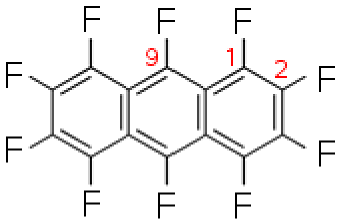


Figure 4.42: Perfluoroanthracene showing substitution sites

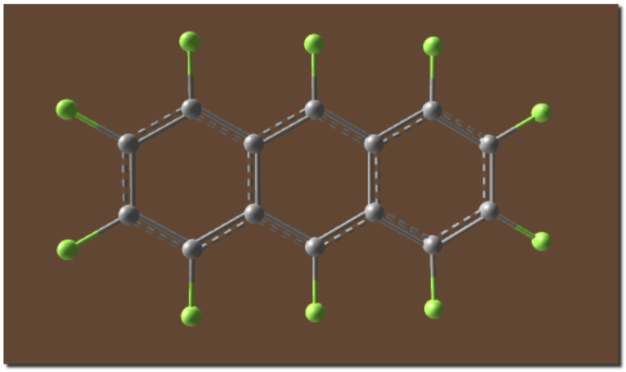


Figure 4.43: Perfluoroanthracene

Figures 4.44 and 4.45 show methoxy substitution at site 1. Experimentally, the actual substitution site is often determined primarily by ^{19}F NMR, and we are going to calculate and compare the ^{19}F NMR spectra for methoxy substitution at all three sites. Such a study has already been published (M. Muir and J. Baker, *J. Fluorine Chem.* 126 (2005) 727) and this example duplicates part of this work, showing how PQS and **PQSMol** can be used in a real research topic.

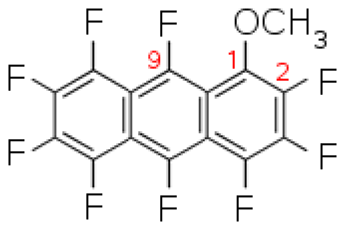


Figure 4.44: 1-methoxy-perfluoroanthracene (substitution at site 1)

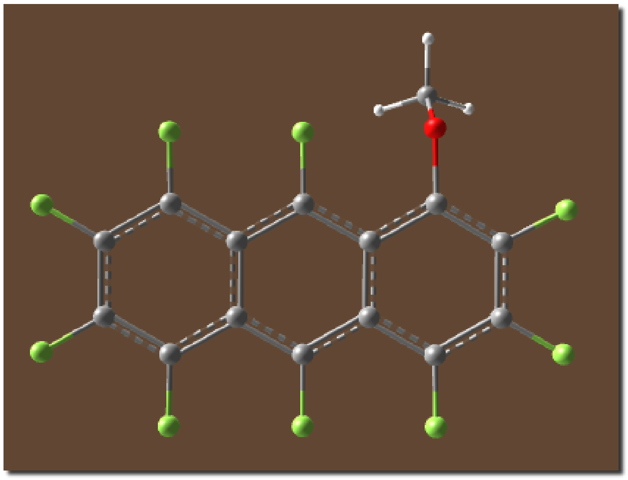


Figure 4.45: 1-methoxy-perfluoroanthracene

> **Note:** During this tutorial perfluoroanthracene and various methoxy-substituted derivatives will be constructed, and input files will be prepared ready for job submission. However, all the output files have been included on the **PQSMol** CD, so there is no need to actually run the jobs. Before starting the tutorial, you should create a test directory and copy all the files in the directory `TUTORIALS/EXAMPLE3` on the CD into this directory. Change directory into this test directory before starting the tutorial.

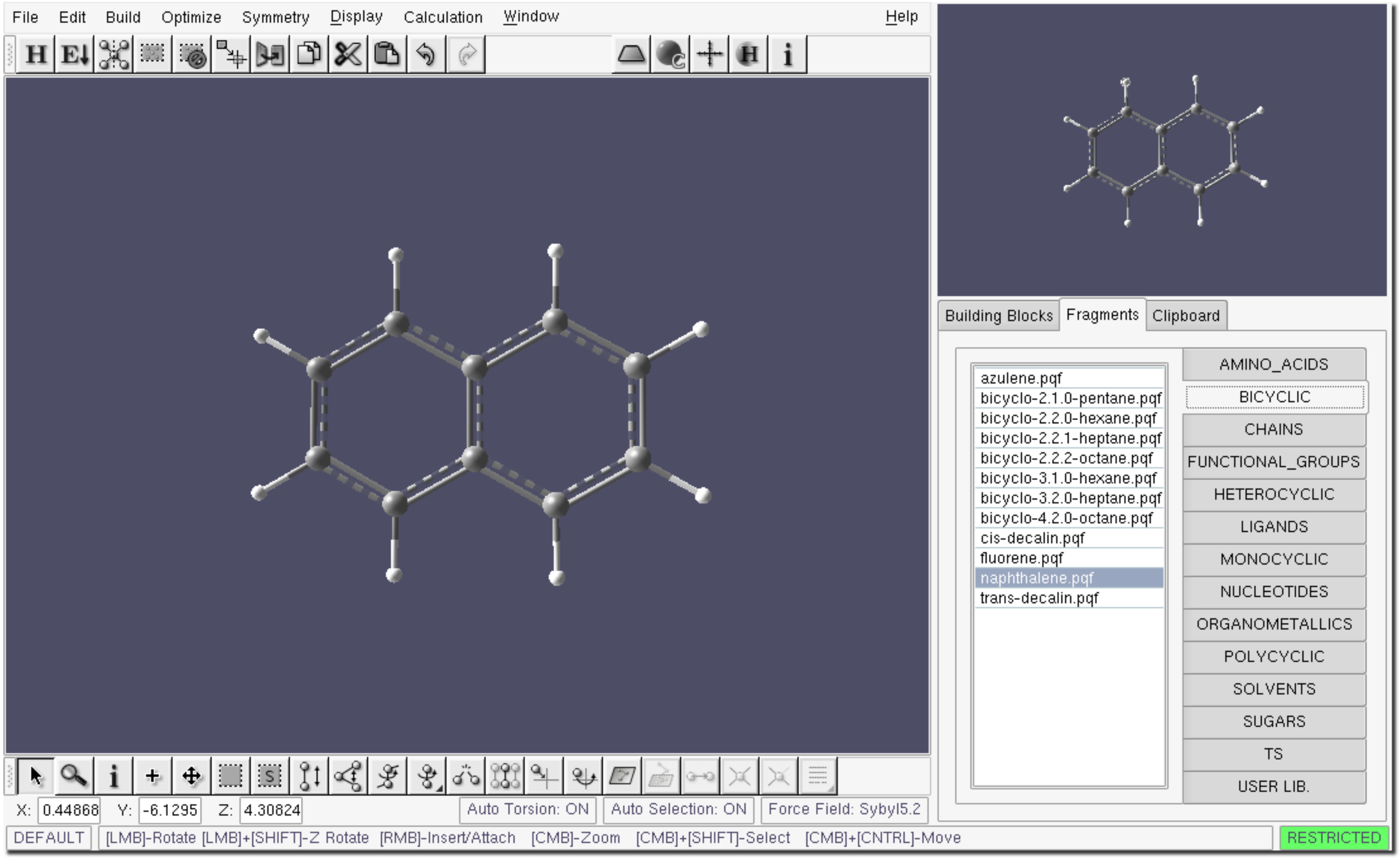
4.3.1 Building Perfluoroanthracene

Step 1 Start the builder by typing `pqsmol` at the command prompt.

First we are going to construct the parent compound, perfluoroanthracene. This comprises three fused aromatic rings, and we are going to build this from two existing fragments: benzene in the *MONOCYCLIC* fragment library, and naphthalene in the *BICYCLIC* fragment library.

Step 2 Insert the naphthalene fragment

In the *Segment window* select the *Fragments tab*, then select *BICYCLIC*. Scroll down to select naphthalene. Insert the Naphthalene fragment into the build area, either by using the **Default** tool and right-clicking or by using the **Add/Attach/Connect** tool +. At this point the *Build window* is shown in Figure 4.46.



X: 0.44868 Y: -6.1295 Z: 4.30824

Auto Torsion: ON

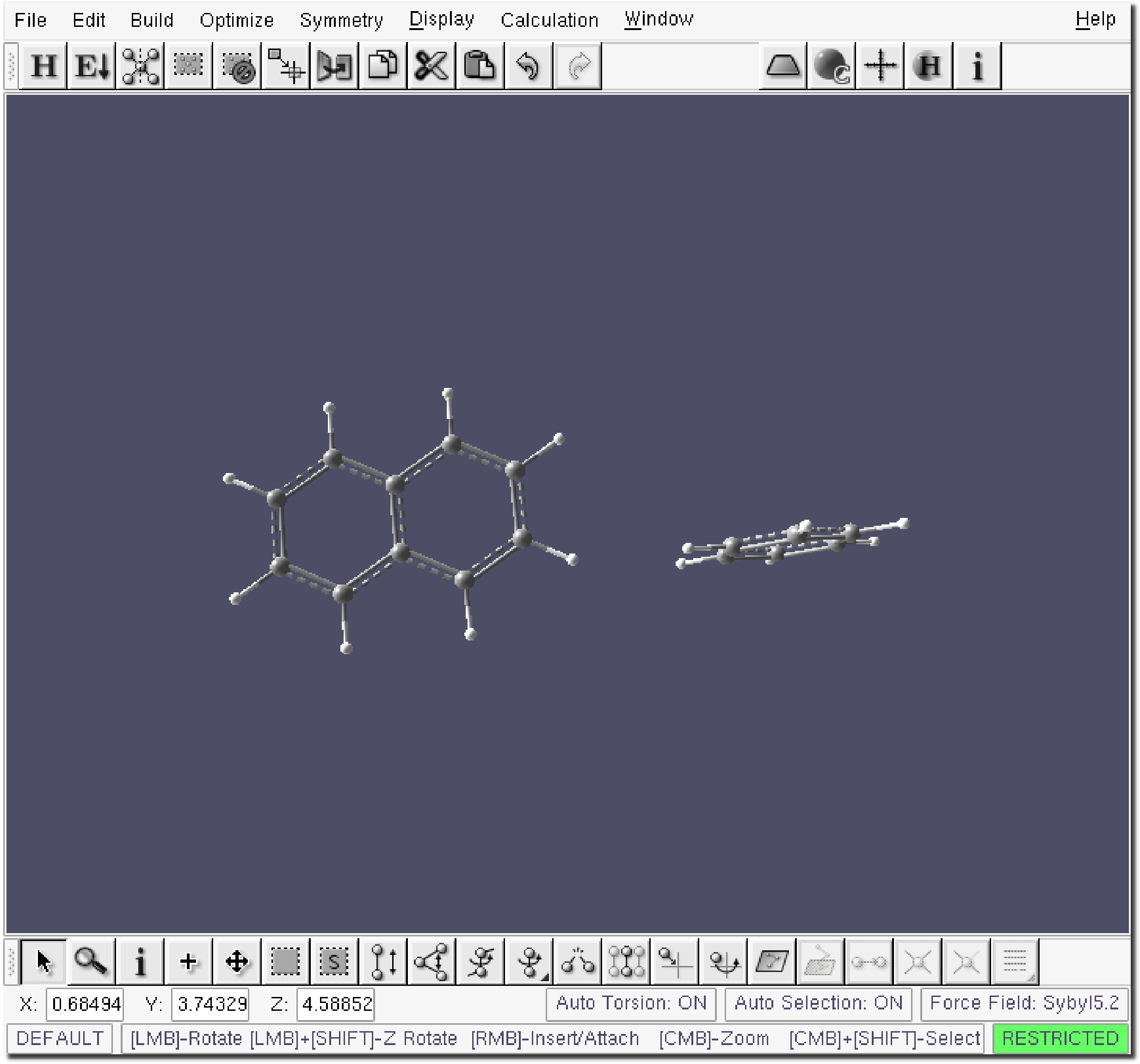
Auto Selection: ON

Force Field: Sybyl5.2

Figure 4.46: Build window - inserting the naphthalene fragment

Step 3 Insert the benzene fragment

Now select the *MONOCYCLIC* fragment library and select benzene. Move the mouse pointer into the *Build window* and insert the fragment in the empty space to the right of the naphthalene fragment. This should add the benzene fragment into the *Build window* as shown in Figure 4.47.



X: 0.68494 Y: 3.74329 Z: 4.58852

Auto Torsion: ON

Auto Selection: ON

Force Field: Sybyl5.2

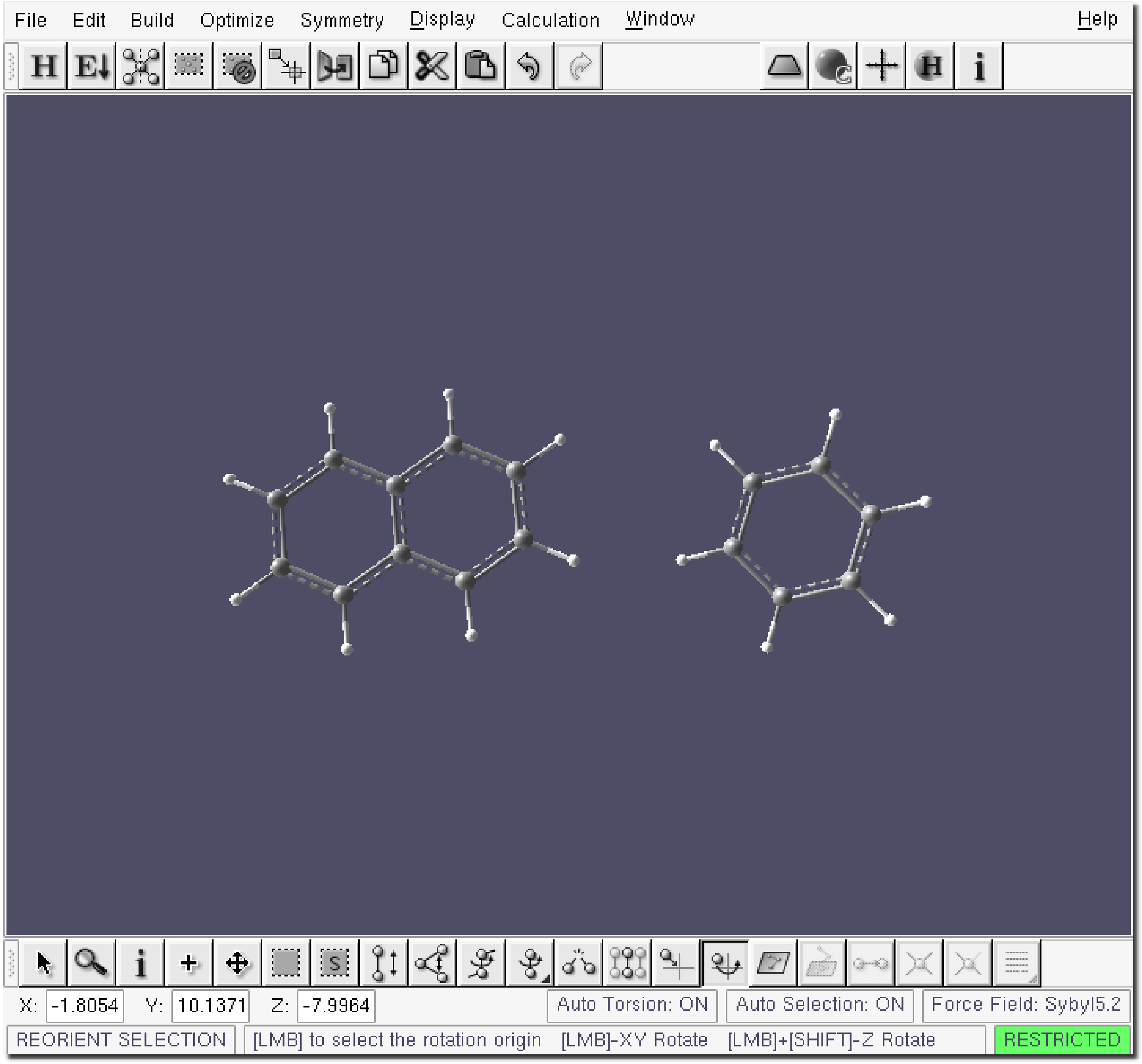
DEFAULT

[LMB]-Rotate [LMB]+[SHIFT]-Z Rotate [RMB]-Insert/Attach [CMB]-Zoom [CMB]+[SHIFT]-Select

RESTRICTED

Figure 4.47: Build window - inserting the benzene fragment

As shown, the benzene fragment is oriented differently from the naphthalene fragment. It can be reoriented into the build plane by selecting the **Reorient Selection** tool and clicking on any atom in the benzene fragment; the atom will be highlighted with a green translucent sphere and the fragment can be reoriented by dragging the mouse vertically. The result is shown in Figure 4.48.



