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VISUALIZER TOOLS GUIDE

MATERIALS VISUALIZER

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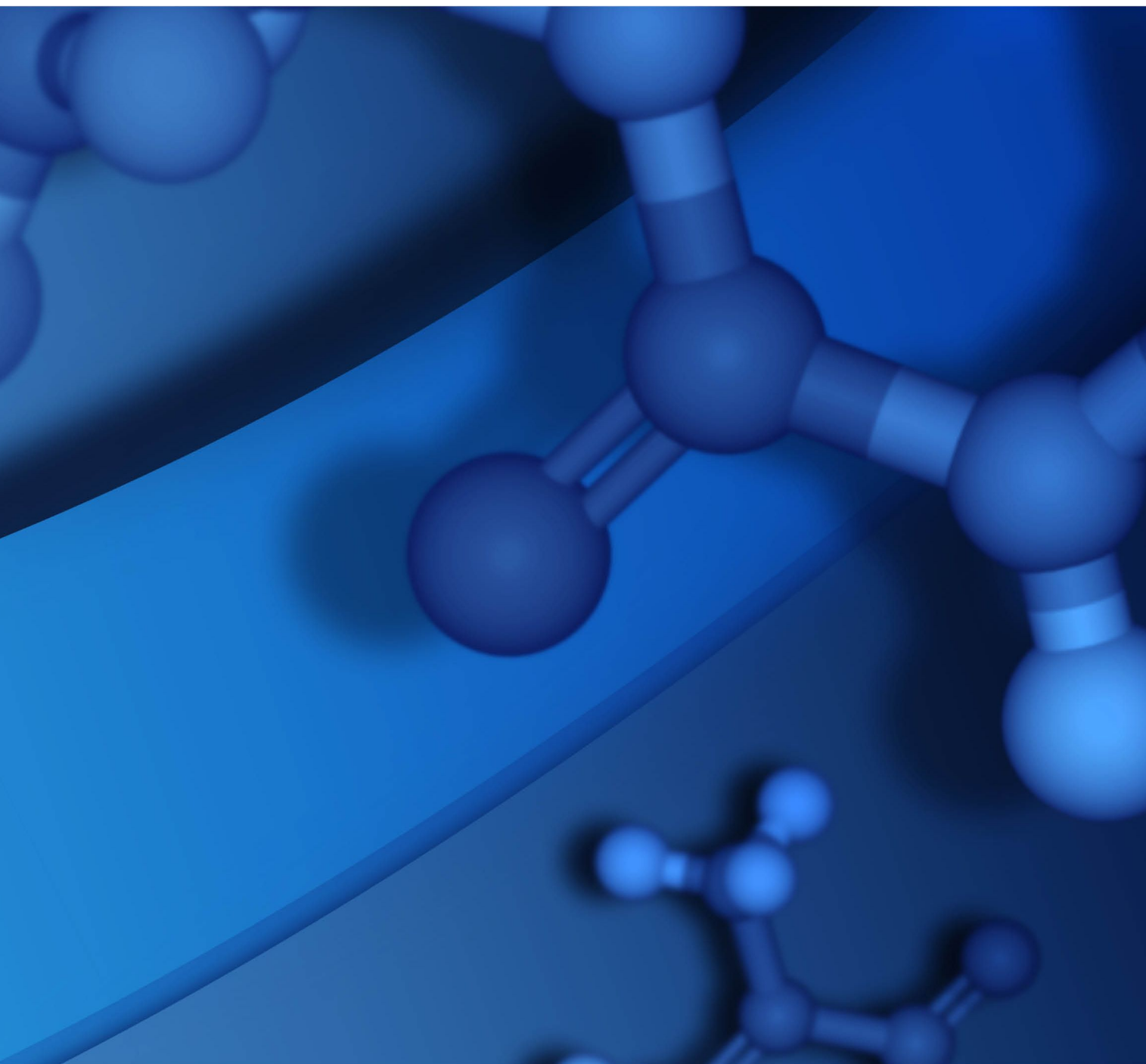
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Visualizer Tools

Introduction

In Materials Studio, the following tools are available:

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- Calculating atom volumes & surfaces
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- Brillouin zone paths
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Further Information

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

Calculating bonds

The *Calculate Bonds* tool allows you to calculate bonds between atoms.

Calculate Bonds

The criteria used to calculate bonds are based on the distance between atoms and the element type. You can edit the bond criteria, save sets of bond criteria as bonding schemes and switch between schemes easily. You can also enable automatic recalculation of bonds to monitor changes in the bonding as the active model is modified, or to investigate the dependence of bonding configurations on bonding criteria.

To calculate bonding

1. Select *Build | Bonds* from the menu bar, or click the *Calculate Bonds* arrow on the Atoms & Bonds toolbar and select *Bond Options* from the dropdown list to open the Bond Calculation dialog.
2. On the *Bonding Scheme* tab, choose the set of bond criteria you wish to use from the dropdown list.
3. Specify the detailed options by checking or unchecking the *Calculate connectivity* and *Calculate bond type* checkboxes.
4. If there are aromatic bonds in the structure, check the *Convert representation to* checkbox and select either *Kekule* or *Resonant* from the dropdown list.
5. If you wish Materials Studio to update the bonding when changes occur in the structure, check the *Monitor bonding* checkbox.
6. Select the *Connectivity Options* tab and set the *Bond-length tolerance* as required by moving the *From* and *To* sliders.
7. If you do not wish to calculate bonding for particular elements, click the *Edit...* button to open the Element Exclusion List dialog.
8. Click the *Calculate* button on the Bond Calculation dialog to calculate bonding for the current 3D Atomistic document.

Default bonding schemes

The default bonding schemes provide the most commonly used criteria for the formation of chemical bonds. The first three sets; No bonding to s- and f-shell, No bonding to d- shell, and Include all elements, differ in the set of elements *not* forming chemical bonds.

The last two sets; Tetrahedral and Anions, are intended for special visualization of atomic arrangements within a sublattice of tetrahedral bonded atoms or within an anion sublattice, respectively. This may be particularly useful for zeolite structures.

Name	Bond-length tolerance		Elements excluded from bonding
	min	max	
No bonding to s- and f-shell (default)	0.6	1.15	1st row elements (Li-Fr) 2nd row elements (Be-Ra) Lanthanide elements
No bonding to d-shell	0.6	1.15	As above + transition metal elements

Name	Bond-length tolerance		Elements excluded from bonding
	min	max	
Include All Elements	0.6	1.15	None
Tetrahedral	0.6	1.5	Oxygen, sulfur
Anions	0.6	2	Aluminum, silicon, phosphorus

Theory in bond calculation

Bond criteria

The *Calculate Bonds* tool creates bonds between two atoms if the following criteria are met:

- Neither of the two atoms is excluded from forming bonds, i.e. they are not elements in the element exclusion list.
- The sum of the covalent radii of the two atoms fulfills the bond-length criterion below.

$$TolFac_{lower} \times ideal\ distance < distance < TolFac_{upper} \times ideal\ distance$$

where

distance = distance between the two atoms forming the bond.

$TolFac_{lower}$ = lower tolerance factor. The lower tolerance factor is set using the Bond-length tolerance options on the Bond Calculation dialog.

$TolFac_{upper}$ = upper tolerance factor. The upper tolerance factor is set using the Bond-length tolerance options on the Bond Calculation dialog.

ideal distance = R_{cov}(Atom1) + R_{cov}(Atom2) and R_{cov} denotes the covalent radius of the atom.

Calculating Bonds

The *Calculate Bonds* tool uses the following procedure:

1. Tests all selected bonds and all bonds attached to a selected atom for compliance with the bond criteria. Deletes non-compliant bonds.
2. Creates atom pairs using all selected atoms and their symmetry images on one side and the whole structure on the other.
3. Forms bonds between all pairs that fulfill the bond criteria.
4. Calculates bond types for all selected and newly created bonds.
5. Converts the display style of resonant bonds to either Kekulé or resonant representation.

Note: If no objects are selected in a structure the bond calculation includes all atoms and bonds.

Monitoring Bonds

The bond monitor is used to automatically recalculate bonds if the document is modified. The bond monitor triggers a bond calculation if one of the events in the following list occurs:

- The selection is changed
- The value of a bond criteria is changed or a new bonding scheme is loaded
- The element type of an atom changes
- An atom changes position
- An atom or bond is deleted or added

Dialogs in bond calculation

Bond calculation functions are available in the following dialogs:

- Bond Calculation dialog
- Element Exclusion List dialog

Bond Calculation dialog

The Bond Calculation dialog allows you to edit the criteria by which bonds are calculated and to save or select a set of bond criteria. You can invoke a single bond calculation or set up a bond monitor. You may also change how resonant bonds are displayed.

The Bond Calculation dialog contains the following tabs:

- Bonding Scheme: Allows you to select a set of bond criteria, invoke a single bond calculation, set up a bond monitor, and change how resonant bonds are displayed.
- Connectivity Options: Allows you to edit the criteria by which bonds are calculated, invoke a single bond calculation, and set up a bond monitor.

Monitor bonding: Enables the automatic recalculation of bonds in the current model document.

> **Tip:** You can also activate *Monitor Bonding* from the Calculate Bonds dropdown menu on the Atoms & Bonds toolbar.

If *Monitor Bonding* is enabled, a checkmark is displayed on the Calculate Bonds tool on the Atoms & Bonds toolbar.

For more information on how the bond monitor operates see Bond monitor procedure.

Calculate: Invokes a single bond calculation. For more information on how bonds are calculated see Bond calculation procedure.

Calculate | 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.

> **Note:** At present *Copy Script* does not copy the setting for any of the options on the *Bonding Scheme* tab. A bond calculation in script will always use the default bonding scheme *No bonding to s- and f-shell* with default options applied.

Help: Displays the Help topic for the current tab.

Access methods

Menu	*Build	Bonds*
Toolbar	*| Bond Options*

Bonding Scheme tab

The *Bonding Scheme* tab allows you to select a set of bond criteria, invoke a single bond calculation, set up a bond monitor and change how resonant bonds are displayed.

Bonding scheme: Allows you to select, rename, save and delete the active bonding scheme. A bonding scheme is the set of bond criteria used to calculate bonds.
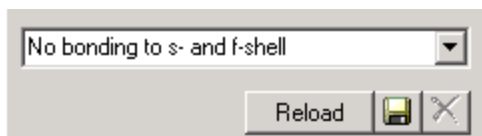
Bonding scheme dropdown

Select the active bonding scheme from the list of default bonding schemes or user defined schemes. The default bonding scheme is No bonding to s- and f-shell. Rename the current bonding scheme by typing a new name in the dropdown list text box, then click the *Save* button.

> **Note:** All modifications to the bond criteria apply to the current active bond scheme only, they do not affect any of the preset or saved user-defined bonding schemes. If you want to modify an existing bonding scheme you need to load the scheme first, modify the settings and save the settings into a new scheme. You may later delete the old bond scheme.

Reload: Loads the default settings for the currently selected bonding scheme.

Save: Saves the current bond criteria into the bonding scheme list.

If a scheme with the same name exists already, the name of the current bonding scheme is modified to provide a unique name.

> **Note:** The *Save* operation never overwrites an existing bond scheme.

> **Note:** The list of bonding schemes is part of the current project. Newly saved bonding schemes are written permanently to disk only if you save the project before exiting Materials Studio.

Delete: Deletes the current bond criteria from the bonding scheme list.

After deleting a scheme from the list the default scheme is loaded.

> **Note:** Preset bonding schemes cannot be deleted from the list. If you load a preset bonding scheme *Delete* is disabled. You may, however, modify the bonding scheme once it is loaded and save it under a new name into the bonding scheme list.

Options

Calculate connectivity: When checked the connectivity is recalculated as the first step of the bond calculation.

Calculate bond type: When checked the bond types are calculated as the last step of the bond calculation.

Convert representation to: When checked during a bond calculation the display style of all selected resonant bonds is modified to either Resonant or Kekule representation. The representation is selected from the list box to the right. Default = Kekule.

Monitor bonding: Enables the automatic recalculation of bonds in the current model document.

Menu	*Build	Bonds	Bonding Scheme*
Toolbar	*	Bond Options	Bonding Scheme*
Toolbar	calculates bonds using the current bond criteria

Connectivity Options tab

The *Connectivity Options* tab allows you to edit the criteria by which bonds are calculated, invoke a single bond calculation and set up a bond monitor.

Bond-length tolerance

The *Bond-length tolerance* specifies the deviation from the ideal bond length that is tolerated for forming a bond between two atoms. The ideal bond length is defined as the sum of the covalent radii of the two atoms forming the bond.

From: Lower tolerance factor. Determines the smallest distance between two atoms for which a bond may still be formed. The distance between the atoms has to be at least the ideal bond length times this value (see also Theory of bond calculation). Range = 0 to 2.

To: Upper tolerance factor. Determines the largest distance between two atoms for which a bond may still be formed. The distance between the atoms has to be smaller than the ideal bond length times this value (see also Theory of bond calculation). Range = 0 to 2.

> **Tip:** Any positive tolerance factor up to 100 may be set using the text box to the right of the slider controls.

Elements excluded from bonding

Edit...: Opens the Element Exclusion List dialog used to edit the list of elements excluded from bonding.

Monitor bonding: Enables the automatic recalculation of bonds in the current model document.

Menu	*Build	Bonds	Connectivity Options*
Toolbar	*	Bond Options	Connectivity Options*
Toolbar	calculates bonds using the current bond criteria

Element Exclusion List dialog

The Element Exclusion List dialog allows you to define a list of elements that do not form covalent bonds. You may also use this functionality to explore different aspects of the connectivity of a structure, for example, by excluding the anions in a zeolite.

Click the *Edit...* button on the Connectivity Options tab of the Bond Calculation dialog to access the Element Exclusion List dialog. Select elements to be excluded from the periodic table.

The following color code is used to indicate whether or not the elements may form covalent bonds.

Color	Meaning
Pink	Excluded from forming bonds
Yellow	May form bonds

A set of elements may be selected from the periodic table using the following operations:

Operation	Meaning
Click on element	Toggle status of element and reset status of all other elements to be included in bond formation.
CTRL + click on element	Toggle status of element without affecting the status of any other element

OK: Accepts the new element exclusion list and makes it the current one.

Cancel: Cancels the changes entered and closes the dialog.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Build	Bonds	Connectivity Options	Edit....*
Toolbar	*	Bond Options	Connectivity Options	Edit...*

Calculating close contacts

The *Calculate Close Contacts* tool allows you to identify close contacts between pairs of atoms in a structure.

Calculate Close Contacts

The distance criterion used to calculate close contacts may be an absolute value or it can be defined in terms of the sum of specified atomic radii. Close contacts can be excluded if the two atoms involved are in the same bonded fragment or set. You can enable automatic recalculation of close contacts to monitor the changes that take place as the structure in the active 3D Atomistic document is modified for example, during a dynamics simulation. Selected close contacts can be labeled in a variety of ways using the options available on the Label dialog.

To calculate close contacts

1. Select *Build | Close Contacts* from the menu bar, or click the *Calculate Close Contacts* arrow on the Atoms & Bonds toolbar and select *Close Contact Options* from the dropdown list to open the Close Contact Calculation dialog.
2. Specify the method for determining closest contacts by selecting either the *Absolute distance* or the *Scaled sum of radii* radio button. If you use the scaled radii, choose the type of radius from the dropdown list, options are VDW (van der Waals), Slater, Metallic, Ionic, and Covalent.
3. Set the distance in Å or the radius using the appropriate slider.
4. If you want Materials Studio to update the close contacts during changes to the structure, check the *Monitor close contacts* checkbox.
5. Choose the *Exclusions* tab and specify the circumstances under which close contacts will be discounted. If you choose membership of the same set, you can create or update sets of atoms by clicking the *Edit Sets...* button to open the Edit Sets dialog.
6. Click the *Calculate* button.

Close contact properties

As with other Materials Studio objects, it is possible to view and manipulate certain properties of close contacts using the Properties Explorer. The list below describes some of the most important close contacts properties that are available.

> **Tip:** Contacts can be labeled with any of these properties, or with custom text, using the options available on the Label dialog.

Gap: Displays the *Length* minus the *RadiusSum* for the selected close contact, in Å.

This value is positive if the particles involved in the close contact are further apart than the sum of their particle radii and it is negative if the close contact is shorter than the sum of the particle radii.

> **Tip:** The value of *Gap* may be useful when studying voids in structures or if you are docking a small molecule into a larger structure.

IsVisible: Controls the visibility of the selected close contact. Available options are on or off.

Length: Displays the distance between the two particles involved in the close contact in Å.

LengthFraction: Displays the *Length* divided by the *RadiusSum* for the selected close contact. This corresponds to the scale used for the *Scaled sum of radii* slider control on the Close Contact Calculation dialog.

Name: Specifies the name of the selected close contact. A default *Name*, based on the *Names* of the particles involved in the contact, is assigned automatically but may be edited using the Properties Explorer.

> **Tip:** By manually editing the Name property and using the Label dialog to display the close contact *Names*, you can generate customized labels for equivalent contacts throughout the current structure.

RadiusSum: Displays the sum of the particle radii for the selected close contact, in Å.

RadiusType: Controls the type of particle radius being used to define the close contact. The value is assigned automatically, based on the selection made on the Close Contact Calculation dialog but may be edited using the Properties Explorer. Available options are:

- Atomic radii
    - VDW
    - Slater
    - Metallic
    - Ionic
    - Covalent
- Mesoscale bead radii
    - Bead

Style: Shows the display style of the selected close contact.

Theory in close contact calculations

The Calculate Close Contacts tool creates contacts between two atoms if the following criteria are met:

- The sum of the chosen atomic radii of the two atoms fulfills the chosen contact-distance criterion below.
- The pair of atoms is not excluded from forming contacts according to the chosen exclusion criterion below.

Absolute distance criterion

The distance criterion is:

```
distance < absolute distance
```

where `distance` = distance between the two candidate atoms and `absolute distance` = the chosen distance set using the slider on the Close Contact Calculation dialog.

Scaled distance criterion

The distance criterion is:

```
distance < TolFac × radius sum
```

where `distance` = distance between the two candidate atoms, `TolFac` = tolerance factor (this is set using the slider on the Close Contact Calculation dialog) and `radius sum` = $R_{Atom1} + R_{Atom2}$, where R denotes the chosen type of radius which is one of:

- VDW
- Slater
- Metallic
- Ionic
- Covalent

> **Note:** You can view and edit the values of the various types of atomic radii using the Element Properties dialog which is accessed from the *Modify* menu.

Bonded connection exclusion criterion

A candidate pair of atoms is excluded if there is a bonded path between the atoms, limited to a specified number of bonds.

Fragment exclusion criterion

A candidate pair of atoms is excluded if there is any bonded path between the atoms.

Set exclusion criterion

A candidate pair of atoms is excluded if both atoms are within the same Set. If the structure has symmetry or periodicity then the contact is only excluded if the atoms are in the same symmetry image of the Set.

Calculating Close Contacts

The Calculate Close Contacts tool uses the following procedure:

1. Between the existing close contacts, it tests for compliance with the above criteria and deletes non-compliant contacts. More specifically, it tests all selected contacts and all contacts attached to selected atoms for compliance. Between these, it deletes non-compliant contacts. Any other contacts remain, regardless of whether they satisfy the criteria.
2. Creates atom pairs using all selected atoms and their symmetry images on one side and the whole structure on the other.
3. Forms close contacts between all pairs that fulfill the above criteria.

> **Note:** If no objects are selected in a structure the contact calculation includes all atoms and contacts.

Monitoring Close Contacts

The close contact monitor is used to automatically recalculate contacts if the document is modified. The close contact monitor triggers a close contact calculation if one of the events in the following list occurs:

- The selection is changed.
- The choice or value of the distance criterion changes.
- The choice of exclusion criterion changes.
- The element type of an atom changes.
- An atom changes position.
- An atom, bond or contact is deleted or added.

If close contact calculation fails

Why close contact calculation may fail

Common reasons for close contact calculation to fail

- An infinite network was encountered when searching for atoms to exclude from the close-contact search. At present, the (default) fragment-based exclusion method cannot operate on systems containing infinite networks.

If close contact calculation fails

- Choose an alternative exclusion method, such as the bond-based method, on the Exclusions tab of the Close Contact Calculation dialog.

Close Contact Calculation dialog

The Close Contact Calculation dialog allows you to specify how close contacts are determined.

It contains the following tabs:

- Contact Distance: Allows you to specify the distance criterion used to determine close contacts.
- Exclusions: Allows you to select groups of close contacts that should be excluded.

Monitor close contacts: When checked, indicates that close contacts will be calculated and displayed dynamically.

Calculate: Performs a close contact calculation.

Calculate | 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.

Help: Displays the Help topic for the current tab.

Access methods

Menu	*Build	Close Contacts*
Toolbar	/ *Close Contact Options*

Contact Distance tab

The *Contact Distance* tab allows you to specify the distance criterion used to determine close contacts. Two different methods are available:

Absolute distance: Specify an absolute value for the distance criterion, either using the slider control or by typing a value in the associated text box. Default = 3.0 Å, slider range = 1.0 to 6.0 Å.

Scaled sum of radii: Alternatively, specify a distance criterion relative to the sum of the selected particle radii. Available particle radii are:

- Atomic radii
  - van der Waals
  - Slater
  - Metallic
  - Ionic
  - Covalent
- Mesoscale bead radii
  - Bead

> **Note:** You can view and edit the values of the various types of particle radii using the Element Properties dialog which is accessed from the *Modify* menu.

Specify the desired scale factor either using the slider control or by typing a value in the associated text box. Default = 0.891, slider range = 0.7 - 1.1.

Access methods

Menu	*Build	Close Contacts	Contact Distance*
Toolbar	![icon] */ Close Contact Options	Contact Distance*

Exclusions tab

The *Exclusions* tab allows you to select groups of close contacts that should be excluded from the close contacts list. Contacts between particle pairs within the specified distance criterion can be excluded based on any of the following:

Connected by *n* bonds or less: Contacts between particles connected by the specified number of bonds or fewer will be excluded.

In same bonded fragment: All contacts between particles in the same structural fragment, regardless of the number of bonds between them, will be excluded.

In same set: All contacts between particles in the same user defined set will be excluded.

Edit Sets...: Provides access to the Edit Sets dialog which allows you to create and modify sets in the current 3D model document.

Access methods

Menu	*Build	Close Contacts	Exclusions*
Toolbar	![icon] */ Close Contact Options	Exclusions*

Calculating hydrogen bonds

The *Calculate Hydrogen Bonds* tool allows you to calculate hydrogen bond patterns in a molecular structure.

