CASTEP GUIDE

MATERIALS STUDIO 2024

Third Party Notification

Your BIOVIA Materials Studio 2024 installation contains third-party software components. For details, refer to the BIOVIA Program Directory at https://media.3ds.com/support/progdir/.

Acknowledgments and References

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Introduction

CASTEP is a state-of-the-art quantum mechanics-based program designed specifically for solid-state materials science. CASTEP employs the density functional theory plane-wave pseudopotential method, which allows you to perform first-principles quantum mechanics calculations that explore the properties of crystals and surfaces in materials such as semiconductors, ceramics, metals, minerals, and zeolites.

Typical applications involve studies of surface chemistry, structural properties, band structure, density of states, and optical properties. CASTEP can also be used to study the spatial distribution of the charge density and wavefunctions of a system.

In addition, you can use CASTEP to calculate the full tensor of second-order elastic constants and related mechanical properties of a crystal (Poisson coefficient, Lamé constants, bulk modulus). The transition-state searching tools in CASTEP enable you to study chemical reactions in either the gas phase or on the surface of a material using linear synchronous transit/quadratic synchronous transit technology. These tools can also be used to investigate bulk and surface diffusion processes.

CASTEP can be used effectively to study properties of both point defects (vacancies, interstitials, and substitutional impurities) and extended defects (for example grain boundaries and dislocations) in semiconductors and other materials.

Furthermore, the vibrational properties of solids (phonon dispersion, total and projected density of phonon states, thermodynamic properties) can be calculated with CASTEP using either the linear response methodology or the finite displacements technique. The results can be used in various ways, for instance, to investigate the vibrational properties of adsorbates on surfaces, to interpret experimental neutron spectroscopy data or vibrational spectra, to study phase stability at high temperatures and pressures, and so on. The linear response method can also be used to calculate the response of a material to an applied electric field - polarizability for molecules and dielectric permittivity in solids - and to predict IR spectra.

CASTEP can be used to calculate the properties required to analyze the results of solid-state NMR experiments, that is, g-tensor, chemical shifts, electric field gradients, and J-couplings on atoms of interest. A detailed review of the CASTEP NMR formalism and numerous examples of practical applications are discussed in Bonhomme et al. (2012).

The CASTEP STM analysis tool allows you to model scanning tunneling microscopy images at different bias voltages in order to solve the surface structures based on the experimental STM images.

In all publications arising from your use of CASTEP, please cite:
Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. J.; Refson, K.; Payne, M. C. "First principles methods using CASTEP", *Zeitschrift fuer Kristallographie*, **220 (5-6)**, 567-570 (2005).

Additional Information

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https://www.3ds.com/support/

Chapter 2: Tasks in CASTEP

The CASTEP module allows you to perform first-principles quantum mechanical calculations in order to explore the properties of crystals and surfaces in the solid state. CASTEP can currently perform several different tasks:

- Single-point energy calculation
- Geometry optimization
- Molecular dynamics
- Elastic constants calculation
- Transition state search
- Transition state confirmation
- Properties

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 CASTEP calculation, which can be grouped as follows:

- **Structure definition:** A periodic 3D Atomistic document containing the system of interest must be specified. There are a number of ways to prepare a structure:
  - Periodic structures can be built using the tools available in the Materials Visualizer for building crystals, surfaces, and single-wall nanotubes.
  - 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 search, 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 using the methods listed above and then use the Reaction Preview tool to generate the trajectory.

  > **Note:** CASTEP can only be used to perform calculations on 3D periodic structures. If you wish to study a molecular system using CASTEP, you will need to construct a supercell to use as the input structure.

  > **Note:** CASTEP cannot handle structures containing pi-system objects. Such objects should be removed from the document prior to running a CASTEP calculation.

  > **Note:** CASTEP performance can be greatly increased if the symmetry of the structure is taken into account. CASTEP offers an option of finding and using the symmetry automatically if the input structure is described as having a P1 symmetry. This option is particularly relevant for calculations on molecular crystals and crystal surfaces, since these structures are typically created as P1 (or p1) systems. Automatic conversion to a higher symmetry structure will honor all atomic properties that are relevant to the current CASTEP settings, such as constraints and electronic configuration.

> **Tip:** The time required for a CASTEP calculation increases with the cube of the number of atoms in the system. Therefore, it is recommended that you use the smallest primitive cell description of your system whenever possible. Select *Build | Symmetry | Primitive Cell* from the menu bar to convert to a primitive cell.

- **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 dynamics calculation, these parameters include the ensemble and its settings, the temperature, and the number and length of the time steps. 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 optical properties. The tools on the CASTEP Analysis dialog may be used to visualize the results of the calculation.

To select a CASTEP task

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.
2. Select the Setup tab.
3. Select the required CASTEP task from the *Task* dropdown list.

CASTEP Energy task

The CASTEP Energy task allows you to calculate the total energy of the specified 3D periodic system, as well its physical properties.

In addition to the total energy, the forces on atoms are reported at the end of the calculation. A charge density file is also created, allowing you to visualize the spatial distribution of the charge density using the Materials Visualizer. The electronic energies at the Monkhorst-Pack k-points used in the calculation are also reported, so that you can generate a density of states chart during CASTEP analysis.

The Energy task is useful for studying the electronic properties of systems for which reliable structural information is available. It can also be used to calculate an equation of state (that is, a pressure-volume and/or energy-volume dependence) for high-symmetry systems with no internal degrees of freedom, as long as the *Stress* property is specified.

> **Note:** In systems with internal degrees of freedom, the equation of state can be obtained using the Geometry Optimization task.

The default unit of energy in CASTEP is the electron-Volt (eV). The relationship between eV and other popular energy units are found in Mohr et al., 2008:

1 eV	0.0367493254 Ha	23.0605 kcal/mole	96.4853 kJ/mole

CASTEP Geometry Optimization task

The CASTEP Geometry Optimization task allows you to refine the geometry of a 3D periodic system to obtain a stable structure or polymorph. This is done by performing an iterative process in which the coordinates of the atoms and possibly the cell parameters are adjusted so that the total energy of the structure is minimized.

CASTEP geometry optimization is based on reducing the magnitude of calculated forces and stresses until they become smaller than defined convergence tolerances. It is also possible to specify an external stress tensor to model the behavior of the system under tension, compression, shear, and so on. In these cases the internal stress tensor is iterated until it becomes equal to the applied external stress.

The process of geometry optimization generally results in a model structure that closely resembles the real structure.

The accuracy of the lattice parameters calculated using CASTEP is illustrated in Figure 1 (Milman et al., 2000).
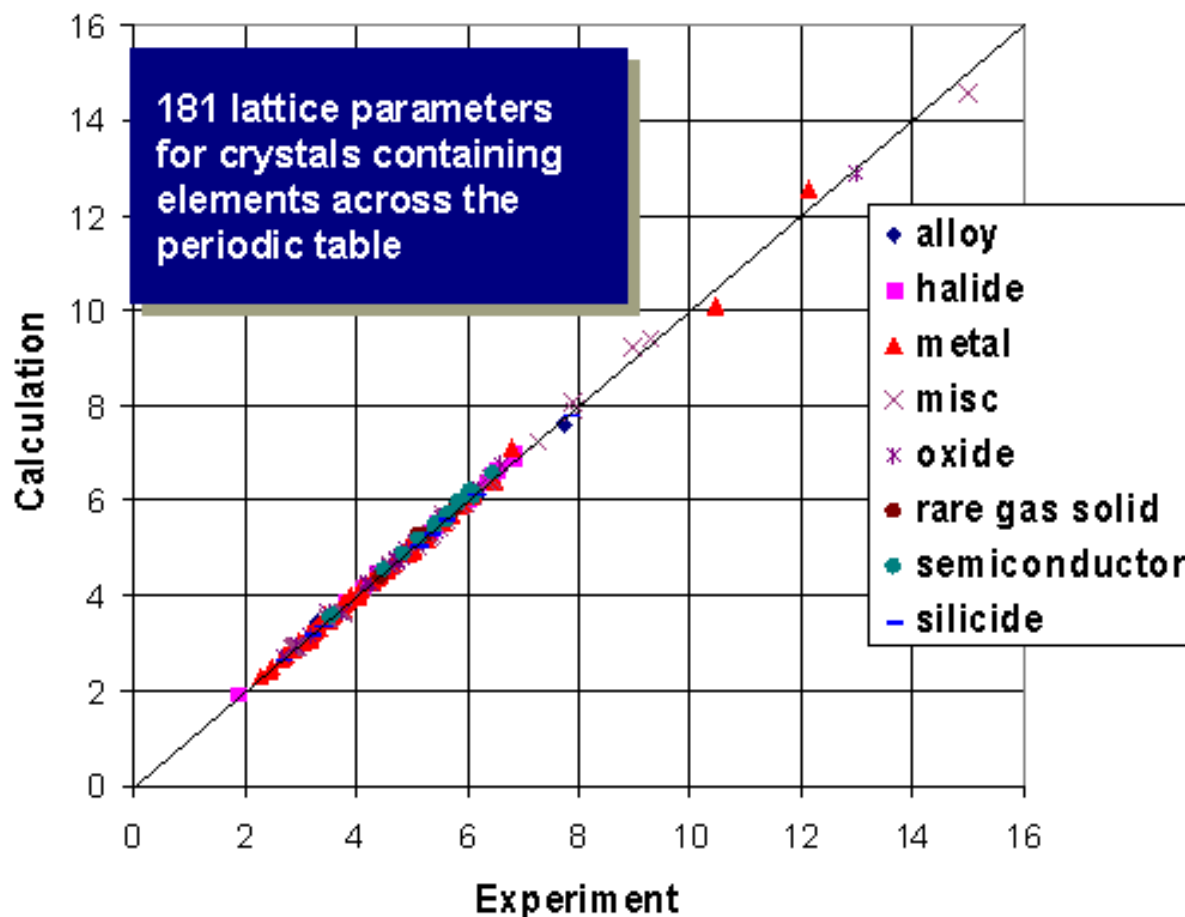
Figure 1. Experimental vs. CASTEP calculated lattice parameters

Equation of state calculation

Geometry optimization under applied hydrostatic pressure can be used to determine the bulk modulus of a material, B, and its pressure derivative, $B'=dB/dP$. The procedure involves calculating a theoretical equation of state, EOS, which describes the dependence of the cell volume on the external hydrostatic pressure. The methodology is very similar to the real experiment: the external pressure is fixed using the Minimizer tab on the Geometry Optimization dialog and the cell volume at that pressure is found by carrying out geometry optimization with CASTEP.

The subsequent analysis of the P-V dataset is exactly the same as in experimental studies (see Winkler, 1999 for more details). An analytical expression is chosen to describe the EOS and its parameters are fitted to the calculated datapoints. The most popular form of EOS is the third order Birch-Murnaghan equation:

$$P = \frac{3}{2} B \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right] * \left\{ 1 + \frac{3}{4} (4 - B') \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] \right\}$$

Where:

V_0 is the equilibrium volume

A detailed comparative study of various analytical forms of EOS was performed by Cohen et al.(2000).

> **Note:** The values of B and B' obtained from such fitting experiments depend on the pressure range used in the calculations. Experimental values obtained using a diamond anvil cell are usually in the range 0-30 GPa, so this is the range recommended for theoretical studies. It is also important to avoid using negative values of pressure in such studies. In addition the pressure values used to create the P-V dataset should not be uniform. More accurate sampling of the low-pressure region is required to obtain an accurate value of the bulk modulus.

Geometry optimization methods

By default, CASTEP uses the BFGS geometry optimization method. This method usually provides the fastest way of finding the lowest energy structure and this is the only scheme that supports cell optimization in CASTEP.

The Damped molecular dynamics method is an alternative that can be as effective as BFGS for systems with a flat potential energy surface, for example molecular crystals or molecules on surfaces.

The TPSD geometry optimization algorithm is a viable alternative for systems where the potential energy surface deviates significantly from the quadratic form. TPSD offers robust convergence and is particularly recommended when user-supplied constraints on lattice parameters are applied during cell optimization (for example, when optimizing a solid-solid interface in a direction perpendicular to the interface plane).

CASTEP Dynamics task

The CASTEP Dynamics task allows you to simulate how the atoms in a 3D periodic structure will move under the influence of computed forces.

Before performing a CASTEP dynamics calculation you can select the thermodynamic ensemble and associated parameters and define the simulation time, temperature, and pressure.

Selecting the thermodynamic ensemble

Integrating Newton's equations of motion allows you to explore the constant-energy surface (NVE dynamics) of a system. However, most natural phenomena occur under conditions where a system exchanges heat with the environment. These conditions can be simulated using NVT ensembles (either the deterministic Nosé ensemble or the stochastic Langevin ensemble).

External pressure can be incorporated into the dynamics calculation by using either the NPH (constant enthalpy) or the NPT (constant temperature) ensemble.

Defining the time step

An important parameter in the integration algorithm is the time step. To make the best use of the computer time, a large time step should be used. However, if the time step is too large it may lead to instability and inaccuracy in the integration process. Typically, this is manifested as a systematic drift in the constant of motion.

> **Note:** Quantum-mechanical molecular dynamics calculations usually require a smaller time step than forcefield based dynamics applications. However, this is less of an issue in CASTEP because wavefunction and density extrapolation are used.

Constraints during dynamics

CASTEP supports constraints during molecular dynamics simulations. However, you can only apply some of the more basic constraints through the Materials Studio interface:

- The center of mass can be fixed.
- Individual atom positions can be fixed.
- Bonds lengths can be fixed.

CASTEP Elastic Constants task

The CASTEP Elastic Constants task allows you to run a set of CASTEP calculations which provides all of the information necessary to obtain the full 6 × 6 tensor of elastic constants for a 3D periodic structure with any symmetry.

CASTEP automatically generates the set of distorted structures that is required by symmetry to produce the full set of elastic constants, then submits jobs for the ideal structure and for all the distorted structures.

The actual calculation of elastic constants, based on the values of initial strains and calculated stresses, is performed at the Analysis stage.

The accuracy of the elastic constants, especially of the shear constants, depends strongly on the quality of the SCF calculation and in particular, on the quality of the Brillouin zone sampling and the degree of convergence of wavefunctions. Therefore, you should use the Fine setting for SCF tolerance and for k-point sampling and a Fine derived FFT grid.

It is not necessary to perform geometry optimization before calculating elastic constants, so you can generate C_{ij} data for the experimentally observed structure. However, more consistent results are obtained if you perform full geometry optimization, including cell optimization and then calculate the elastic constants for the structure which corresponds to the theoretical ground state.

> **Note:** Elastic Debye temperature and averaged sound velocity are not reported if the calculated elastic constants do not produce physically meaningful sound velocities in some directions (for example, if certain C_{ij} values or their combinations are negative when they should be positive). This can happen for low quality calculations or for calculations that were not preceded by a geometry optimization (including optimization of the lattice parameters).

CASTEP minimizes internal coordinates for each distorted structure while keeping the lattice parameters fixed. It is possible to use either the BFGS or the damped MD geometry optimization method. To select a different method you have to select the Geometry Optimization task, change the relevant setting and then return to the Elastic Constants task.

> **Note:** As part of the Elastic Constants task, CASTEP performs a single point energy calculation for the undistorted structure. This allows you to analyze electronic and volumetric properties. The energy and stress from this calculation are not used to evaluate the elastic constants.

CASTEP Transition State Search task

The CASTEP TS Search task allows you to optimize a transition state.

When a 3D periodic molecular or crystal structure is built, it usually needs to be refined to bring it to a stable geometry. The refinement process is known as optimization. It 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, that is, 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.

The TS Search task is particularly useful for predicting barriers to chemical reactions and determining reaction pathways. It can be also used to find diffusion barriers for either solid state diffusion or surface diffusion. The reactants and products can either be optimized separately before running a TS Search or as part of this task. In the latter case partition functions for reactant, product, and transition state can also be calculated. This information can be used to calculate the reaction rate coefficient.

Synchronous transit methods

CASTEP transition state searches are performed using synchronous transit methods. These work best when reasonable structures for the reactants and products exist, but the location of the transition state is unknown.

Starting from reactants and products, the synchronous transit methods interpolate a reaction pathway to find a transition state. The Linear Synchronous Transit (LST) method performs a single interpolation to a maximum energy. The Quadratic Synchronous Transit (QST) method alternates searches for an energy maximum with constrained minimizations in order to refine the transition state to a high degree. The options available through CASTEP include:

- LST Maximum performs a single LST maximization, bracketing the maximum between the reactants and product. This is the quickest but least accurate of the options. The TS structure determined by this method generally requires further refinement.

- LST/Optimization performs an LST maximization, followed by an energy minimization in directions conjugate to the reaction pathway. This yields a structure lower in energy and closer to the true TS than a simple LST. Minimization steps continue until an energy minimum is reached or the number of conjugate directions is exhausted.

- Halgren-Lipscomb is a kind of limited LST/Optimization, and is designed to reproduce the algorithm popularized by Halgren and Lipscomb. After determining the LST maximum, this method performs a conjugate gradient minimization, but only in a single direction.

- Complete LST/QST begins by performing an LST/Optimization calculation. The TS approximation obtained in that way is used to perform a QST maximization. From that point, another conjugate gradient minimization is performed. The cycle is repeated until a stationary point is located or the number of allowed QST steps is exhausted.

A complete description of the algorithms used is given in Govind et al. (2003).

CASTEP TS Confirmation task

The TS Confirmation tool verifies that a TS calculated by an LST or QST search connects the reactant and product as expected. See Setting up a TS confirmation calculation for more details on the mechanics of this method. Materials Studio automatically determines the reactant, TS and product from the given LST or QST trajectory document.

Use the controls on the CASTEP TS Confirmation dialog to specify the convergence criteria for each individual geometry optimization (microiteration), and to specify the number of frames to use in the TS confirmation trajectory.

The output of a TS confirmation calculation is another trajectory document. This one follows the Intrinsic Reaction Path (IRP) as discussed in Reaction pathways. Each successive refinement to the pathway is displayed as a graph in Materials Studio. Use the chart selection tools to choose any point on the graphs and display the corresponding geometry.

In most cases, no minima will be found on the IRP other than your reactant and product. If so, the TS confirmation calculation verifies that the TS does connect your presumed reactant and product.

On the other hand, any other minima located by the TS confirmation are the structures that are actually connected by the TS. These are identified with an asterisk (*). You should perform a geometry optimization to refine the geometry of these minima. Select the structures as described in the Displaying trajectory and chart data topic.

You can generate a detailed map of the entire reaction by repeating TS Search and TS Confirmation for all minima on the IRP.

CASTEP Properties

The CASTEP Properties task allows you to compute electronic, structural, and vibrational properties after the completion of a single-point energy, geometry optimization, or dynamics run on a 3D periodic system.

> **Note:** To calculate properties using the CASTEP Properties task, the results files from a suitable simulation must be present in the current project.

You can also use the Properties tab on the CASTEP Calculation dialog to request calculation of such properties as part of a CASTEP run. You can view the results using the CASTEP Analysis dialog.

The properties that CASTEP can generate are:

- **Band structure:** This calculates electronic eigenvalues along high symmetry directions in the Brillouin zone. These calculations are non-self-consistent for both valence and conduction bands, using electronic charge densities and potentials generated during the simulation.

- **Core level spectroscopy:** This calculates electronic energies on the Monkhorst-Pack mesh of k-points and the matrix elements for electronic interband transitions, either with or without core holes.

- **Density of states:** This calculates electronic eigenvalues on a fine Monkhorst-Pack grid . These calculate are non-self-consistent for both valence and conduction bands, using electronic charge densities and potentials generated during the simulation.

- **Electron density difference:** This calculates the electron density difference with respect to a linear combination of either the atomic densities or the densities of sets of atoms contained in the structure.

- **Electron localization function:** This calculates a simple measure of electron localization in atomic and molecular systems.

- **Electronic excitations (TD-DFT):** This calculates electronic excitations for molecules in a box, using the time-dependent density functional theory (TD-DFT).

- **NMR:** This calculates chemical shielding tensors, electric field gradients, J-couplings, and g-tensors.

> **Note:** NMR in CASTEP is part of the separately licensed module NMR CASTEP. NMR calculations can only be performed if you have purchased this module.

- **Optical properties:** This calculates matrix elements for electronic interband transitions . The CASTEP Analysis dialog allows you to generate grid and chart documents containing measurable optical properties.

- **Orbitals:** This provides information about electronic wavefunctions. This allows you to visualize 3D distribution of various electronic states (orbitals). Visualization of STM profiles also requires this information.

- **Phonons:** For phonon dispersion runs, this calculates phonon frequencies and eigenvectors along high symmetry directions in the Brillouin zone. In the case of phonon density of states calculations, this computes phonon frequencies and eigenvectors on a Monkhorst-Pack grid. Analysis requires this information to display total and projected (partial) phonon densities of states. Calculation of thermodynamic properties including atomic displacement parameters also uses this information. This allows assignment of temperature factors during analysis.

  > **Note:** Phonon calculations take into account existing fixed atom constraints, regardless of the overall *Task* setting. Calculation of vibrational properties does not include such fixed atoms, corresponding to the "partial Hessian" approach.

  > **Tip:** Select the *Fix fractional position* checkbox on the *Atom* tab of the Edit Constraints dialog, accessible from the *Modify* menu.

- **Polarizability, IR and Raman spectra:** This calculates the optical ($\omega = \infty$) and dc ($\omega = 0$) dielectric permittivity or the optical ($\omega = \infty$) and static ($\omega = 0$) molecular polarizability, along with infrared or Raman intensities (response to an electric field in the infrared range). Permittivity is relevant for solid materials, while polarizability and infrared intensities are relevant to molecules prepared using the supercell approach.

- **Population analysis:** This performs Mulliken analysis and Hirshfeld charge analysis. This includes calculation of Mulliken bond populations and angular momentum-resolved atomic charges (as well as magnetic moments for spin-polarized calculations, and production of Hirshfeld atomic charges. Optionally, CASTEP can generate the weights required for partial density of states (PDOS) calculations.

- **Solvation energy:** This calculates the free energy of solvation and writes it to a `seedname_Solv.castep` file. CASTEP automatically prepares calculations using vacuum and implicit solvation schemes and extracts solvation energy from the respective energies of these two calculations.

- **Stress:** This calculates the stress tensor and writes it to a `seedname.castep` file. This information is useful if, for example, you perform a geometry optimization run with fixed cell parameters and you want to verify how far the lattice is from equilibrium. For example, carry out a supercell study of a point defect with the fixed cell that corresponds to the theoretical ground state of the given system. The value of the stress after geometry optimization gives an indication of the magnitude of the elastic effects associated with the supercell approximation.

Modeling disorder in solids

Many crystal structures possess static positional disorder. Materials Studio allows you to model disorder by defining mixture atoms.

Mixture atoms

Atomic sites in a disordered crystal can be described in terms of a hybrid atom, which consists of two or more element types. The relative concentrations can be set for any number of atoms, where the total

concentration must be 100%. The mixture atoms description is the most often used representation of solid solutions, metallic alloys, disordered minerals, and so on.

Technical limitations

Current implementation of the molecular dynamics (MD) algorithms in CASTEP is not yet compatible with the virtual crystal approximation (VCA) formalism, which is used to model disorder in solids. None of the MD schemes (NVE, NPT, and so on) work for disordered crystals in the current version.

The following properties are unavailable for disordered systems:

- Population analysis
- Vibrational properties (phonon dispersion, phonon density of states)
- Optical properties

In addition, geometry optimization based on damped MD is not available (since MD itself is not allowed).

Atom occupancy cannot be used with the current CASTEP implementation of the virtual crystal approximation (VCA). Partial atom occupancy can be considered as a special case of a mixture atom, where one part of the mixture is an atom of "nothing". This case is not supported for a number of technical and fundamental reasons.

The limitations listed above fall into three categories:

- Properties that are ill-defined or do not make sense at all for mixture atoms (population analysis, vibrational properties).
- Features where the calculations might be possible, but which require more theoretical work (optics, partial atomic occupancies).
- Features that are blocked for purely technical reasons (molecular dynamics).

These limitations are imposed by the user interface; if you attempt a run using a combination of settings which is not allowed, a message box explaining why the run cannot be carried out will be displayed when you select *Run* or *Save Files*.

Setting up CASTEP calculations

The topics in this section describe how to set up CASTEP 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 understood by CASTEP which are not currently accessible through the Materials Studio interface. Such options can be utilized by manually editing the CASTEP input files. Information about how to do this is also presented in this section.

An important concept that affects a large number of settings exposed in CASTEP is that of a calculation quality. The *Quality* setting on the Setup tab of the CASTEP Calculation dialog provides a shortcut for setting up a balance between the accuracy and speed of calculations. The range of values from Coarse to Ultra-fine allows you to increase the accuracy gradually by imposing more strict tolerances, improving accuracy of reciprocal space sampling, and increasing the number of basis functions. Nevertheless there are cases where there is no need to systematically change the quality settings and a fast qualitative description is sufficient. The Express quality setting is provided to allow many simple cases to get reasonable results quickly. Please note that these settings cannot be translated into the Coarse - Ultra-fine accuracy scale. This setting is especially useful for semiconductors and insulators and can be fairly accurate for nonmagnetic metals. The study of magnetic metallic systems requires more accurate calculation settings than those defined by the Express quality setting.

Note: CASTEP does not support all possible permutations of electronic settings for all possible properties requests. In cases where the input settings are contradictory the Materials Studio client will display messages explaining the problem. However, sometimes the combinations selected during the setup of a CASTEP calculation are impossible to satisfy. The main source of such contradictions is in the type of pseudopotentials used. For example, NMR calculations and core level spectroscopy calculations require the use of on-the-fly generated (OTFG) pseudopotentials for at least some elements. On the other hand, nonlocal exchange-correlation functionals (for example B3LYP) or linear response phonon calculations are limited to norm-conserving pseudopotentials. It is therefore impossible to use the same settings for requesting, for example, phonon dispersion using linear response and core level spectra, or to calculate band structures with B3LYP and request NMR chemical shifts.

Tip: Accurate calculations for 3D periodic systems may require a large number of k-points if the lattice has a strongly skewed unit cell (for example, some cell angles are very small). In such cases it might be beneficial for the speed of calculations to convert the structure to reduced (Niggli) cell representation using the Redefine Lattice dialog.

Setting electronic options

Electronic options must be set for Energy, Geometry Optimization, Dynamics, Elastic Constants, and TS Search calculations. The settings used for Properties calculations are copied from the input files of the calculation that is to be restarted and are unaffected by any changes made through the interface.

The basic controls used to define the calculations are available on the Setup and Electronic tabs of the CASTEP Calculation dialog. The important settings that you might need to modify are:

- Quality - determines how accurate and how expensive the calculation will be
- System parameters - describe the charge and spin state of the system
- Exchange-correlation functional - determines the level of the DFT description
- Pseudopotentials - affect both the accuracy and the cost of the calculation
- Basis set - specifies the quality of the plane wave basis set
- k-points - determine the accuracy of the Brillouin zone sampling
- SCF - specifies the scheme that is to be used for electronic minimization

Setting the quality of a calculation

An important concept that affects a large number of settings exposed in CASTEP is that of a calculation quality. The *Quality* setting on the Setup tab of the CASTEP Calculation dialog provides a shortcut for setting up a balance between the accuracy and speed of calculations. To help you select appropriate values for CASTEP parameters, four predefined parameter sets are available. The predefined sets vary in quality from Coarse, suitable for quick approximate calculations, to Ultra-fine, for calculations where high precision is required.

CASTEP formalism lends itself naturally to a systematic convergence study by means of increasing the size of the basis set, accuracy of Brillouin zone sampling, and so on. Nevertheless there are cases for which there is no need to systematically change the quality settings and a fast qualitative description is sufficient. The Express quality setting is provided to allow you to obtain reasonable results quickly in many simple cases. This setting can be an order of magnitude faster than the Fine setting, while producing results that are sufficiently accurate for exploratory studies, for investigation of qualitative trends in a high-throughput context for example. The Express setting is especially useful for semiconductors and insulators and can be fairly accurate for nonmagnetic metals. The study of

magnetic metallic systems usually requires more accurate calculation settings than those defined by the Express quality setting.

> **Note:** The Express setting cannot be translated into the Coarse - Ultra-fine accuracy scale.

To help you select appropriate values for CASTEP parameters, four predefined parameter sets are available. The predefined sets vary in quality from Coarse, suitable for quick approximate calculations, to Ultra-fine, for calculations where high precision is required.

To select a quality

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.
2. Select the Setup tab.
3. Choose a *Quality* setting from the dropdown list to select one of the four predefined parameter sets.

When you choose a *Quality* setting, the parameters are set according to the task and the system.

Quality	Express	Coarse	Medium	Fine	Ultra-Fine
Energy tolerances per	Cell	Atom	Atom	Atom	Atom
SCF tolerance (eV/atom)		1.0×10^{-5}	2.0×10^{-6}	1.0×10^{-6}	5.0×10^{-7}
SCF tolerance (eV/cell)	0.0001				
SCF Convergence window	2	3	3	3	3
k-points separation (metals) ($Å^{-1}$)	0.07	0.07	0.05	0.04	0.04
k-points separation (insulators) ($Å^{-1}$)	0.1	0.1	0.08	0.07	0.07
Energy cutoff	Fine	Coarse	Medium	Fine	$1.1 \times$ Fine
FFT Grid Density	Standard	Standard	Standard	Fine	Precise
Apply finite basis set correction	1	1	1	1.2	1.5
Augmentation density scaling factor	Never	Smart	Smart	Smart	Smart

The values of the *Energy cutoff* that correspond to the Coarse, Medium, and Fine settings are element specific and are taken from the pseudopotential files stored in the database. These values were determined from convergence tests for single atoms and diatomic molecules and they roughly correspond to total energy convergences of 2, 0.3, and 0.1 eV atom^{-1}, respectively. The highest value for the selected quality setting among the elements present in the 3D structure document is accepted.

The *Quality* setting also affects the values of the convergence tolerances for tasks such as geometry optimization, elastic constants calculations, and transition-state searching.

> **Note:** The values of force, stress, and displacement tolerances for the Geometry Optimization and Elastic Constants tasks are set to 100 for Express*Quality*. This preset value instructs CASTEP to ignore these tolerances and consider only the energy tolerance as a convergence criterion.

Geometry optimization

Quality	Express	Coarse	Medium	Fine	Ultra-fine
Energy tolerance (eV/atom)		5.0e-5	2.0e-5	1.0e-5	5.0e-6
Energy tolerance (eV/cell)	0.001				
Max. force tolerance (eV/Å)	100	0.1	0.05	0.03	0.01
Max. stress tolerance (GPa)	100	0.2	0.1	0.05	0.02
Max. displacement tolerance (Å)	100	5.0e-3	2.0e-3	1.0e-3	5.0e-4
BFGS Use line search	No	Yes	Yes	Yes	Yes

Note: The values of force, stress, and displacement tolerances are set to 100 for Express*Quality*. This preset value instructs CASTEP to ignore these tolerances and consider only the energy tolerance as a convergence criterion.

The individual tolerances may need to be adjusted in some cases:

- The *Max. force* tolerance can be reduced for molecular systems (isolated molecules, molecules on surfaces, molecular crystals, and so on)
- The *Max. stress* tolerance is generally expressed as a fraction of the bulk modulus of the material, so it should be smaller for soft materials. However, in practice, cell optimization of soft substances (for example, molecular crystals) is difficult and might not be stable enough to impose very stringent convergence criteria.

Elastic constants

Quality	Express	Coarse	Medium	Fine	Ultra-fine
Energy tolerance (eV/atom)		1.0e-5	4.0e-6	2.0e-6	1.0e-6
Energy tolerance (eV/cell)	0.001				
Max. force tolerance (eV/Å)	100	0.02	0.01	0.006	0.002
Max. displacement tolerance (Å)	100	1.0e-3	4.0e-4	2.0e-4	1.0e-4

Note: The values of force, and displacement tolerances are set to 100 for Express*Quality*. This preset value instructs CASTEP to ignore these tolerances and consider only the energy tolerance as a convergence criterion.

Note: These tolerances are five times more strict than the ones used for the Geometry Optimization task.

TS Search

Quality	Express	Coarse	Medium	Fine	Ultra-fine
RMS convergence (eV/Å)	0.1	0.5	0.25	0.05	0.01

Setting system parameters

System charge

CASTEP allows you to perform calculations on charged systems. This is useful for studies of, for example, charged defects in semiconductors (Milman et al., 1993 and Hakala et al., 2000).

> **Note:** Makov-Payne corrections, which improve the convergence of the total energy with respect to the supercell size in charged periodic systems, are not implemented in this version of CASTEP. This means that the results obtained for charged systems with small unit cells are less reliable.

To set system charge

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.
2. Select the Setup tab.
3. Specify the system charge in the *Charge* field.

Spin polarization

Magnetic systems can be studied by carrying out spin-polarized DFT calculations with CASTEP. This setting is recommended for transition metal oxides, certain inorganic surface studies, and metallic systems containing magnetic elements (Fe, Co, Mn, Ni).

Spin-polarized CASTEP calculations are normally carried out with a variable magnetic moment. This procedure, however, does not guarantee finding the lowest energy state. DFT solutions can converge to a variety of local minima, so that the metastable states are found. The most commonly obtained solutions correspond to high spin and low spin states. The state generated by CASTEP depends on the initial magnetic configuration, since the solution is likely to converge to the nearest local minimum rather than to the global minimum.

There are two ways of defining the initial magnetic configuration: either specify the total magnetic moment per unit cell, which gets uniformly distributed over the space, or provide detailed information on the absolute values and direction (up or down) of the spins for each atom in the unit cell. The former method can be used for relatively simple systems where only two solutions are expected (magnetic and non-magnetic). The latter method, which specifies the spin state of the atoms in the system, is more general and gives much more flexibility. It is possible to set up ferromagnetic, ferrimagnetic, or antiferromagnetic calculations to get different starting spin arrangements.

To set up a spin-polarized calculation with a uniformly distributed initial magnetic moment

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.
2. Select the *Setup* tab.
3. Check the *Spin polarized* checkbox and uncheck the *Use formal spin as initial* checkbox.
4. Specify an *Initial spin* value.
5. To optimize the spin value, select the Electronic tab and click the *More...* button to access the CASTEP Electronic Options dialog.
6. Select the SCF tab.
7. Uncheck the *Fix occupancy* checkbox and check the *Optimize total spin* checkbox.

To set up a spin-polarized calculation with a specified ordering of atomic moments

> **Note:** Initial magnetic moments on atoms are treated correctly by CASTEP only when the density mixing scheme is used for electronic structure minimization. CASTEP will ignore atomic information and will use the uniformly distributed magnetic moment for the all bands or EDFT minimizers. The value of the total moment is determined by the sum of formal spins in the system.

1. Set formal spins for the atoms.
2. After setting the formal spins, find and impose the symmetry of the system.
3. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.
4. Select the *Setup* tab.
5. Check the *Spin polarized* and *Use formal spin as initial* checkboxes.
6. Select the *Electronic* tab and click the *More...* button to access the CASTEP Electronic Options dialog.
7. Select the *SCF* tab.
8. Select *Density mixing* as the *Electronic minimizer* setting.
9. Uncheck the *Fix occupancy* checkbox and check the *Optimize total spin* checkbox.

It is important to include a sufficient number of empty bands when optimizing the spin state. The default number of empty bands is 4, which means that the maximum accessible increase in the spin value is 8. A calculation that started with the low spin state will be extremely slow if the actual minimum found by CASTEP corresponds to the high spin state (although this is not the case when a calculation starts with high spin and converges to low spin).

> **Note:** CASTEP might fail to converge the SCF if the number of empty bands is insufficient to accommodate the high spin state, especially in a calculation with variable occupation numbers (metallic systems).

Electric fields

An external electric field can be applied to the system. This causes a force to act on each atom which is proportional to the charge on that atom. This can be used to calculate the polarizability of a dielectric material.

To apply an electric field

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.
2. Select the *Electronic* tab and click the *More...* button to access the CASTEP Electronic Options dialog.
3. Select the *Potentials* tab.
4. Specify the strength of the *Electric field* to apply.
5. Enter the *Field direction* in lattice vectors (A B C).

Setting the exchange-correlation functional

CASTEP supports one local exchange-correlation functional, LDA, three gradient-corrected exchange-correlation functionals, GGA, and a set of nonlocal functionals for the self-consistent total energy calculations.

LDA functional

CA-PZ is the only local (LDA) functional available in CASTEP. It is based on the Ceperley and Alder (1980) data as parameterized by Perdew and Zunger (1981).

GGA functionals

GGA functionals provide a better overall description of the electronic subsystem than the LDA functionals. The LDA description tends to overbind atoms, causing underestimation of the bond lengths and the cell volume by a few percent and overestimation of the bulk modulus. GGA corrects this error but may underbind instead, leading to slightly long bond lengths.

PBE (Perdew et al., 1996) is the default exchange-correlation functional. PBE is especially suitable for studies of molecules interacting with metal surfaces, although it is also fairly reliable for bulk calculations. Use the PW91 (Perdew et al., 1992) functional for comparisons with literature data, as it is the most widely used GGA functional. The results obtained with the PW91 functional are usually very similar to those obtained with PBE. Another nonlocal functional, RPBE (Hammer et al., 1999), is a revised form of the PBE functional designed to improve the description of metallic surfaces. One of the latest GGA potentials, WC, was developed by Wu and Cohen (2006). The authors claim significant improvements for lattice constants, crystal structures, and metal surface energies over the most popular Perdew-Burke-Ernzerhof (PBE) GGA. Another recent functional, PBEsol, was developed specifically to improve the description of exchange in solids, resulting in better structures and energetics for densely packed solids and their surfaces (Perdew et al., 2008).

Meta-GGA functional

In addition to the generalized gradient (GGA) functionals, which depend on the local density and its gradient, CASTEP can handle functionals that depend on the kinetic energy density. The current supported functional is RSCAN (Bartok and Yates, 2019), which is an improved regularized version of the SCAN ("Strongly Constrained and Appropriately Normed") functional developed by Sun et al., 2015. Meta-GGA functionals are considered to be more accurate than pure GGA, and the cost of such calculations is significantly lower than for nonlocal functionals.

> **Note:** There are limitations on the use of meta-GGA in CASTEP. The meta-GGA functional is not compatible with spin-orbit coupling, J-coupling, linear-response phonons, or polarizability calculations. You cannot use the formalism with mixture atoms. You can only use on-the-fly-generated pseudopotentials.

Nonlocal exchange-correlation functionals

Nonlocal exchange-correlation functionals result from the generalized Kohn-Sham procedure (Seidl et al., 1996). The intention is to improve on the description of band gaps in insulators and semiconductors compared with LDA or GGA calculations. This additional accuracy comes at the price of more time consuming calculations.

Several approximations for nonlocal exchange-correlation functionals are available:

- HF
- HF-LDA
- sX
- sX-LDA
- PBE0
- B3LYP
- HSE03
- HSE06

The preferred functionals are sX-LDA, PBE0, B3LYP, and HSE06. The other functionals allow testing against other packages that implement Hartree-Fock schemes for solids.

> **Note:** There are limitations on the use of this approach: you can only use nonlocal exchange for insulators using the all-bands minimizer (not density mixing). It is not compatible with NMR, phonon, or polarizability calculations. You cannot use the formalism with mixture atoms or ultrasoft potentials.

To select the exchange-correlation functional

1. Choose *Modules | CASTEP | Calculation* from the menu bar.

2. Select the *Setup* tab.

3. Choose a local (LDA), a gradient corrected (GGA) or nonlocal functional from the first dropdown list for the *Functional*.

4. Select the specific functional from the second dropdown list.

Setting Up Pseudopotentials

Ultrasoft and Norm-Conserving Pseudopotentials

CASTEP uses on-the-fly generated ultrasoft pseudopotentials (USP) by default. These are generally more accurate and more efficient than norm-conserving pseudopotentials (NCP).

USP implementation allows you to run CASTEP calculations with a lower energy cutoff than their NCP counterparts producing a clear advantage in terms of the calculation time. However, USP formalism is more complex and becomes close to intractable for such complex concepts as linear response implementation for phonons or NMR properties, or for nonlocal exchange-correlation functionals. There is a number of tasks and properties that CASTEP can address only with norm-conserving potentials.

There are two types of pseudopotentials available in Materials Studio: tabulated and generated on-the-fly.

Pseudopotentials Generated On-the-Fly

CASTEP server code allows you to generate pseudopotentials on the fly, that is, you can provide the parameters that govern the generation rather than a tabulated file from the database. This approach has a number of advantages; for example:

- It uses the same exchange-correlation functional in the atomic and solid-state calculations.
- It is possible to generate "softer" or "harder" potentials by changing the core radius.
- It is possible to study excited configurations with a core hole, and so on.

The latest set of OTFG settings for ultrasoft pseudopotentials was developed to minimize the error with respect to fully converged all-electron DFT calculations. The error achieved by this set is 0.4 meV/atom, which puts CASTEP among the most accurate pseudopotential codes available. A full definition of the test framework and the meaning of the error is given by Lejaeghere et al. (2014), and on the website of the Delta project: http://molmod.ugent.be/deltacodesdft. The files that correspond to this set have the _2017R2 suffix. This is the recommended set of OTFG ultrasoft potentials. Use files with the _2017R2ncp suffix when you require norm-conserving potentials. This set has a 1.1 meV/atom error in the Delta project tests. In addition, provides a set of "high throughput" ultrasoft OTFG settings for scripting. This QC5 set generally requires lower cutoff energy and offers faster but less accurate calculations (1.9 meV/atom error in the Delta project tests).

> **Note:** It is not recommended to use the PW91 exchange-correlation functional when requesting on-the-fly generation of pseudopotentials. PBE, RPBE, WC, BLYP, or PBESOL are better options when you require a GGA functional.

This scheme was validated for all elements of the Periodic Table and the files themselves include the results of the tests. You can also create customized versions of the pseudopotential generation settings. In which case, test the resulting potentials thoroughly for convergence and transferability by performing calculations for a variety of systems and at different energy cutoffs. For details of the format of the on-the-fly generation settings file, see CASTEP file formats - OTFG.

On-the-fly generation of pseudopotentials involves the solution of the electronic structure of an atom and a pseudoatom. You can perform this step either in a non-relativistic (Schroedinger) framework, using one of the available scalar relativistic approaches (Koelling-Harmon or ZORA), or using a fully relativistic atomic solver (Dirac). It is important to use a scalar relativistic treatment for improved accuracy of calculations for heavy elements.

> **Notes:**
> - You must use the Dirac solver when you request spin-orbit coupling.
> - You can only compute J-coupling using the Schroedinger or ZORA approach.
> - You can only perform CASTEP NMR calculations using the on-the-fly generation scheme, since the available potentials in the database do not contain sufficient information about all-electron projectors.

Tabulated Pseudopotentials

Tabulated USP files in the database have a `.usp` or `.uspcc` extension, tabulated norm-conserving files have a `.recpot` extension.

> **Note:** Use different tabulated ultrasoft potentials for LDA and GGA exchange-correlation functionals. The naming convention in the database is `<element name>_<ID>.usp[cc]` for LDA functionals and `<element name>_<ID>PBE.usp[cc]` for GGA functionals. By default, Materials Studio tries to find the best fit of the potentials to the exchange-correlation potentials, although you can override this behavior.

The database of NCPs available in Materials Studio is rather old and in some cases might contain potentials that have not been tested sufficiently. An alternative is to use on-the-fly generated pseudopotentials that are more modern and more extensively tested.

Besides changing the global selection of pseudopotentials, it is possible to change the individual selections for each element according to the selected value of the exchange-correlation functional.

> **Tip:** Individual selections are also useful for elements such as oxygen and silicon where additional *soft* versions of the USPs are available. These require a smaller energy cutoff but may be less transferable than the standard potentials.

Nonlinear Core Corrected Pseudopotentials

Materials Studio provides USPs with nonlinear core correction (NLCC) for some elements, most notably transition metals. These potential files have a `.uspcc` extension. In some cases, NLCC potentials are more accurate than the corresponding non-corrected USPs and others they provide a cheaper and less accurate alternative to the non-corrected USPs.

You can distinguish between these two cases by comparing the *Valence* values displayed on the *Potentials* tab of the *CASTEP Electronic Options* dialog.

For example, `Mn_00.usp` and `Mn_00.uspcc` both use seven valence electrons. This means that the NLCC version is more accurate (and it is therefore the default potential for Mn). However, `Cr_00.usp` uses 14 valence electrons, while `Cr_00.uspcc` uses only six. This means that `Cr_00.usp` treats semicore *s* and *p* states explicitly as valence states and is thus more accurate than the NLCC version.

To change global pseudopotential selection

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.

2. Select the *Electronic* tab.

3. Set the *Pseudopotentials* option to either Ultrasoft or Norm-conserving using the list.

To change pseudopotential selection for a given element

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.

2. Select the *Electronic* tab.

3. Click *More...* to open the *CASTEP Electronic Options* dialog.

4. Select the *Potentials* tab.

5. Set the *Pseudopotential* for each element from the list that appears in the appropriate grid cell when it is edited.

   For example, for Mg Materials Studio provides the following pseudopotentials: `Mg_00.usp`, `Mg_00PBE.usp`, `Mg_00PW91.usp`, `Mg_00.recpot`.

6. Click *View* to display the selected pseudopotential scheme.

Pseudopotential Database

Materials Studio provides the pseudopotentials as ASCII text files in the folder `<MS_INSTALL>\share\Resources\Quantum\CASTEP\Potentials`. The headers of these files contain useful information about:

- Recommended cutoff energies for different convergence levels.
- Pseudopotential generation data for core radii, electronic configuration, exchange-correlation potential, etc.
- Convergence testing for energy and forces on atoms for a simple system as a function of the energy cutoff.
- Scientific testing for lattice constants and molecular bond lengths compared to experiment.

This information might be useful when deciding which potential to use, or when writing up the results of a calculation. In addition, you can use the core radii as a guide to selecting a real-space transformation radius.

Setting up the basis set

Energy cutoff

The basis set, as defined by the energy cutoff value, is one of the most important parameters that determine the accuracy (and the cost) of a CASTEP calculation. The easiest way to set this value is by using the *Energy cutoff* option on the *Electronic* tab of the *Calculation* dialog. If you use this method, the cutoff value which is optimal for a given level of the total energy convergence will be determined, based on the information in the pseudopotential data files.

Alternatively, you can specify a custom energy cutoff value on the *Basis* tab of the *Electronic Options* dialog. Custom energy cutoffs may be required in a number of cases, for instance, when modeling a molecule-surface interaction, for example CO on a Pt surface. In such situations, the protocol for the calculation of the binding energy includes separate CASTEP runs for the isolated molecule, the clean Pt surface and finally the CO-Pt complex. The basis sets for the systems containing oxygen will be determined by the convergence properties of the oxygen potential, the hardest element out of O, C, and Pt. In order to achieve maximum error cancellation, it is necessary to set the energy cutoff for the clean Pt surface calculation to the same value as in the other two runs. Therefore, an automatic selection of the energy cutoff is not totally appropriate in this case.

To change the energy cutoff quality

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the *Electronic* tab.
3. Set the *Energy cutoff* quality using the dropdown list.
4. The energy cutoff value that corresponds to the selected quality is displayed next to the dropdown list.

To set a specific energy cutoff value

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the *Electronic* tab.
3. Click the *More...* button to access the *Electronic Options* dialog.
4. Select the *Basis* tab.
5. Check the *Use custom energy cutoff* option.
6. Modify the energy cutoff value.

FFT grid

The size of the FFT grid which is used to represent wavefunctions, charge density and potentials is determined by the energy cutoff value and the reciprocal lattice vectors.

The ideal FFT value is determined by the requirement that there be no wrap-around error in the representation of wavefunctions and potentials (Payne et al., 1992).

This value corresponds to the maximum G-vector of the FFT grid, G_{max}, which is exactly twice the radius of the reciprocal space sphere determined by the energy cutoff E_{cut}.

However, it is possible to use smaller FFT values and still obtain accurate answers even though some wrap-around error will be present. By default CASTEP uses a grid that corresponds to 3/4 of the ideal grid size. This setting can be changed using the *Derived grid* option on the *Basis* tab of the *Electronic Options* dialog. The actual values of the FFT grid are then displayed in the *Divisions* text boxes on the same dialog.

> **Note:** Ultrasoft potentials require a better FFT grid in order to represent the augmentation density accurately. The PW91 exchange-correlation functional also requires a better grid, to represent gradient-dependent terms in the potential.
>
> Therefore, CASTEP derives a finer FFT grid in both of these cases, compared with other exchange-correlation functionals or norm-conserving potentials.

The table below shows the factor by which the actual grid differs from the ideal one depending on (i) *Derived grid* setting and (ii) the use of either the PW91 functional or ultrasoft pseudopotentials.

	Standard	Fine	Precise
No USP, no PW91	0.75	0.875	1.0
Either USP or PW91	0.875	1.0	1.15

> **Tip:** Use the Fine setting (or better) for high-accuracy calculations, especially when the cell optimization is required.

To change the FFT grid quality

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the *Electronic* tab.
3. Click the *More...* button to access the *Electronic Options* dialog.
4. Select the *Basis* tab.
5. Set the *Derived grid* quality from the dropdown list.
6. The FFT grid values that corresponds to the selected quality are displayed below the dropdown list.

Finite basis set corrections

It is recommended that you apply a finite basis set correction to the total energy and to the stress tensor when stress is calculated, including geometry optimization runs with variable cell parameters and NPT/NPH molecular dynamics calculations. The *Apply finite basis set correction* setting corresponding to this is Smart.

> **Note:** Variable cell CASTEP calculations can be carried out in two modes, either fixed basis set quality (that is, fixed energy cutoff), or fixed basis set size (fixed number of plane waves). Finite basis set correction is required only in the former case, and this is accounted for automatically when the Smart setting is used.

CASTEP calculates the correction by determining the total energy at a number of cutoff energies, then evaluating the derivative required in the correction term, numerically. It is normally sufficient to use three reference points in such calculations.

In some cases the value of the derivative may be known from a previous calculation. In such circumstances, the value can be input directly, using the Manual *Correction mode*.

However, under normal circumstances, it is strongly recommended that the finite basis set correction settings are left at their default values. These are:

Apply correction: Smart
Correction mode: Automatic
Numerical differentiation: 3 points

Setting up k-points

The k-point set used in a calculation defines the accuracy of the Brillouin zone sampling. The Monkhorst-Pack k-points used in CASTEP are characterized by divisions along three reciprocal space axes and by an optional origin shift. However, the origin shift should not be used. Thus, the k-points setup procedure simply involves selecting three integer divisions.

The quality of the k-point set can be quantified in a number of ways; CASTEP uses the distance between the points in reciprocal space as a numerical measure. The simplest way to define the set is the following:

Simple way of setting the k-points

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the Electronic tab.
3. Choose the desired *k-point set* from dropdown list.

This method creates either a Monkhorst-Pack set of the selected quality (Coarse, Medium, or Fine) or instructs CASTEP to use only one Γ-point (the origin in reciprocal space).

> **Note:** Explicit selection of Γ-point sampling is not recommended. CASTEP will automatically use this option if the cell is very large in real space, so that the Brillouin zone is small and no sampling is required.
>
> In all other cases, the Γ-point is the least representative of all Brillouin zone points and using it as the only sampling point can distort the results severely.
>
> Puska (2000) showed, for example, that there is a 1-2 eV error in the vacancy formation energy in silicon when the Γ-point is used for cells containing up to 128 atoms.

Finer control over k-point sets can be exercised by using the k-points tab on the CASTEP Electronic Options dialog. This tab allows you to enter the actual Monkhorst-Pack mesh parameters by selecting the Custom grid parameters option.

CASTEP automatically optimizes the mesh parameters according to the point group symmetry of the 3D model. For example, in a cubic crystal the even mesh parameters, N, will generate the set with as many k-points as the one with the odd mesh parameters, N-1. Since the former set provides better sampling, it will be selected automatically when either Quality or k-point separation is used to define the k-point set. Custom grid parameters is the only option which allows you to specify a suboptimal mesh with odd divisions.

The quality of the k-point sampling is particularly important for metallic systems, where rapid changes in electronic structure may occur along the energy band that crosses the Fermi level. Insulators or semiconductors, even when they are treated using variable occupation numbers for electronic states, are less sensitive to the quality of k-point sampling. The default settings used by CASTEP are designed to give accurate sampling for metallic systems. This means that you can get good results for insulators and semiconductors with a slightly less fine k-point mesh than the default.

> **Note:** The total energy is not guaranteed to decrease as more k-points are added. Therefore, when carrying out convergence testing, you should strive to find a set of k-points such that further improvements do not alter the total energy beyond the tolerance level you require. However, the energy is not likely to converge smoothly and oscillations are to be expected.

Setting up SCF parameters

SCF settings determine the algorithm that CASTEP uses to find the ground state of the electronic subsystem, as well as the accuracy required. Most of these settings do not need to be changed by the user. For example, the SCF tolerance is controlled by the global *Quality* option on the *Setup* tab. It can also be modified using the *SCF tolerance* option on the *Electronic* tab, however this is not recommended.

Similarly, the maximum number of SCF cycles, which can be adjusted using *Max. SCF cycles* option on the *SCF* tab on the *CASTEP Electronic Options* dialog, need not be changed under normal circumstances.

The *Max. SCF cycles* setting determines how many SCF steps are taken by CASTEP before it moves atoms according to the task being performed (that is, Geometry Optimization or Dynamics).

> **Note:** The CASTEP server automatically increases the number specified in the interface by a factor of three for metallic systems.

Electronic minimization algorithm

The algorithm that is used to solve the DFT equations is specified by the *Electronic minimizer* option on the *SCF* tab on the *CASTEP Electronic Options* dialog.

Density mixing is the recommended choice, in terms of both robustness and efficiency. It is 2-4 times faster for insulators than the conjugate-gradient based All Bands/EDFT scheme. The Density mixing

scheme is especially good for metallic systems, where speedups for metal surfaces compared to conjugate gradient schemes are in the region of 10-20.

The only case where density mixing may not improve performance is for molecule in a box calculations.

The default density mixing settings use Pulay mixing and conjugate-gradient minimization of each electronic state. You should only attempt to change these parameters if SCF convergence is very poor. Sometimes it helps to reduce the length of the DIIS history from the default value of 20 to a smaller value (5-7). It might also be helpful to decrease the mixing amplitude from the default value of 0.5 to 0.1-0.2.

Variable electronic states occupancies

By default CASTEP uses variable electronic occupancies, thus effectively treating all systems as metallic. This is recommended, as it speeds up density mixing optimization, even for systems with large band gaps. The number of empty bands should be sufficiently large to cater for nearly degenerate bands close to the Fermi level. This is relevant for transition or rare earth metal compounds, where narrow d or f bands can be pinned at the Fermi level.

If the number of bands used for such a system is insufficient, the SCF convergence will be very slow and probably oscillatory. Occupation numbers of the highest electronic states as reported in the `.castep` file are likely to be noticeably nonzero for at least some k-points.

SCF convergence with the Density mixing minimization scheme can sometimes be poor for metallic systems. If this is the case, the alternative All Bands/EDFT scheme, which is based on the ensemble density-functional theory (Marzari et al., 1997) offers a more robust alternative.

> **Tip:** Slow SCF convergence is often indicative of an insufficient number of empty bands, especially in spin-polarized calculations. To check if this is the cause, inspect the occupancies of the highest energy electronic states. They should be very close to zero for all k-points in a calculation which is setup correctly.

Dipole corrections

By default CASTEP does not perform dipole corrections, however, for slab and single molecule systems with P1 symmetry either a Self-consistent or Non self-consistent dipole correction can be applied. The self-consistent scheme is based on the method suggested by Neugebauer and Scheffler (1992) where the correction potential is recalculated at each SCF step. The non self-consistent scheme is based on the approach of Yeh and Berkowitz (1999) where a dipole correction is added after the SCF has converged. In this scenario only the total energy and its gradients are corrected, not the electrostatic potential. As a result, this type of correction is not suitable for electrostatic potential studies such as workfunction calculations.

Dipole corrections can be essential in eliminating nonphysical electrostatic interactions between periodic images, improving accuracy of calculated adsorption energies for molecules on surfaces, for example.

> **Tip:** It is recommended to use the All Bands/EDFT electronic minimization scheme when applying a self-consistent dipole correction to an elongated cell of a slab representing a metal surface; the Density mixing minimization scheme may fail to converge for such systems.

Setting up a geometry optimization

Geometry optimization is one of the tasks most often performed with CASTEP.

Convergence criteria

The accuracy of the calculation is controlled by the *Quality* option on the *Geometry Optimization* dialog.

For a detailed description of the quality settings please refer to the Setting the quality of a calculation topic.

Geometry optimization algorithm

The BFGS algorithm is the recommended algorithm for minimizing structures. The damped molecular dynamics approach is always slower and does not allow cell relaxation. The only case when damped dynamics may be appropriate is in systems with a very flat potential energy surface. BFGS can be extremely slow in such cases and can get stuck in a local minimum.

The TPSD geometry optimization algorithm is a viable alternative for systems where the potential energy surface deviates significantly from the quadratic form. TPSD offers robust convergence and is particularly recommended when user-supplied constraints on lattice parameters are applied during cell optimization (for example, when optimizing a solid-solid interface in a direction perpendicular to the interface plane).

Constraints

Geometry optimization in CASTEP obeys constraints on fractional atomic positions imposed using the Materials Visualizer. You can set such constraints using the Edit Constraints dialog, accessible from the *Modify* menu. Note that atoms must be completely fixed; CASTEP does not support partial constraints on the x, y, and z components of Cartesian atom positions.

> **Tip:** At present, you must check the *Fix fractional position* checkbox on the *Atom* tab of the Edit Constraints dialog in order to apply fixed atom constraints in CASTEP. This has the effect of fixing both fractional and Cartesian positions in a fixed cell calculation, and fixing fractional positions in a variable cell run. In the current version of Materials Studio, checking the *Fix Cartesian position* checkbox has no effect on CASTEP calculations.

More general linear constraints in CASTEP can be specified manually by editing the `.cell` file.

> **Note:** The default setting in CASTEP is to optimize atomic coordinates only. You must choose an option from the *Cell optimization* dropdown list on the Minimizer tab of the Geometry Optimization dialog if cell optimization is required.

Non-linear constraints

Geometry optimization using delocalized internals in CASTEP obeys constraints on interatomic distances, bonds, and/or torsions imposed using the Materials Visualizer. You can set such constraints using the Edit Constraints dialog, accessible from the *Modify* menu.

> **Notes:**
> - All non-linear constraints are only taken into account if you choose the delocalized internal minimizer, by checking the *Use delocalized internals* checkbox on the Options tab of the CASTEP Geometry Optimization dialog.
> - The Damped MD algorithm for geometry optimization acknowledges only constrained bonds (distances) between atoms, all other constraints (torsions and angles) are ignored.
> - Non-linear constraints cannot be applied in conjunction with symmetry constraints. Thus, if your crystal has symmetry other than P1, you will be prompted to convert the crystal symmetry to P1 before you can continue.
> - Non-linear constraints cannot currently be applied to disordered systems.

Potential pitfalls

One of the most difficult parts of geometry optimization in CASTEP is cell optimization. It is important to ensure that you use a finite basis set correction in such calculations, and preferably a fine quality level.

The accuracy of the stresses which are used in the cell optimization algorithm are crucial for the success of geometry optimization. Certain systems, for example, rare-earth compounds with highly localized electronic states, require very stringent criteria for SCF convergence in order to converge the stress tensor. This is particularly true for the Density mixing minimizer.

If cell optimization fails with the following message in the output file:

```
"BFGS: Geometry optimization failed to converge after ... steps",
```

You should try one of the following:

- change electronic minimization algorithm to All Bands/EDFT scheme
- use a stricter SCF tolerance
- use a less strict Max. stress tolerance

Another potential pitfall is the use of the Fixed Basis Size *Cell optimization* setting when the starting geometry is very different from the final one. Finite basis set correction does depend on the cell variables, although this dependence is disregarded by the minimizer. In addition, the effective cutoff energy changes when the cell geometry is modified with the above setting (it is the number of plane waves that is kept fixed). If this change takes the $dE_{tot}/d(ln\ E_{cut})$ function far away from the point that was used to evaluate the finite basis set correction, the results obtained will not be accurate. Therefore, you should compare the starting and final geometries and perform a completely new run starting from the final configuration if the difference between the two is large.

> **Tip:** Fixed Basis Quality is a recommended setting for cell optimization. Even then it is a good idea to perform an additional geometry optimization calculation after successfully completing the first, particularly if there were noticeable changes in the geometry.

Setting up a molecular dynamics calculation

In most cases a dynamics calculation is preceded by structure minimization. It may also be desirable to perform minimizations after the calculation on several of the conformations that were generated.

> **Note:** CASTEP dynamics calculations can be only performed for systems with P1 symmetry.

Defining the time step

A key parameter in the integration algorithms is the integration time step. A common rule-of-thumb used to pick the time step is that the highest frequency vibration should be sampled between 15 and 20 times in one cycle. For example, if the highest frequency is 20 THz, a typical optical mode frequency in an insulator, a time step of 2.5-3.3 fs is appropriate (period = 1/frequency = 50 fs). In water, the stretch frequencies are around 110 THz, indicating that a time step of 0.45-0.6 fs is required. You will probably be able to use a time step that samples the motion as few as 10 times in a cycle. However, you must check your choice of time step by monitoring energy conservation in the NVE ensemble. A thermostat in the NVT ensemble can completely mask inadequate integration.

> **Note:** The *Time step* can be increased to about 4-5 fs when the extended Lagrangian formulation (Steneteg 2010, Niklasson, 2011) is used.

To choose a time step

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the *Setup* tab.
3. Click the *More...* button to open the *Dynamics* dialog.
4. Select the *Dynamics* tab.
5. Set the *Time step* in the text box.

> **Note:** Along with the related value *Number of steps*, *Time step* also determines the *Total simulation time*. Changes to the *Dynamics time* also affect the *Number of steps*.

Choosing an ensemble

You can control temperature of a CASTEP dynamics calculation, in order to simulate a system that exchanges heat with the environment. Under these conditions, the total energy of the system is no longer conserved and extended forms of molecular dynamics are required.

You can simulate several thermodynamics ensembles with a constant number of particles.

Ensemble	Conditions	Description
NVE	Constant-volume/constant-energy dynamics	The Newtonian equations of motion, which conserve the total energy, are used. The unit cell is fixed. The temperature is allowed to vary. Energy is the constant of motion - it can fluctuate slightly, but there should be no systematic drift.
NVT	Constant-volume/constant-temperature dynamics	The unit cell is fixed. A thermostat maintains a constant temperature. The dynamics are modified to allow the system to exchange heat with the environment at a controlled temperature. Several methods of scaling or controlling the temperature are available.
NPH	Constant-pressure/constant enthalpy dynamics	The size of the unit cell is allowed to vary with a barostat to maintain constant pressure. The enthalpy is a constant of the motion. The size of the unit cell is allowed to vary, while the temperature is also allowed to vary. The enthalpy, which is a constant of the motion, is not allowed to vary beyond a set value between dynamics steps.
NPT	Constant-pressure/constant-temperature dynamics	The size of the unit cell is allowed to vary with a barostat to maintain constant pressure. A thermostat maintains a constant temperature. Similar to NPH, except that temperature is controlled. Several methods of scaling or controlling the temperature are available.

To choose an ensemble

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.

2. Select the *Setup* tab.

3. Click the *More...* button to open the *Dynamics* dialog.

4. Select the *Dynamics* tab.

5. Select the required ensemble from the *Ensemble* list.

6. Select the *Options* tab to enter parameters for the selected ensemble.

Constraints

Molecular dynamics in CASTEP obeys constraints on atomic positions and/or interatomic distances (bonds) imposed through the Materials Visualizer. You can set such constraints using the Edit Constraints dialog, accessible from the *Modify* menu.
To fix atomic positions in CASTEP you must check the *Fix fractional position* checkbox on the *Atom* tab of the Edit Constraints dialog.

Setting up a transition state calculation

CASTEP transition-state searches are performed using synchronous transit methods. These work best in situations where the structures of the reactants and products are known, but the location of the transition state is not.

A transition-state search requires a trajectory document (for example, an `.arc` or `.xtd` file) as input. The reactants are taken from the first frame of the trajectory, and the products from the last frame. For quadratic synchronous transit (QST) calculations, the current frame is used for the QST mid-point. The trajectory files generated by any of the other transition state search methods may be used as input to a QST run.

> **Note:** When a transition state search is performed on a periodic system the unit cell is fixed.

For a detailed description of the quality settings please refer to the Setting the quality of a calculation topic.

> **Note:** Synchronous transit calculations are performed in Cartesian coordinates. There is no option to override this.

To set up a synchronous transit calculation

1. Begin by constructing two separate documents, one for the reactants and a second for the products.

2. Determine the correspondence between atoms in the two documents using the Find Equivalent Atoms tool. The synchronous transit method performs a geometric interpolation between the atomic coordinates of the atoms in the reactants and the atoms in the products. In order to accomplish this, it is necessary that the program understand which atom matches to which.

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 CASTEP calculation by clicking the *Run* button.

> **Tip:** To optimize the reactant and product structures as part of the TS Search run, check the *Optimize reactants and products* checkbox on the CASTEP Transition State Search dialog.

Setting up a transition state confirmation calculation

The LST and QST tools locate a maximum energy structure along the reaction path, but this maximum may not, in fact, be the transition state that you are looking for. You can use the TS confirmation tool to confirm that the transition state found does indeed connect your presumed reactant and product.

A TS confirmation calculation requires three structures to proceed - the reactants, the products, and the transition state. The trajectory used as input for this calculation should contain reactants in the first frame and products in the last frame. Transition state structure is taken as the current frame of this trajectory, unless the current frame is either the first or the last - in which case the penultimate frame is used as transition state. This is the frame where CASTEP TS Search calculations store the transition state determined in the synchronous transit search.

To perform a Transition State Confirmation

1. First perform a TS Search using LST or QST. The trajectory computed by this method is used as input to the TS Confirmation. Make sure this trajectory document is in focus when you set up the TS Confirmation.

2. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.

3. Open the Setup tab.

4. Set the *Task* to TS Confirmation.

5. If desired, set additional options by selecting the *More...* button to open the CASTEP TS Confirmation dialog. Normally, the default options will yield adequate results.

