

ECCE 6.x RELEASE NOTES

Version 6.4—August 22, 2012

Version 6.3—April 4, 2012

Version 6.2—December 16, 2011

Version 6.1—July 25, 2011

Version 6.0—April 29, 2009

The intent of this page is to provide information specific to the 6.x versions of ECCE. Version 6.4 is the open source release of ECCE. Version 6.3 is the initial source code release of ECCE with an automated build script along with the first 64-bit platform binary distribution. Version 6.2 replaces password encryption with an in-memory cache of passwords. Version 6.1 supports building periodic systems and setting up NWChem Plane-Wave Density Functional Theory calculations plus more explicit control for password prompting and bundling the latest NWChem 6.0 release. Version 6.0 extends ECCE into the field of reaction kinetics, specifically the prediction of rate constants and equilibrium constants, often including error estimates for rate constants. Version 6.3 notes, the most recent, have titles highlighted in **green text**.

RELEASE NOTES FOR PREVIOUS VERSIONS

[Version 5.x Release Notes – March 10, 2009](#)

[Version 4.x Release Notes – December 27, 2007](#)

[Version 3.2.x Release Notes – April 5, 2006](#)

WHAT'S NEW

Open Source Release

(6.4) ECCE is now available as open source software under the terms of the same Educational Community License (ECL) 2.0 used by NWChem. This eliminates the need to sign an EMSL software use agreement and download the software via the EMSL User Portal. Both binary and source code distributions of ECCE can now be downloaded from the ECCE website at <http://ecce.pnl.gov/using/download.shtml>. ECCE distributions will also be made available from the NWChem wiki at <http://www.nwchem-sw.org>. Other than open source availability and bundling the latest NWChem 6.1.1, the ECCE 6.4 release is otherwise equivalent to the 6.3 release. Because source code is now available the ECCE team is interested in hearing about any enhancements or fixes to ECCE made by the user community and encourages those be contributed back for inclusion in ECCE core distributions. Please contact the ECCE team using the NWChem wiki ECCE forums at <http://www.nwchem->

sw.org/index.php/Special:AWCforum/sc/id4/ECCE: Extensible Computational Chemistry Environment.html if you wish to contribute.

NWChem 6.1.1 Bundled

(6.4) The latest production NWChem release 6.1.1 has been bundled with ECCE 6.4. This is the version that will be used when calculations are run on the host where the ECCE application software is installed. ECCE bundles NWChem as a matter of convenience for those evaluating either ECCE or NWChem with the intent that users running the software for research/production purposes will install NWChem separately on higher performance hardware using platform specific NWChem compilation settings. The 32-bit ECCE binary distribution installs a 32-bit NWChem 6.1.1 binary distribution and the 64-bit ECCE binary distribution installs a 64-bit NWChem 6.1.1 binary distribution. The ECCE source code distribution bundles both a 32-bit and 64-bit NWChem 6.1.1 binary distribution so the appropriate one can be included in the ECCE binary distribution created after ECCE is compiled from source code. Note that these NWChem 6.1.1 binary distributions are generic compilations for Linux workstations using the GNU gfortran compiler, default TCMMSG message passing and other default compilation settings. The build/build_details.doc file of the ECCE source code distribution describes the exact NWChem 6.1.1 compilation settings used.

Source Code Release

(6.3) An ECCE source code distribution is available for the first time. This allows sites to compile ECCE natively on both 32- or 64-bit Linux platforms. A build script automates the process of compiling ECCE including checking for the existence and compatible versions of compilers and other packages needed to build and run ECCE, automating builds of third party software ECCE requires, and compiling ECCE core code. ECCE builds have been tested on a variety of Linux operating systems including 32- and 64-bit releases of Debian 6.0.4, Ubuntu 11.10, OpenSUSE 12.1, Red Hat 5.7, and Mint 12. Build guidance such as the names of prerequisite software packages to install for each of these operating systems is provided. The ECCE source code distribution bundles compatible versions of the third party packages used by ECCE such as the Xerces XML parser, the wxWidgets and wxPython GUI toolkits, and the Apache HTTP server. The README file in the build subdirectory of the source code distribution describes how to use the build_ecce to automate the entire build process and operating system specific guidance. For those having problems compiling the third party software used by ECCE or wishing to try newer versions, details for manually building the third party packages are given in the build_details.doc file in the same directory.

64-bit Binary Distribution

(6.3) A native 64-bit platform binary distribution is now provided in addition the 32-bit distribution that had been the only one available. While both the 32- and 64-bit binary distributions of ECCE are built under the Red Hat Enterprise Linux 5.7 operating system they include operating system dependent shared libraries that allow them to be run on Linux operating systems from many other vendors. The majority of sites do not need to build ECCE from the source code distribution unless they prefer to do so. The quickest way to get up and going with ECCE is to first install the appropriate binary distribution

based on whether it's a 32-bit or 64-bit platform and then test various ECCE applications. If any issues are found then go back and build ECCE from the source code distribution. In addition to the 64-bit ECCE binary distribution being available, the compilers used to build the ECCE binary distributions as well as the versions of the third party software used such as the wxWidgets GUI toolkit and Xerces XML parser have been upgraded to newer releases. The ECCE 6.2 and prior versions used the GNU C++ (g++) 3.2.3 compiler while the 6.3 binary distributions use the 4.1.2 compiler that is native with Red Hat 5.7 where the distributions are built. Note that ECCE source code has been built and tested with the newer g++ 4.x releases including g++ 4.6.

Virtual Machine Distribution

(6.3) The virtual machine distribution of ECCE allows users with only Windows or Mac OS X platforms available to them to run ECCE. However, the VMware distribution of ECCE 6.0 is obsolete and was therefore removed from the download area. Since the ECCE 6.0 release three years ago virtual machine technology has improved dramatically. It is now a much more straightforward process to use these products than when this native VMware distribution of ECCE 6.0 was created. Due to having more flexible no cost products and its less commercial nature, the ECCE team recommends the use of VirtualBox (<http://www.virtualbox.org>) although VMware (<http://www.vmware.com>) remains a well-supported alternative. The previous ECCE 6.0 VMware distribution bundled the CentOS Linux operating system because of its small size and similarity to the Red Hat operating system which was the only operating system where ECCE was compiled prior to the 6.3 release. But, with the added flexibility of both the ECCE 64-bit binary distribution and the ECCE source code distribution any constraints on what Linux operating system can be installed as a virtual machine have been eliminated. From extensive development and testing prior to the ECCE 6.3 source code release the ECCE team recommends Debian, Mint, and Ubuntu for robust and stable Linux operating systems (see the build/README file of the ECCE source code distribution for more details). But, if your facility mandates or favors a different vendor (e.g. OpenSUSE, Red Hat) ECCE is also fully compatible with those operating systems. After installing a virtual machine product like VirtualBox or VMware and then a Linux operating system on a newly created virtual machine, it is a simple matter to install either an ECCE binary distribution or to build ECCE from the source code distribution on the Linux virtual machine. There is no distinction between installing ECCE on a native/local Linux operating system and one running on a virtual machine. One special note is that typically the BIOS settings for a Windows or Linux host do not allow 64-bit virtual machines to be installed even on 64-bit platforms (it isn't possible to install 64-bit virtual machines on 32-bit hosts) without changing default BIOS settings. Simple Google searches will reveal what BIOS changes need to be made to allow 64-bit virtual machines.

NWChem 6.1 Bundled

(6.3) The latest production NWChem release 6.1 has been bundled with ECCE 6.3. This is the version that will be used when calculations are run on the host where the ECCE application software is installed. ECCE bundles NWChem as a matter of convenience for those evaluating either ECCE or NWChem with the intent that users running the software for research/production purposes will install NWChem separately on higher performance

hardware using platform specific NWChem compilation settings. The 32-bit ECCE binary distribution installs a 32-bit NWChem 6.1 binary distribution and the 64-bit ECCE binary distribution installs a 64-bit NWChem 6.1 binary distribution. The ECCE source code distribution bundles both a 32-bit and 64-bit NWChem 6.1 binary distribution so the appropriate one can be included in the ECCE binary distribution created after ECCE is compiled from source code. Note that these NWChem 6.1 binary distributions are generic compilations for Linux workstations using the GNU gfortran compiler, default TCMMSG message passing and other default compilation settings. The build/build_details.doc file of the ECCE source code distribution describes the exact NWChem 6.1 compilation settings used.

