Ab-Initio Multiplet Calculations Using Iterative Algorithms for X-ray Absorption Spectra at Transition Metal $L_{2,3}$ -Edges

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X-ray absorption spectra at the $L_{2,3}$ -edges of transition metals show widely spreading multiplet structure due to the strong electronic correlations between the 2p and 3d electrons. The *ab-initio* multiplet method based on the relativistic configuration interaction (CI) theory is one of the most reliable theoretical methods to reproduce and predict such spectra. In this method, a many-electron Hamiltonian matrix is fully diagonalized in order to obtain the many-electron wavefunctions for the initial and final states of transitions simultaneously. Since the dimension of the Hamiltonian matrix grows exponentially with an increase in the number of active orbitals, the method has been only computationally feasible only for small systems. In the present study, iterative algorithms, including the Davidson-like algorithm for obtaining the wavefunctions for the initial states, and Lanczos algorithm for evaluating the spectral functions solely from the initial states, were implemented. The theoretical spectra obtained by the new algorithms are identical to those obtained by the full-diagonalization method. As the iterative algorithms adopted in this study require much less memory space, the *ab-initio* multiplet method with iterative algorithms can be applied to larger systems that are unmanageable by a conventional full-diagonalization method. [doi:10.2320/matertrans.MD201706]

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1. Introduction

X-ray absorption spectroscopy, which monitors the electronic transitions from the core to unoccupied orbitals, is a powerful technique to investigate the electronic and atomic structures at the nanoscale.^{1,2)} This technique is routinely used in various fields, including solid-state physics, materials science, molecular and bioscience, and catalysis. In many cases, the measured spectra are interpreted by comparing them with the experimental spectra of the reference materials whose atomic and electronic structures are already known. However, the method relies entirely on empirical knowledge and is only usable when the good reference compounds are available. Nanostructural information that can be obtained by such an empirical analysis is very limited. Reliable theoretical calculations that can reproduce and predict spectra without any adjustable parameters, are necessary in order to fully exploit the nanostructural information by experimental spectra.

Various theoretical approaches have been proposed to reproduce X-ray absorption spectra (XAS) from the first-principles manners. So far, no universal theoretical framework that can reproduce all edges of the elements in the periodic table, has been developed. We must choose an appropriate approximation levels for the electronic interactions among the core-hole and excited electrons depending on the element and absorption edges.^{3,4)} One-electron calculations based on the density functional theory (DFT) or the multiple scattering theory are commonly used for simulating XAS.^{5–14)} In these methods, the interaction that an electron feels from other electrons is replaced by the interactions from the electron cloud formed by the other electron. Most of the *K*-edge and *L*-edge spectra of typical elements have been successfully reproduced using these methods.

One-electron calculations, however, break down when the inter-electron interactions are strong, particularly at the $L_{2,3}$ -edges of transition metals (TMs) which are dominated by the electronic transitions between the spatially localized 2p and 3d orbitals. Because of the strong exchange-correlation interactions between the 2p and 3d electrons, the TM- $L_{2,3}$ XAS shows widely spreading multiplet structures whose shape is far different from that of the unoccupied density of states obtained by one-electron calculations. To reproduce TM- $L_{2,3}$ spectra, many-electron calculations that explicitly include the inter-electron interactions are necessary. Multiplet calculations using a model Hamiltonian, such as the Anderson impurity model or the charge transfer multiplet method, are commonly used for the analysis of TM- $L_{2,3}$ XAS.^{15,16)} Though these methods successfully simulated many spectra, they cannot predict the spectra *a priori*, because of the use of adjustable parameters such as the crystal-field splitting and charge transfer energy. The present authors have developed an *ab-initio* multiplet method for simulating TM- $L_{2,3}$ XAS which is based on the relativistic configuration interaction (CI) theory in the quantum chemistry.^{17,18)} The exchange-correlation interactions between the 2p and 3d electrons in TMs were explicitly taken into account by expanding the many-electron wave functions as linear combinations of Slater determinants. The whole relativistic effects on the core 2p levels are treated by solving the Dirac equation instead of the Schrödinger equation.