6. Click the *Run* button.

> **Note:** The *Max. images* is the *upper limit* for the number of frames. Structures that are too similar will be dropped during the calculation.

Users should be aware that TS Confirmation jobs can take a long time to complete. These jobs perform a series of geometry optimizations along the reaction pathway, requiring quite a lot of computer time.

> **Tip:** At the end of the calculation, you can select any geometry on the reaction pathway using the chart/trajectory tools and perform subsequent calculations. In this way you could, for example, perform further geometry optimization on an interesting structure.

Setting up an elastic constants calculation

In most cases, the calculation of elastic constants proceeds by full geometry optimization, including cell optimization. This involves the generation of elastic constants for the theoretical lattice constants. However, you can skip this step and generate elastic constants for the experimental structure.

Elastic constants evaluation involves calculating the stress tensor for a number of distorted structures. Internal coordinates are optimized in each run, while keeping the lattice parameters fixed. The accuracy of the elastic constants depends largely on the accuracy of the SCF part and on the geometry optimization convergence level for each distorted structure.

Note: Elastic Debye temperature and averaged sound velocity are not reported if the calculated elastic constants do not produce physically meaningful sound velocities in some directions (for example, if certain C_{ij} values or their combinations are negative when they should be positive). This can happen for low quality calculations or for calculations that were not preceded by a geometry optimization (including optimization of the lattice parameters).

A CASTEP elastic constants calculation can also produce the piezoelectric strain tensor if you request polarization. The calculation uses the same set of optimized structures, with the applied strain tensor to differentiate numerically calculated polarization with respect to applied strain. This property is even more sensitive to the accuracy of the calculation than elastic coefficients. In particular, you can improve results by using extremely tight SCF convergence criteria and verifying convergence of the results with respect to k-point sampling of the Brillouin zone.

Setting up strain patterns

CASTEP generates the strain patterns automatically, based on the lattice type of the structure. The maximum number of patterns required is six for a monoclinic structure, while one pattern is sufficient for cubic cells. Certain symmetries allow you to modify the patterns so that, whenever possible, the calculation generates volume-conserving strains.

The quality of the calculated values depends strongly on the amplitude of the applied distortions and the number of points used for each strain pattern. Use at least four steps for each strain to obtain a statistically reliable linear fit of the stress-strain relationship. Choose the maximum strain amplitude so that:

- It is sufficiently low that the material stays within the linear elasticity regime.
- It is sufficiently high that the distortion generates stresses significantly higher than the error level of the CASTEP calculation (errors from imperfect SCF convergence, for example).

To set up strain patterns

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the Setup tab.
3. Choose the Elastic Constants task.
4. Click *More...* to open the CASTEP Elastic Constants dialog.
5. Select the Elastic Constants tab.
6. Specify the *Number of steps for each strain* and *Maximum strain amplitude* in the appropriate text boxes.

Convergence criteria

The *Quality* setting on the Minimizer tab of the CASTEP Geometry Optimization dialog controls the accuracy of the calculation.

For a detailed description of the quality settings, see Setting the quality of a calculation.

To change the convergence tolerances

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.

2. Select the Setup tab.

3. Choose the Elastic Constants task.

4. Click *More...* to open the CASTEP Elastic Constants dialog.

5. Select the Options tab.

6. Specify the *Quality* using either the dropdown list or by providing individual convergence tolerances for the energy, maximum force, and maximum displacement in the corresponding text boxes.

> **Note:** For trigonal symmetry, you must use the orientation standard where C lies along the z-axis and A is in the xz plane. For further details on the lattice orientation standard and how its configuration, see Viewing or changing the lattice parameters.

Setting up a DFT+U (LDA+U) calculation

You can run CASTEP DFT+U calculations in either the non-spin-polarized mode, when there is no magnetic solution, or in the spin-polarized mode. Most of the correlated systems that require DFT+U treatment exhibit magnetic properties. They are either ferrimagnetic or anti-ferromagnetic, so you must carefully choose the initial spin moments (see Changing atomic spin). In some cases, you must construct a supercell before starting calculations.

> **Note:** The DFT+U formalism is not compatible with NMR, phonon, or polarizability calculations. You cannot use the formalism with mixture atoms or real-space pseudopotentials.

To prepare a DFT+U calculation

1. Either import a structure from a pre-existing file or construct a new molecule using the sketching tools in the Materials Visualizer.

2. From the menu bar, select *Modify | Electronic Configuration* to display the Hubbard U tab of the Electronic Configuration dialog.Set the U values for the orbitals as required.

   For more information, see Changing Hubbard U values .

   > **Note:** CASTEP provides default effective Hubbard U values as guidelines only, as they are not universal and depend greatly on the chemical environment. The results obtained depend on the value of U as well as the atomic orbitals, so literature values are often inappropriate.

3. On the Spin tab, specify the *Formal spin* parameters for your system. Then close the Electronic Configuration dialog.

4. From the menu bar, choose *Modules | CASTEP | Calculation*.

5. Select the Setup tab.

6. Select a *Functional*. For more information on functionals, see the theory section.

7. Select the *Use DFT+U* checkbox.

8. Click *Run*.

The symmetry used in DFT+U calculations is often lower than the crystallographic symmetry, so the number of k-points required increases. Each step performs more calculations, increasing computation times and requiring more steps to achieve convergence.

> **Tip:** For cubic systems, converting to tetragonal or rhombohedral symmetry may improve performance.

Note: Sometimes the density mixing scheme may not converge. In such cases, switch to an EDFT minimizer to improve results and choose to Optimize total spin after 1 SCF step.

Note: You can only apply the Hubbard U operator to the states that have an LCAO projector in the pseudopotential. If there is no projector for any orbital with nonzero U value, CASTEP returns the following error message:

`Hubbard U is requested for the states which do not have LCAO projectors. Please check HUBBARD_U block in the cell file.`

If you think that the states to which you want to apply Hubbard U are really important, use a different pseudopotential (on-the-fly generated potentials are likely to have more projectors than other pseudopotentials).

Setting up a core hole calculation

Calculations with core holes are designed to describe the electronic structure of a system containing highly exited ions with a hole in a core shell. Such calculations can be relevant to the description of such excitations and relaxations of these excited states.

Core holes can be used in any CASTEP calculation, however they are most relevant to the generation of core level spectroscopy results. It is not recommended to carry out geometry optimizations in the presence of core holes.

Note: CASTEP calculations using core holes are only available for atoms using on-the-fly generated pseudopotentials (OTFG).

To set up a core hole calculation

1. Either import a structure from a pre-existing file or construct a new structure using the sketching and crystal building tools in the Materials Visualizer.
2. Extend the crystal lattice using the Supercell or Redefine Lattice dialog and convert to the primitive representation.
3. Convert the symmetry of the crystal to P1, to prevent core holes being placed on symmetrically equivalent atoms.
4. Select *Modify | Electronic Configuration* from the menu bar to display the Core Hole tab of the Electronic Configuration dialog.
5. Set up the core hole(s) in the structure as desired (see Changing Core Hole values for further guidance). Close the Electronic Configuration dialog.
6. Open the Find Symmetry dialog and select the *Options* tab. Check the *CoreShellWithHole* checkbox in the list of properties. On the *Find* tab click the *Find Symmetry* button then the *Impose Symmetry* button.
7. Choose *Modules | CASTEP | Calculation* from the menu bar to open the CASTEP Calculation dialog.
8. On the Electronic tab check the *Use Core Hole* checkbox.
9. Select *On the fly* from the *Pseudopotentials* dropdown list.
10. Click the *Run* button.

Note: To prevent interactions between periodic images of core hole sites sufficiently large supercells might be necessary.

> **Note:** CASTEP calculations with core holes assume by default that an electron is removed from the system, so it is treated as having a charge of 1 (or one more than specified in the *Charge* field on the Setup tab of the CASTEP Calculation dialog). In some circumstances, for example when studying impurities, it might be more appropriate to consider the system as charge neutral. In order to achieve this you should specify the *Charge* of -1 on the Setup tab, in this way the CASTEP input file will have a zero charge. It is also possible to edit the `seedname.param` file to specify a fractional charge. The strength of the core hole can be adjusted by editing the `seedname.cell` file and modifying the pseudopotential definition string (for example, change `{1s1}` to `{1s0.5}` to use a core hole with the charge of 0.5).

Setting up a work function calculation

The work function is the minimum energy (usually measured in electron Volts) required to remove an electron from a solid to a point immediately outside the solid surface (or the energy needed to move an electron from the Fermi energy level into a vacuum). This energy depends on the orientation of the crystal, different crystallographic surfaces have different work function values. The typical range of values of work function for all crystalline elements is from 2 to 6 eV, and the orientational dependence of the work function is of the order of 1 eV.

A practical way of evaluating work function is to compare the values of the Fermi energy and that of the electrostatic potential in a vacuum away from the surface. CASTEP calculations for crystal surfaces are carried out on slabs with a region of vacuum. Effectively, an infinite array of 2D-periodic slabs of material is separated by wide vacuum spacings. CASTEP produces the Fermi energy for such systems, and the spatial distribution of the electrostatic potential. Materials Studio averages the electrostatic potential in the planes parallel to the surface. This approach allows the value of electrostatic potential in vacuum, and hence the work function, to be determined.

The work function can have a large dependence on the crystal structure and surface orientation. It is recommended that the structure is carefully prepared before calculation of the work function, as described in the steps below. The recommended sequence of steps includes the geometry optimization of the bulk structure, preparation of the surface followed optionally by optimization of atomic coordinates in the surface and bulk layers. It is possible to perform work function calculations without this optimization, so that the effects of surface relaxation on the work function can be investigated. It is reasonable to keep the structure of the middle of the slab as close to the perfect bulk structure as possible, for example by imposing fixed atom constraints on some inner atoms of the slab.

It is important to have a fair representation of the bulk material, by including at least 8-10 Å of material in the slab calculation. It is equally important to provide enough vacuum between layers of materials so that the electrostatic interactions between two sides of a slab are negligible and electrostatic potential reaches its asymptotic value; there should be at least 30 Å of vacuum in the cell.

To set up a work function calculation

1. Either import a structure of the bulk material from a pre-existing file or construct a new structure using the sketching and crystal building tools in the Materials Visualizer.

2. Geometry optimize the bulk structure using CASTEP.

3. Cleave the required crystallographic surface using the Cleave Surface dialog so that the thickness provides a meaningful representation of the bulk.

4. Build a slab using the Build Vacuum Slab Crystal dialog, you should ensure that the distance between the surface and the end of the vacuum is great enough that there can be no potential interactions between the surface and the next layer.

5. Choose *Modules | CASTEP | Calculation* from the menu bar.

6. Select the Setup tab.

7. Choose the Geometry Optimization task.

8. Fix fractional atomic positions of some atoms in the middle of the slab using the Edit Constraints dialog, accessible from the *Modify* menu.

9. Select either the LDA or GGA *Functional* from the dropdown list (see the theory section for more information on functionals).

10. Click the *Run* button.

11. Follow the steps in the Displaying the averaged potential chart for work function calculations topic.

The result of this procedure is a chart of the electrostatic potential as a function of position along the surface normal, with Fermi energy and the vacuum energy level marked as two horizontal lines. The work function value is reported in the chart caption.

Setting up a reaction kinetics calculation

Information generated by CASTEP as part of the transition state search task enables you to predict the reaction rate coefficient of a chemical reaction. The algorithm is based on transition state theory and involves evaluation of the partition functions of reactant(s), product(s), and transition state. Calculation of a partition function involves obtaining the vibration spectra, this in turn is calculated from the Hessian matrix.

The reaction rate calculation requires three main ingredients:

1. Transition state search, performed after optimizing geometry of reactants and products

2. Calculation of the Hessians for all the reaction species

3. Calculation of the partition functions and reaction rates for forward and reverse reactions

Transition state searching in CASTEP can be performed using either the LST or QST formalism. To optimize the reactant and product structures as part of the TS Search run, check the *Optimize reactants and products* checkbox on the CASTEP Transition State Search dialog. It is important to set constraints correctly in the initial documents - this has effect both on the cost of the subsequent calculations, and on the accuracy of the results obtained.

To calculate the Hessians for all the reaction species you should check the *Calculate partition functions* checkbox on the CASTEP Transition State Search dialog. This setting causes vibrational frequencies to be evaluated for reactant, product, and transition state structures. A partial Hessian will be used if there are constrained atoms in the system. Since the calculations rely on finite displacements, the cost can be reduced significantly by fixing coordinates of substrate atoms that are not involved in the surface reaction itself.

The result of the transition state search is an 3D Atomistic Collection Document containing reactant, product, and transition state structures. You can select the "TS" physical system and use the Vibrational Analysis tool to verify the nature of the imaginary mode associated with the reaction.

> **Note:** The reaction rate coefficient can be calculated only if the transition state has exactly one imaginary frequency with its eigenvector along the reaction path.

The 3D Atomistic Collection Document generated will contain all the necessary information to perform the reaction rate calculation itself.

To set up a reaction kinetics calculation

1. Prepare two documents containing reactant and product structures. Set any necessary fixed atom constraints (fixed atoms should be present in both documents and should have the same coordinates).

2. Follow the steps required to set up transition state search calculation.

3. Check the *Optimize reactants and products* checkbox on the CASTEP Transition State Search dialog, unless you have optimized both structures prior to constructing reaction preview document.

   It is recommended to select Ultra-fine for the convergence tolerance for geometry optimization by changing the task to Geometry Optimization, opening CASTEP Geometry Optimization dialog, editing convergence settings, and then changing the task again to TS Search. Such an accurate setting may be necessary to eliminate spurious imaginary modes in the vibrational analysis.

4. Check the *Calculate partition functions* checkbox on the CASTEP Transition State Search dialog.

5. It is recommended to impose more strict convergence criteria than the default values; lack of convergence can result in spurious imaginary modes of the transition state itself.

Setting up a calculation on an isolated molecule

CASTEP can be used to calculate the electronic structure and to optimize the geometry of isolated molecules as well as of solids. In order to study molecules using CASTEP, it is necessary to treat them as periodic systems by assuming that they are in a box. This can be achieved by creating a supercell containing the molecule of interest. There is no limitation on the shape of the supercell, but the simplest approach is to use a rectangular (or even cubic) supercell with a sufficiently large separation between molecules to eliminate spurious interactions between periodic images.

Since both the properties being investigated and the nature of the molecule itself have an influence on the degree of molecular separation required, it is not possible to give a definitive distance that should be established between molecules in a supercell. As a general rule, a box with dimensions that are 4-5 times the size of the molecule should be sufficient. However, it is still important that you check that the size of your supercell is adequate by investigating the convergence of the properties you are interested in against the molecular separation.

> **Tip:** Carrying out a stress analysis is a good way of checking that the molecular separation in a supercell is sufficient to preclude any interactions between periodic images, since the stress value provides a guide as to the size of the cell. Alternatively, you could check the band dispersion: the less dispersion in the valence band, the better the molecular separation in the supercell.

CASTEP is an efficient tool for optimizing the geometry of molecules and also enables you to calculate a range of molecular properties, including:

- Densities of states
- NMR shielding tensors and electric field gradients
- Vibrational properties
- Polarizabilities and IR absorption intensities
- Bond and band populations

> **Note:** It is recommended that only the Γ-point is used for electronic calculations on molecular systems. In addition, the all bands/EDFT electronic minimizer is known to be more efficient for studies of isolated molecules in supercell geometry than the density mixing minimizer. Therefore, it is recommended that you change the *Electronic minimizer* setting to All Bands/EDFT on the SCF tab of the CASTEP Electronic Options dialog when performing such calculations.

> **Tip:** Calculations for "molecule in a box" systems that do not require geometry optimization can be sped up if the molecular symmetry is utilized. Use the Find Symmetry tool to find and apply the symmetry of the molecule to the supercell.

To create a molecule in a box

1. Either import a structure from a pre-existing file or construct a new molecule using the sketching tools in the Materials Visualizer.
2. Construct a crystal using the crystal building tools in the Materials Visualizer.
3. If your system does not require geometry optimization, find and impose the symmetry of the system using the Find Symmetry tool in the Materials Visualizer.

Requesting electronic, structural, and vibrational properties

CASTEP can calculate a number of electronic, structural, and vibrational properties, either as part of an Energy, Geometry Optimization, or Dynamics calculation, or during a separate Properties run.

> **Note:** The descriptions below assume that you are requesting properties as part of another CASTEP calculation. You can also request properties separately after a CASTEP calculation completes, using the Properties option for the *Task* on the Setup tab.
> When you request only calculation of properties, you can configure the run in the same way as described here. However, ensure that the output files from a suitable SCF run are available in the appropriate Project directory.
> You can request multiple properties when preparing a CASTEP job.

> **Tip:** The *Population analysis* checkbox on the Properties tab of the CASTEP Calculation dialog is checked by default.

CASTEP produces electronic properties data by running separate non-self-consistent calculations. This means that *Band structure*, *Density of states*, *Optical properties*, and *Vibrational properties* calculations all generate their own output files. *Population analysis*, *Polarization*, and *Stress* properties are calculated as part of the main run, each storing their output in a `.castep` file. CASTEP generates the *Electric field response* either as part of a *Vibrational properties* calculation, in which case the output is in the appropriate `.castep` file, or as a separate calculation.

Requesting band structure

Calculating band structure properties produces electronic energies along high symmetry directions in the Brillouin zone. The standard path for each lattice type is taken from Bradley and Cracknell (1972). The path can be modified using the CASTEP Band Structure Options dialog. The density of points along

the path, which affects the appearance of the resulting chart, can be controlled by the selection for the *k-point set* dropdown list or the approximate k-point separation can be manually specified in the *Separation* text box, in Å^{-1}, on the Properties tab of the CASTEP Calculation dialog. Conduction band states can be included by specifying a nonzero value in the *Empty bands* text box on the same tab.

> **Note:** You are not required to use the same exchange-correlation functional in the band structure calculation as in the main calculation. This allows you to select a nonlocal screened-exchange functional to study the electronic structure after performing, for example geometry optimization with a variable cell using the GGA functional.

> **Note:** CASTEP does not support the use of nonlocal functionals (screened exchange, exact exchange, and so on) for ultrasoft pseudopotentials, that is, nonlocal functionals can only be requested if all the pseudopotentials for the calculation are specified as norm-conserving.

To calculate band structure

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the Properties tab.
3. Check the *Band structure* option on the Properties list.
4. If necessary, modify the *Number of empty bands* to include more or less states in the conduction band.
5. Optionally, adjust the density of k-points along the high symmetry directions by using *k-point set* dropdown list.
6. Click the *More...* button to open the CASTEP Band Structure Options dialog.
7. Click the *Path...* button to open the Brillouin Zone Path dialog. This dialog allows you to inspect and modify the Brillouin zone path used for the band structure calculation.
8. On the CASTEP Band Structure Options dialog check the *Use separate XC functional for band structure calculation* checkbox to use a nonlocal functional for the electronic structure calculation.
9. Select the alternative *Functional* you wish to use from the dropdown list.

Requesting core level spectroscopy

Calculating core level spectra produces electronic energies on the Monkhorst-Pack mesh of k-points and the matrix elements for electronic interband transitions. The CASTEP Analysis dialog can be used to generate observable core level spectra based on this information. Detailed analysis of the impact of calculation parameters (k-point set, number of empty bands, and so on) on the accuracy of the spectra generated can be found in the core level spectroscopy theory topic.

To calculate core level spectra

1. Choose *Modules | CASTEP | Calculation* from the menu bar.
2. Select the Properties tab.
3. Check the *Core level spectroscopy* option on the properties list.
4. If necessary, modify the number *Energy range* above the Fermi level for which you wish to calculate the spectrum.
5. Optionally, adjust the density of Monkhorst-Pack k-points used for the optical properties calculation by using *k-point set* dropdown list.
6. Click the *More...* button to open the CASTEP Core Level Spectroscopy Options dialog.
7. Select the *Core level spectroscopy k-points* option you want to use and the *Band energy tolerance*.

Note: CASTEP calculations with core holes assume by default that an electron is removed from the system, so it is treated as having a charge of 1 (or one more than specified in the *Charge* field on the Setup tab of the CASTEP Calculation dialog). In some circumstances, for example when studying impurities, it might be more appropriate to consider the system as charge neutral. In order to achieve this you should specify the *Charge* of -1 on the Setup tab, in this way the CASTEP input file will have a zero charge. It is also possible to edit the `seedname.param` file to specify a fractional charge. The strength of the core hole can be adjusted by editing the `seedname.cell` file and modifying the pseudopotential definition string (for example, change `{1s1}` to `{1s0.5}` to use a core hole with the charge of 0.5).

Requesting density of states

Calculating densities of states produces electronic energies on the Monkhorst-Pack mesh of k-points. CASTEP can always produce a density of states plot, based simply on the results of the main self-consistent run. The purpose of a density of states property run is typically to:

- use a finer k-point mesh than in the self-consistent run or
- include more states in the conduction band

Such calculations are intended to provide a better quality density of states over a larger energy range.

This type of run can be also used to request a partial density of states. The quality of the k-points set is controlled by the *k-point set* dropdown list on the Properties tab on the Calculation dialog. Conduction band states can be included by specifying a nonzero value in the *Empty bands* text box on the same tab.

Note: You are not required to use the same exchange-correlation functional in the density of states calculation as in the main calculation. This allows you to select a nonlocal screened-exchange functional to study the electronic structure after performing, for example geometry optimization with a variable cell using the GGA functional.

Note: CASTEP does not support the use of nonlocal functionals (screened exchange, exact exchange, and so on) for ultrasoft pseudopotentials, that is, nonlocal functionals can only be requested if all the pseudopotentials for the calculation are specified as norm-conserving.

Note: To obtain representative density of states it is recommended to use a k-point set which is either the same or finer quality than the one used in the SCF calculations.

To calculate density of states

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.

2. Select the Properties tab.

3. Check the *Density of states* option on the properties list.

4. If necessary, modify the *Number of empty bands* to include more or less states in the conduction band.

5. Optionally, adjust the density of Monkhorst-Pack k-points used for the density of states calculation by using *k-point set* dropdown list.

6. If you would like to generate partial or local densities of states, check *Calculate PDOS*.

7. Click the *More...* button to open the CASTEP Density of States Options dialog. This dialog gives you complete control over setting up the Monkhorst-Pack grid.

8. Check *Use separate XC functional for DOS calculation* on the CASTEP Density of States Options dialog if you want to use, for example, a nonlocal functional for the electronic structure calculation.

9. Select the alternative *Functional* you wish to use from the dropdown list on the same dialog.

Requesting electron density difference analysis

Materials Studio provides the option of generating the electron density difference in two different ways:

- Electron density difference with respect to a linear combination of the atomic densities.
- Electron density difference with respect to a linear combination of the densities of sets of atoms contained in the model.

The former option produces a density difference field which shows the changes in the electron distribution that are due to formation of all the bonds in the system. This object is appropriate for bulk solids to illustrate the charge redistribution due to chemical bonding.

The latter option generates a density difference field which effectively corresponds only to the formation of bonds between atoms in different sets and to charge redistribution within the sets that is due to the presence of other sets. This property is useful to describe such processes as bonding of molecule(s) to external and internal (for example zeolites) surfaces, or creation of large molecules from smaller fragments.

> **Note:** Materials Studio supports the calculation of the density difference with respect to the densities of sets of atoms only for tasks that do not involve changes in atomic geometry. For Geometry Optimization and Dynamics values of the *Task* property, you can request this type of density difference after the run is complete by using the Properties task.

To perform an electron density difference analysis

1. Choose *Modules | CASTEP | Calculation* from the menu bar to open the CASTEP Calculation dialog.

2. Select the Properties tab.

3. Check the *Electron density difference* checkbox on the properties list.

4. Use the radio buttons to select the appropriate type of density difference to be created.

5. When density difference with respect to sets of atoms is requested, it is necessary to create at least one set of atoms in the model. There is a naming convention for sets that are taken into account: they should have "DensityDifference" as part of the set name. In order to create the sets:

   a. Choose *Edit | Edit Sets* from the menu bar.

   b. Make sure that the correct 3D structure document is active.

   c. Select the atoms that will constitute the first set.

   d. Click the *New...* button to create a new set.

   e. Give the set a name, for example DensityDifference1.

   f. Repeat the above steps to create further sets if required.

> **Note:** Multiple sets should be mutually exclusive.

> **Tip:** When only one set with the correct name is present in the structure, Materials Studio assumes that the rest of the atoms should be treated as a second set. Thus, in the case of a molecule-surface interaction, it is sufficient to create a single set that comprises all the atoms in the molecule.

Requesting electron localization function

Electron localization function (ELF) provides a useful qualitative description of chemical bonding. CASTEP can calculate ELF at the end of a run and return the results for volumetric analysis.

To request an ELF calculation

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.

2. Select the Properties tab.

3. Check the *Electron localization function* checkbox in the list of properties.

Requesting electronic excitations (TD-DFT)

CASTEP allows you to calculate electronic excitation energies and the corresponding oscillator strengths (transition probabilities) using time-dependent density functional theory (TD-DFT). These excitation energies correspond to the locations of absorption peaks in the optical spectrum of a material and represent an improvement over Kohn-Sham excitation energies in terms of accuracy. The calculations are carried out using the Tamm-Dankoff approximation (Hirata and Head-Gordon 1999). Knowledge of the excitation energies and corresponding transition probabilities allows one to calculate full set of optical properties.

To calculate TD-DFT optical properties

1. Choose *Modules | CASTEP | Calculation* from the menu bar.
2. Select the Properties tab.
3. Check the *Electronic excitations (TD-DFT)* option in the properties list.
4. Check the *Calculate energies* checkbox to obtain excitation energies.
5. Check the *Calculate optical properties* checkbox to calculate the transition probabilities which can be used for analysis.
6. If necessary, modify the number of excitations which should be calculated.

The excitation data will be reported in the `<seedname>_TDDFT.castep` output file.

In certain applications the lifetime of an excited state can be sufficiently long to justify the need for geometry optimization of this state; this requires calculation of forces within TD-DFT formalism which is provided by CASTEP.

To optimize geometry for a particular excitation

1. Choose *Modules | CASTEP | Calculation* from the menu bar.
2. Select the Properties tab.
3. Check the *Electronic excitations (TD-DFT)* option in the properties list.
4. Check the *Optimize geometry* checkbox.
5. Modify the excitation number which should have its geometry optimized.

The optimized structure for the specified excitation will be saved in the `<seedname>_TDDFT_GO.xsd` output file.

Limitations of electronic excitation calculations in CASTEP

The current version of CASTEP has a number of limitations related to the TD-DFT calculation of electronic excitations:

- The structure must be an insulator (the *Metal* checkbox on the Setup tab of the CASTEP Calculation dialog must be unchecked)
- Norm-conserving pseudopotentials must be used (see the Setting up pseudopotentials topic)
- Fixed orbital occupancies are required (see the Setting up SCF parameters topic)
- Only a Gamma point calculation is allowed, which should be sufficiently accurate for a "molecule in a box" geometry
- LDA+U calculations are not supported

Requesting Fermi surface data

Fermi surfaces are generated from information from CASTEP calculations which is stored in the .bands output file. In order to ensure that the Fermi surface generated is accurate it is recommended that you use as many k-points as is computationally viable. Fermi surfaces can be considered as the equivalent to isosurfaces in reciprocal space.

To generate Fermi surfaces for any CASTEP calculation

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the Electronic tab on the CASTEP Calculation dialog and click the *More...* button to open the CASTEP Electronic Options dialog.
3. Select the k-points tab and click the *Separation* radio button.
4. Specify a value of 0.01 1/Å or less for the k-point separation. This ensures that enough k-points are used over the entire calculation for generating the Fermi surface data.

To generate Fermi surfaces for a CASTEP calculation with DOS properties

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the Properties tab.
3. Check the *Density of states* option on the properties list and set the appropriate DOS options.
4. Click the *More...* button to open the CASTEP Density of States Options dialog.
5. Click the *Separation* radio button and specify a value of 0.01 1/Å or less. This ensures that enough k-points are used for generating the Fermi surface data without requiring such fine settings for the rest of the calculation.

Requesting NMR properties

NMR calculations can generate the shielding tensor and/or electric field gradients for all of the atoms in the selected system. NMR properties are very sensitive to atomic positions, which makes NMR such a useful experimental tool for structure analysis. This means that it is highly recommended to perform a geometry optimization run before the NMR calculation. If the structure of a crystal or molecule under investigation is obtained from an experimental study, it is advisable to optimize positions of hydrogen atoms first of all. If the forces on heavy atoms as reported by CASTEP are high (in excess of 1 eV/Å), complete structure optimization is recommended.

A detailed review of the CASTEP NMR formalism and numerous examples of practical applications are discussed in Bonhomme et al. (2012).

> **Note:** NMR in CASTEP is part of the separately licensed module NMR CASTEP. NMR calculations can only be performed if you have purchased this module.

Chemical shielding tensor

The chemical shielding tensor, σ(r), is defined as the ratio between an external applied magnetic field, **B**, and the non-uniform induced magnetic field, **B**$_{in}$*(r)*:

$$\mathbf{B}_{in}^{(1)}(\mathbf{r}) = -\overleftrightarrow{\sigma}(\mathbf{r})\mathbf{B}$$

The isotropic shielding, σ_{iso}, is given by one third of the trace of $\sigma(\mathbf{r})$. From the symmetric component of the shielding tensor, the chemical shielding anisotropy, σ_{aniso} and the asymmetry parameter, η, can be defined in terms of the principal components of the shielding tensor:

$$\sigma_{aniso} = \frac{\sigma_{zz} - (\sigma_{xx} + \sigma_{yy})}{2}$$

and:

$$\eta = \frac{\sigma_{xx} + \sigma_{yy}}{\sigma_{aniso} + \sigma_{xx}}$$

where:

$$|\sigma_{yy} - \sigma_{iso}| \leq |\sigma_{xx} - \sigma_{iso}| \leq |\sigma_{zz} - \sigma_{iso}|$$

For values of σ_{aniso} close to zero the asymmetry parameter will be ill-defined.

Electric field gradient

The interaction of a quadrupolar nuclei with an external magnetic field can be characterized by the quadrupolar coupling constant, C_Q, and the asymmetry parameter, η_Q. If the principal components of the traceless electric field gradient tensor are labeled, V_{xx}, V_{yy}, and V_{zz} such that:

$$|V_{zz}| \leq |V_{yy}| \leq |V_{xx}|$$

then:

$$C_Q = \frac{eQV_{zz}}{h}$$

where Q is the nuclear electric quadrupole moment, and:

$$\eta_Q = \frac{V_{xx} - V_{yy}}{V_{zz}}$$

For very small values of V_{zz} the asymmetry parameter will be ill-defined.

The value of the quadrupolar moment depends on the actual isotope; CASTEP makes a suggestion based on the most typical isotope used in solid state NMR experiments. The value of Q affects only the quadrupolar coupling constant, C_Q, calculated and printed out by CASTEP. If you find that the wrong value of Q was used you can rescale the generated C_Q constant using a different Q value.

> **Note:** The list of default values is based on the compilation by Pyykkö (2008). CASTEP versions prior to the 5.0 release used an older compilation by Harris (1996), so some results for quadrupolar coupling constants may have changed in later versions.

J-couplings

NMR J-coupling or nuclear spin-spin coupling is an indirect interaction of the nuclear magnetic moments mediated by the bonding electrons. It is manifested as the fine structure in NMR spectra, providing a direct measure of bond strength and a map of the connectivities of the system.

Induced magnetization density and current density are expected to be short-ranged. This forms the basis of using J-coupling as a tool for probing the strength of interatomic bonds. However, in a periodic calculation the perturbing nucleus can be viewed as similar to a defect in a defect calculation. Hence, sometimes it might be necessary to construct a supercell which is large enough to inhibit the interaction between the periodic defects or perturbations. Convergence with respect to the cell size should represent an important test in establishing accuracy of J-coupling calculations in either periodic systems or in molecule in a box calculations.

> **Note:** J-coupling can be calculated only for non-magnetic systems. J-coupling calculations are supported only for systems with P1 symmetry. If your crystal has symmetry other than P1, you will be prompted to convert the crystal symmetry to P1 before you can continue.

To calculate NMR properties

1. Choose *Modules | CASTEP | Calculation* from the menu bar.
2. Choose the Electronic tab on the CASTEP Calculation dialog and select On the fly from the *Pseudopotentials* dropdown list.
3. On the Properties tab, check the *NMR* option on the list of properties.
4. Select the properties you wish to determine:
   - *Shielding*
   - *EFG*
   - *J-coupling*
   - *G-tensor*
5. Choose the method you wish to use to determine the NMR properties from the *System type* dropdown list (Crystal, Molecule, or Auto). The Molecule option refers to the supercell description of isolated molecules.
6. If *J-coupling* is selected, then there are some requirements:
   - At least one atom in the system must be selected, J-couplings will be calculated between the selected atom(s) and all other atoms in the system
   - On-the-fly-generated pseudopotentials must be used
   - The *Relativistic treatment* of the on-the-fly-generated pseudopotentials (on the Electronic tab of the CASTEP Calculation dialog) must be set to either Schroedinger for non-relativistic treatment or ZORA for scalar-relativistic effects to be taken into account.

Note: NMR parameters will be calculated only for the elements for which the on-the-fly-generated pseudopotentials are chosen.

Tip: It is not recommended to use PW91 exchange-correlation functional when requesting NMR properties. PW91 functional may result in sharp real-space features of on-the-fly-generated pseudopotentials; PBE, RPBE, WC, BLYP, or PBESOL are better options when a GGA functional is required.

EPR G-tensor

Electron Spin Resonance (EPR - also known as Electron Paramagnetic Resonance) is a powerful experimental probe of the structure of defects in solids. EPR spectra of spin ½ centers are made up of two contributions:

- the hyperfine parameters
- the g-tensor

The g-tensor arises from the interaction of the electronic spin with external magnetic field. This term plays a somewhat similar role to the shielding in NMR; induced electronic currents in the sample modify the g tensor from its vacuum value.

EPR spectrum can be modeled using the following effective Hamiltonian, bilinear in the total electron spin S, and the applied uniform magnetic field or nuclear spins, B and I_I, respectively:

$$H_{eff} = \frac{\alpha}{2} S \cdot g \cdot B + \sum_I S \cdot A_I \cdot I_I$$

where:
atomic units are used

α is the fine structure constant
the summation I runs over the nuclei

The tensors A_I are the hyperfine parameters, and the tensor g is the EPR g-tensor.

Requesting non-linear optical properties

Second harmonic generation (SHG) coefficients determine the efficiency of non-linear optical (NLO) materials for applications in optoelectronics. The formalism for CASTEP calculations of NLO properties is similar to that for Raman intensity calculations and relies on density functional perturbation theory. All the limitations currently in place for linear response calculations of vibrational properties also apply to the calculation of SHG coefficients, see Requesting vibrational properties for more information.

You can correct numerical values of the calculated SHG coefficients by taking into account systematic underestimation of the band gap in DFT calculations. Use the following workflow for calculation of nonlinear optical properties:

1. Carry out an accurate geometry optimization calculation using a GGA exchange correlation functional, such as WC or PBE. Specify the *Quality* as Ultra-fine.

2. Perform a band structure calculation for the relaxed geometry and extract the value of band gap.

3. Obtain an estimate of a true band gap.

   Use an experimental band gap value when it is available, or perform a band structure calculation. For example, perform a band structure calculation with screened exchange (sX-LDA) functional or a hybrid functional, like HSE0. This can obtain a more accurate band gap than that calculated by a GGA calculation.

4. Use the difference between a GGA band gap and a more accurate value to define the *Scissors operator* value; this effectively shifts the conduction bands up in a CASTEP calculation.

> **Note:** Calculation of non-linear optical properties is only reasonable for crystals without a center of symmetry.

The "Nonlinear Optical Susceptibility" section of the `seed_NLO.castep` output file provides the results of the SHG calculation. The 3×6 d_{ij} tensor reported can contain small numerical noise that violates crystal and Kleinman symmetry. In addition, the tensor's presentation might be in a non-standard lattice orientation, especially for hexagonal and trigonal lattice types. The same output file contains a symmetrized and, where relevant, rotated to standard representation d_{ij} tensor.

> **Note:** Numerical noise in the elements of d_{ij} tensor (that ought to be zero by symmetry) usually reflects the level of convergence with respect to the quality of k-point sampling of the Brillouin zone. If you encounter such noise, you should verify the convergence of the calculated values with respect to the number of k-points. Under-converged results can include significant errors, especially for crystals with small band gaps.

To request calculation of non-linear optical properties

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.

2. Select the Properties tab.

3. Select the *Non-linear optical properties* checkbox in the list of properties.

4. Optionally, alter the accuracy of the calculation by changing the value of the *Convergence tolerance*.

5. If you know the value of the scissors operator, enter this in the *Scissors operator* text box.

Requesting optical properties (DFT)

CASTEP currently implements two approaches for optical properties calculations; one is based on standard DFT Kohn-Sham orbitals and the other uses more accurate but much more time-consuming time-dependent DFT (TD-DFT) theory. In this section we consider only DFT Optical properties. Setting up TD-DFT optical properties calculations are described in the section Requesting electronic excitations (TD-DFT).

Calculating optical properties produces electronic energies on the Monkhorst-Pack mesh of k-points and the matrix elements for electronic interband transitions. The CASTEP Analysis dialog can be used to generate observable optical properties based on this information. Detailed analysis of the impact of calculation parameters (k-point set, number of empty bands, and so on) on the accuracy of the optical properties generated can be found in the Optical properties theory topic.

> **Note:** You are not required to use the same exchange-correlation functional in the optical properties calculation as in the main calculation. This allows you to select a nonlocal screened-exchange functional to study the optical properties after performing, for example, geometry optimization with a variable cell using the GGA functional.

To calculate optical properties

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the Properties tab.
3. Check the *Optical properties* option on the properties list.
4. If necessary, modify the *Number of empty bands* to include more or less states in the conduction band.

> **Note:** The number of empty bands used should be greater when calculating optical properties than for band structure or density of states calculations (see the Optical properties theory topic for more details).

5. Optionally, adjust the density of Monkhorst-Pack k-points used for the optical properties calculation by using *k-point set* dropdown list.
6. Click the *More...* button to open the CASTEP Optical Properties Options dialog. This dialog gives you complete control over setting up the grid.
7. Check *Use separate XC functional for optics calculation* on the CASTEP Optical Properties Options dialog if you want to use, for example, a nonlocal functional for the optical properties calculation.
8. Select the alternative *Functional* you wish to use from the dropdown list on the same dialog.

Requesting orbital analysis

Although wavefunctions are generated by every CASTEP run, they are not returned to the client by default, as the file containing the wavefunctions is very large. To perform orbital analysis it is necessary to explicitly request that these files be returned to the client.

> **Note:** Orbitals are required to calculate the STM profile.

To perform an orbitals analysis

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the Properties tab.
3. Check the *Orbitals* option on the properties list.

Requesting Vibrational Properties

CASTEP allows you to prepare calculations that provide vibrational frequencies and eigenvectors at a selected group of q-vectors in the Brillouin zone. CASTEP provides two approaches to calculating these data:

- Linear response formalism
- Finite displacement method

There are two predefined modes of calculation: the phonon dispersion spectrum along high symmetry directions and the phonon density of states spectrum, which is a prerequisite for the calculation of thermodynamic properties.

> **Note:** Phonon calculations take into account existing fixed atom constraints, regardless of the overall *Task* setting. Such fixed atoms are excluded from the calculation of vibrational properties, which corresponds to the "partial Hessian" approach. Constrained lattice dynamics approach is applied for both linear response and finite displacement approach.

> **Tip:** Select *Fix fractional position* on the *Atom* tab of the Edit Constraints dialog, accessible from the *Modify* menu.

Phonon Frequencies from Linear Response Calculations

The linear response scheme treats atomic displacements as perturbations. In addition, it evaluates an electric field response to calculate a non-analytical correction to longitudinal optical (LO) phonon frequencies at the Γ-point. Longitudinal and transverse modes at the Γ-point are identical (no LO-TO splitting), unless you apply this correction.

The linear response scheme allows the calculation of phonon spectra in any commensurate or incommensurate q-vector of the reciprocal space. This provides full flexibility in the choice of q-vectors to use for calculations. Nevertheless, linear response calculations at a general q-vector are very time consuming and often unnecessary as a real space dynamical matrix that defines vibrational properties is often a short range property. You can use a coarse Monkhorst-Pack mesh to calculate this real space dynamical matrix and then use it to obtain the phonon spectrum at any given q-vector in the Brillouin zone. Thus, there are two major modes of linear response calculations: direct and using interpolation.

Limitation of the Linear Response Implementation in CASTEP

This version of CASTEP supports linear response calculations of phonons or finite displacement calculations that require LO-TO splitting correction only for LDA and GGA exchange correlation functionals and norm-conserving pseudopotentials. For more information, see Setting up pseudopotentials.

CASTEP linear response does not support:

- Spin-orbit coupling
- Non-collinear spin polarization
- DFT+U
- D4 method for DFT-D correction

Phonon Frequencies from Finite Displacements Calculations

CASTEP provides an alternative method of calculating phonon frequencies that is based on the finite displacements method (Montanari and Harrison, 2002). This technique is based on the numerical differentiation of forces on atoms calculated for a number of unit cells with atomic displacements. CASTEP determines the optimum number of such displacements automatically, based on the crystal symmetry. Displacements with a very small magnitude give results that are similar to the linear response

frequencies. An advantage of the finite displacements method is that it is also possible to investigate phonon anharmonicity by increasing the amplitude of the displacements. A further important advantage is that you can use efficient ultrasoft potentials to obtain vibrational frequencies.

The formalism is based on evaluation of the dynamical matrix at a (coarse) commensurate grid of q-points at the cost of creating a supercell. Then the dynamical matrix is re-interpolated onto a requested group of q-points. There are two available approaches to dynamical matrix calculation:

- Create a large supercell with the size defined by a real space cutoff parameter; the supercell size then dictates a coarse grid.
- Create a set of non-diagonal supercells (Lloyd-Williams and Monserrat, 2015) which are commensurate with a q-point group of a coarse grid. In this case, the grid spacing for interpolation defines the coarse grid.

Limitations of the Finite Displacements Implementation in CASTEP

There is a limitation with the implementation of the finite displacements method in CASTEP related to the treatment of the non-analytical term responsible for the LO-TO splitting in insulators. This term is calculated using linear response with an electric field as a perturbation. Therefore, the computational limitation applies to finite displacements calculations if you request LO-TO splitting.

Note: An LO-TO calculation imposes the restriction that applies when you use the linear response technique. You might want to proceed with finite displacement calculations without LO-TO splitting if this restriction affects your study. This case only reliably produces TO modes when there is LO-TO degeneracy in the results.

Requesting Phonon Dispersion

Calculating the phonon dispersion produces phonon frequencies and eigenvectors along high symmetry directions in the Brillouin zone. The standard path for each lattice type is taken from Bradley and Cracknell (1972). You can modify the path using the Brillouin Zone Path dialog. The *Quality* in the *Dispersion* section on the CASTEP Phonon Properties Setup dialog controls the density of points along the path, which affects the appearance of the resulting chart.

To calculate phonon dispersion

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.
2. Select the Properties tab.
3. Select *Phonons* in the list of properties, then select *Dispersion* below the list.
4. If required, select *Calculate LO-TO splitting*.
5. Select the technique to use to calculate the phonon frequencies as the *Method*.
6. Click *More...* to display the CASTEP Phonon Properties Options dialog.
7. For linear response calculations, specify the convergence criterion for the force constants in *Convergence tolerance*.

   If you do not want to carry out a direct calculation, select *Use interpolation* and specify the q-point separation in *q-vector grid spacing for interpolation*.

   For finite displacement calculations, specify the cutoff radius to use to construct the appropriate supercell in *Supercell defined by cutoff radius*.

8. Optionally, adjust the density of q-vectors along the high symmetry directions used for the phonon dispersion calculation using the *Quality* control in the *Dispersion* section.

9. If you want to inspect or modify the Brillouin zone path used for the phonon dispersion calculation, click *Path...* to display the Brillouin Zone Path dialog and alter the path segments accordingly.

10. Optionally, use the partial Hessian approach to accelerate the calculation. Apply fixed atom constraints to the atoms that are not essential to the calculation; for example, the atoms in a molecule on surface calculations.

Requesting Phonon Density of States

Calculating the phonon density of states produces phonon frequencies and eigenvectors on the regular Monkhorst-Pack mesh of q-vectors. CASTEP requires this information to produce either the total or projected (partial) phonon density of states and, thus, to calculate thermodynamic properties. The *Quality* setting in the *Density of states* section on the CASTEP Phonon Properties Options dialog controls the quality of the q-vector.

> **Note:** When you request phonon density of states CASTEP also calculates atomic displacement parameters, allowing assignment of temperature factors during analysis.

To calculate the density of states

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.

2. Select the *Properties* tab.

3. Select *Phonons* in the list of properties, then select *Density of states* below the list.

4. If required, select *Calculate LO-TO splitting*.

5. Select the technique to use to calculate the phonon frequencies as the *Method*.

6. Click *More...* to display the CASTEP Phonon Properties Options dialog.

7. For linear response calculations, specify the convergence criterion for the electronic eigenvalues in *Convergence tolerance*.

   If you do not want to carry out a direct calculation, select *Use interpolation* and specify the q-point separation in *q-vector grid spacing for interpolation*.

   For finite displacement calculations, specify the cutoff radius to use to construct the appropriate supercell in *Supercell defined by cutoff radius*.
   Optionally, use the *Quality* control in the *Density of states* section to adjust the density of Monkhorst-Pack q-vectors used for the phonon density of states calculation.

8. If you want to inspect or modify the setup of the Monkhorst-Pack grid, click *More...* to display the Phonon Density of States Options dialog and alter the settings accordingly.

9. Optionally, use the partial Hessian approach accelerate the calculation. Apply fixed atom constraints to the atoms that are not essential to the calculation; for example, the substrate atoms in a molecule on surface calculations.

> **Tip:** If you choose quality gamma frequencies, then CASTEP only calculates eigenvectors at the Γ-point, which determines most of the experimental data on IR or Raman spectra. This can accelerate finite displacement calculations tremendously as no supercell is constructed for this case. However, the accuracy of thermodynamic properties obtained with this single q-vector is very poor as it does not take into account any acoustic degrees of freedom.

Calculating Vibrational Frequencies of an Isolated Molecule

You can use CASTEP to calculate the vibrational frequencies of isolated molecules as well as the phonon dispersion of solids. Use only the Γ-point for electronic calculations and request the Γ-point when performing either phonon dispersion or phonon density of states calculations. In addition, the all

bands/EDFT electronic minimizer is known to be more efficient for studies of isolated molecules in supercell geometry than the density mixing minimizer. Therefore, change the *Electronic minimizer* to All Bands/EDFT on the SCF tab of the CASTEP Electronic Options dialog when performing such calculations.

> **Tip:** Calculations for "molecule in a box" systems that do not require geometry optimization can be sped up if the molecular symmetry is utilized. Use the Find Symmetry tool to find and apply the symmetry of the molecule to the supercell.

> **Note:** Do not calculate LO-TO splitting for a "molecule in a box" system. There is no physical meaning to this term when studying molecular, rather than crystalline, vibrations.

Guidelines for the Successful Calculation of Vibrational Properties Using CASTEP

1. Parameters for geometry optimization

   Starting from a well-converged geometry for the input structure leads to inaccurate results of a phonon calculation. Well-converged forces ensure a true ground state for the geometry optimization.

   In general, using a *Quality* setting of Ultra-fine for the geometry optimization on the Setup tab of the CASTEP Calculation dialog ensures accurate forces. The safest procedure is to investigate the convergence of the forces as a function of calculation parameters; primarily the k-point sampling. Carry out a series of single-point energy calculations using increasingly dense k-point meshes. Monitor the convergence of the forces until they converge to within the force tolerance criterion.

2. Geometry optimization of the input structure

   Once you have generated reasonably well-converged forces, you can carry out the geometry optimization. Use the same force convergence tolerance as for the force convergence test. A well-converged geometry optimization is of little value if the forces are inaccurate because of convergence errors.

   You may want to perform a fixed-cell or variable-cell geometry optimization, depending on your goals for the calculation. The lattice-dynamical problem is well-defined in either case, but the pressure or stress differs. Also monitor the convergence of the stress before carrying out a variable-cell optimization (though the behavior is usually similar to the convergence of forces).

3. Use of consistent electronic settings

   To be a valid lattice dynamics calculation, the phonon run must use the same specification as the geometry optimization. If you want to change anything of significance, such as the cutoff, XC functional, or k-point sampling, you must carry out a fresh geometry optimization using these new settings before starting the lattice dynamics run.

4. Checking the convergence of the results

   Unfortunately, following the above guidelines does not guarantee that your final phonon frequencies converge to any given tolerance. The only way to determine that this is the case is to verify the convergence behavior of the final properties. This requires a subtle judgment of whether you are measuring a 'primary' change resulting from the convergence of force constants or a 'secondary' one consequent on the slightly different geometry.

   As noted in the literature, and from experience, phonon frequencies are more sensitive to k-point convergence than geometries, assuming tolerance criteria of a few cm^{-1} and a few hundredths of an angstrom. Acoustic phonons near the Γ-point are the most sensitive, as they depend on near-cancellation between large force constant terms in the dynamical matrix. Dielectric properties and Born charges tend to be more sensitive than phonons, on a fractional proportion tolerance.

The ultimate convergence test would require geometry optimization performed for a denser k-point grid, followed by a new phonon calculation - this is the only way to determine whether the k-point sampling has an effect on the accuracy of the calculated vibrational frequencies.

> **Note:** Phonon spectra in metallic compounds are very sensitive to the details of the Fermi surface. To obtain reasonable spectra using the linear response method for metals, the k-point sampling must be extremely dense: much denser than the Fine mesh. Consider specifying a value of less than 0.02 for the *Separation* parameter on the k-points tab of the CASTEP Electronic Options dialog. A clear sign of insufficient quality of k-point sampling is the presence of imaginary acoustic modes near the Γ-point.

Requesting Polarizability, IR, and Raman Spectra

Within the electric field linear response formalism, CASTEP enables you to calculate optical ($\omega = \infty$) and dc ($\omega = 0$) dielectric permittivity or optical ($\omega = \infty$) and static ($\omega = 0$) molecular polarizability. CASTEP calculates these properties when you specify either Efield or Phonon+Efield for the TASK keyword in the input parameters (`.param`) file. Specifying Efield also calculates infrared intensities (response to an electric field in the infrared range) , if the phonon k-points include a Γ-point.

The calculated results are somewhat sensitive to the value of the scissors correction. This correction amounts to the difference between the calculated and experimental band gap. If you have experimental data, you can estimate this correction by performing the band structure run with CASTEP and comparing the calculated band gap with the experimental value.

To calculate polarizability, IR and Raman spectra

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.

2. Select the Properties tab.

3. Select *Polarizability, IR and Raman spectra* in the list of properties.

4. Choose the correct description of the system for the *System type* (Crystal, Molecule, or Linear molecule).

   The last two options refer to the supercell description of isolated molecules.

5. Specify whether to *Calculate Raman intensities*.

6. Click *More...* to open the CASTEP IR and Raman Options dialog.

7. Optionally, alter the accuracy of the calculation by entering a new value in the *Convergence tolerance* field.

8. If you know the value of the scissors operator, enter it as the *Scissors operator* and close the dialog.

Calculating the Polarizability, IR and Raman Spectra of an Isolated Molecule

You can use CASTEP to calculate the electric field response of isolated molecules as well as of solids. Use only the Γ-point for electronic calculations on molecular systems. In addition, the all Bands/EDFT electronic minimizer is known to be more efficient for studies of isolated molecules in supercell geometry than the density mixing minimizer. Therefore, change the *Electronic minimizer* to All Bands/EDFT on the SCF tab of the CASTEP Electronic Options dialog when performing such calculations.

> **Tip:** Calculations for "molecule in a box" systems that do not require geometry optimization can be sped up if the molecular symmetry is utilized. Use the Find Symmetry tool to find and apply the symmetry of the molecule to the supercell.

Note: It is important to select the correct description of the system as the *System type* when calculating the electric field response for a molecular system. The wrong system description can significantly affect the molecular polarizability values obtained.

Limitations of the Electric Field Response Implementation in CASTEP

This version of CASTEP has some limitations related to electric field response calculations. The supported settings for electric field response calculations are:

- Norm-conserving pseudopotentials (see the Setting up pseudopotentials topic)
- Fixed orbital occupancies (see the Setting up SCF parameters topic)

Note: Selecting *Fix occupancy* on the SCF tab of the CASTEP Electronic Options dialog uses fixed orbital occupancies. This is not sufficient if DFT results from a non-spin-polarized calculation indicate that the system under investigation is nonmetallic. Attempting to study a metallic system using fixed orbital occupancies results in poor convergence of the electric field response calculation. The symptoms are very large numbers for IR and Raman intensities and for polarizability in the output file. If this is the case, investigate whether your system is metallic by running either density of states or band structure calculations.

If the configuration violates any of these restrictions, an error message displays with an explanation of the problem. You must change the offending setting to proceed with the calculation.

Requesting polarization

Polarization is a fundamental property that is not easy to define and calculate in an infinite solid. CASTEP implements the Berry phase approach to define spontaneous polarization unambiguously. For a comprehensive explanation of the modern theory of polarization, see Spaldin (2012) .

If the task is Elastic Constants, CASTEP applies predefined strains to the original structure, optimizes atomic coordinates in the deformed structures, and calculates spontaneous polarization. CASTEP then uses calculated values of polarization to evaluate the piezoelectric strain tensor, through numerical differentiation of polarization with respect to applied strain:

$$e_{\alpha,j} = \frac{\partial P_\alpha}{\partial \epsilon_i}$$

The piezoelectric strain tensor is related to the piezoelectric stress tensor, through the elastic coefficients tensor that connects strain and stress responses:

$$d_{\alpha,j} = \frac{\partial P_\alpha}{\partial \sigma_i}$$

In the full unfolded form of these tensors, the connection is:

$$e_{ijk} = C_{jklm} d_{ilm}$$

Note: Polarization calculations are not allowed if you use any of the following settings:

- Ultra-soft pseudopotentials
- Spin-polarized calculation
- DFT+U
- Spin-orbit coupling with non-collinear spins
- External electric field
- Mixture atoms

To request calculation of polarization

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.

2. Select the Properties tab.

3. Check the *Polarization* checkbox in the list of properties.

Requesting population analysis

Performing population analysis produces Mulliken charges, Mulliken magnetic moments, Mulliken partial charges for each angular momentum component, Mulliken bond populations (charge and spin), and Hirshfeld charges. You can use the *Distance cutoff for bond populations* option on the Properties tab to limit the amount of output from the bond population analysis. You can also use the *Calculate band populations* option to calculate the band contributions to the Mulliken charges, so that the results can be used to generate a PDOS chart.

If a system has a P1 symmetry orbital-resolved Mulliken populations are returned for each atom, specifying the amount of charge in, for example, the *px*, *dxy* (and so on) orbitals.

> **Tip:** The *Population analysis* checkbox on the Properties tab of the CASTEP Calculation dialog is checked by default.

> **Note:** It is not possible to specify the number of atomic orbitals to be used in the population analysis explicitly in the CASTEP interface. If the spilling parameter reported in the `.castep` output file is too large (more than 5%), it may be that the default CASTEP parameters were insufficient for this calculation. In such circumstances you should edit the `.cell` file and change the SPECIES_LCAO_ STATES parameters for atomic species, then run the input files again. The `SPECIES_LCAO_` `STATES` parameter for a species should be set such that it results in a complete set of angular momentum states. For example, to use a single *s* and single *p* state `SPECIES_LCAO_STATES` must be 2.

To perform population analysis

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.

2. Select the Properties tab.

3. Ensure that the *Population analysis* option on the properties list is checked.

4. Optionally, modify the *Distance cutoff for bond populations* field to include more or less atomic pairs in the calculation.

5. If you wish to generate partial and local densities of states for the valence band, check the *Calculate band populations* option.

Requesting solvation energy

Calculating solvation energy in CASTEP involves performing two separate calculations for an isolated molecule in a supercell: one to simulate the molecule in a vacuum, and another to include the implicit solvation model. The `seedname_Solv.castep` file reports the solvation energy.

> **Note:** There are certain limitations for solvation energy calculations:
> - The system must represent a molecule in a box.
> - Symmetry of the system must be P1.
> - Calculations must not include spin-polarization.
> - Stress calculations are not available.

Note: Use at least a Fine FFT grid *Density* for solvation calculations; the Precise density is even better. You can specify the FFT grid *Density* on the Basis tab of the CASTEP Electronic Options dialog. Also use an increased value of *Augmentation density scaling factor*, for example 1.5-2.0 instead of the default value of 1.0.

An increased FFT density and energy cutoff can help to eliminate convergence errors for the multigrid solver for electrostatics in a solvent.

To perform a solvation energy calculation

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.

2. Select the Properties tab.

3. Select the *Solvation energy* checkbox in the list of properties.

4. Select the Electronic tab on the CASTEP Calculation dialog. Click **More...:** to open the CASTEP Electronic Options dialog.

5. Select the Solvent tab.

6. From the *Solvent* list, select the solvent to use.

7. If you want, you can specify the dielectric constant of the solvent in the *Dielectric constant* field.

8. Keep selection of the *Include apolar term* and *Account for solute-solvent dispersion repulsion* checkboxes as a robust default setting.

9. If you want, you can specify the surface tension of the solvent in the *Solvent surface tension* field (in units of N/m).

Requesting stress analysis

Calculating stress involves performing a stress tensor calculation, even when the cell parameters are fixed. The stress is a useful measure of the accuracy of the structural description: for example, after performing geometry optimization with a fixed cell, you can get an idea of how accurate the cell parameters are from the magnitude of the remaining stress. Similarly, when studying an isolated molecule in a supercell, the value of the stress provides a guide as to the size of the cell required to remove unphysical interactions between periodic images.

Note: It is important to use finite basis set correction when calculating the stress tensor (see Setting up the basis set for details). Choosing either Smart or Always as the *Apply finite basis set correction* setting on the Basis tab of the CASTEP Electronic Options dialog will achieve this.

To perform a stress analysis

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.

2. Select the Properties tab.

3. Check the *Stress* checkbox in the list of properties.

4. Select the Electronic tab.

5. Click the *More...* button to display the CASTEP Electronic Options dialog.

6. Select the *Basis* tab.

7. Select either Smart or Always from the *Apply finite basis set correction* dropdown list.

Manipulating files

CASTEP is a file-based application which means that all input information is provided in various ASCII text files and the output is delivered in a mixture of text and binary files. This section describes some file handling issues which may arise, especially when the CASTEP server is run in a standalone mode and not through a gateway.

Input files

CASTEP allows you to save input files, for subsequent manual editing instead of running the job directly.

To save input files

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Click the *Files...* button to open *CASTEP Job Files* dialog.
3. Click the *Save Files* button.

> **Note:** The *Save Files* button is enabled only if a suitable 3D model document is active.

Only one input file, .param, is displayed in the Project Explorer. This file contains the parameters specified using the CASTEP interface. However, it also contains a few parameters that allow you to access functionality which is not supported though the interface. The other input files are hidden, since they are unlikely to be edited manually.

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

To run CASTEP using an existing set of input files

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Click the *Files...* button to open *CASTEP Job Files* dialog.
3. Click the *Run Files* button.

> **Note:** The *Run Files* button is enabled only if a suitable .param file is active.

If your server does not support the gateway protocol, you may have to run CASTEP in standalone mode using the `RunCASTEP.sh` or `RunCASTEP.bat` files provided with the installation.

In such circumstances it is necessary to copy all the input files from the Materials Studio Project folder to the appropriate directory on the server machine. The scripts required for standalone execution are provided with accompanying `RunCASTEP.Readme` files that explain, in detail, how to use them. Alternatively, you can obtain help by typing one of the following:

```
RunCASTEP.sh –h
```

```
RunCASTEP.sh
```

> **Note:** The Materials Studio Project folder does not contain the pseudopotential files required to run a job. When transferring input files to the server, you must therefore determine which pseudopotential files are required by examining the .cell file. Then you must locate those potential files in Materials Studio installation, typically in a sub-directory called share\Resources\Quantum\Castep and copy the required files to the same directory on the server as the rest of the input files.

Output files

Only one output file, .castep, is displayed in the Project Explorer. However, there are many more files created during a CASTEP run. These are hidden by Materials Studio. All of these output files are placed in the correct Materials Studio Project folder automatically, when the job is run using the Gateway.

However, if CASTEP is run in standalone mode, the output files must be copied manually from the server to the appropriate Project folder.

Some output files can be quite large. If these files are not likely to be required to restart the job, then it is recommended that you delete or archive them periodically.

Restarting a CASTEP calculation

It is not possible to restart a completed CASTEP job automatically using the interface. However, there are circumstances in which you may wish to do this, for example, if you are running a geometry optimization which does not converge in the given number of steps, or a you wish to continue your calculation with manually modified runtime parameters. To restart such jobs you should edit `.param` file and add the CONTINUATION keyword to the file.

> **Note:** Any additional changes to this file may make it impossible to restart the CASTEP job successfully.

> **Tip:** It is possible to remove everything from `.param` and leave only the CONTINUATION line. This will ensure that all of the settings remain exactly the same as those from the previous run.

> **Note:** In order to restart a job, the output files from the previous run must be present in the Project folder. This check and the subsequent transfer of the files to the server happens automatically whenever CASTEP is used to run an existing file set or to calculate additional properties.

Analyzing CASTEP results

CASTEP results can be analyzed when a job has been completed and all of the output files have been downloaded successfully to the appropriate results folder.

Select the results to be analyzed by opening the structure document in the results folder or the results (`.castep`) file from the CASTEP calculation. This allows you to analyze all related CASTEP results.

> **Note:** The structure is updated automatically on successful download of output files from a completed CASTEP job that was run using a gateway (the structure is not automatically updated if the CASTEP job was run in standalone mode).
>
> The atoms in the updated structure document have an extra property, ServerAtomName, associated with them. This shows the atom sequence numbers as used in the CASTEP output files and can be seen by labeling atoms in the structure with the ServerAtomName property. (This property will be seen only in structures generated from CASTEP and other similar applications).
>
> All other analysis functions require you to perform certain actions using the CASTEP Analysis dialog.

> **Note:** Only structure updates take place automatically after a CASTEP job is completed and the results files have been downloaded successfully (this only applies to jobs that are run on a server through the gateway, not jobs that are run in a standalone mode). All other analysis functions are performed manually, using the options on the CASTEP Analysis dialog.

Displaying trajectory and chart data

Depending on the type of calculation performed, a CASTEP run may produce a trajectory document and one or more chart documents. These documents have a special association with each other because each of the points on the graphs correspond to a frame in the trajectory.

CASTEP produces a trajectory (`.xtd`) file whenever you run a geometry optimization, molecular dynamics or elastic constants calculation, or a transition state search. In all cases, a history of the optimization is returned in a file called *<name>* `Trajectory.xtd`, where *<name>* is the name used for the job description on the Job Control tab of the CASTEP Calculation dialog.

When you run a geometry optimization, two chart documents are generated:

- *<name>* `Energies.xcd`: Contains a plot of total energy vs. frame for all steps of the calculation
- *<name>* `Convergence.xcd`: Contains three (possibly four) plots that describe the degree of convergence of the optimization as a function of frame:
  - Change in energy vs. frame
  - Maximum Cartesian force vs. frame
  - Maximum Cartesian step size vs. frame
  - Maximum stress tensor component vs. frame (for cell optimization runs)

Because these values span several orders of magnitude, the data are plotted on a $\log_{10}$ scale.

Similar charts are produced for each structure in an elastic constants calculation.

When you run a transition state search, a single chart containing a graph of energy vs. reaction coordinate for each step of the calculation, *<name>* `TSSearch.xcd`, is generated. This includes an individual graph for each LST or QST 'uphill' cycle as well as a graph for each conjugate gradient minimization. The CASTEP Transition State Search task topic contains more details.

When you run a molecular dynamics simulation, either two or three chart documents are generated:

- *<name>* `Constant.xcd`: Contains a plot of the constant of motion vs. simulation time
- *<name>* `Temperature.xcd`: Contains a plot of temperature vs. simulation time
- *<name>* `Pressure.xcd`: Contains a plot of pressure vs. simulation time (only produced by the NPH or NPT ensemble)

Trajectory files can be animated using the controls on the Animation toolbar.

If you have access to the Forcite module, you may find some of its dynamics, statistical, and structural analysis features useful for analyzing trajectories. Refer to the Using Forcite Analysis topic for details.

Creating a trajectory and chart

When you run CASTEP using the Materials Studio interface, the creation and display of these trajectories and charts is automatic. If you selected *Automatically view output* on the CASTEP Job Control Options dialog, the graphs will be displayed automatically on completion of the run. If you selected *Update graphs* on the CASTEP Job Control Options dialog, these graphs will be displayed and updated with intermediate results throughout the course of the calculation.

To create charts from output files generated by a standalone calculation

1. Download the files from the compute server to your PC using the procedure described in Running CASTEP in standalone mode. Be sure to retrieve the `.check`, `.castep`, and `.geom`, `.md`, or `.ts` files.
2. Select *Modules | CASTEP | Analysis* from the menu bar.
3. Select Energy evolution from the list on the CASTEP Analysis dialog.
4. Make sure that the `.castep` file is the currently active document.
5. Click the *View* button.

If you used the Materials Studio interface to set up and launch your job, you can regenerate the chart documents by following a similar procedure.

To regenerate charts

1. Open either the `.xsd` or `.castep` file and make it the currently active document.

2. Select *Modules | CASTEP | Analysis* from the menu bar.

3. Select Energy evolution from the list on the CASTEP Analysis dialog.

4. Click the *View* button.

Animating the trajectory

You can use the controls on the Animation toolbar to animate the trajectory, stepping through each of the frames of the document. If the chart is open during the animation, the point corresponding to the active frame will be highlighted.

Chart Viewer point selection

Alternatively, you can use Chart Viewer point selection to display the trajectory frames of the points you select from the chart document.

