Restricted active space calculations of L-edge X-ray absorption spectra: From molecular orbitals to multiplet states

Rahul V. Pinjari,1 Mickael G. Delcey,1 Meiyuan Guo,1 Michael Odelius,2 and Marcus Lundberg1,a)

1) Department of Chemistry - Ångström laboratory, Uppsala University, SE-751 20 Uppsala, Sweden.
2) Department of Physics, Stockholm University, AlbaNova University Center, SE-106 91 Stockholm, Sweden.

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Metal L-edge (2p → 3d) X-ray absorption spectra are affected by a number of different interactions, e.g., electron-electron repulsion, spin-orbit coupling and charge transfer between metal and ligands, which makes them challenging to simulate. The core restricted active space (RAS) method is an accurate and flexible approach that can be used to calculate X-ray spectra of a wide range of medium-size systems without any symmetry constraints. Here, the applicability of the method is tested in detail by applying it to three ferric (3d5) model systems with well-known electronic structure; atomic Fe3+, high-spin [FeCl6]3− with ligand donor bonding, and low-spin [Fe(CN)6]3− that also has metal backbonding. For these systems, the core RAS method performs at a level comparable to that of the commonly used semiempirical charge transfer multiplet model, but without requiring any system-dependent parameters. It handles orbitally degenerate ground states, accurately describes metal-ligand interactions, and includes both single and multiple excitations. To establish the best balance between timing and accuracy, the effects of different model selections have been extensively tested, e.g., active space, number of final states and computational algorithms. A method has also been developed to analyze contributions to the calculated X-ray spectra using a chemically intuitive molecular orbital picture.

Keywords: transition metals, X-ray absorption spectroscopy, metal L-edge, multiconfigurational, wavefunction

I. INTRODUCTION

First-row transition metals are key components in many homogeneous and heterogeneous catalysts. For these systems metal L-edge (2p → 3d) X-ray absorption spectroscopy (XAS) offers an element-specific probe that directly targets the unoccupied or partially unoccupied 3d orbitals that act as electron acceptors during catalytic reactions. To get the most out of the L-edge XAS data requires a theoretical method that can relate the spectral shape to the electronic structure of the system. Due to the complexity of the (2p → 3d) X-ray absorption spectra are affected by a number of different interactions, e.g., electron-electron repulsion, spin-orbit coupling and charge transfer between metal and ligands, which makes them challenging to simulate. The core restricted active space (RAS) method is an accurate and flexible approach that can be used to calculate X-ray spectra of a wide range of medium-size systems without any symmetry constraints. Here, the applicability of the method is tested in detail by applying it to three ferric (3d5) model systems with well-known electronic structure; atomic Fe3+, high-spin [FeCl6]3− with ligand donor bonding, and low-spin [Fe(CN)6]3− that also has metal backbonding. For these systems, the core RAS method performs at a level comparable to that of the commonly used semiempirical charge transfer multiplet model, but without requiring any system-dependent parameters. It handles orbitally degenerate ground states, accurately describes metal-ligand interactions, and includes both single and multiple excitations. To establish the best balance between timing and accuracy, the effects of different model selections have been extensively tested, e.g., active space, number of final states and computational algorithms. A method has also been developed to analyze contributions to the calculated X-ray spectra using a chemically intuitive molecular orbital picture.

In this atomic model, initial and final states are calculated from a full CI including the 3d orbitals, i.e., taking into account all possible 3d electron configurations. Electron correlation is introduced by reducing the electron repulsion integrals from their Hartree-Fock values and spin-orbit coupling is included in the Hamiltonian at the same level as electron-electron repulsion. Ligands are described by an empirical ligand-field splitting of the 3d orbitals.

For highly covalent complexes, the effects of ligands can also be included through the use of additional configurations where one electron has been transferred from or to the ligand, i.e., ligand-to-metal charge transfer (LMCT) and metal-to-ligand charge transfer (MLCT) configurations. Adding these configurations to the CI gives the semiempirical charge-transfer multiplet (CTM) model.6,7 This method gives a balanced description of electron repulsion and spin-orbit coupling and includes all relevant final states. The amount of metal-ligand mixing is typically determined from a system-dependent multi-parameter fit to the experimental spectrum. The number of model parameters increases with decreasing symmetry, and the semiempirical CTM approach thus works best for complexes with a high degree of symmetry.

Ab initio methods offer better predictive power than semi-empirical ones, at least in principle. In the ab initio LFM model the basis for the CI calculations are molecular orbitals (MOs) calculated for small clusters, e.g., the central atom and first-shell ligands. Spin-orbit coupling is introduced at the MO level through a relativis-
active space SCF (RASSCF) method, while electron correlation is introduced through the use of density-functional theory (DFT) to calculate the MOs. To keep the computational cost down, the CI calculation only includes a limited number of determinants, e.g., only those corresponding to single excitations from 2p to 3d, or also those corresponding to single excitations within the 3d space.

In the \emph{ab initio} LFM model the effects of the ligands are accounted for in the calculation of the molecular orbitals. An extension to the method is to include also ligand-centered orbitals in the CI, giving the \emph{ab initio} CTM model. To limit the number of new configurations, typically only single excitations from the ligand orbitals are included in the expansion.

A drawback of the \emph{ab initio} CTM model is that it can only be applied to relatively small clusters. An attempt to overcome this limitation is to first perform a plane-wave local-density approximation (LDA) DFT calculation, and then get localized metal 3d and ligand orbitals using Wannier functions. These functions can then be used to calculate most of the parameters in a CTM model, but e.g., the spherical part of the 2p-3d and 3d-3d Coulomb correlation and the charge-transfer energy still need to be fitted to the experimental data.

A method developed for extended clusters, up to 30 metal atoms, is the DFT restricted-open shell configuration interaction with singles (DFT/ROCIS) approach. In this method the CI is performed on the non-relativistic orbitals only includes single excitations, i.e., the core to valence excitation. To cover all the multiplets that arise from the atomic terms, all relevant spin multiplicities are calculated and the magnetic sublevels are constructed using Wigner-Eckart algebra. The description of electron correlation is improved by parameterizing the configuration interaction matrix, using three system-independent parameters. Finally, SOC is included through a quasi-degenerate perturbation approach on the non-relativistic states, which is the molecular equivalent of atomic L-S coupling.

However, a small CI expansion severely limits the description of the X-ray process, e.g., double excitations are ignored. The importance of higher order excitations has been shown for ferrocene and ferrocenium, although without taking SOC into account. In the complete active space (CAS) self-consistent field (SCF) method a full CI is constructed among the active orbitals. This multiconfigurational wavefunction method has been widely used to model valence excitations, but can adapted for X-ray processes by also including the core orbitals in the active space. As the number of excitations from the core orbitals can typically be restricted to one, it is convenient to use the restricted active space SCF (RASSCF) method, giving the core RAS method. The valence active space in the RASSCF approach can either include only the metal-centered 3d MOs, giving a ligand-field model, or also the important ligand MOs, giving a charge-transfer model. Unlike the other \emph{ab initio} methods, the full CI calculation in the active space not only makes sure that the correct final states are spanned, but also takes care of correlation between the active electrons. The calculation can be further improved by including correlation with the occupied inactive and virtual orbitals using second order perturbation (RASPT2). 21-23 SOC is added on top of the multiconfigurational spin-free states, which is equivalent to L-S coupling.