In the present *ab-initio* multiplet method, a many-electron Hamiltonian matrix is fully diagonalized in order to obtain the eigenstates corresponding to the initial and final states. Subsequently, the photo-absorption cross-section (PACS) is calculated in accordance with the Fermi's golden rule. This method has been successfully applied to reproduce the experimental spectra of various compounds having different oxidation states, coordination numbers, and symmetries, without any adjustable parameters.^{19–22)} However, it is diffi-

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cult to extend this approach to larger systems. As the dimension of the Hamiltonian matrix increases exponentially, as the number of orbitals and electrons increases and the matrix cannot be stored on the physical memory of computers. New algorithms that can handle large Hamiltonian matrices are strongly desirable in order to simulate TM- $L_{2,3}$ XAS from larger systems, such as, TM clusters, TM complexes with large ligands, and magnetic materials in which exchange interactions between magnetic moments of the TM ions plays a crucial role.

In this study, a new method to simulate TM- $L_{2,3}$ XAS using the iterative algorithms is developed, so that the larger Hamiltonian matrices can be handled. In the new method, only the eigenstates corresponding to the initial states of the electronic transitions are computed using the generalized Davidson method. This algorithm has also been implemented in many modern quantum chemistry packages and plane-wave based DFT codes to obtain eigenstates of the Hamiltonian matrix.^{23–26} The PACS can be computed solely from the initial state wavefunctions as the imaginary part of Green's function using the Lanczos algorithm. In these algorithms, the Hamiltonian matrix is requested only during multiplication with a vector whose length is the same as the dimension of the matrix. Owing to the sparse nature of the Hamiltonian matrix, this approach can be applied to the systems with a large Hamiltonian matrix that cannot be handled by the present full-diagonalization algorithm. The theoretical TM- $L_{2,3}$ XAS spectra of simple TM oxides are demonstrated. The theoretical spectra obtained using the iterative algorithms are found to be identical with those obtained by the full-diagonalization method.

2. Theory

As discussed in the previous section, the strong electronic correlation between the spatially localized $2p$ and $3d$ electrons must be explicitly treated in order to reproduce the multiplet structure appearing in the TM- $L_{2,3}$ XAS. We begin with a 'no-pair' Hamiltonian,^{27,28} which is given in the second quantized form as,

$$H = \sum_{i,j=1}^L \langle i|\hat{h}|j\rangle a_i^\dagger a_j + \frac{1}{2} \sum_{i,j,k,l=1}^L \langle ij|r_{12}^{-1}|kl\rangle a_i^\dagger a_j^\dagger a_l a_k, \quad (1)$$

where i, j, k , and l indicate the molecular orbitals (MOs), N is the number of electron in the system, and L ($>N$) is the number of given MOs. $a_i^\dagger$ and a_i are the creation and annihilation operators for an electron in the i -th MO, respectively. $\langle i|\hat{h}|j\rangle$ and $\langle ij|r_{12}^{-1}|kl\rangle$ are the one- and two-electron integrals over MOs, where $\hat{h}$ is the single-particle Dirac operator represented by,

$$\hat{h} = c\alpha \cdot \mathbf{p} + mc^2\beta + v_{nuc}(\mathbf{r}) \quad (2)$$

where $v_{nuc}(\mathbf{r})$ the electrostatic potential from nuclei.

A many-electron wavefunction is expanded as a linear combination of Slater determinants,

$$|\Psi_k\rangle = \sum_{p=1}^M |\Phi_p\rangle C_{pk} \quad (3)$$

where $|\Phi_p\rangle = a_{p_1}^\dagger \cdots a_{p_N}^\dagger |vac\rangle$ is a Slater determinant constructed from $p_1, \dots, p_N$ -th MOs, $|vac\rangle$ denotes the vacuum states, and M is the number of Slater determinants. The coefficients C_{pk} and the corresponding eigenvalues E_k are obtained as eigenpairs of the $M \times M$ Hamiltonian matrix, whose elements can be expressed as

$$\begin{aligned} \langle \Phi_p | \hat{H} | \Phi_q \rangle &= \sum_{i,j=1}^L \langle i|\hat{h}|j\rangle \langle \Phi_p | a_i^\dagger a_j | \Phi_q \rangle \\ &+ \frac{1}{2} \sum_{i,j,k,l=1}^L \langle ij|r_{12}^{-1}|kl\rangle \langle \Phi_p | a_i^\dagger a_j^\dagger a_l a_k | \Phi_q \rangle. \end{aligned} \quad (4)$$

