Quantemol-N Tutorial

Molecule Definition

In the first panel you are required to select your target molecule by selecting each atom individually from the periodic table or simply by typing in the molecular formula. It is important you check the casing of your lettering as, for example, BR is not the same as Br when considering molecules. To give your molecule a positive or negative charge insert a + or - sign respectively. For example to investigate a doubly positively charged methane molecule your input should be CH4++. Note that only atoms up to and including the fourth period are currently selectable.

The 'Import molecule...' option allows you to import molecular data from a variety of chemistry file formats.

Coordinate Entry

Once you have selected your target molecule you are required to position each atom individually. The equilibrium co-ordinates of each separate atom in your molecule can be found here where the atomic positions of several molecules at their equilibrium geometry have already been determined from experimental or calculated data. The choice of which to use is left to the user. If there is no geometry available for your molecule, one can be calculated by consultants at Quantemol.


From here you can also rotate your molecule by any angle around either the X,Y or Z axes or alternatively move it to its centre of mass. This may be necessary when applying the symmetry properties of the system to ensure the planes/points are situated in the correct position on the next panel. You are advised to check your molecule in the preview on the next panel before doing this as this will undoubtedly alter the coordinates you have input.

Symmetry Definition

A preview of your molecule will appear according to the geometry input on the previous panel. Here you are required to select a point group for your molecule. In order to see every aspect of your molecule to determine its symmetry you may wish to orientate it by right-clicking on the image and dragging along your chosen direction. Note that the natural point group for your molecule may not always be available, in this case you must refer to descent symmetry tables.
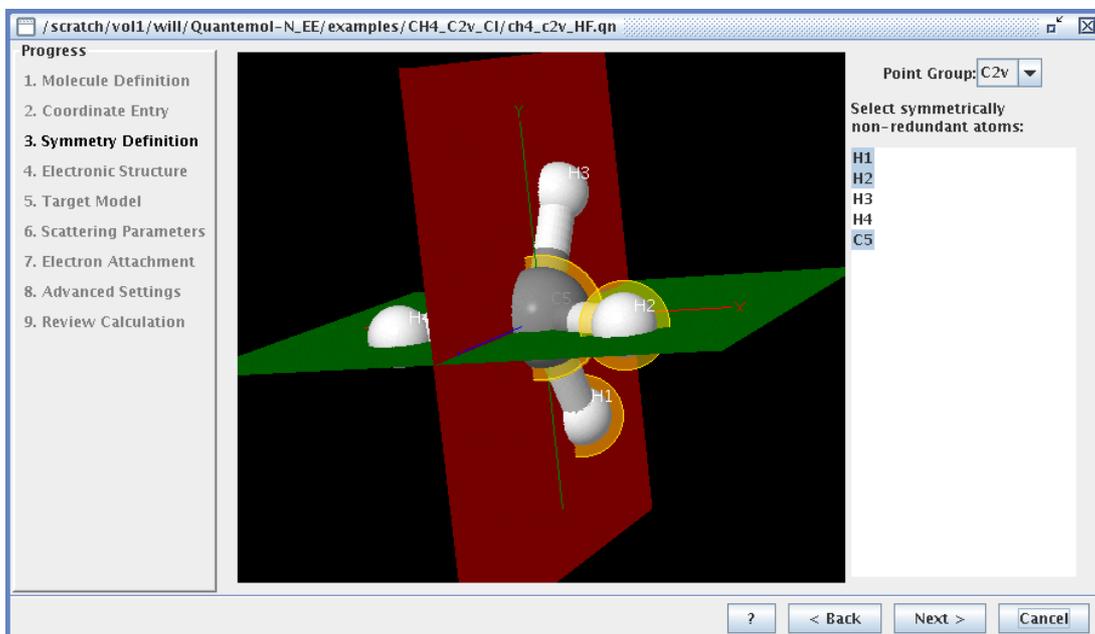
The point groups of many molecules are listed here

Descent (correlation) tables

The Quantemol code only supports Abelian point groups, i.e., those whose symmetry operations are commutative, which means that only point groups with symmetry as high as D2h are selectable. Therefore you will have to choose a lower symmetry sub-group if your molecule does not fit this limitation by referring to a descent symmetry table to check which of the correlated groups are selectable in Quantemol-N. Suggestions of which sub-groups to use for certain natural groups can also be found in the Quantemol help menu.

Non-redundant atoms

The non-redundant atoms of the molecule are those which cannot be generated via symmetry operations. So for the water molecule (which has C_{2v} symmetry) the oxygen atom and one of the hydrogen atoms would be labelled as 'non-redundant,' as the hydrogen atom is generated by the other one by reflection through a plane.

Take methane, in C_2 symmetry as another example, since it can be used as it is a sub-group of T_d, (see descent tables):
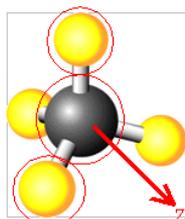
The atoms circled in red represent the non-redundant atoms of methane as these atoms are not re-generated once the molecule is orientated according to the point group, in this case of C_2 symmetry: when the molecule is rotated 180 degrees around the axis of greatest symmetry (z-axis labelled here) you can see that the top circled hydrogen atom (yellow) replaces the far left hydrogen atom and the bottom circled atom replaces the one on the far right (the carbon atom replaces itself).