The core RAS method can be applied to similar systems that are currently treated using standard RASPT2, i.e., systems with around 50 atoms, and does not require any symmetry. It has already been applied e.g., to the X-ray photoelectron spectra (XPS) of U and Yb compounds, and as well as L-edge XAS spectra of transition-metal coordination complexes.

The ability of RASSCF to treat near-degenerate electronic states makes it appropriate for investigations with time-resolved X-ray spectroscopy because the also the photoexcited compounds that undergo changes in chemical bonding can be studied. The recent development of sources for time-resolved resonant inelastic X-ray scattering (RIXS) techniques enables insight into both ultra-fast electron dynamics and nuclear dynamics. The RASSCF framework is suitable for a detailed description of dynamical and polarization dependence in the RIXS and X-ray emission processes and has been applied to calculate the RIXS spectra of aqueous Ni^{2+}, as well as ferrocyanide and ferrocene.

Although core RAS is an \emph{ab initio} method it is possible to tune the accuracy and computational cost through the design of the active space, the choice of excitation levels in the valence space, and the number of final states. This flexibility makes it important to understand how these choices affect the performance, but this has not yet been properly established. In the present study the core RAS method is extensively tested by applying it to a series of L-edge XAS spectra of ferric (3d^5) reference systems with well-known electronic structures. In Oh symmetry the high-spin systems have (t_{2g})^5(e_g)^2 configurations and 4A_{1g} ground states, which give the maximum number of unpaired 3d electrons in any system. The low-spin systems have (t_{2g})^5 configurations and orbitally degenerate 2T_2g ground state, a difficult case for many theoretical models.

The first case, the Fe^{3+} atomic ion in different ligand fields enables a one-to-one comparison with the semiempirical LFM model. The second test case, [FeCl_6]^{3-} (ferric chloride), is a high-spin system with prototypical $\pi$ and $\pi$-donor ligands, see Fig. 1. This system corresponds to a CTM model with an extra LMCT configuration. The third test case, [Fe(CN)_6]^{3-} (ferricyanide), is a low-spin complex where the empty $\pi^*$ CN$^-$ ligands gives rise to $\pi$-backdonation, see Fig. 1. In the CTM model, this corresponds to a three-configuration calculation with an extra MLCT configuration. The tests on these three systems can be used to establish the performance of the core RAS method for a number of different bonding situations, but also to determine the sensitivity of the results.
to the core RAS model selections. This makes it possible to better tune cost and accuracy, which can open up for applications on more complex systems.

One advantage of a molecular orbital approach is that it is possible to analyze the electronic structure in a chemically intuitive way. However, the chemical intuition is often lost in the large CI calculations. To go between molecular orbitals and the many multiplet states in the L-edge XAS, a method will be developed to interpret the spectra in terms of excitations to, and from, different molecular orbitals. This analysis can be used to relate changes in the L-edge XAS spectra to differences in electronic structure, which would add significant value to the theoretical analysis.

II. COMPUTATIONAL DETAILS

A. Core RAS method

The RASSCF/RASPT2 calculations have been performed with MOLCAS 7.9.31 The active space is designated RAS(n,l;m;i,j,k), where, i, j and k are the number of orbitals in the RAS1, RAS2 and RAS3 spaces respectively, n is the total number of electrons in the active space, l the maximum number of holes allowed in RAS1, and m the maximum number of electrons in RAS3. The minimum valence active space consists of the metal-dominated 3d orbitals, and the first additions to this space should be orbitals that correlate strongly with them, i.e., the bonding or antibonding partners. For filled or partly filled d shells, an additional empty shell with the same symmetry with a strong metal 4d character, can be included for correlation, i.e., the double-shell effect.32 The 2p orbitals have been placed in the RAS1 space, allowing maximum one hole. RASSCF optimizations have been performed using the state average (SA) formalism, i.e., the same orbitals are used for all the final states of a specific spin and symmetry. A relatively large level shift of 1.0 hartree (h) has been applied to achieve convergence for all different RAS spaces. To avoid orbital rotation, i.e., that the single excitation occurs from a 3p instead of a 2p orbital, the 2p orbitals have been frozen in the RASSCF optimizations. The calculations performed by relaxing 2p orbitals would slightly lower the energies of the excited states, which can merely alter the shift used to overlay the calculated L-edge spectra on experimental ones, see below.

RASPT2 calculations have been performed using multi-state (MS) RASPT2.33 The default procedure for RASPT2 calculations is that the core orbitals, 1s of C/N and up to 3s of Cl/Fe, are frozen. Calculations where also the core orbitals have been correlated are labeled RASPT2-cc. Calculations have been performed using the default ionization potential electron affinity (IPEA) shift of 0.25 hartree,34 and to reduce problems with intruder states an imaginary shift of 0.3 hartree has been applied.35

Scalar relativistic effects have been included by using a Douglas-Kroll (DK) Hamiltonian36,37 in combination with a relativistic atomic natural orbital (ANO-RCC) basis set.38,39 Unless otherwise specified, a basis set of triple-ζ quality (ANO-RCC-VTZP) has been used. To speed-up calculations without sacrificing accuracy, the density-fitting approximation of the electron repulsion integrals has been used, using auxiliary basis sets from an atomic-compact Cholesky decomposition.40-42

Spin-orbit coupling is included from a one-electron spin-orbit Hamiltonian based on atomic mean field integrals.43 The spin-free eigenstates are used as a basis for computing spin-orbit interaction matrix elements and the spin-orbit eigenstates are then obtained by diagonalizing the spin-orbit interaction matrix,44 giving SOC states (| Λ⟩) that are linear combinations of spin-free states (| I⟩):

$$|Λ⟩ = \sum_I c_I^Λ |I⟩$$

These spin-orbit eigenstates are then utilized to calculate the strength of the electric dipole transitions using the restricted active space state interaction (RASSI) approach.45,46 The intensity of a SO transition is proportional to the square of the expectation value of the dipole operator:

$$\langle Λ | \hat{d} | Θ⟩^2 = \left(\sum_I c_I^Λ \sum_J c_J^Θ \langle I | \hat{d} | J⟩\right)^2$$

An example of the coupling scheme, from RASSCF spin-free states to SOC states, for an L-edge XAS transition is given in Fig. 2.

