



A Combined Wave Function and Density Functional Approach for K-Edge X-ray Absorption Near-Edge Spectroscopy: A Case Study of Hydrated First-Row Transition Metal Ions

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absorption spectra by calculating the metal K pre-edge features of aquated 3*d* transition metal ions in common oxidation states. MC-PDFT results were compared with experimentally measured spectra as well as analyzed against results from restricted active-space second-order perturbation theory (RASPT2) and time-dependent density functional theory (TDDFT). As expected, TDDFT performs well for excited states that can be accurately represented by singly excited configurations but fails for excited states where higher order excitations become important. On the other hand, both RASPT2 and MC-PDFT provide quantitatively accurate results for all excited states



irrespective of their character. While core-level spectroscopy with RASPT2 is accurate, it is computationally expensive. Our results show that MC-PDFT performs equally well with significantly lower computational cost and is an encouraging alternate approach for X-ray spectroscopies.

-ray absorption spectroscopy (XAS) has been used $oldsymbol{\Lambda}$ extensively over the years to study the local structure and chemical environment of different atoms. Depending on the core orbitals where the electrons are excited from, XAS signals are labeled as K-, L- and M-edge spectra corresponding to principal quantum number n = 1, n = 2, and n = 3, respectively. Broadly, XAS encompasses X-ray absorption nearedge structure (XANES), which involves excitations of electrons from core orbitals to bound states, and extended X-ray absorption fine-structure (EXAFS), which involves transitions from the core orbitals to the continuum states. XANES contains information about the local chemical environment, including the charge state, coordination, and local symmetry. Several previous studies have focused on theoretical treatments of XANES spectra for transition metal ions in the solid state and solutions. The K-edge XANES features of cobalt, iron, manganese, and vanadium have been calculated for their oxides and complexes.^{1,2} K-edge features have also been computed for Fe³⁺, Cr^{3+} , and $V^{3+,3}$ K-edge features of Cr^{3+} in α -Al₂O₃ have been studied, but experimental features did not match with computed spectra.⁴ The Fe K-edge spectra have been computed for both Fe²⁺ and Fe^{3+, 5-7} Previous studies have also explored the K-edge XANES features for some solvated first-row transition metal ions like $\operatorname{Cu}^{2+8-13}$ V^{2+/3+/4+/5+,14-16} Mn^{2+/3+/4+,17-19} Cr^{3+20,21} $Co^{2+,22,23}$ Ni^{2+,20,22,23} Zn^{2+,23} and Fe^{2+/3+} aqua complexes²⁴ and, more recently, for almost the entire series of hydrated 3d transition metal ions.²

Despite the studies mentioned above, accurate prediction of XANES for transition metal complexes in solution is still challenging for many ab initio electronic structure methods, either due to the complexity of the nature of excitations involved or due to the size of the models when explicit solvent molecules are included. Time-dependent density functional theory (TDDFT) has been widely used for modeling XANES due to its favorable balance between accuracy and computational cost. However, TDDFT cannot adequately describe core hole relaxation and requires large heuristic shifts to match experimental values and the inability to capture excitations, where higher order configurations are important. Orbital optimized DFT (OO-DFT) approaches can be useful to address the former,^{26,27} but converging the calculation to the correct core excited state can be challenging. While correlated multireference wave function approaches like multireference coupled cluster $(MRCC)^{28}$ or multireference configuration interaction $(MRCI)^{29,30}$ approaches can be used to overcome these issues, they are too expensive for systems beyond a few atoms. The multiconfiguration self-consistent field (MCSCF) method has been widely used for modeling multireference systems, where calculations are based on an active space of

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electrons and orbitals. Complete active-space SCF (CASSCF) performs a full configuration interaction (full-CI) calculations on one active space.³¹ To reduce the computational cost of these calculations, the restricted active-space SCF (RASSCF) method is used, where the active space of a system is divided into three subspaces and only limited excitations are allowed between these subspaces and full-CI calculations are performed within each subspace.³²

Even though MCSCF calculations provide an accurate representation of the wave function of multireference systems, it does not provide accurate energetics due to the missing dynamical correlation. The simplest way to recover dynamical correlations is the configuration interaction approach. While an accurate wave function of a state can be represented with a linear combination of a few configurations, the dynamical correlation converges very slowly with the number of configurations included in the wave function. Post-SCF second-order perturbation theories (PT2) are often used for recovering missing dynamical correlations in MCSCF calculations.^{33–35} Odelius and co-workers have extensively applied the RASPT2 method to study transition metal L-edges.³⁶ However, both PT2 and CI calculations are computationally expensive for large systems.

