Materials Science Suite 2015-2

User Manual

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Contents

Document Conventions

In addition to the use of italics for names of documents, the font conventions that are used in this document are summarized in the table below.

Font	Example	Use
Sans serif	Project Table	Names of GUI features, such as panels, menus, menu items, buttons, and labels
Monospace	`$SCHRODINGER/maestro`	File names, directory names, commands, environment variables, command input and output
Italic	*filename*	Text that the user must replace with a value
Sans serif uppercase	CTRL+H	Keyboard keys

Links to other locations in the current document or to other PDF documents are colored like this: Document Conventions.

In descriptions of command syntax, the following UNIX conventions are used: braces { } enclose a choice of required items, square brackets [ ] enclose optional items, and the bar symbol | separates items in a list from which one item must be chosen. Lines of command syntax that wrap should be interpreted as a single command.

File name, path, and environment variable syntax is generally given with the UNIX conventions. To obtain the Windows conventions, replace the forward slash / with the backslash \ in path or directory names, and replace the $ at the beginning of an environment variable with a % at each end. For example, `$SCHRODINGER/maestro` becomes `%SCHRODINGER%\maestro`.

Keyboard references are given in the Windows convention by default, with Mac equivalents in parentheses, for example CTRL+H (⌘H). Where Mac equivalents are not given, COMMAND should be read in place of CTRL. The convention CTRL-H is not used.

In this document, to *type* text means to type the required text in the specified location, and to *enter* text means to type the required text, then press the ENTER key.

References to literature sources are given in square brackets, like this: [10].

Introduction

The Materials Science suite is a collection of tools and interfaces that are designed to facilitate calculations that are relevant to materials science. The collection leverages the existing Schrödinger software, which was originally designed for basic research and biochemical application, as well as providing new software. The Materials Science interface organizes access to the interactive tools for use in materials science projects. An overview of the features of the interface is given in the first section, and is followed by instructions for running Schrödinger software, including the interface, and starting jobs.

1.1 Overview of Features

The features offered in the Materials Science interface are summarized in the sections below. Some of these features are documented in other manuals. For each feature, links are provided to the relevant sections of this manual or other manuals. The core capabilities are described first, followed by descriptions of the specific features on the Tools and Tasks menus in the interface.

1.1.1 Core Capabilities

The basic structure manipulation, display and management features of the interface are described in the *Maestro User Manual*. Maestro is the underlying interface on which the Materials Science interface is built. In particular you should read the *Maestro Overview*, which gives a basic introduction to the structure of the interface and its workflow. A brief description of the main window

Many of the calculations that can be done are quantum mechanical, so familiarity with the quantum-mechanical program, Jaguar, is highly recommended. You can use the *Jaguar User Manual* and the *Jaguar Quick Start Guide* for this purpose. Semiempirical calculations can also be done—see the *Semiempirical NDDO Guide*.

Molecular dynamics simulations are provided with the Desmond MD program. See the *Desmond User Manual* and the *Desmond Quick Start Guide* for information on the graphical interface and running jobs both from the interface and the command line, and the *Desmond User's Guide* from D.E. Shaw Research for details on the methods and backend command-line input.

Molecular mechanics calculations can be done with the MacroModel program, including minimizations, conformational searches, and coordinate scans. See the *MacroModel User Manual* for more information.

If you want to perform statistical analyses or regressions on properties, you can use Strike from the Materials Science interface (Tasks → Model Building and Statistics). See the *Strike User Manual* for details. You can also use the Canvas interface, which has a wider range of statistical and regression tools available, and can build models based on structural fingerprints as well as properties. See the *Canvas User Manual* for details.

For QSAR models based on 3D features, such as fields or spatial arrangement of atom types or groups, you can use the Field-Based QSAR and Atom-Based QSAR panels (Applications → More Applications → Field-Based QSAR or Applications → More Applications → Phase → Atom-Based QSAR). See *Field-Based QSAR* and Chapter 9 of the *Phase User Manual* for details.

1.1.2 Building Structures

The Materials Science suite offers several specialized tools for building structures:

- Organometallic complexes (Section 2.1 on page 11)
- Structure libraries (Section 2.2 on page 22)
- Element variations (Section 2.3 on page 31)
- Nanotubes and nanosheets (Section 2.4 on page 33)
- Nanoparticles (Section 2.5 on page 37)
- Disordered molecular systems (Section 2.6 on page 39)
- Crystal structures (Section 2.7 on page 45)
- Polymers and amorphous polymer cells (Section 2.8 on page 48)

For information on general structure-building and adjustment tools, see Chapter 5 of the *Maestro User Manual*.

1.1.3 Structure Analysis

Several tools that can be used for analysis of common elements in a set of structures are provided in the Materials Science interface:

- R-group analysis—analyze the properties of a set of structures as a function of the groups at the various attachment points on a common scaffold (*R-Group Analysis* manual)
- Scaffold decomposition—find common scaffolds in a set of molecules (Section 10.5.2 of the *Maestro User Manual*)

- Ligand filtering—Filter a set of structures based on properties of the structures, such as functional group counts or physical properties (Section 10.8 of the *Maestro User Manual*)

1.1.4 Structure Optimization

Tools for minimization of the energy of structures with respect to their geometry (geometry optimization) are available under Tasks → Minimization. These include

- force-field minimization of single structures with MacroModel (Chapter 6 of the *MacroModel User Manual*)
- force-field minimization of periodic structures with Desmond (Section 3.3 of the *Desmond User Manual*)
- semiempirical quantum-mechanical minimizations (*Semiempirical NDDO Guide*).
- ab initio quantum-mechanical minimizations (Chapter 4 of the *Jaguar User Manual*).

Conformational search facilities are available under Tasks → Conformational Search, and include a general search facility (Chapter 8 of the *MacroModel User Manual*), and one specifically designed for locating conformations of macrocycles (Chapter 16 of the *MacroModel User Manual*).

1.1.5 Chemical Reactions

Several tools are provided for calculating reaction energetics, reaction barriers, and reaction rates.

- Transition state search—locate the transition state for a reaction (Section 4.3 of the *Jaguar User Manual*) and generate an IRC or MEP reaction path (Section 4.5 of the *Jaguar User Manual*)
- Reaction path interpolation—create structures along a linear synchronous transit reaction path in internal, distance or Cartesian coordinates, with constraints (Section 3.3 on page 73)
- TST rate calculation—calculate the rate of a reaction based on information from a transition state search (Section 3.5 on page 83)
- Reaction energetics enumeration—calculate reaction enthalpies or reaction barriers for a unimolecular reaction in a series of homologous compounds, based on structures for a prototype reaction (Section 3.4 on page 80)
- Potential energy surfaces—map out the potential energy surface for a selection of coordinates quantum mechanically (Section 4.4 of the *Jaguar User Manual*) or with molecular

mechanics (Chapter 7 of the *MacroModel User Manual*), and display 1D or 2D plots of the results in the Workspace. Use Tasks → Coordinate Scanning and Tools → Plot Coordinate Scan.

- Heat of formation—calculate the enthalpy of formation or the atomization energy of a molecule (Section 5.4 of the *Jaguar User Manual*)
- Bond and ligand dissociation energies—calculate the dissociation enegy for all single bonds or a restricted set of single bonds in a molecule, or the binding energy of each ligand in an organometallic complex (Section 3.2 on page 70)

1.1.6 Optoelectronics

- Optoelectronic properties—calculate oxidation and reduction potentials, reorganization energies, triplet energies, and absorption spectra (Section 4.1 on page 87)
- Charge transfer rate—calculate the Marcus charge transfer rate for electrons or holes in an amorphous structure (Section 4.3 on page 104)
- Genetic optimization—optimize optoelectronic properties by mutating structures using a genetic algorithm.
- Spin states—calculate the lowest state of each spin for specified spin values, with empirical corrections for 3d transition metal complexes.

1.1.7 Molecular Dynamics

Most of the molecular dynamics capabilities are described in the *Desmond User Manual*. The following features are available only in the Materials Science interface:

- Disordered System Builder for building a multicomponent system that is randomly distributed in a simulation box (Section 2.6 on page 39)
- Multistage Simulation Workflow for running multiple MD stages of minimization, molecular dynamics, and simulated annealing (Chapter 5)

1.1.8 Visualization Tools

The graphical interface has a number of visualization tools for display of the results of calculations.

- Plotting spectra—plot UV/Vis, infrared, or VCD spectra from Jaguar, or imported as raw data (Tools → Plot Spectra; Section 3.11 of the *Jaguar User Manual*)
- Plotting potential energy surfaces—plot the results of a coordinate scan in 1 or 2 dimensions (Section 11.2 of the *Maestro User Manual*)

- Scatter plots of properties—plot two properties, with representation of two more in terms of color and size of plot symbols (Section 11.1 of the *Maestro User Manual*)
- Property surfaces—display surfaces generated by Jaguar, such as charge or spin density, molecular orbitals, electrostatic potential (Section 12.4 of the *Maestro User Manual*)

Plotting capabilities are also included in some of the Materials Science panels.

1.2 Running Schrödinger Software

Schrödinger applications can be run from a graphical interface or from the command line. The software writes input and output files to a directory (folder) which is termed the *working directory*. If you run applications from the command line, the directory from which you run the application is the working directory for the job. The Materials Science interface is a customization of the Maestro interface. You can also use the standard Maestro as your working interface.

Linux:

To run any Schrödinger program on a Linux platform, or start a Schrödinger job on a remote host from a Linux platform, you must first set the `SCHRODINGER` environment variable to the installation directory for your Schrödinger software. To set this variable, enter the following command at a shell prompt:

csh/tcsh: `setenv SCHRODINGER` *installation-directory*

bash/ksh: `export SCHRODINGER=`*installation-directory*

Once you have set the `SCHRODINGER` environment variable, you can run programs and utilities with the following commands:

`$SCHRODINGER/`*program* `&`
`$SCHRODINGER/utilities/`*utility* `&`

You can start the Materials Science interface with the following command:

```
$SCHRODINGER/maestro -profile MaterialsScience &
```

It is usually a good idea to change to the desired working directory before starting the Materials Science interface. This directory then becomes the working directory.

Windows:

The primary way of running Schrödinger applications on a Windows platform is from a graphical interface. To start the Materials Science interface, double-click on the Materials Science icon, on a Maestro project, or on a structure file; or choose Start → All Programs → Schro-

dinger-2015-2 → Materials Science. You do not need to make any settings before starting Materials Science or running programs. The default working directory is the Schrodinger folder in your Documents folder.

If you want to run applications from the command line, you can do so in one of the shells that are provided with the installation and have the Schrödinger environment set up:

- Schrödinger Command Prompt—DOS shell.
- Schrödinger Power Shell—Windows Power Shell (if available).

You can open these shells from Start → All Programs → Schrodinger-2015-2. You do not need to include the path to a program or utility when you type the command to run it. If you want access to Unix-style utilities (such as `awk`, `grep`, and `sed`), preface the commands with `sh`, or type `sh` in either of these shells to start a Unix-style shell.

Mac:

The primary way of running Schrödinger software on a Mac is from a graphical interface. To start the Materials Science interface, click its icon on the dock. If there is no Materials Science icon on the dock, you can put one there by dragging it from the SchrodingerSuite2015-2 folder in your Applications folder. This folder contains icons for all the available interfaces. The default working directory is the Schrodinger folder in your Documents folder (`$HOME/Documents/Schrodinger`).

Running software from the command line is similar to Linux—open a terminal window and run the program. You can also start Materials Science from the command line in the same way as on Linux. The default working directory is then the directory from which you start Materials Science. You do not need to set the `SCHRODINGER` environment variable, as this is set in your default environment on installation. To set other variables, on OS X 10.7 use the command

`defaults write ~/.MacOSX/environment` *variable* `"`*value*`"`

and on OS X 10.8, 10.9, and 10.10 use the command

`launchctl setenv` *variable* `"`*value*`"`

1.3 Starting Jobs from the Materials Science Interface

To run a job from the Materials Science interface, you open a panel from one of the menus (e.g. Tasks), make settings, and then submit the job to a host or a queueing system for execution. The panel settings are described in the help topics and in the user manuals. When you have finished making settings, you can use the Job toolbar to start the job.

You can start a job immediately by clicking Run. The job is run on the currently selected host with the current job settings and the job name in the Job name text box. If you want to change the job name, you can edit it in the text box before starting the job. Details of the job settings are reported in the status bar, which is below the Job toolbar.

If you want to change the job settings, such as the host on which to run the job and the number of processors to use, click the Settings button. (You can also click the arrow next to the button and choose Job Settings from the menu that is displayed.)

You can then make the settings in the Job Settings dialog box, and choose to just save the settings by clicking OK, or save the settings and start the job by clicking Run. These settings apply only to jobs that are started from the current panel.

If you want to save the input files for the job but not run it, click the Settings button and choose Write. A dialog box opens in which you can provide the job name, which is used to name the files. The files are written to the current working directory.

The Settings button also allows you to change the panel settings. You can choose Read, to read settings from an input file for the job and apply them to the panel, or you can choose Reset Panel to reset all the panel settings to their default values.

You can also set preferences for all jobs and how the interface interacts with the job at various stages. This is done in the Preferences panel, which you can open at the Jobs section by choosing Preferences from the Settings button menu.

Note: The items present on the Settings menu can vary with the application. The descriptions above cover all of the items. Jaguar has an Edit item and extra functions for the Read and Write items, which are described later in the manual.

The icon on the Job Status button shows the status of jobs for the application that belong to the current project. It starts spinning when the first job is successfully launched, and stops spinning when the last job finishes. It changes to an exclamation point if a job is not launched successfully.

Clicking the button shows a small job status window that lists the job name and status for all active jobs submitted for the application from the current project, and a summary message at the bottom. The rows are colored according to the status: yellow for submitted, green for launched, running, or finished, red for incorporated, died, or killed. You can double-click on a

row to open the Monitor panel and monitor the job, or click the Monitor button to open the Monitor panel and close the job status window. The job status is updated while the window is open. If a job finishes while the window is open, the job remains displayed but with the new status. Click anywhere outside the window to close it.

1.4 The Materials Science Interface

The Materials Science interface is a customized form of the Maestro interface that is specially designed for materials science use. It inherits most of the capabilities of the Maestro interface (though organized differently), and it has features of its own.

If you prefer to use the standard Maestro interface, you can do so. Most of the capabilities of the Materials Science Suite are available from the Materials Science submenu of the Applications menu or the Materials submenu of the Tasks menu.

You can open the Materials Science interface as follows:

- **Windows:** Double-click the Materials Science icon on the desktop
- **Mac:** Go to Applications → SchrodingerSuite2015-2 and double-click the Materials Science icon
- **Linux:** Start Maestro and choose Materials Science in the Choose Profile dialog box, or use the command `$SCHRODINGER/maestro -profile MaterialsScience`

See Section 1.2 on page 5 for more information.

The main window opens with the following features displayed by default:

- **Menu bar.** This is at the top of the window on Linux and Windows, and is the menu bar on a Mac.
- **Manager toolbar.** This toolbar is just below the menu bar on Linux and Windows, and at the top of the window on the Mac. Each label on this toolbar displays or hides another toolbar. By default they are all hidden, as much of their function is available in the Toggle Table. See Section 2.4 of the *Maestro User Manual* for details of the toolbars.
- **Entry List.** This dockable panel is displayed on the left side of the main window. It displays a list of all the structures (“entries”) in the current Maestro project. See Section 9.10 of the *Maestro User Manual* for more information. You can undock it from the main window and redock it with the docking button.

  

  Many other panels are also dockable. You can change the docking behavior in the Preferences panel (Edit → Settings → Preferences, or CTRL+,)

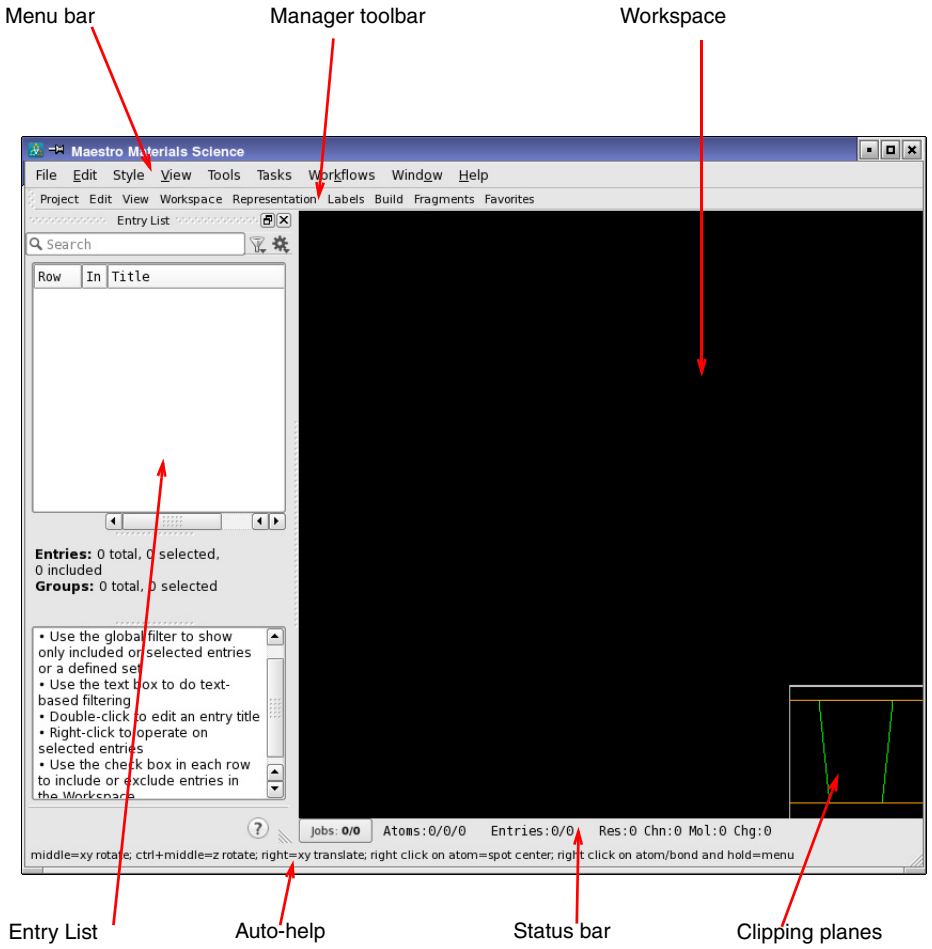

Figure 1.1. The Materials Science main window.

- **Workspace.** This is the large black area that occupies the main part of the main window. It is where 3D structures are displayed, along with any associated objects such as surfaces and text labels.
- **Status bar.** This bar is below the Workspace. At the left is a button that displays information on what jobs are running, which you can click to open the Monitor panel for detailed information on your jobs. When the pointer is not over an atom in the Workspace, the status bar gives information on the contents of the Workspace. When the pointer is over an atom, the status bar gives information on the identity of the atom. For more information, see Section 2.5 of the *Maestro User Manual*.

- **Auto-Help.** This bar at the foot of the panel displays information about the current available actions.
- **Clipping Planes.** This small window displays a top view of the Workspace (from the positive *y* direction), showing the structure and the planes where the structure is clipped.

1.5 Citing the Materials Science Suite in Publications

The use of this suite should be acknowledged in publications as:

Schrödinger Materials Science Suite 2015-2, Schrödinger, LLC, New York, NY, 2015.

Building Structures

Maestro provides facilities for building small molecules either in 2D or 3D, by sketching the structure or by combining predefined and preminimized fragments. These tools are described in Chapter 5 of the *Maestro User Manual*.

In addition to these tools, the Materials Science Suite provides tools for building single structures or multiple structures that are of particular interest in materials applications, such as organometallic complexes, ligand libraries, nanostructures, and crystal structures. These tools are described in the sections below. You can also create molecular complexes with the Probe Scan panel—see Chapter 6.

After building structures, you should perform a minimization on the structures before using them in some other application (if minimization is not part of the procedure.)

2.1 Building Organometallic Complexes

Two tools are available for building octahedral, tetrahedral, or square planar organometallic complexes. The first is a tool to build a single organometallic complex with a single metal center, using one or more ligand types. The second is a tool to build a series of complexes from a set of ligands, in which each complex has only one ligand type (homoleptic complex). In addition, there is a tool for cleaning up the ligand geometry in the complexes, to relieve any steric clashes between large ligands.

2.1.1 Building a Single Complex

You can build a single organometallic complex with a single metal center, in octahedral, tetrahedral, or square planar geometry, in the Build Single Complex panel, which you open by choosing Tools → Build Single Complex.

There are three main steps to building an organometallic complex:

1. Choose the metal and the coordination geometry.
2. Choose the ligands.
3. Choose the arrangement of ligands in the complex.

These steps are described in the sections below.

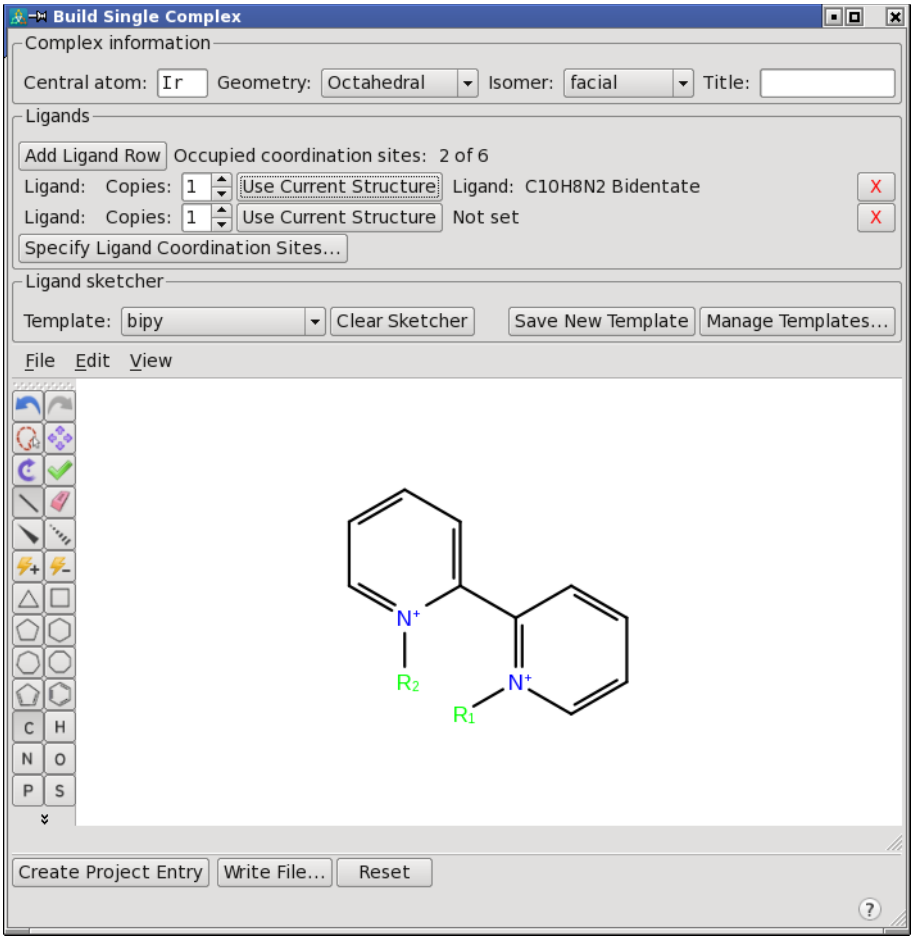

Figure 2.1. The Build Single Complex panel.

2.1.1.1 Choosing the Metal and Coordination Geometry

The metal, coordination geometry, and other information can be set in the Complex information section.

- To choose the metal, type the atomic symbol for the metal in the Central atom text box.
- To set the geometry, choose Octahedral, Tetrahedral, or Square planar from the Geometry option menu.
- To set the title for the structure, enter the text in the Title text box.

2.1.1.2 Choosing the Ligands

In this step, you decide how many different ligands you want to use, how many of each ligand to use, and select or sketch the ligands.

Each ligand is represented by a row in the Ligands section. Each row specifies the number of copies of the ligand, and has a button to assign a ligand structure to this row. For example, for an ML_3X_3 complex, you would have two rows, one for ligand L and one for ligand X, and for each you would set the number of copies to 3. Rows can be added by clicking Add Ligand Row, and deleted by clicking the delete (red X) button for the row.

The actual structures can be defined in the Ligand sketcher section, either by choosing a template for the ligand, which you can modify, or drawing the ligand structure in the sketcher.

- To use an existing ligand template, choose it from the Template option menu. The most recently used ligand is at the top of the menu.
- To modify an existing ligand template, choose it from the Template option menu, then modify it in the sketcher.
- To draw a ligand, choose Custom from the Template option menu, then start drawing in the sketcher.

For information on using the sketcher, see Section 5.5 of the *Maestro User Manual*. This section contains information on the sketcher controls, which are common to several panels.

When creating a new ligand, you must indicate which atoms are the ligating atoms, by adding a bond to them and labeling the terminal atom as R1 for the first ligating atom, and R2 for the second. Right-click on the atom and choose Set R Group → R1 or R2 to perform the labeling. If the ligand forms a dative bond, you must still add a bond and label it, even if it violates the valence of the ligating atom.

If you have drawn a new ligand structure or modified an existing structure, click Save New Template to save the ligand structure as a template, and name the structure in the dialog box that is displayed. The custom templates are stored in your Schrödinger user resources directory. If you want to delete a saved ligand structure, click Manage Templates, select the template from the Template option menu in the Manage Templates panel, and click Delete Template.

When you have drawn or chosen a ligand, click Use Current Structure on the row in the Ligands section that you want to assign the structure to. The ligand formula and whether the ligand is monodentate or bidentate is shown in the ligand row. Pausing the pointer over this information shows the 2D structure of the ligand in a tool tip. In addition, the number of occupied coordination sites listed above the ligand rows is updated.

2.1.1.3 Choosing the Ligand Arrangement

For octahedral complexes with three copies of a single bidentate ligand or three copies of each of two monodentate ligands, you can automatically arrange them in a facial or meridional conformation, by choosing the isomer in the Complex information section. Both isomers are chiral, but only one of the stereoisomers is built. The facial stereoisomer is in the Λ form, the meridional stereoisomer is in the Δ form. The geometry is applied when you save the structure. If the bidentate ligand is symmetric, there are only the two stereoisomers, which are built by choosing the facial or meridional isomer.

For tetrahedral complexes with two pairs of monodentate ligands (i.e. MA_2B_2), you can choose either the cis or the trans isomer in the Complex information section.

For any other type of complex, you must pick the sites on the metal atom for each ligating atom on each ligand, by clicking Specify Ligand Coordination Sites and using the diagram of the complex in the dialog box that opens to pick the sites for each ligand.

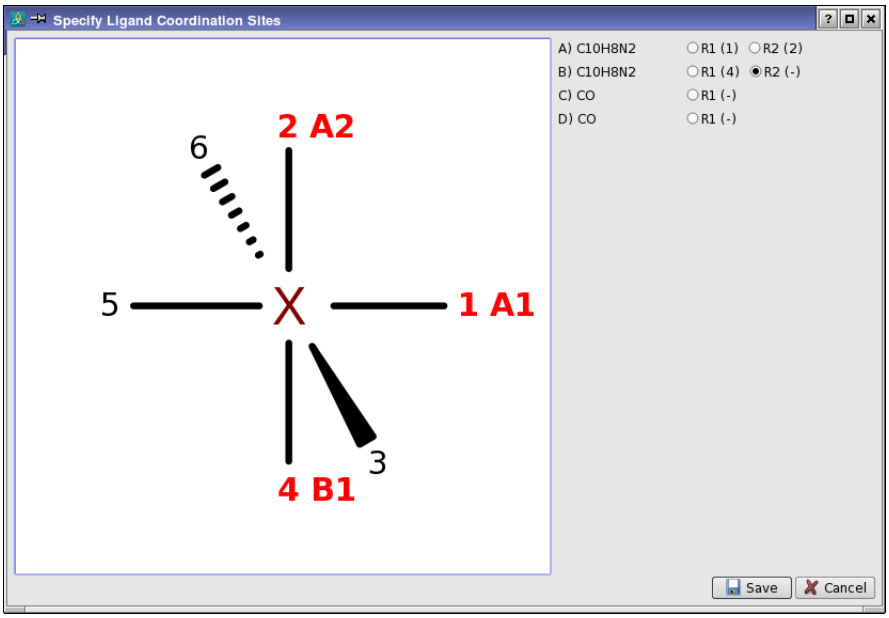

Figure 2.2. The Specify Ligand Coordination Sites dialog box.

By default, the first ligating atom for the first ligand is selected from the list on the right when the dialog box opens. You can click on one of the available coordination sites in the diagram to assign the atom to a site. The site number is colored red and a label identifying the ligand (by a letter) and the ligating atom (by number) is displayed next to the site number. The "-" in parentheses next to the ligating atom label in the list is replaced with the assigned site number. The

next ligating atom is automatically selected, so you can simply click on the sites in the desired order to assign them. You can also select a ligating atom manually to change its assignment.

Pausing the pointer over the ligand name shows its 2D structure in a tool tip.

When you have finished assigning the sites, click Save to save the assignment and close the dialog box.

2.1.1.4 Saving the Complex

When you have finished defining the complex, click one of the action buttons to save it, either to the Maestro project with Create Project Entry or to a file, with Write File.

When you have built the complex, you should consider cleaning it up with the Ligand Cleanup panel, and then running a geometry optimization with Jaguar before proceeding with any calculations on the complex.

2.1.1.5 Summary

The procedures for building complexes and ligands are summarized here.

To build a complex:

1. Enter the atomic symbol for the metal in the Central atom text box.
2. Choose the coordination geometry from the Geometry option menu.
3. Select a ligand template from the Template option menu.
4. (Optional) Modify the template structure if necessary to produce the ligand you want.
5. Click Use Current Structure in the ligand row.

   The ligand formula is displayed to the right, and the count of occupied coordination sites is updated.
6. Set the number of copies of the ligand molecule in the complex using the Copies box.
7. If you want to add another ligand, click Add Ligand Row and repeat Step 3 – Step 6 to set up each ligand.
8. Click Specify Ligand Coordination Sites.
9. Click on the sites in the diagram to assign the ligand coordinating atoms to sites, then click OK.
10. Click Create Project Entry or Write File to save the complex.

To create a new ligand template:

1. Choose Custom from the Template option menu.
2. Sketch the structure in the sketcher.
3. Label the ligating atom or atoms with R1 or R2.
4. Click Save New Template.
5. Enter a name for the template, and click OK.

To delete a saved ligand template:

1. Click Manage Templates to open the Manage Templates panel.
2. Choose the template from the Template option menu.
3. Click Delete Template.

To change the directory used for ligand templates:

1. Click Manage Templates to open the Manage Templates panel.
2. Click Change Custom Template Directory.
3. In the Choose Directory dialog box, select the directory and click Choose.

To clear the panel and return to the default panel settings:

- Click Reset.

2.1.2 Building a Series of Complexes

The Build Multiple Complexes panel is intended for building a series of organometallic complexes from a set of ligands that are variations on a common core. Each complex contains only one of the ligands: thus, the number of complexes generated is equal to the number of ligands that you supply. In addition to the ligand that is varied between complexes, you can specify a "sentinel" ligand: a ligand that stays the same in each complex. The complexes can be octahedral, tetrahedral, or square planar.