Password Caching Redesign

(6.2) Encryption of passwords to file has been eliminated in preparation for the open source release of ECCE in 2012. An in-memory cache of passwords is now kept by ECCE applications for both compute hosts and data servers. The memory cache is synchronized between existing and newly started applications so that a password will only be prompted for a single time when it is first needed by any ECCE application (e.g. Job Launcher, Machine Browser, and Organizer). The Gateway toolbar now prompts for the data server password rather than the ECCE login password (aka encryption key). The ECCE login password (encryption key) prompt dialog previously displayed when first starting ECCE has been eliminated, although the new password prompt dialogs have adopted the same look with the ECCE logo and PNNL/EMSL branding. Because the default administrator configuration of ECCE automatically creates data server accounts for new users when starting ECCE for the first time and this data server password is auto-generated, many users won't know their current data server password. Thus, before running ECCE 6.2 users will need to look up their data server password with the instructions provided in the following release note. New users are now allowed to select their own data server password (6 characters minimum) the first time they run ECCE. Using the "Change..." button on the data server password dialog existing users can change their password to something more easily remembered than the auto-generated password. The Job Launcher and Machine Browser applications still have compute host password entry fields, but if the user does not enter a password in this field a separate password prompt dialog will be displayed when a login is attempted. These prompt dialogs will also appear when accessing an account on a remote host from an application that does not have a password field such as starting remote shells from the Organizer. Of course if the compute host password for this account has previously been prompted for in the same ECCE session such as to launch a job, the password cache will be used by the Organizer and no prompt is displayed.

Lookup Data Server Password

ECCE 6.2 requires users to enter their data server password at startup to access their calculations via the Organizer and other applications. Because the data server password was most likely auto-generated and then encrypted without the user needing to know or remember password, most users will need to retrieve their existing data server password. This can be done without an ECCE administrator resetting the password via the `ecce_htpasswd` server utility script by running ECCE 6.0 or 6.1 (the capability to lookup

data server passwords has been eliminated in ECCE 6.2). For this reason it is recommended that sites make both the new and previous ECCE installation available to users for a period until users are able to retrieve their data server passwords from the previous installation. ECCE administrators should see the “SITE ADMINISTRATOR WHAT’S NEW” release note on installing ECCE 6.2 for details. Here are the steps for users to lookup their data server password:

- Start ECCE 6.0 or 6.1 (will require sourcing the proper runtime_setup file if already setup to run 6.2 by default)
- Enter the encryption key at the login dialog but do not hit return or “OK” as would normally be done to bring up the Gateway toolbar
- Hit the “More...” button
- Hit the newly shown “Lookup Data Server Password” button and the password will be displayed in a popup dialog assuming the correct encryption key was entered
- Write down this password unless you can remember it
- Close the password lookup dialog and select “Quit” from the login dialog for ECCE 6.0/6.1 (note that due to the upgrade to the 6.2 server, ECCE 6.0/6.1 is no longer functional except for looking up passwords)
- Start ECCE 6.2 (will require sourcing the proper runtime_setup file if running from the same window where ECCE 6.0/6.1 was just run)
- The prompt dialog displayed immediately will be for this data server password, not the encryption key prompted for by previous ECCE releases
- Enter the data server password retrieved from ECCE 6.0/6.1
- At this time or a future ECCE session it is recommended that the data server password be changed (6 character minimum) to something that is more easily remembered than the auto-generated one since it will be entered every time ECCE is started

Preferences Directory Rename

(6.2) The .ECCE4 user preferences directory that lives in each user’s home directory has been renamed to .ECCE. Given the password caching changes, this was a good time to tackle this long overdue bit of cleanup. Over the years a number of preference files associated with previous ECCE releases have been deprecated but still exist in .ECCE4 directories. The preference directory rename starts everyone again with fresh preference files—none are copied from the .ECCE4 directory. Since encrypted passwords are no longer saved to preference directory files the most noticeable change for most users will be losing their previous window sizes and locations. Other miscellaneous preference settings will also be set back to defaults, but should be easy for users to restore such as through the Gateway toolbar preferences dialog. Users who don’t anticipate needing to run prior releases can remove their old ~/.ECCE4 preferences directory after transitioning to ECCE 6.2.

NWChem 6.0 Bundled

(6.1) The latest production NWChem release 6.0 has been bundled with ECCE 6.1. This is the version that will be used when calculations are run on the host where the ECCE application software is installed. ECCE bundles NWChem as a matter of convenience for

those evaluating either ECCE or NWChem with the intent that users running the software for research/production purposes will install NWChem separately on higher performance hardware.

Password Prompting Options

(6.1) Figure 1 shows the Login dialog for ECCE 6.1. Of note are the newly added checkboxes labeled “Save encryption key” and “Save machine passwords”. The settings for these options determine when passwords are prompted for by ECCE and thus what is cached on disk to eliminate password prompts selectively, completely, or not at all. Prior to ECCE 6.1 machine passwords, i.e. those needed to access remote machines and submit computational jobs, were always saved, although in encrypted form. This is still the default option for ECCE 6.1 although there is now an option to not save machine passwords and prompt for them each time they are needed. Thus the “Save machine passwords” checkbox is provided for sites and users who have security concerns about storing any passwords to local disk regardless of the encryption applied to them. The “Save encryption key” checkbox controls whether the ECCE Login dialog itself is needed. By choosing to save the encryption key (the default is not to save it), ECCE will bypass the Login dialog asking for the encryption key completely and simply start the ECCE Gateway toolbar. In order for this option to take effect the correct encryption key must be entered when the option is first selected on the dialog. By choosing both to save the encryption key and save machine passwords ECCE won't prompt for any passwords throughout a session other than to initially configure a machine to launch jobs by supplying a valid username/password combination and assuming any username/password combinations used remain valid. Of course “one-time login” type passwords still require prompting regardless of these checkbox settings. By saving neither the encryption key nor machine passwords ECCE will not cache any passwords to disk within or between sessions. ECCE uses an open source 64-bit block cipher encryption algorithm named Blowfish with the encryption key being selected by the user the first time ECCE is run (and changed via the “More...” button options on the Login dialog after that). Because of the underlying Blowfish algorithm and the encryption key itself not being saved on disk unless the “Save encryption key” option is selected, this is an exceptionally strong encryption for machine passwords (the ECCE data server password is also encrypted in the same way) despite being saved to disk in encrypted form. The new checkboxes have been added for those sites/users that either prefer a little extra convenience of not entering an encryption key to start ECCE or need to insure ECCE always prompts rather than maintaining even strongly encrypted passwords. Note that in order to reset the “Save encryption key” option to once again prompt for the key after it is set to not prompt, the “preferences” button on the Gateway toolbar is used to call up a dialog that also contains these two new checkboxes.

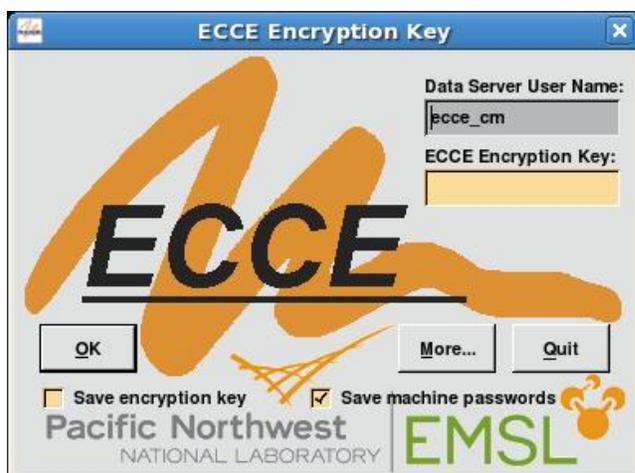


Figure 1. ECCE Login dialog

Periodic System Builder

(6.1) Figure 2 shows the Builder in ECCE 6.1 having imported a CAR file format periodic system. The new Periodic Builder toolkit is at the top of the right-side frame of the Builder in the figure. When loading chemical systems into the Builder using the “Import Chemical System...” item under the File menu, CAR format is now listed in the import dialog. The Periodic Builder toolkit will be shown automatically when a CAR file is imported and is otherwise available from the Tools menu. The “Cell Type” dropdown menu in the Periodic Builder toolkit allows the unit cell to be defined either by the lengths “a, b, c” and angles “alpha, beta, gamma” or by the lattice vectors “a1, a2, a3”. These values can be input by the user at the start of an editing session or they will automatically be set if the user imports a CAR format file. The “Lock” checkbox fixes the coordinates of atoms during any change to the lattice cell definition with the aforementioned fields. If “Lock” is unchecked the atom coordinates will be transformed along with any changes to the lattice cell. The “Center Lattice” checkbox causes the lattice to be centered based on atom coordinate extents with any change to the cell definition. The display of the lattice unit cell can be toggled on and off with the “Show Lattice” checkbox. The “Fold” button will automatically shift atoms by an appropriate periodic distance so that all atoms in the system are inside the unit cell. The resulting structure is equivalent to the starting structure, in a periodic sense. The “Equiv. Rectangle” button can be used to create a unit cell with the same volume as the original unit cell but with all cell angles as 90 degrees. Note that this does not necessarily result in an equivalent lattice. For example, this operation applied to a standard unit cell of a 2D lattice of equilateral triangles will result in a different lattice. However, if this operation is applied to a 2x2 super-lattice of the standard unit cell, the resulting lattice is equivalent to the original triangular lattice. New unit cells can be built using the “Super Lattice” button.