Electronic Structure

It is a requirement of the code to allocate the number of singly/doubly occupied orbitals for each irreducible representation which is determined from the electron configuration of the molecule.
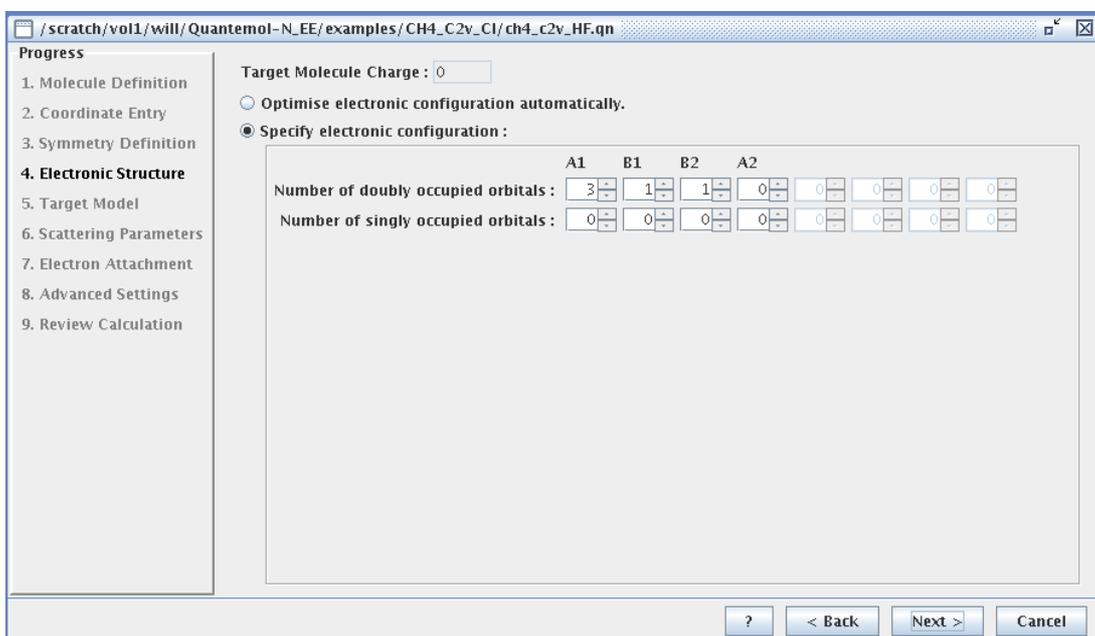

In most cases, Quantemol-N can automatically find the correct electron configuration, but for some it must be entered manually, e.g. molecular oxygen which has a

triplet ground state. If your molecule is not in its natural point group, you will need to convert the irreducable representations of the molecule to the used point group. Exercises on how to do this are included in the documentation.

Target Model

A target model and basis set should be chosen depending on how accurate you wish your calculation to be. The choice of basis set provdied to you by Quantemol-N depends on the elements comprising your molecule.
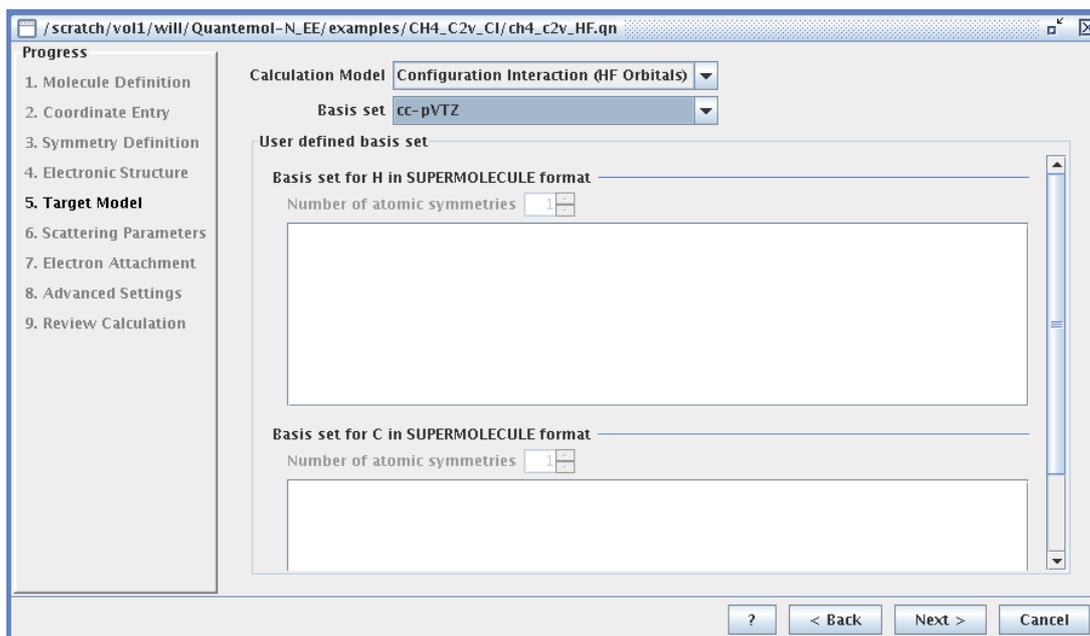
Quantemol-N currently has two selectable calculation models:

1. Self Consistent Field (SCF) approximation

SCF is also known as the Hartree-Fock method, it gives an approximate value of the ground state-wavefunction and ground state energy of the molecule. It is an iterative process which works by selecting an approximate Hamiltonian, solving the Schrodinger equation to obtain more precise sets of orbitals and inserting these results back into the Schrodinger equation and repeating this process until the results converge.

2. Configuration interaction (CI)

CI goes beyond the Hartree-Fock model and involves mixing the many-electron wavefunctions compiled from different configurations to provide an improved many-electron state. CI further increases the accuracy of the solution by replacing one or more occupied orbitals with virtual orbitals. A CI calculation will therefore enable more states (other than the ground state) to be included which is selectable on the next panel.

A number of common basis sets are already defined in Quantemol-N. You may wish to define your own basis set to improve the accuracy of your calculation:

Defining your basis set

Quantemol also gives you the opportunity to define your own basis set. However this must be done with care, as while a more complex basis set may give you a more accurate solution to the Schrodinger equation, it will take up a greater amount of computing time. You can find definitions from the basis set exchange. Simply submit your chosen basis set in SUPERMOLECULE format along with the elements of the molecule you wish to investigate. Copy and paste the orbital-type functions displayed on the web page onto the space provided on the fifth panel for each seperate element. Note that all elements of the molecule must be done in the same basis set.

Scattering Parameters

In the sixth panel you are given the opportunity to choose the maximum number of target states per symmetry you wish to include in your CI calculations, 3 is the recommended value to ensure a reasonable computing time. You are also required to choose the maximum vertical excitation energies of the target states to be included in the calculation, all those above this value will be discarded. A good value for this is the ionisation energy of your molecule as this ensures an adequate number of orbitals are included.
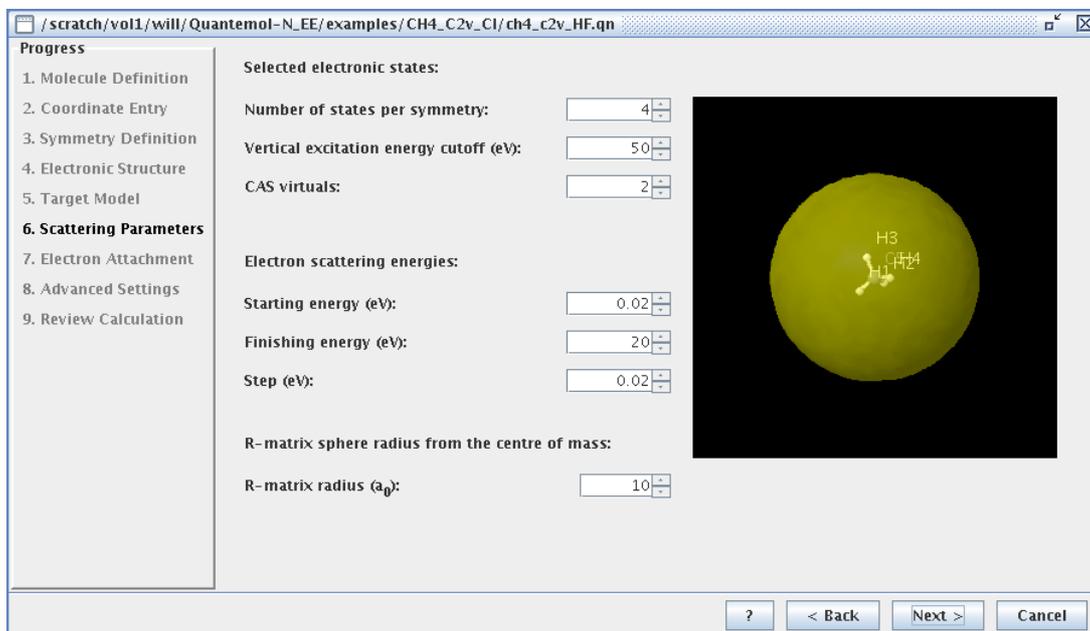
The start and finishing electron energies refer to the region of the electron's scattering energy you wish to investigate. The step size is the magnitude of the incremation between each data point plotted on the eigenphase and cross section graphs.

The last bit of information needed on this panel is the R-matrix radius. Quantemol has a default setting of $10a_0$ which should be good enough for most calculations however you may need to increase this to ensure the target wavefunction is fully contained within the sphere especially when defining your own basis set.

