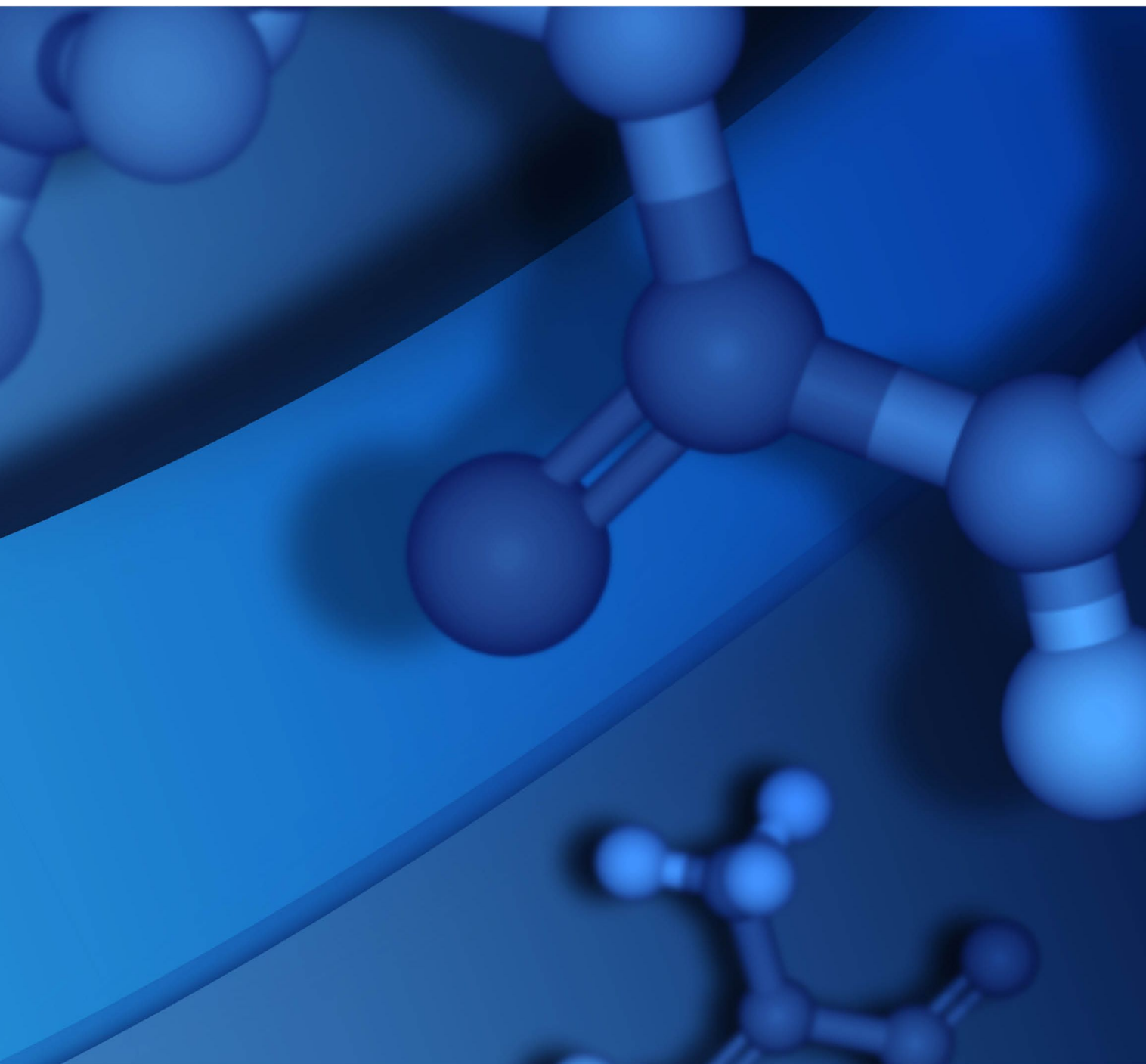


VAMP GUIDE

MATERIALS STUDIO

8.0



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Introduction

VAMP is a semiempirical molecular orbital package capable of predicting geometries, heats of formation, and a host of molecular properties. The program is optimized to be highly numerically stable and fast, so that most calculations can be run interactively on a PC.

VAMP includes routines implementing the natural atomic orbital/point charge (NAO-PC) model for molecular electrostatic properties. It gives accurate dipole and quadrupole, and high quality molecular electrostatic potentials (MEPs), many times faster than comparable methods. NAO-PC is available for the standard semiempirical Hamiltonian methods - MNDO, AM1, and PM3. The other NDDO Hamiltonians that are available are MNDO/C, AM1*, MNDO/d, and PM6. In addition, four ZINDO Hamiltonians are included in VAMP - CNDO/1, CNDO/2, INDO/1, and INDO/2.

VAMP contains many enhancements to geometry optimization and two-electron integral calculations. The program uses Baker's EF routine for geometry optimization, with several options for calculating the initial Hessian matrix. VAMP can successfully optimize geometries. The program also contains three different transition state optimizers: eigenvector following, NLLSQ, and Powell's method.

VAMP simulates solvent effects using numerical self-consistent reaction field (SCRF) calculations for ground and excited states; and COSMO for ground states. The SCRF calculations use Tomasi's numerical method, with a cavity bounded by the solvent-excluded surface. The SCRF calculations also use NAO-PC electrostatic properties.

VAMP also calculates ^{13}C chemical shifts using artificial neural nets.

VAMP reports a number of molecular properties, such as ionization potential, multipole moments, accurate molecular polarizabilities, atomic polarizabilities, and potential-derived charges.

Further Information

For more information about the Materials Studio and other Accelrys software products, visit BIOVIA Support on the Web: <https://community.accelrys.com/index.jspa>

Tasks in VAMP

The VAMP module allows you to predict geometries, heats of formation, and a host of molecular properties, including ionization potential, multipole moments, molecular and atomic polarizabilities, and potential-derived charges. VAMP can currently perform four different tasks:

- Single-point energy calculation
- Geometry optimization
- Transition-state search
- Transition-state optimization

Each of these calculations can be set up so that it generates specified chemical and physical properties. An additional task, known as a properties calculation, allows you to restart a completed job to compute additional properties that were not calculated as part of the original run.

There are a number of steps involved in running a VAMP calculation, which can be grouped as follows:

- **Structure definition:** A 3D Atomistic document containing the system of interest must be specified. There are a number of ways to prepare a structure:
 - Molecules can be built using the sketching tools in the Materials Visualizer
 - Polymers can be constructed using the Polymer Builder in the Materials Visualizer
 - Nanostructures can be prepared using the tools available in the Nanostructure Builder in the Materials Visualizer
 - Existing structures can be modified using the Materials Visualizer sketching tools
 - Structures can be imported from an existing structure file

In the case of a transition-state calculation, a 3D Atomistic Trajectory document containing a reaction sequence is required as the input document. You should define the structures of the reactants and the products in two separate 3D Atomistic documents via the methods listed above and then use the Reaction Preview tool to generate the trajectory.

Note: VAMP can only be used to perform calculations on molecules. Structures with 2D periodicity (surfaces) or 3D periodicity (crystals) cannot be used in VAMP.

- **Calculation setup:** Once a suitable 3D structure document has been defined, then it is necessary to select the type of calculation to be performed and set the associated parameters. For example, in the case of a transition-state optimization, these parameters include the search protocol and the convergence threshold. Finally, the server on which the calculation is to be run should be selected and the job initiated.
- **Analysis of the results:** When the calculation is complete, the files related to that job are returned to the client and, where appropriate, displayed in the Project Explorer. Some further processing of these files may be required to obtain observables such as electron density fields. The tools on the [VAMP Analysis dialog](#) may be used to visualize the results of the calculation.

To select a VAMP task

1. Choose *Modules | VAMP | Calculation* from the menu bar to display the VAMP Calculation dialog.
2. Select the [Setup tab](#).
3. Select the required VAMP task from the *Task* dropdown list.

Energy

Semiempirical methods such as VAMP compute the heat of formation at 298 K. This is in contrast to ab initio methods, which generally compute a total electronic energy. The heat of formation is determined from a combination of computed and parameterized data as discussed by, for example, Stewart ([1990](#)).

The default unit of energy in VAMP is kilocalories per mole.

By comparing the total energies of different systems, you can compute a range of properties that have chemical significance, such as:

- Heats of reaction
- Energy barriers
- Conformational energy differences
- Bond strengths
- Adsorption energies

The heat of formation computed by VAMP for a particular molecular geometry depends upon a number of computational parameters. When comparing energies, it is important that you use the same parameters for each system. When you set up a calculation using the [VAMP Calculation dialog](#), Materials Studio selects reasonable defaults for you, so it is not absolutely necessary to specify values for each of these parameters.

Note: Not all the options available in VAMP are compatible with each other. As a result, some options on the VAMP Calculation dialog will become unavailable when you make certain selections or run calculations on systems for which particular options are not supported. See the [VAMP input restrictions](#) topic for further details.

To perform an energy calculation

1. Either import the structure from a pre-existing file or construct a new system using the sketching tools or the tools for building surfaces and nanostructures in the Materials Visualizer.
2. Choose *Modules | VAMP | Calculation* from the menu bar to display the VAMP Calculation dialog.
3. Select the [Setup tab](#) and choose **Energy** from the *Task* dropdown list.
4. Select the type of *Hamiltonian* you wish to use, **NDDO** or **ZINDO**, from the first dropdown list. Then, choose a particular Hamiltonian from your selected category from the second dropdown list. The Hamiltonian controls the approximations used in computing the heat of formation. For most situations, the **PM3** NDDO Hamiltonian is the best choice.
5. Specify the spin multiplicity and charge of the system and select the type of spin calculation that will be performed from the *Spin* dropdown list.
6. Select the [Electronic tab](#). Select appropriate [electronic options](#) for your calculation. If you wish to specify any additional parameters, click the *More...* button to display the [VAMP Electronic Options dialog](#) and alter the settings accordingly.
7. Select the [Properties tab](#). If you wish to compute any additional properties of the system as part of the VAMP run, check the appropriate checkboxes in the list.
8. Select the [Job Control tab](#) and choose a [server](#) on which to run the VAMP job from the *Gateway location* dropdown list. If necessary, specify the *Queue* to which the job will be submitted. VAMP will automatically assign a name to the job based on the name of the 3D structure document containing the molecule being studied. If you wish to specify an alternative name, uncheck the *Automatic* checkbox and enter the new name in the *Job description* text box.
9. Click the *More...* button to display the [VAMP Job Control Options dialog](#). Select the documents to be used for live updates and set the behavior of VAMP on job completion.

10. Click the *Run* button.
11. If you wish, you can examine the intermediate results to ensure that the calculation parameters are reasonable.
12. After the job has finished, [view the output files](#). You can then [analyze the results](#).

Geometry Optimization

After a structure is built, it usually needs to be refined to bring it to a stable geometry. The refinement process is known as optimization, and is an iterative procedure in which the coordinates of the atoms are adjusted so that the energy of the structure is brought to a stationary point, i.e., one in which the forces on the atoms are zero.

You can request an energy minimization, a search for a relative minimum on the energy hypersurface. The geometry corresponding to this structure should have a close resemblance to an actual physical structure of the system at equilibrium. You can also perform an optimization to a transition state. Searching for a transition state is covered [elsewhere](#). In this section, 'geometry optimization' is taken to mean 'geometry minimization'.

Note: Not all the options available in VAMP are compatible with each other. As a result, some options on the VAMP Calculation dialog will become unavailable when you make certain selections or run calculations on systems for which particular options are not supported. See the [VAMP input restrictions](#) topic for further details.

To perform a geometry optimization (minimization)

1. Choose *Modules | VAMP | Calculation* from the menu bar to display the VAMP Calculation dialog.
2. Select the [Setup tab](#).
3. Set the *Task* to [Geometry Optimization](#).
4. If desired, set additional options by pressing the *More...* button to display the [VAMP Geometry Optimization dialog](#). Normally, the default options will yield adequate results.
5. A checkbox allows you to perform the optimization in either internal or Cartesian coordinates. Cartesian coordinates are generally more reliable for large systems.
6. Click the *Run* button.

Tip: When high accuracy is required in geometry optimization, set the *Quality* to [Fine](#) on the Geometry Optimization dialog. In addition, it is recommended that you set the *SCF quality* to [Fine](#) on the [Electronic tab](#).

TS Search

The Mclver-Kornonicki transition-state optimizer performs a saddle-point optimization, approaching the transition state from two different geometries, one on either side of the barrier. The result is a point close to the real transition state, which can be further refined using the standard [transition-state optimization methods](#).

Input to a transition-state search calculation

TS Search calculations are always performed in Cartesian coordinates.

Note: Unlike other methods, TS Search calculations require a trajectory file as input, rather than a single structure document.

Note: Not all the options available in VAMP are compatible with each other. As a result, some options on the VAMP Calculation dialog will become unavailable when you make certain selections or run calculations on systems for which particular options are not supported. See the [VAMP input restrictions](#) topic for further details.

Perform a TS Search calculation by setting the *Task* to **TS Search** on the [Setup tab](#) of the VAMP Calculation dialog. The *More...* button will be disabled since no additional setup parameters are required.

Note: Barrier height can be calculated by comparing the heats of formation for the transition state with the one for the reactant. Structures of both the reactant and the transition state should be well optimized, using the same VAMP input parameters.

To set up a TS Search calculation

1. Begin with one structure in a 3D model document to represent reactants, and another structure in a second 3D model document to represent products. You can construct or import these structures.
2. Use the Find Equivalent Atoms tool to match equivalent atoms in the two documents. The synchronous transit method performs a geometric interpolation between the atomic coordinates of the atoms in the reactants document and the atoms in the products document. All the atoms in the two documents must be matched in order to accomplish this.
3. Generate a trajectory that converts reactants into products using the Reaction Preview tool. You can animate this document to check that the reactants are converted correctly to products. If you are satisfied with the match, proceed with the calculation. If not, use the Find Equivalent Atoms tool to edit the atom correspondence and try again.
4. Using the document that was created by the Reaction Preview tool, select your options for the *TS Search* calculation and submit the VAMP calculation by pressing the *Run* button.

TS Optimization

Searching for a transition state is similar to performing a geometry minimization. Many of the options are the same, and the setup dialogs are similar. Like the minimization, the transition-state optimization can proceed in Cartesian or internal coordinates.

Starting from a reasonable guess for the transition state, VAMP performs a Newton-Raphson search on the potential energy surface. This searches for an energy maximum along one normal mode and a minimum along all other modes. VAMP generates the required Hessian matrix at the beginning of the calculation.

Calculation parameters

The [VAMP TS Optimization dialog](#) offers you three options for performing the TS optimization: Eigenvector following (**EF**), Powell's method (**Powell**), and non-linear least squares (**NLLSQ**). In most cases, the EF optimizer is faster. However, the Powell optimizer is better at finding transition states on flat potential energy surfaces. NLLSQ only optimizes the atomic forces (gradients) and finds the nearest stationary point; it therefore requires a starting guess that is very close to the actual transition state.

The *Quality* control specifies how closely you want to calculate a stationary point. The optimization will stop when the gradient norm on the atoms is below the specified tolerance.

A checkbox allows you to perform the optimization in either internal or Cartesian coordinates. Cartesian coordinates are generally more reliable for large systems.

Note: Not all the options available in VAMP are compatible with each other. As a result, some options on the VAMP Calculation dialog will become unavailable when you make certain selections or run calculations on systems for which particular options are not supported. See the [VAMP input restrictions](#) topic for further details.

To perform a transition-state optimization

1. Choose *Modules | VAMP | Calculation* from the menu bar to display the VAMP Calculation dialog.
2. Select the [Setup tab](#).
3. Set the *Task* to **TS Optimization**.
4. If desired, set additional options by clicking the *More...* button to display the VAMP TS Optimization dialog. Normally, the default options will yield adequate results.
5. Click the *Run* button.

Properties

Use the [Properties tab](#) on the VAMP Calculation dialog to request that electronic, structural, or vibrational properties be calculated as part of the VAMP run. You can view the results using the [VAMP Analysis dialog](#).

The properties that can be requested through the *Properties* tab are:

- Vibrational frequencies
- Thermodynamic properties
- Localized orbitals
- Electronic states

The following properties are *always* computed as part of a VAMP calculation and so do not appear as options on this tab:

- Canonical molecular orbitals
- Charge density
- Spin density (for UHF cases)
- Electrostatic (Coulomb) potential
- Atomic charges via Mulliken, Coulson, and NAO-PC methods
- Bond orders

To include vibrational frequencies, localized orbitals, or electronic states as part of your VAMP calculation

1. Choose *Modules | VAMP | Calculation* from the menu bar to display the VAMP Calculation dialog.
2. Select the *Properties* tab.
3. Check the checkbox next to the desired property, for example *Frequency*.

To compute thermodynamic properties

1. Choose *Modules | VAMP | Calculation* from the menu bar to display the VAMP Calculation dialog.
2. Select the *Properties* tab.
3. Check the *Frequency* checkbox.
4. Check the *Compute thermodynamic properties* checkbox in the lower half of the dialog. Selecting this option calculates the entropy, enthalpy, and heat capacity as a function of temperature.

See the [Thermodynamic properties selection](#) topic for additional information on these options.

Setting up VAMP calculations

This section describes how to set up VAMP calculations of various types, as well as the ways in which the job control facility can be used.

There are a number of options that are available with VAMP which are not currently available within the Materials Studio interface. These options can be utilized by manually editing the VAMP input files. Information about this is also presented.

Setting up electronic properties

VAMP contains a range of electronic options that control the way that VAMP solves for the electronic wavefunction.

Note: Not all the options available in VAMP are compatible with each other. As a result, some options on the VAMP Calculation dialog will become unavailable when you make certain selections or run calculations on systems for which particular options are not supported. See the [VAMP input restrictions](#) topic for further details.

Convergence scheme

Several options are available to improve the convergence of the SCF wavefunction. These are described in detail in the [Self-consistent field calculations](#) topic. The default option, [Standard](#), will converge most cases. Choose [Pulay](#), [IIS](#), or [Pulay/IIS](#) if the default option fails to achieve convergence.

SCF quality

The *SCF quality* control specifies the accuracy to which the self-consistent field is converged. Normally, a default accuracy of [Medium](#) is sufficient. If you need to converge a geometry optimization to a high degree of accuracy, then [Fine](#) SCF convergence is recommended. For extra control, you can define a specific SCF tolerance on the [VAMP Electronic Options dialog](#), which will result in the *SCF quality* being set to [Customized](#).

CI type

Although SCF calculations are adequate for the vast majority of 'normal' molecules, biradicals and excited states require a more sophisticated treatment. This is often achieved using configuration interaction (CI) methods. VAMP provides several methods for choosing which configurations will be used. The [Full](#) CI option provides accurate results, but leads to very computationally expensive calculations, so this is recommended only for small molecules. A good compromise between cost and accuracy can be achieved using the [PECI](#), or pair-excitation CI, setting. These and the other types of CIs are explained in further detail in the [Configuration interactions](#) topic.

Note: When you choose a type of CI, i.e., when you select a value other than [None](#), you *must* specify the number of orbitals involved in the calculation on the [VAMP Electronic Options dialog](#). If you do not set the number of orbitals to a non-zero value, then a normal SCF calculation will be performed. For a [Full](#) or [CISD](#) calculation, the maximum number of orbitals is 11.

Level shifting

Level shifting helps to achieve SCF by forcing an energy gap between occupied and virtual orbitals. Normally, the level shifting option should be used only as a method of "last resort".

Solvation scheme

VAMP allows you to simulate a solvent around a molecule using one of two continuum models: COSMO or Tomasi (also known as self-consistent reaction field or SCRF). Both these models are discussed further in the [Solvation effects](#) topic. The COSMO model allows you to perform geometry optimizations, but not CI calculations; the Tomasi model only works for single-point energy runs, but allows CI calculations.