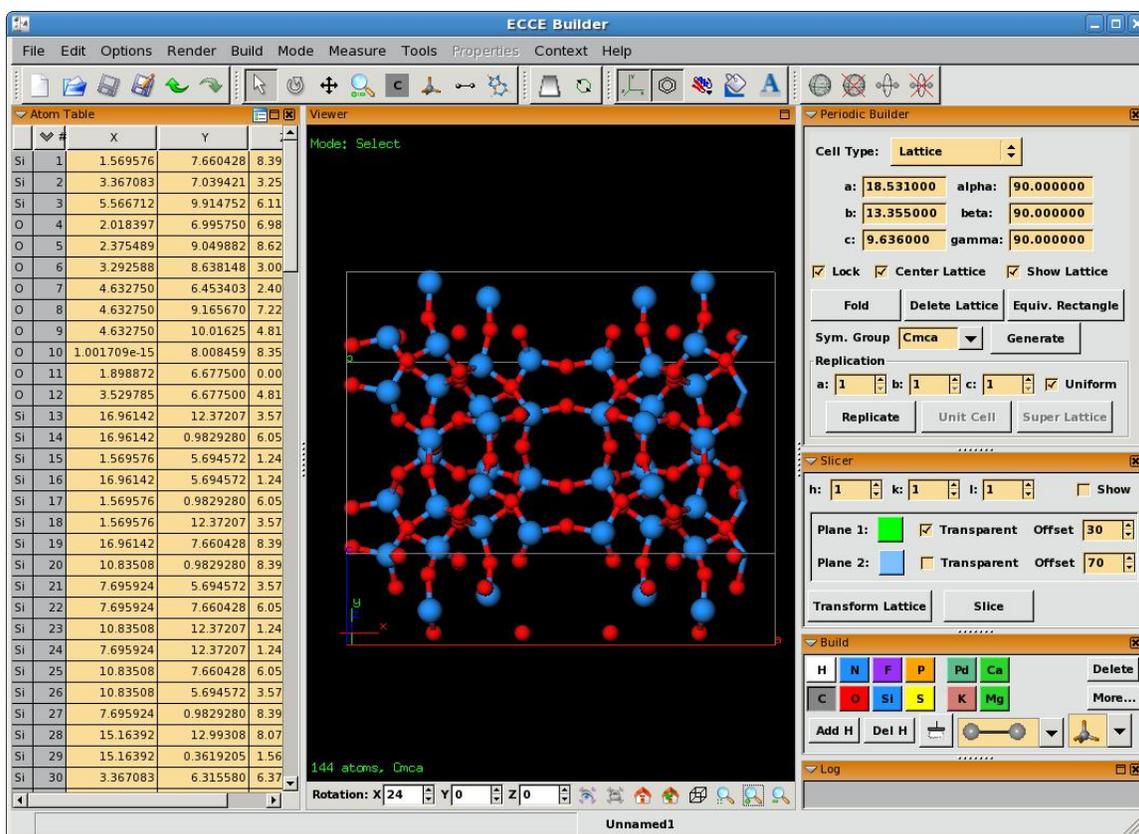


Figure 2. ECCE Builder for periodic systems

If the system is imported from a CAR format file, the symmetry group is automatically set to whatever group was specified in the CAR file. The user can also specify the symmetry group manually. After adding the unique atoms, the full lattice can be generated by pressing the “Generate” button. Visualizations of multiple unit cells can be created using the “Replicate” functionality. The number of cells in each lattice direction can be specified in the three type-in fields labeled “a”, “b”, and “c”. If the “Uniform” checkbox is selected, then all three directions will have the same number of boxes; if it is unchecked, then each axis can have a unique number of boxes. After specifying the number of boxes, pressing the “Replicate” button will generate an image with multiple unit cells. Pressing the “Unit Cell” button will return to the original unit cell. If you want to convert the multiple unit cells into a larger single unit cell, this can be done by pressing the “Super Lattice” button. Note that once a multi-cell system has been converted into a super-lattice cell, it cannot be converted back to the original unit cell.

A second toolkit that is designed to help users manipulate periodic systems is the Slicer, shown below the Periodic Builder toolkit in Figure 2. This toolkit allows users to visualize different crystal planes, slice the system based on these crystal planes, and transform the unit cell so that a desired crystal plane in the original system lies along the 001 direction of the new system. The three type-in fields “h”, “k”, and “l” are the integer components of the vector defining the crystal plane. If the box labeled “Show” is checked, these planes will show in the workspace. The properties of each plane, including their color, transparency, and location can be manipulated with the fields after

the “Plane 1” and “Plane 2” labels. The offset is the relative displacement of the plane (ranging in values from 0 to 100) from the farthest corner or edge of the unit cell. The “Slice” button will remove all atoms from the system that are exterior to the space contained between the two planes. Note that “Slice” only works on the unit cell. To slice a multi-cell system, it first needs to be converted to a single cell using “Super Lattice”. The “Transform” button will transform the original unit cell so that the lattice specified by h, k, and l values is now the 001 vector of the transformed system. This is useful for creating configurations where a desired crystal plane is one of the faces of the unit cell. Note that this transformation does not necessarily conserve the number of atoms. The transformed cell will generally be larger and contain more atoms than the original cell. That lattices represented by both unit cells will be identical though.

NWChem Plane-Wave Density Functional Theory (NWPW) Calculations

(6.1) Figure 3 shows the Calculation Editor Theory Details dialog for the NWChem Plane-Wave Density Functional Theory (aka NWPW) PSPW theory. ECCE GUIs for setting up both PSPW and Band NWPW calculations are now available. The NWPW module PSPW theory additionally includes support for the Car-Parrinello runtime through its own Runtime Details dialog as shown in Figure 4. NWPW calculation support is tightly woven with the periodic system building capability in the Builder that is also new in ECCE 6.1. Note that when selecting either PSPW or Band as the theory for an NWPW calculation in the Calculation Editor that basis set selection is disabled. ECCE Viewer support for plotting a number of per geometry step properties for NWPW and in particular Car-Parrinello calculations has also been added. Figure 5 shows the ECCE Viewer displaying the Geometry Trace and Wave Step Plot properties for a PSPW Car-Parrinello run.