The basic procedure is as follows:

1. Choose the source of the ligand structures, from the Use structures from option menu.
2. Enter the atomic symbol of the metal in the Metal atom text box.
3. Set the geometry of the complex and if necessary, the isomer.
4. (*Optional*) Choose a sentinel ligand, and set the number of copies of this ligand.

5. Choose the coordination sites: for monodentate or bidentate ligands.
6. Enter the atom number in the ligand structure of the coordinating atom or atoms.
7. Select an option for the group to remove from the ligand (if any).
8. Click Build Complexes.

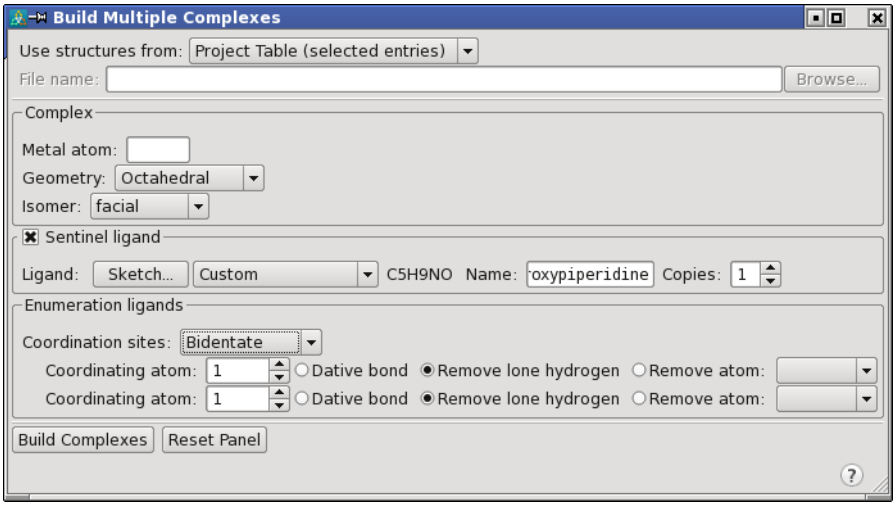

Figure 2.3. The Build Multiple Complexes panel.

More information on the steps in this procedure are given below.

The panel does not build the ligands, but uses ligand structures from the Project Table, the Workspace, or a file. The Workspace ligand must be a project entry, not a scratch entry.

You can build such a set of ligands manually, with Maestro's build tools, you can create a set of elemental variations on ligands with the Elemental Enumeration panel (see Section 2.3 on page 31), or you can use the Interactive Enumeration panel (see Section 2.2 on page 22). This panel allows you to choose a core structure, which is the part of the ligand that is bound to the metal, select side chains on this core as attachment points for new functional groups, and replace the side chains with a range of fragments, to build a set of structures.

The important feature for building a set of complexes is that the core is the same and that it is numbered the same way in all ligands, as the coordinating (ligating) atoms are specified by their atom number. Only one set of atom numbers can be supplied, so it must be the same in all ligands. To find out what the atom numbering is in your ligands, you can label one of the ligands in the Workspace. Include a ligand, then choose Atom Number from the Label All button menu on the Labels toolbar (To display this toolbar, click Labels on the Manager toolbar at the

top of the Workspace). You can then use the numbers displayed on the atoms to specify the coordinating atom (monodentate ligand) or atoms (bidentate ligand).

When specifying the atom that is coordinated, you can request the removal of atoms that are attached to the coordinating atom: for example, if you have a secondary amine in a ring (such as in pyrrole), you might want to remove the attached hydrogen.

- If there are no extra atoms to remove (as for cyano), select Dative bond.
- If there is a single extra hydrogen (as in pyrrole), select Remove lone hydrogen.
- If some other functional group is attached to the coordinating atom, select Remove atom, and choose the atom from the list, which shows the atomic symbol and the atom number. This option requires a structure in the Workspace, so that the atoms connected to the coordinating atom can be determined. The attached atom and all atoms in the side chain originating at the attached atom are removed when the complex is built.

  For example, if the atom to remove is the C in a $CONH_2$ group, the entire $CONH_2$ group is removed. Likewise, if the atom is part of a phenyl group, the entire phenyl group is removed. If the atom to remove and the coordinating atom are part of the same ring system, no additional atoms are removed beyond the specified atom to remove.

If you have a ligand structure in the Workspace, the coordinating atom or atoms are marked in the Workspace with green markers, and the atoms to be removed are marked with red markers.

If you want to construct complexes with a common ligand, while enumerating other ligands, you can select Sentinel ligand, then specify the ligand to use as the common ("sentinel") ligand and the number of copies of this ligand to use. The ligand can be monodentate or bidentate. The remaining sites in the complex are filled with the "enumeration" ligands, as described above.

You can choose the sentinel ligand from the Ligand option menu, or sketch a new ligand by clicking Sketch and drawing it in the Ligand Sketcher. For information on using the sketcher, see Section 5.5 of the *Maestro User Manual*. You must indicate which atoms are the ligating atoms, by adding a bond to them and labeling the terminal atom as R1 for the first ligating atom, and R2 for the second. Right-click on the atom and choose Set R Group → R1 or R2 to perform the labeling. When you have finished sketching the ligand, click Use This Structure to use it for this run only, or click Save New Template, to save it as a "template" ligand, which is added to the list of ligands on the Ligand option menu (and stored in a resource file for future use).

To specify the complex geometry, choose Octahedral, Tetrahedral, or Square planar from the Geometry option menu.

For octahedral complexes of bidentate ligands, two geometric isomers are possible: facial and meridional. You can choose the isomer from the Isomer option menu, which is only available if you have bidentate ligands and an octahedral complex. Both isomers are chiral, but only one of the stereoisomers is built. The facial stereoisomer is in the Λ form, the meridional stereoisomer is in the Δ form. If the ligands are symmetric, there are only the two stereoisomers, which are built by choosing the facial or meridional isomer.

Square planar complexes have two geometric isomers if the ligand is asymmetric and bidentate: cis and trans. You can choose the isomer from the Isomer option menu.

Tetrahedral complexes of asymmetric bidentate ligands have two stereoisomers, only one of which is built.

To build the complexes, click Build Complexes. When the complexes have been created, they are added to the Project Table as single entries, named M(L)n, where M is the atomic symbol of the metal, L is the title of the ligand, and n is the number of ligands.

If you want to clear the panel settings and reset them to the defaults, click Reset Panel.

When you have built the complexes, you should consider cleaning them up with the Ligand Cleanup panel, and then running a geometry optimization with Jaguar before proceeding with any calculations on the complexes.

2.1.3 Building with the Build Panel

If you want to build complexes with coordination geometries other than octahedral, tetrahedral, or square planar, you can use the metal fragments and metal ligands in the Fragments tab of the Build panel, which you open with Edit → 3D Builder → Fragments, or click the Fragments button on the Fragments toolbar.

To build a complex, choose a metal center from the Metal center button menu on the Fragments toolbar, and click in the Workspace. The centers available have from one to sixteen ligands.

The metal center is placed with hydrogens as the default ligands, and a generic metal. To set the metal, choose Other from the Set element button menu on the Build toolbar, and select the metal in the periodic table that is displayed, then click on the metal center.

You can also go to the Atom Properties tab in the Build panel, choose Element from the Property option menu, select the metal in the periodic table, then click on the metal center.

The ligand set contains common monodentate ligands (CO, CN, NO, H_2O, NH_3, and PH_3), and a set of η-coordinated ligands (ethylene, acetylene, allyl, butadiene, cyclopentadiene, and benzene). To use these ligands, choose Metal ligands from the Fragments option menu.

To add a ligand, choose a ligand from the available set and click on one of the coordination sites (hydrogens). You can also add other organic fragments, and these will be treated as covalently bonded to the metal.

If you want to build a complex with bidentate ligands, you should start with one of the specialized builder panels, then edit the resulting complex. You can replace the metal center in an existing complex by choosing one of the metal centers and clicking on the metal atom. The existing ligands remain in place and occupy coordination sites of the new center type.

To build a porphyrin or phthalocyanine system, choose Rings from the Fragments option menu, select the appropriate ring system and click in the Workspace to place the ring.

2.1.4 Cleaning Up the Structures of the Complexes

After building complexes, you should clean up the structures of the complexes. You can do this in the Clean Up Complexes panel, which cleans up the structure of one or more complexes by performing a force-field minimization. The metal atom is treated as though the metal-ligand bonds are at their equilibrium distances, with a generic force field whose minimum is at the current distance, and likewise with the bending parameters. The geometry around the metal is therefore not likely to change much, so the minimization will largely affect the ligand geometries.

To open the panel, choose Tools → Clean Up Complexes.

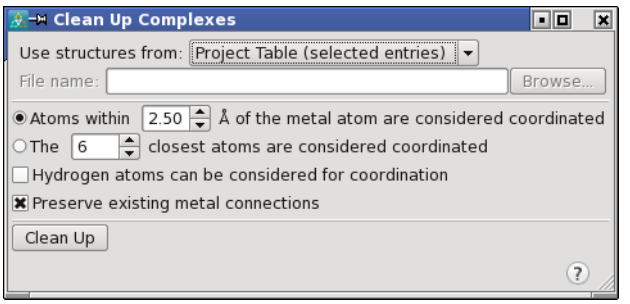

Figure 2.4. The Clean Up Complexes panel.

To clean up a set of complexes:

1. Choose the source of structures. The choices are:
   - Project Table (selected entries)—Use the entries that are currently selected in the Project Table.
   - Workspace—Use the contents of the Workspace, including any scratch entries, as a single structure.
   - File—Use the structures from the specified file. When this option is selected, the File name text box and Browse button are activated. Click Browse and navigate to the file you want to use. The file name is displayed in the text box when you click Open in the file selector. You can also enter the file name in the text box.
2. Choose an option for determining which atoms are coordinated to the metal:
   - Atoms within *d* Å of the metal atom are considered coordinated—specify the distance cutoff for detecting atoms that are coordinated to the metal.
   - The *N* closest atoms are considered coordinated—specify the number of atoms to be coordinated to the metal in order of proximity.
   - Hydrogen atoms can be considered for coordination—Consider hydrogen atoms to be bonded to the metal if they are within bonding distance of the metal.
   - Preserve existing metal connections—Keep existing bonds to the metal, regardless of whether they satisfy the above criteria for coordination.

   The set of atoms coordinated to the metal is the union of the set of atoms with existing bonds and the sets determined by distance or order of proximity.
3. Click Clean Up.

   The cleanup job is run locally.

The complex is minimized with the OPLS_2005 force field, to a convergence of 0.05 kcal mol^{-1} $Å^{-1}$. Bonds to the metal from the coordinating atoms are replaced with single bonds or dative bonds (which appear as zero-order bonds in the Workspace).

Structures from the Workspace or the Project Table are replaced by the cleaned-up structures. If you choose to clean up structures from a file, the minimized structures are written to a file named *filestem*`-minimized.maegz`.

There is likely to be strain around the metal center even after the cleanup. It is therefore recommended to perform a QM (Jaguar) optimization on the complexes after they have been cleaned up. The cleanup should provide a much better starting geometry for the optimization than the raw structure. Choose Tasks → Minimization → Ab Initio QM to set up the geometry optimization and run the job. Details of geometry optimization can be found in Chapter 4 of the *Jaguar User Manual*.

2.2 Building Structure Libraries by Adding to a Scaffold

The search for new materials can involve tuning the structure of a molecule, such as a ligand in an organometallic complex, to optimize a particular property or set of properties. Computationally, this can easily be done by replacement of one or more target groups on a scaffold with sets of fragments (functional groups), enumerating all the structures and using them in calculations of the desired properties. From there QSPR models can be developed for prediction of properties of new molecules, for example.

The Interactive Enumeration panel provides a convenient way of setting up libraries of fragments that can be attached to a scaffold at various points, then enumerating all the structures. The basic tasks in this panel are to import a scaffold, define the attachment bonds, set up fragment collections, choose collections for each attachment point, and enumerate the resulting structures. The technique is borrowed from combinatorial chemistry, and thus the library of enumerated structures is called a "combinatorial library".

To open the Interactive Enumeration panel, choose Tools → Interactive Enumeration.

2.2.1 Importing a Scaffold

The first step is to import a scaffold, or "core-containing molecule", which is used to define the combinatorial library. The choices are:

- Maestro file—Import the core-containing molecule from a Maestro file. Click Browse to navigate to the file and select it. The first structure in the file is imported.
- Combinatorial definition—Import a combinatorial library definition from file, including all the attachments. Click Browse to navigate to and select a combinatorial library definition (`-comdef.tar.gz`) file.
- Sketcher—Sketch the core-containing molecule using the 2D Sketcher. Click Sketch to open this panel. When you close it, the structure is converted to 3D with LigPrep and imported. For information on this panel, see Section 5.5 of the *Maestro User Manual*.
- Workspace—Import the core-containing molecule from the Workspace. The Workspace must contain only the core-containing molecule as a single entry. Click Import to import the molecule.
- Project Table—Import the core-containing molecule from the Project Table. The project entry for the core-containing molecule must be the only entry selected. Click Import to import the molecule.

When you have imported the core-containing molecule, it is displayed in the display area.

2.2.2 Defining or Changing Attachment Points

If you imported a combinatorial definition, or a molecule that already has attachment bonds defined, the bonds are marked by colored arrows on the 2D structure, and rows in the Combinatorial definition table are added for each attachment bond. The arrow color matches the rows in the table. The head of the arrow indicates the fragment or atom that will be removed when a fragment (R group) is attached in this position.

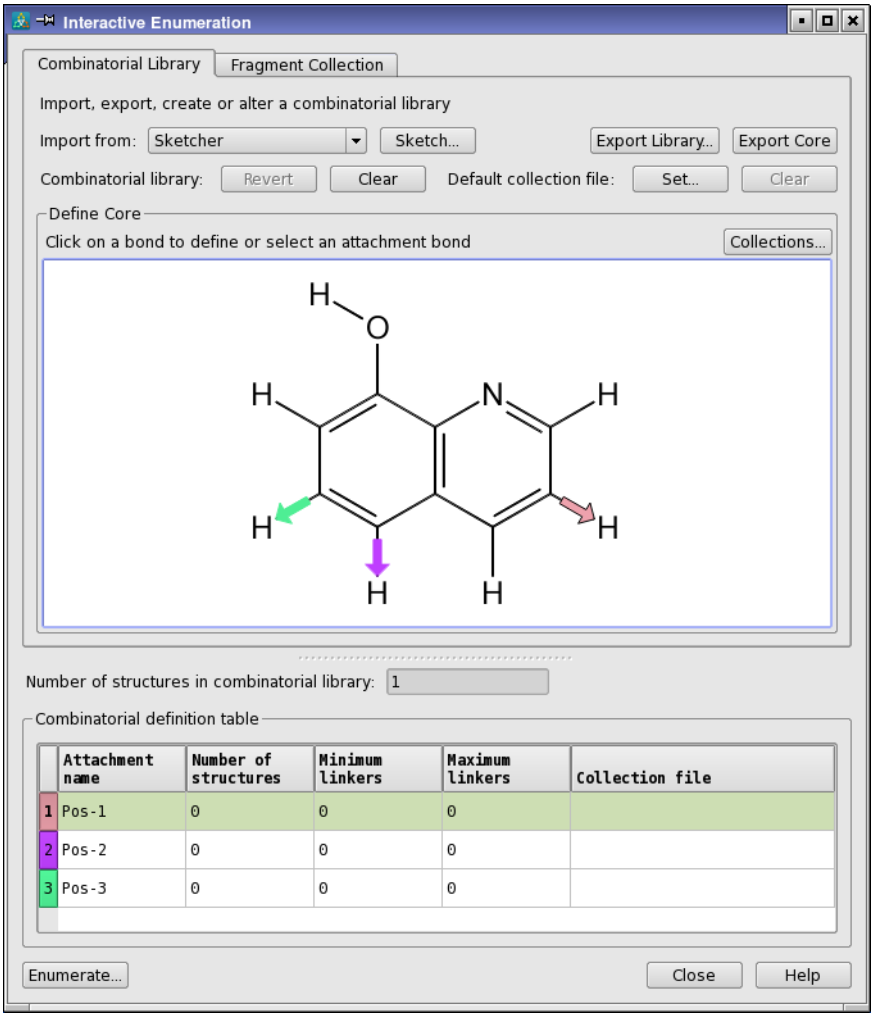

Figure 2.5. The Combinatorial Library tab of the Interactive Enumeration panel.

If you are starting with a new structure, or if you want to modify the attachment points on a structure that already has them, you can pick bonds in the structure to define new attachment points, or "core positions".

If you right-click on an existing attachment bond, the shortcut menu allows you to switch the direction of the arrow or delete it. Clicking again on the bond also changes the direction of the arrow. The direction is only changed, however, if it would not invalidate existing attachment points: all arrows must be pointing away from each other.

Each time you create a new attachment point, it is added to the Combinatorial definition table. The selected position is highlighted in olive-green in the table and the arrow is outlined in black in the display area.

The Combinatorial definition table lists each attachment point (core position), along with information about the position and its attachments. The first column is an index and is color-coded to match the position in the display area of the Combinatorial Library tab. The other table columns are described in Table 2.1. The fragment collection for a given core position is shown in the Fragment Collection tab, which is described in Section 2.2.4 on page 25.

Table 2.1. Combinatorial definition table columns.

Column	Description
Attachment name	Name given to the attachment on the core-containing structure. The name can be edited.
Number of structures	Number of structures in the collection for this attachment. Noneditable. When the collection changes, both the number in the Fragment Collection tab and the number in the collection file are reported.
Minimum linkers	Minimum number of methylene linkers to add between the core and the fragment. This value can be edited. Default is zero.
Maximum linkers	Maximum number of methylene linkers to add between the core and the fragment. This value can be edited. Default is zero.
Collection file	Name of the collection file used for this attachment point. To set or change the file, right-click on the table row and choose Browse for new collection file. A file selector opens so that you can navigate to and select the file.

To delete an attachment point, right-click on the arrow in the display area or in the table row and choose Delete. The arrow and the table row are removed.

The number of structures in the combinatorial library is displayed in a noneditable text box above the Combinatorial definition table.

If you want to export the core molecule with the attachments marked, so you can use it later, click Export and choose the location to export it to.

2.2.3 Applying an Existing Fragment Collection

To create a combinatorial library, a collection of fragments must be applied to each attachment point (core position). Collections are stored in files with a `.bld` extension. If you already have fragment collections saved, you can apply them with one of the following methods:

- Define a default collection file, and this collection is applied automatically when you select an attachment bond. To do this, click Set, and browse to the collection file. To clear the default collection file, click Clear.
- Click Collections, and drag one of the collection files from the Collections panel to the desired attachment bond on the molecule in the display area. You can add directories to this panel, so your collections can be made available.
- Right-click on a row in the table and choose Replace Collection or Append to Collection, then browse to the collection in the file selector. The selected collection replaces the collection at that core position or adds to it, according to your choice.

Two standard locations are included in the Collections panel and in the file selector:

- Schrodinger Collections, which points to a location in the installation that contains a collection of 43 fragments in the file `default_fragments.bld`
- My Collections, which points to the `cg/interactive_fragments` subdirectory of your user resources directory (`$HOME/.schrodinger` on Linux and Mac, `%APPDATA%\Schrodinger` on Windows) as a convenient location for storing your fragment collections.

If you want to modify a collection or create a new collection, you can use the tools in the Fragment Collection tab, which is described in the next section.

2.2.4 Setting Up Fragment Collections

The Fragment Collection tab provides the tools to select and manage your own fragment collection. A fragment collection is a set of molecules, each of which has a bond marked as the attachment bond. As for the core, there is a direction associated with the attachment bond: one part of the molecule is discarded when it is attached to the core, the other (the fragment, or R group) is kept.

To create new fragments, you have to label them with the attachment bond. Creating new fragments (or modifying existing fragments) can be done in the Create Fragment Collection panel, which you open by clicking Create. This task is described in the next section.

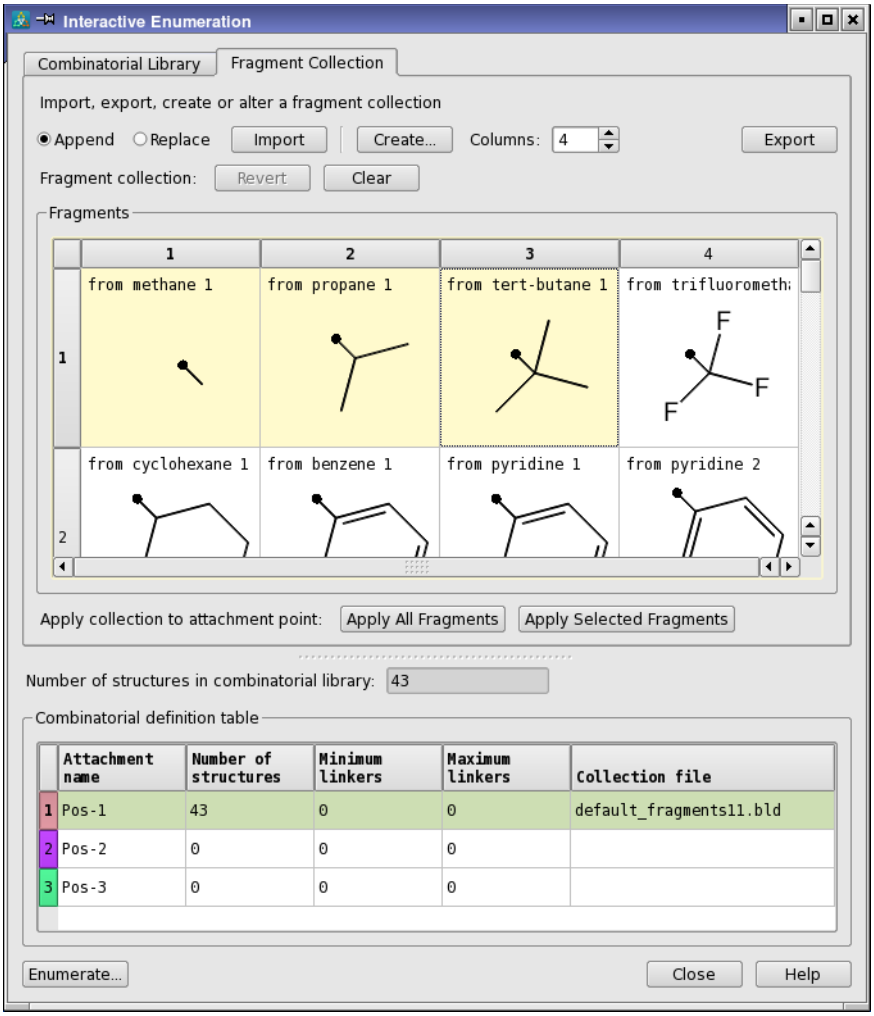

Figure 2.6. The Fragment Collections tab of the Interactive Enumeration panel.

The main task of the Fragment Collection tab is to select a set of fragments that you can apply to an attachment point. The 2D structures of the current fragment collection are displayed in the Fragments table. The filled circle indicates the connection point to the core. You can set the number of columns of structures in the table in the Columns box.

The basic procedure is as follows:

1. Choose whether to add to or replace the fragment collection:
    - To add fragments to the table, select Append.
    - To replace the entire table, select Replace.
2. Choose the source of the new fragments:
    - Click Import to import fragments from a file, the Project Table, or the Workspace.
    - Click Create to create new fragments.

    You can repeat the addition of new fragments as many times as you like.
3. Edit the collection as desired. You can select structures in the table, and right click to perform an action:
    - Delete selected structures—Delete the selected structures from the collection.
    - Retain only selected structures—Keep only the selected structures, and delete the rest from the collection.
    - Delete this structure—Delete the structure that you clicked on from the collection.
    - Retain only selected structures—Keep only the structure that you clicked on, and delete the rest from the collection.
4. Apply the collection to the current attachment point:
    - Click Apply All Fragments to use the entire collection for the current attachment point.
    - Select fragments in the table and click Apply Selected Fragments to use a selection of fragments for the current attachment point.

The table row for the core position is colored red when you add to or edit the collection, to indicate that the displayed collection is not the same as the collection associated with the position. The fragment collection is written to a file when you apply it, and the new file name is shown in the Combinatorial definition table.

There are various other actions you can perform to manage the structures:

- If you started with a particular collection file at an attachment point, made changes, and want to revert to the original set, click Revert.
- To clear the collection entirely, click Clear. The collection is cleared, and the current attachment point is also cleared. This allows you to create a collection independent of an attachment point.
- To rename a fragment, right click and choose Rename structure.
- To view the 3D structure, right-click and choose Show this structure in Workspace.

- To add a structure to the Project Table, right-click and choose Export this structure to Project Table.

When you want to save a collection, you can click Export to export it to a file or to the Project Table. A menu is displayed so that you can choose the destination. If you export to the Project Table, it is exported as an entry group named after the collection file. If you export to a file, the default file location is My Collections, which is described in the previous section.

2.2.5 Creating a Fragment Collection

To create a new fragment collection by selecting from a set of structures, you can use the Create Fragment Collection panel. In this panel, you can import or draw structures, select the desired structures, define their attachment bonds, and add them to the fragment collection.

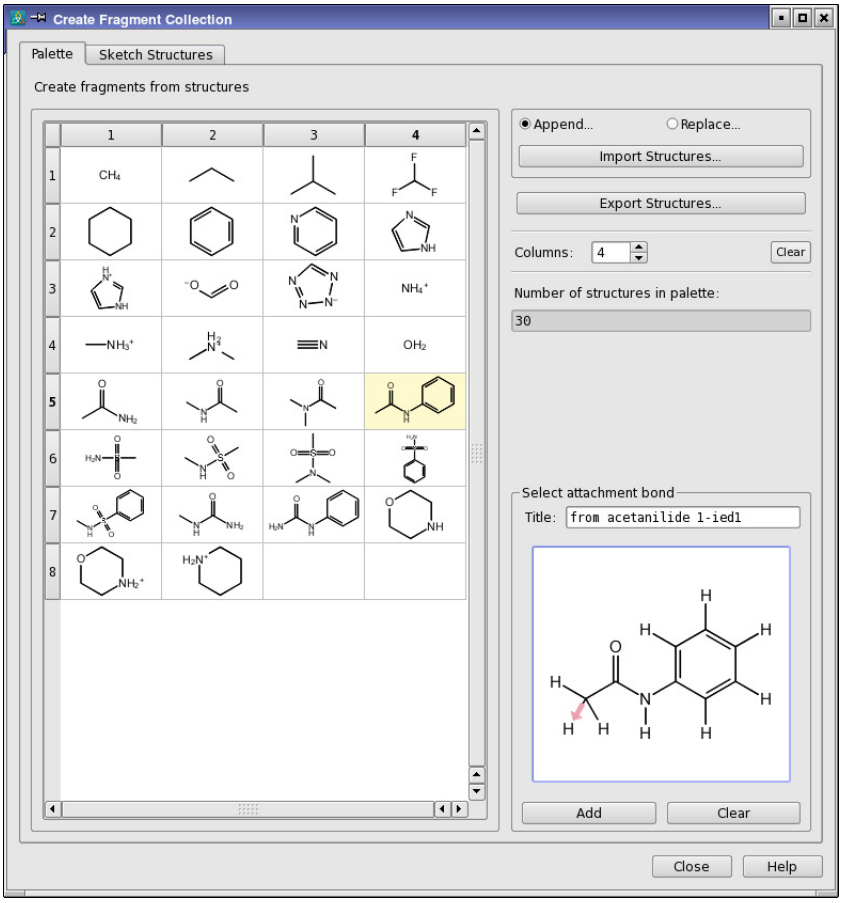

Figure 2.7. The Palette tab of the Create Fragment Collection panel.

To open the Create Fragment Collection panel, click Create. The panel opens with the Palette tab displayed.

The palette—the display area for the structures—is initially empty. The palette is a table of structures that can be selected for addition of an attachment bond, after which it can be added to the fragment collection. You can set the number of columns in the Columns box, and resize the table cells by dragging the row or column boundary in the table margin. You can clear the palette by clicking Clear.

To import structures into the palette, click Import Structures. A menu is displayed that allows you to choose whether to import from a file, the selected entries in the Project Table, or the Workspace. If you choose Import from File, a file selector opens, and you can navigate to and select the file. The file can be a Maestro file, without attachment bonds defined, or a reagent file with attachment bonds defined (`.bld`). The file selector opens in a directory that contains a default set of structures that are useful in a palette. When you click Open, the file name is displayed in the Filename text box, and the structures are shown in 2D form in the palette.

If you already have structures, you can append to the list by selecting Append and importing structures. If you want to replace the existing structures with a new set, select Replace before importing the structures.

To draw structures, click the Sketch Structures tab. In this tab you can draw structures with the 2D Sketcher, then add them to the palette. You can place multiple structures on the drawing area, and when you click Add Structures, all of them are added as independent fragments, after checking for duplicates. For information on the 2D Sketcher, see Section 5.5 of the *Maestro User Manual*.

You can select multiple structures in the palette (with shift-click and control-click). The shortcut menu offers the choice of keeping only the selected structures or deleting them, or keeping only the structure clicked on or deleting it. This allows you to define new palette collections for later use.

If you want to save a particular set of structures, click Export Structures. The menu that is displayed offers the choice of exporting to a Maestro file or to the Project Table. Attachment bond information is not written with the structures. If you choose to export to a file, a file selector opens, in which you can navigate to a location and name the file. The export option is useful for creating a new file for future use in a palette after importing and possibly deleting structures from several files.

After you have added structures to the palette, you can proceed to select a structure, add an attachment bond, and then add the structure to the current fragment collection.

When you click on a structure in the palette, the structure is displayed in the Select attachment bond section, so that you can define the attachment bond. The stereochemistry is indicated by

wedge and dashed bonds. The title of the structure is displayed in the Title text box, and the structure itself in the display area. To select the attachment bond, click on a bond in the display area. Clicking a second time on the same bond changes the direction of the attachment bond, if the bond is not terminal. The arrow on the bond points towards the part that is removed to attach the fragment to the core.

To add this fragment to the collection, click Add. The fragment flashes, and it is added to the current Fragment Collection display of the Interactive Enumeration and Docking panel. It is therefore a good idea to have both panels visible and next to each other, so that you can see the fragment being added to the fragment collection.

If you want to add the same fragment with a different attachment point, you can select a different attachment bond and click Add. The fragment is added to the collection again with the new attachment bond.

2.2.6 Saving or Enumerating the Library

When you have finished adding fragments to each attachment point on the core, you can save the library or enumerate it.

To save the library definition, click Export Library, and navigate to the desired location in the file selector that opens. The core molecule with the defined attachments and the fragment collections are exported to a tar archive with the suffix `-comdef.tar.gz`.

To enumerate the library, click Enumerate. The fragments are added to all the attachment positions in the job that is run. No minimization or untangling of the enumerated structures is performed, so you must sort out any bad structures afterwards. It is recommended that you do a minimization, at least.

2.3 Varying the Elements in a Structure

If you want to create variations on a structure that involve a change of element, such as replacement of CH groups with N, you can use the Elemental Enumeration panel to perform the transmutations on the Workspace structure. All possible transmutations are performed on the selected atoms, within defined bounds. The new structures are added to the project.

Substituting elements can be used to tune the electronic properties of a molecule, which could be used as a ligand in an organometallic complex, for example.

To open the Elemental Enumeration panel, choose Tools → Elemental Enumeration.