X: -1.8054 Y: 10.1371 Z: -7.9964

Auto Torsion: ON

Auto Selection: ON

Force Field: Sybyl5.2

REORIENT SELECTION

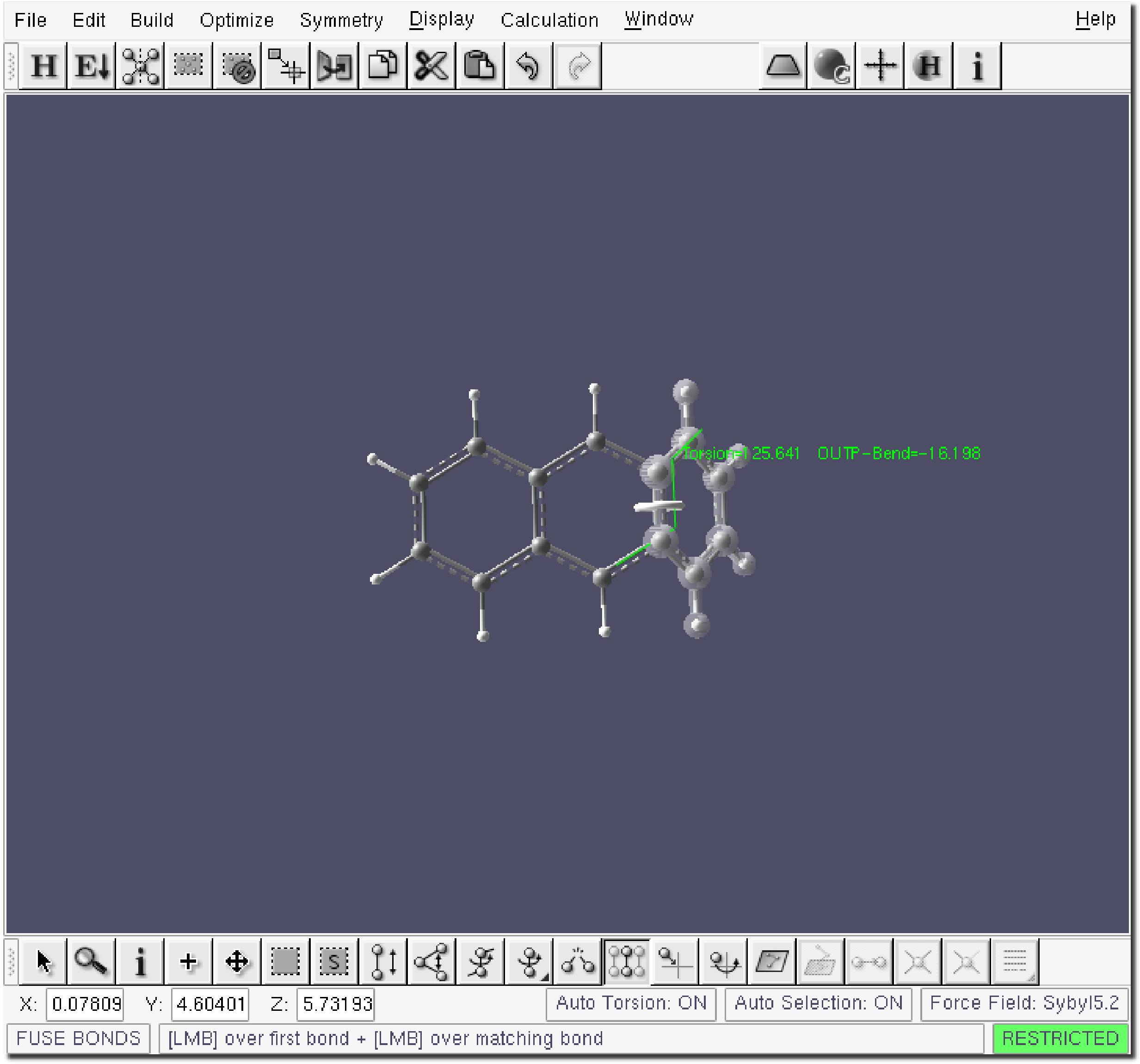
[LMB] to select the rotation origin [LMB]-XY Rotate [LMB]+[SHIFT]-Z Rotate

RESTRICTED

Figure 4.48: Build window - reorienting the benzene fragment

Step 4 Fuse the naphthalene and benzene fragments

Select the **Bond Fuse** tool . Click on the (approximately) vertical ring bond in the naphthalene fragment closest to the benzene. Click on the corresponding bond in the benzene fragment. The two rings will be fused at the selected bonds. When the segments are fused, the newly fused bond is automatically defined as a *rotation bond* and designed with a white torus, Figure 4.49.



X: 0.07809 Y: 4.60401 Z: 5.73193

Auto Torsion: ON

Auto Selection: ON

Force Field: Sybyl5.2

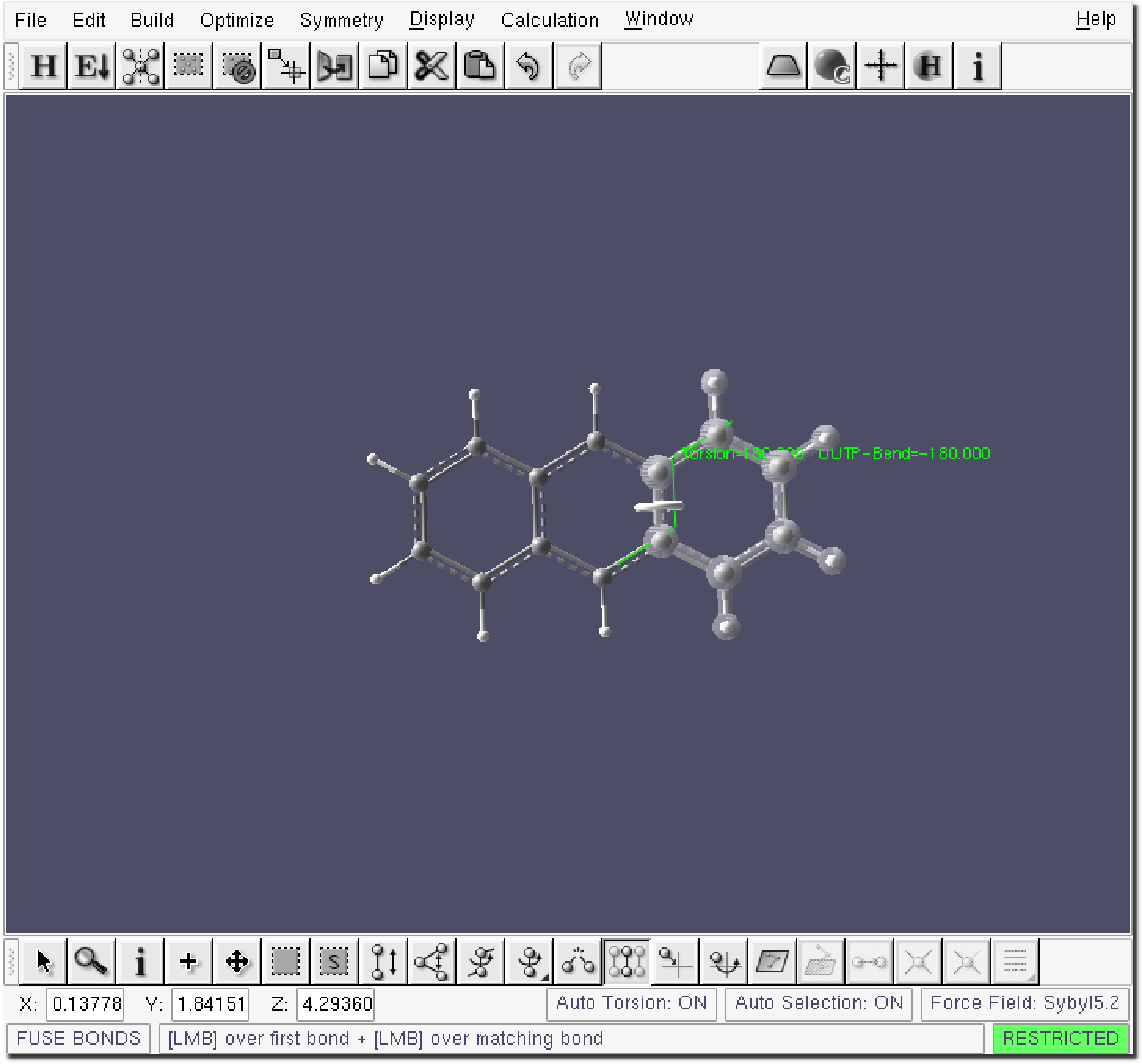
FUSE BONDS

[LMB] over first bond + [LMB] over matching bond

RESTRICTED

Figure 4.49: Build window - fusing the naphthalene and benzene fragments, attachment

Drag the mouse to rotate about the *rotation bond*, or select the dihedral angle (180°) from the rotation preset window that automatically appears. The final result should be as shown in Figure 4.50.



X: 0.13778 Y: 1.84151 Z: 4.29360

Auto Torsion: ON

Auto Selection: ON

Force Field: Sybyl5.2

FUSE BONDS

[LMB] over first bond + [LMB] over matching bond

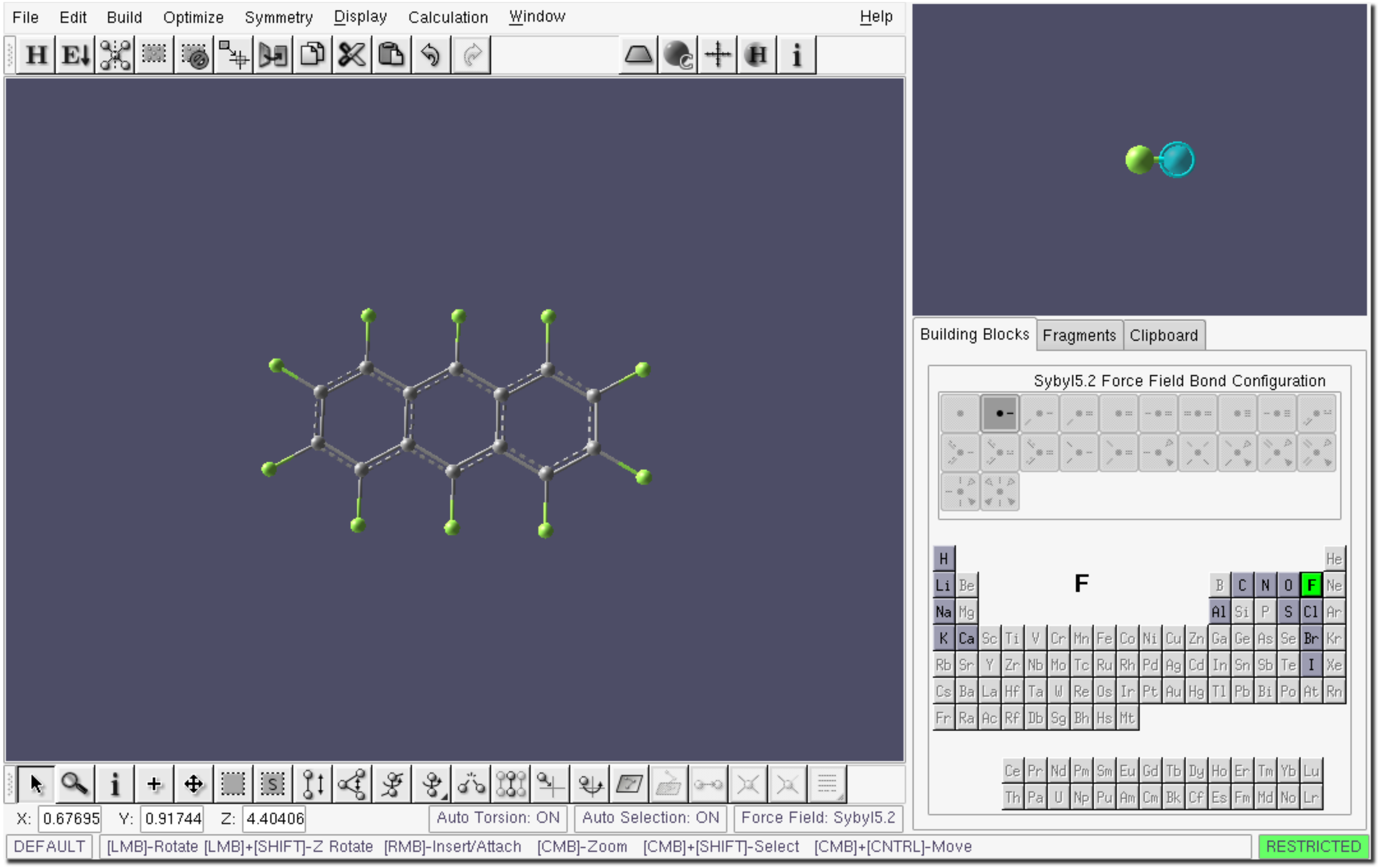
RESTRICTED

Figure 4.50: Build window - fusing the naphthalene and benzene fragments, rotation

Double click inside the build area to clear the selection and set the angle.

Step 5 Add the fluorine atoms

Select *Building Blocks tab* in the *Segment window* and select fluorine from the periodic table. In the default Sybyl 5.2 force field there is only one fluorine building block which will be shown in the *Segment buffer*. Select the **Add/Attach/Connect** tool + and replace every ring hydrogen atom by fluorine. You have now built perfluoroanthracene, Figure 4.51.



X: 0.67695 Y: 0.91744 Z: 4.40406 Auto Torsion: ON Auto Selection: ON Force Field: Sybyl5.2

[LMB]-Rotate [LMB]+[SHIFT]-Z Rotate [RMB]-Insert/Attach [CMB]-Zoom [CMB]+[SHIFT]-Select [CMB]+[CNTRL]-Move

Figure 4.51: Build Window - hydrogen replaced with fluorine

The structure can be optimized by clicking on the **Optimize** button E↓ and the symmetry found by clicking on the **Check Symmetry** button. The resulting point group should be `d2h`, Figure 4.52.