Calculate Hydrogen Bonds

The criteria used to assign hydrogen bonds are the distance between the hydrogen and the acceptor atom and the donor-hydrogen-acceptor angle. You can edit the list of possible donor and acceptor elements, save sets of bond criteria as bonding schemes and switch between schemes easily. You can also enable automatic recalculation of hydrogen bonds to monitor changes to the hydrogen bond pattern during modification of the active document, or to investigate the dependence of hydrogen bonding configurations on bonding criteria.

To calculate hydrogen bonds

1. Select *Build | Hydrogen Bonds* from the menu bar, or click the *Calculate Hydrogen Bonds* arrow on the Atoms & Bonds toolbar and select *Hydrogen Bond Options* from the dropdown list to open the Hydrogen Bond Calculation dialog.
2. On the *H-bonding Scheme* tab, choose the set of bond criteria you wish to use from the dropdown list.
3. You can define which elements can serve as hydrogen bond donors or acceptors by clicking the *Edit...* button to open the Donor Acceptor List dialog.
4. If you wish Materials Studio to update the hydrogen bonding when changes occur in the structure, check the *Monitor hydrogen bonding* checkbox.
5. Select the *H-bond Geometry* tab and set the *Maximum hydrogen-acceptor distance* in Å and the *Minimum donor-hydrogen-acceptor angle* in ° by moving the sliders.
6. Click the *Calculate* button to calculate hydrogen bonds in the current 3D Atomistic document.

Default hydrogen bonding schemes

The default hydrogen bonding schemes include the three most commonly used sets of elements which act as donors or acceptors in hydrogen bonds. Details of the settings for the different schemes are listed in the table below.

Name	Hydrogen bond geometry		Terminals	
	max. length	min. angle	Donor	Acceptor
N, O, S	2.5 Å	90°	nitrogen, oxygen, sulfur	nitrogen, oxygen, sulfur
N, O, S + halogens (default)	2.5 Å	90°	N, O, S + fluorine, chlorine	N, O, S + fluorine, chlorine
N, O, S + halogens + carbon as donor	2.5 Å	90°	N, O, S + halogens + carbon	N, O, S + halogens

Theory in hydrogen bonding calculations

Hydrogen bond criteria

The Hydrogen Bond Calculation tool creates a hydrogen bond between two atoms if the following criteria are met:

- One atom is a hydrogen atom. The hydrogen atom is single bonded and the attached atom may act as a hydrogen bond donor.
- The second atom may act as a hydrogen bond acceptor and has at least one lone electron pair.
- The distance between the hydrogen atom and the acceptor is less than or equal to the Maximum hydrogen-acceptor distance.
- The value of the angle formed by the donor, hydrogen and acceptor atoms is at least the Minimum donor-hydrogen-acceptor angle.
- If both the hydrogen and acceptor atom are within the same molecule, they are separated by at least four nearest neighbor shells.

> **Note:** In this version of Materials Studio the Hydrogen Bond Calculation tool does not consider implicit hydrogen atoms. In order to calculate hydrogen bonds correctly hydrogen atoms must be present.

Calculating hydrogen bonds

The hydrogen bond calculation tool uses the following procedure.

1. Tests all selected hydrogen bonds for compliance with the hydrogen bond criteria. Deletes noncompliant bonds.
2. Creates donor-acceptor pairs using all selected atoms and their symmetry images on one side and the whole structure on the other.
3. Creates hydrogen bonds between all pairs that fulfill the hydrogen bond criteria.

> **Note:** If no object is selected in the structure, the hydrogen bond calculation includes all atoms and hydrogen bonds.

Monitoring hydrogen bonds

The hydrogen bond monitor is used to automatically recalculate hydrogen bond patterns if the document is modified. The hydrogen bond monitor triggers a hydrogen bond calculation if one of the following events occurs.

- The selection of atoms or hydrogen bonds is changed.
- The value of a hydrogen bond criteria is changed, the donor-acceptor list is modified or new bonding scheme is loaded.
- An atom changes position.
- An atom, bond or hydrogen bond is deleted or added.

Dialogs in hydrogen bond calculation

Hydrogen bond calculation functions are available in the following dialogs:

- Hydrogen Bond Calculation dialog
- Donor Acceptor List dialog

Hydrogen Bond Calculation dialog

The Hydrogen Bond Calculation dialog allows you to edit the criteria by which hydrogen bonds are assigned and to save or select a set of bond criteria. You can invoke a single hydrogen bond calculation or set up an automatic recalculation of hydrogen bonds.

The Hydrogen Bond Calculation dialog contains the following tabs:

- H-bonding Scheme: Allows you to save or select a set of bond criteria, invoke a single hydrogen bond calculation, or set up an automatic recalculation of hydrogen bonds.
- H-bond Geometry: Allows you to edit the criteria by which hydrogen bonds are assigned, invoke a single hydrogen bond calculation, or set up an automatic recalculation of hydrogen bonds.

Monitor hydrogen bonding: Enables the automatic recalculation of hydrogen bonds in the current model document.

> **Tip:** You can also activate *Monitor Hydrogen Bonding* from the Calculate Hydrogen Bonds dropdown list on the Atoms & Bonds toolbar.

If *Monitor Hydrogen Bonding* is enabled a checkmark is displayed on the Calculate Hydrogen Bonds tool on the Atoms & Bonds toolbar.

For more information on how the hydrogen bond monitor operates see Monitoring hydrogen bonds.

> **Note:** The hydrogen bond monitor will watch all selected atoms and bonds in the current active document (it will be deactivated temporarily if the active document is not an atomistic model). Frequent recalculation of hydrogen bonds is CPU intensive. To avoid performance degradation you should deactivate the hydrogen bond monitor when it is no longer required.

Calculate: Invokes a single calculation of the hydrogen bond pattern. For more information on how hydrogen bonds are calculated see Calculating hydrogen bonds.

Calculate | 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.

> **Note:** At present *Copy Script* does not copy the setting for any of the options on the *H-bonding Scheme* tab. A hydrogen bond calculation in script will always use the default scheme N, O, S + Halogens.

Help: Displays the Help topic for the current tab.

Access methods

Menu	*Build	Hydrogen Bonds*
Toolbar	*| Hydrogen Bond Options*

H-bonding Scheme tab

The *H-bonding Scheme* tab allows you to save or select a set of bond criteria, invoke a single hydrogen bond calculation or set up an automatic recalculation of hydrogen bonds.

Hydrogen bonding schemes: Allows you to select, save, rename and delete the active bonding scheme. A bonding scheme is the set of criteria used to assign hydrogen bonds.
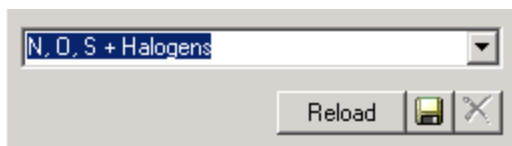
Hydrogen bonding scheme dropdown

Select the active bonding scheme from the list of pre-set bonding schemes or user defined schemes. The default bonding scheme is N, O, S + Halogens. Rename the current bonding scheme by typing a new name in the dropdown list text box, then click the *Save* button.

> **Note:** All modifications to the bond criteria apply to the current active bond scheme only, they do not affect any of the preset or saved user-defined bonding schemes. If you want to modify an existing bonding scheme you need to load the scheme first, modify the settings and save the settings into a new scheme. You may later delete the old bond scheme.

Reload: Loads the default settings for the currently selected bonding scheme.

Save: Saves the current bond criteria into the bonding scheme list.

If a scheme with the same name exists already, the name of the current bonding scheme is modified to provide a unique name.

> **Note:** The *Save* operation never overwrites an existing bond scheme.

> **Note:** The list of bonding schemes is part of the current project. Newly saved bonding schemes are written permanently to disk only if you save the project before exiting Materials Studio.

Delete: Deletes the current bond criteria from the bonding scheme list.

After deleting a scheme from the list the default scheme is loaded.

> **Note:** Pre-set bonding schemes cannot be deleted from the list. If you load a pre-set bonding scheme *Delete* is disabled. You may, however, modify the bonding scheme once it is loaded and save it under a new name into the bonding scheme list.

Donor-acceptor list

Edit...: Opens the Donor Acceptor List dialog which allows you to edit the list of elements that may act as hydrogen bond donors or acceptors.

Access methods

Menu	*Build	Hydrogen Bonds	H-bonding Scheme*
Toolbar	*	Hydrogen Bond Options	H-bonding Scheme*
Toolbar	calculates hydrogen bonds using the current bond criteria

H-bond Geometry tab

The *H-bond Geometry* tab allows you to edit the criteria by which hydrogen bonds are assigned, invoke a single hydrogen bond calculation or set up an automatic recalculation of hydrogen bonds.

Hydrogen bond geometry

Maximum hydrogen-acceptor distance: Specify the maximum distance (in Å) between the hydrogen and the acceptor atom for which hydrogen bonding is possible. Range = 0 to 4 Å.

> **Tip:** Any positive values up to 10 Å may be set using the text box to the right of the slider controls.

Minimum donor-hydrogen-acceptor angle: Specify the minimum angle between the donor, hydrogen and acceptor atom in degrees for which hydrogen bonding is possible. Range = 0 to 180°.

Access methods

Menu	*Build	Hydrogen Bonds	H-bond Geometry*
Toolbar	*	Hydrogen Bond Options	H-bond Geometry*
Toolbar	calculates hydrogen bonds using the current bond criteria

Donor Acceptor List dialog

The Donor Acceptor List dialog allows you define a list of elements which act as hydrogen bond donors or acceptors.

Click the *Edit...* button on the H-bonding Scheme tab of the Hydrogen Bond Calculation dialog to access the Donor Acceptor List dialog. Select elements from the periodic table and click on the appropriate buttons to designate them as donors, acceptors, both, or neither.

Periodic table

The following color code is used to show the possible role of an element in hydrogen bonding.

Color	Meaning
Red color	Element may act as a hydrogen bond donor only
Blue color	Element may act as a hydrogen bond acceptor only
Purple color	Element may act as either a hydrogen bond donor or acceptor
Yellow color	Element may not be a hydrogen bond donor *and* may not be a hydrogen bond acceptor

A set of elements may be selected from the periodic table using the following operations:

Operation	Meaning
Click on element	Toggle selection status of element and reset status of all other elements to non-selected
CTRL + Click on element	Toggle selection status of element without affecting the status of any other element

Donor: Assigns donor-only status to all elements currently selected in the periodic table.

Acceptor: Assigns acceptor-only status to all elements currently selected in the periodic table.

Both: Assigns donor-or-acceptor status to all elements currently selected in the periodic table.

Neither: Removes all selected elements from the donor-acceptor list.

> **Note:** Changing the donor-acceptor status of one or more elements causes the color coding of the periodic table to be updated to reflect the new donor-acceptor list settings.

OK: Accepts the new donor acceptor list and makes it the current one.

Cancel: Cancels the changes entered and closes the dialog.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Build	Hydrogen Bonds	H-bonding Scheme	Edit...*
Toolbar	*	Hydrogen Bond Options	H-bonding Scheme	Edit...*

Calculating charges

Classical simulation forcefields include electrostatic interaction terms. In order to be able to calculate these terms atomic charges must be specified. Atomic charges can be inferred, in some simple cases, from experimental data. It is also possible to use *ab initio* methods to calculate charges for small systems. However, for large systems, such as polymers, it is not practical to obtain point charges by either experimental or *ab initio* approaches and an alternative approach is required.

Materials Studio provides two methods for calculating approximate atomic point charges, QEq and Gasteiger.

The QEq method is based on the atomic configuration and the electronegativities of the various atoms of which the systems is comprised. Unlike the Gasteiger method, which depends on connectivity, the QEq algorithm does not make use of the bonding pattern. The calculation is iterative for structures that contain hydrogens.

The Gasteiger method rapidly calculates atomic changes in bonded and nonconjugated systems. Atoms are characterized by their orbital electronegativities. In the calculation, only the connectivities of the atoms are considered, so only the topology of a molecule is important. Through an iterative procedure, partial equalization of orbital electronegativity is obtained.

Assigning atomic charges

The Charges dialog allows you to calculate approximate atomic point charges for a whole system or a selection of atoms, using either the Gasteiger (Gasteiger and Marsili, 1980) or the QEq (Rappe and Goddard, 1991) method.

To calculate atomic point charges using the Gasteiger method

> **Note:** If no atoms are selected in the active document, charges will be calculated for all atoms.

1. Select the atoms for which you wish to calculate atomic charges.
2. Choose *Charges* from the Modify menu.
3. Select the Calculate tab on the Charges dialog.
4. Specify Gasteiger using the *Method* dropdown list.
5. If desired, use the *More...* button to access the Gasteiger Options dialog. This allows you to set alternative values for the *Maximum iterations*, *Convergence limit* and *Parameter set*.
6. Click the *Calculate* button to determine atomic point charges for the selected atoms.

To calculate atomic point charges using the QEq method

> **Note:** If no atoms are selected in the active document, charges will be calculated for all atoms.

1. Select the atoms for which you wish to calculate atomic charges.
2. Choose *Charges* from the Modify menu.
3. Select the Calculate tab on the Charges dialog.
4. Specify QEq using the *Method* dropdown list.
5. If desired, use the *More...* button to access the QEq Options dialog. This allows you to set alternative values for the *Initial charge*, *Maximum iterations*, *Convergence limit* and *Parameter set*.
6. Click the *Calculate* button to determine atomic point charges for the selected atoms.

Editing charges

The Charges dialog allows you to modify the values of existing charges on atoms or beads.

To modify point charges for selected particles

> **Note:** If no particles are selected in the active document, any modifications will be applied to all particles.

1. Select the atoms or beads whose charges you wish to modify.
2. Choose *Charges* from the Modify menu.
3. Select the Edit tab on the Charges dialog.
4. Choose one of the charge editing methods from the *Edit charges* section:
   - *Set all charges to* - this method will set all charges on the currently selected particles to the value specified.
   - *Set total charge to* - this method will calculate the current total charge, compare it with the required total charge and adjust the charge of all selected particles by the same amount to give the desired total charge.
   - *Scale charges by* - this method multiplies all select charges by the specified value.
   - *Average all charges* - this methods calculates the average charge on all the select particles and then sets the charge of all selected particles to this value.
5. Click the *Assign* button to modify the charges on the selected particles.

Assigning charge groups

The Charges dialog allows you to calculate charge groups automatically or specify them manually. In addition, you can also remove existing charge groups.

To perform an automatic charge groups calculation

1. Ensure that the active document is the 3D Atomistic document containing the structure that you wish to create charge groups for. The complete structure must be charge neutral (within the specified tolerance) and should not contain any existing charge groups. If the structure is periodic, it must be composed of discrete atoms or fragments rather than being an infinite network of covalently bonded atoms.
2. Choose *Modify | Charges* from the menu bar to display the Charges dialog.
3. Select the Charge Groups tab.
4. Specify a value for the *Total charge tolerance*.
5. Specify the *Method*. If you choose *Subunits*, Materials Studio will attempt to create charge groups based on the repeat unit hierarchy already defined in the model. If you choose *Divide-and-conquer*, Materials Studio will assign charge groups by repeatedly partitioning the molecule into neutral sections.
6. Click the *Calculate* button.

To assign charge groups manually

1. Ensure that the active document is the 3D Atomistic document containing the atoms that you wish to define a charge group for.

2. Choose *Modify | Charges* from the menu bar to display the Charges dialog.

3. Select the *Charge Groups* tab.

4. Select the atoms that will form the charge group in the active structure document.

5. Click the *Define from selected atoms* button. Materials Studio will attempt to create a single charge group from the selected atoms. A charge group will not be created if any of the selected atoms are already part of an existing charge group.

6. Repeat this procedure for each charge group that you wish to define.

> **Note:** Great care must be taken when assigning or editing charge groups manually. Most applications that use charge groups require that every atom in the input structure belongs to a charge group and that there is no overlap between charge groups. Calculations may fail if you assign charge groups that do not conform to these requirements.
>
> This is especially true for applications that use `.car`/`.mdf` files. Due to the nature of the CAR/MDF file format, all atoms within a charge group must also belong to the same molecule or repeat unit, in addition to the above requirements. If the charge groups do not conform to all these requirements, they will not be written to the file.

> **Tip:** If you are unsure whether a document contains molecules or repeat units, check the *Filter* dropdown list in the Properties Explorer, which lists all the objects present in the currently active document. Some of these objects can be visualized independently, but others can only be seen by coloring atoms using the Display Style dialog.

To remove charge groups

1. Ensure that the active document is the 3D Atomistic document containing the charge group(s) that you wish to delete.

2. Choose *Modify | Charges* from the menu bar to display the Charges dialog.

3. Select the *Charge Groups* tab.

4. Select the atoms that comprise the charge group(s) to be removed in the active structure document. If no atoms are selected, all the charge groups in the document will be removed.

5. Click the *Remove charge groups* button. Materials Studio will attempt to delete the charge group(s) defined for the selected atoms. For a charge group to be removed, all of its constituent atoms must be selected.

Charging algorithms

Materials Studio provides two methods for calculating approximate atomic point charges, Gasteiger (Gasteiger and Marsili, 1980) and QEq (Rappé and Goddard, 1991). Both of these methods exploit the notion of electronegativity. There are a number of definitions of electronegativity but to determine charges, Mulliken's definition is used:

Eq. 1

$$\chi = \frac{I + E}{2}$$

where *I* is the ionization potential and *E* is the electron affinity.

Gasteiger

The basis of the Gasteiger method is the equalization of atomic electronegativities over a network of sigma bonded atoms.

The concept of electronegativity can be extended to apply to individual atomic orbitals, and specifically to those valence orbitals that participate in bonding. The electronegativity of an orbital is a function of the occupancy or more simply the charge located within the orbital. An empty orbital will be able to attract electrons whereas a fully occupied orbital will not. This can be expressed quantitatively as:

Eq. 2

$$\chi_i = a_i + b_i Q + c_i Q^2$$

where Q is the total charge on the atom regardless of which orbitals in which it is located. The coefficients a_i, b_i and c_i are a function of the element and hybridization combination. Generally, a_i and b_i > c_i, so that this relation indicates that as charge density increases the electronegativity will decrease.

The heart of the algorithm is an iterative loop that transfers charge between atoms until the electronegativities on each orbital participating in a sigma bond are equal. Suppose atom a is bonded to atom b, and let the electronegativities of the orbitals that form the sigma bond between these atoms be χ_a and χ_b such that $\chi_b > \chi_a$, so that there is a tendency for charge to move from a to b. For the jth iteration the charge transferred for this pair is estimated to be:

Eq. 3

$$\Delta q_i = \frac{\chi_b - \chi_a}{\chi_{a+}} \left(\frac{1}{2} \right)^j$$

where χ_a^+ is the electronegativity the orbital on a would have if it were empty. The transfer of charge will alter the electrostatic field and tend to prevent further transfer of charge. This is recognized in Eq. 3 by the factor $(1/2)^j$, which damps the charge transfer between atoms in a given iteration. This calculation is repeated for all other atoms bonded to a, with the additional requirement that if $\chi_b < \chi_a$, χ_b^+ is used in place of χ_a^+ in Eq. 3. The total charge transferred between atom a and its sigma bonded neighbors is found by summing Δ_q^j, and then added to the current charge on a. This procedure is applied to all other atoms. The new charges are then used to recalculate the orbital electronegativities using Eq. 3 (the change in electronegativities will tend to inhibit further transfer hence the need for a damping mechanism). This completes a single iteration. The process is repeated until the largest change in charge for any atom is less that a specified tolerance.

QEq

The basis of the QEq method is the equilibration of atomic electrostatic potentials with respect to a local charge distribution.

The energy of an atom as a function of charge, can be written as a Taylor expansion:

Eq. 4

$$E_A(Q) = E_{A0} + Q_A \left(\frac{\partial E}{\partial Q} \right)_{A0} + \frac{1}{2} Q_A \left(\frac{\partial^2 E}{\partial Q^2} \right)_{A0} + \ldots$$

where the expansion has been truncated to second order. E_A^0 is the energy of an atom with zero charge. By considering the energy of an atom when it carries a charge of +1 or -1, it is straightforward to show that:

Eq. 5

$$\left(\frac{\partial E}{\partial Q}\right)_{A0} = \frac{1}{2}(IP + EA) = \chi_A^0$$

and

Eq. 6

$$\left(\frac{\partial^2 E}{\partial Q^2}\right)_{A0} = IP - EA = J_{AA}^0$$

where J_{AA}^0 is the Coulomb repulsion between two electrons in the same orbital. Thus, the energy of an isolated atom as a function of charge, can be written as:

Eq. 7

$$E_A(Q) = E_{A0} + \chi_A^0 Q_A + \frac{1}{2} J_{AA}^0 Q_A^2$$

The value of J_{AA}^0 depends on the size of the atom but can be approximated using:

Eq. 8

$$J_{AA}^0 = \frac{14.4}{R_{A^0}}$$

The quadratic expansion of Eq. 7 is only valid for a range of charges so, during a charge equilibration calculation, atomic charges are confined to this range. The range depends on the atom in question and is determined by the maximum and minimum oxidation states of the valence shell, thus:

$-7 < Q_{Li} < +1$
$-4 < Q_C < +4$
$-2 < Q_O < +6$

Isolated atoms are of limited interest in molecular simulation and Eq. 7 must be adjusted to account for the affects of the charges on surrounding atoms. This is done by introducing Coulombic interactions:

Eq. 9

$$E(Q_1 \dots Q_N) = \sum \left(E_{A0} + \chi_A^0 Q_A + \frac{1}{2} J_{AA}^0 Q_A^2\right) + \sum_{A<B} Q_A Q_B J_{AB}$$

$$E(Q_1 \dots Q_N) = \sum \left(E_{A0} + \chi_A^0 Q_A\right) + \frac{1}{2}\sum_{A,B} Q_A Q_B J_{AB}$$

where N is the number of atoms in the model and J_{AB} is a Coulomb term for the interaction of charges on different atoms. Differentiation of Eq. 7 leads to an atomic scale chemical potential:

Eq. 10

$$\chi_A(Q_1 \dots Q_N) = \frac{\partial E}{\partial Q_A} = \chi_A^0 + \sum_B J_{AB} Q_B$$

The optimal value for the charges will occur when the chemical potential is the same on all atoms, that is:

Eq. 11

$$\chi_1 = \chi_2 = \ldots = \chi_N$$

This relation gives N - 1 independent linear equations in N unknowns and together with the restriction on total charge:

Eq. 12

$$Q_{tot} = \sum_{i=1}^{N} Q_i$$

can be written as:

Eq. 13

$$CQ = -D$$

where

Eq. 14

$$D_1 = -Q_{tot}$$
$$D_i = \chi_i^0 - \chi_1^0 \text{ for } i \geq 2$$

and

Eq. 15

$$C_{1i} = Q_i$$
$$C_{ij} = J_{ij} - J_{1j} \text{ for } i \geq 2$$

Eq. 13 can be solved by matrix inversion and will, in principle, lead to a complete set of charges.