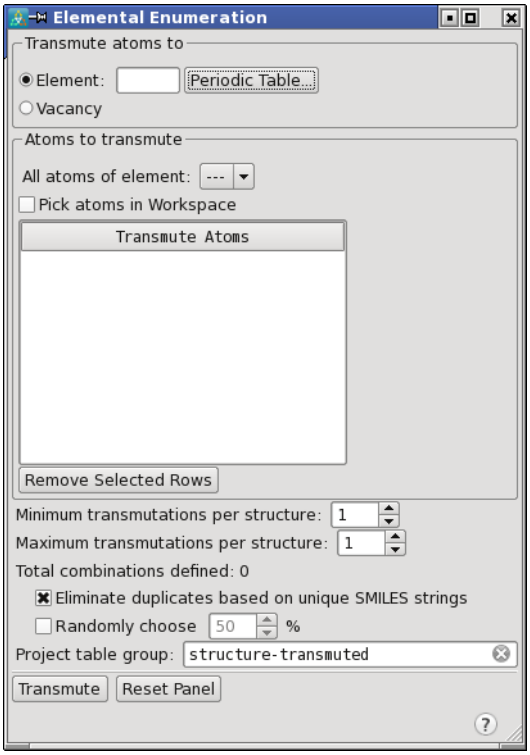

Figure 2.8. The Elemental Enumeration panel.

To run an elemental enumeration:

1. Include the source structure in the Workspace.
2. Enter the element symbol for the target element or click Periodic Table to choose the element; or select Vacancy to delete atoms (create vacancies).

3. Pick the atoms to transmute on the Workspace structure or choose the element to transmute.
4. Specify limits on the minimum and maximum number of transmuted atoms.
5. Choose whether to keep or eliminate duplicate structures.
6. If you want a random selection from the set of all possible structures, select Randomly choose and specify the percentage of structures to choose at random from the full set.
7. Specify an entry group name for the transmuted structures.
8. Click Transmute.

When you pick atoms for transmutation, each atom is added to the table after it has been picked. If you choose an element from the All atoms of element option menu, all atoms of that element are added to the table. You can remove atoms from the transmutation list by selecting them in the table and clicking Remove Selected Rows.

Atoms chosen for transmutation are marked with a cyan-colored marker in the Workspace. To remove the markers, clear the Transmute atoms table, or reset or close the panel.

The transmuted structures are added to the Project Table as a new entry group. All possible combinations are created (unless you chose to make a random selection). This means that for a structure with high symmetry, like benzene, there will be redundant structures, unless you choose to eliminate duplicates. The structure titles include information on the transmutation performed.

In order to keep atom numbering as consistent as possible in the enumerated structures, the atom ordering is changed so that all heavy atoms occur first and all hydrogen atoms follow. This is done because the number of hydrogens may change in the transmutation. The reordered parent structure is also added as part of the new group. The atom numbers appearing in the title of each enumerated structure refer to the atom numbers of the reordered structures.

The number of attached hydrogens is changed so that the proper valence of the target element is satisfied. If the target is a vacancy, hydrogens are not added to the elements bonded to the removed atom, so they may have unsatisfied valences. The charge state is not modified, so if for example you change a benzene carbon to an oxygen, the oxygen atom will have three bonds and no charge. You will have to change the charge or the bond orders before using the structure for calculations.

This panel is primarily designed for transmutation to a single element, for example conversion of a set of aromatic hydrocarbons into a set of N-heterocycles. If you want to transmute to other elements, you must display each of the structures from a transmutation in turn, and then perform the next transmutation.

You can also change elements manually, by using the Build toolbar. Click the arrow next to the Set element button, and choose the new element, then click on the desired atoms in the Workspace.

The number of hydrogens is adjusted to satisfy the valency. You can save each structure as a new project entry. The automated procedure in the Elemental Enumeration panel is quicker if you want to create multiple structures.

2.4 Building Nanostructures

The Nanostructure Builder panel allows you to build nanotubes or nanosheets from a specified unit cell and geometry to a given size. Multi-walled nanotubes and multi-layer nanosheets can be constructed as well as single-walled nanotubes and single nanosheets, and nanotubes with a range of chiral indices can be generated.

All structures are based on the usual honeycomb pattern of connectivity, with three neighbors for each atom. The edges can be terminated with a single bond to a chosen terminating group, or left with no terminating group.

A formal assignment of bonding is made between the atoms. On this basis, the atoms in the nanostructure can be trivalent, so that each atom has three single bonds (as in BN), or tetravalent, so that each atom has two single bonds and one double bond (as for carbon). Other than this, no attempt is made to assign bond orders or formal charges based on valence, and no checking is done on the validity of this assignment, as nanostructures can be built with this panel out of any elements.

If you plan to use the nanostructures in modeling with force fields (such as molecular dynamics), you will have to choose atoms that are supported by the force field, and have appropriate sp^2 atom types. If the atoms you choose are not trivalent or tetravalent, you will have to assign bond orders and formal charges before using the structure for modeling.

For quantum mechanical modeling, connectivity and atom typing is not relevant. You could, for example, generate PbO nanosheets, and ignore the bonding. Generating nanostructures is quicker if you choose not to add double bonds.

To open the Nanostructure Builder panel, choose Tools → Build Nanosheets or Build Nanotubes in the main window.

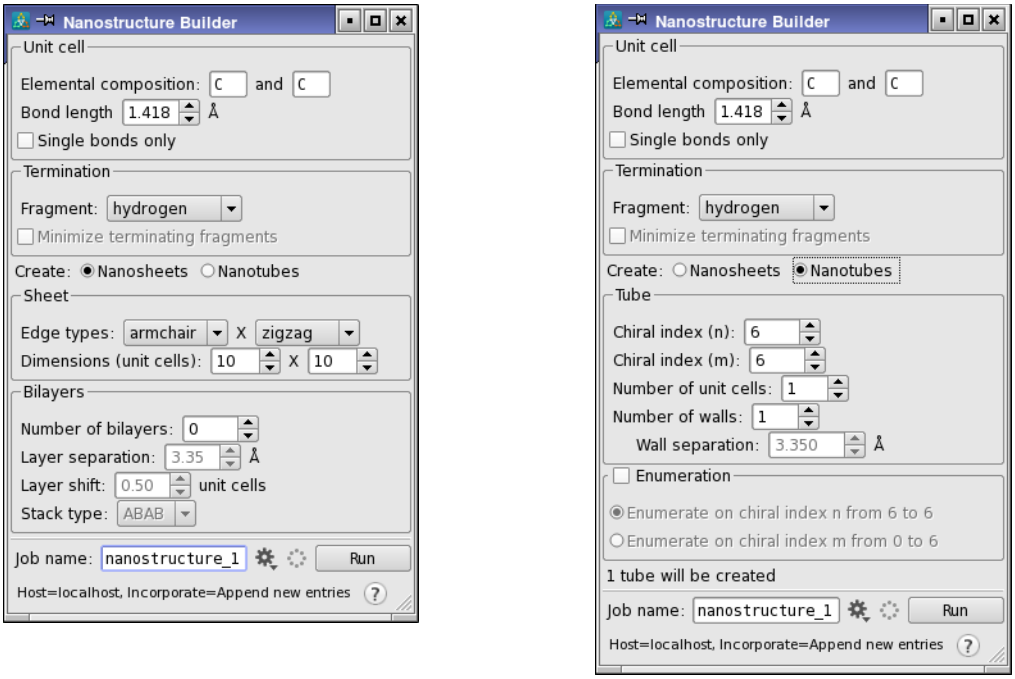

Figure 2.9. The Nanostructure Builder panel, showing controls for nanosheets (left) and nanotubes (right).

2.4.1 Defining the Composition and Bonding

The first step is to define the basic building block and choose how to terminate the sheets or tubes. This task is common to both types of nanostructure.

1. Specify the composition of the unit cell, by entering the element symbols in the Elemental composition text boxes.

   There are no limitations imposed on the elemental composition, and no imposition of valence rules or assignment of formal charges in the construction of the nanostructure. All atoms have bonds to three neighboring atoms within each sheet or tube (including the terminating groups).

2. Define the length of the bond between the two atoms, by entering a value in the Bond length text box.

   This length is used for all bonds between the atoms, regardless of bond order.

3. Set the type of bonding pattern.

By default, there is a double bond between the atoms of the unit cell. Select Single bonds only to create a structure with single bonds only. For example, you would want double bonds for carbon nanostructures (tetravalent atoms), but single bonds for BN nanostructures (trivalent atoms).

4. Choose an organic fragment to terminate the bonds on the ends of the tubes or the edges of the sheet, from the Fragment option menu. If the fragment is polyatomic, you can also perform a minimization of the fragments when they are attached.
5. (Optional) Select Minimize terminating fragments to relieve any steric crowding of the terminating fragments.

   The atom in the fragment that is attached to the nanostructure is held fixed, as is the nanostructure itself. The minimization of the fragment is done with a force field (with backup general atom typing for unrecognized atom types in the nanostructure). This option is only available if the terminating fragment is polyatomic.

When you have finished making these settings, you can proceed to define the structure. You can switch between nanosheet and nanotube creation with the Create options. The controls below are updated according to your choice.

2.4.2 Building Nanosheets

You can build structures that consist of a single nanosheet or of multiple bilayers. First, the size and shape of each nanosheet in the structure must be set.

1. Choose the edge types for the two edges of the sheet, from armchair and zigzag.
2. Set the dimensions of the sheet in terms of the unit cell size (hexagons) along each edge.

   The actual number of atoms depends on the edge type. For the zigzag edge, the symmetry operations to add the next unit place some atoms over atoms in an existing unit, and only the unique atoms are added, whereas for the armchair edge, all of the added atoms are unique.

If you want a multi-sheet structure, there are further parameters to specify:

3. Set the number of bilayers in the Number of bilayers box.

   A value of 0 produces a single nanosheet, whereas a positive integer produces the specified number of bilayers, and the number of layers is twice this number.
4. Set the layer separation, in angstroms, in the Layer separation box.

   The same separation is used between all layers (there is no distinction between intra-bilayer and inter-bilayer separation).

5. Set the amount by which each layer is shifted relative to the layer below it, in the Layer shift box.

   The shift is applied to both directions in the plane of the sheet (here regarded as the horizontal plane). To produce a vertically aligned stack, set the shift to zero. The direction of the shift (positive or negative) for each sheet is determined by the stacking geometry.

6. Choose the stacking geometry from the Stack type option menu. There are two options:

   - ABAB—the direction of the shift is reversed for each layer that is added. The result is that the odd-numbered layers are vertically aligned, and the even-numbered layers are vertically aligned but are shifted relative to the odd-numbered layers.
   - ABCD—the shift is applied in the same direction as each layer is added.

2.4.3 Building Nanotubes

You can build single-walled or multi-walled nanotubes, for a fixed set of chiral indices, and you can also build nanotubes with a range of chiral indices. The first stage is to set up the parameters that define the geometry and number of tubes.

1. Set the chiral indices (n,m) for the tube (or the innermost tube) in the Chiral index (n) and Chiral index (m) boxes.

   The indices must be in the range $0 \le m \le n$. If you choose to generate a set of nanotubes with different chiral indices, these values are the limits of the range of indices used. If you choose to build a multi-walled nanotube, these are the indices for the innermost tube.

2. Specify the length in terms of the number of repeating units, in the Number of unit cells box.

   This determines the length of the nanotube. The number is adjusted for each wall to obtain tubes of approximately the same length as the inner tube.

For multi-walled nanotubes, the following settings must also be made.

3. Set the number of walls in the Number of walls box.
4. Set the wall separation in the Wall separation box.

   This value is used along with the chiral indices given for the innermost tube (above) to construct the outer walls to match as closely as possible the chiral angles of the innermost tube. Given the geometric constraints on the tube, the wall separation may not be reproduced exactly.

If you want to generate nanotubes with a range of chiral indices, select Enumeration and choose an enumeration option.

- Enumerate on chiral index n from *m* to *n*—Generate all possible nanotubes with the chiral index n taking values from the m value given in the Tube section to the n value given in the Tube section. The values reported in the text change as you adjust the values in the Tube section.
- Enumerate on chiral index m from 0 to *m*—Generate all possible nanotubes with the chiral index m taking values from 0 to the m value given in the Tube section. The value reported in the text changes as you adjust the m value in the Tube section.

2.4.4 Running the Job

When you have finished setting options, set the job name and click Run to run the job. The structures are written to a Maestro structure file, and by default are incorporated into the current Maestro project. If you want to change any of the job options, click the Settings (gear) button.

2.5 Building Nanoparticles

The Nanoparticle Builder panel allows you to build a nanoparticle of a particular shape and size from the structure in the Workspace. To open the Nanoparticle Builder panel, choose Tools → Build Nanoparticles in the main window.

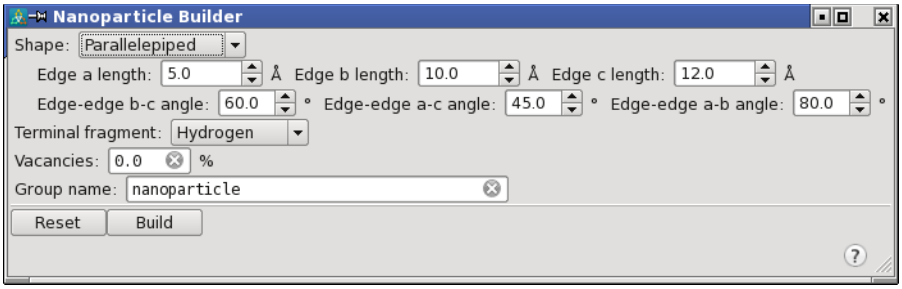

Figure 2.10. The Nanoparticle Builder panel.

Nanoparticles are built from a larger structure by imposing a particular shape on the particle, and removing atoms from the larger structure that are outside the surface of the shape.

Possibly the easiest way to create the larger structure from a crystal structure is to use the Extents button on the Periodicity toolbar

to extend the unit cell with as many replicas as needed to create a structure of the required size.

There is no restriction on the structure from which you create the nanoparticle—it does not have to be a crystal. If you use organic molecules (even if in a molecular crystal), these molecules will be cut at the boundaries and the dangling bonds will be terminated with the fragment you choose.

As the shape used to create the nanoparticle is symmetrically placed about the origin, you might want to align the parent structure to obtain the desired symmetry of the nanoparticle. Maestro provides a tool for aligning structures on the coordinate axes or planes, and updating the coordinates of the aligned structure. Choose Edit → Align to open the Align Atoms panel, in which you can perform an alignment (click Update Coordinates to change the structure coordinates to match the Workspace view).

To build a nanoparticle:

1. Choose the shape of the nanoparticle.

   Text boxes for specifying the shape parameters are displayed below this option menu that are appropriate for the shape.

2. Specify the size of the nanoparticle in the text boxes, by specifying the edge lengths, angles, radius, as appropriate.

   Lengths are specified in angstroms, angles in degrees.

3. Choose a fragment to terminate dangling bonds on the surface of the nanoparticle.

   Each neighboring atom that is removed from an atom at the surface of the nanoparticle is replaced with the terminating fragment.

4. (Optional) Specify the percentage of vacancies to create in the nanoparticle.

   The number of vacancies is determined from the percentage by rounding to the nearest integer. This number of atoms (or molecules, if the structure has more than one molecule) is removed from the nanoparticle at random.

5. Specify the name of the entry group in the project that contains the output entries.

   The entries themselves are also named with this name. The nanoparticle has the name *groupname*`-`*shape*. If you also build a nanoparticle with vacancies, this entry is named *groupname*`-`*shape*`-`*X*`% vacancies`.

6. Click Build.

An entry group is created for the structures, containing an entry for the nanoparticle itself (without vacancies), an entry for the shape of the nanoparticle (if it is a polyhedron), and an entry for the nanoparticle with vacancies if a vacancy percentage was set.

2.6 Building a Disordered Molecular Mixture

If you want to create a disordered mixture of compounds that can be used for molecular dynamics simulations or other purposes, you can build the mixture in the Disordered System Builder panel, which you open by choosing Tools → Disordered System Builder. This panel allows you to build just the mixture, or to build it on one of three types of substrate: the entire surface of a particle such as a nanoparticle, quantum dot, or a solute molecule; a plane such as a particular face of a crystalline solid or the surface of an amorphous solid; or the interior of a structure such as a nanotube, zeolite, or metal-organic framework. The mixture can even have a single component, i.e. is a pure substance, but placed in a disordered fashion.

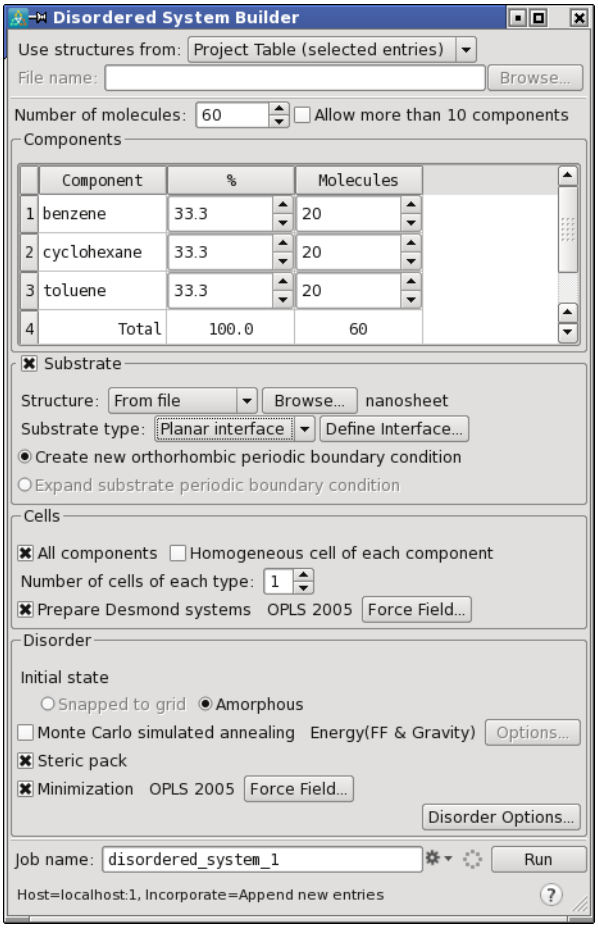

Figure 2.11. The Disordered System Builder panel.

The disordered system, with its substrate, is placed in an orthorhombic box (with some exceptions), whose lengths are adjusted to best accommodate the system after it has been built.

2.6.1 Specifying the Mixture Composition

The first stage is to set up the mixture composition and provide the structures of each component.

1. Choose the compounds you want to use.

   You can take structures from the selected entries in the Project Table, the Workspace, or a single file that contains all the compounds. The compounds are listed in the Components table when the source is chosen.

   For most purposes, a mixture containing 10 or less components is adequate. If you need to build a system with more than 10 components, select Allow more than 10 components. This option is present mainly to prevent inadvertent selection of a large number of components, which could take a long time to process.

2. Set the total number of molecules to use in the Number of molecules box.

   If you choose (later on in the process) to initially place the molecules on a grid, this value is used to determine the cubic grid on which the molecules are placed: the number of points in any direction is the cube root of the number of molecules, rounded up to the nearest integer. To ensure that the simulation box (if you create one) does not have any spaces, you should choose a number that is a perfect cube, or a number that results in only one or two layers of molecules missing from the cube (that is, n^3• n^2 or n^3• $2n^2$). Other values will result in incomplete layers of molecules that may take a long simulation time to fill.

   You might have to adjust the number of molecules inside a container-type substrate to ensure that the container is not overloaded. If you try to put too many molecules in it, the job to create the system will fail.

3. Specify the proportions of each component in the mixture, by editing the cells in the Components table.

   The percentages are initially set to be equal. As you edit the cells, the values in the unedited cells are adjusted so that the percentage values add up to 100. Once you have edited all cells, you can change any value, but the other values are no longer adjusted.

   The percentages are used to determine the number of molecules of each type, by multiplying them by the total number of molecules, and dividing by 100, then rounding up to the nearest integer. The percentages or proportions you provide will therefore not be exact, and must be regarded as a target value.

However, you must ensure that the number of molecules for each component, which is reported in the Molecules column, adds up to the total. If it does not, you must adjust either the percentages or the number of molecules, by editing either the percentage column or the Molecules column.

For example, if you have an odd number of molecules in a two-component mixture, the default percentages are both 50, and the number of molecules does not add up to the total, as both are rounded up. You must change one of the components to have one more molecule than the other.

The larger the number of molecules in the box, the closer the actual proportions will be to the target values. Of course, the resources for the simulation also increase with the number of atoms in the simulation, and also resources for display of results in Maestro. For guidance, Maestro can display up to about 500,000 atoms comfortably on a machine with 4GB memory, and a Desmond simulation with about 100,000 atoms run on 8 cores would take about 1 day per ns of simulation. You should in any case ensure that the simulation box is not too small: each side must be at least 20 Å, which means a minimum of around 3000 atoms.

4. Ensure that All components is selected in the Cells section.

   This is the option that creates the disordered mixture.

5. If you want to create separate periodic boxes for each of the (pure) components, select Homogeneous cell of each component in the Cells section.

   The total number of molecules specified for the mixture is also used for the simulation box for each component. This allows you to do simulations on the pure compounds to compare with the mixture.

6. If you want to create multiple cells of each type (mixture and pure components), specify the number of cells in the Number of cells of each type box.

   Each of the cells is created using the random number seed in the Model parameters section. The resulting cells are written to separate files with an index. Having multiple cells with the same composition but different random placement of the components can be useful for checking the dependence of the results on the initial conditions, or for accumulating statistics about the system.

7. If you want to prepare the disordered system for Desmond simulations, select Prepare Desmond systems.

   You can choose the force field is added when the Desmond model system is built by clicking the Force Field button and making your selection in the dialog box that opens. This dialog box also allows you to set custom charges on the atoms.

2.6.2 Building on a Substrate

To build a disordered system on a substrate, you must load the substrate and identify the type of substrate it is. You can load the substrate from a file or from the Workspace, using the Structure option menu and associated button. The file must be a Maestro file.

The type of substrate that you loaded must be chosen from the Substrate type option menu, as this affects the actions taken when building the disordered system on the substrate. There are three types of substrate:

- Immersed—The substrate is surrounded by the disordered system. This type of substrate can be used for nanoparticles or quantum dots immersed in a molecular mixture, or for a molecule of interest in a mixed solvent. The disordered system is placed in a box whose dimensions are set to accommodate the given number of molecules at the specified density, enlarged if necessary to ensure that there is enough space between the substrate and the box walls to fit any of the molecules of the mixture.
- Container—The molecules are placed inside cavities in the substrate. This type of substrate can be used for nanotubes, zeolites, and metal-organic frameworks, for example. The size of the cavities is fixed by the substrate structure itself, so can only accommodate a set number of molecules of a given size.
- Planar interface—The substrate surface is planar, or approximately so, and the disordered system is placed above this surface. This type of interface applies to a particular face of a crystal structure, or the surface of an amorphous solid, which could be somewhat irregular, or a graphene sheet, for example. The box in which the disordered system is placed has the entire surface of the substrate as one face, and the height of the box above the surface is adjusted to contain the disordered system. If the substrate already has crystal parameters defined, you can choose to extend the existing cell along one of the crystal vectors (which might be at an angle to the surface), by choosing Expand substrate periodic boundary condition. Otherwise, a new orthorhombic box is created, with the surface as its base. If the surface is not rectangular, the base of the box is chosen to include the entire surface.

  To specify the surface to be used and any buffer distances between the substrate and the mixture, click Define Interface. The Define Interface dialog box opens, and the substrate is displayed in the Workspace with the default interface (surface plane) shown, and the direction of growth of the disordered system is indicated with an arrow. There are three options for the plane:

  - Best fit to all atoms—Define the interface plane as the best fit to all atoms in the structure. As the fitting on its own places the plane in the middle of the substrate, the plane is moved after fitting so that it rests on the surface of the structure.

- Crystal vector—Define the interface as the plane that is perpendicular to one of the crystal vectors and at the surface of the substrate, and select the vector (a, b, or c). The cell is extended in this direction to accommodate the disordered system.

  If you want to choose a different crystal plane, you must prepare the substrate structure so that the desired plane is exposed, and then a new set of periodic boundary conditions is defined as part of building the disordered system.

- Choose at least 3 atoms to define the plane—Define the interface plane as the best fit to the chosen atoms. Select Pick and pick the atoms in the Workspace. The plane is fit to the atoms as you pick, after the third atom is picked, and the plane and arrow marker in the Workspace are centered at the centroid of the picked atoms. No adjustment is made to place the plane at the surface of the substrate.

If the location of the plane and the direction of growth of the disordered system is on the wrong face of the substrate, click the Flip Direction button. The arrow is reversed and the plane is moved to the other side of the substrate, except for the manual choice of the plane, where the direction is simply reversed.

In addition to defining the plane, you can add a gap between the substrate and the disordered system, if you do not want the system in contact with the surface; and you can add a gap between the top of the disordered system and the boundary of the cell, where the image of the other side of the substrate is situated in a periodic system. A large gap can be used to simulate an isolated surface. A zero gap on both sides of the disordered system produces a layered system.

2.6.3 Specifying the Placement and Distribution

The next stage is to specify how the molecules are to be placed and distributed in the box or in relation to the substrate. The molecules are placed initially in the box, and then undergo up to three processes to produce a final placement.

If you are not using a substrate, there are two options for the initial state, Snapped to grid and Amorphous. If you are using a substrate, only the Amorphous option is available. The Snapped to grid option places randomly chosen molecules on a regular grid in the cubic box, in such a way that there are no clashes for any possible rotation of the molecules. This option tends to generate systems that are closer to cubic than the Amorphous option. The Amorphous option places randomly chosen molecules at random locations and orientations in the box, or in the substrate if it is a container type, or around the substrate if it is to be immersed.

The processes that can be applied to modify the initial state of the system, in order of their application, are as follows. You can choose any combination of these processes.

- Monte Carlo simulated annealing—Perform a Metropolis Monte Carlo simulated annealing calculation to minimize the energy of the system. The weights and sizes of translation and rotation moves, the temperatures, the number of iterations, and the energy terms to use can be set in the Simulated Annealing Options dialog box, which you open by clicking the Options button.

  There are two choices for the energy terms: a force field, which you can select, or a "gravity" term, whose energy is negative and linear in the distance between the nearest atom of a molecule to a substrate atom, or to the cell center if there is no substrate. The two terms can be combined.

- Steric pack—Maximize the density of the system by moving the molecules towards the substrate (if one is defined) or the center of the cell, while avoiding steric clashes. Options for the van der Waals scaling (for defining clashes), the initial density, the property to keep constant, and the number of attempts at placement are available in the Disorder Options dialog box, which you open by clicking the Disorder Options button at the lower right of the panel.

  Once the molecules are distributed in the cell, starting at the center or the surface and moving outward or upward, each molecule is moved toward the origin along the vector between the molecular center and the origin. The point closest to the origin that causes no steric collisions is the new location of the molecule. No rotation is performed and no other movement is performed. Molecules are allowed to pass through each other to find the closest-to-the-origin cavity along the vector. Atoms are considered hard spheres and any overlap is considered a steric collision.

- Minimization—Minimize the final configuration of the structure using the specified force field. Click the Force Field button to specify the force field to use. The current force field is reported to the left of the button.

Several other options are available in the Disorder Options dialog box, including setting a random seed, randomizing the orientations of molecules when snapped to a grid, coloring molecules by component rather than the default coloring by element, setting limits on the number of placement attempts for each molecule and the number of attempts to build a more densely packed cell in the steric packing process.

After the initial placement and any procedures applied to produce a final location for each molecule, the unit cell is redefined to produce the densest fit to the final disordered system, while remaining orthorhombic.

2.6.4 Running the Job

After the parameters are set, use the Job toolbar to run the job to create the disordered system. See Section 1.3 on page 6 for more information on this toolbar.

If you chose to prepare the systems for Desmond simulations, the result is one or more CMS files, which can be used directly as input to Desmond. The file containing the model system for the mixture is named *jobname*`.cms`, so you should choose a descriptive job name (rather than the default). The files containing the model systems for the components are named *jobname*`-component`*n*`.cms`, where *n* is the component number in the Components table. If you chose to generate multiple cells of each type, a suffix *_N* is added, where *N* indexes the multiple cells of each type.

If you chose not to prepare Desmond model systems, the results are written to Maestro files (`.maegz`), including the periodic box properties.

Molecular dynamics simulations can be set up by choosing the task from Tasks → Molecular Dynamics.

2.7 Building a Crystal Structure

The crystal structure builder allows you to build a crystal structure, either from text data, which may be taken from a publication, for example, or from an existing 3D structure. The crystal structure is stored as a project entry with crystal properties, and can be used in Schrödinger applications that require crystal data, or exported and used in other applications.

Choose Tools → Build Crystal Structure to open the New Crystal Structure panel.

To create a crystal structure from text data:

1. Enter the space group number or the space group name in the appropriate text box under Space Group, or click Choose to choose the space group from a list.

   The Select Space Group dialog box, which opens when you click Choose, allows you to filter the list of space groups by the crystal system and by the lattice type. Similarly, a list of space group names is shown below the text box if you type in the space group name, and it is filtered as you type. You can choose the space group name from this list.

   The space group is displayed to the right of the group number text box. The text boxes for the parameters are updated so that only the unique parameters can be specified.

2. Enter the unique cell parameters in the text boxes.

   The remaining parameters are set from the unique parameters.

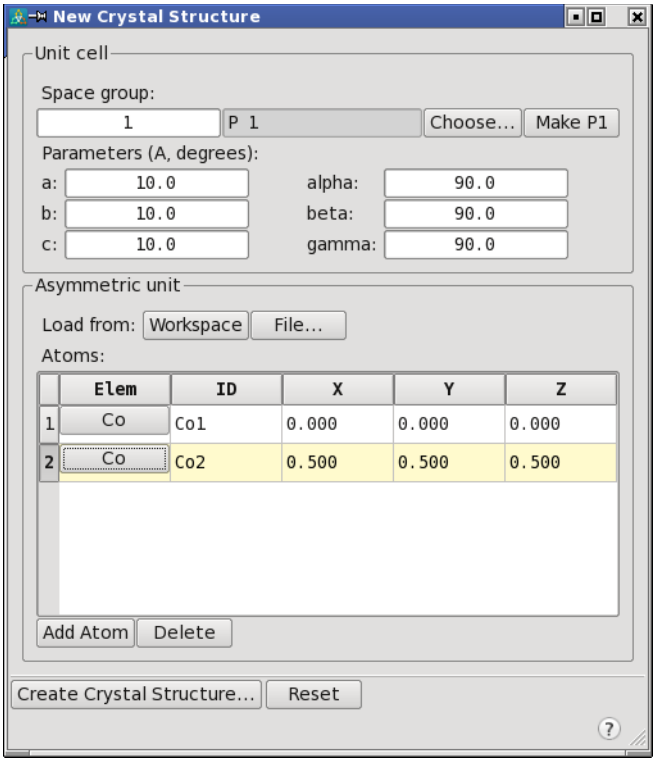

Figure 2.12. The New Crystal Structure panel.

3. Click Add Atom (under the Atoms table) to add an atom to the asymmetric unit.

   A new atom is added to the table with fractional coordinates of (0, 0, 0).

4. Change the element by clicking on the element button and choosing the element from the periodic table that is displayed.

5. Enter the fractional coordinates of the atom in the F1, F2, and F3 columns.

   The fractional coordinates must be in the range [-0.5, 0.5] or [0.0, 1.0]. The range used determines the origin of the unit cell.

6. (Optional) Change the ID for the atom.

