AMTC Letters
Vol. 1 (2008)

Ab initio Calculations and Interpretation of X-ray Absorption and Electron Energy Loss Spectra*

J. J. Rehr[1], A. P. Sorini[1], K. Jorissen[1,2], J. J. Kas[1]

[1] Department of Physics, University of Washington, Seattle, WA 98195-1560, USA
[2]EMAT, Universiteit Antwerpen, Antwerp B-2020, Belgium

There has been substantial progress in recent years in theories of core-level spectra, e.g., electron energy loss spectra (EELS) and x-ray absorption spectra (XAS) [1]. Here we focus on the real-space Green's function (RSGF) approach which is widely used for calculating these core-level spectra [2]. This approach is essentially the real-space analog of the KKR band structure method, and is formally similar to other periodic approaches [3]. A major challenge for the theory is that such spectra depend on the excited state electronic structure, which differs significantly from that of the ground state. Thus calculations should take into account effects of inelastic losses in the final state and the influence of the core-hole. However, owing to the difficulty of calculating such "many-body" effects, simplified models have been used in practice.

The RSGF approach is based on a quasi-particle approximation and the final state rule [2], which builds in many of the most important many-body effects. In particular the final states are calculated with a Hamiltonian that includes a complex self-energy which builds in inelastic losses, and a fully screened core-hole. Semi-empirical screening models (e.g., the plasmon-pole self energy of Hedin and Lundqvist) are reasonable at high energies, and yield spectra with quantitative near edge structure, e.g, both energy-loss near edge structure (ELNES) and x-ray absorption near edge structure (XANES). However accurate self-energies depend on details of the dielectric response, and hence require calculations going beyond the independent particle approximation. Moreover, corrections (e.g., from local fields) can be important in the spectra even far above an absorption edge. Thus we have endeavored to develop efficient *ab initio* approaches for treating these many body effects as extensions to the (RSGF) formalism. Starting from the dielectric response function, we have derived a many-pole representation of the dielectric function, which is then used to obtain system-dependent self-energies and inelastic mean free paths. Local fields and core-hole screening are treated using a combination of time-dependent density functional theory (TDDFT) and the Bethe-Salpeter equation (BSE). Finally by calculating the spectral function using a quasi-boson approximation, we obtain an approximate treatment of losses due to multiple-electron excitations [3]. All of these effects are important to calculations of EELS and XAS over a broad spectrum, and we find that the approach yields efficient calculations of various spectra from the UV to hard x-ray energies. Moreover, the approach also improves both the near edge and the extended fine structure. The extension to finite momentum transfer (NRIXS) [4] and to relativistic effects in electron energy loss spectra (EELS) is also briefly discussed [5]. We have also succeeded in extending the RSGF code FEFF8 for calculating relativistic EELS. The code is applicabile to all types of materials through the periodic table, regardless of symmetry. In particular, the code takes into account the effects of transverse fields on the effective momentum-transfer which appears in the relativistic expression for the EELS double-differential cross-section (DDCS). These effects are especially important in the treatment of anisotropic systems (e.g., graphite), and are exemplified by the large relativisitic corrections to the EELS “magic angle” in anisotropic systems. Within the dipole approximation, the relativistic EELS spectrum can be written as an integral of an effective momentum-transfer dyadic contracted with the “absorption tensor.” The absorption tensor contains all of the energy-dependence of the spectrum and sample information. An example of the absorption tensor for graphite [5] is shown in Fig. (1).

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*Supported by DOE Grant DE-FG03-97ER45623,

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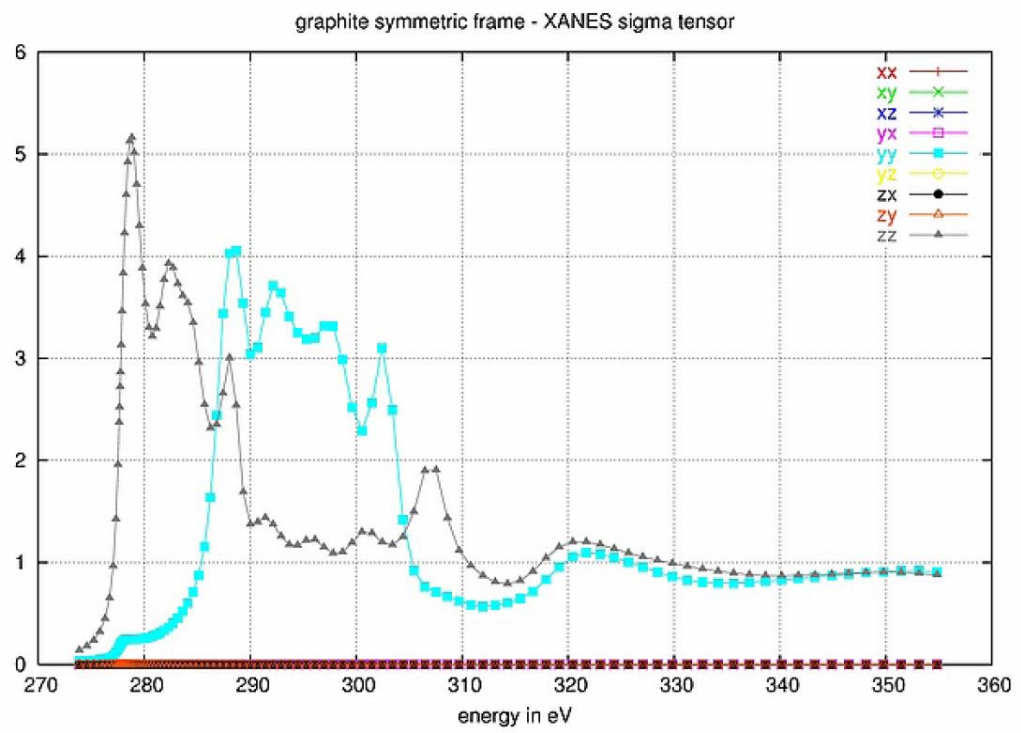

FIG. 1. Components of the x-ray absorption tensor σ_{ij} of graphite, evaluated in the principle-axis frame. The *zz* component corresponds to absorption along the *c*-axis, whereas the *xx* and *yy* components (which are identical) correspond to absorption perpendicular to the *c*-axis. All other components of the absorption tensor are identically zero in this frame.