Ab initio EELS : beyond the fingerprint

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ABSTRACT: A new scheme is presented for the calculation of Energy Loss Near Edge Structure (ELNES) within the framework of a Density Functional Theory (DFT) total energy code. It includes a highly efficient approach to the Brillouin zone integrations, and deals with the single particle core hole effects within the supercell approximation with significant improvements on comparison to experiment for bulk Diamond.

1 INTRODUCTION

Electron Energy Loss Spectroscopy (EELS) probes the unoccupied electronic states of materials, transitions taking place from core or valence band states — giving rise to ELNES (and at higher energy, extended structure) or Low Loss spectra respectively (see the left hand panel in Figure 1). Knowledge of the spectral properties (i.e. variation with energy and symmetry) of these states is important in several ways. Since the local potential directly effects the energy distribution of the electronic states they are a *fingerprint* of local structure (the focussed beam of electrons in a STEM forms a local probe). The unoccupied states also give indirect access to occupied states, and hence to information as to the bonding energetics (Muller 1996). Finally, since they dictate the electronic — e.g. optical and transport — properties of the system, direct observation of the unoccupied states themselves is of interest.

With the development of computer power and theoretical tools the interpretation of ELNES can be taken beyond the fingerprint level through calculation. If these calculations are well controlled they can demonstrate clearly the degree to which the energy loss spectra is understood. If theory and experiment do not agree the understanding is then proved to be incomplete and theory must be further developed. Once a model of the spectra has been developed it may be used as an aid to intuition (suggesting further experimental possibilities) or as a quantitative tool in the interpretation of experimental results. In this paper a scheme for the *ab initio* calculation of ELNES is presented, building on earlier work (Pickard 1995), based on a DFT planewave pseudopotential total energy code — CASTEP (Payne 1992).

2 ENERGY LOSS NEAR EDGE STRUCTURE

In the subsequent discussion the focus is on the ELNES region of the energy loss spectrum. For a fast incident electron (treated as a planewave) which looses an energy E and momentum $\mathbf{q}$ the differential cross section can be related to the imaginary part of the dielectric constant, given within the single particle approximation for a periodic system by:

$$\epsilon_2(\mathbf{q},E) = \frac{2e^2\pi}{\Omega\epsilon_0 q^2}\sum_{\mathbf{k},c}|\langle\psi^c_{\mathbf{k}}|e^{i\mathbf{q}\cdot\mathbf{r}}|1\mathrm{s}\rangle|^2\delta(E^c_{\mathbf{k}}-E_{1\mathrm{s}}-E),$$

in the specific case of an excitation from a 1s core state, where Ω is the unit cell volume.

In this scheme the final states and energies — $|\Psi^c_{\mathbf{k}}\rangle$ and $E^c_{\mathbf{k}}$ — derive from an *ab initio* electronic structure calculation described in Section 3. The sum is over the first Brillouin zone $\mathbf{k}$ and unoccupied bands c, i.e. all final states. The two main elements to the calculation of ELNES within this scheme is the evaluation of the density of states (DOS) term, which is described further in Section 4, and the transition matrix elements, which are dealt with in Section 5.

3 THE PLANEWAVE PSEUDOPOTENTIAL APPROACH

A DFT planewave total energy code (CASTEP) is used to obtain the final electronic states and energies. It is based on DFT within the Local Density Approximation. A planewave basis set and periodic boundary conditions are used (and hence summations over all states become sums over bands and an integration over the first Brillouin zone). Non-local pseudopotentials are used to deal with the rapidly varying core regions of the wavefunctions. The technique is reviewed by Payne *et al* (1992).

4 BRILLOUIN ZONE INTEGRATION

A highly efficient Brillouin Zone integration scheme has been developed which uses a very low **k**-point sampling. It is important to use an extrapolative approach, since interpolative ones are hindered by band crossing at low sampling densities, introducing spurious singularities in the DOS. The information for the extrapolation is obtained using **k.p** perturbation theory to second order (to obtain the correct analytic behaviour at van Hove singularities) within a set of sub-volumes into which the Brillouin zone is divided (efficiently chosen to make full use of symmetry at low sampling densities) — some corrections are required for the use of non-local pseudopotentials. The resulting piecewise quadratic representation of the bandstructure is directly converted do a DOS using the analytic quadratic approach of Methfessel (1983). The right panel of Fig. 1 show the convergence properties of this scheme (which is described in greater detail in Pickard 1997).