To display a trajectory frame for a point on a chart document

1. Choose the *Selection* tool on the Chart Viewer toolbar to enter selection mode.

2. Making sure you have the corresponding trajectory document open, select a data point on the chart document.

3. The corresponding trajectory frame is displayed.

4. Drag the mouse over other data points on the chart document to display their corresponding trajectory frames.

5. If CASTEP generated multiple chart documents, the related data points will be highlighted on all of them.

> **Tip:** To make it easier to see the chart and trajectory documents, close all the other documents and then maximize the sizes of these two documents by selecting *Window | Tile Vertically* from the menu bar.

Visualizing volumetric data

You can visualize the spatial distribution of electronic charge, electron density difference, electron localization function, and electrostatic potential calculated by CASTEP. In addition, charge densities of particular orbitals and the approximate STM profile for surfaces in a slab supercell geometry can be visualized. The relevant data from the CASTEP results files are used to add a field to the model. This field can be visualized in a variety of ways (direct field visualization, isosurfaces, slices, and so on).

- Electronic charge
- Electron density difference
- Electron localization function
- SCF local potential
- Orbitals
- STM profile
- Field visualization

Electronic charge

Materials Studio uses the information stored in the CASTEP binary output file to create a field that corresponds to the electronic charge. When you analyze a spin-polarized calculation, you can create

additional separate fields for the density of spin-up (alpha) or spin-down (beta) electrons, as well as a field for the spin density (the difference between the density of alpha and beta electrons). The latter field allows you to visualize the spatial distribution of the magnetic moment in a spin-polarized system.

> **Note:** Maxima in the electronic density field correspond to interatomic bonds or to the position of atoms that have semicore states which are explicitly treated as valence. When there are no semicore states in the system (this can be verified by analyzing the atomic charges displayed on the Potentials tab of the CASTEP Electronic Options dialog), the density will display minima at the positions of atomic nuclei. This is to be expected in the pseudopotential formalism.

To create a density field

1. Choose *Modules | CASTEP | Analysis* from the menu bar to open the CASTEP Analysis dialog.
2. Select Electron density from the list of properties.
3. Ensure that the 3D Atomistic document to be analyzed is the active document.
4. For spin-polarized calculations, select the type of field required from the *Density field* dropdown list.
5. Optionally, check the *View isosurface on import* checkbox to automatically create an isosurface when the density field is imported.
6. Click the *Import* button.

You also have the option of creating a plain text file which contains the values of charge (and spin, when appropriate) density on a regular grid along three lattice vectors. The file has the extension `.charg_frm` and is hidden by default. Select *Tools | Folder Options...* in the Windows File Explorer to open the Folder Options dialog, then select the *View* tab and click the *Show hidden files and folders* radio button to reveal the hidden file. The format of the file is self-explanatory:

```
a       b       c       Charge
1       1       1       1.8133362740
2       1       1       1.5071161497
3       1       1       1.1111633102
4       1       1       0.9584556846
```

or, for a spin-polarized calculation:

```
a       b       c       Charge          Spin
        1       1       1       1.8130116660    0.0006370238
        2       1       1       1.5068114569    0.0004814296
        3       1       1       1.1108593919    0.0002249406
        4       1       1       0.9580778273    0.0001768619
```

> **Note:** The charge and spin density in the `.charg_frm` file are in the same units as those used by CASTEP during calculations. The values are normalized to the number of electrons per cell. The density fields displayed in the 3D model are, however, normalized to the number of electrons per $Å^3$.

To create a plain text density file

1. Choose *Modules | CASTEP | Analysis* from the menu bar to open the CASTEP Analysis dialog.
2. Select Electron density from the list of properties.
3. Click the *Save density to file* button.

Electron density difference

Materials Studio provides the option of generating the electron density difference in two different ways:

- Electron density difference with respect to a linear combination of the atomic densities
- Electron density difference with respect to a linear combination of the densities of sets of atoms contained in the model

The former option produces a density difference field which shows the changes in the electron distribution that are due to formation of all the bonds in the system. This object is appropriate for bulk solids to illustrate the charge redistribution due to chemical bonding.

The latter option generates a density difference field which effectively corresponds only to the formation of bonds between atoms in different sets and to charge redistribution within the sets that is due to the presence of other sets. This property is useful to describe such processes as bonding of molecule(s) to external and internal (for example, zeolites) surfaces or creation of large molecules from smaller fragments.

To create a density difference field

1. Choose *Modules | CASTEP | Analysis* from the menu bar to open the CASTEP Analysis dialog.
2. Select Electron density difference from the list of properties.
3. Ensure that the 3D Atomistic document to be analyzed is the active document.
4. Use the *Use atomic densities* checkbox to request the density difference with respect to a linear combination of the atomic densities. The density difference with respect to the sets of atoms will be produced when this checkbox is unchecked.
5. Optionally, check the *View isosurface on import* checkbox to automatically create an isosurface when the potential field is imported.
6. Click the *Import* button.
7. A field is created in the model; its name is either "CASTEP density difference from atoms" or "CASTEP density difference from sets", depending on whether the *Use atomic densities* checkbox is checked.

> **Note:** Analysis based on atomic densities requires the presence of a binary file with the extension `.chdiff`; analysis based on sets of atoms requires that for each set of input files, `seed_Subset*.*`, there are binary files with the extension `.check` present. The *Import* button is disabled if the files required for the current setting of the *Use atomic densities* checkbox are not present in the results folder.

Electron localization function

Materials Studio uses the information stored in the CASTEP binary output file to create a field that corresponds to the localization of electrons.

To create an electron localization function field

1. Choose *Modules | CASTEP | Analysis* from the menu bar to open the CASTEP Analysis dialog.
2. Select Electron localization function from the list of properties.
3. Ensure that the 3D Atomistic document to be analyzed is the active document.
4. Optionally, check the *View isosurface on import* checkbox to automatically create an isosurface when the density field is imported.
5. Click the *Import* button.
6. A field is created in the model, named "CASTEP electron localization function".

SCF local potential

Materials Studio uses the information stored in the binary `.cst_esp` file to create a field that corresponds to the local part of the Kohn-Sham potential. In fact, the data in the file correspond to minus a Kohn-Sham potential. Thus, this field is closely related to the electrostatic potential used in quantum chemistry programs, where it represents the electrostatic energy of a proton at a given point. The units of the potential are eV/electron.

The local SCF potential analyzed in Materials Studio includes all the DFT contributions, except for the nonlocal part of the pseudopotential: the Hartree term, the local pseudopotential term, and the exchange-correlation term. This potential can be used to analyze important solid-state properties such as band offsets and work function (the latter is a specific case of the band offset calculation where one of the materials is a vacuum). An excellent description of the formalism for band offset calculations based on CASTEP results is given by Al Allak and Clark (2001).

To create a local potential field

1. Choose *Modules | CASTEP | Analysis* from the menu bar to open the CASTEP Analysis dialog.
2. Select Potentials from the list of properties.
3. Ensure that the 3D Atomistic document to be analyzed is the active document.
4. Select the type of field required from the *Potential field* dropdown list.

> **Note:** Materials Studio currently supports only the local SCF potential field type.

5. Optionally, check the *View isosurface on import* checkbox to automatically create an isosurface when the potential field is imported.
6. Click the *Import* button.

Orbitals

Materials Studio uses the information stored by CASTEP in a binary `.check` file to create a field that corresponds to any of the orbitals in the system. In this context, the orbital is the square of the absolute value of the wavefunction for a given electronic band, summed over all k-points. A band is defined by the position of its eigenvalue in the ordered list of electronic energies at each k-point. For example, orbital (or band) number 3 is obtained by summation over all k-points of the wavefunctions with the third lowest energy. The sum of the "orbital densities" obtained in this way gives the total electron density of the crystal.

> **Note:** Because of the size of the `.check` file orbital analysis is only available if orbitals are explicitly requested.

The *Filter* dropdown list, which becomes available on the CASTEP Analysis dialog when Orbitals is selected from the list of properties, allows you to control which orbitals are displayed in the table:

- *Alpha* displays data for alpha-spin orbitals (spin up) only
- *Beta* displays data for beta-spin orbitals (spin down) only

> **Note:** For non-spin-polarized calculations, this option is not available.

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

- *N* - number of the orbital, with 1 corresponding to the lowest energy orbital.
- *s* - spin: + for alpha, - for beta.

> **Note:** In a non-spin-polarized calculation, all orbitals are labeled +.

- *From* - lowest value of the energy of the Nth band at any k-point (in eV)
- *To* - highest value of the energy of the Nth band at any k-point (in eV)

You can artificially change the band gap value for insulators or semiconductors by using the scissors operator. This parameter effectively describes the difference between the theoretical and experimental band gap values. When the experimental value is known, you can perform a band structure calculation to find the theoretical band gap. Then, simply set the scissors operator to the difference between the two values. The eigenvalues of the conduction band states displayed in the scrollable list will be shifted upward by the value of the scissors operator.

To create an orbital field

1. Choose *Modules | CASTEP | Analysis* from the menu bar to open the CASTEP Analysis dialog.

2. Select Orbitals from the list of properties.

3. Ensure that the 3D Atomistic document to be analyzed is the active document.

4. From the scrollable list, select the row(s) corresponding to the orbital(s) you wish to display.

   > **Tip:** Multiple selections are allowed. To select more than one orbital, hold down the SHIFT key and click on the first and last orbitals in the block you want to select, or hold down the CTRL key and click to select orbitals individually.

5. Optionally, check the *View isosurface on import* checkbox to automatically create an isosurface when the potential field is imported.

6. Click the *Import* button.

> **Note:** The units for the isovalues are e/Å^3 and correspond to the wavefunction density, ψ^2.

STM profile

CASTEP models the scanning transmission microscope (STM) profile by representing it as an isosurface of the electron density generated only by states at a certain energy away from the Fermi level. The distance from the Fermi level corresponds to the applied bias in actual STM experiments. Positive bias corresponds to the imaging of empty (conduction) states, while negative bias produces images of occupied (valence) states. This approach neglects the actual geometry of the STM tip and makes use of the Tersoff-Hamman approximation for tunneling transport (Tersoff and Hamman, 1985).

STM profile visualization makes sense only for models that represent surfaces in the slab supercell geometry. In addition, information about charge density at a distance from the surface is likely to be inaccurate as a result of the DFT failing to reproduce the asymptotics of the wavefunction decay into a vacuum.

> **Note:** Because of the size of the `.check` file STM analysis is available only if orbitals are explicitly requested.

> **Note:** Visualization of the images created by conduction band states requires that the calculation was performed with an increased number of empty bands. The recommended procedure is to use electronic density of states (DOS) calculations and specify a sufficiently high number of empty states.

To create an STM profile

1. Choose *Modules | CASTEP | Analysis* from the menu bar to open the CASTEP Analysis dialog.
2. Select STM profile from the list of properties.
3. Ensure that the 3D Atomistic document to be analyzed is the active document.
4. Specify the *STM bias* value.
5. Optionally, check the *View isosurface on import* checkbox to automatically create an isosurface when the potential field is imported.
6. Use field visualization tools to create an isosurface that represents the STM profile.
7. Click the *Import* button.

Field visualization

Materials Studio provides a number of tools for field visualization. They are accessed from 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.

> **Note:** The default settings for field visualization result in the fields being displayed over one unit cell of a structure. Use the In-Cell display mode for the lattice (accessible from the Lattice tab of the Display Style dialog) to make sure that the field is positioned around the displayed atoms.

Displaying band structure charts

Band structure charts show how electronic energies depend on k-vector, along high symmetry directions in the Brillouin zone. These charts provide a useful tool for qualitative analysis of the electronic structure of a material, for example, it is easy to identify the narrow bands of *d* and *f* states as opposed to the free electron like bands that correspond to *s* and *p* electrons. It is also instructive to look for directions with relatively flat, dispersionless bands, as these directions are likely to contribute strongly to optical absorption. Thus, allowing explanation of the anisotropy of optical properties. The

energy band gap is also easily deduced from the band structure plots as it normally corresponds to the energy difference between two states at high symmetry points.

An example of the CASTEP output for band structure is shown in Figure 1. Electronic states with different spins are presented using different colors and the Fermi level is shown with the dashed line. All energies are relative to the Fermi level (or to the top of the valence band in the case of insulators or semiconductors). The labels along the X axis of the band structure graph correspond to the standard definitions of high symmetry points for the given lattice type (Bradley and Cracknell, 1972). The Γ-point is denoted by a *G*.

The density of states included in this plot was created using Interpolation as an *Integration method* and Alpha and Beta as the *DOS display*.

> **Note:** If you have calculated DOS for a spin polarized system with a non-zero initial spin and the total spin is not optimized two charts will automatically be displayed, *<seedname>* Band Structure Alpha.xcd and *<seedname>* Band Structure Beta.xcd.
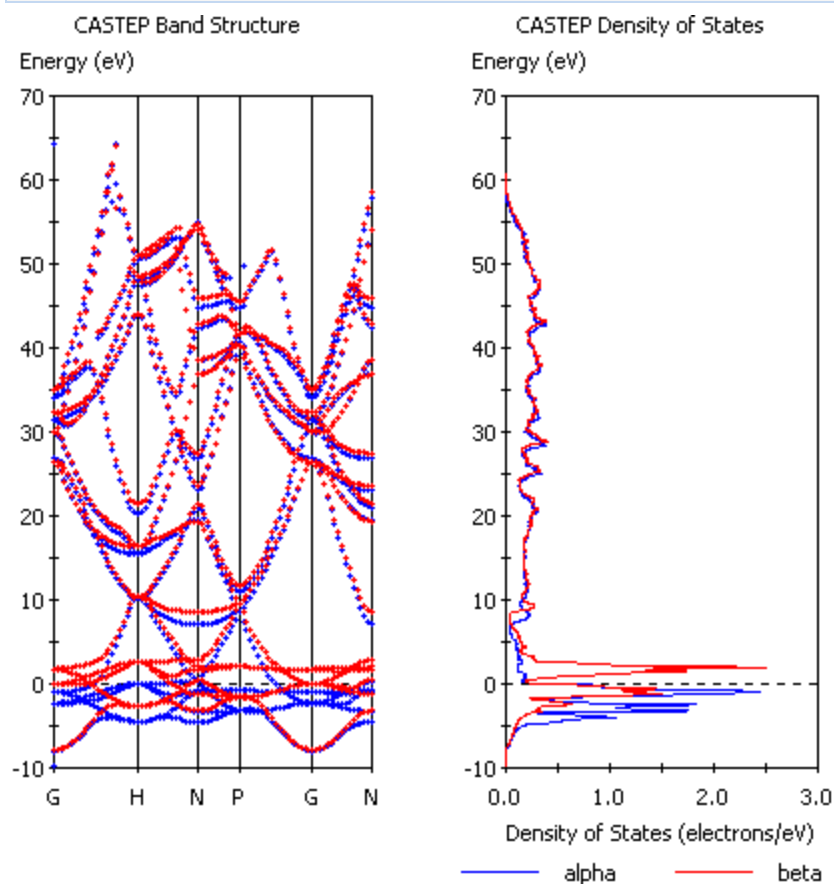
Figure 1. Band structure with DOS for Fe (spin-polarized GGA calculation).

To create a band structure chart

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.

2. Select Band structure from the list of properties.

3. Use *Results file selector* to pick the appropriate results file (it should have a BandStr suffix).

4. Select a required display style (Points or Lines) from the *Graph style* dropdown list.

5. Optionally, check *Show DOS* and set the relevant DOS options.

6. Click the *View* button.

7. A new chart document, *seedname* Band Structure.xcd, is created in the results folder.

Displaying core level spectra

The CASTEP Analysis dialog can be used to generate observable core level spectra based on electronic energies on the Monkhorst-Pack mesh of k-points obtained during a calculation. Detailed analysis of the impact of calculation parameters (k-point set, number of empty bands, and so on) on the accuracy of the spectra generated can be found in the core level spectroscopy theory topic.

> **Note:** Core level spectra can only be calculated for single atoms. One atom should be selected in the active 3D Atomistic document before carrying out a core level spectroscopy analysis.

To create a core level spectrum

1. Choose *Modules | CASTEP | Analysis* from the menu bar to open the CASTEP Analysis dialog.

2. Select Core level spectroscopy from the list of properties.

3. In the 3D Atomistic document containing the 3D periodic structure, select the atom for which you wish to simulate a core level spectrum. Click the *Atom Selection* button on the CASTEP Analysis dialog to open the Atom Selection dialog.

4. Use the Results file selector to pick the results file or make the *seedname*_EELS.castep file the active document.

5. Select the electron configuration of the *Spectrum*.

6. Specify the *Type* of spectrum you want to calculate, options are Absorption and Emission.

7. Click the *More...* button to open the CASTEP EELS Analysis Options dialog.

8. Set the *Instrumental smearing* value.

9. Specify whether to take *Lifetime effects* into account by checking or unchecking the checkbox, if checked set the *Core level broadening* value.

10. Specify whether to take *Include spin-orbit splitting* into account by checking or unchecking the checkbox, if checked set the *Spin-orbit splitting* value and close the CASTEP EELS Analysis Options dialog.

11. Select the incident radiation polarization from the *Calculation* dropdown list. If you specify Polarized radiation choose the direction of the *Polarization* of the incident radiation in fractional (lattice) coordinates.

12. Make the 3D periodic structure the active document and click the *View* button.

13. A new chart document, *seedname* EELS.xcd, is created in the results folder and becomes the active document.

> **Note:** If you carry out several core level spectroscopy analyses, each new spectrum will be displayed in a new chart document.

Displaying density of states charts

Density of states (DOS) and partial density of states (PDOS) charts give a quick qualitative picture of the electronic structure of a material and sometimes they can be related directly to experimental spectroscopic results.

> **Note:** If you have calculated DOS for a spin polarized system and the total spin is not optimized two charts will automatically be displayed, *<seedname>* DOS Alpha.xcd and *<seedname>* DOS Beta.xcd.

Full density of states

Materials Studio can produce DOS plots from any .bands CASTEP output file. These files are hidden in the Project Explorer but a .bands file is generated with every .castep file. All the files that can be used in the analysis of the current calculation will be presented in the results file selector. However, it is recommended that you create DOS plots based on the results of a band structure calculation that only uses k-points in high-symmetry directions.

> **Tip:** When evaluating DOS, use only the results of eigenvalues calculations on the Monkhorst-Pack grid. If you have more than one such set of results, for example, DOS and Optics, select the one with the highest density of k-points, that is, the highest Monkhorst-Pack mesh parameters.

To create a DOS chart

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.
2. Select Density of states from the list of properties.
3. Use Results file selector to pick the right results file.
4. Select Full to display the total DOS.
5. For spin-polarized calculations, select the required DOS component from the *DOS display* dropdown list.
6. Specify the *Function* to use, either DOS or Integrated DOS.
7. Optionally, click the *More...* button to open the CASTEP DOS Analysis Options dialog. Set the *Integration method* and other options, Interpolation gives more accurate results than the Smearing method, although it is slightly slower.
8. Click the *View* button.
9. A new chart document, *seedname* DOS.xcd, is created in the results folder.

Partial density of states

Materials Studio produces PDOS plots for certain angular momenta on selected atoms. The Sum curve represents the local density of states (LDOS) when one atom is selected. If more than one atom is selected, the contributions in each angular momentum channel from all selected atoms are added together. When no atoms are selected the behavior is the same as if all atoms were selected.

> **Note:** PDOS analysis formalism is not valid for high energy states in the conduction band: PDOS representation will usually decay to zero at about 20 eV above the Fermi level. This is related to the fact that expansion of essentially free electron states in terms of a limited number of atomic-like basis functions is impossible to carry out with any degree of accuracy. Only the valence band and lower part of the conduction band are meaningful in the PDOS plot.
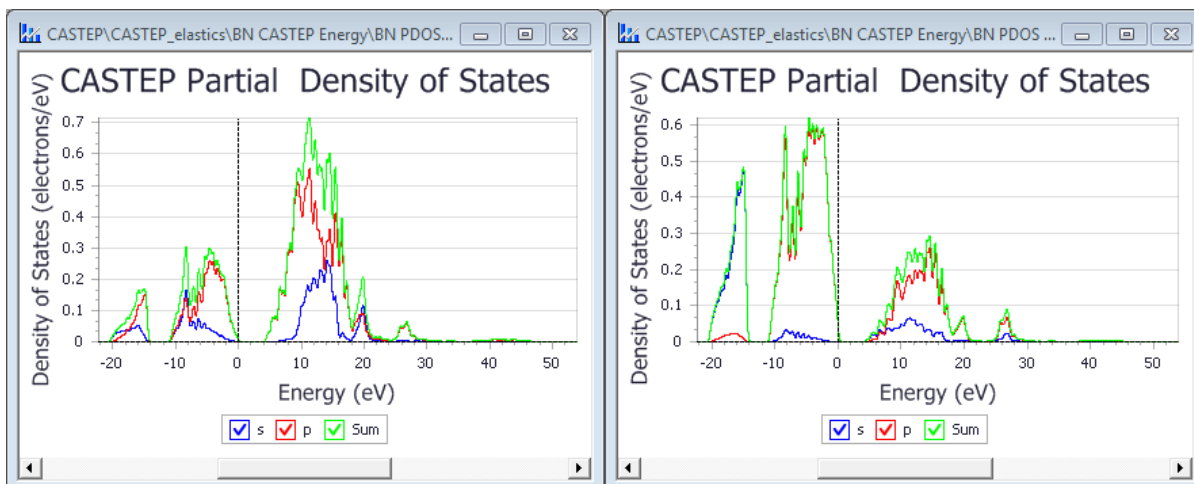
Figure 1. PDOS for BN. The left window is for boron, the right for nitrogen.

To create a PDOS chart

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.

2. Select Density of states from the list of properties.

3. Use Results file selector to pick the right results file.

4. Select Partial to display the partial DOS.

5. Check the required angular momentum components for the PDOS.

6. Select the atom or atoms in the model, for which the PDOS is to be created.

7. For spin-polarized calculations, select the required DOS component from the *DOS display* dropdown list.

8. Optionally, set additional CASTEP DOS analysis options. The Interpolation *Integration method* gives more accurate results than the Smearing method, although it is slightly slower.

9. Click the *View* button.

10. A new chart document, *seedname* PDOS.xcd, is created in the results folder.

> **Tip:** You should rename this file to indicate the atoms on which it is based. In the example above (see Figure 1) suitable names for the two files created might be BN N PDOS.xcd and BN B PDOS.xcd (the default names are BN PDOS.xcd and BN PDOS (2).xcd).

Calculating elastic constants

The CASTEP Elastic Constants task return results as a group of .castep output files. Each of them represents a geometry optimization run with a fixed cell, for a given strain pattern and strain amplitude. The naming convention for these files is:

seedname_cij__m__n

Where *m* is the current strain pattern and *n* is the current strain amplitude for the given pattern.

You can then use CASTEP to analyze the calculated stress tensors for each of these runs and generate a file with information about elastic properties. The information in this file includes:

- A summary of the input strains and calculated stresses.
- Results of linear fitting for each strain pattern, including the quality of the fit.
- The correspondence between calculated stresses and elastic constants for a given symmetry.
- A table of elastic constants, C_{ij}, and elastic compliances, S_{ij}.
- The derived properties such as bulk modulus and its inverse, compressibility, Young modulus and Poisson ratios for three directions, and the Lamé constants required for modeling the material as an isotropic medium.

If you requested the polarization property, the main output file, `seedname.castep`, contains the piezoelectric tensor output at the end, for example:

```
      Symmetrized Piezoelectric Stress Tensor (C/m^2)
      -------------------------------------------------
  0.000000   0.000000   0.000000   0.000000  -0.918444   0.000000
  0.000000   0.000000   0.000000  -0.918444   0.000000   0.000000
 -0.600778  -0.600778   1.321444   0.000000   0.000000   0.000000
```

To calculate elastic constants

1. From the Materials Studio menu bar, select *Modules | CASTEP | Analysis*.
2. From the list of properties, select Elastic constants.
3. Use the Results file selector to pick the appropriate results file.
4. Click *Calculate*.
5. This creates a new text document, `seedname Elastic Constants.txt`, in the results folder.

Description of the elastic constants file

Here, the example of a tetragonal rutile crystal, TiO_2, illustrates the contents of the `Elastic Constants.txt` output file produced by CASTEP.

This lattice type requires two strain patterns. For each strain pattern, there is a summary of the calculated stresses as extracted from the respective `.castep` files:

```
         Summary of the calculated stresses
         ***********************************

 Strain pattern:      1
 ====================

 Current amplitude: 1
 Transformed stress tensor (GPa) :
       0.719908       -0.000000       -0.000000
      -0.000000        0.331220        0.369780
      -0.000000        0.369780        0.174538

 Current amplitude: 2
 Transformed stress tensor (GPa) :
       0.115598       -0.000000       -0.000000
      -0.000000       -0.019103        0.146509
      -0.000000        0.146509       -0.144727
                                           ....
```

This provides information about the connection between components of the stress, strain, and elastic constants tensors. At this stage, each elastic constant's representation is a single compact index rather

than by a pair of *ij* indices. Later, the file provides the correspondence between the compact notation and the conventional indexing:

```
Stress corresponds to elastic coefficients (compact notation):
  1  7  8  4  0  11

as induced by the strain components:
  1  1  1  4  0  1
```

A linear fit of the stress-strain relationship for each component of the stress has the following format:

```
                    Stress    Cij      value of        value of
                    index    index      stress          strain
                      1        1       0.719908       -0.003000
                      1        1       0.115598       -0.001000
                      1        1      -0.509448        0.001000
                      1        1      -1.066455        0.003000
C (gradient)     :    299.206750
Error on C       :      4.882222
Correlation coeff:      0.999734
Stress intercept :     -0.185099
```

The gradient provides the value of the elastic constant (or a linear combination of elastic constants). The quality of the fit, indicated by the correlation coefficient, provides the statistical uncertainty of that value. The stress intercept value is not used in further analysis. It is an indication of how far the converged ground state was from the initial structure.

The output file then summarizes the results for all the strain patterns:

```
============================
 Summary of elastic constants
============================

id  i  j       Cij (GPa)
1   1  1     299.20675 +/-    4.882
3   3  3     500.96355 +/-    2.004
4   4  4     126.32975 +/-    4.509
6   6  6     229.09375 +/-    0.826
7   1  2     168.90265 +/-    4.411
8   1  3     158.33975 +/-    4.590
11  1  6       0.00000 +/-    0.000
```

This includes the errors only when the strain amplitude uses more than two values, since there is no statistical uncertainty associated with fitting a straight line to only two points.

The output files present the elastic constants in a conventional 6×6 tensor form, followed by a similar 6×6 representation of the compliances:

```
========================================
 Elastic Stiffness Constants Cij (GPa)
========================================

   299.20675   168.90265   158.33975     0.00000     0.00000     0.00000
   168.90265   299.20675   158.33975     0.00000     0.00000     0.00000
   158.33975   158.33975   500.96355     0.00000     0.00000     0.00000
     0.00000     0.00000     0.00000   126.32975     0.00000     0.00000
     0.00000     0.00000     0.00000     0.00000   126.32975     0.00000
     0.00000     0.00000     0.00000     0.00000     0.00000   229.09375


=========================================
 Elastic Compliance Constants Sij (1/GPa)
```

```
       ========================================
   0.0051958   -0.0024785   -0.0008588    0.0000000    0.0000000    0.0000000
  -0.0024785    0.0051958   -0.0008588    0.0000000    0.0000000    0.0000000
  -0.0008588   -0.0008588    0.0025391    0.0000000    0.0000000    0.0000000
   0.0000000    0.0000000    0.0000000    0.0079158    0.0000000    0.0000000
   0.0000000    0.0000000    0.0000000    0.0000000    0.0079158    0.0000000
   0.0000000    0.0000000    0.0000000    0.0000000    0.0000000    0.0043650
```

The final part of the file contains the derived properties:

```
Bulk modulus                 =     220.35108 +/-  2.572 (GPa)

Compressibility              =       0.00454 (1/GPa)

Elastic Debye temperature =     812.49749 K
Averaged sound velocity   =  5939.32973 (m/s)

   Axis     Young Modulus          Poisson Ratios
            (GPa)
    X        192.46266      Exy=  0.4770 Exz=  0.1653
    Y        192.46266      Eyx=  0.4770 Eyz=  0.1653
    Z        393.84553      Ezx=  0.3383 Ezy=  0.3383
```

The elastic Debye temperature evaluation uses the recipe by Anderson ([1963](#)), where the averaged sound velocity is evaluated numerically as an integral over all propagation directions. The Debye temperature is proportional to the averaged sound velocity, v_m:

$$\theta = \frac{h}{k}\left[\frac{3q}{4\pi}\frac{N\rho}{M}\right]^{1/3}v_m$$

Where:

h is the Planck constant
k is the Boltzmann constant
N is Avogadro's number
ρ is the density
M is the molecular weight of the solid
q is the number of atoms in the molecule.

Note: Elastic Debye temperature and averaged sound velocity are not reported if the calculated elastic constants do not produce physically meaningful sound velocities in some directions (for example, if certain C_{ij} values or their combinations are negative when they should be positive). This can happen for low quality calculations or for calculations that were not preceded by a geometry optimization (including optimization of the lattice parameters).

The last section of the file contains average properties that describe the elastic response of a polycrystal, for example:

```
       =======================================================
        Elastic constants for polycrystalline material (GPa)
       =======================================================
                                    Voigt       Reuss        Hill
Bulk modulus                 :    230.06015   220.35108   225.20562
Shear modulus (Lame Mu)      :    137.27031   116.19120   126.73075
Lame lambda                  :    138.54661   142.89028   140.71845
Young modulus                :    343.49337   296.46492   320.14092
Poisson ratio                :      0.25116     0.27576     0.26308
```

```
Hardness (Tian 2012)          :       16.68027    12.87984    14.74764
Fracture toughness  (MPa m^0.5):        2.62165     2.36054     2.49228

Universal anisotropy index:        0.95115
```

This output contains the bulk modulus, shear modulus, Young modulus, and Poisson ratio averaged according to Voigt, Reuss, and Hill schemes (Nye 1957).

In addition, a universal anisotropy index suggested by Ranganathan and Ostoja-Starzewski (2008) is evaluated.

The Vickers hardness in GPa evaluation uses Tian's (2012) empirical formula. This expresses hardness in terms of the polycrystalline bulk, B, and shear, G, moduli (using Pugh's modulus ratio, $k=G/B$):

$$H_V = 0.92 k^{1.137} G^{0.708}$$

The correlation between the results from this macroscopic model and experimentally measured hardness values is quite good when hardness is larger than 5 GPa. However, the empirical formula overestimates the hardness of softer materials.

Niu et al. (2019) introduced a similar empirical model to estimate fracture toughness, K_{IC}, from the polycrystalline moduli:

$$K_{IC} = V_0^{1/6} G (B/G)^{1/2}$$

> **Note:** The empirical expressions for Vickers hardness and for fracture toughness cannot be applied if the calculated shear modulus is negative. This can happen when the calculation settings are not sufficiently accurate. In such a case, the summary report does not include the hardness or the fracture toughness.

Visualizing Fermi surfaces

Fermi surfaces are generated from information from CASTEP calculations which is stored in the .bands output file. Fermi surfaces can be considered as the energy isosurfaces in reciprocal space.

> **Tip:** To ensure that the generated Fermi surface(s) are reliable you must use as many k-points as computational resources will allow when setting up the calculation.

To create a Fermi surface

1. Choose *Modules | CASTEP | Analysis* from the menu bar to open the CASTEP Analysis dialog.
2. Select Fermi surface from the list of properties.
3. Ensure that the 3D Atomistic document to be analyzed is the active document.
4. Select the *Band* for which to display the Fermi surface.
5. Click the *Import* button.

To change the Fermi level used for the Fermi surface

1. Create a Fermi surface according to the steps above.
2. Open the Display Style dialog and select the Isosurface tab.
3. In the *Generation* section change the *Isovalue*. The Fermi surface will be updated appropriately.

Visualizing vibrational spectra

When a CASTEP calculation returns a Hessian (dynamical matrix) at the Γ-point, then vibrational frequencies for the bonds in the system being studied can be calculated and visualized using the Vibrational Analysis tool.

Note: After a CASTEP job that included calculation of the electric field response (that is, the *Polarizability, IR and Raman spectra* checkbox was checked on the *Properties* tab of the CASTEP Calculation dialog) is complete and the results files have been downloaded successfully, Materials Studio will automatically import the Hessian matrix, provided that the CASTEP job was not a Properties run.

A dynamical matrix is returned if the TASK keyword in the input parameters (`.param`) file is set to either Efield or Phonon+Efield and there is a Γ-point among the phonon k-vectors. You can achieve this either by checking the *Polarizability, IR and Raman spectra* checkbox on the Properties tab of the CASTEP Calculation dialog or, alternatively, if you wish to calculate the phonon dispersion or phonon density of states, by checking the *Phonons* checkbox in the list on the *Properties* tab, checking the *Dispersion* or *Density of states* checkboxes, as appropriate, that appear below the list, and ensuring that there is a Γ-point in the q-vector set.

IR spectra

In order to carry out a vibrational analysis, you will need to import a Hessian matrix from the output of a CASTEP run.

To import a Hessian and display an IR spectrum

1. Choose *Modules | CASTEP | Analysis* from the menu bar to display the CASTEP Analysis dialog.

2. Select IR spectrum from the list of options at the top of the dialog.

3. Ensure that the 3D Atomistic document to be updated is the active document.

4. Click the *Import Hessian from CASTEP output* button.

If you requested that the electric field response be calculated as part of the CASTEP job by checking the *Polarizability, IR and Raman spectra* checkbox on the *Properties* tab of the CASTEP Calculation dialog, you will be able to display vibrational mode frequencies and absorption intensities for the structure being studied in the form of a list of values or graphically as a vibrational spectrum using the Vibrational Analysis tool.

Raman spectra

To display a Raman spectrum

1. Choose *Modules | CASTEP | Analysis* from the menu bar to display the CASTEP Analysis dialog.

2. Select Raman spectrum from the list of options at the top of the dialog.

3. Use Results file selector to pick the right results file.

4. Ensure that the 3D Atomistic document containing the structure is the active document.

5. Select the *Function* of the mode to be calculated.

6. If the *Function* is set to Intensity set the *Temperature*.

7. Set the *Smearing* value to be used.

8. Select the *Units* for the X axis.

9. Specify whether to reverse the wavenumber and intensity axes.

10. Click the *View* button.

11. A new chart document, *seedname* `Raman.xcd`, is created in the results folder.

Displaying NMR results

A CASTEP NMR calculation computes the chemical shielding tensor and the electric field gradients for all of the atoms in the system.

> **Note:** NMR in CASTEP is part of the separately licensed module NMR CASTEP. NMR calculations can only be performed if you have purchased this module.

> **Note:** NMR properties are dynamic (that is, they are not present on atoms until they are assigned during analysis).

To display the shielding tensor

1. Choose *Modules | CASTEP | Analysis* from the menu bar to display the CASTEP Analysis dialog.
2. Select NMR from the list of properties.
3. Make sure that the desired 3D Atomistic document is the active document.
4. Click the *Assign isotropic chemical shielding to structure* button to import the data into the model.
5. Right-click in the 3D Viewer and select *Label* from the shortcut menu. Set the *Object type* to Atom, select NMRShielding from the *Properties* list, and click the *Apply* button to display the shielding tensors.

To display the electric field gradients

1. Choose *Modules | CASTEP | Analysis* from the menu bar to display the CASTEP Analysis dialog.
2. Select NMR from the list of properties.
3. Make sure that the desired 3D Atomistic document is the active document.
4. Click the *Assign electric field gradients to structure* button to import the data into the model.
5. Right-click in the 3D Viewer and select *Label* from the shortcut menu. Set the *Object type* to Atom, select EFGQuadrupolarCoupling or EFGAsymmetry, as appropriate, from the *Properties* list, and click the *Apply* button to display the electric field gradients.

To display the J-coupling constants

1. Choose *Modules | CASTEP | Analysis* from the menu bar to display the CASTEP Analysis dialog.
2. Select NMR from the list of properties.
3. Use Results file selector to pick the right results file; in this case it should be a *seedname_* NMRJC.castep file.
4. Click the *Show J-coupling constants* button to generate and open a study table reporting the calculated J-coupling constants. The study table document will be named *seedname_*NMRJC JCoupling.std.

   The study table contains two sheets, one with the summary of the results (atom pairs, corresponding interatomic distances, and isotropic and anisotropic components of the J-coupling tensor) and one with the detailed breakdown of contributions to the isotropic coupling (Fermi contact term, spin-dipole term, paramagnetic, and diamagnetic contributions).
5. Right-click in the 3D Viewer and select *Label* from the shortcut menu. Set the *Object type* to Atom, select ServerAtomName from the *Properties* list, and click the *Apply* button to display the atom names that are shown in the first two columns of the Summary sheet of the study table.

Displaying optical properties

Analysis of optical properties involves two main steps.

Dielectric function calculation

When a CASTEP calculation returns the matrix elements for electronic interband transitions (Eq. CASTEP 56) in the (hidden) file .cst_ome, it is necessary to calculate the dielectric function using Eq. CASTEP 55. This calculation results in the creation of a grid document that contains two sheets. The first is the

summary of the calculation that includes the value of the scissors operator, the geometry of the calculation and the smearing applied. The second sheet contains a table of the real and imaginary parts of the dielectric function versus the photon energy (eV).

It is important to set the parameters for this type of calculation correctly in order to be able to compare the results obtained with experimental optical constants.

Scissors operator: This parameter effectively describes the difference between the theoretical and experimental band gap values. When the experimental value is known, you can perform a band structure calculation to find the theoretical band gap. Then simply set the scissors operator to the difference between the two values.

> **Tip:** When there is no experimental band gap value but there are data on the dielectric function, you can repeat the calculations with varying scissors operator values and select the one that gives a theoretical absorption edge which matches the experimental value.

In the absence of any experimental data, use a fixed proportion of the theoretical band gap as the scissors operator, for example 25%. This approach allows you to study trends in optical properties across a family of similar compounds.

Calculation: This parameter and the related *Polarization* or *Incidence* settings, specify the experimental geometry. These are irrelevant for optically isotropic crystals but they are necessary to study anisotropy of optical properties in crystals with lower symmetry. A good example of the theoretical study of optical anisotropy of crystalline polymers was given by Ambros-Drachl et al. (1995). A more detailed discussion of the meaning of these settings is given in the Optical properties theory topic.

Smearing: This parameter specifies the width of the Gaussian broadening that is used to produce the dielectric function. It is similar to the broadening that is used in density of states calculations.

To create a dielectric function grid

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.

2. Select Optical properties from the list of properties.

3. Use Results file selector to pick the right results file.

4. Select the geometry of the calculation from the *Calculation* dropdown list.

   - If Polarized geometry is selected, specify the *Polarization* direction in the text boxes.
   - If Unpolarized geometry is selected, specify the *Incidence* direction in the text boxes.
   - If Polycrystalline geometry is selected, no additional parameters need to be specified.

5. Specify a *Smearing* value in the text box (0.5 eV is a good default setting).

6. Click the *Calculate* button.

7. A new grid document, *seedname* `Optical Properties.xgd`, is created in the results folder and becomes the active document.

Display optical constants

The following optical constants can be evaluated based on the calculated dielectric function:

- Reflectivity
- Absorption
- Refractive index, *n* and *k*
- Complex optical conductivity
- Energy loss function

Any of these constants and the complex dielectric function itself, can be plotted using Materials Studio. The only additional information that might be required are the Drude correction parameters.

The empirical Drude contribution to the spectra is due to intraband excitations that are not included in the spectra calculated by CASTEP. The Drude contribution, which may be non-zero only for metals and semi-metals, is determined by the *DC Conductivity* and *Drude Damping* parameters. Appropriate values for these quantities cover a wide range and are usually taken from experiment. A typical value of the *Drude Damping* parameter for metals is 0.05 eV. Typical values for the *DC Conductivity* in metals are around 250 eV. But it must be 0 for insulators. Another common unit for the *DC conductivity* is 1/ (Ohm*cm). The conversion factor between this unit and eV is 1/(Ohm*cm) = 5.924×10^{-4} eV.

To create a chart with optical properties

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.
2. Select Optical properties from the list of properties.
3. Ensure that the grid document, *seedname* Optical Properties.xgd, is active.
4. Specify the property to be plotted using the *Function* dropdown list.

   > **Tip:** If the system is a molecule in the box the only relevant property to display is the Absorption calculated for Polycrystalline geometry.

5. Specify the energy units for the plot using *Units* dropdown list.
6. Set the Drude correction parameters for metallic systems. Click the *More...* button to access the Optics Analysis Options dialog.

   > **Tip:** Ensure that the Drude term is ignored for the nonmetallic systems, that is, check that the *DC Conductivity* is 0 on the CASTEP Optical Properties Options dialog.

7. Click the *View* button.
8. A new chart document, *seedname* Optical Properties.xcd, is created in the results folder. The summary from the first sheet of the grid document is used as the graph title to assist in identification of the graphs.

> **Note:** The *View* button is enabled only if a suitable grid document is active.

> **Tip:** If the only experimental information available is the value of the static dielectric constant, it is still possible to assess the value of the scissors operator. Calculate the refractive index repeatedly, using different scissors operator values and select the one that gives the best fit between the calculated n(0) value and the square root of the experimental static dielectric constant.

Displaying phonon dispersion and density of states

Phonon dispersion curves show how phonon energy depends on the q-vector, along high symmetry directions in the Brillouin zone. This information can be obtained experimentally from neutron scattering experiments on single crystals. Such experimental data are available for only a small number of materials and thus, theoretical dispersion curves are useful for both establishing the validity of a modeling approach and to demonstrate the predictive power of *ab initio* calculations.

In certain circumstances it is possible to measure the density of states (DOS) rather than the phonon dispersion. Furthermore, the electron-phonon interaction function, which is directly related to the phonon DOS can be measured directly in the tunneling experiments (see, for example, Yanson, 1988). It is therefore important to be able to calculate phonon DOS from first principles, in order to compare the results with experimentally observed spectra.

Materials Studio can produce phonon dispersion and DOS charts from any `.phonon` CASTEP output file. These files are hidden in the Project Explorer but a `.phonon` file is generated with every `.castep` file that has a PhonDisp or PhonDOS suffix. All the files that can be used in the analysis of the current calculation will be presented in the results file selector. However, it is not recommended that you create phonon DOS plots based on the results of a phonon dispersion calculation that only uses q-vectors in high-symmetry directions.

> **Tip:** When evaluating phonon DOS, use only the results of the phonon calculations on the Monkhorst-Pack grid.

To create a phonon dispersion chart

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.
2. Select Phonon dispersion from the list of properties.
3. Use *Results file selector* to pick the appropriate results file (it should have a PhonDisp suffix).
4. Select the required frequency units for the chart from the *Units* dropdown list.
5. Select a required display style (Points or Line) from the *Graph style* dropdown list.
6. Optionally, check *Show DOS* and set the relevant DOS options.
7. Click the *View* button.
8. A new chart document, *seedname* `Phonon Dispersion.xcd`, is created in the results folder.

To create a phonon DOS chart

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.
2. Select Phonon density of states from the list of properties.
3. Use *Results file selector* to pick the right results file (it should have a PhonDOS suffix).
4. Select a required DOS type (Full or Partial) from the *DOS display* dropdown list.
5. Optionally, set additional CASTEP Phonon DOS analysis options. The Interpolation *Integration method* gives more accurate results than the Smearing method, although it is slightly slower.
6. Click the *View* button.
7. A new chart document, *seedname* `DOS.xcd`, is created in the results folder when Full density of states is selected. A document *seedname* PDOS.xcd, is created in the results folder when Partial density of states is selected.

Displaying population analysis results

A CASTEP calculation can compute atomic charges, spins, and bond orders using Mulliken analysis, and atomic charges using Hirshfeld analysis.

> **Note:** CASTEP bond orders may be incorrect for small unit cells, when an atom is bonded to a number of periodic images of itself. For example, bond orders for the primitive cell of silicon are reported as 3.0, while the same calculation for the conventional cell gives 0.75. The factor of four appears because CASTEP sums up the bond orders for the four bonds that link the Si atom at the origin with the periodic images of itself in the primitive cell. A manual analysis of the multiplicities is required in such cases, specifically: determine the number of bonds to periodic images of the same atom and divide the bond order by that number. In cases where the bonds are not symmetry equivalent, you can only obtain an average bond order.

Displaying computed charges, spins, and bond orders

Mulliken charge analysis is one of the most common types of charge analysis. The spin density matrix and atomic overlap matrix are used to partition charges among the atoms. An alternative method of charge partitioning is based on deformation density and produces so-called Hirshfeld charges.

To import and display computed atomic charges, spins, and bond orders, you need to have the structure file (`.xsd`) and CASTEP output file (`.castep`) in a folder within the current project.

To display atomic charges or spins

1. Choose *Modules | CASTEP | Analysis* from the menu bar to display the CASTEP Analysis dialog.
2. Select Population analysis from the list of properties at the top of the dialog.
3. Make sure that the structure file from the CASTEP calculation is the active document.
4. Select the type of charges (Mulliken or Hirshfeld) that you wish to apply from the dropdown list.
5. Click the *Assign charges to structure* or *Assign Mulliken spins to structure* button, as appropriate, to import the charge or spin data into the structure.
6. Right-click in the 3D Viewer and select *Label* from the shortcut menu to display the Label dialog.
7. Set the *Object type* to Atom, select Charge or Spin, as appropriate, from the *Properties* list, and click the *Apply* button to display the charges or spins.

To display bond orders

1. Choose *Modules | CASTEP | Analysis* from the menu bar to display the CASTEP Analysis dialog.
2. Select Population analysis from the list of properties at the top of the dialog.
3. Make sure that the structure file from the CASTEP calculation is the active document.
4. Click the *Assign Mulliken bond orders to structure* button to import the bond order data into the structure.
5. Right-click in the 3D Viewer 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.

Calculating reaction kinetics

Reaction kinetics are described in terms of reaction rate coefficients. The rate coefficients are evaluated in the transition state theory framework using information about the energies, geometries, and vibrational frequencies of reactants, products, and transition state. In order to achieve better agreement with experiment it might be advantageous to increase the reaction threshold value from the DFT calculated one and to scale calculated harmonic frequencies to account for DFT deficiency and for anharmonic effects.

The threshold correction can be applied either on a basis of more accurate ab initio calculations or based on the comparison of calculated and experimental rate coefficients. It appears that a value in the region of 6-7 kcal/mol describes DFT error adequately.

The recommended correction factors for DFT frequencies can be found at the NIST website for a variety of exchange-correlation functionals: https://cccbdb.nist.gov/vibscalejust.asp.

To calculate reaction kinetics

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.

2. Select Reaction kinetics from the list of properties.

3. Ensure that the desired 3D Atomistic collection document (`seedname.xod`) is the currently active document.

4. Specify the temperature range of interest.

5. Check the *Apply tunneling correction* checkbox if the reaction involves motion of light elements.

6. Optionally specify a *Threshold correction* and a *Vibrational frequencies scaling* factor.

7. Click the *Calculate* button.

8. A new study table document, `seedname.std`, is created in the results folder.

Displaying the averaged potential chart for work function calculations

The CASTEP Analysis dialog can be used to generate plots of the change in electrostatic potential through a slab, which is related to the energy required to remove an electron from the bulk into the vacuum (the work function). The plots are created by averaging the electrostatic potential in the planes perpendicular to the slab normal.

> **Note:** Work function can only be calculated for structures constructed in a slab geometry so that they contain atomic planes separated by a vacuum layer.

The averaged electrostatic potential is reported along the fractional coordinate of the unit cell in the direction of the vacuum. The Fermi level is reported on the work function chart.

To create an averaged potential chart

1. Choose *Modules | CASTEP | Analysis* from the menu bar to open the CASTEP Analysis dialog.

2. Select Potentials from the list of properties.

3. Make the 3D Atomistic document containing the 3D periodic slab the active document.

4. Use the *Results file selector* to pick the results file.

5. Select the *Potential field* from the dropdown list.

6. Optionally check the *View isosurface on import* checkbox.

7. Click the *Import* button.

8. A new chart document, `seedname Potential Profile.xcd`, is created in the results folder and becomes the active document. The selected potential field is imported into the 3D Atomistic document and may be displayed as an isosurface.

Updating structure

Updating cell parameters and atomic coordinates after Geometry Optimization or a Dynamics run should be the first step in the Analysis process.

> **Note:** Structure updates happen automatically after a CASTEP job is completed and the results files have been downloaded successfully. The description below is, therefore, only relevant for jobs which were run in standalone mode and where the results files were transferred manually, or results files in which the final structure produced by CASTEP has been manually modified and you wish to revert to the unmodified form.

You can update the structure if the chemical composition (the number of atomic species and the number of atoms of each kind) has not been changed since Materials Studio saved the structure in the

results folder. After the update, the cell parameters and atom coordinates are set to the values returned by the CASTEP run in the (hidden) binary `.check` file.

To update the structure

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.

2. Select Structure from the list of properties.

3. Ensure that the 3D model document to be updated is active.

4. Click the *Update* button.

> **Note:** An error message is generated if the output `.check` file is incomplete, or if the chemical composition of the model has been changed.
> The *Update* button is enabled only if the output `.check` file is present and the active document is the 3D model to be updated.

Creating a trajectory file

> **Note:** A trajectory file, *seedname*.xtd, is automatically created when a CASTEP job is completed and the results files have been downloaded successfully. The description below is, therefore, only relevant for jobs which were run in standalone mode and where the results files were transferred manually.

The CASTEP server returns a number of ASCII text files to the client PC that can be used to create a trajectory file for either a geometry optimization or a dynamics calculation. This trajectory is saved in a hidden *seedname* `Trajectory.trj` file in the results folder.

This file contains complete information on the structure evolution, including changes in the energy, temperature, stress, velocities and forces. Materials Studio does not currently provide tools for analyzing this information. Although, it is possible to animate the trajectory.

> **Note:** To perform statistical analysis of the results or to visualize atomic vectors (forces and velocities) you can use Forcite Analysis.

To create a trajectory

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.

2. Select *Structure* from the list of properties.

3. Ensure that the current document is either the 3D model in the results folder or the `.castep` file of the corresponding calculation.

4. Click the *Create* button.

Displaying thermodynamic properties

Phonon calculations in CASTEP can be used to evaluate the temperature dependence of the energy, entropy, free energy and lattice heat capacity of a crystal in a quasiharmonic approximation. These results can be used to compare with experimental data (for example on heat capacity measurements), to predict phase stability of different structural modifications, and so on (see Baroni et al., 2001). Warren et al. demonstrated applicability of CASTEP to theoretical studies of phase transitions (Warren and Ackland, 1996 and Warren et al., 1998).

An example of the CASTEP output for thermodynamic properties is shown in Figure 1. All energy-related properties are plotted on one graph, and the calculated value of the zero-point energy is included. The heat capacity is plotted separately on the right.

> **Note:** The entropy is presented as an S*T product to allow comparison with the energy.

CASTEP Thermodynamic Properties

Zero point energy=1.3792910 eV

Energy (eV)

Heat capacity (cal/mol.K)

Enthalpy
Free Energy
T*Entropy
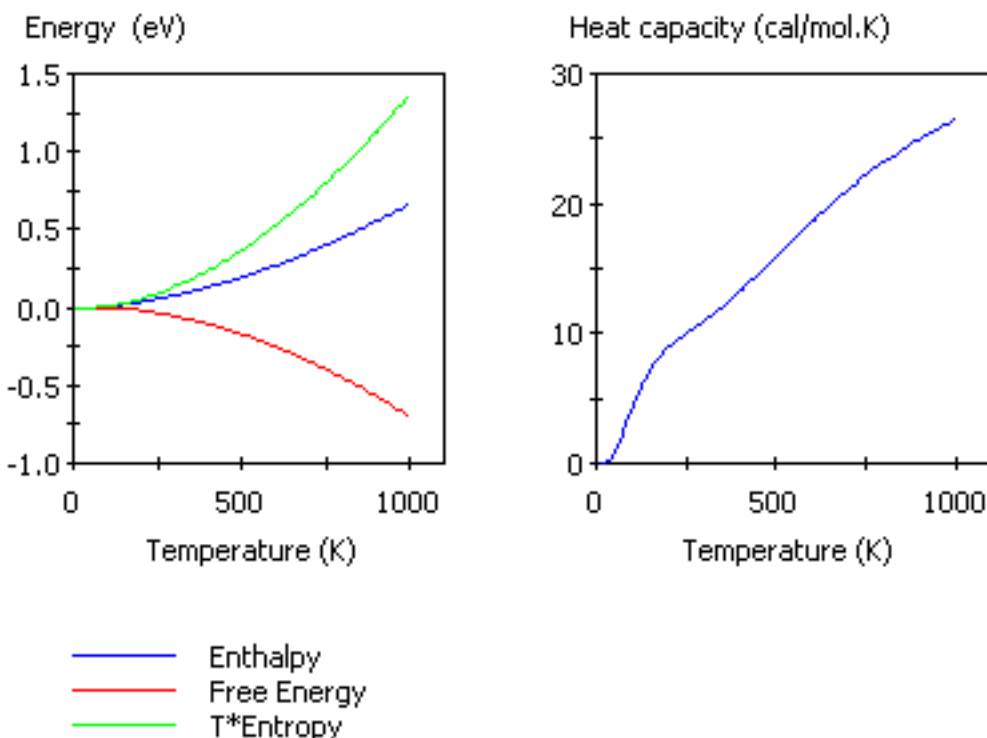
Figure 1. Thermodynamic properties of MgH$_2$

> **Note:** Thermodynamic properties calculated using the quasiharmonic approximation can be inaccurate for temperatures comparable to the Debye temperature.

To create a thermodynamic properties chart

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.

2. Select Thermodynamic properties from the list of properties.

3. Use the *Results file selector* to pick the appropriate results file (it should have a PhonDOS suffix).

4. Optionally, check *Plot Debye temperature*.

5. Select the desired temperature range.

6. Click the *View* button.

7. A new chart document, *seedname* Thermodynamic Properties.xcd, is created in the results folder.

8. If *Plot Debye temperature* is checked, an additional chart document, *seedname* Debye Temperature, is created in the results folder.

9. Optionally, click the *Assign temperature factors to structure* button to add temperature factor information to the structure.

Chapter 3: CASTEP jobs

The topics in this section cover controlling and running remote CASTEP jobs, details of a sample remote run, running jobs in standalone mode, and potential reasons why CASTEP might fail.

Using CASTEP job control

Materials Studio runs CASTEP jobs as background processes on a server. The following tools are provided to setup and control the jobs:

- Use the Job Control tab on the CASTEP Calculation dialog to select the gateway location and job parameters for future jobs.
- Use the Server Console application 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 CASTEP Job Control Options dialog.

Running CASTEP jobs in parallel

CASTEP jobs can run in parallel on a server that supports MPI. The CASTEP interface uses the gateway framework of Materials Studio to extract the relevant information for each gateway server. You can select the number of cores to use, up to the maximum number available, as indicated by the text to the right of the *Run in parallel on* control.

> **Note:** It is recommended to use the number of cores which is commensurate with the number of k-points in the calculation. You can determine the number of k-points by using the *Display points...* button on the k-points tab of the *CASTEP Electronic Options* dialog.

CASTEP jobs can run in parallel using hybrid OpenMP/MPI parallelization. CASTEP uses the Materials Studio gateway framework to extract the relevant information for each gateway server. You can select the number of cores to use, up to the maximum number available, as indicated by the *Run in parallel on* option on the Job Control tab of the CASTEP Calculation dialog. Furthermore, on Linux gateways you can specify the desired number of threads to be used for each MPI process. The number of threads must be commensurate with the number of cores requested and should not exceed the number of cores on each execution host.

This functionality can substantially decrease the amount of memory required for a job (although it could somewhat decrease speed).

Remote CASTEP jobs

CASTEP uses a client-server architecture that allows you use your PC to control calculations of the total energy and electronic properties of a system or geometry optimizations and dynamics simulations of structures 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 supercomputer from your Windows desktop PC. It also allows you to make use of spare CPU cycles on other desktop PCs.

Execution of server code can be somewhat reconfigured. In particular, for Linux clusters it can be useful to set *MaxCoresPerProcessor* to the actual number of cores per *chip* for homogeneous clusters. For

example, if a cluster node contains two 6-core chips, the value can be set to 6. This modification can speed up parallel jobs for some architectures.

CASTEP jobs are controlled by input files that are generated by Materials Studio when you start a job. CASTEP 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.

CASTEP remote jobs run according to the standard sequence of processes described in A sample remote job run with the differences explained in the Sample CASTEP run help topic.

A sample CASTEP run

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

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: Materials Studio creates a chart document called $[seedname]$ `Energies.xcd`, showing the total energy versus SCF iteration, and another chart document called $[seedname]$ `Convergence.xcd`, showing, on the logarithmic scale, the convergence of the total energy versus SCF iteration.

- *Update textual results* is checked: Materials Studio downloads a text file called `Status.txt` that contains a summary of the calculation performed (task, DFT functional, energy cutoff for plane wave basis set, electronic minimization method, system charge and spin, and so on), the SCF iteration number, the total energy, and the total energy convergence (that is, the change from the previous iteration).

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 total energy versus optimization step, and another chart document called $[seedname]$ `Convergence.xcd`, showing, on the logarithmic scale, the total energy change, the maximum displacement, the maximum force, and the maximum stress versus optimization step.

- *Update textual results* is checked: Materials Studio downloads a text file called `Status.txt` that contains a summary of the calculation performed (task, DFT functional, energy cutoff for plane wave basis set, electronic minimization method, system charge and spin, and so on), the SCF iteration number, the total energy, the total energy convergence (that is, the change from the previous iteration), the maximum displacement, the maximum force, and the maximum stress for the last completed optimization step.

For Dynamics 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*] Constant.xcd, showing the constant of motion versus simulation time, and another chart document called [*seedname*] Temperature.xcd, showing the temperature versus simulation time. In addition, the chart document [*seedname*] Pressure.xcd is created if the calculation is run using the NPH or NPT ensembles.
- *Update textual results* is checked: Materials Studio downloads a text file called Status.txt that contains a summary of the calculation performed (task, DFT functional, energy cutoff for plane wave basis set, electronic minimization method, system charge and spin, and so on), the number of completed dynamics steps, the temperature, and the constant of motion for the last completed optimization step.

For Elastic Constants calculations, if

- *Update structure* is checked: there is no effect, as no structural changes are associated with the original structure. CASTEP performs an Energy calculation for the initial structure.
- *Update graphs* is checked: Materials Studio creates a chart document called [*seedname*] Energies.xcd, showing the total energy versus optimization step, and another chart document called [*seedname*] Convergence.xcd, showing, on a logarithmic scale, the total energy change, the maximum displacement, and the maximum force versus optimization step. These charts refer to the structure currently being processed, as indicated by the index of the strain pattern and of the strain magnitude for that pattern.
- *Update textual results* is checked: Materials Studio downloads a text file called Status.txt that contains a summary of the calculation performed (task, DFT functional, energy cutoff for plane wave basis set, electronic minimization method, system charge and spin, and so on), a description of the structure currently being processed (as indicated by the index of the strain pattern and of the strain magnitude for that pattern), the number of completed optimization steps, the total energy, and the total energy convergence (that is, the change from the previous iteration), the maximum displacement, and the maximum force for the last completed optimization step.

For TS Search 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*] TSSearch.xcd, showing the total energy versus reaction coordinate. For each phase of the transition-state search, a separate graph is displayed within the chart document.
- *Update textual results* is selected: Materials Studio downloads a text file called Status.txt that contains a summary of the calculation performed (task, DFT functional, energy cutoff for plane wave basis set, electronic minimization method, system charge and spin, and so on), a description of the phase of the transition-state search currently being processed, the reaction path coordinate, the total energy, the total energy convergence (that is, the change from the previous iteration), the maximum displacement, and the maximum force for the last completed search step.

For Properties runs or for any other task where electronic structure properties (band structure, density of states, or optical properties) are requested, textual updates are modified as follows.

When the CASTEP run enters the properties stage, the task description in the Status.txt file is changed to either Eigenvalues (for band structure or density of states) or Eigenvalues + Optical Properties (for optical properties). This file now contains a summary of the calculation, the number of

completed non-self-consistent iterations of the eigenvalues calculation, the maximum convergence of electronic energies, and the maximum change in electronic energies on the last completed iteration for any band or k-point.

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 CASTEP output files.

- For Geometry Optimization runs, Materials Studio downloads all the CASTEP 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 Dynamics runs, Materials Studio downloads all the CASTEP output files, updates the structure it has copied into the results folder to show the configuration at the beginning of the dynamics run, and creates a trajectory file, [*seedname*].xtd, that describes the molecular dynamics calculation. The trajectory file can be animated using the tools on the *Animation* toolbar.

- For Elastic Constants runs, Materials Studio downloads all the CASTEP output files for all strain patterns and strain amplitudes.

- For TS Search runs, Materials Studio downloads all the CASTEP output files, updates the structure it has copied into the results folder to show the resulting configuration, 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.

If a remote CASTEP job fails

Materials Studio verifies most of the data and settings required to perform a CASTEP job before it starts. If it cannot start the job, this generates error messages detailing the reasons.

However, sometimes jobs may fail for reasons that Materials Studio cannot verify before starting the job. In such cases, an error message giving more detailed information appears in the [*seedname*].castep file produced by the job or in the project log file. Other files stored in the job directory on the server, for example, Castepexe.log, may also contain further clues. To view the server-side files, you can use the Remote Gateway Web Page facility of the Job Explorer.

Note: You cannot access a Remote Gateway Web Page for Linux SSH gateways. If you need files from completed, stopped, or failed jobs, you must access them through the file system on the Linux SSH gateway machine itself.

Note: You cannot access a Remote Gateway Web Page for 3DEXPERIENCE Cloud jobs.

Below is a list of the most common reasons for CASTEP jobs to fail. It may help you to identify and fix any problems you have with your remote CASTEP jobs. For generic reasons for remote job failures, see If a remote job fails in the Materials Studio Online Help.

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

Common reasons for a CASTEP job to fail to start

Server-side problems

▪ Parallel CASTEP job fails with Error writing ... message under Linux.

Depending on the options selected, CASTEP may use significant amounts of disk space to store scratch files. Each node creates scratch files during the execution of a parallel CASTEP job. CASTEP uses the value of the environment variable GATEWAY_TMP as the location to use to save these files. <MS_INSTALL>/etc/Gateway/ms_vars.sbd defines this variable, you can change its value using the Remote Gateway Web Page. Ensure that the location that to use on each node points to a file system with at least 1 GB of free space.

> **Note:** The ./tmp setting for GATEWAY_TMP corresponds to using the common file space on the head node, in the actual job directory, to store the temporary files. This setting can have a detrimental effect on the performance of Linux clusters.

An additional problem may occur if you define the GATEWAY_TMP as a location on a shared disk resource that is NFS mounted from the nodes. Mount the NFS in a synchronous mode using hard mounts.

> **Tip:** It is important to identify the reason for the failure of a CASTEP job before taking any action. In most cases, the error message produced gives a good indication of the reason for the failure. If the error message indicates that the job failed, but does not provide specific reasons, review the [*seedname*].castep file produced by the job or the project log.

Running CASTEP in standalone mode

The most convenient way of running CASTEP is through the Materials Studio interface, which performs all the preparatory tasks required to run a CASTEP job. However, in some circumstances, it may be necessary to run CASTEP 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, that is, a computer that does not communicate with your Materials Studio client (perhaps because a firewall prevents automatic file transfer and job launch).

For more general information on using standalone mode, see the Running jobs in standalone mode help topic.

Generate the input files

CASTEP requires various input files that contain details of the calculation. More information about these files can be found in the CASTEP 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 CASTEP Job Files dialog, see the Running jobs in standalone mode help topic for further information.

> **Tip:** Only the .param input file is displayed in the Project Explorer. The other input files are saved as hidden files. You should ensure that your Windows folder settings allow you to view hidden files so that you are able to see all of the files you need to copy to the server in order to run CASTEP. It may also help to turn off the Windows option of hiding file extensions for known file types.

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

Usage:

`RunCASTEP.sh [-h] [-np number of cores] [-nt number of threads] [-q queue name] seedname` (Linux)

or

`RunCASTEP [-h] [-np number of cores] [-q queue name] seedname` (Windows)

Argument	Description
`-h`	Displays the help text.
`-np`	Specifies the number of cores on which to run CASTEP. When this option is not specified a single core is used.
`number of cores`	The number of cores to use.
`-nt`	Specifies desired number of threads. When this option is not specified a single thread for each process is used.
`number of threads`	The number of threads to use.
`-q`	Submits the job to the specified queue.
`queue name`	The name of the queue on which to run the job.
`seedname`	The seed used to identify the set of CASTEP input and output files. The input files should be present in the directory in which the CASTEP script is started.

If you wish to calculate properties, you should execute the script with all the seednames as parameters for the `RunCastep.sh`:

`RunCASTEP.sh -np 4 seedname seedname_BandStr seedname_DOS seedname_Optics`

> **Note:** By default large `seedname.check` files are removed after the execution to save space. In most cases the `seedname.castep_bin` files are enough to restart the calculation. However, if check files are needed they can be requested by adding the following command:
>
> `-extraoptions KeepCheckFiles:Yes`
>
> For example:
>
> `RunCASTEP.sh -extraoptions KeepCheckFiles:Yes seedname`

Download the output files from the server

When the CASTEP calculation is complete, you must transfer the output files back to your PC for analysis in Materials Studio. See Running jobs in standalone mode for further information.

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 CASTEP file formats topic. All of the files, *seedname.**, *seedname_BandStr.**, *seedname_DOS.**, *seedname_Optics.**, *seedname_PhonDOS.**, *seedname_ PhonDisp.**, and *seedname_Subset*.**, 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 `.castep` 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 CASTEP analysis options described in the topic Analyzing CASTEP results. Specifically, you can open the 3D Atomistic document containing the starting structure and update it, create a trajectory document and animate it, visualize volumetric properties, calculate DOS and optical spectra, and plot band structure.

CASTEP file formats

The CASTEP server program is a file-based application. It requires input files and produces a number of output files. The precise number and type of output files produced depends on the details of the CASTEP job being performed.