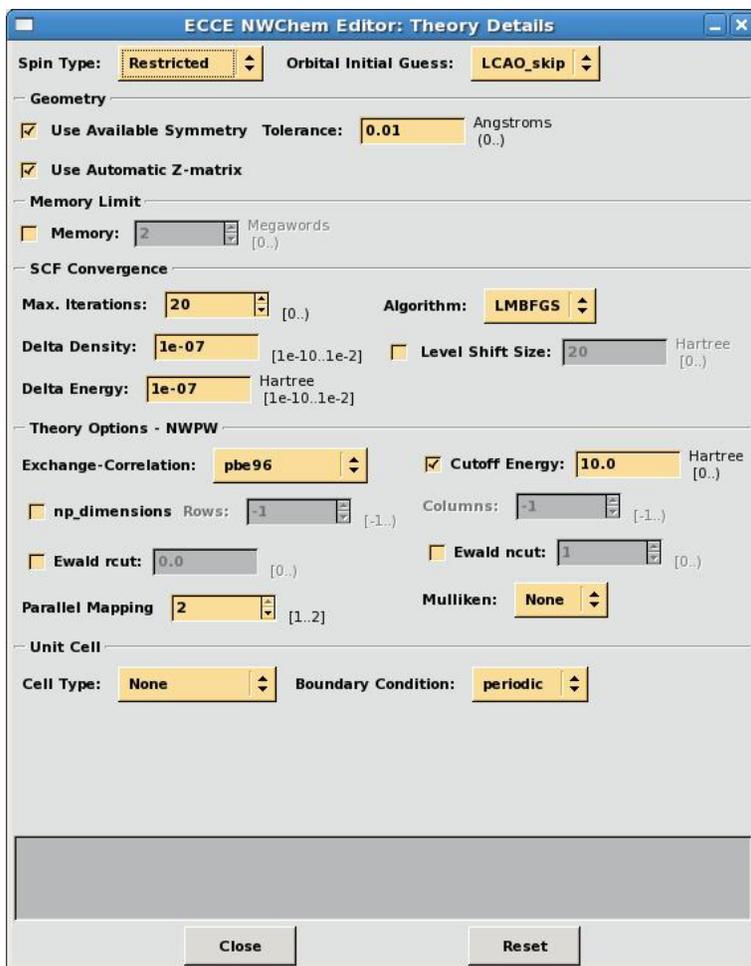


Figure 3. NWPW PSPW Theory Details dialog

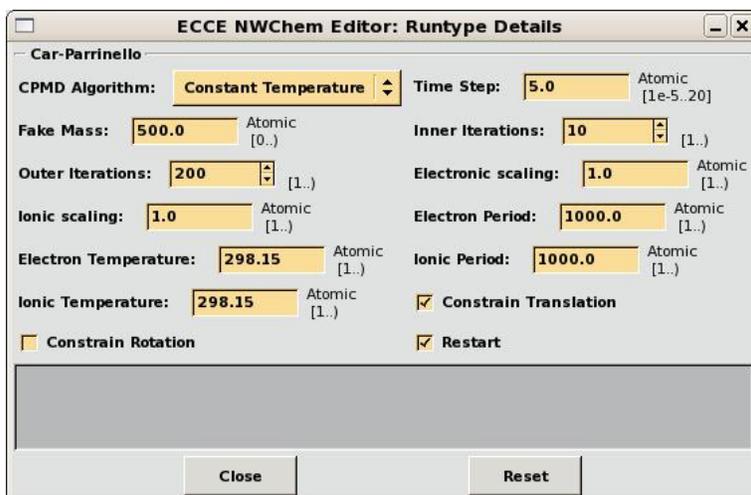


Figure 4. NWPW Car-Parrinello Runtime Details dialog

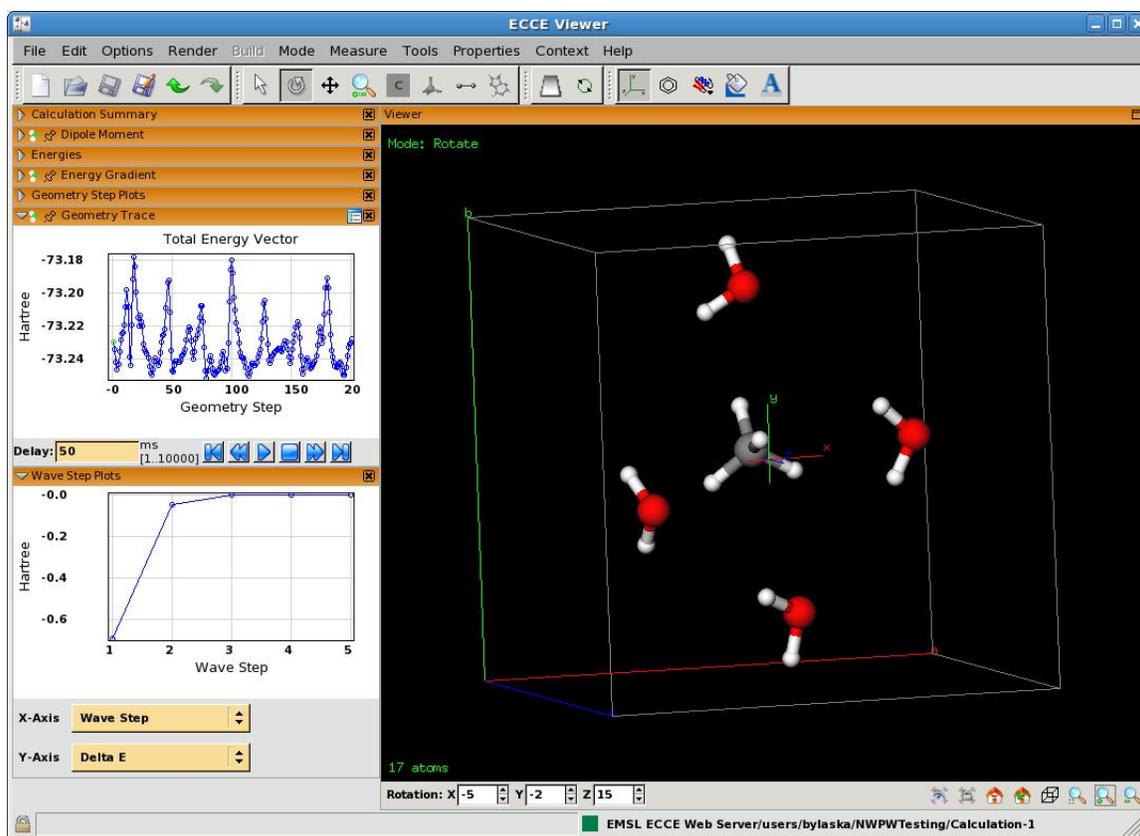


Figure 5. ECCE Viewer showing NWPW PSPW Car-Parrinello results

Reaction Rate Constant Prediction

(6.0) The NWChem DirDyVTST module has been integrated with the POLYRATE code (see <http://comp.chem.umn.edu/polyrate>) into the ECCE user environment yielding a powerful capability to predict gas phase chemical reaction rate constants. This is done through two new ECCE applications, the NWChem DirDyVTST (Direct Dynamics Variational Transition State Theory) Editor and the POLYRATE Editor, as well as extensions to several other ECCE applications including the Organizer, Builder, Basis Set Tool, and Viewer. This work was sponsored by the U. S. Department of Defense, Air Force Office of Scientific Research under a Small Business Technology Transfer effort (contract number: FA9550-07-C-0008) led by Spectral Sciences, Inc., Burlington, MA. Support from the ECCE team as well as documentation for this new capability is limited to the work done during the contract period. These release notes and a new online movie that demonstrates a simple reaction rate calculation make up the full documentation that is available for the initial release.

Organizer

Figure 6 is a screen capture of the ECCE Organizer application showing a reaction study named “ethaneBondRotation”. The reaction rate prediction capability uses the same workflow paradigm as molecular dynamics for chaining together the output of discrete calculations or tasks as the input to subsequent tasks. The Organizer “File” menu now contains an item to create a “New Reaction Study...” as well as the previous “New MD

Study...” menu item. Reaction studies contain DirDyVTST and POLYRATE sub-tasks along with the different electronic structure calculations on the transition state, reactant, and product components of the chemical reaction. In Figure 6, the DirDyVTST calculation of the reaction has been selected in the left-hand pane, which displays the ECCE applications available for working on that sub-task in the right-hand pane. Like MD studies, by selecting the reaction study parent task in the left-hand pane, a workflow view showing the flow of data between all sub-tasks is displayed in the right-hand pane.

