OptaDOS – a tool for EELS calculations

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Electron energy loss spectroscopy (EELS) provides information about the composition and bonding within a sample. Spectrometers allowing EELS analysis are now common additions to (scanning) transmission electron microscopes ((S)TEMs), and, with the addition of monochromators, it is possible for the fine structure to contain a large amount of detail. Simulated spectra can often aid the interpretation of experimental data. Several computer codes exist which simulate EELS spectra, including CASTEP [1], Feff 9 [2] and WIEN2k [3]. OptaDOS [4] is an analysis tool which calculates the density of states (DOS) and spectral properties for the output of a bandstructure code, such as CASTEP. Both low-loss and core-loss spectra can be simulated.

OptaDOS uses the energy bands computed by the bandstructure code to calculate DOS and joint DOS (jDOS). Spectral properties, such as EELS spectra, can be thought of as weighted DOS or jDOS. These can be produced by OptaDOS using the appropriate matrix elements as calculated by the bandstructure code. Further details about the technical aspects of OptaDOS can be found in [5].

The DOS per unit energy (E) is given by [6]:

\[ \rho(E) = \frac{1}{N_k} \sum_i \delta(\varepsilon_{i,k} - E) \]  

where \( N_k \) is the number of k-points, \( \varepsilon_{i,k} \) is the energy of the \( i^{th} \) state at k-point \( \vec{k} \). To plot the DOS, the delta functions in equation (1) can be replaced by Gaussian functions. The width of the Gaussian has an effect on how smooth the DOS looks, and whilst a narrow DOS will wash out fewer of the details, it will take more k-points to converge. OptaDOS uses several methods to plot the DOS. The first method applies a fixed Gaussian broadening and will be referred to as fixed broadening. An adaptation of the fixed broadening uses information about the band gradient to determine the width of the Gaussian [7]. This method is referred to as adaptive broadening. A linear-extrapolative broadening method is also available, details of which can be found in [8].

Figure 1 shows the DOS of cubic boron nitride (cBN) calculated using both fixed and adaptive broadenings for a 12x12x12 k-point grid. The fixed smearing was 0.4eV, which was the minimum that could be used for this k-point grid without unphysical oscillations appearing in the spectrum due to under-sampling. The finer features captured by the adaptive smearing method are washed out by the fixed smearing. For a particular k-point grid, the adaptive smearing method produces a DOS closer to the 'true' density of states.

Both the projected DOS (pDOS), obtained by projecting the DOS onto different atomic orbitals, and core-loss EELS spectra can be thought of as weighted DOS [9]. Calculations of both rely on an accurate calculation of the DOS.

The jDOS is given by:

\[ jDOS(E) = \frac{1}{N_k} \sum_{i,j,k} \delta(\varepsilon_{i,k} - \varepsilon_{j,k} - E) \]  

and is related to the energy difference between states \( i \) and \( j \). It is also possible to calculate the jDOS using both the fixed and adaptive broadening methods. Figure 2 shows the jDOS of cBN calculated using both methods for a k-point grid of 12x12x12. The value of the fixed smearing is 0.4eV. Again this value is the minimum for which under-sampling does not cause unphysical oscillations. The main features of the spectrum are present in both jDOS, but, as with the DOS, the fine details shown in the adaptive smearing jDOS are not present in the fixed smearing jDOS.
OptaDOS uses the approach outlined by Pickard [10] to calculate the imaginary part of the dielectric function, which can be thought of as a weighted jDOS. The Kramers Kronig relation can be used to calculate the real part of the dielectric function, and then low-loss EELS spectra can be simulated.

In summary, OptaDOS is a tool for calculating DOS and EELS spectra based on the output of a bandstructure calculation. DOS and jDOS can be calculated using several smearing methods. For a particular k-point grid, the adaptive broadening method will produce a DOS closer to the ‘true’ density of states than the fixed broadening [11].

References

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Figure 1. DOS of cBN calculated with both fixed and adaptive broadenings

Figure 2. jDOS of cBN calculated with both fixed and adaptive broadenings