Before Eq. 13 can be solved the value of the Coulomb term, J_{AB}, must be specified. For large distances J_{AB} can be approximated as:

Eq. 16

$$J_{AB} = \frac{14.4}{R}$$

For short distances, where there is significant overlap of the charge distribution, this expression is not be appropriate since it tends to infinity, rather than a value related to J_{AA} or J_{BB}. A more accurate expression must account for the overlap of electron density. This is effected in Materials Studio by calculating an approximate overlap integral using Slater type orbitals.

Using Eq. 1 to calculate the electronegativity of hydrogen gives a value of 7.17 eV which is inconsistent with other measures of electronegativity. By examining the charges on a number of hydrides, Rappé and Goddard (1991) showed that the J_{HH} Coulombic term is charge dependent and given by:

Eq. 17

$$J_{HH}(Q_H) = (1 + Q_H / \zeta_H^0) J_{HH}^0$$

where J_{HH}^0 is the Coulomb overlap integral for an isolated Hydrogen atom and ... is the exponent that appears in the Slater type orbitals used to calculate J_{HH}^0. If the model for charges includes hydrogen atoms, then J_{HH} must be used leading to a set of non-linear equations. These equations are solved

iteratively by assuming an initial value for Q_H, the iterating until the charges on all atoms are self consistent.

QEq parameter file format

The *Parameter set* list on the QEq Options dialog contains an entry for each file in the `Resources\Simulation` directory (which can be found in `Materials Studio\share` in a standard Materials Studio installation) with a name of the form `QEq*.chg`. You can edit these files in order to extend them to cover new atom types or you can add new files to the directory to create new parameter sets.

The QEq parameter file consists of one line for each element recognized by the charging system. Each line contains seven fields, occupying the columns listed below.

Field	Columns	Description
1	1-2	The element symbol for the atom.
2	11-15	The principal quantum number of the valence shell for the atom.
3	16-20	The minimum possible formal charge (the formal charge on the atom when the valence shell is full).
4	21-25	The maximum possible formal charge (the formal charge on the atom when the valence shell is empty).
5	26-35	The electronegativity of the atom.
6	36-45	The idempotential (or "hardness") J^0_{AA} for the atom (see Eq 6).
7	46-55	The characteristic atomic size R^0_A of the atom.

Note: Lines beginning with # are interpreted as comments and ignored. Only spaces should be used to separate fields, as tabs may not be interpreted in the way they are intended.

Gasteiger parameter file format

The *Parameter set* list on the Gasteiger Options dialog contains an entry for each file in the `Resources\Simulation` directory (which can be found in `Materials Studio\share` in a standard Materials Studio installation) with a name of the form `Gast*.chg`. You can edit these files in order to extend them to cover new atom types or you can add new files to the directory to create new parameter sets.

The Gasteiger parameter file consists of two sections. The first defines the atom types recognized by the charging system. The second defines the damping factor used for the calculation.

ATOM_TYPING Section

This section defines the parameters for each atom used in the model. It begins with a line containing the token ATOM_DATA and ends with the token END. For example:

```
ATOM_DATA
#  Desc    Val.State   a       b       c       Chi+    q0      qAdd
#-------------------------------------------------------------------
H   DEFAULT             7.1700  6.2400  -0.5600  20.0200  0.0000  0.0000
END
```

Each line contains nine fields, occupying the columns listed below. Fields 1, 2, and 3 together, uniquely specify an atom type, the remaining fields provide parameter values for atoms in the model which match this type. Field 3 may be left blank, to make a more general type.

> **Note:** Atoms will be assigned the parameters of the most specific atom type which matches.

Field	Columns	Description	
1	1-2	The element symbol for the atom.	
2	5-14	The chemical environment of the atom. This field may take one of the following values:	
		DEFAULT	any atom in any environment
		CARBOXY	oxygen atom in a carboxy group
		NITRO	nitrogen or oxygen atom in a nitro group
		PHOSPHATE	oxygen atom in a phosphate group
		AMIDE	nitrogen or oxygen atom in an amide group
		CATION	nitrogen, oxygen, or sulfur atom as cation
		ANION	oxygen or carbon atom as anion
		HYPERVAL	sulfur atom with more than three bonds
		S_6_4	sulfur atom with 4 bonds and total bond order of 6
		S_4_4	sulfur atom with 4 bonds and total bond order of 4
		S_4_3	sulfur atom with 3 bonds and total bond order of 4
		ISOLATED	any atom with no bonds
3	16-26	The hybridization state of the atom. This field may be left blank to match an atom with any hybridization, or may take one of the following values: LINEAR, TRIGONAL, TETRAHEDRAL.	
4	28-35	The coefficient a_i in Eq. 2 for the atom.	
5	38-45	The coefficient b_i in Eq. 2 for the atom.	
6	48-55	The coefficient c_i in Eq. 2 for the atom.	
7	57-64	The orbital electronegativity of the positive ion (see Eq. 3). This field may be left blank, in which case the value will be calculated from the coefficients a_i, b_i and c_i.	
8	66-73	The charge assigned to the atom at the start of the calculation; this is typically 0.	
9	75-82	The charge correction added to the charge on the atom at the end of the calculation; this is typically 0.	

DAMPING_FACTORS Section

This section defines the damping factor, $(1/2)^j$ of [Eq 3](#). It has the format shown below. You should change only the numerical value in columns 10-17. The damping factor must be non-negative.

```
DAMPING_FACTORS
DEFAULT    0.5000
END
```

> **Note:** Lines beginning with # are interpreted as comments and ignored. Only spaces should be used to separate fields, as tabs may not be interpreted in the way they are intended.

If charging fails

Why charging may fail

Common reasons for charging to fail

1. Parameters are not defined for all the elements in the structure.
2. Not enough atoms are selected. For example, the QEq algorithm requires at least two atoms.
3. The model carries a net charge. The QEq method requires the total initial charge on the atoms in a periodic model to be 0. This restriction does not apply to nonperiodic models.
4. The Gasteiger and QEq charging methods are iterative and may not converge within the specified number of cycles. In such situations, the atomic charges in the structure will be updated, but they may not be as accurate as possible. A warning message will be displayed to inform you that this is the case.

> **Tip:** Use *View | Project Log* to see if any error or warning messages have been reported.

If charging fails

1. Choose a parameter file that contains parameters for all atoms in the structure, deselect those atoms for which parameters are not available or add the atoms to the [Gasteiger](#) or [QEq](#) parameter file.
2. Choose a different *Initial charge* setting using the [QEq Options](#) dialog.
3. Increase the *Maximum iterations* or *Convergence limit* for the charging calculation using the [Gasteiger Options](#) or [QEq Options](#) dialog.

Charges dialog

The Charges dialog allows you to equilibrate atomic charges across a bonded system using either Gasteiger or QEq methods, modify individual atomic charges, and define charge groups.

The Charges dialog contains the following tabs:

- [Calculate](#): Allows you to select a charge equilibration method.
- [Edit](#): Allows you to modify individual atomic charges.
- [Charge Groups](#): Allows you to create or remove charge groups.

Help: Displays the Help topic for the current tab.

Access methods

Menu	*Modify	Charges*

Calculate tab

The *Calculate* tab allows you to select a charge equilibration method.

Charge equilibration method

Charge equilibration uses the specified method to redistribute the overall charge on the atoms in the current 3D Atomistic document.

Method: Select the method to be used for charge equilibration from the dropdown list. Available options are:

- QEq - takes into account the geometry and the electronegativities of the various atoms. Molecular conformation, as well as connectivity, affects the charge calculation. The calculation is iterative for structures that contain hydrogens.
- Gasteiger - atoms are characterized by their orbital electronegativities. Only the connectivities of the atoms are considered, so only the topology of a molecule is important. Through an iterative procedure, partial equalization of orbital electronegativity is obtained.

More...: Provides access to further options for the selected charge equilibration method.

Calculate: Determines the atomic charges on the atoms in the current selection using the specified charge equilibration method.

> **Note:** The *Calculate* button is enabled only when the current selection contains atoms, or if nothing is selected the 3D Atomistic document must contain atoms.

Access methods

Menu	*Modify	Charges	Calculate*

Gasteiger Options dialog

The Gasteiger Options dialog allows you to set parameters for the Gasteiger charge equilibration method.

Maximum iterations: Specify the maximum number of iteration cycles for the charge calculation. If this number of cycles is reached, then the calculation will stop, even if the convergence criteria are not satisfied.

Convergence limit: Specify the maximum transfer of charge permitted between any two atoms. The calculation will stop when the maximum transfer of charge is less than this value.

Parameter set: Select the Gasteiger element-based parameter set to be loaded from the dropdown list. Three different Gasteiger parameter sets are available:

Parameter set	Description
Gast_original1.0	The parameters presented in the original publication on the method (Gasteiger & Marsili, 1980). It contains parameters for C, H, O, N, S, and the halogens.
Gast_polygraf1.0	An augmented version of the original, containing in-house enhancements for the treatment of nitro, carboxylate, phosphate, 4-valent nitrogen, and hypervalent sulfur functional groups. These refinements were first introduced in the PolyGraf code.

Parameter set	Description
Gast_quanta1.0	An augmented version of the original, containing in-house enhancements for the treatment of amide, carbanion, formally charged oxygen and nitrogen, aluminum, phosphorus, and sulfur in a variety of chemical environments. These refinements were first introduced in the Quanta code.

Tip: Add more atom types to the Gasteiger parameter file by editing it manually.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modify	Charges	Calculate	More...*

QEq Options dialog

The QEq Options dialog allows you to set parameters for the QEq charge equilibration method.

Note: Due to the nature of the algorithm used for QEq charge equilibration, it is not recommended to use this charging algorithm with structures larger than about 200 atoms. Above this size the computation times can become excessive.

Initial charge: Select how the initial charges on the atoms will be set from the dropdown list. Available options are:

Value	Meaning
Current	The current atomic charges will be used.
Formal	The formal charges on each atom will be used.
Zero	All charges will be set to 0.

Maximum iterations: If the structure contains hydrogen atoms, the QEq calculation is iterative. Specify the maximum number of iteration cycles for the charge calculation. If this number of cycles is reached, then the calculation will stop even if the convergence criteria are not satisfied.

Convergence limit: Specify the maximum change in charge permitted on a hydrogen atom. The calculation will stop when the maximum change in charge is less than this value.

Parameter set: Select the QEq parameter set to be loaded from the dropdown list. A number of different QEq parameter sets are available and each set is optimized for a different type of system:

Parameter set	Description
QEq_neutral1.0	The parameter set from the original work on the QEq method (Rappé and Goddard, 1991). Recommended for systems containing neutral oxidation state metals (for example, alloys).
QEq_charged1.0	Originally generated for positive metal ions. Recommended for systems containing metal ions (for example, organometallics).
QEq_charged1.1	Largely the same as QEq_charged1.0, but has revised parameters for better treatment of group 13 (B, Al, Ga, In, Tl), group 14 (C, Si, Ge, Sn, Pb), and group 15 (N, P, As, Sb, Bi) elements. Recommended for the calculation of zeolite charges.

> **Tip:** Add more atom types to the QEq parameter file by editing it manually.

All parameter sets above were supplied by Dr A. K. Rappé.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modify	Charges	Calculate	More...*

Edit tab

The *Edit* tab allows you to modify individual charges on selected atoms or beads.

Edit charges

Total charge: Displays the total charge on all selected particles (or on the entire system if no particles are selected).

Set all charges to: When selected, indicates that the charge on each selected atom or bead will be set to the specified value.

Set total charge to: When selected, indicates that a calculated fixed charge will be added to each selected particle such that the total charge on all selected particles equals the specified value.

Scale charges by: When selected, indicates that the charge on each selected particle will be multiplied by the specified value.

Average all charges: When selected, indicates that the charge on each selected atom or bead will be set to the arithmetic mean of the charges on all the selected particles.

Assign: Makes the specified changes to the charges on the selected particles.

> **Note:** The *Assign* button is enabled only when the current document is a 3D Atomistic document.

Access methods

Menu	*Modify	Charges	Edit*

Charge Groups tab

The *Charge Groups* tab allows you to create or remove charge groups.

Charge group calculation

Total charge tolerance: Specify the maximum absolute value of the total charge for a group of atoms that can form a valid charge group.

Method: The method used to assign charge groups. If Subunits method is selected, the calculation attempts to create charge groups based on the repeat unit hierarchy already defined in the model. If Divide-and-conquer method is chosen, charge groups are assigned by repeatedly partitioning the molecule into neutral sections.

Calculate: Computes charge groups in the currently active 3D Atomistic document.

> **Note:** The calculation will fail if the selection already contains charge groups or if the complete structure is not charge neutral (within the specified tolerance). In the case of periodic systems, charge groups can only be calculated for structures composed of discrete atoms or fragments and not for infinite networks of covalently bonded atoms.

Color by charge group: When checked atoms will be recolored according to their charge group after a *Calculate*, *Define*, or *Remove* operation.

Edit charge groups

Total charge: Displays the total charge on all selected particles (or on the entire system if no particles are selected).

Define from selected atoms: Attempts to create a single charge group from the selected atoms.

> **Note:** A charge group will not be created if any of the selected atoms are already part of an existing charge group.

Remove charge groups: Deletes the charge groups defined for the selected atoms. For a charge group to be removed, all of its constituent atoms must be selected.

> **Note:** Great care must be taken when assigning or editing charge groups manually. Most applications that use charge groups require that every atom in the input structure belongs to a charge group and that there is no overlap between charge groups. Calculations may fail if you assign charge groups that do not conform to these requirements.
>
> This is especially true for applications that use `.car/.mdf` files. Due to the nature of the CAR/MDF file format, all atoms within a charge group must also belong to the same molecule or repeat unit, in addition to the above requirements. If the charge groups do not conform to all these requirements, they will not be written to the file.

> **Tip:** If you are unsure whether a document contains molecules or repeat units, check the *Filter* dropdown list in the Properties Explorer, which lists all the objects present in the currently active document. Some of these objects can be visualized independently, but others can only be seen by coloring atoms using the Display Style dialog.

Access methods

Menu	*Modify	Charges	Charge Groups*

Charge Groups dialog

The *Charge Groups* dialog is used by multiple modules and allows you to create or remove charge groups.

Charge group calculation

Total charge tolerance: Specify the maximum absolute value of the total charge for a group of atoms that can form a valid charge group.

Method: The method used to assign charge groups. If Subunits method is selected, the calculation attempts to create charge groups based on the repeat unit hierarchy already defined in the model. If Divide-and-conquer method is chosen, charge groups are assigned by repeatedly partitioning the molecule into neutral sections.

Calculate: Computes charge groups in the currently active 3D Atomistic document.

Note: The calculation will fail if the selection already contains charge groups or if the complete structure is not charge neutral (within the specified tolerance). In the case of periodic systems, charge groups can only be calculated for structures composed of discrete atoms or fragments and not for infinite networks of covalently bonded atoms.

Color by charge group: When checked atoms will be recolored according to their charge group after a *Calculate*, *Define*, or *Remove* operation.

Edit charge groups

Total charge: Displays the total charge on all selected particles (or on the entire system if no particles are selected).

Define from selected atoms: Attempts to create a single charge group from the selected atoms.

Note: A charge group will not be created if any of the selected atoms are already part of an existing charge group.

Remove charge groups: Deletes the charge groups defined for the selected atoms. For a charge group to be removed, all of its constituent atoms must be selected.

Note: Great care must be taken when assigning or editing charge groups manually. Most applications that use charge groups require that every atom in the input structure belongs to a charge group and that there is no overlap between charge groups. Calculations may fail if you assign charge groups that do not conform to these requirements.

This is especially true for applications that use `.car`/`.mdf` files. Due to the nature of the CAR/MDF file format, all atoms within a charge group must also belong to the same molecule or repeat unit, in addition to the above requirements. If the charge groups do not conform to all these requirements, they will not be written to the file.

Tip: If you are unsure whether a document contains molecules or repeat units, check the *Filter* dropdown list in the Properties Explorer, which lists all the objects present in the currently active document. Some of these objects can be visualized independently, but others can only be seen by coloring atoms using the Display Style dialog.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modules	[Module name]	Calculation	Energy	Forcefield More...	Charge Groups More...*
Toolbar	*	Calculation	Energy	Forcefield More...	Charge Groups More...*
	*	Calculation	Energy	Forcefield More...	Charge Groups More...*
	*	Calculation	Energy	Forcefield More...	Charge Groups More...*
	*	Calculation	Energy	Forcefield More...	Charge Groups More...*
	*	Calculation	Energy	Forcefield More...	Charge Groups More...*
	*	Calculation	Energy	Forcefield More...	Charge Groups More...*
	*	Calculation	Energy	Forcefield More...	Charge Groups More...*
	*	Powder Refinement	Energy	Forcefield More...	Charge Groups More...*
	*	Calculation	Energy	Forcefield More...	Charge Groups More...*

Constraints

During a simulation, it is often desirable, or necessary, to constrain the motion of an atom, bead or a group of these particles. The application of a constraint, in general, reduces the number of degrees of freedom required to describe the system and often speeds up a calculation.

There are many forms of constraints; one important class is symmetry constraints, which restrict the motion of particles so that the symmetry of a system is preserved. The constraints discussed here are particle constraints, which fall into two categories:

- fixed, where the coordinates of a particle are fixed absolutely in space.
- rigid body, where the coordinates of each particle in a specified collection of particles (a motion group) are fixed relative to the coordinates of all the other particles in the group.

An example of the use of fixed atoms is in the simulation of sorbate-surface interactions. The details of the motion of those atoms that are in the surface or, more often, below it do not generally impact the dynamics of the sorbate to any great degree and fixing these atoms can speed up the simulation.

Rigid bodies are useful in the optimization of molecular crystal structures, as they allow known functional group configurations to be maintained during optimization, as well as reducing the calculation time required for a simulation.

> **Note:** There is an important distinction between constraints and restraints. A constraint prevents motion, placing an absolute restriction on a calculation. A restraint allows motion, but imposes a penalty if it occurs. This produces an energetic bias that tends to lead a calculation in a particular direction.

Imposing constraints

The Materials Visualizer allows you to set a number of different constraints on particles:

- Fixed particles - individual Cartesian coordinates of atoms or beads can be fixed in any direction
- Fixed measurement - distance, angle, and torsion measurements can be constrained to constant values
- Motion groups - specified collections of particles can be defined such that the group can be translated or rotated while the coordinates of each particle in the group remain fixed relative to the coordinates of all the other particles in the group

To fix particles

1. Make the 3D structure document containing the atoms or beads to be constrained the active document and select the appropriate particles. If no particles are selected, all particles will be deemed to be in scope, by default.
2. Choose *Modify | Constraints* from the menu bar to display the Edit Constraints dialog.
3. Select the Atom tab.
4. Check the *Fix Cartesian position* checkbox if you wish to fix the selected particles in Cartesian space. Check the appropriate checkboxes to fix the positions of the selected particles in the required Cartesian directions.
5. For atoms in periodic structures only, check the *Fix fractional position* checkbox if you wish to fix the positions of the selected atoms within the lattice.

To fix measurements

1. Make the 3D structure document containing the measurements to be constrained the active document and select the appropriate measurements. If no measurements are selected, all measurements will be deemed to be in scope, by default.
2. Choose *Modify | Constraints* from the menu bar to display the Edit Constraints dialog.
3. Select the Measurement tab.
4. Check the appropriate checkbox to fix the selected measurement.

> **Note:** Some modules in Materials Studio only honor certain types of constraints. Other modules ignore all constraints. See the Support for constraints in Materials Studio topic for more details.

To create a motion group

1. Make the 3D structure document that you wish to add the motion group to the active document.
2. Choose *Modify | Motion Groups* from the menu bar to display the Motion Groups dialog.
3. If you want Materials Studio to automatically assign motion groups for all free fragments in the currently active document, click the *Assign automatically* button.

> **Note:** If the structure already contains motion groups, an error message will be generated when *Assign automatically* is pressed. The existing motion groups must be deleted before automatic assignment of motion groups can be carried out.

Alternatively, to define motion groups manually, select the atoms that you want to include in the motion group and click the *Create from selected atoms* button.

> **Note:** If any of the selected atoms are already part of a motion group, an error message will be generated when *Create from selected atoms* is pressed. You must either delete the existing motion group or deselect any atoms that already belong to a motion group in order to create a new motion group.

It is not always clear what constraints are currently imposed on a structure, so the Materials Visualizer provides tools to assist you in visualizing constraints.

To color fixed particles

1. Choose *View | Display Style* from the menu bar, click the *Display Style* button on the 3D Viewer toolbar, or right-click in the 3D structure document and select *Display Style* from the shortcut menu to display the Display Style dialog.
2. Select the Atom tab.
3. Choose *Color by* in the *Coloring* section and select Constraint from the dropdown list. Constrained particles will be colored red and unconstrained atoms will appear gray.
4. To revert to standard colors, choose Element or Bead Type from the *Color by* dropdown list.

To color fixed measurements

1. Choose *View | Display Style* from the menu bar, click the *Display Style* button on the *3D Viewer* toolbar, or right-click in the 3D structure document and select *Display Style* from the shortcut menu to display the Display Style dialog.
2. Select the Measurement tab.
3. Choose *Color by* in the *Coloring* section and select Constraint from the dropdown list. Constrained measurements will be colored red and unconstrained measurements will appear gray.
4. To revert to standard measurement colors, choose Type from the *Color by* dropdown list.

Motion groups on a structure are represented by semi-transparent gray ellipsoids. The coloring and display style of motion groups cannot be altered, although they can be hidden or made visible using the Properties Explorer.

Support for constraints in Materials Studio

Materials Studio can maintain information about constraints in a 3D structure document. These constraints are imposed and modified using the Edit Constraints dialog. However, some modules in Materials Studio only honor certain types of constraints, while others ignore all constraints.

The modules that currently support constraints are listed below, along with details of the types of constraints that are supported:

- **CASTEP:** Supports atom positions fixed in Cartesian space, fixed lattice parameters, and fixed interatomic distances, angles, and torsions, but ignores all combinations of constraints on the x, y, and z components of Cartesian atom positions and geometric constraints.

  > **Note:** It is not possible alter constraints between simulations when using the *Restart* option.

- **DFTB+:** Supports atom positions fixed in Cartesian or fractional space and fixed lattice parameters, but ignores partial constraints on the x, y, or z components of Cartesian atom positions and geometric constraints. Supports fixed distance measurements in dynamics.
- **DMol^3:** Supports atom positions fixed in Cartesian space, and partial constraints on the x, y, or z components of Cartesian atom positions, but ignores constraints on fractional positions and lattice parameters. Additionally, DMol^3 supports fixed interatomic distances, angles, and torsions in nonperiodic structures.

  > **Note:** DMol^3 does not support constraints for the TS Search task.