You can choose the type of solvent to be used in the solvation simulation on the VAMP Electronic Options dialog. The default solvent is water.

Setting up a geometry optimization

After building or importing a molecule, it usually needs to be refined to bring it to a stable geometry. The refinement process is known as optimization, and is an iterative procedure in which the coordinates of the atoms are adjusted so that the energy of the structure is brought to a stationary point, i.e., one in which the forces on the atoms are zero.

When you set the *Task* to [Geometry Optimization](#) on the [Setup](#) tab, you actually request an energy minimization, a search for a relative minimum on the energy hypersurface. The geometry corresponding to this structure should have a close resemblance to an actual physical structure. The [VAMP Geometry Optimization](#) dialog allows you to more control over the quality and precise behavior of the minimization.

Generating a Hessian

The nature of a stationary point can be characterized by the number of imaginary eigenvalues for the Hessian matrix at the stationary point. The VAMP Geometry Optimization dialog offers two Hessian generation scenarios:

- **Partial:** This is the default method for energy minimization. The diagonal elements of the Hessian matrix are calculated for all internal parameters except bond lengths to hydrogen, for which estimated values are used. This was chosen as a compromise between the need for an accurate initial Hessian, and the desire to reduce the CPU time required for the first cycle. This method can also be selected by omitting the keyword HESS from the input file.
- **Exact:** This is the default for transition state searching, and is available as an option for minimization. The entire Hessian matrix is calculated in the first optimization cycle. This is time-consuming, but may be worthwhile for very difficult optimizations where it is suspected that the final geometry is close to the initial coordinates. This method can also be selected by adding the keyword HESS=1 to the input file.

Computing the full Hessian will be a more costly calculation, but may improve the speed of convergence.

Using internal coordinates

Usually, using internal coordinates is more efficient, so the calculation will converge more quickly. However, there are instances when an optimization may fail, for example due to bonds becoming linear, which may be resolved by optimizing in Cartesian space. To optimize in Cartesian space uncheck the *Optimize using internal coordinates* checkbox on the VAMP Geometry Optimization dialog.

To perform a geometry optimization

1. Choose *Modules | VAMP | Calculation* from the menu bar to display the VAMP Calculation dialog.
2. Select the [Setup tab](#).
3. Set the *Task* to [Geometry Optimization](#).
4. If desired, set additional options by clicking the *More...* button to display the [VAMP Geometry Optimization dialog](#).
5. Select a *Quality*, set values for the *Gradient norm* and *Max. step size*.
6. Choose whether to generate a [Partial](#) or [Exact](#) Hessian and whether to *Optimize using internal coordinates*.
7. Click the *Run* button.

Note: Not all the options available in VAMP are compatible with each other. As a result, some options on the VAMP Calculation dialog will become unavailable when you make certain selections or run calculations on systems for which particular options are not supported. See the [VAMP input restrictions](#) topic for further details.

Tip: When high accuracy is required in geometry optimization, set the *Quality* to [Fine](#) on the VAMP Geometry Optimization dialog. In addition, it is recommended that you set the *SCF quality* to [Fine](#) on the [Electronic tab](#).

Setting up a transition-state optimization calculation

When a molecular structure is imported or built, it usually needs to be refined to bring it to a stable geometry. The refinement process is known as optimization (or minimization) and is an iterative procedure in which the coordinates of the atoms are adjusted so that the energy of the structure is brought to a stationary point, i.e., one in which the forces on the atoms are zero. A transition state is a stationary point that is an energy maximum in one direction (the direction of the reaction coordinate) and an energy minimum in all other directions.

During the course of chemical reaction, the total energy naturally changes. Starting from the reactants, the energy increases to a maximum and then decreases to the energy of the products. The maximum energy along the reaction pathway is known as the activation energy; the structure corresponding to this energy is called the transition state. By performing a TS optimization you can predict barriers to chemical reactions and determine reaction pathways.

Which method to use?

VAMP offers three different choices of optimizer:

- **Eigenvector following** - This is generally the most robust of the three methods and should be the first method you try. The normal mode with the largest imaginary frequency will be followed to the transition state.
- **Powell's method** - Also known as NS01A, yields results similar to eigenvector following. In some cases, the eigenvector following is faster than NS01A. However, the NS01A optimizer is better at finding transition states on flat potential energy surfaces.
- **NLLSQ** - If both NS01A and TS optimizers fail to find the transition state, the non-linear least squares optimizer (NLLSQ) is often successful where the initial geometry is very close to a transition state. NLLSQ only optimizes the atomic forces (gradients) and therefore finds the nearest stationary point, in this case the transition state.

Note: Not all the options available in VAMP are compatible with each other. As a result, some options on the VAMP Calculation dialog will become unavailable when you make certain selections or run calculations on systems for which particular options are not supported. See the [VAMP input restrictions](#) topic for further details.

To perform a transition-state optimization

1. Choose *Modules | VAMP | Calculation* from the menu bar to display the VAMP Calculation dialog.
2. Select the [Setup tab](#).
3. Set the *Task* to [TS Optimization](#).
4. If desired, set additional options by pressing the *More...* button to display the [VAMP TS Optimization dialog](#). Normally, the default options will yield adequate results.
5. Click the *Run* button.

Verifying a transition state

At the conclusion of a successful transition-state calculation, you will have a stationary point. It is more difficult to prove that the stationary point actually corresponds to a transition state. To do this, you must perform a vibrational analysis. A true transition state will have one imaginary vibrational frequency whose normal mode corresponds to the reaction coordinate; all other eigenvalues will be real. A structure with two or more imaginary frequencies is not a true transition state. In such cases, it will be possible to locate a lower energy barrier by following one of the modes.

Tip: You can request that a vibrational frequency calculation be performed automatically following a successful transition-state optimization or transition-state search. Simply check the *Frequency* checkbox on the *Properties* tab.

Requesting electronic, structural, and vibrational properties

It is possible to request via the [Properties tab](#) on the VAMP Calculation dialog that electronic, structural, or vibrational properties be calculated as part of the VAMP run. You can view the results using the [VAMP Analysis dialog](#).

The properties that can be requested through the *Properties* tab are:

- Vibrational frequencies
- Thermodynamic properties
- Localized orbitals
- Electronic states

As discussed in the [Properties](#) topic, a number of other molecular properties are computed automatically as part of every VAMP job. The properties discussed here are more time consuming and, so, you are given the option of whether to calculate them.

When you select an [Energy](#) calculation as the *Task*, the properties are computed at the geometry supplied in the input. When you select a [Geometry Optimization](#) or [TS Optimization](#) task, then the properties are evaluated at the final geometry.

Note: Not all the options available in VAMP are compatible with each other. As a result, some options on the VAMP Calculation dialog will become unavailable when you make certain selections or run calculations on systems for which particular options are not supported. See the [VAMP input restrictions](#) topic for further details.

Setting up a frequency calculation

To compute vibrational frequencies as part of your VAMP calculation

1. Choose *Modules | VAMP | Calculation* from the menu bar to display the VAMP Calculation dialog.
2. Select the *Properties* tab.
3. Check the *Frequency* checkbox.

When the calculation is complete, you can display the vibrational frequencies using the Vibrational Analysis tool.

Setting up thermodynamic properties

If you include thermodynamic properties as part of your VAMP calculation, you must also perform a vibrational calculation.

To perform a vibrational calculation including thermodynamic properties

1. Choose *Modules | VAMP | Calculation* from the menu bar to display the VAMP Calculation dialog.
2. Select the *Properties* tab.
3. Check the *Frequency* checkbox.
4. In the lower half of the dialog, check the *Compute thermodynamic properties* checkbox.
5. Set the lowest and highest temperatures at which you wish to compute the properties in the *From* and *To* fields, respectively. Set the increment that you wish the temperature to be increased by at each step in the *Step size* field.

When the calculation is complete, you can display the enthalpy, entropy, and heat capacity as a function of temperature using the [Thermodynamic properties](#) options on the VAMP Analysis dialog.

Setting up a localized orbital calculation

To compute localized orbitals as part of your VAMP calculation

1. Choose *Modules | VAMP | Calculation* from the menu bar to display the VAMP Calculation dialog.
2. Select the *Properties* tab.
3. Check the *Localized orbitals* checkbox.

When the calculation is complete, you can display localized orbitals using the [Localized orbitals](#) options on the VAMP Analysis dialog.

Setting up a UV-Vis calculation

To compute electronic states as part of your VAMP calculation

1. Choose *Modules | VAMP | Calculation* from the menu bar to display the VAMP Calculation dialog.
2. Select the *Properties* tab.
3. Check the *UV-Vis* checkbox.
4. Ensure that you have selected a configuration interaction treatment, i.e., *CI type* on the [Electronic tab](#) is *not* set to *None*.
5. Ensure that you have specified a sufficient number of orbitals to include in the [configuration interaction](#) calculation on the [VAMP Electronic Options dialog](#).

When the calculation is complete, you can use the [Electronic levels](#) options on the VAMP Analysis dialog to view excitation data for the electronic states of the structure being studied and generate its UV-Vis spectrum.

VAMP input restrictions

Not all the options available in VAMP are compatible with each other. As a result, some options on the VAMP Calculation dialog will become unavailable when you make certain selections or run calculations on systems for which particular options are not supported.

Unsupported systems

There are some restrictions on the systems that can be input to a VAMP calculation. The *Run* button on the VAMP Calculation dialog is disabled if the system in the active structure document is unsuitable for a VAMP job. The following types of systems cannot be used with VAMP:

- 3D periodic systems (crystals)
- Empty systems (not containing any atoms)
- System containing mixture atoms
- Systems containing pseudo-atoms (dummy atoms)
- Systems containing an element for which none of the available Hamiltonians are parameterized

Task restrictions

Some VAMP tasks are unavailable for certain types of systems and some require specific types of input documents. The following input restrictions apply:

- ZINDO Hamiltonians can only be used when performing single-point energy calculations. This means that only the [Energy](#) task is available for systems containing elements, such as transition metals, that are parameterized only for ZINDO Hamiltonians and not for NDDO Hamiltonians.
- A 3D Atomistic Trajectory document containing a reaction sequence is required as the input document for a transition-state calculation. As a result, the [TS Search](#) task is available only if the currently active document is a 3D Atomistic Trajectory document.

Electronic restrictions

The electronic structure of the input system imposes certain restrictions on the calculations that can be performed. The following restrictions are governed by the number of electrons in the input system:

- When the input system contains an even number of electrons, only singlet, triplet, and quintet multiplicities can be calculated, so only the [Auto](#), [Singlet](#), [Triplet](#), and [Quintet](#) options are available from the *Multiplicity* dropdown list on the [Setup tab](#) of the VAMP Calculation dialog. Selecting [Auto](#) will result in a singlet calculation being performed.
- When the input system contains an odd number of electrons, only doublet, quartet, and sextet multiplicities can be calculated, so only the [Auto](#), [Doublet](#), [Quartet](#), and [Sextet](#) options are available from the *Multiplicity* dropdown list on the *Setup* tab of the VAMP Calculation dialog. Selecting [Auto](#) will result in a doublet calculation being performed.

NDDO Hamiltonians

The following restrictions apply when using NDDO Hamiltonians:

- The restricted open-shell Hartree-Fock formalism cannot be used to calculate the spin polarization. The [ROHF](#) option will not be available from the *Spin* dropdown list on the *Setup* tab of the VAMP Calculation dialog.
- A configuration interaction scheme can be specified only if the restricted Hartree-Fock formalism is used to calculate the spin polarization. Only the [None](#) option will be available from the *CI type* dropdown list on the [Electronic tab](#) of the VAMP Calculation dialog unless you select [RHF](#) from the *Spin* dropdown list on the *Setup* tab.
- The conductor-like screening model solvation scheme is not available when the PM6, MNDO/d, and AM1* Hamiltonians are used. The [COSMO](#) option will not be available from the *Solvation scheme* dropdown list on the *Electronic* tab of the VAMP Calculation dialog when the PM6, MNDO/d, and AM1* Hamiltonians are used.
- The self-consistent reaction field solvation scheme is available only when performing single-point energy calculations. The [SCRF](#) option is only available from the *Solvation scheme* dropdown list on the *Electronic* tab of the VAMP Calculation dialog for the [Energy](#) task.

ZINDO Hamiltonians

The following restrictions apply when using ZINDO Hamiltonians:

- ZINDO Hamiltonians can only be used when performing single-point energy calculations.
- Only the restricted Hartree-Fock and restricted open-shell Hartree-Fock formalisms can be used to calculate the spin polarization for ZINDO Hamiltonians. The [UHF](#) and [A-UHF](#) options will not be available from the *Spin* dropdown list on the *Setup* tab of the VAMP Calculation dialog when ZINDO Hamiltonians are used.
- The restricted Hartree-Fock spin polarization formalism is available only for systems with an even number of electrons and only if the *Multiplicity* is set to [Auto](#), [Singlet](#), or [Triplet](#) on the *Setup* tab of the VAMP Calculation dialog.
- When the restricted Hartree-Fock spin polarization formalism is used, the only solvation scheme that can be used is CIS. Only [None](#) and [CIS](#) will be available from the *CI type* dropdown list on the *Electronic* tab of the VAMP Calculation dialog when [RHF](#) is selected as the *Spin* on the *Setup* tab.
- When the restricted open-shell Hartree-Fock spin polarization formalism is used, the only solvation scheme that can be used is RumerCI. Only [None](#) and [RumerCI](#) will be available from the *CI type* dropdown list on the *Electronic* tab of the VAMP Calculation dialog when [ROHF](#) is selected as the *Spin* on the *Setup* tab.

Properties restrictions

Some properties can be calculated only if certain options are used for a calculation. The following restrictions apply to properties calculations:

- UV spectra can be calculated only if a configuration interaction scheme is specified. If [None](#) is selected from the *CI type* dropdown list on the *Electronic* tab of the VAMP Calculation dialog, you will not be able to calculate the UV spectrum of the input system.
- Frequencies and thermodynamic properties can be calculated only if NDDO Hamiltonians are used.

Manipulating files

VAMP is a file-based application: all input and output is delivered in a mixture of text and binary files. This section describes some file handling issues which may arise, especially when the VAMP server is run in a standalone mode and not via a gateway.

Input files

The [VAMP Job Files dialog](#) allows you to save input files for subsequent manual editing or for running in standalone mode.

To save input files

1. Choose *Modules | VAMP | Calculation* from the menu bar to display the VAMP Calculation dialog.
2. Click the *Files...* button to display the VAMP Job Files dialog.
3. Click the *Save Files* button.

Note: The *Save Files* button is enabled only if the active document is a 3D Atomistic document.

The input file, *rootname.input*, is displayed in the Project Explorer. This file contains the parameters specified using the VAMP interface. You can add to it parameters that access functionality not supported through the interface.

To edit the input file

1. Select the desired file in the Project Explorer.
2. Double-click to open the file in the text editor.
3. Make your changes, adding, deleting, or modifying input, as desired.
4. Choose *File | Save* from the menu bar to save your changes.

Input files can be run on a server after they have been edited.

To run VAMP using an existing set of input files

1. Choose *Modules | VAMP | Calculation* from the menu bar to display the VAMP Calculation dialog.
2. Click the *Files...* button to display the VAMP Job Files dialog.
3. Double-click on the input file.
4. Click the *Run Files* button.

Note: The *Run Files* button is enabled only if the active file is a VAMP input file. The corresponding reference structure document (.xsd) must be present in the current folder.

Output files

The output file, *.out*, is displayed in the Project Explorer. You can view this by double-clicking on it. There may be several other files created during a VAMP run. Though they are not visible in the Project Explorer, all of these output files are placed in the correct Materials Studio project folder automatically when the job is run using the gateway. These files are used by the [VAMP Analysis](#) tools. The various files are described in detail in the [VAMP file formats](#) topic.

Analyzing VAMP results

VAMP results become available for analysis on completion of the VAMP run, once all the output files have been successfully downloaded to the results folder.

Select the results to be analyzed by opening the structure document (.xsd) in the results folder. This allows all related VAMP results to be analyzed.

Note: The structure is updated automatically on successful download of output files from a completed VAMP job.

The atoms in the updated structure document have an extra property, *ServerAtomIndex*, associated with them. This shows the atom sequence numbers as used in the VAMP output files and can be seen by labeling atoms in the structure with the *ServerAtomIndex* property (this property will be seen only in structures generated from VAMP and other similar applications).

All other analysis functions require you to perform certain actions using the [VAMP Analysis dialog](#).

Tip: If you have calculated a Hessian matrix (i.e., by checking the *Frequency* checkbox on the [Properties tab](#) of the VAMP Calculation dialog) as part of a VAMP run, you can create a list of vibrational modes and view the spectrum for the structure using the Vibrational Analysis tool.

Note that vibrational intensities can only be obtained for nonperiodic systems. Without intensities, the displayed spectrum consists of points on the frequency axis only.

Updating structure

Updating the atomic coordinates after geometry optimization or TS optimization is the recommended first step in the analysis process.

When a VAMP job is completed successfully, the output files are copied from the server to the results folder and the structure is updated automatically. The procedure described below can be used to restore the coordinates of a structure if you have modified it.

Note: If the chemical composition (i.e., number of atomic species or number of each kind of atoms) has changed since Materials Studio saved the .xsd file in the results folder, you cannot update the structure.

As a result of the update, the coordinates of the atoms are set to the values returned by the VAMP run in the (hidden) .car file. If a VAMP Hessian file ([.vres](#)) is present in the same folder, it is read into the model when you request the update.

To update the structure

1. Choose *Modules | VAMP | Analysis* from the menu bar to display the [VAMP Analysis dialog](#).
2. Select *Structure* from the list of properties.
3. Make sure that the 3D Atomistic document you wish to update is the currently active document.
4. Click the *Update* button.

An error message is displayed if the .car structure file is incomplete or if the chemical composition of the model has been changed (i.e., atoms were added, removed, or modified). The *Update* button is disabled if the .car file is not present or if the current document cannot be updated.

Visualizing volumetric data

Materials Studio allows you to visualize the spatial distribution of electron density, electrostatic potential, canonical molecular orbitals, or localized molecular orbitals computed by VAMP. The relevant data from VAMP are used to add fields to the model. Fields can be subsequently visualized in a variety of ways, for example direct field visualization, isosurfaces, or slices.

When you request a field in VAMP analysis, the data needed to display it are computed "on the fly" by the Materials Studio client. This is in contrast to DMol³ volumetric analysis, for example, in which the server computes the field data and the Materials Studio client simply displays it.

A progress meter shows how much field data has been computed. If a calculation is taking too long, you can cancel it by pressing the ESC (escape) key.

Electron density

Materials Studio uses the information generated by VAMP to create a field that corresponds to the total electron density. When you analyze a spin-unrestricted calculation, you can also create a field for the spin density (the difference between the density of alpha and beta electrons). This field allows you to visualize the spatial distribution of the magnetic moment in a spin-unrestricted system.

To create a density field

1. Choose *Modules | VAMP | Analysis* from the menu bar to display the [VAMP Analysis dialog](#).
2. Select *Electron density* from the list of properties.
3. Make sure that the 3D Atomistic document containing the output structure from the VAMP calculation is the currently active document.
4. From the *Density field* dropdown list, select the type of density you wish to display ([Total density](#) or [Spin density](#)). [Total density](#) is available for all calculations. [Spin density](#) is only available for open-shell calculations.
5. Optionally, uncheck the *View isosurface on import* checkbox if you wish to import the volumetric data as a 3D field rather than an isosurface. This checkbox is checked by default.
6. Click the *Import* button.