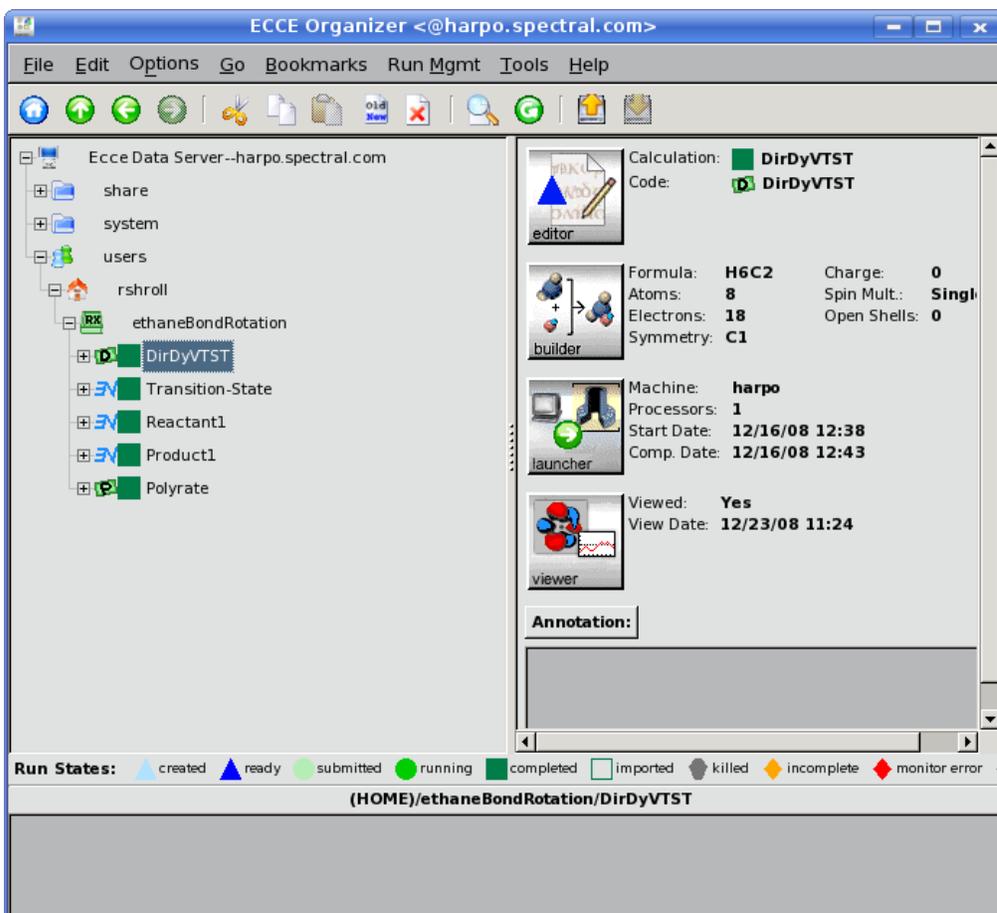


Figure 6. ECCE Organizer in the context of a reaction study

DirDyVTST Editor

The DirDyVTST Editor controls NWChem’s DirDyVTST module, which calculates molecular properties over the reaction path necessary for the transition state calculations. This routine provides the key to interfacing the NWChem quantum chemistry calculations with the POLYRATE transition state theory rate constant predictions and is thus central to the ECCE reaction rate constant prediction capability. The enhancements made allow the user access to a broad range of quantum chemistry theory types for this purpose. Figure 7 shows the main window of the DirDyVTST Editor. The editor helps the user organize and run up to five separate electronic structure calculations for the

reactants, products, and the transition state. Note that thumbnail visualizations of each of the reaction component chemical systems are displayed on the main DirDyVTST Editor window. This allows at-a-glance feedback on the chemical systems that are part of the computation without bringing up the Builder application on each component. The example shown is for internal rotation about the C-C bond of ethane. This is a unimolecular process and thus “Reactant 2” and “Product 2” are unused.

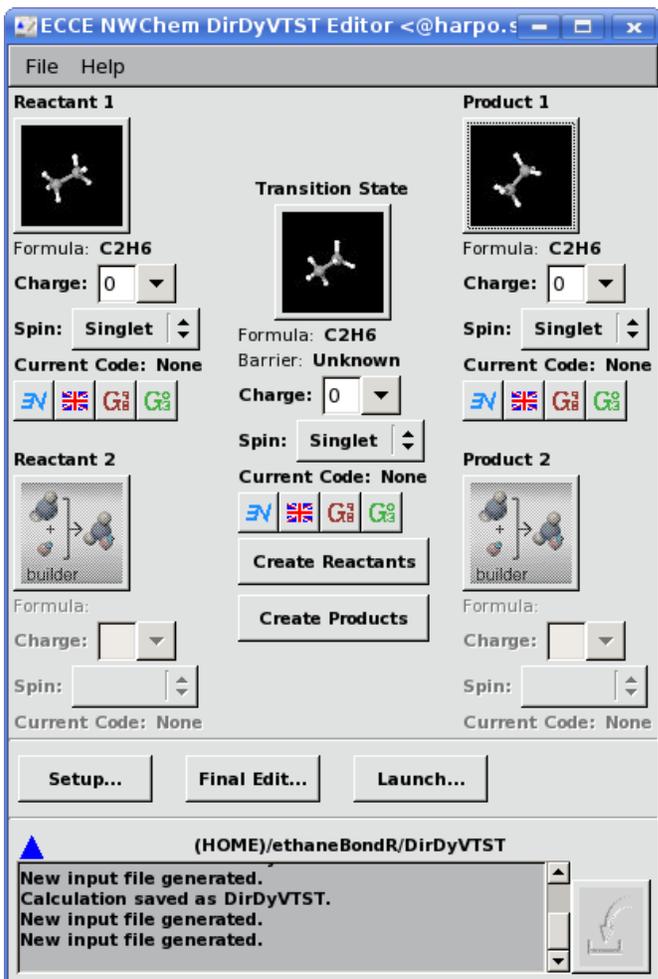


Figure 7. The DirDyVTST Editor is used to initialize quantum chemistry calculations for each molecule and the DirDyVTST routine. Thumbnail images show the reactants, products, and transition state for an example reaction

The organization of the DirDyVTST Editor represents the reaction as proceeding from reactants to products from left to right. On the left, there are two areas for each of the two reactants, where Reactant 2 is optional depending on the reaction being studied. Each area has a title like “Reactant 1” and buttons for launching the ECCE Builder and the electronic structure calculation editors. The Builder is launched by clicking on the thumbnail image, which prior to any input is the generic Builder icon shown under Reactant 2 and Product 2 in Figure 7. The user inputs and saves a molecular structure

and its image is displayed as a thumbnail with the chemical formula underneath. The system charge and spin multiplicity are also selected through this interface. This is done for the reaction as a whole and not separately for each molecule, since there are restrictions that must be applied over the entire reaction path. One such restriction is charge conservation, where the total charge of the reactants must be the same as the total charge of the products. Displayed in this single interface, the user can see the charge and spin multiplicity of the entire reaction at once. ECCE will enforce these restrictions, so for instance, if the total system charge for a bimolecular reaction is -1 and the user changes the charge on Reactant 1 from -1 to 0 then ECCE will update the charge on Reactant 2 from 0 to -1. ECCE will thus maintain a viable calculation. When the change is performed, the display is updated and the user is shown that their change has altered the calculation for Reactant 2. Underneath the spin selection, there are four buttons for launching calculation editors for the four supported electronic structure codes. These editors provide similarly structured interfaces to the different codes simplifying their use. The transition state area has two additional buttons for creating the reactants and products. When the DirDyVTST Editor is first launched, the user is guided towards inputting the transition state (Builder access will be disabled for the reactants and products until a transition state is defined). Once this is done, the reactants and products are generated from the transitions state. For instance, atoms composing one of the reactants are selected and Create Reactants is chosen. ECCE then generates one reactant from the selected atoms and one reactant from the remaining (unselected) atoms. ECCE fills in the Reactant entry fields and sets up default values for the system charge and spin.

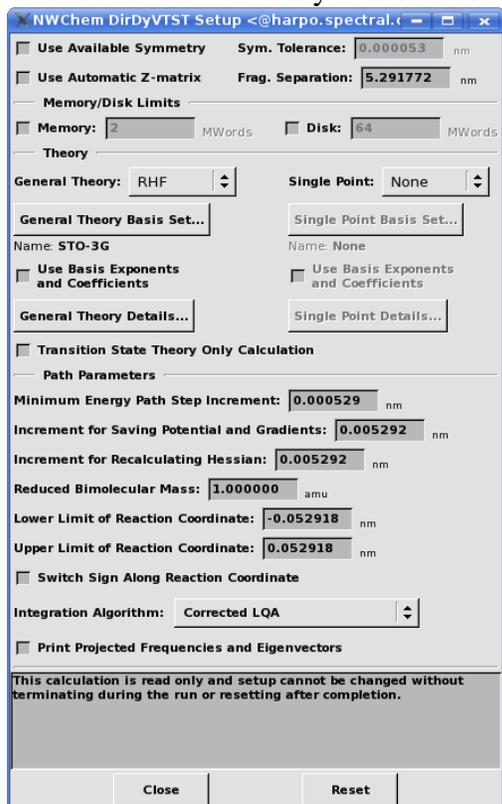


Figure 8. The DirDyVTST Editor Setup window is used to configure the DirDyVTST calculation

Through the DirDyVTST Editor Setup window (available from the main window), the full range of registered NWChem theory types for the DirDyVTST calculation is supported for both a “General” and “Single Point” calculation. Figure 8 shows the DirDyVTST Editor Setup window. The single point calculation ability is critical to accurate rate constant prediction because a much more accurate and computationally demanding theory may be used to correct the faster theories necessary to follow the reaction path.

The DirDyVTST calculation follows the reaction just before and just after the transition state. It performs many quantum chemistry calculations and is computationally the most expensive step in the entire rate constant calculation process. It does this to locate the free energy maximum, which may be offset from the energy maximum located at the transition state. All of the controls for this calculation are present in the DirDyVTST interface. Upon its initial launch, the input fields are all filled with default values applicable to most cases. Alterations to the defaults may be made to better represent specific systems. This is primarily done through the Theory and Path Parameters sections. In the Theory section the general and single point theories are selected. The general theory is the theory used to perform the path calculation and single point is an optional higher level theory that may be used to correct the lower level theory used by the general calculation. Both calculations require selecting electronic structure methods, basis sets, and basic computational parameters such as self consistent field (SCF) convergence criteria. At the bottom of the Theory section is a toggle labeled “Transition State Theory Only Calculation”. This is the most basic type of calculation and does not require location of the free energy maximum via calculation over the reaction path near the transition state. If this is selected, the Path Parameters section is grayed out. Otherwise, the path calculation is performed. The Path Parameters section allows the user to change the path calculation characteristics such as number of points calculated, the distance between the points, and the integration algorithm used.