An alternative post-SCF method for recovering dynamical correlation is to use a combined wave function and density functional theory (DFT) approach.^{37,38} In this class of approaches, only the DFT/ROCIS method has been applied to X-ray spectroscopy of different transition metal systems.^{39–42} However, a shortcoming with this method involves empirical parameters, and the ground state wave function is single reference in nature. A more general combined wave function and DFT approach is multiconfiguration pair-density functional theory (MC-PDFT) developed by Li Manni and coworkers.³⁷ It has provided accurate results for a wide range of chemical problems including a wide range of valence excitations, ^{37,38} but it has not been explored to study corelevel excitations, which is the focus of this letter.

In MC-PDFT, the energy of an electronic state is calculated by

$$E^{MC-PDFT} = V_{nn} + \langle \psi | T + V_{ne} | \psi \rangle + V_c[\rho] + E_{ot}[\rho, \Pi]$$

where $|\psi\rangle$ is the converged MCSCF wave function, $\langle \psi|T +$ $V_{ne}|\psi\rangle$ is the summation of the kinetic and electron-nuclear energy, $V_c[\rho]$ is the classical Coulomb energy, and $E_{ot}[\rho, \Pi]$ is the on-top energy.³⁷ The MC-PDFT method requires a multireference wave function to generate the total density and the on-top pair-density (Π) for an electronic state. Π is the probability of finding two electrons at a given point in space. The on-top energy is analogous to the exchange-correlation energy of Kohn-Sham DFT, but instead of spin densities, the on-top energy depends on the total density and the on-top pair-density. It includes a correction to the MCSCF kinetic energy in addition to the exchange and correlation. On-top energy functionals are translated forms of traditional KS-DFT exchange-correlation functionals. For example, tPBE is the translated form of the PBE exchange-correlation functional. The multiconfigurational wave function in MC-PDFT is obtained from converged MCSCF calculations. For studying core-level excitations, RASSCF is particularly useful as it is possible to restrict excitations from a core-level orbital to one.

Recently, Ghosh and co-workers have reported a detailed study of the K pre-edge XANES of aquated 3*d* transition metal ions with *d*-orbital occupancies: d^2 (V³⁺), d^3 (V²⁺, Cr³⁺), d^5

(Fe³⁺, Mn²⁺), and $d^{7,8,9,10}$ (Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺).²⁵ This series is particularly relevant for assessing the accuracy of a computational method as it contains a good balance of systems with single- and multireference character. Core-level excitations change both qualitatively and quantitatively depending on the 3*d* orbital occupancy of the metal ions. Additionally, the availability of high quality experimental data makes this series an ideal reference set. The study also demonstrated that a suitable description of the solvent environment is needed for quantitative agreement with experiment.

In this letter, we have investigated the accuracy of MC-PDFT for the computation of K-edge XANES. We have compared our results with those obtained from TDDFT, RASPT2, and experimental measurements. All the metal aqua ions studied here are high-spin and hexacoordinated with water molecules except for the structure of the Cu^{2+} aqua ion, where two axial Cu–O bond distances are appreciably elongated compared with other Cu–O bond distances. The structures for all of the systems studied were obtained from ref 25.

For the V^{2+} ion (Figure 1), the experimentally measured spectrum shows a broad peak between 5464.5 and 5467.5 eV.



Figure 1. 1s-3d pre-edge spectra for V^{2+} from computation and experiment. The calculated spectra have been aligned with experiment.

TDDFT predicts two peaks, but the overall spectrum is narrower compared with the experiment. RASPT2 shows two peaks at ~5464.5 and ~5467 eV, as well as a small shoulder at ~5467.5 eV. MC-PDFT also shows one broad peak between ~5465 and ~5467 eV and a shoulder at ~5467.5 eV. Analysis of the multireference wave function reveals that the first peak has appreciable contributions from double or higher excited configurations. Specifically, these involve 1s to 3d orbital excitations of a single electron and rearrangement of electrons within occupied and unoccupied 3d orbitals, but all configurations in these cases have singly occupied 3d orbitals. However, excited states corresponding to the second peak are essentially configurations with doubly occupied *d* orbitals. The small shoulder in RASPT2 and MC-PDFT at ~5467.5 eV is again primarily composed of configurations with singly occupied d orbitals.

The experimentally measured spectrum of V^{3+} ion (Figure 2) has three distinct peaks at ~5465, ~5467.5, and ~5468.5 eV, respectively. TDDFT, RASPT2, and MC-PDFT spectra



Figure 2. 1s-3d pre-edge spectra for V^{3+} from computation and experiment. The calculated spectra have been aligned with experiment.

are similar and match with the experiment for the first two peaks. However, in the case of the first peak at ~5464.5 eV, MCSCF wave functions for excited states have significant contributions from higher than singly excited configurations, which cannot be captured with TDDFT. These higher excited state configurations involve a combination of 1s to 3d transitions and rearrangement of 3d electrons similar to V²⁺. Although TDDFT cannot capture these higher excited configurations, it still reproduces the first two peaks, albeit for the wrong reason. The ~5468.5 eV peak, like the first peak, has appreciable higher order excited configurations and is correctly captured by both MC-PDFT and RASPT2 but not with TDDFT.