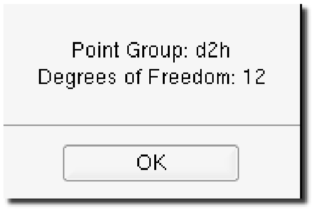

Point Group: d2h
Degrees of Freedom: 12

Figure 4.52: Symmetry dialog

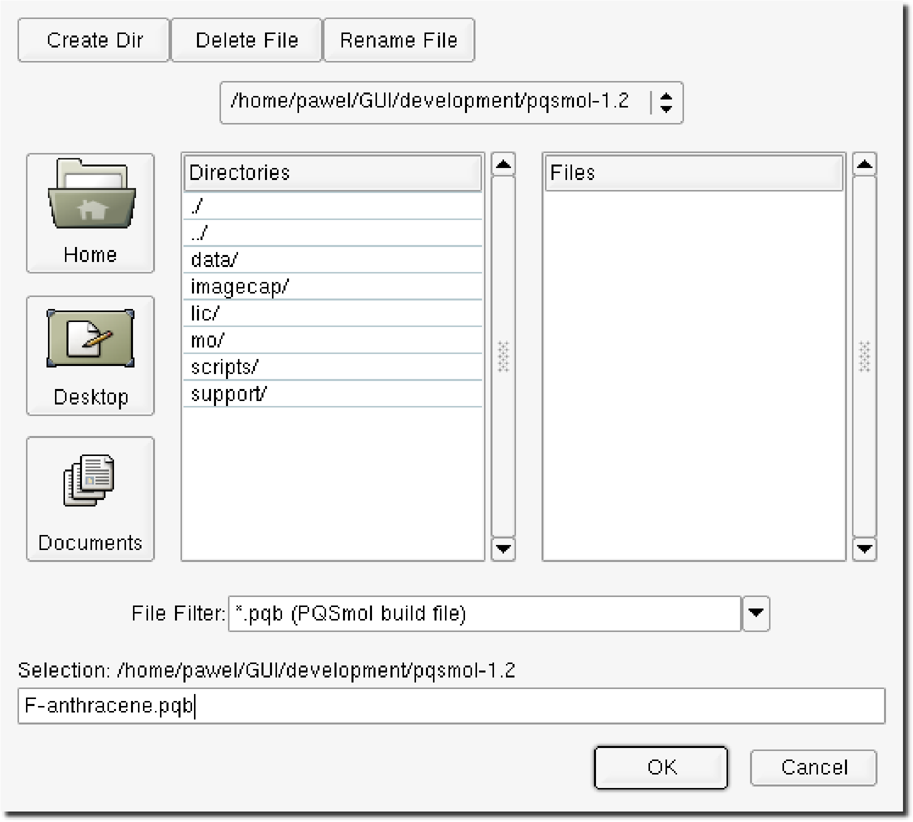
The entire procedure up to this point could have been considerably simplified, as the *POLYCYCLIC* fragment library already contains an Anthracene fragment, which could have been selected directly instead of fusing the naphthalene and benzene rings. But where's the fun in that?

4.3.2 Creating a PQS input file

Step 6 Preparing the input file

Once perfluoroanthracene has been successfully built, the PQS input file can be prepared. We are going to optimize the geometry using DFT and then compute vibrational frequencies (to characterize the nature of the stationary point, i.e., to ensure that it is a minimum) and NMR chemical shifts.

Select the **Calculation→Job Input** menu item to start the input generator. Since our build file has not yet been named, the File Save dialog (Figure 4.53) will appear, prompting you to provide a filename. By default the empirical formula will be provided as a filename; this can be changed by typing in an alternative name. Here the file has been named `F-anthracene.pqb` (the file extension must be pqb).



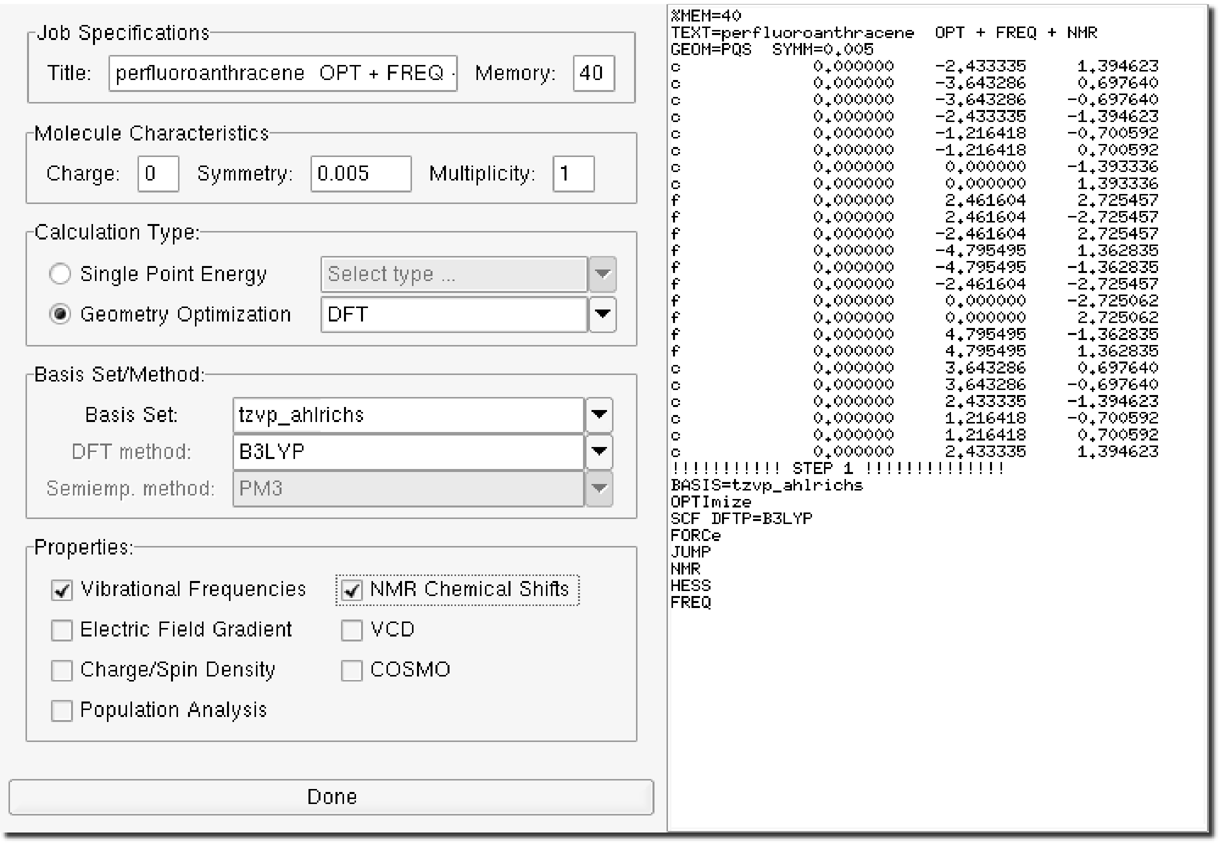
File Filter: *.pqb (PQSmol build file)

Selection: /home/pawel/GUI/development/pqsmol-1.2

F-anthracene.pqb

Figure 4.53: File Save dialog

Once the file has been successfully named, the input preparation window will appear, Figure 4.54. As shown, the job has been set up as a B3LYP/tzvp_ahlirchs optimization + frequency + NMR.



Job Specifications

Title: perfluoroanthracene OPT + FREQ

Memory: 40

Molecule Characteristics

Charge: 0

Symmetry: 0.005

Multiplicity: 1

Calculation Type:

○ Single Point Energy — Select type ...

● Geometry Optimization — DFT

Basis Set/Method:

Basis Set: tzvp_ahlrichs

DFT method: B3LYP

Semiemp. method: PM3

Properties:

☑ Vibrational Frequencies
☑ NMR Chemical Shifts
☐ Electric Field Gradient
☐ VCD
☐ Charge/Spin Density
☐ COSMO
☐ Population Analysis

```
%MEM=40
TEXT=perfluoroanthracene  OPT + FREQ + NMR
GEOM=PQS  SYMM=0.005
c              0.000000   -2.433335    1.394623
c              0.000000   -3.643286    0.697640
c              0.000000   -3.643286   -0.697640
c              0.000000   -2.433335   -1.394623
c              0.000000   -1.216418   -0.700592
c              0.000000   -1.216418    0.700592
c              0.000000    0.000000   -1.393336
c              0.000000    0.000000    1.393336
f              0.000000    2.461604    2.725457
f              0.000000    2.461604   -2.725457
f              0.000000   -2.461604    2.725457
f              0.000000   -4.795495    1.362835
f              0.000000   -4.795495   -1.362835
f              0.000000   -2.461604   -2.725457
f              0.000000    0.000000   -2.725062
f              0.000000    0.000000    2.725062
f              0.000000    4.795495   -1.362835
f              0.000000    4.795495    1.362835
c              0.000000    3.643286    0.697640
c              0.000000    3.643286   -0.697640
c              0.000000    2.433335   -1.394623
c              0.000000    1.216418   -0.700592
c              0.000000    1.216418    0.700592
c              0.000000    2.433335    1.394623
!!!!!!!!!!! STEP 1 !!!!!!!!!!!!!!
BASIS=tzvp_ahlrichs
OPTImize
SCF DFTP=B3LYP
FORCe
JUMP
NMR
HESS
FREQ
```

Figure 4.54: Input generation window - finished input

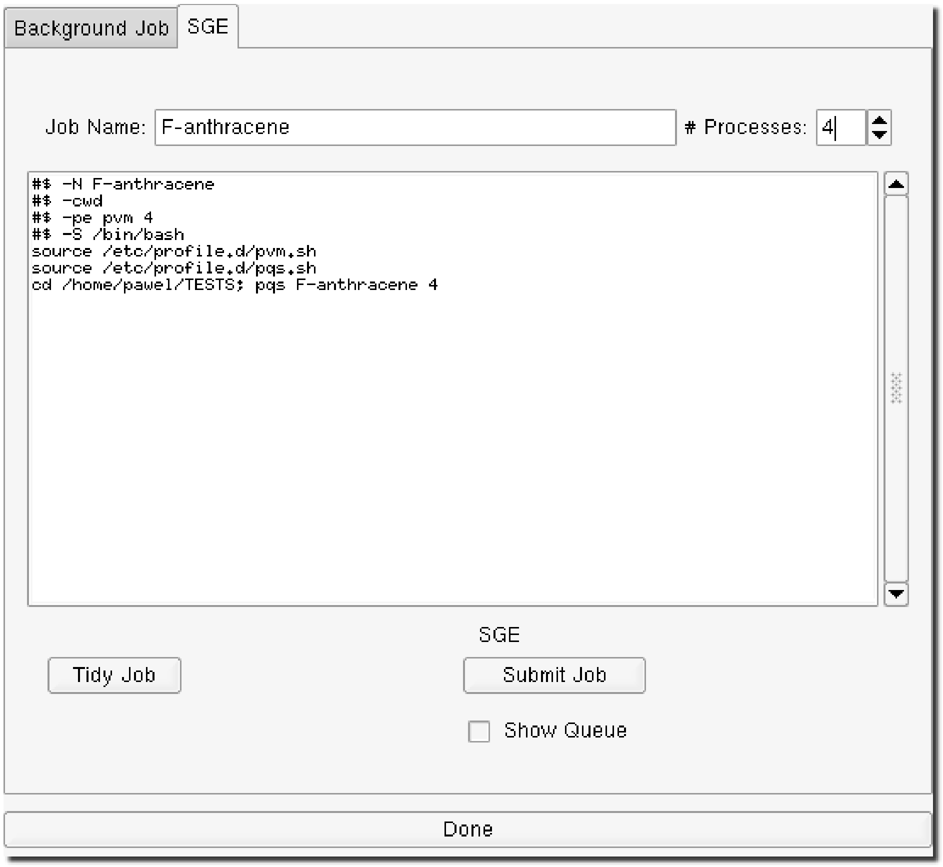
Press the **Done** button to save the changes to the input file.

4.3.3 Submitting a PQS job

Step 7 Submit the **PQS** job.

Once the input has been prepared select the **Calculation→Submit Parallel Job** menu item, Figure 4.55.

> **Note:** The **Calculation→Submit Parallel Job** menu item is only active in parallel installations of the PQS ab initio package. If you do not have a QuantumCube^{TM} or other parallel system, this option will be greyed out and the job will have to be submitted in serial mode; however, all the jobs in this example have been run in advance, and all output files should be available to you in the `TUTORIAL/EXAMPLE3` directory on the **PQSMol** CD, so there is no need to actually run the job.



Job Name: F-anthracene

Processes: 4

```
#$ -N F-anthracene
#$ -cwd
#$ -pe pvm 4
#$ -S /bin/bash
source /etc/profile.d/pvm.sh
source /etc/profile.d/pqs.sh
cd /home/pawel/TESTS; pqs F-anthracene 4
```

Figure 4.55: Parallel Job Submission dialog

The Job Submission window will appear (Figure 4.55). The job is being submitted to the parallel SGE job queue. The job submission script appears in the large window and requires two user-supplied entries; the job name (F-anthracene) and the number of processors (in this case 4). Pressing the **Submit Job** button will send the script to the job queue.

At this point you can exit **PQSMol** (unless you actually want to run this job). We will use the files copied from the TUTORIAL/EXAMPLE3 directory on the **PQSMol** CD at the beginning of this example. Click on Done in the Job Submission window and then select the **File→Quit** menu item.

4.3.4 Visualizing the PQS job output

Step 8 Capture the ^{19}F NMR spectrum of perfluoroanthracene.

Note: Make sure you are in the directory where the files from the `TUTORIAL/EXAMPLE3` directory were copied.

To view the output of the perfluoroanthracene job, start **PQSMol** in **View mode** by typing `pqsview F-anthracene.out` at the command prompt, Figure 4.56.