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

File type	Input or Output	Brief description
.param	Input	General input file (text)
.cell [*]	Input	Structure input file (text)
.castep	Output	Report on the calculation (text)
.check, .castep_bin [*]	Output	Charge density, wavefunctions, structure, and so on (binary)
.bands [*]	Output	Eigenvalues (text)
.cst_esp [*]	Output	Electrostatic potentials (binary)
.geom [*]	Output	Geometry optimization trajectory data (text)
.md [*]	Output	Molecular dynamics trajectory data (text)

File type	Input or Output	Brief description
.ts *	Output	Transition state search trajectory data (text)
.phonon *	Output	Phonon data (text)
.pdos_weights *	Output	Weights required to calculate PDOS (binary)
.cst_ome *	Output	Matrix elements required to calculate optical properties (binary)
.elf *	Output	Electron localization function, ELF (binary)
.bib	Output	Bibliography file in BibTeX format (text)
.otfg *	N/A	Information required for generating pseudopotential files on the fly stored on the client (text)
.tddft	Output	Results of a CASTEP calculation of excitations in the time-dependent DFT approach

* These files are hidden by default, so they will not appear in the Materials Studio Project Explorer; these files are only visible in the Windows File Explorer if Windows on your machine is configured to show hidden files.

CASTEP file formats - PARAM

The .param file contains all of the control parameters required to run a CASTEP job, including the type of calculation, the charge, the spin state, and convergence tolerances. The file consists of lines containing keywords and associated values.

A .param file is generated by Materials Studio when you launch a calculation or when you click the *Save Files* button on the CASTEP Job Files dialog. Job options selected using the interface appear as keywords in the resulting .param file.

Under certain circumstances, you may wish to manually add keywords to a .param file. The procedure is described in the topic Running CASTEP in standalone mode.

The following rules govern keywords in the .param file:

- Keywords may appear in any order.
- The keywords and values are case- and punctuation-insensitive.
- Only one keyword and its options may appear on a line.
- Keywords that do not appear in the .param file are set to their default values.
- Units may be specified for physical quantities.

Note: Recognized units and their identifiers are listed in the UNIT keyword topics. If no units are specified, the default units will be assumed.

- Comment lines (those beginning with #, ;, ! or COMMENT) and blank lines are ignored.

Keywords and their values are fully described in the topic CASTEP keywords.

CASTEP file formats - CELL

The .cell file contains geometry information, including cell parameters, atomic coordinates, and k-point coordinates and weights. The file consists of lines containing keywords and data blocks, and

associated values.

A `.cell` file is generated by Materials Studio when you launch a calculation or when you click the *Save Files* button on the CASTEP Job Files dialog.

Under certain circumstances, you may wish to manually add keywords to a `.cell` file. The procedure is described in the topic Running CASTEP in standalone mode.

The following rules govern keywords and data blocks in the `.cell` file:

- Keywords and data blocks may appear in any order.
- The keywords, data blocks, and values are case- and punctuation-insensitive.
- Only one keyword and its options may appear on a line.
- Data blocks are preceded by `%BLOCK <keyword>`, followed by a series of data lines, and terminated by `%ENDBLOCK <keyword>`.
- Keywords and data blocks that do not appear in the `.cell` file are set to their default values.
- Units may be specified for physical quantities.

> **Note:** Recognized units and their identifiers are listed in the UNIT keyword topics. If no units are specified, the default units will be assumed.

- Comment lines (those beginning with `#`, `;`, `!` or COMMENT) and blank lines are ignored.

Keywords and their values are fully described in the topic CASTEP keywords.

CASTEP file formats - CASTEP

The `.castep` file contains the numerical output of a CASTEP job in ASCII format. The header describes the settings used, followed by the calculation results.

CASTEP file formats - binary checkpoint files

The `.check` and `.castep_bin` files contain the numerical output of a CASTEP job in binary format. The difference between the two files is that the `.check` file stores electronic wavefunctions in addition to all other information (calculation parameters, structure, electron density, electronic, and vibrational properties) and can become very large for large systems.

At least one of these files is required by the Materials Studio client to analyze CASTEP results. The CASTEP module in Materials Studio allows you to choose which of the two binary files to download after job execution.

> **Note:** Visualization of orbitals or of STM images requires information about electronic wavefunctions, hence the `.check` file is always downloaded if any of these properties were requested.

CASTEP file formats - BANDS

The `.bands` file contains electronic eigenvalues for all k-points in a CASTEP job. The data in this file are used for band structure plotting and optics, DOS, and PDOS calculations.

The file has the following format:

The eigenvalues are given in atomic units. The k-points are specified using fractional coordinates, which are followed by the corresponding k-point weight.

CASTEP file formats - CST_ESP

The `.cst_esp` file contains the electrostatic potentials output from a CASTEP job.

CASTEP file formats - task-specific files

CASTEP produces additional output files only when certain tasks are selected:

- `.geom` - Geometry optimization
- `.md` - Molecular dynamics
- `.ts` - Transition state search

These files contain trajectory information and have the following format:

```
        -1.82539879E+002        -1.82539879E+002                        <-- E
```

Values are always specified in atomic units and one of the following letter codes will be present:

- E - total energy and enthalpy
- T - temperature
- R - atomic coordinates (Cartesian)
- h - cell matrix
- hv - derivatives (velocities) of the cell matrix
- F - forces
- V - velocities
- S - stress tensor
- P - pressure

CASTEP file formats - PHONON

The `.phonon` file contains phonon frequencies and eigenvectors for all q-vectors in a CASTEP phonon calculation. The data in this file are used for phonon dispersion plotting, phonon DOS, and projected (partial) phonon DOS calculations. Phonon frequencies are always given in wavenumbers (cm^{-1}).

CASTEP file formats - TDDFT

The `.tddft` file contains detailed information about the results of a CASTEP calculation of excitations in the time-dependent DFT approach.

The header contains information about the structure, this block is followed by the representation of excited states as a superposition of Kohn-Sham one-electron bands. The overlap between occupied and unoccupied states gives a useful indication of the degree of charge transfer in every given excitation (if the value is significantly lower than 1.0, the TD-DFT description might be inaccurate since it does not take charge transfer into account).

The final section contains spectroscopic data; excitations energy, singlet or triplet character, level of convergence, and transition dipoles (the position operator between the ground-state wavefunction and the first order response wavefunction for the Nth excited state from TDDFT, $< u^0|\mathbf{r}|u^N >$). The transition dipole is projected onto the Cartesian axes. The character can be marked as "spurious" to reflect the fact that there are mathematically valid solutions to the linear-response TDDFT eigenvalue problem that are not physical (Heßelmann and Görling, 2009). These are solutions that provide a pure Kohn-Sham orbital transition, with no contribution from the exchange-correlation action. In terms of observables, the matrix elements will be zero (numerically so for computed quantities), and therefore harmless unless you want to select a specific state, for example for a structure optimization.

CASTEP file formats - PDOS_WEIGHTS

The `.pdos_weights` file contains the weights that are required to generate partial densities of state (PDOS), based on the results of a CASTEP job.

CASTEP file formats - CST_OME

The `.cst_ome` file contains the matrix elements for electronic interband transitions that are required to generate the dielectric function and other optical properties, based on the results of a CASTEP job. This is a binary file which contains the array of matrix elements; M(band1,band2,coord,k,spin). The loop is over the number of bands (band1, band2), x, y, z components (coord), k-points (nk), and spins (ns).

CASTEP file formats - ORBITALS

The `.orbitals` file contains the electronic wavefunctions from a CASTEP job. This file is created only for band structure or optics runs; the wavefunctions for all other types of CASTEP calculations are stored in the `.check` file. The `.orbitals` file is required to carry out analysis of orbitals and of the STM profile based on the output of band structure or optics calculations.

CASTEP file formats - CHDIFF

The `.chdiff` file contains the electron density difference calculated as part of a CASTEP job. The density difference is evaluated by subtracting the sum of the atomic densities from the total electron density of the system.

CASTEP file formats - ELF

The `.elf` file contains the electron localization function output from a CASTEP job.

CASTEP file formats - OTFG

The information required for generating CASTEP pseudopotential files on the fly is stored on the client in the files with the `.otfg` extension. These files are intended for the use on the client only, they are not expected to be transferred to the gateway server. The purpose of these files is to create a correct string in the SPECIES_POT block in `.cell` file.

The `.otfg` files can be edited manually, and new files with this extension can be created and stored in the Resources\Quantum\Castep\Potentials folder on the client. The most likely purpose for the editing would be to change the default core radius in order to create a softer (bigger core radius) or a more accurate and hard (smaller core radius) version of a pseudopotential for a given element. Occasionally, when core holes are used for some elements different settings are more appropriate.

The latest set of OTFG settings for ultrasoft pseudopotentials was developed to minimize the error with respect to fully converged all-electron DFT calculations. The error achieved by this set is 0.4 meV/atom, which puts CASTEP among the most accurate pseudopotential codes available. A full definition of the test framework and the meaning of the error is given by Lejaeghere et al. (2014), and on the website of the Delta project: http://molmod.ugent.be/deltacodesdft. The files that correspond to this set have the `_2017R2` suffix. This is the recommended set of OTFG ultrasoft potentials. Use files with the `_2017R2ncp` suffix when you require norm-conserving potentials. This set has a 1.1 meV/atom error in the Delta project tests. In addition, provides a set of "high throughput" ultrasoft OTFG settings for scripting. This QC5 set generally requires lower cutoff energy and offers faster but less accurate calculations (1.9 meV/atom error in the Delta project tests).

See Prof. David Vanderbilt's website on pseudopotential generation for more information: http://www.physics.rutgers.edu/~dhv/uspp/

The format can be described as:

- The order of the blocks and of single lines with keywords in the file is irrelevant.
- The order of the lines inside the BLOCK constructs is irrelevant.
- The separator between the keyword and the value can be any of the **designated separators**: "=",":", tab, space.
- The case of the keyword is irrelevant.
- The comments are allowed after the value as long as they are separated by at least one designated separator.
- The **compulsory fields** are the ones in red in the description above.
- The string fields have to be enclosed in single quotation marks.
- The energy shifts, CHANNEL_INFO_SHIFT, can be given either as shifts relative to the atomic eigenvalues or as an absolute value (in which case, the value should be preceded by VAL and a designated separator).
- The level shifts, CHANNEL_INFO_LEVELSHIFT, are artificial shifts of atomic eigenvalues relative to their DFT positions. Such shifts can be used to correct DFT error in relative positions of bands in a solid state calculation, see Profeta et al. (2004) for details.
- Information about multiple projectors in the CHANNEL_INFO lines should be separated by "&&", and there should be also at least one of the designated separators on either side of the "&&" construct.
- CHANNEL_INFO_TYPE, CHANNEL_INFO_SHIFT and CHANNEL_INFO_BETA_RC values within a CHANNEL_INFO block are all optional; if either of these entries is omitted CASTEP will use the default values for the respective property. The default setting is to use two ultrasoft projectors, using atomic eigenvalues as reference energies, and using BETA_RADIUS value specified elsewhere in the `.otfg` file.
- If two or three out of CHANNEL_INFO_TYPE, CHANNEL_INFO_SHIFT and CHANNEL_INFO_BETA_RC fields are present, then each of these fields should contain the same number of values.
- A block enclosed in STARTCOMMENT and ENDCOMMENT tags can be inserted anywhere in the file; its contents are ignored and can be used to keep a record of, for example, convergence testing and validation studies.
- The only value currently allowed on the COMPATIBILITY line is 'compat7'. The generator has been improved in the 8.0 release, so that it produces slightly different (although functionally equivalent) pseudopotential from the same input. The COMPATIBILITY option has been added to all `00.otfg` files to ensure compatibility with the earlier releases.

Note: COARSE, MEDIUM and FINE values are used by the CASTEP GUI in order to determine the cutoff energy for the calculations carried out at the specified level of accuracy. If you are generating a new file, you would have to carry out the convergence testing to determine the appropriate values for the new potentials.

In order to ensure that the OTFG for core holes is appropriate some conditional settings have been appended for certain elements, in a section which is only used when core holes are requested. If core holes are not being used in the calculation the `CORE_HOLE_INFO` keywords are ignored and the preceding settings are used.

Reaction Kinetics Study Table

The results of the reaction rate calculation are collected in a study table which contains the following tabs:

- *Summary* - contains a summary of the results, reporting the main parameters of the calculation, fit coefficients, and root-mean-square error (RMSE) which is calculated for ln(k(T)). If the fit parameters (also shown on the *Graphs* tab) produce too high n, or Ea becomes negative, the corresponding lines in the study table are highlighted in red.

- *Structures* - contains the collection document representing the entire reaction as well as one atomistic document for each of the reactants and products.

- *Graphs* - contains the temperature dependence of the reaction rates coefficients ($k(T)$) for forward and backward reactions together with equilibrium constants. It also contains results of the fit using Arrhenius form (see Kinetics constants theory) with temperature $T_0 = 298.15$ K together with standard Arrhenius form ($n = 0$, the temperature independent pre-exponential coefficient).

- *Partition Function* - contains the calculated partition functions for reactant(s), product(s), and transition state.

Chapter 4: Theory in CASTEP

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

CASTEP background theory

This section provides information specific to the implementation of DFT in the CASTEP program. The general overview provides information on the concepts of charge density, DFT functionals, the SCF procedure, and band structures, which are applicable to any computational implementation of DFT.

This section provides background information on aspects of DFT that are specific to CASTEP.

CASTEP provides a robust and efficient implementation of DFT that is based on the following concepts:

- Pseudopotential description of the electron-ion interaction
- Supercell approach with periodic boundary conditions
- Plane wave basis set
- Extensive use of fast Fourier transform (FFT) for evaluation of the Hamiltonian terms
- Iterative schemes for the self-consistent electronic minimization
- Implementation of the most popular DFT expressions for the exchange-correlation functional, including the screened and exact exchange schemes.

This section provides information on some of these topics. For more detailed information, refer to the links listed at the end of this topic.

Supercell approach

CASTEP is based on a supercell method, you must perform all studies on a periodic system, even when the periodicity is superficial. For example, you must represent a crystal surface by a finite-length slab (Figure 1). To study molecules, you must assume that they are in a box and treat them as periodic systems. There is no limitation on the shape of the supercell.
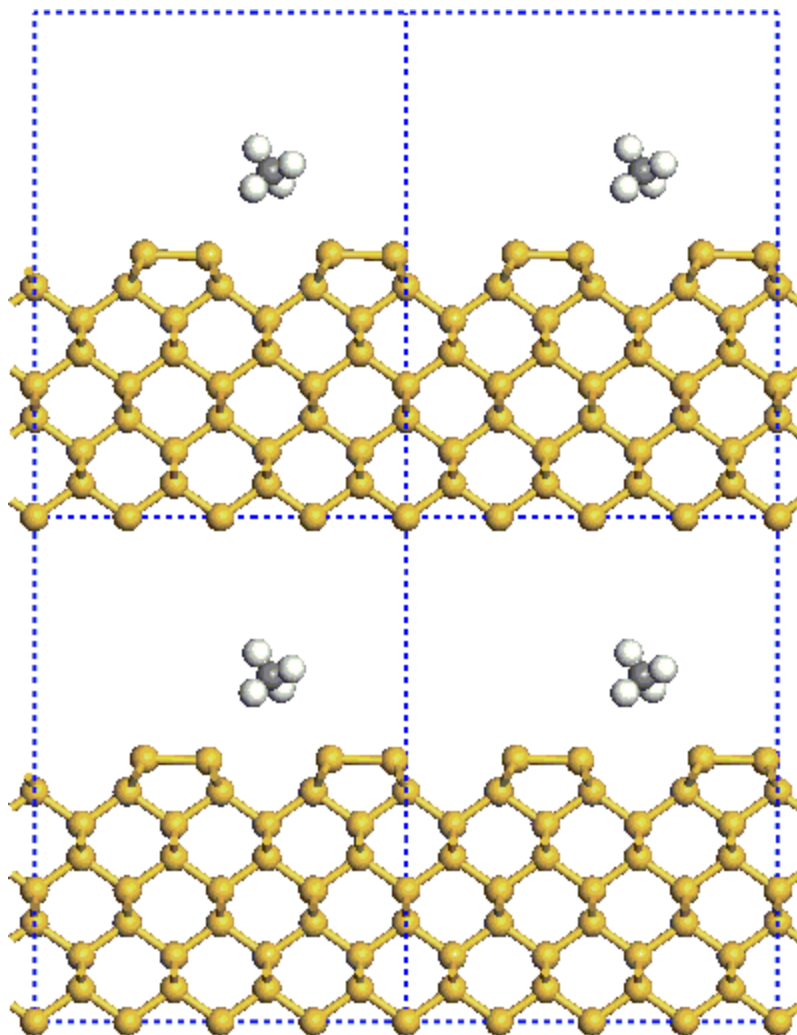
Figure 1. Schematic representation of the supercell calculation of a small molecule adsorption on a surface

The main advantage of imposing periodic boundary conditions relates to Bloch's theorem. This states that in a periodic system you can write each electronic wavefunction as a product of a cell-periodic part and a wavelike part (Payne et al. 1992).

Eq. CASTEP 1

$$\psi_i(\mathbf{r}) = e^{ik\mathbf{R}} \psi_i(\mathbf{r})$$

You can then expand the cell periodic part, ψ, using a basis set consisting of a discrete set of plane waves whose wave vectors are reciprocal lattice vectors of the crystal:

Eq. CASTEP 2

$$\psi_i(\mathbf{r}) = \sum C_{i,\mathbf{G}} e^{i\mathbf{G} \ \mathbf{R}}$$

Therefore, you can write each electronic function as a sum of plane waves, $\exp[i(\mathbf{k}+\mathbf{G})\cdot\mathbf{R}]$. For details of the advantages and technical details of the plane wave basis set, see Plane wave basis set on page 108.

Among the major gains is the simplified form of the Kohn-Sham equations:

Eq. CASTEP 3

$$\sum \left[|\mathbf{k}+\mathbf{G}|^2 \delta_{\mathbf{G}\mathbf{G}'} + V_{ion}(\mathbf{G}-\mathbf{G}') + V_H(\mathbf{G}-\mathbf{G}') + V_{xc}(\mathbf{G}-\mathbf{G}') \right] C_{i,\mathbf{k}+\mathbf{G}'} = \varepsilon_i C_{i,\mathbf{k}+\mathbf{G}}$$

In this form, the kinetic energy is diagonal, and the various potentials (electron-ion, Hartree, exchange-correlation) are described in terms of their Fourier transforms.

Another advantage of the plane wave basis set is the ease of calculating derivatives of the total energy with respect to atomic displacements (that is, stresses and forces are computationally cheap in this approach). This enables the implementation of efficient geometry optimization and molecular dynamics schemes. It is also straightforward to study and improve convergence of plane-wave basis set calculations, as there is a systematic way of adding more basis functions.

However, there is an additional cost to using the supercell approach for systems that lack periodicity in three dimensions inherently (isolated molecules, defects in solids, surfaces, and so on). In a study of a single defect, for example, the properties of an infinite array of defects (Figure 2) would always be calculated. Therefore, it is essential to introduce enough separation between artificial images of such nonperiodic objects to ensure that there is no appreciable interaction between them. The situation is similar for surface calculations carried out in a slab geometry. Ensure that the vacuum layer is thick enough to eliminate artificial interactions between the slabs.
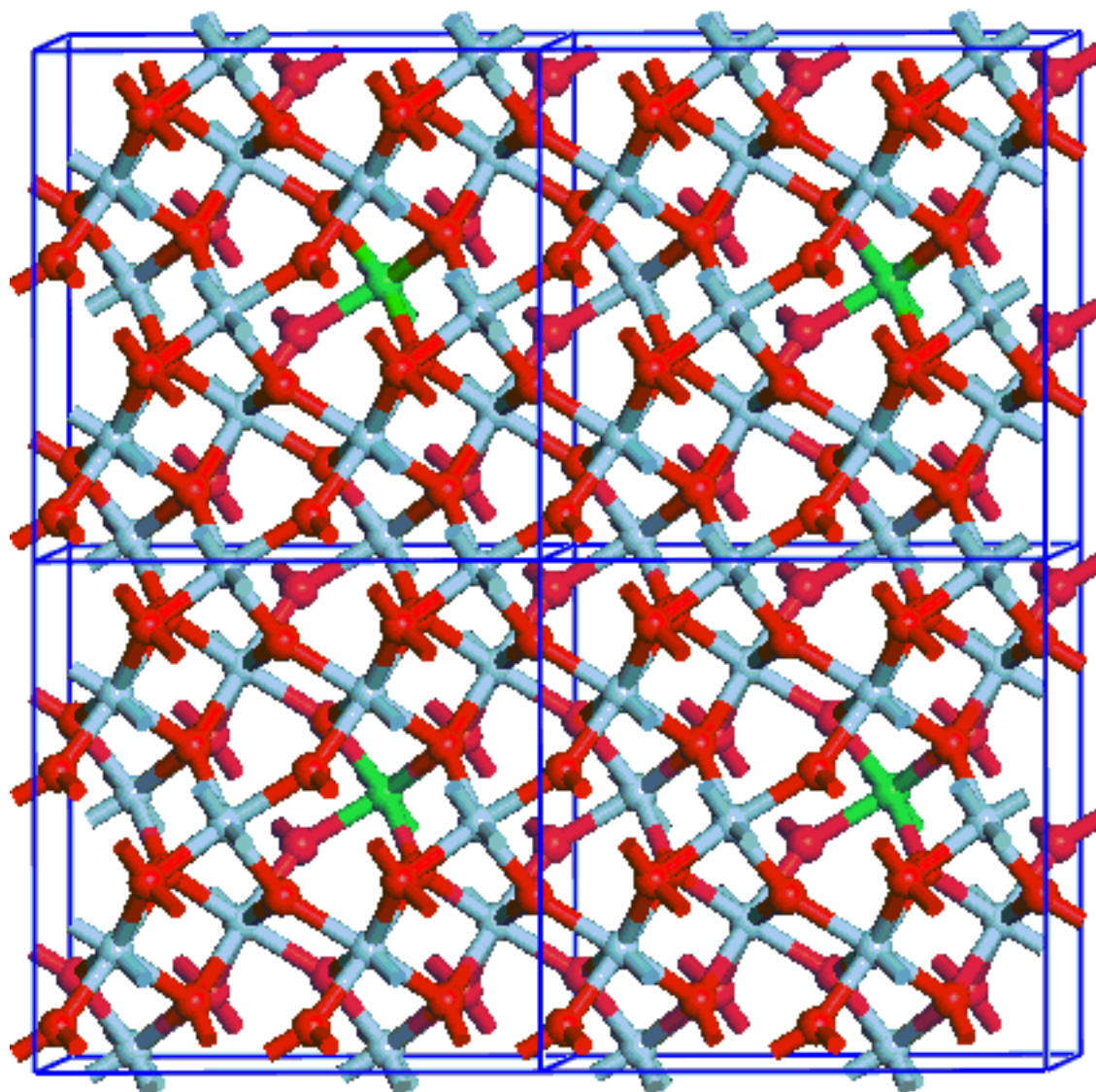

Figure 2. Schematic representation of the supercell calculation of a substitutional impurity

Fast Fourier transforms (FFT) in CASTEP

One of the major computational steps in CASTEP is the calculation of the product of the Hamiltonian with a wavefunction, $\mathbf{H}\psi$. Studies have shown that above $\mathbf{H}\psi$ the kinetic energy operator of the Hamiltonian has a diagonal representation in reciprocal space. The same is true of the Hartree operator and of the local pseudopotential operator. However, the exchange-correlation potential has a diagonal representation in real space. This means that there is a need for an efficient way of transforming various entities (wavefunctions, potentials, search directions) from real to reciprocal space and back. FFT provide this, so that the gain from evaluating various parts of the Hamiltonian in their "natural" representations is not offset by the cost of the transformation.

Exchange-correlation functionals in CASTEP

CASTEP implements a number of exchange-correlation functionals: local (LDA), gradient-corrected (GGA), and fully nonlocal (based on the exact and screened exchange formalism).

Local exchange-correlation functionals in CASTEP

The exchange-correlation energy is given by Eq. DFT 7. CASTEP only provides one local functional, the Perdew and Zunger (1981) parameterization of the numerical results of Ceperley and Alder (1980), CA-PZ.

This particular prescription for the local representation of the exchange-correlation potential is considered one of the most accurate descriptions available (Srivastava and Weaire, 1987).

Gradient corrected exchange-correlation functionals in CASTEP

The so-called nonlocal or gradient-corrected functionals depend on $d\rho/dr$ as well as on ρ. This provides a considerable increase in the accuracy of predicted energies and structures, but with an additional cost. The nonlocal functionals available in CASTEP include:

Name	Description	Reference
PW91	Perdew-Wang generalized-gradient approximation, PW91.	Perdew and Wang
PBE	Perdew-Burke-Ernzerhof functional, PBE.	Perdew et al.
RPBE	Revised Perdew-Burke-Ernzerhof functional, RPBE.	Hammer et al.
WC	More accurate GGA functional, based on a diffuse radial cutoff for the exchange hole in real space and the analytical gradient expansion of the exchange energy for small gradients.	Wu and Cohen
PBEsol	A version of the PBE functional that improves the equilibrium properties of densely packed solids and their surfaces.	Perdew et al.
BLYP	Becke exchange, Lee-Yang-Parr correlation.	Becke; Lee, Yang, Parr

The PBE functional has been designed to give essentially the same results as the PW91 functional but it is more robust in systems with rapidly varying electron density. The RPBE functional was designed specifically to improve the DFT description of the adsorption energies of molecules on metallic surfaces. For a detailed comparison of these three functionals when applied to surface science problems, see Marlo and Milman, 2000. One of the latest developments, PBEsol functional, is explicitly designed to improve the first-principles gradient expansion for exchange over a wide range of density gradients. This therefore improves the description of equilibrium properties of densely packed solids and their surfaces.

Implementation of all gradient-corrected functionals in CASTEP follow the method described by White and Bird (1994). The application of gradient-corrected exchange-correlation functionals in total-energy calculations using a plane-wave basis set is less straightforward than in localized basis set approaches

(used in other programs such as DMol³). The usual form of the exchange-correlation potential includes gradients whose calculation requires the use of a high-quality representation of the density. This is computationally expensive in both memory and time. These problems are overcome by defining an exchange-correlation potential for the discrete set of grid points consistent with the discretized form of the exchange-correlation energy used in the plane-wave total-energy calculations. This potential is calculated exactly on the minimum fast Fourier transform grid and gives improved convergence and stability as well as computational efficiency.

Meta-GGA functional

In addition to the generalized gradient (GGA) functionals, which depend on the local density and its gradient, CASTEP can handle functionals that depend on the kinetic energy density. The current supported functional is RSCAN (Bartók and Yates, 2019), which is an improved regularized version of the SCAN ("Strongly Constrained and Appropriately Normed") functional developed by Sun et al., 2016. Meta-GGA functionals are considered to be more accurate than pure GGA, and the cost of such calculations is significantly lower than for nonlocal functionals.

The SCAN functional satisfies all known constraints that a semi-local functional can satisfy. The remaining free parameters are fitted to reproduce exact or accurate reference values, or norms, of exchange and correlation energies.

The RSCAN modification eliminates the unphysical divergence of the exchange-correlation potential, which occurs in some free atoms. It also fixes the feature of the switching function in SCAN, which introduces rapidly oscillating regions in the exchange-correlation potential. These improvements make the SCAN functional usable in the context of robust pseudopotential generation. CASTEP's implementation has shown that RSCAN is transferable and accurate for a broad range of solid state and molecular systems.

> **Note:** There are limitations on the use of meta-GGA in CASTEP. The meta-GGA functional is not compatible with spin-orbit coupling, J-coupling, linear-response phonons, or polarizability calculations. You cannot use the formalism with mixture atoms. You can only use on-the-fly generated pseudopotentials.

Nonlocal exchange-correlation functionals in CASTEP

Kohn-Sham schemes based on LDA and GGA functionals have a common feature: they underestimate the band gap substantially. This does not affect the accuracy of the description of the total energy and related properties of crystals and molecules (equilibrium structure, vibrational spectra, elastic constants, and so on). However, you often require an accurate description of the details of the electronic structure to understand the properties of semiconductors and insulators. Then a DFT error of up to 50% in the calculated band gap energy becomes unacceptable.

It is possible to correct for the DFT band gap error by introducing an empirical scissors correction. This is effectively a rigid shift of the conduction band with respect to the valence band. This approach produces satisfactory results for such properties as optical spectra, provided the experimental band gap is accurate. The scissors operator scheme is very difficult to use in predictive studies and in the context of band gap engineering, when there is little or no experimental information about the electronic structure. In addition, the scissors operator approach does not help when you require an improvement in the description of the electronic structure of metallic systems.

There are a wide variety of techniques designed to deal with the band-gap problem in DFT. Most of them are exceedingly complex and time consuming. One of the most practical solutions is the so-called screened exchange, or sX-LDA scheme, developed in the context of the generalized Kohn-Sham procedure (Seidl et al., 1996). Generalized Kohn-Sham schemes allow one to split the exchange contribution to the total energy into a screened, nonlocal and a local density component.

CASTEP implements the following generalized Kohn-Sham schemes:

- HF: exact exchange, no correlation
- HF-LDA: exact exchange, LDA correlation
- sX: screened exchange, no correlation
- sX-LDA: screened exchange, LDA correlation
- PBE0: combination of PBE functional with a predefined amount of exact exchange (Adamo and Barone, 1998)
- B3LYP: combination of Hartree-Fock exchange with DFT exchange-correlation (Becke, 1993)
- HSE03: hybrid functional based on a screened Coulomb potential (Heyd et al., 2003)
- HSE06: similar to HSE03, but with optimized screening parameters (Krukau et al., 2006)

> **Tip:** Use the sX-LDA or HSE06 scheme for band gap calculations.

The implementation of screened exchange in CASTEP follows closely the recipe suggested by Seidl et al. (1996). This uses the Thomas-Fermi screening function (the case of zero screening length, k_{TF}, corresponds to the exact exchange formalism).

CASTEP provides a number of schemes for evaluating the screening length. The most straightforward to use is average density. This is a reasonable approach for bulk solids, but not for systems with large amounts of vacuum in the cell, for example molecules, surfaces, porous materials, and so on.

Alternatively, you can use the k_{TF} value associated with the self-weighted average density of the system. The self-weighted average is given by the integral of the density squared divided by the integral of the density. This removes the problems connected with large regions of vacuum. Otherwise, you can evaluate the self-weighted average of the screened exchange energy density.

Nonlocal functionals have certain limitations compared with LDA and GGA functionals. For example, the optical properties calculated using these functionals might be inaccurate. This problem is related to the introduction of a fully nonlocal component of the Hamiltonian. The addition of a nonlocal potential breaks the usual expressions for transforming the optical matrix element from the position operator to the momentum operator, because the commutator with the Hamiltonian becomes exceedingly complex (Asahi et al., 1999). However, even with the significant computational overhead of the screened exchange formalism, it provides a state-of-the-art scheme for predictive studies of electronic and optical properties of crystals.

> **Tip:** CASTEP only implements nonlocal functionals for norm-conserving potentials, not for ultrasoft ones.

> **Note:** There is an important difference between standard DFT calculations with local exchange-correlation potentials and the nonlocal exchange case. The potential used in the latter scenario depends on the SCF k-points, while in the former case, the potential depends only on electron density. This difference can make all properties calculations a lot more expensive in terms of memory usage and CPU time. Limit the number of SCF k-points that you use in such situations. This is particularly relevant for small unit cells, where the default settings might generate a very large k-point set.

Spin Orbit Coupling

Spin orbit coupling between the electron's spin and its orbital angular momentum couples the direction of spin with the underlying lattice. This is a relativistic effect that increases in magnitude with the nuclear charge, Z. For materials with heavy elements a scalar relativistic treatment (that is, one that neglects the

spin orbit interaction) is insufficient to model the electronic band structure. In magnetic systems, the spin orbit coupling introduces a preferential direction (or set of directions) for the spin density.

The prediction of many physical properties requires the inclusion of spin orbit coupling. For example, effective masses in semiconductors (modeling light and heavy holes), the anomalous Hall effect, Berry curvature, topological insulators, and magnetoelectrics.

The plane waves and pseudopotential model only explicitly models the pseudized valence electrons. These electrons have a velocity, $v << c$, and as such the standard (non-relativistic) Kohn-Sham (KS) equations are appropriate. Work by Dal Corso et al. (2005) allowed the development of j-dependent pseudopotentials so that CASTEP can include spin orbit coupling . These pseudopotentials act on KS spin or wavefunctions and an electron density with a vector spin at each grid point.

DFT+U (LDA+U)

DFT can only give access to the ground state properties of a system, even if you know the exact exchange-correlation potential. To model electronic excitations, CASTEP substitutes Kohn-Sham equations with the Dyson equation, using the energy-dependent self-energy operator instead of the unknown exchange-correlation potential. The local and energy-independent exchange-correlation potential can represent this operator, in which case you can recover the Kohn-Sham equations for one-electron excitations. However, this approach is not appropriate for a large class of compounds, so-called correlated systems. These systems require a mixture of the Hubbard model theory and DFT. The most popular implementation is the DFT+U method, as introduced by Anisimov and coworkers (1991).

The CASTEP implementation of DFT+U adopts a simplified, rotationally invariant approach (Cococcioni and de Gironcoli, 2005, Dudarev et al., 1998). The only external parameter required for this approach is the effective value of the on-site Coulomb parameter, U, for each affected orbital. You can calculate this parameter theoretically (Cococcioni and de Gironcoli, 2005). However, experience shows that the best results are achieved when the U parameter can vary depending on the property of interest. CASTEP therefore does not calculate the value of U, but uses it as an input parameter.

Symmetry in CASTEP

You can trace back the original idea of using space group symmetry in plane-wave total energy calculations to the *k290* package (Kunc et al., 1985). The importance of this issue for achieving high performance has long been recognized. Often a high symmetry system has a fairly small unit cell. This means that the Brillouin zone is quite large and efficient Brillouin zone sampling requires a high number of k-points. When you recognize a relationship between the contributions to the charge density from wavefunctions with k-vectors related by symmetry, you can greatly reduce this number. It is then sufficient to use only one k-point from each star of symmetry-related points. Because the cost of a CASTEP calculation increases linearly with the number of k-points, any symmetry-related reduction in the number of k-points gives a direct computational speedup.

CASTEP during geometry optimization also uses space group symmetry. CASTEP always *symmetrizes* forces on atoms, the stress tensor, and consequently atomic displacements and changes in the cell parameters, so that the space group symmetry can never become lower. However, CASTEP does not perform symmetry analysis. Instead, it uses symmetry information provided by Materials Studio.

Pseudopotentials

The concept of a pseudopotential is a crucial one for plane-wave total energy methods since the alternative full Coulomb potential of the electron-ion interaction decays too slowly to be accurately represented by a small number of Fourier components.

Another way of looking at the problem is to analyze wavefunctions. Consider a solid as a collection of valence electrons and ion cores. The ion cores contain nuclei and tightly bound core electrons. The

valence-electron wavefunctions are orthogonal to core-electron wavefunctions. All-electron DFT methods treat core and valence electrons on an equal footing. In the pseudopotential approach ion cores are considered to be *frozen*. This means that properties of molecules or solids are calculated on the assumption that the ion cores are not involved in chemical bonding and do not change as a result of structural modifications.

All-electron wavefunctions of valence electrons exhibit rapid oscillations in the core region in order to satisfy the orthogonality constraint. It is impractical to represent such functions using plane waves as the size of the basis set would be prohibitive. The pseudopotential approximation replaces core electrons and the strong Coulomb potential by a weaker pseudopotential that acts on a set of pseudo wavefunctions. This potential can be represented with only a small number of Fourier coefficients. Pseudo wavefunctions ideally should have no nodes inside the core regions and thus they only require a small basis set. It is now well known that the combination of the power of plane wave technology and the pseudopotential concept is extremely useful for the description of chemical bonding (for a review see Srivastava and Weaire, 1987).

Traditionally, pseudopotentials are constructed so as to reproduce faithfully the scattering properties of the full ionic potential. The phase shift produced by the ionic core is different for each angular momentum component (*s*, *p*, *d*, and so on) of the valence wavefunction. Thus, the scattering from the pseudopotential must be angular momentum dependent. The most general form for a pseudopotential is:

Eq. CASTEP 4

$$NL = \sum |lm\rangle V_l \langle lm|$$

where $|lm\rangle$ are the spherical harmonics and V_l is the pseudopotential for angular momentum l. A pseudopotential that uses the same potential in each angular momentum channel is called a local pseudopotential. Local pseudopotentials are computationally much more efficient than a nonlocal ones, however, only a few elements can be described accurately using local pseudopotentials.

An important concept in the pseudopotential applications is the degree of *hardness* of a pseudopotential. A pseudopotential is considered *soft* when it requires a small number of Fourier components for its accurate representation and *hard* otherwise. Early development of accurate norm-conserving pseudopotentials quickly showed that the potentials for transition metals and for first row elements (O, C, N, and so on) turn out to be extremely hard (Bachelet et al., 1982; Kerker, 1980). Various schemes have been suggested to improve convergence properties of norm-conserving pseudopotentials (Troullier and Martins, 1991). Norm-conserving potentials in CASTEP are generated using the kinetic energy optimization scheme developed by Lin et al., (1993) and Lee (1996).

A more radical approach was suggested by Vanderbilt (1990), which involves relaxing the norm conservation requirement in order to generate much softer pseudopotentials. In the ultrasoft pseudopotential scheme the pseudo-wavefunctions are allowed to be as soft as possible within the core region, so that the cutoff energy can be reduced dramatically. Ultrasoft potentials (USP) have another advantage besides being much softer than the norm-conserving potentials. The generation algorithm guarantees good scattering properties over a pre-specified energy range, which results in much better transferability and accuracy of the pseudopotentials. USP usually also treats shallow core states as valences by including multiple sets of occupied states in each angular momentum channel. This also adds to high accuracy and transferability of the potentials, although at a price of computational efficiency.

Transferability is the main benefit of the pseudopotential technique over all electron DFT implementations. Pseudopotentials are constructed from a fixed electronic configuration of an isolated atom or ion and thus they reproduce the scattering properties of a nucleus in that particular configuration. They can also be used reliably for any other atomic configuration or in various solid-state

environments due to the way in which they are generated, which guarantees the correct scattering properties over a wide energy range. An example of the accuracy that can be achieved across a number of structures and chemical environments is given by Milman et al. (2000).

Nonlocal pseudopotentials, even in their most efficient separable representation (Kleinman and Bylander, 1982), still consume a large share of the computational time in pseudopotential total-energy calculations. In addition, the cost of applying nonlocal pseudopotentials in reciprocal space increases with the cube of the number of atoms. Therefore, it becomes one of the dominant operations for large systems. The nonlocality of the pseudopotential, however, extends only over the region occupied by the core of the atom. As the core region is relatively small, especially if the system has a lot of vacuum in it (slab calculations, open zeolite systems, and so on), it is more efficient in this case to apply the pseudopotential in real space. The computational cost of this method increases with the square of the number of atoms and so is preferable for big systems. CASTEP uses the scheme developed originally for norm-conserving potentials (King-Smith et al., 1991) and was subsequently generalized for the case of ultrasoft pseudopotentials.

The separation of electrons into core and valence creates a problem when treating exchange-correlation interactions. Within the core region of the nucleus the densities of the two subsystems overlap which makes it difficult to cleanly *descreen* the pseudopotential during its generation. The only term in the potential energy operator that is nonlinear with respect to the electron density is the exchange-correlation energy. It has been shown by Louie et al. (1982) that there is a simple explicit scheme for treating the nonlinear exchange and correlation interaction between the core and the valence charge densities. This approach leads to significant improvements in the transferability of the potential. In particular, the spin-polarized calculations become noticeably more accurate. The nonlinear core correction (NLCC) term is especially important when semicore states are not explicitly treated as valences. On the other hand, their explicit inclusion into the valence subsystem essentially removes the need for the NLCC treatment.

Norm-Conserving Pseudopotentials

The main requirement of the pseudopotential approach is that it reproduces the valence charge density associated with chemical bonds. For pseudo and all-electron wavefunctions to be identical beyond the core radius, R_c, the integrals of squared amplitudes of the two functions must be the same (Hamann et al., 1979). This is equivalent to requiring norm-conservation from pseudo wavefunctions, that is, each should carry exactly one electron. This condition ensures correct reproduction of the scattering properties of the pseudopotential.
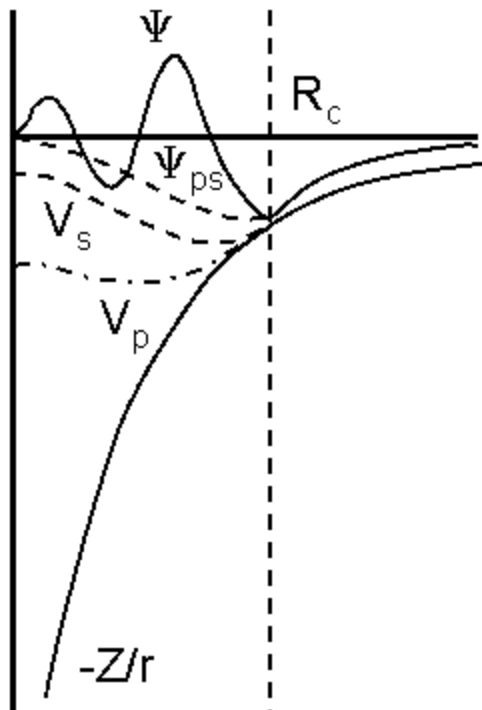
Figure 1. Schematic representation of the all-electron and pseudized wavefunctions and potentials

The typical method for generating pseudopotentials is as follows:

- All-electron calculations are carried out for an isolated atom in a chosen electronic configuration (not necessarily in the ground state). This provides valence electron eigenvalues and valence electron wavefunctions for the atom (shown as ψ in Figure 1).
- Selection of a parameterized form for the ionic pseudopotential (or the pseudo wavefunction).
- The parameters are then adjusted, so that a pseudoatom calculation with the same exchange-correlation potential as in the all-electron atom gives:
  - Pseudowavefunctions, ψ_{ps} (Figure 1), that match the valence wavefunctions outside some cutoff radius, R_c.
  - Pseudoeigenvalues that are equal to the valence eigenvalues.

This procedure involves direct inversion of the radial Kohn-Sham equation for parameterization of the pseudowavefunctions rather than the pseudopotential. Normalizing each wavefunction, pseudo and all-electron, to one, results in automatically satisfaction of the norm-conservation constraint because of matching the wavefunctions outside R_c.

The ionic pseudopotentials construction uses R_c ranging from one to two times the value of the physical core radius. The smaller the value of R_c, the harder and more transferable the potential. The conflicting effect of R_c creates an obvious trade-off between accuracy and efficiency.

Optimized Pseudopotentials

A number of recipes exist for producing pseudopotentials that are optimized with respect to the energy cutoff required in solid-state calculations.

Lin et al. (1993) suggested the following generation scheme based on the earlier work of Rappé et al. (1990).

1. The pseudo wavefunction $\psi_l(\mathbf{r})$ inside a cutoff radius is expressed as:
   Eq. CASTEP 5

$$\Psi_l^{ps}(\mathbf{r}) = \sum_{i=1}^{4} \alpha_i j_l(q_i r)$$

   Where:

$$\frac{j_l'(q_i R_c)}{j_l(q_i R_c)} = \frac{\phi_l'(R_c)}{\phi_l(R_c)}$$

   $j_l(q_i r)$ are spherical Bessel functions with $(i\text{-}1)$ zeros between $r=0$ and $r=R_c$. The cutoff radius value is as large as possible, consistent with satisfactory transferability of the potential.

2. Minimization of the kinetic energy beyond the cutoff vector q_c determines the coefficients α_i:
   Eq. CASTEP 6

$$\Delta E_l(\{\alpha_i\}, q_c) = -\int_0^{\infty} d\mathbf{r} \Psi_l^{ps*}(\mathbf{r}) \nabla^2 \Psi_l^{ps}(\mathbf{r}) - \int_0^{qc} d\mathbf{q} q^2 \left| \Psi_l^{ps}(\mathbf{q}) \right|^2$$

   where q_c is chosen to be equal to q_4 from Eq. CASTEP 5. Lagrange multipliers satisfy some additional constraints:

   - The normalization of the pseudowavefunction.
   - The continuity of the first two derivatives of the pseudowavefunction at R_c.

3. The standard step of inverting the radial Kohn-Sham equation produces a smooth pseudopotential with optimal convergence properties.

Lee (1996) suggested further enhancements and it is essentially this scheme that generated the bulk of norm-conserving pseudopotentials in the CASTEP database. This generation method eliminates the condition that the second derivative of the pseudo wavefunction must be continuous at a given cutoff radius because it automatically satisfies the second derivative constraint. The scheme allows you to tune q_c for a given R_c to optimize the accuracy and efficiency of a pseudopotential.

The USP implementation allows you to run CASTEP calculations with a lower energy cutoff than their NCP counterparts; producing a clear advantage in terms of the calculation time. However, USP formalism is more complex and becomes close to intractable for such complex concepts as linear response implementation for phonons or NMR properties, or for nonlocal exchange-correlation functionals. There is a number of tasks and properties that CASTEP can address only with norm-conserving potentials. The database of tabulated NCPs available in Materials Studio is rather old and in some cases might contain potentials that have not been tested sufficiently. A recommended alternative is to use on-the-fly generated norm-conserving pseudopotentials that are more accurate and much better tested.

Ultrasoft pseudopotentials

Ultrasoft pseudopotentials (USP) were introduced by Vanderbilt (1990) in order to allow calculations to be performed with the lowest possible cutoff energy for the plane-wave basis set. Since it is understood that there are inherent limits on optimizing the convergence of norm-conserving pseudopotentials, a completely different approach has been designed.

The rationale behind USP is that, in most cases, a high cutoff energy is only required for the plane-wave basis set when there are tightly bound orbitals that have a substantial fraction of their weight inside the core region of the atom. In these situations, the only way to reduce the basis set is to violate the norm-conservation condition by removing the charge associated with these orbitals from the core region. The

pseudo wavefunctions are thus allowed to be as soft as possible within the core, yielding a dramatic reduction in the cutoff energy.

Technically, this is accomplished by introducing a generalized orthonormality condition. In order to recover the full electronic charge, the electron density given by the square moduli of the wavefunctions is augmented in the core regions. The electron density can thus be subdivided into a soft part extending through the unit cell and a hard part localized in the core regions.

USP formalism in solid state

The total energy in the USP scheme has the same form as other pseudopotential plane-wave methods, with the nonlocal potential V_{NL} given as:

Eq. CASTEP 7

$$V_{NL} = \sum_{nm,I} D_{nm}^{(0)} \left| \beta_n^I \right\rangle \left\langle \beta_m^I \right|$$

where the projectors β and coefficients $D^{(0)}$ characterize the pseudopotential and differ for different atomic species. The index I refers to an atomic site. The electron density in the expression for the total energy is given by:

Eq. CASTEP 8

$$n(\mathbf{r}) = \sum_i \left[\left| \phi_i(\mathbf{r}) \right|^2 + \sum_{nm,I} Q_{nm}^I(\mathbf{r}) \left\langle \phi_i | \beta_n^I \right\rangle \left\langle \beta_m^I | \phi_i \right\rangle \right]$$

where ϕ are the wavefunctions and $Q(\mathbf{r})$ are the augmentation functions that are strictly localized in the core regions. The ultrasoft potential is fully determined by the local part, $V_{loc}{}^{ion}(\mathbf{r})$ and by the coefficients $D^{(0)}$, Q, and β. The algorithm that generates these quantities is described [below](#).

The relaxation of the norm-conserving constraint is achieved by introducing a generalized orthonormality condition:

Eq. CASTEP 9

$$\left\langle \phi_i \left| S \right| \phi_i \right\rangle = \delta_{ij}$$

where S is a Hermitian overlap operator:

Eq. CASTEP 10

$$S = 1 + \sum_{nm,I} q_{nm}^i \left| \beta_n^I \right\rangle \left\langle \beta_m^I \right|$$

where coefficients q are obtained by integrating $Q(\mathbf{r})$. Kohn-Sham equations can be rewritten for the USP case as:

Eq. CASTEP 11

$$H \left| \phi_i \right\rangle = \varepsilon_i S \left| \phi_i \right\rangle$$

where H can be presented as a sum of kinetic energy and local potential:

Eq. CASTEP 12

$$H = T + V_{eff} + \sum_{nm,I} D_{nm}^I \left| \beta_n^I \right\rangle \left\langle \beta_m^I \right|$$

where V_{eff} contains $V_{loc}{}^{ion}(\mathbf{r})$, Hartree and exchange-correlation terms. All the terms arising from the augmented part of the electron density are grouped with the nonlocal part of the pseudopotential (Eq. CASTEP 7) by defining new coefficients:

Eq. CASTEP 13

$$D_{nm}^I = D_{nm}^{(0)} + \int d\mathbf{r} V_{eff}(\mathbf{r}) Q_{nm}^I(\mathbf{r})$$

The difference compared with the norm-conserving case is the presence of the overlap operator S, the wave-function dependence of the coefficients D and the fact that the number of projector function β is typically twice as large. A number of calculations related to augmentation charges can be carried out in real space because of the localized nature of the function involved, so that the overall impact of these extra steps on efficiency is not large.

Further technical details of the USP implementation, including expressions for the derivatives of the total energy, can be found in Laasonen et al. (1993).

Pseudopotential generation

As in the norm-conserving case, an all-electron calculation is carried out on a free atom, leading to a screened atomic potential, $V_{AE}(r)$. For each angular momentum a set of reference energies, ε_l, is chosen. Typically two reference energies are sufficient. These energies should cover the range over which good scattering properties are required. At each reference energy the solution of the radial Kohn-Sham equation which is regular at the origin is obtained. Next cutoff radii R_{cl} are chosen and for each all-electron wavefunction ψ generated above, a pseudo wavefunction ϕ is constructed. The only constraint is that it should join smoothly to ψ at R_{cl}. A smooth local potential, $V_{loc}(r)$, is generated to match $V_{AE}(r)$ smoothly at a cutoff radius, R_{loc}. An auxiliary radius, R, is defined to be slightly higher than all of the core radii. Finally, the local orbitals are formed (they vanish beyond R):

Eq. CASTEP 14

$$|\chi_n\rangle = (\varepsilon_n - T - V_{loc}) |\phi_n\rangle$$

and their matrix of inner products:

$$B_{nm} = \langle \phi_n | \chi_m \rangle$$

It is now possible to define the quantities needed for the solid state calculation ($V_{loc}{}^{ion}(\mathbf{r})$, $D^{(0)}$, Q, and β):

Eq. CASTEP 15

$$Q_{nm}(r) = \Psi_n^*(r)\Psi_m(r) - \phi_n^*(r)\phi_m(r); q_{nm} = \int dr Q_{nm}(r)$$

Eq. CASTEP 16

$$|\beta_n\rangle = \sum_m (B^{-1})_{nm} |\chi_m\rangle$$

and $V_{loc}{}^{ion}(\mathbf{r})$, $D^{(0)}$ are produced using a descreening procedure:

Eq. CASTEP 17

$$V_{loc}^{ion}(r) = V_{loc}(r) - V_H(r) - V_{xc}(r)$$

Eq. CASTEP 18

$$D_{nm}^{(0)} = B_{nm} + \varepsilon_m q_{nm} - \int dr V_{loc}(r) n(r)$$

> **Note:** The non-linear core correction term can be introduced in the descreening procedure, Eq. CASTEP 17, in exactly the same way as in the norm-conserving case.

> **Note:** The formalism described above is based on the non-relativistic Schroedinger approach. With CASTEP you can also use a scalar-relativistic approach either as a Koelling-Harmon (1977) scheme or as its approximation commonly referred to as ZORA, zeroth order regular approximation (Lenthe et al. 1994).

The following conditions are satisfied in this scheme:

- The pseudo eigenvalues are equal to the all-electron ones, and the corresponding orbitals match exactly outside the core radii.
- The scattering properties are correct at each reference energy. Thus, the transferability can be systematically improved by increasing the number of such energies.
- The valence charge density is precisely equal to the all-electron valence density in the reference configuration.

Nonlinear core correction

The nonlinear core correction (NLCC) was first proposed by Louie et al. (1982) as a way of obtaining accurate pseudopotential descriptions of magnetic systems. It has been shown, however, that NLCC is equally important for spin non-polarized systems with semicore electrons.

The reason that the NLCC is required is found in the total energy expression in DFT:

Eq. CASTEP 19

$$E_{tot} = T\{\rho\} + E_{ion}\{\rho\} + E_{ee}\{\rho\} + E_{xc}\{\rho\}$$

In the pseudopotential formalism, the charge density is divided into core and valence contributions. The energy of the core is assumed to be constant and is subtracted out. Thus, in Eq. CASTEP 19 above the total charge density is replaced by a (pseudo) valence charge density and E_{ion} is evaluated using pseudopotentials.

As a result all interaction between core and valence electrons is transferred to the pseudopotential. This implies linearization with respect to charge density which can only be an approximation to the kinetic energy and the *explicitly* nonlinear exchange-correlation energy.

This linearization is obviously a good approximation when core and valence densities are well separated in space. However, if there is significant overlap between the two densities, it will be the source of systematic errors and will lead to reduced transferability of the potential.

The solution to the NLCC problem lies in a modifying the pseudopotential generation procedure and the solid-state algorithm. In a typical generation scheme a screened atomic potential V^l is produced for each angular momentum channel subject to certain constraints, for example norm-conservation, matching eigenvalues to all-electron values, and so on.

These screened potentials give rise to atomic pseudowavefunctions that represent valence states only. The valence pseudo charge density is constructed from these wavefunctions and is used to descreen the potential to produce the bare ionic potential:

Eq. CASTEP 20

$$V_{iob}^l(\mathbf{r}) = V^l(\mathbf{r}) - V_{ee}\left[\rho_\nu(\mathbf{r})\right] - V_{xc}\left[\rho_\nu(\mathbf{r})\right]$$

Since the exchange-correlation potential is a nonlinear function of the charge density, it can be shown that this procedure, especially for spin-polarized systems, creates ionic pseudopotentials that are

dependent on the valence configuration. Louie et al. (1982) suggested substituting Eq. CASTEP 20 with the following expression:

Eq. CASTEP 21

$$V_{iob}^l(\mathbf{r}) = V^l(\mathbf{r}) - V_{ee}\left[\rho_\nu(\mathbf{r})\right] - V_{xc}\left[\rho_\nu(\mathbf{r}) + \rho_c(\mathbf{r})\right]$$

Here the total exchange-correlation potential is subtracted from the screened atomic potential. In addition, the core charge must now be added to the valence charge whenever the exchange-correlation potential is calculated. This additional atomic information has to be passed on to CASTEP and the core charge is deemed to be the same in all applications. A drawback of this is that the core charge is difficult to represent accurately on the Fourier grid used in pseudopotential calculations. Furthermore, the core density is usually bigger than the valence density, so its presence might mask effects related to valence charge density.

The next step in developing the formalism was to introduce the partial core correction. This approach recognizes the fact that only the area of overlap between the core and valence densities is of interest. Core density close to the nucleus is of no consequence although this is precisely the part of the core density that causes the problems described above. Partial NLCC replaces the full core density with a function that coincides with ρ_c outside a certain radius, and falls off smoothly toward the nucleus.

CASTEP uses a partial core correction with numerical core density in the case of ultrasoft pseudopotentials for certain elements. The database of norm-conserving potentials does not, however, include NLCC information.

Real-space representations of pseudopotentials

The nonlocality of the pseudopotential only extends over the region occupied by the core of the atom. As the core region is relatively small, it should be possible to deal efficiently with the nonlocality of the pseudopotential by working in real space. Only a small number of operations should be required to project the angular momentum components of each wavefunction in the core of each atom. Furthermore, the number of operations needed to project the angular momentum components of a single wavefunction around a single atom in real space is independent of the size of the system, leading to better scaling with system size than in the reciprocal space projection scheme. The computational cost of the real-space implementation increases with the square of the number of atoms, compared with the cubic relationship that exists for reciprocal space projection methods (Payne et al., 1992).

CASTEP uses the scheme developed originally for norm-conserving potentials (King-Smith et al., 1991) and subsequently generalized for the case of ultrasoft pseudopotentials.

The reciprocal-to-real space transformation involves the following steps:

- Select the plane wave cutoff, G_{max}, which is to be used in the solid-state calculation.
- Set $\chi_l(q) = V_l(q)$ for $0 < q < G_{max}$ and $\chi_l(q) = 0$ for $q > \gamma$, where γ is the difference between the ideal Fourier grid size with no wrap-around errors for potential evaluation (at least $4G_{max}$). The Fourier transform of the pseudopotential $V_l(q)$, is defined as:

Eq. CASTEP 22

$$V_l(q) = \int_0^\infty r^2 V_l(r) j_l(qr) dr$$

where $V_l(r)$ is the original nonlocal projector and $j_l(qr)$ is the spherical Bessel function.

- Select a real-space cutoff radius, R_0. Generally this is about $1.5\text{-}2.0 \times R_c$, where R_c is the core radius used in pseudopotential generation.
- Variationally select $\chi_l(q)$ in the intermediate region, $G_{max} < q < \gamma$ by minimizing:

Eq. CASTEP 23

$$I = \int_{R_0}^\infty [r\chi_l(r)]^2 dr$$

The object of this step is to achieve the best possible convergence of the modified potential in real space.

- Transform $\chi_l(q)$ back to real space to get $\chi_l(r)$ which is now used in the real-space evaluation of nonlocal potential matrix elements in solid-state calculations.

The modified real-space projectors are no longer identically zero outside R_c, although the minimization in Eq. CASTEP 23 ensures the best possible convergence compatible with the removal of the wrap around error. A quantitative measure of the error introduced by the transformation is given by:

Eq. CASTEP 24

$$W_l(\mathbf{k} + \mathbf{G}) = \int_0^{R_0} r^2 \chi_l(r) j_l \left(|\mathbf{k} + \mathbf{G}| r \right) dr$$

This error function should be small (less than 0.001) for all wavevectors, q, and can be inspected in the CASTEP output file.

One should bear in mind that the use of real-space scheme represents an approximation and that more accurate results are obtained with the reciprocal-space version. The accuracy of the real-space transformation is controlled by the value of the cutoff radius, R_0. The default set of these values in CASTEP is designed to be for accuracy rather than performance. It is advisable to carry out independent tests on small systems before embarking on large-scale calculations with drastically reduced R_0 values.

The real space transformation of the pseudopotential depends on the cutoff energy for plane wave basis set, and thus it is not possible to precalculate real-space projectors in the same way as the reciprocal space potentials (which are provided in CASTEP database).

Plane wave basis set

Bloch's theorem states that the electronic wavefunctions at each k-point can be expanded in terms of a discrete plane-wave basis set. In principle, an infinite number of plane waves is required for such an expansion. However, the coefficients, $C_{\mathbf{k}+\mathbf{G}}$, for the plane waves with small kinetic energies, $|\mathbf{k} + \mathbf{G}|^2$, are more important than those with large kinetic energies. Thus, the plane wave basis set can be truncated to include only plane waves that have kinetic energies that are smaller than some particular

cutoff energy as illustrated in Figure 1 (the radius of the sphere is proportional to the square root of the cutoff energy).
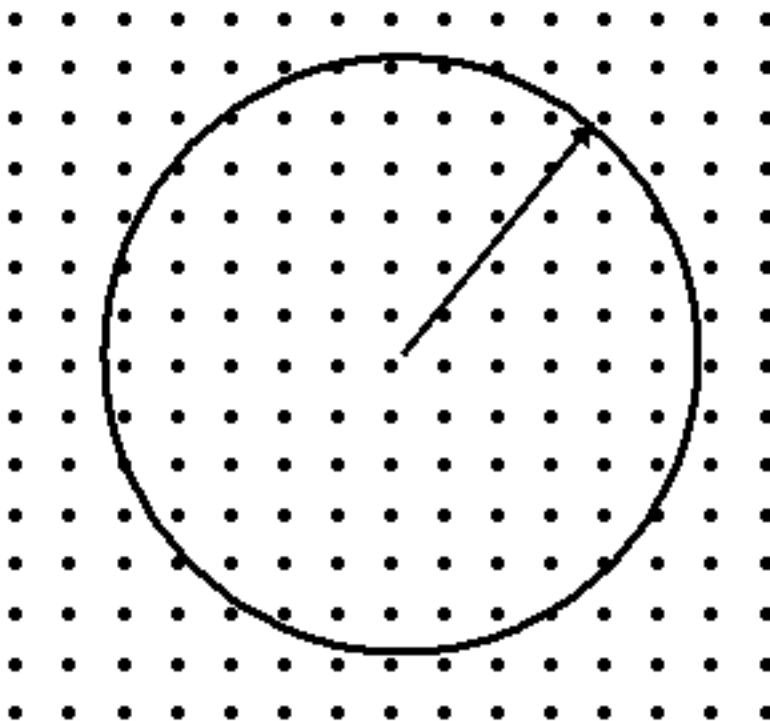

Figure 1. Schematic representation of the cutoff energy concept

Such that:

$$E_{cut} = \frac{1}{2}G_{max}^2$$

The truncation of the basis set at a finite cutoff energy will lead to an error in the computed total energy and its derivatives. It is possible to reduce the magnitude of the error in a systematic way by increasing the value of the cutoff energy. In principle, the cutoff energy should be increased until the calculated total energy converges within the required tolerance. This would be the recommended procedure if, for example, you were conducting a phase stability study where the absolute values of total energies of different structures are compared. However, the energy differences for the *same* structure converge at much lower cutoff energies than the total energy itself. This is due to the cancellation of errors and allows one to use moderate basis sets for reliable geometry optimization or molecular dynamics studies. These arguments are also valid for the convergence testing of Brillouin zone sampling.

Finite basis set correction

One of the difficulties associated with the use of plane-wave basis sets is that the number of basis states changes discontinuously with cutoff energy. In general these discontinuities will occur at different cutoffs for different k-points in the k-point set. In addition, at a fixed cutoff energy, a change in the size or shape of the unit cell will cause discontinuities in the plane wave basis set. This problem can be reduced by using a denser k-point set, so that the weight attached to any particular plane wave basis state is reduced. However, the problem is still present even with quite dense k-point samplings. It can be handled approximately by applying a correction factor that accounts for the difference between the number of a states in a basis set with an infinitely large number of k-points and the number of basis states actually used in the calculation (Francis and Payne, 1990).

The finite basis set correction is of the utmost importance when cell optimization is performed with a basis set that is not absolutely converged. For example, the norm-conserving silicon pseudopotential is sufficiently soft and provides accurate results with a cutoff energy for plane waves of about 200 eV. However, if one calculates the equation of state using this cutoff (that is, the volume dependence of the total energy and pressure), the volume that corresponds to the minimum in total energy does not coincide with the volume that gives zero pressure. As one repeats such EOS calculations at progressively higher cutoff energies and with better k-point sampling, the difference between the two volume values becomes smaller and smaller. In addition, the E-V curve calculated at low cutoff energy is jagged but becomes more and more smooth as the cutoff energy is increased. The reason for the jagged appearance of the E-V curve is the discontinuous change in the number of plane waves used at the same cutoff energy but for different lattice constants. The finite basis set correction, when added to the total energy, allows one to perform calculations with a fixed number of basis states and to interpolate the results as if the more physical condition of a fixed energy cutoff were used. A detailed description of the recommended use of this technique can be found in Milman et al. ([1994](#)).

The only parameter that must be known in order for this correction term to be evaluated is $dE_{tot}/d\,lnE_{cut}$, where E_{tot} is the total energy of the system and E_{cut} is the cutoff energy. CASTEP can calculate this term automatically or you can input this parameter manually.

The value of the $dE_{tot}/d\,lnE_{cut}$ gives a good indication of the convergence of the calculation with respect to the energy cutoff and k-point sampling. When its value per atom (that is, the value reported in the CASTEP output file divided by the number of atoms) is smaller than 0.01 eV/atom, the calculation can be considered very well converged. A value of 0.1 eV/atom is sufficient for most calculations.

Self-consistent electronic minimization

CASTEP offers a choice of methods for electronic relaxation. The default method is the most efficient and is based on density mixing ([Kresse and Furthmuller, 1996](#)). In this scheme, the sum of electronic eigenvalues is minimized in the fixed potential instead of the self-consistent minimization of the total energy. The new charge density at the end of the minimization is mixed with the initial density and the process is repeated until convergence is reached. A number of options are supported for this scheme: linear mixing, Kerker mixing, Broyden mixing, and Pulay mixing, in order of increasing robustness. The conjugate gradient-based approach is used to minimize the sum of eigenvalues. A slightly more elaborate scheme that involves separate mixing of spin density has been developed for spin-polarized calculations.

CASTEP also supports a more traditional scheme for electronic relaxation, involving minimization of the total energy. The electronic wavefunctions are expanded using a plane-wave basis set and the expansion coefficients are varied so as to minimize the total energy. This minimization is performed by using an all-bands method that allows simultaneous update of all wavefunctions. The scheme uses a preconditioned conjugate gradients technique ([Payne et al., 1992](#)).

The main advantage of the density mixing method is its robustness for metallic systems, especially for metallic surfaces. A traditional total energy minimization scheme might become unstable in a metallic system with the cell elongated in one dimension, which is the typical setup for supercell calculations on surfaces. The density mixing scheme converges equally well for insulating and metallic cases, and offers at least a factor of three increase in speed for moderately sized insulator systems.

> **Note:** When using the density mixing method, the SCF energy no longer decreases monotonically to the final converged SCF energy and unconverged energies may have values lower than the final converged energy. This behavior is due to the fact that in the density mixing method, the Harris functional for the energy is used, rather than the Kohn-Sham functional. Unlike the Kohn-Sham functional, the Harris functional does not necessarily have a minimum at the SCF solution.