Tips:

- If you select *View isosurface on import*, you should see a 3D contour after the field has been imported. To change the value of the contour, open the Display Style dialog and select the *Isosurface* tab. If you do not see an isosurface, the default value is possibly outside of the range of the field values. Select the *Isosurface* tab and choose a different value.
- If you do *not* check the *View isosurface on import* checkbox, you will not see a volumetric data display.
- Use the Volume Visualization toolbar and Display Style dialog to control the display of the field data.

Electrostatic potential

Materials Studio uses the information generated by VAMP to create a field that corresponds to the electrostatic, or Coulomb, potential. The potential is computed based on the multipole expansion ([Horn et al., 2005](#)). Positive regions correspond to electron-deficient areas and are subject to nucleophilic attack; negative regions correspond to electron-rich areas and are subject to electrophilic attack.

To create an electrostatic potential field

1. Choose *Modules | VAMP | Analysis* from the menu bar to display the VAMP Analysis dialog.
2. Select *Potentials* from the list of properties.
3. Make sure that the 3D Atomistic document containing the output structure from the VAMP calculation is the currently active document.
4. From the *Potential field* dropdown list, select the type of potential you wish to display. The choice is currently limited to [Electrostatic potential](#).
5. Optionally, uncheck the *View isosurface on import* checkbox if you wish to import the volumetric data as a 3D field rather than an isosurface. This checkbox is checked by default.
6. Click the *Import* button.

If you wish to use the potential to color an isosurface, see the [Color and contour mapping](#) topic.

Tips:

- If you select *View isosurface on import*, you should see a 3D contour after the field has been imported. To change the value of the contour, open the Display Style dialog and select the *Isosurface* tab. If you do not see an isosurface, the default value is possibly outside of the range of the field values. Select the *Isosurface* tab and choose a different value.
- If you do *not* check the *View isosurface on import* checkbox, you will not see a volumetric data display.
- Use the Volume Visualization toolbar and Display Style dialog to control the display of the field data.

Molecular orbitals

Materials Studio uses the information generated by VAMP to create a field that corresponds to any of the canonical molecular orbitals in the system. These are the orbitals that diagonalize the Hamiltonian. The highest occupied orbital (HOMO) and lowest unoccupied orbital (LUMO) are especially important in determining the chemical reactivity of a system.

The *Filter* dropdown list allows you to control which orbitals have their information displayed in the table:

- [All](#) - displays data for all orbitals.
- [Minimal](#) - displays data for the HOMO and for the 3 occupied and 3 virtual orbitals immediately above and below the HOMO.
- [Spin up](#) - displays data for alpha-spin orbitals only. In the unrestricted case, this is the same as [All](#).
- [Spin down](#) - displays data for beta-spin orbitals only. In the unrestricted case, no data are displayed.

The orbital analysis table provides you with a list of eigenvalues and information about each orbital. The list of eigenvalues starts with the lowest core orbital. The accompanying information includes:

- *N* - indicates the number of the orbital, with [1](#) corresponding to the lowest energy orbital. In an unrestricted calculation, the alpha- and beta-spin orbitals are numbered separately.
- *s* - indicates spin, [+](#) for alpha, [-](#) for beta. In a spin-restricted calculation, all orbitals are labeled as [+](#).
- *Eigenvalue* - indicates the orbital eigenvalue in eV.
- *Type* - indicates the *HOMO* and *LUMO*. These labels appear in the appropriate row.

To create a canonical molecular orbital field

1. Choose *Modules | VAMP | Analysis* from the menu bar to display the VAMP Analysis dialog.
2. Select *Orbitals* from the list of properties.
3. Make sure that the 3D Atomistic document containing the output structure from the VAMP calculation is the currently active document.
4. From the grid, select the row corresponding to the orbital you wish to display.
5. Optionally, uncheck the *View isosurface on import* checkbox if you wish to import the volumetric data as a 3D field rather than an isosurface. This checkbox is checked by default.
6. Click the *Import* button.

Tips:

- If you select *View isosurface on import*, you should see a 3D contour after the field has been imported. To change the value of the contour, open the Display Style dialog and select the *Isosurface* tab. If you do not see an isosurface, the default value is possibly outside of the range of the field values. Select the *Isosurface* tab and choose a different value.
- If you do *not* check the *View isosurface on import* checkbox, you will not see a volumetric data display.
- Use the Volume Visualization toolbar and Display Style dialog to control the display of the field data.

Localized orbitals

Materials Studio uses the information generated by VAMP to create a field that corresponds to any of the localized molecular orbitals in the system. These orbitals have been spatially localized using the method of [Perkins and Stewart](#). The localization procedure is applied to the occupied orbitals only, so the list of localized orbitals will be shorter than that for [canonical orbitals](#).

The *Filter* dropdown list allows you to control which orbitals have their information displayed in the table:

- **All** - displays data for all orbitals.
- **Minimal** - displays data for the 4 localized orbitals obtained from the 4 HOMOs. For open shells, there are 7 orbitals obtained from the HOMO and 3 highest orbitals of each spin.
- **Spin up** - displays data for alpha-spin orbitals only. In the unrestricted case, this is the same as **All**.
- **Spin down** - displays data for beta-spin orbitals only. In the unrestricted case, no data are displayed.

The orbital analysis table provides you with a list of information about each orbital, including:

- *N* - indicates the number of the orbital, with **1** corresponding to the lowest energy orbital. In an unrestricted calculation, the alpha- and beta-spin orbitals are numbered separately.
- *s* - indicates spin, **+** for alpha, **-** for beta. In a spin-restricted calculation, all orbitals are labeled as **+**.
- *Energy* - indicates the orbital energy in eV.

To create a localized molecular orbital field

1. Choose *Modules | VAMP | Analysis* from the menu bar to display the VAMP Analysis dialog.
2. Select *Localized orbitals* from the list of properties.
3. Make sure that the 3D Atomistic document containing the output structure from the VAMP calculation is the currently active document.
4. From the grid, select the row corresponding to the orbital you wish to display.
5. Optionally, uncheck the *View isosurface on import* checkbox if you wish to import the volumetric data as a 3D field rather than an isosurface. This checkbox is checked by default.
6. Click the *Import* button.

Tips:

- If you select *View isosurface on import*, you should see a 3D contour after the field has been imported. To change the value of the contour, open the Display Style dialog and select the *Isosurface* tab. If you do not see an isosurface, the default value is possibly outside of the range of the field values. Select the *Isosurface* tab and choose a different value.
- If you do *not* check the *View isosurface on import* checkbox, you will not see a volumetric data display.
- Use the Volume Visualization toolbar and Display Style dialog to control the display of the field data.

Field visualization

Materials Studio provides a number of tools for field visualization. They are accessed via the Volume Visualization toolbar and *Field*, *Isosurface*, and *Slice* tabs on the Display Style dialog.

The *Volume Visualization* toolbar provides access to the Volumetric Selection dialog, which enables you to specify the field to be visualized and set visibility attributes for fields, slices, and isosurfaces. This toolbar also contains controls for creating new isosurfaces and slices, including the shortcuts for orienting the slice based on either the cell axes or the coordinates of selected atoms. The Color Maps dialog, which can also be accessed from the *Volume Visualization* toolbar, provides control over the coloring of volumetric objects (it also provides useful shortcuts for determining the minimum and maximum values of the field).

The *Field* tab of the Display Style dialog allows you to visualize the field directly using either the *Dots* or *Volume* display styles.

The *Isosurface* tab of the Display Style dialog allows you to alter the visualization style of a selected isosurface, change its isovalue, or use another field for color mapping.

The *Slice* tab of the Display Style dialog allows you to alter the visualization style of a selected slice.

Note: The volumetric visualization tabs on the Display Style dialog are displayed only if an object of the relevant type is present in the active document. If a field, isosurface, or slice is selected, for example by using the Volumetric Selection dialog, the volumetric visualization tabs that are not relevant to the selection will be removed from the Display Style dialog.

Tip: Field visualization in Materials Studio fully supports periodic display. You can use the *Field* tab on the Display Style dialog to change the range of a field to display more or less than one unit cell of a structure.

Displaying atomic charges and bond orders

VAMP can calculate atomic charges using three different methods: Mulliken, Coulson, or ESP charge analysis. Bond orders are computed in VAMP using a Coulson analysis.

Displaying computed charges

To import and display computed atomic charges, you need to have the structure file (.xsd) and VAMP output file available in a folder in the Project Explorer.

To display charges

1. Choose *Modules | VAMP | Analysis* from the menu bar to display the [VAMP Analysis dialog](#).
2. Select *Population analysis* from the list of properties.
3. Make sure that the 3D Atomistic document containing the output structure from the VAMP calculation is the currently active document.
4. Select the type of charge you wish to use ([Mulliken](#), [Coulson](#), or [ESP](#)) from the *Charges* dropdown list.

Note: You cannot assign [ESP](#) charges if you have performed your calculation using the AM1*, MNDO/d, or MNDO/C NDDO Hamiltonians, or any of the ZINDO Hamiltonians.

5. Click the *Assign chosen charges to structure* button to import the charge data into the structure document.
6. Right-click in the 3D view and select *Label* from the shortcut menu to display the Label dialog.
7. Set the *Object type* to [Atom](#), select [Charge](#) from the *Properties* list, and click the *Apply* button to display the charges.

Once you have imported the charges using the *Assign* button, you can export a .car file that contains these charges.

To display bond orders

1. Choose *Modules | VAMP | Analysis* from the menu bar to display the VAMP Analysis dialog.
2. Select *Population analysis* from the list of properties.
3. Make sure that the 3D Atomistic document containing the output structure from the VAMP calculation is the currently active document.
4. Click the *Assign bond orders to structure* button to import the bond order data into the structure document.
5. Right-click in the 3D view and select *Label* from the shortcut menu to display the Label dialog.
6. Set the *Object type* to [Bond](#), select [BondOrder](#) from the *Properties* list, and click the *Apply* button to display the bond orders.

Displaying UV-Vis spectra

VAMP enables you to calculate the electronic states of the final output structure from a run. The [Electronic levels](#) options, accessed from the VAMP Analysis dialog, allows you to view excitation data and to generate UV-Vis spectra in both chart and grid form.

To view excitation data or create UV-Vis spectrum, you need to have the structure file (.xsd) and VAMP output file in a folder in the Project Explorer.

To calculate electronic states

In order to calculate the electronic states of a structure, you need to perform a CI-type calculation.

1. Choose *Modules | VAMP | Calculation* from the menu bar to display the VAMP Calculation dialog.
2. Select the [Electronic tab](#).
3. Select a configuration interaction treatment, i.e., make sure that *CI type* is *not* set to **None**.
4. Click the *More...* button to display the [VAMP Electronic Options dialog](#).
5. In the *Number of orbitals* field, specify a sufficient number of orbitals to include in the [configuration interaction](#) calculation.
6. Select the [Properties tab](#) and check the *UV-Vis* checkbox.
7. Select a *Task* on the [Setup tab](#) and alter the other settings on the VAMP Calculation dialog as appropriate for your particular calculation.
8. Click the *Run* button. When the job is complete, you can view the calculated excitation data using the [VAMP Analysis dialog](#).
9. Choose *Modules | VAMP | Analysis* from the menu bar to display the VAMP Analysis dialog.
10. Select *Electronic levels* from the list of properties.
11. Make sure that the 3D Atomistic document containing the output structure from the VAMP calculation is the currently active document.
12. Click the *View electronic energy levels* button. This generates a grid document containing a list of electronic states for the structure being studied. The grid document gives the energy (in eV), the excitation wavelength (in nm), the multiplicity (spin arrangement), and the oscillator strength (transition dipole moment) for each electronic state listed.

To generate a UV-Vis spectrum

In order to predict the UV-Vis spectrum for a system, you need to perform a CI-type calculation and request that electronic properties be computed as part of the VAMP run, as described above. You can then use the [Electronic levels](#) options on the VAMP Analysis dialog to generate the UV-Vis spectrum.

1. Choose *Modules | VAMP | Analysis* from the menu bar to display the VAMP Analysis dialog.
2. Select *Electronic levels* from the list of properties.
3. Make sure that the 3D Atomistic document containing the output structure from the VAMP calculation is the currently active document.
4. Click the *More...* button to display the [VAMP UV-Vis Spectrum Options dialog](#).
5. Select an *Integration method* to be used to smooth the peaks and set the peak width parameter associated with the specified smoothing function (*Smearing width* for **Gaussian** and *FWHM parameter* for **Lorentzian**).

Note: Selecting **None** for the *Integration method* will produce a spectrum consisting solely of vertical lines (deltas) at the excitation wavelength with heights proportional to the excitation intensity.

6. Set the *Accuracy level*, which defines the quality of the interpolation for generation of the spectrum.
7. Click the *OK* button to close the VAMP UV-Vis Spectrum Options dialog and then click the *View Spectrum* button on the Electronic levels dialog to generate the UV-Vis spectrum.

The UV-Vis spectrum is constructed from the allowed transitions between the ground state and all the excited electronic states identified in the VAMP calculation, provided these transitions have non-zero intensity and appear at wavelengths above 100 nm. Allowed transitions are defined as transitions between states with the same multiplicity, i.e., singlet-singlet, triplet-triplet, etc. Transitions between electronic states with different multiplicity, for example singlet-triplet, are considered forbidden.

8. If you wish to see the data used to generate the UV-Vis spectrum presented in tabular form, click the *View Grid* button. This produces a grid document containing the energies (in nm) and oscillator strengths of the allowed excitations used to construct the UV-Vis spectrum.

Improving SCF convergence

The following message is displayed when an SCF calculation fails to converge:

```
""""""""""UNABLE TO ACHIEVE SELF-CONSISTENCE
```

```
DELTA E=  value1    DELTA P=  value2
```

Check that the calculation is closed shell

Check that the calculation is closed shell, i.e., has no unpaired electrons. An open-shell calculation using RHF, the default, is indicated by lines such as:

```
<>      RHF calculation with    27 doubly occupied levels

        and    1 singly occupied levels
```

in the output. A closed-shell calculation has doubly occupied levels only.

Try an alternative to RHF in an open-shell calculation

If the calculation is open shell, the convergence failure is usually caused by using the RHF (half-electron) method. The alternatives are to use UHF (unrestricted Hartree-Fock) or AUHF (annihilated UHF), both of which should converge much better than RHF.

If you still want to use RHF, check the steps given above for closed-shell molecules and try to improve the convergence as described. If this fails, the calculation is probably trying to decide between degenerate, or very nearly degenerate, singly occupied orbitals. In this case, using the VAMP keyword OPEN(1,2) will request that the singly occupied orbital be distributed over two orbitals in the reference RHF wavefunction. Generally, the calculation will then converge very quickly.

Refer to the [SCF formalism](#) topic for more information on RHF and UHF calculations, including [using UHF to allow electrons to become unpaired](#) and [strategies to avoid spin contamination in UHF calculations](#).

Try a different converger

If the geometry is correct, try a different SCF converger and increase the number of allowed SCF cycles to a large value. Attempt the calculation again, beginning with the first converger listed below:

1. IIS - [Badziag and Solms's](#) technique. This is the most reliable converger, but it can be slow.
2. Pulay.
3. [SHIFT=1000](#) (if all others fail).

Check the geometry

If the calculation is closed shell and DELTA E and DELTA P are small, for example 1.0^{-3} , first check that the geometry is correct. Bad geometries often give poor SCF convergence.

Increase maximum SCF iterations

Increase the maximum number of SCF iterations on the [VAMP Electronic Options dialog](#). This will help if the SCF was already converging, but needed more iterations in order to achieve the requested convergence.

Request lower accuracy

Request lower accuracy in the SCF convergence on the [Electronic tab](#). The SCF might be able to achieve [Coarse](#) accuracy in cases where it could not achieve [Medium](#) or [Fine](#) convergence.

Reduce the step size

If you are performing a geometry optimization and you got this error message after a few steps of the optimization, try reducing the maximum step size on the [VAMP Geometry Optimization dialog](#). Sometimes, an optimization will take a step that results in a skewed geometry that is hard to converge. Reducing the maximum step size reduces the likelihood of this.

VAMP jobs

The topics in this section cover [controlling](#) and running [remote](#) VAMP jobs, running jobs in [standalone](#) mode, details of a [sample](#) remote run, and potential reasons why VAMP might [fail](#).

Using VAMP job control

VAMP jobs are run as a background process on a server (via a gateway). The following tools are used to set up and control the jobs:

- Use the [Job Control](#) tab of the VAMP Calculation dialog to select the gateway location and job parameters.
- Use the Server Console to add new servers and to monitor multiple jobs.
- Use the Job Explorer to monitor multiple jobs.

For further information on using job control see the main job control and live updates help topics. Live updates can be requested on the [VAMP Job Control Options](#) dialog.

Remote VAMP jobs

VAMP in Materials Studio uses a client-server architecture that allows you to use your PC to control calculations running on a remote computer.

This separation of the client user interface from the server system, which runs the calculations, allows you to use a high performance super computer from your Windows desktop PC. It also allows you to make use of spare CPU cycles on other desktop PCs. VAMP jobs are controlled by input files that are generated by Materials Studio when you start a job.

VAMP writes the results of the calculations to various output files, which are downloaded from the server to the appropriate Materials Studio project when the job is completed.

A sample VAMP run

Whether you perform a single-point energy calculation, minimize a structure, or perform a transition-state search, the sequence of steps that is executed to run a remote VAMP job is always the same. When you click the *Run* button on the VAMP Calculation dialog, the steps described in A sample remote job run happen with the following differences:

The exact behavior of Materials Studio on receipt of update information depends on the type of calculation that is being performed.

For [Energy](#) calculations, if

- *Update structure* is checked: there is no effect, as no structural changes are associated with this task.
- *Update graphs* is checked: there is no effect.
- *Update textual results* is checked: there is no effect.

For [Geometry Optimization](#) calculations, if

- *Update structure* is checked: Materials Studio downloads a snapshot of the structure and modifies a copy of the original structure accordingly.
- *Update graphs* is checked: Materials Studio creates a chart document called [*seedname*] Energies.xcd, showing the computed heat of formation versus optimization step, and another chart document called [*seedname*] Convergence.xcd, showing, on the logarithmic scale, the total energy change and the RMS force versus optimization step.
- *Update textual results* is checked: Materials Studio downloads a text file called Status.txt that contains the job name, the type of calculation performed, the current optimization step, and the heat of formation and gradient norm for the last completed optimization step.

For [TS Search](#) and [TS Optimization](#) calculations, the behavior is the same as for a [Geometry Optimization](#) run.

Once the job has finished, Materials Studio will transfer the output files back to your PC, where you can [view and edit](#) them, [analyze the results](#), or use them for further calculations. Additional output files may be generated or modified depending on the type of calculation you performed.

- For [Energy](#) runs, Materials Studio downloads all the VAMP output files.
- For [Geometry Optimization](#) runs, Materials Studio downloads all the VAMP output files, updates the structure it has copied into the results folder to show the final geometry, and creates a trajectory file, [*seedname*].xtd, that contains the history of the optimization process. The trajectory file can be animated using the tools on the Animation toolbar.
- For [TS Search](#) and [TS Optimization](#) runs, the behavior is the same as for a [Geometry Optimization](#) run.

If a VAMP job fails

Materials Studio checks most of the data and settings required to perform a VAMP job prior to launch. If it cannot start the job, error messages are generated detailing the reasons.

However, sometimes jobs may fail for reasons which cannot be checked prior to launch. In such cases, an error message giving more detailed information appears in the output file produced by the job and, in some situations, in the job log window as well. Other files stored in the job directory on the server may contain further clues. To view the server-side files, you can use the Remote View facility of the Job Explorer.