5 ELNES MATRIX ELEMENTS

In the pseudopotential approximation the core states are not explicitly calculated, and the pseudowavefunctions differ from the true ones within a radius r_c from the nucleus (r_c is typically of the order of 0.5Å). In the evaluation of the matrix elements the initial core states are taken from all electron calculations for isolated atoms — consistent with the frozen core approximation on which the pseudopotential approximation is based. In practice the dipole approximation is taken, but it has been shown that it is straightforward to go further in this formalism (Pickard 1997). The matrix elements are then directly evaluated and corrected for the pseudopotential error using the Projector Augmented Wave approach of van de Walle and Blöchl (1993) — see the left panel of Fig. 2 (further details are given in Pickard 1997). In this way the matrix elements are evaluated quantitatively, resulting in an absolute prediction for the cross-section. This is in contrast to many previous approaches — which frequently are simply symmetry projected local DOS.

6 SINGLE PARTICLE CORE HOLE EFFECTS

The "single particle" core hole effects derive from the un-screening of the nuclear charge as an electron is excited from a localised core state. In a metal this potential is almost entirely re-screened and there is very little effect due to the core hole. In an insulator the screening

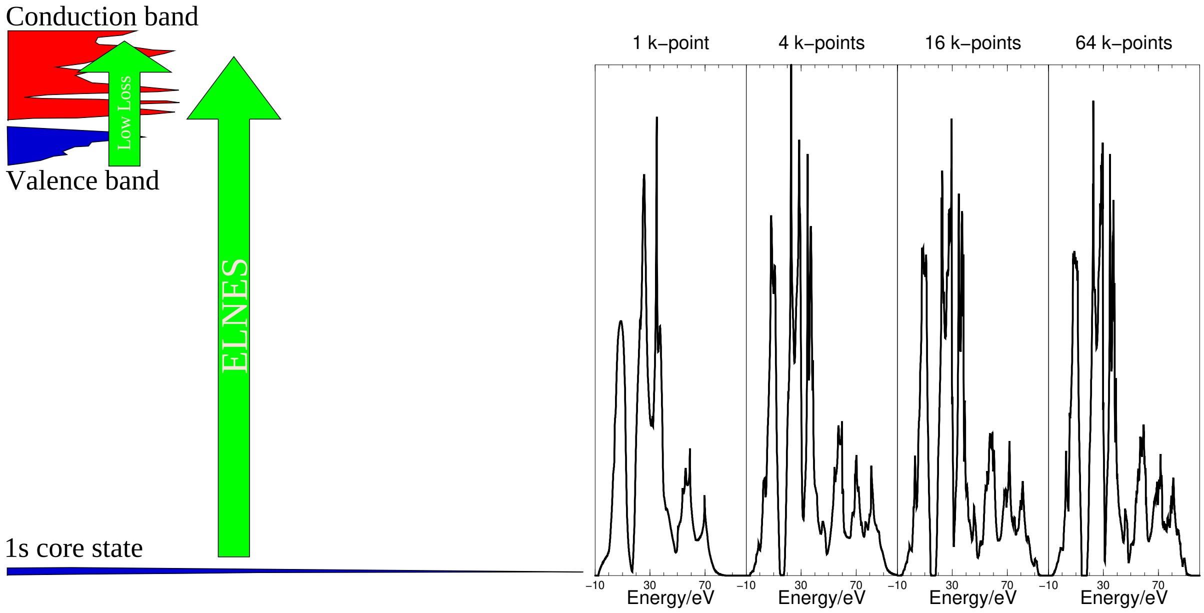

Figure 1: *Left:* Pictorial representation of the energy loss process for Diamond. *Right:* Convergence of the K-edge of Diamond (including occupied states) with number of **k**-points for the piecewise quadratic extrapolative method using the primitive 2 atom unit cell.

of the hole by the valence electrons is only partially achieved. Physically, the excited atom is like an impurity in the material with an associated distortion of the electronic structure (and no atomic relaxation on the time-scale of the excitation). In fact, impurity models — such as the Clogston-Wolff model — have been used to model core hole effects in systems where the screening is almost complete and hence the impurity potential differs only slightly from the unperturbed one. Weijs (1990) studied the core hole effects in the X-ray absorption spectra of transition metal silicides in this way.