   The default ID is the element symbol followed by an index that indexes atoms for each element. It is updated if you change the element. Once edited, the custom ID is kept.

7. Repeat the above four steps for each atom in the asymmetric unit.

8. Click Create Crystal Structure, and provide a title for the structure in the dialog box that opens.

   The structure is added as an entry to the Project Table, with the crystal data as properties.

To create a crystal structure from a 3D structure that has no crystal information:

1. Enter the space group number or the space group name, or click Choose to choose the space group.
2. Enter the unique cell parameters in the text boxes.
3. Click one of the Load from buttons to add the atoms from the 3D structure to the asymmetric unit: Workspace, if the structure is in the Workspace, or File, to read a structure from a Maestro file.
4. (Optional) Change data for any of the atoms.
5. Click Create Crystal Structure, and provide a title for the structure in the dialog box that opens.

   The structure is added as an entry to the Project Table, with the crystal data as properties.

To create a new crystal structure from a 3D structure that already has crystal information:

1. Click one of the Load from buttons to load the crystal information and add the atoms from the 3D structure to the asymmetric unit: Workspace, if the structure is in the Workspace, or File, to read a structure from a Maestro, PDB, or CIF file.
2. (Optional) Change cell parameters
3. (Optional) Change data for any of the atoms.
4. Click Create Crystal Structure, and provide a title for the structure in the dialog box that opens.

To convert a structure to P 1 symmetry:

1. Click Make P1.

   The structure is converted to P 1 symmetry by applying the symmetry operations of the current space group, and the Atoms table is populated with the symmetry-degenerate atoms.

2. Click Create Crystal Structure, and provide a title for the structure in the dialog box that opens.

2.8 Building Polymers

If you want to build a polymer from one or more monomer units, you can use the Polymer Builder panel. The polymer can be linear, branched, or dendritic; with different monomers it can also be a periodic or block copolymer or a random copolymer. You can specify the composition, arrangement and configuration of the monomers; the initiator, cascader (if any), and terminator; backbone dihedrals, and nonstandard couplings. You can also use the polymer to build an amorphous cell of polymers.

To open the Polymer Builder panel, you can:

- Choose Tools → Build Polymer in the main window.
- Choose Applications → Materials Science → Build Polymer in the main window.

The panel has three tabs, the Groups tab, in which you specify the chemical groups you want to use for the polymer: initiator, cascader, terminator, and monomers; the Configuration tab, in which you specify how the monomers are arranged to form the polymer, and the number of repeat units in the polymer; and the Amorphous Cell tab, in which you can build an amorphous cubic cell containing a specified number of polymers. After making settings in these tabs, click Run to run the job.

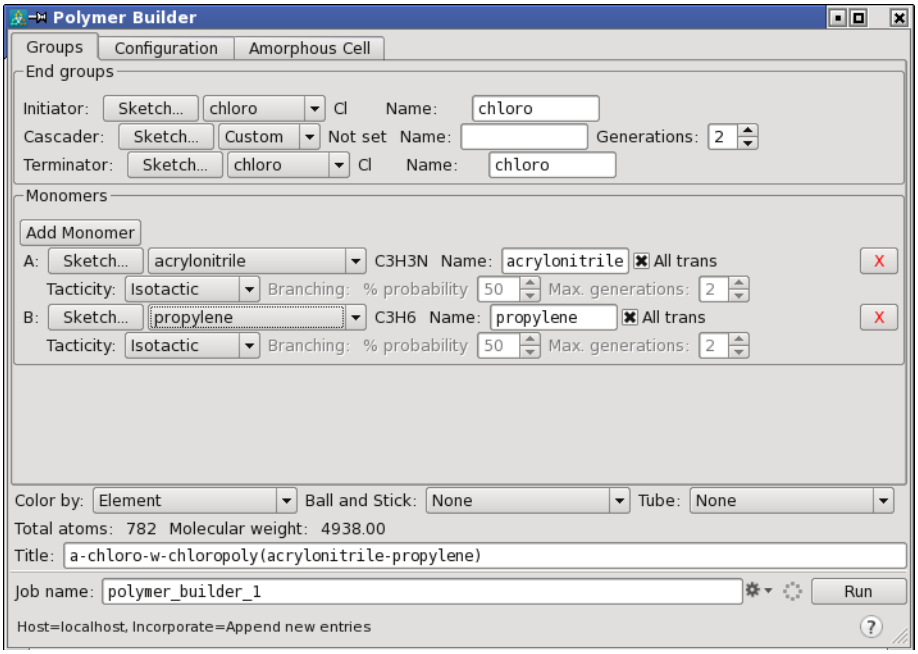

Figure 2.13. The Polymer Builder panel, Groups tab.

2.8.1 Choosing Monomer and End Groups

The first task in building a polymer is deciding on the groups from which the polymer is built: the initiator, the terminator, the cascader for dendritic structures, and the monomer, or monomers for a copolymer.

The end groups (initiator, cascader, and terminator) can be chosen in the End groups section. A short list of common groups is available from the option menu for each group type. When you choose one of these groups, the empirical formula is given next to the option menu, and the name is added to the Name text box.

If the group that you want is not on the option menu, you can draw it, by clicking Sketch and using the tools in the sketcher panel that opens. When you close the sketcher panel by accepting the sketched structure, the choice on the option menu is set to Custom and the formula is given next to the option menu. You can then name it in the Name text box. You can also add new groups (templates) to the option menu for current and later use. More details are given in the next section.

Choosing the monomers is similar. You can select a monomer from the option menu in the Monomers section, or click Sketch to draw the monomer or add a new template monomer. When you choose one of these groups, the empirical formula is given next to the option menu, and the name is added to the Name text box.

For a copolymer, you can add monomers by clicking the Add Monomer button. A new set of controls for a monomer unit is added below the last set of monomer controls. The monomers are labeled with letters, A, B, C, and so on. These letter codes are used in the Configuration tab to specify the order in which the monomer units are used. To delete a monomer, click the delete (X) button on the right. The controls for the monomer are removed from the panel and the information on the monomer is discarded.

2.8.2 Sketching Polymer Groups

If you want to supply your own end groups or monomers, you can sketch them in 2D. Click the Sketch button for the group to open a panel in which you can sketch the structure. In addition to drawing the structure, you will also have to label groups as R groups, which you can do from the shortcut menu for the atom to be converted to an R group. The labels and their requirements are discussed with the group types, below.

Each instance of this panel has an option menu and several buttons at the top, which you can use to load or save templates, or clear the drawing area.

- Template option menu—Choose an existing template to customize, or choose Custom to draw a new group.

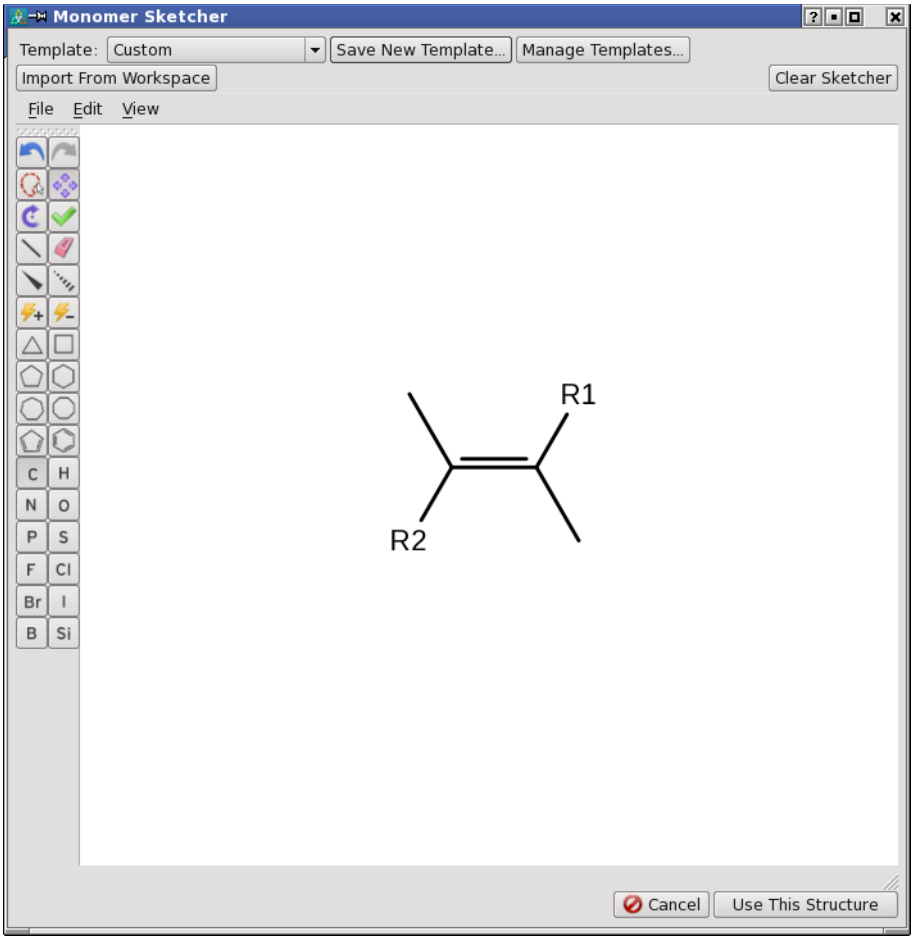

Figure 2.14. The Monomer Sketcher.

- Save New Template button—Save the current structure as a new template. Opens a dialog box in which you can name the template.
- Manage Templates button—Manage the custom templates. You can do the following:
  - Delete a template. Choose a template to delete from the Template option menu and click Delete Template.
  - Set the template directory. Click Change Custom Template Directory and navigate to a new location for the templates, or click Use Default Directory to return to the default directory for custom templates.

- Import from Workspace button—Import the current Workspace structure into the panel. The structure is drawn in 2D, and you can modify and label it.
- Clear Sketcher button—Clear the drawing area of all structures (which are discarded).

Below the drawing area there is a Cancel button, to return to the main panel without setting up a structure for the group, and a Use This Structure button, to use the drawn structure for the group and close the panel.

The menu, toolbar and drawing area are all common components that are used in multiple places. These features are described in detail in Section 5.5 of the *Maestro User Manual*.

When you have sketched a group, you must label it to identify the points at which other groups will be attached. To do this, you should add a bond to a carbon atom to the atom that will be attached to another group, and then change that carbon atom to the appropriate kind of R group, as follows:

- Initiator—must have at least one R1 group. For example, if your initiator is a Cl atom, build an ethane molecule, change one carbon to Cl (hover over the atom and type Cl), and change the other to R1 (right-click and choose Set R Group → R1). The molecule you end up with should be represented as Cl–R1.

  You can add multiple R1 labels, and the (same) polymer is built from each point on the initiator that is so labeled. This enables you to build dendrimers (along with cascaders).
- Cascader—must be labeled with one R1 group and two or more R2 groups. The R2 groups define points at which the chain from the initiator is replicated, to form a dendritic structure.
- Terminator—must have exactly one R1 group defined (and no others).
- Monomer—must have a single R1 group for the head, and a single R2 group for the tail. For example, for polyethylene, the monomer must have a single C–C bond, with two hydrogens and one R group at each end. To create this monomer, you would draw butane, and convert the terminal carbons to an R1 and an R2.

  If you want to create branched polymers, you can add an R3 group to the monomer to designate a point where a new chain can be attached.

2.8.3 Building Dendrimers

To build a dendrimer, you must choose a cascader in the End groups section. In addition to the controls to define the cascader group, there is a Generations box, in which you can define the number of replications of the polymer chain in the dendrimer. The minimum number is 2, which means that there is one cascader on each chain from the initiator, to which copies of this chain are attached in place of the R2 groups of the cascader.

You do not have to use an initiator with multiple R1 groups to start building a dendrimer, but you can do so if you wish.

2.8.4 Building Branched Polymers

If the monomer group you choose has an R3 group, you can use it to build a branched polymer. The Branching controls are enabled, and you can specify the probability of branching and the maximum number of generations when branching.

The branching probability is applied to each monomer unit independently, to decide whether it will branch or not. (This is different from choosing the specified percentage of monomers at random, which guarantees approximately the specified percentage of branches. Here, there is a small but finite probability of none of the monomers branching, or of all of them branching.)

Each branch is created by taking a copy of the chain before branching and attaching it to the branch point. If you specify more than two generations, branch points are chosen at random for each added chain, so the branch points can be different in each chain that is added in each generation. The process is repeated for each subsequent generation.

If an R3 group is not chosen as a branch point in the random selection, it is replaced with the terminating group.

2.8.5 Defining the Polymer Composition

In the Composition section of the Configuration tab, you specify how the monomers are arranged to form the polymer, and the number of repeat units in the polymer. The type of polymer that can be formed depends on the number of monomer units, and is reflected in the options of this section. These three options, with their controls, are described below.

2.8.5.1 Homopolymer

If there is only one monomer specified, this is the only option available and it is selected by default. You can specify the length of the polymer chain in the Number of monomers box. The polymer can be branched if you specified a branch point on the monomer. In this case each of the branches has the number of monomers specified in the Number of monomers box. Likewise, if the polymer is dendritic, each of the branches has the specified number of monomers.

2.8.5.2 Block or Periodic Copolymer

If you specified more than one monomer, you can construct a block or periodic copolymer by selecting Block or periodic copolymer. You can then specify the repeat unit and the number of repeat units.

To specify the repeat unit, enter the sequence of letter codes for the monomer units in the Repeat unit text box. These letter codes with the monomer names are shown to the right of the Block or periodic copolymer option. If there are repeated monomer units, you can instead use a repeat count following the letter code, e.g. A3 is the same as AAA.

If you want to enumerate several polymers in which one or more positions has each of the monomers, you can use a * to designate an enumeration site. A list of repeat units is constructed that contains each of the possible monomers at this site. For example, if you have three monomer units, then AB* generates the three repeat units ABA, ABB, and ABC. Each of these is used in a separate polymer: ABAABAABA..., ABBABBABB..., and ABCABCABC...; only one repeat unit is used in each polymer. You can have more than one enumeration site. For example, with two monomers, A*B* would generate four repeat units, AABA, AABB, ABBA, and ABBB. The number of polymers generated is shown to the right of the number of repeat units as Enumerated polymers.

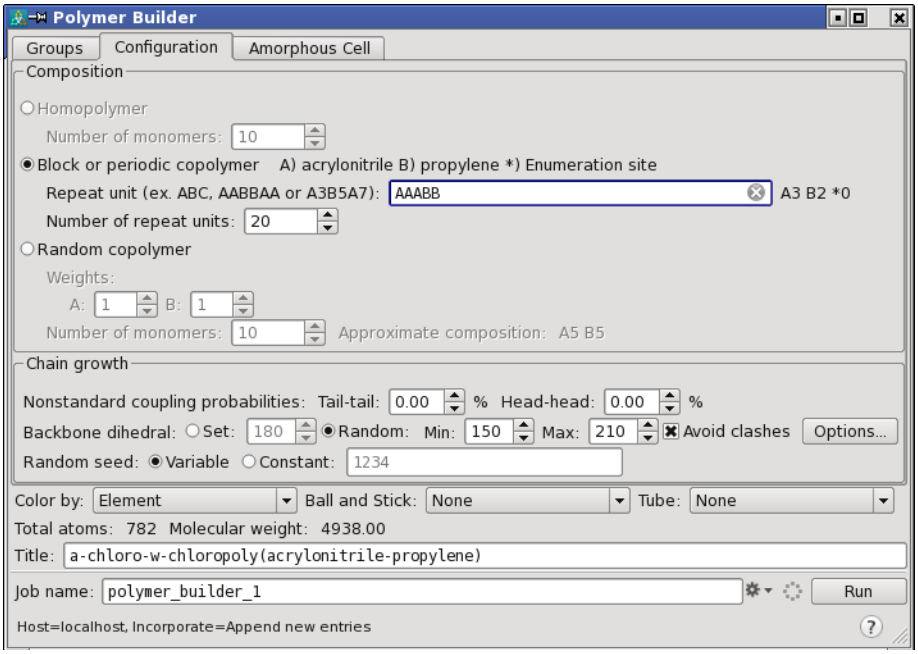

Figure 2.15. The Polymer Builder panel, Configuration tab, for block copolymers.

When you have specified the repeat units, you can set the number of repeat units (as defined above) in each polymer chain, by entering the number in the Number of repeat units box. If the polymer is branched or dendritic, each chain that is initiated from a branch point or cascader has this length.

2.8.5.3 Random Copolymer

If you specified more than one monomer, you can construct a random copolymer by selecting Random copolymer. For each monomer, you can specify the relative probability of choosing it for addition to the polymer at each polymerization step, by setting the values in the Weights boxes. These boxes are labeled with the letter code for the monomer. The letter codes with the monomer names are shown to the right of the Random copolymer option. The approximate composition is given to the right of the Number of monomers box.

You can specify the number of monomers in the copolymer chain in the Number of monomers box. If the polymer is branched or dendritic, each chain that is initiated from a branch point or cascader has this length.

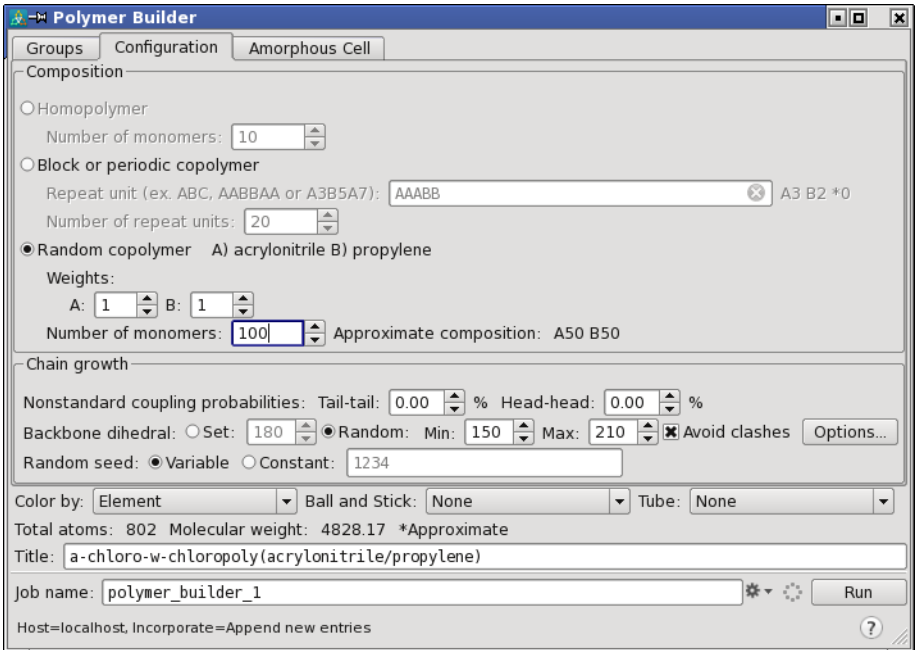

Figure 2.16. The Polymer Builder panel, Configuration tab, for random copolymers.

2.8.6 Setting the Chain Configuration

The chain configuration can be set by specifying backbone dihedrals, and if the monomer is chiral, the tacticity.

You can set the backbone dihedral angle between the monomer units or specify a range of angles with the Backbone dihedral options. The backbone dihedral is the dihedral angle between adjacent monomer units; the three vectors are the vectors that connect the head and

tail of each monomer, and the vector that connects one monomer to the next. In a standard coupling, it is the head1-tail1-head2-tail2 dihedral, where head*n* and tail*n* are the head and tail atoms in the monomers.

- Set—Select this option to set the backbone dihedral to a specific angle in degrees, which you enter in the box.
- Random—Select this option to allow random selection of a backbone dihedral within a specified range of angles. You can set the limits of the range in the Min and Max boxes. Select Avoid clashes to retry dihedrals if there is a clash (the nonbonded interatomic distance is less than the scaled sum of the atomic van der Waals radii). You can set the number of retries and the scaling factor by clicking Options and making changes in the dialog box that opens.

You can also set the dihedral angles within each monomer unit to the trans configuration (180°), by selecting All trans for the monomer in the Monomers section of the Groups tab. If you deselect this option, the dihedral angles along the monomer are set from the geometry obtained by minimization when the 2D structure is converted to 3D.

If the monomer unit is chiral in the polymer, you can set the tacticity for the polymer with the Tacticity option menu, to Isotactic (same chirality for each monomer unit), Syndiotactic (alternating chirality for each monomer unit), or Atactic (chirality chosen at random). No information on the chirality is taken from the structure.

2.8.7 Allowing Nonstandard Couplings

If you want to allow tail-to-tail or head-to-head couplings, instead of the normal head-to-tail couplings, you can set the percentage probability that a nonstandard coupling occurs on the addition of another monomer, in the Tail-tail and Head-head boxes in the Chain growth section of the Configuration tab. The random number generator is used in conjunction with these percentage probabilities to determine whether the coupling of the next monomer unit is nonstandard, when building the polymer. To introduce multiple nonstandard couplings, you must set probabilities for both types.

2.8.8 Setting the Seed for Random Number Generation

Several of the options for building polymers involve random selection. The random number generator that is used for the random selection processes is initialized by a seed, which you can specify, by selecting one of the Random seed options:

- Variable—Select this option to use a different seed each time a new polymer is built. As the seed changes each time, you will get a different polymer each time you build, even from the same settings.

- Constant—Select this option and supply a seed value, to use the same seed each time a polymer is built. This option allows you to reproduce your results, as the same random seed is used to initialize the random sequence each time.

2.8.9 Setting Color and Molecular Representation

You can set the color and molecular representation that are used in Maestro to display the polymer when it is built.

To set the color, choose one of the following schemes from the Color by option menu:

- Element—Color each atom by element. This is the standard Element color scheme, with gray carbons, red oxygens, blue nitrogens, and so on. See the Atom Color Schemes help topic for information on standard color schemes.
- Monomer—Color each monomer type with a unique color. Initiators, cascaders, and terminators are considered separate monomer types for coloring. This is useful for identifying the sequence of monomers in a copolymer.
- Chirality—Color monomers that have R chirality in green, those that have S chirality in cyan, and those with no chirality in red (including initiators, cascaders, and terminators).
- Backbone/side group—Color the backbone atoms green, the side groups cyan, and anything else red (initiators, cascaders, terminators, H attached to backbone).
- Molecule—Color each polymer molecule with a unique color. This scheme is useful when creating an amorphous cell, to distinguish the polymers in the cell.

By default, the polymer is drawn in the wire frame scheme: wires (lines) for bonds, and atoms are at the ends of the wires, with no explicit representation. You can set the representation for different regions or groups in the polymer to ball and stick or tube representation by choosing from the Ball and stick and Tube option menus. You can choose different items from these menus to represent different parts of the polymer. These option menus have the same items:

- None—Do not render anything in the chosen representation.
- Backbone—Render the backbone atoms in the chosen representation.
- Side group—Render the side group atoms in the chosen representation.
- R chirality—Render monomer units that have R chirality in the chosen representation.
- S chirality—Render monomer units that have S chirality in the chosen representation.
- Head—Render the head atom in each monomer in the chosen representation. This is the atom attached to the R1 group. The atom attached to R1 for initializers, terminators and cascaders are also considered head atoms.

- Tail—Render the tail atom in each monomer in the chosen representation.
- Head and tail—Render the head and tail atoms in the chosen representation. The bond between the monomer units will also be rendered in the chosen representation.

2.8.10 Setting the Structure Title

To specify the title for the polymer, you can edit the text in the Title text box. A default title is built up from the IUPAC name of the polymer, as far as possible. This default scheme does not work for more complicated polymers.

2.8.11 Creating an Amorphous Cell of Polymers

As well as building a single polymer chain or dendrimer, you can create an amorphous cubic cell consisting of multiple polymer chains. The cell may have a nonuniform composition of the polymers if you chose any random element in the generation of the polymer chain.

The cell is built by randomly orienting and placing polymers one by one, and checking for clashes. If a clash is found, the latest polymer to be placed is placed again at random, and this process is repeated until a non-clashing placement is found or the number of tries is exceeded. If a non-clashing placement isn't found, building of the cell is tried again from the beginning. If the cell can't be built from the beginning after a specified number of trials, the density or the scaling factor for clash detection is decreased, and the process starts again.

Settings for creating the cell can be made in the Amorphous Cell tab. You can choose to create a model system for Desmond MD simulations instead of just a structure. After the job is run, the structure or the model system (whichever you chose) is incorporated into the project.

To create an amorphous cell, select Create amorphous cell, then make settings for the cell, as follows.

1. Specify the number of polymers to place in the cell, in the Number of polymers text box.
2. Specify the initial density of the polymer in g $cm^{\bullet 3}$ in the Initial density text box.

   The density may be adjusted to avoid clashes, depending on the option for the value to keep constant, below.
3. Specify the initial scaling factor for detecting clashes in the Initial clash VDW scale factor text box.

   A clash is considered to occur if the nonbonded interatomic distance between two atoms is smaller than the scaled sum of the atomic van der Waals radii of the atoms.
4. Choose one of the Keep constant options for the quantity to keep constant when constructing the cell, from Density or VDW scale factor.

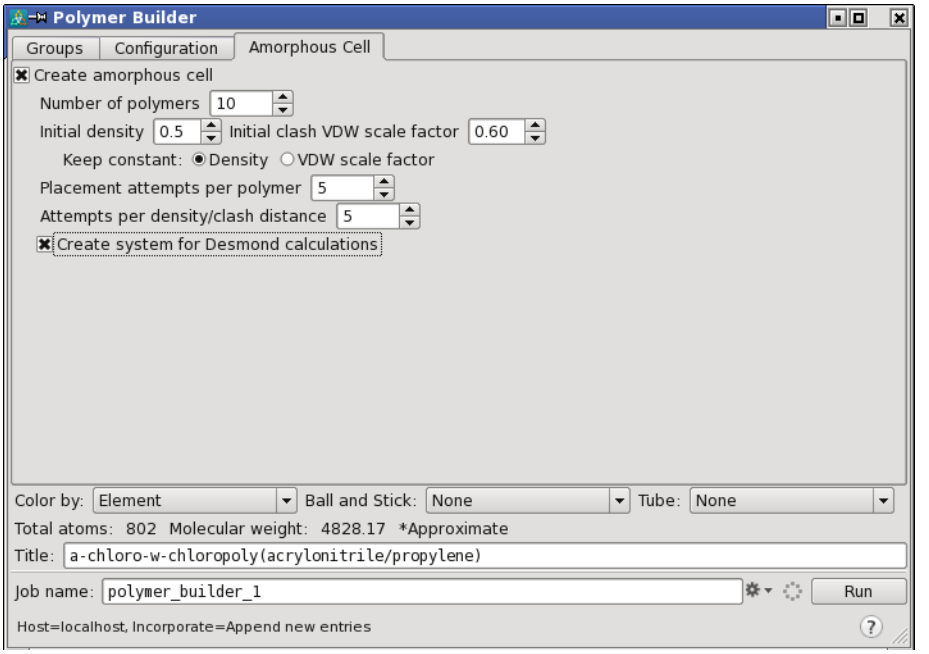

Figure 2.17. The Polymer Builder panel, Amorphous Cell tab.

The other quantity is adjusted during the placement of polymers to avoid clashes. Choosing Density keeps the density at its initial value and changes the scale factor for clashes to eliminate clashes. This option might result in polymers that are too close. Choosing VDW scale factor keeps the clash detection the same, and adjusts the density to eliminate clashes. This might result in a density that is lower than desired.

5. Specify the maximum number of attempts to be made when placing a polymer in the cell, in the Placement attempts per polymer text box.
6. In each attempt, the polymer is oriented at random and placed in the cell at random. If a clash is detected, the attempt is regarded as failed, and a new attempt is made. If the maximum number of attempts is exceeded, the cell is discarded and a new cell is built.
7. Specify the maximum number of attempts at building a cell, in the Attempts per density/clash distance text box.

   If a non-clashing cell cannot be built in this number of attempts, the density is lowered or the van der Waals scaling factor is lowered, depending on the Keep constant option. The process continues until a non-clashing cell can be built, or the density or scale factor are very small.

8. (Optional) Select Create system for Desmond calculations to create a model system for molecular dynamics simulations with Desmond, instead of just a structure. The result (model system or structure) is incorporated into the project.

2.8.12 Creating the Polymer or Amorphous Cell

When you have made all the settings you want to make, click Run. The job should take less than a minute for a polymer, and somewhat longer for an amorphous cell. The polymer or the amorphous cell (or Desmond model system) is added as an entry to the Project Table, and is displayed in the Workspace.

If you want to create another polymer or cell, you can choose Reset from the Job settings button menu to clear the panel, resetting all settings to their defaults, and start building a new polymer.

2.8.13 Summary of Basic Procedures

To sketch an initiator, cascader, terminator, or monomer group:

1. Click Sketch.

   The Sketcher panel for the group type opens.

2. Draw the group as it appears in the polymer using the drawing tools.

   This means that monomers should not have double bonds as they exist in the isolated monomer, but single bonds as they exist in the polymer. See Section 5.5 of the *Maestro User Manual* for details on how to use the drawing tools.

3. Add a bond to an extra atom (a carbon, for example) to each point on the group that will be attached to another group in the polymer.

   For example, if you are building an ethylene monomer, add an extra carbon to each end. At this point the ethylene monomer would look like butane.

4. Label the extra atoms as R groups, by right-clicking on them and choosing one of the R group options from the Set R Group submenu.

   The labels to use for each group type are:

   - Initiator: Use R1 for each extra atom. All of the atoms so labeled will initiate a chain.
   - Monomer: Label the extra atom at the head as R1, and the extra atom at the tail as R2. If the monomer can have a branch point, label the extra atom for the branch as R3.

- Terminator: Label the extra atom as R1. There should be only one extra atom for a terminator.
- Cascader: Label the extra atom that is attached to the main chain as R1, and the extra atoms for initiating the new chains as R2.

5. To save the group as a template:
   i. Click Save New Template.
   ii. Enter a name for the template in the text box of the Template Name dialog box.
   iii. Click OK.

   The template is added to the Template menu and is selected.
6. To use the group without saving it, click Use This Structure.

Instructions for building the basic kinds of polymers are given below. More complicated polymers can be built, but they follow the same basic procedure.

To build a simple unbranched polymer:

1. Choose or sketch an initiator group.
2. Choose or sketch a terminator group.
3. Choose or sketch a monomer.
4. If the monomer has a chiral group, choose the tacticity from the Tacticity option menu.
5. In the Configuration tab, set the number of monomers in the polymer.
6. Click Run.

The polymer is built, added to the project, and displayed in the Workspace.

To build a branched polymer:

1. Choose or sketch an initiator group.
2. Choose or sketch a terminator group.
3. Choose or sketch a monomer.

   The monomer must be labeled with R1 for the head group, R2 for the tail group, and R3 for the branch point.
4. If the monomer has a chiral group, choose the tacticity from the Tacticity option menu.
5. Set the percentage probability of branching.

This determines how frequently branches are likely to occur within a given chain. The percentage probability is applied to each monomer unit independently to determine which ones will branch.

6. Set the number of generations.

   This determines how many times another set of chains is added to the previous generation of chain additions. The first generation is the original generation from the initiator: thus, two generations means that a set of chains is added once, to the selected branch points on the original chain. Branch points are chosen randomly in each generation.

7. In the Configuration tab, set the number of monomers in each chain of the polymer.
8. Click Run.

The polymer is built, added to the project, and displayed in the Workspace.

