Band Structure Calculations; Electronic and Optical Properties

Stewart Clark
University of Durham

Outline

- Introduction to band structures
- Calculating band structures using Castep
- Calculating optical properties
- Examples results
- Some applications

Band Structures

- Bloch's theorem introduces a wavevector **k**.
- It can always be confined to the 1st BZ (any **k** outside the 1st BZ can be mapped back into it).
- The band index appears in Bloch's theorem because for each **k** there are many solutions.

$$H\Psi_{n.k} = E_{n,k}\Psi_{n,k}$$

This leads to a description of the energy levels of electrons in a periodic potential in terms of a family of continuous functions $E_{n,k}$.

This is the *band structure* of the solid.

Simple Methods

Free electrons give parabolic bands

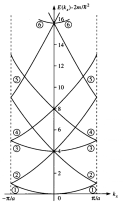


Fig. 7.5 Free electron bands for a square lattice shown along the [1 0] direction.

Using a basic basis set for the wavefunctions improves results slightly

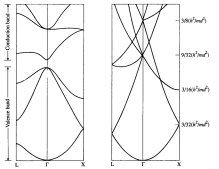


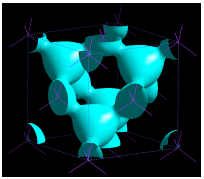
Fig. 7.6 Comparison between the LCAO bands for Ge, computed with an sp^3 basis, and the free electron bands. From Harrison (1980).

In Castep we use an accurate plane wave basis set.

Calculating Band Structures

- After calculating the electronic structure of a material we have the charge density n(r) , the potential V(r) and hence the complete Hamiltonian:

$$H = -\frac{1}{2}\nabla^2 + V_{e-e}[n(r)] + V_{i-e}[n(r)] + V_{xc}[n(r)]$$

n(r)  V(r)

Algorithm

- Calculate self-consistent density and potential.
- For a chosen *k*-point in the band structure calculate it's eigenvalues and eigenvectors (wavefunctions) as follows:
- Start from random wavefunction.
- For the first band, calculate the search direction using self-consistent potential.
- Assuming parabolic energy curve, step wavefunction coefficients to bottom in given direction.
- Repeat previous two steps (using orthogonal search direction) until no change occurs.
- For subsequent bands at this *k*-point, perform similar process, ensuring the bands remain orthogonal to all lower bands.

Castep Input Files

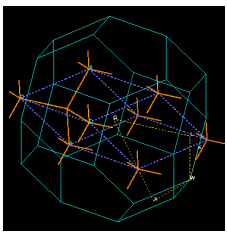
- Can control k-points used in band structures by several `cell` keywords
  - `bs_kpoints_list`
  - `bs_kpoints_path`
  - `bs_kpoints_mp_grid`
- Controlled by `param` keyword `task`
  - `task : BandStructure`

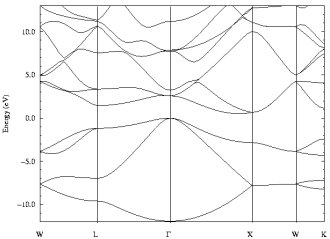
Example: Silicon

```
%block lattice_cart
2.7 2.7 0.0
2.7 0.0 2.7
0.0 2.7 2.7
%endblock lattice_cart

%block positions_frac
Si 0.00 0.00 0.00
Si 0.25 0.25 0.25
%endblock positions_frac

%block bs_kpoints_path
0.0 0.0 0.0
0.5 0.0 0.5
0.5 0.5 0.5
0.0 0.0 0.0
%endblock bs_kpoints_path

Symmetry_generate
```

```
task : BandStructure
```

Silicon Band Structure





Conventional Cell?

- Although the full set of levels can be described with restricted **k**, it is often useful to allow **k** to range over more of *k*-space.
- The set of wavefunctions and energy levels for 2 values of **k** differing by a reciprocal lattice vector **K** are identical.