Although the model systems have O_h or D_{4h} symmetry, calculations are effectively performed in D_{2h} which is the highest symmetry Abelian point group. This point group has inversion symmetry and as only the 2p orbitals are of ungerade symmetry, the lowest excited states of ungerade symmetry are all core excited states. Thus in the RASSCF calculations of the final state, all four irreducible representations with ungerade symmetry in D_{2h} (A_{1u}, B_{1u}, B_{2u}, and B_{3u}) have been included, in combination with all possible (2p)^5(3d)^5 spin states, i.e.,
doublet, quartet and sextet states. For the atomic calculations, where only the five 3d orbitals are placed in the active space, all possible final states are included in the calculations. For $B_{1u}$, $B_{2u}$, and $B_{3u}$ this means 72 doublet, 37 quartet and 4 sextet states each, while the corresponding numbers for $A_{1u}$ symmetry are 69, 39 and 0. Including also ligand orbitals in the active space gives a very large number of possible final states. For these systems, calculations have been performed with a fixed number of final states per symmetry and spin multiplicity. Up to 120 states have been calculated for all the twelve symmetry-spin combinations, which gives a total of 1440 final states before spin-orbit coupling.

**B. Analysis of orbital contributions**

In the core RAS approach the L-edge XAS spectrum can be analyzed in terms of chemically intuitive molecular orbitals and their occupation numbers. Natural occupation numbers for the active orbitals are available for each RASSCF state, and can be constructed for MS-RASPT2 and RASSI-SO states as they are just linear combinations of RASSCF states, see Fig. 2. The differences in occupation numbers between the ground state and each final state allows for an intuitive interpretation of the spectrum in terms of orbital excitations. However, the spin-free states mix heavily under the influence of the strong spin-orbit coupling in the final state. This complicates a straightforward analysis and instead an approximate scheme was designed in which only the spin-free states contributing to the final intensity of a transition between SOC states were taken into account. Assuming that the effect of the cross-terms in Equation 2 are similar for the different spin-free contributions and therefore can be neglected this gives:

$$\langle \Lambda | \hat{d} | \Theta \rangle^2 \approx \sum_I \omega_I^\Lambda \sum_J \omega_J^\Theta (I | \hat{d} | J)^2$$  (3)

with the weights $\omega_I^\Lambda = (c_I^\Lambda)^2$. This summation uses only information printed in the MOLCAS output, although the code has been modified to include all contributions with weights $> 10^{-5}$. The change in natural occupation number between the spin-free states is then weighted by the estimate in Equation 2. Using $n^i_I$ for the natural occupation number of orbital $i$ in the spin-free state $I$ and $f(I \rightarrow J)$ the intensity of the transition between spin-free states $I$ and $J$, the contribution of orbital $i$ to the intensity of a transition from the initial state $\Lambda$ to the final state $\Theta$, $f_i(\Lambda \rightarrow \Theta)$, was computed as:

$$f_i(\Lambda \rightarrow \Theta) = \frac{\sum_I \omega_I^\Lambda \sum_J \omega_J^\Theta f(I \rightarrow J)(n^i_I - n^f_I)}{\sum_I \omega_I^\Lambda \sum_J \omega_J^\Theta f(I \rightarrow J)} f(\Lambda \rightarrow \Theta)$$  (4)

Because of the large number of transitions, an analysis for each transition is not desirable, and instead a graphical representation has been made where the contributions from all transitions have been added.

**C. Core RAS model systems**

To simulate a ligand-field splitting in the atomic system six negative charges are placed at the vertices of the octahedron, 2.0 Å away from the Fe$^{3+}$ center. Calculations have been performed with zero charges, and with charges that give the same splittings between two lowest states as in the RASPT2 calculations of ferric chloride (high spin) and ferricyanide (low spin). The high-spin system has charges of -5.3 au, which gives an energy difference between the lowest $^6A_{1g}$ and $^2T_{2g}$ states of 220 eV. The low-spin system has charges of -12.4 au, which gives an energy difference between two lowest states ($^2T_{2g}$ and $^4T_{1g}$) of 261 eV. In this crystal field model the charges have to be unphysically large to get the correct spin-state energetics because in molecular systems the splitting is mainly due to the different mixing of metal centered orbitals with the ligand orbitals.

All spectral simulations have been performed using the ground state geometries. Calculations on $[\text{FeCl}_6]^{3-}$...
have been performed on an $O_h$ symmetric structure with Fe–Cl distances of 2.40 Å, which is in the 2.39-2.41 Å range given by X-ray diffraction. The [Fe(CN)$_6$]$^{3-}$ geometry is optimized at the CASPT2/ANO-RCC-VTZP (9.0,0,0.10,0) level, giving four Fe–C distances of 1.939 Å, and two distances of 1.916 Å, in good agreement with experimental estimates of 1.941 Å. The C–N distances are 1.178 (1.180) Å. Ferricyanide thus has $D_{4h}$ symmetry, but as will be shown below, the effects of this distortion are relatively small and $O_h$ symmetry will be used to discuss the results.

E. Experimental comparisons

The experimental spectra of ferric chloride and ferricyanide are taken from references Wasinger et al. and Hocking et al. respectively. To obtain L-edge XAS spectra from the core RAS and VBCL multiplet model, the transition intensities are plotted using a Lorentzian broadening with a full-width-at-half-maximum (FWHM) of 0.4 and 0.8 eV for the $L_3$ and $L_2$ edge. The spectra are further convoluted with an experimental Gaussian broadening of 0.4 eV. With this broadening, the simulated spectrum has a FWHM for the first major transition in the ferricyanide spectrum similar to the one in the experimental spectrum. For high-spin complexes the energies of the calculated spectra are shifted so that the high-spin complexes are aligned to the experimental spectra at the most intense peak, whereas spectra of low-spin complexes are aligned to the first intense transition. The energy shifts for selected spectra are given in Table SI 2. The absolute value of the shift decreases for RASPT2 compared to RASSCF and when using larger basis sets. Unless specified, the total integrated intensities of the calculated spectra are scaled to match the total intensity of the experimental spectra.

III. RESULTS

A. Atomic system

Results are presented in order of increasing complexity of the electronic structure, starting with the simple monoatomic Fe$^{3+}$ system with six point charges in $O_h$ symmetry. The RAS1 space includes the three 2p orbitals ($t_{1u}$) while the RAS2 space includes the five 3d orbitals ($t_{2g}$ and $e_g$), see Fig. 1. This gives a total of 11 active electrons. With one excitation allowed from the RAS1 space, and no orbitals in the RAS3 space, the active space is written RAS(1,1,0,3,5,0). In all atomic calculations, the ANO-RCC...3s2p1d basis set contraction has been used.

The core RAS and semiempirical ligand-field multiplet model L-edge XAS spectra of the Fe$^{3+}$ ion without external field, with a weak field, and with a strong field, are displayed in Fig. 3. For the systems with a high-spin $^6A_g$ ($t_{2g})^3(e_g)^2$ ground state, the core RAS and multiplet spectra agree very well for the $L_3$ edge up to 717 eV. Above that energy the core RAS spectra have a minor peak, not present in the multiplet calculations, see Fig. 3a-b. The region above 720 eV is also significantly different. For the low-spin $^2T_{2g}$ ($t_{2g})^5(e_g)^0$ system, there is relatively good agreement between core RAS and multiplet spectra over the entire energy region. One of the minor differences is that the $L_2$ edge is shifted to lower energy in the core RAS spectrum compared to the multiplet results.

