OptaDOS - a new tool for EELS calculations

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Abstract. Many modern (Scanning) Transmission Electron Microscopes ((S)TEMs) are equipped with an energy loss spectrometer. The Electron Energy Loss (EEL) spectra collected provide an experimental method of probing the bonding within a material. With the extra addition of monochromators, the energy resolution obtainable means that even more information is revealed within the fine structure of the spectra. Interpreting the fine structure can often be aided by simulation. Density-functional theory (DFT) is one method of simulating EEL spectra. DFT allows us to simulate DOS and EEL spectra from different structures. This comparison between simulation and experiment enables us to explore how changes in the spectrum are related to changes within the sample. CASTEP is a pseudopotential DFT code which can simulate both low-loss and core-loss EEL spectra. Recent developments have resulted in a separate analysis tool, OptaDOS. This package computes various spectral properties including DOS, projected DOS, joint DOS, core-loss and low-loss EEL spectra and optical spectra. One of the important aspects of the code is the way in which the DOS is calculated. This is done via linear extrapolation or adaptive smearing, methods which are not currently available within CASTEP (or indeed any other code) and which allow detailed analysis of spectral properties. This paper summarises these developments and what they mean for the interpretation of EEL spectra.

1. Introduction

Spectrometers which allow electron energy loss (EEL) spectroscopy to be performed are now quite common additions to (Scanning) Transmission Electron Microscopes ((S)TEMs). The EEL spectra they produce contain information about the bonding within the sample and with the addition of monochromators, it is possible for the fine structure to contain a large amount of detail. Comparison of the experimental data with simulated spectra can help aid interpretation. Several computer codes exist which are able to simulate spectra, for example CASTEP \cite{1}, Feff9 \cite{2} and WIEN2k \cite{3}.

In this paper, we will outline a new analysis tool, OptaDOS, which calculates the density of states (DOS) and spectral properties from the output of an electronic structure code, such as CASTEP, and discuss how it can help in the interpretation of EEL spectra.

2. OptaDOS

OptaDOS (www.optados.org) is an analysis tool which is run after an electronic structure calculation and uses the computed energy bands to calculate DOS and joint DOS (jDOS). Spectral properties, such as core-loss and low-loss EEL spectra, can be thought of as weighted
DOS or jDOS. These can be produced by OptaDOS using appropriate matrix elements as calculated by the electronic structure program. OptaDOS was developed for use with the pseudopotential code CASTEP, but there is no reason why it cannot also be used as a tool with other electronic structure programs. Further details about the technical aspects of OptaDOS can be found in Morris et al. [4].

2.1. Density of States (DOS)

The DOS per unit energy (E) is given by [5]

$$\rho(E) = \frac{1}{N_k} \sum_{i,k} \delta(\epsilon_{i,k} - E)$$

where $N_k$ is the number of k-points, and $\epsilon_{i,k}$ is the energy of the $i^{th}$ state at k-point $k$. In order to plot the DOS, the delta functions can be replaced by Gaussians. The width of the Gaussian has an effect on how smooth the DOS looks, and whilst a narrow Gaussian will wash out fewer of the details, it will take more k-points to obtain a converged DOS. OptaDOS uses two methods based on Gaussian broadening to plot DOS, the first is a fixed Gaussian broadening, which shall be referred to as fixed broadening, and the second method, which shall be referred to as adaptive smearing, uses the gradient of the band to determine the width of the Gaussian [6].

Figure 1 shows the DOS of diamond calculated using both fixed and adaptive broadenings for a 12x12x12 k-point grid. The fixed smearing width is 0.4eV, which is the smallest that can be used for this k-point grid without the spectrum showing unphysical oscillations due to under-sampling. It can be seen that the fine features of the DOS which are captured by the adaptive smearing are washed out by the fixed smearing. If a finer k-point grid is used, the smearing width at which there are no artificial oscillations for the fixed smearing will be reduced and will need to be re-determined. For a particular k-point grid, the adaptive smearing method
produces a DOS closer to the ‘true’ density of states. It also has the additional benefit of a single parameter (k-points) controlling the quality of the DOS rather than the two parameters (k-points and smearing width) needed for the fixed smearing.

2.2. Partial DOS, joint DOS and spectral properties

The partial DOS (pDOS) is obtained by projecting the DOS onto different atomic orbitals

\[ pDOS(E) = \frac{1}{N_k} \sum_{i,k} | \langle \psi_{i,k} | \psi_{atomic,k} \rangle |^2 \delta(\epsilon_{i,k} - E) \]  

(2)

By comparing equations 1 and 2, it can be seen that the pDOS is a DOS weighted by a matrix element. Core-loss spectra, which are calculated by OptaDOS using the approach of Pickard [7, 8, 9]

\[ I(E) = \frac{4\pi e^2}{\Omega} \sum_{i,k} | \langle \psi_{i,k} | \hat{u} \cdot \mathbf{r} | \psi_{core,k} \rangle |^2 \delta(\epsilon_{i,k} - E) \]  

(3)

can also be thought of as weighted DOS. Both pDOS and core-level spectrum calculations rely on an accurate calculation of the DOS.

The jDOS is given by

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

(4)

and is related to the energy difference between states i and j. It is also possible to calculate the jDOS using the two approaches outlined earlier. Figure 2 shows the jDOS of diamond calculated using both methods for a k-point grid of 12x12x12. The value of the fixed smearing is 0.4eV, which is the smallest smearing it is possible to use for this case without getting oscillations due to the under-sampling. The jDOS calculated with fixed smearing has the main features seen in the adaptive smearing jDOS, but, as with the DOS, the finer details are not present.

OptaDOS uses the approach outlined by Pickard [8] to calculate the imaginary part of the dielectric function which is given by

\[ \epsilon_2(E) = \frac{2\pi e^2}{\Omega \varepsilon_0} \sum_{i,j,k} | \langle \psi_{i,k} | \hat{u} \cdot \mathbf{r} | \psi_{j,k} \rangle |^2 \delta(\epsilon_{i,k} - \epsilon_{j,k} - E) \]  

(5)

By comparing equations 4 and 5, it can be seen that \( \epsilon_2 \) takes the form of a weighted jDOS. Once \( \epsilon_2 \) has been calculated, \( \epsilon_1 \) is obtained using the Kramers Kronig relation. The loss function (which is what is obtained in a low-loss EEL spectroscopy experiment) is related to the dielectric function by \( \text{Im}[-1/\epsilon] \).

3. Core-loss spectra

Good DOS calculations are vital for accurate calculation of theoretical spectra. OptaDOS allows the calculation of a spectrum based on the DOS produced with adaptive smearing. The advantage of this is that it is possible to compare the spectrum with the pDOS (also produced by OptaDOS) which can help assign the origin of peaks in the spectra. Once the theoretical spectrum has been understood, OptaDOS can then be used to convolve the spectrum with appropriate broadening representing lifetime and instrumentation effects.
4. Low-loss spectra

Low-loss spectra can be calculated using the OptaDOS ‘optics’ task, which calculates the
dielectric function ($\epsilon(\omega)$) using the random phase approximation without local field effects.
In many cases neglecting local field effects gives qualitative agreement with experiment. The
precise importance of local field effects depends on the material and the spectral features of
interest [10]. As well as the real and imaginary parts of $\epsilon(\omega)$ and the loss function, the optics
task also calculates the absorption coefficient, conductivity, reflection coefficient and refractive
index. All of these properties can be calculated for a polycrystalline material or for $q$ in a
specific direction. It is also possible to calculate the average response in a plane perpendicular
to a specific direction.

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