- **Forcite:** Supports atom positions fixed in Cartesian space and fixed lattice parameters, but ignores partial constraints on the x, y, or z components of Cartesian atom positions and geometric constraints. Supports fixed distance measurements in dynamics.
- **GULP:** Supports atom positions fixed in Cartesian or fractional space, but ignores constraints on lattice parameters, partial constraints on the x, y, or z components of Cartesian atom positions, and geometric constraints.
- **Mesocite:** Supports bead positions fixed in Cartesian or fractional space and fixed lattice parameters, but ignores partial constraints on the x, y, or z components of Cartesian bead positions and geometric constraints. Fractional constraints are not supported for Dynamics calculations. Supports fixed distance measurements in dynamics.
- **ONETEP:** Supports atom positions fixed in Cartesian space and fixed lattice parameters, but ignores all combinations of constraints on the x, y, and z components of Cartesian atom positions and geometric constraints.

  > **Note:** ONETEP cannot change lattice geometry.

- **QMERA:** The support of constraints depends on the task and algorithm chosen. All geometry optimizations and the Baker transition state optimization algorithms can use atoms fixed in Cartesian space, but will ignore partial constraints on the x, y, or z components of Cartesian atom positions. QMERA also supports fixed interatomic distances, angles, and torsions in HDLC geometry or transition state optimizations. For QMERA dynamics, the only type of constraint available is fixed bond lengths.

> **Note:** In QMERA HDLC transition state optimizations, the atoms allowed to move are determined by the *TS core* atoms and constraints set in the structure document are silently ignored.
>
> For HDLC optimizations fixed torsions, angles, or distances are only considered when all atoms involved are not fixed in Cartesian space. If a fixed atom is included in a measurement constraint, the measure will be silently ignored and the atomic constraint respected.

- **Reflex/Reflex Plus (Powder Refinement and Powder Solve):** Supports fixed interatomic torsions and fixed lattice parameters, but ignores constraints on Cartesian and fractional atom positions and other geometric constraints.

> **Note:** All the other Materials Studio modules ignore all the types of constraints that can be defined using the Edit Constraints dialog.

Motion groups

A motion group is a collection of particles that can be translated or rotated such that the coordinates of each particle in the group remain fixed relative to the coordinates of all the other particles in the group. The default point of rotation for a motion group is its center of mass. Motion groups are often used to model rigid bodies, which are employed in modules such as Reflex and Polymorph to constrain the geometries of fragments or functional groups, while allowing their location and orientation within a crystal cell to be optimized. Rigid body methods often speed up calculations.

> **Note:** While motion groups are often used to define rigid bodies, they do not impose any constraints directly. You can alter the location of an atom or a bead in a motion group using the standard editing tools in the Materials Visualizer.

Constraints dialogs

Most atomic constraints can be imposed using dialogs which can be accessed from the Modify menu.

Edit Constraints dialog

The Edit Constraints dialog allows you to identify structural properties that you want to remain fixed during subsequent simulations.

The types of constraints which may be applied include fixed positions and lattice parameters, as well as geometric constraints, such as fixed distances.

> **Note:** Some modules in Materials Studio only honor certain types of constraints. Other modules ignore all constraints. See the Support for constraints in Materials Studio topic for more details.

The Edit Constraints dialog contains the following tabs:

- Atom: Allows you to specify constraints on the motion of atoms or beads during simulations.
- Measurement: Allows you to specify constraints on the motion of atoms or beads during simulations.
- Lattice: Allows you to specify constraints on the stretch and shear of a structure with symmetry.

Help: Displays the Help topic for the current tab.

Access methods

Menu	*Modify	Constraints*

Atom tab

The *Atom* tab of the Edit Constraints dialog allows you to specify constraints on the motion of atoms during simulations.

Fix Cartesian position: When checked, indicates that the *XYZ* position property in Cartesian space will be held constant for the selected particle.

X, Y, Z: When checked, indicate that the x, y, or z components of a particle's position will be held constant for the selected particle.

> **Note:** These options are enabled only if *Fix Cartesian position* is checked.

Fix fractional position: When checked, indicates that the *FractionalXYZ* position property in the fractional space of the lattice will be held constant for the selected atom.

> **Note:** This option is enabled only if the currently active structure is periodic.
>
> Reorientation of a lattice or changing its angular cell parameters may cause a partial Cartesian constraint to change direction.

If multiple particles are selected, a checkmark indicates that all particles are fixed. A gray checkmark indicates that only some of the selected atoms are fixed.

Access methods

Menu	*Modify	Constraints	Atom*

Measurement tab

The *Measurement* tab of the Edit Constraints dialog allows you to specify constraints on the motion of particles during simulations.

In this case, the constraints are defined in terms of geometric relationships between particles. In order to apply such constraints, measurements must first be made using the Measure/Change tool on the *Sketch* toolbar.

Fix distance: When checked, indicates that the selected distance will be held constant.

Fix angle: When checked, indicates that the selected angle will be held constant.

Fix torsion: When checked, indicates that the selected torsion angle will be held constant.

If multiple measurements of the same type are selected, a checkmark indicates that all measurements fixed. A gray checkmark indicates that only some of the selected measurements are fixed.

Access methods

Menu	*Modify	Constraints	Measurement*

Lattice tab

The *Lattice* tab allows you to specify constraints on the stretch and shear of a structure with symmetry.

Lattice Type: Displays the lattice type of the currently active structure. This may impose a minimum set of constraints.

If the lattice parameters of the currently active structure are constrained to certain values by its symmetry, these constraints are reported on the dialog and the appropriate checkboxes are checked and disabled.

Fix Lengths: When checked, indicate that lattice parameters a, b, or c (for a crystal), or u or v (for a surface) will be held constant for the currently active structure.

Fix Angles: When checked, indicate that lattice parameters α, β, or γ (for a crystal), or θ (for a surface) will be held constant for the currently active structure.

Access methods

Menu	*Modify	Constraints	Lattice*

Motion Groups dialog

The Motion Groups dialog allows you to specify motion groups for use with a number of simulation methods.

Assign automatically: Attempts to automatically assign motion groups in the currently active 3D structure document. A motion group will be defined for any free fragment that is located, with all the atoms in the fragment being included in the motion group.

> **Note:** This button is enabled only if a 3D structure document is in focus.
>
> If the structure already contains motion groups, an error message will be generated when *Assign automatically* is pressed. The existing motion groups must be deleted before automatic assignment of motion groups can be carried out.

Create from selection: Creates a motion group from the currently selected atoms or beads in the active 3D structure document.

> **Note:** This button is enabled only if a 3D structure document is in focus and at least one particle is selected.
>
> If any of the selected atoms or beads are already part of a motion group, an error message will be generated when *Create from selection* is clicked. You must either delete the existing motion group or deselect any particles that already belong to a motion group in order to create a new motion group.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modify	Motion Groups*

Restraints

Restraints impose an energy penalty for any deviation from the restrained value (distance, angle, torsion). They have been used in a wide variety of applications, such as steered molecular dynamics and to aid structural refinement.

> **Note:** There is an important distinction between constraints and restraints. A constraint prevents motion, placing an absolute restriction on a calculation. A restraint allows motion, but imposes a penalty if it occurs. This produces an energetic bias that tends to lead a calculation in a particular direction.

Imposing restraints

The Materials Visualizer allows you to add restraints to distance, angle, and torsion measurements with specific minimum energy value and force constants.

To restrain measurements

1. Make the 3D structure document containing the measurements to be restrained the active document and select the appropriate measurements. If no measurements are selected, restraints will be created for all measurements.
2. Select *Modify | Restraints* from the menu bar to open the Restraints dialog.
3. Specify the *Force constant* in kcal/mol for the restraint's functional form.
4. Choose how to define the minimum energy of the restraint, either the current value or a user-defined energy minimum value can be specified.
5. Click the *Create* button.

To delete restraints

1. Make the 3D structure document containing the restraints to be deleted the active document.
2. Select the restraint by clicking on the restraint symbol, typically a large dot near the measure, or if both the restraint and measure are to be deleted click on the measure label or on one of its solid lines to select both objects.
3. Delete the restraint using one of these methods:
   - Press the DELETE key
   - Right-click in the 3D structure document and choose *Delete* from the shortcut menu
   - Select *Edit | Delete* from the menu bar.

Support for restraints in Materials Studio

Materials Studio can maintain information about restraints in a 3D structure document. These restraints are imposed and modified using the Restraints dialog. However, some modules in Materials Studio honor restraints, while others ignore all restraints.

The modules that currently support restraints are listed below:

- **Forcite**
- **Mesocite**

> **Note:** All the other Materials Studio modules ignore all the types of restraints that can be defined using the Restraints dialog.

Restraints dialog

The Restraints dialog allows you to define and add restraints to existing measurements in a 3D Atomistic document. Restraints cannot be added when more than one type of measurement is selected or when the current system is symmetric.

Restraints can only be created for one type of measurement at a time.

Functional form: The type of functional form to use to describe the interaction of the particles involved in the selected measurement. Options are:

- Harmonic

Force constant: The value for the force constant component of the functional form (for the Harmonic *Functional Form* this is K_b).

Minimum at current value: When selected, the current value of the measure will dictate the position of the minimum restraint energy (E).

Minimum at: When selected, specify the value at which the restraint energy (E) is a minimum.

Create: Adds a restraint to the selected measurement(s).

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modify	Restraints*

Vectors

Atoms and beads can have vector properties such as force and velocity. Likewise groups of atoms, such as molecules, can have vector properties such as force, velocity and dipole moment. The Vector tools help visualize these properties.
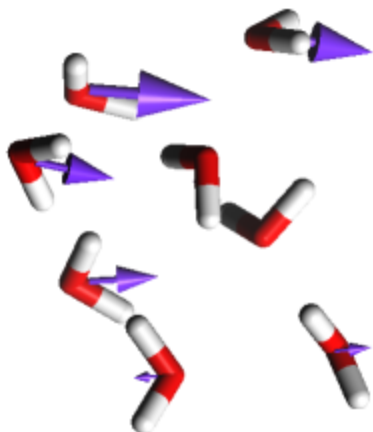
The display of vector properties is controlled using the Vectors dialog.

The appearance of vectors can be altered using the Vector tab on the Display Style dialog.

By default, vectors are colored according to the property being displayed:

- Velocity - **green**
- Momentum - **turquoise**
- Force - **brown**
- Dipole moment - **purple**

Working with vectors

In order to generate vectors for a structure, it must contain at least one of the following:

- Charges - for dipole moment vectors (for molecules, subunits, charge groups, motion groups, or substructures)
- Forces - for force vectors
- Velocity - for velocity and momentum vectors

> **Tips:**
> - Charges can be calculated and assigned to a structure using the Charges dialog.
> - Forces and velocities can be generated by dynamics simulations.
> - Substructures can be generated using the Find Patterns dialog.

To create vectors

1. Activate the 3D structure document containing the atoms or beads which should have vectors and select the appropriate particles. If no particles are selected vectors will be created on all particles.
2. Select *Tools | Vectors* from the menu bar to open the Vectors dialog.
3. Choose the *Object Type* and the *Property* for the vector.
4. Click the *Apply* button.

To edit vector display

1. On the *Vectors* dialog choose the *Object Type* and the Property for the vector(s).
2. Click the *Select* button, the vector(s) will be highlighted in yellow in the 3D Viewer.
3. Open the Display Style dialog and select the Vector tab.
4. Choose the *Display style*, *Scale Factor*, and the *Coloring* for the vector(s).

To delete vectors

1. On the *Vectors* dialog choose the *Object Type* and the Property for the vector(s).
2. Click the *Remove* button, the vector(s) will be deleted.

To orient the view with a vector

1. Create vectors using the steps above.
2. Select one vector in the 3D Viewer.
3. Choose View Onto or View Across from the *3D Viewer Recenter* dropdown list on the *3D Viewer* toolbar.

Vectors dialog

The Vectors dialog allows you to add and remove vector property symbols in a 3D Atomistic document.

First, select a type of object and a vector property, then choose to apply, remove, or select the vectors that meet those criteria.

All tasks operate on the current selection, or if there is no selection then on the whole document.

Object type: Specifies the type of object whose vectors are to be manipulated. Available options depend on the current selection, and may include:

- Atom
- Bead
- Molecule
- SubUnit
- ElectrodeTip
- ChargeGroup
- MotionGroup
- PhysicalSystem
- Substructure

Property: Specifies the vector property to use for creation, selection, or deletion of vectors. Only the properties defined on the selected object(s) are listed. Options may include:

- Atom
  - Force
  - Momentum
  - Relative velocity
  - Velocity
- Bead
  - Force
  - Momentum
  - Relative velocity
  - Velocity
- Molecule or SubUnit
  - Dipole moment
  - Net force
  - Net momentum
  - Net velocity
- ElectrodeTip
  - Dipole moment
- ChargeGroup, MotionGroup, or Substructure
  - Dipole moment
  - Net force
  - Net momentum
  - Net velocity
- PhysicalSystem
  - Dipole moment
  - Net force
  - Net momentum
  - Net velocity
  - Server dipole moment

Apply: Adds symbols to the document for the specified vector property.

Select: Selects the specified vectors.

Remove: Removes the specified vectors from the selection.

> **Note:** You can only create vector property symbols for object property combinations that are available in the 3D atomistic document in focus. If the selected object property combination is not available for the current selection the *Apply* button will be disabled.
>
> For example, velocities and forces are only available if you have previously run a molecular mechanics simulation, such as a geometry optimization or molecular dynamics. Some properties may only be generated by a subset of the molecular mechanics engines in Materials Studio.

Note: When vectors are applied, a default scale factor in the 3D Viewer is chosen based upon the magnitude of the vector property value.

When vectors are applied to more than one selected object at the same time, the scaling is chosen based upon the largest property magnitude. In this case, the vectors on the other objects may be proportionately shorter in length. If vectors are instead applied to multiple objects in separate actions, then a different scale factor may be chosen each time.

The Display Style dialog provides additional control over the use of display scale factors for vectors after they have been applied. This offers the ability to change the scaling to a new uniform value, or to display vectors with fixed length in order to emphasize only the directions.

If vectors are applied for a property whose values are all zero, a warning is produced.

Note: Relative velocity is only useful for 3D periodic systems in which the cell is changing, such as from a shear dynamics simulation. Otherwise, this is the same as the Velocity.

Help: Displays the Help topic in a browser.

Access methods

| Menu | *Tools | Vectors* |

Bead types

Beads are fundamental objects in certain types of mesoscale modeling, to some extent analogous to atoms in atomistic modeling. In the same way that each atom has many of its properties defined by its element type, each bead has many of its properties defined by its bead type.

Bead types can be created and have their properties edited using the Bead Types dialog.

Beads that have been created in a mesoscale structure document can have their bead type changed using the Modify Bead Type dialog, a task analogous to changing the element type of an atom in an atomistic structure.

Changing bead type

Changing the type of a bead in a mesoscale structure is analogous to changing the element type of an atom in an atomistic structure.

To modify the bead type for selected beads

1. Open the Modify Bead Type dialog by either of the following means:
   - Choose *Modify | Modify Bead Type* from the main menu.
   - In the Properties Explorer, ensure that the *Filter* is set to Bead. Double-click on the *BeadTypeName* property.
2. If desired, check the *Filter by current document* to restrict the list of bead types shown.
3. Select the new bead type that is required for the selected beads.
4. If the desired bead type is not known to the project you should close this dialog and create the bead type before continuing with the current task.
5. Click the *OK* button. The dialog will close and the selected beads will have their bead type changed to the new value.

Modify Bead Type dialog

The Modify Bead Type dialog allows you to change the bead type for one or more selected beads in a document to another, already existing, bead type.

Bead Type: Lists, in alphabetical order, the bead types, either all those known to the project or those used by the current document, depending on the setting of the *Filter by current document* checkbox. Choose the desired new bead type for selected beads, by clicking on the bead type name. If the desired new bead type does not already exist it should be created using the Bead Types dialog.

Color: This shows the colors assigned to each of the bead types.

Filter by current document: If this is checked, the set of bead types that is displayed in the grid will be restricted to just those that are used in the current document. Default = unchecked.

OK: Change the bead type of the selected beads to that chosen from the *Bead Type* list, and close the dialog.

Cancel: Close this dialog without making any changes to the document in focus.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Modify	Modify Bead Type...*
Properties Explorer	With *Bead* shown in the *Filter*, double-click on the *BeadTypeName*

Calculating atom volumes & surfaces

The Atom Volumes & Surfaces tool allows you to create a variety of surfaces that characterize the geometry and solvent interaction of molecules or 3D periodic systems. It allows the creation of Connolly, van der Waals, solvent, and smoothed solvent surfaces (and accessible variants), collectively known as atom volume surfaces.

The Atom Volumes & Surfaces tool can be used to probe the available surface area in a zeolite pore or to examine the free or solvent volume in an amorphous polymer, for example. The solvent radius and/or Connolly radius can be varied interactively to simulate different solvent sizes, providing a rapid method for screening the accessibility of different solvents in porous materials. The surface area, occupied volume, and (where relevant) unoccupied volume of each atom volume surface is reported.

The following steps describe how to create, analyze, and modify atom volume surfaces.

To create and manipulate atom volume surfaces

1. Ensure that a 3D model document is active.
2. Choose *Tools | Atom Volumes & Surfaces* from the menu bar to display the Atom Volumes & Surfaces dialog.
3. Select the type of surface(s) you wish to generate from the *Task* dropdown list on the *Setup tab*.
4. Optionally, adjust the settings relevant to the surface(s) you are creating on the *Setup* tab.
5. Click the *Create* button to create an Atom Volumes field. Depending on the settings specified on the *Setup* tab, one or more atom volume surfaces will be displayed. The numeric properties (volumes and areas) of all the surfaces created are reported in the *Results* field on the Analysis tab.

> **Note:** The *Create/Recreate* button may be disabled if the current document is a 3D Atomistic Collection document containing more than one physical system. Atom volume surfaces cannot be generated for selections which span physical systems. To enable the *Create/Recreate* button, you need to select all or part of a single physical system.
>
> The *Create/Recreate* button is also disabled if the current document (or currently selected physical system) contains a 2D periodic surface.

6. Show or hide surfaces using the visibility controls in the tree view on the *Analysis* tab.
7. Use the spin controls to adjust the *Solvent radius* and/or *Connolly radius* on the *Analysis* tab. The *Results* field is updated in response to any changes you make to the radii.
8. If desired, modify the settings on the *Setup* tab and click the *Recreate* button to recreate the atom volumes field and the surface(s) using the new settings.
9. Alternatively, if the current structure has changed, perhaps through the addition or movement of atoms, click the *Refresh* button on the *Analysis* tab to update the current surface(s) without changing the settings.

Working with atom volume fields and surfaces

The Atom Volumes & Surfaces tool creates a field that contains values of some distance function, such that isosurfaces of that field characterize the geometry and solvent interaction of an atomistic structure in a variety of ways. Thus, atom volume fields and atom volume surfaces are specialized versions of the equivalent general-purpose volumetric objects.

Once these objects have been created using the Atom Volumes & Surfaces tool, the resulting atom volume fields and surfaces are displayed on the *Analysis* tab of the Atom Volumes & Surfaces dialog.

The first volumetric object displayed in the tree view is named the Atom Volumes Field.

- For the Connolly task, this is a field whose value at each point in space corresponds to the depth in the nearest Connolly probe of a given radius, as it rolls over the van der Waals surface of the atomistic structure.
- For the Solvent task, this is a field whose value at each point in space corresponds to the distance to the nearest point on the van der Waals surface of the atomistic structure.
- For the Both task, this is a field that combines both of the above properties.

See the Atom volumes & surfaces algorithms topic for more information about how an atom volumes field is calculated. The different atom volume surfaces are listed below the Atom Volumes Field in the tree view. These surfaces are automatically named according to their physical meaning.

With these fields defined, the *Solvent radius* specified on the *Analysis* tab is a special type of isovalue associated with an atom volume surface. The changes which result from altering the *Solvent radius* of a surface can be rapidly visualized by regenerating the isosurface.

The *Connolly radius* can also be changed interactively; however, recalculation of the atom volume field is required in order for any changes you make to become visible.

You can use the general volumetric visualization tools for viewing atom volume surfaces. For example:

- Use the tools on the Volume Visualization toolbar to create additional isosurfaces and slices.
- Use the Display Style dialog to change the appearance of fields, slice, and isosurfaces.
- Use the Color Maps dialog to control the range of values displayed in fields and slices and to vary their coloring.

> **Tip:** If you have a graphics card with hardware acceleration for OpenGL, you may wish to uncheck the *Fast render on move* option on the Graphics tab of the Display Options dialog when viewing the atom volumes.

> **Tip:** To visualize the interaction of two molecules, place each molecule in turn into a 3D Atomistic Collection document, create an atom volume field for each molecule, then map the atom volume field of one molecule onto a surface of the other molecule by setting Mapped Field on the *Isosurfaces* tab of the Display Style dialog.

Creating new atom volume surfaces

You can create new atom volume surfaces on an atom volume field using the *Create Isosurfaces* tool on the Volume Visualization toolbar. Initially, any new atom volume surface will be a solvent surface and will be named accordingly in the tree view on the *Analysis* tab of the Atom Volumes & Surfaces dialog. Subsequently, you can modify the properties of the new atom volume surface using the Isosurface tab on the Display Style dialog. This may change the nature and name of the atom volume surface.

The isosurface properties that change the nature of an atom volume surface are:

- *Isovalue:* Has a value of zero or greater. This is synonymous with the *Solvent radius* value specified on the *Analysis* tab of the Atoms & Volumes dialog.
- *Isosurface kind:* Indicates whether the surface is solvent-accessible or not.
- *High values inside:* Indicates whether the inside of the surface is the side with higher field values or lower field values. Isosurfaces created using the tools on the Volume Visualization toolbar have the *High values inside* checkbox checked, but this should typically be unchecked when the isosurface is used with an atom volume field. When the *High values inside* checkbox is unchecked, the isosurfaces wrap around the atoms in the system rather than around the voids or cavities.