To build a block or periodic copolymer:

1. Choose or sketch an initiator group.
2. Choose or sketch a terminator group.
3. Choose or sketch the first monomer.
4. Click Add Monomer to add another monomer definition.
5. Choose or sketch the next monomer.
6. Repeat the previous two steps for each additional monomer.
7. If any monomer has a chiral group, choose the tacticity from its Tacticity option menu.
8. In the Configuration tab, ensure that Block or periodic copolymer is selected.
9. Specify the repeat unit in the Repeat unit text box by typing in the letter codes for the monomers in the desired sequence, eg. AABBBB.
10. Set the number of repeat units in the polymer.
11. Click Run.

The polymer is built, added to the project, and displayed in the Workspace.

To build a dendrimer:

1. Choose or sketch an initiator group.

   To make a dendrimer that branches from the initiator, ensure that you have multiple R1 groups on the initiator. You can check this by pausing the pointer over the empirical formula for the initiator. The 2D structure is shown in a tool tip.

2. Choose or sketch a cascader group.

   This group must have one R1 group and two or more R2 groups, depending on how many branches you want to have at each branch point.

3. Set the number of generations for the cascader.

   The cascader terminates the generation of a polymer chain (and initiates a new generation) except for the last termination, where the terminator is added.

4. Choose or sketch a terminator group.
5. Choose or sketch a monomer.
6. If the monomer has a chiral group, choose the tacticity from the Tacticity option menu.
7. In the Configuration tab, set the number of monomers in each chain of the dendrimer.
8. Click Run.

The dendrimer is built, added to the project, and displayed in the Workspace.

Chemical Reactions

The Materials Science suite contains a number of tools for investigating chemical reactions: reaction channel enumeration, for generating possible products from reactants; reaction path interpolation, for generating structures along an approximate reaction path by linear interpolation; reaction enthalpies and barriers for a series of homologous compounds, and TST rate calculations. These tools are described in this chapter.

Energetics and barriers are calculated quantum mechanically, with Jaguar. For a single calculation of reaction energies, transition states, and reaction paths, you can use the Jaguar program directly (or semiempirical NDDO, for more qualitative results). These tasks can be found under Tasks → Quantum Mechanics. For more information, see the *Jaguar User Manual* and the *Jaguar Quick Start Guide*. Finding and forming a complex in the right pose for a reaction can be done with the Probe Scan panel—see Chapter 6.

3.1 Reaction Channel Enumeration

Before proceeding with the calculation of a reaction path or reaction energetics, you might want to explore the possible reaction channels. This can be done in the Reaction Channel Enumeration panel, which you open from the Tools menu.

Given a set of reactants, this panel can be used to enumerate the products for reaction channels of several possible types of reactions, either by choosing specific channels, by random selection, or by exhaustive enumeration. You can enumerate reaction channels for multiple molecules by including them all in the Workspace, then setting up the enumerations.

The reactant and product structures can then be used as input for reaction path interpolation or a transition state search, for example. As the numbering of the atoms in both reactant and product structures is the same, they are suitable for use with Jaguar for a transition state search; however, there is no attempt made to form a pre- or post-reactive complex.

To start, you must display the molecules you want to use in the Workspace. If you are interested in a specific reaction, display the one or two molecules that are involved in the reaction. If you want to sample all possible reactions between a set of molecules, or between one reactant and a set of other reactants, include them all in the Workspace.

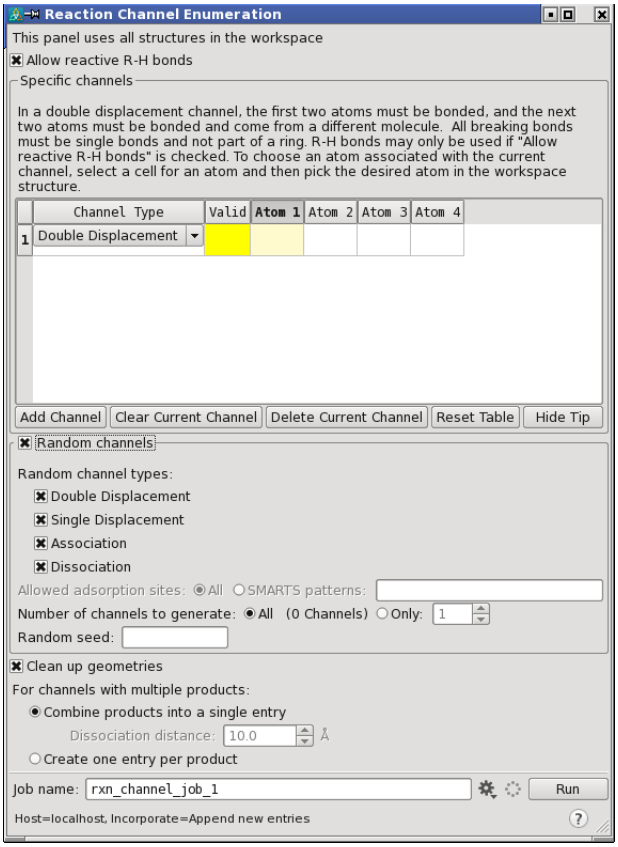

Figure 3.1. The Reaction Channel Enumeration panel.

3.1.1 Setting Up Enumeration of Specific Channels

If you want to generate the reaction channels for specific reactions, i.e. breaking or forming specific bonds, you can use the tools in the Specific channels section. Each reaction channel is defined in a row of the table in this section. The table initially contains one reaction channel but with no data.

- To set up a reaction channel, choose the channel type from the option menu in the Channel Type column, then pick the required atoms in the Workspace. Details are given below.
- To add a new reaction channel, click Add Channel.
- To clear the data from a reaction channel, select it in the table and click Clear Current Channel.
- To remove a reaction channel, select it in the table and click Delete Current Channel.

- To remove all the reaction channels, click Reset Table.

When you choose a channel type, text is displayed above the table describing how to pick the atoms that define the channel. You can hide this text by clicking Hide Tip; the button changes to Show Tip when you click it, so that you can redisplay the text. The channel types are described in Table 3.1.

The channel is defined by a set of atoms that define the bonds to be broken or formed. Depending on the channel type, this number can be from 2 to 4. Table cells are filled in with the atom number as you pick the atoms in the Workspace, The cell that is "active" has a colored background. Cells that are not needed for the channel type are grayed out.

The status of the channel is indicated by the Valid cell color: Red indicates that one of the atoms picked is invalid; i yellow means that picking is incomplete, green means that the picking is complete and all the atoms are valid.

If you need to change the atom in any cell, click on the cell and pick an atom in the Workspace. The active cell moves to the next empty cell in the same row once you have picked an atom, so you don't need to click in each cell to pick atoms sequentially.

Table 3.1. Description of channel types.

Channel type	Description
Double displacement	Reaction of the type A-B + C-D → A-C + B-D, A-D + B-C, in which one bond in each molecule is broken, and both combinations of fragments are generated.
Single displacement	Reaction of the type A + B-C → A-B + C, A-C + B, in which one bond is broken in one reactant, and both combinations of the fragments with the other molecule are generated. (This could be a typical SN2 reaction, for example).
Association	Reaction of the type A + B → C, in which a bond is formed between two molecules.
Dissociation	Reaction of the type A → B + C, in which a bond in a single molecule is broken to form two molecules.

3.1.2 Setting Up Random Enumeration or Exhaustive Enumeration

If you want to generate a random selection of reaction channels, or exhaustively enumerate all possible reaction channels, you can do so in the Random channels section.

All molecules in the Workspace are considered in the generation of channels, so if you do not want to consider reactions between some of the molecules, you should ensure that the Workspace contains only those molecules whose reactions you do want to consider. You can run the

enumeration multiple times to cover the reactions you do want to consider. For example, if you wanted to consider the association reaction of one molecule with a series of other molecules, you would have to do each independently; if you include all of the series, reactions between the members of the series will be considered.

First, you must select the Random channels option. The channels generated in this section are in addition to (and exclusive of) the channels generated in the Specific channels section.

The enumeration can take into account more than one channel type. You can select the channel types to consider under Random channel types. The channel types are described in Table 3.1.

When enumerating adsorption reactions on a surface (association), you can specify which sites on the surface to adsorb onto, with the Allowed adsorption sites options. The choices are All, to consider adsorption onto all possible sites, or SMARTS patterns, to specify sites by their SMARTS patterns. Atoms from the SMARTS pattern are chosen at random for the site to use for adsorption, so the pattern should include only atoms at which you want to consider adsorption.

The options so far are common to both random and exhaustive enumeration. The choice between random and exhaustive enumeration is done by selecting an option for the number of channels to generate.

- If you select All, all possible reaction channels are generated in an exhaustive search. This could take some time.
- If you select Only, channels are generated at random, and you must specify the number of channels to generate. The seed used for random number generation can be specified in the Random seed text box. This can be useful for reproducing the results of a random selection. The channels are generated by random selection of molecules, then random selection of channel types, then random selection of atoms.

3.1.3 Post-Processing and Output

The reaction products for a given channel are created by breaking bonds and forming new bonds. The product structures can be minimized with the OPLS_2005 force field by selecting Clean up geometries. The reactant structures are also minimized if you choose this option. You should ensure that the reactant structures are positioned in the Workspace so that they do not clash, both to prevent minimization problems with the reactants, and because the product structures are formed by making the minimum changes to the reactant structures and so will occupy a similar region of space.

The product molecules for a given channel can be written out as a single structure (entry), where they retain the atom numbering of the corresponding reactant atoms, or they can be written as separate structures (entries). You can specify which you want by making a selection

under For channels with multiple products. For dissociation reactions, the distance between the product molecules in the final structure can be specified.

A reaction channel could exchange identical groups, and regenerate the reactants instead of new products. A reaction channel could also result in the same products as another channel. To eliminate these redundancies, you can select Unique products only.

The structures are written to a file, which is incorporated into the project by default. All the reactant molecules are in the first entry, followed by entries containing the products. The products for each channel are placed consecutively. If you chose to create one entry per product, the product molecules for a given product set for a given channel are placed consecutively.

As each reaction involves only one or two reactants, if you included more than the required number of molecules for a single reaction in the Workspace, the other molecules are spectators and are included in the output reactant and product structures. Before using these structures for other calculations, you should remove the spectators. You can do this by simply deleting the spectators in Maestro: the atom numbering of the reactants and products will remain consistent after removal of the spectators.

3.1.4 Summary of Procedures

To set up an enumeration for a random selection of channels:

1. Display the reactant molecules in the Workspace.
2. Choose whether to allow bonds to hydrogen to be considered in the reaction channels, by selecting or deselecting Allow reactive R-H bonds.
3. Choose whether to keep only the nonredundant channels by selecting or deselecting Unique products only.
4. Select Random channels.

   You can ignore the Specific channels section, which will not be used unless it has data.
5. Choose the channel types that you want to consider in the random selection, under Random channel types.
6. For Number of channels to generate, select Only and set the number of channels.
7. (Optional) Specify the seed to be used in the random selection.
8. If you want to minimize the structures with the OPLS_2005 force field, select Clean up geometries.
9. If you want to place each product molecule into a separate project entry, select Create one entry per product.

10. Click Run to run the job.

To set up an enumeration of all possible channels:

1. Display the reactant molecules in the Workspace.
2. Choose whether to allow bonds to hydrogen to be considered in the reaction channels, by selecting or deselecting Allow reactive R-H bonds.
3. Choose whether to keep only the nonredundant channels by selecting or deselecting Unique products only.
4. Select Random channels.
5. Choose the channel types that you want to consider in the exhaustive enumeration, under Random channel types.
6. For Number of channels to generate, select All.
7. If you want to minimize the structures with the OPLS_2005 force field, select Clean up geometries.
8. If you want to place each product molecule into a separate project entry, select Create one entry per product.
9. Click Run to run the job.

To set up an enumeration for specific channels:

1. Display the reactant molecules in the Workspace.
2. Choose whether to allow bonds to hydrogen to be considered in the reaction channels, by selecting or deselecting Allow reactive R-H bonds.
3. Choose whether to keep only the nonredundant channels by selecting or deselecting Unique products only.
4. Specify the first reaction channel by choosing a channel type and picking atoms in the Workspace. See below for instructions for each channel type.
5. To add another channel, click Add Channel, then choose the channel type and pick atoms.
6. If you want to minimize the structures with the OPLS_2005 force field, select Clean up geometries.
7. If you want to place each product molecule into a separate project entry, select Create one entry per product.
8. Click Run to run the job.

To set up a dissociation channel, A-B → A + B:

1. Choose Dissociation from the menu in the Channel Type column of the channels table.
2. Pick the two atoms in the reactant molecule to define the bond to be broken.

   The Atom 1 and Atom 2 columns of the table row are filled in.

To set up an association channel, A + B → A-B:

1. Choose Association from the menu in the Channel Type column of the channels table.
2. Pick the atom in one reactant molecule that you want to form a bond with the other reactant molecule.

   The Atom 1 column of the table row is filled in.
3. Pick the atom in the other reactant molecule that you want to form a bond with the first molecule.

   The Atom 2 column of the table row is filled in.

To set up a single-displacement channel, A-B + C → A + B-C, B + A-C:

1. Choose Single displacement from the menu in the Channel Type column of the channels table.
2. Pick the two atoms in one reactant molecule to define the bond to be broken in that reactant.

   The Atom 1 and Atom 2 columns of the table row are filled in.
3. Pick the atom in the other reactant molecule that the fragments from the first molecule should bond to.

   The Atom 3 column of the table row is filled in.

To set up a double-displacement channel, A-B + C-D → A-C + B-D, A-D + B-C:

1. Choose Double displacement from the menu in the Channel Type column of the channels table.
2. Pick the two atoms in one reactant molecule to define the bond to be broken in that reactant.

   The Atom 1 and Atom 2 columns of the table row are filled in.
3. Pick the two atoms in the other reactant molecule to define the bond to be broken in that reactant.

   The Atom 3 and Atom 4 columns of the table row are filled in.

3.2 Bond and Ligand Dissociation Energies

When evaluating compounds for their reactivity or stability, it can be useful to know what the bond energies are. This information may be useful in the assessment of chemical lifetimes of optoelectronic materials, for example. Similarly, when evaluating ligands for use in transition metal complexes, the ligand binding energy can help to determine the usefulness of the ligand.

The Materials Science suite provides a workflow that evaluates the change in energy for dissociating molecules into all possible combinations of two fragments that come from breaking covalent single non-ring bonds (by homolytic dissociation) or from removing ligands from a metal atom. This workflow is available from the Bond and Ligand Dissociation panel, which you open by choosing Tasks → Bond and Ligand Dissociation or Applications → Materials Science → Bond and Ligand Dissociation in the main window.

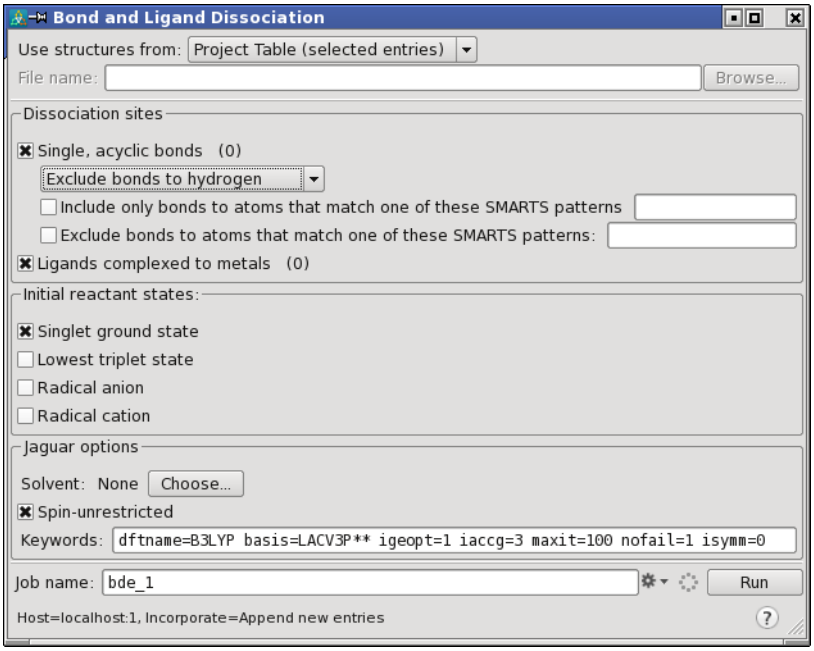

Figure 3.2. The Bond and Ligand Dissociation panel.

Dissociation energy calculations can be performed on multiple molecules in the same run. You can choose the source of the structures from the Use structures from option menu:

- Project Table (selected entries)—Use the entries that are currently selected in the Project Table.

- Workspace (included entries)—Use the entries that are currently included in the Workspace, treated as separate structures. The Workspace should not contain a scratch entry.
- File—Use the structures from the specified file. When this option is selected, the File name text box and Browse button are activated. Click Browse and navigate to the file you want to use. The file name is displayed in the text box when you click Open in the file selector. You can also enter the file name in the text box.

You can calculate both bond dissociation and ligand dissociation energies in the same run. To choose the kinds of dissociation to be considered, choose one or both of the Dissociation Site options:

- Single, acyclic bonds —Calculate dissociation energies for the breaking of all single bonds in each molecule that are not part of a ring.

  By default, bonds to hydrogen are not included. If you want to consider bonds to hydrogen as well, choose Include bonds to hydrogen from the option menu. If you want to consider only bonds to hydrogen, to calculate hydrogen abstraction energies, choose Include only bonds to hydrogen from the option menu.

  You can include or exclude bonds to other atoms by selecting the Include only bonds to atoms that match one of these SMARTS patterns or Exclude bonds to atoms that match one of these SMARTS patterns options and providing the SMARTS patterns in the text boxes. You can include multiple SMARTS patterns, separated by spaces, in each text box. Any bond that has an atom that matches any of the SMARTS patterns is either included or excluded.

  If the molecule is a metal complex, bonds between monodentate ligands and the metal are included as well as bonds within the ligands.
- Ligands complexed to metals—Calculate dissociation energies for the removal of single ligand molecules that are complexed to metals. This may involve the breaking of more than one metal-ligand bond, if the ligand is polydentate.

The input molecules that you provide must be closed-shell singlet molecules. This includes transition-metal complexes. However, you can choose from a variety of initial states that are actually used in the calculations, and you can perform the calculations for more than one initial state, by choosing from the Initial reactant state options:

- Singlet ground state—Calculate dissociation energies from the ground state of the input molecule, which must be a closed-shell singlet.
- Lowest triplet state—Calculate the dissociation energies from the lowest triplet state of the input molecule. For bond dissociation, the fragments are always treated as doublets.

- Radical anion—Calculate dissociation energies from the negative ion doublet state. As the negative charge can be on either of the fragments, both the neutral and the charged fragments are calculated. The output from this case is two reactions, rather than just one.
- Radical cation—Calculate dissociation energies from the positive ion doublet state. As the positive charge can be on either of the fragments, both the neutral and the charged fragments are calculated. The output from this case is two reactions, rather than just one.

The calculations are performed with Jaguar, and the geometry is optimized for all fragments and all input states. To maximize efficiency, a unique set of fragments for the entire input is assembled, and calculations are performed on the unique fragments. This means, for example, that if a phenyl ring occurs in more than one place either within a single molecule or in different molecules, only one calculation is performed on the phenyl ring. Likewise, dissociation from a singlet and a triplet state produce the same set of fragments, so the cost of calculating both is not much more than that of calculating one of the initial states. (The extra cost is just the cost of the extra initial states).

By default, the calculations are run in the gas phase. To run the calculations in solution, click Choose to set the solvent. The Solvent Model dialog box opens, where you can select the PBF solvent model and choose a solvent. The other controls in this dialog box are the same as in the Solvation tab of the Jaguar panel—see Section 3.7 of the *Jaguar User Manual*.

If you want to add keywords for the Jaguar calculations, you can do so in the Keywords text box. A default set of keywords is provided for the method and basis set as well as some accuracy and convergence settings.

In the output structure file, there is an entry for each reaction, which contains the reactant and product structures for that reaction, as well as the reaction energy property. The reactant structure is placed on the negative side of the *x* axis, with the broken bond highlighted and placed along the *x* axis. The product structures are placed on the positive side of the *x* axis, and displaced in the *y* direction so they don't overlap. They have the same orientation as in the reactant structure (unless the same fragment is used for multiple reactions). The atoms on the end of each broken bond are highlighted in the product structures. For polydentate ligands, each atom that ligates the metal is marked, and each metal-ligand bond is marked in the reactant.The average of the vectors defined by the broken bonds in the reactant is aligned on the *x* axis.

In addition to the entries for the reactions, there are entries for each reactant molecule and each product molecule. The product titles contain an index for the fragment and the job name.

3.3 Reaction Path Interpolation

Locating the transition state for a reaction is a critical task in determining the kinetics of a reaction. It is also a difficult task, as it is usually necessary to have a good guess at the desired transition state. For the search, it is also necessary to maintain a proper correspondence between the atoms in the reactant and product structures and the transition state guess.

The Reaction Path Interpolation panel provides a convenient way to set up an approximate reaction path using a linear interpolation of a set of Cartesian, distance, or redundant internal coordinates. The structures produced along this path can then be examined and used as input to a search for the transition state. To open the Reaction Path Interpolation panel, choose Tools → Reaction Path Interpolation.

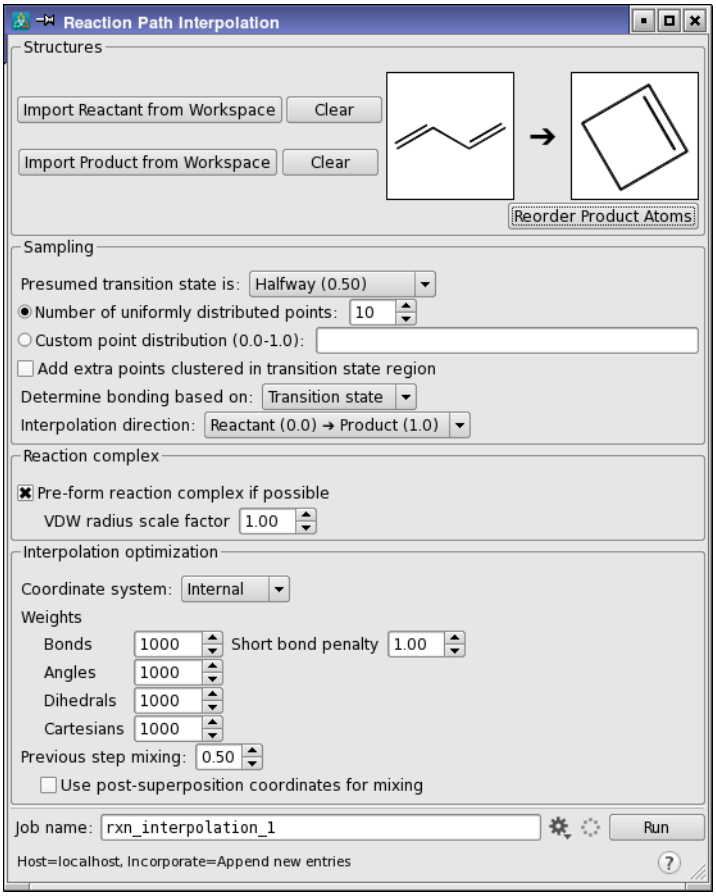

Figure 3.3. The Reaction Path Interpolation panel.

The reaction path interpolation procedure is based on the work of Halgren and Lipscomb [1].

3.3.1 Choosing Reactant and Product Structures

In general, the reaction and product structures should be constructed so that the structures are pre-positioned for reaction (in either direction). It is highly recommended that you build the product structures by modifying the reactant structures, breaking bonds and forming new bonds as necessary but not deleting any atoms. Keeping all the atoms is critical to maintaining the atom ordering, which is critical for constructing the path. The atom numbering must match, otherwise the reaction path will be meaningless. (To ensure that no automatic deletion of hydrogens is done, deselect Allow united atom types while building and Adjust number of hydrogens following additive build operations under Builder – Behavior in the Preferences panel.)

If you build the products from the reactants, you should do a restrained minimization of the structures that relieves strain but does not significantly reposition the product structures.

If you have structures that do not have corresponding atom numbers, the panel offers you ways to change the atom numbering and position the reactants and products, as explained below.

To select the structures:

1. Display the reactant structure in the Workspace.
2. Click Import Reactant from Workspace.
3. Display the product structure in the Workspace.
4. Click Import Product from Workspace.

If you import the wrong structure, you can click the Clear button.

2D sketches of the reactants and the products are displayed in the reaction diagram. These 2D sketches do not necessarily represent the 3D geometry or stereochemistry.

3.3.2 Renumbering Atoms

You can renumber the atoms if the reactant and product numbering schemes do not match, in the Reorder Atoms dialog box, which you open by clicking Reorder Product Atoms. This dialog box shows 2D images of the reactant and product complexes, and allows you to visually select the corresponding atoms for renumbering. The reactants constitute the reference structure and the products constitute the comparison structure (the one that is reordered). Atoms are indicated by their atom numbers, and are colored by element.

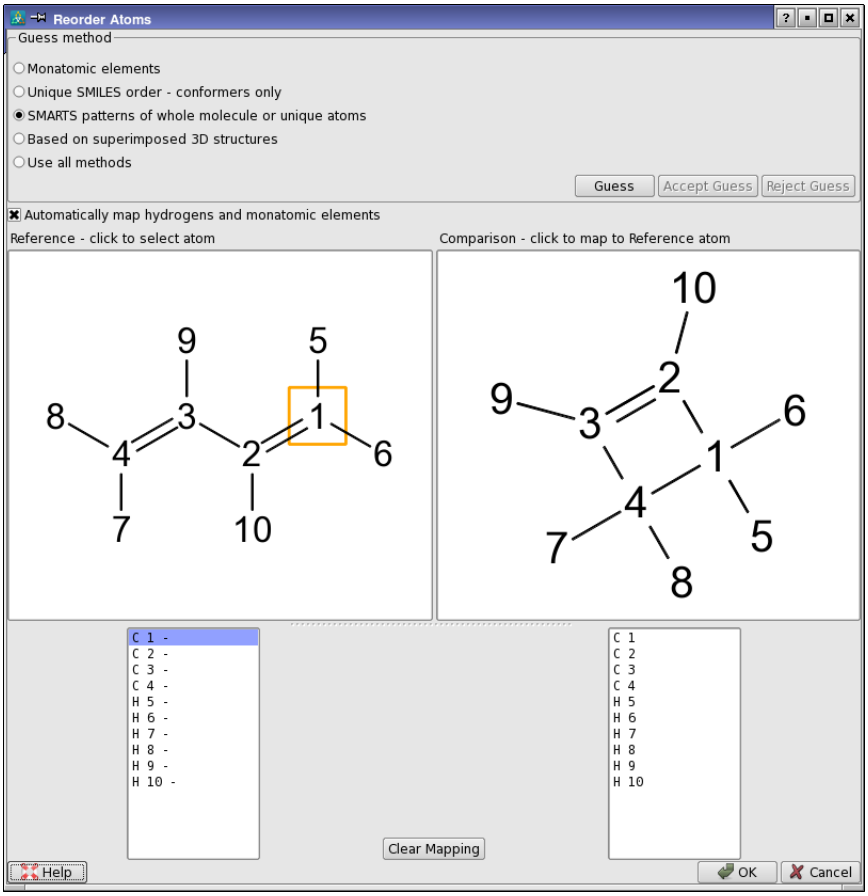

Figure 3.4. The Reorder Atoms dialog box.

There are several ways in which you can use this dialog box to map the atoms of the comparison structure to those of the reference structure.

A. Use the automated detection (guess) tools. Select a guess method and click Guess. The guessed atoms are marked in light blue. If the guess is good, click Accept Guess; if not, click Reject Guess. The atoms are marked in green if the guess is accepted; if it is rejected the markers are removed. The guess methods do the following:

   - Monatomic elements—Map atoms for elements that only occur once in the reference structure and in the comparison structure.
   - Unique SMILES order - conformers only—Map atoms on the basis of the order in the unique SMILES string for the entire reference structure or comparison structure.

The reference structure and the comparison structure must be conformers (no changes in bonding). This method might not be able to determine the mapping of hydrogen atoms.

- SMARTS patterns of whole molecule or unique atoms—Map atoms on the basis of SMARTS patterns, either of individual atoms or of whole molecules. If a SMARTS pattern has only one match in the reference structure and one match in the comparison structure, use that pattern to map the atom numbers. The SMARTS patterns for unique atoms identify individual atoms solely on the basis of their bonding pattern, with no account taken of the identity of the atoms to which they are bonded.
- Based on superimposed 3D structures—Superimpose the comparison structure on the reference structure, and map each comparison atom to the closest reference atom of the same element. If there is no nearby atom of the same element, the mapping of the atom is not done. This method uses the already-mapped atoms for the superposition, so there must be at least three atoms mapped before this method can be used.
- Use all methods—Use all of the applicable methods to determine the mapping between the reference and comparison atoms.

B. Pick corresponding atoms in the two diagrams. First, pick a reference atom, which is then marked with a yellow square. Then pick the corresponding comparison atom. The atoms are marked with green markers.

   If you pause the pointer over a mapped atom, it is marked with a green square, and the mapped atom in the comparison structure is also marked with a green square. This also happens if you select a mapped atom, which allows you to identify which atom it is currently mapped to.

C. Pick corresponding atoms in the two atom lists, reference first. The atoms are identified by element and atom number. The atoms are marked in the diagrams when you pick rows in the lists. The reference rows are terminated with a dash prior to mapping; the mapped comparison atom number is added after the dash when a reference atom is mapped. Rows for unmapped atoms are colored white; rows for mapped atoms are colored green; rows for guessed mappings are colored light blue.

You can also combine any method with automatic mapping of hydrogens and monatomic elements, by selecting Automatically map hydrogens and monatomic elements. Whenever a change is made to the mapping, any hydrogens attached to mapped atoms are mapped if possible, and any remaining atoms that are the only remaining unmapped instances of an element are also mapped. The mapping of hydrogens is done as follows:

- If the reference atom and the corresponding comparison atom have only one hydrogen, that hydrogen is mapped.

- If the reference atom and the corresponding comparison atom have the same number of hydrogens (more than one), and the dihedral angles for the hydrogens in the reference structure can be matched to dihedral angles for the hydrogens in the comparison structure, the hydrogens are mapped.

If you make a mistake in the mapping, you can simply select the mis-mapped atom in the reference diagram or list, and then select the correct atom in the comparison diagram or list.

If you want to clear the entire mapping and start over, click Clear Mapping.

3.3.3 Positioning the Reactants and Products

If you have not already positioned the reactants and products in a pre-reactive or post-reactive complex, you should do so before proceeding. Structures that are pre-positioned close to the transition state provide better reaction paths than structures that are at their equilibrium geometries and far from the transition state. You can use the Probe Scan panel to find pre-positioned states for bimolecular reactions—see Chapter 6. If you do, you will probably need to renumber the atoms in the product complex to match the reactant complex.

For certain reaction types, you can select Pre-form reaction complex if possible to form a complex of the reactants and a complex of the products, to assist in defining the path. The reactive atoms are identified and the structures are positioned with respect to each other to form a pre-reactive or post-reactive complex. This feature is limited to unimolecular decompositions that form two molecules and bimolecular combination reactions that do not involve exchange of atoms (any leaving group comes from only one of the original molecules) So, for example, an S_N2 reaction is acceptable, as the nucleophile combines with the substrate and the leaving group comes from the substrate, but a hydrolysis reaction is not acceptable because the water donates a hydrogen and accepts another fragment.

