Strong two-particle interaction in high energy ELNES/XANES

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Near edge structures of a core-electron energy loss spectrum using X-ray and electron, namely X-ray absorption near edge structure (XANES) and electro energy loss near edge structure (ELNES), are powerful analytical methods to investigate the local atomic and electronic structures of materials. Theoretical methods for calculating ELNES/XANES have advanced in parallel with the development of experimental facilities. Now, we know that the spectrum calculation is categorized into three theoretical frameworks: the one-particle method, the two-particle method and the multi-particle method [1,2].

On the other hand, an open question still remains in the ELNES/XANES calculation. Namely, the effect of the two-particle interaction, namely excitonic interaction, at the high-energy ELNES/XANES is not sufficiently revealed. The exciton in the ELNES/XANES spectrum is a “core-exciton” between the excited electron at the conduction band and the hole at the core orbital, namely core-hole. In the one-particle calculation, the excitonic interaction is approximated using the DFT–LDA/GGA framework. If the energy distance between the excited electron and core-hole is large, such as the case in high-energy spectrum, one can easily expect that the one-particle approximation works well to describe the core-excitonic interaction.

However, it is known that exciton behavior is strongly dependent on the electronic structure of material. For example, excitonic interaction at the band gap, i.e., the exciton in the band-gap, is influenced by the band gap and band dispersion. Furthermore, it is known that low-dimensional materials, such as carbon nanotube, show strong excitonic interaction due to the presence of the strongly confined wave functions. Contrary to such exciton at the band gap, the possibility of the presence of a strong "core"–excitonic interaction in high-energy ELNES/XANES has not been sufficiently discussed.

In this study, we performed both the one-particle calculation and two-particle calculation to study the excitonic interaction in the high energy ELNES/XANES. We focused on oxygen-K edge of perovskite oxides. Oxygen-K edge locates around 530eV, and has been believed that the two particle interaction is not strong. The first-principles full-potential linearized augmented plane-wave method based on DFT–GGA, as implemented in the Elk code, was used for the one-particle calculation and the two particle calculation, namely Bethe-Salpeter Equation (BSE) method, in this study.

As a reference, experimental and calculated oxygen K-edge of MgO is shown in Fig.1(left). It is clearly seen that both GGA and BSE can reproduce the experimental spectrum. Figure 1(right) shows the experimental oxygen K-edge spectrum for CaTiO₃ with the GGA and BSE calculated spectra. To investigate the fine profiles in detail, the experimental and calculated spectra were aligned using peak C, indicated by arrows in Fig. 1(right). The experimental spectrum is composed of sharp peak A, which is followed by broad peak B, a distinct peak C, and small shoulder D. The GGA calculation reproduces the characteristic features of the experimental spectrum (Fig. 1(right)). Because Ti has six-fold octahedral symmetry, peaks A and B can be ascribed
to the hybridized peak with Ti-d $t_{2g}$ and $e_g$-type components, respectively. Peaks C and D come from the O p-orbital hybridized with the Ca d-orbital. Because Ca is coordinated by 12 oxygens point symmetry, peaks C and D can be ascribed to hybridized peaks with Ca-d $e_g$- and $t_{2g}$-type components, respectively.

Detailed investigation of the peaks highlighted several discrepancies between the experimental spectrum and the spectrum calculated using GGA. The distance between peaks A and C in the experimental spectrum was 5.2 eV, whereas it was 4.1 eV in the spectrum calculated using GGA, i.e., a 1.1 eV error is present in the GGA calculation. Furthermore, peak B is less intense in the GGA calculation than the experimental spectrum. On the other hand, the BSE calculation well reproduces the A–C peak distance and small peak B well. This result clearly suggests that, contrary to the case of MgO (Fig. 1(left)), the two particle interaction in the oxygen K-edge of CaTiO$_3$ is not negligible. We also investigated the two particle interactions in the oxygen-K edge of other perovskite oxides [3,4].

References
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Fig. 1: Oxygen K edge of (left) MgO and (right) CaTiO$_3$. Both calculated spectra using BSE and GGA are compared with experimental spectra.