To better understand the core RAS results, the spectrum from the low-spin $^2T_{2g}$ ground state is analyzed in more detail, starting with the effects of 2p and 3d SOC, see Fig. 4. As expected, without any SOC there is a single edge, split by ligand-field and multiplet effects. Proper inclusion of 2p spin-orbit coupling, grey line in Fig. 4, not only splits the spectrum into $L_3$ ($J'_{2p} = \frac{3}{2}$) and $L_2$ ($J'_{2p} = \frac{1}{2}$) edges but also leads to major changes in spectral shape because of the mixing of states with different multiplicity. To form the correct spin-orbit states requires all three 2p orbitals and the size of the core RAS1 space can therefore not be decreased. Due to mixing caused by the 2p-3d multiplet interactions the final states are not pure $J'_{2p} = \frac{3}{2}$ and $J'_{2p} = \frac{1}{2}$ states, and $J'$ has therefore been used as a convenient label.

3d SOC is much weaker than 2p SOC, with a coupling constant of 0.05 eV for 3d compared to 8 eV for 2p. Despite the small effect on the final state energies, tak-
FIG. 3. L-edge XAS spectra of the Fe$^{3+}$ ion, with different ligand-field splitting, calculated using RASPT2(11,1,0,3,5,0) (red) and the ligand-field multiplet model (green). The lengths of the arrows give the approximate sizes of the ligand-field splittings.

FIG. 4. Core RAS L-edge XAS spectra of the Fe$^{3+}$ ion with different treatments of 2p and 3d SOC. (i) Spectrum calculated without SOC, (ii) Spectrum with 2p SOC but using one of the $^2T_{2g}$ ground states, i.e., without considering splitting from 3d SOC. (iii) Spectrum calculated from the $\Gamma^+_7$ ($J'_{\text{sd}}=\frac{3}{2}$) SOC ground states. (iv) Spectrum calculated from a Boltzmann distribution of $\Gamma^+_7$ ($J'_{\text{sd}}=\frac{3}{2}$) and $\Gamma^+_6$ ($J'_{\text{sd}}=\frac{1}{2}$) states.

When SOC is taken into account, the spectral shape changes are connected to differences in selection rules for the different SOC states. In Bethe double-group notation, the first peak in the spectrum when including also sextets is very small. However, the selection rules for spin-orbit coupling, $\Delta S = 0, \pm 1$, means that also quartet states need to be included to get a correct description of the spectrum, see Fig. SI 3.$^{1,54}$ Sextet states have indirect effects through their interactions with the quartets, but the changes in the spectrum when including also sextets is very small. Results are similar for the high-spin sextet ground state, with large effects of quartet states, and small effects of doublet states, see Fig. SI 3.$^{1,54}$ In short, final states with $\Delta S = \pm 2$ compared to the initial state can be ignored, unless the initial state itself is a mixture of different spin states.

The previous analysis illustrates how an L-edge XAS spectrum is formed by the interactions between a large number of electronic states of different multiplicity. Despite this complexity, the spectral shape can be analyzed using an intuitive picture of molecular orbital excitations. The first peak in the $L_3$ edge of the low-spin Fe$^{3+}$ ion, see Fig. 3c, serves as a simple example. The $\Gamma^+_7$ ground state is formed from the three degenerate $T_{2g}$ spin-free MS-RASPT2 states, with equal ($\frac{1}{3}$) weights, see Fig. 2. Each MS-RASPT2 state is formed from a single dominant RASSCF state, where each RASSCF state represents a different position of an unpaired electron in the three $t_{2g}$ orbitals ($d_{xy}, d_{xz}, d_{yz}$). The full CI between the 3d orbitals in the RASSCF calculation gives occupation numbers of 4.96 and 0.04 for the $t_{2g}$ and $e_g$ orbitals.
respectively, compared to 5.0 and 0.0 for an SCF calculation. The deviation from integer values is due to the use of excited determinants to describe correlation in wavefunction theory, which is different from the physical excitation process connected to the absorption of a photon.

The $2p \rightarrow t_{2g}$ excitation in the $L_3$ edge, caused by absorption of an X-ray photon, gives quadruply-degenerate $T_{2g}$ ($t'_{2g} = \frac{3}{2}$) final states. They are formed by linear combinations of the $T_{1u}$ spin-free MS-RASPT2 states, each of which has a dominant contribution (92%) from a single RASSCF state with occupation numbers of 5.91 for $t_{2g}$ and 0.09 for $e_g$. Compared to the ground state, there is thus stronger $t_{2g}$-$e_g$ correlation in the final state. Weighing the contributions from all different configurations, the formal $2p \rightarrow t_{2g}$ excitation leads to the loss of one 2p electron, and a gain of 0.95 $t_{2g}$ and 0.05 $e_g$ electrons.

A graphical analysis of the orbital contributions to all final states, described in the Methods section, is shown in Fig. SI 4.54 For the atomic systems which only have $t_{2g}$ and $e_g$ orbitals in the valence active space the analysis is straightforward. The low-spin system has a clear separation of $t_{2g}$ and $e_g$ resonances, and the small negative $t_{2g}$ contributions in the $e_g$ resonance reflect differences in correlation between initial and final state. For the high-spin system (weak field), the first peak is mainly $2p \rightarrow t_{2g}$ excitation, while the second resonance is a mixture between different multiplets reached by both $2p \rightarrow t_{2g}$ and $2p \rightarrow e_g$ transitions, where excitations to $e_g$ orbitals dominate at higher incident energies.

B. Ferric chloride [FeCl$_6$]$^{3-}$

Ferric chloride is a complex with prototypical $\sigma$ and $\pi$-donor bonding. In $O_h$ symmetry, the eighteen filled 3p Cl$^-$ orbitals form six $\sigma$ symmetry adapted linear combinations (SALCs) and twelve $\pi$ SALCs. The two $\sigma$ SALCs of $e_g$ symmetry mix with metal 3d $e_g$ orbitals to create bonding ($\sigma$) and antibonding ($\sigma^*$) combinations, see Fig. 1. The bonding orbitals have predominant ligand character, while the $\sigma^*$ orbitals are usually referred to as metal 3d $e_g$ orbitals. The three filled $\pi$ SALCs of $t_{2g}$ symmetry mix with the 3d $t_{2g}$ orbitals to form sets of weakly bonding and antibonding molecular orbitals.