The “General Theory Details” and “Single Point Details” dialogs available from the DirDyVTST Editor Setup window allow the user to specify options such as SCF convergence criteria and theory specific algorithms to use for the general and single point calculations, respectively. Figure 9 shows a Theory Details dialog for the RDFT (restricted density functional theory) level of theory. A small number of fields on the electronic structure NWChem Theory Details dialog are excluded when the dialog is invoked in the context of a DirDyVTST calculation. The symmetry and memory limit fields are among these as the DirDyVTST Setup window includes these fields instead of the lower level NWChem Theory Details dialog.

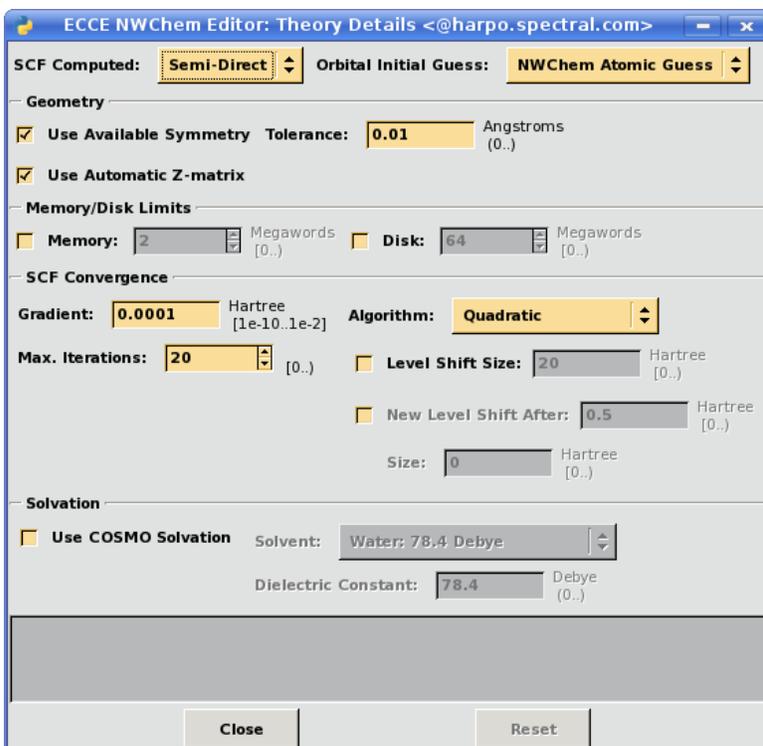


Figure 9. The DirDyVTST Editor Theory Details dialog is where the chosen quantum chemistry method is configured

Electronic structure geometry optimizations can be run on reaction components (transition state, reactants, products) prior to invoking the DirDyVTST calculation using NWChem, Gaussian 03, Gaussian 98, or GAMESS-UK. This option to run calculations on the reaction components is accessed via icons representing each code, shown below each of the chemical system thumbnail visualizations on the DirDyVTST Editor main window.

The DirDyVTST Editor enforces consistency between the transition state chemical system number of electrons, overall charge, spin multiplicity, and level of theory. Based on the number of electrons and charge set by the user, the spin multiplicity and theory choices are restricted to maintain the integrity of the overall calculation. This consistency encompasses the reaction component calculations and the follow-on POLYRATE calculation, described next. This kind of guaranteed consistency is a primary reason ECCE is so valuable in setting up these complex, detail oriented, and multi-step calculations.

POLYRATE Editor

Figure 10 shows two screen captures of the POLYRATE Editor used to create the input file for the POLYRATE code.

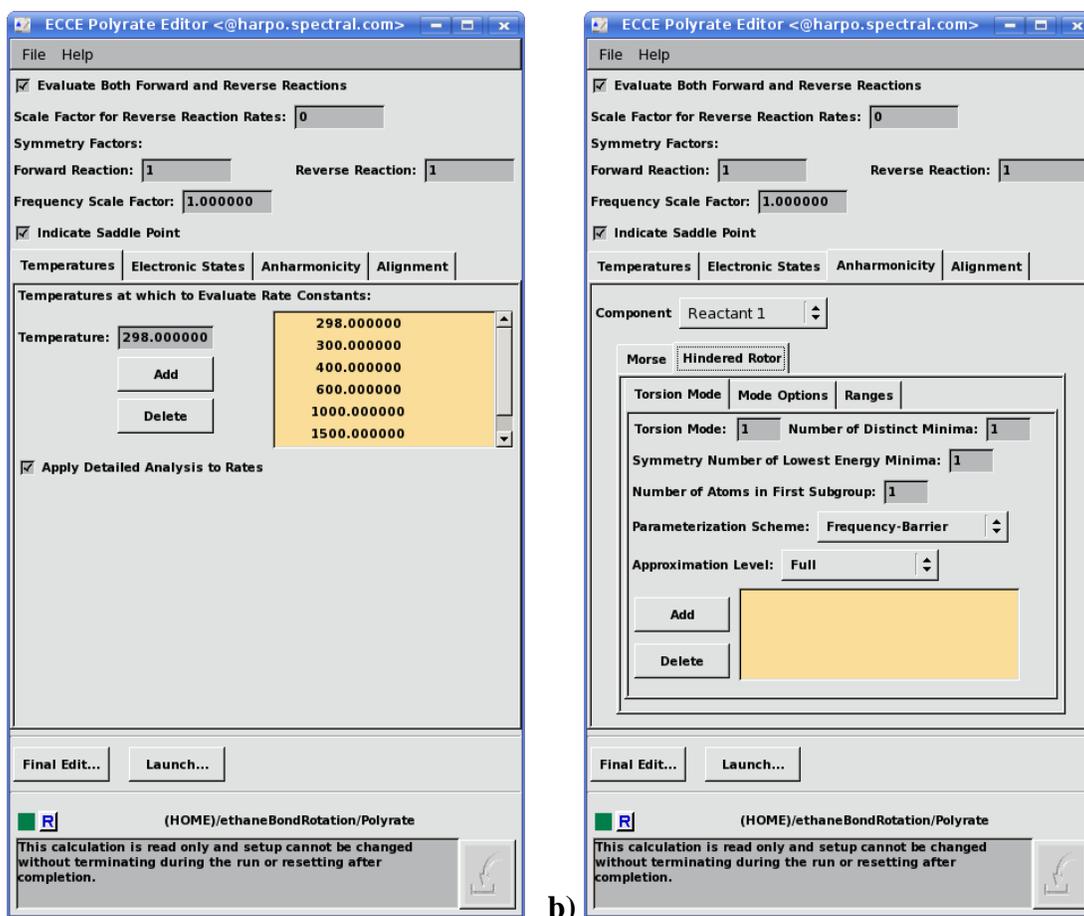


Figure 10. The POLYRATE Editor is used to enter parameters for the transition state theory rate constant calculation. Four tabs are available with input fields associated with Temperatures, Electronic States, Anharmonicity, and Alignment. The editor is shown with a) the Temperature tab selected on the left and b) the Anharmonicity tab selected on the right

The POLYRATE Editor is composed of three main areas. The top area is where basic information relevant to all rate constant calculations may be entered, such as calculating both forward and reverse rate constants and the use of symmetry factors. The middle is where more complex parameters may be entered. The interface is structured for the user to enter parameters for their system via four tabs. The parameters under each tab have default values assuming a broad range of temperatures, one electronic ground state, and no anharmonicity. Starting with these values, a user may make alterations based on their specific system. The bottom of the interface has an option for making a “Final Edit”, where users may edit the POLYRATE input file just prior to running the calculation. This provides the more advanced user with access to any feature of POLYRATE that is not directly supported by the editor.

Support for running POLYRATE calculations through ECCE is accomplished by generating the POLYRATE “fu5” primary input file and copying the “fu30” file from the NWChem DirDyVTST calculation to the directory where POLYRATE will run on the compute resource selected through the ECCE Launcher. This final step gives ECCE the

ability to run an entire kinetics calculation from basic electronic structure calculations to the final transition state theory rate constant prediction.