Dissociative Attachment Options

By default the option to estimate dissociative attachment cross-sections is turned off. However if you wish to use the Quantemol-N estimator this panel is where you can specify the details. Please note this calculation is not fully *ab-initio*, and is instead designed to create quick but accurate estimations of the dissociative attachment process.

Firstly the option must be checked to tell Q-N to calculate these cross-sections. Now some details must be established, firstly the ground state vibrational frequency of the neutral target molecule in question must be chosen, this can either be a default value, or a user-specified value from experiment or in the literature (given in wavenumbers cm^{-1}), no matter what option is chosen, a value of the dissociation energy of the neutral must also be chosen and given (in eV). This can be taken from experiment or from the scientific literature on the chosen molecule. *As the panel below shows, an error message will show and you will not be allowed to proceed until a suitable, positive value of the dissociation energy is chosen.*

The user must also specify the way in which they would like the neutral-electron compound to break-up. This can either be the default, radical and anion breakup, or instead the user can define the exact 2 species they wish the compound to break up into, providing they also define the electron affinity of species B (in eV), again this can be taken from the scientific literature.
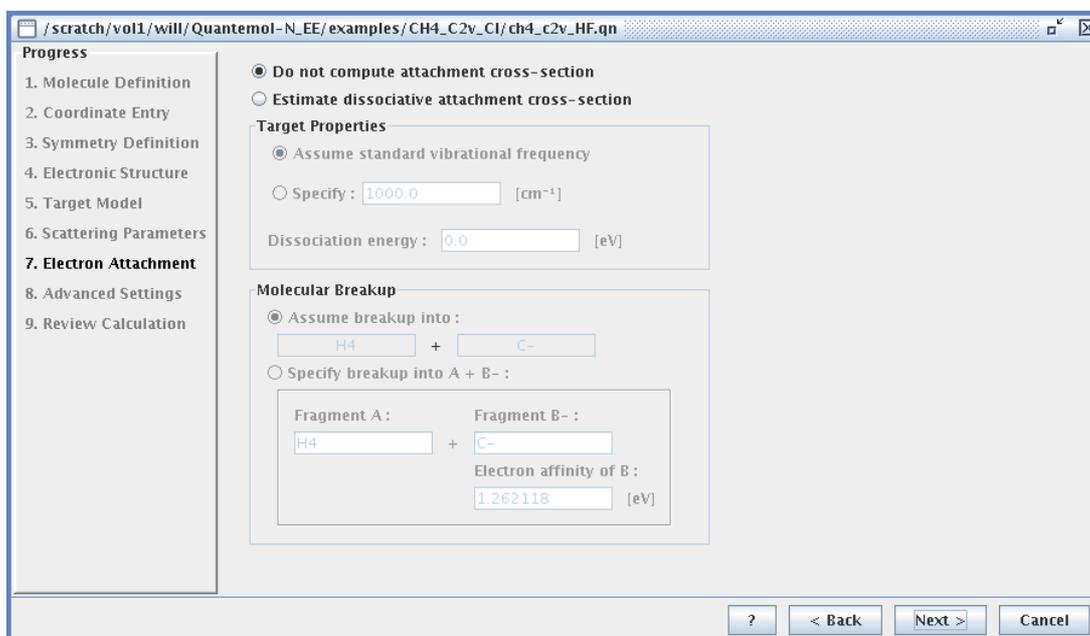
Once the user has specified the options and correctly filled in the required information, click the 'Next' button to proceed to the final panel of the wizard.

Output options

You are required to save your calculation before running it. Quantemol-N files have the extension *.qn*. If you ommit it, it will be appended automatically. It is also prbably wise to give your job files descriptive names, and not use spaces to facilitate command line jobs in the event that you use this feature.
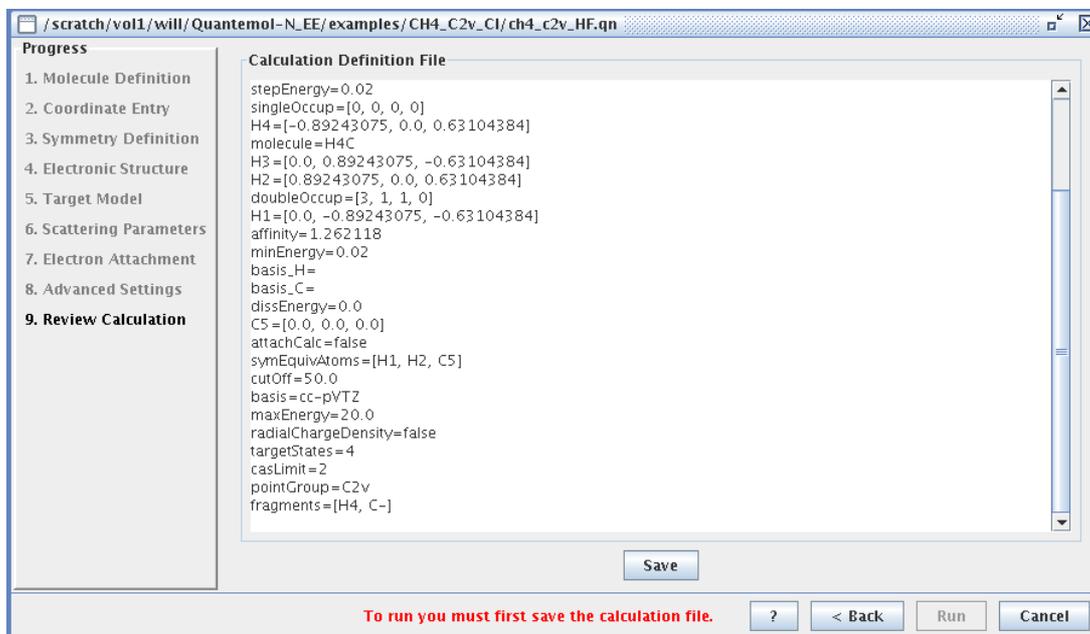
Once you are finished saving you will be asked to confirm starting a new calculation.