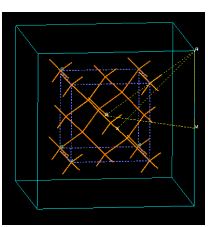
$$\Psi_{n,k+K}(r) = \Psi_{n,k}(r)$$

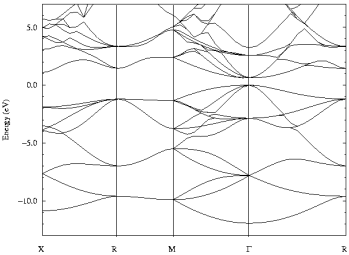
$$E_{n,k+K} = E_{n,k}$$

By not using a primitive cell, the band structure contains redundant information.

For each of the **k**=**k**+**K** we can map them back into the 1st Brillouin zone of the primitive cell.

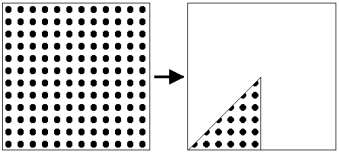
Non-primitive Cell





Density of States

- Many electronic properties depend on the electronic structure throughout the whole Brillouin zone.
- A band structure usually shows the electronic states along lines of high symmetry.
- Instead, we need to sample the whole Brillouin zone in a method similar to the SCF.



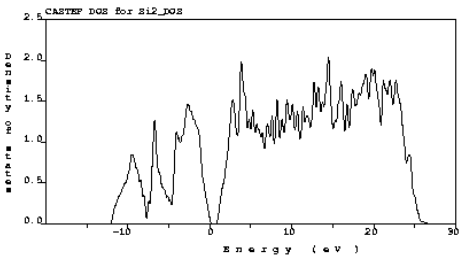
Castep Input files

For DOS calculations, get regular sampling grid using:

```
bs_kpoints_mp_grid : i j k
```

Plotting a DOS from k-points on high symmetry lines (from `bs_kpoints_path`) is not correct

Example of DOS Calculation



Magnetic Materials

- By default CASTEP calculations are non-magnetic
- All bands are doubly degenerate
- To release this constraint use either:
  - `spin_polarised : true`
  - `nspins : 2`

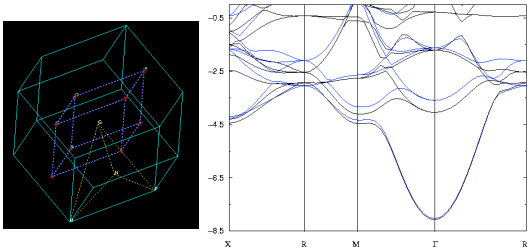
Magnetic Materials

- Can also set initial magnetic state (`param` file):
  - `spin : 3`
- Can constrain spin (`param` file):
  - `spin_fix : 6`
- Can initialise atom spin states (`cell` file):

```
%block positions_frac
Fe 0.0 0.0 0.0 MAGMOM= 0.25
Fe 0.5 0.5 0.5 MAGMOM=-0.25
%endblock positions_frac
```

(NB: MAGMOM to be obsolete in v4.1. Use SPIN instead)

Magnetic Materials



Calculating Optical Properties

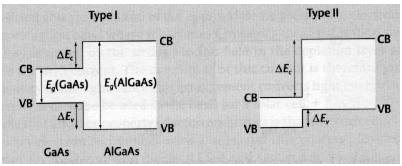
- `task` keyword in `param` file
  - `task : Optics`
- In the cell file use one of
  - `optics_kpoints_list`
  - `optics_kpoints_path`
  - `optics_kpoints_mp_grid`
- Calculation similar to bandstructure, but optical matrix elements also calculated

Optical Properties

- Properties include
  - Reflectivity
  - Absorption
  - Refractive Index
  - Dielectric Function
  - Conductivity
- For
  - Polarised light
  - Unpolarised light
  - Polycrystalline materials

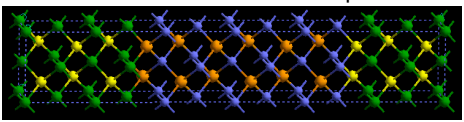
BS Application – Band Offsets

- Heterojunctions are formed when two different types of semiconductor are joined together.
- Heterostructures are used extensively in the electronic (e.g. transistors) and optoelectronic (e.g. LED's) industry.