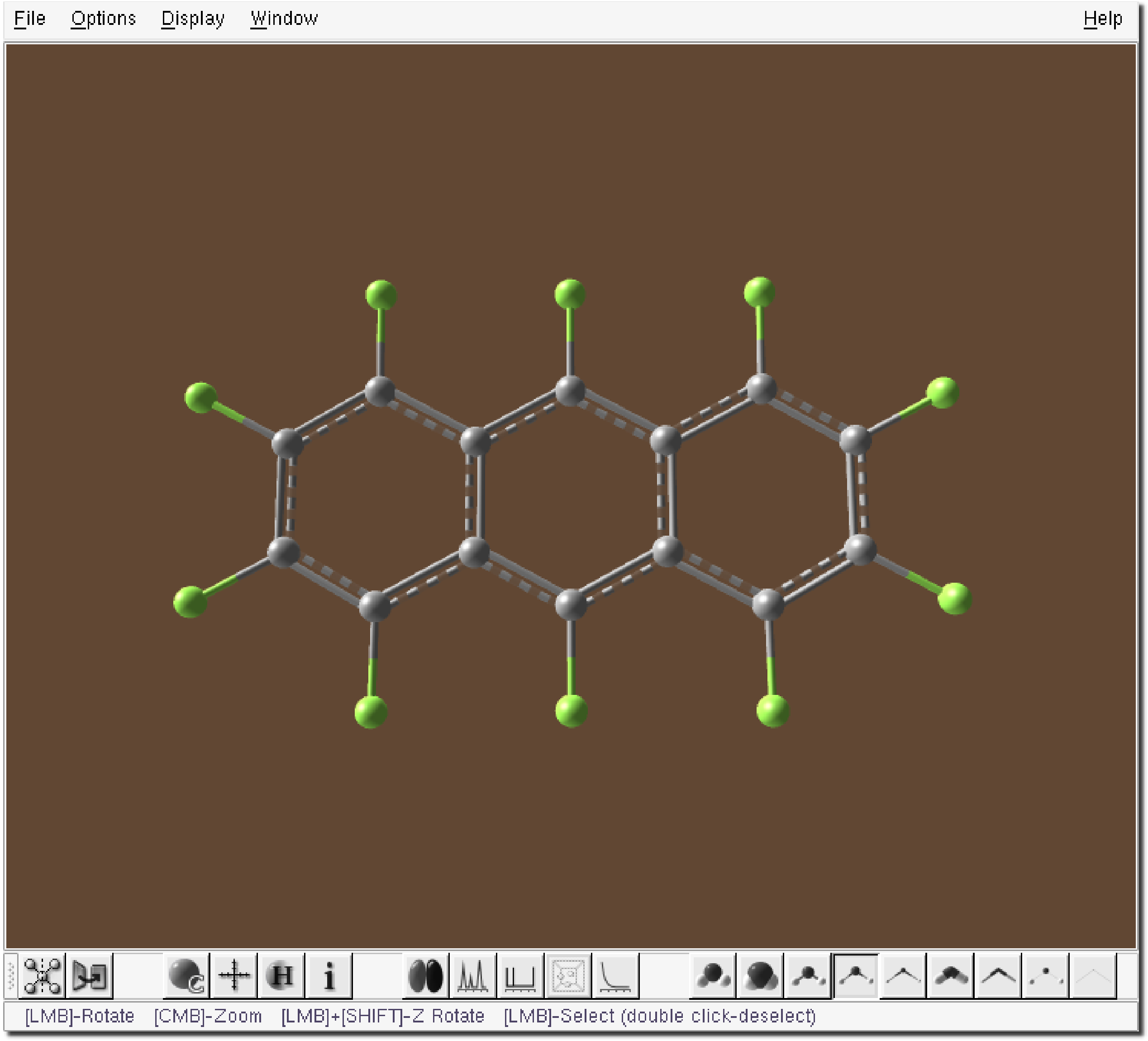
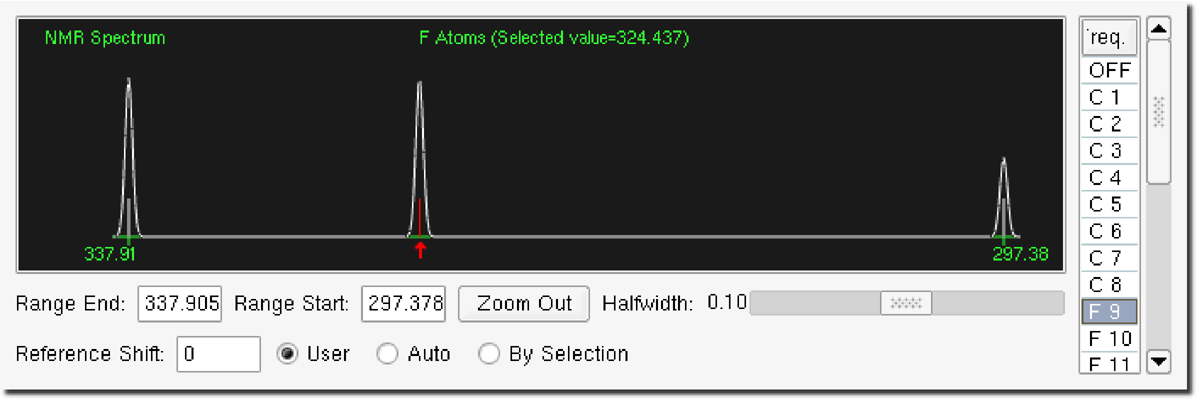


Figure 4.56: View window - perfluoroanthracene job visualization

We are going to visualize and capture an image of the NMR spectrum. Press the **NMR** button in the toolbar at the bottom of the *View window*. This will initially display the ^{13}C NMR spectrum (carbon being the first atom listed). To display the ^{19}F NMR spectrum you can either select a fluorine atom, e.g., F9, from the NMR spectrum window, or click on one of the fluorine atoms of perfluoroanthracene in the *View window*. The resulting NMR spectrum is shown in Figure 4.57 (Note the red arrow below the peak corresponding to the selected fluorine atom, F9.)



NMR Spectrum

F Atoms (Selected value=324.437)

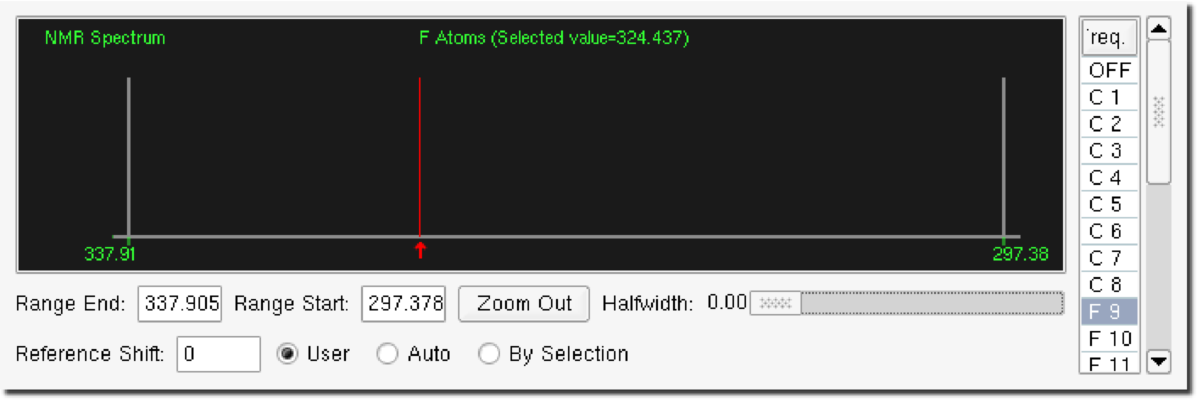
Range End: 337.905 Range Start: 297.378

Halfwidth: 0.10

Reference Shift: 0 ● User ○ Auto ○ By Selection

Figure 4.57: NMR window - Initial ^{19}F NMR spectrum of perfluoroanthracene

The halfwidth of the peaks can be controlled using the slider bar; sliding this all the way to the left reduces the half width to zero and simply displays a vertical line, 4.58.



NMR Spectrum

F Atoms (Selected value=324.437)

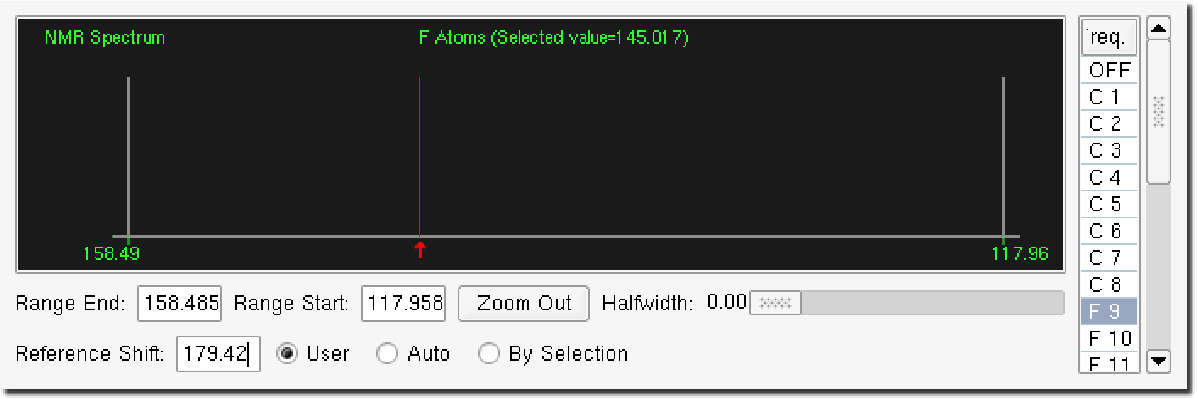
Range End: 337.905 Range Start: 297.378

Halfwidth: 0.00

Reference Shift: 0 ● User ○ Auto ○ By Selection

Figure 4.58: NMR window - ^{19}F NMR spectrum with zero halfwidth

The NMR spectra shown in Figures 4.57 and 4.58 display the raw average shielding values as computed by PQS. Experimental chemical shifts are all given with respect to a reference, and a common one for ^{19}F NMR spectra is the ^{19}F signal in CF_3Cl. This can be taken to be 179.42 (see M. Muir and J. Baker, *J. Fluorine Chem.* 126 (2005) 727) and typing this value into the *Reference Shift* entry in the bottom left corner of the *NMR window* results in the spectrum shown in Figure 4.59.



NMR Spectrum

F Atoms (Selected value=145.017)

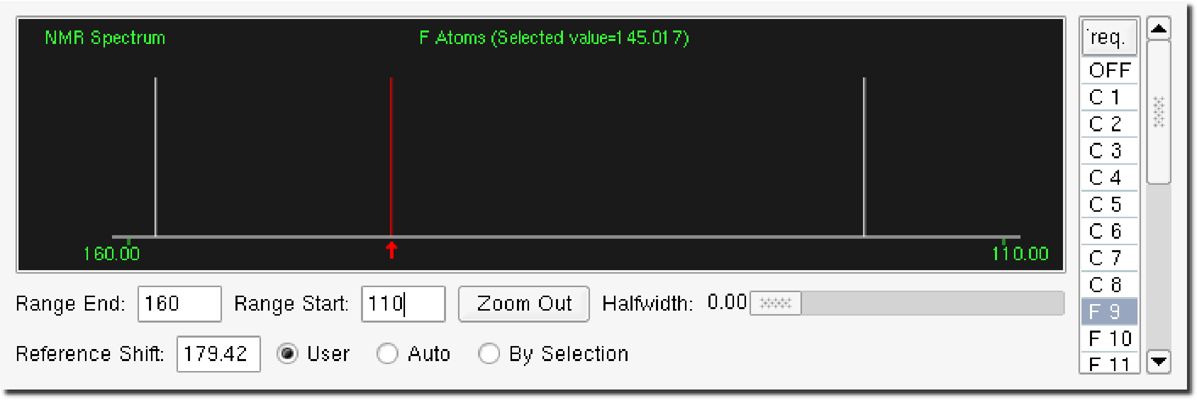
Range End: 158.485 Range Start: 117.958

Halfwidth: 0.00

Reference Shift: 179.42 ● User ○ Auto ○ By Selection

Figure 4.59: NMR window - ^{19}F NMR spectrum using CF_3Cl as reference

Using a non-zero reference of course changes the relative chemical shift values and thus the spectrum range. In order to directly compare different NMR spectra, i.e., in this case the ^{19}F spectra of perfluoroanthracene with its methoxy-substituted derivatives, it is helpful if the different spectra cover the same spectral range. To facilitate this, we are going to change the *Range End* entry to 160 ppm and the *Range Start* entry to 110 ppm. This changes the starting and ending values on the X-axis of the NMR spectrum, as shown in Figure 4.60.

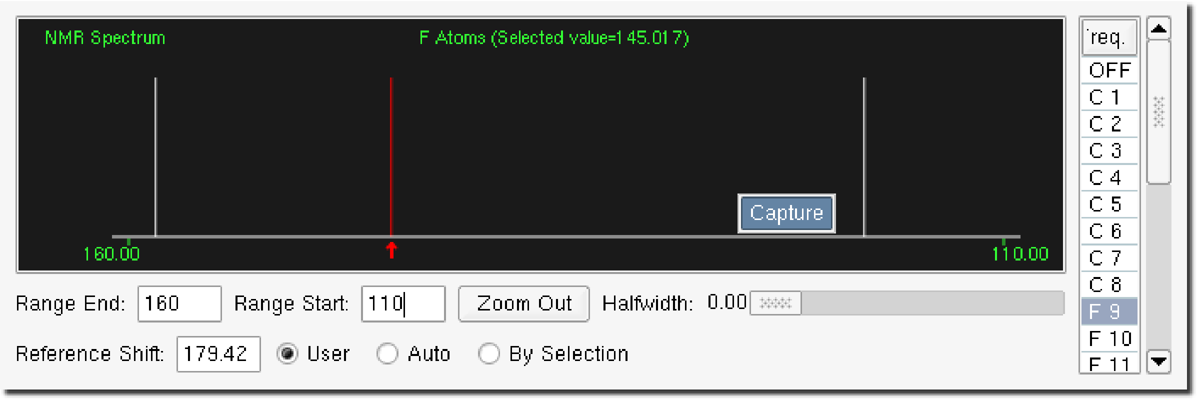


Range End: 160
Range Start: 110
Halfwidth: 0.00
Reference Shift: 179.42 ● User ○ Auto ○ By Selection

Figure 4.60: NMR window - ^{19}F NMR spectrum with modified range

Changing the range in this way has the effect of slightly compressing the spectrum.

Finally, we are going to capture an image of the NMR spectrum. Position the mouse pointer anywhere inside the NMR spectrum graph and press the right mouse button; this will produce a popup menu with a single menu item labeled *Capture* (see Figure 4.61).

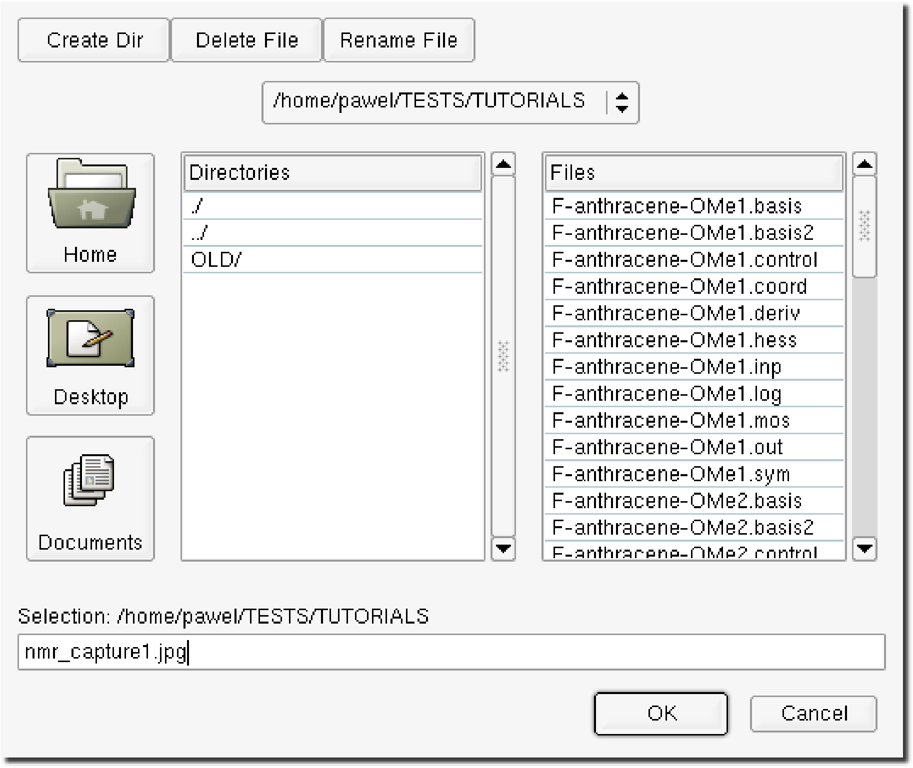


Range End: 160
Range Start: 110
Halfwidth: 0.00
Reference Shift: 179.42 ● User ○ Auto ○ By Selection

Figure 4.61: NMR window - Capturing an image of the ^{19}F NMR spectrum

Note: The spectrum image captured in this example has a white NMR plot line on a black background. This color combination may not be the suitable for printed media. You can change the background color of the spectrum with the **Options→Graph Background** menu item and the plot color with **Options→Graph Plot**.