In Figure 3, the experimentally measured spectrum of Cr^{3+} shows three peaks, a main peak at ~5993 eV with a weak shoulder at ~5993.5 eV, and a third peak at ~5995.5 eV. The TDDFT spectrum only shows two peaks with a significantly underestimated splitting. The RASPT2 spectrum is composed



Figure 3. 1s-3d pre-edge spectra for Cr^{3+} from computation and experiment. The calculated spectra have been aligned with experiment.

of four peaks. The first broad experimental peak is represented by two peaks in RASPT2 (~5992.5 and ~5993.5 eV). Among these two RASPT2 peaks, the first peak at ~5992.5 eV is primarily composed of doubly excited configurations, and the excited states corresponding to the second peak, at ~5993.5 eV, can be represented accurately by singly excited state configurations. The third and fourth peaks in the RASPT2 spectrum of Cr^{3+} , at ~5995.5 and ~5996.2 eV, are primarily singly excited configurations, and these are predicted correctly with TDDFT. Interestingly, the MC-PDFT spectrum matches very well with the experimentally measured spectrum for Cr³⁺. MC-PDFT predicts two broad peaks at ~5993 and ~5995.5 eV. A closer look at the excitation energies shows that both of the broad peaks have two peaks, but the splitting between these two peaks is significantly smaller compared to the RASPT2 spectrum.

Both Mn^{2+} and Fe^{3+} aqua ions have d^5 configurations, and the Co^{2+} aqua ion has a d^7 electronic configuration. K-edge XANES of these metal ions are primarily singly excited configurations. The experimentally measured spectrum (Figure 4) of Mn^{2+} has one broad peak between ~6538 and ~6541 eV. The TDDFT spectrum has two peaks at ~6539 and ~6540 eV, while the RASPT2 and MC-PDFT spectra show two peaks at ~6538.5 and ~6539.5 eV. Experimental, RASPT2, MC-PDFT, and TDDFT computed spectra have two distinct peaks at ~7112.5 and ~7114 eV. The Fe^{2+} experimental spectrum (Figure 4) shows two equal intensity peaks at ~7112 and ~7114.5 eV. TDDFT, RASPT2, and MC-PDFT predict these two peaks accurately. However, the intensities of these peaks are not equal for the computed spectra. This may be attributed to the lack of configuration averaging in our calculations. The experimentally measured spectrum of Co^{2+} (Figure 4) has one peak at ~7708 eV and a second peak at ~7709.5 eV. TDDFT correctly predicts these two peaks for Co²⁺. RASPT2 and MC-PDFT spectra have two peaks as well, but at ~7709 and ~7709.5 eV, suggesting a smaller splitting. Unlike TDDFT and MC-PDFT, the RASPT2 spectrum has a weak peak at ~7712 eV. Even though the excited states corresponding to the third RASPT2 peak are computed in the MC-PDFT spectrum, the splitting between the second and third peaks in MC-PDFT is significantly smaller compared to RASPT2, resulting in the absence of a separate third peak. See Table S6 in the Supporting Information.

Due to the d^8 and d^9 electronic configurations of the Ni²⁺ and Cu²⁺ aqua ions, the t_{2g} 3*d* orbitals are doubly occupied. All three methods, RASPT2, MC-PDFT, and TDDFT, show single peaks similar to the experimentally measured spectrum for Ni²⁺ and Cu²⁺ ions (Figure 5). The excitations involved in these two aqua ions are single in nature.

Table 1 shows the energy shift needed for TDDFT, RASPT2, and MC-PDFT to align the calculated spectra with the experimentally measured spectra. The shift required for TDDFT is significantly larger compared to RASPT2 and MC-PDFT. It is also important to note that the shifts needed for TDDFT are negative, while shifts are positive for RASPT2 and MC-PDFT. This is an indication that the nature of the errors are different in TDDFT and multireference methods. In the case of TDDFT, the excited state wave function is not variationally optimized, and the self-interaction error of the exchange-correlation functional can be a contributing factor. On the other hand, in RASPT2 and MC-PDFT, the excited state wave functions are variationally optimized. However, to prevent variational collapse, the core orbital is kept frozen



Figure 4. 1s-3d pre-edge spectra for (a) Mn^{2+} , (b) Fe³⁺, and (c) Co²⁺ from computation and experiment. The calculated spectra have been shifted to align with experiment.



Figure 5. 1s-3d pre-edge spectra for (a) Ni^{2+} and (b) Cu^{2+} from computation and experiment. The calculated spectra have been aligned with experiment.