Calculating Band Offsets

- Knowledge of the band structures of the two individual materials is not sufficient to determine the band offset.
- Band energies are determined with respect to the average potential in the solid.
- It is also necessary to perform a *supercell* calculation to determine how the potentials

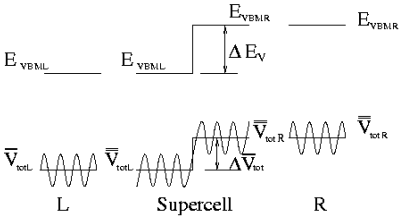


The Average Potential

- The potential can be averaged across the *x-y* planes (junction normal to *z*).
- This is the *microscopic average* potential.
- The *macroscopic average* potential is calculated over the period over the microscopic potential.
- The band structures are measured relative to the macroscopic average.

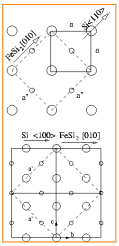
$$\overline{\overline{V}}_{tot}(z) = \frac{1}{\lambda\lambda'} \int_{z-\lambda/2}^{z+\lambda/2} \int_{z'-\lambda'/2}^{z'+\lambda'/2} \overline{V}_{tot}(z'')dz''dz'$$

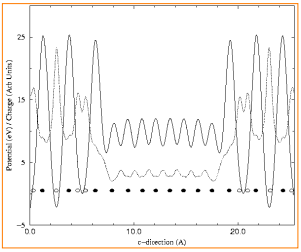
Band Line-up Using Potential



$$\Delta E_v = \left(\overline{\overline{V}}_{totL} + E_{vbmL}\right) - \left(\overline{\overline{V}}_{totR} + E_{vbmR}\right)$$

An Example: $FeSi_2$ on Si





Offset is 0.4eV – useful for LED's and near-IR detectors

Applications - Surfaces

- We can also use the *supercell* method to calculate the band structures of surfaces.
- The wavefunctions at surfaces decay exponentially into the vacuum region.

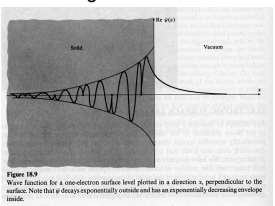
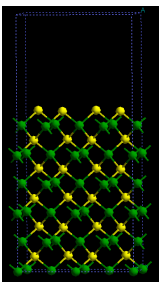
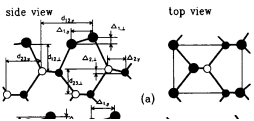


Figure 18.9
Wave function for a one-electron surface level plotted in a direction x, perpendicular to the surface. Note that ψ decays exponentially outside and has an exponentially decreasing envelope inside.

Details of GaAs Surface



Surface supercell

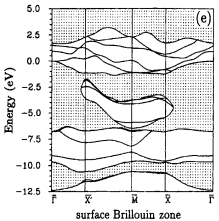


There is *reconstruction* of the surface – this is calculated first.

A band structure of the *supercell* is then used for the surface band structure.

The GaAs Band Structure

- *K*-points are chosen using the *surface Brillouin zone*.
- Many regions have a *continuous* energy spectrum, while *gaps* still exist.
- The details of the surface band structure depend on the details of the surface reconstruction.



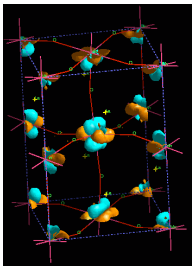
Applications - Orbitals

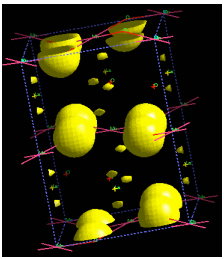
- In addition to the energy eigenvalues for a given material, a band structure calculation also gives the eigenvectors (wavefunctions) for any point in the Brillouin zone.
- It should be noted that no proof exists which confirms that the DFT *single particle* wavefunctions generated here correspond to the *many particle* wavefunction.
- However, the orbitals generated can lead to useful physics and give further insight in the the nature of the bonding in materials.

Example of DFT Orbitals

- Instead of summing up the squares of all the wavefunctions from each electron, we can look at each one individually.
- Each one will be the charge density for a Kohn-Sham orbital.
- This gives a *chemistry* point of view!
- We can examine the electronic structure electron by electron.
- Note: Kohn-Sham orbitals/one electron orbitals: meaning is not necessarily well defined!

Example of Orbitals





Example shown is for $LaMnO_3$ – a magnetic material.