The ground state of ferric chloride is the high-spin $^6A_g$ state with a formal $(t_{2g})^3(e_g)^2$ electron configuration. The RAS1 space consists of the three $t_{1u}$ Fe 2p orbitals. The design of the RAS2 space starts with the three predominantly metal $t_{2g}$ orbitals and the two metal-dominated $e_g$ orbitals. As the $e_g$ orbitals participate in strong covalent interactions, the first extension is to include correlating orbitals in the same bond, i.e., the two ligand-dominated $\sigma$ orbitals. The half-filled metal $t_{2g}$ orbitals can either correlate with their bonding partners, the filled ligand-dominated $t_{2g}$ ($\pi$) orbitals, or a set of empty 4d $t_{2g}$ orbitals ($t'_2$). In the ground state RASSCF calculation the correlation is stronger with the $t'_{2g}$ orbitals and they are therefore included in the active space, giving a total of ten RAS2 orbitals, see Fig. SI 5.54

As the calculations are performed using state-average RASSCF, the orbital optimization depends on which states that are included. In excited state calculations, the optimal orbitals may therefore be different from those in the ground state. For [FeCl$_6$]$^{3-}$ the lowest-lying unoccupied orbitals of $t_{2g}$ symmetry are SALCs from the Cl 4p orbitals, and in some calculations with a large number of states the 4d $t_{2g}$ orbitals rotate out of the active space and become replaced by the empty Cl 4p $t_{2g}$ orbitals, see Fig. SI 5.54 What appears to be large changes in the structure of the active-space orbitals caused by the core hole potential can often be just a consequence of orbital rotation in the RASSCF optimization. This does not compromise the applicability of the RASSCF method as long as the energies are accurately calculated, but can complicate the analysis of the X-ray process.

The L-edge XAS spectrum calculated at the RASPT2-cc(15,1,0;3,10,0)/ANO-RCC-VTZP level with 120 states per final state symmetry and spin state is shown in Fig. 5. The core RAS spectrum predicts all the major and minor peaks of [FeCl$_6$]$^{3-}$, albeit the intensities of the first two peaks are underestimated, and the peak at 714 eV appears at 713.2 eV with too high intensity. The semiempirical CTM model gives a slightly better estimate of the experimental shape, but as the core RAS results have been obtained without any parameter fitting, the results must be considered very good. The core RAS results are also significantly better than those previously obtained by the DFT/ROCIS method.11

To test the sensitivity to the geometry used in the calculation, the spectrum was calculated with Fe-Cl distances that differ by $\pm$ 0.03 Å compared to the default...
2.40 Å, see Fig. SI 6. A larger Fe-Cl distance increases the intensity of the first peak and gives better agreement with experiment. Parts of the differences compared to the experimental spectrum could thus come from possible errors in the geometry. In the present model the polarization of the complex from the crystal environment is also neglected, which could also have an effect on the calculated spectrum.

The X-ray spectrum of [FeCl₆]³⁻ can be analyzed using the same approach as for the atomic systems, see Fig. 6. The first band at 707 eV is mainly a 2p → t₂g transition, while transitions in the main peak are mixtures of multiplets formed from t₂g and e_g excitations. The negative contributions from the σ orbitals highlight changes in correlation between metal and ligand orbitals when going from the ground to the final state, and indicate that it is important to include the ligand orbitals in the active space. As a comparison, the contributions from the metal t′₂g orbitals are almost negligible. The insight provided by the orbital picture is even clearer in the analysis of the peak at 713.2 eV. Here the contributions from the ligand σ orbitals correspond to the loss of approximately one electron. The peak can therefore directly be assigned to a 2p excitation combined with a σ → 3d transition, i.e., a shake-up transition of LMCT type. This assignment is in agreement with a previous analysis using the semiepipirical CTM model.

Although the core RAS results are very good, the core RASPT2-cc (15,1,0;3,10,0)/ANO-RCC-VTZP calculation is much more expensive than e.g., the DFT/ROCIS method. It is therefore interesting to see whether the computational cost can be decreased without any significant loss in accuracy. An obvious solution is to decrease the size of the active space. Fig. 7 shows that there are no major differences between the original (15,1,0;3,10,0) active space and a (15,1,0;3,7,0) space where the empty orbitals of t₂g symmetry orbitals have been removed. The effect is only noticeable in the 710-715 eV region, with a blue shift of the ligand-to-metal shake-up transition by ∼1.0 eV. These results indicate that, for the systems dominated by σ-bonding, an active space involving seven valence orbitals are sufficient to predict the L-edge spectra with good accuracy. Decreasing the active space by removing also the filled ligand σ orbitals would further reduce computational cost, but this alternative could not be tested as it leads to convergence problems in the RASPT2 calculations. The poor convergence is a clear indication that there is strong correlation between e_g and σ, and that the latter should be included to get proper results.

An alternative to reducing the number of active orbitals is to put some orbitals in the RAS3 space where the number of excitations can be limited. Putting the e_g orbitals in the RAS3 space and allowing a maximum of three electrons, (15,1,3;3,5,2), means that only one additional electron is allowed in the e_g orbitals from the (t₂g)³(e_g)² ground state configuration. Among the effects is that the shake-up transition disappears, which further confirms that this peak requires more than single-electron excitations.

After the design of the active space, the choice of basis set has the largest effect on the computational cost. The basis set dependence of the L-edge XAS spectra were evaluated using ANO-RCC basis sets from double-ζ (VDZP) to quadruple-ζ basis on all atoms (VQZP), see Fig. SI 7. The spectral shape does not change significantly when going from double to quadruple-ζ, with only minor changes in the intensity of the first minor peak and in the shake-up transition.

Compared to the calculations of valence excitations, simulating an L-edge XAS spectrum is more expensive, partly because of the large number of excited states that need to be calculated. To probe the effect of the number of final states, the RASPT2-cc (15,1,0;3,10,0) spectra
were calculated with between 20 and 120 states per symmetry and spin multiplicity, see Fig. 8. The L_3 edge is relatively insensitive to the number of states, although the intensity of the shoulders of the main peak changes slightly. The situation is very different for the L_2 edge for which the shape is very dependent on the number of states without any clear convergence even for a large number of states.

The number of states affects the core RAS calculations in several different ways. In the SA-RASSCF calculation the shapes of the orbitals depend on the states that are included in the optimization. This has been tested by calculating the same number of final states (80) but using the orbitals optimized for 20, 40, 60 and 80 states, see Fig. SI 8. The test shows that the spectrum, and thus the shape of the orbitals, do not change significantly after 40 states. A similar calculation using only 20 final states leads to the same conclusion see Fig. SI 8. Another important point is that all states with significant transition intensity must be included, but also spin-free states without significant intensity can affect the core RAS spectrum through mixing in the SOC calculation. To illustrate these effects, spectra were calculated with 20, 40, 60 and 80 states, in all cases the same RASSCF orbitals, those optimized for 80 states. There are large differences between the different spectra, especially in the L_2-edge, see Fig. SI 9. This shows that the shape of the L_2-edge is not only affected by the J''_{2p} = \frac{3}{2} states but also by the large number of high-energy valence-excited states with J''_{2p} = \frac{3}{2} in the same energy region.