Below is a list of the most common reasons for VAMP jobs to fail. It may help you to identify and fix any problems you have with your remote VAMP jobs. For generic reasons for remote job failures please consult the [If a remote job fails](#) help topic.

Tip: Select *View / Project Log* from the menu bar to see if any error or warning messages have been reported.

Cannot start a VAMP job

Run button is grayed out.

- The active document is not a 3D Atomistic document.
If something other than a 3D Atomistic document is the current document, a chart or text document, for example, then the *Run* button will be grayed out. To run the calculation, select an appropriate document.
- The active document is periodic.
VAMP can only operate on molecules.

Common reasons for a VAMP job to fail to finish successfully

Server-side problems

1. Out of memory.

If the server machine runs out of virtual memory or swap space when trying to start up a process or while running, various errors may occur. VAMP might also stop with the message:

Not enough memory available

Unable to continue: Terminating program

These errors depend on the operating system of the server machine. In order to proceed, you will need to find a different computer with more physical memory and/or virtual memory. Alternatively, you could try to reduce the size of the molecule you are studying. For example, you could remove side-groups that are not absolutely necessary.

2. Molecular becomes almost linear.

VAMP might stop with the message:

Rerun optimization in Cartesian coordinates using keyword XYZ
and add keyword GEO-OK

This occurs when an optimization is performed using internal coordinates and three atoms become almost linear. This creates a problem because the torsion angle relating the atoms cannot be computed. If this happens, rerun the optimization with Cartesian coordinates. Open the [VAMP Geometry Optimization dialog](#) and make certain the *Optimize using internal coordinates* checkbox is *not* checked. This will run in Cartesian space and add all the recommended keywords to the VAMP input.

Tip: Generally, when you receive this error message, you will have a partially optimized geometry. You can save time by starting the Cartesian optimization using this partially optimized result rather than starting over from the original geometry. To do this, launch the VAMP calculation using the 3D Atomistic document (.xsd file) in the results folder rather than using the original .xsd file.

3. Degenerate energy levels detected in CI-calculation.

When you run a [CI calculation](#), VAMP tests for sets of orbitals that are almost degenerate, but that are not all included in the CI calculation. If this happens, the CI calculation is stopped with the message:

Job stopped. To continue, specify "LEV-OK"

To continue, check the *Ignore degenerate orbitals* checkbox on the [VAMP Electronic Options dialog](#); this will add the keyword LEV-OK to the input file.

4. Failure of the SCF to converge.

If VAMP cannot converge the wavefunction, it will terminate with the message:

""""""""""UNABLE TO ACHIEVE SELF-CONSISTENCE

Refer to the [Improving SCF convergence](#) topic for procedures and options to try.

5. Failure of geometry optimization to converge.

The default number of geometry steps in an optimization is 1000. If the geometry does not converge within this number of steps, VAMP will return the message:

Maximum number of cycles reached

There are several actions you can take when this happens.

- Simply accept the final geometry - Examine the final norm of the gradient. If it is already small (less than about 2 or 3), then the geometry and energy will change very little. Further optimizations might not even be able to achieve the requested convergence.
 - Restart the optimization using Materials Studio - The geometry that gets returned to Materials Studio is the final geometry from the optimization. Submitting an optimization from this starting point will essentially pick up where the other job left off. If the norm of the gradient is already rather small, consider loosening the optimization criteria on the [VAMP Geometry Optimization dialog](#).
 - Restart the optimization but reduce the maximum step size of the optimization - Sometimes an optimization will take steps that result in oscillatory behavior. Reducing the step size on the VAMP Geometry Optimization dialog can help alleviate this problem.
6. Failure of a vibrational calculation (FORCE calculation) to start.

When you request a vibrational frequency calculation, VAMP first computes the gradients on the atoms. If these gradients are too large, then VAMP returns the error message:

```
Gradients are too large to allow calculation of the force matrix
(Limit=10)
```

This occurs because vibrations are only meaningful near a stationary point. If you have requested a geometry optimization, then VAMP continues, performing the optimization and then the frequencies calculation. However, if you have requested a single-point energy with frequencies, then VAMP will stop. The maximum allowed gradient is 10 kcal mol⁻¹ Å⁻¹ or the GNORM value. If necessary, you can work around this by using the LET keyword, which allows larger gradients.

7. VAMP may terminate with the following message:

```
Analytical gradients are not yet available for d-orbitals.
Please specify NUMCI
```

This indicates that numerical CI gradients must be used, in case the elements have d orbitals. This may occur when AM1*, MNDO/d, or PM6 Hamiltonians are used to perform CI calculations. For example, a CI is also used in the case of open-shell systems and restricted calculations. The remedy is to add the NUMCI keyword to the input data.

Tip: It is important to identify the reason for the failure of a VAMP job before taking any action. In most cases, the error message will give a good indication of the reason for the failure. If the error message indicates that the job failed, but does not provide specific reasons, check the output file produced by the job or check the project log.

Running VAMP in standalone mode

The most convenient way of running VAMP is via the Materials Studio interface, which performs all the preparatory tasks required to run a VAMP job. However, in some circumstances, it may be necessary to run VAMP in standalone mode with a set of input files prepared elsewhere. For example, you may wish to run a calculation on a server that has not been configured as a gateway, i.e., a computer that does not communicate with your Materials Studio client (perhaps because a firewall prevents automatic file transfer and job launch).

Generate the input files

VAMP requires various input files that contain details of the calculation. More information about these files can be found in the [VAMP file formats](#) topic. You can create these files using a text editor, such as

WordPad on Windows or vi on Linux. However, because the information contained in the input files is quite complex, you should use Materials Studio to generate them for you. You can create the required files using the VAMP [Job Files dialog](#), see the Running jobs in standalone mode topic for further information.

Note: The Materials Studio project folder does not contain the parameter files required to run a job. Therefore, when transferring input files to the server, you must locate the parameter files in the Materials Studio installation, typically in a sub-directory called `..\share\Resources\Quantum\VAMP\`, and copy them to the same directory on the server as the rest of the input files.

Transfer the input files to the server

If you generated the input files manually using a text editor on the server machine, then no file transfer is required. However, if you generated the files on your PC using Materials Studio, you must transfer them to the server before you can start the calculation.

If you are unable to access the hard drive on the server, you should use the File Transfer tool to transfer files from the client to the server.

Execute the job

To assist you in running VAMP in standalone mode, a batch/shell file called RunVAMP is supplied. It can be found in the directory in which the VAMP executables are located, usually `etc/VAMP/bin/` in the main Materials Studio directory. RunVAMP scripts are used to start VAMP jobs in standalone mode. RunVAMP .sh is provided for Linux servers, while RunVAMP .bat is provided for Windows servers.

Usage:

RunVAMP.sh [-h] *seedname*(Linux)

or

RunVAMP [-h] *seedname*(Windows)

Argument	Description
-h	Displays the help text.
<i>seedname</i>	The seed used to identify the set of VAMP input and output files. The input files should be present in the directory in which the VAMP script is started.

Download the output files from the server

When the VAMP calculation is complete, you must transfer the output files back to your PC for analysis in Materials Studio.

To transfer the output files back to your PC

1. Transfer the output files to the client PC using either copy and paste or the File Transfer tool.
2. A complete list of the output files that are generated and descriptions of their contents can be found in the [VAMP file formats](#) topic. All of the files, *seedname.out*, *seedname.sdf*, *seedname.vmp*, and *seedname.vres*, should be downloaded from the server.

Tip: After you have transferred the output files, you may wish to modify their attributes such that all of them except the .out file are hidden files. This avoids cluttering up the display in the Project Explorer.

Tip: If you have transferred files into a Materials Studio project folder, but you cannot see them in the Project Explorer, try using the *Refresh* button  to update the Project Explorer.

Open the output files in Materials Studio

Provided that you have transferred the correct files from the server to your PC and stored them in a folder in a Materials Studio project, you should be able to make use of the VAMP analysis options described in the topic [Analyzing VAMP results](#). Specifically, you can open the 3D Atomistic document containing the starting structure and update it or create a trajectory document and animate it.

VAMP file formats

The VAMP server program requires a number of different input files and produces a number of output files. The number and type of input files required and output files produced depend on the details of the VAMP job to be performed.

The table below summarizes information on the format and purpose of the major file types, and provides links to further information.

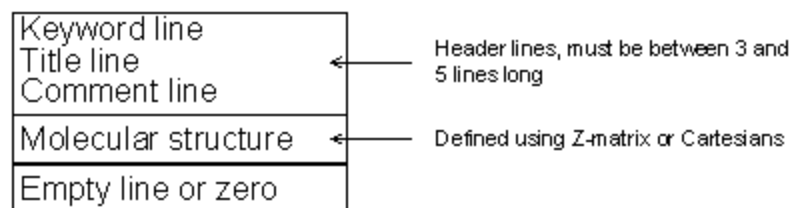
File type	Input or Output	Brief description
.input	Input	General input file
.out	Output	General output file
.sdf	Output	LCAOMO coefficients; atomic charges
.vmp	Output	Final coordinates; NAO-PC charges
.vres	Output	Hessian matrix
.varc	Output	Archive file

INPUT

The Materials Studio interface will create VAMP input files that allow you to access all of the commonly-used features. Occasionally users may need to access features that have not been exposed via Materials Studio. This help topic describes briefly the format of the input file so that users may modify it if necessary.

Each calculation requires a VAMP input file consisting of several different sections. Some sections are mandatory and some are optional, as described below. The input file is free format, i.e., the columns and rows must be in the correct order, but the positioning of individual parameters within each line is unimportant. Parameters must be separated by at least one space or by commas, and lines cannot be longer than 80 characters.

A general scheme for a simple VAMP input file is shown below:



Layout of VAMP input file

Keyword and title lines

All input files must start with at least one keyword line. This is followed by two further lines, which may be either a comment line and a title line, or more keyword lines.

Keyword lines contain keywords that define the calculation, output options, any time limits, etc.

Keywords should be separated by at least one space to ensure that there are no ambiguous definitions

By default, the second and third lines of the input file are simply read by VAMP and printed to the output and archive files during the calculation. You can use these lines as required, but they must be present in the input file.

You can use the plus character, +, to show that the following line is an additional keyword line. The maximum total number of header lines is five. You can use the ampersand character, &, to show that the next line is replaced by a keyword line. The maximum total number of header lines is three.

Examples

Some examples of possible Header lines for VAMP input files are:

Example 1	Example 2	Example 3	Example 4
keywords comment title rest of file	keywords1 + keywords2 + keywords3 + comment title rest of file	keywords1 & keywords2 title rest of file	keywords1 & keywords2 & keywords3 rest of file

Molecular structure data

The molecule structure lines define the structure of the molecule, using either a Z-matrix, or Cartesian coordinates. For all structures greater than four atoms, VAMP recognizes which type of structure definition is used in the input file. For structures with less than four atoms, a Z-matrix is required.

Atoms are defined using their atomic symbols (upper or lower case in any combination), or atomic numbers. There are two special cases for defining atoms:

- **Dummy atoms** are defined using the atomic symbol XX or the atomic number 99. Dummy atoms are imaginary atoms that are not included in the actual calculations, but are often necessary to define molecules correctly in a given symmetry. They can also be used very efficiently to orient the molecule in space.
- **Isotopes** are characterized by the atomic symbol of the element, followed by the atomic weight of the isotope. Note that there is no blank between the symbol and the mass. A deuterium atom is thus defined by H2, tritium by H3, ¹³C by C13, etc. This option only has an effect when vibrational frequencies or thermodynamics are being calculated, because isotopes are otherwise identical within the Born-Oppenheimer approximation used for the SCF calculations.

Cartesian coordinates

Materials Studio generates input files using Cartesian coordinates. Note that this does not limit your ability to perform geometry optimizations: by default, all VAMP optimizations are carried out using internal coordinates. When you input a structure using Cartesian coordinates, it is recommended that you use the XYZ keyword to perform the optimizations in Cartesian space.

When using Cartesian coordinate format, the position of each atom (characterized by its symbol) is defined by the x, y, and z coordinates (Å), followed by an optimization flag.

If the molecule is defined by Cartesian coordinates, it is not possible to use symmetry conditions. Connectivity does not need to be defined because the positions are given explicitly, and not derived from earlier atoms. VAMP automatically recognizes whether the molecule is defined by a Z-matrix or by Cartesian coordinates. The last atom should also be followed by a blank line.

In the example below, the Cartesian coordinates are provided for methanol.

Example Cartesian coordinate input

```
C   -0.36732038   1  -0.18984837   1   0.00000000   1
O    1.14148649   1  -0.12918107   1   0.00000000   1
H   -0.72650149   1  -0.74108568   1   0.93093418   1
H   -0.72650149   1  -0.74108568   1  -0.93093418   1
H   -0.78862211   1   0.86932729   1   0.00000000   1
H    1.46745898   1   0.93187351   1   0.00000000   1
0
```

Internal coordinates

The most usual form for molecule structure lines is the Z-matrix ([Stewart, 1990](#); [Pople, et al., 1986](#); [Clark, 1985](#)) which is a way of defining a molecular structure, one line per atom, in terms of bond lengths, bond angles and dihedral (torsional) angles.

VAMP builds up the molecule, atom-by-atom and sequentially, using the geometric parameters given in the Z-matrix file.

The first atom is always placed at the origin, so only a definition of its atomic symbol is needed.

The second atom is placed along the x-axis, and is defined using the following:

- the atomic symbol
- a bond length to the first atom
- a flag (1 or 0) indicating whether to optimize the parameter.

Therefore, a Z-matrix for HCl is:

```
H
Cl 1.3 1
```

This Z-matrix defines HCl, with a bond length of 1.3 Å, to be optimized during the calculation.

The third atom is placed in the xy-plane and is therefore defined using:

- the atomic symbol
- the bond length
- the bond angle
- a dummy dihedral angle (although this parameter has no real meaning).

Because two atoms are already defined, the atoms to which the bond length and bond angle are made should also be defined. A possible Z-matrix for water would be:

```
H
O 0.97 1
H 0.97 1 106.0 1 0.0 0 2 1 0
```

In this case, the third atom is defined as making a bond to atom 2 of 0.97 Å which is to be optimized. It makes an angle with atom 1 of 106.0°, which is also to be optimized. The dummy dihedral angle 0.0° is defined relative to nonexistent atom 0 and is not optimized.

The remaining atoms in a larger molecule are defined analogously, except that dihedral angles are now required. These are obtained by imagining a Newman-projection from the atom defining the bond

(atom 2 in the above example) to that defining the angle (atom 1 above), and giving the angle between the bond to the atom being defined and a suitable reference atom.

Thus, a possible Z-matrix for ammonia would be:

```
H
N 1.0 1
H 1.0 1 110.0 1 0.0 0 2 1 0
H 1.0 1 110.0 1 120.0 1 2 1 3
```

OUT

The output file, `.out`, is a text file that contains information about the VAMP calculation.

The first section of the output is a header showing the time the job was run.

Next comes the z-matrix for the input geometry, even if the original input was in Cartesian coordinates. The method used to create initial Hessian (or force constant) matrices for geometry optimization are indicated by:

- #: calculated diagonal values are included in the initial Hessian matrix. By default, all parameters that are to be optimized are calculated, except hydrogen bond lengths.
- *: estimated diagonal values included in the initial Hessian matrix (by default, only hydrogen bond lengths are estimated).

This is followed by the input Cartesian coordinates in Å.

The symmetry of the input geometry is reported (it may change during the optimization). VAMP allows small inaccuracies in the geometry when determining the point group.

References for the Hamiltonian parameters are printed next.

If you are running a geometry optimization followed by frequencies, then a summary of the energy and gradients at the starting geometry is printed.

The diagonal elements of the force constant matrix are calculated for the parameters marked with a "#".

For each step of the geometry optimization (Or TS Optimization) VAMP prints:

- The number of the optimization cycle
- The time in seconds required by the most recent cycle
- The time in seconds remaining until time expires
- The norm of the gradients in kcal/mole/Å
- The heat of formation in kcal/mole
- The number of imaginary modes in the Hessian. For a minimization, this number should be zero. For a TS, it should be one. If the final values are different from this, then you probably have not converged to the correct geometry.
- The vibrational frequencies of the lowest few modes in cm^{-1}

The cycles stop then the printed gradient norm falls below the value of GNORM request in the input.

At the conclusion of a geometry optimization, VAMP echoes the input data again and prints a summary of the final heat of formation and electronic energies, as well as some properties.

A z-matrix for the final geometry is printed even if the calculation was performed in Cartesian coordinates.

Molecular orbital eigenvectors and eigenvalues are printed. Orbital eigenvalues are in eV.

The Coulson charges are printed.

The Mulliken population results are printed. This begins with the overlap populations and concludes with the net atomic Mulliken charges.

Additional properties are computed at the final geometry.

Finally, the vibrational frequencies are computed. There will be a line printed for each degree of freedom, equal to three times the number of atoms.

The frequencies and the eigenvectors of the Hessian are printed.

SDF

A `.sdf` (structure data file) is created for all successful calculations. This file contains a number of results that are needed to perform VAMP analysis. The following data are read from the file by Materials Studio:

- Mulliken charges
- Coulson charges
- NAO-PC
- Coulson bond orders
- LCAO-MO coefficients for canonical and localized orbitals
- Orbitals eigenvalues

The `.sdf` is not intended to be read or edited by the user.

VMP

The `.vmp` file contains the final coordinates and atomic charges from the VAMP calculation.

It contains the following lines:

- line 1: `ncenters (i4)`
The number of centers (atoms for a typical `.vmp` file, charge centers if the keyword NAO-PC is used) is defined.
- lines 2 through `2+ncenters (i4,4f8.3)`
`atomic no. x-coord y-coord z-coord charge`
The positions and atomic numbers or point charges for each center are defined.
For atom centers, `atomic no.` is the atomic number; for charge centers, `atomic no.` is zero.
The `coords` are the Cartesian coordinates of each center, in Å.
The `charge` is the atomic charge in units of electronic charges. By default, these charges are NAO-PC. If the keyword COULSON is used, this overrides NAO-PC and Coulson charges appear in the `.vmp` file. If the keyword MULLIKEN is used, this overrides both COULSON and NAO-PC and Mulliken charges appear in the `.vmp` file.

- next line: `-nbonds (i5)`
The number of bonds multiplied by -1 is specified.

- next "`nbonds`" lines (`3i5`)
`atom1 atom2 bond type`

Where `atom1` and `atom2` are the numbers of the atoms involved in the bond (according to the `ncenters` list above). The following `bond types` are available:

- 1 = single bond
- 2 = double bond
- 3 = triple bond
- 4 = strong partial bond
- 5 = weak partial bond

Note: This bonding information is *not* read by Materials Studio.

VRES

The VAMP .vres file contains a Hessian matrix and atomic polar tensors. These are used by Materials Studio to perform a vibrational analysis. This is a binary file and is not intended to be read by users.

The .vres file is created whenever you request [frequencies](#) as part of a VAMP job. The file is returned to the Project Explorer as a hidden file, where it is opened and the data are automatically read into the model. Once the Hessian data have been imported, you can perform a vibrational analysis.

If, for some reason, the data in .vres are not imported automatically, you can manually import the information in one of two ways:

- Update the structure using the VAMP [structure analysis](#).
- Choose *Edit / Insert from...* from the Materials Studio menu bar to read the data from the .vres file.

Note: The .vres file is returned to the Project Explorer as a hidden file, so it is not visible. To open a file using *Edit / Insert From...* you must first browse to the hidden file using Windows Explorer and unmark it as a hidden file.

VARC

Note: This file is written to ensure backward compatibility of VAMP and is not returned to the client when run using Materials Studio.

Archive (filename.varc) files are ASCII files that contain information in a concise format about the calculation that has been performed.