Results

Output

Once you run the calculation the output will immediately open. Several messages will appear; however, some of the ones you may wish to pay attention to including orbital energies, target states and CASCI which are explained in the Quantemol-N documentation.

Graphs

Once your calculation is complete you will receive a message telling you so and up to five graphs will simultaneously appear depending on your chosen target model. Be aware that these calculations are likely to take a while therefore do not be discouraged if you do not receive results quickly, Quantemol will return an error message if a mistake in the input is detected. The commands for the scattering and target properties are then displayed in the output which can be obtained from the work directory.

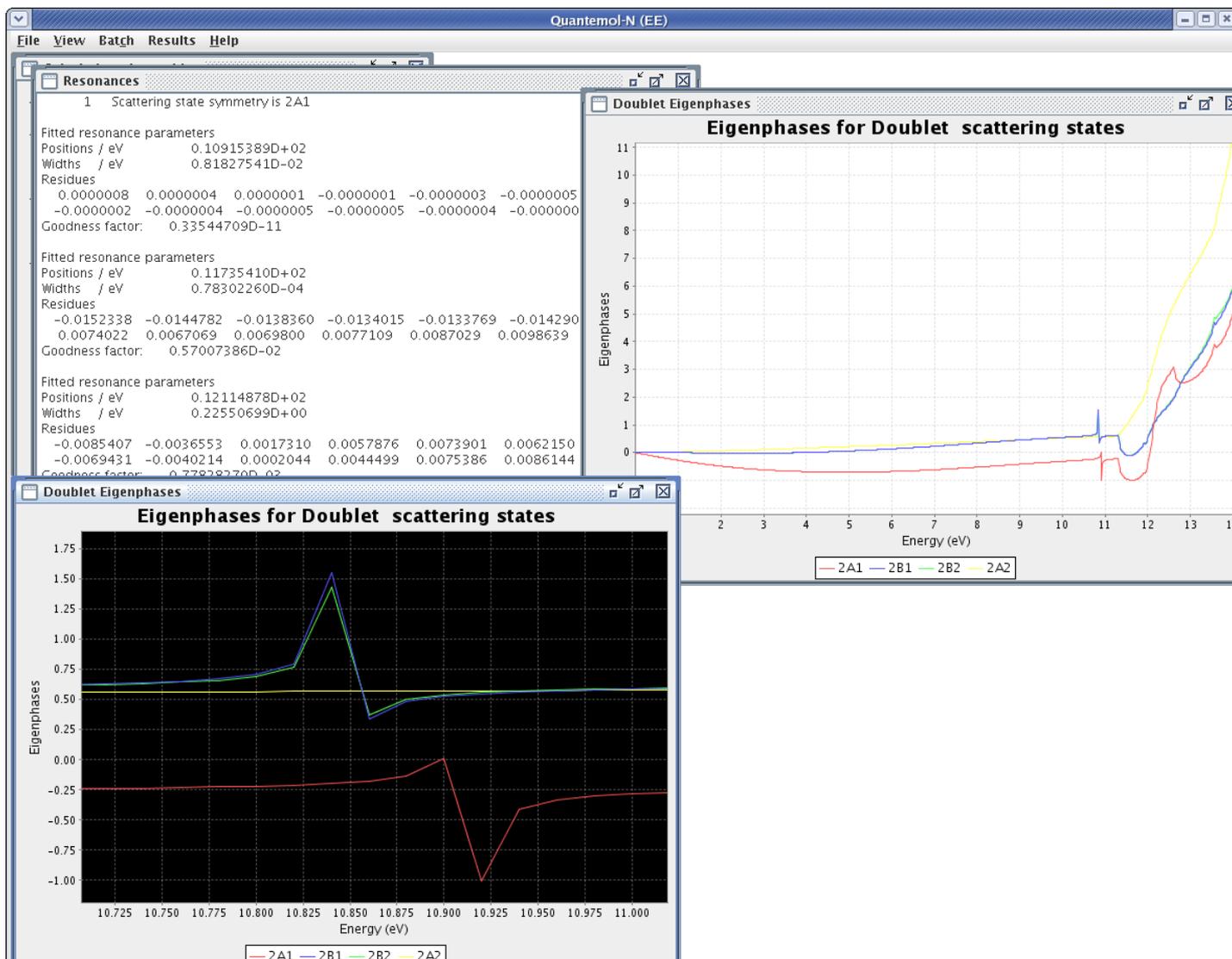The graphs that will potentially appear are:

- Eigenphases vs. electron scattering energy.
- Total elastic cross-section vs. electron scattering energy.
- Total elastic cross-section (without Born correction) vs. electron scattering energy.
- Excitation cross-sections vs. electron scattering energy.
- Elastic scattering: rate co-efficients vs. temperature (for CI calculations only).
- BEB (Binary Encounter Bethe) ionization cross-section vs. electron scattering energy.
- Estimated Attachment Cross Section vs. Scattering Electron Energy
- BE scaled born cross section - A high energy approximation for dipole allowed transitions

These graphs will allow to determine various properties of your calculation such as the dipole moment of your molecule and the resonance parameters

Example Graphs

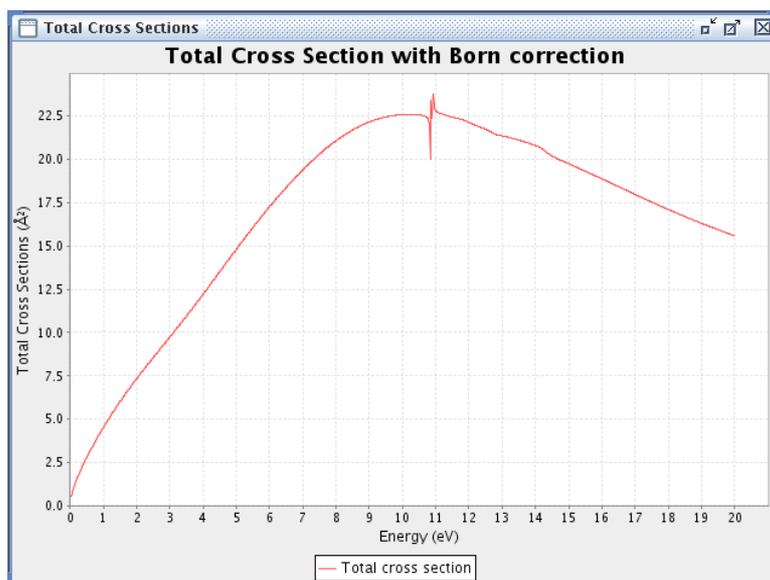### Eigenphases vs. electron scattering energy

The graph enables you to determine how reliable your data is, an erratic or highly oscillatory trace is often associated with unreliable data. A jump in π is indicative of resonance, sometimes these jumps are very quick, and may appear as a discontinuity; other times they are slower. It is a good idea to open the "Resonances" results tab when viewing these graphs, to confirm whether a region of the graph is showing a resonance or not. The eigenphase is modulo π. Attempts have been made to remove arbitrary jumps in π, any remaining jumps can safely be ignored. They are not resonances. There is also a background though, so if the background is changing the eigenphase in the opposite direction to the resonance, then it may be hard to see.

Here, the eigenphases for doublet scattering states have been opened twice, with the one window zoomed in on the resonances around 10.85eV for the B$_1$ and B$_2$ symmetries and 10.9eV for the A$_1$ symmetry. As seen in the "resonance" results pane, the A$_1$ symmetry is at 10.915eV. The "D" in the resonance pane is equivalent to an E. i.e. 10.915... x 10^2 eV for the first resonance. The width of a resonance can help to verify the validity of a model, with better models converging on thinner resonances. Some resonances are inherently wide however.

Total elastic cross-section vs. electron scattering energy

You will also be presented with a graph of the total elastic (kinetic energy conserved before and after the collision) cross-sections in units angstrom^2 (10^{-20}m^2) as a function on the electron's scattering energy.

Excitation cross-section vs. electron scattering energy (for CI calculations only)

The excitation cross-sections per symmetry will also be plotted for CI calculations.

You may find that there is no trace is found for the excitation cross sections. This is because the electron scattering energy is below the threshold value i.e. it is not large enough to excite the molecule to a higher state. It can therefore be concluded that all the vertical excitation energies of the molecule are higher than the highest energy labelled on the graph and no excitation cross sections are present. To rectify this you are recommended to increase the maximum electron energy on the sixth