### C. Ferricyanide ([Fe(CN)]_6)^3−

In [Fe(CN)]_6^3− each cyanide ligand contributes one filled σ orbital and two empty antibonding orbitals of π type. Assuming O_h symmetry, two σ SALCs of e_g symmetry mix with metal 3d e_g orbitals to give ligand-dominated bonding (σ) and metal-dominated antibonding (e_g or σ*) orbitals, see Fig. 1. Three empty CN π SALCs mix with Fe 3d t_2g orbital, to form metal-centered bonding (t_2g) and ligand-centered antibonding (π*) orbitals that describe π backdonation.

In O_h symmetry the ground state of ferricyanide is the low-spin 2T_2g state with a nominal (t_2g)^5(e_g)^0 electron configuration. Five electrons in three t_2g orbitals lead to a Jahn-Teller distortion to D_{4h} symmetry, but as the t_2g orbitals are only weakly bonding the distortion is small, see the Computational details. Labels appropriate for O_h symmetry will be used, with effects of deviation from this symmetry discussed separately. The RAS1 space again consists of the three t_1u, Fe 2p orbitals. The RAS2 space has 10 orbitals. The empty metal-dominated e_g orbitals correlate with the two filled ligand σ, while the partially filled metal t_2g orbitals can either correlate with the ligand π* orbitals or the metal 4d t'_2g orbitals. In the ground state the t'_2g orbitals are better correlating partners and stay in the active space during the RASSCF optimization, see Fig. SI 10. However, state-average optimizations with sufficient number of excited states, in order to include direct π* excitations, can lead to solutions where the π* orbitals are included in the active space instead of the t_2g orbitals, see Fig. SI 10.

The experimental L-edge XAS spectrum of ferricyanide, see Fig. 9, has three distinct peaks in the L_3 edge; a first peak at 705.8 eV assigned to a 2p → t_2g transition, a second peak with a maximum around 710 eV, assigned to e_g transitions, and a third peak at around 712 eV assigned to π* transitions. The L-edge XAS spectrum calculated at the RASPT2-cc/ANO-RCC-VTZP 120 (15,1,0;3,10,0) level of theory captures all the major features of the experimental spectrum, e.g., the difference in intensity of the t_2g peaks in the two edges, the shape of the e_g resonance, the high intensity of the π* resonance, as well as its high-energy shoulder, see Fig. 9. The main differences are that the π* peak is shifted to higher energy by ~1.5 eV and that the splitting between the L_3 and L_2 edges is underestimated by ~1.0 eV. The accuracy of the core RAS spectrum is comparable to that achieved with the semiempirical CTM model.

For [Fe(CN)]_6^3− all calculations have been made on the geometry optimized at CASPT2/ANO-RCC-VTZP, which gave four Fe−C distances of 1.939 Å and two distances of 1.916 Å, but the Jahn-Teller distortion to D_{4h} does not significantly affect the ground state energy levels, see Fig. SI 11. A comparison of spectra calculated using a constrained O_h and the optimized D_{4h} geometry, see Fig. SI 12 also shows very small differences. However, the choice of geometry is still important. Many calculations are, due to the lack of CASPT2 analytical gradients, made on geometries optimized with DFT. For ferricyanide geometry optimization with B3LYP/ANO-RCC-VTZP gives Fe−C bonds that are longer by ~0.06 Å and C−N bonds that are shorter by ~0.02 Å, differences large enough to affect the calculated spectrum, see
The molecular orbital contributions to the [Fe(CN)$_6$]$^{3-}$ L-edge XAS spectrum can be analyzed in a similar way as previously done for Fe$^{3+}$ and [FeCl$_6$]$^{3-}$, see Fig. 10. All resonances, except the first $2p \rightarrow t_{2g}$ transition, are comprised of excitations to large number of different multiplet states. For the broad $2p \rightarrow e_g$ resonance the low-energy shoulder is a relatively pure $e_g$ transitions but as the energy of the different ($t_{2g}$)$^5$(e$_g$)$^1$ multiplets increase they mix more strongly with other excited configurations, seen as an increasing loss of electrons from the $t_{2g}$ orbitals. The reason for the high intensity of the $\pi^*$ peak, despite the small metal contributions to the $\pi^*$ orbital, can also be rationalized. The contributions from direct excitations into the $\pi^*$ orbitals are relatively small, and instead the major contribution is intensity borrowing from $e_g$ excitations. There are also large changes in the occupation number of the $t_{2g}$ orbitals, which reflects the increased weight of configurations with less than five $t_{2g}$ electrons at this energy.

The calculations of ferric chloride showed that the number of orbitals in the RAS2 space could be decreased from ten to seven without significant changes to the spectrum. However in ferrocyanide the three highest orbitals of $t_{2g}$ symmetry are not included to describe correlation, but are ligand $\pi^*$ orbitals required to describe the $\pi^*$ peak. To save computational time, orbitals can instead be moved to the RAS3 space where the number of excitations can be limited. Calculations with $e_g$ and $\pi^*$ orbitals in the RAS3 space with either two, RAS(15,1,2;3,5,5), or three electrons allowed, RAS(15,1,3;3,5,5), are shown in Fig. 11. As one of these electrons comes from the core excitation, these RAS calculations represent single and double excitations in the valence space respectively. Allowing only two RAS3 electrons leads to significant changes in the spectrum, e.g., the $\pi^*$ peak in the $L_3$-edge almost disappears. This is consistent with the orbital analysis above where the $\pi^*$ peak had significant contributions from states with multiple excitations. Instead allowing three RAS3 electrons gives significantly better results and the main difference compared to the original calculation is a shift of the $e_g$ peaks to higher energy.

The basis set dependence was evaluated using double-$\zeta$ (VDZP), triple-$\zeta$ on Fe and double-$\zeta$ on ligands (VD(T)Z), and triple-$\zeta$ (VTZP), see Fig. SI 14. The splitting of the $t_{2g}$ and $e_g$ peaks change by 0.3 eV between double and triple-$\zeta$, and the relative intensity of the different peaks also change slightly. These differences can be considered relatively small, at least on the energy scale of the L-edge XAS.

For ferric chloride, the number of final states had signif-
D. Core RAS algorithms

To fully understand the stability of the results and find the best compromise between accuracy and computational time, the computational algorithms should also be evaluated. For most systems the computational bottleneck is the MS-RASPT2 calculation. This algorithm is in general better than the standard state specific RASPT2 method when several states of the same symmetry interact strongly. However, for calculations of a very large number of states, the standard RASPT2 procedure has some advantages. The total cost is lower compared to the MS-RASPT2 algorithm, and RASPT2 calculations of individual states can be performed separately, making this step trivially parallelizable. Comparisons of the RASPT2 and MS-RASPT2 spectra for both ferric chloride and ferricyanide are shown in Fig. SI 16. In both complexes the spectrum does not change significantly, which suggests the standard RASPT2 method can be used for larger calculations. These calculations should further be facilitated by the recent implementation of parallel RASPT2 in Molcas. The default for the RASPT2 calculations is that the core orbitals are not included in the correlation calculation. For valence excited states this saves computational time without significantly affecting results as the contributions of core excited determinants are small. This could potentially change when the 2p orbitals are placed in the active space, and all calculations were therefore performed by also correlating the core orbitals (RASPT2-cc). However, a direct comparison of the two approaches shows that the difference compared to the default procedure is relatively small, both for ferric chloride and ferricyanide, see Fig. SI 17.