The positioning is done with rigid-body movement of the molecules. The distance between the molecules is controlled by a molecular radius parameter, set in the VDW radius scale factor text box. When the molecules are positioned in the complex, the intermolecular distances are must be no smaller than the sums of the scaled radii of the molecules involved. A larger scaling factor places the molecules further apart. The molecular diameter is taken to be the largest atom-atom distance plus the van der Waals radii of the atoms involved; the molecular radius is half this value.

3.3.4 Specifying the Reaction Path

The points along the reaction path can be chosen as an evenly-spaced set or as a list of points. The path is defined with a value of 0 for the reactants and 1 for the products. The points that you specify do not include the reactant or product structures, so for example if you choose 10 evenly spaced points, 12 structures are returned: the reactant, the product, and the structures for

each point. Likewise, any points you enter in the Custom point distribution text box are in addition to the reactant point at 0.0 and the product point at 1.0.

You can add points around the approximate location of the transition state, spaced at 0.02 in the path coordinate with 5 points on each side, by selecting Add extra points clustered in transition state region. The presumed transition state location can be chosen as early (25%), midway (50%) or late (75%) in the reaction path, from the Presumed transition state is option menu. Any existing points that fall in the range covered by the added points are removed.

For display purposes, you may want to specify how the bonds (connectivity) are assigned in the interpolated structures. There are three choices on the Determine bonding based on option menu:

- Reactant—Use the connectivity from the reactant for all structures
- Product—Use the connectivity from the products for all structures.
- Transition state—Change the connectivity from that of the reactant to that of the product along the reaction path, with the change occurring in the region of the presumed transition state. In this region, bonds that are broken or formed are represented as zero-order bonds.

3.3.5 Choosing a Coordinate System for the Interpolation

The choice of a coordinate system that is interpolated is critical to finding a suitable reaction path. Cartesian coordinates may be suitable for some reactions, such as the classic S_N2 reaction, $X^- + CH_3Y \rightarrow CH_3X + Y^-$ (if the halides X and Y and the carbon atom remain in the same order). The rearrangement of HCN to HNC cannot be done with Cartesian interpolation, however, as the hydrogen would have to pass through both heavy atoms. A better coordinate system for this reaction is the set of distance coordinates: the HC distance has to increase in a linear interpolation, which forces the hydrogen to go around the CN rather than through.

Three choices of coordinates are offered on the Coordinate system option menu:

- Internal—Use the internal coordinates of the structures (bond distances, bond angles, dihedrals). This is a set of redundant internal coordinates that includes the union of the coordinate sets for both products and reactants. This option can be used to avoid some kinds of atomic collisions along the path, and works for the greatest number of reactions.
- Distance—Use the set of all interatomic distances. This option can help avoid over-estimation of bond lengths.
- Cartesian—Use the Cartesian coordinates of all atoms.

The algorithm proceeds by performing a linear interpolation of the coordinates between the reactants and the products, to produce a set of target coordinates. Interpolation of internal and distance coordinates do not, however, produce a consistent set of Cartesian coordinates, so a Cartesian interpolation is also done as a starting guess, and these Cartesian coordinates are adjusted in a nonlinear least-squares procedure to minimize the difference between the internal or distance coordinates generated from the Cartesian coordinates and those determined from the interpolation.

The orientation of the structures is important for the Cartesian interpolation. Before the interpolation, begins, the product structure is superimposed onto the reactant structure, using the nonreactive (or least reactive) atoms to perform the superposition. This procedure minimizes the changes in the coordinates. It also prevents the lines between corresponding atoms (on which the linear Cartesian interpolation is done) from passing through the same point.

The structure obtained at each step of the interpolation is also superimposed on the reactant structure. This process helps prevent drift (translation or rotation of the entire structure), and also makes visualization of the path easier.

3.3.6 Setting Parameters for Optimizing the Path

As a nonlinear least squares procedure is required for optimizing the path for distance and internal coordinates, some parameters can be set to control the optimization. Further, since short distances are to be avoided, a penalty function can be added for short distances.

To help improve convergence, weight factors are used for the squared coordinate differences in the least squares procedure. These weights can be set in the Bonds, Angles, Dihedrals, and Cartesians boxes. The weights that are available depend on the coordinate type. Increasing the value increases the rigidity of the interpolated coordinates (damps changes). If convergence difficulties are encountered, changing the weights can help. Increasing or decreasing the Cartesian weight can usually remedy troublesome reaction paths more effectively than changing the other weighting terms. When optimizing on distances, each distance is considered a “bond” for weighting purposes.

To avoid short distances, you can specify a penalty in the Short bond penalty box. The penalty is applied as *value*/R, where R is any bond distance. This penalty is available when using internal or distance coordinates.

Another means of controlling convergence is to mix part of the previous step into the current guess. If the previous step was far from the Cartesian interpolation, mixing in some of the previous step should improve the starting guess for the current step. You can specify the amount of the optimized Cartesian coordinates from the previous step to mix into the interpolated guess for the current step in the Previous step mixing text box. Mixing can help to avoid collisions and to create continuous reaction paths. You can also choose to apply the mixing

before or after superposition on the reactant structure, by deselecting or selecting Use post-superposition coordinates for mixing.

Finally, you can choose which end of the reactant to start the interpolation, by choosing from the Interpolation direction option menu: from reactant to product or from product to reactant. For a simple Cartesian interpolation, the path is independent of the direction, but for other coordinate systems, the path may vary with the direction if step mixing is used. The steps are taken in reverse order, but no changes are made in the step numbering or the path coordinate.

3.3.7 Output

When the path has been generated, the output Maestro file contains all of the structures: first the reactants, then the reactant complex (if requested), the steps in the path, the product complex (if requested), then the products. The step index and distance along the path (in the range 0 to 1) are included as entry properties, and the reactive atoms are identified with an atom-level property. To see these properties in the Project Table, you will have to choose to show them explicitly, or show all properties, as they are not shown by default.

3.4 Reaction Energetics for a Compound Series

When studying the effect of substituents on a reaction barrier or a reaction enthalpy, it is useful to have a semiquantitative guide to the relative effects of the substituents at an approximate level before performing full calculations. The more expensive calculations can then be focused on the substituents that are most likely to produce the desired energetics. The semiquantitative results can also be used to construct a QSAR model for the prediction of the barrier or enthalpy for screening of other compounds.

The capability to calculate reaction barriers or reaction enthalpies of a unimolecular rearrangement reaction for a series of related compounds is provided in the Reaction Energetics Enumeration panel. To open the Reaction Energetics Enumeration panel, choose Tasks → Reaction Energetics Enumeration.

The reaction for each compound must be based on a prototype reaction, in which substitutions are made on the structures in the prototype reaction. The structures for the series of compounds are enumerated by addition of functional groups to the structures for the prototype reaction at designated locations. For useful results, the reaction pathway and products should not depend very much on the substituents: the transition states and the products must have similar geometries to those of the prototype structures for the common atoms.

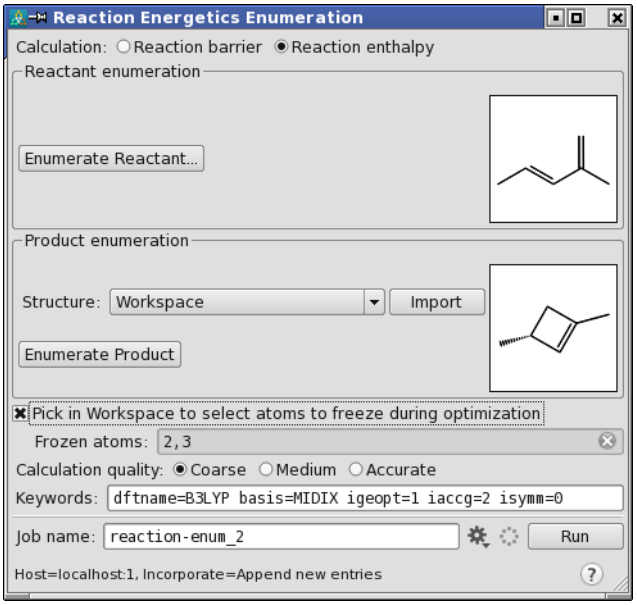

Figure 3.5. The Reaction Energetics Enumeration panel.

Prior to using this panel, you should optimize the geometry of the prototype reactant molecule, and either do a transition state search or optimize the product geometry. All structures must be unimolecular: reactant, transition state, and product. The geometries of these prototype structures are held fixed during the remainder of the calculations. When the structures are enumerated, the geometry of the additional functional groups is optimized in each structure to relieve strain.

The atom numbering in the prototype reactant and the prototype transition state or product must be the same. This is necessary because the attachment points for the substituents must be on the corresponding atoms in these structures. For a transition state, the atom numbering must be the same as that of the reactant used in the search. For a product that is not used in a transition state search, the numbering is not required to be the same as that of the reactant, so you must make sure that it is. One way to do this is to build the product from the reactant in the Workspace with the build tools, breaking and forming bonds *without deleting any atoms*. To ensure that no automatic deletion of hydrogens is done, deselect Adjust number of hydrogens following additive build operations under Builder – Behavior in the Preferences panel.

The reaction enthalpy or reaction barrier for each reaction is calculated from two single point calculations, one on the reactant structure, the other on the transition state or the product structure, and reported as a Maestro property of the reactant structure.

1. Choose the type of calculation.

   The choices are Reaction barrier or Reaction enthalpy. The choice determines whether you need a transition state structure or a product structure in the second enumeration.

2. Enumerate the reactant structures.

   When you click Enumerate Reactant, the Interactive Enumeration panel opens (see Section 2.2 on page 22). In this panel you should import the prototype reactant structure that you optimized, specify the bonds at which you want to substitute other functional groups, and define the set of functional groups to substitute. The structures are enumerated combinatorially when you click Enumerate: all possible substitutions are made, to create a combinatorial library. The enumerated structures are added to the Project Table. This set of structures is used for the reactants.

3. Enumerate the transition state structures or the product structures.

   First choose the source of the prototype structure from the Structure option menu. If you choose File, click Import to import the structure, which is then added to the project. When you click Enumerate Product, the same sets of functional groups that you chose for the reactant are added to the same bonds in the transition state or the product, to create a combinatorial library.

4. (Optional) Pick atoms to freeze during geometry optimization.

   Select Pick in Workspace to select atoms to freeze during optimization. The prototype reactant structure is placed in the Workspace, and you can pick the atoms to freeze. These atoms are marked in the Workspace and listed in the Frozen atoms text box. If you want to clear the frozen atom list, click the X button in this text box. The atoms are frozen in all reactant and product structures. This feature is only available for reaction enthalpies.

5. Run the job.

   When the reactant and transition state or product structures have been enumerated, you can start the calculation. Choose a calculation quality, and make any Jaguar keyword settings that you want to add. The three quality options represent different levels of theory and basis set, which are shown in the Keywords text box. For information on the keywords, see Chapter 9 of the *Jaguar User Manual*.

   Before you click Run to run the job, click the Settings button (gear icon) to make settings for the job. You can distribute the job over multiple processors to reduce the turnaround time, as well as selecting a host on which to run the job.

When the job finishes, the reactant structures and either the transition state structures or the product structures are added to the Project Table, if you chose the output option to append new

entries in the Job Settings dialog box. The reaction enthalpy or the reaction barrier in kcal/mol is added to the reactant structures as a property.

3.5 TST Rate Calculation

The TST Rate Calculation panel allows you to calculate the rate of a reaction using transition state theory, from the output of quantum mechanical calculations on the reactants and the transition state. The calculations allow you to select the prefactor partition functions to use and to include the Wigner tunneling correction.

To open the TST Rate Calculation panel, choose Tasks → TST Rate Calculation.

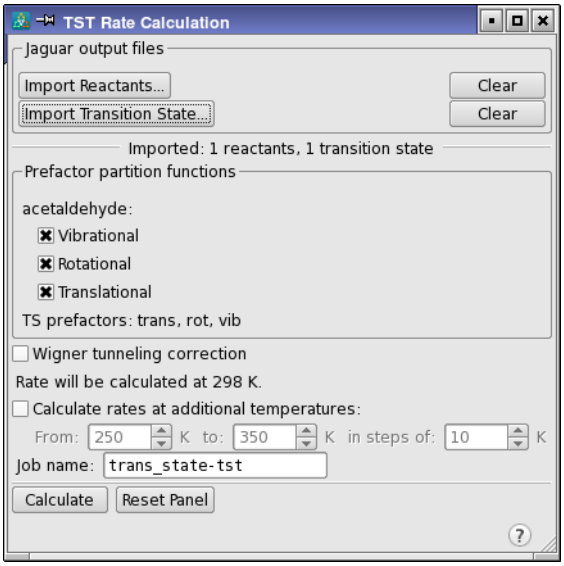

Figure 3.6. The TST Rate Calculation panel.

To run the quantum mechanical calculations:

1. Run a transition state search with Jaguar for the desired reaction and calculate the vibrational frequencies at the transition state.

   Choose Tasks → Quantum Mechanics → Transition State Search to set up the job.

   You must supply the required structures. It is highly recommended that you do a reaction path interpolation calculation, as described in Section 3.3 on page 73, to produce the reactant, product and transition state guesses, and use a QST search.

Choose Vibrational frequencies in the Properties tab to calculate the frequencies after the search, but do *not* select Use available Hessian, as the Hessian from the search is not accurate enough for the frequency calculation.

2. Optimize the geometries of the reactants as separate molecules and calculate their vibrational frequencies.

   Choose Tasks → Quantum Mechanics → Geometry Optimization to set up the job. If the structures are in the Project Table, you can select them and choose Project Table (selected entries) from the Use structures from option menu to run the optimizations in the same job. When you start the job you can distribute the calculations over multiple processors.

   Choose Vibrational frequencies in the Properties tab to calculate the frequencies at the end of the optimization, but do *not* select Use available Hessian, as the Hessian from the geometry optimization is not accurate enough for the frequency calculation.

   The reactants must be in their ground state geometry, not pre-positioned for reaction in a reaction complex. If the reactants are only available in the pre-reactive complex, you can use Entry → Split → By Molecule in the Project Table to split the entry into separate molecules, and then run the geometry optimization on each of these molecules.

3. If you want to calculate the backward rate as well as the forward rate, optimize the geometries of the products as separate molecules and calculate their vibrational frequencies, using the same procedure as for the reactants.

When the jobs finish, you can perform the rate calculation in the TST Rate Calculation panel.

To calculate the rates:

1. Specify the Jaguar output files to use for the rate calculation.

   These files are the text output (`.out`), not the structure output files.

   Click Import Reactants to import the reactant output files. You can use this button more than once to import reactant files separately, or you can select multiple files to import them all at the same time. Each file must contain the results of a calculation on a reactant at its minimum geometry. This is not the same as the "reactant" file you use in the transition state search, which must contain all the reactants, pre-positioned for the search.

   Click Import Transition State to import the transition state output file. Clicking this button again and choosing another file replaces the previous transition state.

   If you make a mistake, you can click the Clear button to remove the reactants or the transition state.

2. Choose the prefactor partition functions to use.

   By default, all three partition functions are used in the prefactor, on the assumption that the molecule is free to move. If it is confined but still able to rotate, deselect Translational; if it is not able to translate or rotate, deselect both Translational and Rotational. For the transition state, a rotational partition function is used if all reactants have a rotational partition function or are monatomic, and a translational partition function is used if all reactants have a translational partition function.

3. If you want to include the Wigner tunneling correction in the rate calculation, select Wigner tunneling correction.

4. If you want to calculate rates at a range of temperatures as well as 298.15 K, select Calculate rates at additional temperatures and specify the temperature limits and interval in the boxes.

5. Enter a job name, and click Calculate.

When the calculation finishes, the rate is displayed in a panel that opens. If you calculated rates over a temperature range, they are displayed in a table and plotted. You can copy the results from the table to the clipboard (with CTRL+C or ⌘C), and then paste them into another application. The rates are also available in the log file for the job (*jobname*`.log`). If the job fails, the log file reports the reason for the failure. No structural output is produced for this job.

To start again or to calculate a new rate, click Reset, which clears all data from the panel and resets all settings to their defaults.

If you have calculated the forward rate for a reaction and want to calculate the backward rate, you can clear the reactants files, and import the optimized product outputs as the "reactants", then proceed with the rest of the setup and the calculation.

3.6 Heats of Formation

Heats of formation and atomization energies can be calculated with the Heat of Formation panel, which you open by choosing Tasks → Heat of Formation. This panel is described in detail in Section 5.4 of the *Jaguar User Manual*.

Optoelectronics

The Materials Science suite provides some capabilities for calculating properties that are relevant to optoelectronics, in addition to existing Jaguar features for calculating molecular properties.

4.1 Optoelectronic Properties

Electronic properties of molecules relevant to optoelectronics can be calculated via the Optoelectronics Calculations panel, and viewed in the Optoelectronics Results panel. These properties are the oxidation and reduction potentials, hole and electron reorganization energies, singlet-triplet excitation energies, triplet reorganization energy, and electronic absorption spectra.

To open the Optoelectronics Calculations panel, choose Tasks → Optoelectronics → Perform Calculations. To view the results, choose Tasks → Optoelectronics → View Results.

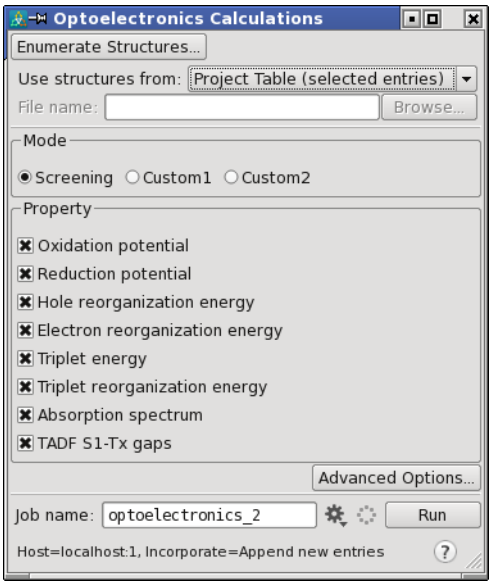

Figure 4.1. The Optoelectronics Calculations panel.

One of the main intended uses of this panel is to screen a set of related molecules for properties that are of importance in optoelectronics. For this purpose, it is useful to generate the set of related molecule by varying a functional group at a particular position on a reference molecule. This can be done in the Interactive Enumeration panel, which you can open by clicking the Enumerate Structures button, or from the Tools menu. (See Section 2.2 on page 22 for details.) As the structures are optimized as part of the optoelectronics calculation procedure, any structural deficiencies in the enumeration should no longer be present when the properties are calculated. The results can be used as the basis for a QSPR model, or simply examined directly to locate structures that show improvements in key properties. The Optoelectronics Results panel allows you to show scatter plots of any two properties, and the Spectrum Plot panel allows you to plot multiple spectra for comparison.

4.1.1 Properties and Methods

All calculations begin with a gas phase optimization of the ground state, neutral molecule. This calculation is only performed once and used for all properties. All successive calculations are run with the same method and basis set. If calculations on the cation or anion are required for more than one property, they are only calculated once. For the anion calculations, it may be advisable to add diffuse functions to the basis set.

4.1.1.1 Screening Calculations

The Screening calculation method (Mode) is intended to produce high quality results with a small basis set. The properties calculated with this method include corrections based on experimental data (see below).

This method uses the MIDI! basis set (Jaguar basis MIDIX). Because this basis set lacks d functions on carbon atoms, calculations generally run much faster with this basis set than with more common basis sets such as 6-31G*. Because d functions are included on other heavy atoms including N, O and F, results are similar to 6-31G* in quality and significantly improved over 3-21G(*). However, MIDI! does not have coverage for many elements in the periodic table, so by default the following algorithm is used to assign the basis set for screening calculations, so that they can be run over most of the periodic table. For any element for which MIDI! is not defined, 6-31G* is used if it is defined for that element; if 6-31G* is not defined for that element, LACV3P is used. If the basis set for screening is changed to any basis set other than MIDI! (`basis=midix`), this algorithm is not applied.

4.1.1.2 Oxidation and Reduction Potentials

Two different methods can be used for oxidation and reduction potentials: a Koopmans' approximation and an adiabatic method. The selection of the methods can be made in the Advanced Options dialog box.

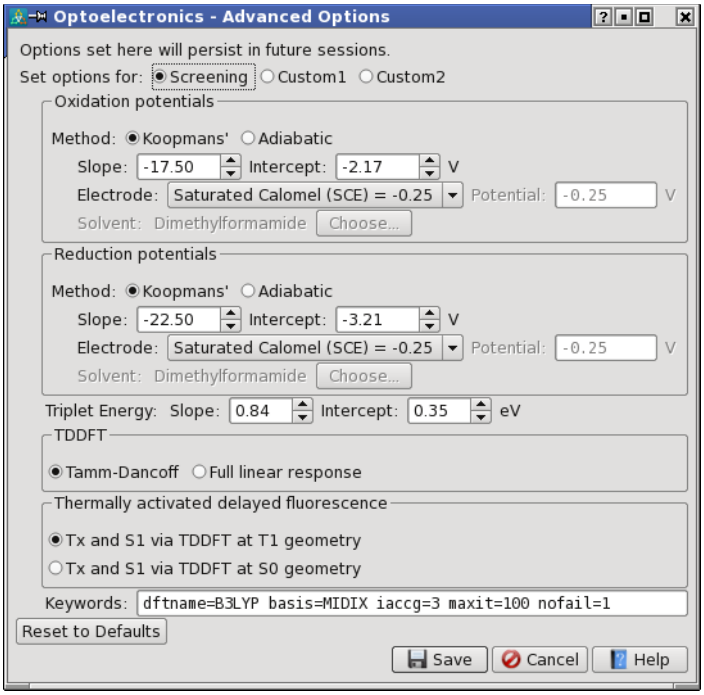

Figure 4.2. The Optoelectronics - Advanced Options dialog box.

For the Koopmans approximation, the potential is calculated with the following formula:

Potential = slope * Orbital_energy + intercept

The value of Orbital_energy is taken to be the HOMO energy from the neutral molecule for the oxidation potential, and the LUMO energy for the reduction potential. The values of the slope and intercept were obtained by linear regression against experimental oxidation and reduction potentials over a wide range of OLED materials, including hole and electron transporting materials, emitting materials, organics and organometallic complexes. These values were developed using B3LYP with the default basis set for screening calculations and are not directly applicable to other methods and basis sets.

Koopmans' approximation only requires a single calculation on the neutral molecule in the ground state. It is the default method for Screening calculations, and is significantly faster and more robust than the adiabatic method. Because it has been parameterized to experimental data, it is likely to produce results that are as good as or better than the adiabatic method.

The adiabatic potentials are calculated with the following formulae:

Oxidation Potential = –(E_electrode + E_electron + E_ion – E_neutral)
Reduction Potential = –(E_electrode + E_ion – E_neutral – E_electron)

This method requires calculations on the neutral species and the ions. The ion geometries are optimized in the gas phase, just as for the neutral molecule. Single-point calculations are performed with aqueous continuum solvation (PBF) at the optimized gas-phase geometries. E_electron is taken as –4.44 eV and E_electrode is the potential of the electrode chosen in the Advanced Options dialog box.

It is advisable to include diffuse functions in the basis set when calculating reduction potentials with the adiabatic method, to provide a proper description of the anion.

4.1.1.3 Hole and Electron Reorganization Energies

The reorganization energy is the difference between the energy required for the neutral molecule to relax from the ion geometry to the neutral geometry and the energy required for the ion to relax from the neutral geometry to the ion geometry.

E_reorg = (E_opt_neutral – E_vert_neutral) – (E_opt_ion – E_vert_ion)

Geometry optimizations are performed on the neutral and the ionic species, and single-point calculations for the neutral at the ion geometry (E_vert_neutral) and the ion at the neutral geometry (E_vert_ion) are then performed, all in the gas phase.

4.1.1.4 Triplet Energy and Triplet Reorganization Energy

The triplet energy property is the energy of the relaxed lowest triplet state relative to the energy of the relaxed ground state. The formula used includes corrections that can be parametrized:

E_trip = slope * (E_triplet_state - E_ground_state) + intercept

The energy of the triplet state is calculated using unrestricted DFT (UDFT) to optimize its geometry. The slope and intercept were parametrized for the Screening calculation method, using B3LYP and the default screening basis set.

The triplet reorganization energy is defined in a similar manner to the hole and electron reorganization energies:

E_trip_reorg = (E_opt_ground – E_vert_ground) – (E_opt_triplet – E_vert_triplet)

Geometry optimizations are performed on the ground state and the triplet state, and single-point calculations for the ground state at the triplet geometry (E_vert_ground) and the triplet at the ground state geometry (E_vert_triplet) are then performed, all in the gas phase.

4.1.1.5 Absorption Spectrum

The absorption spectrum is calculated from vertical excitation energies computed with TD-DFT (`itddft=1`) at the neutral molecule geometry. You can choose to use the full linear response instead of the Tamm-Dancoff approximation (`itda=1`, the default) in the Advanced Options dialog box. Five states are calculated (nroot=5). The spectrum can be viewed by importing the spectrum file (*jobname*`_uvv.spm`) into the Spectrum Plot panel, which can be opened with Tools → Plot Spectra.

In addition, this calculation computes properties based on the full spectrum. This full spectrum is obtained by line-broadening the computed transitions. The broadening is done by placing a Lorentzian curve centered on each transition. Each curve has a line width of 40 nm and a height equal to the oscillator strength of the transition. The sum of all curves is then taken to form the full absorption spectrum. The same method is used when plotting the spectrum in the Spectrum Plot panel. From this full spectrum, the following properties are computed.

- Lmax—The wavelength in the visible region for which the spectrum has the highest intensity. This might not correspond to the wavelength of the lowest energy transition because a) a higher energy transition may have higher intensity, or b) two transitions may add together to form a peak centered on neither transition. Since 390 nm is considered the short wavelength cutoff of the visible spectrum, an absorption spectrum with no or only trivial peaks in the visible spectrum will typically show an Lmax value of 390.
- Red Area/Green Area/Blue Area— These are the integrated areas under the absorption spectrum in the stated red, green or blue region. For the purposes of these properties, the region definitions are:

  blue: 390-490
  green: 490-590
  red: 590-750

  These areas are useful in a relative comparison of the shifting absorption window between structures. They can, for instance, offer a quick analysis of which structure in a series has the most (or least) absorption in the green region. Since the spectra are scaled by the computed oscillator strength of the transitions, a change in area can occur due to a change in intensity or a shifting of the peak to shorter or longer wavelengths.

4.1.1.6 Thermally-Activated Delayed Fluorescence (TADF)

The energy gap between the lowest three triplet states (T1, T2, and T3) and the first excited singlet state (S1) state is calculated using TDDFT, using the S0 (ground) state as the reference. The gap can be calculated either at the equilibrium geometry of the T1 state or the equilibrium geometry of the S0 state, which you can choose in the Advanced Options dialog box. This gap is useful for assessing the possibility of thermally-activated delayed fluorescence.

4.1.2 Setting Up and Running the Calculation

To set up a calculation:

1. Choose the source of the structures for the current task from the Use structures from option menu.
   - Project Table (selected entries)—Use the entries that are currently selected in the Project Table.
   - Workspace (included entries)—Use the entries that are currently included in the Workspace, treated as separate structures. The Workspace should not contain a scratch entry.
   - File—Use the structures from the specified file. Click Browse and navigate to the file you want to use. You can also enter the file name in the text box.
2. Select an option for the type of calculation that is done.
   - Screening—rapid calculation based on a well-parametrized model for the redox potentials and triplet energy using a small basis set, and suitable for screening a larger number of molecules.
   - Custom1 and Custom2—run a custom calculation to your own specifications. The customization is done in the Optoelectronics - Advanced Options dialog box.
3. Select the properties that you want to calculate.

   By default, all of them are selected.
4. Enter a name for the job in the Job name text box.
5. Click Run, or click the Settings button to make job settings before running the job.

You can distribute the job over multiple processors. The number of processors should not exceed the number of molecules in your input. See Section 1.3 on page 6 for more information on job submission tools.

4.1.3 Viewing the Results

The Optoelectronics Results panel can be used to detect trends and outliers in properties calculated with the Optoelectronics Calculation panel. The panel contains a table that displays all the data, and a plot that displays user-specified properties.

The plot makes it easy to find interesting outliers, such as compounds that have a high triplet energy but a low reduction potential. Points can be colored by a third property, which may show (for example) that a cluster of outliers on a plot of triplet energy vs Lmax all tend to have high oxidation potentials. Spectral data can also be conveniently plotted from this panel.

To open the Optoelectronics Results panel, choose Tasks → Optoelectronics → View Results.

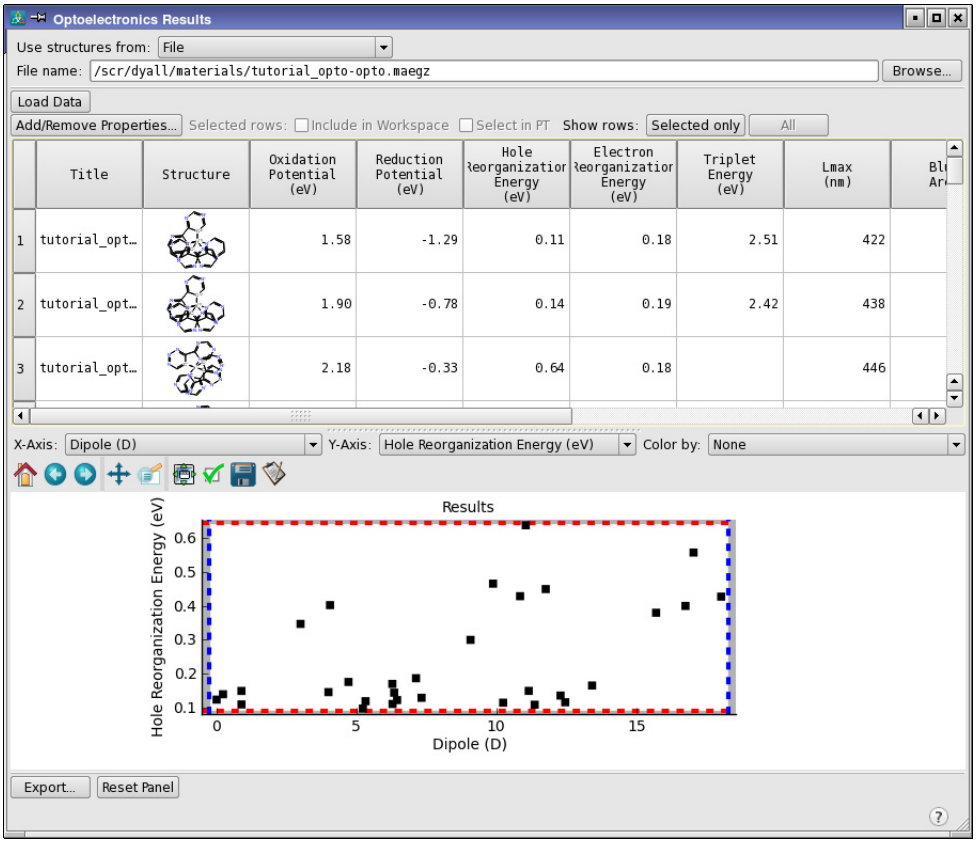

Figure 4.3. The Optoelectronics Results panel.

