Accurate X-Ray Spectral Predictions: An Advanced Self-Consistent-Field Approach
Inspired by Many-Body Perturbation Theory

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Constrained-occupancy delta-self-consistent-field (∆SCF) methods and many-body perturbation
theories (MBPT) are two strategies for obtaining electronic excitations from first-principles. Using
the two distinct approaches, we study the O 1s core excitations that have become increasingly
important for characterizing transition-metal oxides and understanding strong electronic correlation.
The ∆SCF approach, in its current single-particle form, systematically underestimates the pre-
edge intensity for chosen oxides, despite its success in weakly correlated systems. By contrast, the
Bethe-Salpeter equation within MBPT predicts much better lineshapes. This motivates one to
reexamine the many-electron dynamics of X-ray excitations. We find that the single-particle ∆SCF
approach can be rectified by explicitly calculating many-electron transition amplitudes, producing
X-ray spectra in excellent agreement with experiments. This study paves the way to accurately
predict X-ray near-edge spectral fingerprints for physics and materials science beyond the Bethe-
Salpeter equation.

X-ray absorption spectroscopy (XAS) is a powerful
colorization technique in physics, chemistry, and ma-
terials science, owing to its element specificity and orbital
selectivity. With the help of density-functional theory
(DFT), the interpretation of XAS is greatly facilitated
by simulating spectral fingerprints for hypothetical
structures from first-principles. Satisfactory X-ray absorption
spectra have been simulated across a wide range of sys-
tems from small molecules [1, 2] to condensed matter
[3–9] and even complex interfaces [10].

In this letter, we introduce a novel first-principles
theory for simulating X-ray absorption spectra extend-
ing the constrained-occupancy delta-self-consistent-field
(∆SCF) method [6, 7, 9]. The ∆SCF method assumes a
fixed core-hole potential and employs only single-particle
orbitals for finding transition amplitudes. It is generally
thought this theory cannot capture certain many-electron
effects as incorporated in many-body perturbation the-
ories, such as the Bethe-Salpeter Equation (BSE) [11–14].
However, if the one-body transition amplitude in the
∆SCF method is recast into a many-body formal-
isim, we show that the method can in fact capture many-
electron effects in X-ray excitations. Furthermore, we
outline how the excitation spectrum can be enriched by
considering multiple electron-hole (e-h) excitations, per-
mitting extensions beyond the BSE, on the level of the
Mahan-Nozières-De Dominicis (MND) theory [15, 16].

For our examples, we choose the O K edges (1s → np
transitions) of transition-metal oxides (TMOs) to illus-
trate the utility of the many-body ∆SCF method. The
study of the O K edges for TMOs is fueled by the quest
for next-generation energy materials, for recharge-
able battery cathodes [17–20], fuel cells [21, 22], water-
splitting catalysts [23–25], and transparent conductive
layers [26]. Many of these materials are TMOs with com-
plex chemical properties due to their d orbitals. Addi-
tionally, XAS has been employed to understand electron
correlations inherent in TMOs, such as metal-insulator
transitions [27–29], high-Tc superconductivity [30, 31],
and emergent phenomena at perovskite interfaces [32].
XAS can also serve as powerful guides to advance theories
for correlated electron systems, including the DFT+U
method [33], dynamical mean-field theory [34], and ex-
act diagonalization approaches [35, 36]. In almost all of
the aforementioned examples [17, 19–21, 23–28, 30–33, 35, 36], there are measurements at the O K edge.
Despite its utility, very few studies have simulated this
absorption edge for TMOs from first-principles.

Five TMOs are selected for benchmarking: the rutile
TiO2, VO2, and CrO2 as well as the corundum α-Fe2O3
and the perovskite SrTiO3. They vary greatly in struc-
ture, band gap, or magnetism. The rutile VO2 (> 340K)
and CrO2 are metallic, whereas TiO2 and SrTiO3 are insu-
ling. CrO2 is ferromagnetic (FM) while Fe2O3 is antiferromagnetic (AFM). The O K edges from previ-
ous experiments [23, 27, 37–39] are shown in Fig. 1 (a).
These spectra are angularly averaged except for CrO2,
where the polarization is perpendicular to the magneti-
zation axis [38]. The TM-3d-O-2p hybridization mani-
fests as sharp double peaks around 530 eV, which result
from the t2g-e_g splitting in the octahedral field. The in-
tensity ratio of the two peaks often serves as a diagnostic
tool. Understanding gained through these simple TM
compounds will find great utility in interpreting XAS for
more complex contexts, e.g., liquids, interfaces, heteroge-

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The text continues with detailed discussions about the X-ray absorption spectra of various TMOs, their characteristic features, and the implications of these studies for understanding electron correlations in transition-metal oxides.
The near-edge lineshape.

