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Effect of the van der Waals interaction on the electron energy-loss near edge structure theoretical calculation

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ABSTRACT

The effect of the van der Waals (vdW) interaction on the simulation of the electron energy-loss near edge structure (ELNES) by a first-principles band-structure calculation is reported. The effect of the vdW interaction is considered by the Tkatchenko-Scheffler scheme, and the change of the spectrum profile and the energy shift are discussed. We perform calculations on systems in the solid, liquid and gaseous states. The transition energy shifts to lower energy by approximately 0.1 eV in the condensed (solid and liquid) systems by introducing the vdW effect into the calculation, whereas the energy shift in the gaseous models is negligible owing to the long intermolecular distance. We reveal that the vdW interaction exhibits a larger effect on the excited state than the ground state owing to the presence of an excited electron in the unoccupied band. Moreover, the vdW effect is found to depend on the local electron density and the molecular coordination. In addition, this study suggests that the detection of the vdW interactions exhibited within materials is possible by a very stable and high resolution observation.

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1. Introduction

In recent years, the investigation of the local atomic/electronic structure of materials has drawn increasing attention [1–3] owing to their importance on the macroscopic properties. In this regard, the electron energy-loss near edge structure (ELNES) in the electron energy-loss spectrum (EELS) is useful because the ELNES profile reflects the partial electronic density of states (PDOS), namely, the atomic/electronic structures of the objective atoms, and can be obtained from a very localized area using transmission electron microscopy (TEM) and scanning TEM (STEM) [4]. In the past decade, TEM and STEM have made substantial progress from the development of aberration correction technology to achieve atomic resolution [5,6]. Moreover, STEM-EELS has accomplished a very high energy resolution using a monochromator system [7–10]. These developments have made it possible to determine detailed atomic/electronic structures and detect their small but important changes at the atomic scale through the interpretation of the ELNES spectra.

To enable the attribution of the experimental ELNES peaks to the atomic and electronic structures, such as the bonding state, coordination environment, and valence state, theoretical calculation of the ELNES is essential [11–14]. ELNES calculations can be categorized into three theoretical frameworks, that is the one-

particle method, the two-particle method, and the multi-particle method as reviewed in the manuscript [14]. The one-particle calculation is based on density functional theory (DFT) within the local density approximation (LDA) or generalized gradient approximation (GGA) [13–16]. The two-particle calculation can correctly consider the two-particle interaction between an excited electron and an electronic hole [17–21]. The multi-particle interactions, including electron–electron and electron–hole, are considered in the multi-particle calculation [22–25]. By selecting the suitable theoretical framework and consider the core-hole effect correctly, the calculation can reproduce the experimental ELNES very well, and it provides the correct interpretations of the ELNES peaks.

While the ELNES simulation with the first-principles calculation is well established and can reproduce the experimental spectrum with high accuracy, there is still room for improvement, for example, the effect of the van der Waals (vdW) interaction [26] on the ELNES calculation. The effect of the vdW interaction in materials has not been considered in the ELNES calculation to date, because the spectrum change derived from the vdW interaction has been believed to be below the measurable limit owing to its much smaller interaction than that of ionic and covalent bonding. However, the vdW interaction is present in every material, even in non-polar material, and the ELNES provides a great benefit to investigate the vdW interaction at a local region such as an interface and a surface.

Thus, in this study, we investigated the effect of the vdW interaction on the first-principles ELNES calculation, and discussed

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the extent and type of spectral changes that are generated from the vdW interaction. Since the vdW effect differs depending on the state, the influence of the vdW interaction on the ELNES calculation of the solid, liquid, and gaseous states were systematically investigated.

2. Methodology

Here, the calculation models, the conditions of the theoretical calculations, and the way to consider the vdW interaction are presented. We investigated the solid, liquid and gaseous models, and calculated their ELNES spectra. We selected layered compounds, hexagonal boron nitride (h-BN) and hexagonal graphite, where the vdW interaction plays a major role [27], as the solid models, and water and methanol as both the liquid and gaseous models because these have been well-studied and have simple molecular structures. $3 \times 3 \times 2$ supercells comprising the unit cells of h-BN and graphite, which correspond to $7.513 \times 7.513 \times 13.212 \text{ \AA}$ and $7.386 \times 7.386 \times 13.414 \text{ \AA}$, respectively, were used as the solid structures to exclude the interaction between the adjacent core-holes. The liquid structures of water and methanol were constructed by classical molecular dynamics (MD) calculation with a force field [28]. In the liquid water and methanol models, supercells containing 27 and 16 molecules were calculated, and the MD simulation time and time step were set to 10 ps and 0.01 fs, respectively. The temperature was maintained at 298 K in a *NPT* ensemble, namely number of atoms (*N*), pressure (*P*), and temperature (*T*) are fixed in the MD simulation. The size of the supercell for the liquid models were $9.737 \times 9.737 \times 9.737 \text{ \AA}$ and $11.387 \times 10.846 \times 10.361 \text{ \AA}$ for water and methanol, respectively. The gaseous models were constructed by placing an isolated methanol and water molecule inside a $10 \times 10 \times 10 \text{ \AA}$ supercell. These supercell structures are shown in Fig. 1(a)–(f). The details of the MD simulation is summarized in Fig. 2.