Depending on the values of these properties, and those of the atom volume field (marked *), the following atom volume surfaces can be created:

Automatic name	Connolly radius*	Isovalue	Accessible mode?	High inside?	Meaning
vdW Surface	0.0	0.0	No	No	The surface that intersects with the van der Waals radii of the atoms in the structure. This is equivalent to a solvent surface with a solvent probe radius of zero and to a Connolly surface with a Connolly probe radius of zero.
vdW Surface	0.0	0.0	No	Yes	As vdW Surface, but inside out.
Accessible vdW Surface	0.0	0.0	Yes	No	As vdW Surface, except only those regions that are externally accessible are shown.
Solvent Surface@N.N	0.0	> 0.0	No	No	The surface which is the locus of the probe center as the probe rolls over the scaled vdW surface. This surface describes a space which could, in principle, be occupied by a probe of given radius, ignoring the accessibility of such points.
Solvent Surface@N.N	0.0	> 0.0	No	Yes	As Solvent Surface, but inside out.
Accessible Solvent Surface@N.N	0.0	> 0.0	Yes	No	As Solvent Surface, except that the surface is only defined over externally accessible regions.
Connolly Surface	> 0.0	0.0	No	No	The surface at the boundary between the Connolly probe and the atoms (as represented by their scaled van der Waals radii), not at the locus of the probe center.
Connolly Surface	> 0.0	0.0	No	Yes	As Connolly Surface, but inside out.
Accessible Connolly Surface	> 0.0	0.0	Yes		As Connolly Surface, except only those regions that are externally accessible are shown.
Smoothed Solvent Surface@N.N	> 0.0	> 0.0 < Connolly radius	No	No	A solvent surface that is smoothed at the discontinuities (creases and cusps) in the same way that a Connolly surface is a smoothed vdW surface.

The following table lists some property values which are not valid, along with the reasons why:

Automatic name	Connolly radius*	Isovalue	Accessible mode?	High inside?	Meaning
Non-Physical	Any	< 0.0	Any	Any	A negative isovalue indicates a negative solvent radius, which cannot be meaningful.
Non-Physical	Any	Any	Yes	Yes	On an atom volume field, an isosurfaces in accessible mode must not have the *High values inside* checkbox checked. In other words, accessible isosurfaces must not be inside out. A region is deemed accessible if it can be reached from outside the field on a path of values outside the isosurface. When the *High values inside* checkbox is checked, this means that a region would be deemed accessible if it can be reached via low field values. For an atom volume field, low values occur in the vdW radii of atoms. This would mean that the probe-accessible regions would be those that are occupied by atoms, which cannot be meaningful.
Non-Physical	Any	> *Max. solvent radius*	Any	Any	The atom volume field is only guaranteed to be valid for solvent radii up to the maximum solvent radius.

Atom volume field properties

As with other Materials Studio objects, it is possible to view and manipulate the properties of atom volume fields using the Properties Explorer. Modifying any of these properties will cause the atom volume field to be recalculated. In addition to the properties possessed by many other fields, the atom volume field has some unique properties. These are listed below:

ConnollyRadius: Specifies the radius, in Å, of the Connolly probe used in calculating the atom volume field. Range = 0.0 to 10.0 Å.

With a value of 0.0, no Connolly calculations are performed, resulting in calculation of a field suitable for vdW and solvent surfaces. For more details, see Atom volumes & surfaces algorithms.

GridInterval: Specifies the desired spacing, in Å, between points on the regular grid on which the atom volume field is calculated. In practice, the actual separation used will be at least that good, possibly slightly better, to allow for a whole number of grid points within the field's region. Range = 0.1 to 2.0 Å.

> **Note:** A small grid interval will give higher visual quality and more accurate numeric properties, but can significantly increase the calculation time. If numeric properties are required with a high degree of accuracy, it is recommended that a *GridInterval* value of 0.25 Å or less is used.

Care should be taken with larger systems, as both the memory requirements and computation time increase cubically as the grid interval decreases. For a given system, reducing the *GridInterval* value from 0.4 to 0.1 will take at least 4^3 (64) times longer to compute.

MaxSolventRadius: Contributes to a cutoff value, in Å, beyond which atoms are not considered when calculating the values in the atom volume field. The actual cutoff used is the sum of *MaxSolventRadius*

and the largest scaled vdW radius in the system. A larger *MaxSolventRadius* value will allow examination of a wider range of probe radii, but will increase the calculation time. In a nonperiodic or molecular case, the *MaxSolventRadius* distance determines the size of the margins around the molecule. Range = 0.0 to 10.0 Å.

With a value of 0.0 Å, minimal solvent calculations are performed, resulting in calculation of a field suitable for Connolly or vdW surfaces, depending on the *ConnollyRadius* value. For more details, see Atom volumes & surfaces algorithms.

VDWScaling: Specifies a factor to uniformly modify all van der Waals radii, representing a hard shell into which a probe may not pass. Alternatively, you may edit the van der Waals radii of an individual element using the Element Properties dialog. Range = 0.1 to 3.0.

Atom volumes & surfaces algorithms

When the *Create* button on the Setup tab of the Atom Volumes & Surfaces dialog is pressed, an atom volume field and up to three special isosurfaces corresponding to the van der Waals surface, the solvent surface, the accessible solvent surface, and/or the Connolly surface are created. Each of these atom volume surfaces is automatically named according to the parameters used to create it.

Defining van der Waals and solvent surfaces

Figure 1 shows a volume field for a simple diatomic molecule created using the Solvent task. A slice has been added, showing the location of a van der Waals (vdW) surface and two solvent surfaces. The blue and red circles illustrate solvent probe position and radius.
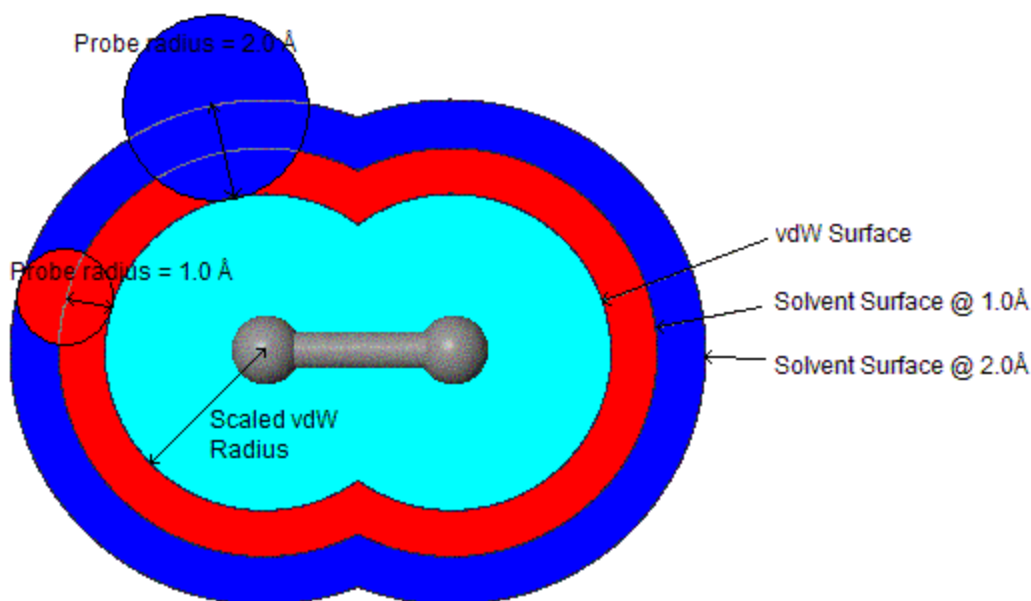
Figure 1. van der Waals and solvent surfaces

The surfaces shown above are defined as follows.

van der Waals surface: The surface that intersects with the vdW radii of the atoms in the structure. This is equivalent to a solvent surface with a solvent probe radius of zero and to a Connolly surface with a Connolly probe radius of zero (the van der Waals surface is shown in cyan in Figure 1).

Solvent surface: The surface which is the locus of the probe center as the probe rolls over the scaled vdW surface. This surface describes a space which could, in principle, be occupied by a probe of given

radius, ignoring the accessibility of such points (the two solvent surfaces are shown in red and blue in Figure 1).

Accessible solvent surface: The surface which is the locus of the probe center as the probe rolls over the scaled vdW surface, in accessible regions only. This is the same as the solvent surface, except that the surface is only defined over externally accessible regions. External accessibility is determined by a flooding algorithm that fills from the external faces of the field (see Figure 2).

Figure 2 shows a fairly thin section of surfaces on a C_{60} molecule. The diagram distinguishes between a solvent surface (left) and an accessible solvent surface (right) at a probe radius of 1.0 Å.
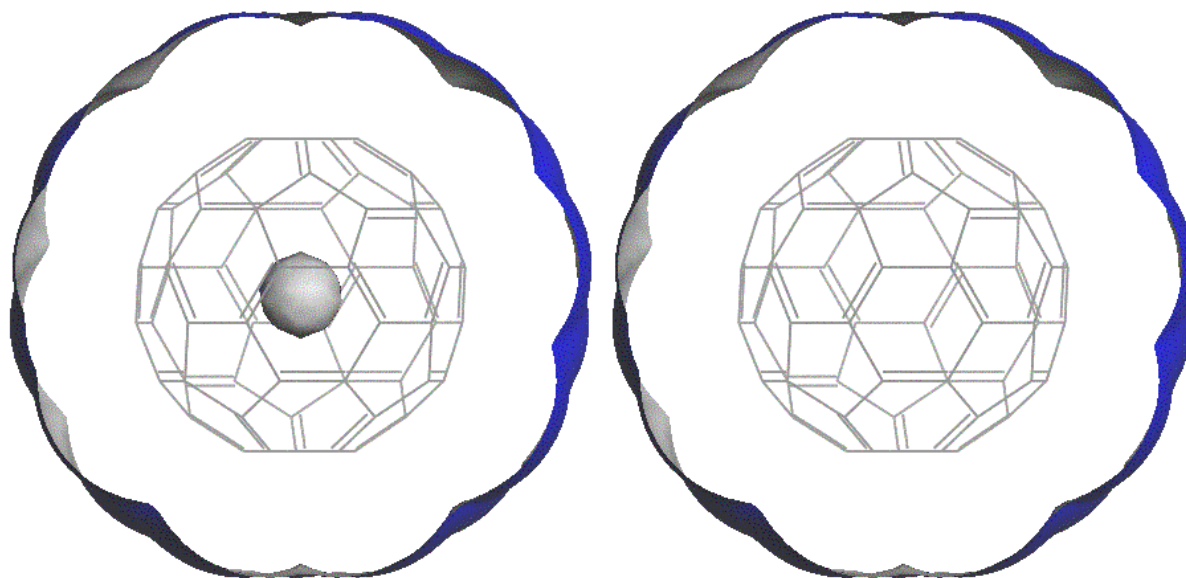
Figure 2. Solvent surface vs. accessible solvent surface

There is an inaccessible region within the C_{60} cage, so the accessible surface is not present in that region. The occupied volume associated with the accessible surface is greater than the solvent volume by the volume of the small central sphere.

Defining Connolly surfaces

The solvent surfaces described above are similar to Connolly surfaces (Connolly, 1983). However, they are not generally the same.

Figure 3 shows three atom volume fields created using the Connolly task. A slice has been added to each, showing the location of the Connolly surfaces between the white and pink contours. The blue spheres illustrate Connolly probe position and radius. The radii of the Connolly probes shown in Figure 3 are 0.5, 1.0, and 2.0 Å from left to right.
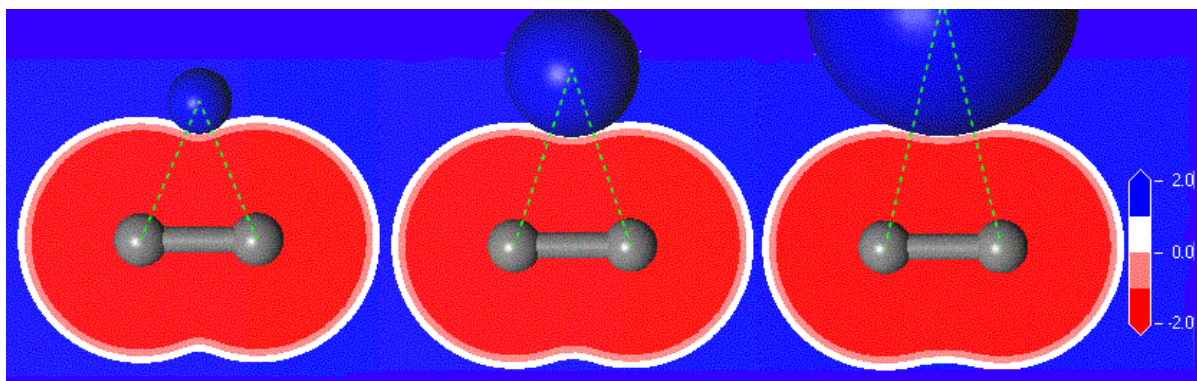
Figure 3. Connolly surface

A Connolly surface is at the boundary between the Connolly probe and the atoms (as represented by their scaled vdW radii), not at the locus of the probe center. Varying the Connolly probe radius of a Connolly surface tends to change the curvature at cusp points and creases on the vdW surface, but away from such areas, the Connolly surface follows the vdW surface.

In Figure 3, the Connolly surface departs from the vdW surface only in the region enclosed by the dotted lines. Only in the case of a solvent probe radius of zero and a Connolly probe radius of zero are solvent surfaces and the Connolly surfaces the same. In this situation, they both become equivalent to the vdW surface.

For an atom volume surface to be considered a Connolly surface in Materials Studio, the solvent probe radius must be 0.0 Å (i.e., an isovalue of 0.0) and the atom volume field on which the surface is based must have a positive, non-zero, Connolly probe radius associated with it.

Defining smoothed solvent surfaces

Figure 4 shows a slice through an atom volume field created using the Both task with a Connolly radius of 1.0 Å and a maximum solvent radius of 2.0 Å. Four isosurfaces have been added. The field's display range was truncated so that only the edge of the isosurfaces protruding through the slice can be seen. The transparent sphere illustrates one Connolly probe position.
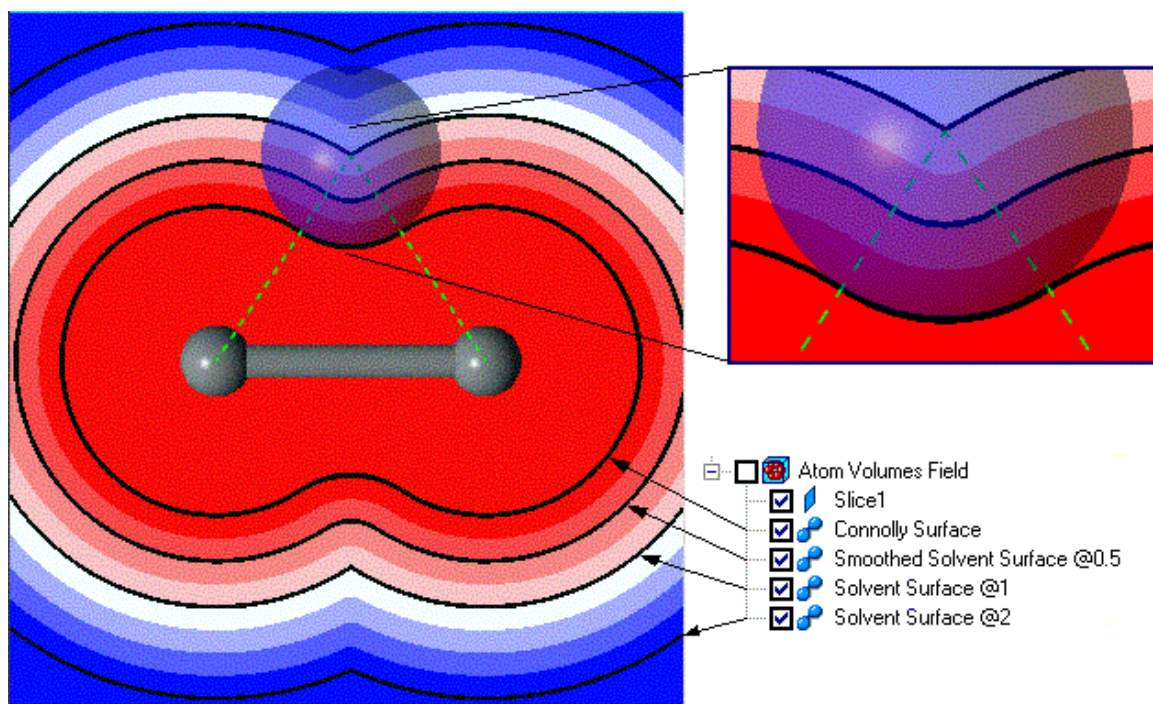
Figure 4. Smoothed solvent surfaces

Again, only the region within the dotted lines differs between the Connolly and solvent surfaces. The inset shows how the field values, and hence the surfaces, vary within this region. Here, the field values are of the depth within the nearest Connolly probe, out to a distance equal to the Connolly probe radius beyond the vdW surface. This can been seen in the spherical form of slice contours inside the Connolly probe.

Considering the isosurfaces shown in Figure 4 in turn:

- At an isovalue of 0.0, there is a Connolly surface

  This can be considered to be a smoothed vdW surface in that it is smoothed by a sphere with a radius equal to that of the Connolly probe.

- At an isovalue of 0.5, there is a smoothed solvent surface

  This can be considered to be a solvent surface with a solvent radius of 0.5 Å, but smoothed by a probe of radius 0.5 Å (Connolly radius - solvent radius). A normal solvent surface has a constant nearest distance to the vdW surface. A smoothed solvent surface has a constant nearest distance to the Connolly surface.

- At isovalues above the Connolly radius, there are solvent surfaces that are not smoothed

  These surfaces show the normal sharp creases and cusps (see the outer two surfaces in Figure 4).

A smoothed solvent surface is a solvent surface that is smoothed at the discontinuities (creases and cusps) in the same way that a Connolly surface is a smoothed vdW surface. A smoothed solvent surface has a constant nearest distance to the Connolly surface.

For an atom volume surface to be considered a smoothed solvent surface in Materials Studio, its solvent probe radius (or isovalue) must be between 0.0 Å and the Connolly radius used to generate the atom volume field. Smoothed solvent surfaces have characteristics similar to both Connolly and solvent surfaces, and can exist only when these surfaces have been created.

Properties of atom volume surfaces

Atom volume surfaces have the following properties.

Occupied volume: The volume on the atom side of the atom volume surface. In the default state, after the *Create* button has been pressed, this is the inside (gray side) of the isosurface.

> **Note:** The default color assignment may change if the *High values inside* checkbox is checked on the Isosurface tab of the Display Style dialog.

The occupied volume is always physically meaningful and so it is always displayed in the *Results* field on the Analysis tab of the Atom Volumes & Surfaces dialog.

Free volume: The volume on the side of the atom volume surface without atoms. In the default state, after the *Create* button has been pressed, this is the outside (colored side) of the isosurface.

The free volume is only physically meaningful for 3D periodic systems and so it is only displayed in the *Results* field on the *Analysis* tab of the Atom Volumes & Surfaces dialog when such systems are in scope.

Surface area: The surface area of an atom volume surface.

The surface area is always physically meaningful and so it is always displayed in the *Results* field on the *Analysis* tab of the Atom Volumes & Surfaces dialog.

Values within atom volume fields

Solvent task

When created using the Solvent task, the values within an atom volume field vary as shown in Figure 5.

This graph shows the values at grid points along the axis of a simple diatomic molecule. The scaled vdW radius is 1.7 Å, the maximum solvent radius is 2.0 Å, and the grid interval is 0.1 Å.
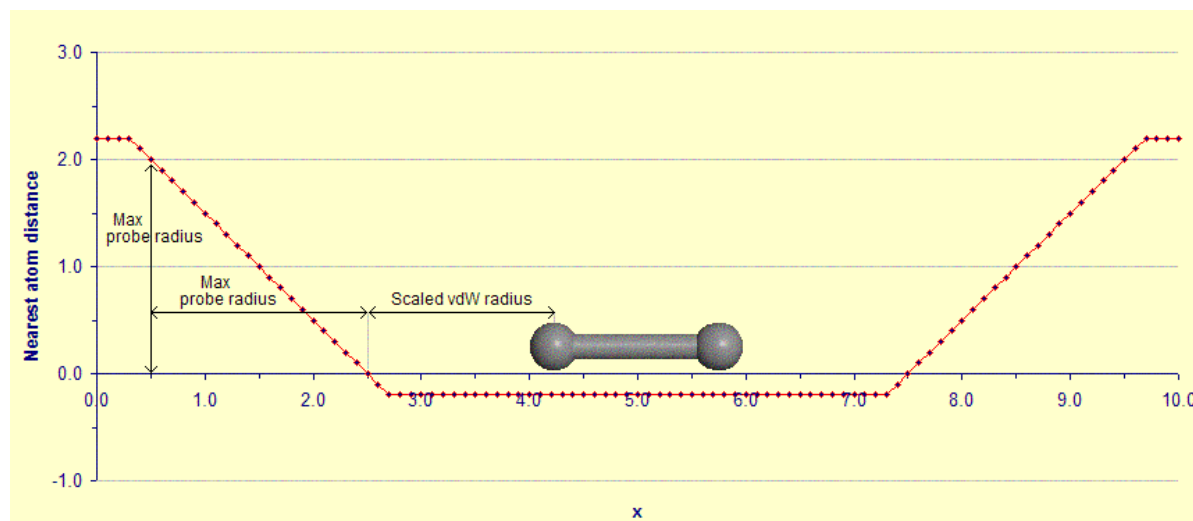
Figure 5. Values within an atom volume field - Solvent task

In the case of the Solvent task, it is possible to think of the atom volume field as simply containing values equal to the distance to the nearest vdW surface. This reflects a model where both atoms and the solvent probe are treated as hard spheres.

This treatment is similar to that used by Voorintholt et al. (1989); however, in Materials Studio, the actual distances are stored, rather than a quadratic interpolation approximation.

In practice, the actual treatment varies between certain regions:

- Inside an atom

    Grid points at a distance less than the scaled vdW radius from the center of the nearest atom are not calculated, but are set to a small constant negative value.

- On the atom's vdW surface

    Grid points at a distance equal to the scaled vdW radius from the center of the nearest atom have a value of zero.

- Outside atoms, but not too far out

    Grid points beyond the scaled vdW shell by a distance less than the maximum solvent radius have values equal to the distance to the nearest vdW shell.

- Too far out

    Grid points at a distance greater than the maximum solvent radius from the scaled vdW shell are not calculated, but are set to a fixed value slightly above the maximum solvent radius.

Connolly task

Traditionally a Connolly surface is created by combining three kinds of surface: convex, saddle, and concave.

Field for the convex part of the surface

When the Connolly probe rolls over a single atom, the resulting surface is the same as the vdW surface. Given that the Connolly surface is defined as having an isovalue of zero, this step is simply the same as for the Solvent task, but with a maximum solvent radius of zero, since there is no need for the field to extend far beyond the atom.

An optimization is applied at this point. In dense crystals, there may be no point in space where the Connolly probe may fit. This can be seen by calculating the distance to the nearest vdW surface for the whole field and checking whether the largest distance found is less than the Connolly probe radius. In such cases, there is no point in continuing to the next steps as no valid Connolly surface can be produced. The field is reduced to its minimum size (2 × 2 × 2) to conserve memory as it can contain no valid data.