Table 1. Energy Shifts $(E_{expt} - E_{comp})$ in eV for Computational Spectra Obtained from TDDFT, RASPT2, and MC-PDFT To Align with Experimentally Measured Spectra

	E_{TDDFT}	E_{RASPT2}	$E_{MC-PDFT}$
V ³⁺	108.4	-14.7	-7.1
V ²⁺	108.4	-14.7	-7.1
Cr ³⁺	122.3	-12.0	-3.6
Mn ²⁺	131.4	-15.8	-6.8
Fe ³⁺	143.8	-19.5	-9.5
Co ²⁺	157.3	-19.5	-9.0
Ni ²⁺	171.2	-21.0	-10.4
Cu ²⁺	189.1	-20.4	-9.7

during the optimization, which can contribute to the shifts needed for RASPT2 and MC-PDFT, respectively. The RASSCF optimization uses a state-average approach for optimizing the orbitals for a core excited state, where an average optimization is performed for all core excited states. This also contributes to the shifts. MC-PDFT has a smaller shift compared to RASPT2. A possible reason for this is because RASPT2 can only recover the correlation originating from double excitations, while MC-PDFT, in principle, can recover the dynamical correlation originating from all possible excitations.

In summary, through a detailed study, we have demonstrated the predictive ability of MC-PDFT as a promising alternative to RASPT2 for studying the K-edge XANES for a series of complex transition metal systems. We have compared our results with experimental measurements, TDDFT, and RASPT2. While TDDFT yields sufficiently accurate results when the excitations are dominated by singly excited configurations, it fails as expected when the excitations involved are higher order in nature. RASPT2 and MC-PDFT both perform well irrespective of the nature of excitations. This distinction between TDDFT and the two multireference methods, MC-PDFT and RASPT2, can be clearly seen in the spectra of the V^{3+} , V^{2+} , and Cr^{3+} aqua ions, where both RASPT2 and MC-PDFT are not only accurate compared with experiment but also capture the nature of the different excited states correctly. We have demonstrated that MC-PDFT is qualitatively similar to RASPT2, but with significantly lower computational cost. The offset needed to align the computed spectra to experimental spectra is also smallest for MC-PDFT. Nevertheless, we also note that unlike TDDFT, both RASPT2 and MC-PDFT are not black-box methods, and the affordability of these methods depends on the cost of the underlying MCSCF calculation. Embedding approaches⁴³⁻⁴⁷ offer the possibility to extend multireference calculations for studying core-level excited states in larger complexes in realistic environments.

COMPUTATIONAL METHODS

The DFT and TDDFT results and all the geometries of the transition metal aqua ions including the solvent environment

parameters were taken from ref 25. The geometries were optimized using the PBE0 exchange-correlation functional⁴ together with the dispersion correction⁴⁹ with 40 explicit water molecules in the presence of the COSMO solvent model.⁵⁰ In our RASSCF calculations, the RAS1 subspace contains only the 1s orbital, while the RAS2 subspace contains five 3dorbitals. Only one hole was allowed in the RAS1 space during core excited state calculations. RASSCF optimizations were performed using the state-average formalism for all of the core excited states, while the ground state was optimized separately. To ensure core excitations occur from the 1s orbital, this orbital was kept frozen during the RASSCF optimization.⁵ For the V^{2+} , V^{3+} , and Cr^{3+} aqua ions, a total of 20 core excited states were computed in the RASSCF calculation. For Mn²⁺ and Fe³⁺, and Ni²⁺, a total of 5 core excited states were computed in the RASSCF calculation. For Co^{2+} and Cu^{2+} , a total of 10 and 1 states were computed, respectively, in the RASSCF calculation. RASPT2 calculations are performed using the ANO-RCC-VTZP basis set, an imaginary shift of 5.44 eV, and without any IPEA shift.

To account for the effect of the solvent in the RASSCF, RASPT2, and MC-PDFT calculations, the COSMO implicit solvent charges for all of the aqua ion structures were obtained from NWChem DFT calculations.^{25,51} Multireference calculations were performed in the presence of those charges on the aqua ion structures. In Table S9 of the Supporting Information, taking the Cr³⁺ ion as a test case, we show that the COSMO charges mainly affect the intensities of the core excited states but do not have a large effect on the excitation energies. All MC-PDFT calculations shown in this paper were performed with the OpenMolcas software package (v22.02, tag 112-ge90b62921).⁵² The MC-PDFT calculations were performed using the RASSCF wave function and translated PBE (tPBE) on-top pair-density functional using the ANO-RCC-VTZP⁵³ basis set. The restricted active-space state interaction (RASSI) method was used to compute transition dipole moments between ground and core excited states.⁵⁴ To compare with experimental spectra, a Lorentzian broadening of 1.5 eV was applied to all of the computed spectra.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.3c00611.

Details and character of the K-edge excitations for all systems studied (PDF)

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Notes

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