Preconditioning

All electronic relaxation methods in CASTEP use preconditioning to speed up the rate of convergence (Payne et al., 1992). The idea is to find a matrix which, when multiplied with the residual vector, gives the exact error in the wavefunction. Formally, this matrix can be written down as:

Eq. CASTEP 28

$$\frac{1}{\mathbf{H} - \varepsilon_n}$$

where ε_n is the exact eigenvalue for the band being optimized. It in not possible to evaluate this matrix, but by recognizing that the kinetic energy dominates the Hamiltonian for large G-vectors, it is possible to approximate the matrix by a diagonal function which converges to G^{-2} for large G-vectors and is constant for small G-vectors. The actual form of the matrix is (Payne et al., 1992):

Eq. CASTEP 29

$$\mathbf{K}_{GG'} = \delta_{GG'} \frac{27 + 18x + 12x^2 + 8x^3}{27 + 18x + 12x^2 + 8x^3 + 16x^4}$$

where x is the ratio of $|\mathbf{k} + \mathbf{G}|^2$ to the kinetic energy of the given state.

Application of the preconditioning scheme causes all of the large wave-vector components of a wavefunction to converge at nearly the same rate.

Density mixing schemes

CASTEP supports four schemes for generating new starting charge densities from the results of the previous SCF step (Kresse and Furthmuller, 1996). The simplest is the linear mixing scheme. This method requires one parameter and the output density is produced as a linear combination of the input and output densities on the last iteration.

Kerker mixing recognizes the fact that small-G components of the charge density should be mixed with smaller weights in order to prevent charge sloshing during SCF optimization. The new density is given by:

Eq. CASTEP 30

$$\rho_{new}(G) = \rho_{in}(G) + A \frac{G^2}{G^2 + G^2_{max}} (\rho_{out}(G) - \rho_{in}(G))$$

The Kerker scheme is, consequently, defined by two parameters, the mixing amplitude, A, and the cutoff wavevector, G_{max}.

The most efficient mixing scheme is Pulay's scheme. In this approach, the input charge density and the residual vectors are stored over a number of SCF optimization steps. A new input density is obtained in each step as a linear combination of charge densities of all previous steps. The new density is determined such that it minimizes the normal of the residual vector subject to the constraint of conserving the number of electrons. Pulay's scheme starts with a Kerker-type step, so it is effectively controlled by three parameters: the mixing amplitude, A, the cutoff wavevector, G_{max}, and the depth of the optimization history.

Broyden mixing is very similar to the Pulay scheme, except that it performs a quasi-Newton relaxation instead of DIIS minimization of the residuals.

Treatment of metallic systems

The main difference between metals and insulators, from the technical point of view, is that the number of occupied bands is not the same at different k-points in the Brillouin zone. The number of occupied bands for insulators is calculated as one half the total number of valence electrons, but this approach is

not suitable for metals. Partial occupancies are introduced to eliminate discontinuous changes in total energy that are created when an energy band crosses a Fermi level during SCF minimization.

The overall strategy for treating metallic systems in CASTEP is as follows. The number of bands has to be slightly higher than would be required for an insulator. It may be necessary to add more bands if convergence is slow, especially for spin-polarized systems. An artificial electronic temperature is then introduced by assuming Gaussian-like smearing of each energy level ([de Vita, 1992](#)). Occupation numbers are deduced from the ratio of the area of the Gaussian that falls below the Fermi level to its total area. Thus, a level deep in the valence band has an occupation number of 1, a level directly on the Fermi surface has an occupation number of 0.5, and a level high above the Fermi energy is empty. In some sense, this is the same as giving the Kohn-Sham particles a finite temperature. Therefore, CASTEP uses the Mermin finite temperature expression for the total energy ([Marzari, 1997](#)):

$$E = E_{KS} - TS$$

where:

T is the temperature (that is, smearing width)
S is the Mermin entropy due to the different ways in which the partially filled bands could have been filled

The CASTEP output is as follows. The line

```
Final energy, E = -861.8315373731 ev
```

gives the Kohn-Sham energy, E_{KS}, which ignores the entropy. However, it is the total Mermin free energy that is minimized by CASTEP and reported in the SCF cycles in the line

```
Final free energy (E-TS) = -861.8315374521 ev
```

If you were actually interested in the electronic states at some reasonable nonzero temperature, you would smear the Fermi level with a thermal (that is, Fermi-Dirac) smearing method and the free energy reported by CASTEP would be the value you require.

> **Note:** Temperature equivalent of energy is given by the conversion factor of 11604.5 K/eV; so the default smearing width of 0.1 eV corresponds to a very high temperature of 1160 K.

However, it is often the T = 0 K value that is required and the smearing is necessary to improve the convergence of the numerical algorithm. As the smearing ('temperature') is increased, the TS term increases and the free energy, $E_{KS} - TS$, goes down. At the same time, as the entropy contributes more and more to the free energy, the electronic minimization pays less attention to the E_{KS} term, so the final E_{KS} increases. Because the dependence of the free energy and the Kohn-Sham energy on the smearing width is the same (to first order), averaging the two values gives a much better approximation to the T = 0 K result:

```
NB est. 0K energy (E-0.5TS) = -861.8315374126 ev
```

The total energy calculated by CASTEP for metals is thereby corrected for the fact that it now includes the artificial electronic entropy contribution. This correction is possible because a closed analytical form for the dependence of the total energy on the smearing width (or electronic temperature), s, exists. In principle, evaluation of E_{tot} (s -> 0) is necessary in order to obtain a physically meaningful energy. In the past, values for s as low as 0.01 eV have been used to calculate the converged energy. The total energy correction described above allows the use of a much higher smearing width (up to 1 eV), while still giving results converged with respect to s. The advantage is the added stability of the calculation, since occasional Fermi-level crossings do not create instabilities. However, there is no simple expression for a similar correction for either atomic forces or stress on the unit cell.

The error in the forces introduced by this limitation is generally small and acceptable. Nonetheless, geometry optimizations for metals should be performed with some caution. You should use smaller

smearing values than for single-point energy runs. The calculated forces will be more accurate, but there is a risk of instability, since changes in atomic geometry are likely to cause reordering of bands and some Fermi-level crossings. Cell optimization is also more difficult for metallic systems, since the stress tensor could be affected by nonphysical contributions from nearly empty conduction bands.

Disorder in solids

Many crystal structures possess static positional disorder. The crystal may either contain fewer atomic species than there are crystallographically equivalent sites to populate, or there might, for example, be statistical occupancy of a given crystallographic site by more than one type of atom in different unit cells. This positional disorder is typically manifested in site occupancy factors of less than unity for the average unit cell.

Materials Studio allows you to model positional disorder by specifying atom occupancy and by defining mixture atoms.

Atom occupancy

The vast majority of atoms will have an occupancy of unity. However, in the case of an atom on a partially occupied interstitial position, you can specify an occupancy ranging from 0.0 to 1.0.

Atom occupancies can be modified in the Properties Explorer.

Mixture atoms

Atomic sites in a crystal can also be described in terms of a hybrid atom that consists of two or more element types. The relative concentrations can be set for any number of atoms, but the total concentration must not exceed 100%. The mixture atoms description is the most often used representation of solid solutions, metallic alloys, disordered minerals, and so on.

Disorder and first principles calculations

There are a number of different approaches for dealing with disorder in first principles calculations:

- Virtual crystal approximation (VCA): this offers technically the simplest approach, allowing calculations on disordered systems to be carried out at the same cost as calculations for ordered structures. VCA ignores any possible short range order and assumes that on each potentially disordered site there is a virtual atom which interpolates between the behavior of the actual components. This approach neglects such effects as local distortions around atoms and cannot be expected to reproduce the finer details of the disordered structures very accurately.

- Using large ordered supercells followed by configurational averaging: this is a very expensive approach with limited applicability. For example, it is not possible to treat arbitrary and particularly small concentrations.

- Coherent potential approximation (CPA): this method approximates a configurationally random alloy with an effective medium that is determined self-consistently from the condition of stationary scattering. The CPA technique is used extensively with model Hamiltonians with well-known scattering properties or in the context of multiple scattering methods of band structure calculation (KKR, LMTO). CPA is not well suited to total energy calculations or geometry optimization tasks.

- "Computational alchemy": this method uses the perturbation theory to calculate the response to the difference between the true and VCA potentials. This approach is very demanding computationally, as are all linear response calculations.

The basic ideas of the workable VCA implementation for DFT methods, in particular for the pseudopotential-based techniques, were set out by Bellaiche and Vanderbilt (2000). The main statement for the implementation of VCA with ultrasoft potentials can be expressed as:

Eq. CASTEP 86

$$V_{ext}(r, r') = \sum_I \sum_\alpha w_\alpha^I V_{ps}^\alpha(r - R_{I\alpha}, r' - R_{I\alpha})$$

where the total external potential is generated as the sum of the nonlocal potentials of each atomic species, α, taken with the weights, w, of the component atoms in the mixture atom. This means that all the key components of the ultrasoft potentials, that is, the local part, V_{loc}, and the D and Q matrices, are all weighted according to the site occupancies.

The VCA scheme described above has been applied successfully to study disorder in the perovskites Pb(ZrTi)O$_3$ (Bellaiche and Vanderbilt, 2000) and BiScO$_3$-PbTiO$_3$ (Iniguez et al., 2000), and Al-Si disorder in silicates such as hollandite and gehlenite (Winkler et al., 2002).

> **Note:** Ramer and Rappé (2000) suggested an alternative scheme where the pseudopotentials are generated on the fly for the mixture atoms. Their scheme appears to be less readily generalized for the case of more than two disordered species or where the mixture atom's components have different chemical valences.

Limitations of VCA implementation in CASTEP

The VCA approach is not intended as a universal method for conducting studies of disordered materials. It often produces useful results, but it is important to be aware of its limitations.

Theoretical limitations

VCA is not expected to be better than 50% accurate for excess properties of solid solutions, even for the applications that use simple forcefields. The deviation from the Vegard law, for example, can only be reproduced qualitatively for many systems. In fact, CASTEP calculations for NaCl/KCl mixtures with norm-conserving potentials fail to describe even the shape of the excess volume curve (the difference between the calculated volume at a given concentration and the linear combination of the volumes of the end-members). It should be noted that the excess properties are very sensitive to the accuracy of the data for the end-members and, in general, this is not the preferred application of VCA in CASTEP. On the other hand, properties such as the bulk modulus of the NaCl/KCl solid solution are described very well within the same framework (see Figure 1).

An important aspect of the VCA implementation has not been discussed by the authors of the formalism (Bellaiche and Vanderbilt, 2000). One should always test the pseudopotentials for the presence of ghost states. They often manifest themselves in the solid state calculations as a strong change in the total energy as a function of the energy cutoff of the plane wave basis set. It seems that the ultrasoft potentials are prone to generating ghost states in the VCA framework, while none of the individual potentials has a ghost state. The NaCl/KCl system could not be studied with the ultrasoft potentials for this very reason - the finite basis set correction calculated for solid solutions was orders of magnitude higher than for the end-members. This is a clear indication of a ghost state in the calculation. There is no easy way of testing the VCA approach for ghost states, so one should always examine the value of the derivative of the total energy as displayed in the output file during the finite basis set correction calculation. It should be of the same order as the derivatives for the end-member structures.

Technical limitations

Atom occupancy cannot be used with the current CASTEP implementation of the virtual crystal approximation (VCA). Partial atom occupancy can be considered as a special case of a mixture atom,

where one part of the mixture is an atom of "nothing". This case is not supported for a number of technical and fundamental reasons.

Current implementation of the molecular dynamics algorithms in CASTEP is not yet compatible with the VCA formalism. None of the MD schemes (NVE, NPT, and so on) works for disordered crystals in the current version.

Linear response calculations (phonons, polarizability) are not supported for disordered crystals.

Test results

The VCA implementation in CASTEP is capable of correctly describing a number of mixture atoms, as shown by the results below.

Bulk modulus of NaCl/KCl solid solution

The bulk modulus of the halite-sylvite mixture (NaCl/KCl) has been calculated as a function of concentration by calculating the *P-V* equation of state for different Na concentration and fitting them with the third-order Birch-Murnaghan analytical expression. The results agree with the experimental data (Figure 1) to better accuracy than is typically achieved for the ordered crystals. The norm-conserving pseudopotentials were used in this study (all other tests described below were carried out with ultrasoft pseudopotentials).
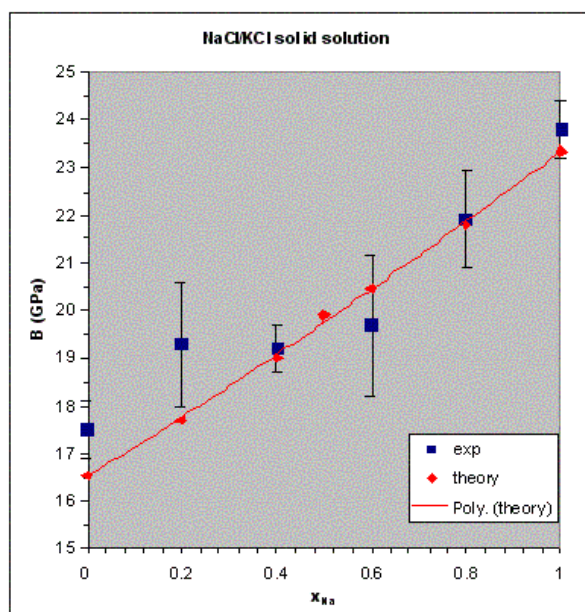
Figure 1. Dependence of the bulk modulus of the NaCl/KCl solid solution on concentration.
Experimental data are from Walker et al. (2004). The solid line shows a polynomial fit to the calculated results.

The structure of bicchulite

The structure of the cubic mineral bicchulite, $Ca_2[Al_2SiO_6](OH)_2$, was calculated and compared to the experimental results (Sahl, 1980). Each Si/Al site is completely disordered in this structure, so the weights are 2/3 and 1/3 for Al and Si atoms, respectively. The lattice parameter is calculated as 8.675 Å, or 1.7% lower than the experimental value. The interatomic distances calculated for the structure are (Si,Al)-O = 1.6968 Å (-1.1%) and Ca-O = 2.3009 Å (-0.4%) and 2.3794 Å (-3.2%). This level of accuracy in the structural description is acceptable for a DFT calculation.

The structure and stability of Pb(Zr,Ti)O$_3$ perovskites

The structures and energies of three different modifications of the 1:1 PZTO ceramics were calculated and the results compared with the experimental data and the earlier VCA results (Ramer and Rappé, 2000). The modifications studied include tetragonal *P4mm* and rhombohedral *R3m* and *R3c* phases. The results are summarized in the tables below.

Table 1. Structure of the *P4mm* tetragonal phase of PZTO. Experimental data are from Frantti et al. (2000)**, earlier VCA results are from** Ramer and Rappé (2000)**.**

	a (Å)	*c* (Å)	*c/a*	Ti*z*	O1*z*	O2*z*	Pb-O2 (Å)	Ti-O1 (Å)	Ti-O2 (Å)
CASTEP	4.0481	4.1283	1.020	0.5573	0.6112	0.0926	2.600	1.918	2.036
exp.	4.0303	4.1449	1.028	0.5649	0.6110	0.0921	2.508	1.960	2.024
VCA	3.9760	4.1050	1.033	-	-	-	-	-	-

Table 2. Structure of the *R3m* rhombohedral phase of PZTO. Experimental data are from Amin et al. (1981)**, earlier VCA results are from** Ramer and Rappé (2000)**.**

	a (Å)	*α* (°)	O*x*	O*y*	Pb*x*	Ti*x*	Pb-O (Å)	Ti-O (Å)
CASTEP	4.0749	89.535	-0.0040	0.5080	0.5586	0.0250	2.516	1.973, 2.115
exp.	4.0809	89.676	-0.0046	0.5092	0.5620	0.0216	2.537	1.994, 2.098
VCA	4.0215	90 (fixed)	-	-	-	-	-	-

Table 3. Structure of the *R3c* rhombohedral phase of PZTO. Experimental data are from Jirak and Kala (1988)**, earlier VCA results are from** Ramer and Rappé (2000)**.**

	a (Å)	*α* (°)	O*x*	O*y*	O*z*	Pb*x*	Ti*x*	Pb-O (Å)	Ti-O (Å)
CASTEP	5.7726	59.589	0.4942	0.0284	-0.0180	0.0283	0.2632	2.565	1.979, 2.111
exp.	5.8240	59.600	0.4860	0.0330	-0.0190	0.0341	0.2620	2.487	2.024, 2.109
VCA	5.6790	60 (fixed)	-	-	-	-	-	-	-

Table 4. Energy differences between the three phases of PZTO, in meV per 5 atom cell. Earlier VCA results are from Ramer and Rappé (2000)**.**

	E(R3m) - *E(P4mm)*	*E(R3c)* - *E(P4mm)*
CASTEP	-4.7	-6.3
VCA	9	6

These results indicate that the structural features are reproduced quite accurately within VCA. Note that the experimental data for rhombohedral phases are for Zr concentrations slightly different from 0.5, since these phases are not stable for the 1:1 composition. The energy differences between the phases

are extremely small in recent studies and earlier work by Ramer and Rappé (2000). DFT energies cannot be trusted at this level of accuracy to judge the relative stability of the polymorphs. For example, the fact that the angles were fixed to 90 and 60° in the earlier VCA work suggests that after the full optimization, the rhombohedral phases are likely to become more stable than the tetrahedral phase, in agreement with the CASTEP results (Table 4).

The structure of leucite

Tetragonal leucite, $KAlSi_2O_6$, contains three different sites with a fully disordered distribution of Al and Si cations. The structure is only slightly distorted with respect to the cubic cell and the accuracy of reproduction of this distortion is a measure of the quality of the VCA description. The results presented below (Table 5) show exceptionally good agreement with the experimental data. Furthermore, atomic positions are also predicted very accurately. The highest deviation from the experimental data for any individual fractional coordinate is 0.001 in the CASTEP calculations, compared with maximum deviations of up to 0.007 in the forcefield modeling.

Table 5. Lattice parameters of leucite compared to experimental data (Mazzi et al., 1976) and the results of forcefield calculations (Winkler et al., 1991).

	a (Å)	*c* (Å)	*c/a*
CASTEP	13.1497	13.8318	1.052
exp.	13.09	13.75	1.050
empirical	12.9884	13.8000	1.062

Geometry optimization

CASTEP supports a number of schemes for geometry optimization: BFGS, TPSD, and damped molecular dynamics.

BFGS geometry optimization

The main advantage of the BFGS minimizer (Pfrommer et al., 1997) is the ability to perform cell optimization, including optimization at fixed external stress. The BFGS scheme uses a starting Hessian that the optimization updates recursively. The CASTEP implementation involves a Hessian in the mixed space of internal and cell degrees of freedom, allowing optimization of both lattice parameters and atomic coordinates.

The LBFGS algorithm (low-memory BFGS) is expected to perform better for large systems. This approach uses only a limited number of inverse Hessian updates to construct a new Hessian. This scheme scales linearly in memory, while BFGS scales as a square of the system size (Aarons, 2011). The LBFGS algorithm also implements a universal sparse preconditioner that accelerates geometry optimization by a factor of two for small systems and a factor of ten for very large ones (Packwood et al., 2016).

When you require cell optimization, use a finite basis set correction term. Calculating the term is not too costly (10-30% of the self-consistent electronic minimization at the first iteration) relative to the advantages that it provides. Cell optimization runs may be problematic if the finite basis set correction is not used or if the energy cutoff is so low that the correction is not accurate. In these circumstances, the optimization run may stop with a message that states that the energy has converged, but that the stress is still non-zero. The minimizer attempts to find the energy minimum rather than the stress zero-point, since the former is more meaningful under the circumstances.

Another potential pitfall is the use of the Fixed Basis Size *Cell optimization* setting when the starting geometry is very different from the final one. The finite basis set correction depends on the cell size and

shape, although the minimizer disregards this dependence. When using Fixed Basis Size modifies the cell geometry, the effective cutoff energy changes but the number of plane waves remains fixed. If this change takes the $dE_{tot}/d(\ln E_{cut})$ function far away from the point used to evaluate the finite basis set correction, the results are not accurate. Therefore, compare the starting and final geometries and perform a completely new run starting from the final configuration if the difference between the two structures is large.

Constraints

CASTEP can perform geometry optimization with constraints applied. The simplest type of constraint is to fix the atom positions. In CASTEP, this means fixing the fractional coordinates of the atoms.

> **Note:** You do not need to manually fix atoms on special positions as the symmetry treatment in CASTEP ensures the correct behavior of such atoms.

It is also possible to fix lattice parameters. You do not need to fix lattice parameters, except for parameters *not* fixed by symmetry. This type of constraint is often useful in phase stability studies when, for example, you want to fix the angles to 90° (Winkler and Milman, 1997).

It is also possible to impose more general linear constraints on atomic coordinates. A matrix that transforms the Cartesian coordinates of all atoms to the subspace of unconstrained coordinates specifies these constraints. You can use this facility to fix, for example, the z-coordinates of atoms in slab calculations of surface processes.

Non-linear constraints

Non-linear constraints refer to constraints on interatomic distances (bonds), angles, and torsions. You can impose such constraints using the delocalized internals optimizer.

Estimated compressibility

You can facilitate cell optimization convergence by making a reasonable initial estimate of the bulk modulus for the material. The initial changes to lattice vectors are calculated on the basis of this value, based on the calculated stress tensor. When the estimated bulk modulus is too high, the steps become smaller than is ideal for the minimizer. Therefore, it is conceivably possible that you could reduce the number of geometry optimization steps by reducing this value. Conversely, too small a bulk modulus for a hard material could result in an oscillating behavior, where the first step is too big. Thus, prior knowledge of the hardness of the material could help to reduce the number of steps required for calculations. The table below illustrates the effect of a judicious choice of the initial bulk modulus value. The times are relative to the same calculation using an initial value of 500 GPa.

Compound	Estimated bulk modulus (GPa)	Number of steps	Relative time
Cubane	5.000	15	0.98
	50.00	15	0.87
	250.0	15	0.82
	500.0	20	1.00
	1000.0	24	1.29

Compound	Estimated bulk modulus (GPa)	Number of steps	Relative time
Glycine	5.000	46	1.29
	50.00	42	1.03
	250.0	39	0.92
	500.0	37	1.00
	1000.0	54	1.24
$YBa_2Cu_3O_7$	5.000	12	0.81
	50.00	13	0.74
	250.0	12	0.81
	500.0	17	1.00
	1000.0	13	0.81

TPSD geometry optimization

The BFGS algorithm as implemented in CASTEP uses the assumption that the potential is quadratic to determine an optimal step length per iteration. When this is not the case, the BFGS algorithm does not perform well and may take a long time to optimize the structure. A more robust Barzilai-Borwein (1988) Two-Point Steepest Descent (TPSD) algorithm allows you to solve a larger range of problems. It is specifically more efficient when you request cell optimization with custom constraints. This scenario describes, for example, optimization of solid-solid interfaces strained to a substrate: that is, with fixed lateral cell parameters and all cell angles, only allowing relaxation of the cell dimension in the direction normal to the interface.

The TPSD algorithm requires only the gradient and position of the system at the current and previous iteration, meaning that the calculation consumes a relatively small amount of memory. The difference of each value between the iterations generates a step size for use in the direction of the most negative gradient from the current iteration. TPSD optimization converges reliably in a number of situations where the BFGS algorithm takes too long to converge.

Damped molecular dynamics

Damped molecular dynamics presents an alternative method for geometry minimization that involves only internal coordinates (with fixed cell parameters). The method uses the critical damping regime as a way of dealing with the ground state. The regime can be implemented either by using one damping coefficient for all degrees of freedom (coupled modes) or by using different coefficients for different degrees of freedom (independent modes). The latter approach allows you to freeze all modes, both fast and slow, simultaneously. Alternatively, you can perform steepest descents damping with a fixed coefficient. However, this is a less efficient approach. Indeed, it is not, strictly speaking, a molecular dynamics technique, since it solves first-order equations of motion and not second-order equations.

Both independent modes and coupled modes damped molecular dynamics runs can be performed with a bigger time step than undamped molecular dynamics simulations. When the system gets close to equilibrium, the time step can be increased even further, since the fast modes freeze out before the slow ones. CASTEP can automatically adjust the time step, leading to increased efficiency of the algorithm. It is also recommended that you recalculate the damping coefficients periodically during a damped

molecular dynamics run. A full description of the method implemented in CASTEP can be found elsewhere (Probert, 2003).

Dynamics

Molecular dynamics (MD) involves the stepwise integration of Newton's equations from a given starting point. It is the most natural method of performing equilibrium statistical-mechanical calculations using a simulation. Additionally, MD may be used to explore conformations, such as molecular adsorption sites on a surface. If frictional forces are added to the equations of motion, Langevin dynamics becomes possible, as does geometry optimization using damped MD. Finally, extended Lagrangian methods allow thermostatic control of the temperature.

Molecular dynamics in total-energy DFT schemes is implemented in essentially the same way as in conventional forcefield based methods. The main difference is that the energy and atomic forces are derived by solving DFT equations rather than from empirical potentials of interatomic interactions. Electrons are kept on the Born-Oppenheimer surface by means of explicit electronic structure optimization after each MD step. A side effect of this is that evaluation of force and energy from first principles is always the most computationally expensive part of *ab initio* MD. As a result, the efficiency of the MD step itself has no impact on the speed of the calculation.

MD in CASTEP is based on the velocity Verlet algorithm for integration of the equation of motion. The default time step can be as high as 1 fs with this algorithm because of its numerical stability and the conservation of the constant of motion.

The efficiency of the method is due in large part to the introduction of wavefunction extrapolation between MD steps (Arias et al., 1992). In addition, charge density extrapolation (Alfe, 1999) has been introduced.

Wavefunctions and density extrapolation

The main idea behind the interpolation schemes is to provide a good starting model of the electronic structure for the SCF optimization, after the geometry change. This can be achieved by using the multi-linear extrapolation as proposed by Arias et al. (1992).

The problem with wavefunction interpolation is that wavefunctions may be multiplied by an arbitrary phase factor or ordered in different ways in two contiguous steps. So, before the extrapolation is performed, the two subspaces $\{\psi_{n,\mathbf{k}}(t)\}$ and $\{\psi_{n,\mathbf{k}}(t\text{-}dt)\}$ are aligned so that $\Sigma_{n,\mathbf{k}}|\psi_{n,\mathbf{k}}(t)\text{-}\psi_{n,\mathbf{k}}(t\text{-}dt)|$ is minimized.

Then the wavefunctions at the next time step, $t+dt$, can be written as:

Eq. CASTEP 31

$$\Psi_{n,\mathbf{k}}(t+dt) = \Psi_{n,\mathbf{k}}(t) + \alpha\left[\Psi_{n,\mathbf{k}}(t) - \Psi_{n,\mathbf{k}}(t-dt)\right] + \beta\left[\Psi_{n,\mathbf{k}}(t-dt) - \Psi_{n,\mathbf{k}}(t-2dt)\right]$$

and similarly for the charge density:

Eq. CASTEP 32

$$\rho(t+dt) = \rho(t) + \alpha\left[\rho(t) - \rho(t-dt)\right] + \beta\left[\rho(t-dt) - \rho(t-2dt)\right]$$

The coefficients α and β are calculated by determining the best quadratic extrapolation of the atomic positions. This extrapolation scheme not only speeds up the calculation but also improves conservation of the constant of motion and dramatically reduces the "electronic drag" effect (Payne et al., 1992).

An improvement suggested by Alfe (1999) recognizes the fact that the charge density is mostly determined by the superposition of the atomic charge densities. Therefore one can write:

Eq. CASTEP 33

$$\rho(t) = \rho_{at}(t) + \delta\rho(t)$$

where $\rho(t)$ is the self-consistent charge density at time t, and $\rho_{at}(t)$ is the sum of the atomic charge densities. The charge at time $t+dt$ is simply extrapolated as:

Eq. CASTEP 34

$$\rho(t + dt) = \rho_{at}(t + dt) + \delta\rho(t + dt)$$

where the change of $\delta\rho$ is given by:

Eq. CASTEP 35

$$\delta\rho(t + dt) = \delta\rho(t) + \alpha\left[\delta\rho(t) - \delta\rho(t - dt)\right] + \beta\left[\delta\rho(t - dt) - \delta\rho(t - 2dt)\right]$$

The atomic charge density can be calculated exactly and cheaply using the same methods as for Mulliken population analysis. The resultant scheme includes extrapolation of wavefunctions using Eq. CASTEP 31, extrapolation of charge density *difference* using Eq. CASTEP 35 and recalculation of the atomic charge densities.

Experience shows that the second-order extrapolation scheme described above is not necessarily the best or the fastest algorithm. CASTEP therefore offers a selection of extrapolation schemes that differ in the way the coefficients are selected: 1st order extrapolation with variable coefficients; 2nd order extrapolation with variable coefficients; alternating first and second order extrapolation steps with variable coefficients; and similar combinations of 1st and 2nd order schemes with fixed coefficients. The actual setting is controlled by the values of the and MD_EXTRAP_FIT keywords in the .param file. The fixed coefficient scheme is based essentially on a Taylor expansion, while the variable coefficients schemes are based on the best fit between extrapolated and MD-predicted atomic coordinates. It has been shown that the accuracy of wavefunction extrapolation improves greatly when the coefficients are chosen based on the extrapolation of atomic coordinates.

An alternative to using wavefunction extrapolation is to use extended Lagrangian formulation, XL-BOMD (Steneteg 2010, Niklasson 2011) . The XL-BOMD scheme allows simultaneous propagation of nuclear and electronic degrees of freedom and shows good energy conservation at time steps that are unusually high for first principles calculations.

Ensembles

Integrating Newton's equations of motion allows you to explore the constant-energy surface of a system. However, most natural phenomena occur under conditions where the system is exposed to external pressure and/or exchanges heat with the environment. Under these conditions, the total energy of the system is no longer conserved and extended forms of molecular dynamics are required.

Several methods are available for controlling temperature and pressure. Depending on which state variables (the energy E, enthalpy H (that is, $E + PV$), number of particles N, pressure P, stress S, temperature T, and volume V) are kept fixed, different statistical ensembles can be generated. A variety of structural, energetic, and dynamic properties can then be calculated from the averages or the fluctuations of these quantities over the ensemble generated.

Both isothermal (where heat is exchanged with a temperature bath to maintain a constant thermodynamic temperature) and adiabatic (where no heat exchange occurs) ensembles are available:

Table 1. Thermodynamic ensembles handled by CASTEP

Ensemble
Constant temperature, constant pressure (NPT)
Constant energy, constant volume (NVE)
Constant pressure, constant enthalpy (NPH)
Constant temperature, constant volume (NVT)

NVE ensemble

The constant-energy, constant-volume ensemble (NVE), also known as the *microcanonical ensemble*, is obtained by solving the standard Newton equation without any temperature and pressure control. Energy is conserved when this (adiabatic) ensemble is generated. However, because of rounding and truncation errors during the integration process, there is always a slight fluctuation, or drift in energy.

True constant-energy conditions (that is, without temperature control) are not recommended for the equilibration phase of the simulation because, without the energy flow facilitated by temperature control, the desired temperature cannot be achieved.

However, during the data collection phase, if you are interested in exploring the constant-energy surface of the conformational space, or if for some other reason you do not want the perturbation introduced by temperature- and pressure-bath coupling, this is a useful ensemble.

Nosé NVT dynamics

The Nosé thermostat (Nosé, 1984) generates deterministic dynamics, with the temperature controlled by a fictitious additional coordinate, s, added to the Lagrangian of the system. The thermostat employs a feedback loop between the instantaneous kinetic energy and the required temperature. The rate of feedback is determined by the mass parameter, Q. This parameter should be chosen so that the natural oscillation frequency of the Nosé coordinate is close to the characteristic frequency of the actual system.

The mass parameter is related to the thermostat relaxation time by:

Eq. CASTEP 36

$$Q = g \frac{k_B T}{\tau^2}$$

Where:

g is the number of degrees of freedom (usually 3N - 3, where N is the number of atoms)
k_B is the Boltzmann constant
T is the thermostat temperature
τ is the relaxation time.

An improvement on the standard Nosé thermostat (or Nosé-Hoover thermostat) is the Nosé-Hoover chain method, described in detail by Tuckerman et al. (2001). In this method the kinetic energy fluctuations of the thermostat variable are controlled by coupling it to another thermostat variable. The kinetic energy fluctuations of the second thermostat are, in turn, controlled by coupling to a third thermostat, and so on, to form a chain of M thermostats. This new coupling (the Nosé-Hoover "chain" thermostatting mechanism) leads to a more general canonical dynamics method.

Langevin NVT dynamics

The Langevin thermostat generates stochastic dynamics using a Brownian motion model, implemented using the fluctuation-dissipation theorem. It is controlled by the damping time parameter, which controls the rate of decay of fluctuations in the temperature. In practice, this should be chosen such that it is larger than the time scale of any motions of interest. An advantage of the Langevin description is that it can be proved to provide ergodic results. The Nosé thermostat, on the other hand, provides good short term dynamics, but fails to give ergodicity.

Nosé-Hoover-Langevin thermostat

The Nosé-Hoover-Langevin (NHL) thermostat suggested by Leimkuhler et al. (2009) combines the advantages of the Nosé-Hoover chain method with the ergodicity of Langevin dynamics. In practical terms this thermostat converges to equilibrium faster than the Nosé-Hoover chain method and offers much better conservation of the constant of motion.

NPT ensemble

The constant-temperature, constant-pressure ensemble (NPT) allows control over both the temperature and pressure. The unit cell vectors are allowed to change, and the pressure is adjusted by adjusting the volume of the unit cell.

Pressure is currently controlled in CASTEP using either the Andersen or Parrinello-Rahman method.

> **Note:** Only the size, and not the shape, of the unit cell can be changed with the Andersen method.

Temperature can be controlled using either the Nosé or the Langevin thermostat.

NPT is the ensemble of choice when the correct pressure, volume, and densities are important in the simulation. This ensemble can also be used during equilibration to achieve the desired temperature and pressure, before changing to the constant-volume or constant-energy ensemble when data collection starts.

Andersen method of pressure control

In the Andersen (1980) method of pressure control, the volume of the cell can change, but its shape is preserved by only allowing the cell to change isotropically.

The Andersen method is useful for liquid simulations since the box could become quite elongated in the absence of restoring forces if the shape of the cell were allowed to change. A constant shape also makes the dynamics analysis easier.

However, this method is not very useful for studying materials under anisotropic stress or undergoing phase transitions, which involve changes in both cell lengths and cell angles (in these situations, the Parrinello-Rahman method should be used where available).

The basic idea is to treat the volume V of the cell as a dynamic variable in the system. The Lagrangian of the system is modified so that it contains a kinetic energy term with a user-defined mass M and a potential term which is the pV potential derived from an external pressure P_{ext} acting on volume V of the system.

Parrinello-Rahman method of pressure and stress control

The Parrinello-Rahman method of pressure and stress control can allow simulation of a structure under externally applied stress. This is useful for studying the stress-strain relationship of materials. Both the shape and the volume of the cell can change, so that the internal stress of the system can match the externally applied stress.

The method is discussed in more detail in Parrinello and Rahman, 1981 and is only summarized here.

The Lagrangians of the system are modified such that a term representing the kinetic energy of the cell depends on a user-defined mass-like parameter $\mathbf{W}$. An elastic energy term $p\Omega$ is related to the pressure and volume or the stress and strain of the system. The equations of motion for the atoms and cell vectors can be derived from this Lagrangian. The motion of the cell vectors, which determines the cell shape and size, is driven by the difference between the target and internal stress.

With hydrostatic pressure only:

Eq. CASTEP 37

$$L = \frac{1}{2}\sum_{i=1}^{N} m_i \dot{\mathbf{s}}_i' \mathbf{G} \dot{\mathbf{s}}_i - \sum_{i=1}^{N}\sum_{j>1}^{N} \phi(\mathbf{r}_{ij}) + \frac{1}{2} W \text{Tr}\left[\dot{h}'\dot{h}\right] - p\Omega$$

Where:

$h=\{\mathbf{a \cdot b \cdot c}\}$ is the cell vector matrix
$\mathbf{G}=h'h$
$\mathbf{r}_i=h\mathbf{s}_i$
ϕ is the interaction potential
Ω is the volume of the cell
Tr is the trace of a matrix

The dots above some symbols indicate time derivatives and the primes indicate matrix transposition.

With stress, the elastic term $p\Omega$ is replaced by:

Eq. CASTEP 38

$$p(\Omega - \Omega_0) + \Omega_0 \text{Tr}\left[(\mathbf{S} - p\mathbf{I})\varepsilon\right]$$

Where:

S is the applied stress
Ω_0 is the initial volume
ε is the strain
ε is also a tensor, defined as:

$$\frac{\left(h_0'^{-1}\mathbf{G}h_0^{-1} - 1\right)}{2}$$

Note: It is the user-defined variable $\mathbf{W}$, which determines the rate of change of the volume/shape matrix.

A large $\mathbf{W}$ means a heavy, slow cell. In the limiting case, infinite $\mathbf{W}$ reverts to constant-volume dynamics. A small $\mathbf{W}$ means fast motion of the cell vectors. Although that may mean that the target stress can be reached faster, there may not be enough time for equilibration.

NPH ensemble

The constant-pressure, constant-enthalpy ensemble (Andersen, 1980) is the analogue of constant-volume, constant-energy ensemble, where the size of the unit cell is allowed to vary.

Constraints

CASTEP supports linear constraints defined using the matrix $\mathbf{A}_{ij}$:

Eq. CASTEP 39

$$\sum_i^{Ni} \sum_j^{Nc} \mathbf{A}_{ij} \cdot \mathbf{R}_i = C$$

The summations are over N_i ions and N_c constraints. Vector $\mathbf{R}_i$ is the Cartesian position of the ith atom and C is a constant. These constraints can be used to, for example:

- Fix some of the Cartesian coordinates of the atom
- Fix the *x*-separation between a pair of atoms
- Constrain an atom to lie in a plane
- Constrain the center of mass to be fixed

Example

The example below (Figure 1) shows the results of an NVE calculation for a nitrogen diatomic molecule with using a time step of 1 fs. The energy conservation is excellent, the energy drift over 500 steps (0.5 ps) is less than 0.1 kcal/mole. The power spectrum of the trajectory gives the vibrational frequency as 2340 cm^{-1}, which is within 1% of the experimental value of 2360 cm^{-1}.
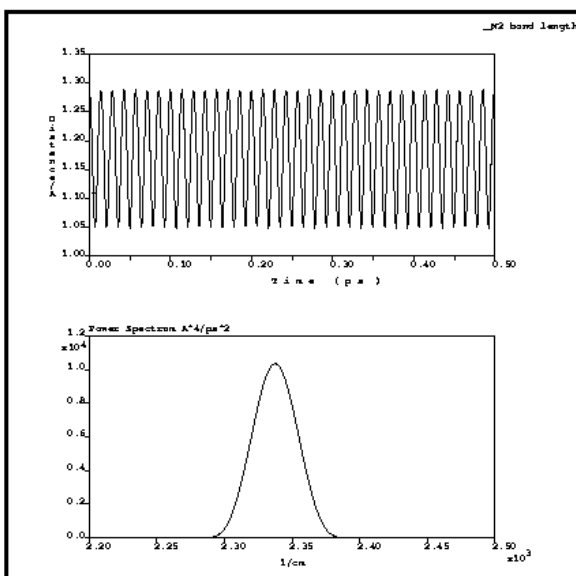
Figure 1. Bond length of the N_2 molecule and power spectrum of the trajectory

Core level spectroscopy

CASTEP can calculate spectroscopic properties of solids that are due to electronic transitions from a core level of an ion to the conduction band (X-ray absorption) and from the valence band to a core level (X-ray emission). This can be used to describe a wide variety of experimental results connected to such processes. Core holes can be created by X-ray or electron incident radiation.

The core level is localized, so core level spectroscopy provides a detailed element-specific picture of the local electronic structure around a given atomic site. There is no contribution from the other atoms in the system, so the electronic states for a specific atom can be investigated.

In the case of anisotropic systems, angular-dependent experiments enable the separation of states with different symmetries for the involved orbitals. An important consequence is that symmetry states, which result solely from chemical bonding, can be studied.

Emission spectroscopy

X-ray emission spectroscopy (XES) is a classical technique used to study the electronic structure of bulk samples. It is ideally suited to these systems due to the large information depth (around 0.1 m for soft X-rays). In XES the core hole created by an X-ray absorption process is filled by the decay of a valence electron. For this process energy is conserved by the emission of an x-ray photon of matching energy. A selective, resonant excitation of a core hole state at the atomic center of an adsorbate can be used to probe surfaces.

Absorption spectroscopy

Electron energy-loss near-edge structure (ELNES or EELS) and x-ray absorption near-edge structure (XANES) spectroscopies provide information on the unoccupied electronic states by exciting one electron from a core level into an unoccupied state. Scanning transmission electron microscopes with an electron energy-loss spectrometer attached have been used extensively in the study of nanoscale materials, providing information on local composition, structure, and electronic structure. However, the probing electron or x-ray interacts with a system that has been perturbed by the probe itself. The system being studied has had an inner-shell electron removed, leaving a core hole.

Core hole effects

The relaxation of a system with a core hole will affect the observed core level excitation spectra so that interpretation of the experimental spectrum becomes a more challenging task. A satisfactory theory of optical spectra or core excited spectra should calculate two particle electron-hole interactions in a reliable and accessible way. In the core level excitation process, the core hole is localized on a single atomic site. Using an atom with a reduced occupation in the core level in a supercell approximation has been a good and popular description for the calculation of core level spectroscopy using standard density functional theory (DFT).

Recent developments in core-level spectroscopy calculations using the Bethe-Salpeter equation or time-dependent DFT (or a combination of the two) provide more rigorous approaches for a core-level spectra calculation. In these methods many-body effects, such as the broadening of spectra due to electron-hole lifetime, can be taken into account in a natural way. While good agreement with experimental results has been achieved, this necessarily comes with a much greater computational burden in comparison to standard ground state calculations.

A systematic observation of core hole effects and a quantitative estimation of the core hole strength in materials can assist in the simulation and interpretation of core level spectra. Applying empirical rules, a core-level spectrum is not likely to be heavily influenced by core-hole effects, so information on the ground electronic structure of a material can be inferred directly from the experimental spectrum. In this case, traditional ground state calculations should predict the main features of experimental results and allow interpretation of the spectrum. If this is not the case, inclusion of the influence of the core hole is essential in the theoretical simulation. Analysis of experimental results should take into account that near-edge fine structure includes influences in the core excitation processes beyond the ground state electronic structure.

There is an open question regarding the best way of handling the charge of core holes; depending on the nature of the system it might be appropriate to treat the system either as having lost an electron and thus having a charge of 1 or as neutral. Materials Studio assumes the former treatment.

Energy broadening

The ELNES calculation can be performed with an energy resolution far better than that used to obtain experimental results. Therefore, the calculated ELNES must be broadened before comparing it with the experiment. The broadening observed in the experimental spectra has three origins: the lifetime of the core hole, the lifetime of the excited state, and instrumental broadening. A good description of this subject was given by Hebert (2007).

Instrumental broadening is easiest to simulate: it can be modeled by a Gaussian with a FWHM given by the instrument. For a TEM equipped with a field emission gun, this is usually about 0.6-0.7 eV. Some instruments are equipped with a monochromator to improve energy resolution to about 0.1 eV. In nearly all cases the energy distribution can be modeled by a Gaussian curve.

The broadening by the core hole lifetime depends on the atom and the edge. Values for lifetime broadening are tabulated and can be found in the literature, see Fuggle and Inglesfield (1992). Broadening due to the lifetime of the core hole is, however, relatively low for edges accessible in EELS (about 0.2 eV for the Ni or Cu L3 edge). The broadening of core hole lifetimes can be modeled by a Lorentzian (Fuggle and Inglesfield, 1992).

The broadening by the excited state lifetimes is more complicated. At the edge onset (where the lifetime of the excited state approaches infinity) the broadening is zero and increases with increasing energy. Different methods have been employed to obtain the broadening factor, see Hebert (2007) for a comparative review. An empirical linear function $\Gamma(E) = 0.1\,E$ (where E is the energy above the threshold) gives good results when compared to the experiment - this is the option employed in CASTEP.

Spin-orbit splitting

Experimental spectra record transitions involving core states that are split as a result of the spin-orbit interactions; so one should distinguish between states such as $p_{1/2}$ and $p_{3/2}$ and so on. The CASTEP implementation lacks spin-orbit terms, so the calculations can only produce "generic" spectra for p, d, or f states. In spectroscopic terms this means producing (for example) $L_{2,3}$ spectra rather than just L_2. The simplest, albeit slightly approximate, way to model experimental spectra is to modify the calculated spectrum as follows:

- Find the experimental value of the spin-orbit splitting of the core states.
- Generate an approximate L_3 spectrum by shifting the L_2 spectrum.
- Apply intensity scaling based on the occupancy of the respective electronic shell. The intensity ratios for L spectra are 2:4 and for M spectra 4:6, and so on.
- Add the two shifted and scaled spectra together.

For a more general discussion of the core level spectroscopy and details of its implementation see S.-P. Gao et al. (2008) and references.

Phonon density of states

Phonon density of states (or vibrational density of states) is defined in exactly the same way as the electronic densities of state, see the DOS equation. The integral over the Brillouin zone goes over all 3N phonon bands, where N is the number of atoms in the cell. There are two popular conventions regarding normalization of the phonon DOS. Either it can be normalized to unity or to the total number of vibrational modes, 3N.

The partial (or projected) phonon density of states is determined as a contribution from the given atom to the total phonon DOS. This is a useful concept that allows one to understand the nature of various

branches in the phonon spectrum. The contribution to the partial density of states on atom i, from each phonon band, is evaluated using:

Eq. CASTEP 41

$$N_i(E) = \int \frac{d\mathbf{k}}{4\pi^3} |e_j(i)|^2 \delta(E - E_j(\mathbf{k}))$$

where e_j is the eigenvector (normalized to unit length) associated with the mode of energy E_j. The projected density of states is then obtained by summation of these contributions over all phonon bands. By construction all the projected phonon DOS sum up to the true phonon DOS.

Electron localization function

Formulation of electron localization function

The electron localization function (ELF) was introduced by Becke and Edgecombe as a "simple measure of electron localization in atomic and molecular systems" (Becke and Edgecombe, 1990). Becke and Edgecombe associated the localization of an electron with the probability density for finding a second like-spin electron near the reference point. For small probability densities, $D(\mathbf{r})$ is also small and the electron is more localized.

Eq. CASTEP 87

$$D(\mathbf{r}) = \sum_i^\sigma |\nabla \Psi_i(\mathbf{r})|^2 - \frac{1}{4} \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})}$$

The Pauli repulsion between two like-spin electrons, described by the size of $D(\mathbf{r})$, is taken as a measure of the electron localization. Using the corresponding factor found for a uniform electron gas, $D_h(\mathbf{r})$, Becke and Edgecombe, defined ELF as:

Eq. CASTEP 88

$$\eta(\mathbf{r}) = \frac{1}{[1 + \chi_{BE}^2(\mathbf{r})]}$$

where

Eq. CASTEP 89

$$\chi_{BE}(\mathbf{r}) = \frac{D(\mathbf{r})}{D_h(\mathbf{r})}$$

$$D_h(\mathbf{r}) = \frac{3}{5}(6\pi^2)^{2/3} \rho(\mathbf{r})^{5/3}$$

Becke and Edgecombe attributed the ratio $\chi_{BE}(\mathbf{r})$ to a dimensionless localization index, calibrated with respect to the uniform electron gas. This reference was chosen arbitrarily, so ELF is only a relative measure of the electron localization. High ELF values show that at the examined position the electrons are more localized than in a uniform electron gas of the same density. For example, when $\eta(\mathbf{r}) = 1/2$ the effect of the Pauli repulsion is the same as in a uniform electron gas of the same density.

The ELF formulation originates from the Hartree-Fock description of electron gas. A formulation for ELF in DFT has been developed by Savin et al. (1992). This DFT-ELF approach evaluates the Pauli kinetic energy density based on the diagonal elements of the one-particle density matrix (the electron density).

The Pauli kinetic energy is the energy due to the redistribution of the electrons in accordance with the Pauli principle and is the integral of the Pauli kinetic energy density:

Eq. CASTEP 90

$$t_p(\mathbf{r}) = t(\mathbf{r}) - \frac{1}{8}\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})}$$

The Pauli kinetic energy density itself does not resolve the bonding situation. It is an arbitrary division of $t_P(\mathbf{r})$ by the kinetic energy density of a uniform electron gas of the same electron density, this yields all the information:

$$t_h(\mathbf{r}) = c_F\rho(\mathbf{r})^{5/3}$$

where c_F is the Fermi constant:

$$c_F = \frac{3}{10}(3\pi^2)^{2/3}$$

For a closed shell system the ratio:

$$\chi_S(\mathbf{r}) = \frac{t_P(\mathbf{r})}{t_h(\mathbf{r})}$$

is formally identical to the ratio $\chi_{BE}(r)$ in the HF approximation. The same applies for an open shell system, where the kinetic energy densities are computed for the corresponding spin part only. So the ELF formulas based on $\chi_{BE}(r)$) and $\chi_S(r)$ are identical. In the interpretation of Savin and coworkers (1992) ELF is a measure of the influence of Pauli principle as given by the Pauli kinetic energy density, *relative* to a uniform electron gas of the same density. Similarly, for the original definition ELF does not mirror $t_P(\mathbf{r})$.

How to interpret ELF

The values of ELF are fairly straightforward to calculate but may not be easy to interpret. The ELF website (http://www.cpfs.mpg.de/ELF/index.php?content=06interpr.txt) provides a very useful article on physical meanings of ELF and, in particular, on what ELF is not.

> **Note:** ELF was developed for all electron descriptions. ELF in CASTEP and ONETEP is calculated for valence electrons only, so it might be less meaningful. In particular, ELF values from CASTEP and ONETEP do not span the full range from 0 to 1. Extremely localized or delocalized electrons may be poorly described.

Mulliken population analysis

CASTEP can perform Mulliken charges and bond populations calculations according to the formalism described by Segall et al. (1996a and 1996b).

Introduction

A disadvantage of the use of a plane wave (PW) basis set is that, because of the delocalized nature of the basis states, it provides no information regarding the localization of the electrons in the system. In contrast, a Linear Combination of Atomic Orbitals (LCAO) basis set provides a natural way of specifying quantities such as atomic charge, bond population, charge transfer, and so on.

CASTEP performs population analysis using a projection of the PW states onto a localized basis using a technique described by Sanchez-Portal et al. ([1995](#)). Population analysis of the resulting projected states uses the Mulliken formalism ([Mulliken, 1955](#)). This technique is widely used in the analysis of electronic structure calculations performed with LCAO basis sets.

Formalism

The eigenstates $|\psi_\alpha(\mathbf{k})>$, obtained from the PW calculation when sampling at a given wavevector $\mathbf{k}$, are projected onto Bloch functions formed from an LCAO basis set $|\phi_\mu(\mathbf{k})>$. In general, such a localized basis set is neither orthonormal nor complete. Therefore, care must be taken when performing the projection.

The overlap matrix of the localized basis set, $\mathbf{S}(\mathbf{k})$, is defined as:

Eq. CASTEP 63

$$S_{\mu\nu}(\mathbf{k}) = \langle \phi_\mu(\mathbf{k})|\phi_\nu(\mathbf{k})\rangle$$

The quality of the projection can be assessed by calculating a *spilling parameter*:

Eq. CASTEP 64

$$\sigma = \frac{1}{N_\alpha} \sum_{\mathbf{k}} w_{\mathbf{k}} \sum_\alpha \langle \psi_\alpha(\mathbf{k})| (1 - \hat{p}(\mathbf{k}))| \psi_\alpha(\mathbf{k})\rangle$$

Where:

N_α is the number of PW states.
$w_{\mathbf{k}}$ are the weights associated with the calculated k-points in the Brillouin zone.
$p(\mathbf{k})$ is the projection operator of Bloch functions with wavevector $\mathbf{k}$ generated by the atomic basis set:

Eq. CASTEP 65

$$\hat{p}(\mathbf{k}) = \sum_\mu |\phi_\mu(\mathbf{k})\rangle \langle \phi_\mu(\mathbf{k})|$$

Where $|\phi_\mu(\mathbf{k})>$ are the duals of the LCAO basis, such that:

Eq. CASTEP 66

$$\langle \phi_\mu(\mathbf{k})|\phi^\nu(\mathbf{k})\rangle = \langle \phi^\mu(\mathbf{k})|\phi_\nu(\mathbf{k})\rangle = \delta_{\mu\nu}$$

The spilling parameter varies between one, when the LCAO basis is orthogonal to the PW states, and zero, when the projected wavefunctions perfectly represent the PW states.

The density operator may be defined:

Eq. CASTEP 67

$$\hat{p}(\mathbf{k}) = \sum_\alpha^{occ} n_\alpha |\chi_\alpha(\mathbf{k})\rangle \langle \chi^\alpha(\mathbf{k})|$$

Where:
n_α are the occupancies of the PW states.
$|\chi_\alpha(\mathbf{k})>$ are the projected PW states $p(\mathbf{k})|\psi_\alpha(\mathbf{k})>$.
$|\chi^\alpha(\mathbf{k})>$ are the duals of these states.

From this operator, you can calculated the density matrix for the atomic states as follows:

Eq. CASTEP 68

$$P_{\mu\nu}(\mathbf{k}) = \langle \phi^\mu(\mathbf{k})| \hat{\rho}(\mathbf{k})| \phi^\nu(\mathbf{k})\rangle$$

The density matrix $\mathbf{P(k)}$ and the overlap matrix $\mathbf{S(k)}$ are sufficient to perform population analysis of the electronic distribution. In Mulliken analysis ([Mulliken, 1955](#)) the charge associated with a given atom, A, is determined by:

Eq. CASTEP 69

$$Q(A) = \sum_{\mathbf{k}} w_{\mathbf{k}} \sum_{\mu}^{onA} \sum_{\nu} P_{\mu\nu}(\mathbf{k}) S_{\nu\mu}(\mathbf{k})$$

The overlap population between two atoms, A and B, is:

Eq. CASTEP 70

$$n(AB) = \sum_{\mathbf{k}} w_{\mathbf{k}} \sum_{\mu}^{onA} \sum_{\nu}^{onb} 2P_{\mu\nu}(\mathbf{k}) S_{\nu\mu}(\mathbf{k})$$

The weight of a band on a given orbital can be calculated by projecting the band onto the selected orbital. So, the weight of band α on orbital μ is given by:

Eq. CASTEP 71

$$W_{\alpha\mu}(\mathbf{k}) = \langle \psi_\alpha(\mathbf{k}) | \phi_\mu(\mathbf{k}) \rangle \langle \phi^\alpha(\mathbf{k}) | \psi_\alpha(\mathbf{k}) \rangle$$

The contribution of each band α to the density of states is multiplied by the weight $W_{\alpha\mu}(\mathbf{k})$ to get the projected density of states for orbital μ.

LCAO Basis Set

In this case, the natural choice of basis set is that of pseudo-atomic orbitals, generated from the pseudopotentials used in the electronic structure calculation. These are generated automatically during population analysis. The orbitals are calculated by solving for the lowest energy eigenstates of the pseudopotential in a sphere, using a spherical Bessel basis set.

By default, the basis set used on an atom of a given species is that of the orbitals in the closed valence shell of that species. This is usually a sufficiently good basis set for population analysis and partial density of states projection. If the spilling parameter indicates that the basis set does not represent the PW states with sufficient accuracy, the number of orbitals in the atomic basis set can be increased. A spilling parameter in the region of a few percent or less is sufficiently good for population analysis and partial density of states projection. Take care when increasing the basis set dramatically, as this can lead to artificial transfers of charge.

Implementation details

The elements of the overlap matrix $\mathbf{S(k)}$ are computed in reciprocal space, as the imposition of periodic boundary conditions implies that the orbitals need only be evaluated on a discrete reciprocal space grid. The overlaps between orbitals on different atomic sites are calculated on the same grid with the application of a phase factor.

The overlaps between the plane wave states and the basis functions are also calculated in reciprocal space as this is the natural representation of the plane wave states:

Eq. CASTEP 72

$$T_{\alpha\mu}(\mathbf{k}) = \langle \psi_\alpha(\mathbf{k}) | \phi_\mu(\mathbf{k}) \rangle$$

The duals of the orbitals are constructed as follows:

Eq. CASTEP 73

$$|\phi^{\mu}(\mathbf{k})\rangle = \sum_{\nu} S_{\mu\nu}^{-1}(\mathbf{k}) \, |\phi_{\nu}(\mathbf{k})\rangle$$

The duals of the projected wavefunctions are generated in a similar manner:

Eq. CASTEP 74

$$|\chi^{\alpha}(\mathbf{k})\rangle = \sum_{\beta} \mathbf{R}_{\alpha\beta}^{-1}(\mathbf{k}) \, |\chi_{\beta}(\mathbf{k})\rangle$$

Where $\mathbf{R}(k)$ is the overlap matrix between projected states:

Eq. CASTEP 75

$$R_{\alpha\beta}(\mathbf{k}) = \langle \chi_{\alpha}(\mathbf{k})|\chi_{\beta}(\mathbf{k})\rangle = \sum_{\mu\nu} T_{\alpha\nu}(\mathbf{k}) S_{\nu\mu}^{-1}(\mathbf{k}) T_{\beta\mu}^{*}(\mathbf{k})$$

Two auxiliary matrices can be defined for efficiency, namely:

Eq. CASTEP 76

$$\mathbf{U}(\mathbf{k}) = \mathbf{T}(\mathbf{k})\mathbf{S}^{-1}(\mathbf{k})$$

Eq. CASTEP 77

$$\mathbf{V}(\mathbf{k}) = \mathbf{R}^{-1}(\mathbf{k})\mathbf{U}(\mathbf{k})$$

These matrices are used to calculate the spilling parameter:

Eq. CASTEP 78

$$\sigma = 1 - \frac{1}{N_{\alpha}} \sum_{\mathbf{k}} w_{\mathbf{k}} \sum_{\alpha} \sum_{\mu\nu} T_{\alpha\mu}(\mathbf{k}) S_{\mu\nu}^{-1}(\mathbf{k}) T_{\alpha\mu}^{*}(\mathbf{k}) = 1 - \frac{1}{N_{\alpha}} \sum_{\mathbf{k}} w_{\mathbf{k}} \sum_{\alpha} \sum_{\nu} U_{\alpha\mu}(\mathbf{k}) T_{\alpha\nu}^{*}(\mathbf{k})$$

Similarly, the density matrix can be straightforwardly calculated as:

Eq. CASTEP 79

$$P_{\mu\nu}(\mathbf{k}) = \sum_{\alpha\beta} \sum_{\kappa\lambda} n_{\alpha}(\mathbf{k}) S_{\mu\nu}^{-1}(\mathbf{k}) T_{\alpha\nu}^{*}(\mathbf{k}) R_{\alpha\beta}^{-1}(\mathbf{k}) T_{\beta\lambda}(\mathbf{k}) S_{\lambda\nu}^{-1}(\mathbf{k}) = \sum_{\alpha} U_{\alpha\mu}^{*}(\mathbf{k}) V_{\alpha\nu}(\mathbf{k})$$

For spin dependent systems, the populations of the two spin components are calculated separately and the sum and difference of the atomic and overlap populations are calculated to find the net charge and spin, respectively.

Interpreting the results

It is widely accepted that the absolute magnitude of the atomic charges yielded by population analysis have little physical meaning. Tthey display a high degree of sensitivity to the atomic basis set with which they were calculated (Davidson and Chakravorty, 1992). However, consideration of their relative values can yield useful information (Segall et al., 1996a; Segall et al., 1996b; Winkler et al., 2001), provided that you use a consistent basis set for their calculation.

The spilling parameter should be in the region of a few percent or less to ensure that the results are reliable. If this is not the case, the number of orbitals in the basis set should be increased with care. If this does not significantly improve the spilling parameter, it may be that atomic orbitals do not provide a good representation of some of the states in the system.

Note: Normally CASTEP reports a "charge spilling parameter", obtained from summation of σ (see Eq CASTEP 78) over all occupied bands. Additionally, CASTEP can calculate an "all bands spilling parameter", obtained from the sum over all bands, including unoccupied states. Its value is typically higher and it describes the accuracy of the representation of conduction states through LCAO-type functions.

In addition to providing an objective criterion for bonding between atoms, the overlap population can be used to assess the covalent or ionic nature of a bond. A high value of the bond population indicates a covalent bond, while a low value indicates an ionic interaction. You can obtain a further measure of ionic character from the effective ionic valence, defined as the difference between the formal ionic and Mulliken charges on the anion species. A value of zero indicates a perfectly ionic bond, while values greater than zero indicate increasing levels of covalency. See Segall et al. (1996b) for more details.

Take care when interpreting the bond order values for small unit cells. The results are incorrect whenever an atom is bonded to a number of periodic images of itself. For example, bond orders for the primitive cell of silicon are reported as 3.0, while the same calculation for the conventional cell gives 0.75. The factor of four appears because CASTEP sums the bond orders for the four bonds that link the Si atom at the origin its periodic images, in the primitive cell. A manual analysis of the multiplicities is required in such cases, specifically: determine the number of bonds to periodic images of the same atom and divide the bond order by that number.

Note: The physical meaning of Mulliken charges or bond populations for metallic systems is unclear. This calculation is allowed, but the scientific interpretation of the results is left to the user.

Hirshfeld charge analysis

Hirshfeld charges (Hirshfeld, 1977) are defined relative to the deformation density, this is the difference between the molecular and unrelaxed atomic charge densities.

For quantitative descriptions of charge distributions in molecules or solids it is convenient to divide a system into well-defined atomic fragments. A general and natural choice is to share the charge density at each point between the atoms, in proportion to their free-atom densities at the corresponding distances from the nuclei. This prescription yields well-localized bonded-atom distributions each of which closely resembles the molecular density in its vicinity. Integration of the atomic deformation densities - bonded minus free atoms - defines the net atomic charges and multipole moments which concisely summarize the molecular charge reorganization. This permits calculation of the external electrostatic potential and the interaction energy between molecules or between parts of the same molecule.

Calculating NMR shielding tensors using pseudopotentials

A uniform external magnetic field, **B**, applied to a sample induces an electric current. In an insulating non-magnetic material, only the orbital motion of the electrons contributes to the this current. In addition, for the field strengths typically used in NMR experiments, the induced electric current is proportional to the external field, **B**. This first-order induced current, $\mathbf{j}^{(1)}(\mathbf{r})$, produces a non-uniform magnetic field:

Eq. CASTEP 42

$$\mathbf{B}_{in}^{(1)}(\mathbf{r}) = \frac{1}{c} \int d^3 r' \mathbf{j}^{(1)}(\mathbf{r}') \times \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3}$$

The shielding tensor, $\sigma(\mathbf{r})$, connects the induced magnetic field to the applied magnetic field:

Eq. CASTEP 43

$$\mathbf{B}_{in}^{(1)}(\mathbf{r}) = -\overleftrightarrow{\sigma}(\mathbf{r})\mathbf{B}$$

and the isotropic shielding is given by:

Eq. CASTEP 44

$$\sigma(\mathbf{r}) = \frac{\mathrm{Tr}\left[\overleftrightarrow{\sigma}(\mathbf{r})\right]}{3}$$

All-electron magnetic response with pseudopotentials

Information about $\sigma(\mathbf{r})$ at nuclear positions can be obtained from NMR experiments. In CASTEP, the first-order induced current, $\mathbf{j}^{(1)}(\mathbf{r})$, is calculated and then used to evaluate the induced magnetic field, $\mathbf{B}^{(1)}$ through Eq. 42. Calculations are performed with the gauge-including projector augmented-wave method (GIPAW) developed by Pickard and Mauri (2001). The projector augmented-wave formalism originally introduced by Blöchl (1994) makes it possible to obtain expectation values of all-electron operators in terms of pseudo-wavefunctions coming from a pseudopotential calculation and the GIPAW formalism reconciles the requirement of translational invariance of the crystal in a uniform magnetic field with the localized nature of Blöchl's projectors. The theory was initially applied with Troullier-Martins norm-conserving pseudopotentials (Pickard and Mauri, 2001) and has been extended subsequently to the case of ultrasoft pseudopotentials (Yates, 2007).

The first-order perturbation wavefunction, $\Psi^{(1)}$:

Eq. CASTEP 45

$$\left|\bar{\Psi}_n^{(1)}\right\rangle = G(\varepsilon_n)\bar{H}^{(1)}\left|\bar{\Psi}_n^{(0)}\right\rangle$$

is proportional to the magnetic perturbation, $H^{(1)}$, which, in pseudopotential calculations, contains a contribution due to the non-locality of the pseudopotential, in addition to the usual term:

Eq. CASTEP 46

$$\frac{1}{2c}\mathbf{L}\cdot\mathbf{B}$$

Calculation of perturbed wavefunctions

In order to obtain the first-order perturbation wavefunction $\Psi^{(1)}$, the application of the Green function in Eq. 46 is performed in CASTEP by solving a system of linear equations:

Eq. CASTEP 47

$$\left(\varepsilon_n - \bar{H}^{(0)}\right)\left|\bar{\Psi}_n^{(1)}\right\rangle = Q\bar{H}^{(1)}\left|\bar{\Psi}_n^{(0)}\right\rangle$$

where Q is the projection operator onto the unoccupied Hilbert subspace. The system is solved by a conjugate gradient minimization scheme, whereby the tedious summation over unoccupied states is avoided. The method is, thus, comparable in computational cost to the calculation of the ground-state electronic structure.

NMR properties of molecules and crystals

The calculation of the induced current involves evaluation of expectation values of the position operator, whose definition for extended systems is not straightforward. Two approaches have been developed (Pickard and Mauri, 2001) and implemented in CASTEP. For translationally invariant systems with well-defined Blöch vectors, $\mathbf{k}$, the application of the position operator can be reduced to calculating the gradient in k-space. Alternatively, for finite systems, which are represented by supercell structures (a molecule in a box) in CASTEP, one can apply a real-space representation of the position operator. The artificial periodicity imposed on the system causes the position operator to acquire a sawtooth shape. Thus, in the vicinity of the box boundaries, the position operator is distorted. Because of this, a sufficiently large supercell must be constructed so that the electronic density does not reach the regions where the position operator behaves unphysically. This condition is easily satisfied by the usual physical requirement that the molecules in neighboring boxes do not interact.