Field for the saddle part of the surface

When the Connolly probe rolls over a pair of atoms, it is possible that it will become jammed between the atoms. This could yield a saddle surface between the atoms, as the probe orbits around the common axis. Or in cases where the probe only just jams between the atoms, points are created on each atom.
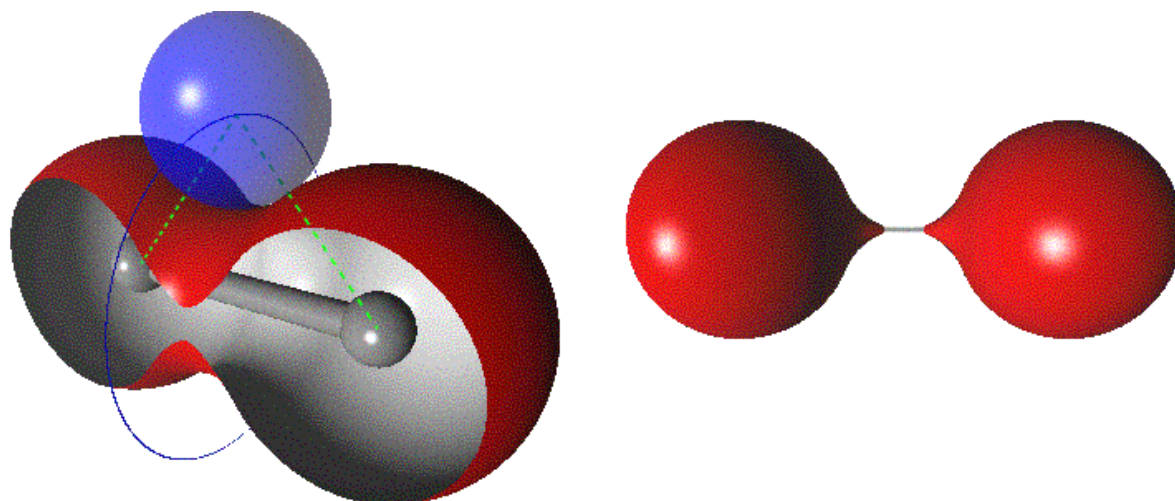
Figure 6. Connolly probe orbiting the common axis of two atoms

Pairs of atoms sufficiently close to jam a probe between them are identified. A double-cone region that is swept out by the probe and the two atoms is identified. Within that region, the field is set to the distance *within* the nearest probe position. Points outside the nearest probe have a negative value.

The actual region updated is reduced as there is no need to update the field far away from the Connolly surface. The distance beyond the Connolly surface that is guaranteed updated in the field is governed by the maximum solvent radius. For the Connolly task, the maximum solvent radius is zero.

Field for the concave part of the surface

When the Connolly probe rolls over three atoms, it is possible that it will become jammed between the atoms, both above and below the plane of the atoms. This would yield a concave or dish-like surface between the atoms.

In Figure 7 the concave areas of the surface formed by the probe touching three atoms are highlighted in blue. The probe positions are not shown, The upper probe position would be at the apex of the tetrahedron formed by the dotted lines. The lower position would simply be a reflection of the upper position below the plane of the atoms.
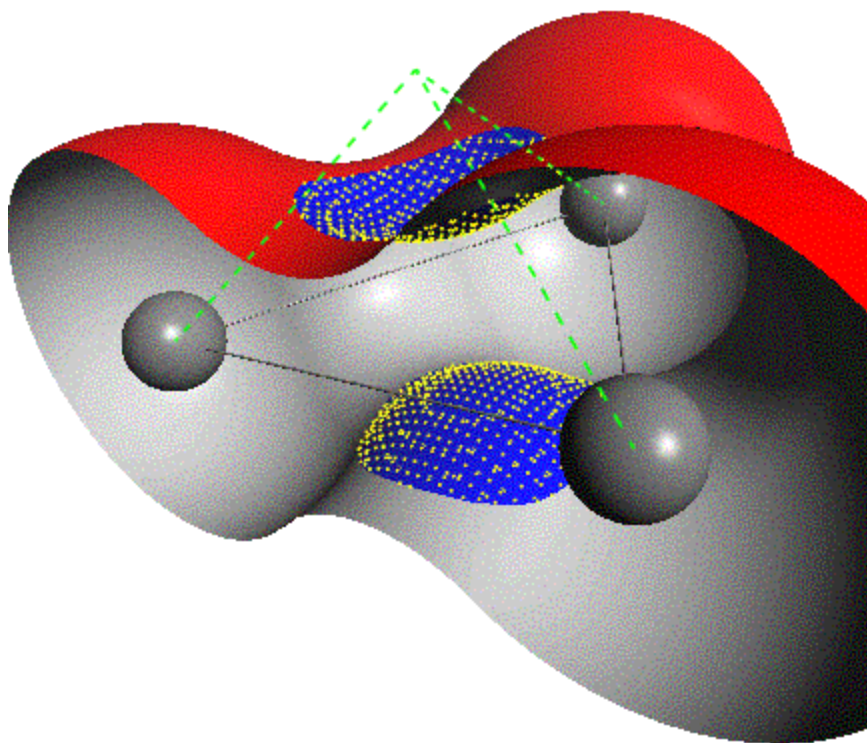
Figure 7. Connolly probe touching three atoms

Groups of three atoms sufficiently close to jam a probe between them are identified. A double tetrahedron region is identified between the two probe positions and the three atoms. Within that region, the field is set to the distance *within* the nearest probe position. Points outside the nearest probe have a negative value.

The actual region updated is reduced as there is no need to update the field far away from the Connolly surface. The distance beyond the Connolly surface that is guaranteed updated in the field is governed by the maximum solvent radius. For the Connolly task, the maximum solvent radius is zero.

Both Task

The Both task simply involves the execution of the Connolly task, but with the addition of updating the field further beyond the Connolly surface, such that the solvent and smoothed solvent surfaces are also supported. This is achieved by allowing the maximum solvent radius to be greater than zero.

Atom volumes & surfaces warnings

Certain situations can prevent atom volumes & surfaces calculations from being performed successfully. If this is the case, a warning message will be displayed to alert you to the problem. Further details about these warnings are provided below.

Field creation failed - try increasing the grid interval to reduce the memory requirements.

If you try to perform an atom volume field calculation that cannot be satisfied with the memory available you should reduce the resolution of the field (that is, increase the *Grid interval*). The total number of grid points required will decrease by a factor of 8 when the *Grid interval* is halved.

The accessible mode of an isosurface was turned off due to lack of memory

Determining the accessible regions of a field may require a large amount of memory. If insufficient memory is available, the isosurface will be changed automatically from an accessible surface to a normal surface.

> **Tip:** Atom volume fields can be very large, taking up as much as 1 GB of memory or even more. When these large fields are saved, the resulting files are equally large (up to 1.6 GB). In addition, reloading large fields can take a great deal of time, sometimes even longer than it took to calculate the field in the first place. As a result, you should be cautious about saving large atom volume fields.

Atom Volumes & Surfaces dialog

The Atom Volumes & Surfaces tool allows you to create a variety of surfaces that characterize the geometry and solvent interaction of molecules or 3D periodic systems. It allows the creation of Connolly, van der Waals, solvent, and smoothed solvent surfaces (and accessible variants), collectively known as atom volume surfaces.

The Atom Volumes & Surfaces tool can be used to probe the available surface area in a zeolite pore or to examine the free or solvent volume in an amorphous polymer, for example. The solvent radius and/or Connolly radius can be varied interactively to simulate different solvent sizes, providing a rapid method for screening the accessibility of different solvents in porous materials. The surface area, occupied volume, and (where relevant) unoccupied volume of each atom volume surface is reported.

The Atom Volumes & Surfaces dialog contains the following tabs:

- Setup: Allows you to specify preliminary settings for Atom Volumes & Surfaces calculations.
- Analysis: Allows you to interactively control the generation and visualization of all atom volume fields and surfaces in the current document.

Help: Displays the Help topic for the current tab.

Access methods

Menu	*Tools	Atom Volumes & Surfaces*

Setup tab

The *Setup* tab on the Atom Volumes & Surfaces dialog allows you to specify preliminary settings for Atom Volumes & Surfaces calculations. Every time the *Create* button is pressed, the settings on the *Setup* tab are used to create a set of objects in the current document that provide visual representations and numeric properties (volumes and surface areas) for the current structure.

Task: Select the kind of surfaces that are to be supported from the dropdown list. Available options are:

- Connolly surface - Creates a field that supports Connolly surfaces and, typically, also creates a Connolly surface.
- Solvent surfaces - Creates a field that supports vdW, solvent, and accessible solvent surfaces and, typically, also creates these surfaces.
- Both - Creates a field that supports Connolly, solvent, accessible solvent, and smoothed solvent surfaces and, typically, also creates these surfaces.

Grid resolution: Select a resolution level for the atomistic surface grid from the dropdown list. Available values and the corresponding *Grid interval* values are:

- Coarse - 0.75 Å
- Medium - 0.4 Å
- Fine - 0.25 Å
- Ultra-fine - 0.15 Å

Grid interval: Specify a value, in Å, for the grid interval. Setting this parameter to a value other than one of the preset values listed above will cause the *Grid resolution* to be set to Customized. Range = 0.1 to 2.0 Å.

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

Care should be taken with larger systems, as both the memory requirements and computation time increase cubically as the grid interval decreases. For a given system, reducing the *GridInterval* value from 0.4 to 0.1 will take at least 4^3 (64) times longer to compute.

vdW scale factor: Specify a factor to uniformly modify all van der Waals radii, representing a hard shell into which a probe may not pass. Alternatively, you may edit the van der Waals radii of an individual element using the Element Properties dialog. Default = 1.0; range = 0.1 to 3.0.

Max. solvent radius: Specify the maximum radius, in Å, of the solvent probe that is to be supported by the created field. *Max. solvent radius* is a cutoff distance that determines how far beyond the van der Waals surface of each atom the volume field is calculated. Default = 2.0 Å; range = 0.0 to 10.0 Å.

After you click *Create/Recreate*, this value governs the range of valid solvent radii on the Analysis tab. Increasing this value allows a wider range of solvent surfaces to be investigated without recalculation, but larger values take longer to compute. For more details, see Atom volumes & surfaces algorithms.

> **Note:** This option is disabled if the Connolly surface task is selected.

Connolly radius: Specify the radius, in Å, of the Connolly probe used in calculating the atom volume field. Range = 0.0 to 10.0 Å.

> **Note:** This option is disabled if the Solvent surfaces task is selected.

> **Note:** Calculation time can increase rapidly with *Connolly radius*, depending on the structure. Because of this, care should be taken when using large values of *Connolly radius*.

The *Default isosurfaces* section contains options which control the initial settings of the default isosurfaces. The default set of isosurfaces are always created when you first click the *Create* button. Once the isosurfaces have been created, these settings can be changed interactively on the *Analysis* tab.

Initial solvent radius: Specify the initial solvent probe radius, in Å, used to display solvent and accessible solvent surfaces. Range = 0.5 to 10.0 Å.

> **Note:** This option is disabled if the Connolly surface task is selected.

Show isosurfaces: Select the surfaces you want to be made visible once they have been created. After you click *Calculate/Recalculate*, these settings map to the visibility shown in the tree view on the *Analysis* tab. The set of isosurfaces generated will depend on the *Task* selected.

Recreate default isosurfaces: When checked, indicates that, when the *Recreate* button is pressed, all existing isosurfaces will be removed and replaced by the default set of isosurfaces (from the set Connolly Surface, vdW Surface, Solvent Surface, and Accessible Solvent Surface, depending on the *Task* selected).

Create/Recreate: Creates (or recreates) an atom volume field and, typically, some associated surfaces in the currently active document using the parameters specified on the *Setup* tab.

> **Note:** The *Create/Recreate* button may be disabled if the current document is a 3D Atomistic Collection document containing more than one physical system. Atom volume surfaces cannot be generated for selections which span physical systems. To enable the *Create/Recreate* button, you need to select all or part of a single physical system.
>
> The *Create/Recreate* button is also disabled if the current document (or currently selected physical system) contains a 2D periodic surface.

Create/Recreate | 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.

Access methods

Menu	*Tools	Atom Volumes & Surfaces	Setup*

Analysis tab

The *Analysis* tab on the Atom Volumes & Surfaces dialog allows you to interactively control the generation and visualization of all atom volume fields and surfaces in the current document. It also displays the results of atom volumes & surfaces calculations in the currently active document. The *Analysis* tab will be blank and disabled until atom volume fields and surfaces have been created.

Once the *Create* button has been pressed, the tree view on the *Analysis* tab allows you to select atom volume fields and surfaces in the current 3D model document and to control their visibility. The tree view also supports deletion, using the DELETE key, and allows renaming of fields and surfaces. Typically, one or more of the following atom volume surfaces are available, depending on the *Task* selected on the Setup tab.

- Connolly Surface - The surface at the boundary between the Connolly probe and the atoms (as represented by their scaled van der Waals radii), not at the locus of the probe center.
- vdW Surface - The surface that intersects with the van der Waals radii of the atoms in the structure. This is equivalent to a solvent surface with a solvent probe radius of zero and to a Connolly surface with a Connolly probe radius of zero.
- Solvent Surface - The surface which is the locus of the probe center as the probe rolls over the scaled vdW surface. This surface describes a space which could, in principle, be occupied by a probe of given radius, ignoring the accessibility of such points.
- Smoothed Solvent Surface - This is a solvent surface that is smoothed at the discontinuities (creases and cusps) in the same way that a Connolly surface is a smoothed vdW surface.
- Accessible Solvent Surface - This is the same as a solvent surface, except that the surface is only defined over externally accessible regions.

The tree view on the *Analysis* tab displays all of the atom volume surfaces in the current 3D model document, together with the atom volume field(s) from which they are derived. To collapse or expand the tree view, click the + or - symbol next to the node you want to collapse or expand.

> **Note:** These controls function in exactly the same way as those on the Volumetric Selection dialog. You can also use the techniques described in Selecting fields, surfaces, slices, and mesoscale molecules to control the visibility of the atom volume surfaces and to rename or delete atom volume fields or surfaces using the tree view.

Each item in the tree view has the following features:

- Visibility control - When checked, turns on display of the corresponding atom volume surface or field. The initial visibility here, once the *Create* button has been pressed, reflects the selection from the *Show isosurfaces* list on the *Setup* tab.

- Icon - Click on an icon (for example 🔲 Atom Volume Field or 🔗 Atom Volume Surface) to select the corresponding object in the 3D Viewer.

- Name - The name of the atom volume field or surface. To rename an atom volume field or surface, select the object, click on the name, then type in the new name.

> **Note:** To revert to the default/automatic name, select the object, then click on the existing custom name and delete it.

Solvent radius: Specify the size of the solvent probe radius for the selected surfaces. The solvent probe radius determines the distance of the solvent surface from the structure. Enter a new value or use the spin controls to change the value. Any changes you make are reflected interactively in the current document. Valid *Solvent radius* values must fall between 0.0 and the *Max. solvent radius*. Invalid values will results in surfaces named Non-Physical.

Connolly radius: Specify the Connolly probe radius for the selected surfaces. Enter a new value or use the spin controls to change the value. Any changes you make are reflected interactively in the current document.

> **Note:** If a value of 0.0 is shown, then Connolly surfaces have not been calculated. Changing the *Connolly radius* requires that the atom volume field is recalculated. For large systems, this may take some time.

> **Tip:** If you type in a value for the *Solvent radius* or *Connolly radius*, you must tab out of the text box before the change will take effect.

> **Note:** The *Solvent radius* and *Connolly radius* settings reflect the common settings for all of the atom volume surfaces currently selected in the active 3D model document or, equivalently, those selected in the tree view. A solvent radius or Connolly radius will only have a displayed value if it is the same for all selected atom volume surfaces or, if nothing is selected, if it is the same for all atom volume surfaces in the structure. If no atom volume surfaces are present in the structure, the *Solvent radius* and *Connolly radius* controls will be disabled. See Selecting fields, surfaces, slices, and mesoscale molecules for details on how to select atom volume surfaces.

Results: Reports volume and surface area properties for *all* atom volume surfaces in the currently active 3D model document. Entries take the form *<surface type> @<solvent radius>*, followed by details of the properties listed below, as appropriate:

- *Occupied Volume* - The volume on the atom side of the surface. It may map to the enclosed volume or the external volume of an atom volume surface, depending on whether the *High value inside* checkbox is checked on the Isosurfaces tab of the Display Style dialog.

- *Free Volume* - The volume on the side of the atom volume surface that is free of atoms (for 3D periodic systems only).

- *Surface Area* - The calculated area covered by the specified atom volume surface.

In the case of 3D periodic systems, these property values are for a single periodic cell. In nonperiodic or molecular systems, these property values apply to the whole structure.

Refresh: Recalculates the atom volume field, taking into account any changes to the currently active 3D model document, such as a change in the number or position of the atoms. Any atom volume surfaces will also be updated to reflect any such changes.

Access methods

Menu	*Tools	Atom Volumes & Surfaces	Analysis*

Finding equivalent atoms

The Find Equivalent Atoms dialog allows you to match atoms in one 3D model document with the equivalent atoms in another document. Atom matching is necessary in order to determine the proper correspondence between pairs of atoms in the reactant and product structures and thus generate a reaction pathway using the Reaction Preview dialog.

The Find Equivalent Atoms dialog can be accessed in two ways

- by selecting the *Find Equivalent Atoms* option on the Tools menu
- by pressing the *Match...* button on the Reaction Preview dialog

If you open the Find Equivalent Atoms dialog directly from the *Tools* menu, you must begin by specifying the two 3D model documents you wish to match, using the document chooser at the top of the dialog.

> **Note:** To be suitable for matching, the two 3D model documents selected must contain the same numbers of atoms of each element type. In addition, if any constrained atoms are present, there must be the same number and type of these in both documents. Finally, periodic 3D model documents must have P1 symmetry.
>
> If two unsuitable 3D model documents are selected, hint text describing the nature of the problem will be displayed below the main text area.

If you open the Find Equivalent Atoms dialog indirectly using the *Match...* button, the *Reactant* and *Product* 3D model documents specified on the Reaction Preview dialog are selected automatically.

When two suitable 3D model documents have been selected, preliminary sorting is performed based on element type and atom constraints.

After preliminary sorting, all of the atoms in each document are grouped into two folders; *matched atoms* and *unmatched atoms* and displayed in the text area below the corresponding filename.

Atoms in the red *unmatched atoms* folders are further grouped into subfolders by element type and atom constraints. Thus, a subfolder labeled 2xC contains two unmatched carbon atoms and one labeled 4xH contains four unmatched hydrogen atoms.

To find further matches automatically

1. Click the *Auto Find* button.

The *Auto Find* operation locates new matches using topological and geometrical algorithms.

To match atoms manually

1. Select an unmatched atom from one list. If you have already used *Auto Find*, a likely match for that atom will be highlighted in the second list, with a blue circle.

> **Note:** The selected atom is shown in yellow and any likely match is shown in blue in the corresponding 3D model document windows

2. Select the atom in the second list which you want to match with the atom you selected from the first list. This can be the likely match suggested by *Auto Find* or any other unmatched atom in the appropriate subfolder.
3. Click the *Set Match* button to define a match between the two selected atoms.

Atom matching strategy

In order to determine a reaction pathway using the Reaction Preview dialog, you must first match the atoms in the reactant with equivalent atoms in the product. This atom matching is performed using the options available on the Find Equivalent Atoms dialog.

Typically, the atom matching process involves several steps.

First, two suitable 3D model documents must be selected and some preliminary sorting is performed, based on element type and atom constraints.

After this preliminary sorting, all of the atoms in each document are grouped into two folders; *matched atoms* and *unmatched atoms*.

Further matches between unmatched atoms can be identified automatically, with the *Auto Find* button.

The *Auto Find* operation locates new matches using topological and geometrical algorithms. These algorithms use any existing atom matches as a starting point for generating new ones. Therefore, it is possible to improve the results of *Auto Find* by setting up some initial matches first, using the *Set Match* button.

This strategy is particularly useful for 3D models which have ambiguous topology, since in these situations *Auto Find* may generate an incorrect atom match. Use the following procedure to correct any errors of this type:

1. Unset all of the matches made by the *Auto Find* operation using the *Reset* button or the *Undo* option on the Edit menu.
2. Use the *Set Match* button to match manually one of the atoms that was incorrectly matched by *Auto Find*.
3. Click the *Auto Find* button again to generate a new set of atom matches based on the additional atom match information you supplied.

After the *Auto Find* operation is performed, any remaining unmatched atoms are grouped into subfolders based on atom type and topology. A likely match for each atom is also determined.

The *Set Match* button can be used manually match these atoms.

Find Equivalent Atoms dialog

The Find Equivalent Atoms dialog allows you to match atoms in one 3D model document with the equivalent atoms in another document. Atom matching is necessary in order to determine a reaction pathway using the Reaction Preview dialog.

Select two 3D model documents to be matched using the document chooser dropdown lists at the top of the Find Equivalent Atoms dialog. The document choosers filter the files in the current project so that only currently loaded 3D model documents are displayed.

> **Note:** To be suitable for matching, the two 3D model documents selected must contain the same numbers of atoms of each element type. In addition, if any constrained atoms are present, there must be the same number and type of these in both documents. Finally, periodic 3D model documents must have P1 symmetry.
>
> If two unsuitable 3D model documents are selected, hint text describing the nature of the problem will be displayed below the main text area.

When two suitable 3D model documents have been selected, preliminary sorting is performed based on element type and atom constraints.

After preliminary sorting, all of the atoms in each document are grouped into two folders; *matched atoms* and *unmatched atoms* and displayed in the text area below the corresponding filename:
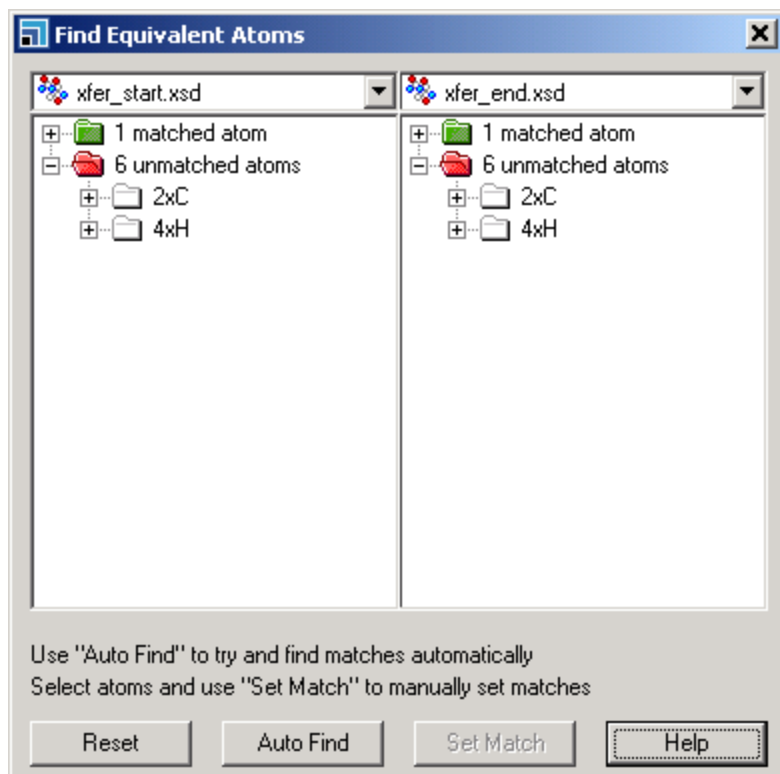
Find Equivalent Atoms dialog after two suitable 3D model documents have been selected, showing the results of preliminary sorting

Select an atom in a green *matched atoms* folder to highlight the atom it has been matched with in the other 3D model document. Both atoms are shown in yellow in the corresponding 3D model document windows.