In the original *ab-initio* multiplet method, this $M \times M$ matrix is fully diagonalized by using the dense matrix decomposition algorithm. The multiplet energies and wavefunctions corresponding to the initial and final states of the TM- $L_{2,3}$ XAS are explicitly computed. Then, the PACS is evaluated in accordance with the Fermi's golden rule as,

$$\sigma_{abs}(\omega) = \sum_f 4\pi^2 \alpha |\langle \Psi_f | \hat{A} | \Psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega), \quad (5)$$

where α is the fine structure constant, and $\hat{A}$ is the transition operator, which represents the interaction of photons with the electrons. Here, Ψ_i and Ψ_f are the many-electron wavefunctions corresponding to the initial and final states, respectively, while E_i and E_f are their energies, respectively. During the calculation, the entire matrix elements are required to be stored the memory. The computational time and the required memory space scale as $O(M^3)$, and $O(M^2)$, respectively. Using computers with modern CPUs and memory size, a matrix with size up to $M = 50,000$ can be tractable in a practical computational time. However, the dimension of M grows rapidly with an increase in the number of MOs (L) and number of electrons (N) which may easily more than 10^5 and may exceed 10^7 for larger systems. Full diagonalization of such a large Hamiltonian matrix is infeasible.

A Hamiltonian matrix element in eq. (4) is zero if more than two MO indices constituting Slater determinants Φ_p and Φ_q are different. Therefore, a significant number of matrix elements are zero. In other words, the CI Hamiltonian matrix is sparse. In addition, the magnitude of the diagonal matrix elements is larger than that of the non-diagonal elements, i.e., the Hamiltonian matrix is diagonally dominant. There are efficient iterative algorithms for computing only a few among the largest/smallest eigenpairs of such kinds of matrices.²⁹ In this work, the generalized Davidson method^{30–32} was adopted to compute the eigenstates corresponding to the initial states. In this algorithm, only the non-zero elements of the Hamiltonian matrix, H , are required for computing the matrix-vector product of the form, $\mathbf{v} = H\mathbf{c}$. The required memory space for this algorithm can be much smaller than that required for a full diagonalization method, and hence, this can handle a larger CI matrix.

With the generalized Davidson method, the eigenstates corresponding to the final states of the XAS are unavailable, hence, the PACS cannot be calculated directly using eq. (5). Alternatively, the PACS is evaluated as the imaginary part of a spectral function, G_A , which is derived from the Green's function formalism:

$$\sigma_{\text{abs}} \propto \lim_{\eta \rightarrow 0} \text{Im } G_A(\hbar\omega + i\eta)$$

$$G_A(\hbar\omega + i\eta) = -\frac{1}{\pi} \langle \Psi_i | \hat{A}^\dagger (\hbar\omega + E_i - H + i\eta)^{-1} \hat{A} | \Psi_i \rangle. \quad (6)$$

The two formalisms described in eqs. (5) and (6) are mathematically identical. As can be seen from eq. (6), the PACS can be obtained solely from the initial states. The information of the final states is indirectly introduced by applying the inverse Hamiltonian matrix of the form, $(z - H)^{-1}$, to a vector $|\Psi_A\rangle = \hat{A}|\Psi_i\rangle$, where $z = \hbar\omega + E_i + i\eta$. The direct computation of the inverse Hamiltonian matrix, $(z - H)^{-1}$, is computationally inefficient and memory consuming because the inverse of a sparse matrix is usually not sparse. Instead, a linear equation, $\mathbf{y} = (z - H) \mathbf{x}$, is solved using an iterative algorithm in which the Hamiltonian matrix is only used for the matrix-vector multiplications. In this study, the Lanczos method is adopted so that the spectral function, G_A , is evaluated as a continued fraction,³³⁾

$$G_A(\hbar\omega + i\eta) = \frac{\langle \Psi_A | \Psi_A \rangle}{z - \alpha_1 - \frac{\beta_2^2}{z - \alpha_2 - \frac{\beta_3^2}{z - \alpha_3 - \dots}}}, \quad (7)$$

where, the coefficients α_k and β_k are calculated recursively as,

$$\begin{aligned} \beta_{k+1} v_{k+1} &= (z - H - \alpha_k) v_k - \beta_k v_{k-1} \\ \alpha_k &= v_k^\dagger (z - H) v_k \\ \beta_k &= (v_k^\dagger v_k)^{\frac{1}{2}} \end{aligned} \quad (8)$$

starting from $v_1 = |\Psi_A\rangle$. We terminate the Lanczos iterations when the residual norm is smaller than a threshold value, ε . For theoretical XAS, $\varepsilon = 10^{-6}$ is appropriate.