To load a set of results, choose the source of the structures from the Use structures from option menu, open the file if you chose File, and click Load Data. The results are read in, analyzed, and displayed in the table. (The structures do not actually need to have optoelectronic properties, as the panel is a general-purpose tool that can be used for any set of results.)

To clear all data from the panel and reset all settings to the defaults, click Reset.

4.1.3.1 Properties Table

The properties table displays properties for the structures. By default, the entry title, the 2D structure, and the primary properties for optoelectronics calculations are shown. You can select multiple rows, to apply an action. You can also copy and paste data from the table in to another application, using CTRL+C (⌘C). You can resize the columns or the rows by dragging the borders in the heading row or the row number column.

If you want to add other properties from the Project Table, or remove properties from the table, click Add/Remove Properties. A property selector opens, in which you can choose the properties to show in the table. By default, only optoelectronics properties are displayed. This allows you to show correlations between optoelectronic properties and other molecular properties.

The panel can interact with the Project Table and the Workspace. To do this you can select options for actions to take on the selected rows. The options are:

- Include in Workspace—Display the entries for the selected rows in the Workspace. All other entries are excluded.
- Select in PT—Change the Project Table selection to only those entries that correspond to the selected rows in the properties table (deselecting all other entries).

The action is applied automatically as you change the row selection.

You can restrict the range of rows shown in the table and plotted in the plot area by selecting them in the table and clicking Selected Only. To redisplay all rows, click All.

If the Absorption Spectrum property was selected in the Optoelectronics Calculations panel when computing the current results, the properties table includes a Spectrum column that contains a button labeled Plot for each row where the absorption window calculation was successful. Clicking this button opens the Spectrum Plot panel and shows the computed absorption spectrum. If the current working directory is different from the directory in which the calculation results are stored, a file dialog open requesting the location of the Jaguar spectrum file for this entry.

If you want to import the properties into a spreadsheet, you can export the table contents to a CSV file. Clicking Export opens a file selector, in which you can navigate to a location and name the file.

4.1.3.2 Property Scatter Plot

The plotting tool allows you to show a scatter plot of two properties, which you can choose from the X-Axis and Y-Axis option menus. Only numerical properties shown in the table can be selected.

You can color the plot points by a chosen property, using a blue-green-red color ramp, with blue for low values and red for high values. This feature allows you to display the dependence on a third property.

The panel has a toolbar that you can use to configure the plot or to save an image of the plot. The toolbar buttons are described below.

Reset
Reset the plot to the original pan and zoom settings.

Back
Display the previous view of the plot in the view history

Next
Display the next view of the plot in the view history

Pan/zoom
Pan the plot by dragging with the left mouse button, zoom by dragging with the right mouse button.

Zoom to rectangle
Drag out a rectangle on the plot to zoom in to that rectangle.

Configure subplots
Configure the margins and spacing of each plot in the panel.

Edit axis and curve parameters
Make settings for the title, range, labeling, and scale of the axes; the color, style, and width of lines; and the color, style, and size of markers.

Save image
Save an image of the plot to file. Opens a file selector in which you can browse to a location, select the image format, and name the image.

Copy to clipboard
Copy an image of the plot to the clipboard. You can then paste it into another application. This button is only available in some panels.

The plot shows horizontal red dotted lines and vertical blue dotted lines. These lines can be dragged in the plot area to create a selection square. The rows in the properties table corresponding to the points in the white central square are selected. Rows corresponding to the points in grey outer regions of the plot are deselected.

4.2 Optimization of Optoelectronic Properties

The Materials Science suite provides a tool for modifying structures to optimize a selection of optoelectronic properties, by mutating structures with a genetic algorithm. The goal is to generate a diverse set of structures that have the desired properties. In this sense, it is a discovery tool rather than an optimization tool. Each structure is considered an “individual” in a population, and is mutated by changing aspects of its chemistry into another structure.

The optimization can be set up and run in the Genetic Optimization panel, which you open by choosing Tasks → Optoelectronics → Genetic Optimization in the main window.

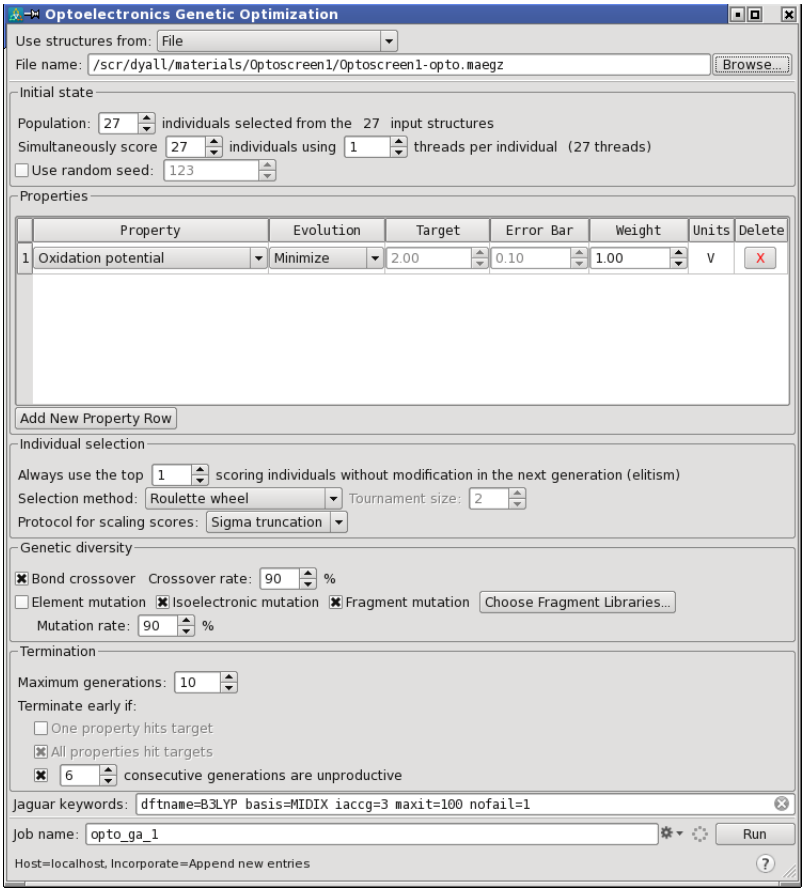

Figure 4.4. The Optoelectronics Genetic Optimization panel.

4.2.1 Selecting the Initial Structures and Initial State

The first step is to set up the initial state for the evolution of the structures.

As the goal of the optimization is to find new, diverse structures, the input structures should not be closely related (as in a congeneric series, for example). You can choose the source of the structures for the current task from the Use structures from option menu:

- Project Table (selected entries)—Use the entries that are currently selected in the Project Table.

- File—Use the structures from the specified file. Click Browse and navigate to the file you want to use. The file name is displayed in the text box when you click Open in the file selector. You can also enter the file name in the text box.

The input structures you specify do not all have to be used in the genetic algorithm: the initial population can be a random selection from these structures. You can specify the number of individuals (structures) to use from the set of input structures in the Population box. The number must be less than or equal to the number of input structures. If it is less than the input number, a selection is made at random. The population (number of individuals) is maintained at each generation of the genetic optimization.

As random processes are used in the optimization, you can specify the seed used for the random number generator, by selecting Use random seed and specifying the seed in the box. This option allows you to reproduce the results of an optimization with the same input structures. Otherwise a default seed is used, which changes for each run.

4.2.2 Selecting the Properties to Optimize

You can optimize several properties simultaneously, if you wish, set targets for the properties, and set weights in the optimization for each property.

Each property to be optimized is specified by a row in the Properties table. You can choose the property to be optimized from the option menu in the Property column, and set the goal for the optimization of the property in the Evolution column. If the goal is to achieve a specific value or at least a certain minimum or maximum value or, you can set the target value in the Target column, and for a specific value, the allowed deviation from the final value in the Error Bar column.

You can adjust the weight of the property in the scoring function by setting it in the Weight column. You might want to use this value to compensate for different units or property ranges.

To add another property row to the table, click Add New Property Row. To delete a property row, click the button in the Delete column.

4.2.3 Setting Up the Selection Process

Several controls are provided on how to individuals are selected as parents for the next generation. The selection may be based on the scoring function for the fitness of the individuals.

To specify the number of individuals to carry forward to the next generation without modification, set the number in the Always use the top *N* scoring individuals without modification in the next generation box. The individuals with the highest scores are selected (elitism). Set the value to 0 to turn off this feature.

For the remaining individuals for the next generation, you can choose a method for selecting the individuals that are used as the parents for the next generation from the Selection method option menu. The selection is done to fill the places in the population after the highest-scoring individuals are selected (if any). The choices are:

- Rank—Select individuals at random, with the probablility of selection proportional to the rank of the individual. The rank is the index of the individual in a list sorted by increasing score: the highest scoring individual has the highest index and thus the highest rank. (This is a roulette wheel method in which the pocket size is the rank.)
- Roulette wheel—Select individuals at random, with the probability of selection (pocket size) proportional to the score.
- Tournament—Select the highest-scoring individual from a randomly selected pool of the size specified in the Tournament size box. The selection of members of the pool is done by uniform random sampling.
- Tournament with roulette—Select the highest-scoring individual from a randomly selected pool of the size specified in the Tournament size box. The selection of members of the pool is done by roulette-wheel random sampling, where the probability of selection is proportional to the score.
- Uniform—Select individuals by uniform random selections. In this method, all individuals have the same probability of selection: there is no bias toward the fitter individuals.

You can also choose a protocol for scaling scores to differentiate between individuals towards the end of the optimization, where scores may not be well separated. The protocols are standard genetic algorithm protocols, information on which can be found in textbooks or online.

4.2.4 Setting Up the Mutations

The types of mutations that are made to produce new structures can be specified in the Genetic diversity section. You can choose one or more of the following mutation types:

- Bond crossover—Swap fragments from two structures. An acyclic single bond that does not involve hydrogen is chosen at random in each structure, to create two fragments in each structure. One of the fragments in one structure is exchanged with one of the fragments in the other structure, to create two new structures. The frequency at which this occurs can be set in the Crossover rate box.
- Element mutation—Mutate an element in the structure to another element in the same group of the periodic table, e.g. O to S. Hydrogen is mutated to a halogen.
- Isoelectronic mutation—Mutate an element in the structure to another element in the same row of the periodic table, with addition or deletion of hydrogens to maintain the same

number of electrons, e.g. NH to O or to CH2.

- Fragment mutation—Replace a fragment on a structure with a fragment selected at random from the specified fragment libraries. The fragment that is replaced is one that has a single acyclic bond that is not to a hydrogen atom. Click Choose Fragment Libraries to select the libraries to use.

  The available standard libraries include some of the fragment libraries available in the Build panel, the CombiGlide default library, and an optoelectronics library. You can also specify your own set of fragments by selecting Custom and opening a file that contains the structures. All hydrogen atoms on these structures are considered as candidates for removal to form a bond to the individual that is being mutated, and one of these is chosen at random.

The mutation rate (the frequency of mutations) for the element, isolelectronic, and fragment mutations can be set in the Mutation rate box.

4.2.5 Setting Termination Criteria

You can terminate the optimization in several ways.

To limit the length of the run, you can specify the maximum number of generations in the Maximum generations box, after which the optimization stops.

Otherwise, you can terminate the optimization early by selecting options for conditions on the property values and their targets:

- One property hits target—Stop the optimization if the target for one of the properties is attained (greater than, equal to, or less than the target value). This option is only available if at least one property has a target value.
- All properties hit targets—Stop the optimization if the targets for all of the properties are attained (greater than, equal to, or less than the target value). This option is only available if more than one property has a target value.
- *N* consecutive generations are unproductive—Stop the optimization if there is no improvement in the total score after the specified number of generations.

4.2.6 Setting Job Options and Starting the Job

The optimization involves running a set of Jaguar jobs on each structure in each generation. You can run these jobs simultaneously, by specifying the number of simultaneous jobs in the Simultaneously score *N* invididuals box, and you can use multiple threads for each job by setting the value for using *M* threads per individual. You should not set the number of jobs to more than the number of individuals (the population size). If you have more processors avail-

able than the population size, setting the number of threads per individual to a value greater than 1 will give faster turnaround. If not, it is more efficient to set the number of simultaneous jobs as high as possible.

You can also set keywords for the Jaguar calculations in the Jaguar keywords box, if you want to use something other than the defaults. A geometry optimization is performed on each structure, so you may want to consider including optimization-related keywords if you encounter failures.

When you have made all the settings you want, enter a job name in the Job name text box, and click Run to start the job immediately, or click the Settings button to make job settings first. If you are running jobs simultaneously or using multiple threads, you should click the Settings button to choose a multiprocessor host for your job.

4.2.7 Monitoring and Examining the Results

As the jobs can take a long time, it may be useful to examine the results as it is running, for example to assess the progress or success of the optimization, or to make use of structures that meet some criteria before the job finishes. You can do this in the Optoelectronics Genetic Optimization Viewer panel, which you open by choosing Tasks → Optoelectronics → Genetic Optimization Monitor in the main window.

When you click Load New Job a panel opens so you can select the job. You can either select Load from job database, then select a job from the table of jobs, or you can select Manually locate GA directory and click Browse to open a directory selector and navigate to a directory that contains the job results. This allows you to examine a job for which the job record no longer exists in the job database.

Clicking Refresh Current Job updates the results for the job that is loaded. This action is only effective if the job is still running.

To view 2D structures together with scores and property values, arranged in a grid in a separate window, select Show structure window. You can set the number of columns in the grid, and display the structures from each generation in a separate row. You can select multiple structures, and either incorporate them into the project or remove them from the structure window. Structures are not incorporated again if they have already been incorporated.

The Summary tab provides a summary of the job, including the properties chosen for optimization and the criteria for optimizing the properties, the parameters set for the genetic algorithm, and the log file for the job.

The panel has three tabs, which offer different ways of assessing the progress of the optimization.

4.2.7.1 Min/Max Plot

In the Min/Max Plot tab, you can display the minimum value and the maximum value of any property as a function of the generation. For the scores, if the maximum is not increasing, then the optimization is not making progress. If the maximum is not increasing much and the spread between the maximum and the minimum is increasing, the process is generating structures whose properties are less desirable. You then might want to adjust the parameters to increase the generation of improved structures, or you might want to consider what kinds of mutations you are performing.

You can choose the property to display in the plot area and select the statistics to plot. If you select both the minimum and the maximum, the area between the lines is colored light green, to highlight the range of values observed. Pausing the pointer over a point displays the 2D structure and property values for that structure; the points (circles) are only plotted for the minimum and maximum. Clicking (or right-clicking) on a point displays a menu that allows you to add the structure to the Structure Window, incorporate the structure into the project, or incorporate all structures into the project.

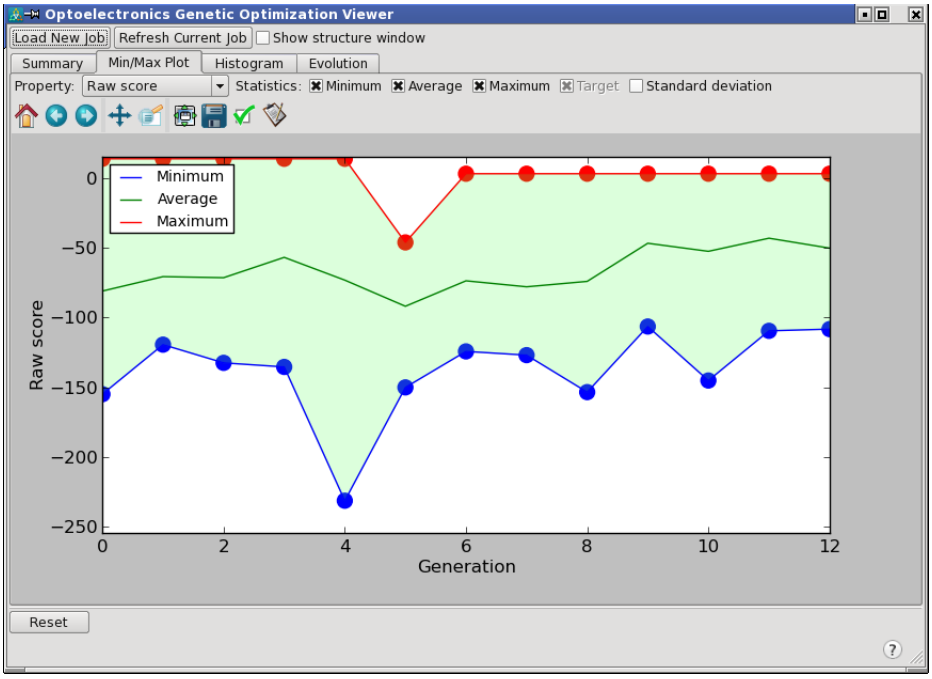

Figure 4.5. The Optoelectronics Genetic Optimization Viewer panel, Min/Max Plot tab.

4.2.7.2 Histogram

In the Histogram tab, you can view how many structures had a particular range of values, color coded by generation. From this view you can assess whether the number of structures in the desirable ranges is increasing with each generation. You can choose the property to display, and set the number of bins for the property values.

Each bar in the histogram is partitioned into regions by generation and color-coded according to the legend on the left. Pausing the pointer over a region shows information on the properties for the generation represented in that region of the bar. If there are fewer than 4 structures represented, information on all properties for each structure is shown, including the 2D structure. If there are 4 or more structures represented, the ranges of all properties are shown.

If you click on a region, a menu is shown, which allows you to show the structures from that generation and bin (the region) or the structures from the entire bin (the bar); and to incorporate structures into the project from the generation and bin, the entire bin, or the entire set of structures.

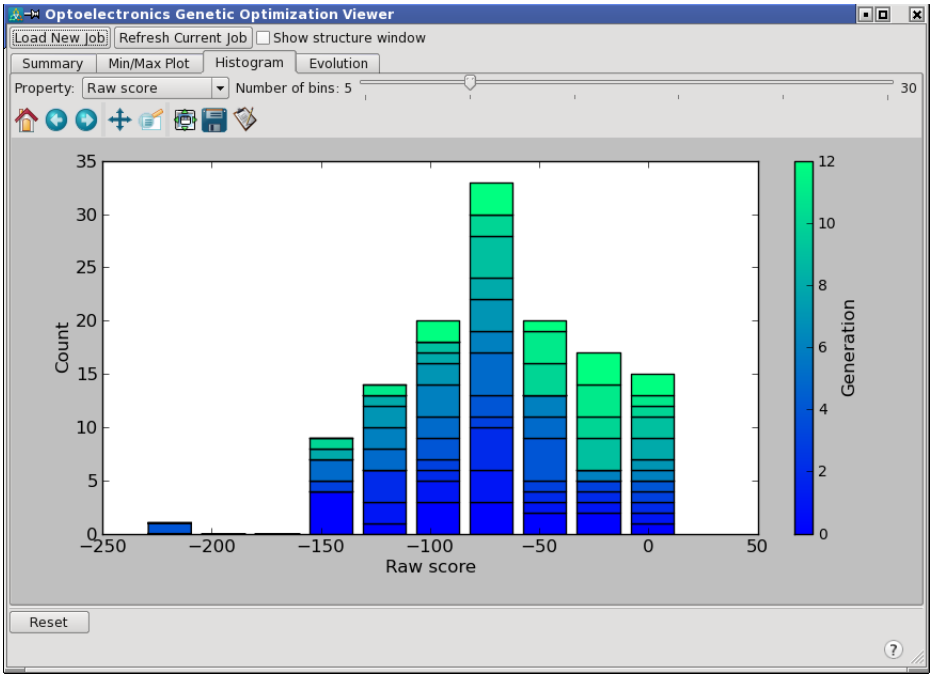

Figure 4.6. The Optoelectronics Genetic Optimization Viewer panel, Histogram tab.

4.2.7.3 Evolution

In the Evolution tab, you can view the family tree of any particular individual in any generation. The tree is marked with green lines to the parents and blue lines to the children, and the individuals are colored by a property value. This allows you to see how the property value is changing between generations. The properties of the family (parents, individual, children) are shown in the Structure Window so you can examine all the properties, not just the one used for coloring. You can choose the property to display and the color map for coding the property values.

Each generation is shown as a horizontal bar, partitioned into rectangles for each individual. The rectangles are color coded by the property value. The tooltip for a rectangle shows the 2D structure and all of the properties.

Clicking a rectangle displays a green line connecting the individual to the parent (for mutation) or parents (for crossover), and a blue line connecting the individual to its children. It also adds all of these structures to the Structure Window. Shift-clicking on any of the parent or children rectangles extends the family tree to the previous or next generation from that individual.

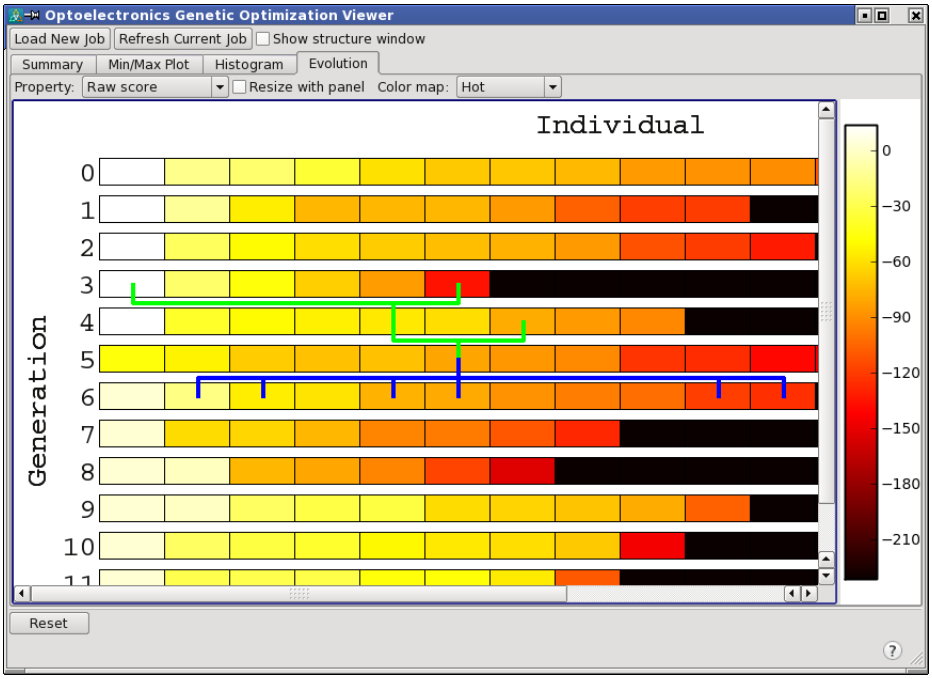

Figure 4.7. The Optoelectronics Genetic Optimization Viewer panel, Evolution tab.

Right-clicking in a rectangle displays a menu, which you can use to show the structure in the Structure Window, incorporate the structure, the generation, or all structures into the project, or clear the family tree display.

4.3 Charge Transfer Rate

The Electron Coupling panel can be used to calculate carrier hopping rates in an amorphous structure. It is mainly designed for the results of an MD simulation with a homogeneous system, but it can be used for any structure consisting of multiple molecules. Marcus theory is used for the hopping rate, based on DFT calculations for the electron transfer between donors and acceptors with either full wave function or dimer frontier orbital splitting calculations of the coupling matrix element. Reference 2 gives an excellent review of this area.

To open the Electron Coupling panel, choose Tasks → Optoelectronics → Electron Coupling.

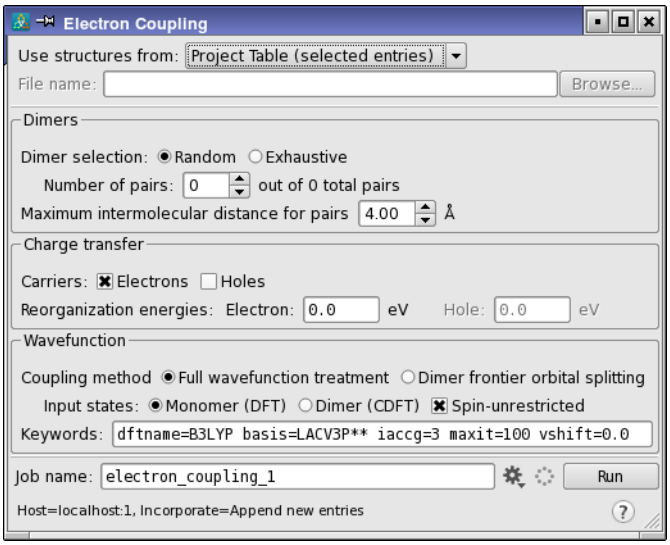

Figure 4.8. The Electron Coupling panel.

The basic procedure for running a calculation is as follows:

1. Create a structure that contains multiple molecules.

   To set up the structure with MD, you can use the Disordered System Builder panel (see Section 2.6 on page 39) and then run a simulation with the Molecular Dynamics panel. You can also import structures from other sources into Maestro. Although you can use the panel for mixtures, further approximations are made in this case that could adversely affect the results.

2. Select the structure for use in the calculations.

   You can choose the source of the structure from the Use structure from option menu.

3. Choose how to select the pairs of molecules ("dimers") between which the hopping rate is calculated.

   You can choose to select dimers at random or to perform an exhaustive calculation based on all possible dimers that are neighbors (have atoms within 4 Å). Random selection is a compromise between speed and accuracy. If you decide on random selection, you must also specify the number of pairs of molecules to choose, in the Number of pairs box.

4. Choose the carrier type, from Electrons or Holes, or both.

5. Specify the reorganization energies for the carriers.

   You can calculate the reorganization energy with the Optoelectronics Calculations panel (see Section 4.1 on page 87). The reorganization energy is assumed to have been calculated for the isolated, ground state relaxed molecule, and is assumed to be independent of the geometry in the mixture. If you have a heterogeneous system, you must decide how to treat the reorganization energy, which is specified here as a single value and thus cannot be given for different components.

6. Choose the coupling method.

   - Full wavefunction treatment—Use the wave functions for the species in which the charge is localized on one or the other monomer to calculate the coupling matrix element. You can use either dimer wave functions or monomer wave functions by choosing one of the Input states options. You can also choose to run either UDFT or RODFT calculations by selecting or clearing the Spin-unrestricted option.
   - Dimer frontier orbital splitting—Use the dimer frontier orbital approximation to calculate the coupling matrix element. In this approximation, the matrix element is calculated from the difference between the LUMO and the LUMO+1 orbital energies for electron transfer, and the difference between the HOMO and the HOMO+1 orbital energies for hole transfer, taken from calculations on the neutral dimer.

7. If Full wavefunction treatment was chosen, choose the type of input states to use.

   The matrix elements for the hopping are calculated using QM wave functions based on DFT calculations. All calculations are run as single-point Jaguar calculations at the geometry of the input structure. The two alternatives are:

   - Monomer (DFT)—Run calculations on the donor and acceptor of a pair independently, with the charge localized on one or the other of the two. As the calculations are independent, they can be run with normal DFT methods. This involves a calculation on each of the monomers with and without the charge, 4 calculations in all.

- Dimer (CDFT)—Run two calculations on the dimer and constrain the charge to lie on the donor in one and the acceptor in the other, using constrained DFT (CDFT).

8. If you want to set any Jaguar keywords for the calculation, add them to the Keywords text box.

   The default keywords are recorded, but you can change them if you want. If you modify the basis set, you should choose a basis set that has polarization and diffuse functions, if possible, as these are important for calculating the electron transfer rate.

   There is a chance that a QM calculation can result in an excited state rather than the ground state. CDFT calculations appear to be particularly susceptible to this issue. Therefore, it is always important to check the HOMO and LUMO values listed in the Project Table for the initial and final states to verify that the HOMO energy is lower than the LUMO energy. If these values are reversed, the calculation should be repeated, adding the setting `vshift=0.0` in the Keywords text box. By default, the value is 0.2 for hybrid DFT functionals and 0.3 for pure DFT.

9. Run the job.

   When the job is run, each Jaguar job is run sequentially, but you can run individual Jaguar jobs in parallel. Doing this is useful if the molecule or the basis set is large. You can run dimer splitting jobs or DFT (monomer) jobs in parallel, but you cannot run CDFT (dimer) jobs in parallel.

The output of the calculation depend on the coupling method chosen. For each dimer, a set of structures is produced. For the dimer frontier orbital splitting method, the structural output consists of a dimer structure, and includes properties for the hopping rate and the coupling matrix element (in eV), as well as the Jaguar properties for the neutral dimer. For the full wave function treatment, the output includes two dimer structures in addition to the DFT or CDFT structures. The dimer structures have the rate properties, one for the forward rate and one for the reverse rate. The properties are the charge transfer coupling (T_i->f in the Jaguar output), and the hopping rate. If you choose to calculate both hole and electron rates, there is one set of structures for each carrier type.

The hopping rate is defined by

$$K = \frac{4\pi^2}{h} e^{-L/(4kT)} \frac{H_{ab}^2}{\sqrt{4\pi LkT}} \tag{1}$$

where L is the reorganization energy, H_{ab} is the electron transfer coupling matrix element, k is the Boltzmann constant and T is the temperature, and all energies are given in joules. The rate is in units of $s^{\bullet 1}$.

4.4 Spin States

The location of different spin states is important when searching for spin-forbidden transitions, for example in transition metal complexes. The Spin States panel enables you to generate spin states for transition metal complexes. It is primarily intended for complexes with a single metal, where the possible occupations of the d orbitals can be explored. You can search for the ground state, a specific spin state, or all spin states, either for the default initial guess of the orbital occupations, or for all occupations generated from the open d shell.

It is also possible to generate spin states for organic molecules. In this case, the unpaired electrons go into the lowest unoccupied molecular orbitals after the paired electrons have been assigned to orbitals.

To open the Spin States panel, choose Tasks → Spin States.

4.4.1 Preparing Complexes

Tools for building complexes are described in Section 2.1 on page 11.

For mononuclear transition metal complexes, you must assign formal charges to the metal center and the ligands so that the ligands are represented as closed-shell molecules. Assigning atomic formal charges helps Jaguar to construct initial guesses for metal complexes that sample different arrangements of electrons in the d orbitals of the metal center. The spin states facility was designed to sample only the open-shell character of the d orbitals, and requires the ligands to be closed shell. The formal charge on the entire complex is ignored: only the atomic formal charges are taken into account. The charge on the complex can of course be constructed from the atomic formal charges.

To assign formal charges to a complex:

1. Ensure that all metal-ligand bonds are of zero order.

   You can use the Decrement bond order button on the Build toolbar to do this.

   

2. Display formal charges on the atoms.

   Choose Formal Charge from the Label All button menu on the Labels toolbar to display the formal charges in the Workspace. Make sure that Reapply when Workspace Changes is selected on this button menu, so that the labels are added as you change the charges.

   

To add the Label All button to the Labels toolbar, right click in the toolbar and choose Customize. The button is under Workspace Annotation in the Available buttons list.

3. Set the formal charges on the ligand atoms and the metal atom.

   You can use the Increment formal charge and Decrement formal charge buttons on the Build toolbar to do this.

You should consider the bonding as ionic, and make the ligands negative and the metal positive. For example, halogens should have a charge of • 1, and the two nitrogens in a porphyrin that bond to the metal should have a charge of • 1. The nitrosyl ligand would generally be treated as NO• , but may be treated as NO+ when studying solvation effects. The overall charge of the complex is reported in the status bar.

These classical atomic formal charge and closed shell ligand assignments are used simply to provide flexibility in the SCF initial guesses. They have no relation to the final converged wave functions, which can have any distribution of atomic charges and spins.

