Setting up a work function calculation

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

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

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

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

To set up a work function calculation

1. Either import a structure of the bulk material from a pre-existing file or construct a new structure using the sketching and crystal building tools in the Materials Visualizer.
2. Geometry optimize the bulk structure using CASTEP.
3. Cleave the required crystallographic surface using the Cleave Surface dialog so that the thickness provides a meaningful representation of the bulk.
4. Build a vacuum slab using the Build Vacuum Slab Crystal dialog, you should ensure that the distance between the surface and the end of the vacuum is great enough that there can be no potential interactions between the surface and the next layer.
5. Choose Modules | CASTEP | Calculation from the menu bar.
6. Select the Setup tab.
7. Choose the Geometry Optimization task.
8. Fix Cartesian atomic positions of some atoms in the middle of the slab using the Edit Constraints dialog, accessible from the Modify menu.
9. Select either the LDA or GGA Functional from the dropdown list (see the theory section for more information on functionals).
10. Click the Run button.
11. Follow the steps in the Displaying the averaged potential chart for work function calculations topic.

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

Displaying the averaged potential chart for work function calculations

The CASTEP Analysis dialog can be used to generate plots of the change in electrostatic potential through a vacuum slab, which is related to the energy required to remove an electron from the bulk into the vacuum (the work function). The plots are created by averaging the electrostatic potential in the planes perpendicular to the slab normal.

The averaged electrostatic potential is reported along the fractional coordinate of the unit cell in the direction of the vacuum. The Fermi level is reported on the work function chart.

To create an averaged potential chart

1. Choose Modules | CASTEP | Analysis from the menu bar to open the CASTEP Analysis dialog.
2. Select Potentials from the list of properties.
3. Make the 3D Atomistic document containing the 3D periodic vacuum slab the active document.
4. Use the Results file selector to pick the results file or make the *seedname*.outmol file the active document.
5. Select the Potential field from the dropdown list.
6. Optionally check the View isosurface on import checkbox.
7. Click the Import button.
8. A new chart document, *seedname* Potential Profile.xcd, is created in the results folder and becomes the active document. The selected potential field is imported into the 3D Atomistic document and may be displayed as an isosurface.