A more drastic alternative would be to skip the RASPT2 step completely and instead calculate the spectra at the RASSCF level of theory. Evaluating the effects of dynamical correlation shows that it has large effects on the spectra, especially for [Fe(CN)]

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FIG. 13. Analysis of the total computational cost for the various steps in the calculation the L-edge XAS spectra of \([\text{Fe(CN)}_6]^{3-}\) as function of active space, basis set, and computational algorithm. The timings refer to an architecture of the type Intel Xeon E5-2660 “Sandy Bridge” processor at 2.2 GHz using 8 GB RAM. The numbers of doublet configuration state functions in \(B_{1g}\) symmetry are also shown for comparison.

Finally, the total computational cost for the L-edge spectrum of the \([\text{Fe(CN)}_6]^{3-}\) XAS simulation has been evaluated for the different active space, basis set and RASPT2 calculations, see Fig. 13. In all cases the reference calculation is RASPT2-cc/ANO-RCC-VTZP (15,1,3:3,5,5) with 80 states, which has a total computational cost of 161 core hours with similar weights for the RASSCF and RASPT2 steps. Allowing for a full CI among the active valence orbitals more than doubles the computational cost both for RASSCF and RASPT2 steps. Allowing for a full CI among the active valence orbitals more than doubles the computational cost both for RASSCF and RASPT2 steps. Placing the 2p orbitals in the RAS3 instead of the RAS1 space, required for systems that lack inversion symmetry, further increases the CI expansion from 36 848 to 122 348. Increasing the size of that basis set mainly affects the cost of the RASPT2 calculation. Calculations with the smaller VDZP and the mixed VD(T)ZP basis set are thus dominated by the RASSCF step. The relative savings when using a smaller basis set are thus more important in systems with a larger number of atoms or small active spaces. When it comes to the algorithm for the RASPT2 calculations, neglecting core correlation reduces the cost of the RASPT2 step significantly, from 90 to 26 hrs, and state specific calculations takes even less time (15 hrs), without significant loss in accuracy. These results shows that it is possible to tune computational cost and accuracy, especially important for simulations of L-edge XAS spectra of larger molecular systems.

IV. DISCUSSION

The results show that the core RAS method can predict L-edge XAS spectra with high accuracy, at a level comparable to that of the semiempirical CTM model. While the semiempirical CTM model describes donation and backdonation through additional charge-transfer configurations, the core RAS model includes these effects by increasing the number of orbitals in the active space. An important difference is that adding configurations to the CTM model increases the number of model parameters, while the core RAS calculations are essentially parameter free independent of the type of electronic structure that is described.

The two methods are most directly comparable for the \(\text{Fe}^{3+}\) ion that lack any charge-transfer parameters. However, there are still differences in the description of electron correlation and spin-orbit coupling. In the multiplet model electron-electron repulsion is treated at the HF level, with a parameterized reduction of the integrals by 80% to mimic electron correlation. The core RAS model improves on this description by calculating the 3d-3d and 2p-3d interactions through a full CI, while correlation with other electrons are included through second-order perturbation theory.

The core RAS method evaluates the spin-orbit coupling strengths on the correlated spin-free states through a perturbation approach, and subsequent diagonalization of the state interaction matrix gives SOC states that are linear combinations of spin-free states. This approach, corresponding to molecular L-S coupling, is expected to work better for weak perturbations like 3d SOC than for the strong 2p SOC coupling. The multiplet model improves on that description as it diagonalizes a state interaction matrix that includes both electron repulsion and spin-orbit coupling. In the core RAS calculations the low-energy \(J' = \frac{1}{2}\) states in the \(L_2\) edge mix strongly with high-energy \(J' = \frac{3}{2}\) states, and this coupling could be the reason for the larger deviations between the methods for energies above 715 eV, including the additional peak in the high-spin systems that is present only in the core RAS calculations, see Fig. 3a-b.

With performance comparable to that of the multiplet model, but with essentially no adjustable parameters and without principal symmetry restrictions, the core RAS approach is an attractive alternative for any small and medium-size systems. It can be applied to systems with complicated electronic structures, e.g., orbitally degenerate ground states, and with proper design of the active space both effects of ligand donor bonding and backdonation can be accurately described. As all possible excitations are included, the method can reproduce all spectral features, also those arising from multiple excitations, e.g., shake-up and shake-down transitions. The
major drawback of the core RAS method is the relatively high computational cost. While it gives better results for [FeCl$_6$]$^{3-}$ than the DFT/ROCIS method, the latter can be applied to much larger systems. The core RAS method is thus best suited for spectra that are dominated by local effects. The current calculations have been performed on relatively small metal clusters without taking counter ions or adjacent metal ions into account. One possible improvement is to include a better description of the environmental effects. However, considering the good agreement with experimental spectra, it is reasonable to assume that effects beyond the first coordination shell are limited for the currently tested systems.

One of the appealing features of the core RAS approach is that the L-edge XAS spectrum can be analyzed in terms of contributions from chemically intuitive molecular orbitals. A new scheme was therefore developed that takes into account the changes in natural occupation number of the orbitals in the active space. This analysis highlights the importance of correlation between metal and ligand orbitals, but can also be used to identify the nature of an unknown peak, e.g., the [FeCl$_6$]$^{3-}$ shake-up transition. However, this analysis does not take into account changes in the shape of the orbitals during the RASSCF optimization, e.g., when the [FeCl$_6$]$^{3-}$ metal-centered $t_{2g}$ orbitals are replaced by Cl 4p orbitals. Fortunately, orbital rotation mainly occurs for weakly correlating orbitals that have small changes in occupation number. Another important point is that many metal-ligand bonds will be described as too ionic in RASSCF and although the RASPT2 step corrects the energies it does not change the reference wavefunction. Care must therefore be taken when trying to extract quantitative metal-ligand covalencies directly from the RASSCF orbitals.

When applying the core RAS method to medium-size systems it is important to choose combinations of active space, number of states, basis set, and computational algorithms that give accurate spectra while still limiting the computational cost. The most important consideration is the size of the active space. Systematic investigations of transition metal complexes show that large active spaces are required to calculate relative energies of different states, with one important factor being the double-shell effect. In [FeCl$_6$]$^{3-}$ spectrum trying to include a set of empty $t_{2g}$ orbitals did not have any major effects on the calculated [FeCl$_6$]$^{3-}$ spectrum, see Fig. 7. The main reason is that the target accuracy for calculations of L-edge XAS spectra is relatively low as they span a wide energy range, more than 30 eV. The same observation is valid also for the size of the basis set, where the basis set effects are relatively small and for most systems a triple or even double-$\zeta$ basis should be sufficient. The results are also relatively stable with respect to choices of parameters in the computational algorithms, e.g., IPEA and imaginary shifts. However, it should be noted that the low sensitivity is partly due to the use of complexes that lack low-lying excited states and therefore have well-defined ground states.