Activating the **Capture** menu item will cause the Save Image As dialog shown in Figure 4.62 to appear, prompting you for a file name to save a JPEG image. As shown, the default name is `nmr_capture1.jpg`. Change this to, e.g., `F-anthracene.jpg` and press the *OK* button to save the image.



/home/pawel/TESTS/TUTORIALS

Directories:
./
../
OLD/

Files:
F-anthracene-OMe1.basis
F-anthracene-OMe1.basis2
F-anthracene-OMe1.control
F-anthracene-OMe1.coord
F-anthracene-OMe1.deriv
F-anthracene-OMe1.hess
F-anthracene-OMe1.inp
F-anthracene-OMe1.log
F-anthracene-OMe1.mos
F-anthracene-OMe1.out
F-anthracene-OMe1.sym
F-anthracene-OMe2.basis
F-anthracene-OMe2.basis2

Selection: /home/pawel/TESTS/TUTORIALS

nmr_capture1.jpg

Figure 4.62: Save dialog - naming the NMR spectrum image

This completes the first part of this tutorial. At this point we have obtained and saved as a JPEG image the simulated ^{19}F NMR spectrum of perfluoroanthracene. We will now build the various methoxy-substituted derivatives and obtain their NMR spectra.

4.3.5 Building 1-Methoxy-Perfluoroanthracene

Step 9 Import the prebuilt perfluoroanthracene

Start the builder by typing `pqsmol` at the the command prompt.

As we have already constructed, and optimized, the geometry of perfluoroanthracene, we can start with that. Select the **File→Import** menu item, Figure 4.63.

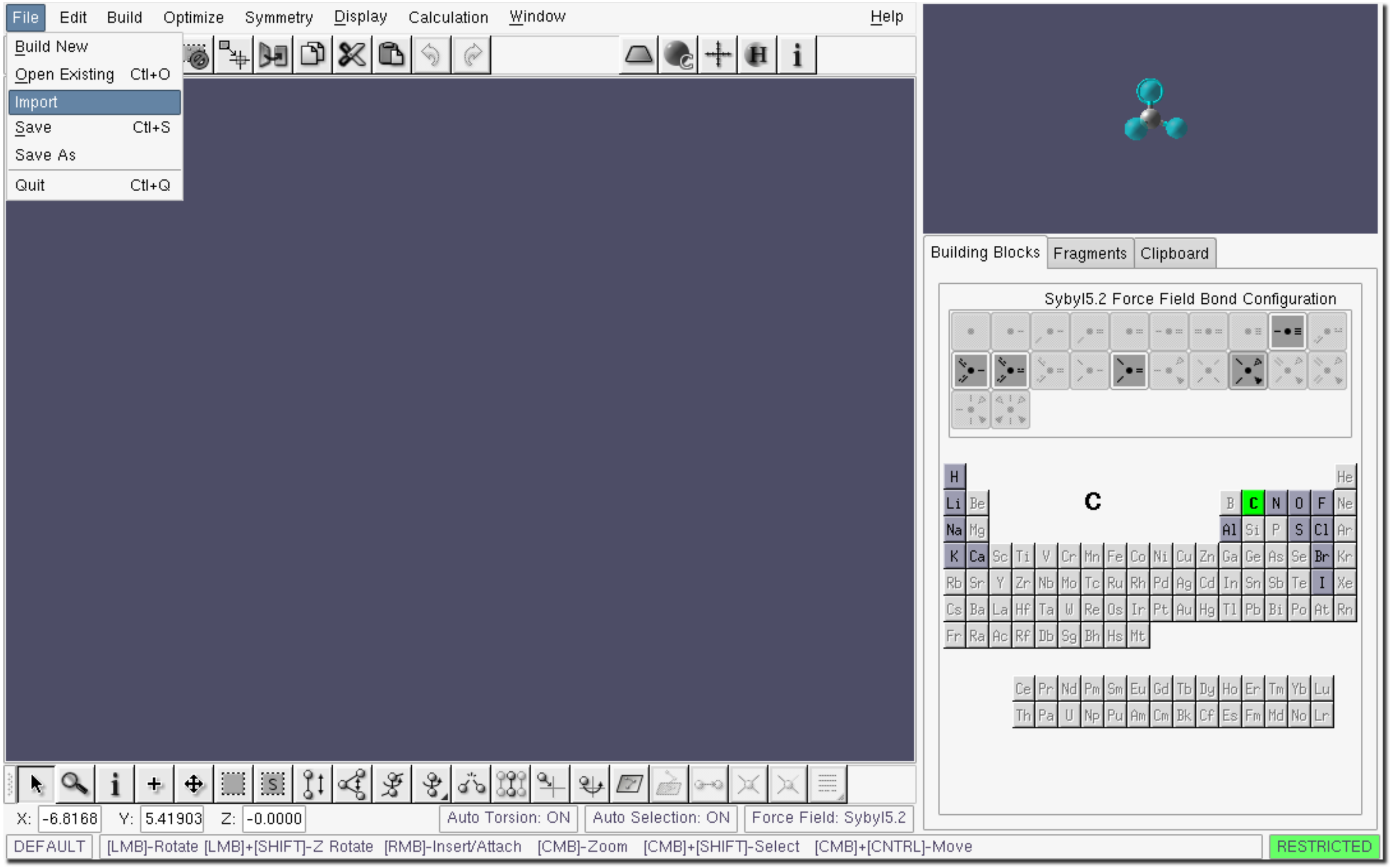


Figure 4.63: Build window - importing an existing structure into **PQSMol**

The Import Geometry dialog (Figure 4.64) will open, allowing various file types to be imported. We are going to import the final converged geometry of perfluoroanthracene which is available in the `.coord` file, `F-anthracene.coord`. In the *File Filter* dropdown list select `*.coord (coordinates)` and select the file `F-anthracene.coord` from those shown in the *Files* list.

> **Note:** As all jobs for this tutorial have been run in advance, the `.coord` files for all structures are already available; normally of course only the `.coord` file for perfluoroanthracene – the job run in the first part of this tutorial – would be present.

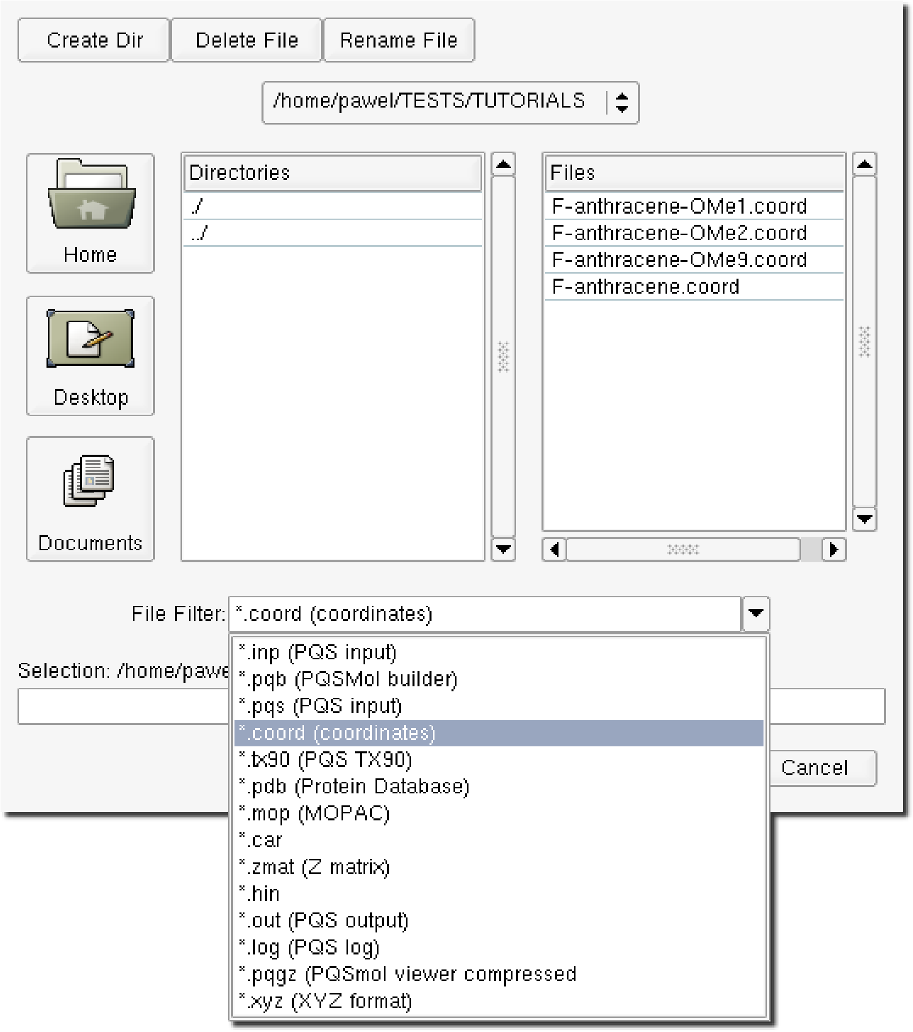


Figure 4.64: Import dialog - importing a `.coord` file into **PQSMol**

As the structure is imported into the *Segment buffer* the dialog in Figure 4.65 should appear. When an existing (and compatible) `.pqb` file is found with the same name as the file being imported, **PQSMol** will extract forcefield data (atom types and connectivity) from this file.

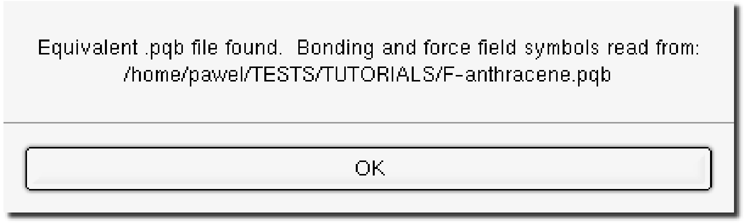
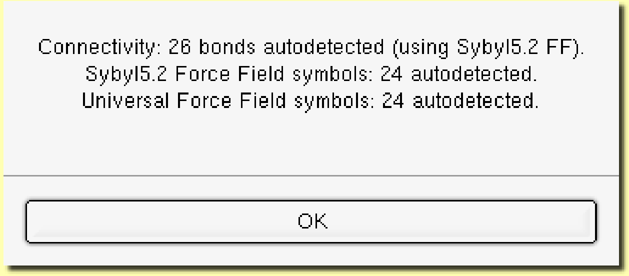

Equivalent .pqb file found. Bonding and force field symbols read from:
/home/pawel/TESTS/TUTORIALS/F-anthracene.pqb

Figure 4.65: Import info dialog - geometry imported with an existing `.pqb` file.

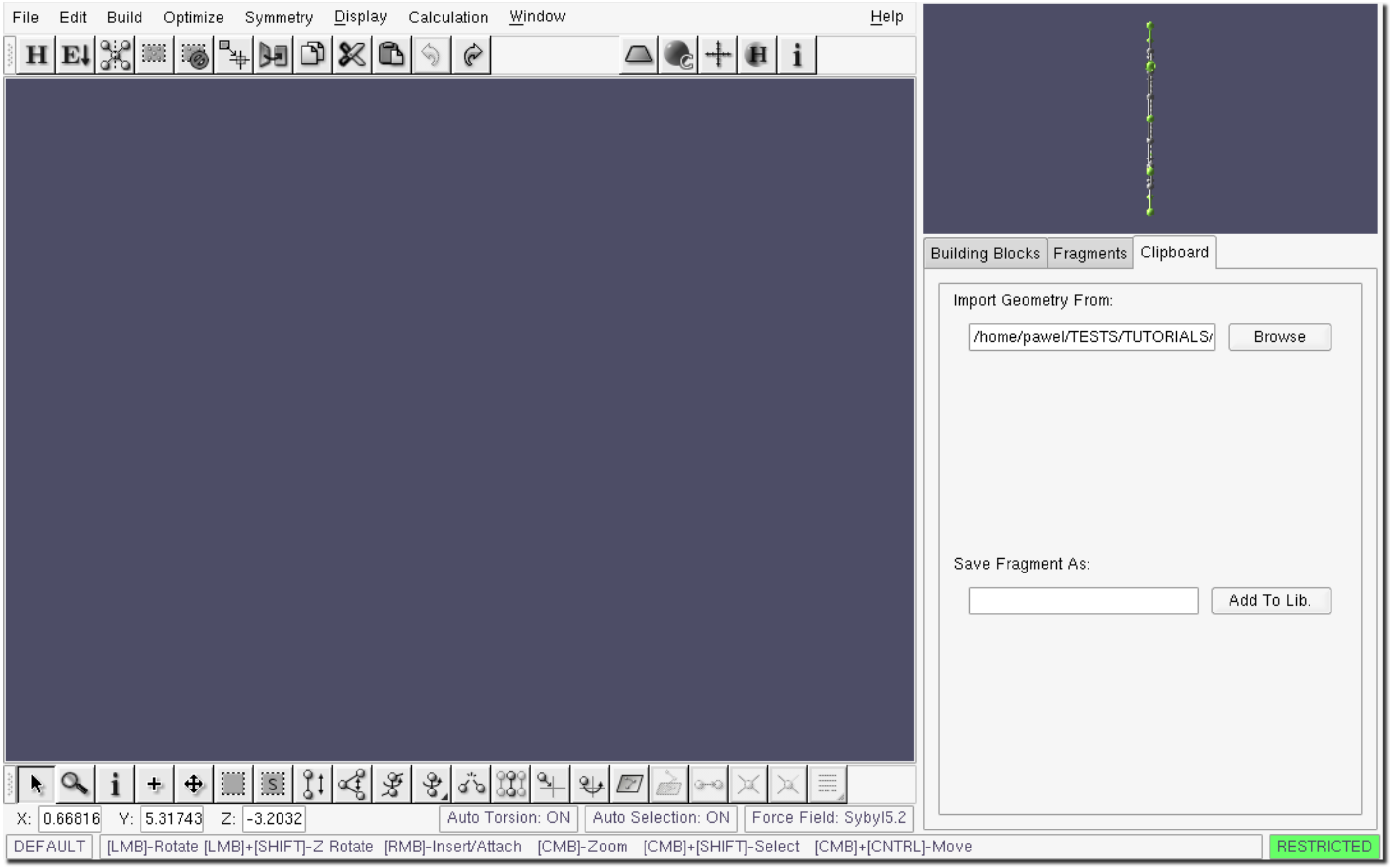
Note: If a corresponding `.pqb` is not found in the same directory as the file to be imported, i.e., you are importing raw structural data, then **PQSMol** will attempt to derive forcefield data using an internal algorithm. The import info dialog in this case would look like the one in Figure 4.66.



Connectivity: 26 bonds autodetected (using Sybyl5.2 FF).
Sybyl5.2 Force Field symbols: 24 autodetected.
Universal Force Field symbols: 24 autodetected.

Figure 4.66: Import info dialog - geometry imported without an existing `.pqb` file.

