

ELNES and XANES From First Principles Using the Bethe-Salpeter Equation

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Both electron energy loss near edge structures (ELNES) and X-ray absorption near-edge structures (XANES) provide information on the chemical environment in a wide range of materials by probing the excited states, or more specifically, the transition probability between core electrons and unoccupied states. For the important class of solids with band-gap, excitonic effects may significantly modify the absorption spectra, as bound states, *core-excitons*, can form due to the Coulomb attraction between the excited electron and core-hole. We perform *ab initio* calculations utilizing the Bethe-Salpeter equation (BSE), carefully taking into account the correlated motion of the electron and hole, in order to study the influence of excitonic effects on the absorption spectra [1]. The BSE computations are implemented within the full-potential linearized augmented planewave (FPLAPW) plus local-orbital method, using the WIEN2k code [2]. An advantage with the present methodology is that apart from obtaining the spectra, it is also possible to estimate binding energies as well as wave functions of the individual core-exciton states.

Investigations have been performed for a number of materials, including; the B *K*-edge (*1s*) in c-BN and h-BN, the Be *K*-edge in BeO and BeS, the Mg *L*_{2,3}-edge (*2p*) in MgO and the Li *K*-edge in Li-halides, with a general good agreement to experiment. The BSE result for the XANES spectra of the Li *K*-edge in the wide band-gap insulator LiBr is shown in Fig. 1, with comparison to experiment [3] and the commonly used method of explicitly introducing a core-hole at a single atom in a supercell within density functional theory (DFT), see for example Ref. [4]. The theoretical results are aligned to experiment at the point of the arrow. In this case BSE reproduces the fine details of the spectra, while the supercell calculation gives a different result. Here one can also remark that not taking the core-hole into account at all (e.g. ground state calculation), as expected, produces a much worse spectra. In Fig. 2, a demonstration is made for the core-exciton in real space, plotting the absolute part of the wave function for one of the degenerated higher binding energy *p*-like core-excitons, corresponding to the main peak in Fig. 1.

In brief, the BSE method gives a consistent way of treating the electron-hole interaction, both providing a useful tool for the careful analysis of excitonic effects in the absorption spectra, and as a reference for more approximative theoretical methods.

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References

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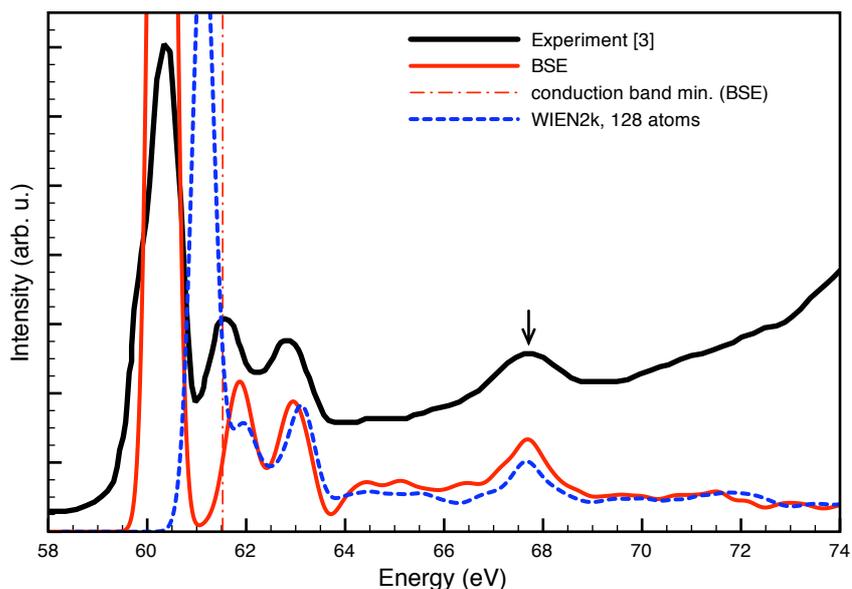


FIG. 1. The XANES spectra for the Li K-edge in LiBr. BSE (red line) is compared with experiment (black line) and 128 atoms supercell core-hole calculation using WIEN2k (blue, dashed line).

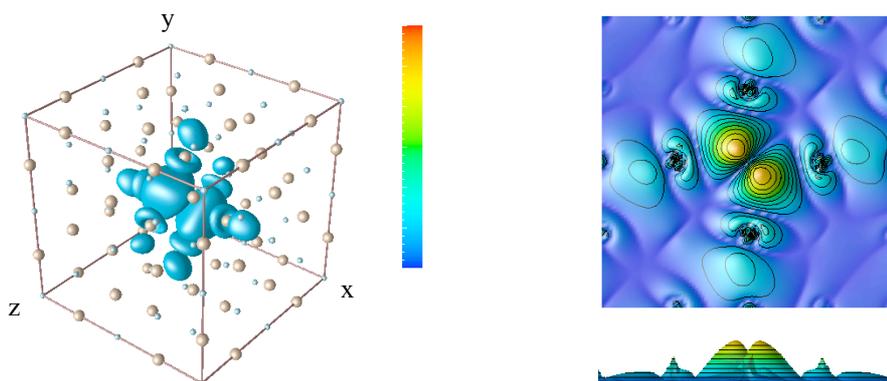


FIG. 2. The absolute part of the wave function for one of the higher binding energy, *p*-like, core-excitons corresponding to the Li (small atoms) *K*-edge in rock-salt structure LiBr (left). The core-hole is fixed at the Li-atom in the center. A contour plot through the (001)-plane is shown (right).