NMR shielding tensor

Finally, the induced magnetic field, $\mathbf{B}^{(1)}$, is calculated from the induced current and its value at the nuclear position determines the NMR shielding tensor. The calculated tensor is rather sensitive to numerical errors in both the unperturbed wavefunction, $\Psi^{(0)}$, and its first-order perturbation, $\Psi^{(1)}$, so the convergence requirements for NMR calculations are more stringent than, for example, routine band structure calculations. To obtain reliable results, the convergence of the wavefunction with respect to the number of basis functions (plane waves) must be ensured and a well-converged conjugate gradient procedure put in place to determine the coefficients of the plane waves. Apart from that, in calculating solid-state NMR properties (a small unit cell as opposed to a molecule in a box) the convergence of the k-space sum over the Brillouin zone must be achieved. The NMR observables are not particularly sensitive to uncertainties in the ground-state density distribution in the system, which determines the unperturbed Hamiltonian. Here, the usual convergence criteria for self-consistent DFT calculations are sufficient.

Chemical shift (or shielding) can be calculated for paramagnetic materials where the total spin is zero, even if a spin-polarized treatment is applied. This opens the possibility of using the DFT+U method as implemented by Shih and Yates (2017). The nonlocal Hubbard correction potential has been reexamined in order to comply with the gauge-including projector augmented-wave transformation under an external uniform magnetic field. The resulting expression is suitable for chemical shift calculations using both norm-conserving and ultrasoft pseudopotentials in the projector augmented-wave scheme. As a result more accurate results can be obtained for transition metal and rare earth oxides.

Note: It is important to examine the results and establish that the solution is indeed paramagnetic. If the total spin of the final state is non-zero, or the spin arrangement is antiferromagnetic, the results are likely to be meaningless.

Sensitivity of NMR to calculation parameters

NMR properties calculations are very sensitive to the number of k-points in the Brillouin zone. It is hard to construct a general rule for the number of k-points required, so it is recommended that you carry out convergence tests. An example convergence test for gallium phosphide is given below (these results are obtained for the experimentally observed structure of cubic GaP, ultra-fine settings, on the fly generated ultrasoft pseudopotentials, PBE functional).

Table 1. Convergence test for GaP

	k-point mesh	chemical shift (ppm)
P	2 × 2 × 2	-578.60
	4 × 4 × 4	302.72
	8 × 8 × 8	376.18
	12 × 12 × 12	375.45
	16 × 16 × 16	375.34
Ga	2 × 2 × 2	920.61
	4 × 4 × 4	1335.72
	8 × 8 × 8	1352.50
	12 × 12 × 12	1352.21
	16 × 16 × 16	1352.20

It follows from Table 1 that a grid of at least 12 × 12 × 12 is required to achieve convergence of the chemical shift to within 1-2 ppm, and finer grids might be needed to achieve higher accuracy.

NMR properties are very sensitive to atomic positions, which makes NMR such a useful experimental tool for structure analysis. This implies that it is highly recommended to perform a geometry optimization run prior to the NMR calculation. If the structure of a crystal or molecule under investigation is obtained from an experimental study, it is advisable to optimize positions of hydrogen atoms first of all. If the forces on heavy atoms as reported by CASTEP are high (in excess of 1 eV/Å) then complete structure optimization is recommended.

NMR J-couplings

NMR J-coupling or nuclear spin-spin coupling is an indirect interaction of the nuclear magnetic moments mediated by the bonding electrons. It is manifested as the fine structure in NMR spectra, providing a direct measure of bond strength and a map of the connectivities of the system.

The J-coupling mechanism is an essential component of many NMR experiments. Joyce *et al.* (2007) developed a method to calculate J-coupling constants from first-principles in extended systems in a planewave-pseudopotential density functional theory framework, using the projected augmented wave method (PAW) to reconstruct the all-electron properties of the system. This method has been validated for a small number of systems containing light atoms against quantum chemical calculations and against experimental data (see for example, Joyce *et al.*, 2008). This technique has been further developed by Green and Yates (2014) to incorporate scalar relativistic effects in the ZORA (zeroth-order regular approximation) approach and hence to provide a highly efficient method for predicting J-coupling in extended systems containing heavy ions at negligible extra computational cost compared to the non-relativistic method.

A general review of the formalism is given by Yates (2010), this discusses various aspects of the calculations which should be taken into account when comparing results with solid-state NMR experiments including anisotropy and orientation of the J tensors, the reduced coupling constant, and the relationship between the J-coupling and crystal structure.

J-coupling interactions can be decomposed into four mechanisms:

- two due to interactions of the electron spins with the nuclear moments
- two due to electron currents induced by the nuclear moments

When spin-orbit coupling is neglected these can be treated separately.

The spin term can be decomposed into an analog of a spin-dipole interaction plus a Fermi-contact term, which is due to the finite probability of the presence of an electron at the nucleus.

Induced current operators can be decomposed into diamagnetic and paramagnetic current operators.

Joyce *et al.* (2007) found that the Fermi-contact contribution to be consistently the largest component, while the diamagnetic and spin-dipolar contributions were very small for all the cases studied.

Experimental interest is focused primarily on the isotropic coupling constant which is obtained from the trace of the J-coupling tensor and is measured in Hertz. Recent extensive validation studies (for example, by Green and Yates 2014) demonstrate that the pseudopotential PAW approach for J-coupling calculations gives results in good qualitative and quantitative agreement with experiment both for light and heavy elements.

It is important to note that solid state calculations of J-couplings using CASTEP correctly account for long-range effects in the periodic systems and reproduce the differences between solution and solid-state values (Joyce *et al.*, 2008).

Note: Induced magnetization density and current density are expected to be short-ranged. This forms the basis of using J-coupling as a tool for probing the strength of interatomic bonds. However, in a periodic calculation the perturbing nucleus can be viewed as similar to a defect in a defect calculation. Hence, sometimes it might be necessary to construct a supercell which is large enough to inhibit the interaction between the periodic defects or perturbations. Convergence with respect to the cell size should represent an important test in establishing accuracy of J-coupling calculations in either periodic systems or in molecule in a box calculations.

EPR G-tensor

Electron Spin Resonance (EPR - also known as Electron Paramagnetic Resonance) is a powerful experimental probe of the structure of defects in solids. EPR spectra of spin ½ centers are made up of two contributions:

- the hyperfine parameters
- the g-tensor

The g-tensor arises from the interaction of the electronic spin with external magnetic field. This term plays a somewhat similar role to the shielding in NMR; induced electronic currents in the sample modify the g tensor from its vacuum value.

EPR spectrum can be modeled using the following effective Hamiltonian, bilinear in the total electron spin S, and the applied uniform magnetic field or nuclear spins, B and I_I, respectively:

$$H_{eff} = \frac{\alpha}{2} S \cdot g \cdot B + \sum_I S \cdot A_I \cdot I_I$$

where:
atomic units are used
α is the fine structure constant
the summation I runs over the nuclei

The tensors A_I are the hyperfine parameters, and the tensor g is the EPR g-tensor.

The Gauge Including Projector Augmented Waves (GIPAW) approach has been used to compute g tensors in several crystalline materials including defects in α-quartz and zirconia.

The hyperfine tensor can be obtained from the ground state charge density. In CASTEP it is computed using the PAW approach of Van de Walle and Blöchl ([1993](#)). The calculation of the g-tensor is more involved, requiring the linear response currents. These are computed using the GIPAW approach of Pickard and Mauri ([2001](#)). The total g-tensor is obtained as:

$$g = g_e + \Delta g_{Z-KE} + \Delta g_{SO} + \Delta g_{SOO} = g_e + \Delta g$$

Where the contributions to the total change in the g-tensor are the electron Zeeman kinetic energy, spin-orbit, and the spin-other-orbit correction. The calculation of these terms follows the approach of Pickard and Mauri ([2002](#)) extended for the use of ultrasoft potentials by Yates *et al.* ([2007](#)). The GIPAW approach has been used to compute g-tensors in several crystalline materials including defects in quartz and zirconia by Pietrucci *et al.* ([2006](#)).

Optical properties

Definition of optical constants

CASTEP can calculate the optical properties of solids that are due to electronic transitions.

In general, the difference in the propagation of an electromagnetic wave through vacuum and some other material can be described by a complex refractive index, N:

Eq. CASTEP 48

$$N = n + ik$$

In vacuum N is real, and equal to unity. For transparent materials it is purely real, the imaginary part being related to the *absorption coefficient* by:

Eq. CASTEP 49

$$\eta = \frac{2k\omega}{c}$$

The absorption coefficient indicates the fraction of energy lost by the wave when it passes through the material, so that the intensity at the distance x from the surface is:

$$I(x) = I(0)\exp(-\eta x)$$

where *I(0)* is the intensity of the incident light.

The *reflection coefficient* can be obtained for the simple case of normal incidence onto a plane surface by matching both the electric and magnetic fields at the surface:

Eq. CASTEP 50

$$R = \left|\frac{1-N}{1+N}\right|^2 = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

However, when performing calculations of optical properties it is common to evaluate the complex dielectric constant and then express other properties in terms of it. The complex dielectric constant, ε *(ω)*, is given by:

Eq. CASTEP 51

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 = N^2$$

and hence the relation between the real and imaginary parts of the refractive index and dielectric constant is:

Eq. CASTEP 52

$$\varepsilon_1 = n^2 - k^2$$
$$\varepsilon_2 = 2nk$$

Another frequently used quantity for expressing optical properties is the *optical conductivity*, $\sigma(\omega)$:

Eq. CASTEP 53

$$\sigma = \sigma_1 + i\sigma_2 = -i\frac{\omega}{4\pi}(\varepsilon - 1)$$

Optical conductivity is usually used to characterize metals, however CASTEP is aimed more toward the optical properties of insulators and semiconductors. The main difference between the two is that intraband transitions play important role in the IR part of the optical spectra of metals and these transitions are not considered at all in CASTEP.

A further property that can be calculated from the complex dielectric constant is the energy loss function. It describes the energy lost by an electron passing through a homogeneous dielectric material and is given by:

Eq. CASTEP 54

$$Im\left(\frac{-1}{\varepsilon(\omega)}\right)$$

Connection to experimental observables

Experimentally, the most accessible optical parameters are the absorption, $\eta(\omega)$, and the reflection, $R(\omega)$, coefficients. In principle, given the knowledge of both of these, the real and imaginary parts of N can be determined, through Eq. CASTEP 49 and Eq. CASTEP 50. Eq. CASTEP 51 allows expression in terms of the complex dielectric constant. However, in practice, the experiments are more complicated than the case of normal incidence considered above. Polarization effects must be accounted for and the geometry can become quite complex (for example, transmission through multilayered films or incidence at a general angle).

CASTEP supports spin-polarized calculations of optical properties for magnetic systems. Only transitions between the states with the same spin are allowed. For a more general discussion of the analysis of optical data see Palik (1985).

Connection to electronic structure

The interaction of a photon with the electrons in the system is described in terms of time dependent perturbations of the ground state electronic states. Currently CASTEP provides two approaches to optical properties calculations; one is based on standard DFT Kohn-Sham orbitals and the other uses more accurate but much more time-consuming time-dependent DFT (TD-DFT) theory.

DFT optics

In this approach excited states are represented as unoccupied Kohn-Sham states. Transitions between occupied and unoccupied states are caused by the electric field of the photon (the magnetic field effect is weaker by a factor of v/c). When these excitations are collective they are known as plasmons (which are most easily observed by the passing of a fast electron through the system rather than a photon, in a technique known as Electron Energy Loss Spectroscopy, described by Eq. CASTEP 54 , since transverse photons do not excite longitudinal plasmons). When the transitions are independent they are known as

single particle excitations. The spectra resulting from these excitations can be thought of as a joint density of states between the valence and conduction bands, weighted by appropriate matrix elements (introducing selection rules).

Evaluation of the dielectric constant

CASTEP calculates the imaginary part of the dielectric constant, which is given by:

Eq. CASTEP 55

$$\varepsilon_2 \left(\mathbf{q} \to O_{\hat{u}}, \hbar\omega \right) = \frac{2e^2\pi}{\Omega\varepsilon_0} \sum_{\mathbf{k},\nu,c} \left| \left\langle \Psi_{\mathbf{k}}^c \left| \mathbf{u} \cdot \mathbf{r} \right| \Psi_{\mathbf{k}}^\nu \right\rangle \right|^2 \delta \left(E_{\mathbf{k}}^c - E_{\mathbf{k}}^\nu - \hbar\omega \right)$$

where **u** is the vector defining the polarization of the incident electric field.

This expression is similar to Fermi's Golden rule for time dependent perturbations, and $\varepsilon_2(\omega)$ can be thought of as detailing the real transitions between occupied and unoccupied electronic states. Since the dielectric constant describes a causal response, the real and imaginary parts are linked by a Kramers-Kronig transform. This transform is used to obtain the real part of the dielectric function, $\varepsilon_1(\omega)$.

Details of the calculation

Evaluation of matrix elements

The matrix elements of the position operator that are required to describe the electronic transitions in Eq. CASTEP 55 may normally be written as matrix elements of the momentum operator allowing straightforward calculation in reciprocal space. However, this depends on the use of local potentials (Read and Needs, 1991), while in CASTEP nonlocal potentials are more often used. The corrected form of the matrix elements is:

Eq. CASTEP 56

$$\left\langle \Psi_{\mathbf{k}}^c \left| \mathbf{r} \right| \Psi_{\mathbf{k}}^\nu \right\rangle = \frac{1}{i\omega m} \left\langle \Psi_{\mathbf{k}}^c \left| \mathbf{P} \right| \Psi_{\mathbf{k}}^\nu \right\rangle + \frac{1}{\hbar w} \left\langle \Psi_{\mathbf{k}}^c \left| \left[V_{nl}(r), \mathbf{r} \right] \right| \Psi_{\mathbf{k}}^\nu \right\rangle$$

Ultrasoft pseudopotentials produce an additional contribution to optical matrix elements that is also included in CASTEP results.

Drude correction

The intraband contribution to the optical properties affects mainly the low energy infrared part of the spectra. It can be described sufficiently accurately using a semiempirical Drude term in the optical conductivity:

Eq. CASTEP 57

$$\varepsilon_D(\omega) = 1 - \frac{\omega_P^2}{\omega(i\gamma_D + \omega)}$$

in terms of the plasma frequency ω_P and damping parameter γ_D which depends on many details of the material and is usually obtained from experiment. The Drude damping parameter describes the broadening of the spectra due to effects not included in the calculation. Examples of processes that contribute to this broadening are electron-electron scattering (including Auger processes), electron-phonon scattering, and electron-defect scattering. This last contribution is usually the most important. As a result an a priori determination of the broadening would require knowledge as to the concentrations and kinds of defects present in the sample under study.

Polarization

For materials that do not display full cubic symmetry, the optical properties will display some anisotropy. This can be included in the calculations by taking the polarization of the electromagnetic field into account. As mentioned above, the unit vector **u** defines the polarization direction of the electric field. When evaluating the dielectric constant there are three options:

- *polarized*: requires a vector to define the direction of the electric field vector for the light at normal incidence to the crystal.
- *unpolarized*: requires a vector to define the direction of propagation of incident light at normal incidence to the crystal. The electric field vector is taken as an average over the plane perpendicular to this direction.
- *polycrystal*: no direction need be specified, the electric field vectors are taken as a fully isotropic average.

Scissors operator

As discussed below, the relative position of the conduction to valence bands is erroneous when the Kohn-Sham eigenvalues are used. In an attempt to fix this problem, inherent in DFT, a rigid shift of the conduction band with respect to the valence band is allowed. This procedure of artificially increasing the band gap is know as a *scissor operator*.

Limitations of the method

Local field effects

The level of approximation used here does not take any local field effects into account. These arise from the fact that the electric field experienced at a particular site in the system is screened by the polarizability of the system itself. So, the local field is different from the applied external field (that is, the photon electric field). This can have a significant effect on the spectra calculated (see the example of bulk silicon calculation below) but it is prohibitively expensive to calculate for general systems at present.

Quasiparticles and the DFT bandgap

In order to calculate any spectral properties it is necessary to identify the Kohn-Sham eigenvalues with quasiparticle energies. Although there is no formal connection between the two, the similarities between the Schrödinger-like equation for the quasiparticles and the Kohn-Sham equations allow the two to be identified. For semiconductors, it has been shown computationally (by comparing GW and DFT band structures) that most of the difference between Kohn-Sham eigenvalues and the true excitation energies can be accounted for by a rigid shift of the conduction band upward with respect to the valence band (Godby et al., 1992). This is attributed to a discontinuity in the exchange-correlation potential as the system goes from (N)-electrons to (N+1)-electrons during the excitation process. There can, in some systems, be considerable dispersion of this shift across the Brillouin zone, and the scissor operator used here will be insufficient.

Excitonic effects

In connection with the absence of local field effects, excitonic effects are not treated in the present formalism. This will be of particular importance for ionic crystals (for example NaCl) where such effects are well known.

Other limitations

- The nonlocal nature of the GGA exchange-correlation functionals is not taken into account when evaluating the matrix elements but it is expected that this will have a small effect on the calculated spectra.

- Phonons and their optical effects have been neglected.

- Finally, there is an intrinsic error in the matrix elements for optical transition due to the fact that pseudowavefunctions have been used (that is they deviate from the true wavefunctions in the core region). However, the selection rules will not be changed when going from pseudo- to all-electron wavefunctions.

Sensitivity of optical properties to calculation parameters

Number of conduction bands

This parameter defines the energy range covered in the calculation, and it also determines the accuracy of the Kramers-Kronig transform. It is clear from Figure 1 that $\varepsilon_2(\omega)$ converges rapidly with the number of conduction bands included.
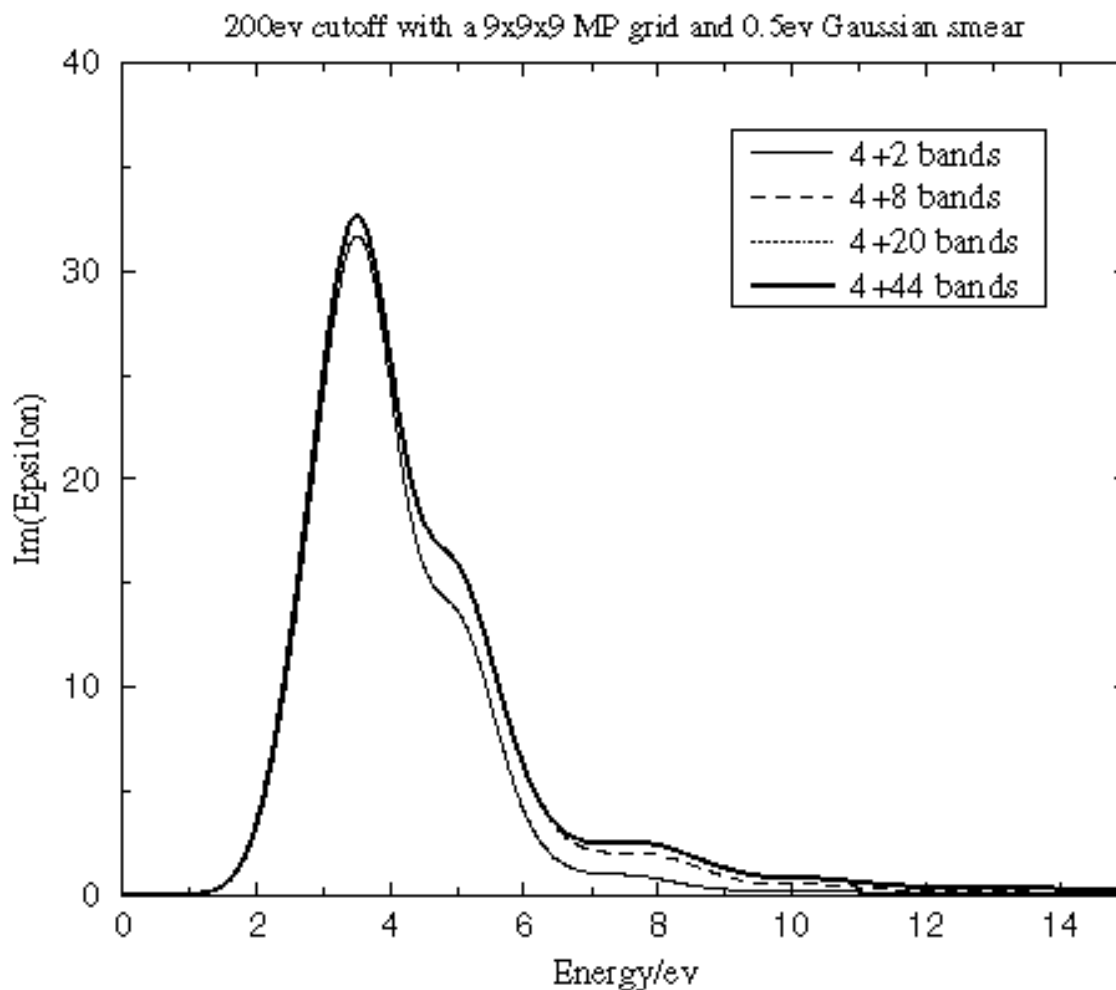
Figure 1. Convergence of the dielectric function with the number of conduction bands

Energy cutoff

The value of the energy cutoff that was used in the original SCF calculation of the ground state electron density is an important factor that determines the accuracy of the calculated optical properties. A bigger basis set provides more accurate self-consistent charge density and more variational freedom when searching for wavefunctions of unoccupied states. Figure 2 shows that while it is important to converge the calculation with respect to the planewave cutoff to obtain the correct energies for the spectral features, the shape of those features is reached rapidly.
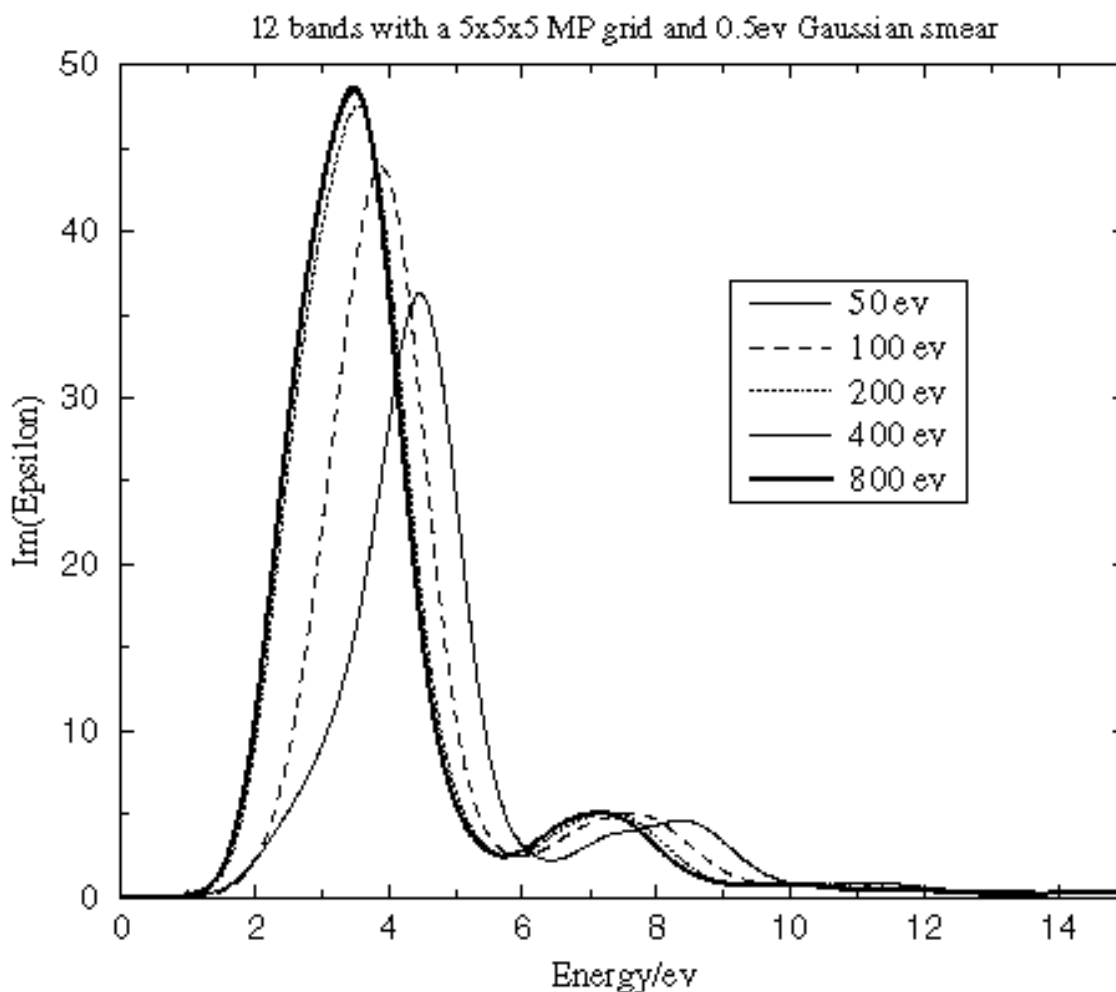
Figure 2. Convergence of the dielectric function with the cutoff energy

Number of k-points in the SCF calculation

The accuracy of the ground state electron density depends on the number of k-points used in the SCF run as well as on the basis set quality. Figure 3 reveals that the optical properties converge rapidly with the number of k-points used in the SCF run, which implies low sensitivity to the details of the charge density.
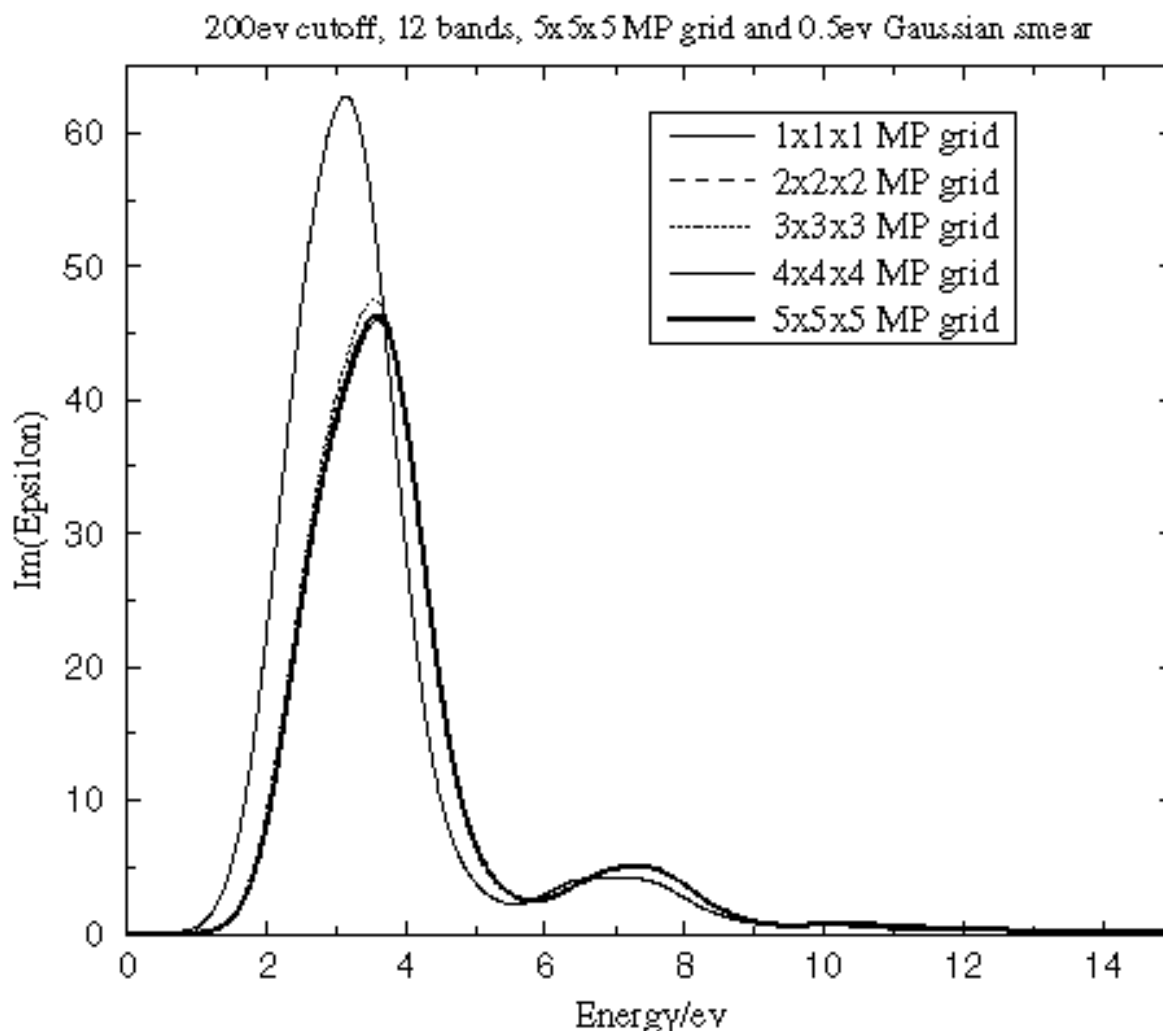
Figure 3. Convergence of the dielectric function with the number of k-points in the SCF calculation

Number of k-points for Brillouin zone integration

It is important to use a sufficient number of k-points in the Brillouin zone when running optical matrix element calculations. The matrix element changes more rapidly within the Brillouin zone than electronic energies themselves. Therefore, one requires more k-points to integrate this property accurately than are needed for an ordinary SCF calculation. Figure 4 clearly demonstrates the importance of converging the Brillouin zone integration for the optical properties with respect to the k-point density. Both energies and spectral features are strongly affected by the accuracy of this integration.
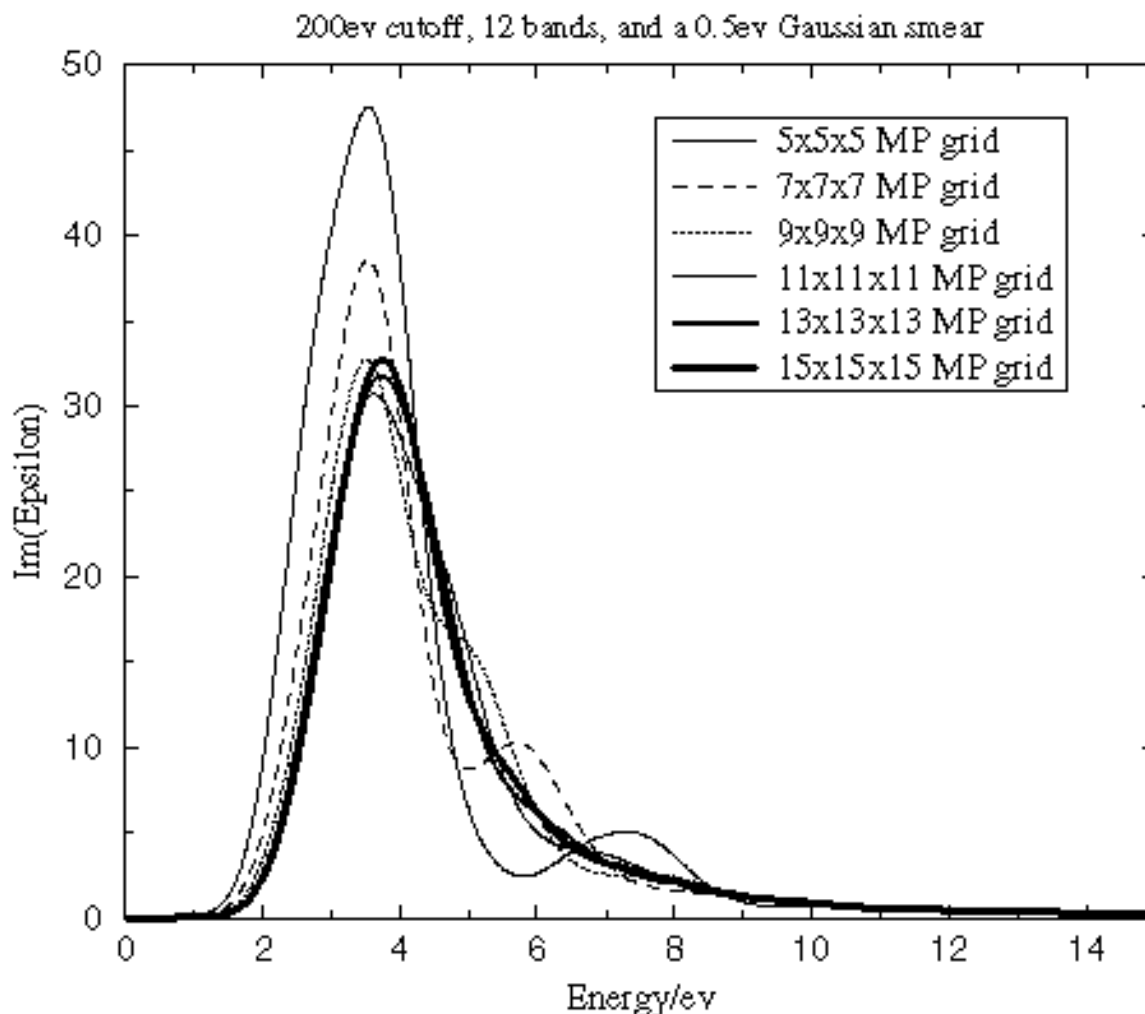
Figure 4. Convergence of the dielectric function with the number of k-points in the optical matrix elements calculation

TD-DFT optics

TD-DFT is a formally exact treatment of electronic excited states. The implementation in CASTEP follows the work of Hutter (2003), which takes a linear response approach to computing excitation energies directly. A benefit of this method is that the response wavefunctions for excited states are calculated and can then be used to derive further properties such as optical matrix elements and atomic forces. In the case of atomic forces, a geometry optimization or molecular dynamics run can be performed for a chosen excitation.

Hutter reformulated the equations of time-dependent Hartree-Fock in the Tamm-Dancoff approximation applied to TD-DFT (Hirata and Head-Gordon, 1999) so that they could be efficiently implemented in a plane-wave basis set. This self-consistent eigenvalue problem is solved in CASTEP by the user's choice of conjugate gradient or block-Davidson minimizers. The result is a set of electronic excitation energies and linear response wavefunctions.

A technical report on the implementation details of the TD-DFT minimizers can be found at http://www.hector.ac.uk/cse/distributedcse/reports/castep02/.

A second report on the implementation of excited state forces can be found at
http://www.hector.ac.uk/cse/distributedcse/reports/castep03/.

Non-linear optical properties

The development of highly efficient non-linear optical (NLO) crystals is of great importance to extending the frequency range provided by conventional laser sources into the ultraviolet and infrared regions. Therefore, the search for new NLO crystals is very active. There is a number of sometimes conflicting requirements for good NLO materials: large second harmonic generation (SHG) coefficients, a wide transparent and phase matchable region, good optical quality, and a high damage threshold. Computational screening of possible NLO materials has potential for generating good candidate crystals, and study of known NLO systems is useful for understanding the fundamental reasons for their good performance.

The prerequisite in searches for NLO materials is the ability to calculate both linear (refractive index, n) and nonlinear (second harmonic generation coefficient, SHG) optical properties that are related to second order susceptibility $\chi^{(2)}$. The early formalism for calculating the static limit of $\chi^{(2)}$ using CASTEP methodology is described and applied by Lin et al. (1999). A number of applications where SHG coefficients d_{ij} were calculated using CASTEP are cited in a review by Milman et al. (2010).

For small electric fields the dielectric polarization density (P) can be expressed as a Taylor expansion in terms of the electric field (E):

$$P = \varepsilon_0 \left(\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots \right)$$

Here, we assume the polarization is instantaneous and lossless, satisfying the Kramers-Kronig constraints. The linear polarizability $\chi^{(1)}$ is related to the dielectric permittivity, discussed above.

In principle, the second order polarizability $\chi^{(2)}$ is non-zero for any material without inversion symmetry and gives rise to 3-wave-mixing phenomena. It is a rank-3 tensor quantity related to the third derivative of the total energy with respect to electric field. These third order derivative quantities are computed in CASTEP using the 2n+1 theorem of the Density Functional Perturbation Theory following the method of Miwa (2011), also used for DFPT Raman calculations. The CASTEP implementation includes neither the phonon contribution, nor the frequency-dependence for energies above the bandgap, which modify the response at infrared and ultraviolet regions of the spectrum respectively, and therefore is appropriate for the visible optical range.

For a material where the susceptibility is dispersionless, the Kleinman symmetry condition is satisfied. This allows a contraction of the 27-element $\chi^{(2)}$ tensor into an 18-element tensor, d, that is symmetric in its last two indices:

$$d_{ijk} = 1/2 \chi^{(2)}_{ijk}$$

Using the following contraction, we define d_{il}.

jk	11	22	33	23, 32	31, 13	12, 21
l	1	2	3	4	5	6

Depending on the space group of the crystal, there are at most 10 symmetry-distinct elements of the d matrix.

The full form of the 3 × 6 matrix is:

$$d_{il} = \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{16} & d_{22} & d_{23} & d_{24} & d_{14} & d_{12} \\ d_{15} & d_{24} & d_{33} & d_{23} & d_{13} & d_{14} \end{bmatrix}$$

Measured quantities are most often reported in picometers per Volt, (pm/V). The book by Boyd ([2003](#)) contains more detailed background and discussion.

Phonons

The basic theory of phonons, or lattice vibrations, in crystals is well understood and has been described in detail in text books such as those by [Born and Huang (1954)](#) and [Ashcroft and Mermin (1976)](#). The importance of the phonon interpretation of lattice dynamics is illustrated by the large number of physical properties that can be understood in terms of phonons: infrared, Raman, and neutron scattering spectra; specific heat, thermal expansion, and heat conduction; electron-phonon interactions and, thus, resistivity and superconductivity, and so on.

A number of approximations are made in order to arrive at the phonon description of lattice vibrations. First of all, it is assumed that the mean equilibrium position of each ion, i, is a Bravais lattice site, $\mathbf{R}_i$. Secondly, it is assumed that the amplitude of atomic displacements is small compared to interatomic distances. This leads to a harmonic approximation which is sufficiently accurate to describe most of the lattice dynamical effect of interest. However, further refinement, in the form of anharmonic theory, is required to explain physical properties at elevated temperatures when the harmonic approximation breaks down.

The N-ion harmonic crystal can be considered as 3N independent harmonic oscillators, whose frequencies are those of 3N classical normal modes. Thus, at each wave vector, $\mathbf{q}$, in the Brillouin zone there are 3N vibrational modes. There are two equivalent descriptions of this system, either in terms of normal modes or phonons. Phonons are the quanta of the ionic displacement field that describe classical sound; they are similar to photons, the quanta of the radiation field that describe classical light.

The properties of phonons can be described using a harmonic approximation based on the knowledge of just one fundamental quantity, the force constants matrix:

Eq. CASTEP 58

$$D_{\mu\nu}(\mathbf{R} - \mathbf{R}') = \left. \frac{\partial^2 E}{\partial u_\mu(\mathbf{R}) \partial u_\nu(\mathbf{R})} \right|_{u=0}$$

Here u refers to the displacement of a given atom and E is the total energy in the harmonic approximation. This force constants matrix (or Hessian matrix) can also be represented in reciprocal space and the result is commonly referred to as the dynamical matrix:

Eq. CASTEP 59

$$D_{\mu\nu}(\mathbf{q}) = \frac{1}{N_{\mathbf{R}}} \sum_{\mathbf{R}} D_{\mu\nu}(\mathbf{R}) \exp(-i\mathbf{q}\mathbf{R})$$

Classical equations of motion can be written in the language of dynamical matrices, as an eigenvalue problem. Each atomic displacement is described in the form of plane waves:

Eq. CASTEP 60

$$\mathbf{u}(\mathbf{R}, t) = \varepsilon e^{i(\mathbf{q}\mathbf{R} - \omega(\mathbf{q})t)}$$

where the polarization vector of each mode, ε, is an eigenvector with the dimension of 3N of the eigenvalue problem:

Eq. CASTEP 61

$$M\omega^2(\mathbf{q})\varepsilon = D(\mathbf{q})\varepsilon$$

The dependence of the frequency, ω, on the wave vector is known as the phonon dispersion.

Each lattice always has three *acoustic* modes. Their dispersion relation at small values (near the Γ point) is linear, which is characteristic of sound waves. The rest of the vibrational modes, 3N - 3, in a Bravais lattice with basis are known as *optical* modes because the long wavelength optical modes in ionic crystals can interact with electromagnetic radiation and are therefore responsible for much of the characteristic optical behavior of such crystals. The frequencies of optical modes are finite at $\mathbf{q} = 0$. A simplistic characterization of acoustic and optical branches (Ashcroft and Mermin, 1976) would be: All ions in a primitive cell move essentially in phase in an acoustic mode and the dynamics is determined by the interaction between cells; an optical mode is one in which the ions within each cell exhibit a molecular vibration mode which is broadened into a band of frequencies due to intercellular interactions.

A popular way of classifying lattice vibrations is based on the relationship between the orientation of the polarization vector, ε, and the propagation direction, $\mathbf{q}$. In an isotropic medium for the case of a monatomic primitive cell it is always possible to choose three solutions for a given $\mathbf{q}$ so that one branch (*longitudinal*) is polarized along the propagation direction and the other two branches (*transverse*) are polarized perpendicular to this direction. This simple relationship does not hold for an arbitrary q-vector in an anisotropic crystal, nor for a Bravais lattice with basis. It is still common to classify vibrational modes along high symmetry directions in simple lattices based on the transverse and longitudinal description.

Long wavelength vibrations in polar materials deserve a special mention. The long range character of the Coulomb forces gives rise to macroscopic electric fields for longitudinal optic (LO) phonons at the Γ-point in polar semiconductors and insulators. The coupling between longitudinal phonons and the nonperiodic electric field gives rise to LO-TO splitting at the Γ-point. The value of the splitting is determined by the static dielectric constant of the crystal and by the Born effective charge of the ions. The Born effective charge tensor of the sth ion is the partial derivative of the macroscopic polarization with respect to a periodic displacement of all the periodic images of that ion at zero macroscopic electric field. A good review of the practical methods of dealing with this effect is given by Baroni et al., (2001).

Thermodynamic properties of crystals can be evaluated in a fairly straightforward way based on a knowledge of the phonon frequencies across the Brillouin zone (see Ashcroft and Mermin, 1976; Baroni et al., 2001). These quasiharmonic results are quite accurate at moderate temperatures and only small corrections to calculated phase transition properties can be found at temperatures as high as 1000-2000 K (Kern et al., 1999).

Practical schemes for phonon calculations

A good review of the existing schemes can be found in Baroni et al., (2001). The theoretical study of phonon properties has to rely on one of the three available methods for determining the force constants matrix: analytical calculations, supercell calculations, or linear response calculations. The analytical approach is only viable when the energy model is sufficiently simple to allow a direct evaluation of the second derivatives of the energy with respect to atomic displacements (for example, empirical pair potential models). Therefore, it is unsuitable for first principles calculations. Further alternatives such as extracting vibrational properties from molecular dynamics runs (Arias et al., 1992) are less transparent and noticeably more computationally expensive.

The supercell method involves perturbing the positions of the atoms slightly and calculating the reaction forces (Ackland et al., 1997). It is necessary to use supercells of the original cell when interatomic interaction in the system is long ranged. The main advantage of this method (and of the closely related frozen phonon technique) is that there is no need for a new formalism; any total energy scheme like CASTEP can be used to evaluate the forces at a number of carefully selected distorted configurations. The original frozen phonon scheme requires a displacement with the given wave vector and has been successfully used since the early 1980s (Yin and Cohen, 1982; Ho et al., 1984). The force constants matrix evaluation in this formalism has been used to calculate interplanar force constants (Wei and Chou, 1994) and, thus, phonon dispersion along high symmetry directions. More recent applications are based on the full reconstruction of the force constants matrix (Ackland et al., 1997; Parlinski et al., 1997; and references in Baroni et al., 2001).

Linear response calculations seek to evaluate the dynamical matrix directly for a set of q-vectors. The starting point of the linear response approach is evaluation of the second-order change in the total energy induced by atomic displacements. The main advantage of the scheme is that there is no need to artificially increase the cell size in order to accommodate small values of the q-vectors, as in the frozen phonon method, or to overcome the long range interaction problem (force constants matrix from supercell calculations). A more detailed description of the linear response method can be found in Baroni et al., (2001). The CASTEP implementation is described in the Linear response topic.

Interpolation schemes

The force constant matrix (Eq. CASTEP 58) for non-polar insulators and most metals decays proportionally to r^{-5} or even faster. This fact allows the introduction of an effective interpolation scheme to accelerate phonon calculations within both the finite displacement and linear response formalisms through the introduction of a cutoff radius, R_c, beyond which all the elements of the force constant matrix can be treated as zero. If an approximation for the force constant is available, the dynamical matrix for any given reciprocal vector can be calculated using Eq. CASTEP 59.

Finite displacement: supercell method

In the supercell method, finite displacement calculations are carried out in the supercell, circumventing the sphere described by the cutoff radius, which directly give all the non-zero elements of the force constant matrix.

Linear response: Fourier interpolation

In the Fourier interpolation method, calculations are performed on the regular reciprocal mesh (with a spacing corresponding to the real space cutoff radius). The set of dynamical matrices obtained in these calculations can be used to construct the force constant matrix using Fourier transformation.

Symmetry analysis of vibrations

Symmetry considerations in vibrational analysis are useful for various reasons. For example, the use of symmetry in the CASTEP implementation reduces computational time and the automatic assignment of spectroscopic labels allows you to interpret experimentally measured modes at Γ-points with greater confidence. Symmetry analysis and the subsequent enforcing of symmetry is carried out along the lines suggested by Warren and Worlton (1974). The nomenclature suggested by these authors for labeling symmetry elements is adopted in the CASTEP output. The notation for irreducible representation labels that are common in spectroscopic analysis is specified by IUPAC recommendations (1997).

Infrared spectra

In the infrared energy range (typically below 1 eV), vibrations are an important component of optical spectra. In the case of metals, this process is screened considerably by the plasmon (intraband)

electronic contribution, while for semiconductors and insulators, it is vibrations that are mainly responsible for absorbing light energy.

Theoretically, infrared absorption intensities are described in terms of a dynamical matrix (also known as a Hessian) and Born effective charges (also known as atomic polarizability tensors, ATP). The Born effective charge tensor of an ion is the partial derivative of the macroscopic polarization with respect to a periodic displacement of all the periodic images of that ion at zero macroscopic electric field. A good review of the practical methods of dealing with this effect is given by Baroni et al. (2001). The Born effective charge tensor is calculated within the linear response formalism by applying a Gonze approximation. Once these data are known, it is straightforward to calculate IR intensities (see Calculating vibrational frequencies). IR absorption intensities are printed in the CASTEP output file for any run where phonons at the Γ-point and LO-TO splitting are calculated.

The concept of IR absorption intensities is mostly used in the analysis of molecules. CASTEP can be used to model isolated molecules if the molecule in question is assumed to be contained within a box (see Setting up a calculation on an isolated molecule. This approach allows accurate prediction of IR absorption intensities. Figure 1 compares the results of such calculations obtained using DMol^3 and CASTEP for a variety of molecules.
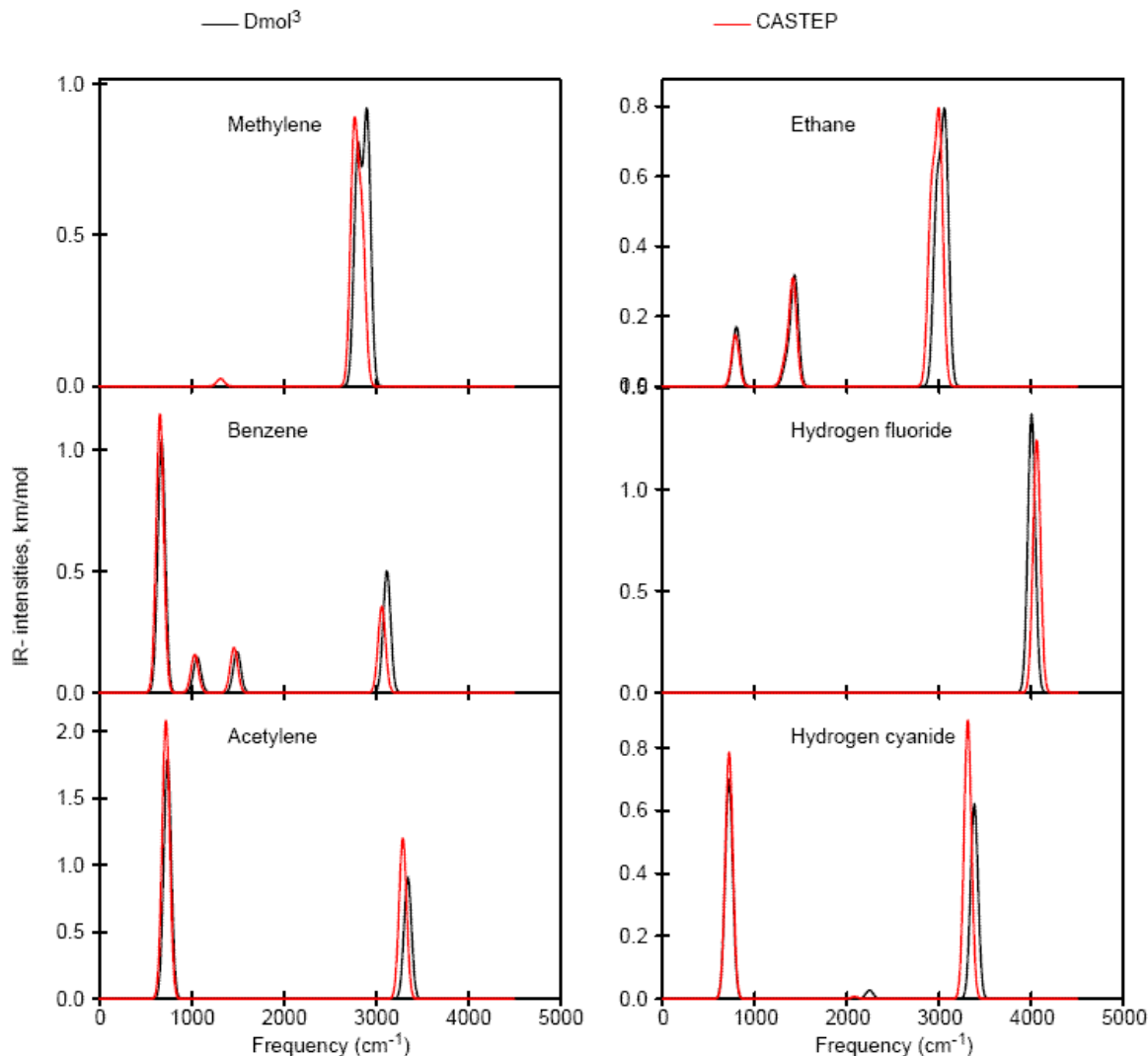
Figure 1. Comparison of IR spectra calculated using DMol^3 and CASTEP for a range of molecules

Linear response

Linear response, or density functional perturbation theory (DFPT), is one of the most popular methods of *ab initio* calculation of lattice dynamics (Baroni et al. 2001). However, the applicability of the method extends beyond the study of vibrational properties. Linear response provides an analytical way of computing the second derivative of the total energy with respect to a given perturbation. Depending on the nature of this perturbation, a number of properties can be calculated. A perturbation in ionic positions gives the dynamical matrix and phonons; in magnetic field - NMR response; in unit cell vectors - elastic constants; in an electric field - dielectric response, and so on.

The force constants matrix can be obtained by differentiating the Hellmann-Feynman forces on atoms, with respect to ionic coordinates. This procedure reveals that the force constants matrix depends on the ground state electron charge density and on its linear response to a distortion of atomic positions. Due to the variational principle of the density functional formalism, the second order change in energy depends on the first order change in the electron density.

The DFPT formalism is, in many ways, very similar to the density functional theory (DFT) itself. DFT states that the total energy is the functional of the electron density; thus one can solve the DFT equations by minimizing the total energy. Similarly, the DFPT problem can be solved by minimizing the second order perturbation in the total energy, which gives the first order changes in density, wavefunctions and potential (Gonze et al. 1994, Gonze 1997).

This variational technique for solving DFPT problems is a more robust and accurate method than the original Green's function, iterative scheme suggested by Baroni et al. 1987. Both methods should converge to the same solution but the Green's function method does not rely on the variational principle and its convergence properties are thus inferior. Moreover, once the first order change in wavefunctions, $\psi^{(1)}$, is evaluated, then the Green's function scheme evaluates the second order energy, which is not stationary with respect to first-order errors in $\psi^{(1)}$. Thus, the variational scheme of Gonze 1997 is expected to be more accurate.

The electronic second order energy, which is minimized in this approach, as implemented in CASTEP, is:

Eq. CASTEP 62

$$E^{(2)} = \sum_{\mathbf{k},n} \left[\left\langle \Psi_{\mathbf{k},n}^{(1)} \left| H^{(0)} - \varepsilon_{\mathbf{k},n}^{(0)} \right| \Psi_{\mathbf{k},n}^{(1)} \right\rangle + \left\langle \Psi_{\mathbf{k},n}^{(1)} \left| V^{(1)} \right| \Psi_{\mathbf{k},n}^{(0)} \right\rangle + \left\langle \Psi_{\mathbf{k},n}^{(0)} \left| V^{(1)} \right| \Psi_{\mathbf{k},n}^{(1)} \right\rangle \right]$$

$$+ \frac{1}{2} \int \frac{\delta^2 E_{xc}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} n^{(1)}(\mathbf{r}) n^{(1)}(\mathbf{r}') + \sum_{\mathbf{k},n} \left\langle \Psi_{\mathbf{k},n}^{(0)} \left| V^{(2)} \right| \Psi_{\mathbf{k},n}^{(0)} \right\rangle$$

where the superscripts refer to the ground state (0) and first (1) and second (2) order changes, respectively. Similar terms have to be evaluated for the ionic terms in the total energy. The preconditioned conjugate gradients minimization scheme can be used to find the minimum of this functional with respect to the first order wavefunctions. The dynamical matrix for a given $\mathbf{q}$ is then evaluated from the converged first order wavefunctions and densities (Gonze 1997).

Raman spectra

Raman spectroscopy is used to study the vibrational, rotational, and other low-frequency modes in a system. It is based on the Raman effect of inelastic scattering of monochromatic light. This interaction with vibrations results in the energy of incident photons being shifted up or down. The energy shift is defined by the vibrational frequency and the proportion of the inelastically scattered light is defined by the spatial derivatives of the macroscopic polarization, technical details are described by Porezag and Pederson (1996).

Spatial derivatives of the macroscopic polarization are calculated numerically along eigenvectors of each Raman active phonon mode by calculating the polarization for each displacement using a linear response formalism. Once these derivatives are known, it is straightforward to calculate the Raman cross-section through appropriate space averaging.

Raman activities defined by Porezag and Pederson (1996) characterize phonon mode contributions to the intensity of peaks in Raman spectra. These intensities depend on some other factors such as the temperature and incident light wavelength. It is important to specify these parameters in order to simulate a realistic Raman spectrum that can be compared to experimental results.

The Raman susceptibility tensor from which the Raman intensity can be calculated is defined as:

$$A^m_{\alpha\beta} = \sqrt{V} \sum_{I\gamma} \frac{d\chi^{(1)}_{\alpha\beta}}{dR_{I\gamma}} \frac{v^m_{I\gamma}}{\sqrt{M_I}}$$

where:
$\chi^{(1)}$ is the first order dielectric susceptibility
v is a phonon eigenvector (the direction in which atoms, I, at equilibrium positions R, move under excitation of a phonon mode, m in a unit cell with volume V)
Greek subscripts denote Cartesian directions

The derivative of $\chi^{(1)}$ inside the sum can be calculated in CASTEP using a finite difference approach, making small atomic displacements corresponding to the eigenvectors of each Raman active mode. However, the derivative can be written in full as:

$$\frac{d\chi^{(1)}_{\alpha\beta}}{dR_{I\gamma}} = -\frac{1}{V} \frac{d^3 E}{d\epsilon_\alpha d\epsilon_\beta dR_{I\gamma}}$$

where:
ϵ is the electric field of a photon in a Raman experiment exciting the phonon
E is the total energy of the system.

We can use the (2n+1) theorem in quantum mechanics to evaluate this in a more direct manner, see Miwa (2011). This theorem states that, under a perturbation, if the perturbed wavefunctions are known to order n then we can evaluate the perturbed energy up to order 2n+1. In particular, in a CASTEP phonon calculation, we need to evaluate the perturbed wavefunctions up to first order and therefore we should have access to the 3rd order energy perturbation, $E^{(3)}$, from which we can compute the susceptibility derivatives.

For Raman intensities, the full expression for this third derivative is given by equations (28)-(31) of Miwa (2011). These expressions are implemented in CASTEP for norm-conserving pseudopotentials.

The finite difference method and the "2n+1" linear response method lead to the same Raman susceptibility tensor, however the mathematical, and hence computational, routes are rather different. In the finite difference method, the phonon eigenvectors are calculated during a phonon task, and are then used to calculate the third order derivative for each mode one at a time. This means that there is a separate Raman intensity calculation for each Raman active mode to obtain its intensity. Computationally, this is usually the most time consuming part of a Raman intensity calculation.

Alternatively, in the linear response method, we first precompute the 9 second order derivatives with respect to electric field: equation 19 of Miwa (2011) and then construct the full set of Raman tensors during the phonon perturbations: equation (28) of Miwa (2011). Computationally, this means that in the linear response Raman intensity method there is an initialization stage and each phonon perturbation calculation has slightly more work to do than in the finite difference method. However, the computational work is then complete, unlike in the finite difference method where additional electric field perturbations are required for every Raman intensity.

For small cells the linear response method will be slower as the initialization stage and the extra cost of each phonon perturbation does not outweigh the effort of calculating the finite difference Raman tensor. For example, a linear response calculation for the primitive cell of boron nitride in the diamond structure takes about twice as long as the finite displacement calculation. However, the linear response method quickly becomes significantly more efficient as the number of degrees of freedom increases. Calculations for molecular crystals containing 50-100 atoms per unit cell can be an order of magnitude faster using the linear response method compared to the finite difference method.

> **Note:** It is important to remember that Raman intensities are effectively third order derivatives, so to obtain reasonable results very accurate calculations are required. Both the energy cutoff and k-point sampling can contribute significantly to a convergence error, so a careful convergence test is necessary to obtain reliable Raman intensities.

Thermodynamic calculations

The results of a calculation of phonon spectra can be used to compute energy (E), entropy (S), free energy (F), and lattice heat capacity (C_v) as functions of temperature. The CASTEP total energy yields the total electronic energy at 0 K. The vibrational contributions to the thermodynamic properties are evaluated to compute E, S, F, and C_v at finite temperatures as discussed below.

> **Note:** Thermodynamic calculations can be performed only if the system is in the ground state, that is, geometry optimization is fully converged. This means that all the phonon eigenfrequencies must be real and non-negative.

When you perform a vibrational analysis with CASTEP the results of the thermodynamic calculations can be visualized using the thermodynamic analysis tools.

The formulas below are based on work by Baroni et al. (2001).

The temperature dependence of the energy is given by:

Eq. CASTEP 80

$$E(T) = E_{tot} + E_{zp} + \int \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1} F(\omega)d\omega$$

where E_{zp} if the zero point vibrational energy, k is the Boltzmann constant, $\hbar$ is the Planck constant and $F(\omega)$ is the phonon density of states. E_{zp} can be evaluated as:

Eq. CASTEP 81

$$E_{zp} = \frac{1}{2} \int F(w)\hbar\omega d\omega$$

The vibrational contribution to the free energy, F, is given by:

Eq. CASTEP 82

$$F(T) = E_{tot} + E_{zp} + kT \int F(\omega) \ln\left[1 - \exp\left(-\frac{\hbar\omega}{kT}\right)\right] d\omega$$

The vibrational contribution to the entropy, S, can be obtained using:

Eq. CASTEP 83

$$S(T) = k \left\{ \int \frac{\frac{\hbar\omega}{kT}}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1} F(\omega)d\omega - \int F(\omega)ln\left[1 - \exp\left(-\frac{\hbar\omega}{kT}\right)\right] d\omega \right\}$$

The lattice contribution to the heat capacity, C_v, is:

Eq. CASTEP 84

$$C_\nu(t) = k \int \frac{\left(\frac{\hbar\omega}{kT}\right)^2 exp\left(\frac{\hbar\omega}{kT}\right)}{\left[\exp\left(\frac{\hbar\omega}{kT}\right) - 1\right]^2} F(\omega)d\omega$$

A popular representation of the experimental data on heat capacity is based on the comparison of the actual heat capacity to that predicted by the Debye model. This leads to the concept of the temperature dependent Debye temperature, $\Theta_D(T)$. Heat capacity in Debye model is given by (Ashcroft and Mermin, 1976):

Eq. CASTEP 85

$$C_\nu^D(T) = 9Nk\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2}dx$$

where N is the number of atoms per cell. Thus, the value of the Debye temperature, Θ_D, at a given temperature, T, is obtained by calculating the actual heat capacity, Eq. CASTEP 84, then inverting Eq. CASTEP 85 to obtain Θ_D.

Implicit solvation model

CASTEP offers a minimal-parameter implicit solvation model. This is based on the iso-density scheme first proposed in a series of papers (Fattebert and Gygi (2002), Fattebert and Gygi (2003), Scherlis *et al.* (2006)). Dziedzic made refinements to the scheme, see Dziedzic *et al.* (2011).

DFT describes the solute, while a dielectric continuum with a spatially varying permittivity represents the solvent. Unlike most traditional solvation models, here the permittivity changes smoothly, approaching the bulk value far from the solute, and 1 in the vicinity of the solute. This is achieved by relating the permittivity to the electronic density of the solute. In this way, definition of the solute cavity is natural, avoiding the need for parameterizing its shape – the model is free of the ionic radii needed in most models.

This requires only two parameters to define the model; the density where the permittivity drops to half the bulk value and the steepness of this transition. With suitable, transferable values determined in advance. These are independent of solute, solvent, and details of the DFT calculation, such as pseudopotentials or exchange-correlation functionals.

Two physical characteristics describe the solvent itself: bulk permittivity (dielectric constant) and surface tension.

Apart from electrostatic effects of the solvent, the CASTEP model includes the apolar contribution to solvation-cavitation energy, and solute-solvent dispersion-repulsion energy. The SASA (solvent-

accessible surface area) approximation calculates both of these terms, so they are proportional to the surface area of the cavity.

Dziedzic *et al.* (2011) includes a brief description of the model, discussion of its implementation, and comparison to other approaches. Dziedzic *et al.* (2013) provides a more detailed description of the choice of numerical parameters. Fox *et al.* (2014) presents an example application to solvation of an entire protein.

Chapter 5: Dialogs in CASTEP

The following topics describe the dialogs in CASTEP:

- CASTEP Calculation dialog
- CASTEP Analysis dialog

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

CASTEP Calculation dialog

The Calculation dialog allows you to set up and run a CASTEP calculation.

It contains the following tabs:

- Setup: Allows you to choose the type and quality of calculation that CASTEP will perform, along with other basic input options, including exchange-correlation functional, spin polarization, and total charge.
- Electronic: Allows you to set the parameters associated with the electronic Hamiltonian. These include the basis set, pseudopotentials, SCF convergence criteria, and integration accuracy.
- Properties: Allows you to select the properties that will be computed as part of a CASTEP calculation. These include electronic properties (such as band structure, density of states, and population analysis), optical properties, vibrational properties, and stress.
- Job Control: Allows you to specify settings for the CASTEP job.

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

> **Note:** This button is enabled only when the current 3D model document contains a periodic structure.

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 CASTEP Job Files dialog which allows you to save input files for a CASTEP 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 CASTEP server program in standalone mode, or who wish to edit the CASTEP input files in order to gain access to features not supported by the CASTEP interface.
Help: Displays the Help topic for the current tab.

Access methods

Menu	*Modules	CASTEP	Calculation*
Toolbar	*| Calculation*

Setup tab

The *Setup* tab allows you to choose the type and quality of calculation that CASTEP performs, and other basic input options such as exchange-correlation functional, spin polarization, and total charge.

Task: Select the type of calculation for CASTEP to perform. Available options are:

- Energy - performs a single-point energy calculation.
- Geometry Optimization - searches for a minimum energy structure.
- Dynamics - performs a molecular dynamics calculation.
- Elastic Constants - performs an elastic constants calculation.
- TS Search - performs a transition state search.
- TS Confirmation - produces a refined reaction path based on a TS search.
- Properties - calculates properties based on the results obtained from one of the other tasks.

More...: Provides access to further options for the selected task: opening the CASTEP Geometry Optimization, CASTEP Dynamics, CASTEP Elastic Constants, CASTEP Transition State Search , or CASTEP TS Confirmation dialogs.

Quality: Select the overall quality of a single-point energy, geometry optimization, or dynamics calculation. This quality affects the basis set, k-point, SCF convergence criteria, and the convergence criteria for the Geometry Optimization, Elastic Constants, and TS Search tasks. Available options are:

- Express
- Coarse
- Medium
- Fine
- Ultra-fine

> **Tip:** Use the Coarse quality setting for a quick assessment of the calculation. Use the Express quality to achieve a good compromise between speed and accuracy that is appropriate for most calculations. Use Fine and Ultra-fine quality settings for calculations that require very high accuracy, at the expense of longer calculation times. Carry out convergence testing for highly sensitive calculations by increasing the quality setting and possibly by increasing the accuracy of the basis set and the k-point sampling.

The *Quality* setting affects all relevant task parameters that control the precision of the simulation. If any parameter has a value different from that specified by the overall quality level, the *Quality* displays as Customized.

Functional: Select the type of DFT exchange-correlation potential to use in the calculation. Choose the class of functional from the first list, then select the specific functional from the second list.