Press the **OK** button to import the structure. The result is given in Figure 4.67 which shows perfluoroanthracene imported into the *Segment buffer*. Because of the symmetry of this molecule and the orientation of the coordinate axes in the *Segment buffer*, the structure is shown "on edge". Drag the mouse pointer in the *Segment window* to reorient the structure.



/home/pawel/TESTS/TUTORIALS/

X: 0.66816 Y: 5.31743 Z: -3.2032

Auto Torsion: ON

Auto Selection: ON

Force Field: Sybyl5.2

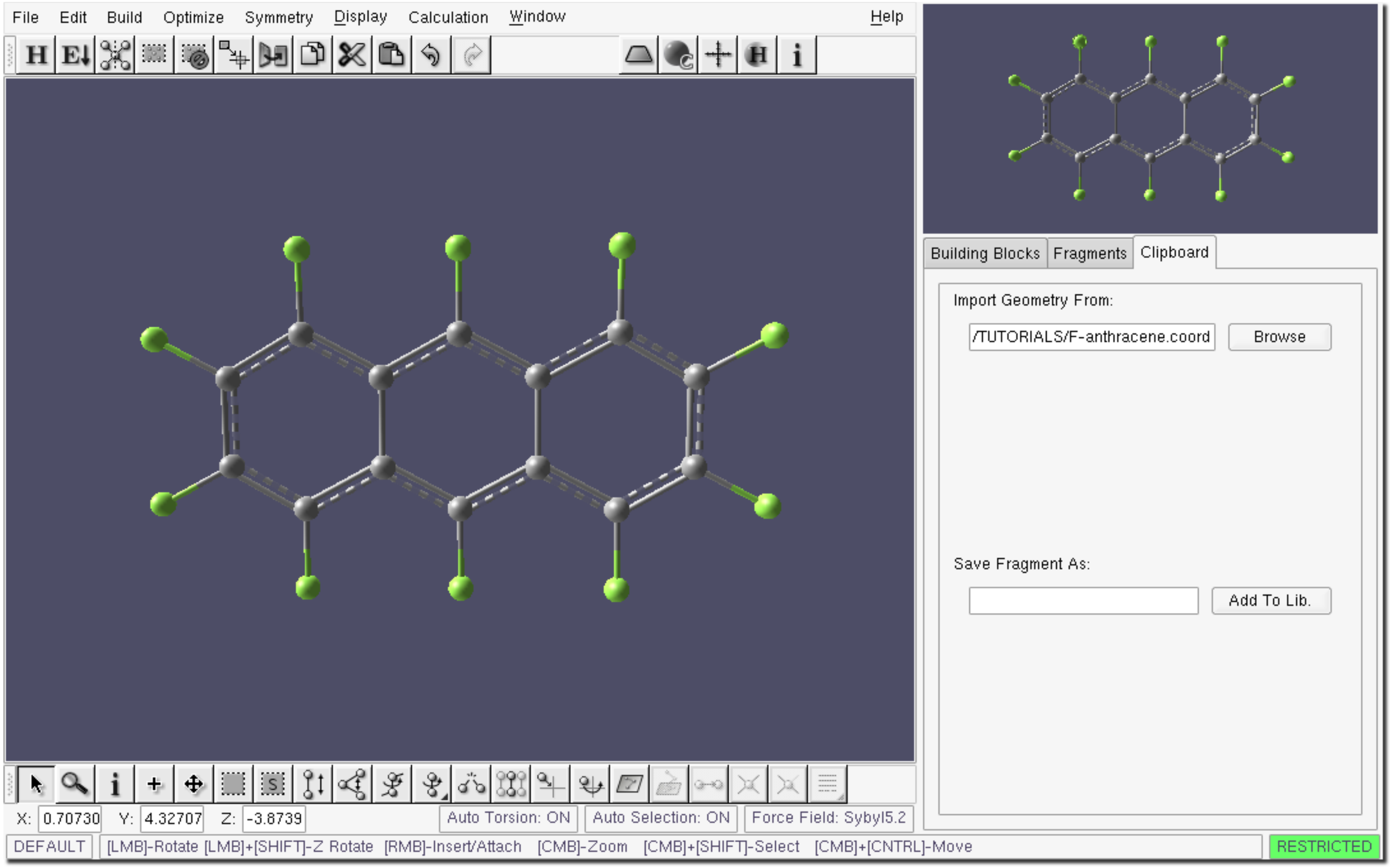
DEFAULT

[LMB]-Rotate [LMB]+[SHIFT]-Z Rotate [RMB]-Insert/Attach [CMB]-Zoom [CMB]+[SHIFT]-Select [CMB]+[CNTRL]-Move

RESTRICTED

Figure 4.67: Build window - perfluoroanthracene imported into the Segment buffer

Using either the **Add/Attach/Connect** tool or the overloaded right-click in the **Default** tool insert the perfluoroanthracene segment into the build area, Figure 4.68.



Import Geometry From: /TUTORIALS/F-anthracene.coord

Save Fragment As:

X: 0.70730 Y: 4.32707 Z: -3.8739

Auto Torsion: ON

Auto Selection: ON

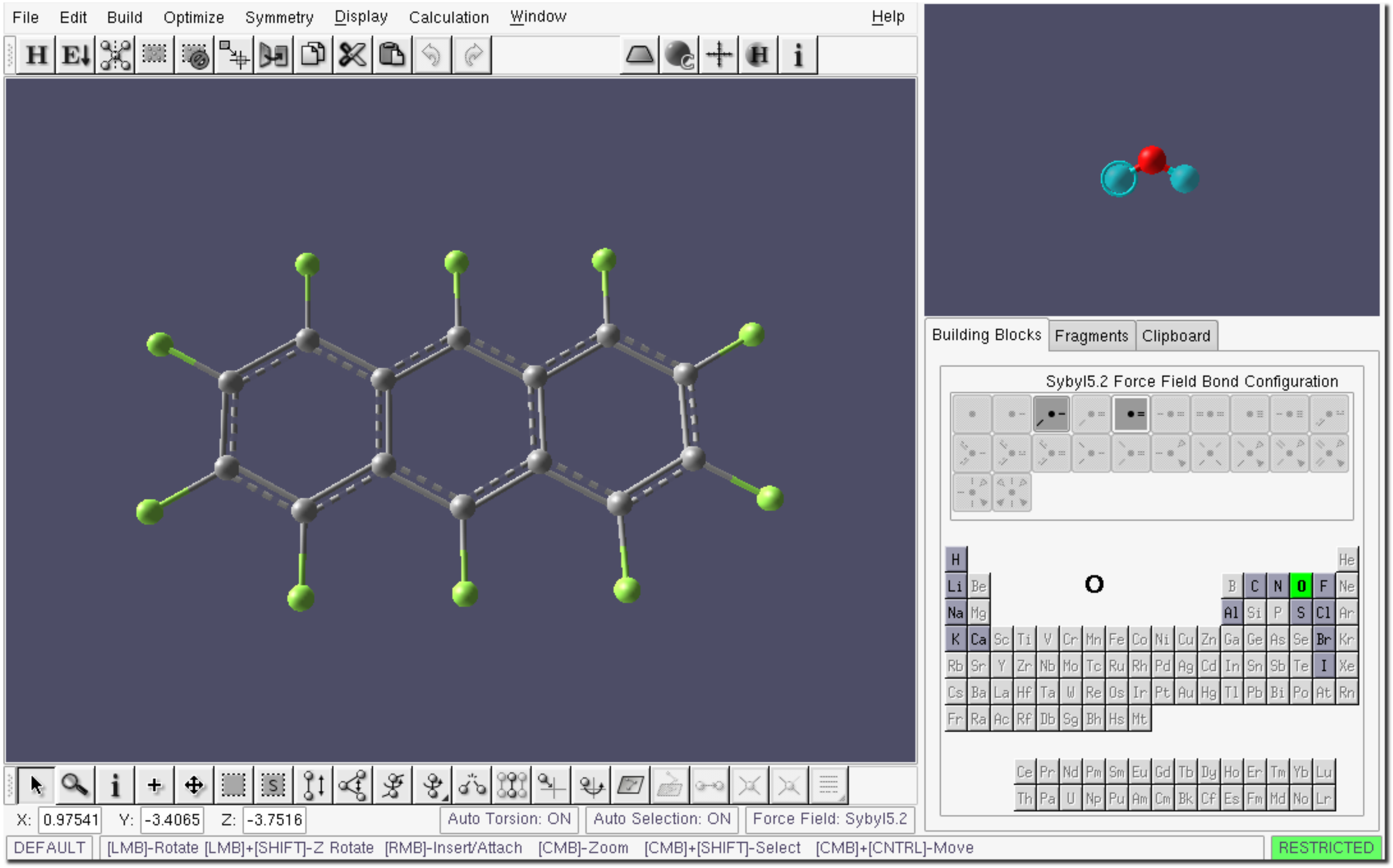
Force Field: Sybyl5.2

DEFAULT [LMB]-Rotate [LMB]+[SHIFT]-Z Rotate [RMB]-Insert/Attach [CMB]-Zoom [CMB]+[SHIFT]-Select [CMB]+[CNTRL]-Move RESTRICTED

Figure 4.68: Build window - perfluoroanthracene inserted

Step 10 Attach the oxygen building block

Select the *Building Blocks tab* in the *Segment window* and select oxygen in the periodic table. The result is shown in Figure 4.69. There are only two possible building blocks for oxygen in **restricted mode**, either a double bond or a bent configuration with two single bonds, with the latter, which is the one we want, as the default.



X: 0.97541 Y: -3.4065 Z: -3.7516

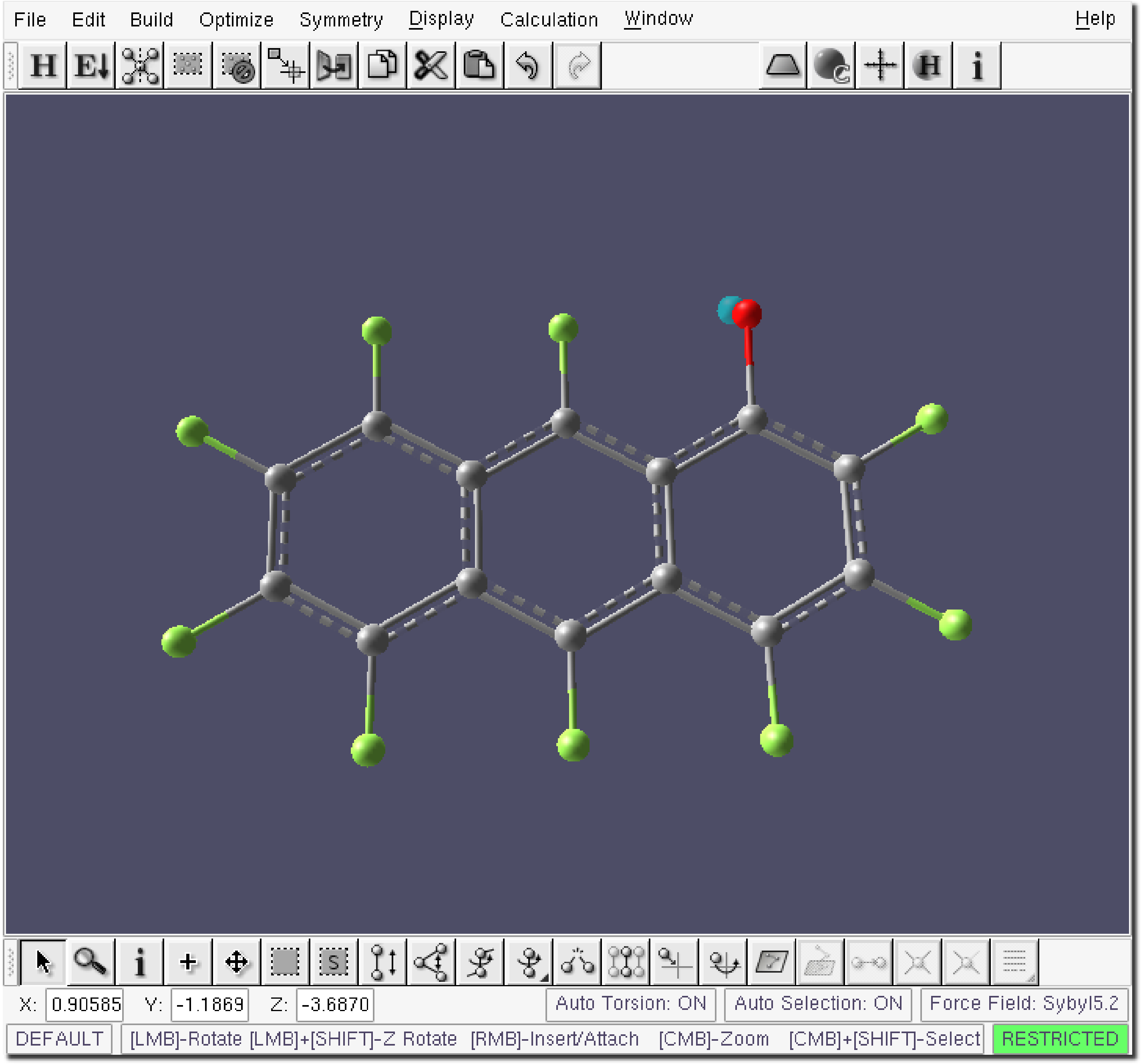
Auto Torsion: ON

Auto Selection: ON

Force Field: Sybyl5.2

Figure 4.69: Build window - bent oxygen building block selected

Using either the **Add/Attach/Connect** tool or the overloaded right-click in the **Default** tool attach the oxygen building block to the to top fluorine in the right-most benzene ring. This is the 1-position. The result is shown in Figure 4.70.