Note: The type of optimization performed and whether it was successful are defined. For example, an archive file is written by optimizations that do not finish within the maximum number of cycles.

Theory in VAMP

The following topics provide specific details about the theory behind VAMP.

Overview of semiempirical molecular theory

Background

The name semiempirical molecular orbital theory indicates that the methods used have been parameterized to reproduce experimental results.

Semiempirical techniques use the same Linear Combination of Atomic Orbitals-Self Consistent Field (LCAO-SCF) theory as *ab initio* programs. However, many of the more complex integrals are removed or replaced using simple approximations. Empirical parameters and functions are used to compensate for the errors introduced by removing integrals. These empirical parameters are fitted to reproduce experimental data.

The basic approximations for neglecting less important integrals were developed by Pople's group in the 1950s and 1960s. The methods that arose from this period are the CNDO ([Pople et al., 1966](#)), INDO ([Pople et al., 1967](#)), and NDDO ([Pople et al., 1965](#)) approximations. These methods are still in use, although usually in modifications intended for interpreting molecular spectra.

More suitable methods for the evaluation of energetic data have been developed by Dewar's group and by Stewart. These are usually known by the acronyms MINDO/3 ([Bingham et al., 1975](#)), MNDO ([Dewar and Thiel, 1977](#)), AM1 ([Dewar et al., 1985](#)), and PM3 ([Stewart, 1989](#)). Of these, either AM1 or PM3 is usually the method of choice, although MNDO is also still in use.

The comparative merits of these methods are frequently discussed. Generally, AM1 is most reliable for organic C, H, N and O containing molecules and PM3 should be used for molecules containing phosphorus and sulfur or for the main group elements that are not parameterized for AM1.

MINDO/3 is now largely obsolete and MNDO has the major disadvantage that it cannot reproduce hydrogen bonds. VAMP performs MINDO/3, MNDO, MNDO/d, AM1, AM1*, PM3, and MNDO/C ([Thiel, 1981](#)) calculations (MNDO/C is a variation of MNDO that is parameterized including a perturbational correlation correction).

The recently implemented PM6 method ([Stewart, 2007](#)), based on the NDDO approximation, delivers the highest accuracy results for a widest range of elements and should be used as the default method for any task.

Basic theory and approximations used

VAMP uses semiempirical calculations to determine a molecular wavefunction ([Pople and Beveridge, 1970](#) and [Stewart, 1990](#)). This wavefunction can then be used to derive molecular properties such as energy, dipole moment, etc.

The molecular wavefunction, Ψ , is built up by a Slater-determinant consisting of molecular spin orbitals, Ψ_i . These are described by the usual LCAO method, in which the molecular orbitals are obtained as a linear combination of the atomic orbitals, ϕ_m :

VAMP Eq. 1

$$\Psi_i = \sum_{\mu} c_{\mu i} \phi_{\mu}$$

In *ab initio* theory, these atomic orbitals are usually described by Gaussian functions, allowing an easier and faster calculation of the two-electron integrals ([Pople et al., 1986](#) and [Szabo and Ostlund, 1989](#)).

Semiempirical MO theory uses Slater-type atomic orbitals rather than Gaussian functions. Slater functions are much more difficult to handle exactly than Gaussians, but represent the electron density far from the nucleus better. Semiempirical methods can use Slater functions by evaluating the two-electron integrals via a multipole approximation ([Dewar and Thiel, 1977](#)), rather than an exact calculation. The so-called basis set of atomic orbitals are defined in the `Vhamil.par` file.

Molecular orbitals can then be built up by an iterative procedure that optimizes the LCAO coefficients, $c_{\mu i}$. This variational self-consistent field (SCF) method is based on Hartree-Fock-Roothaan-Hall theory, and constitutes the main part of most MO programs. It is also a part in which many approximations are implemented because of the very time consuming iterative procedure.

Once the wavefunction is determined, the program uses it to evaluate the energy of the molecule, the atomic forces, and many other electronic properties. The energy and the atomic forces are used to optimize the geometry of the molecule to a stationary point (usually a minimum or transition state) at which the atomic forces are ideally all zero.

MINDO/3 is a modification of Pople's INDO method, whereas MNDO, MNDO/d, AM1, AM1* and PM3 are based on NDDO. AM1 and PM3, which are quantum mechanically identical but vary in their parameterizations, are extensions of MNDO in which the nuclear repulsion energy function has been modified to provide better results, especially for hydrogen bonded systems.

The molecular wavefunction calculated depends on a number of variables, which are user defined and are stated explicitly in the input file to the VAMP calculation.

Applications

Semiempirical programs should be used for molecules that are too large for geometry optimization at the Hartree-Fock split-valence level of *ab initio* theory or with comparable basis sets with DFT.

Currently, this means using semiempirical programs for molecules in the range of 50 to 400 atoms, but these numbers can change as hardware and software become more powerful. Molecules larger than this range should be treated by forcefield methods or mixed QM/MM calculations, and the smaller ones by *ab initio* or density functional theory.

Ab initio and density functional programs can handle molecules up to about 100 atoms, but for most problems, the computation time needed to optimize geometries is prohibitive. Because of this, semiempirical programs are often used in industry and application oriented research. Examples of their use include:

- rapid calculation of optimized geometries and molecular orbitals
- transition state searching and optimization
- calculation of accurate and reliable molecular electrostatic properties, potentials, and fields
- calculation of spectroscopic properties including ESR, NMR, IR, and Raman frequencies, together with hyperpolarizabilities for nonlinear optical studies
- investigation of solvent effects and solvatochromic shifts

Self-consistent field calculations

Evaluating the semiempirical energy expression requires VAMP to solve a set of coupled equations self-consistently. This results in a description of the average field that each electron experiences, called a self-consistent field (SCF) approximation. All calculations involve at least one SCF calculation.

Semiempirical parameters

- NDDO (neglect of diatomic differential overlap)
- ZINDO (Zerner's intermediate neglect of differential overlap)

NDDO Hamiltonians

MENDO

H																He		
Li	Be											B	C	N	O	F	Ne	
Na	Mg											Al	Si	P	S	Cl	Ar	
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh		
* lanthanides			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
** actinides			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

MNDO is not recommended for use with hypervalent compounds because it uses only s and p atomic orbitals. AM1 or PM3 are recommended over MNDO for use with biological systems as MNDO does not reproduce hydrogen bonds and shows larger deviations from experimental heats of formation than these methods.

MNDO/C

MNDO/C ([Thiel, 1981](#); [Schweig and Thiel, 1981](#)) is an MNDO method designed to be used with a perturbational theory correction for electron correlation. It performs well in situations when excited states are important. MNDO/C is parameterized for the following elements:

H																	He	
Li	Be											B	C	N	O	F	Ne	
Na	Mg											Al	Si	P	S	Cl	Ar	
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh		
* lanthanides			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
** actinides			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

MNDO/d

MNDO/d ([Thiel and Voityuk, 1996](#); [Thiel, 1996](#)) consists of the normal MNDO parameters for the elements in orange:

H																	He		
Li	Be											B	C	N	O	F	Ne		
Na	Mg											Al	Si	P	S	Cl	Ar		
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba		*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra		**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh		
* lanthanides			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb			
** actinides			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No			

Elements shown in green have MNDO/d parameter sets which include d orbitals, those in blue have MNDO/d parameter sets with only s and p orbitals.

MNDO/d performs significantly better than the other Hamiltonians for most phosphorus compounds, hypervalent compounds, and for the halogens. Like MNDO, it does not reproduce hydrogen bonds.

MINDO/3

This method is accessible only through the MINDO/3 keyword, when running VAMP in standalone mode and not the Materials Studio interface. The literature citations for the parameter sets used are

given by the program at run time.

AM1

AM1 (Austin model 1; [Dewar et al., 1985](#)) is an s and p orbital-based MNDO-like method, but it differs from MNDO in that extra Gaussian potentials are added to the core-core repulsion energy to allow it to form hydrogen bonds. AM1 is parameterized for the following elements:

H																He		
Li	Be											B	C	N	O	F	Ne	
Na	Mg											Al	Si	P	S	Cl	Ar	
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh		
* lanthanides			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
** actinides			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

Note: AM1 is the default Hamiltonian when VAMP is run from the Materials Studio user interface.

Errors in heats of formation with AM1 are, on average, only about half those obtained with MNDO. Of the s and p orbital-based methods, AM1 underestimates bond torsion barriers least and is therefore the method of choice for many applications involving π systems, including amides.

The geometry of hydrogen bonds is not correct in AM1, but the energetic effects of this error are small. AM1 is a good general method for organic compounds, peptides, etc., although it is not recommended for use with phosphorus and sulfur compounds. Three-coordinate nitrogen centers are generally too flat in AM1.

Standard AM1 parameters can be replaced with the RM1 parameters ([Rocha et al., 2006](#)) provided with the Materials Studio VAMP distribution. The RM1 parameters are a public domain set providing improved accuracy over the original set and also addressing some failures of PM3. To enable the RM1 set the EXTERNAL keyword must be used.

AM1*

AM1* is a new Hamiltonian developed for Materials Studio. It uses AM1 parameters and theory unchanged for the elements H, C, N, O and F. The elements P, S, and Cl have been reparameterized using an additional set of d orbitals in the basis set ([Voityuk and Roesch, 2000](#)) and with two-center core-core parameters, rather than the Gaussian functions used to modify the core-core potential in AM1.

Recently, parameters for Br, I ([Kayi and Clark, 2009a](#)), Cu, Zn ([Kayi and Clark, 2007](#)), Co, Ni ([Kayi and Clark, 2010a](#)), Cr, V ([Kayi and Clark, 2009c](#)), Au ([Kayi, 2010c](#)), Mn and Fe ([Kayi and Clark, 2010b](#)), and Pd and Ag ([Kayi and Clark, 2011](#)) became available and they were shown to provide excellent performance exceeding that of the PM5 and PM6 methods.

AM1* is parameterized for the following elements:

H																		He
Li	Be											B	C	N	O	F		Ne
Na	Mg											Al	Si	P	S	Cl		Ar
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh		
* lanthanides			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
** actinides			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

Elements in green have parameter sets which include d orbitals, those in blue have only s and p orbitals. AM1* gives identical results to AM1 for compounds containing only H, C, N, O, and F.

PM3

PM3 (parameterization model 3; [Stewart, 1989; 1990](#)) is quantum mechanically identical to AM1, but more parameters were treated as variables during the parameterization and so it performs somewhat better than AM1 for heats of formation. PM3 also gives the correct geometries for hydrogen bonds. However, rotation barriers of partial π bonds are very low in PM3. It performs poorly for peptides, for example, for which it often gives non-planar nitrogen coordination.

PM3 is parameterized for the following elements:

H																		He
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh		
* lanthanides			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
** actinides			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

Although PM3 was parameterized to treat hypervalent compounds, it still gives large errors for their heats of formation because it is limited to s and p atomic orbitals. PM3 is not recommended for use with phosphorus compounds.

PM6

PM6 is a most recent NDDO-type method developed by Stewart ([2007](#)). It contains modified NDDO core-core interaction terms and a new, completely optimized set of atomic and diatomic parameters. 70

elements have been successfully parameterized allowing excellent description of main group and hypervalent compounds. Several long-standing faults in AM1 and PM3 have been corrected and significant improvements have been made in the prediction of geometries.

H																	He	
Li	Be											B	C	N	O	F	Ne	
Na	Mg											Al	Si	P	S	Cl	Ar	
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh		
* lanthanides			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
** actinides			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

Note: As the PM6 method is still under development, several errors with some systems are known and described on the developer's page: Accuracy of PM6 (http://openmopac.net/manual/index_accuracy.html). Fixes for these errors will be implemented in VAMP as soon as they become available.

ZINDO Hamiltonians

ZINDO ([Zerner et al., 1980](#)) was parameterized for accurate calculation of the spectroscopic properties of molecules. It provides a number of different model Hamiltonians that can be selected according to the desired property. The default Hamiltonian for ZINDO calculations in VAMP is INDO/1.

The difference between versions /1 and /2 of the ZINDO class methods is in the way the core Hamiltonian elements have been parameterized. In CNDO/1 and INDO/1, these parameters are obtained by fitting to the atomic ionization energies only, while in CNDO/2 and INDO/2, the fitting is to the average of the ionization potential and the electron affinity, making these methods more applicable to cases where electrons are gained or lost. More information on the ZINDO Hamiltonians and their parameterized elements is given below.

CNDO

CNDO (complete neglect of differential overlap; [Pople and Santry, 1965](#)) is the crudest and least rigorous semiempirical approximation. In CNDO, all integrals involving different atomic orbitals are ignored.

CNDO/1 is parameterized for the following elements:

H																			He
Li	Be												B	C	N	O	F		Ne
Na	Mg												Al	Si	P	S	Cl		Ar
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br		Kr
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I		Xe
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At		Rn
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh			
* lanthanides			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb			
** actinides			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No			

INDO/2 is parameterized for:

H																			He
Li	Be												B	C	N	O	F		Ne
Na	Mg												Al	Si	P	S	Cl		Ar
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br		Kr
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I		Xe
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At		Rn
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh			
* lanthanides			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb			
** actinides			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No			

Since INDO and CNDO execution time is comparable and INDO contains some important integrals that are neglected in the CNDO method, INDO performs much better than CNDO, especially in the prediction of molecular spectral properties.

SCF formalism

VAMP performs one of three different types of SCF calculation, controlled by the presence of unpaired electrons or by the input options:

- [Restricted Hartree-Fock \(RHF\)](#) - used by default. A closely related method, RHF Half-Electron (HE), is used when there is an odd number of electrons or for triplet and higher spin states. The appropriate method, RHF or HE, is invoked automatically by VAMP.
- [Unrestricted Hartree-Fock \(UHF\)](#) - used only when requested using the UHF keyword.
- [Annihilated Unrestricted Hartree-Fock \(AUHF\)](#) - similar to UHF, but when AUHF is used, any spin contamination is eliminated during each SCF cycle to give results similar to those obtained using the RHF method.

Restricted Hartree-Fock (RHF)

In a Restricted Hartree-Fock (RHF) calculation, only one set of molecular orbitals is calculated, and these are constrained to be either doubly occupied or empty. A Half-Electron (HE) calculation is really a RHF calculation in which the unpaired electron is represented by two paired half electrons.

Half-electron and RHF calculations are the basis for the Configuration Interaction (CI) calculations performed by VAMP. HE geometry optimizations can be slow, or even fail, because the electron pairing correction to the energy has caused errors in the atomic forces. Usually, in an RHF calculation, each occupied molecular orbital contains two electrons. In an HE calculation, this does not need to be the case.

You can use the keyword OPEN(n,m) to define partially occupied orbitals (useful for degenerate states in conjunction with CI calculations, for instance), where n denotes the number of electrons to be distributed evenly over m orbitals. For example, if you use the keyword OPEN(2,2), two electrons will be distributed in two orbitals, resulting in a biradical reference wavefunction. (This feature is not available through the Materials Studio interface).

Tip: When dealing with transition metal ions and complexes with a high spin multiplicity, the UHF or AUHF methods are recommended. The lowest state of an open shell system cannot be determined with restricted Hartree-Fock (RHF).

Using UHF to allow electrons to become unpaired

If the calculation is closed-shell and DELTA or DELTAP are large, for example 1.0^{-1} , there is a fundamental problem with the calculation. This is most often because the molecule itself wants to be open-shell (for example a triplet), but may also be because the geometry is bad. If the geometry is correct, try using the keyword UHF for an unrestricted Hartree-Fock calculation that will allow the electrons to become unpaired. At the same time, you can use the SCF convergers listed above and increase the number of SCF cycles. First perform a single energy calculation and check the output file for the values of <S**2>, given in the lines:

```
<> Expectation value for <S**2>: 0.00000
<> Original (UHF) <S**2> : value
```

If the UHF <S**2> value is large, for example, 0.5 or more, the molecule has at least some open-shell character, which will require a CI calculation, or may even be a triplet, which can be calculated using the TRIPLET and UHF options.

Unrestricted Hartree-Fock (UHF)

In contrast to Restricted Hartree-Fock or Half-Electron calculations, for which there is no specific keyword, to use Unrestricted Hartree-Fock (UHF) calculations, you must request them using the keyword UHF.

In UHF formalism, two sets of molecular orbitals (alpha and beta) are calculated. The alpha orbitals are populated by spin-up electrons and their beta counterparts by electrons of the opposite spin. There are always at least as many (or more) alpha-electrons as beta. Alpha and beta orbitals for a pair of electrons are usually similar, but not identical.

When an input file uses UHF for a system with n unpaired electrons (i.e., an uneven number of electrons, or a triplet or higher spin state), VAMP performs a UHF calculation with n more alpha electrons than beta.

When an input file uses UHF for a system with an even number of electrons, a singlet state is calculated, but the initial guess (the MOs used as a starting point for the SCF iterations) is perturbed randomly so that the UHF calculation will not converge to the RHF solution if the UHF wavefunction is more stable.

If the UHF energy is lower than that given by RHF, this indicates that there is a biradical contribution to the molecular wavefunction that should ideally be treated using the CI method. The biradical contribution is seen as spin contamination, arising because the UHF wavefunction is not an Eigenfunction of the total spin operator. Spin states higher than those requested by the user mix into the wavefunction, giving rise to larger than expected values for spin operators.

Both the expected and calculated spin operators (S^2) are reported in the output file. Expected S^2 values for pure singlet, doublet and triplet states are 0.0, 0.75, and 2.0, respectively. You should treat UHF calculations that give significantly (20%) larger values than these with caution.

Strategies to avoid spin contamination in UHF calculations

Generally, unrestricted Hartree-Fock (UHF) is the best option for open-shell systems; it is very much faster than RHF. However, UHF calculations sometimes suffer from so-called spin contamination, affecting the results of the calculation.

In general, if the value of the UHF $\langle S^2 \rangle$ is no more than about 110% of the expectation value, the calculation is OK. Higher values indicate significant mixing of higher spin states (for example, triplets for a singlet calculation or quartets for a doublet) into the wavefunction. If this is the case, try the calculation again using annihilated UHF (AUHF, a method unique to VAMP) or RHF.

Tip: The different methods give different energies, so make sure that any species you plan to compare are calculated using the same method.

SCF convergers

The SCF calculation is an iterative procedure and therefore sometimes either fails to converge (oscillates), or converges very slowly. The default maximum number of iterations allowed for convergence is 200. You can set this value on the [VAMP Electronic Options dialog](#) or by using the keyword ITRY=n.

VAMP offers several different methods to enforce SCF convergence. All are accessible from the [Electronic tab](#), or by adding the appropriate VAMP keyword.

- **Standard converger** - used by default, no associated keyword. If this converger fails after (ITRY-10) iterations, the Level shift method and Pulay convergers are tried for up to ITRY further iterations.
- **IIS converger** - [Badziag and Solm's](#) IIS technique, requested using the IIS keyword. This is the most reliable SCF converger, but can be slow to converge. You might need to increase the number of SCF cycles allowed using the keyword ITRY=n.
- **Pulay converger** - [Pulay's](#) SCF converger, requested using the PULAY keyword. This converger can give a very fast convergence. However, there are no simple rules to indicate when it is suitable.
- **Level shift method** - requested using the SHIFT=n.n keyword or by checking the *Use level shifting* checkbox on the [Electronic tab](#). SCF convergence is enforced by increasing the energy of the virtual molecular orbitals, which are usually responsible for oscillations. nnnn denotes the additional energy in eV. Use this method with caution, especially for CI calculations.

A further option to control SCF behavior is to set the degree of convergence on [Electronic tab](#), or by using the keyword SCFCRT=n.nn. This alters the convergence criterion for the SCF calculation. It is often useful to make this criterion tighter, but usually, you should not relax it.