The use of a RAS3 space for the valence orbitals gives considerable flexibility in the quality of the CI calculation and can lead to significant time savings. Allowing the excitation of a single electron into the RAS3 space captures the main 2p excitation, while exciting two electrons also makes it possible to describe shake-up (and shake-down) transitions, as shown for [FeCl$_6$]$^{3-}$ in Fig. 7. However, in the RAS calculations excitations are also used to describe electron correlation within the active space. Correlation requires at least double-excitations in the valence space, and for [Fe(CN)$_6$]$^{3-}$ allowing three excitations, including the core excitation, gives a spectrum similar to the full CI while the calculation with only two excitations did not, see Fig. 11. In this respect the RASPT2 step does not help as it only adds correlation between different orbital spaces, and do not recover missing correlation within the active space.

In addition to the number of excitations in the RAS space, the spectral simulation is also sensitive to the number of final states, most evident from the large changes in the shape of the $L_2$ edge, see Figures 8 and 12. However, unlike the active space, where it is clear that a larger space leads to better results, it is less straightforward to determine the right number of final states. From the ferrocyanide simulations it is clear that a large number of states have to be included in the RASSCF calculation to properly describe the important $\pi^*$ orbitals. Exactly how many states that are required depend on the ordering of high-energy states of different character, and can be strongly affected by both active space and choice of basis set. As an example, fewer states are required with the $e_g$ and $\pi^*$ orbitals in RAS3 because of the reduction in the total number of states. The spectrum may therefore appear extremely sensitive to basis set or active space selection, but this sensitivity would disappear with a higher number of states. At the same time, including too many states may lead to suboptimal active spaces where orbitals with strong correlation are removed in favor of empty ligand orbitals that neither correlate with the metal orbitals nor have any significant transition intensity, e.g., the 4p Cl orbitals in ferric chloride. If there is an optimum number of states, this number would then depend on both symmetry and spin multiplicity. To make it simple, the current calculations have been performed with the same number of states for all symmetry-spin combinations, but this could possibly be improved in future calculations.

The spectral simulations in this study have been performed with the 2p orbitals in the RASI space allowing maximum one hole. This is the preferred approach for centrosymmetric systems as all valence excitations keep “gerade” symmetry and only 2p excitations leads to states with “ungerade” symmetry. In absence of inversion symmetry the large number of valence excited states with lower energy than the core hole excited states must first be removed. Another possibility is to put the 2p orbitals in the RAS3 space and allowing a maximum of
5 electrons. One drawback of the core RAS3 approach is that 3-4 times more determinants have to be calculated compared to the core RAS1 approach. Moreover, the RAS3 space can no longer be used to tune the number of valence excitations. Independent of which active space the 2p orbitals are placed in, the current procedure requires that the 2p orbitals are excluded from the RASSCF orbital optimization. The effect of neglecting core relaxation has not been evaluated, but as the sudden approximation performs well for many X-ray processes it is believed to be relatively small, at least when it comes to the relative energy of different final states.

As the core RAS method accurately describes all kind of final states reached through core excitations, it can potentially be applied to a large number of different X-ray experiments. The direct connection between the X-ray spectrum and a molecular orbital picture makes it attractive when analyzing the electronic structures of different compounds, and the method can be used to extract the electronic structure of a complex without any prior assumptions. One potential application is for heme systems that are primarily studied using the intense porphyrin $\pi \rightarrow \pi^*$ transitions in UV/Vis region, but where insights into the electronic structure of the iron is complicated as the intense ligand features obscure the Fe center. Another possibility is to analyze the electronic structure of transition-metal catalysts in photovoltaic systems, where the chromophores obscure many UV/Vis probes of the catalyst itself. The explicit calculation of the excited states also makes it possible to follow the nuclear dynamics of core excited states created in ultra-fast X-ray experiments.

V. CONCLUSIONS

Multiconfigurational wavefunction (RASSCF/RASPT2) theory has great potential for simulations of X-ray processes as it includes a high-level description of electron-electron correlation together with a perturbation treatment of spin-orbit coupling. The core RAS method can be applied to any medium-sized system without any formal symmetry constraints. Among the advantages is that it can handle orbitally degenerate ground states, describes metal-ligand charge transfer, and includes all possible electron excitations, at least within the active orbitals. For the calculation of L-edge XAS spectra of a series of ferric systems, the core RAS method performs at a level comparable to that of the commonly used semiempirical CTM multiplet model, but without the use of any system-dependent parameters.

The flexibility of the method makes it possible to tune the balance between accuracy and computational cost. Compared to valence excitations, the size of the valence active space can be reduced as the required accuracy is typically much lower. The number of valence excitations can be limited through the use of a RAS3 space, although it is recommended to allow at least two valence excitations, in addition to the core excitation, to get results comparable to a full CI in the active space. The RASPT2 calculations can be effectively performed as state-specific calculations performed on individual processors without any major difference compared to R multi-state RASPT2 calculations. A relatively small basis set, e.g., double or triple-$\zeta$, is also sufficient for most systems.

As the results are very accurate, they can be used to fingerprint the electronic structure of a system without any prior assumptions. The analysis of the X-ray spectra in terms of molecular orbital contributions enables a direct connection between a spectrum and the electronic structure features. The core RAS method can therefore be of great use in the interpretation of a wide variety of different X-ray experiments.

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54See supplementalmaterialathttp://dx.doi.org/...forMultipletparameters,shiftofenergiesoftheL-edgespectrum,schematicsofsocenelevelsmolecularorbitalsandvariouscore-RAS

calculatedL-edgespectraofferricyanideandferricchloride.


$[\text{FeCl}_6]^{3-}$

$6\text{Cl}^-$

$\pi^* (t_{2g})$

$t_{2g}'$

$4\text{p}$

$\pi^*(t_{2g})$

$\text{t}_{1u}$

$\pi^* (t_{1g} + t_{1u} + e_{g})$

$\sigma (a_{1g} + t_{1u} + e_{g})$

$\pi^* (t_{1g} + t_{2g} + t_{1u} + t_{2u})$

$\sigma (a_{1g} + t_{1u} + e_{g})$

$\text{Fe in field}$

$4\text{d}$

$\text{t}_{1u}$

$2\text{p}$

$\text{e}_{g}$

$\text{t}_{2g}$

$3\text{p}$

$\sigma (e_{g})$

$\pi(t_{2g})$

$\pi(t_{2g})$

$\sigma (e_{g})$

$\pi(t_{2g})$

$\sigma (e_{g})$

$\pi(t_{2g})$
The graph shows the intensity of different transitions in the incident energy range of 700 to 735 eV. The labels on the right axis indicate the types of transitions: Total, \( t'_{2g} \), \( e_g \), \( t_{2g} \), \( \sigma \), and \( 2p \). Peaks and valleys in the graph correspond to changes in intensity for each type of transition.