The electronic structure and ELNES spectra of these models were calculated using the first-principles plane-wave basis pseudopotential method (CASTEP code) [29]. CASTEP is the DFT based band structure calculation method, and the exchange-correlation functional was approximated by GGA-PBE [30]. The plane wave cutoff energy was set to 500 eV. In the ELNES calculation, $1 \times 1 \times 1$ k-point sets for the liquid and gaseous structures, and $2 \times 2 \times 1$ k-point sets for the solid structures were used because the size of the supercells is sufficiently large. The B-K edges were calculated for h-BN. The C-K edges were calculated from graphite, liquid and gaseous methanol, and the O-K edges from liquid and gaseous water.

Consideration of the core-hole effect is mandatory for the ELNES calculation. To include the core-hole effect in the pseudopotential method, an excited pseudopotential including a core hole is generated and used it for the excited atom whereas the ground state pseudopotentials were used for the other atoms [15,31]. The core-hole was introduced to the 1 s orbital and an excited electron was put into the lowest unoccupied orbital. Namely, neutral charged supercells were used. The transition energy was defined as the total energy difference of the excited and the ground state, and it was conducted by the method reported previously [32]. The theoretical ELNES was obtained by calculating the electron transition probability. The calculated transition probability was broadened using Gaussian function with FWHM=0.5 eV for comparison with the experimental spectrum. In the liquid models, the ELNES spectra were calculated from all molecules, and all the spectra were summed to provide the ELNES spectrum of the whole structure, in the same manner as that used in Ref. [33].

To introduce the vdW interaction into the ELNES calculation, we applied the semi-empirical vdW-TS approach of Tkatchenko

and Scheffler [34], which is implemented in CASTEP code [35]. This TS method is advantageous in that the impact of the vdW interaction differs in every atom depending on the electron density distribution and the distances to the other atoms. This method corrects the DFT energy by adding the following term,

$$E_{vdW} = -\frac{1}{2} \sum_B \int_{damp} (R_{AB}) C_{6AB}^{eff} R_{AB}^{-6} \quad (1)$$

where $\int_{damp}(R_{AB})$ is the damping function preventing the vdW energy, E_{vdW} , from diverging at a short atomic distance. R_{AB} is the distance between atoms A and B. C_{6AB}^{eff} is the effective dispersion coefficient expressed by

$$C_{6AB}^{eff} = \frac{2C_{6AA}^{eff}C_{6BB}^{eff}}{\frac{\alpha_B^{eff}}{\alpha_A^{eff}}C_{6AA}^{eff} + \frac{\alpha_A^{eff}}{\alpha_B^{eff}}C_{6BB}^{eff}} \quad (2)$$

The effective coefficient for two equivalent atoms C_{6AA}^{eff} and the polarizability of the atom A in a molecule α_A^{eff} are defined by

$$C_{6AA}^{eff} \propto \left(\frac{V_A^{free}}{V_A^{eff}} \right)^2 C_{6AA}^{free}, \quad \alpha_A^{eff} = \frac{V_A^{free}}{V_A^{eff}} \alpha_A^{free} \quad (3)$$

where C_{6AA}^{free} is the homonuclear coefficient reported by Chu and Dalgarno [36]. α_A^{free} is the polarizability of the free atom A. V_A^{free} and V_A^{eff} are the Hirshfeld volumes of atom A in a molecule and in isolation, respectively [37].

$$V_A^{eff} = \int r^3 w_A(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r}, \quad V_A^{free} = \int r^3 n_A^{free}(\mathbf{r}) d^3\mathbf{r} \quad (4)$$

$$w_A(\mathbf{r}) = \frac{n_A^{free}(\mathbf{r})}{\sum_B n_B^{free}(\mathbf{r})} \quad (5)$$

where r^3 is the cube of the distance from the nucleus of the atom A, $n(\mathbf{r})$ is the total electron density, $n_A^{free}(\mathbf{r})$ is the electron density of the free atom A. $w_A(\mathbf{r})$ is called the Hirshfeld atomic partitioning weight of the atom A. C_{6AB}^{eff} of Eq. (2) can be summarized by substituting Eq. (3) into Eq. (2) as follows

$$C_{6AB}^{eff} \propto V_A^{eff} V_B^{eff} \cdot \frac{2C_{6AA}^{free}C_{6BB}^{free}}{V_A^{free} V_B^{free} \left(\frac{\alpha_B^{free}}{\alpha_A^{free}} C_{6AA}^{free} + \frac{\alpha_A^{free}}{\alpha_B^{free}} C_{6BB}^{free} \right)} \quad (6)$$

The second term is determined only by the elemental species of the atoms A and B, whereas the first term varies with the surrounding environment of the atoms A and B. This indicates that the effective volumes V_A^{eff} and V_B^{eff} are the main factors in determining the impact of the vdW interaction in materials.

Since V_A^{eff} cannot be calculated directly, the Hirshfeld charges, defined by Eq. (7), were used to discuss the relationship between the magnitude of the vdW interaction and the electronic structure.

$$q_A = Z_A - \int w_A(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r} \quad (7)$$

in which Z_A is the atomic number. Since both Eqs. (4) and (7) contain the $w_A(\mathbf{r}) n(\mathbf{r})$ term, V_A^{eff} (namely C_{6AB}^{eff}) can be speculated from q_A .

In addition to this TS scheme, another scheme proposed by Grimme, namely DFT-D2, was also examined for a comparison [38]. Different from the TS scheme, The DFT-D2 is the completely "element" dependent parameter method and is independent of the local atomic (molecular) configuration and chemical bonding.

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