Geometry optimizations

When a structure is built, it usually needs to be refined to bring it to a stable geometry. The refinement process is known as optimization, and is an iterative procedure in which the coordinates of the atoms are adjusted so that the energy of the structure is brought to a stationary point, where the forces on the

atoms are zero. Several options are available in VAMP to perform the optimization as efficiently as possible.

Eigenvector following

The default VAMP optimizer is the Eigenvector Following (EF) routine ([Baker, 1986](#)), which was chosen for its reliability and excellent general performance. EF can derive geometrical changes from several different types of force constant (Hessian) matrix, and these options obviously have a large effect on the progress of the optimization.

A typical geometry optimization starts either by calculating all or part of the Hessian matrix, or by estimating its diagonal values. The choice of starting Hessian can have a significant impact on the speed of a geometry optimization, so is covered in some depth here. The initial Hessian is then progressively updated and improved as more information about the energy hypersurface is gathered during the optimization cycles. VAMP several different initial Hessian options, two of which are available through the Materials Studio interface.

- **Approximate Hessian:** This is the default method for energy minimization. The diagonal elements of the Hessian matrix are calculated for all internal parameters except bond lengths to hydrogen, for which estimated values are used. This was chosen as a compromise between the need for an accurate initial Hessian, and the desire to reduce the CPU time required for the first cycle. This method may be selected by setting the *Generate Hessian* option to [Partial](#) on the [VAMP Geometry Optimization dialog](#), or by omitting the keyword HESS from the input file.
- **Exact Hessian:** This is the default for transition state searching, and is available as an option for minimization. The entire Hessian matrix is calculated in the first optimization cycle. This is time-consuming, but may be worthwhile for very difficult optimizations where it is suspected that the final geometry is close to the initial coordinates. This method may be selected by setting the *Generate Hessian* option to [Exact](#) on the [VAMP Geometry Optimization dialog](#), or by adding the keyword HESS=1 to the input file.

VAMP offers several other ways to specify the starting Hessian that are *not* available through the Materials Studio interface:

- **HESS=0:** The initial diagonal values of the Hessian matrix are estimated. This is often useful for "normal" acyclic molecules and has the advantage that the first cycle, in which the initial Hessian is normally calculated, is very fast. HESS=0 may also be useful for very large molecules, for which the calculation of the partial Hessian matrix may be very time-consuming. Because the estimated initial Hessian is probably not a very close approximation to the real one, optimizations using HESS=0 usually require far more cycles than the default method.
- **HESS=-1:** Allows you to specify which diagonal values are calculated. Diagonal elements are calculated for all parameters with an input file optimization flag set to 2 (normally 0 or 1). All other diagonal values are estimated.
- **HESS=2:** Allows a Hessian matrix to be read from a .res file calculated during a previous force calculation.
- **HESS=5:** #Uses an approximate Hessian generated from the Amber forcefield.

An optimization will continue until the gradient norm on the atoms falls below the threshold specified in the input. This value may be controlled from the [VAMP Geometry Optimization dialog](#).

The speed of a geometry optimization can be improved by using internal coordinates (Z-matrix) rather than Cartesian coordinates (XYZ keyword). However this option may fail if the molecule is so flexible that linear bends occur during optimization. For some molecules Z-matrix may not be the best representation of internal coordinates, and geometry optimization may take many steps to converge. It is recommended that geometry optimization runs be limited to systems containing fewer than about 500 atoms.

Transition state searching

VAMP offers three different transition state optimizers:

- **EF:** Requested by setting the *Method* option to **EF** on the [VAMP TS Optimization dialog](#) or by using the keyword EF. The default EF optimizer is set to find a transition state rather than a minimum.
- **Powell:** Requested by setting the *Method* option to **Powell** on the [VAMP TS Optimization dialog](#) or by using the keyword NS01A.

These two procedures are used in the same way and so are not discussed separately here. In some cases, the **TS** optimizer is faster than **Powell**. However, the **Powell** optimizer is better at finding transition states on flat potential energy surfaces.

Unfortunately, there does not seem to be a general rule to use in choosing which transition state optimizer to use for a problem. For many problems, both optimizers are suitable. For some problems, only one (and occasionally neither) method will work.

- **NLLSQ:** Requested by setting the *Method* option to **NLLSQ** on the [VAMP TS Optimization dialog](#) or by using the keyword NLLSQ.

The nonlinear least squares optimizer, **NLLSQ**, is often successful when both the **Powell** and **TS** optimizers fail to find the transition state, particularly where the initial geometry is very close to a transition state.

Note: **NLLSQ** only optimizes the atomic forces (gradients) and therefore finds the nearest stationary point.

The HESS=1 option is automatically turned on for all TS optimizations.

It is always necessary to test the nature of the structure by computing the vibrational frequencies at the final geometry. Structures with a single imaginary frequency are transition states; structures with more than one imaginary frequency should be optimized to eliminate one of the imaginary modes.

Fixing atoms

VAMP allows you to apply restraints to fix certain atoms at their initial input position, or at any position you specify. You can achieve this by manually editing the input file. At the end of the input file, add a blank line followed by:

```
> <fixed.atoms>
force fvalue
position l1 x y z
position l2 x y z
...
distance k l dvalue1
angle    k l m dvalue2
dihedral k l m n dvalue3
```

The default force constant of 100 is applied to the positions of the atoms and to the specified monitors (distances, angles, and torsions) unless it is redefined by *fvalue*.

fvalue is the value of the force constant to be applied to the fixed atoms. A larger *fvalue* reduces changes of fixed coordinates and monitors.

l1, *l2* and so on are the atom numbers in the initial input to be fixed at the specified coordinates. Coordinates *x y z* are in Å.

All coordinates of fixed atoms are frozen. The *position* command must be followed by three coordinates.

Restraints to specified distances, angles, and torsions can be applied as shown in the example above (it is possible to restrain numerous monitors). There can be a number of such restraints in the input file, but increasing their number introduces a high risk of failing geometry optimization when VAMP is unable to satisfy all the required restraints.

Note: The restraint technique does not really freeze the coordinates of fixed atoms, but it makes sure that these coordinates change significantly less than those of free atoms.

Force calculations

Force calculations aim to calculate the normal vibrational modes of the molecule or structure. The force constant matrix (Hessian) is calculated, mass-weighted, and then diagonalized. The results of force calculations may be used as follows:

- The frequencies of the normal vibrational modes indicate whether the structure is a minimum (all frequencies positive), a transition state (one negative frequency), or a higher order stationary point (hilltops etc., with more than one negative frequency). This test of the structure should always be performed, especially for transition-state optimizations.

You can display the vibrational frequencies, view the vibrational spectrum, and animate normal modes using the Vibrational Analysis tools in the Materials Visualizer. You can also examine the VAMP output file to see the results.

The accuracy of the IR spectra calculated by VAMP is illustrated in [Figure 1](#), where simulated IR spectra from VAMP calculations are compared to the data published by the US National Institute of Standards and Technology (NIST).

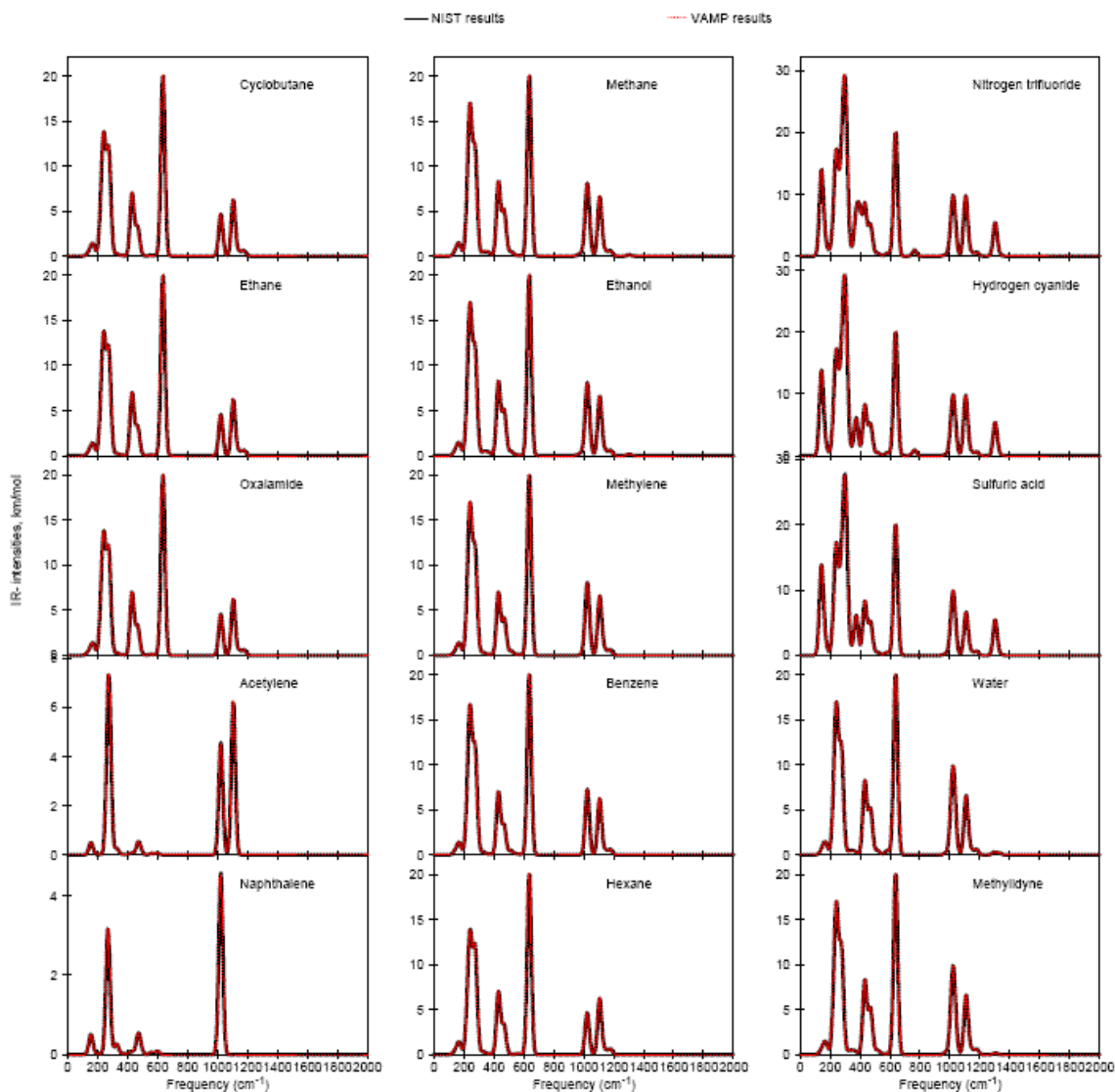


Figure 1. Comparison of IR spectra calculated using VAMP with reference spectra published by NIST

- The normal vibrational modes of a structure are necessary for calculations of thermodynamic properties and isotope effects. You can perform thermodynamic analysis using the [Thermodynamic properties](#) options on the VAMP Analysis dialog or by examining the VAMP output file.
- The Hessian matrices returned by a FORCE calculation may be used as initial Hessians by other programs. For example, DMol³ can use the VAMP Hessian as a starting point in geometry optimizations.

To use a VAMP Hessian in a DMol³ calculation

1. Perform a VAMP calculation ([Energy](#), [Geometry Optimization](#), or [TS Optimization](#)). Request that the frequencies be computed at the final geometry, as described in [Requesting electronic, structural, and vibrational properties](#).
2. When the job is complete, open the final 3D Atomistic document (.xsd) file in the Project Explorer. This should automatically load the Hessian from the [.vres](#) file.
3. When you are ready to submit this model to DMol³, open the DMol3 Geometry Optimization dialog and check the *Use starting Hessian* checkbox. The Hessian computed by VAMP will be used as the starting Hessian for DMol³.
4. If the *Use starting Hessian* checkbox is grayed out, the VAMP Hessian has not been imported. If this is the case, use the [Structure](#) options on the VAMP Analysis dialog to refresh the structure and import the Hessian.

Force calculations assume that the input file contains an optimized geometry. If the gradients norm is too large (set using the GNORM keyword), the structure will be re-optimized before the requested force calculation is performed. You can avoid re-optimizing the geometry by using the keyword LET.

Thermodynamic calculations

In principle, if the molecular geometry, energy, and vibrational frequencies are known, the thermodynamics properties (enthalpy, entropy, free energy) of the molecule can be calculated ([Stull and Prophet, 1971](#)). The results can be displayed using the [Thermodynamic properties](#) options on the VAMP Analysis dialog, or viewed in the VAMP output file.

There is, however, a fundamental inconsistency inherent in the parameterization of semiempirical methods to reproduce heats of formation. The energy calculated by VAMP is the internal energy of a hypothetical motionless (Born-Oppenheimer) state. To relate this energy to heats of formation at 298 K, an atom-based scheme is used, assuming that the energy difference between the Born-Oppenheimer state and the molecule at 298 K can be treated in an additive fashion. This means that the zero-point energy and the energy required to warm the molecule to 298 K are assumed to be identical for isomers. This is clearly not the case and can lead to errors of up to 5 kcal mol⁻¹.

A further problem arises in the calculation of the thermodynamic properties. As the methods are parameterized to reproduce the heat of formation at 298 K, this temperature must be used as the reference point for thermodynamics calculations. The calculation, however, gives an energy for a motionless molecule. This leads to a basic inconsistency. Thermodynamics calculations yield entropy, enthalpy, and free energy changes between the Born-Oppenheimer state and the temperature in question. The heat of formation scale must, however, be adjusted so that the value at 298 K is the same as that given in the normal calculation.

The result is that, in effect, a fictitious Born-Oppenheimer energy is used in thermodynamics calculations. The best procedure is simply to ignore the "heat of formation" and to calculate thermodynamic quantities for reactions based on the Born-Oppenheimer energy and the calculated entropy and enthalpy changes, as for ab initio calculations.

Using the thermodynamic data

Once the enthalpy, entropy, and free energy of the molecule are calculated as a function of temperature, the results can be used to compute the heat of formation at any temperature. The heat of formation at 298 K is written to the VAMP output file and can be adjusted for different temperatures as follows:

1. Display the results using the [Thermodynamic properties](#) options on the VAMP Analysis dialog or view them in the VAMP output file.
2. For the temperature of interest, say 100 K, compute the temperature-dependent contribution, enthalpy minus temperature times entropy (E - TS).
3. Compute E - TS at 298 K. If you did not compute the thermodynamics at exactly 298 K, pick the temperature closest to it (for example 300 K) or estimate it by interpolation.
4. Compute the difference in E - TS at the two temperatures and adjust the heat of formation at 298 K by that amount. For example, say that E - TS at 100 K is 0.5 kcal mol⁻¹ and the value at 298 K is 2.2 kcal mol⁻¹. You would compute the heat of formation at 100 K by subtracting 1.7 kcal mol⁻¹ (2.2 - 0.5) from the heat of formation at 298 K given in the VAMP output file.

Configuration interactions

Although self-consistent field (SCF) calculations are adequate for the vast majority of 'normal' molecules, biradicals and excited states require a more sophisticated treatment. This is often achieved using configuration interaction (CI) methods. In CI calculations, the molecular orbitals (MOs) for the ground state are calculated and then used unchanged to construct a series of further electronic configurations (microstates) that are mixed to form new electronic states. VAMP CI calculations give not only the ground state, but also the excited states that result from mixing the microstates used. They can, therefore, be used for the calculation of UV-Vis spectra, optimization of excited states, second-order hyperpolarizabilities (sum-over-states method) etc.

VAMP includes several types of standard CI expansion where the microstates used are predefined. Standard CI expansions in VAMP are defined by specifying the number of MOs to be used. If *n* MOs are requested, the program will use one of three different sets of permutations of the electrons over these *n* MOs:

- **Even *n*:** The highest *n*/2 occupied orbitals and the lowest *n*/2 unoccupied orbitals are used for closed-shell reference wavefunctions (the reference wavefunction is that of the SCF state used to obtain the MOs).
- **Odd *n*, even number of electrons:** One more occupied orbital is used than unoccupied orbitals.
- **Odd *n*, odd number of electrons:** The singly occupied orbital counts as if it were doubly occupied within the above rules.

VAMP tests for 'degenerate' sets of orbitals that are not fully included in the CI calculation by making sure that the energy difference between MOs within the active space and those outside is at least 0.1 eV. If this is not the case, the CI calculation is stopped after the SCF. This test can be overridden by checking *Ignore degenerate orbitals* on the [VAMP Electronic Options dialog](#) or by adding the keyword LEV-OK to the input file.

The sort of CI to be used can be controlled using the *CI type* dropdown list on the [Electronic tab](#) of the VAMP Calculation dialog. Available options are:

- **Full** - All available permutations of the electrons within the n MOs are used. This option is very useful for small values of n , but leads to very large numbers of microstates as n becomes larger.
- **CIS** - All single excitations (relative to the reference configuration) are included in the CI calculations. This allows you to consider a large number of orbitals in the CI calculation. This option is often a useful alternative to PECO for calculating spectra.
- **CISD** - All single and double excitations (relative to the reference configuration) are included in the CI calculations. This option is very useful for CI calculations on odd-electron species, but does not include all the necessary microstates to complete all the spin sets, so that some states with incorrect spins may result from the CI calculation.
- **PECI** - All single excitations and all double excitations in which a complete electron pair is promoted from one MO to another (pair doubles) are included in the CI. This is a very economical and effective CI expansion for closed-shell molecules and is used in VAMP for the calculation of spectra or hyperpolarizabilities. PECO should not be used for systems with unpaired electrons in the reference wavefunction.
- **RumerCI** - Rumer CI is a configuration interaction technique based on selecting the microstates to be included in the CI on the basis of Rumer diagrams ([Rumer et al., 1932](#)). Rumer diagrams are derived from valence bond theory and use the Rumer-Pauling rules. Rumer CI in VAMP can treat spin multiplicities other than singlets and uses a restricted open-shell Hartree-Fock (ROHF) reference wavefunction. The technique was introduced for INDO/S by Pauncz et al. ([2000](#)). A similar approach has been described by Ramesesha ([1986](#)) and Sarma and Ahsan ([1998](#)). Spin-orbit coupling was introduced for the Rumer CI in ZINDO by Kotzian et al. ([1991](#)). Rumer CI can be used to investigate singlets or systems with higher spin states within VAMP. It must be used with an ROHF reference wavefunction. The use of Rumer diagrams guarantees that all the necessary spin states will be included in the CI calculation.

CI calculations are available only for RHF and ROHF wavefunctions. Any spin state (singlet, doublet, etc.) can be requested.

Natural atomic orbital/point charge model

The natural atomic orbital/point charge (NAO-PC) model ([Rauhut and Clark, 1993](#)) may be used in conjunction with the Hamiltonian methods MNDO, AM1, and PM3 in VAMP. The electron cloud of the molecule is represented as an array of negative point charges (eight per non-hydrogen atom) in this model. This allows the fast and accurate calculation of a variety of one-electron properties of the molecule. Molecular electrostatic potentials, multipole moments, electrostatic fields, etc., can then be calculated from the NAO-PC model using classical electrostatics.

The **.vmp** file generated by VAMP contains the NAO-PC model of the molecule with the negative point charges defined as atoms of atomic number zero. This feature can be turned off using the **keyword** COULSON, which results in a **.vmp** file containing an atom-centered point charge model using Coulson charges (the atomic charges normally given by the population analysis), or the keyword MULLIKEN, which results in a **.vmp** file containing an atom-centered point charge model using Mulliken charges.