panel so that the excitation cross sections are displayed.
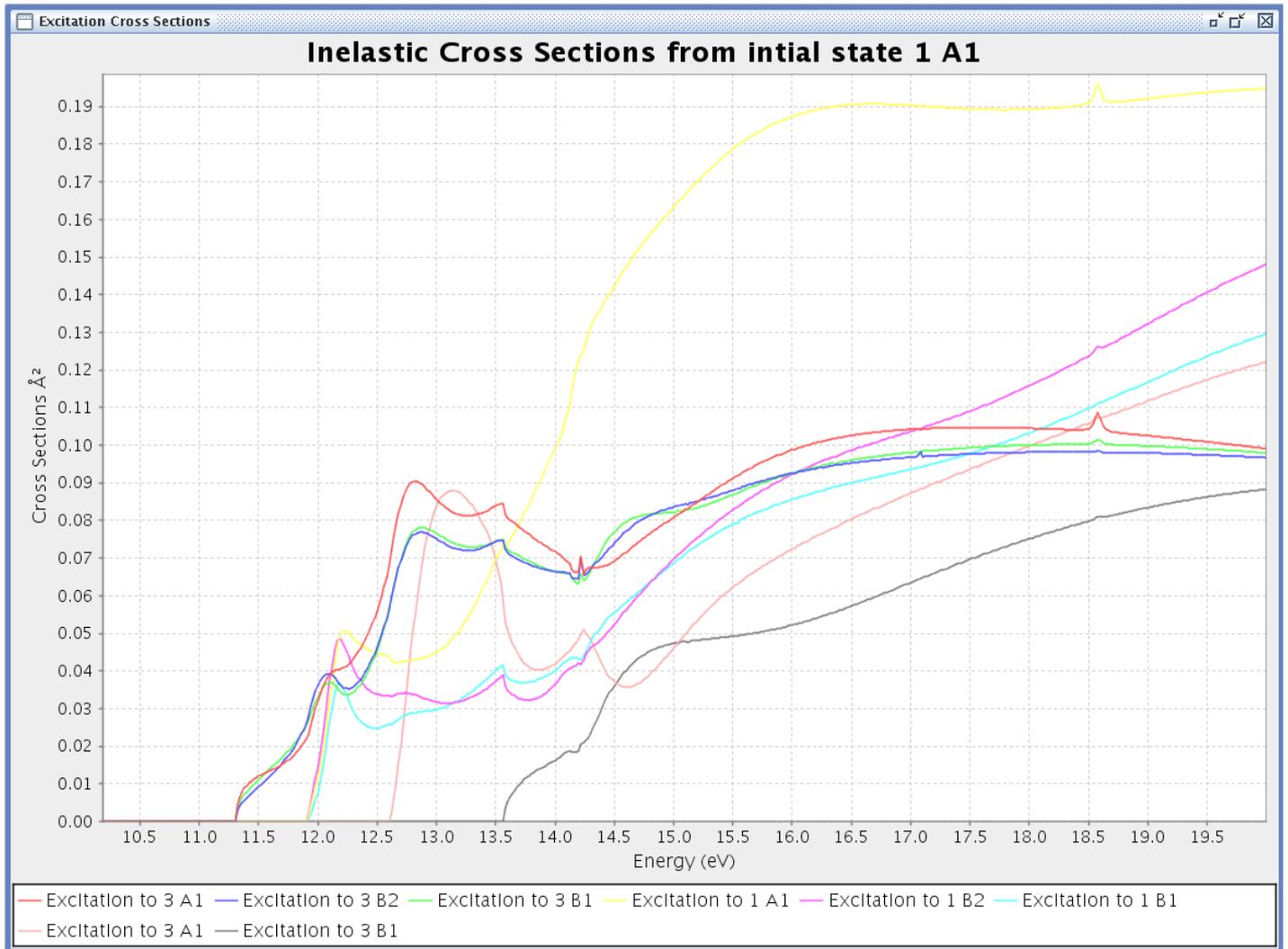
Here the graph has been cropped to illustrate the region of interest. By Koopman's theorem the ionisation energy of methane is 14.8eV, and so features above this energy should be treated with care.

Recall that methane is a member of the symmetry group T_d, and that the subgroup C_{2v} is used for the calculations. This means that the C_{2v} symmetries B_1 and B_2 are always degenerate, with each other and also one of A_1 or A_2 (T_2 and T_1 in the T_d group respectively). A_1 and A_2 can also be degenerate with one another (irrep. E), or non degenerate (A_1 and A_2 in T_d).

Note that the legend shows only the spin multiplicity of the state, and it's symmetry. This means that some lines may have the same label. By observing the threshold at which the channel opens, one can deduce (trivially) which instance of the symmetry the line refers to. (i.e. the red line is 1 $^3A_1$ symmetry. The peach coloured line is 2 $^3A_1$ symmetry)