Atoms in the red *unmatched atoms* folders are grouped into subfolders by element type and atom constraints. Thus, a subfolder labeled 2×C contains two unmatched carbon atoms and one labeled 4×H contains four unmatched hydrogen atoms.

Use the *Auto Find* button to identify matches between unmatched atoms automatically:
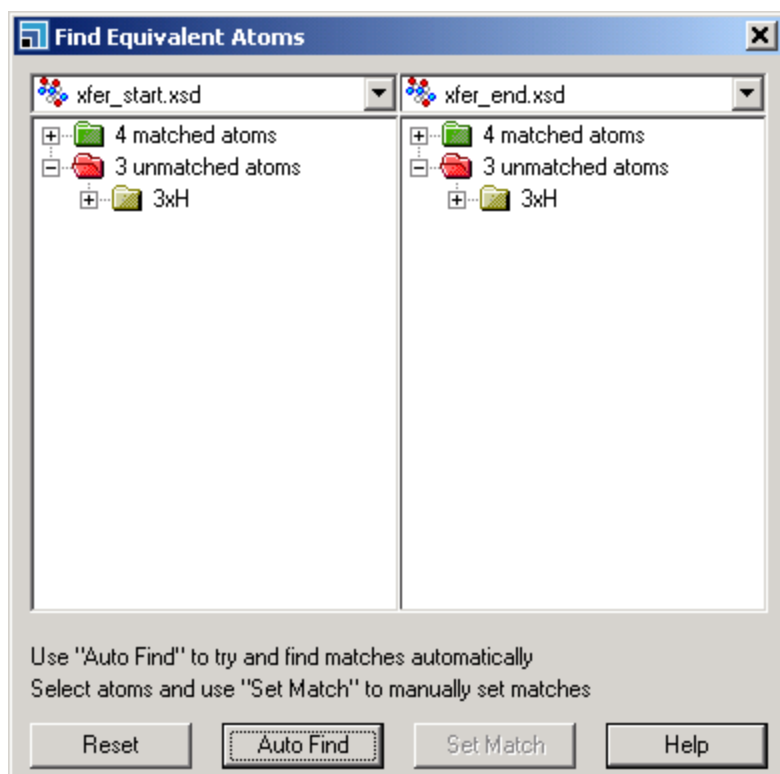
Find Equivalent Atoms dialog after Auto Find has been used to identify matches between unmatched atoms

Select an atom in one of the *unmatched atoms* folders to highlight its likely match in the other structure. The selected atom is shown in yellow and the likely match is shown in blue:
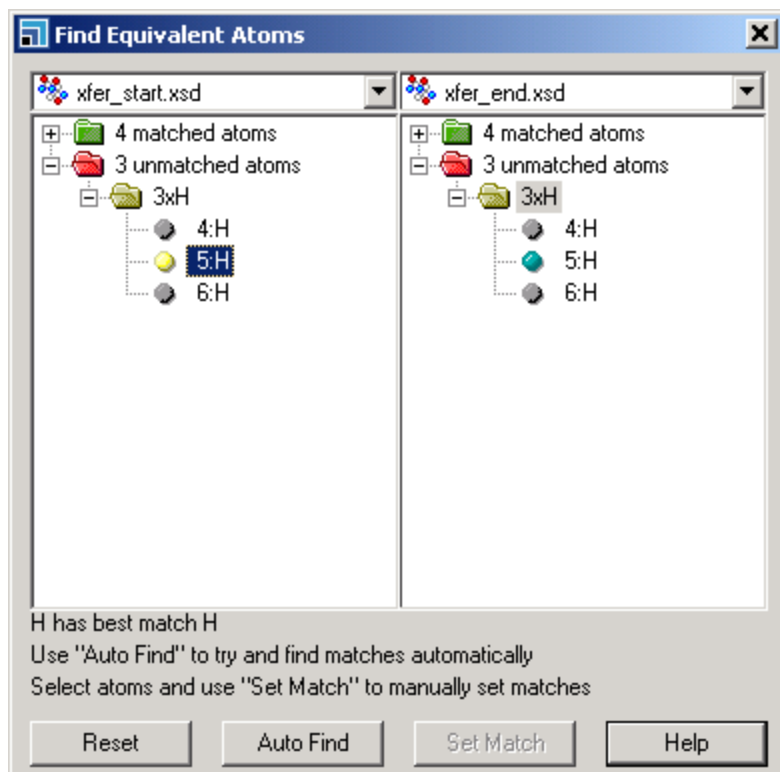
Find Equivalent Atoms dialog with an unmatched atom and its likely match highlighted

Both atoms are also highlighted in the corresponding 3D model document windows.

> **Note:** Likely matches between unmatched atoms are displayed only after the *Auto Find* operation has been performed.

Reset: When a folder or any unmatched atom is selected, *Reset* unsets all of the matches made using *Auto Find* and *Set Match* during the current session. When a matched atom is selected, *Reset* unsets only that match.

> **Tip:** The *Undo* and *Redo* options on the Edit menu can also be used to unset matches.

Auto Find: Identifies matches between atoms in two selected 3D model documents automatically, using topological and geometrical algorithms.

> **Note:** The *Auto Find* button is enabled only if there are atoms present in the *unmatched atoms* folder.

Set Match: Defines a match between the currently selected pair of atoms.

> **Note:** The *Set Match* button is enabled only if two suitable unmatched atoms are selected.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Tools	Find Equivalent Atoms*

Previewing reaction pathways

The Reaction Preview dialog allows you to interpolate between the reactant and the product of a chemical reaction in order to obtain a reaction pathway. The interpolated pathway is determined geometrically, using Linear Synchronous Transit (LST). The results of the interpolation can be used for transition state searching with, for example, DMol^3.

To preview a reaction pathway

1. Select *Reaction Preview* from the Tools menu.
2. Specify the *Reactant* and *Product* 3D model documents, using the document chooser.
3. If the reactant and product are unmatched, click the *Match...* button to open the Find Equivalent Atoms dialog. This allows you to match atoms in one 3D model document with the equivalent atoms in another document.

> **Note:** To be suitable for matching, the reactant and product 3D model documents selected must contain the same numbers of atoms of each element type. In addition, if any constrained atoms are present, there must be the same number and type of these in both documents.

4. Specify the number of steps over which the interpolation should be performed.
5. If necessary, check the *Superimpose Structures* option to perform a least squares best superposition on the reactant and product atom coordinates.
6. Choose whether the display settings of the reactant or those of the product should be used in the results file.
7. Click the *Preview* button to generate a reaction pathway and write the results to a trajectory file.

The results of the reaction preview are presented in a new 3D model document window. Use the animation controls, accessible from the Animation toolbar, to view the reaction pathway.

> **Note:** Since reaction pathways typically involve breaking bonds and making new ones, it is best to view them with *Monitor bonding* option, accessible from the Atoms & Bonds toolbar, switched on.

Reaction Preview dialog

The *Reaction Preview* dialog allows you to interpolate between the reactant and the product of a chemical reaction in order to obtain a reaction pathway. The interpolated pathway is determined geometrically, using Linear Synchronous Transit (LST). The results of the interpolation can be used for transition state searching with, for example, DMol^3.

Reactant: Select the 3D model document containing the desired reactant using the document chooser.

Product: Select the 3D model document containing the desired product using the document chooser.

> **Note:** The document chooser filters the files in the current project so that only currently loaded 3D model documents are displayed.

> **Note:** The two 3D model documents selected must be matched using the Find Equivalent Atoms dialog, before a reaction pathway can be previewed.

Number of frames: Specify the number of steps over which the interpolation should be performed.

Superimpose structures: When checked, indicates that a least squares best superposition will be performed on the reactant and product atom coordinates. In the resulting preview the initial atom positions are identical to those of the reactant and the final atom positions are those given by the rotation and translation of the product atom positions that gives the best least squares fit. Default = unchecked.

> **Note:** The *Superimpose structures* option is enabled only if nonperiodic 3D model documents are selected.

> **Note:** The reaction preview uses the original coordinates, not the displayed coordinates, when creating the trajectory. The user is encouraged to use the Original display style when mapping atoms.

Base preview on reactant: When selected, indicates that trajectory will use the display styles, monitors, etc. of the reactant document.

Base preview on product: When selected, indicates that trajectory will use the display styles, monitors, etc. of the product document.

Match...: Provides access to the Find Equivalent Atoms dialog which allows you to match atoms in one 3D model document with the equivalent atoms in another document. Atom matching is necessary in order to determine a reaction pathway using the *Reaction Preview* dialog.

Preview: Generates a reaction pathway based on the reactant and product specified in the *Reaction Preview* dialog, using Linear Synchronous Transit (LST) and writes the results to a trajectory (XTD format) file.

> **Note:** The *Preview* button is enabled only if two matched 3D model documents are selected.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Tools	Reaction Preview*

Superposing structures

The Superpose Structures tool takes a number of molecular structures and determines a set of transformations that aligns them, either with another structure or with each other, and calculates a measure of structural similarity for each pair of structures considered. The transformations are applied to generate a set of aligned structures that can be compared visually or, alternatively, the structural similarity measure can be used for numeric comparison.

The following scenarios provide examples of situations where aligning a set of structures could be useful:

- Determining structural similarity

  Similar structures may exhibit similar chemical activity; thus, identifying similar structures could be useful in predicting their properties.

- Preparing structures for a reaction preview

  The Reaction Preview tool provides a first approximation of the trajectory from a reactant to a product via a transition state. The trajectory is easier to interpret if the reactant and the product from which it is generated are correctly aligned.

- Preparing structures for other calculations

  When calculating vector or tensor properties (for example, dipole or quadrupole moment) for a series of structures, it is generally easier to compare the values if the structures are aligned.

Superposing molecular fragments

The Superpose Structures tool takes a number of molecular structures and determines a set of transformations that aligns them. The transformations are then applied to generate a set of aligned structures that can be compared visually or used as the input for further calculations.

To align structures

>

1. Either import structures from pre-existing files or construct new molecules using the sketching tools in the Materials Visualizer. To be aligned using the Superpose Structures tool, input and target structures must be molecular. Periodic systems cannot be used with Superpose Structures.

2. Make the 3D Atomistic document or 3D Atomistic Collection document containing the structures to be aligned the active document.

   > **Note:** If a subset of atoms are selected in the active document, then only those selected atoms will be included in the alignment calculation.

3. Choose *Tools | Superpose Structures* from the menu bar to display the Superpose Structures dialog.
4. Select the Alignment tab.
5. Choose the alignment strategy you wish to use by selecting the appropriate radio button. *Consensus* fitting will align the input structures to each other to produce the best overall fit between them all. *Target* fitting will align the input structures on an individual basis with a specified target system to produce the best fit between each input structure and the target.

   If you are fitting the structures to a target molecule, click on *Target document* and select the 3D Atomistic document containing the target structure from the dropdown tree view of the current project.

> **Note:** Consensus alignment can only be applied to 3D Atomistic Collection documents containing more than one structure.

> **Note:** If a subset of atoms are selected in the target document, then only the selected atoms will be included in the alignment calculation.

6. Select the method that will be used to align the structures from the *Fit method* dropdown list. For RMS Atoms fitting, the optimal alignment of one structure relative to another is defined as that which minimizes the root mean square distance between equivalent atoms in the two structures. For Field fitting, the optimal alignment is defined as that which maximizes a weighted average of the steric field overlap and the electrostatic field overlap between the two structures. For Moments fitting, the optimal alignment is obtained by aligning the moments of inertia or the electrostatic moments (i.e., dipole and/or quadrupole moments).

7. If you want the structures in the input document(s) to be updated to reflect the orientations that produce the optimal alignment, check the *Update original structures* checkbox.

8. If you wish to create a study table containing the aligned structures, together with values for the similarity measure, check the *Output to study table* checkbox.

9. Select the Fit Method tab.

10. Depending on the *Fit method* you selected on the *Alignment* tab, further options are available.

   If you are using the RMS Atoms fitting method, you should ensure that equivalent atoms are matched across all the input structures. If you want Superpose Structures to automatically match atoms between the input documents, check the *Find atom matches* checkbox. Alternatively, click the *Match...* button to display the Superpose Structures Equivalent Atoms dialog and match atoms across the input structures manually.

   If you are using the Field or Moments fitting methods, set the steric and electrostatic contributions to the forcefield used to align the structures in the *Steric weight* and *Electrostatic weight* fields. The values must be in the range 0.0 to 1.0 inclusive and should total 1.0. Select either *Moments of inertia* or *Electrostatic moments* as the property that will be used to determine the direction in which the structures will be aligned.

> **Note:** In order to use a non-zero electrostatic weight or electrostatic moments you must have atomic charges defined on the structures.

11. Select the Options tab.

12. Select the type of movements that will be allowed when the structures are aligned from the *Alignment type* dropdown list. Rigid fitting involves the translation and re-orientation of the structures that are being aligned. In addition to translation and re-orientation, Flexible fitting also includes variation of torsion angles in order to increase the structural similarity of the aligned structures. You should define the torsion angles you wish to vary in the input document using the Measure/Change Torsion tool on the *Sketch* toolbar.

   If you are performing a Flexible alignment, you may check the *Use bump checking* checkbox to include a close-contact penalty function in the alignment calculation. This will tend to exclude conformations that produce large overlaps of the van der Waals radii of the atoms in the structure.

> **Note:** If a subset of the defined torsions are selected in the active document, then only those selected torsions will be allowed to vary in a Flexible fitting run.

13. If you wish to align the structures using a substructure that is common to all the input molecules, check the *Find pattern* checkbox. Select the document containing the structural motif from the dropdown tree view of the current project. Superpose Structures will automatically perform a search for the specified pattern in the other input structures (in both the active document and the target document, if applicable) as part of the alignment process. Only those atoms that match the specified pattern will then be included in the alignment calculation.

> **Note:** If a subset of atoms are selected in the pattern document, then only the matching atoms in the active document and the target document will be included in the alignment calculation.

14. Click the *Superpose* button.

Depending on the output options you specified on the *Alignment* tab, Superpose Structures will update the input documents with the orientations of the structures that produce the optimal alignment, according to the specified settings, and/or output the aligned structures to a study table document, along with values calculated for the overlap during the fitting run.

The study table infrastructure provides extensive functionality for sorting, filtering, and processing the structures in the study table. It also enables you to calculate additional properties.

Matching atoms for alignment

In order to align structures using the RMS Atoms fitting method, it is necessary to determine the proper correspondence between atoms in the structures to be aligned. This correspondence can be set using the Superpose Structures Equivalent Atoms dialog.

To perform a targeted alignment, you need to match atoms in the target 3D Atomistic document with the equivalent atoms in the document to be aligned, which could be another 3D Atomistic document or a 3D Atomistic Collection document.

To find matches automatically

1. Either import structures from pre-existing files or construct new molecules using the sketching tools in the Materials Visualizer. The input structures for atom matching must be molecular. Periodic systems cannot be matched using the Superpose Structures Equivalent Atoms dialog.
2. If you are aligning to a target structure, select the `.xsd` document containing the target structure from the dropdown tree view of the current project using the document chooser on the left.
3. Select the `.xsd` or `.xod` document containing the structures to be aligned using the document chooser on the right.
4. Select the atoms you want to find matches for in each document or deselect everything if you want to find matches for all of the atoms.

> **Note:** To be suitable for matching, the same number and type of atoms must be selected in each of two or more structures.

5. Click the *Auto Find* button. The *Auto Find* operation locates new matches, including exact matches and groups of equivalent atoms, using topological and geometrical algorithms. The new matches are shown in the grid.

To set matches manually

1. Either import structures from pre-existing files or construct new molecules using the sketching tools in the Materials Visualizer. The input structures for atom matching must be molecular. Periodic systems cannot be matched using the Superpose Structures Equivalent Atoms dialog.

2. If you are aligning to a target structure, select the `.xsd` document containing the target structure from the dropdown tree view of the current project using the document chooser on the left.

3. Select the `.xsd` or `.xod` document containing the structures to be aligned using the document chooser on the right.

4. Select the atoms you want to set matches for in each document. You must select only one atom in each of any two or more structures.

5. Click the *Set* button. The new match is shown in the grid.

To remove matches

1. If you are aligning to a target structure, select the `.xsd` document containing the target structure from the dropdown tree view of the current project using the document chooser on the left.

2. Select the `.xsd` or `.xod` document containing the structures to be aligned using the document chooser on the right.

3. Select the atoms you want to remove matches from in each document (or deselect everything if you want to remove all matches for all of the atoms).

4. Click the *Reset* button. The selected matches are removed from the grid.

To review matches

1. If you are aligning to a target structure, select the `.xsd` document containing the target structure from the dropdown tree view of the current project using the document chooser on the left.

2. Select the `.xsd` or `.xod` document containing the structures to be aligned using the document chooser on the right.

3. Select one of the matches listed in the grid. If it is an exact match, the equivalent atoms in the alignment and (if applicable) target document will be selected. If the match is partial, the groups of equivalent atoms will be selected in the alignment and (if applicable) target document.

Superpose Structures dialog

The Superpose Structures dialog allows you to align two or more structures using a range of methods.

The Superpose Structures dialog contains the following tabs:

- Alignment: Allows you to select the alignment method, specify a fitting method, and set output options.
- Fit Method: Allows you to set further options associated with the selected fitting method.
- Options: Allows you to specify rigid or flexible fitting and to restrict the alignment calculation to a core structure common to all the systems being studied.

Superpose: Update the input documents with the orientations of the structures that produce the optimal alignment, according to the specified settings, and/or output the aligned structures to a study table document, along with values calculated for the overlap during the fitting run.

Help: Displays the Help topic for the current tab.

Access methods

Menu	*Tools	Superpose Structures*

Alignment tab

The *Alignment* tab allows you to select the alignment method, specify a fitting method, and set output options.

Consensus: When selected, indicates that the input structures will be aligned with each other to produce the best overall fit between them all. The input structures must be presented in the form of a single 3D Atomistic Collection document (`.xod`) containing multiple physical systems.

> **Tip:** A consensus fit can be thought of as the alignment of all the input structures to a virtual target that represents the 'average' conformation of the input structures. As a result, this strategy does not necessarily give the best fit for any given pair of structures in a set of consensus-aligned systems.

Target: When selected, indicates that all the input structures will be aligned on an individual basis with a specified target system to produce the best fit between each input structure and the target. The target system must be a single structure contained in a 3D Atomistic document.

> **Note:** To be aligned using the Superpose Structures tool, input or target structures must be molecular. Periodic systems cannot be used with Superpose Structures.

Target document: Select the 3D Atomistic document containing the target structure from the dropdown tree view of the current project.

> **Note:** The 3D Atomistic document containing the target molecular structure must be a loaded document in the current project. Either create the desired structure using the sketching tools in the Materials Visualizer or import the required molecule into the project before starting an alignment.

Fit method: Select the property that will be minimized when the structures are aligned from the dropdown list. Available options are:

- RMS Atoms - Aligns structures by calculating the best superposition of a defined set of matched atoms common to all the systems being studied using the root mean square difference in positions of matched atoms. If a study table is requested, the average distance between matched atoms is reported, in Angstrom. A value of 0 corresponds to perfect alignment.

  > **Note:** The RMS Atoms fitting method requires that equivalent atoms are matched across all the input structures. This correspondence can be set using the Superpose Structures Equivalent Atoms dialog, which can be accessed via the Fit Method tab.

- Field - Aligns structures by calculating the steric and electrostatic fields around them and then altering the orientation of the structures to maximize a weighted average of the steric field overlap and the electrostatic field overlap between the two structures. Here, the steric field is defined as the Lennard-Jones potential seen by a probe carbon atom.
- Moments - Aligns structures in terms of either their moments of inertia or electrostatic moments (i.e., dipole and/or quadrupole moments), according to the setting specified on the *Fit Method* tab.

Update original structures: When checked, indicates that the positions of the structures in the input document(s) will be updated to the orientation that is calculated to produce the optimal alignment.

Output to study table: When checked, indicates that the aligned structures will be output to a study table document, along with details of the structural similarity or overlap.

Access methods

Menu	*Tools	Superpose Structures	Alignment*

Fit Method tab

The *Fit Method* tab allows you to set further options associated with the selected fitting method.

Find atom matches: When checked, indicates that atom matches between the input documents will be determined automatically before an RMS fit is attempted.

Match...: Provides access to the Superpose Structures Equivalent Atoms dialog, which allows you to manually match atoms in one structure with the equivalent atoms in another.

> **Note:** The *Find atom matches* option and the *Match...* button are enabled only if the *Fit method* is set to RMS Atoms on the Alignment tab.

Steric weight: Specify the steric contribution, as a fractional value, to the forcefield used in the Field and Moments fitting methods. This value must be equal to 1.0 minus the electrostatic contribution.

Electrostatic weight: Specify the electrostatic contribution, as a fractional value, to the forcefield used in the Field and Moments fitting methods. This value must be equal to 1.0 minus the steric contribution.

> **Note:** The *Steric weight* and *Electrostatic weight* controls are disabled if the *Fit method* is set to RMS Atoms on the *Alignment* tab.

Moments of inertia: When selected, indicates that the principle moments of inertia of the input structures will be used to align structures for the Moments fitting method. This process will also be used as a pre-alignment step for Field fitting.

Electrostatic moments: When selected, indicates that the dipole and/or quadrupole moments of the input structures will be used to align structures for the Moments fitting method. This process will be also be used as a pre-alignment step for Field fitting

> **Note:** The *Moments of inertia* and *Electrostatic moments* controls are disabled if the *Fit method* is set to RMS Atoms on the *Alignment* tab.

Access methods

Menu	*Tools	Superpose Structures	Fit Method*

Superpose Structures Equivalent Atoms dialog

The Superpose Structures Equivalent Atoms dialog allows you to set a correspondence between atoms in one 3D Atomistic document with the equivalent atoms in another 3D Atomistic document or in a 3D Atomistic Collection document, or to set a correspondence between atoms in different structures in the same 3D Atomistic Collection document. Atom matching is necessary in order to align structures using the RMS Atoms fitting method.