The X-ray absorbance $\sigma(\omega)$ is obtained from Fermi’s golden rule

$$
\sigma(\omega) \propto \omega \sum_f \langle \Psi_f | \epsilon \cdot R | \Psi_i \rangle^2 \delta(E_f - E_i - \hbar \omega)
$$

where $\epsilon$ and $R$ are the photon polarization and many-body position operator respectively. $|\Psi_i\rangle$ is the initial (ground) state and $|\Psi_f\rangle$ is any excited eigenstate of the system, while $E_i$ and $E_f$ are their energies. Predicting X-ray absorption requires: (a) an accurate prediction of the excitation energies $E_f$ and (b) a reliable approximation to the amplitude $\langle \Psi_f | \epsilon \cdot R | \Psi_i \rangle$. We first contrast the single-particle $\Delta$SCF core-hole approach and the BSE using the five TMOs, and identify a systematic failure in the current $\Delta$SCF method. We argue that the failure is due to the omission of many-electron response to the core hole, which motivates us to develop an advanced $\Delta$SCF approach by using many-electron wavefunctions instead of single-particle orbitals.

$\Delta$SCF and BSE Approaches In the $\Delta$SCF core-hole approach the core-excited atom is treated as a single impurity with one electron removed from the excited core level. Depending on whether or not the X-ray photoelectron is included, it is termed as an excited-electron and core-hole (XCH) or full core-hole (FCH) calculation [6, 7, 9]. One places the core-excited atom in a sufficiently large supercell and then finds the equilibrated electron density using constrained-occupancy DFT. This equilibrated state, with the presence of a core hole, is referred to as the final state [13], and that of the pristine system as the initial state. The working approximation is to use single Kohn-Sham orbitals for finding the transition amplitude

$$
\langle \Psi_f | \epsilon \cdot R | \Psi_i \rangle \approx S(\tilde{\psi}_f | \epsilon \cdot \mathbf{r} | \psi_h)
$$

where $\tilde{\psi}_f$’s are the unoccupied orbitals in the final state (with tilde) and $\psi_h$ is the core orbital in the initial state. $S$ is a many-body overlap that reflects the excited-state response of the remaining electrons other than the photoexcited one, and is normally treated as a constant in the sudden approximation [40]. The excitation spectrum $E_f - E_i$ is approximated based on differences in DFT orbital energies, $\tilde{\varepsilon}_f - \varepsilon_h$, with some further realignment reflecting the local atomic context and the experimental energy scale [41].

To account for strong electron correlations in TMOs, the DFT+U theory [33] is employed where the DFT energy is captured by the Perdew-Burke-Ernzerhof (PBE) functional, and the on-site Coulomb potential $U$ are from Ref. [42]. We interpret the DFT+U orbital energies as quasiparticle (QP) energies and perform FCH rather than XCH calculations so as not to favor any particular occupation. More numerical details can be found in the Supplemental Material [56].

Strikingly, the FCH approach systematically underestimates the intensity of the near-edge peak associated with the $t_{2g}$ manifold for all selected TMOs (Fig. 1 (b)). The $t_{2g}$ peak at $\sim 529.2$ eV of CrO$_2$ [38] suffers from the most severe underestimation. It becomes a weak, broad feature in the FCH simulation as compared to the strong, sharp peak in experiment. The $t_{2g}$-$e_g$ peak intensity ratios of VO$_2$ and Fe$_2$O$_3$ are also too low - both are predicted as 0.7, compared with 1.7 and 1.0 as measured, respectively.

In the BSE formalism [12, 43, 44], the final state is assumed to be a superposition of effective e-h pairs and the matrix elements are calculated as

$$
\langle \Psi_f | \epsilon \cdot R | \Psi_i \rangle = \sum_c A_{c}^{f} \langle \psi_c | \epsilon \cdot \mathbf{r} | \psi_h \rangle
$$

where $\psi_c$’s are the initial-state orbitals and $c$ iterates over empty orbitals only. The exciton amplitude $A_c^f$ and energy $E_f$ can be solved from the BSE as in Ref. [11–14]. The core-level BSE calculations in this work employ the OCEAN code [14, 45].

As is shown in Fig. 1 (c), the BSE substantially improves on the O K-edge line shapes. The $t_{2g}$ peak intensity is retrieved for each investigated TMO, particularly for CrO$_2$. The simulated $t_{2g}$-$e_g$ intensity ratios are
almost as measured for TiO$_2$, α-Fe$_2$O$_3$, and SrTiO$_3$ (below 537 eV). These BSE spectra are also in better agreement with experiments than the previous results using the initial-state rule [46, 47].