Elastic scattering: Rate co-efficients vs. Temperature

Here the rate coefficients are plotted as a function of the kinetic temperature which is defined according to the Maxwell-Boltzmann distribution.
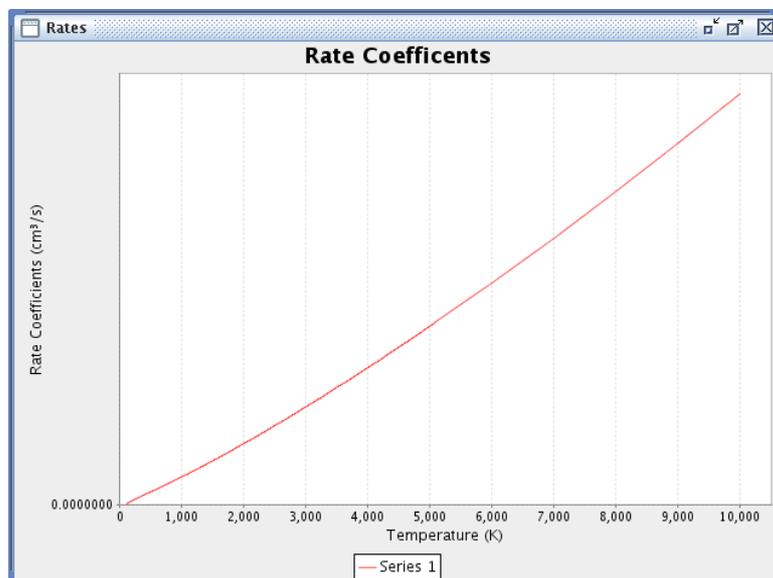

From this graph it is noted that the scattering rate increases rapidly up to approximately 2500K before gradually dying down as the temperature is further increased.

There is currently a minor bug in quantemol in which the Rate coeficcients may not be shown on the Rates axis. this is because they are very small (< 1E-7) and there

is an issue drawing the numbers. It will be remedied soon, but until then, you may still obtain the plot data. Firstly, you may right click on the graph, and navigate properties.../plot/range axis/range to view the range of the axis (in this example, it is 4.15548E-8.) Or alternatively, you may open the rates.dat file, and copy the data points into a graphing program of your choice.

BEB Ionization cross-section: cross-section vs. scattering emergy

Here the BEB ionization cross-section is plotted as a function of the electron scattering energy.
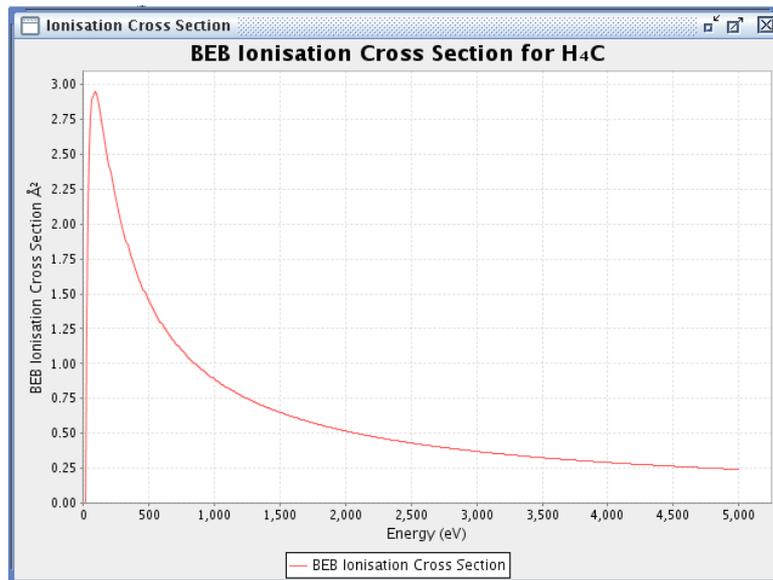
For more information on BEB cross-sections please visit here.

BE scaled born cross section

For Dipole allowed transitions, a scaled born cross section is given. This is not a very reliable method at low energies, however, it is a good approximation for high energies.
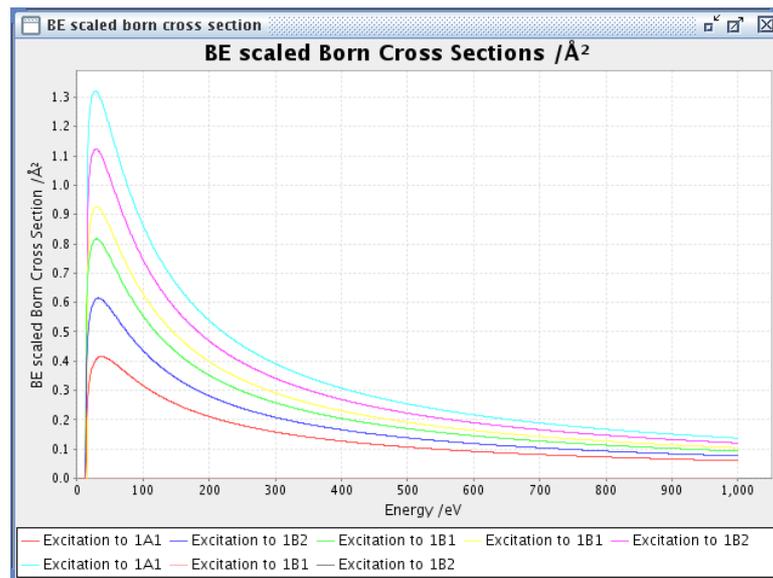
One can determine which curves here correspond to which in the inelastic cross sections graph by zooming in on the lower end of the scale and matching the thresholds.