X: 0.90585 Y: -1.1869 Z: -3.6870

Auto Torsion: ON

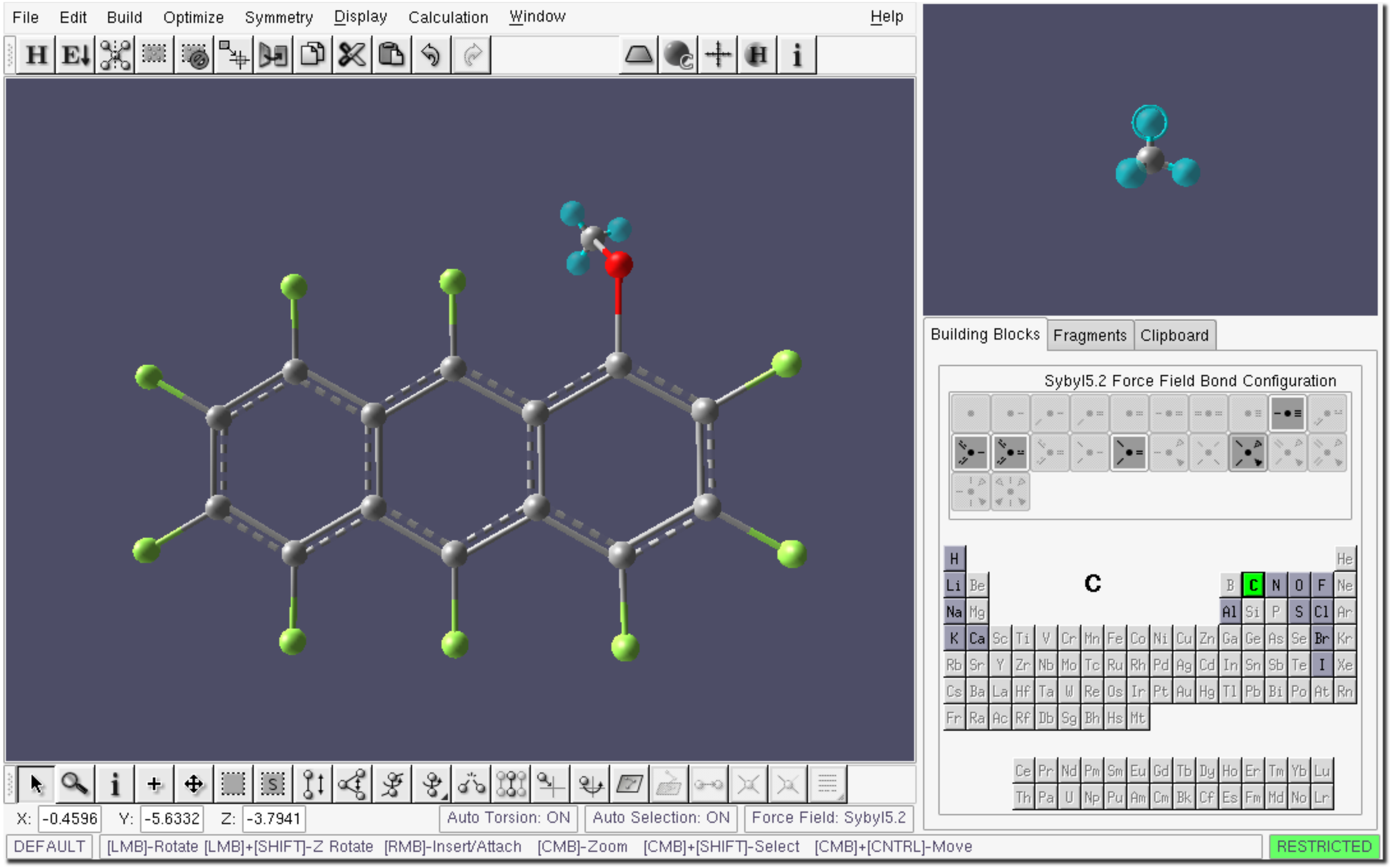
Auto Selection: ON

Force Field: Sybyl5.2

Figure 4.70: Build window - perfluoroanthracene with the oxygen building block attached at position 1

Step 11 Attach the tetrahedral carbon building block.

In the periodic table select carbon. This will show the five building blocks available for carbon, with the 4-bond sp3 hybridized carbon again the one we want the default. Position the mouse pointer over the free valence (the green dummy atom) on the oxygen atom and right click to attach the carbon atom. The result is shown in Figure 4.71.



X: -0.4596 Y: -5.6332 Z: -3.7941

Auto Torsion: ON

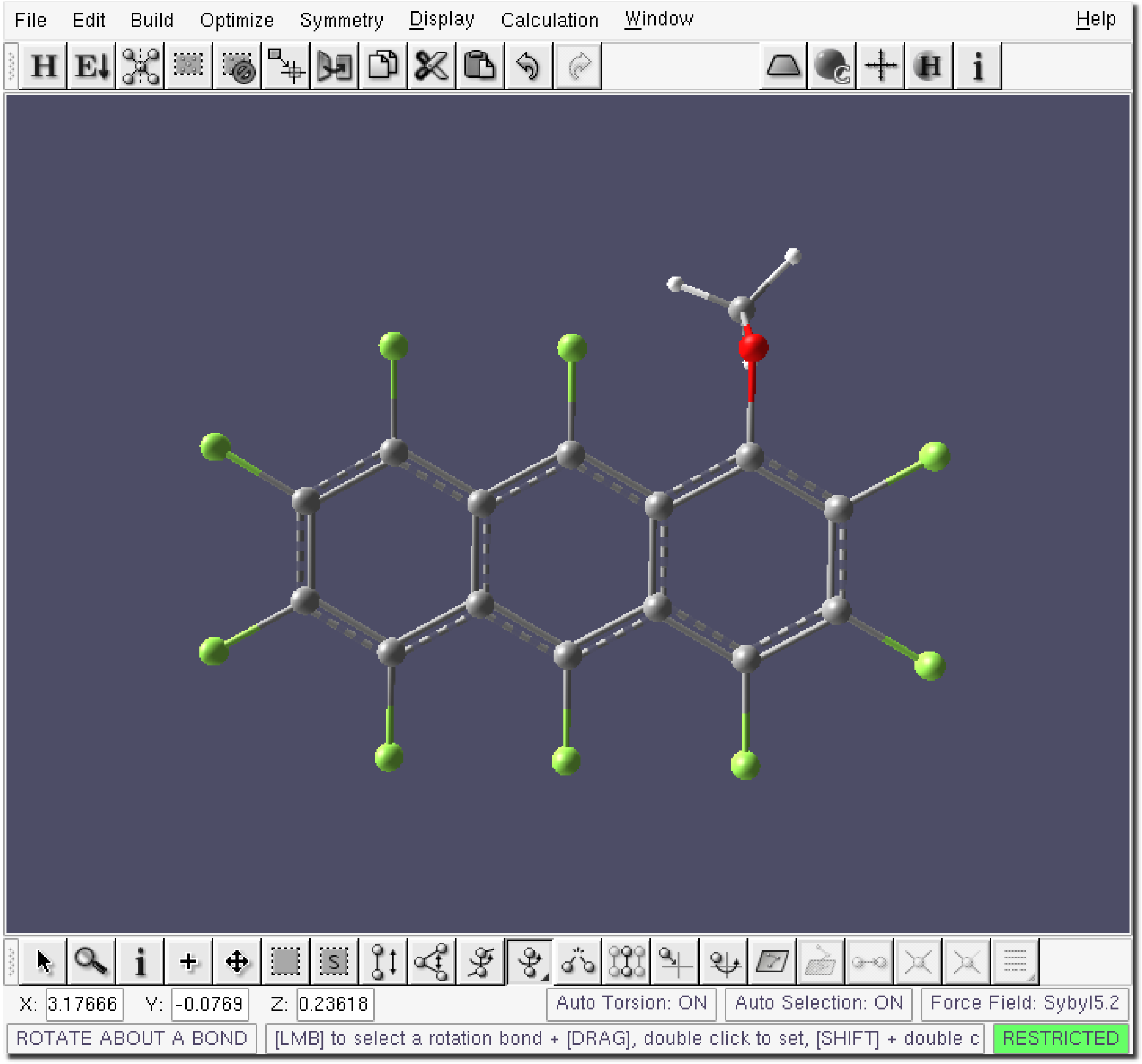
Auto Selection: ON

Force Field: Sybyl5.2

[LMB]-Rotate [LMB]+[SHIFT]-Z Rotate [RMB]-Insert/Attach [CMB]-Zoom [CMB]+[SHIFT]-Select [CMB]+[CNTRL]-Move

Figure 4.71: Build window - attaching the tetrahedral carbon building block

Finally, press the **Hydrogen Fill** button H in the top toolbar to fill the three free valencies on the newly attached carbon atom with hydrogens. This completes the building of 1-methoxy-perfluoroanthracene Figure 4.72.



X: 3.17666 Y: -0.0769 Z: 0.23618

Auto Torsion: ON

Auto Selection: ON

Force Field: Sybyl5.2

ROTATE ABOUT A BOND

[LMB] to select a rotation bond + [DRAG], double click to set, [SHIFT] + double c

RESTRICTED

Figure 4.72: Build window - 1-methoxy-perfluoroanthracene

At this point we could optimize the geometry of 1-methoxy-perfluoroanthracene using the Sybyl5.2 force field. However, as we have imported the already-optimized geometry of perfluoroanthracene (optimized at our desired level of theory) and all we have done is replace a fluorine by a methoxy group, then it might be better to start the *ab initio* optimization using the structure "as is" without the force field preoptimization. (The methoxy group can be rotated about the C-O bond to any desired position.)

We can now repeat Step 6 above and prepare the input file. If desired, you can skip this step and go direct to the examination of the output. The output file is called `F-anthracene-OMe1.out`.

4.3.6 Visualizing the PQS job output

Step 12 Capture the ^{19}F NMR spectrum of 1-methoxy-perfluoroanthracene

This is basically a repeat of Step 8 with perfluoroanthracene replaced by 1-methoxy-perfluoroanthracene. View the output file for the 1-methoxy derivative by typing `pqsview F-anthracene-OMe1.out` at the command prompt, Figure 4.73.

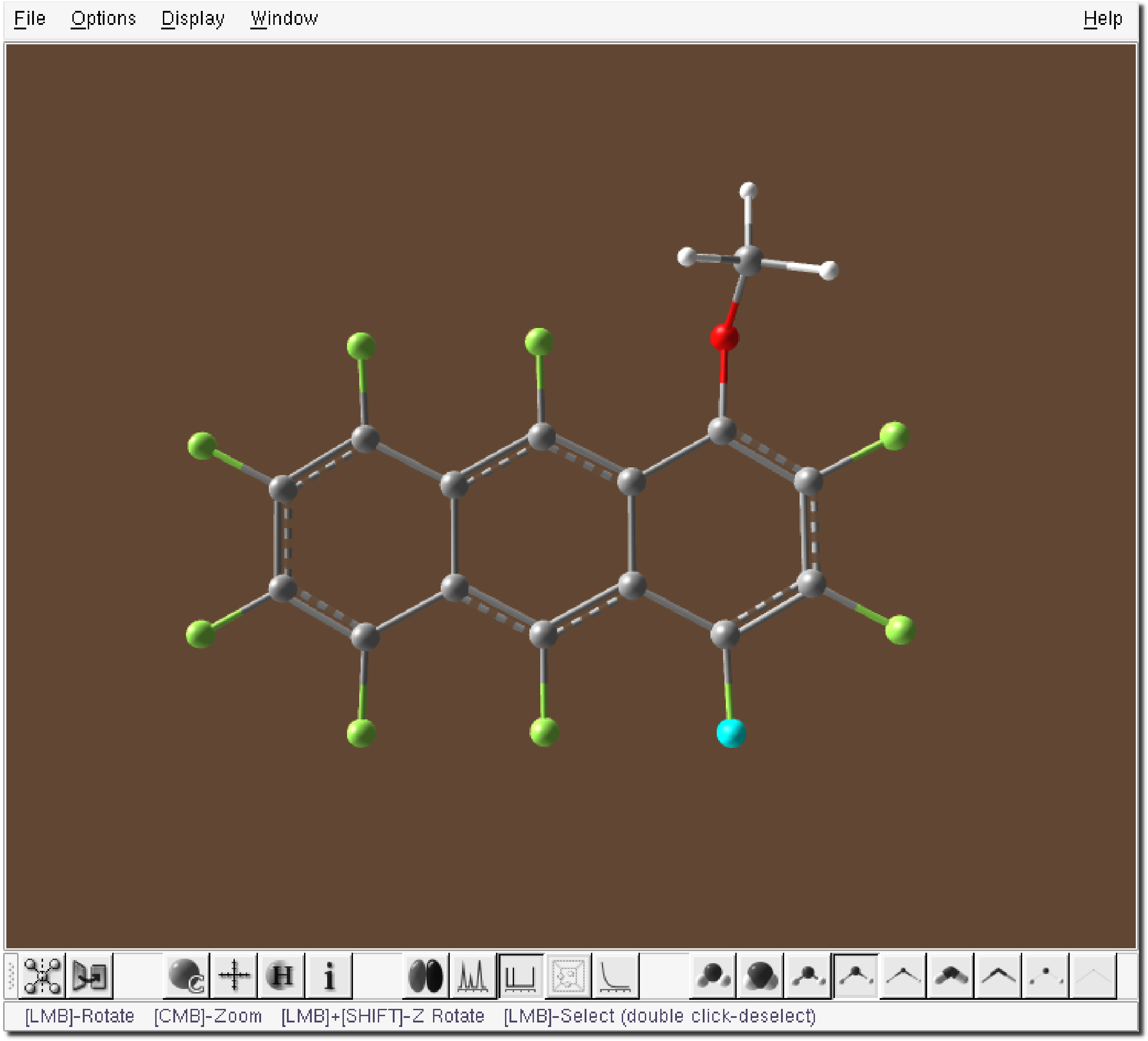
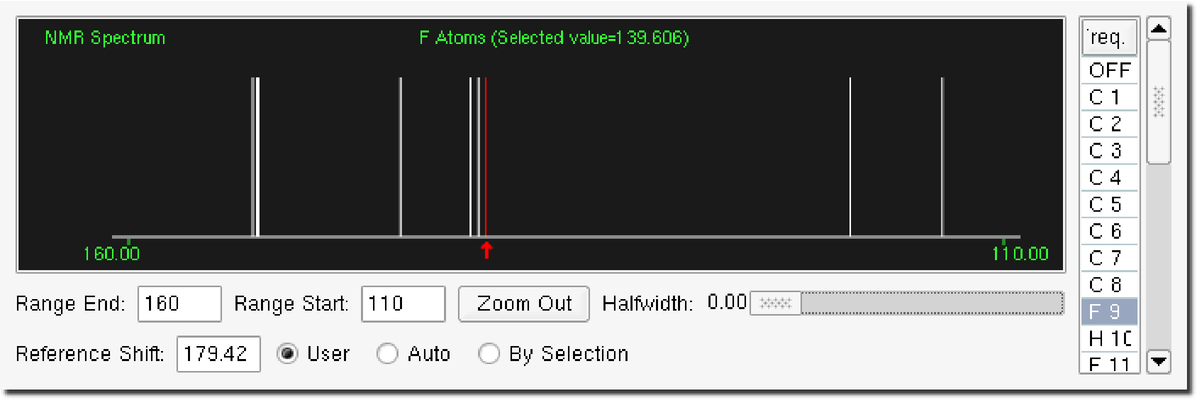


Figure 4.73: View window - 1-methoxy-perfluoroanthracene, fluorine atom no. 9 selected

Exactly the same sequence of operations as described in Step 8 should result in the following ^{19}F NMR spectrum, Figure 4.74.



Range End: 160 Range Start: 110 Halfwidth: 0.00

Reference Shift: 179.42 ● User ○ Auto ○ By Selection

Figure 4.74: NMR window - 1-methoxy-perfluoroanthracene, ^{19}F NMR spectrum

4.3.7 Building 2- and 9-Methoxy-Perfluoroanthracene and Visualizing the PQS job outputs

Steps 9 through 12 can be repeated to construct and capture the ^{19}F NMR spectra of the 2- and 9-methoxy derivatives. The output files are available as `F-anthracene-OMe2.out` and `F-anthracene-OMe9.out`, respectively. The structures and NMR spectra are shown in Figures 4.75 - 4.78.