The NAO-PC model is analyzed to give the molecular monopole, dipole, quadrupole, and octupole moments ([Beck et al., 1994](#)) and atomic monopole, dipole, and quadrupole moments for the non-hydrogen atoms. This simple type of distributed multipole analysis provides a more exact picture of the molecular electronics than the normal population analysis. Note that molecular quadrupoles calculated with the MNDO, AM1, or PM3 Hamiltonians agree at least as well with experimentally determined values as those calculated using ab initio theory at the MP2/6-31G* level ([Beck et al., 1994](#)).

The NAO-PC atomic multipoles are also used as input descriptors for a neural net that estimates the ^{13}C chemical shift of carbon atoms in the molecules calculated ([Clark et al., 1995](#)). The standard deviation of the calculated chemical shift from experimental values is currently about 7 ppm, but the largest

deviations may be around 20 ppm. A warning will be printed if the descriptors for a given carbon are out of the range known to the net, which usually suggests that the net was not trained on molecules containing carbons of this type.

At present, the natural atomic orbital/point charge (NAO-PC) model is not available for the AM1*, MNDOD/d, PM6, and MNDO/C NDDO Hamiltonians or any of the ZINDO Hamiltonians.

Solvent effects

Self-consistent Reaction Field

VAMP simulates solvent effects on ground and excited states using the numerical Self-Consistent Reaction Field (SCRF) method described by Rauhut, Clark and Steinke ([1993](#)).

The SCRF method has been extended to include the calculation of absorption and fluorescence energies by Gedeck and Schneider ([1997](#)). At present, the SCRF technique can be used only for single point calculations (not for optimizations).

The current implementation of the numerical SCRF technique in VAMP is rather CPU intensive but much faster than in earlier versions of VAMP. Nevertheless, it usually gives good results for solvatochromic shifts and moderate agreement with experimental results for solvation energies of ground states.

VAMP can simulate a variety of solvents and treat excited states. The calculation of the dispersion energy is based on calculated reaction field and polarizability tensors.

The calculation of dispersion energy is, however, not origin independent and so is calculated relative to the center of mass of the system. This would give unrealistically large dispersion energies for molecules where the center of mass lies outside the Van der Waals' volume of the molecule, for example U-shaped molecules. This special case is detected by VAMP and the reaction field is artificially damped to preclude very large dispersion contributions.

In these cases, the program prints warnings that the reaction field has been damped and that the dispersion energy may not be reliable (seldom required).

To perform SCRF calculations, choose [SCRF](#) from the list of *Solvation schemes* on the [Electronic tab](#) or add the SCRF keyword to the input file. You can control the type of solvent that is used on the [VAMP Electronic Options dialog](#). Available solvents are:

Solvent	Keyword SCRF=
Acetone	ACE
Acetonitrile	CH3
Benzene	C6H6
Carbon tetrachloride	CCL
Chloroform	CHC
Diethyl ether	ETH
Dimethyl sulfoxide	DMS
Ethanol	ETO
Methanol	MEO
Methylene chloride	CH2

Solvent	Keyword SCRF=
n-Hexane	HEX
n-Hexadecane	NHD
Nitrobenzene	NIT
Pyridine	PYR
Water	H2O

For example, to choose water as the solvent, set the *Solvent* to [Water](#) on the [VAMP Electronic Options dialog](#), or add the keyword SCRF=H2O to the input file.

The continuum model cannot account adequately for specific effects such as hydrogen bonding, and therefore results for water, methanol, and ethanol are generally less reliable than those for other solvents.

COSMO

COSMO, the CONductor-like Screening MOdel developed by Klamt and Schüürmann ([1993](#)) is a continuum solvation model in which the solute molecule forms a cavity within the dielectric continuum of permittivity, ϵ , that represents the solvent.

Unlike the SCRF solvent model, you can perform geometry optimization or TS optimizations using COSMO. You cannot, however, perform CI calculations.

The charge distribution of the solute polarizes the dielectric medium. The response of the dielectric medium is described by the generation of screening (or polarization) charges on the cavity surface. In contrast to other implementations of CSMs, COSMO does not require solution of the rather complicated boundary conditions for a dielectric in order to obtain screening charges, but instead calculates the screening charges using a much simpler boundary condition for a conductor.

The deviations of this COSMO approximation from the exact solution are rather small. For strong dielectrics like water they are less than 1%, while for nonpolar solvents with ϵ of about 2 they may reach 10% of the total screening effects. However, for weak dielectrics, screening effects are small, and the absolute error therefore amounts to less than one kcal/mol.

You can select the [COSMO](#) method using the *Solvation scheme* option on the [Electronic tab](#) or by adding EPS=nn.nn to the input file where nn.nn is the dielectric constant of the solvent. You can choose the type of solvent that is used on the [VAMP Electronic Options dialog](#).

A list of common solvents is available via the *Solvent* dropdown list. However, you can use *any* solvent if you know its dielectric constant. Simply type the known dielectric constant in the *Dielectric constant* field on the [VAMP Electronic Options dialog](#).

Polarizabilities

VAMP 9.0 now calculates parameterized polarizabilities within the additive partitioned (M4) model ([Martin et al., 2000](#)) as the default and only method. This method has been parameterized for MNDO, AM1, and PM3, and the elements shown in blue:

H																	He	
Li	Be											B	C	N	O	F	Ne	
Na	Mg											Al	Si	P	S	Cl	Ar	
K	Ca	*	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra		**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	
* lanthanides			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
** actinides			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

MNDO/C calculations use the optimized MNDO parameters and analytical values for the parameters are used for all other elements. A warning is displayed in the output file if elements for which no optimized parameters are available are present. In this case, the calculated polarizabilities will not be as accurate as those for the elements that have been polarized.

Polarizabilities are not calculated for charged species or for methods that use d orbitals (currently PM6, MNDO/d, and AM1*).

Dialogs in VAMP

The following topics and subtopics describe the VAMP dialogs:

- [VAMP Calculation dialog](#)
- [VAMP Analysis dialog](#)

Use the Save settings... option to save the current dialog settings.

VAMP Calculation dialog

The VAMP Calculation dialog allows you to set up and display the parameters for a VAMP calculation.

The VAMP Calculation dialog contains the following tabs:

- [Setup](#): Allows you to choose the type of calculation that VAMP will perform, along with other basic input options, such as the Hamiltonian, spin state, and total charge.
- [Electronic](#): Allows you to set the parameters associated with the electronic Hamiltonian, including the SCF convergence scheme and the solvent environment.
- [Properties](#): Allows you to select the properties that will be computed as part of the VAMP calculation, in addition to all the other properties that VAMP computes by default.
- [Job Control](#): Allows you to specify job settings for the VAMP calculation.

Run: Runs a job using the settings specified. The results are placed in a subfolder of the current Materials Studio project directory.


Run | Copy Script: Converts the current settings to a script and copies the script to the clipboard. Refer to the Generating scripts topic for more information on using sections of scripts generated from a dialog.

Files...: Provides access to the [VAMP Job Files](#) dialog which allows you to save input files for a VAMP calculation without running the job, or to run a job using an existing set of input files.

This functionality is provided for users who need to run the VAMP server program in standalone mode, or who wish to edit the VAMP input files in order to gain access to features not supported by the VAMP interface.

Help: Displays the Help topic for the current tab.

Access methods

Menu	<i>Modules VAMP Calculation</i>
Toolbar	 / Calculation

Setup tab

The *Setup* tab allows you to choose the type of calculation that VAMP will perform, along with other basic input options, such as the Hamiltonian, spin state, and total charge.

Task: Select the type of calculation that you wish to perform from the dropdown list. Available options are:

- [Energy](#) - performs a single-point energy calculation
- [Geometry Optimization](#) - searches for a minimum energy structure
- [TS Search](#) - searches for a transition state
- [TS Optimization](#) - searches for a transition state by refining a transition-state structure

More...: Provides access to further options for the selected task.

Hamiltonian: Select the [Hamiltonian](#) that will be used in the calculation.

Choose either the neglect of diatomic differential overlap ([NDDO](#)) or the Zerner's intermediate neglect of differential overlap ([ZINDO](#)) approximation from the first dropdown list. Then select the particular Hamiltonian from the second dropdown list. Seven NDDO ([MNDO/C](#), [MNDO](#), [AM1](#), [PM3](#), [AM1*](#), [MNDO/d](#), and [PM6](#)) and four ZINDO ([CNDO/1](#), [CNDO/2](#), [INDO/1](#), and [INDO/2](#)) Hamiltonians are available.

Multiplicity: Select the multiplicity from the dropdown list to perform a calculation on a specific spin state. Available options are:

- [Auto](#)
- [Singlet](#)
- [Doublet](#)
- [Triplet](#)
- [Quartet](#)
- [Quintet](#)
- [Sextet](#)


When [Auto](#) is selected, VAMP will attempt to determine the ground spin state when performing a spin-unrestricted calculation ([UHF](#), [A-UHF](#), or [ROHF](#)).

Spin: Select the [spin state](#) that will be used in the calculation from the dropdown list. Available options are:

- [RHF](#) - restricted Hartree-Fock
- [UHF](#) - unrestricted Hartree-Fock
- [A-UHF](#) - annihilated unrestricted Hartree-Fock (half-electron method)
- [ROHF](#) - restricted open-shell Hartree-Fock

Charge: Specify the total charge on the molecule. Only integer values can be specified.

Access methods

Menu	Modules VAMP Calculation Setup
Toolbar	 Calculation Setup

VAMP Geometry Optimization dialog

The VAMP Geometry Optimization dialog is accessed by clicking the *More...* button on the [Setup tab](#) of the VAMP Calculation dialog, when [Geometry Optimization](#) is selected from the *Task* dropdown list. It provides access to detailed options for control of the [geometry optimization](#).

Quality: Specifies the geometry optimization convergence threshold for *Gradient norm*. The optimization will stop when the *Gradient norm* convergence criterion is satisfied. Available options are:

- [Coarse](#) - 1.0 kcal/mol/Å
- [Medium](#) - 0.4 kcal/mol/Å
- [Fine](#) - 0.1 kcal/mol/Å

Changing the *Gradient norm* to any other value will result in the *Quality* being set to [Customized](#).

Gradient norm: Specifies the gradient norm convergence criterion for the geometry optimization calculation. The calculation ends when the gradient norm falls below this threshold.

Max. step size: Specifies the maximum allowed change of any Cartesian coordinate. Geometric displacements are truncated such that they are less than this value. This prevents the optimizer from taking unreasonable steps.

Generate Hessian: Specifies how the initial Hessian matrix is to be computed. Available options are:

- **Partial** - only the diagonal elements are calculated.
- **Exact** - the full Hessian matrix is calculated.


Tip: Computing the full Hessian will be a more costly calculation, but may improve the speed of convergence.

Optimize using internal coordinates: When checked, indicates that internal coordinates are to be used for optimizing the structure, rather than Cartesian coordinates.

Tip: Usually, using internal coordinates is more efficient, so the calculation will converge more quickly. However, there are instances when an optimization may fail, for example due to bonds becoming linear, which may be resolved by optimizing in Cartesian space.

Help: Displays the Help topic in a browser.

Access methods

Menu	<i>Modules VAMP Calculation Setup More...</i>
Toolbar	 <i>Calculation Setup More...</i>

VAMP TS Optimization dialog

The VAMP TS Optimization dialog is accessed by clicking the *More...* button on the [Setup tab](#) of the VAMP Calculation dialog, when the **TS Optimization** option is selected from the *Task* dropdown list. It provides access to detailed options for control of the [transition state optimization](#).

Method: Specifies the method used to search for the transition state. Available options are:

- **EF** - eigenvector following
- **Powell**
- **NLLSQ** - non-linear least squares

Information about these methods is available under the topic [Setting up a transition state optimization calculation](#).

Quality: Sets the transition state optimization convergence threshold for *Gradient norm*. The optimization stops when the gradient norm convergence criterion is satisfied. The available options are:

- **Coarse** - 1.0 kcal/mol/Å
- **Medium** - 0.4 kcal/mol/Å
- **Fine** - 0.1 kcal/mol/Å

Changing the *Gradient norm* to any other value will result in the *Quality* being set to **Customized**.

Gradient norm: Specifies the gradient norm convergence criterion for the transition state optimization calculation. The calculation ends when the gradient norm falls below this threshold.

Max. step size: Specifies the maximum allowed change of any Cartesian coordinate. Geometric displacements are truncated such that they are less than this value. This prevents the optimizer from taking unreasonable steps.


Note: This option is disabled if the [Powell](#) transition state search method is selected.

Optimize using internal coordinates: When checked, indicates that internal coordinates are to be used for optimizing the structure, rather than Cartesian coordinates.

Tip: Usually, using internal coordinates is more efficient, so the calculation will converge more quickly. However, there are instances when an optimization may fail due to bonds becoming linear, for example, which may be resolved by optimizing in Cartesian space.

Help: Displays the Help topic in a browser.

Access methods

Menu	<i>Modules VAMP Calculation Setup More...</i>
Toolbar	 <i>Calculation Setup More...</i>

Electronic tab

The *Electronic* tab allows you to set the parameters associated with the electronic [Hamiltonian](#), including the SCF convergence scheme and the solvent environment.

Convergence scheme: Select the [convergence scheme](#) to be used in the calculation. Available options are:

- **Standard** - Use the standard converger. If this fails after the maximum number of iterations, the level shift method and Pulay convergers are tried for further iterations.
- **Pulay** - Use the Pulay converger.
- **IIS** - Use the IIS converger.
- **Pulay/IIS** - Use a combination of Pulay and IIS.

Tip: Refer to the [Improving SCF convergence](#) topic for details of remedies for unsatisfactory convergences.

SCF quality: Sets the SCF tolerance threshold used to determine whether an SCF calculation has converged. Available options and associated thresholds are:

- **Coarse** - 2×10^{-4} eV atom⁻¹
- **Medium** - 10^{-5} eV atom⁻¹
- **Fine** - 5×10^{-7} eV atom⁻¹

The *SCF tolerance* can be set directly on the [VAMP Electronic Options dialog](#). Specifying a value other than those listed above will result in the *SCF quality* being displayed as **Customized**.

CI type: Select the [configuration interaction](#) (CI) treatment to be used in the calculation. Available options are:

- **None** - No CI calculation will be performed
- **Full** - All available permutations of the electrons in the specified molecular orbitals will be used
- **CIS** - All single excitations will be included
- **CISD** - All single and double excitations will be included
- **PECI** - All single and all double excitations in which a complete electron pair is promoted will be included
- **RumerCI** - Excitations drawn from Rumer diagrams (beyond the singlet level of excitation) will be included

Use level shifting: When checked, indicates that the level shifting method will be used in the calculation. Specify the amount, in eV, by which to increase the energy of the virtual orbitals in the text box.


Solvation scheme: Select the method to be used to simulate the [solvent environment](#) for the calculation. Available options are:

- **None** - No solvent environment simulation will be performed
- **COSMO** - Use the conductor-like screening model
- **SCRF** - Use the self-consistent reaction field method

Note: The **SCRF** method is only available for single-point energy calculations.

More...: Provides access to the [VAMP Electronic Options dialog](#), which allows you to specify additional parameters, such as the solvent and the number of orbitals to include in the CI calculation.

Access methods

Menu	<i>Modules VAMP Calculation Electronic</i>
Toolbar	 <i>Calculation Electronic</i>

VAMP Electronic Options dialog

The *Electronic options* dialog allows you to specify additional parameters associated with the electronic [Hamiltonian](#). The parameters supplement those provided on the [Electronic](#) tab and are intended for more expert users.

SCF tolerance: Specify the threshold used to determine whether an SCF calculation has converged. Setting this to an arbitrary value will result in the *SCF quality* on the *Electronic* tab being set to [Customized](#).

Max. SCF cycles: Specify the maximum number of cycles used in attempting to converge the SCF. If the calculation has not converged after this threshold has been reached, it will stop.

Tip: It is not recommended to reduce this parameter below the default value of 200.

Total CI orbitals: Specify the number of orbitals to include in the [configuration interaction](#) calculation.

Note: For the *CI type* being **Full** or **CISD** this value should be a number between 2 and 11.

Virtual CI orbitals: Specify how many of them are virtual (the rest will be considered as occupied). This should be a number between 1 and the value of *Total CI orbitals*.

Note: This option is available only if the *CI type* on the [Electronic tab](#) is set to **RumerCI**.

Ignore degenerate orbitals: When checked, indicates that degenerate orbitals will be ignored in the configuration interaction calculation.

Note: If the *CI type* on the [Electronic tab](#) is set to **None** these options are disabled.

Solvent: Select a solvent from the dropdown list to be used as the [solvent environment](#). Selecting a solvent also sets the value of the associated *Dielectric constant*.


Note: If the *Solvation Scheme* on the [Electronic tab](#) is set to **None** this option is disabled.

Dielectric constant: Specify the value of the solvent dielectric constant.

Note: This parameter is visible only when the *Solvation Scheme* is set to **COSMO**.

Help: Displays the Help topic in a browser.

Access methods


Menu	<i>Modules VAMP Calculation Electronic More...</i>
Toolbar	 <i>Calculation Electronic More...</i>

Properties tab

The *Properties* tab allows you to select the properties that will be computed as part of the VAMP calculation, in addition to all the other properties that VAMP computes by default.

Choose the properties you wish to compute by checking the appropriate checkboxes in the list. Once you select a properties checkbox, additional options may be displayed below the list.

Access methods

Menu	<i>Modules VAMP Calculation Properties</i>
Toolbar	 <i>Calculation Properties</i>

Frequency selection

Choosing *Frequency* on the [Properties tab](#) displays options for computing the Hessian that is used to calculate the vibrational frequencies and intensities for a structure.

Vibrational mode frequencies and absorption intensities can be displayed in the form of a list of values or graphically as a vibrational spectrum using the Vibrational Analysis tool.

Calculating vibrational frequencies also enables you to compute certain [thermodynamic data](#).


Compute thermodynamic properties: When checked, indicates that the enthalpy, entropy, and heat capacity will be computed across a specified temperature range.

From: Specify the lower limit of the temperature range for which thermodynamic properties will be computed.

To: Specify the upper limit of the temperature range for which thermodynamic properties will be computed.

Step size: Specify the size of the temperature steps for which thermodynamic properties will be computed.


Access methods

Menu	<i>Modules VAMP Calculation Properties Frequency</i>
Toolbar	 / <i>Calculation Properties Frequency</i>

Localized orbitals selection

Choosing *Localized orbitals* on the [Properties tab](#) causes details of localized orbitals to be reported in the output of the calculation. Canonical orbitals are always created by default.

Access methods

Menu	<i>Modules VAMP Calculation Properties Localized orbitals</i>
Toolbar	 / <i>Calculation Properties Localized orbitals</i>


UV-Vis selection

Choosing *UV-Vis* on the [Properties tab](#) causes the electronic states of the structure being studied to be calculated and the energy (in eV and nm), multiplicity, and oscillator strength to be reported for each state in the output of the VAMP run.

The UV-Vis spectrum and corresponding grid document as well as the list of calculated electronic excited states can be displayed using the [Electronic Levels](#) VAMP analysis tool.

Note: UV-Vis spectrum can be computed only when a CI method is used in the calculation.

Access methods

Menu	<i>Modules VAMP Calculation Properties UV-Vis</i>
Toolbar	 / <i>Calculation Properties UV-Vis</i>

Job Control tab

VAMP calculations run in the background on a server via the gateway. The *Job Control* tab allows you to select a server for the VAMP calculation and to control some aspects of how the calculation will be performed.

Note: The options specified on the *Job Control* tab only apply to new jobs. They do not affect jobs that are already running.

Gateway location: Select a server for the VAMP calculation from the list of available server machines. You can add servers to the list using the Server Console.

Queue: Specify the queue to which the job will be submitted. Select the desired queue from the dropdown list, which displays the available queues on the chosen gateway. See [Working with queues](#) for additional details.