In fact, the core-hole effects predicted by the ∆SCF method in these oxides are counterintuitive. Typically, excitonic effects tend to sharpen the absorption edge due to e·h attraction [5, 11, 12, 43]. In Fig. 2, we show the core-hole effects from ∆SCF by comparing the initial- and final-state spectra. The core-hole attraction does redshift the spectra by over 1 eV in both the TM 3d pre-edge and the 4p [48] region (near 544 eV). However, the FCH core-hole effect substantially reduces the $t_{2g}$ peak intensity. Similarly underestimated pre-peak intensity was encountered before [49–51] but no satisfactory explanation has been provided to date.

Within the independent-KS-orbital approximation, the ground state $|\Psi_i\rangle$ can be constructed as a Slater determinant built from the $N$ lowest occupied valence orbitals of the pristine supercell and the core orbital of the impurity atom. Here, $N$ is the number of valence electrons in the supercell. Similarly, the final state $|\Psi_f\rangle$ can be constructed as a Slater determinant of arbitrary $N+1$ KS orbitals in the final-state picture. To enumerate the many-electron final states, we generalize the final state index $f$ to represent any excited configuration of these $N+1$ electrons: $f$ now represents a unique $(N+1)$-tuple, $f=(f_1,f_2,\ldots,f_{N+1})$, where $f_i$’s label distinct final-state orbitals that the $N+1$ electrons can occupy.

The single-particle orbitals necessary for constructing $|\Psi_i\rangle$ and $|\Psi_f\rangle$ can be readily obtained from respective ∆SCF calculations performed over the supercell. However, $|\Psi_i\rangle$ and $|\Psi_f\rangle$ are represented with the initial- and final-state orbital basis respectively. To eventually access $\langle\Psi_f|e\cdot R|\Psi_i\rangle$, we perform the orbital transformation from the initial to final state: $|\psi_i\rangle = \sum_j \xi_{ij} |\psi_j\rangle$, in which $\psi_i$ and $\psi_j$ are the $i$th final-state and $j$th initial-state orbitals in the supercell, respectively. $\xi_{ij}$ is the transformation coefficient. The resulting matrix element has the same form as in Eq. (3) but the amplitude of a given final state $f$ becomes a single determinant of the transformation coefficients [56]

$$A_f^j = \det \begin{bmatrix} \xi_{f_1,1} & \xi_{f_1,2} & \cdots & \xi_{f_1,N} & \xi_{f_1,c} \\ \xi_{f_2,1} & \xi_{f_2,2} & \cdots & \xi_{f_2,N} & \xi_{f_2,c} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \xi_{f_{N+1},1} & \xi_{f_{N+1},2} & \cdots & \xi_{f_{N+1},N} & \xi_{f_{N+1},c} \end{bmatrix}$$  \hfill (4)

Within the independent-KS-orbital approximation, the energy of $|\Psi_f\rangle$ can be found by summing up the energy of
energies of the occupied KS orbitals in the final state

\[ E_f = \sum_{j=1}^{N+1} \tilde{\varepsilon}_{f_j} \]  
(5)

The energy difference \( E_f - E_i \) for producing spectra may employ a similar alignment scheme as in the single-body approach, since the initial (ground)-state energy \( E_i \) is fixed. In the following discussion, it is more meaningful to define the relative energy \( \Omega_f = E_f - E_{\text{th}} \), where the threshold energy, \( E_{\text{th}} = \sum_{j=1}^{N+1} \tilde{\varepsilon}_j \), corresponds to the lowest-energy final-state configuration \((1, 2, ..., N + 1)\).

Determinant expressions similar to Eq. (4) were also obtained in previous work [52–54] but they are rarely applied in a solid-state context from first-principles. Thus it is of great interest to examine whether the many-electron \( \Delta SCF \) formalism in Eq. (4) and (5) can reproduce the correct lineshapes for the investigated TMOs.

Evaluating the many-electron \( A_f^c \) seems formidable at first glance because a solid contains many electrons, which leads to a combinatorially huge number of final states. To facilitate the calculation, we regroup the final-state configurations according to the number of e-h pairs excited. For example, we denote a single configuration with one core-excited e-h pair as \( f^{(1)} = (1, 2, \cdots, N, f_{N+1}) \), which is used in producing the one-body \( \Delta SCF \) XAS and \( f_{N+1} \) is the single unoccupied orbital in the final state. Based on this configuration, we can define a double configuration with one more valence e-h pairs as \( f^{(2)} = (1, \cdots, i-1, i+1, \cdots, N, f_N; f_{N+1}) \), where \( f_{N+1} > f_N > N \), and so forth (Fig. 3).

Despite a large number of excitation configurations, not all of them contribute equally to the near-edge XAS, particularly near the absorption onset. First, for an insulator, \( \Omega_f \) will increase proportionally with the number of e-h pairs excited across the band gap \( (E_g) \): \( \Omega_f \geq (n - 1)E_g \). This significantly reduces the number of necessary final-states for producing the first few eVs of XAS for an insulator. Second, the many-electron transition amplitude may decrease rapidly with increasing number of e-h pairs excited, as we will show next.