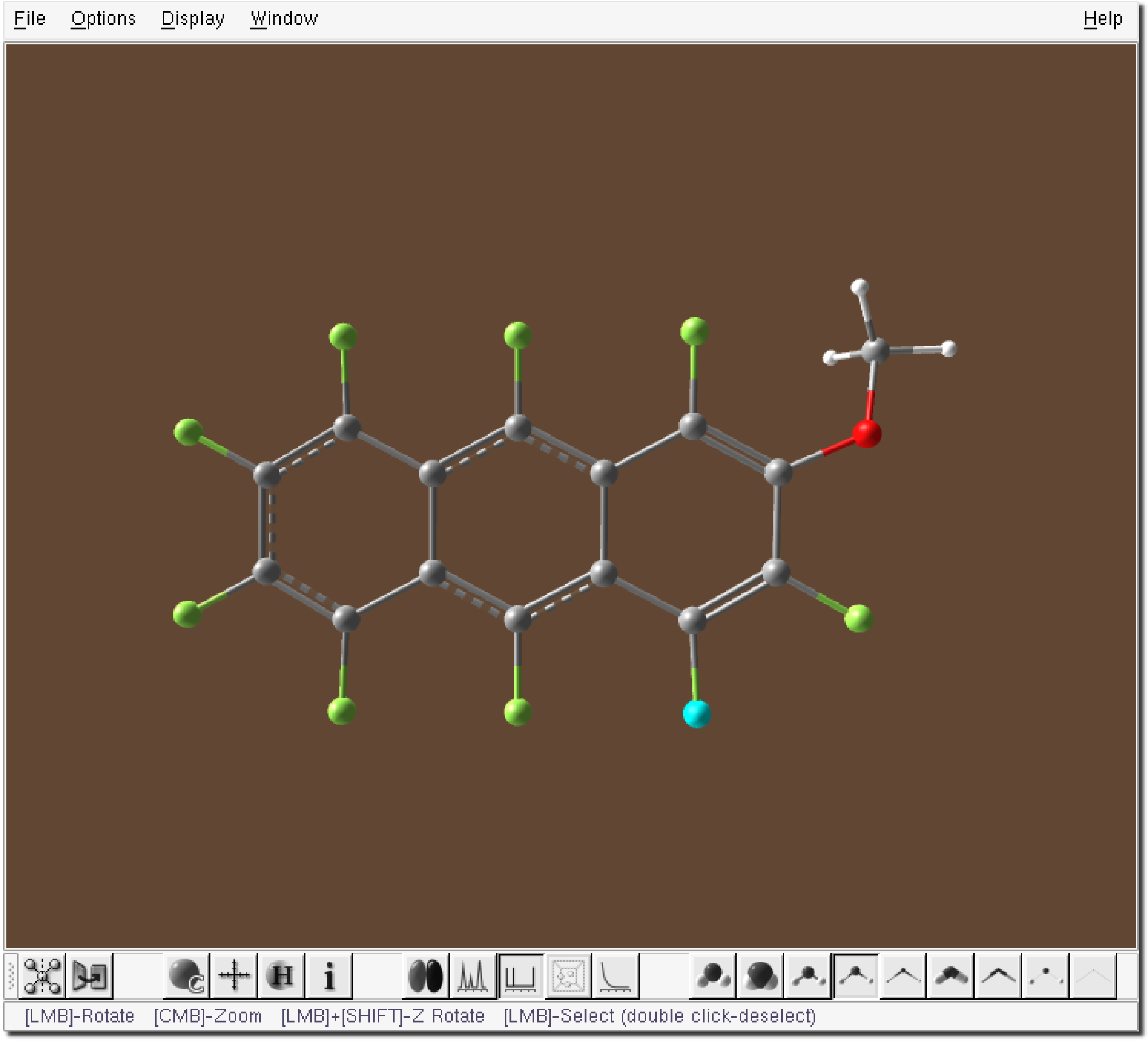
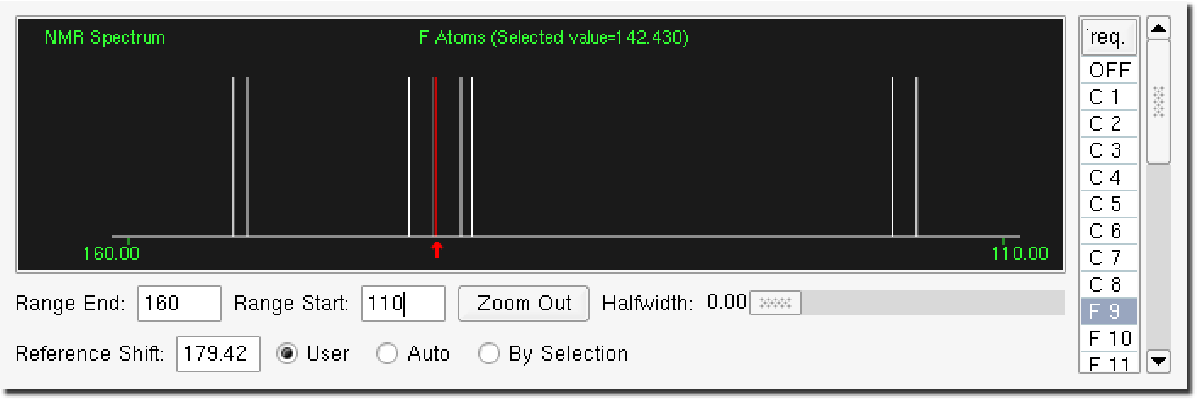


Figure 4.75: View window - 2-methoxy-perfluoroanthracene, atom no. 9 selected



Range End: 160 Range Start: 110

Halfwidth: 0.00

Reference Shift: 179.42 ● User ○ Auto ○ By Selection

Figure 4.76: NMR window - 2-methoxy-perfluoroanthracene, ^{19}F NMR spectrum

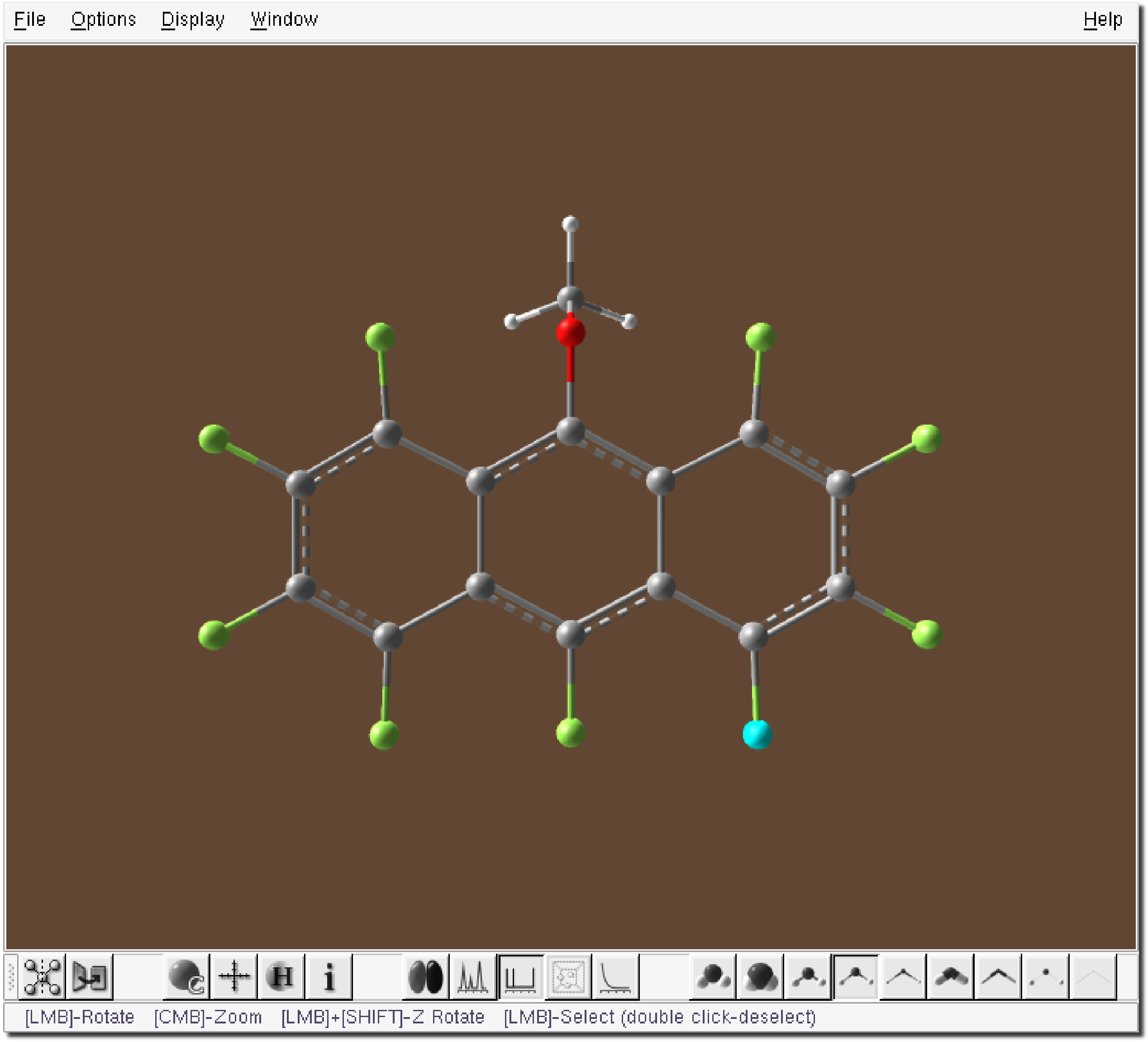
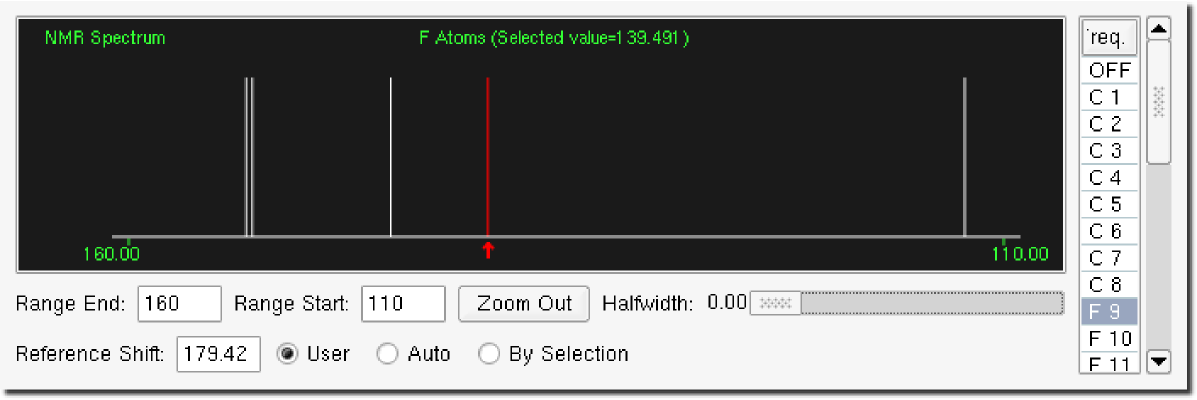


Figure 4.77: View window - 9-methoxy-perfluoroanthracene, fluorine atom no. 9 selected



Range End: 160 Range Start: 110 Halfwidth: 0.00

Reference Shift: 179.42 ● User ○ Auto ○ By Selection

Figure 4.78: NMR window - 9-methoxy-perfluoroanthracene, ^{19}F NMR spectrum

4.3.8 Comparing the NMR Spectra of perfluoroanthracene, 1-, 2-, and 9-methoxy- perfluoroanthracene

All four ^{19}F NMR spectra are shown together in Figure 4.79. The parent perfluoroanthracene is at the top, followed by the 1-, 2- and 9-methoxy derivatives. Because the ranges were set to the same on all four spectra, they can be directly compared.

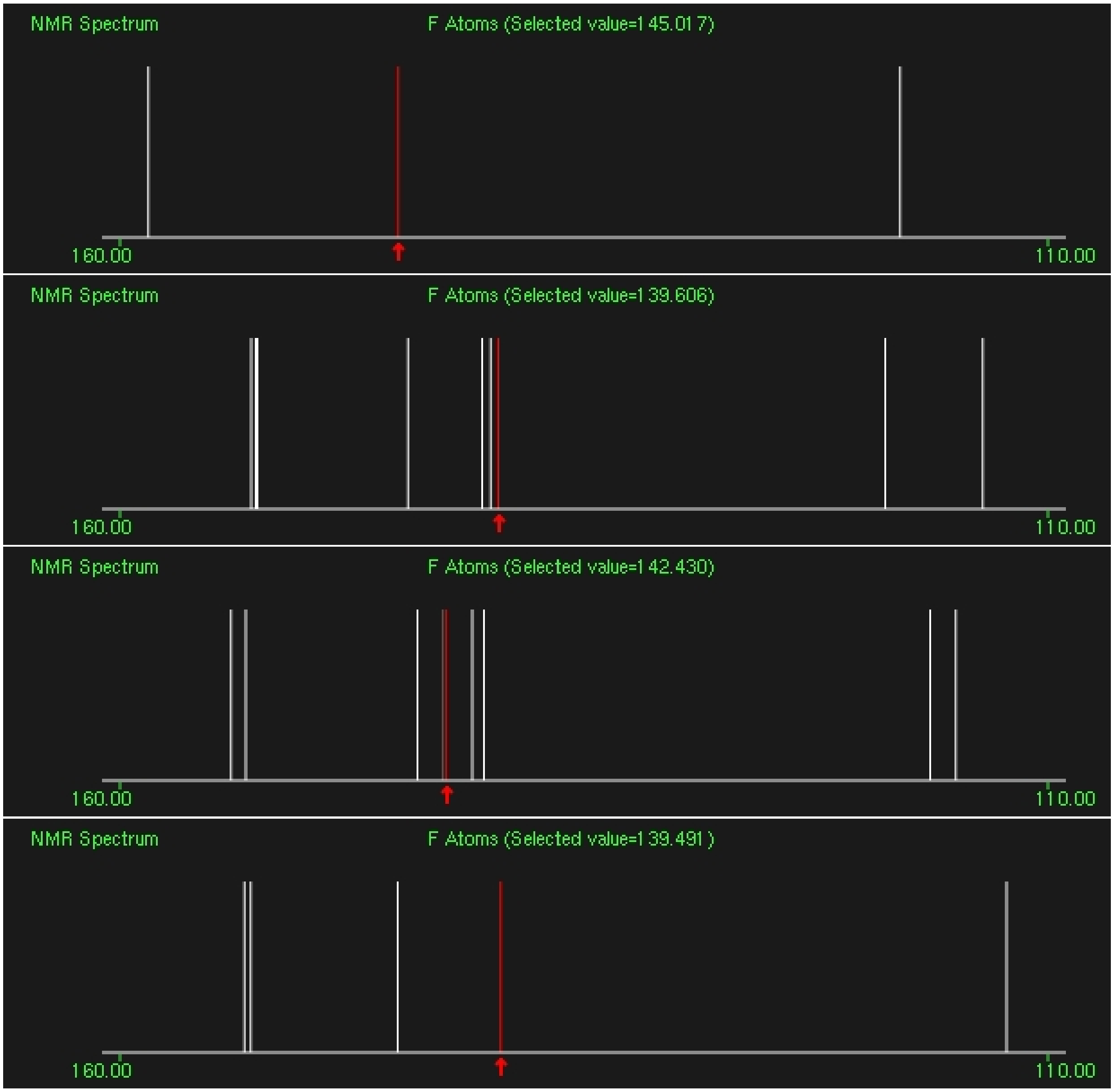


Figure 4.79: ^{19}F NMR spectra (from the top): perfluoroanthracene, 1-methoxy-perfluoroanthracene, 2-methoxy-perfluoroanthracene and 9-methoxy-perfluoroanthracene, atom no. 9 selected

In all three derivative spectra, the three main signals observed in the parent are split (due of course to the loss of symmetry) and are shifted downfield. The spectra of the three isomers are sufficiently different that in, e.g., a reaction between perfluoroanthracene and methoxide ion in methanol, provided one isomer was dominant in the reaction mix, it should be possible to determine the actual substitution site – whether at positions 1, 2 or 9 – by comparing the experimentally observed ^{19}F NMR spectrum with the theoretically simulated spectra.

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