The documents containing the atoms to be matched are selected using the dropdown tree views of the current project at the top of the dialog. The document chooser on the left only shows 3D Atomistic documents (.xsd). The document chooser on the right shows both 3D Atomistic documents and 3D Atomistic Collection documents (.xod).

> **Note:** The target document and/or the document containing the structure(s) for atom matching must be part of the current project. Either create the desired molecules using the sketching tools in the Materials Visualizer or import the required structures into the project before selecting input documents for matching.

> **Tip:** If you wish to set equivalences between atoms in different structures in a single 3D Atomistic Collection document, select the appropriate `.xod` document from the document chooser on the right and leave the document chooser on the left blank.

The grid shows any atom matches in the selected document or documents, including exact matches, indicated by a green icon, and matched groups, i.e., groups of atoms in different structures that are deemed to be equivalent, but for which the correspondence between individual atoms in the group is not known.

The grid will contain some of the following columns, depending on the documents selected:

- *Match size* - Shows the size of the matched groups of atoms in each structure for each match.
- *Target atom(s)* - Shows the names (if available) of the matched atoms in the target document. This column is not displayed if a target document has not been selected from the document chooser on the left.
- *Matched atom(s)* - Shows the names (if available) of the matched atoms in the 3D Atomistic document to be aligned. This column is displayed only if both the target document and the document to be matched are 3D Atomistic documents.
- *Num. matched systems* - Shows the number of structures in the 3D Atomistic document to be aligned that contain a matched atom or group of atoms. This column is not displayed if both the target document and the document to be matched are 3D Atomistic documents.

Clicking on an exact match in the grid causes the corresponding equivalent atoms in the specified document(s) to be selected. Clicking on a match group in the grid causes the corresponding groups of equivalent atoms in the selected document or documents to be highlighted.

> **Note:** If a single matched atom is selected in one of the specified documents then the corresponding item in the grid and the equivalent atoms in the documents are selected.

Reset: Removes matches on each of the selected atoms in the specified 3D structure document(s) or removes all matches if nothing is selected.

> **Tip:** The *Undo* and *Redo* options on the Edit menu can also be used to unset matches.

Auto Find: Automatically identifies matches between selected atoms in the specified 3D structure document(s) using topological and geometrical algorithms.

> **Note:** The *Auto Find* button is enabled only if the same number and type of atoms are selected in each of two or more structures.

Set Match: Defines a match between the currently selected pair of atoms.

> **Note:** The *Set Match* button is enabled only if a single atom is selected in each of two or more structures.

Access methods

Menu	*Tools | Superpose Structures | Fit Method | Match...*

Options tab

The *Options* tab allows you to specify rigid or flexible fitting and to identify core structures common to all the systems being studied.

Alignment type: Select the type of movements that will be allowed when the structures are aligned. Available options are:

- Rigid - Structures will be aligned using only rigid translation and rotation of one model relative to another.
- Flexible - Structures will be aligned by rigid translation and rotation of one model relative to another and, in addition, by varying defined torsion angles in order to improve the similarity of aligned structures.

> **Note:** The torsion angles that are to be varied must be defined in the input document using the Measure/Change Torsion tool on the *Sketch* toolbar.

Use bump checking: When checked, indicates that a close-contact penalty function will be included in torsional optimization during a Flexible fit. This will tend to exclude conformations that produce large overlaps of the van der Waals radii of the atoms in the flexible structure. Default = unchecked.

> **Note:** This option is enabled only if Flexible fitting is selected.

Find pattern: When checked, indicates that all structures in the input documents will be searched for a structural motif defined in the pattern document using the Find Patterns functionality in the Materials Visualizer. Select the document containing the substructure pattern from the dropdown tree view of the current project. Default = unchecked.

> **Tip:** This option is useful in cases where the structures being studied have a common core and you wish to align them using this substructure.

> **Note:** Find Patterns matches atoms or beads by one of the atom or bead properties, but it ignores bond types. However, Superpose Structures always matches both atoms and bonds based on their ElementType and ChemicalType respectively.

Access methods

Menu	*Tools	Superpose Structures	Options*

Brillouin zone paths

The Brillouin zone is a uniquely defined primitive cell of the reciprocal lattice, a path through this zone can be used to connect important symmetry points. The critical points available depend on the symmetry of the lattice.

The Brillouin zone path to the k-point in particular is essential to the graphical representation of band structure and phonon dispersion in CASTEP, DMol[3], and GULP.
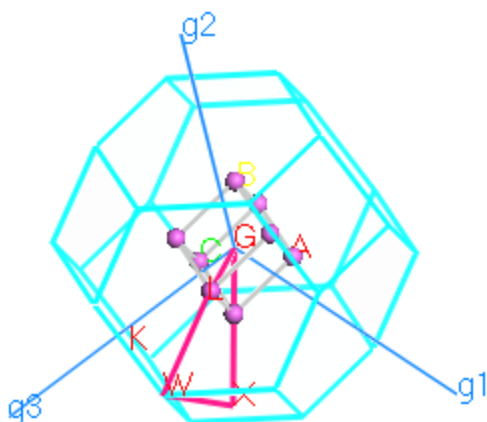
By default the crystal lattice is displayed in white, the reciprocal lattice in light blue, its axes in bright blue, and the Brillouin zone path and critical points in magenta.

Viewing the reciprocal lattice

The reciprocal lattice contains the Brillouin zone and its special points.

To view a reciprocal lattice and add paths

1. Either import a crystal structure from an existing file or construct a new lattice using the Crystal Builder tools in the Materials Visualizer.
2. Select *Build | Symmetry | Primitive Cell* from the menu bar to convert to the primitive crystal lattice.
3. Select *Tools | Brillouin Zone Path* from the menu bar to open the Brillouin Zone Path dialog.
4. Click the *Create* Brillouin zone path button. The reciprocal lattice and axes are displayed in the 3D Viewer and the default Brillouin zone paths are plotted.

   > **Tip:** You may wish to hide the crystal lattice to prevent the 3D Viewer from becoming cluttered.

5. Click the *Add path segment* button on the Brillouin Zone Path dialog to add a new row to the grid.
6. Edit the name of the point (the letter) and its coordinates. The coordinates are expressed as fractional X Y Z with no separating commas or brackets but must be separated from the point name by a colon (:).
7. The order of the paths can be changed and unnecessary paths can be deleted.
8. Click the *Reset* button to restore the default paths.
9. Uncheck the *Display reciprocal lattice* checkbox to hide the reciprocal lattice in the viewer.

To set the reciprocal lattice display style

1. Choose *View | Display Style* from the menu bar, click the *Display Style* button [image] on the 3D Viewer toolbar, or right-click in the 3D structure document and select *Display Style* from the shortcut menu to open the Display Style dialog.
2. Select the *Reciprocal* tab and specify whether to display the reciprocal lattice in the *Display style* section.
3. Use the *Scale* setting to determine the size of the reciprocal lattice relative to the parent crystal lattice.
4. Choose how the *Paths* are represented. They can be drawn with solid or dashed lines, or not drawn at all. The color and line width can be adjusted using the appropriate controls.
5. Choose how the *Brillouin zone* is represented. Its color and transparency can be adjusted and its limits can be drawn with solid or dashed lines, or not drawn at all.
6. Specify whether to *Display axes* for the reciprocal lattice.

Brillouin zone theory

The first Brillouin zone is a uniquely defined primitive cell of the reciprocal lattice. Its stems from the Bloch wave description of waves in a periodic medium, in which it is found that the solutions can be completely characterized by their behavior in any primitive cell of the reciprocal lattice. The main advantage of the Brillouin zone between the waves is that these polyhedra implicitly possess the highest point symmetry. So the Brillouin zone represents the point symmetry of the underlying reciprocal lattice.

Taking surfaces at the same distance from one element of the lattice and its neighbors, the volume included is the first Brillouin zone. Another definition is as the set of points in k-space that can be reached from the origin without crossing any Bragg plane. Equivalently, this is the Voronoi cell around the origin of the reciprocal lattice.

For example for an FCC lattice the reciprocal lattice is a truncated octahedron:
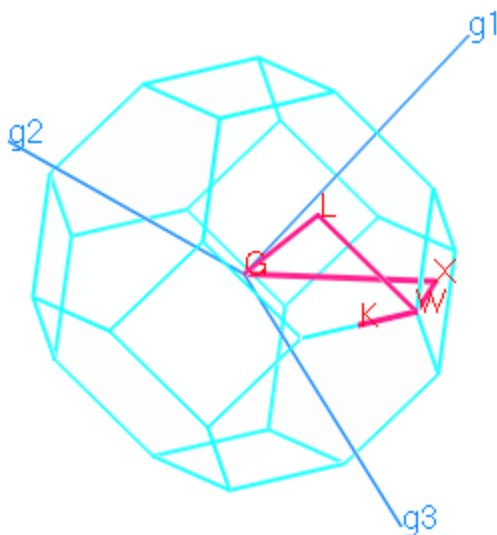
The reciprocal lattice with Brillouin zone for an FCC system, the high symmetry points and lines are indicated in red.

The following notation is used to label the critical points:

Symbol	Description
Γ (G)	Center of the Brillouin zone
Simple cube	
M	Center of an edge
R	Corner point
X	Center of a face
Face-centered cubic	
K	Middle of an edge joining two hexagonal faces
L	Center of a hexagonal face
U	Middle of an edge joining a square and a hexagonal face. Symmetrically equivalent to K.
W	Corner point
X	Center of a face
Body-centered cubic	
H	Corner point joining four edges
N	Center of a face
P	Corner point joining three faces
Hexagonal	
A	Center of a hexagonal face
H	Corner point
K	Middle of an edge joining two rectangular faces
L	Middle of an edge joining a hexagonal and a rectangular face
M	Center of a rectangular face

The reciprocal lattice vectors are labeled g1, g2, and g3 in Materials Studio.

There are also second, third, etc., Brillouin zones, corresponding to a sequence of disjoint regions (all with the same volume) at increasing distances from the origin, but these are used more rarely. As a result, the first Brillouin zone is often called simply the Brillouin zone. (In general, the n-th Brillouin zone consist of the set of points that can be reached from the origin by crossing n - 1 Bragg planes.)

Brillouin Zone Path dialog

The Brillouin Zone Path dialog displays information about the Brillouin zone of the current structure and the path. The display style of the reciprocal lattice for a Brillouin zone path can be modified on the Reciprocal tab on the Display Style dialog.

Reset Brillouin zone path: Resets the k-point path to the default path for the current structure. If the active document is not 3D periodic this is not available.

Create Brillouin zone path: Creates the k-point path to the default path for the current structure. This is only available if the active document contains a 3D periodic system without a path.

Each row of the grid corresponds to a segment of the path, showing the symmetry label, the start and end points of the segment and the number of divisions.

The end points of each segment can be edited, either by typing the required coordinates into the grid or by selecting a new symmetry label from the dropdown list.

Path segments can be added and deleted, the order of segments can be changed and the direction of a segment can be reversed using the buttons on the toolbar beneath the grid.

Add path segment: Copies the selected path segment to a new row at the bottom of the grid.

Delete path segment: Deletes the selected row from the grid.

Earlier in path: Moves the selected row above the preceding row in the grid.

Later in path: Moves the selected row below the subsequent row in the grid.

Reverse path segment: Transposes the coordinates and symmetries of the start and end points of the selected path segment.

Display reciprocal lattice: When checked the reciprocal lattice will be displayed.

Help: Displays the Help topic in a browser.

Access methods

Menu	*Tools	Brillouin Zone Path*
Menu	*Modules	CASTEP	Calculation	Properties	Band Structure	More...	Path...*
Toolbar	*	Calculation	Properties	Band Structure	More...	Path...*
Menu	*Modules	CASTEP	Calculation	Properties	Phonons	More...	Path...*
Toolbar	*	Calculation	Properties	Phonons	More...	Path...*
Menu	*Modules	DFTB+	Calculation	Properties	Band structure	Path...*
Toolbar	*	Calculation	Properties	Band structure	Path...*
Menu	*Modules	DMol3	Calculation	Properties	Band structure	Path...*
Toolbar	*	Calculation	Properties	Band structure	Path...*
Menu	*Modules	GULP	Calculation	Properties	Frequencies	Path...*
Toolbar	*	Calculation	Properties	Frequencies	Path...*

Vibrational analysis

Materials Studio allows you to calculate the vibrational modes of molecules which have a suitable Hessian matrix associated with them. Such matrices can either be calculated directly using Materials Studio modules, for example DMol[3], or they can be imported.

To analyze vibrational frequencies

1. Open a 3D Atomistic document containing the results of a calculation in which one of the properties requested was *Frequency* and a Hessian matrix was produced.
2. Select *Tools | Vibrational Analysis* from the menu bar to open the Vibrational Analysis dialog, select the Analysis tab.
3. Click the *Calculate modes* button. Any vibrational modes are identified and listed according to their Frequency (in cm^{-1}) and Intensity (in km/mol). Positive values are normal modes, negative frequencies indicate imaginary vibrations.
4. Select a negative frequency and click the *Animate* button to view the vibration is represents.
5. Click the *Grid* button to display a Grid document containing the frequency and intensity data.
6. Click the *Spectrum* button to display the calculated IR spectrum for the structure, the properties of the spectrum can be set on the Options tab.

Calculating vibrational frequencies

Harmonic vibrational frequencies may be obtained from the matrix of Cartesian second derivatives, also known as the Hessian matrix, of a molecular or periodic system (Wilson et al., 1955).

The Hessian matrix can be computed using Forcite or quantum mechanical methods. It can take up considerable space in memory for a large structure, so you may wish to remove it when it is no longer required.

For the case of molecule (or any finite system) the elements of the Hessian, $H_{i,j}$, are given by the second derivative of the total energy E:

Eq. 1

$$H_{i,j} = \frac{\partial^2 E}{\partial q_i \partial q_j}$$

where q_i is a Cartesian coordinate of a system with N atoms, so that $1 < i < 3N$.

For the periodic case, there is an infinite number of atoms, but due to the periodicity ($H_{i,j} = H_{i+T,j+T}$), the infinite Hessian matrix can be Fourier transformed into an infinite set of 3N x 3N matrices, where N now stands for number of atoms in the unit cell.

Eq. 2

$$H_{i,j}^{\mathbf{k}} = \frac{1}{V} \sum_{\mathbf{T}} H_{i,j+\mathbf{T}e^{i\mathbf{k}\mathbf{T}}}$$

Here, **T** is the lattice translations vector and **k** represents the vector in the first Brillouin zone.

For many phenomena, such as infrared spectra, for example, the most important factor is the Hessian matrix for the case where **k** = 0, i.e., at the Γ-point. Thus, the Hessian for periodic systems will hereafter be referred to as the Hessian at the Γ-point.

The mass-weighted Hessian is obtained by dividing Hessian elements by the square roots of the atomic masses:

Eq. 3

$$F_{i,j} = \frac{H_{i,j}}{\sqrt{m_i m_j}}$$

According to the harmonic approximation, the vibrational frequencies are the square roots of the eigenvalues of F and the normal modes are the eigenvectors of F.

Calculating vibrational intensities

The infrared intensities are obtained from the atomic polar tensors (A), which are conventionally called Born effective charges in solid-state calculations, of all atoms in the system. A is a second derivative of the total energy with respect to the Cartesian coordinates and dipole moments.

Eq. 4

$$A_{i,j} = \frac{\delta E}{\delta q_i \delta \mu_i}$$

The intensity of a given mode can be evaluated as a square of all transition moments of this mode and expressed in terms of the A matrix and eigenvectors of the mass-weighted Hessian, F:

Eq. 5

$$I_i = \left(\sum_{j,k} F'_{i,j} A_{j,k} \right)^2$$

Here, F' are eigenvectors of the normal mode, i.

Infrared spectra

A chart displaying infrared absorbance as a function of frequency is called an infrared spectrum. In Materials Studio, the frequency of vibrational modes is expressed in cm^{-1} and their intensity (closely related to macroscopic absorbance) is expressed in $km\ mol^{-1}$ (kilometers per mole).

A molecule composed of N atoms has 3N degrees of freedom, of which six are translations and rotations of the molecule itself. This leaves 3N - 6 degrees of vibrational freedom (or 3N - 5 if the molecule is linear). The frequency at which a given vibration occurs is determined by the strengths of the bonds and the masses of the atoms involved. The number of observed absorption peaks is usually different from what would be predicted by the formula above, since their number may be increased by additive and subtractive interactions, leading to combination tones and overtones of the fundamental vibrations. Furthermore, the number of observed absorption peaks may be decreased by molecular symmetry and spectroscopic selection rules.

Negative eigenvalues

Negative eigenvalues correspond to modes in which the energy is not a local minimum. Generally, these indicate that the system is in a transition state. The normal mode corresponding to this eigenvalue is the mode that moves the system in the direction of a local energy minimum.

The frequencies obtained from negative eigenvalues are obviously imaginary numbers. However, by convention, such frequencies are given as real negative numbers.

Translations and rotations

Diagonalizing the mass-weighted Hessian yields 3N frequencies. Of these, 3N - 6 correspond to the normal modes of vibration and the remainder to translations and rotations of the entire system. (For a

linear molecule, there are 3N - 5 normal modes; for a periodic system, there are 3N - 3). If the geometry of the system has been optimized so that the atomic forces are small (~1.0×10^{-4} Hartree Bohr^{-1}), then the frequencies corresponding to translations and rotations will only be a few wavenumbers in magnitude. If, however, the geometry of the system has not been optimized, then the frequencies of the translations and rotations can be rather large, of the order of several hundred wavenumbers.

It is possible to remove the translations and rotations from the Hessian matrix before computing the frequencies. This will result in values for the translational and rotational modes that are rigorously zero. The procedure involves constructing a matrix representation of the translations and rotations, P, which is used to project the translations and rotations from the Hessian. The remaining normal modes and frequencies are slightly altered from the unprojected values.

> **Note:** The vibrational frequencies computed at non-optimized geometries are, at best, approximations to the actual frequencies. Depending on the magnitude of the forces on the atoms, the calculated frequencies could actually be quite inaccurate. The main purpose of computing frequencies at such geometries is to identify modes of negative curvature which may be used to locate transition states.

Vibrational Analysis dialog

The Vibrational Analysis dialog allows you to calculate the vibrational modes and intensities of molecules in suitable 3D model documents.

To be suitable for vibrational analysis, the 3D model document must have a single Hessian matrix associated with it. This matrix can either be calculated directly using, for example DMol^3, or it can be imported into the model using the *Insert From...* command on the Edit menu. If the Hessian file contains atomic polar tensor information (used in the DMol^3 and CASTEP modules, for example), vibrational mode intensities will also be calculated and displayed.

The Vibrational Analysis dialog contains the following tabs:

- Analysis: Allows you to determine vibrational frequencies and intensities, and the spectrum for the active 3D model document, and to display the results.
- Options: Allows you to control how vibrational modes are calculated and how the results of the calculation are displayed.

Help: Displays the Help topic for the current tab.

Access methods

Menu	*Tools	Vibrational Analysis*

Analysis tab

The *Analysis* tab allows you to determine vibrational frequencies and IR intensities, and the spectrum for the active 3D model document, and to display the results.

Calculate modes: Determines and displays a list of the frequencies and IR intensities of the vibrational modes calculated for the active 3D model document.

Calculate modes | 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.

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

Animation: Creates an animation in a trajectory file (XTD file format) for the selected vibrational mode in a new 3D model document window using the options specified on the Options tab and automatically animates it. Select a mode from the list to make it the active mode and enable the *Animation* button. Click the *Animation* button or double-click on a mode from the list to create a trajectory file for that mode in a new 3D model document window and animate it automatically.

> **Tip:** If the Animation toolbar is not already displayed, it is opened automatically when you click the *Animation* button. Use the animation controls on the *Animation* toolbar to control the playback of the animation.

> **Note:** The *Animation* button is enabled only when a vibrational mode of the molecule in the active 3D model document is selected.

Grid: Creates a grid document (XGD file format) containing the current set of calculated vibrational frequencies and IR intensities.

> **Tip:** Materials Visualizer supports easy transfer of such grid data into both internal and external spreadsheet applications for further analysis.

> **Note:** The *Grid* button is enabled only when the vibrational modes of the molecule in the active 3D model document have been calculated and displayed.

Spectrum: Displays the calculated IR spectrum for the structure and creates a chart document (XCD file format), based on the calculated frequencies and IR intensities, using the options specified on the Options tab.

> **Note:** The *Spectrum* button is enabled only when the vibrational modes of the molecule in the active 3D model document have been calculated and displayed.

IR intensities are reported as zero if the computational server that generated vibrational frequencies has not produced atomic polarizability tensors.

Access methods

Menu	*Tools	Vibrational Analysis	Analysis*

Options tab

The *Options* tab allows you to control how vibrational modes are calculated and how the results of the calculation are displayed.

Project out zero frequency modes: When checked, indicates that zero frequency vibrational modes (which correspond to rotations and translations in nonperiodic systems and just translations in periodic systems) will be removed from consideration. Default = checked.

Scale amplitudes by intensities: When checked, indicates that mode animation magnitude will be scaled depending on its IR intensity. The highest intensity mode will be animated with the specified *Max. amplitude* value. Default = unchecked.

Max. amplitude: Specify the value, in Å, to be used to scale the apparent motion of atoms when a mode is animated. The distance, which can take a minimum value of 0.1 Å and a maximum value of 2.0 Å, corresponds to the largest displacement of an atom from its rest position. Default = 1.0 Å.

Number of steps in file: Specify the number of steps or frames to be used when a mode is animated. Values are restricted to positive multiples of 4. Each animation represents a single cycle of a vibrational mode. Consequently, for N steps, the rest positions are shown at steps N/2 and N and the maximum displacements at steps N/4 and 3N/4. Default = 20.

Reverse wavenumber axis: When checked, indicates that the x-axis of the generated spectrum will be reversed, with frequencies increasing from right to left. Default = checked.

Reverse intensity axis: When checked, indicates that the y-axis of the generated spectrum will be reversed, with intensities increasing from top to bottom. Default = checked.

Show smoothed spectrum: When checked, indicates that the generated spectrum will be smoothed with a Lorentzian function. When this checkbox is unchecked, the spectrum will consist only of vertical bars at normal mode frequencies. Default = checked.

FWHM: Specify, in cm^{-1}, the full width at half maximum parameter of the Lorentzian function used for smoothing of the IR spectrum. This parameter defines, in general, how broad the IR peaks are. Default = 5.0 1/cm.

Graph quality: Specify the quality of spectrum smoothing to be used along the wavenumber scale. Available options are:

- Coarse
- Medium
- Fine
- Ultra-fine

Access methods

Menu	*Tools	Vibrational Analysis	Options*