- LDA: local functional
  - CA-PZ: Ceperley and Alder, 1980; data as parameterized by Perdew and Zunger, 1981
- GGA: gradient-corrected functionals
  - PBE: Perdew et al., 1996
  - RPBE: Hammer et al., 1999
  - PW91: Perdew et al., 1992
  - WC: Wu and Cohen, 2006
  - PBESOL: Perdew et al., 2008
  - BLYP: exchange from Becke, 1988; correlation from Lee, Yang, Parr, 1988
- m-GGA: meta-GGA functional
  - RSCAN: Bartók and Yates, 2019; regularized version of the SCAN functional by Sun et al., 2016
- Nonlocal: Nonlocal functionals
  - HF
  - HF-LDA
  - sX
  - sX-LDA
- Hybrid: Hybrid functionals
  - PBE0
  - B3LYP
  - HSE03
  - HSE06

> **Notes:**
> - The m-GGA functional is not compatible with spin-orbit coupling, J-coupling, linear-response phonons, or polarizability calculations. You cannot use this formalism with mixture atoms. You can only use on-the-fly generated pseudopotentials with m-GGA.
>
> - You can only use Nonlocal and Hybrid functionals for insulators using All Bands/EDFT Electronic minimizer tasks. They are not compatible with NMR, phonon, or polarizability calculations. You cannot use these formalisms with mixture atoms. You can only use norm-conserving potentials with Nonlocal and Hybrid.
>
> - There is an important difference between standard DFT calculations with local exchange-correlation potentials and the nonlocal exchange case. The potential used in the latter scenario depends on the wavefunctions at SCF k-points, while in the former case, the potential depends only on electron density. This difference can make calculations a lot more expensive in terms of memory usage and CPU time, so it is advisable to limit the number of SCF k-points that you use in such situations. This is particularly relevant for small unit cells, where the default settings may generate a very large k-point set.

Use method for DFT-D correction: When selected, dispersion corrections use the chosen method. Available options are:

- TS for GGA PBE, PBESOL, RPBE, BLYP, PW91; also for PBE0 and B3LYP
- Grimme for GGA PBE, GGA BLYP, and B3LYP
- OBS for GGA PW91 and LDA
- D4 for GGA PW91, PBE, PBESOL, RPBE; also for PBE0, HSE03, HSE06, and RSCAN
- MBD* for GGA PBE; also for HSE03, HSE06, and PBE0

The selected value might change when you select a different exchange-correlation functional; if there is no support for the previous DFT-D scheme with the new functional. For example, if you selected the OBS method and the LDA functional, the selection becomes invalid when you change the functional to GGA PBE. In this case, the value of the dispersion correction method changes automatically to a valid option; TS when possible, and D4 for the RSCAN functional. The DFT-D correction field becomes disabled if the selected functional has no validated options, for example, for GGA WC. In this case, you can only apply dispersion corrections by specifying custom values on the DFT-D tab of the CASTEP Electronic Options dialog.

> **Note:** The option selected automatically updates the *Use custom DFT-D parameters* option on the DFT-D tab of the CASTEP Electronic Options dialog.

Spin polarization: Select how to treat spin density. Available options are:

- Non-polarized also known as 'spin-restricted' calculation, uses the same orbitals for alpha and beta spins.
- Collinear also known as 'spin-unrestricted' calculation, separate calculation for majority and minority spin projections.
- Non-collinear the calculation allows spin density to vary the quantization axis in each point of space.

Use formal spin as initial: When selected, indicates that the calculation takes the initial value for the number of unpaired electrons from the formal spin specified for each atom. The calculation optimizes this starting value. If you do not select this option, you can specify the initial value for the number of unpaired electrons. Default = checked.

> **Note:** You can only specify *Use formal spin as initial* if you select Non-collinear or Collinear for the *Spin polarization*.

> **Note:** CASTEP only uses atom-resolved initial spin if the *Electronic minimizer* is Density mixing on the SCF tab of the CASTEP Electronic Options dialog or if you select *DFT+U*.

Use DFT+U: When checked, CASTEP uses DFT+U (also known as the LDA+U formalism). You can specify the actual values of U on the Hubbard U tab of the Electronic Configuration dialog.

> **Note:** The DFT+U formalism is not compatible with NMR or polarizability calculations. You cannot use this formalism with mixture atoms or real-space pseudopotentials.

Include spin-orbit coupling: When selected, adds spin-orbit coupling to the Hamiltonian.

> **Note:** You can only specify *Include spin-orbit coupling* if you select Non-collinear or Collinear for the *Spin polarization*. You can only use the spin-orbit coupling formalism for norm-conserving pseudopotentials, either on-the-fly generated or tabulated, with no LDA+U corrections. In addition, it is not compatible with calculations of:
>
> - NMR
> - Dipole corrections
> - Electron localization function
> - Linear response, including polarizability calculation
> - Electronic excitations
> - Partial density of states
> - Hirshfeld population analysis
>
> You cannot visualize the electrostatic potential.

Metal: When selected, this indicates that the system is metallic so that you can create and edit empty bands. Default = checked.

If you do not specify that a system is metallic:

- *Fix occupancy* on the SCF tab of the CASTEP Electronic Options dialog is selected.
- The default k-point separation value is coarser.

> **Note:** In some calculations, it is not sufficient to use fixed orbital occupancies if DFT results indicate that the system under investigation has a band gap. This applies to calculations that use the linear response formalism for vibrational properties and to calculations of electric field responses (polarizability and IR and Raman spectra). Attempting to study a metallic systems using fixed orbital occupancies results in poor convergence and usually in unphysical results for IR and Raman intensities and for polarizability. If this is the case, verify whether your system is metallic by running either density of states or band structure calculations.

Charge: Specify the total charge on the unit cell.

Access methods

Menu	*Modules | CASTEP | Calculation | Setup*
Toolbar	≋▼ | *Calculation | Setup*

CASTEP Geometry Optimization dialog

The Geometry Optimization dialog allows you to set up and display the parameters that control the Geometry Optimization task.

It contains the following tabs:

- Minimizer: Provides access to the parameters that specify the convergence level of the minimization and the external pressure and allows you to control cell optimization.
- Options: Provides access to the parameters that control the minimization algorithm.
- Stress: Provides access to the parameters that control the external stress or hydrostatic pressure on the structure.

Help: Displays the Help topic for the current tab.

Access methods

Menu	*Modules	CASTEP	Calculation	Setup	More...*
Toolbar	*	Calculation	Setup	More...*

Minimizer tab

The *Minimizer* tab allows you to specify the convergence level of the minimization and the external pressure, and to control cell optimization.

Quality: Set the geometry optimization convergence thresholds for energy change, maximum force, maximum stress, and maximum displacement between optimization cycles. The optimization will stop when all of these criteria are satisfied.

Four sets of convergence thresholds are available:

- Coarse
- Medium
- Fine
- Ultra-fine

The values of the convergence thresholds in each set are given in the table below:

Value	Coarse	Medium	Fine	Ultra-fine
Energy (eV/atom)	5×10^{-5}	2×10^{-5}	1×10^{-5}	5×10^{-6}
Max. force (eV/Å)	0.1	0.05	0.03	0.01
Max. stress (GPa)	0.2	0.1	0.05	0.02
Max. displacement (Å)	0.005	0.002	0.001	5×10^{-4}

Alternatively, thresholds can be specified independently for *Energy*, *Max. force*, *Max. stress*, and *Max. displacement*. If you enter your own values for any of these settings, the *Quality* is displayed as Customized on both the *Minimizer* tab and the Setup tab of the CASTEP Calculation dialog.

> **Note:** When the main quality is set to Express the geometry optimization quality is also set to Express. In this case energy tolerance will be displayed in eV/cell rather than eV/atom, the default value is 0.001 eV/cell. All other tolerances are ignored and geometry optimization runs stop when the energy change is less than the tolerance regardless of the values of forces or displacements.

Energy: Specify the convergence threshold for the maximum energy change, in eV/atom, during the geometry optimization. The units are eV/cell if the *Quality* is set to Express.

Max. force: Specify the convergence threshold for the maximum force, in eV/Å, during the geometry optimization. If the *Quality* is set to Express, this tolerance by default will be set to a very high value and will effectively be ignored in the calculation.

Max. stress: Specify the convergence threshold for the maximum stress, in GPa, during the geometry optimization. If the *Quality* is set to Express, this tolerance by default will be set to a very high value and will effectively be ignored in the calculation.

Max. displacement: Specify the convergence threshold for the maximum displacement, in Å, during the geometry optimization. If the *Quality* is set to Express, this tolerance by default will be set to a very high value and will effectively be ignored in the calculation.

Max. iterations: Specify the maximum number of geometry optimization cycles. If this number of cycles is reached, then the calculation will stop, even if the convergence criteria are not satisfied.

Cell optimization: Specify whether the cell should be optimized and how. Default = None. Options are:

- None - No cell optimization is requested and the *Basis set for variable cell* and *Compressibility* options are not available.
- Full - Complete optimization of the cell.
- Fixed Volume - The cell is optimized while keeping the volume fixed, cell angles and cell lengths are varied.
- Fixed Shape - The cell is optimized while keeping the cell angles and cell length ratios fixed, the cell volume is varied.

Basis set for variable cell: Specify the desired behavior of the basis set when the cell size changes. Default = Fixed Basis Quality. Options are:

- Fixed Basis Quality - The number of plane waves changes to maintain the fixed cutoff energy (finite basis set correction is required)
- Fixed Basis Size - The number of plane waves is kept constant, so the effective cutoff energy changes (finite basis set correction is not required)

> **Tip:** Fixed Basis Quality is the recommended option.

Compressibility: Specify an estimated compressibility value for the crystal under investigation in order to accelerate the geometry optimization. Each entry in the dropdown list is interpreted as a preset value:

- Soft - 25 GPa, suitable for soft materials like molecular crystals
- Medium - 200 GPa, suitable for most transition metals
- Hard (default) - 500 GPa, suitable for minerals, ceramics, and hard metals

> **Note:** CASTEP geometry optimization will respect constraints on the fractional coordinates of atoms. These constraints may be imposed using the controls on the Atom tab of the Edit Constraints dialog.
>
> Nonlinear constraints are respected only for P1 structures that do not contain mixture atoms and only when the delocalized internals optimizer is used, that is, the *Use delocalized internals* checkbox is checked on the Options tab of the CASTEP Geometry Optimization dialog.

Access methods

Menu	*Modules	CASTEP	Calculation	Setup	More...	Minimizer*
Toolbar	*	Calculation	Setup	More...	Minimizer*

Options tab

The *Options* tab allows you to specify the minimization algorithm and the parameters controlling the algorithm.

Algorithm: Specify the minimization algorithm. These algorithms are supported by CASTEP:

- LBFGS
- BFGS
- Damped MD
- TPSD

The LBFGS algorithm is generally recommended, especially for large systems. It implements a universal sparse preconditioner that accelerates geometry optimization (Packwood et al., 2016). However, if there are constraints TPSD might be a better choice (see the Geometry optimization theory topic for further details).

The TPSD geometry optimization algorithm is a viable alternative for systems where the potential energy surface deviates significantly from the quadratic form. TPSD offers robust convergence and is particularly recommended when user-supplied constraints on lattice parameters are applied during cell optimization (for example, when optimizing a solid-solid interface in a direction perpendicular to the interface plane).

> **Note:** The Damped MD algorithm is not used when cell optimization is performed.

Use line search: When checked, indicates that optimization should use the advanced line search algorithm.

> **Note:** This checkbox is checked by default, except when the main quality is set to Express. If you specify the Express quality setting and then request line search, the *Quality* is displayed as Customized on both the Minimizer tab and the Setup tab of the CASTEP Calculation dialog. In the latter scenario, you must set convergence criteria for gradients and displacements to sensible values, as the line search algorithm cannot function using only the energy change criterion.

Use delocalized internals: When checked, indicates that delocalized internal coordinates should be used during geometry optimization, instead of Cartesian coordinates. This setting typically speeds up the calculation by 2-3 times.

> **Note:** The *Use delocalized internals* option is enabled only if the BFGS algorithm is selected.

> **Note:** The delocalized internals minimizer does not currently support cell optimization. As a result, CASTEP will automatically switch over to Cartesian coordinates when the cell is allowed to vary.
>
> The delocalized internals minimizer respects nonlinear constraints only for P1 structures that do not contain mixture atoms.

Damping algorithm: Specify the algorithm for the Damped MD method. The supported algorithms are:

- Independent - the damping constant is chosen independently for each mode, so that all modes lose energy at the same rate.
- Coupled - the same damping constant is used for all modes at each step.
- Steepest Descent

The Independent damping algorithm is recommended (see the Geometry optimization theory topic for details).

Damping coefficient recalculation frequency: During the damped MD optimization, the damping coefficients are recalculated occasionally to improve the damping rate. This value specifies the number of MD steps between these recalculations.

> **Note:** The *Damping coefficient recalculation frequency* value is not used by the steepest descent algorithm.

Wavefunction extrapolation: Specify the method to be used for wavefunction extrapolation between MD steps.

- None - no extrapolation is performed.
- 1st VV - first-order extrapolation with variable coefficients.
- 2nd VV - second-order extrapolation with variable coefficients.
- 2/1 VV - alternate second- and first-order extrapolation with variable coefficients.
- 1st CC - first-order extrapolation with constant coefficients.
- 2nd CC - second-order extrapolation with constant coefficients.
- 2/1 CC - alternate second- and first-order extrapolation with constant coefficients.

Time step: Specify the time step to be used in the damped MD geometry optimization.

Auto-update time step: When checked, indicates that the time step will be automatically updated to speed up the geometry optimization.

> **Note:** The *Time step* and *Auto-update time step* controls are enabled only if the Damped MD algorithm is selected.

Access methods

Menu	*Modules	CASTEP	Calculation	Setup	More...	Options*
Toolbar	*	Calculation	Setup	More...	Options*

Stress tab

The *Stress* tab allows you to specify an external stress or hydrostatic pressure on the structure for geometry optimization.

> **Note:** The options on this tab are applicable only when cell optimization has been requested.

External stress: Specify any element of the external stress tensor on the structure, in GPa.

Equivalent hydrostatic pressure: Specify the hydrostatic pressure on the structure.

The hydrostatic pressure is one third of the trace of the stress tensor. When a value is specified here, the diagonal elements of the stress tensor are modified so as to leave any anisotropic term unchanged.

> **Note:** A positive value of external stress and hydrostatic pressure indicates that the structure is compressed.

Reset external stress to zero: Sets all elements of the stress tensor to zero.

Access methods

Menu	*Modules	CASTEP	Calculation	Setup	More...	Stress*

Toolbar		*Calculation	Setup	More...	Stress*
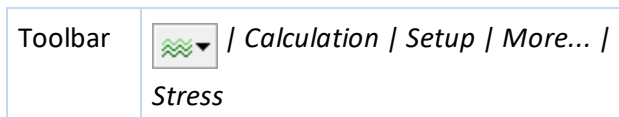
CASTEP Dynamics dialog

The CASTEP Dynamics dialog allows you to set up and display the parameters that control the Dynamics task.

It contains the following tabs:

- Dynamics: Provides access to the main parameters that specify the dynamics, including choice of ensemble, temperature, pressure, and the length of the run.
- Options: Provides access to the parameters that control the details of the dynamics algorithm, including thermostat, barostat and wavefunction extrapolation settings.
- Stress: Provides access to the parameters that control the external stress or hydrostatic pressure on the structure.

Help: Displays the Help topic for the current tab.

Access methods

Menu	*Modules	CASTEP	Calculation	Setup	More...*
Toolbar	*	Calculation	Setup	More...*

Dynamics tab

The *Dynamics* tab allows you to specify the main parameters for controlling dynamics simulations.

Ensemble: Specify the ensemble to be used in the dynamics simulation.

- NVE - dynamics at fixed volume and constant energy.
- NVT - dynamics at fixed volume with a thermostat to maintain a constant temperature.
- NPH - dynamics at constant enthalpy with a barostat to maintain a constant pressure.
- NPT - dynamics with a thermostat to maintain a constant temperature and with a barostat to maintain a constant pressure.

Initial velocities: Select the method of velocity initialization to be used for the dynamics calculation. The available options are:

- Random - set initial velocities to random value (default).
- Current - set initial velocities to values currently defined on the structure.

Temperature: Specify the temperature of the dynamics simulation. For the NVE ensemble, the initial random velocities of the atoms are scaled to this temperature.

Pressure: Specify the external pressure for the dynamics simulation in the NPH or NPT ensemble. For Parrinello barostat full stress tensor can be specified on the Stress tab.

Time step: Specify the time step for the dynamics simulation.

Total simulation time: Specify the total time for the dynamics simulation. When modified the number of steps is adjusted appropriately for the current time step.

Number of steps: Specify the total number of steps for the dynamics simulation.

Basis set for variable cell: Specify the desired behavior of the basis set when the cell size changes.

- **Fixed Basis Quality** - the number of plane waves changes to maintain the fixed cutoff energy (finite basis set correction is required).
- **Fixed Basis Size** - the number of plane waves is kept constant, so the effective cutoff energy changes (finite basis set correction is not required).

> **Tip:** Fixed Basis Quality is the recommended option.

Access methods

Menu	*Modules	CASTEP	Calculation	Setup	More...	Dynamics*
Toolbar	≋▼	*	Calculation	Setup	More...	Dynamics*

Options tab

The *Options* tab allows you to specify parameters which control the details of the dynamics algorithm.

Thermostat: Specify the thermostat to be used for NVT or NPT dynamics. Available options are:

- Langevin
- Nose
- NHL

> **Note:** This option in enabled only if the NVT or NPT ensemble is selected on the Dynamics tab. The Nosé-Hoover-Langevin (NHL) thermostat is only available for the NVT ensemble.

Barostat: Specify the barostat to be used for NPH or NPT dynamics. Available options are:

- Andersen - scales the cell uniformly
- Parrinello - allows variation in the cell shape

> **Note:** This option in enabled only if the NPT or NPH ensemble is selected on the Dynamics tab.

Langevin constant: Specify the damping time of temperature fluctuations during Langevin NVT dynamics. This time should normally be larger than the time scale of any motions of interest.

Nose Q ratio: Specify a scaling factor for the fictitious mass Q of the Nosé thermostat for Nosé or Nosé-Hoover-Langevin NVT dynamics. A larger Q ratio implies increased damping of temperature fluctuations.

Cell time constant: Specify the characteristic cell time, which is used to estimate the mass associated with the barostat. A larger value implies increased damping of pressure fluctuations.

Wavefunction extrapolation scheme: Specify the method to be used for wavefunction extrapolation between molecular dynamics steps. This selection is not available when *Use Extended Lagrangian (XL-BOMD)* is selected.

- None - no extrapolation is performed.
- 1st VV - 1st order extrapolation with variable coefficients.
- 2nd VV - 2nd order extrapolation with variable coefficients.
- 2/1 VV - Alternate 2nd and 1st order extrapolation with variable coefficients.
- 1st CC - 1st order extrapolation with constant coefficients.
- 2nd CC - 2nd order extrapolation with constant coefficients.
- 2/1 CC - Alternate 2nd and 1st order extrapolation with constant coefficients.

Use eXtended Lagrangian (XL-BOMD): When checked, indicates that the extended Lagrangian molecular dynamics (Steneteg 2010, Niklasson 2011) is used instead of the wavefunction extrapolation schemes. The extended Lagrangian formulation allows significantly higher time step values to be used, while conserving the constant of motion. This option is available only for fixed-cell (NVE and NVT) ensembles. Default = checked.

Fix center of mass: When checked, indicates that the center of mass will be fixed during the dynamics simulation. Default = unchecked.

Access methods

Menu	Modules | CASTEP | Calculation | Setup | More... | Options
Toolbar	| Calculation | Setup | More... | Options

Stress tab

The *Stress* tab allows you to specify an external stress or hydrostatic pressure on the structure for molecular dynamics.

> **Note:** The options on this tab are available only when the NPT or NPH ensemble is selected on the Dynamics tab.

External stress: Specify any element of the external stress tensor on the structure, in GPa.

Equivalent hydrostatic pressure: Specify the hydrostatic pressure on the structure.

The hydrostatic pressure is one third of the trace of the stress tensor. When a value is specified here, the diagonal elements of the stress tensor are modified so that any anisotropic term remains unchanged.

> **Note:** A positive value of external stress and hydrostatic pressure indicates that the structure is compressed.

> **Note:** When the Andersen barostat is selected on the Options tab only hydrostatic pressure is used by CASTEP.

Reset external stress to zero: Sets all elements of the stress tensor to zero.

Access methods

Menu	Modules | CASTEP | Calculation | Setup | More... | Stress

Toolbar	*| Calculation | Setup | More... |* *Stress*

CASTEP Elastic Constants dialog

The CASTEP Elastic Constants dialog is accessed from the *More...* button on the Setup tab, when the Elastic Constants option is selected from the *Task* dropdown list.

It contains the following tabs:

- Elastic Constants: Allows you to specify the strains applied to the crystal, used for calculating elastic constants.

- Options: Allows you to set the convergence level of the elastic constants calculation.
Help: Displays the Help topic for the current tab.

Access methods

Menu	*Modules | CASTEP | Calculation | Setup | More...*
Toolbar	*| Calculation | Setup | More...*

Elastic Constants tab

The *Elastic Constants* tab allows you to set parameters that define how the elastic constants will be calculated.

Number of steps for each strain: Specify the number of distorted structures generated for each strain pattern. An odd value implies that the undistorted structure will be among those generated. Even values are, therefore, recommended.

Maximum strain amplitude: Set the maximum distortion used. Values in excess of 0.01 are not recommended, since the crystal is likely to be beyond linear elasticity. However, values of 0.001 and below will generate a set of structures that are very similar to one another. In these circumstances, computational noise may become significant when comparing the calculated stress values for similar structures.

Use volume-conserving strains: When checked indicates that the strain patterns will be modified to use volume-conserving strains, when possible. This option should only be used if the standard set of strains is producing unsatisfactory results.

Strain pattern: Displays a matrix showing the nonzero components of the strain tensor for each generated strain. For example, the line:

```
    1  0  0  1  0  0
```

means that the xx, yz (and zy) components of the strain tensor will be non-zero.

> **Note:** This matrix is not editable.

> **Note:** For trigonal symmetry, the orientation standard where C lies along the z-axis and A is in the xz plane must be used. For further details on the lattice orientation standard and how to set it, see the Viewing or changing the lattice parameters topic.

Access methods

Menu	*Modules	CASTEP	Calculation	Setup	More...	Elastic Constants*
Toolbar	〰️▾ *	Calculation	Setup	More...	Elastic Constants*

Options tab

The *Options* tab allows you to specify the convergence level of the elastic constants calculation.

Quality: Sets the convergence thresholds for energy change, maximum force, and maximum displacement between cycles. This is used for the geometry optimization runs that are required for the elastic constants calculation. The calculation will stop when all of these criteria are satisfied.

Four sets of convergence thresholds are available; Coarse, Medium, Fine and Ultra-fine. The values of each convergence threshold in each set are given in the table below:

Quality	Energy (eV/atom)	Force (eV/Å)	Displacement (Å)
Coarse	1×10^{-5}	0.02	0.001
Medium	4×10^{-6}	0.01	4×10^{-4}
Fine	2×10^{-6}	0.006	2×10^{-4}
Ultra-fine	1×10^{-6}	0.002	1×10^{-4}
Customized	User defined	User defined	User defined

Alternatively, thresholds can be specified independently. If user defined values are used, the *Quality* displayed is Customized.

> **Note:** When the main quality is set to Express the elastic constants quality is also set to Express. In this case energy tolerance will be displayed in eV/cell rather than eV/atom, the default value is 0.001 eV/cell. All other tolerances are ignored and geometry optimization runs stop when the energy change is less than the tolerance regardless of the values of forces or displacements.

Energy: Specify the convergence threshold for the maximum energy change, in eV/atom. The units are eV/cell if the *Quality* is set to Express.

Max. force: Specify the convergence threshold for the maximum force, in eV/Å. If the *Quality* is set to Express, this tolerance by default will be set to a very high value and will effectively be ignored in the calculation.

Max. displacement: Specify the convergence threshold for the maximum displacement, in Å. If the *Quality* is set to Express, this tolerance by default will be set to a very high value and will effectively be ignored in the calculation.

Max. iterations: Specify the maximum number of elastic constants cycles. If this number of cycles is reached, then the calculation will stop even if the convergence criteria are not satisfied.

Access methods

Menu	*Modules	CASTEP	Calculation	Setup	More...	Options*
Toolbar	*≋▾	Calculation	Setup	More...	Options*

CASTEP Transition State Search dialog

The CASTEP Transition State Search dialog allows you to set up and display the parameters that control the TS Search task, including the protocol to be used and the quality of the search.

> **Note:** CASTEP transition-state searches require a trajectory document (for example, an `.arc` or `.xtd` file) as input. You will not be able to start a transition-state search run unless a suitable document is in scope.

> **Note:** When a transition state search is performed on a periodic system the unit cell is fixed.

Search protocol: Select the type of synchronous transit that will be performed from the dropdown list. Available options are:

- LST Maximum - performs a single linear synchronous transit (LST) maximization, bracketing the maximum between the reactants and product
- Halgren-Lipscomb - performs an LST maximization, followed by a single-line search minimization
- LST/Optimization - performs an LST maximization, followed by a full conjugate gradient minimization
- Complete LST/QST - performs an LST, followed by repeated conjugate gradient minimizations and quadratic synchronous transit (QST) maximizations until a transition state has been located
- QST/Optimization - starting from a QST, performs repeated maximizations and conjugate gradient minimizations until a transition state has been located

Quality: Set the TS search convergence thresholds for the root mean square (RMS) forces on the atoms. The search will stop when this criterion is satisfied.

Five quality settings are available:

- Express
- Coarse
- Medium
- Fine
- Ultra-fine

The value of the convergence threshold for each setting is given in the table below:

	Express	Coarse	Medium	Fine	Ultra-fine
RMS convergence (eV Å^{-1})	0.1	0.5	0.25	0.05	0.01

RMS convergence: Specify the value, in eV Å^{-1}, at which convergence is considered to take place in terms of the RMS of the gradients.

Max. number QST steps: Specify the maximum number of QST maximization cycles. If this number of cycles is reached, then the calculation will stop, even if the convergence criteria are not satisfied.

Optimize reactants and products: Specifies that the input structure for the reactant and product in a TS search calculation should be optimized to a local minimum. Selecting this allows the TS search to start from a "raw" trajectory, where the reactant and product structures have not already been optimized.

> **Note:** This choice may lead to reactant and product structures deviating substantially from the input structures, so it is recommended that you carefully check the final path.

Calculate partition functions: Specifies whether to calculate partition functions based on the Gamma-point dynamical matrix for the reactants, products, and the transition state. This data will be stored in the output 3D Atomistic Collection document.

> **Note:** This is not available unless *Optimize reactants and products* is checked.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modules | CASTEP | Calculation | Setup | More...*
Toolbar	≋▼ | *Calculation | Setup | More...*

CASTEP TS Confirmation dialog

The CASTEP TS Confirmation dialog allows you to set up and display the parameters that control the simulation in a CASTEP TS Confirmation task.

Quality: Set the geometry optimization convergence thresholds for energy change, maximum force, and maximum displacement between optimization cycles. The optimization will stop when the energy convergence is satisfied along with either the displacement or gradient criteria.

Four sets of convergence thresholds are available:

- Coarse
- Medium
- Fine
- Ultra-fine

The values of the convergence thresholds in each set are given in the table below:

Value	Coarse	Medium	Fine	Ultra-fine
Energy (eV/atom)	1×10^{-4}	2×10^{-5}	1×10^{-5}	5×10^{-6}
Max. force (eV/Å)	0.5	0.1	0.05	0.02
Max. displacement (Å)	0.05	0.005	0.004	0.003

Alternatively, thresholds can be specified independently for *Energy*, *Max. force*, and *Max. displacement*. If you enter your own values for any of these settings, the *Quality* is displayed as Customized on both the CASTEP TS Confirmation dialog and the Setup tab of the CASTEP Calculation dialog.

> **Note:** When the main quality is set to Express the transition state confirmation quality is also set to Express. In this case the energy tolerance will be displayed in eV/cell rather than eV/atom, the default value is 0.002 eV/cell.

Energy: Specify the convergence threshold for the maximum energy change, in eV/atom, during the geometry optimization. The units are eV/cell if the *Quality* is set to Express.

Max. force: Specify the convergence threshold for the maximum force, in eV/Å, during the geometry optimization.

Max. displacement: Specify the convergence threshold for the maximum displacement, in Å, during the geometry optimization.

Altering the value of any threshold is allowed and results in the *Quality* being set to Customized.

Max. images: The number of intermediate NEB images used during the transition state confirmation.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modules	CASTEP	Calculation	Setup	More...*
Toolbar	*	Calculation	Setup	More...*

Electronic tab

The *Electronic* tab allows you to specify the parameters associated with the electronic Hamiltonian. These include the basis set, pseudopotentials, SCF convergence criteria, and k-point set.

Energy cutoff: Select the precision used for the plane wave basis set.

- Coarse
- Medium
- Fine
- Ultra-fine

The actual value of the energy cutoff corresponding to the selected quality for the current structure also displays.

> **Note:** Calculation of the NMR parameters may require a higher *Energy cutoff* than for total energy or geometry optimization calculations. Study the convergence of the results as you increase the *Energy cutoff* value. Generally, a cutoff between 270 and 400 eV produces convergence of the shielding constant to about 1 ppm. In some cases, you might need to increase the cutoff up to 550 eV.

SCF tolerance: Select the threshold used to determine whether an SCF has converged. Available options and associated convergence thresholds are:

- Coarse - 10^{-5} eV/atom
- Medium - 2×10^{-6} eV/atom
- Fine - 10^{-6} eV/atom
- Ultra-fine - 5×10^{-7} eV/atom

> **Note:** When the main quality is Express, the SCF tolerance is automatically Express. This corresponds to 10^{-4} eV/cell.

Energy tolerances per: Specifies whether to calculate energy tolerances as the energy change per atom (Atom is the default) or per unit cell. The Cell value is enforced when the main quality, and hence the SCF tolerance quality, is Express.

k-point set: Define the number of integration points to use to integrate the wavefunction in reciprocal space. Available options are:

- Gamma - a single point at (0, 0, 0)
- Coarse
- Medium
- Fine

Pseudopotentials: Select the type of pseudopotential to use. Two different types of pseudopotentials are available, ultrasoft and norm-conserving; both of them are available as either generated on the fly (OTFG) potentials or as tabulated potentials. OTFG potentials are generally preferred for reasons of accuracy and consistency. NMR calculations required OTFG potentials.

- OTFG ultrasoft (default) - the preferred option, ultrasoft pseudopotentials allow calculations with lower energy cutoffs. On-the-fly generation produces potentials that are consistent between solid state and pseudo-atom calculations since they use the same exchange-correlation functional throughout. The OTFG ultrasoft pseudopotentials introduced in Materials Studio 8.0 provides results in close agreement with all electron calculations and is very accurate for describing ground state structures.

- OTFG norm conserving - typically harder and therefore more computationally expensive than ultrasoft pseudopotentials. Linear response-based calculations of phonon properties and of polarizabilities and calculations with nonlocal exchange-correlation functionals (for example, screened exchange) require norm-conserving potentials.

- Ultrasoft - tabulated ultrasoft pseudopotentials, provided for compatibility with earlier versions of Materials Studio.

- Norm conserving - tabulated norm-conserving pseudopotentials, provided for compatibility with earlier versions of Materials Studio.

> **Notes:**
> - Do not use the PW91 exchange-correlation functional when requesting on the fly generation of pseudopotentials. When you require a GGA functional, use PBE, RPBE, WC, BLYP, or PBESOL.
> - When you specify the type of pseudopotential to use in this way, the calculation uses the default pseudopotential of that type for each element.

> **Tip:** Use the Electronic Options dialog to exercise more control over which pseudopotentials to use for each element.

Relativistic treatment: The way OTFG pseudopotentials incorporate relativistic effects. Options are:

- Schroedinger
- Koelling-Harmon (default)
- ZORA
- Dirac

> **Note:** Use the Dirac solver when requesting spin-orbit coupling and on the fly generated pseudopotentials.

Use core hole: Specify whether to include core holes in the calculation. You can use core holes in core level spectroscopy calculations. Define core holes using the Core Hole tab of the Electronic Configuration dialog.

> **Note:** For calculations exploiting core holes, you must use on-the-fly pseudopotentials.
> If you do not select the *Use core hole* checkbox, the calculation does not preserve any core holes in the input system.

> **Note:** CASTEP calculations with core holes assume by default that an electron is removed from the system, so it is treated as having a charge of 1 (or one more than specified in the *Charge* field on the Setup tab of the CASTEP Calculation dialog). In some circumstances, for example when studying impurities, it might be more appropriate to consider the system as charge neutral. In order to achieve this you should specify the *Charge* of -1 on the Setup tab, in this way the CASTEP input file will have a zero charge. It is also possible to edit the `seedname.param` file to specify a fractional charge. The strength of the core hole can be adjusted by editing the `seedname.cell` file and modifying the pseudopotential definition string (for example, change `{1s1}` to `{1s0.5}` to use a core hole with the charge of 0.5).

Use solvation model: When selected, uses the implicit solvation model. The Solvent tab of the CASTEP Electronic Options dialog allows you to define the solvent characteristics.

> **Note:** The implicit solvation model allows you to simulate a solvent environment only for "molecule in a box" calculations. Materials Studio automatically positions isolated molecule structures roughly in the center of a cell. Ensure that the cell is large enough to contain a significant amount of vacuum surrounding the molecule.

> **Note:** Use at least a Fine FFT grid *Density* for solvation calculations; the Precise density is even better. You can specify the FFT grid *Density* on the Basis tab of the CASTEP Electronic Options dialog. Also use an increased value of *Augmentation density scaling factor*, for example 1.5-2.0 instead of the default value of 1.0.
>
> An increased FFT density and energy cutoff can help to eliminate convergence errors for the multigrid solver for electrostatics in a solvent.

More...: Provides access to the CASTEP Electronic Options dialog, where you can configure further details of the electronic Hamiltonian.

Access methods

Menu	*Modules	CASTEP	Calculation	Electronic*
Toolbar	*	Calculation	Electronic*

CASTEP Electronic Options dialog

The CASTEP Electronic Options dialog allows you to configure and display the details of the electronic Hamiltonian used in CASTEP calculations. These parameters are relevant for the Energy, Geometry Optimization, Dynamics, Elastic Constants, and TS Search tasks.

It contains the following tabs:

- **Basis** : Provides access to the plane-wave energy cutoff, FFT grid specification, and finite basis set correction.
- **SCF**: Provides access to the parameters that control the electronic minimization algorithm.
- **k-points**: Provides more detailed access to the k-point set.
- **Potentials**: Provides control over which pseudopotentials to use for each element in the structure.
- **DFT-D**: Provides access to the parameters for van der Waals dispersion correction calculations.
- **Solvent**: Provides access to the parameters for solvation calculations.

Help: Displays the Help topic for the current tab.

Access methods

Menu	*Modules	CASTEP	Calculation	Electronic	More...*
Toolbar	⚉▾ *	Calculation	Electronic	More...*

Basis tab

The *Basis* tab provides access to basis set information, including the plane-wave energy cutoff, FFT grid specification, and finite basis set correction.

Use custom energy cutoff: When selected, you can specify a custom value for the energy cutoff in the adjacent text box. Otherwise the text box displays the energy cutoff appropriate for the *Energy cutoff* quality parameter on selected on the Electronic tab.

Density: Specify the quality of the FFT grid. Three options are available:

- Standard
- Fine
- Precise

The FFT grid parameters are chosen such that they provide a good representation of the electron density. The Precise level provides an exact representation of the density for the given energy-cutoff. The Standard and Fine levels use a reduced FFT grid to speed up the calculation. Some aliasing occurs as a result, but the effect on the SCF solution is usually small. The FFT grid parameters used in the CASTEP calculation display as derived, using the current energy-cutoff and unit cell parameters.

Augmentation density scaling factor: Specify a finer grid for representation of the augmentation charge density in the atomic core region. By default, CASTEP uses the same grid as for the standard electron density. It is reasonable in some cases to increase the augmentation grid by a factor of up to 4, to improve the accuracy of calculations. You can control this with the *Quality* option on the Setup tab of the CASTEP Calculation dialog.

Apply finite basis set correction: Specify when to use a finite basis set correction in the evaluation of energy and stress. You can control this with the *Quality* option on the Setup tab of the CASTEP Calculation dialog.

This correction gives a volume dependent addition to the energy that may result in a significant correction to any calculated stress. It is particularly important where you require an accurate stress or cell geometry optimization. Three options are available:

- **Smart** - apply the correction only when stress is required. This includes any cell geometry optimization.
- **Always** - apply the correction to all calculations.
- **Never** - do not apply a correction, even when calculating stress. Any result for stress or cell geometry may be unreliable.

Correction mode: Specify how to calculate the finite basis set correction. The evaluation of the correction requires an estimate for the derivative of the total energy with respect to the logarithm of the plane-wave energy cutoff. The options are:

- **Automatic** - automatically calculates the energy derivative using numerical differentiation.
- **Manual** - allows you to manually specify the energy derivative.

Numerical differentiation using: Specify the number of energy points to use in evaluating the energy derivative required for the finite basis set correction. This evaluates a converged SCF energy at each point.

> **Note:** Available only if you select the Automatic *Correction mode*.

Energy derivative w.r.t. cutoff: Specify the value of the energy derivative required for the finite basis set correction.

> **Note:** Available only if you select the Manual *Correction mode*.

Access methods

Menu	*Modules	CASTEP	Calculation	Electronic	More...	Basis*
Toolbar	≋▼ | *Calculation	Electronic	More...	Basis*

SCF tab

The *SCF* tab on the CASTEP Electronic Options dialog provides access to parameters that control the electronic minimization algorithm.

SCF tolerance: Specify the SCF convergence threshold. This overrides the *SCF tolerance* option specified on the Electronic tab.

> **Note:** When calculating linear response properties (for example phonons, polarizabilities, NMR properties), it is important that the SCF convergence threshold is sufficiently strict from the computational point of view to accurately calculate these properties. When you request the calculation of linear response properties, CASTEP uses a convergence threshold of 10^{-8} eV atom^{-1}, unless the specified threshold is lower. To force CASTEP to use a less stringent threshold, manually add the ELEC_ENERGY_TOL parameter to the input parameters (`.param`) file for the property calculation.

Max. SCF cycles: Set the maximum number of SCF iterations allowed for an energy calculation. The energy calculation ends after the specified number of iterations, even if the SCF has not converged.

Convergence window: The convergence tolerance window for SCF. This is the number of SCF iterations in a row for which convergence criteria are fulfilled. This parameter prevents occasional oscillations.

Electronic minimizer: Specify the electronic minimization method to use for the SCF calculation. Two options are available, Density Mixing and All Bands/EDFT.

> **Tip:** The Density Mixing option is recommended, particularly for variable occupancy calculations. The All Bands/EDFT method is usually slower and requires more memory. However, use the EDFT scheme for metallic systems where converging electronic structure using the Density Mixing option proves problematic.

Charge: Specify the amplitude for charge density mixing (that is, the amplitude of the output charge density to mix with the input charge density to obtain input for the next iteration).

> **Note:** Available only when you select the Density Mixing minimization method.

Spin: Specify the amplitude for spin density mixing, that is, the amplitude of the output spin density to mix with the input spin density to obtain input for the next iteration.

> **Note:** Available only for spin-polarized calculations using the Density Mixing minimization method.

More...: Provides access to the CASTEP Density Mixing Options dialog, where more detailed control over the Density Mixing electronic minimization method is available.

> **Note:** Available only when you select the Density Mixing minimization method.

Fix occupancy: When selected, this fixes thee electronic occupation numbers during electronic minimization. CASTEP includes only the lowest occupied states in the calculation. Default = checked.

More...: Provides access to the CASTEP Occupancy Options dialog, where more detailed control over the occupancies is available.

Apply dipole corrections: Select the type of dipole corrections to apply from the list. Available options are:

- None (default)
- Non self-consistent
- Self-consistent

Self-consistent is the most accurate option, as this affects the electrostatic potential as well as the total energy and its gradients. This is the only option that is suitable to investigate the effect of dipole corrections, for example on surface workfunctions.

> **Tip:** It is recommended to use the All Bands/EDFT electronic minimization scheme when applying a self-consistent dipole correction to an elongated cell of a slab representing a metal surface; the Density mixing minimization scheme may fail to converge for such systems.

Use Non self-consistent for cases where it is hard to converge the SCF with *Apply dipole corrections*. You can only use this option for *Energy* calculations, it is not compatible with phonon calculations.

> **Note:** CASTEP applies dipole corrections only if the system is either molecule in the box or a periodic slab with the vacuum layer of at least 8 Å.

> **Note:** To apply dipole corrections, CASTEP converts the symmetry of the system to P1 to bring the molecule (or slab) into the center of the unit cell.

Access methods

Menu	*Modules	CASTEP	Calculation	Electronic	More...	SCF*

Toolbar	≋▾	*Calculation	Electronic |* *More...	SCF*

CASTEP Density Mixing Options dialog

The CASTEP Density Mixing Options dialog allows you to specify the parameters that control the Density Mixing method of electronic minimization.

Mixing scheme: Specify the method used for mixing the input densities and output densities from the current iteration to obtain the input density for the next iteration in the iterative solution for the SCF. The supported methods are:

- Linear - the input density and the output density are mixed in a simple linear combination.
- Kerker - the input density and output density are mixed using a reduced mixing factor for the long length scale Fourier coefficients of the density.
- Pulay (default) - the output density is mixed with densities from a number of previous iterations, using the RMM-DIIS method, leading to more rapid convergence.
- Broyden - the output density is mixed with densities from a number of previous iterations, using the quasi-Newton relaxation method. The overall convergence is similar to that of Pulay mixing.

The Pulay or Broyden method is recommended. The Linear method is not usually suitable for large systems.

Charge mixing amplitude: Specify the amplitude of the output charge density to mix with the input charge density to obtain input for the next iteration.

Charge mixing cutoff: Specify the length scale used. Charge mixing is reduced for Fourier coefficients at reciprocal lattice vectors less than about this value.

> **Note:** This option is enabled only if the Kerker, Broyden, or Pulay density mixing method is selected.

DIIS history list: Specify the number of previous iterations to be considered in the DIIS for the Pulay or Broyden density mixing method.

> **Note:** This option is enabled only if the Pulay or Broyden density mixing method is selected.

Spin mixing amplitude: Specify the amplitude of the output spin density to mix with the input spin density to obtain input for the next iteration.

> **Note:** This option is enabled only for spin-polarized calculations.

Spin mixing cutoff: Specify the length scale used. Spin mixing is reduced for Fourier coefficients at reciprocal lattice vectors less than about this value.

> **Note:** This option is enabled only for spin-polarized calculations using the Kerker, Broyden, or Pulay density mixing methods.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modules	CASTEP	Calculation	Electronic	More...	SCF	More...*
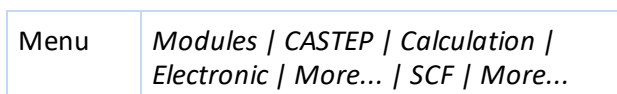
| Toolbar | ≋▾ | *Calculation* | *Electronic* |
More... | SCF | More... |

CASTEP Occupancy Options dialog

The CASTEP Occupancy Options dialog provides access to parameters that control occupancies in CASTEP calculations.

By default, CASTEP calculations are performed with variable occupancy. The fixed occupancy option is only suitable for structures that are known to be insulators or closed shell systems at the level of theory used in the CASTEP calculation.

Empty bands: Specify the number of additional bands to be included in an electronic minimization as a percentage of the number of occupied bands.

> **Note:** This option is enabled only for variable occupancy calculations.

Smearing: Specify the broadening to be applied to the electronic occupation.

> **Note:** This option is enabled only for variable occupancy calculations.

Optimize total spin after: Specify the number of SCF iterations for which the total electronic spin will remain fixed before being allowed to vary.

> **Note:** This option is enabled only for spin-polarized variable occupancy calculations.

> **Note:** The spin will be fixed throughout the calculation (including possible steps of geometry optimization) if the checkbox is unchecked.

> **Tip:** In spin-polarized systems there may be more than one stable SCF solution with different total spin values. By setting the initial spin on the Setup tab and by fixing the total spin value for a number of SCF iterations, it is possible to exert some control over which solution is found.

Help: Displays the Help topic in a browser.

Access methods

| Menu | *Modules | CASTEP | Calculation |*
Electronic | More... | SCF | More... |
| Toolbar | ≋▾ | *Calculation* | *Electronic* |
More... | SCF | More... |

k-points tab

The *k-points* tab provides access to more detailed options for controlling the k-point set used in CASTEP calculations.

You can specify the Monkhorst-Pack k-point grid to use in several ways. For cubic cells and for the C direction of hexagonal cells, the even and odd grids for the Monkhorst-Pack scheme give the same number of k-points. However, the even grid provides better sampling and CASTEP always uses this automatically under these conditions. This achieves a good grid with k-point separation at (or less than) the specified target more economically. As a consequence, such lattices may have much finer

separations than requested as CASTEP excludes odd grids - even if they would have been closer to the specified separation - and takes the better even grids in preference.

Gamma point only: When selected, indicates that the density of states calculation uses a single k-point at (0,0,0).

Quality: When selected, generates the k-point grid using a k-point separation appropriate to the specified quality level. Select the desired quality level from the list. Available options are:

- Coarse
- Medium
- Fine

The k-point separations associated with the three *Quality* settings depend on whether you select the *Metal* checkbox on the Setup tab:

Quality	k-point separation ($Å^{-1}$)	
	Metal selected	**Metal not selected**
Coarse	0.07	0.1
Medium	0.05	0.08
Fine	0.04	0.07

Separation: When selected, generates the k-point grid according to the specified k-point separation. Specify the k-point separation, in $Å^{-1}$, in the associated text box.

> **Note:** When you select the *Separation*, the Monkhorst-Pack parameters are derived to give the specified separation between neighboring grid points.

Custom grid parameters: When selected, generates the k-point grid using the Monkhorst-Pack grid parameters and the origin shift in fractional reciprocal space coordinates specified in the *Grid parameters* and *Origin shift* text boxes, respectively.

Grid parameters: Specify the Monkhorst-Pack grid parameters in each of the lattice directions.

Actual spacing: Displays the k-point separation, in $Å^{-1}$, resulting from the currently specified Monkhorst-Pack grid parameters in each of the lattice directions.

Origin shift: Specify the offset of the Monkhorst-Pack grid in fractional reciprocal space coordinates.

> **Note:** The *Grid parameters* and *Origin shift* controls are enabled only if you select the *Custom grid parameters* option.

Display points...: Displays the number and fractional coordinates of the reciprocal space mesh points generated using the specified parameters.

> **Note:** The actual set of k-points used in the calculations may change if the symmetry of the system changes or if you request a DFT+U calculation.

Access methods

Menu	*Modules	CASTEP	Calculation	Electronic	More...	k-points*

Toolbar	![icon]	*Calculation | Electronic |*
		More... | k-points
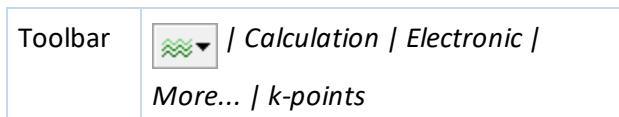
Potentials tab

The *Potentials* tab allows you to control which pseudopotentials to use for each element in the structure.

Scheme: Select the type of pseudopotential to use. Two different types of pseudopotentials are available, ultrasoft and norm-conserving. Both of these are available as either generated on the fly (OTFG) potentials or as tabulated potentials. OTFG potentials generally provide better accuracy and consistency. You can only perform NMR calculations with OTFG potentials.

- OTFG ultrasoft (default) - the preferred option, ultrasoft pseudopotentials allow you to perform calculations with lower energy cutoffs. On-the-fly generation produces potentials that are consistent between solid state and pseudo-atom calculations since they use the same exchange-correlation functional throughout. The set of OTFG ultrasoft pseudopotentials introduced in Materials Studio 8.0 provides results in close agreement with all electron calculations and is very accurate for describing ground state structures.

- OTFG norm conserving - typically harder and therefore more computationally expensive than ultrasoft pseudopotentials. Norm-conserving potentials are required for linear response-based calculations of phonon properties and of polarizabilities and for calculations with nonlocal exchange-correlation functionals (for example, screened exchange).

- Ultrasoft - tabulated ultrasoft pseudopotentials, provided for compatibility with earlier versions of Materials Studio.

- Norm conserving - tabulated norm-conserving pseudopotentials, provided for compatibility with earlier versions of Materials Studio.

Note: The latest set of OTFG settings for ultrasoft pseudopotentials was developed to minimize the error with respect to fully converged all-electron DFT calculations. The error achieved by this set is 0.4 meV/atom, which puts CASTEP among the most accurate pseudopotential codes available. A full definition of the test framework and the meaning of the error is given by Lejaeghere et al. (2014), and on the website of the Delta project: http://molmod.ugent.be/deltacodesdft. The files that correspond to this set have the _2017R2 suffix. This is the recommended set of OTFG ultrasoft potentials. Use files with the _2017R2ncp suffix when you require norm-conserving potentials. This set has a 1.1 meV/atom error in the Delta project tests. In addition, provides a set of "high throughput" ultrasoft OTFG settings for scripting. This QC5 set generally requires lower cutoff energy and offers faster but less accurate calculations (1.9 meV/atom error in the Delta project tests).

Note: Do not use the PW91 exchange-correlation functional when requesting on the fly generation of pseudopotentials. PBE, RPBE, WC, BLYP, or PBESOL are better options when you require a GGA functional.

Note: When you specify the type of pseudopotential to use in this way, the default pseudopotential of that type for each element will be used in the calculation.

Representation: Choose between Reciprocal space and Real space representations of the pseudopotentials.

Tip: The real space representation may give a performance advantage for large systems.

More...: Provides access to the CASTEP Real Space Potentials dialog, which allows you to specify details of the transformation of pseudopotentials to a real space representation.

> **Note:** This is enabled only if you select Real space from the *Representation* list.

Selected potentials: Displays information about the selected pseudopotentials for each element in a grid.

There is a row in the grid for each element displaying the element type, current pseudopotential, energy, and valence (Z). To select a different pseudopotential for a particular element, click in the appropriate pseudopotential grid cell and choose a new pseudopotential from the list.

If you change the default pseudopotentials, the *Scheme* displays as Custom.

Show potentials for all elements: When selected, the *Selected potentials* list displays information about all elements in the periodic table for which pseudopotentials are available. Otherwise, only elements present in the current structure are displayed in the list. Default = unchecked.

View: Displays a modal view on the selected pseudopotential file.

External Potential

Electric field: Specify the external electric field strength, in eV/Å/e.

Field direction (X Y Z): Vector specifying the direction of the electric field.

> **Note:** Only systems that contain molecules or slabs are appropriate for electric field calculations. For slabs, the field must be along the surface normal. In both cases, you must position atoms in the middle of the cell and the symmetry must be P1.

> **Note:** The field direction is specified in Cartesian coordinates. The values of the X, Y, and Z direction components of the electric field are interrelated. The three field components define a unit vector. When you start a job, the direction components are normalized to give a unit vector, which is then multiplied by the field magnitude to give the actual field components. Entering a vector with all zero components has the same effect as entering a (111) vector.

Access methods

Menu	*Modules	CASTEP	Calculation	Electronic	More...	Potentials*
Toolbar	*	Calculation	Electronic	More...	Potentials*

CASTEP Real Space Potentials dialog

The CASTEP Real Space Potentials dialog allows you to specify the parameters describing the transformation of pseudopotentials to a real space representation.

Core radius: Specify the real space core radius of the element displayed. Change the element type using the dropdown list.

> **Tip:** Enter zero to reset the core radius for the displayed element to the default value.

Note: The real space core radius determines the radius of real space integration to be used in the calculation. It should be larger than the core radius used in pseudopotential generation, normally by a factor of 1.5 to 2.0, so as to overcome the aliasing problems inherent in the real space integration method.

Reset all core radii to defaults: Sets all core radii to the default values.

Use custom energy cutoff for transformation: When checked, a value may be specified for the energy cutoff used in the transformation to the real space form of pseudopotentials. Otherwise a value will be calculated automatically based on the plane-wave energy cutoff to be used in the calculation. Default = unchecked.

Impose tolerance: When checked, the real space pseudopotential transformation will be tested to ensure it is of the quality specified in the dropdown list. Default = checked.

If the transformation is not of the requested quality, then the CASTEP calculation will not proceed. This should ensure that the results obtained from a real space pseudopotential calculation accurately reproduce those of a similar calculation using reciprocal space pseudopotentials.

Note: If this option in unchecked, the CASTEP calculation will be performed regardless of the quality of the real space pseudopotential transformation.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modules | CASTEP | Calculation | Electronic | More... | Potentials | More...*
Toolbar	≋▾ | *Calculation | Electronic | More... | Potentials | More...*

DFT-D tab

The *DFT-D* tab allows you to prepare customized parameters for van der Waals dispersion corrections. This can involve the definition of DFT-D corrections for exchange functionals that Materials Studio does not usually support, the definition of support for additional elements, or changing existing parameters.

Use custom DFT-D parameters: Specify whether to use custom DFT-D parameters. When selected, you can choose the van der Waals scheme to use from the list, options are:

- TS (default)
- Grimme
- OBS
- MBD*

Note: You cannot customize the parameters of the D4 method.

Note: The option selected automatically updates the *Use method for DFT-D correction* option on the Setup tab of the CASTEP Calculation dialog.

> **Note:** The schemes that rely on calculated electron densities, namely TS and MBD*, may not work well in calculations with small unit cells, where the diameter of van der Waals spheres is comparable to the lattice parameters. The MBD* scheme is particularly sensitive to such situations. In such cases, the CASTEP output file contains a warning explaining the problem. The MBD* scheme can also fail if the geometry is far from equilibrium, in which case it is useful to perform a preliminary geometry optimization with the TS scheme. The main area of application of the MBD* scheme is molecular crystals, so it may experience problems with highly ionic systems.

Atomic parameters

This table allows you to edit the dispersion correction parameters for each of the atomic species. The type and number of parameters depend on the DFT-D scheme selected. Refer to the original literature for the meaning and usage of each parameter.

The units for all parameters are in eV for energies and in Å for lengths. The available columns are:

Atom: Denotes the element to edit.

C6 (eV Å^6): Available for TS, MBD*, and Grimme schemes.

R0 (Å): Available for TS, MBD*, and Grimme schemes.

alpha (Å^3): Available for TS, MBD*, and OBS schemes.

I (eV): Available for the OBS scheme.

Rvdw (Å): Available for the OBS scheme.

> **Note:** The *Atomic parameters* table only lists the elements in the active document.

> **Note:** Each scheme includes a radius (**R0** for TS and Grimme, **Rvdw** for OBS) that must be non-zero for each of the active elements.

Scheme parameters

Scheme parameters are dimensionless numbers that define the functional form of each scheme.

Refer to the original literature for the meaning and usage of each parameter.

Depending on the van der Waals scheme selected for the *custom DFT-D parameters* setting, the *Scheme parameters* that you can specify are:

- TS: **sR, d**
- Grimme: **s6, d**
- OBS: **lambda, n**
- MBD*: **sR**

> **Note:** The default values for these parameters depend on the exchange correlation functional selected on the Setup tab of the CASTEP Calculation dialog.

> **Note:** Both scheme parameters must be non-zero for the calculations to start and for Materials Studio to write to the input files.

Reset All: Restores the default settings for each element in the grid.

Access methods

Menu	*Modules | CASTEP | Calculation | Electronic | More... | DFT-D*
Toolbar	⧀⧀▾ | *Calculation | Electronic | More... | DFT-D*

Solvent tab

The *Solvent* tab allows you to configure a simulated solvent environment for the calculation.

Solvent: Select a solvent to use as the solvent environment for the calculation. Available options are:

- Acetone
- Acetonitrile
- Benzene
- Carbon tetrachloride
- Chlorobenzene
- Chloroform
- Cyclohexane
- Diethyl ether
- Dimethyl sulfoxide
- Ethanol
- Methanol
- Methylene chloride
- n-hexane
- n-hexadecane
- Nitrobenzene
- Pyridine
- Water

When you select a solvent, the *Dielectric constant* field automatically updates with the appropriate value.

> **Note:** If you specify the *Dielectric constant* parameter to a value different from that dictated by the selected solvent, the *Solvent* displays as Customized.

Dielectric constant: Specify a value for the solvent dielectric constant. This parameter automatically updates to the appropriate value when you select a solvent from the *Solvent* dropdown list. However, you can enter your own custom value if you want.

Include apolar term: Request calculation of apolar (non-electrostatic) contributions to the solvation energy. These contributions arise from cavitation and solute-solvent dispersion-repulsion. Calculations without the apolar term cannot reliably estimate solvation energies, especially for neutral molecules, and particularly so if these molecules are large.

> **Note:** The *Solvent surface tension* and *Account for solute-solvent dispersion repulsion* controls are enabled only when you select the *Include apolar term* checkbox.

Solvent surface tension: The surface tension of the solvent (in N/m) for evaluation of the apolar term.

Account for solute-solvent dispersion repulsion: The CASTEP solvation model suggests scaling of the surface tension that enters the expression for the apolar term, to account for the solute-solvent dispersion-repulsion. The default dimensionless scaling factor is 0.281075 (see Dziedzic, 2011).

> **Note:** Use at least a Fine FFT grid *Density* for solvation calculations; the Precise density is even better. You can specify the FFT grid *Density* on the Basis tab of the CASTEP Electronic Options dialog. Also use an increased value of *Augmentation density scaling factor*, for example 1.5-2.0 instead of the default value of 1.0.
>
> An increased FFT density and energy cutoff can help to eliminate convergence errors for the multigrid solver for electrostatics in a solvent.

Access methods

Menu	*Modules	CASTEP	Calculation	Electronic	More...	Solvent*
Toolbar	≋▼	*Calculation	Electronic	More...	Solvent*

Properties tab

The *Properties* tab allows you to select the properties that will be computed as part of a CASTEP calculation.

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	*Modules	CASTEP	Calculation	Properties*
Toolbar	≋▼	*Calculation	Properties*

Band structure selection

Checking the *Band structure* checkbox on the Properties tab displays options for calculating electronic energies along high symmetry directions in the Brillouin zone.

Energy range: Specify the maximum energy above the Fermi level for which band structure will be calculated. Default = 10 eV.

k-point set: Specify the quality of the k-point set for the band structure calculation. Each setting corresponds to a particular approximate separation between consecutive k-points on the reciprocal space path. Default = Medium.

Quality	k-point separation (Å^{-1})
Coarse	0.04
Medium	0.025
Fine	0.015

Separation: Specify the approximate separation between k-points in Å^{-1}. The default depends on the selected *k-point set*.

More...: Provides access to the CASTEP Band Structure Options dialog, which allows you to set additional parameters, including the reciprocal space path.

Access methods

Menu	*Modules	CASTEP	Calculation	Properties	Band structure*
Toolbar	≋▾ *	Calculation	Properties	Band structure*

CASTEP Band Structure Options dialog

The Band Structure Options dialog allows you to specify a custom reciprocal space path and the eigenvalue convergence criterion used for band structure calculations.

Use separate XC functional for band structure calculation: When checked, allows you to select a different exchange-correlation functional for the band structure calculation from the one used in the self-consistent calculation.

> **Tip:** This feature is particularly useful for carrying out expensive, screened exchange calculations. Perform the main run with the LDA or GGA functional, then invoke screened or exact exchange in non self-consistent mode during the band structure calculation.

> **Note:** There is an important difference between standard DFT calculations with local exchange-correlation potentials and the nonlocal exchange case. The potential used in the latter scenario depends on the SCF k-points, while in the former case, the potential depends only on electron density. This difference can make all properties calculations a lot more expensive in terms of memory usage and CPU time, so it is advisable to limit the number of SCF k-points that you use in such situations. This is particularly relevant for small unit cells, where the default settings may generate a very large k-point set.

Functional: Select the type of exchange-correlation potential to be used in the band structure calculation.

Choose the type of functional from the first dropdown list. Available options are:

- LDA
- GGA
- HF
- HF-LDA
- sX
- sX-LDA
- PBE0
- B3LYP
- HSE03
- HSE06

Then, if appropriate, select the specific functional from the second dropdown list. Depending on the functional type selected from the first dropdown list, some of the following options may be available:

- CA-PZ
- PBE
- RPBE
- PW91
- WC
- PBESOL
- BLYP

> **Note:** This option is enabled only when *Use separate XC functional for band structure calculation* is checked.

Band energy tolerance: Specify the convergence criterion for electronic eigenvalues during the band structure calculation. The calculation will stop when all electronic eigenvalues change by less than this value over a single iteration of the electronic structure.

> **Note:** More information about the symmetry labels used in the Band Structure Options dialog can be found in Bradley and Cracknell (1972).

Path...: Provides access to the Brillouin Zone Path dialog, which allows you to specify a custom reciprocal space path.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modules	CASTEP	Calculation	Properties	More...*
Toolbar	≋▾ | *Calculation | Properties | More...*

Core level spectroscopy selection

Checking the *Core level spectroscopy* checkbox on the Properties tab displays options for calculating core level spectra.

Energy range: Specify the energy limit above the Fermi level for which core level spectra will be calculated. Default = 25 eV.

k-point set: Specify the quality of the k-point set for the core level spectroscopy calculation. Each setting corresponds to a particular separation between consecutive k-points on the reciprocal space path. Default = Medium.

Quality	k-point separation ($Å^{-1}$)
Coarse	0.04
Medium	0.025
Fine	0.015

More...: Provides access to the CASTEP Core Level Spectroscopy Options dialog, which allows you to set additional parameters, including the k-point set specification.

Access methods

Menu	*Modules	CASTEP	Calculation	Properties	Core level spectroscopy*
Toolbar	![icon]	*Calculation	Properties	Core level spectroscopy*

CASTEP Core Level Spectroscopy Options dialog

The CASTEP Core Level Spectroscopy Options dialog allows you to specify the density of the k-point set and the eigenvalue convergence criterion used for core level spectra calculations.

The Monkhorst-Pack k-point grid to be used in the calculation can be specified in one of four ways:

Gamma point only: When selected, indicates that the density of states calculation uses a single k-point at (0,0,0).

Quality: When selected, generates the k-point grid using a k-point separation appropriate to the specified quality level. Select the desired quality level from the list. Available options are:

- Coarse
- Medium
- Fine

The k-point separations associated with the three *Quality* settings are as follows:

Quality	k-point separation (Å⁻¹)
Coarse	0.07
Medium	0.05
Fine	0.04

Separation: When selected, generates the k-point grid according to the specified k-point separation. Specify the k-point separation, in $Å^{-1}$, in the associated text box.

> **Note:** When you select the *Separation*, the Monkhorst-Pack parameters are derived to give the specified separation between neighboring grid points.

Custom grid parameters: When selected, generates the k-point grid using the Monkhorst-Pack grid parameters and the origin shift in fractional reciprocal space coordinates specified in the *Grid parameters* and *Origin shift* text boxes, respectively.

Grid parameters: Specify the Monkhorst-Pack grid parameters in each of the lattice directions.

Actual spacing: Displays the k-point separation, in $Å^{-1}$, resulting from the currently specified Monkhorst-Pack grid parameters in each of the lattice directions.

Origin shift: Specify the offset of the Monkhorst-Pack grid in fractional reciprocal space coordinates.

> **Note:** The *Grid parameters* and *Origin shift* controls are enabled only if you select the *Custom grid parameters* option.

Display points...: Displays the number and fractional coordinates of the reciprocal space mesh points that would be generated using the currently specified parameters.

> **Note:** The actual set of k-points that will be used in the calculations may be altered if the symmetry of the system changes.

Band energy tolerance: Specify the convergence criterion in eV for electronic eigenvalues during the core level spectroscopy calculation. The calculation will stop when all electronic eigenvalues change by less than this value over a single iteration of the electronic structure.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modules	CASTEP	Calculation	Properties	Core level spectroscopy	More...*
Toolbar	≋▾ | *Calculation	Properties	Core level spectroscopy	More...*

Density of states selection

Checking the *Density of states* checkbox on the Properties tab displays options for calculating electronic energies on the Monkhorst-Pack mesh of k-points.

Energy range: Specify the maximum energy above the Fermi level for which density of states will be calculated. Default = 10 eV.

k-point set: Specify the quality of the k-point set for the density of states calculation. Each setting corresponds to a particular separation between neighboring k-points in the Monkhorst-Pack grid. Default = Medium.

Calculate PDOS: When checked, indicates that the information required to generate partial and local densities of states will also be calculated.

More...: Provides access to the CASTEP Density of States Options dialog, which allows you to set additional parameters, including the k-point set specification.

Access methods

Menu	*Modules	CASTEP	Calculation	Properties	Density of states*
Toolbar	≋▾ | *Calculation	Properties	Density of states*

CASTEP Density of States Options dialog

The CASTEP Density of States Options dialog allows you to specify the k-point set and the eigenvalue convergence criterion used for density of states calculations.

The Monkhorst-Pack k-point grid to be used in the calculation can be specified in one of four ways:

Gamma point only: When selected, indicates that the density of states calculation uses a single k-point at (0,0,0).

Quality: When selected, generates the k-point grid using a k-point separation appropriate to the specified quality level. Select the desired quality level from the list. Available options are:

- Coarse
- Medium
- Fine

The k-point separations associated with the three *Quality* settings are as follows:

Quality	k-point separation ($Å^{-1}$)
Coarse	0.07
Medium	0.05
Fine	0.04

Separation: When selected, generates the k-point grid according to the specified k-point separation. Specify the k-point separation, in $Å^{-1}$, in the associated text box.

> **Note:** When you select the *Separation*, the Monkhorst-Pack parameters are derived to give the specified separation between neighboring grid points.

Custom grid parameters: When selected, generates the k-point grid using the Monkhorst-Pack grid parameters and the origin shift in fractional reciprocal space coordinates specified in the *Grid parameters* and *Origin shift* text boxes, respectively.

Grid parameters: Specify the Monkhorst-Pack grid parameters in each of the lattice directions.

Actual spacing: Displays the k-point separation, in $Å^{-1}$, resulting from the currently specified Monkhorst-Pack grid parameters in each of the lattice directions.

Origin shift: Specify the offset of the Monkhorst-Pack grid in fractional reciprocal space coordinates.

> **Note:** The *Grid parameters* and *Origin shift* controls are enabled only if you select the *Custom grid parameters* option.

Display points...: Displays the number and fractional coordinates of the reciprocal space mesh points that would be generated using the currently specified parameters.

> **Note:** The actual set of k-points that will be used in the calculations may be altered if the symmetry of the system changes.