Viewer

The results for a POLYRATE reaction rate constant calculation are presented by the Viewer in Figure 11. The Viewer displays the transition state and the option to view calculation output in tables and plots inside panels on the left. Figure 11 shows three expanded plots for the equilibrium constant, rate constant, and a comparison between transition state theory and variational transition state rate constants. The plots and tables may be detached from the Viewer, as shown in Figure 12, and expanded.

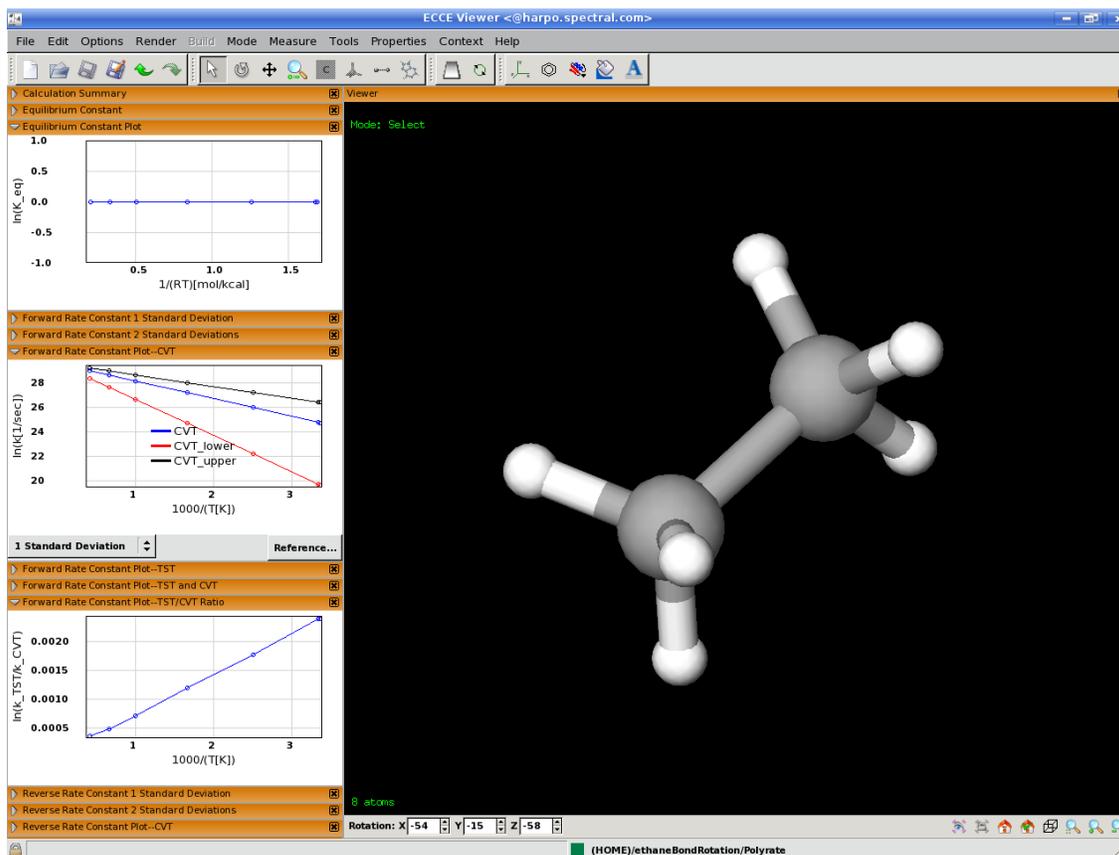


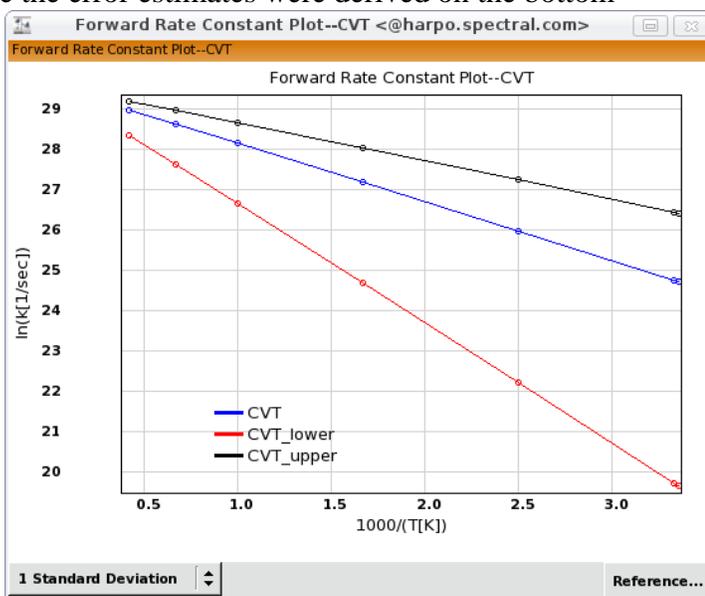
Figure 11. The ECCE Viewer displaying the results of a POLYRATE calculation. The transition state is displayed on the right along with the options to view tables and plots of calculation output on the left. The plots for the equilibrium constant, rate constants, estimated error, and a comparison between rate constants are shown

T	1000/T	ln(k_TST)	ln(k_TST-lower)	ln(k_TST-upper)	ln(k_CVT)	ln(k_CVT-lower)	ln(k_CVT-upper)	ln(k_TST/k_CVT)
298.000000	3.355705	24.726609	19.660630	26.415269	24.724215	19.658236	26.412875	0.002394
300.000000	3.333333	24.759416	19.727210	26.436818	24.757028	19.724822	26.434431	0.002388
400.000000	2.500000	25.980761	22.206607	27.238813	25.978989	22.204834	27.237040	0.001772
600.000000	1.666667	27.196369	24.680266	28.035070	27.195179	24.679076	28.033880	0.001190
1000.000000	1.000000	28.157051	26.647389	28.660271	28.156341	26.646679	28.659562	0.000709
1500.000000	0.666667	28.631322	27.624881	28.966802	28.630844	27.624403	28.966324	0.000478
2400.000000	0.416667	28.983991	28.354966	29.193667	28.983629	28.354604	29.193305	0.000362

Figure 12. A table of rate constants and predicted errors detached or “floated” from the main Viewer window

Error Estimates

Error estimates will be displayed and plotted for predicted reaction rate constants for specific combinations of level of theory and basis set. Currently only two basis sets are supported: 6-31++G** and aug-cc-pVTZ. For the 6-31++G** basis, the level of theory must be either MP or DFT, the latter with an exchange-correlation functional of “Modified Perdew-Wang 1K”, “B3LYP”, or “BB1K”. For the aug-cc-pVTZ basis, the level of theory must be CC. The use of any other combination of basis sets and levels of theory will produce predicted reaction rates without error estimates. It is important to note that the same basis set and level of theory should be applied to any reaction component geometry optimizations as well as the DirDyVTST calculation in order to be confident in the integrity of the results and specifically the error estimates. An example of plotted error estimates is shown in Figure 13. The detached Viewer plot shows the predicted rate constant (CVT, blue line) and the errors estimated for one sigma (CVT_lower, CVT_upper, red and black lines). The plot allows the user to change the value of sigma via the menu on the bottom-left. There is also access to a reference citing where the error estimates were derived on the bottom-



right.

Figure 13. A plot of the Variational Transition State Theory rate constant (CVT), shown with estimated errors (CVT_lower and CVT_upper)

ECCE Rate Constant Prediction Demonstration Walkthrough

This section provides an end-to-end description of a demonstration of the reaction rate constant prediction capability, the same demonstration as the online movie. The steps assume a basic familiarity of the underlying ECCE software.