We reexamine two extreme cases: the insulating \( \text{TiO}_2 \) and the metallic \( \text{CrO}_2 \). Fig. 4 shows the XAS calculated from the many-body formalism as in Eq. (4) and (5). The orbitals used for calculating the transformation coefficients \( \xi_{ij} \) in \( A_f^c \) are obtained from the same set of ground-state and FCH calculations [56] as previously described. For simplicity, only the states at the \( \Gamma \)-point of the supercell Brillouin zone are used for producing the XAS. Remarkably, the simulated XAS lineshapes (Fig 4) with the many-electron formalism are in excellent agreement with experiments. In particular for \( \text{CrO}_2 \), the edge sharpness is completely retrieved (Fig 4 (b)) despite the disappearance of the first peak in a single-electron theory.

We find calculated XAS for \( \text{TiO}_2 \) converges at the order of \( f^{(1)} \). As expected, the contributions from \( f^{(2)} \) (Fig 4 (c)) appear at higher energies due to the sizable band gap, and are much weaker due to reduced wavefunction overlap. However, it is more challenging to achieve numerical convergence in the metallic \( \text{CrO}_2 \). While the first peak is retrieved mainly from \( f^{(1)} \) excitations, the correct peak-intensity ratio can only be reproduced when the next-order, \( f^{(2)} \), is taken into account, which substantially increases the intensity of the absorption feature \( \sim 4 \) eV above onset (Fig 4 (b)). Meanwhile, we find \( f^{(3)} \) can be neglected up to the first 8 eV (Fig 4 (d)).

Both the BSE (Fig. 1) and the many-electron formalism (Fig 4) yield very similar spectra for \( \text{TiO}_2 \), but the many-electron formalism produces a spectrum for \( \text{CrO}_2 \) in closer agreement with experiment than the BSE. The experimental peak-intensity ratio is 1.7; 1.6 from the many-electron formalism; but only 1.3 from the BSE. We attribute this improvement the explicit inclusion of many-electron response to the core-hole potential via the
transition amplitude $A^{f}_{n}$ [Eq. (4)]. Since the Slater determinants are exact solutions to the independent-electron model, the many-electron formalism has taken into account all possible many-electron processes in the MND theory. In addition to the e-h ladder diagrams in the BSE, the MND theory also considers non-ladder diagrams, such as diagrams with crossing Coulomb lines and bubble diagrams that account for the orthogonality catastrophe [15, 16, 52]. Instead of adopting a diagrammatic approach, the many-electron formalism considers these processes via incorporating response of each electron to the core hole in the determinant amplitude $A^{f}_{n}$. Therefore, the many-electron formalism goes beyond the two-particle correlation in the BSE. For insulators like TiO$_2$, the many-electron formalism produces results very similar to the BSE because the non-ladder diagrams are not important near the absorption edge. However, this is not the case for CrO$_2$ since multiple e-h-pair production is more likely in a metal and the non-ladder diagrams become significant for determining the near-edge lineshape. The significance of the multiple electron response can also be appreciated from the fact that the CrO$_2$ spectrum converges at a higher-order $f^{(n)}$.

At last, we briefly discuss the validity of the independent-KS-orbital approximation. On the $f^{(1)}$ level, there is a one-to-one correspondence between the many-electron configurations and the empty single-particle final-state orbitals, and the latter are typically good approximations to QP band topology and wavefunctions [43, 55]. This approximation may break down if there are one or more valence e-h pairs. For example, valence e-h pairs in the $f^{(2)}$ configurations of an insulator may hybridize to form bound excitons; the two excited electrons in the $f^{(2)}$ configurations may interact through strong on-site Coulomb repulsion. In the case of CrO$_2$, however, the strong metallic screening can largely reduce e-h binding energy, maintaining the independent-KS-orbital approximation. As for strongly correlated effects, it will be worthwhile to further consider embedded models based on the current determinant formalism.

Conclusions We have shown that the BSE and a newly developed many-electron ∆SCF approach are highly predictive for O K-edge fingerprints of TMOs. The systematic underestimation of the peak-intensity ratio within the original one-body ∆SCF approach is attributed to the absence of many-electron response in this formalism. We have demonstrated how to rectify these shortcomings by (1) extending the wavefunctions in the original ∆SCF to a many-electron form (2) calculating the determinant form of the transition amplitude. This many-electron formalism is transferable and not at all peculiar to TMOs. We leave the discussion of shakeup effects, improvement of efficiency, and other examples to near-future work.

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[56] See Supplemental Material [url], which includes Refs. [57–58].