4.4.2 Setting Up the Calculation

The Spin States panel offers a selection of the most important settings available in the Jaguar panel, but you can add settings if you need to.

Use structures from—Choose the source of the structures for the current task.

- Project Table (selected entries)—Use the entries that are currently selected in the Project Table.
- Workspace (included entries)—Use the entries that are currently included in the Workspace, treated as separate structures. The Workspace should not contain a scratch entry.
- File—Use the structures from the specified file. Click Browse and navigate to the file you want to use.

Theory—Choose the theoretical DFT method used to calculate the states of the transition metal complex from the option menu. The method is displayed in the text box. You can choose Other to specify a method that is not listed, and enter a DFT method in the text box. The name you enter must be a valid value for the **dftname** keyword in the Jaguar input file.

For octahedral complexes of 3d transition metals, the B3LYP method includes a local correlation correction (LOC) that is designed to produce excitation energies that are of much higher accuracy than the standard DFT method.

Basis set—Choose a basis set for the calculation from the option menu. If the basis set you want to use is not on the menu, you can choose Other and enter the basis set name in the text box, including any polarization or diffuse function labels (as the option menus will be blank).

Optimization—Select Minimize geometry if you want to find the geometry of each spin state. The energy differences between the states are then the adiabatic excitation energies. By default, only an energy calculation is done, and the energy differences are the vertical excitation energies. If you choose to minimize the geometry, you can also obtain vibrational frequencies by selecting Calculate frequencies. Each option you select substantially increases the time taken for the job.

Solvent—Choose a solvent model from the Model option menu. The choices are None, which requests a calculation in vacuum, and PBF, which uses the Poisson-Boltzmann solver with a continuum solvent. If you select the latter option, you can then choose the solvent from the Solvent option menu.

Run type—Choose the states for which you want to perform calculations in this section. The first option menu allows you to choose whether to do calculations for just the selected spin state or all spin states, and for the default initial guess of the d-orbital occupations, or all possible initial guesses. If you are running the calculation on an organic molecule or a complex with more than one transition metal, the initial guess options are not available.

If you choose to select the spin state, the State option menu is activated, and you can choose to optimize the low-spin state (singlet or doublet) or the high spin state (triplet or quartet for organics or systems with more than one metal, highest allowed spin state for single-metal complexes). For octahedral complexes with a single 3d transition metal, a third option, ground, is available, which uses a spin multiplicity value that has been predicted by a physical model to be that of the ground electronic state. In the case of spin-crossover systems, choosing ground selects all of the relevant quasi-degenerate spin multiplicities.

Extra sections—Specify extra sections for the Jaguar input file. You can add the text for these sections in the text box. The Generate &atomic section option adds an atomic section with formal charge (**formal**) and multiplicity (**multip**) for the metal atom. You could, for example include **zvar** and **coord** sections to do a coordinate scan.

Additional keywords—Specify additional keywords for the gen section of the input file. For example, adding `iplotspn=1` requests a spin-density calculation. For information on the keywords, see Chapter 9 of the *Jaguar User Manual*.

4.4.3 Running the Job

After making settings, you can run the job. To make settings for the host and number of CPUs, and how subjobs are distributed, click the Settings button and make your choices in the Job Settings dialog box, then click Run to run the job.

If you are running calculations on more than one complex, the calculations can be distributed over multiple processors (cores) by selecting CPUs under Distribute subjobs across, and entering the number of processors to use (which should not be more than the number of complexes).

If you are running a single complex, you can distribute the work across multiple processors by choosing MPI processes and threads, and specify the number of MPI processes and OpenMP threads to use. See Section 11.4 of the *Jaguar User Manual* for more information on how to set these numbers.

To run the job with the current job settings, enter a name in the Job name text box and click Run.

Molecular Dynamics

The Materials Science suite provides access to the Desmond molecular dynamics program. The Desmond panels in the standard Maestro are mostly designed for general applications and for protein modeling. The Materials Science suite provides some panels that are specifically designed for materials applications.

5.1 Multistage Simulation Workflow

The molecular dynamics panels that are provided in the standard Maestro interface as well as the Materials Science interface are suitable for the most common workflows, and include a stage for relaxing the model system before performing the main simulation.

Sometimes more complex workflows are needed. For this purpose, the Materials Science suite provides the Multistage Simulation Workflow panel for constructing a workflow that can contain multiple stages of minimization, simulated annealing, and molecular dynamics.

The panel was primarily designed to allow processing of the initial condensed phase model generated from the Disordered System Builder, using a series of NVE, NVT, and finally target temperature NPT simulations to predict the amorphous system density and structure. However it can be used for any Desmond simulation, and compute properties such as the coefficient of thermal expansion or T_g.

To open this panel, choose Tasks → Molecular Dynamics → Multistage Simulation Workflow.

Like all Desmond MD simulations, a prepared model system is required as input. You can load the model system from the Workspace (if it is displayed) or read it from a `.cms` file.

When the panel opens, a single simulation step is shown below the Model system section. You can add steps in three ways:

- Click Append Step to add a new default step at the end of the list.
- Click the Duplicate button (two squares) at the top right of a step to duplicate the step with all its settings, below the source step.
- Click the Append Steps from File button, and import the steps from a previous simulation. A file selector opens so you can locate the desired `.msj` file. You can only import steps from a minimization, molecular dynamics, or simulated annealing run, or a multistage run from this panel. The steps are added at the end of the list.

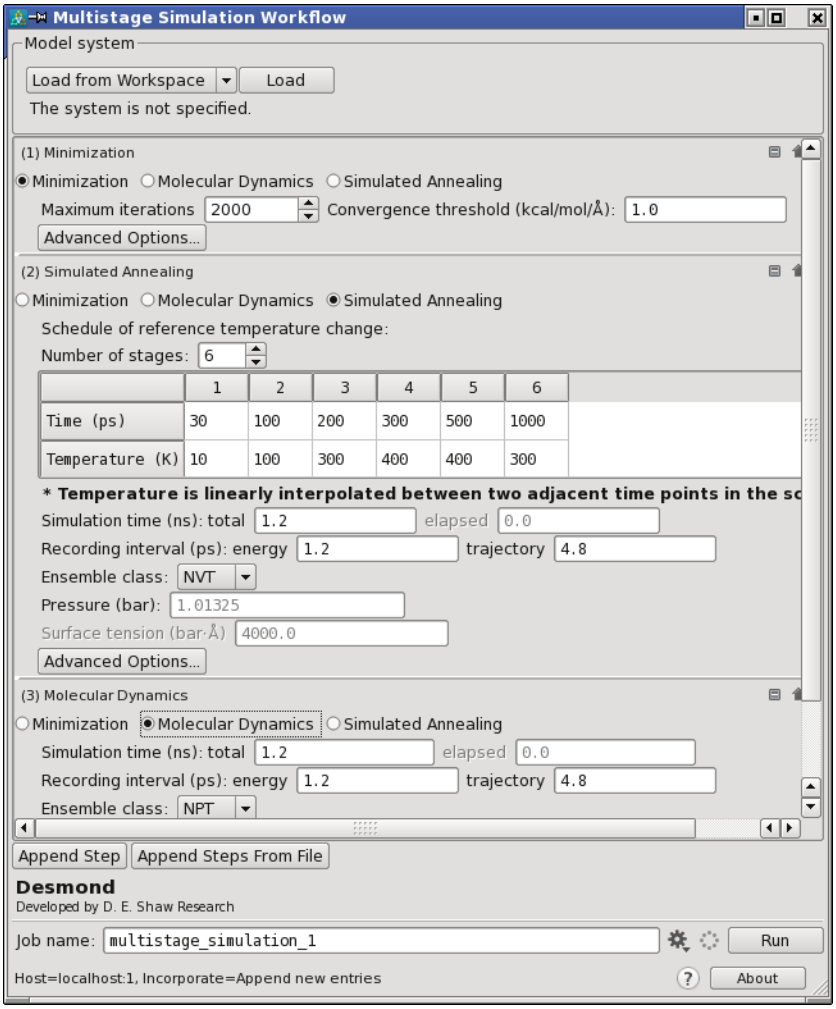

Figure 5.1. The Multistage Simulation Workflow panel.

You can rearrange steps with the arrow buttons at the top right of the steps. This makes it easy to duplicate an earlier step then move it down into the desired location, and modify the settings.

If you want to see only some of the steps, you can show or hide the options with the show and hide buttons. This is useful when you have a number of steps and want to compare two separated steps, for example.

A summary of the button operations is given below.


Show or hide the simulation options.


Move the step down or up one place in the workflow.


Duplicate the step.The duplicate is placed below the current step.


Delete the step.

Each simulation step has controls for a single step of the simulation.

The step label indicates the step number and the type of the step. It is updated if the step type is changed or the step is moved. If the step settings are hidden, the label gives a brief summary of the main step parameters.

For a given step, you can select the type of simulation step, from Minimization, Molecular Dynamics, and Simulated Annealing. When you select a step type, the label is updated with the type, and the relevant settings are displayed below these options.

You can then set options for the simulation step. The options depend on the simulation type. They are the same as in the corresponding Desmond panels, except that the relaxation options are not present. Links to the descriptions are given here:

- Minimization—Section 3.3 of the *Desmond User Manual*
- Molecular Dynamics—Section 3.4 of the *Desmond User Manual*
- Simulated Annealing—Section 3.5 of the *Desmond User Manual*

Note: You must submit the job to a Linux host, as Desmond only runs under Linux.

5.2 Simulation Analysis

Information on bulk properties can be extracted from an analysis of an MD trajectory. The MS MD Trajectory Analysis panel analyzes a trajectory from a Desmond MD simulation and presents information about bulk properties derived from the simulation, in graphical form. The properties displayed are volume and density, heat of vaporization, cohesive energy, and solubility parameter.

To generate the analysis data, click the Load button and select an output `-out.cms` file that has an associated trajectory, and run the analysis. Once the analysis is run, you can load the event analysis file (`.eaf`) and examine the various graphical representations of the bulk properties.

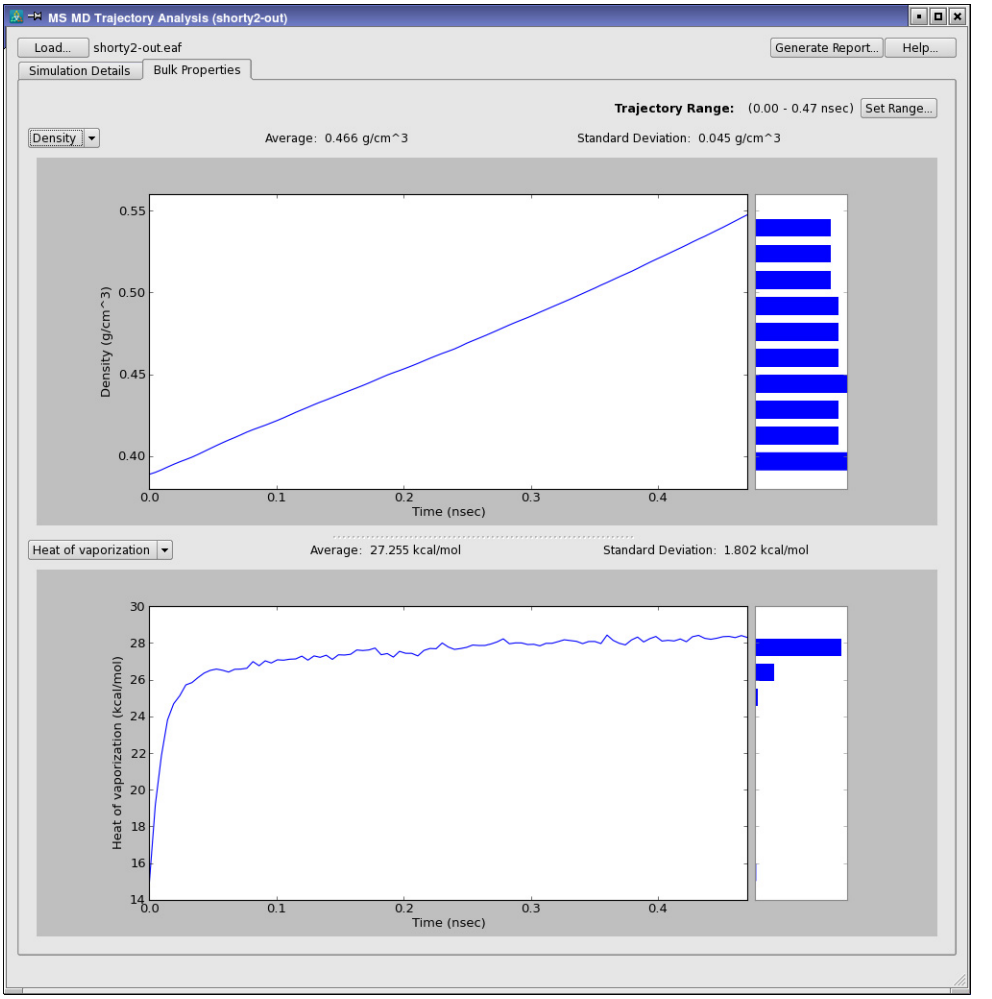

Figure 5.2. The MS MD Trajectory Analysis panel.

The Simulation Details tab shows data on the simulation. At the top is information on the job that was run, including details of the running of the job and the job input. Below this information is information on each molecule in the simulation, including a SMILES string, molecular formula, and 2D structure, the number of molecules in the simulation box, number of atoms, molecular weight, charge, and number of rotatable bonds.

The Bulk Properties tab displays plots of various bulk properties as a function of simulation time.

The simulation time range over which the properties are evaluated is displayed at the top right. You can set the range by clicking Set Range, and setting the lower and upper frame limits for the analysis in the dialog box that opens. This is useful for removing the initial equilibration from the analysis so that the average values are for the converged simulation.

There are two plot areas, each of which has the following features:

- Property menu, from which you can choose the bulk property to display on the plot.
- Average and standard deviation of the property computed over the simulation time, displayed above the plot.
- Plot of property as a function of time.
- Bar chart (histogram) showing the distribution of property values during the course of the simulation. There are 10 bins, divided equally over the range of property values.

In the upper plot area there are two related properties that you can plot, the simulation cell volume and the density. If either of these properties is changing significantly, the simulation has not converged. With the OPLS force field (FF), the density of organic and inorganic condensed matter can be obtained with an error of less than 3% compared to experiment.

In the lower plot area there are three properties that you can plot:

- Cohesive energy—The cohesive energy is calculated as the energy of the cell divided by the number of molecules in the cell, minus the energy of a single molecule in the gas phase,

  $$E_{\mathrm{coh}} = (E_{\mathrm{cell}}/N) - E_{\mathrm{mol}}$$

- Solubility parameter—The solubility parameter δ for a pure liquid is defined as

  $$\delta = \sqrt{(\Delta H_v - RT)/V_m}$$

  where ΔH_v is the heat of vaporization and V_m is the molar volume. In addition to the solubility parameter, the van der Waals (vdW) and electrostatic contributions to (the square of) this quantity can be selected and plotted. Data on the contributions are added to the report as well.

- Heat of vaporization—The heat of vaporization is calculated from the energy of the periodic unit cell minus the sum of energies of the N individual molecules, E_i, averaged over the MD trajectory, as

$$\Delta H_v = E_{\text{cell}} - \sum_{i=1}^{N} E_i + RT$$

You can create a PDF file that contains all the charts in the panel, along with explanatory text, or you can export just the charts as images. You can also export the data to a plain text file if you want to do your own analyses or processing of the data. To do this, click Generate Report and choose one or more formats:

- PDF report—Generate a PDF file that contains the diagrams with explanatory text and other data.
- Plots—Save all the diagrams in the panel in PNG or SVG format.
- Data—Export the data used to generate the diagrams as plain text files.

Scanning Probe-Target Interactions

Finding out how one molecule interacts with another is an important task in many areas of materials science, from determining low-energy adsorption sites of a molecule on some substrate, which might be another molecule, a nanoparticle, a catalytic oxide, to finding the pre-positioned reactant and product complexes on either side of the barrier in a transition state search, or finding likely sites for nucleophilic attack.

The Probe Scan panel allows you to explore the quantum-mechanical potential energy surface of a molecule with respect to a probe, which can be a point charge, an atom, or a molecule. Thus you can obtain an electrostatic potential surface, an atom-molecule potential surface, or a molecule-molecule potential surface. With optimization of the probe-target interaction, you can locate local minima on the surface and thus identify low-energy complexes.

To open the Probe Scan panel, choose Tasks → Grid Scan in the main window.

This panel is designed to produce a potential energy map around a target molecule for a specified probe. The probe can be a point charge, an atom, or a molecule with a designated probe atom. The probe atom is placed at points on a grid, and the QM energy of the system is evaluated, with optional optimization. The grid points are computed to lie on one or more surfaces, which are placed at a specified distance from the van der Waals surface of the target.

When the probe atom is placed, it is considered to be bonded to the nearest target atom. You can optimize the target molecule geometry in the target probe system, the probe molecule geometry, the distance between the target atom and the probe atom, and the orientation of the probe with respect to the target atom. These options all allow optimization to a local minimum near the target atom: more optimization gives higher accuracy but with higher cost. You can also do a full optimization of the system, with no restraints.

The result is a set of structures at each grid point with an energy, indices of target and probe atoms, grid coordinates, and probe-target atom direction vector. You can choose to return all the results, or you can choose to group the results by the target atom that the probe atom is closest to, and return only the lowest-energy structure per target atom.

6.1 Specifying the Target

The target is specified at the top of the panel, by choosing a source from the Target structure option menu

- Workspace (included entry)—Use the entry that is currently included in the Workspace. Only one entry must be included in the Workspace.
- File—Use the (first) structure from the specified file. Click Browse and navigate to the file you want to use. The file name is displayed in the text box when you click Open in the file selector. You can also enter the file name in the text box.

If you want to use the Workspace structure for the target, and also use a molecular probe, you should display the probe first and import it, then display the target structure.

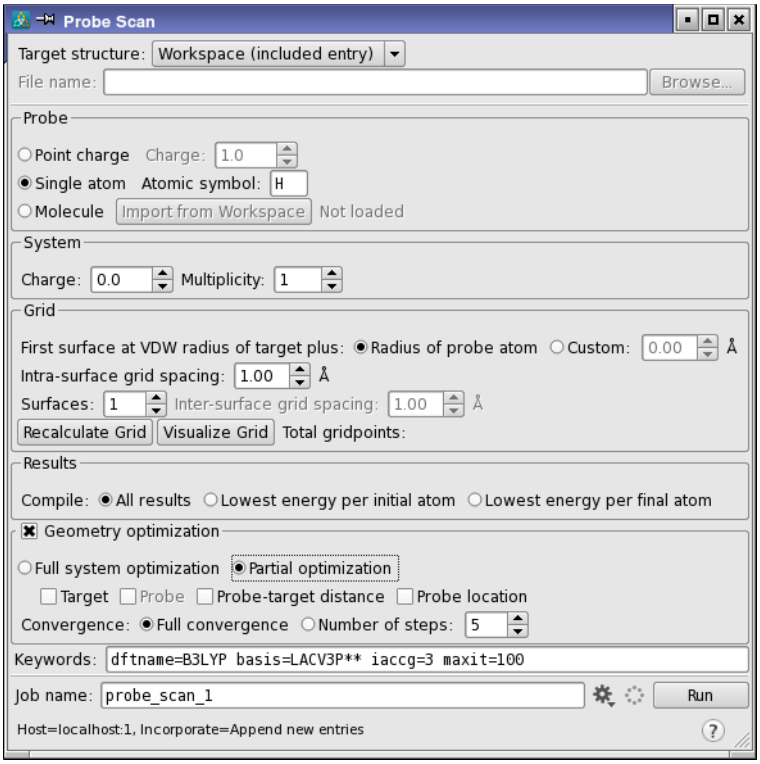

Figure 6.1. The Probe Scan panel.

6.2 Specifying the Probe

There are three choices for specifying the probe to use:

- Point charge—Use a point charge as the probe, and specify the charge value in the Charge text box.
- Single atom—Use a single atom as the probe, and specify the atomic symbol in the Atomic symbol text box.
- Molecule—Use the molecule that is in the Workspace as the probe. Click Import from Workspace when the desired molecule (and no other) is displayed in the Workspace. The Import Probe dialog box opens, which you use to pick the probe atom, and specify the orientation of the probe with respect to the nearest target atom when the probe is placed on the grid. The arrow that is displayed represents the vector from the grid point to the target atom.

The choice of probe affects which geometry optimization options are available.

6.3 Setting System Parameters

With the probe-target system defined, you will need to specify the charge and spin of the system, and set any other parameters you want to use for the QM calculation with Jaguar.

- Charge—Specify the total charge on the probe-target system in this box. If you chose a point charge or a charged atom or molecule as a probe, the target charge is the value given in this box minus the probe charge.
- Multiplicity—Specify the spin multiplicity of the probe-target system in this box. If the multiplicity is greater than 1, a spin-unrestricted calculation is performed by default. Point charges are considered spinless, so they do not contribute to the multiplicity.
- Keywords—Specify any **gen** section keywords for the Jaguar (QM) calculations.

6.4 Specifying the Grid

The grid on which the probe or probe atom is placed is constructed at a specified distance from the van der Waals surface of the target, and thus represents a surface around the target. You can specify multiple surfaces, if you want to map a volume rather than a surface.

To set the distance from the target, choose one of the First surface at VDW radius of target plus options. The default is the van der Waals radius of the probe atom (Radius of probe atom), which is zero for a point charge. You can set the value in angstroms by choosing Custom and specifying the distance in the text box.

The spacing of the grid on this (and any other) surface can be set in the Intra-surface grid spacing box. The grid is placed on the surface so that the points are at least the specified distance from any other grid point.

If you want to specify multiple surfaces, use the Surfaces box to specify the number of surfaces. Setting this value greater than 1 produces a volume rather than a surface. The distance between surfaces can be set in the Inter-surface grid spacing box.

If you do specify multiple surfaces, you should avoid optimizing the probe-target distance (or location), as it could easily collapse onto a point from another shell, and the volume generated might not be very useful.

You can visualize the grid in a 3D plot by clicking Visualize Grid. The target atoms are represented as red spheres, and the grid points as spheres in another color. A different color is used for each surface if you choose to generate multiple surfaces. If you have made changes to the grid parameters and want to visualize the grid again, click Recalculate Grid, to regenerate the grid. This button is not necessary to set the grid for the calculation, as the current set of parameters is always used when you run the job.

6.5 Optimizing the Geometry

If you want to optimize the geometry of the target or the probe (or both) at each grid point, select the Geometry optimization option. For each grid point, the target and probe geometries are set to their input geometries, and then optimized.

There are a number of choices of the parts of the system to optimize.

- Choose Full system optimization if you want to optimize the target and the probe fully at each grid point. This option will give a set of structures at local minima around the target. The probe atom is not confined to the grid point with this option, so it is possible that when the probe is placed at nearby grid points, the same minimum is found.It is probably best to combine this option with the choice to return the lowest energy per final atom for the output.
- Choose Partial optimization if you want to examine the surface as a function of the probe location, with or without relaxation. There are several options to select the parts of the system that you want to optimize.
    - Target—Optimize the target structure.
    - Probe—Optimize the probe structure. Only available if the probe is a molecule.
    - Probe-target distance—Optimize the distance between the probe atom and the nearest target atom, along the vector connecting the two.

- Probe location—Optimize the orientation of the probe molecule around the probe atom–target atom vector as well as the distance.

With either optimization, you can specify the extent to which the geometry optimization is required to converge.

- Full convergence—Converge to the default accuracy specifications.
- Number of steps—Run the optimization for the specified number of steps. This option is useful for a faster calculation, with a lower accuracy.

6.6 Specifying the Output

For some kinds of scans, it may not be useful to return all the results, so you can choose an option that determines which of the resulting structures you want to return as the results of the scan.

- All results—return all structures. This is probably the most useful for examining the energy surface.
- Lowest energy per initial atom—Group the results by the atom in the target that is initially nearest to the probe atom, and return only the lowest-energy structure from each group.
- Lowest energy per final atom—Group the results by the atom in the target that is nearest to the probe atom at the end of any optimization, and return only the lowest-energy structure from each group. (This is the same as the initial atom option if no optimization of the probe-target distance or location is performed.)

The structures are written to the output file. In addition to the usual Jaguar properties, several entry properties related to the scan are added, and one atom property. These properties are described in Table 6.1.

Table 6.1. Scan properties added to structures

Property	Description
point initial atom	Index of the target atom that is initially closest to the probe atom
point final atom	Index of the target atom that is closest to the probe at the end of the job
atom source	Atom-level property that indicates whether an atom is a target atom or a probe atom (value `target` or `probe`)
probe tip atom	Index of the probe atom that is placed at the grid point
probe vector	Vector from the probe tip atom to the nearest target atom
grid point q	Grid point x, y, and z coordinates

References

1. Halgren, T. A.; Lipscomb, W. N. The synchronous-transit method for determining reaction pathways and locating molecular transition states. *Chem. Phys. Lett.* **1977**, *49*, 225.

2. Coropceanu,V.; Cornil, J.; da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Brédas, J.-L. Charge Transport in Organic Semiconductors. *Chem. Rev.* **2007**, *107*, 926.i

Getting Help

Information about Schrödinger software is available in two main places:

- The `docs` folder (directory) of your software installation, which contains HTML and PDF documentation. Index pages are available in this folder.
- The Schrödinger web site, http://www.schrodinger.com/, In particular, you can use the Knowledge Base, http://www.schrodinger.com/kb, to find current information on a range of topics, and the Known Issues page, http://www.schrodinger.com/knownissues, to find information on software issues.

Finding Information in Maestro

Maestro provides access to nearly all the information available on Schrödinger software.

To get information:

- Pause the pointer over a GUI feature (button, menu item, menu, ...). In the main window, information is displayed in the Auto-Help text box, which is located at the foot of the main window, or in a tooltip. In other panels, information is displayed in a tooltip.

  If the tooltip does not appear within a second, check that Show tooltips is selected under General → Appearance in the Preferences panel, which you can open with CTRL+, (⌘,). Not all features have tooltips.

- Click the Help button in the lower right corner of a panel or press F1, for information about a panel or the tab that is displayed in a panel. The help topic is displayed in the Help panel. The button may have text or an icon:

  

- Choose Help → Online Help or press CTRL+H (⌘H) to open the default help topic.
- When help is displayed in the Help panel, use the navigation links in the help topic or search the help.
- Choose Help → Documentation Index, to open a page that has links to all the documents. Click a link to open the document.

- Choose Help → Search Manuals to search the manuals. The search tab in Adobe Reader opens, and you can search across all the PDF documents. You must have Adobe Reader installed to use this feature.

For information on:

- Problems and solutions: choose Help → Knowledge Base or Help → Known Issues → *product*.
- New software features: choose Help → New Features.
- Python scripting: choose Help → Python Module Overview.
- Utility programs: choose Help → About Utilities.
- Keyboard shortcuts: choose Help → Keyboard Shortcuts.
- Installation and licensing: see the *Installation Guide*.
- Running and managing jobs: see the *Job Control Guide*.
- Using Maestro: see the *Maestro User Manual*.
- Maestro commands: see the *Maestro Command Reference Manual*.

Contacting Technical Support

If you have questions that are not answered from any of the above sources, contact Schrödinger using the information below.

Web:	http://www.schrodinger.com/supportcenter
E-mail:	help@schrodinger.com
Mail:	Schrödinger, 101 SW Main Street, Suite 1300, Portland, OR 97204
Phone:	+1 888 891-4701 (USA, 8am – 8pm Eastern Time)
	+49 621 438-55173 (Europe, 9am – 5pm Central European Time)
Fax:	+1 503 299-4532 (USA, Portland office)
FTP:	ftp://ftp.schrodinger.com

Generally, using the web form is best because you can add machine output and upload files, if necessary. You will need to include the following information:

- All relevant user input and machine output
- Materials Science Suite purchaser (company, research institution, or individual)
- Primary Materials Science Suite user
- Installation, licensing, and machine information as described below.

Gathering Information for Technical Support

The instructions below describe how to gather the required machine, licensing, and installation information, and any other job-related or failure-related information, to send to technical support. Where the instructions depend on the profile used for Maestro, the profile is indicated.

For general enquiries or problems:

1. Open the Diagnostics panel.
   - **Maestro:** Help → Diagnostics
   - **Windows:** Start → All Programs → Schrodinger-2015-2 → Diagnostics
   - **Mac:** Applications → Schrodinger2015-2 → Diagnostics
   - **Command line:** `$SCHRODINGER/diagnostics`
2. When the diagnostics have run, click Technical Support.

   A dialog box opens, with instructions. You can highlight and copy the name of the file.
3. Upload the file specified in the dialog box to the support web form.

   If you have already submitted a support request, use the upload link in the email response from Schrödinger to upload the file. If you need to submit a new request, you can upload the file when you fill in the form.

If your job failed:

1. Open the Monitor panel, using the instructions for your profile as given below:
   - **Maestro/Jaguar/Elements:** Tasks → Monitor Jobs
   - **BioLuminate/MaterialsScience:** Tasks → Job Monitor
2. Select the failed job in the table, and click Postmortem.

   The Postmortem panel opens.
3. If your data is not sensitive and you can send it, select Include structures and deselect Automatically obfuscate path names.
4. Click Create.

   An archive file is created, and an information dialog box with the name and location of the file opens. You can highlight and copy the name of the file.
5. Upload the file specified in the dialog box to the support web form.

   If you have already submitted a support request, use the upload link in the email response from Schrödinger to upload the file. If you need to submit a new request, you can upload the file when you fill in the form.

6. Copy and paste any log messages from the window used to start the interface or the job into the web form (or an e-mail message), or attach them as a file.
   - **Windows:** Right-click in the window and choose Select All, then press ENTER to copy the text.
   - **Mac:** Start the Console application (Applications → Utilities), filter on the application that you used to start the job (Maestro, BioLuminate, Elements), copy the text.

If Maestro failed:

1. Open the Diagnostics panel.
   - **Windows:** Start → All Programs → Schrodinger-2015-2 → Diagnostics
   - **Mac:** Applications → SchrodingerSuite2015-2 → Diagnostics
   - **Linux/command line:** `$SCHRODINGER/diagnostics`
2. When the diagnostics have run, click Technical Support.

   A dialog box opens, with instructions. You can highlight and copy the name of the file.
3. Upload the file specified in the dialog box to the support web form.

   If you have already submitted a support request, use the upload link in the email response from Schrödinger to upload the file. If you need to submit a new request, you can upload the file when you fill in the form.
4. Upload the error files to the support web form.

   The files should be in the following location:

- **Windows:** `%LOCALAPPDATA%\Schrodinger\appcrash`
  (Choose Start → Run and paste this location into the Open text box.)
  Attach `maestro_error_`*`pid`*`.txt` and `maestro.exe_`*`pid_timestamp`*`.dmp`.
- **Mac:** `$HOME/Library/Logs/CrashReporter`
  (Go → Home → Library → Logs → CrashReporter)
  Attach `maestro_error_`*`pid`*`.txt` and `maestro_`*`timestamp_machinename`*`.crash`.
- **Linux:** `$HOME/.schrodinger/appcrash`
  Attach `maestro_error_`*`pid`*`.txt` and `crash_report_`*`timestamp_pid`*`.txt`.

If a Maestro panel failed to open:

1. Copy the text in the dialog box that opens.
2. Paste the text into the support web form.

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San Diego, CA 92122

155 Gibbs St
Suite 430
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