A. Finding the Transition State

1. Create a new Reaction Study in the ECCE Organizer
2. Launch the NWChem DirDyVTST Editor (right mouse button popup over the task or main menubar Tools menu) after selecting on the DirDyVTST task in the right-hand side Organizer workflow view of the Reaction Study
3. Launch the ECCE Builder for the transition state in the DirDyVTST Editor
4. Build ethane, CH₃-CH₃
5. Edit a torsion to generate eclipsed ethane--i.e. ethane with D_{3h} symmetry or if you look down the C-C bond you only see 3 hydrogen atoms (eclipsed) instead of 6 (staggered). This can be done by selecting H-C-C-H, in that order and changing the torsional angle from 60 to 0. Clear the torsion measure and selection
6. Optional: Use symmetry toolkit to find (verify) D_{3h} symmetry (no need for symmetry clean operation)
7. Save and exit Builder
8. Open the NWChem Electronic Structure Editor by hitting the NWChem code icon button in the DirDyVTST Editor under "Current Code" label for the transition state
9. Select the STO-3G basis set from the Quick Basis Menu in the NWChem Editor
10. Select Theory RHF and Runtime GeoVib
11. Open the Runtime Details window and set the "Find" field to "Minimum". Typically, we would search for a transition state. For this case, symmetry restrictions will cause the Minimum to be located at the transition state.
12. Hit "Launch..." button, select appropriate machine from the Launcher and launch the job
13. The transition state is located (calculation completes) in just a few seconds
14. Launch the Viewer for the Transition-State task (right mouse button popup over the Transition-State icon in the Organizer workflow view) and verify that you have one negative frequency. Animate the negative frequency to verify that it is the ethane bond rotation frequency that is of interest

B. Finding the Reactants and Products

1. Launch Viewer for the completed transition state calculation from the DirDyVTST Editor by hitting the transition state thumbnail
2. Select All (Ctrl-A) in the Viewer

3. Hit “Create Reactants” button in the DirDyVTST Editor
4. Hit “Create Products” button in the DirDyVTST Editor
5. Close the Viewer for the transition state calculation
6. Open Builder for the reactant by hitting the reactant thumbnail in the DirDyVTST Editor
7. Select 4 atoms H-C-C-H (in that order), whose torsion angle is 0 in the transition state structure
8. Set torsion angle to -60
9. Find (verify) symmetry as D3d
10. Save and exit Builder
11. Repeat steps 6-10 for the product, setting the torsion angle to 60 this time

C. The DirDyVTST Calculation

1. From the DirDyVTST Editor open the Setup window
2. Divide the symmetry tolerance by 10 (making it 0.0001 Bohr or 0.00000529 nm depending upon the units selected)
3. Set the general theory to RHF (leave single point theory as None)
4. Click on “General Basis Set...”
5. Double-click to select STO-3G, save and exit the Basis Set Tool
6. Set the following Path Parameters in the DirDyVTST Editor Setup window:
 - a. Minimum Energy Path Step Increment 0.002 nm (0.0378 Bohr)
 - b. Increment for Saving 0.002 nm (0.0378 Bohr)
 - c. Increment for Recalculating Hessian 0.004 nm (0.0756 Bohr)
 - d. Lower Limit -0.01 nm (-0.189 Bohr)
 - e. Upper Limit 0.01 nm (0.189 Bohr)
7. Set the Integration Algorithm to “Corrected LQA”
8. Optional: Click on Final Edit in the DirDyVTST Editor to show the NWChem input file ECCE has created via the GUI
9. Launch the DirDyVTST calculation via the Launcher. Note: NWChem DirDyVTST requires a special patch to run on more than a single processor. As of NWChem release 5.1.1, this patch had not been incorporated into the standard NWChem release.
10. As the calculation is running, open the Viewer and look at the Reaction Trace property where the geometry can be animated over the dividing surface. Depending on machine, the job will take a few minutes to complete

D. The POLYRATE Calculation

1. In the Organizer, create a POLYRATE task under the Reaction Study
2. Open the POLYRATE Editor on this newly created task

3. Select Final Edit (no changes needed) to view the ECCE generated input file
4. Hit “Launch...” button, select appropriate machine from the Launcher and launch the job. Job completes almost immediately
5. Open Viewer and look at reaction rate and equilibrium constant tables and plots
6. If desired, hit "Shell in Calculation Run Directory..." from the Organizer and look at regular POLYRATE output files

Builder Lasso Selection

(6.0) The capability to select multiple atoms and bonds at once in the Builder or Viewer by surrounding them with a rectangular “lasso” has been restored. This feature was temporarily lost when direct atom dragging was added in ECCE 5.0.1. Both of these features use the left mouse button in select mode and thus the user must choose their preferred behavior from the menu item labeled “Select Mode Action” under the “Options” menu. The default behavior is “Atom Drag” although if “Lasso Select” is specified instead, ECCE will remember this setting as a preference and restore it in subsequent Builder invocations.

Higher Order Spin Multiplicities

(6.0) The electronic structure Calculation Editor now supports spin multiplicities beyond “nontet” (eight open shells). The entry field for multiplicity has been changed from a non-editable choice box to an editable drop-down combo box. The same set of values (“singlet”, “triplet”, etc. for an even number of total electrons and “doublet”, “quartet”, etc. for an odd number of total electrons) will be displayed when clicking on the drop-down menu button next to the entry field. But, it is also possible to type directly into the text field and enter a value without selecting from the drop-down menu items. For values above “nontet”, an integral number must be entered (9=“nontet”). For “nontet” and values below, either an integral number can be entered (e.g. 1 for “singlet”) or the full name can also be entered (lower-case, upper-case, or the first letter capitalized). If an inappropriate value is entered (less than 1, greater than the total number of electrons, invalid based on whether the total number of electrons is even or odd, or just a typo in the spin multiplicity name), a feedback area message will be issued and the value will be reset to maintain a consistent calculation. This capability was primarily added in anticipation of an upcoming ECCE release that adds support for building periodic (lattice) systems and running NWChem Plane-Wave DFT calculations, where chemistry on higher spin state systems is common.

SITE ADMINISTRATOR WHAT’S NEW

Upgrade of Apache HTTPD

(6.3) The Apache HTTPD server (see <http://httpd.apache.org>) used for the ECCE data server has been upgraded from release 2.2.21 to 2.2.22, the latest stable production release. This version of the source code distribution of HTTPD is bundled with the ECCE source code distribution and ECCE binary distributions have this version of HTTPD built and ready to run after ECCE is installed.

Prerequisite Software Check

(6.3) The ECCE binary distribution installation script now includes a check for prerequisite software needed to run ECCE such as the java runtime environment, python and perl scripting languages, and the underlying Gtk user interface toolkit. If the package is found then a check for an ECCE compatible version is performed. This prerequisite software check is a new menu item available from the main installation menu and thus the previous item numbers have changed. These checks are analogous to those done for building ECCE from the source code distribution via the build_ece script except that checks are only made for software needed to run ECCE instead of software needed both to run and build ECCE. Therefore if the binary distribution of ECCE being installed has been built from source code on the current platform there is no need to perform the prerequisite software check when installing.

Installing ECCE 6.2

(6.2) Because ECCE 6.2 requires users to enter their data server password and most existing users will not know this password (it is not the same as the ECCE login password or encryption key that was entered on startup prior to ECCE 6.2), it is recommended that sites run both ECCE 6.2 and their existing ECCE 6.0 or 6.1 concurrently. This is possible because the default ECCE server ports for the Apache HTTPD data server and Apache ActiveMQ message server have been changed allowing a 6.2 ECCE server to run concurrently with a 6.0/6.1 server on the same host. To be able to run both the old and new ECCE either a “Full upgrade” (option 2) or “Server upgrade” (option 6) should be selected at the main installation menu. This will allow users to lookup their existing data server password using ECCE 6.0/6.1 and then use the password to gain access to ECCE 6.2. Note that because of the upgrade process user calculation data will no longer be accessible from ECCE 6.0/6.1 so this old version is functional only for retrieving passwords (hitting “OK” on the login dialog yields an error dialog about the server not having user data and the Gateway toolbar will not be displayed). After some period of time at the discretion of the site administrator the 6.0/6.1 server can be shutdown. At this time any users who didn’t retrieve their data server password will need their password reset by contacting the site administrator before running ECCE 6.2. If the site administrator doesn’t want to run concurrent ECCE servers then the ECCE 6.0/6.1 server can be shut down immediately when installing ECCE 6.2 and all users will need to have their data server password reset with the new passwords being communicated to users before they can run 6.2. The ecce_htpasswd utility script in the ecce-utils directory under the top-level ECCE server directory is used to reset data server passwords. Simply run ecce_htpasswd as the same user who installed ECCE (for write permissions) with the username as the only command line argument. The new password will then be prompted for by ecce_htpasswd.

Upgrade of Apache HTTPD

(6.2) The Apache HTTPD server (see <http://httpd.apache.org>) used for the ECCE data server has been upgraded from release 2.2.15 to 2.2.21, the latest stable production release. Due to changes necessitated by the new password caching, both the ECCE 6.2 server and application software must be upgraded together rather than solely the application software.

Upgrade of ECCE Data Server

(6.1) The Apache HTTPD server (see <http://httpd.apache.org>) used for the ECCE data server along with the bundled mod_dav module has been upgraded from release 2.2.10 to 2.2.15. When installing, we highly recommend upgrading the ECCE server and application software together rather than solely the application software to get the latest HTTPD server enhancements and security patches. The ECCE application software is not compatible with ECCE server versions prior to the ECCE 5.0 release such as ECCE 4.5.x.