This CI method is known to systematically overestimate the absolute transition energies. This can be ascribed to the incompleteness of our basis MOs and the limitation on the number of Slater determinants. In this study, the transition energy was corrected by considering the energy difference between MOs for the Slater's transition state as a reference.³⁴⁾

3. Results and Discussions

TM- $L_{2,3}$ XAS of simple TM oxides were computed to test the performance of the new iterative algorithm for the *ab-initio* multiplet method. We selected a few TM oxides with different numbers of d-electrons, namely, SrTiO₃ (Ti⁴⁺, d⁰), MnO (Mn²⁺, d⁵), CoO (Co²⁺, d⁷) and NiO (Ni²⁺, d⁸), as benchmarking systems. In these compounds, the TM ions are located at the octahedral site with an O_h symmetry. The atomic positions of these compounds were obtained from the experimental crystalline structures.^{35–38)} The bond lengths between a TM and its first neighboring oxygen ion is 1.950, 2.222, 2.129, and 2.090 Å for SrTiO₃, MnO, CoO, and NiO, respectively.

Initially, relativistic molecular orbital calculations were performed by solving the Dirac equations within the framework of a local density approximation. Four-component rel-

ativistic MOs were expressed as linear combinations of atomic orbitals (LCAO). The numerically generated four-component relativistic atomic orbitals (AOs), namely, 1s-4p for TM and 1s-2p for O, were used as the basis functions for MOs. Cluster models composed of a single TM ion and six neighboring oxygen ions were used for the calculations. The total number of electrons in a cluster model was counted on the basis of the formal charges of the constituents. To take account of the effective Madelung potential, an array of point charges was placed at the external atomic sites of the clusters using the method proposed by Evjen.³⁹⁾

Once relativistic MOs were obtained, one-electron integrals, $\langle i | \hat{h} | j \rangle$, and two-electron integrals, $\langle ij | r_{12}^{-1} | kl \rangle$, which are required to construct the many-electron Hamiltonian matrices, were directly evaluated by numerical integration. All the ligand-field effects can be considered by evaluating these integrals over all the possible combinations of MOs. Subsequently, the Slater determinants were constructed as the basis functions for many-electron wavefunctions in the CI. Because of the limited computational resources, we restricted the number of Slater determinants. As TM- $L_{2,3}$ XAS is mainly ascribed to 2p-3d excitations, the Slater determinants corresponding to the $(2p)^6(3d)^n$ and $(2p)^5(3d)^{n+1}$ configurations were used for describing the wavefunctions of the initial and final states, respectively. The configurations having two or more holes on TM-2p MOs were not considered since the multiplet energies of such configurations are much higher and do not interact with the two configurations described above. The number of Slater determinants expanding the initial and final states are ${}_6C_6 \times {}_{10}C_n$ and ${}_6C_5 \times {}_{10}C_{n+1}$, respectively. In the case of NiO, the oxygen-to-metal charge transfer is known to have a significant influence on the spectral shape of the Ni- $L_{2,3}$ XAS.¹⁸⁾ Thus, the charge transferred electronic configurations, namely, $(2p)^6(\text{O-}2p)^{35}(3d)^{n+1}$ and $(2p)^5(\text{O-}2p)^{35}(3d)^{n+2}$, were taken into account for the calculating the Ni- $L_{2,3}$ XAS of NiO.

Relativistic CI calculations were performed for the systems mentioned above using the generalized Davidson algorithms to obtain a few of the smallest eigenvalues corresponding to the initial states of TM- $L_{2,3}$ XAS. The Davidson recursion process converged by setting the relative accuracy of eigenvalues to 10^{-10} without any numerical instability. The multiplet energies obtained by the two different algorithms were identical. The composition of each electronic configuration in every wavefunction was found to be the same in both the algorithms.

The theoretical TM- $L_{2,3}$ XAS of SrTiO₃, MnO, CoO, and NiO were calculated by the Lanczos method (eqs. (6)–(8)) from the initial states wavefunctions obtained by the generalized Davidson method. In practical calculation, the parameter, η , should be a finite value, otherwise, the continued fraction in eq. (7) becomes divergent. In this work, $\eta = 0.2$ eV was used. The theoretical spectra were also calculated by the full-diagonalization method using eq. (5), where the δ -function in eq. (5) was replaced by a Lorentz function and its full-width at half maximus (FWHM) was 2η (= 0.4 eV). The theoretical TM- $L_{2,3}$ spectra for SrTiO₃, MnO, CoO, and NiO obtained by the two different algorithms are shown in the lower panels of Figs. 1–4, where the spectra obtained by the iterative algorithms and full-diago-