Job description: Specify the name to be used to identify the job.

A default job description is automatically assigned. An alternative description can be chosen by unchecking the *Automatic* checkbox and typing the new name in the *Job description* text box.

Automatic: When checked indicates that a job description will be selected automatically. Default = [checked](#).

More...: Displays the [VAMP Job Control Options dialog](#), which provides options for monitoring the calculation.

Access methods

Menu	<i>Modules / VAMP / Calculation / Job Control</i>
Toolbar	 <i>Calculation / Job Control</i>

VAMP Job Control Options dialog

The VAMP Job Control Options dialog allows you to set the options associated with monitoring and controlling the results of a VAMP calculation on a gateway.

Note: The options specified on the *Job Control* tab only apply to new jobs. They do not affect jobs that are already running.

Update structure: When checked, indicates that intermediate results will be used to update the displayed structure as the job progresses. Default = [unchecked](#).

Update graphs: When checked, indicates that intermediate results will be used to update the displayed graphs as the job progresses. Default = [checked](#).

Two graphs are created for a geometry optimization or transition state optimization:

- total energy vs. optimization cycle
- change of energy, force grad. vs. optimization cycle.

Update textual results: When checked, indicates that intermediate results will be used to update textual results files as the job progresses. Default = [checked](#).

Tip: Intermediate updates are useful shortly after initiating a job to assess if it is progressing as expected.

Update every: Specify the time interval, in seconds, between requests for intermediate updates.

Note: The rate at which new results appear is limited by the time it takes for the VAMP server to perform a single iteration step of the chosen task. This may be significantly longer than the chosen update interval. If a calculation finishes before the specified update interval, a summary file may not be created.

Retain server files: When checked, indicates that the folder on the server containing the job files will be retained after the job is complete. Default = [unchecked](#).

If this checkbox is left unchecked, the job files on the server will be deleted. Regardless of whether it is checked or unchecked, copies of the results files will *always* be retrieved from the server, placed in the associated project on the local machine, and displayed in the Project Explorer.


Automatically view output: When checked, the output files from the job will be opened automatically when the calculation is completed. Files opened may include a structure document and an output file. Default = [checked](#).

Notify on job completion: When checked, indicates that a dialog will be displayed when the job is complete. Default = [checked](#).

Tip: If you run several short jobs in one session, you may find it useful to stop the automatic display of job completion notices and results files.

Help: Displays the Help topic in a browser.

Access methods

Menu	<i>Modules VAMP Calculation Job Control More...</i>
Toolbar	 <i>Calculation Job Control More...</i>

VAMP Job Files dialog

The VAMP Job Files dialog allows you to save input files for a VAMP calculation without running the job or to run a job using an existing set of input files.

This functionality is provided for users who need to run the VAMP server program in standalone mode or who wish to edit the VAMP input files in order to gain access to features not supported by the VAMP interface.

Save Files: Saves the input files required to run the VAMP job on the server, but does not submit the job.

Note: The *Save Files* button is enabled only if the active document is a 3D Atomistic document.

The input files are placed in a subfolder of the current Materials Studio project directory and the primary VAMP input file is displayed in the Materials Visualizer.

Run Files: Runs a VAMP job using an existing set of input files.


Note: The *Run Files* button is enabled only if the active file is a VAMP input file. The corresponding reference structure document (.xsd) must be present in the current folder.

The job is submitted using the settings specified on the [Job Control tab](#).

The results files are placed in a subfolder of the current Materials Studio project directory.

Help: Displays the Help topic in a browser.

Access methods

Menu	<i>Modules VAMP Calculation Files...</i>
Toolbar	 <i>Calculation Files...</i>

VAMP Analysis dialog

The VAMP Analysis dialog allows you to analyze the results of a VAMP calculation.

A list of properties that may be analyzed is displayed at the top of the dialog. Select the property you wish to analyze from the list. Options relating to the analysis of that property are displayed at the bottom of the dialog.


The types of analysis that can be performed include:

- Display of [electron density](#) plots, including the charge and spin densities
- Computation of electronic levels and display of [UV-Vis spectra](#)
- Display of the [energy evolution](#) history of the calculation
- Display of [localized orbital](#) energies and plotting in three dimensions
- Display of orbital eigenvalues and plotting of [molecular orbitals](#) in three dimensions
- Display of computed charges and bond orders from Coulson and Mulliken [population analysis](#)
- Display of [electrostatic potential](#) plots
- Display of [thermodynamic properties](#)
- Calculation of vibrational spectra and animation of normal modes of vibrations

Note: To use any of these analysis functions, you must first perform a VAMP calculation and ensure that the output structure document is active. Analyses only apply to the active document and require that an associated .out file also exists (other [data files](#), such as .vmp, .sdf, and .vres, may also be required for certain analyses).

Help: Displays the Help topic for the currently selected analysis.

Access methods

Menu	<i>Modules VAMP Analysis</i>
Toolbar	 Analysis

Electron density selection

Select the *Electron density* option on the VAMP Analysis dialog to display the Electron density controls. These controls allow you to specify the type of density field to be calculated.

Note: The calculation is based on the specified .out results file and the active structure document.

Results file: Displays the name of the VAMP output file associated with the active structure document.

Density field: Select the type of density to be plotted. Available options are:

- [Charge density](#)
- [Spin density](#)

Note: If an [RHF](#) calculation was performed, you will not be able to plot the spin density.

View isosurface on import: When checked, indicates that a 3D isosurface will be created when the *Import* button is pressed. By default, the following isosurfaces are generated:

- [Charge density](#) - 0.017 electrons Å⁻³
- [Spin density](#) - 10% of the maximum value


If *View isosurface on import:* is unchecked, the volumetric data are imported as a 3D field.

Once you have imported the volumetric data, you can refine the display using the volume visualization controls.

Import: Loads the specified volumetric density data into the active document.

Grid...: Provides access to the [VAMP Grid Parameters dialog](#), which allows you to specify the resolution and extents of the calculated volumetric data. If you wish to change these values, you must do so prior to importing the field.

Access methods

Menu	<i>Modules VAMP Analysis Electron density</i>
Toolbar	 <i>Analysis Electron density</i>

Electronic levels selection

Select the *Electronic levels* option on the VAMP Analysis dialog to display the Electronic levels controls. These controls allow you to view excitation data for the electronic states of the structure being studied and to generate its UV-Vis spectrum in both chart and grid form.

Note: The calculation is based on the specified .out results file and the active structure document.

Results file: Displays the name of the VAMP output file associated with the active structure document.


View Electronic energy levels: Generates a grid document containing a list of electronic states for the structure being studied. The grid document gives the energy (in eV), the excitation wavelength (in nm), the multiplicity (spin arrangement), and the oscillator strength (transition dipole moment) for each electronic state listed.

View Spectrum: Generates a chart document containing the predicted UV-Vis spectrum for the structure being studied. The spectrum takes the form of a plot of oscillator strength against wavelength.

More...: Provides access to the [VAMP UV-Vis Spectrum Options dialog](#), which allows you to set additional options associated with generation of the UV-Vis spectrum.

View Grid: Generates a grid document containing a list of wavelengths (in nm) and peak oscillator strengths for the allowed excitations used to generate the UV-Vis spectrum.

Access methods

Menu	<i>Modules VAMP Analysis Electronic levels</i>
Toolbar	 <i>Analysis Electronic levels</i>

VAMP UV-Vis Spectrum Options dialog

The VAMP UV-Vis Spectrum Options dialog allows you to set additional options associated with generation of the UV-Vis spectrum for the structure being studied.

Integration method: Select an integration method to use to broaden the predicted peaks and, thus, generate a smoothed spectrum. Available options are:

- [Gaussian](#) (default)
- [Lorentzian](#)
- [None](#)

Smearing width: Specify the smearing width, in nm, for the Gaussian smoothing function. Range = [0.1](#) - [100](#) nm. Default = [20](#) nm.

Note: This option is enabled only if [Gaussian](#) is selected as the *Integration method*.

FWHM parameter: Specify the full width at half maximum, in nm, for the Lorentzian smoothing function. Range = [0.1](#) - [100](#) nm. Default = [20](#) nm.


Note: This option is enabled only if [Lorentzian](#) is selected as the *Integration method*.

Accuracy level: Select the quality of the interpolation to be carried out, i.e., the number of integration points per energy unit. Available options are:

- Coarse
- Medium (default)
- Fine
- Ultra-fine

Help: Displays the Help topic in a browser.

Access methods

Menu	<i>Modules VAMP Analysis Electronic levels More...</i>
Toolbar	 <i>Analysis Electronic levels More...</i>

Energy evolution selection

Select the *Energy evolution* option on the VAMP Analysis dialog to display the optimization history of a VAMP geometry optimization.

Note: The calculation is based on the specified .out results file and the active structure document.

Results file: Displays the name of the VAMP output file associated with the active structure document.


View: Generates charts containing the following plots for a geometry optimization or transition state optimization:

- Total energy vs. optimization cycle
- Change in energy, gradient norm vs. optimization cycle

These charts are the same as those that are generated when you check the *Update graphs* checkbox on the [VAMP Job Control Options dialog](#). Charts can be generated using the Energy evolution dialog whether or not you checked *Update graphs* for the original calculation.

Note: Every time you perform a calculation with the *Update graphs* option checked, the existing chart documents are overwritten. Hence, any changes or annotations you make to the charts will be lost.

Access methods

Menu	<i>Modules VAMP Analysis Energy evolution</i>
Toolbar	 <i>Analysis Energy evolution</i>

Localized orbitals selection

Select the *Localized orbitals* option on the VAMP Analysis dialog to display the Localized orbitals controls. These controls provide a list of orbital energy values for the system and allow you to generate 3D volumetric images of the localized orbitals.

Note: The calculation is based on the specified .out results file and the active structure document.

Results file: Displays the name of the VAMP output file associated with the active structure document.

Filter: Select which orbitals are displayed in the table. Available options are:

- **All** - displays energy values for all the occupied orbitals that were included in the VAMP output file. No virtual orbitals are included.
- **Minimal** - displays only the four highest energy orbitals. Only if localized orbitals were computed as part of a VAMP job will data appear here. If the list of available orbitals is empty, perform another calculation, specifying localized orbitals on the [Properties tab](#) of the VAMP Calculation dialog.
- **Spin up** - displays only eigenvalues from alpha-spin (spin-up) orbitals. If the calculation is closed shell, this filter displays no orbitals.
- **Spin down** - displays only eigenvalues from beta-spin (spin-down) orbitals. If the calculation is closed shell, this filter displays no orbitals.

The grid below the *Filter* control displays a list of localized orbital energy values, along with additional information about each of them:

- **N**: Indicates the orbital number, starting from 1 for the lowest energy orbital.
- **s**: Indicates the spin of the orbital. For spin-restricted calculations, all orbitals are unlabeled. For spin-unrestricted calculations, alpha-spin orbitals are labeled + and beta-spin orbitals are labeled -.
- **Energy**: Indicates the energy value of each orbital in eV.

Note: Localized orbitals will only be available for rendering if they were computed as part of a VAMP job. See the [Localized orbitals selection](#) topic for information about setting up a localized orbitals calculation.


View isosurface on import: When checked, indicates that a 3D isosurface will be created when the *Import* button is pressed. By default, two isosurfaces are created with values of ± 0.03 au. If unchecked, the volumetric data are imported as a 3D field.

Once you have imported the volumetric data, you can refine the display using the volume visualization controls.

Import: Loads the specified molecular orbital data into the active document for volumetric display.

Grid...: Provides access to the [VAMP Grid Parameters dialog](#), which allows you to specify the resolution and extents of the calculated volumetric data. If you wish to change these values, you must do so prior to importing the field.

Access methods

Menu	<i>Modules VAMP Analysis Localized orbitals</i>
Toolbar	 <i>Analysis Localized orbitals</i>

Orbitals selection

Select the *Orbitals* option on the VAMP Analysis dialog to display the Orbitals controls. These controls provide a list of orbital eigenvalues for the system and allow you to generate 3D volumetric images of the orbitals.

Note: The calculation is based on the specified .out results file and the active structure document.

Results file: Displays the name of the VAMP output file associated with the active structure document.

Filter: Select which orbitals are displayed in the table. Available options are:

- **All** - displays eigenvalues for all the orbitals that were included in the VAMP output file. This includes all of the occupied orbitals and the first eight virtual orbitals.
- **Minimal** - displays only the four eigenvalues about the HOMO.
- **Spin up** - displays only eigenvalues from alpha-spin (spin-up) orbitals. If the calculation is closed shell, this filter displays no orbitals.
- **Spin down** - displays only eigenvalues from beta-spin (spin-down) orbitals. If the calculation is closed shell, this filter displays no orbitals.

The grid below the *Filter* control displays a list of molecular orbital eigenvalues, along with additional information about each of them:

- *N*: Indicates the orbital number, starting from 1 for the lowest energy orbital.
- *s*: Indicates the spin of the orbital. For spin-restricted calculations, all orbitals are labeled +. For spin-unrestricted calculations, alpha-spin orbitals are labeled + and beta-spin orbitals are labeled -.
- *Eigenvalue*: Indicates the eigenvalue of each orbital in eV.
- *Type*: Indicates the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).


View isosurface on import: When checked, indicates that a 3D isosurface will be created when the *Import* button is pressed. By default, two isosurfaces are created with values of ± 0.03 au. If unchecked, the volumetric data are imported as a 3D field.

Once you have imported the volumetric data, you can refine the display using the volume visualization controls.

Import: Loads the specified molecular orbital data into the active document for volumetric display.

Grid...: Provides access to the [VAMP Grid Parameters dialog](#), which allows you to specify the resolution and extents of the calculated volumetric data. If you wish to change these values, you must do so prior to importing the field.

Access methods

Menu	<i>Modules VAMP Analysis Orbitals</i>
Toolbar	 <i>Analysis Orbitals</i>

Population analysis selection

Select the *Population analysis* option on the VAMP Analysis dialog to display the Population analysis controls. These controls allow you to import atomic charges and bond orders and assign them to the atoms in the active structure document.

Note: The calculation is based on the specified .out results file and the active structure document.

Results file: Displays the name of the VAMP output file associated with the active structure document.

Charges: Select the type of charge to assign. The choice is limited to the charges generated as part of the VAMP calculation. Available options are:

- **Coulson**
- **Mulliken**
- **ESP**


Note: You cannot assign [ESP](#) charges if you have performed your calculation using the AM1*, MNDO/d, or MNDO/C NDDO Hamiltonians, or any of the ZINDO Hamiltonians.

Assign chosen charges to structure: Imports the selected charges into the active 3D Atomistic document and assigns partial charges to each atom. You can see the charges by labeling the atoms by charge.

Assign bond orders to structure: Imports the bond order into the active 3D Atomistic document and assigns bond orders to each bond. You can see the bond orders by labeling the bonds by bond order.

Note: This may result in new bonds being created or existing ones being deleted.

Access methods

Menu	<i>Modules VAMP Analysis Population analysis</i>
Toolbar	 <i>Analysis Population analysis</i>

Potentials selection

Select the *Potentials* option on the VAMP Analysis dialog to display the Potentials controls. These controls allow you to specify the type of potential field to be generated.

Note: The calculation is based on the specified .out results file and the active structure document.

Results file: Displays the name of the VAMP output file associated with the active structure document.

Potential field: Select which type of potential will be plotted. At present, the only option available is [Electrostatic potential](#).


View isosurface on import: When checked, indicates that a 3D isosurface will be created when the *Import* button is pressed. By default, two isosurfaces are created with values of $\pm 10 \text{ kcal mol}^{-1}$ (0.016 au). If unchecked, the volumetric data are imported as a 3D field.

Once you have imported the volumetric data, you can refine the display using the volume visualization controls.

Import: Loads the specified volumetric data into the active document.

Grid...: Provides access to the [VAMP Grid Parameters dialog](#), which allows you to specify the resolution and extents of the calculated volumetric data. If you wish to change these values, you must do so prior to importing the field.

Access methods

Menu	<i>Modules VAMP Analysis Potentials</i>
Toolbar	 <i>Analysis Potentials</i>

Structure selection


Select the *Structure* option on the VAMP Analysis dialog to display the Structure controls. These controls allow you to update the structure displayed in the active structure document based on the latest set of VAMP results. Use this option if you have made modifications to the structure and wish to restore the original geometry produced by VAMP, or you wish to re-import the Hessian.

Note: Every VAMP calculation generates a structure containing the final geometry. For most types of calculation, the final geometry is different from the initial geometry. However, if an energy calculation is performed, the final geometry is normally the same as the initial geometry, unless snap to symmetry is used, in which case the final geometry may differ slightly from the initial geometry.

Results file: Displays the name of the VAMP output file associated with the active structure document.

Update structure from VAMP output: Updates the structure in the active 3D Atomistic document with the geometry contained in the .out file (and associated .vmp file). This button also re-imports the Hessian into the model, if one exists.

Access methods

Menu	<i>Modules VAMP Analysis Structure</i>
Toolbar	 <i>Analysis Structure</i>

Thermodynamic properties selection


Select the *Thermodynamic properties* option on the VAMP Analysis dialog to display the Thermodynamic properties controls. These controls allow you to compute and display a chart of thermodynamic properties as a function of temperature. You can use this option if your VAMP calculation included [vibrational analysis](#). The properties you can calculate are the enthalpy, entropy, and heat capacity. The methods used to calculate these thermodynamic properties are described in the [Thermodynamic calculations](#) topic.

Note: The calculation is based on the specified .out results file and the active structure document.

Results file: Displays the name of the VAMP output file associated with the active structure document.

View thermodynamics from VAMP output: Generates a chart containing plots of the enthalpy, entropy, and heat capacity as functions of temperature. If no thermodynamic data are present in the .out file, this control will be disabled.

Access methods

Menu	<i>Modules VAMP Analysis Thermodynamic properties</i>
Toolbar	 <i>Analysis Thermodynamic properties</i>

VAMP Grid Parameters dialog

The Grid Parameters dialog allows you to set the resolution and extents of the grid used to calculate the volumetric properties [Electron density](#), [Potentials](#), [Orbitals](#) and [Localized orbitals](#).

Grid resolution: Specify the resolution of the grid. Available values are:

- **Fine** - 0.15 Å grid interval
- **Medium** - 0.25 Å grid interval
- **Coarse** - 0.4 Å grid interval





Grid interval: Alternatively, specify a user-defined value for the grid spacing. Setting this parameter to a value other than one of those listed above will cause the *Grid resolution* to be set to **Customized**.

Tip: A smaller grid interval (i.e., finer resolution) produces a higher quality grid, but is more costly to compute and display.

Border: Specify the size of the border to impose about the molecular extents when creating the volumetric grid.

Note: The values set in this dialog will be used for the computation of *all* volumetric properties, regardless of where the dialog was accessed from.

Access methods

Menu	<i>Modules VAMP Analysis Electron density Grid...</i> <i>Modules VAMP Analysis Orbitals Grid...</i> <i>Modules VAMP Analysis Localized orbitals Grid...</i> <i>Modules VAMP Analysis Potentials Grid...</i>
Toolbar	 <i>Analysis Electron density Grid...</i>  <i>Analysis Orbitals Grid...</i>  <i>Analysis Localized orbitals Grid...</i>  <i>Analysis Potentials Grid...</i>

VAMP keywords

This section describes the input keywords and data blocks that are recognized by VAMP, including some that are not accessible from the VAMP setup dialogs.

Tip: For information on VAMP keywords, please refer to the Materials Studio Online Help.

Note: The keywords and keyword blocks in the input files are not case-sensitive.

VAMP References

A list of published papers describing calculations using VAMP can be found on the Materials Studio website: <http://accelrys.com/products/materials-studio/publication-references/vamp-references.html>.

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