For many systems the hybridisation due to core hole potential cannot be treated perturbatively, and the effects must be calculated explicitly. Within a bandstructure approach this is achieved by performing a supercell calculation in which there is a single excited potential in each cell. The spectra is then evaluated for that excited atom. The supercell must be large enough that the neighbouring excited potentials do not interact with each other. Such calculations have previously been performed for Diamond (Mauri 1995) and Graphite (Ahuja 1996). Within the pseudopotential approximation, the more common Z+1 approximation is improved upon by generating a special pseudopotential with partially occupied core states. Comparisons for Diamond show the Z+1 approximation to be generally good (Pickard 1997), but there are some small differences at the threshold.

The right-hand panel in Fig. 2 show the effects of the core hole on the Diamond K-edge. A significant improvement in the calculated spectra is observed, but the total intensity at the threshold is overestimated. According to Batson (1993) the passage of a swift electron in an EELS measurement has an effect on the excitation process, reducing the expected excitonic enhancement. It should be noted that, in contrast with the usual picture, the core hole has an effect well above the threshold. In Diamond, there is effectively a second threshold at 17eV above the first and so it is not surprising that there is also distortion there.

7 CONCLUSION

ELNES can be calculated within the framework of a total energy pseudopotential code. The description of the wavefunctions in terms of planewaves allows the straightforward direct evaluation of the transition matrix elements, and corrections for the pseudopotentials can be

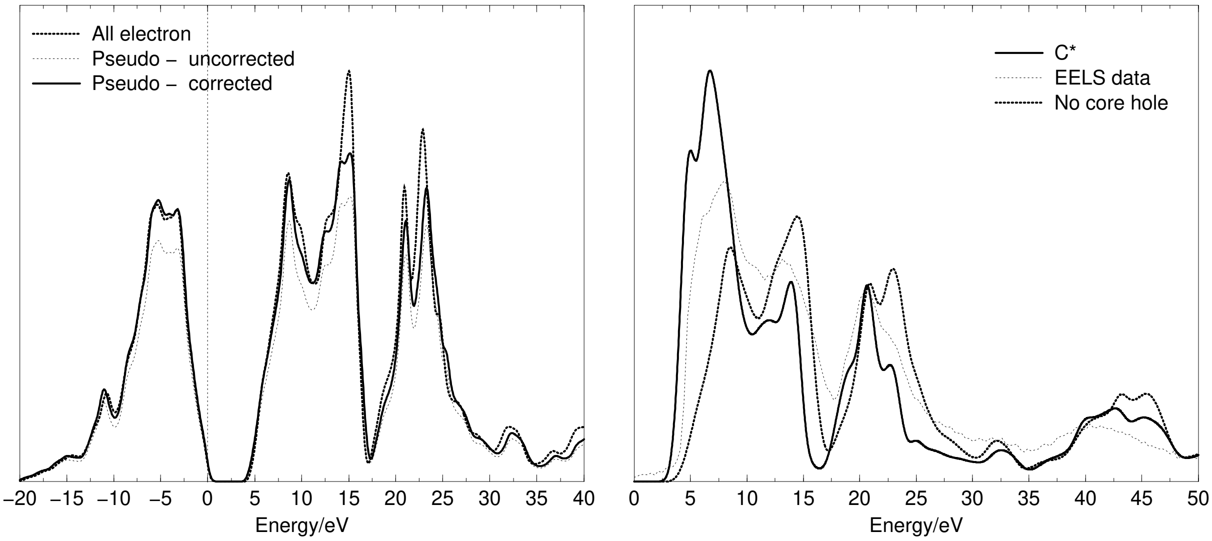

Figure 2: *Left:* The effect of correcting the ELNES matrix elements for a Diamond K-edge. Comparison is made with an all electron planewave calculation. *Right:* The inclusion of core hole effects in Diamond using a 16 atom supercell and a single excited atom. Improved agreement with experiment is observed at the threshold. Experimental data by Brian Rafferty.

included. Some of the computational expense of the technique is offset by efficient Brillouin zone integrations, and the importance of including the core hole potential is demonstrated. It is envisioned that such an scheme, in concert with the structure prediction of these *ab initio* techniques will prove to be a powerful tool in the investigation of microstructure.

ACKNOWLEDGEMENTS

C J Pickard would like to thank the EPSRC for funding, and L M Brown, E Sandre, J Yuan and P Rez for many helpful comments in the course of this work.

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