Density Functional Theory as a Tool for the Electron Microscopist

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Ab-initio calculations have reached a fantastic level of accuracy for the calculation of electronic structure, lattice constants, binding energy as well as optical, magnetic, and electronic properties. A large number of methods is in use nowadays, many of them as commercially available program packages.

Of particular interest for the electron microscopist is the understanding of ionisation edges, low losses and their relation to the electronic, optical and mechanical properties of modern materials. The ab-initio methods used in electron energy loss spectrometry can be divided into two groups:
• multiple scattering methods which work in real space and are widely used for the calculation of X-ray absorption spectra (XAS) and ELNES (energy loss near edge structures)
• band-structure methods, based on the density functional theory (DFT) working in reciprocal space. Despite of the fact that the output of the DFT is electrons where they are and not where they could be the calculation of ELNES and of low-loss spectra with the DFT works pretty well (the method is not intended for the calculation of empty states – a fact that lead the Nobel laureate Walter Kohn to the statement that calculation of empty states is an "illegitimate child" of the DFT).

In the following, we give an overview of recent developments in the field, where the simulations are mainly based on the Wien97 code [1], the TELNES program [2] and the dynamical scattering theory.

Fe_3B was used as a test example to demonstrate that calculated ELNES can be used to distinguish phases with the same composition but with slight distortions of the unit cell (Fe_3B orthorhombic and tetragonal) in a nanocrystalline material composed of different phases, without the use of reference spectra taken on pure samples [3].

An exciting question in this context was whether a random alloy could be distinguished from a regular arrangement of atoms by use of ELNES. In the substitutional alloy CuNi DFT calculations based on a 2x2x1 supercell and on single cells with superstructure showed that differences in the fine structure of the Cu L_3 edge between a random substitutional alloy and an ordered alloy are well visible. Calculations based on the Virtual Crystal Approximation showed that the supercell calculation is needed in order to reproduce the random alloy [4].

The question of the core-hole left by the excited electron is often considered as a problem since it complicates the calculation of insulators because of the necessary supercell. On the other hand the comparison between calculations with different partial core holes in single cells and full core hole in a supercell made for the Cu L_3 edge in copper showed that half a core hole is needed for perfect agreement between experiment and calculation, which could be interpreted by a non perfect screening of the core hole by valence electrons [5].

Chemical analysis under channelling condition has been studied since the seventies. More recent is the question of the influence of channelling on the ELNES. We could show that the central quantity in this

context is the Mixed Dynamic Form Factor (MDFF) which can be interpreted as an interference term. Under proper experimental conditions, information on the position of ionised atoms in the unit cell, on non-dipole transitions and on centro-symmetry can be extracted. Very recently we could interpret faint variations of the O-K ELNES in terms of different final states in the 1s->2p transition in TiO_2 depending on channelling [6].

An interesting observation which is certainly of great importance for the next future is that the MDFF is closely related to an interference term leading to the phenomenon of circular dichroism in XAS [7].

The subject of angular resolved low-losses and the dispersion of plasmons seems to attract interest anew after it lay dormant for nearly two decades. This has to do with the tremendous computing capacity of modern equipment. The Bethe-Salpeter equation seems to be well adapted to the description of this intricate many-body problem. It was shown in a few cases recently that local field effects are most important in understanding the dispersion features in the low-loss region e.g.[8].

Finally, we want to point out that one of the biggest challenges will be the energy filtered imaging of the electronic structures of crystals at atomic resolution [9] [10].

References
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