Use separate XC functional for DOS calculation: When checked, indicates that a different exchange-correlation functional will be used for the density of states calculation from the one used in the self-consistent calculation.

> **Tip:** This feature is particularly useful for carrying out expensive screened exchange calculations: perform the main run with the LDA or GGA functional, then invoke screened or exact exchange in non-self-consistent mode during the density of states calculation.

> **Note:** There is an important difference between standard DFT calculations with local exchange-correlation potentials and the non-local exchange case. The potential used in the latter scenario depends on the SCF k-points, while in the former case, the potential depends only on electron density. This difference can make all properties calculations a lot more expensive in terms of memory usage and CPU time, so it is advisable to limit the number of SCF k-points that you use in such situations. This is particularly relevant for small unit cells, where the default settings may generate a very large k-point set.

Functional: Select the type of DFT exchange-correlation potential to be used in the density of states calculation.

Choose the type of functional from the first dropdown list. Available options are:

- LDA
- GGA
- HF
- HF-LDA
- sX
- sX-LDA
- PBE0
- B3LYP
- HSE03
- HSE06

Then, if appropriate, select the specific functional from the second dropdown list. Depending on the functional type selected from the first dropdown list, some of the following options may be available:

- CA-PZ
- PBE
- RPBE
- PW91
- WC
- PBESOL
- BLYP

> **Note:** The *Functional* control is enabled only if the *Use separate XC functional for DOS calculation* checkbox is checked.

Band energy tolerance: Specify the convergence criterion, in eV, for electronic eigenvalues during the density of states calculation. The calculation will stop when all electronic eigenvalues change by less than this value over a single iteration of the electronic structure.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modules	CASTEP	Calculation	Properties	Density of states	More...*

Toolbar	≋▼	*Calculation	Properties |* *Density of states	More...*

Electron density difference selection

Checking the *Electron density difference* checkbox on the Properties tab displays options for calculating an electron density difference field.

Calculation of atomic difference with respect to the sum of the densities of a subsystem requires that sets of atoms have been created in the input structure. Only sets with DensityDifference as part of the set name will be taken into account, and only if they contain atoms (it is possible for such sets to contain other objects like bonds or monitors; only atoms will be considered in electron density difference calculations). Use the Edit Sets dialog, accessed by selecting *Edit | Edit Sets* from the menu bar, to create the required sets in the 3D Atomistic document.

> **Note:** Sets of atoms should not overlap; that is, no atom can belong to more than one 'DensityDifference' set.

> **Tip:** When only one set with the correct name is present in the structure, Materials Studio assumes that the rest of the atoms should be treated as a second set. Thus, in the case of a molecule-surface interaction, it is sufficient to create a single set that comprises all the atoms in the molecule.

Atomic densities: When selected, indicates that only the density difference with respect to the sum of atomic densities will be calculated.

Sets of atoms: When selected, indicates that only the density difference with respect to the sum of the densities of sets of atoms will be calculated.

Both atomic densities and sets of atoms: When selected, indicates that both kinds of density difference will be calculated.

Access methods

Menu	*Modules	CASTEP	Calculation	Properties	Electron density difference*
Toolbar	≋▼ *	Calculation	Properties	Electron density difference*

Electron localization function selection

Checking the *Electron localization function* checkbox on the Properties tab causes ELF to be calculated as part of the CASTEP run.

Access methods

Menu	*Modules	CASTEP	Calculation	Properties	Electron localization function*
Toolbar	≋▼ *	Calculation	Properties	Electron localization function*

Electronic excitations (TD-DFT) selection

Checking the *Electronic excitations (TD-DFT)* checkbox on the Properties tab displays options for calculating electronic excitations.

Calculate energies of: Specify the number of excited states which will be calculated. Default = 6.

The excitation data will be reported in the `<seedname>_TDDFT.castep` output file.

Calculate optical properties: If checked, the transition probabilities for these states will be calculated to provide access to optical properties.

Optimize geometry for: Specify the excited state whose geometry should be optimized. Default = 1 (that is, the first excited state).

The optimized structure for the specified state will be saved in the `<seedname>_TDDFT_GO.xsd` output file.

Access methods

Menu	*Modules	CASTEP	Calculation	Properties	Electronic excitations (TD-DFT)*
Toolbar	≋▼ | *Calculation	Properties	Electronic excitations (TD-DFT)*

NMR selection

Checking the *NMR* checkbox on the Properties tab displays options for calculating shielding tensors and electric field gradients.

> **Note:** NMR in CASTEP is part of the separately licensed module NMR CASTEP. NMR calculations can only be performed if you have purchased this module.

Shielding: Determines the chemical shielding tensor for each atom in the system.

> **Note:** The shielding tensor is ill-defined for spin-polarized calculations. NMR calculations are allowed wth a spin-polarized setting for a paramagnetic system, but you should check that the final electronic state is indeed paramagnetic. Similarly, such calculations are not recommended for metallic systems without a band gap; however, it is legitimate to use variable orbital occupancies and metallic settings while modeling an insulator.

EFG: Determines the electric field gradients for each atom in the system.

J-coupling: Determines the J-coupling between the selected atom(s) and all other atoms in the system. At least one atom must be selected in the input 3D Atomistic document.

> **Note:** J-coupling can be calculated only for non-magnetic systems. The *Relativistic treatment* of the OTFG pseudopotentials (on the Electronic tab of the CASTEP Calculation dialog) must be set to either Schroedinger for non-relativistic treatment or ZORA for scalar-relativistic effects to be taken into account. J-coupling calculations are supported only for systems with P1 symmetry. If your crystal has symmetry other than P1, you will be prompted to convert the crystal symmetry to P1 before you can continue.

G-tensor: Calculates the change in the EPR g-tensor for a molecule in a box or a defect in a crystal, as well as the tensor of hyperfine parameters.

Note: The g-tensor and hyperfine parameters can only be calculated with spin-polarization turned on and for systems with P1 symmetry. If your crystal has symmetry other than P1, you will be prompted to convert the crystal symmetry to P1 before you continue.

System type: Specify the type of system used in the calculation. Options are:

- Crystal
- Molecule
- Auto - CASTEP will assess the system and treat it as a crystal or molecule as appropriate

Note: Calculations in the Molecule mode can only be performed for systems with P1 symmetry. If your crystal representing molecule in the box has symmetry other than P1, you will be prompted to convert the crystal symmetry to P1 before you can continue.

More...: Provides access to the CASTEP NMR Options dialog, which allows you to specify the nuclear quadrupolar moment for each element.

Note: Calculation of the NMR parameters requires higher accuracy for the wavefunctions than total energy or geometry optimization calculations. This affects how you choose the *Energy cutoff* quality parameter on the Electronic tab, even choosing Ultra-fine may not be sufficient to obtain high quality NMR parameters. Therefore, it is advisable to study the convergence of the results as the *Energy cutoff* parameter is increased. Generally, setting the cutoff to between 270 and 400 eV should produce convergence of the shielding constant to about 1 ppm, but in some cases, the cutoff has to be increased up to 550 eV.

Access methods

Menu	*Modules	CASTEP	Calculation	Properties	NMR*
Toolbar	≋▾ *	Calculation	Properties	NMR*

CASTEP NMR Options dialog

The CASTEP NMR Options dialog allows you to set additional parameters affecting a NMR calculations.

Maximum number of steps: Specify the maximum number of conjugate gradient steps taken for each electronic band in the electronic minimizer during an NMR calculation of the first-order perturbed wavefunctions. Default = 250.

Nuclear quadrupolar moment

This section allows you to specify the nuclear quadrupolar moment, Q, used for electric field gradient calculations. The value of the quadrupolar moment depends on the actual isotope. CASTEP makes a suggestion based on the most typical isotope used in solid state NMR experiments. The value of Q affects only the quadrupolar coupling constant, C_Q, calculated and printed out by CASTEP. If you find that the wrong value of Q was used you can rescale the generated C_Q constant using a different Q value. The list of default values is based on the compilation by Pyykkö (2008).

Note: CASTEP versions before Materials Studio 5.0 used an older compilation by Harris (1996), so some results for quadrupolar coupling constants may have changed in later versions.

> **Note:** NMR in CASTEP is part of the separately licensed module NMR CASTEP. NMR calculations can only be performed if you have purchased this module.

Q moment: Specify the nuclear quadrupolar moment of the element displayed. Change the element type using the dropdown list.

> **Tip:** To reset the nuclear quadrupolar moment for the displayed element to the default value, enter 0 for the *Q moment*.

Reset all Q values to defaults: Sets all nuclear quadrupolar moments for all elements to the default values.

Help: Displays the Help topic in a browser.

Menu	*Modules | CASTEP | Calculation | Properties | NMR | More...*
Toolbar	*| Calculation | Properties | NMR | More...*

Non-linear optical properties selection

Checking the *Non-linear optical properties* checkbox on the Properties tab causes second harmonic generation coefficients to be calculated as part of the CASTEP run.

Convergence tolerance: Specify the value, in $Å^3$, for the required convergence for the second-order response to the electric field. Default = 1.0 e-5 $Å^3$.

Scissors operator: Specify the value, in eV, of the scissors operator to use in calculating the response to the electric field. Default = 0.0 eV.

> **Note:** Calculation of non-linear optical properties is only reasonable for crystals without a center of symmetry.

Access methods

Menu	*Modules | CASTEP | Calculation | Properties | Non-linear optical properties*
Toolbar	*| Calculation | Properties | Non-linear optical properties*

Optical properties selection

Checking the *Optical properties* checkbox on the Properties tab displays options for calculating electronic intraband transitions.

Energy range: Specify the maximum energy above the Fermi level for which optical properties will be calculated. Default = 10 eV.

> **Note:** It is important to include a significant number of empty bands when calculating optical properties. The exact number required will depend on the nature and size of the system under consideration.

k-point set: Specify the quality of the k-point set for the optical properties calculation. Each setting corresponds to a particular separation between neighboring k-points in the Monkhorst-Pack grid. Default = Medium.

More...: Provides access to the CASTEP Optical Properties Options dialog, which allows you to set additional parameters, including the k-point set specification.

Access methods

Menu	*Modules | CASTEP | Calculation | Properties | Optical properties*
Toolbar	* | Calculation | Properties | Optical properties*

CASTEP Optical Properties Options dialog

The CASTEP Optical Properties Options dialog allows you to specify the density of the k-point set and the eigenvalue convergence criterion used for optical properties calculations.

The Monkhorst-Pack k-point grid to be used in the calculation can be specified in one of four ways:

Gamma point only: When selected, indicates that the density of states calculation uses a single k-point at (0,0,0).

Quality: When selected, generates the k-point grid using a k-point separation appropriate to the specified quality level. Select the desired quality level from the list. Available options are:

- Coarse
- Medium
- Fine

The k-point separations associated with the three *Quality* settings are as follows:

Quality	k-point separation ($Å^{-1}$)
Coarse	0.07
Medium	0.05
Fine	0.04

Separation: When selected, generates the k-point grid according to the specified k-point separation. Specify the k-point separation, in $Å^{-1}$, in the associated text box.

> **Note:** When you select the *Separation*, the Monkhorst-Pack parameters are derived to give the specified separation between neighboring grid points.

Custom grid parameters: When selected, generates the k-point grid using the Monkhorst-Pack grid parameters and the origin shift in fractional reciprocal space coordinates specified in the *Grid parameters* and *Origin shift* text boxes, respectively.

Grid parameters: Specify the Monkhorst-Pack grid parameters in each of the lattice directions.

Actual spacing: Displays the k-point separation, in $Å^{-1}$, resulting from the currently specified Monkhorst-Pack grid parameters in each of the lattice directions.

Origin shift: Specify the offset of the Monkhorst-Pack grid in fractional reciprocal space coordinates.

> **Note:** The *Grid parameters* and *Origin shift* controls are enabled only if you select the *Custom grid parameters* option.

Display points...: Displays the number and fractional coordinates of the reciprocal space mesh points that would be generated using the currently specified parameters.

> **Note:** The actual set of k-points that will be used in the calculations may be altered if the symmetry of the system changes.

Use separate XC functional for optics calculation: When checked, indicates that a different exchange-correlation functional will be used for the optical properties calculation from the one used in the self-consistent calculation.

> **Tip:** This feature is particularly useful for carrying out expensive, screened exchange calculations. Perform the main run with the LDA or GGA functional, then invoke screened or exact exchange in non self-consistent mode during the band structure calculation.

> **Note:** There is an important difference between standard DFT calculations with local exchange-correlation potentials and the non-local exchange case. The potential used in the latter scenario depends on the SCF k-points, while in the former case, the potential depends only on electron density. This difference can make all properties calculations a lot more expensive in terms of memory usage and CPU time, so it is advisable to limit the number of SCF k-points that you use in such situations. This is particularly relevant for small unit cells, where the default settings may generate a very large k-point set.

Functional: Select the type of DFT exchange-correlation potential to be used in the optical properties calculation.

Choose the type of functional from the first dropdown list. Available options are:

- LDA
- GGA
- HF
- HF-LDA
- sX
- sX-LDA
- PBE0
- B3LYP
- HSE03
- HSE06

Then, if appropriate, select the specific functional from the second dropdown list. Depending on the functional type selected from the first dropdown list, some of the following options may be available:

- CA-PZ
- PBE
- RPBE
- PW91
- WC
- PBESOL
- BLYP

Note: The *Functional* control is enabled only if the *Use separate XC functional for optics calculation* checkbox is checked.

Band energy tolerance: Specify the convergence criterion, in eV, for electronic eigenvalues during the optical properties calculation. The calculation will stop when all electronic eigenvalues change by less than this value over a single iteration of the electronic structure.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modules	CASTEP	Calculation	Properties	Optical properties	More...*
Toolbar	*	Calculation	Properties	Optical properties	More...*

Orbitals selection

Checking the *Orbitals* checkbox on the Properties tab causes the orbitals (wavefunctions) to be calculated as part of the CASTEP run.

Note: Orbitals are required to calculate the STM profile.

Access methods

Menu	*Modules	CASTEP	Calculation	Properties	Orbitals*
Toolbar	*	Calculation	Properties	Orbitals*

Phonons selection

Selecting *Phonons* on the Properties tab displays options for calculating phonon properties.

Density of states: When selected, computes the phonon density of states as part of the CASTEP run.

Dispersion: When selected, computes the phonon dispersion as part of the CASTEP run.

Both: When selected, computes both the phonon density of states and dispersion during the CASTEP run.

Calculate LO-TO splitting: When selected, applies a non-analytical correction to the dynamical matrix. This calculates the LO-TO phonon frequency splitting at the Γ-point along the directions connecting the Γ-point with the neighboring points along the reciprocal space path. Default = checked.

Method: Select the technique to use to calculate phonon frequencies. Available options are:

- Linear response
- Finite displacement

Finite displacement phonons are available only at the commensurate q-points (at the cost of creating a supercell). However, in this case, you can obtain the phonon frequencies with no limitations on the settings so that, for example, you can use ultrasoft potentials.

> **Note:** If you request LO-TO splitting, then the restrictions on the system type and settings (insulator, norm-conserving potentials) are the same for both the linear response and finite displacement techniques.

More...: Provides access to the CASTEP Phonon Properties Setup dialog, where you can specify additional parameters affecting a phonon calculation, including the convergence tolerance.

Access methods

Menu	*Modules	CASTEP	Calculation	Properties	Phonons*
Toolbar	*	Calculation	Properties	Phonons*

CASTEP Phonon Properties Setup dialog

The CASTEP Phonon Properties Setup dialog allows you to specify additional parameters affecting a phonon calculation.

Method: Select the technique to use to calculate phonon frequencies. Available options are:

- Linear response
- Finite displacement

With ultrasoft potentials, you can only use the finite displacement technique.

> **Note:** If you request LO-TO splitting, then the restrictions on the system type and settings (insulator, norm-conserving potentials) are the same for both the linear response and finite displacement techniques. Select *Calculate LO-TO splitting* on the Properties tab of the CASTEP Calculation dialog when Phonons to request LO-TO splitting.

Linear response

Use interpolation: When selected, calculates the real space dynamical matrix using the Monkhorst-Pack mesh defined by the separation parameter.

q-vector grid spacing for interpolation: Specify the q-point separation parameter, in $Å^{-1}$, which represents the average distance between Monkhorst-Pack mesh q-points used in the real space dynamical matrix calculations. A smaller separation parameter produces a denser mesh, giving more accurate results at the expense of longer calculation times.

Adjust phonon q-vector grid: When selected, adjusts the phonon Monkhorst-Pack mesh to always connect points on the electronic k-vector grid. This can significantly improve convergence especially for metallic cases.

> **Note:** You can only specify the *q-vector grid spacing for interpolation* and *Adjust phonon q-vector grid* if you select *Use interpolation*.

Convergence tolerance: Specify the convergence criterion, in eV $Å^{-2}$, for the force constants during a phonon properties run.

> **Note:** You can only specify the *Convergence tolerance* if you select Linear response as the *Method*.

Finite displacement

Use: Select the method to calculate the dynamic matrix using finite displacement. Available options are:

- Several small supercells - uses the Monkhorst-Pack mesh defined by the separation parameter. When you select Finite displacement as the *Method*, this invokes the nondiagonal supercell approach of Lloyd-Williams and Monserrat (2015).
- One large supercell

q-vector grid spacing for interpolation: Specify the q-point separation parameter, in $Å^{-1}$. This represents the average distance between Monkhorst-Pack mesh q-points used in the real space dynamic matrix calculations. A smaller separation parameter produces a denser mesh, giving more accurate results at the expense of longer calculation times.

> **Note:** You can only specify the *q-vector grid spacing for interpolation* if you select Several small supercells.

Supercell defined by cutoff radius: Specify the real space cutoff radius, in Å, for dynamical matrix calculations. CASTEP uses this value to construct an appropriate supercell. A larger cutoff radius produces more accurate results at the expense of longer calculation times.

If the cutoff radius specified creates a large supercell, its size is reported as a factor of the size of the current cell, indicating that the calculation may be computationally expensive. If the cutoff radius is reasonable, the report confirms that the original cell is large enough. For non-3D periodic systems, you receive a reminder that Materials Studio cannot construct a supercell.

> **Note:** You can only specify the *Supercell defined by cutoff radius* if you select One large supercell.

Dispersion

Quality: Specify the quality of the q-vector used for the phonon dispersion calculation. The quality level affects the approximate separation between consecutive q-vectors on the reciprocal space path. Available options and the corresponding q-vector separations are:

Quality	q-vector separation ($Å^{-1}$)
Coarse	0.04
Medium	0.025
Fine	0.015

Separation: Specify the approximate separation between q-vectors in $Å^{-1}$. The default depends on the selected *Quality* of the q-vector.

Path...: Provides access to the Brillouin Zone Path dialog, which allows you to specify a custom reciprocal space path.

Density of states

Quality: Specify the quality of the q-vector to use for the phonon density of states calculation. The quality level affects the separation between neighboring q-vectors in the Monkhorst-Pack grid. Available options and the corresponding q-vector separations are:

Quality	k-point separation ($Å^{-1}$)
Gamma	uses a single q-vector at (0,0,0)
Coarse	0.07
Medium	0.05
Fine	0.04

> **Note:** For Linear response calculations, if you select Gamma point and select the *Use interpolation*, this calculates the frequencies using the interpolation method. This involves calculations of phonon frequencies at multiple q-vectors in the Brillouin zone and is therefore an expensive way of generating Gamma point phonons. The only justification for such calculations is as a way of testing the accuracy of the interpolation scheme (directly calculated frequencies are more accurate). To run calculations only at the Gamma point, clear selection of *Use interpolation*.

More...: Provides access to the CASTEP Phonon Density of States Options dialog, where you can specify the q-vector to use.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modules	CASTEP	Calculation	Properties	Phonons	More...*
Toolbar	≋▾	*Calculation	Properties	Phonons	More...*

CASTEP Phonon Density of States Options dialog

The CASTEP Phonon Density of States Options dialog allows you to specify the q-vector set for phonon density of states calculations.

The Monkhorst-Pack q-vector grid to be used in the calculation can be specified in one of four ways.

> **Note:** The option selected here propagates from the *Quality* setting in the *Density of States* section on the CASTEP Phonon Properties Setup dialog. As a result, altering the selection here will also change the setting on the CASTEP Phonon Properties Options dialog.

Gamma point only: When selected, indicates that a single q-vector at (0,0,0) will be used for the density of states calculation.

Quality: When selected, indicates that the q-vector grid will be generated using a q-vector separation appropriate to the specified quality level. Select the desired quality level from the dropdown list. Available options and the associated q-vector separations are:

Quality	k-point separation (Å⁻¹)
Coarse	0.07
Medium	0.05
Fine	0.04

Separation: When selected, indicates that the q-vector grid will be generated according to the specified q-vector separation. Specify the q-vector separation, in Å⁻¹, in the associated text box.

> **Note:** When the *Separation* option is selected, the Monkhorst-Pack parameters are derived so as to produce the specified separation between neighboring grid points.

Custom grid parameters: When selected, indicates that the q-vector grid will be generated using the Monkhorst-Pack grid parameters and the origin shift in fractional reciprocal space coordinates specified in the *Grid parameters* and *Origin shift* text boxes, respectively.

Grid parameters: Specify the Monkhorst-Pack grid parameters in each of the lattice directions.

Actual spacing: Displays the k-point separation, in Å⁻¹, resulting from the currently specified Monkhorst-Pack grid parameters in each of the lattice directions.

Origin shift: Specify the offset of the Monkhorst-Pack grid in fractional reciprocal space coordinates.

> **Note:** The *Grid parameters* and *Origin shift* controls are enabled only if you select the *Custom grid parameters* option.

Display points...: Displays, in a new window, the number and fractional coordinates of the reciprocal space mesh points that would be generated using the currently specified parameters.

> **Note:** The actual set of q-vectors that will be used in the calculation may be altered if the symmetry of the system changes.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modules	CASTEP	Calculation	Properties	Phonons	More...	More...*
Toolbar	[icon] ▾	*Calculation	Properties	Phonons	More...	More...*

Polarizability, IR and Raman spectra selection

Checking the *Polarizability, IR and Raman spectra* checkbox on the Properties tab displays options for calculating dielectric permittivity and molecular polarizability.

System type: Select the option from the dropdown list that best describes the system being studied or choose Auto for automatic detection. Available options are:

- Auto
- Crystal
- Molecule
- Linear

Calculate Raman intensities: When checked, activities for Raman active vibrations will be calculated. Subsequently CASTEP analysis can be used to construct Raman mode intensities for a given temperature and laser wavelength from calculated activities.

More...: Provides access to the CASTEP IR and Raman Options dialog, which allows you to set additional parameters affecting a polarizability, IR and Raman calculation, including the convergence tolerance and Raman frequency range.

Access methods

Menu	*Modules | CASTEP | Calculation | Properties | Polarizability, IR and Raman spectra*
Toolbar	≋▾ | *Calculation | Properties | Polarizability, IR and Raman spectra*

CASTEP IR and Raman Options dialog

The CASTEP IR and Raman Options dialog allows you to set additional parameters affecting a polarizability, IR, and Raman calculation.

Convergence tolerance: Specify the value, in $\mathring{A}^3$, of the required convergence for the second-order response to the electric field. Default = 1.0e-5 $\mathring{A}^3$.

Scissors operator: Specify the value, in eV, of the scissors operator to be used in calculating the response to the electric field.

Method: Select the technique to use to calculate Raman intensities from the dropdown list. Available options are:

- Linear response
- Finite displacement

Initial frequency: Specify the value, in cm^{-1}, of the minimal frequency for which Raman modes are calculated. Default = 0 cm^{-1}.

Final frequency: Specify the value, in cm^{-1}, of the maximal frequency for which Raman modes are calculated. Default = 10000 cm^{-1}.

> **Note:** The frequency range can only be specified only if *Method* is set to Finite displacement.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modules | CASTEP | Calculation | Properties | Polarizability, IR and Raman spectra | More...*

| Toolbar | | *Calculation | Properties |* *Polarizability, IR and Raman spectra |* *More...* |

Polarization selection

Checking the *Polarization* checkbox on the Properties tab includes calculation of polarization as part of the CASTEP run. If the task is Elastic Constants, CASTEP uses calculated values of polarization to evaluate the piezoelectric strain tensor.

> **Note:** Polarization calculations are not allowed if you use any of the following settings:
>
> - Ultra-soft pseudopotentials
> - Spin-polarized calculation
> - DFT+U
> - Spin-orbit coupling with non-collinear spins
> - External electric field
> - Mixture atoms

Access methods

| Menu | *Modules | CASTEP | Calculation | Properties | Polarization* |
| Toolbar | | *Calculation | Properties |* *Polarization* |

Population analysis selection

The *Population analysis* checkbox is checked by default. When this is checked the Properties tab displays options for controlling the calculation of Mulliken charges (including partial charges for each angular momentum component), Mulliken spins (for spin-polarized calculations), and Mulliken bond populations. Hirshfeld charges are always calculated when the *Population analysis* checkbox is checked.

Distance cutoff for bond populations: Specify the maximum interatomic distance, in Å, to be considered in the bond population calculation. Default = 3.0 Å.

Calculate band populations: When checked, indicates that the contribution to Mulliken populations from each band will be calculated, in addition to the Mulliken charges.

> **Note:** For disordered crystals population analysis cannot be performed and any these settings will be not be used.

Access methods

| Menu | *Modules | CASTEP | Calculation | Properties | Population analysis* |
| Toolbar | | *Calculation | Properties |* *Population analysis* |

Solvation energy

Checking the *Solvation energy* checkbox on the Properties tab causes calculation of the free energy of solvation, as a separate CASTEP run. This additional run evaluates the energy of a molecule in a box both in vacuum and in the presence of an implicit solvent. Then CASTEP produces the energy of solvation from these results.

There are certain limitations for solvation energy calculations:

- The system must represent a molecule in a box.
- Symmetry of the system must be P1.
- Calculations must not include spin-polarization.
- Stress calculations are not available.

You can specify the options for the solvation energy calculation on the Solvent tab of the CASTEP Electronic Options dialog.

> **Note:** Use at least a Fine FFT grid *Density* for solvation calculations; the Precise density is even better. You can specify the FFT grid *Density* on the Basis tab of the CASTEP Electronic Options dialog. Also use an increased value of *Augmentation density scaling factor*, for example 1.5-2.0 instead of the default value of 1.0.
>
> An increased FFT density and energy cutoff can help to eliminate convergence errors for the multigrid solver for electrostatics in a solvent.

Access methods

Menu	*Modules	CASTEP	Calculation	Properties	Solvation energy*
Toolbar	⚋ ▾	*Calculation	Properties	Solvation energy*

Stress selection

Checking the *Stress* checkbox on the Properties tab causes the stress tensor to be calculated as part of the CASTEP run.

Access methods

Menu	*Modules	CASTEP	Calculation	Properties	Stress*
Toolbar	⚋ ▾	*Calculation	Properties	Stress*

Job Control tab

CASTEP calculations run in the background on a server using the gateway. The *Job Control* tab allows you to select a server for the CASTEP 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 CASTEP 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 to submit the job. Select the required queue from the list, to display the available queues on the chosen gateway. For more information, see Working with queues.

> **Note:** For 3DEXPERIENCE Cloud jobs you cannot specify a *Queue* or choose a value for the *Run in parallel on* number of cores. Instead, select the *Category* for the job, these options automatically determine the number of cores to use for the job.

Category: For 3DEXPERIENCE jobs, select the compute power to use.

Job description: Specify the name to use to identify the job.

Materials Studio automatically assigns a default job description. You can specify an alternative description by clearing the *Automatic* checkbox and entering the new name in the *Job description* text box.

> **Note:** Do not use this field for *Properties* task since in this case CASTEP Analysis will not be able to associate results files with the original structure.

Automatic: Use the automatically generated job description. Default = checked.

Run in parallel on: Runs the job on the selected gateway using the specified number of computer cores. The text to the right of the *Run in parallel on* control indicates the maximum number of cores available on the selected gateway.

> **Note:** It is recommended to use the number of cores which is commensurate with the number of k-points in the calculation. You can determine the number of k-points by using the *Display points...* button on the k-points tab of the *CASTEP Electronic Options* dialog.

Using up to: Specify the maximum number of threads allowed to be used by each MPI process. If the number of threads is greater than 1, the hybrid OpenMP/MPI parallelization will be invoked. The actual number of threads in use will depend on the details of the hardware configuration and the queuing system setup. For example, under with some queuing systems you can set up the gateway to guarantee exclusive use of nodes when number of threads is greater than 1.

> **Note:** This functionality is available only on Linux gateways. To ensure it works as expected when a gateway is using a queuing system, check that the queuing system is set up consistently. See Working with queues for additional details.

> **Note:** Hybrid OpenMP/MPI parallelization can substantially decrease the amount of memory required for a job (though it could somewhat decrease speed).

Runtime optimization: Specify the strategy used to balance memory use and speed during the calculation. Available options are:

- Default - Balance speed and memory use. Wavefunction coefficients for all k-points in a calculation will be kept in memory during, rather than be paged to disk. Some large work arrays will be paged to disk.
- Memory - Minimize memory use. All wavefunctions and large work arrays are paged to disk.
- Speed - Maximize speed. No paging to disk.

> **Note:** This option does not apply to calculations using the nonlocal exchange correlation potential. In this case paging does not save any memory and *Speed* optimization is enforced.

More...: Provides access to the CASTEP Job Control Options dialog which allows you to set additional options associated with monitoring and controlling the results of a CASTEP calculation.

Access methods

Menu	*Modules	CASTEP	Calculation	Job Control*
Toolbar	≈▾	*	Calculation	Job Control*

CASTEP Job Control Options dialog

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

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.

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 CASTEP server to perform a single iteration step of the chosen task. This may be significantly longer than the chosen update interval.

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.

> **Note:** For 3DEXPERIENCE Cloud jobs, selecting *Retain server files* does *not* cause the 3DEXPERIENCE server to save the job files.

> **Tip:** It may be useful to retain the server files so that standalone CASTEP runs can performed.

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 a CASTEP output (`.castep`) file for the main task performed by the job. 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.

Return BibTeX list of references: When checked, indicates that a BibTeX formatted list of references used for this run will be returned when the job has completed.

Return complete check file: When checked, indicates that the full check file will be returned when the job has completes. Availability of this file (which can be very large) can accelerate the restart of a job.

> **Note:** This option does not apply to calculations using the nonlocal exchange correlation potential. In this case the check file is always returned so that restarts are enabled.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modules | CASTEP | Calculation | Job Control | More...*
Toolbar	≈▼ *| Calculation | Job Control | More...*

CASTEP Job Files dialog

The CASTEP Job Files dialog allows you to save input files for a CASTEP 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 CASTEP server program in standalone mode, or who wish to edit the CASTEP input files in order to gain access to features not supported by the CASTEP interface.

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

> **Note:** The *Save Files* button is enabled only when the current 3D model document contains a suitable periodic structure.

The input files are placed in a subfolder of the current Materials Studio project directory and the primary CASTEP input (.param) file is displayed in the Project Explorer.

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

> **Note:** The *Run Files* button is enabled only when the current document is a CASTEP input (.param) file.

The job is submitted using the settings specified on the *Job Control* tab.

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

When band structure, density of states or optical properties are requested, additional input files will be produced for each property. This is because these properties must each be calculated using a separate run of the CASTEP server. These additional input files are named according to the property they are intended to calculate.

In such situations, selecting the input file for the main task and pressing the *Run Files* button runs all of the input files in a single job.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modules	CASTEP	Calculation	Files...*
Toolbar	*	Calculation	Files...*

CASTEP Analysis dialog

The Analysis dialog allows you to analyze the results of a CASTEP 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 analysis of that property are displayed at the bottom of the dialog.

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

Access methods

Menu	*Modules	CASTEP	Analysis*
Toolbar	*| Analysis*

Band structure selection

The following options are available when Band structure is selected from the list of properties.

Results file: Select the CASTEP results file from which the band structure information will be taken.

When more than one set of results is available, use the [...] button to browse the current directory and appropriate subdirectories for results files.

Energy units: Specify the energy units to be used for the dispersion graph. Available options are:

- eV
- Ha

Scissors: Specify the scissors operator to be used in plotting the band structure.

The scissors operator is only applied for insulating systems, which have a clear separation between valence band and conduction band states. It is ignored for metallic systems.

Graph style: Specify the style to be used for the band structure graph. Available options are:

- Points
- Line

Show DOS: When checked, indicates that a density of states from the specified results file will be displayed, together with the band structure graph.

Full DOS: When selected, indicates that the total density of states will be displayed.

Partial: When selected, indicates that the partial density of states (PDOS) will be displayed.

The angular momenta to be included in the PDOS display can be controlled using the *s, p, d, f,* and *Sum* checkboxes.

Note: When the appropriate structure document is active and atoms are selected, the contribution to the density of states from the selected atoms will be plotted. Otherwise, the contribution from all atoms is considered.

Display DOS: Specify which spin components should be plotted in the density of states graph. For a spin-polarized calculation, the supported options are:

- Total - contributions from both spin-up and spin-down eigenstates are summed
- Alpha - contributions from spin-up eigenstates only
- Beta - contributions from spin-down eigenstates only
- Alpha and Beta - contributions from both spin-up and spin-down eigenstates are displayed in a butterfly plot
- Spin - difference between contributions from spin-up and spin-down eigenstates is displayed
- Total and Spin

When a non-spin-polarized CASTEP calculation is analyzed, only the Total option is available.

Function: Specify whether to plot the untreated DOS or the integrated density of states (the number of states).

More...: Provides access to the CASTEP DOS Analysis Options dialog which allows you to specify parameters controlling the density of states integration method.

Note: The *Full*, *Partial*, *Display DOS*, and *More...* options are enabled only if *Show DOS* is checked.

View: Displays the band structure using the options specified.

Note: If you have calculated DOS for a spin polarized system with a non-zero initial spin and the total spin is not optimized two charts will automatically be displayed, *<seedname>* Band Structure Alpha.xcd and *<seedname>* Band Structure Beta.xcd.

Access methods

Menu	*Modules	CASTEP	Analysis	Band structure*
Toolbar		*Analysis	Band structure*

Core level spectroscopy selection

The following options are available when Core level spectroscopy is selected from the list of properties.

Results file: Select the CASTEP results file from which the core level spectroscopy information will be taken. When more than one set of results is available, use the button to browse the current directory and appropriate subdirectories for results files.

Note: Core level spectra can only be calculated for single atoms. One atom should be selected in the active 3D Atomistic document before carrying out a core level spectroscopy analysis.

Tip: If you included a core hole in your calculation, you can select the relevant atom using the Atom Selection dialog.

Spectrum: Specify the type of spectrum that will be calculated. If there is a core hole in the shell a *
symbol is included in the spectrum name, for example 1s*[K1]. Available options (with and without core
holes) are:

- 1s[K1]
- 2s[L1]
- 2p[L23]
- 3s[M1]
- 3p[M23]
- 3d[M45]
- 4s[N1]
- 4p[N23]
- 4d[N45]
- 5s[O1]
- 5p[O23]

Type: Specify the type of spectrum that will be calculated. Available options are:

- Absorption - the predicted absorption spectrum
- Emission - the predicted emission spectrum

More...: Opens the CASTEP EELS Analysis Options dialog.

Calculation: Specify the polarization of the incident radiation for the core level spectroscopy calculation.

Polarization: Specify the direction of the polarization of the incident radiation in fractional (lattice)
coordinates. Not available when Unpolarized is selected for *Calculation*.

Atom Selection...: Opens the Atom Selection dialog.

View: Displays the selected core level spectrum.

A chart document is created using the information contained in the active grid document.

> **Note:** If the requested spectrum is not available, a warning message will be returned explaining the
> reasons.

Access methods

Menu	*Modules | CASTEP | Analysis | Core level spectroscopy*
Toolbar	≋▼ *| Analysis | Core level spectroscopy*

CASTEP EELS Analysis Options dialog

The CASTEP EELS Analysis Options dialog allows you to specify the parameters controlling the core level
spectroscopy broadening options.

Spectrum: Reports the spectrum specified on the CASTEP Analysis dialog when Core level spectroscopy
is selected.

Instrumental smearing: Specify the Gaussian broadening from the instrument to be used.
Default = 0.2 eV.

Lifetime effects: When checked, lifetime broadening effects will be taken into account.

Core level broadening: Specify the broadening to be used at the core level. Default values for lifetime broadening are tabulated based on the compilation by Fuggle and Inglesfield (1992).

Reset broadening to default: Resets the *Core level broadening* to its default value.

Include spin-orbit splitting: When checked, spin-orbit splitting for the core level is added to the spectrum.

Spin-orbit splitting: Specify the value of the core level spin-orbit splitting to be used. Default values for spin-orbit splitting are taken from atomic spectroscopic data (see the WebElements Periodic Table: http://www.webelements.com). These values represent the difference between reported binding energies for core electrons of the given species, for example the difference between $2p_{1/2}$ and $2p_{3/2}$ gives the $L_{2,3}$ splitting.

Reset spin-orbit splitting to default: Resets the *Spin-orbit splitting* to its default value.

Normalize spectrum: When checked, the resulting spectrum will be normalized to 1 at maximum.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modules | CASTEP | Analysis | Core level spectroscopy | More...*
Toolbar	![icon] *| Analysis | Core level spectroscopy | More...*

Density of states selection

The following options are available when Density of states is selected from the list of properties.

Results file: Select the CASTEP results file from which the density of states information will be taken.

When more than one set of results is available, use the [...] button to browse the current directory and appropriate subdirectories for results files.

Energy units: Specify the energy units to be used for the density of states graph. Available options are:

- eV
- Ha

Full DOS: When selected, indicates that the total density of states will be displayed.

Partial: When selected, indicates that the partial density of states (PDOS) will be displayed.

> **Note:** PDOS analysis formalism is not valid for high energy states in the conduction band: PDOS representation will usually decay to zero at about 20 eV above the Fermi level. This is related to the fact that expansion of essentially free electron states in terms of a limited number of atomic-like basis functions is impossible to carry out with any degree of accuracy. Only the valence band and lower part of the conduction band are meaningful in the PDOS plot.

The angular momenta to be included in the PDOS display can be controlled using the *s, p, d, f,* and *Sum* checkboxes.

> **Note:** When the appropriate structure document is active and atoms are selected, the contribution to the density of states from the selected atoms will be plotted. Otherwise, the contribution from all atoms is considered.

Display DOS: Specify which spin components should be plotted in the density of states graph. For a spin-polarized calculation, the supported options are:

- Total - contributions from both spin-up and spin-down eigenstates are summed
- Alpha - contributions from spin-up eigenstates only
- Beta - contributions from spin-down eigenstates only
- Alpha and Beta - contributions from both spin-up and spin-down eigenstates are displayed in a butterfly plot
- Spin - difference between contributions from spin-up and spin-down eigenstates is displayed
- Total and Spin

When a non-spin-polarized CASTEP calculation is analyzed, only the Total option is available.

Note: If you have calculated DOS for a spin polarized system with a non-zero initial spin and the total spin is not optimized only the Total option is available. In this case, two charts will automatically be displayed, *<seedname>* DOS Alpha.xcd and *<seedname>* DOS Beta.xcd.

Function: Specify whether to plot the untreated DOS or the integrated density of states (the number of states).

Scissors: Specify the scissors operator to be used in plotting the density of states.

The scissors operator is only applied for insulating systems, which have a clear separation between valence band and conduction band states. It is ignored for metallic systems.

Atom Selection...: Opens the Atom Selection dialog.

More...: Provides access to the CASTEP DOS Analysis Options dialog, which allows you to specify parameters controlling the density of states integration method.

View: Displays the density of states using the options specified.

Access methods

Menu	*Modules	CASTEP	Analysis	Density of states*
Toolbar	⚛▼ *	Analysis	Density of states*

CASTEP DOS Analysis Options dialog

The CASTEP DOS Analysis Options dialog allows you to specify the parameters controlling the density of states integration method.

Integration method: Select the method to be used for integrating the density of states results from the dropdown list. Supported methods are:

- Smearing - Gaussian broadening is applied to the eigenvalues obtained from the CASTEP calculation.
- Interpolation - eigenvalues (and partial weights for a partial density of states) from the CASTEP calculation are interpolated onto a finer k-point grid.

The Interpolation method provides an improved representation of the density of states. However, it can only be used when eigenvalues are available on a Monkhorst-Pack grid with 3 or more points in each direction. The k-point set for density of states calculations can be specified on the CASTEP Density of States Options - Properties tab on the CASTEP Calculation dialog. If the Interpolation method cannot be used for the selected results, it will be absent from the dropdown list.

Smearing width: Specify the Gaussian broadening to be used.

> **Note:** This option is enabled only if the Smearing integration method is selected.

Accuracy level: Specify the quality of the interpolation to be used. Available options are:

- Coarse - Interpolates onto a k-point grid of about 50×50×50
- Medium - Interpolates onto a k-point grid of about 100×100×100
- Fine - Interpolates onto a k-point grid of about 200×200×200

Instrument broadening: Specify an additional broadening to be applied to the interpolated density of states.

> **Note:** The *Accuracy level* and *Instrument broadening* options are enabled only if the Interpolation integration method is selected.

Number of points per: Specify number of points per 1 eV or per 1 Ha energy range. Use high settings to generate charts that remain smooth after a zoom-in operation.

OK: Updates the settings with any changes and closes the dialog.

Cancel: Closes the dialog without updating any settings.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modules | CASTEP | Analysis | Density of states | More...*
Menu	*Modules | CASTEP | Analysis | Band structure | More...*
Toolbar	〜▼ *| Analysis | Density of states | More...*
Toolbar	〜▼ *| Analysis | Band structure | More...*

Elastic constants selection

The following options are available when Elastic constants is selected from the list of properties.

Results file: Select the CASTEP results file from which the elastic constants information will be taken.

When more than one set of results is available, use the ⬚ button to browse the current directory and appropriate subdirectories for results files.

Calculate: Analyzes stress-strain relationship and calculates the tensors of the elastic constants and the compliances. These results are used to produce the bulk modulus, compressibility, averaged sound velocity, elastic Debye temperature, Young modulus, Poisson ratio, Lamé constants, Vickers hardness, and universal anisotropy index. All of these properties including polycrystalline averages using Voigt, Reuss, and Hill schemes, are written to a new text document, *seedname* `Elastic Constants.txt`, in the results folder.

> **Note:** The empirical expressions for Vickers hardness and for fracture toughness cannot be applied if the calculated shear modulus is negative. This can happen when the calculation settings are not sufficiently accurate. In such a case, the summary report does not include the hardness or the fracture toughness.

Access methods

Menu	*Modules	CASTEP	Analysis	Elastic constants*
Toolbar	*	Analysis	Elastic constants*

Electron density selection

The following options are available when Electron density is selected from the list of properties.

Results file: Select the CASTEP results file from which the electron density information will be taken.

When more than one set of results is available, use the button to browse the current directory and appropriate subdirectories for results files.

Density field: Select the type of density field to be imported. For a spin-polarized calculation, the supported options are:

- Total density - the total electron density
- Spin density - the difference between alpha- and beta-electron densities
- Alpha density - the density of spin-up electrons
- Beta density - the density of spin-down electrons

When a non-spin-polarized CASTEP calculation is analyzed, only the Total density option is available.

View isosurface on import: When checked, an isosurface will be created automatically when the density field is imported.

Save density to file: Creates a plain text file that contains either the charge density or, for spin-polarized calculations, the charge and spin density on a uniform grid in real space. The file has the extension `.charg_frm`.

> **Note:** This file is hidden by default. Use the *Tools | Folder Options... | View | Show hidden files and folders* option in the Windows File Explorer to access the file.

Import: Imports the selected density field from the CASTEP results file into the current structure document.

Access methods

Menu	*Modules	CASTEP	Analysis	Electron density*
Toolbar	*	Analysis	Electron density*

Electron density difference selection

The following options are available when Electron density difference is selected from the list of properties.

Results file: Select the CASTEP results file from which the information required to visualize the electron density difference will be taken. When more than one set of results is available, use the [...] button to browse the current directory and appropriate subdirectories for results files.

Use atomic densities: When checked, the electron density difference with respect to the sum of the atomic densities will be created. If unchecked, the density difference with respect to the sum of the densities of sets of atoms will be created.

View isosurface on import: When checked, an isosurface will be created automatically when the electron density difference field is imported.

Import: Imports the selected electron density difference field from the CASTEP results file into the current structure document.

> **Note:** Analysis based on atomic densities requires the presence of a binary file with the extension `.chdiff`; analysis based on sets of atoms requires that for each set of input files, `seed_Subset*.*`, there are binary files with the extension `.check` present.

Access methods

Menu	Modules | CASTEP | Analysis | Electron density difference
Toolbar	| Analysis | Electron density difference

Electron localization function selection

The following options are available when Electron localization function is selected from the list of properties.

Results file: Select the CASTEP results file from which the ELF information will be taken. When more than one set of results is available, use the [...] button to browse the current directory and appropriate subdirectories for results files.

View isosurface on import: When checked, an isosurface will be created automatically when the ELF field is imported.

Import: Imports the ELF field from the CASTEP results file into the current structure document.

Access methods

Menu	Modules | CASTEP | Analysis | Electron localization function
Toolbar	| Analysis | Electron localization function

Energy evolution selection

The following options are available when Energy evolution is selected from the list of properties.

Results file: Select the CASTEP results file from which the energy evolution information will be taken.

When more than one set of results is available, use the [...] button to browse the current directory and appropriate subdirectories for results files.

View: Generates chart documents as described in the Displaying trajectory and chart data topic.

These charts are the same as would be generated by selecting *Update graphs* in the CASTEP Job Control Options dialog. Charts generated using Energy evolution can be generated whether or not you chose *Update graphs* in the original calculation.

> **Note:** Each time you select *Update graphs* the existing chart documents are rewritten, and any changes or annotations you have made to the charts will be lost.

Access methods

Menu	*Modules	CASTEP	Analysis	Energy evolution*
Toolbar	[≋▾]	*Analysis	Energy evolution*

Fermi surface selection

The following options are available when Fermi surface is selected from the list of properties.

Results file: Select the CASTEP results file from which the band structure data will be taken. When more than one set of results is available, use the [...] button to browse the current directory and appropriate subdirectories for results files.

Filter: Choose how to filter the available Fermi surfaces, options are:

- All - all Fermi surfaces are available.

Show only bands crossing Fermi level: When checked only the bands which traverse the Fermi level will be listed in the table below.

- *Band* - the index of the band in this row
- *Spin* - the spin for this band
- *From* - lowest value of the energy for the band (in eV)
- *To* - highest value of the energy for the band (in eV)

Import: Imports the selected Fermi surface from the CASTEP results file into the current structure document.

Access methods

Menu	*Modules	CASTEP	Analysis	Fermi surface*
Toolbar	[≋▾]	*Analysis	Fermi surface*

IR spectrum selection

The following options are available when IR spectrum is selected from the list of properties.

Results file: Select the CASTEP results file from which the Hessian (dynamical matrix) and ATP tensor (Born charges) information will be taken. When more than one set of results are available, use the [...] button to browse the current directory and appropriate subdirectories for results files.

Import Hessian from CASTEP output: Imports the Hessian and ATP tensor data, if present, from the selected CASTEP results file into the current structure document.

> **Note:** This only is enabled if the currently active document contains a structure for which CASTEP results for the dynamical matrix at the Γ-point are available.

Once a Hessian has been imported, vibrational mode frequencies and, if ATP tensors were calculated, absorption intensities can be displayed in the form of a list of values or graphically as a vibrational spectrum using the Vibrational Analysis tool.

View vibrational analysis: Opens the Vibrational Analysis dialog. This is only enabled when the Hessian is imported into the current structure document.

Access methods

Menu	*Modules	CASTEP	Analysis	IR spectrum*
Toolbar	*	Analysis	IR spectrum*

NMR selection

The following options are available when NMR is selected from the list of properties.

> **Note:** NMR in CASTEP is part of the separately licensed module NMR CASTEP. NMR calculations can only be performed if you have purchased this module.

Results file: Select the CASTEP results file from which the NMR information will be taken. When more than one set of results is available, use the [...] button to browse the current directory and appropriate subdirectories for results files.

Assign isotropic chemical shielding to structure: Adds the *NMRShielding* property to the atoms for which NMR shielding data are available.

Assign electric field gradients to structure: Adds the *EFGQuadrupolarCoupling* and *EFGAsymmetry* properties to the atoms for which electric field gradient data are available.

Once added, all three of these properties are accessible in the Properties Explorer and can be used for labeling.

Show J-coupling constants: Generates and opens a study table reporting the calculated J-coupling constants. This option is only available when the Results file selector is set to use a *seedname_* `NMRJC.castep` file.

Access methods

Menu	*Modules	CASTEP	Analysis	NMR*
Toolbar	*	Analysis	NMR*

Optical properties selection

The following options are available when Optical properties is selected from the list of properties.

Results file: Select the CASTEP results file from which the optical properties information will be taken.

When more than one set of results is available, use the [...] button to browse the current directory and appropriate subdirectories for results files.

Calculation: Specify the type of optical properties calculation to be performed. Available options are:

- Polarized - optical properties are calculated for plane polarized light with the specified polarization direction.
- Unpolarized - optical properties are averaged over polarization directions perpendicular to the specified incident direction.
- Polycrystalline - optical properties are averaged over all polarization directions, thereby imitating an experiment on a polycrystalline sample.

Smearing: Specify the Gaussian broadening to be used for calculating the dielectric function.

Scissors: Specify the scissors operator to be used for calculating the dielectric function.

The scissors operator is only applied for insulating systems, which have a clear separation between valence band and conduction band states. It is ignored for metallic systems.

Polarization: Specify the polarization of the incident radiation for the optical properties calculation. The direction is specified in fractional (lattice) coordinates.

> **Note:** This option is enabled only if a Polarized calculation is selected.

Incidence: Specify the incident direction of radiation the for optical properties calculation. The direction is specified in fractional (lattice) coordinates.

> **Note:** This option is enabled only if an Unpolarized calculation is selected.

Function: Specify which optical property should be displayed as a function of frequency when the *View* button is pressed. Available options are:

- Reflectivity
- Absorption
- Refractive Index - both the real part, n, and imaginary part, k, of the complex optical constant are displayed.
- Dielectric Function - both the real and imaginary parts are displayed.
- Conductivity - both the real and imaginary parts are displayed.
- Loss Function

Units: Specify the frequency units used for the display of optical properties.

More...: Provides access to the Optics Analysis Options dialog, which allows you to specify any Drude contribution to the optical properties.

Calculate: Calculates the dielectric function from the optical matrix elements and eigenvalues in the CASTEP results file.

A grid document is produced containing the calculated dielectric function.

View: Displays the selected optical property as a function of frequency.

Note: This button is enabled only if the current document is a grid document containing a dielectric function.

A chart document is created using the dielectric function information contained in the active grid document.

Access methods

Menu	*Modules	CASTEP	Analysis	Optical properties*
Toolbar	*	Analysis	Optical properties*

Optics Analysis Options dialog

The CASTEP Optics Analysis Options dialog allows you to specify the Drude contribution to the optical properties.

Plasma frequency: Specify the value of the plasma frequency which is used in the Drude term.

Tip: A value of zero, no Drude correction, should be used for insulators and semiconductors. For metals, a typical value range is 2-10 eV.

Drude damping: Specify the lifetime broadening for the Drude contribution.

Tip: Typical values range from 0.02 eV to 0.08 eV.

OK: Updates the settings with any changes and closes the dialog.

Cancel: Closes the dialog without updating any settings.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modules	CASTEP	Analysis	Optical properties	More...*
Toolbar	*	Analysis	Optical properties	More...*

Orbitals selection

The following options are available when Orbitals is selected from the list of properties.

Results file: Select the CASTEP results file from which the orbitals information will be taken. When more than one set of results is available, use the button to browse the current directory and appropriate subdirectories for results files.

Filter: Choose which orbitals are displayed in the table:

- Alpha - displays data only for alpha-spin orbitals (spin up)
- Beta - displays data only for beta-spin orbitals (spin down)

Note: For non-spin-polarized calculations, this option is not available.

The orbital analysis table, below the *Filter* dropdown list, lists the eigenvalues and other information about each orbital. The list starts with the lowest energy orbital. Other information contained in the table includes:

- *N* - number of the orbital, with 1 corresponding to the lowest energy orbital
- *s* - spin, + for alpha, and - for beta.

> **Note:** In a non-spin-polarized calculation, all orbitals are labeled +.

- *From* - lowest value of the energy of the Nth band at any k-point (in eV)
- *To* - highest value of the energy of the Nth band at any k-point (in eV)

Scissors: Specify the scissors operator to be used in displaying the orbital eigenvalues.

The scissors operator is only applied for insulating systems, which have a clear separation between valence band and conduction band states. It is ignored for metallic systems.

View isosurface on import: When checked, an isosurface will be created automatically when the orbital field is imported. The units for the isovalues are e/Å^3.

Import: Imports the selected orbital field from the CASTEP results file into the current structure document.

Access methods

Menu	*Modules	CASTEP	Analysis	Orbitals*
Toolbar	*	Analysis	Orbitals*

Phonon dispersion selection

The following options are available when Phonon dispersion is selected from the list of properties.

Results file: Select the CASTEP results file from which the phonon dispersion information will be taken.

When more than one set of results is available, use the [...] button to browse the current directory and appropriate subdirectories for results files.

Units: Specify the frequency units to be used for the phonon dispersion graph. Available options are:

- THz
- meV
- cm^{-1}

Graph style: Specify the style to be used for the band structure graph. Available options are:

- Points
- Line

Show DOS: When checked, indicates that a phonon density of states from the specified results file will be displayed, together with the phonon dispersion graph.

Display DOS: Specify the type of the phonon density of states that will be displayed. Available options are:

- Full
- Partial

> **Note:** When atoms are selected in the active structure document, the contribution to the phonon density of states from only the selected atoms will be plotted. Otherwise, the contribution from all atoms is considered.

More...: Provides access to the CASTEP Phonon DOS Analysis Options dialog which allows you to specify parameters that control the density of states integration method and DOS normalization scheme.

> **Note:** The *DOS display* and *More* options are enabled only if *Show DOS* is checked.

View: Displays the phonon dispersion using the options specified.

Access methods

Menu	*Modules	CASTEP	Analysis	Phonon dispersion*
Toolbar	≋▾ *	Analysis	Phonon dispersion*

Phonon density of states selection

The following options are available when Phonon density of states is selected from the list of properties.

Results file: Select the CASTEP results file from which the phonon density of states information will be taken. When more than one set of results is available, use the ⋯ button to browse the current directory and appropriate subdirectories for results files.

Display DOS: Specify the type of the phonon density of states that will be displayed. Available options are:

- Full
- Partial

> **Note:** When atoms are selected in the active structure document, the contribution to the phonon density of states from only the selected atoms will be plotted. Otherwise, the contribution from all atoms is considered.

Units: Specify the frequency units to be used for the phonon dispersion graph. Available options are:

- THz
- meV
- cm^{-1}

More...: Provides access to the CASTEP Phonon DOS Analysis Options dialog which allows you to specify parameters that control the density of states integration method.

View: Displays the phonon density of states using the options specified.

Access methods

Menu	*Modules	CASTEP	Analysis	Phonon density of states*
Toolbar	≋▾ *	Analysis	Phonon density of states*

CASTEP Phonon DOS Analysis Options dialog

The CASTEP Phonon DOS Analysis Options dialog allows you to specify the parameters that control the phonon density of states integration method.

Integration method: Select the method to be used for integrating the density of states results from the dropdown list. Supported methods are:

- Smearing - Gaussian broadening is applied to the eigenvalues obtained from the CASTEP calculation.
- Interpolation - eigenvalues (and partial weights for a partial density of states) from the CASTEP calculation are interpolated onto a finer k-point grid.

The Interpolation method provides an improved representation of the density of states. However, it can only be used when eigenvalues are available on a 3 × 3 × 3 or larger Monkhorst-Pack grid. If the Interpolation method cannot be used for the selected results, it will be absent from the dropdown list.

Smearing width: Specify the Gaussian broadening to be used.

> **Note:** This option is enabled only if the Smearing *Integration method* is selected.

Accuracy level: Specify the quality of the interpolation to be used. Available options are:

- Coarse - Interpolates onto a k-point grid of about 50 × 50 × 50.
- Medium - Interpolates onto a k-point grid of about 100 × 100 × 100.
- Fine - Interpolates onto a k-point grid of about 200 × 200 × 200.

Instrument broadening: Specify an additional broadening to be applied to the interpolated density of states.

> **Note:** The *Accuracy level* and *Instrument broadening* options are enabled only if the Interpolation integration method is selected.

Normalization: Select the required normalization scheme from the dropdown list. Available options are:

- 1 - the integral of the generated density of states is 1.
- 3N - the integral of the generated density of states is the total number of vibrational degrees of freedom.

OK: Updates the settings with any changes and closes the dialog.

Cancel: Closes the dialog without updating any settings.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modules	CASTEP	Analysis	Phonon Density of states	More...*
Toolbar	*	Analysis	Phonon Density of states	More...*

Population analysis selection

The following options are available when Population analysis is selected from the list of properties.

Results file: Select the CASTEP results file from which the population analysis information will be taken.

When more than one set of results is available, use the [...] button to browse the current directory and appropriate subdirectories for results files.

Assign charges to structure: Imports the selected charges into the active structure document and assigns them to each atom. You can see the charges by labeling the atoms according to their charge. Select the type of charges that you wish to import from the dropdown list, available options are:

- Mulliken
- Hirshfeld

Assign spins to structure: Imports the selected spins into the active structure document and assigns them to each atom. You can see the spins by labeling the atoms according to their spin. Select the type of spins that you wish to import from the dropdown list, available options are:

- Mulliken
- Hirshfeld

Assign Mulliken bond orders to structure: Imports Mulliken bond orders into the active structure document and assigns them to each bond.

Access methods

Menu	*Modules	CASTEP	Analysis	Population analysis*
Toolbar	≋▼ *	Analysis	Population analysis*

Potentials selection

The following options are available when Potentials is selected from the list of properties.

Results file: Select the CASTEP results file from which the potentials information will be taken. When more than one set of results is available, use the [...] button to browse the current directory and appropriate subdirectories for results files.

> **Note:** The local potential cannot be analyzed for calculations with spin-orbit interaction taken into account.

Potential field: Indicates the type of potential field to be imported. Currently only SCF local potential is available.

View isosurface on import: When checked, an isosurface will be created automatically when the potential field is imported.

Import: Imports the selected potential field from the CASTEP results file into the current structure document. If the structure is a slab with a region of vacuum, a Chart document named `<seedname> Potential Profile.xcd` is also displayed containing a plot of the potential averaged in the planes perpendicular to the surface normal. This chart document also contains the value of work function calculated as a difference between the potential level in a vacuum and the Fermi energy.

> **Note:** When calculating a work function from a periodic slab model, you should ensure that the self-consistent dipole correction is activated on the SCF tab of the CASTEP Electronic Options dialog.

Access methods

Menu	*Modules | CASTEP | Analysis | Potentials*
Toolbar	⋙ ▾ | *Analysis | Potentials*

Reaction kinetics selection

Select the *Reaction kinetics* option on the CASTEP Analysis dialog to display the Reaction kinetics dialog.

Results file: Indicates the document containing the reaction ingredients. This field displays the name of the active document. You can change the active document by clicking on the desired document window or by double-clicking on the document name in the Project Explorer.

> **Note:** Reaction kinetics calculation can be performed only if the collection document contains well-defined reaction ingredients: the reactant(s), the product(s), and the transition state. All the structures must have Hessians and total energy calculated. Reactant(s) and product(s) systems must be in the ground state - that is all the eigenfrequencies must be real and non-negative.The transition state must be a valid saddle point with one and only one imaginary frequency for which eigenvectors represent the reaction path.

From: To: Specify the temperature range for the output of the calculated rate coefficient.

Apply tunneling correction: When checked, indicates that the reaction rate coefficient will be calculated taking into account the tunneling correction.

Threshold correction: Specify the value to be added to the DFT reaction threshold. This correction compensates for the underestimation of reaction barriers at the DFT level of theory.

> **Note: Vibrational frequencies scaling:** Specify the value of the scaling coefficient to be applied to calculated vibrational frequencies before evaluation of vibrational partition functions.

> **Note:** In some reactions, the transition state may have optical isomers with degeneracy n. These require the prefactor of the Arrhenius rate to be corrected by a factor n. Materials Studio does not automatically include this prefactor, users are encouraged to add it to the results study table by hand.

Calculate: Calculate and display a study table containing rate coefficients for the forward and reverse reactions.

> **Note:** The prefactor for the modified Arrhenius equation is calculated using T_0= 298.15 K as reference temperature.

Access methods

Menu	*Modules | CASTEP | Analysis | Reaction kinetics*
Toolbar	⋙ ▾ | *Analysis | Reaction kinetics*

Raman spectrum selection

The following options are available when Raman spectrum is selected from the list of properties.

Results file: Select the CASTEP results file from which the Hessian (dynamical matrix) and ATP tensor

(Born charges) information will be taken. When more than one set of results are available, use the [...] button to browse the current directory and appropriate subdirectories for results files.

Function: Specify whether to calculate the Intensity or the Activity of the vibrational mode.

Temperature: If the intensity of the vibrational mode is being calculated set the temperature in Kelvin.

Incident light: If the intensity of the vibrational mode is being calculated specify the wavelength of the incident light in nm. The default value of 514.5 nm corresponds to a standard Ar laser. Other popular wavelengths for laser Raman spectrometers include 632.8 nm (He-Ne), 785 nm (diode), and 1064 nm (Nd:YAG).

Smearing: Specify the type of broadening (Gaussian or Lorentzian) and width to be used. Default Lorentzian broadening with width = 20.0 cm-1.

Units: Specify the units for the X axis of the spectrum, options are:

- meV
- THz
- cm-1

Reverse wavenumber axis: When checked, indicates that the values on the X axis will decrease from right to left.

Reverse intensity axis: When checked, indicates that the values on the Y axis will decrease from bottom to top.

Once a Hessian has been imported, vibrational mode frequencies and, if ATP tensors were calculated, absorption intensities can be displayed in the form of a list of values or graphically as a vibrational spectrum using the Vibrational Analysis tool.

View: Displays the selected Raman spectrum.

Access methods

Menu	*Modules | CASTEP | Analysis | Raman spectrum*
Toolbar	≋ ▾ | *Analysis | Raman spectrum*

STM profile selection

The following options are available when STM profile is selected from the list of properties.

Results file: Select the CASTEP results file from which the information required to model the STM profile

will be taken. When more than one set of results is available, use the [...] button to browse the current directory and appropriate subdirectories for results files.

> **Note:** STM analysis is only available if orbitals were requested.

> **Note:** When more than one set of results is available, it is preferable to use output files for DOS calculation, especially when STM images of empty bands are required.

STM bias: Specify the value of the bias for STM modeling. Positive bias corresponds to the imaging of empty (conduction) states, negative bias to the imaging of occupied (valence) states.

View isosurface on import: When checked, an isosurface will be created automatically when the STM profile field is imported.

Import: Imports the selected STM profile field from the CASTEP results file into the current structure document.

Menu	*Modules	CASTEP	Analysis	STM profile*
Toolbar	*	Analysis	STM profile*

Structure selection

The following options are available when Structure is selected from the list of properties.

Results file: Select the CASTEP results file from which the structure information will be taken. When more than one set of results is available, use the [...] button to browse the current directory and appropriate subdirectories for results files.

Update structure from CASTEP output: Restores atomic coordinates and cell parameters from the CASTEP results file.

> **Note:** This button is enabled only if the current document contains a structure for which CASTEP results are available.

Create trajectory: Creates a trajectory (`.xtd`) file from the results of a CASTEP Geometry Optimization, Dynamics or TS Search task.

> **Note:** This button is enabled only if the current document contains a structure for which CASTEP trajectory results are available.

Access methods

Menu	*Modules	CASTEP	Analysis	Structure*
Toolbar	*	Analysis	Structure*

Thermodynamic properties selection

The following options are available when Thermodynamic properties is selected from the list of properties.

Results file: Select the CASTEP results file from which the information about phonon frequencies will be taken in order to evaluate thermodynamic properties. When more than one set of results is available, use the [...] button to browse the current directory and appropriate subdirectories for results files.

> **Note:** Thermodynamic calculations can be performed only if the system is in the ground state, that is, geometry optimization is fully converged. This means that all the phonon eigenfrequencies must be real and non-negative.

From: To: Specify the temperature range for the output of the calculated thermodynamic properties.

> **Tip:** The lower limit should be no less than be 5 K to avoid numerical noise due to inadequate Brillouin zone sampling at low temperatures. The upper limit should not be significantly greater than the Debye temperature because of the limited accuracy of the quasiharmonic approximation at high temperatures.

Plot Debye temperature: When checked, indicates that a separate chart with the temperature dependence of the Debye temperature will be displayed.

Assign temperature factors to structure: Adds temperature factor information to the structure.

View: Displays the thermodynamics properties using the options specified.

> **Note:** Thermodynamic calculations performed only at the Γ-point give very poor results, as no acoustic degrees of freedom can be taken into account.

> **Note:** Heat capacity is measured in calories per unit cell per Kelvin. The unit cell can contain several formula units.

Access methods

Menu	*Modules | CASTEP | Analysis | Thermodynamic properties*
Toolbar	*| Analysis | Thermodynamic properties*

Results file selector

The Results file selector dialog allows you to browse CASTEP results (.castep) files in the current directory and appropriate subdirectories and select the file you wish to use as the source of data for analysis of the chosen property.

Choose results file: Select the results file you wish to use as the source of data for analysis of the chosen property.

All CASTEP results files that are relevant to the current document and that contain results for the chosen property will be displayed.

OK: Updates the file selection on the CASTEP Analysis dialog and closes this dialog.

Cancel: Closes the dialog without updating the selection.

Help: Displays the Help topic in a browser.

Chapter 6: CASTEP keywords

A wide range of input keywords and data blocks are recognized by CASTEP, including some that are not accessible from the CASTEP setup dialogs.

> **Tip:** For information on CASTEP keywords, refer to the Materials Studio Online Help.

Appendix I: CASTEP References

A list of papers published using CASTEP can be found at the Dassault Systèmes website:
https://www.3ds.com/products-services/biovia/search/?cloudview.r=%2Bf%2Fsearchmodulefacet%2Fcastep.

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