nalization method are visualized by dotted lines and solid lines, respectively. The spectra are also compared to the experimental spectra obtained from the literatures (upper panels of Figs. 1–3).^{40–42)} The experimental spectrum of NiO (upper panel of Fig. 4) was measured at the BL25SU in SPring-8 (Harima, Japan). For all the compounds, the two theoretical spectra obtained by the different algorithms have identical shapes. The results indicated that the iterative algorithms for the *ab-initio* multiplet calculations were implemented successfully. The new iterative algorithm enables us to compute TM- $L_{2,3}$ XAS spectra without explicitly comput-

ing the final state wavefunctions explicitly.

Finally, we discuss the computational costs of the new methods developed in the present study for the *ab-initio* multiplet method. The generalized Davidson algorithm used for computing the eigenstates is more efficient in terms of the required memory space compared to the full-diagonalization algorithm. Usually, the sparsity, which is the ratio of non-zero elements in a matrix, decreases with an increase in the dimension of many-electron Hamiltonian matrix, which is about a few tens percent.^{43,44)} Comparison of the computational time between the generalized Davidson and full-di-

Fig. 1 Theoretical Ti- $L_{2,3}$ XAS of SrTiO_3 obtained by the Davidson and Lanczos algorithms (lower panel, dotted line) and that obtained by the full-diagonalization method (lower panel, solid line). These are compared with the experimental spectrum from the literature⁴⁰⁾ (upper panel).

Fig. 2 Theoretical Mn- $L_{2,3}$ XAS of MnO obtained by the Davidson and Lanczos algorithms (lower panel, dotted line) and that obtained by the full-diagonalization method (lower panel, solid line). These are compared with the experimental spectrum from the literature⁴¹⁾ (upper panel).

Fig. 3 Theoretical Co- $L_{2,3}$ XAS of CoO obtained by the Davidson and Lanczos algorithms (lower panel, dotted line) and that obtained by the full-diagonalization method (lower panel, solid line). These are compared with the experimental spectrum from the literature⁴²⁾ (upper panel).

Fig. 4 Theoretical Ni- $L_{2,3}$ XAS of NiO obtained by the Davidson and Lanczos algorithms (lower panel, dotted line) and that obtained by the full-diagonalization method (lower panel, solid line). These are compared with the experimental spectrum (upper panel).

agonalization methods is not straightforward, as the convergence of Davidson recursion strongly depends on the property of the matrix. A significant advantage of the former method is, however, that it can be applied to a much larger matrix than that manageable by the latter. The Green's function formalism for a theoretical spectrum is more computationally demanding compared to the Fermi's golden rule in eq. (5), because the spectrum function in eq. (6) must be evaluated at each transition energy, $\hbar\omega$. However, the computing multiplet levels corresponding to the final states for a larger system is infeasible, thus, the method would be useful for applying to such systems. In addition, calculations of the spectral function in (6) can be simultaneously performed for different transition energies. Hence, the increase in computational time for spectral functions is not a serious problem for practical applications.

4. Conclusion

In this study, two new algorithms for simulating the multiple structures appearing in TM- $L_{2,3}$ XAS were developed. The first was the generalized Davidson method to solve eigenvalue problems in the many-electron Hamiltonian matrix in the CI. Only the eigenstates corresponding to the initial states of TM- $L_{2,3}$ XAS were calculated by this method. The second was the Lanczos recursion method to compute the spectral function as given in (6). With this method, the PACS for TM- $L_{2,3}$ XAS can be calculated using only the initial state wavefunctions.

Benchmarking calculations were performed for the TM- $L_{2,3}$ XAS of simple TM oxides using small-sized clusters. The eigenvalues and eigenvectors obtained by the generalized Davidson method were identical to that obtained by the full-diagonalization algorithm. The shapes of the spectral functions obtained by the Lanczos recursion method were same as those for the PACS, computed by full-diagonalization algorithm in accordance with the Fermi's golden rule. The results demonstrate that the algorithms described above are properly implemented, and have the potential to quantitatively reproduce and predict the TM- $L_{2,3}$ XAS. The algorithms developed in this study are more suitable for simulating the spectra from larger systems, such as metal clusters and TM complexes whose ligands are composed of multiple of atoms. Further research in this direction is underway.

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