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Lock-in Amplifiers up to 600 MHz
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ABSTRACT

Ab initio calculations of resonant inelastic x-ray scattering (RIXS) often rely on damped response theory, which prevents the divergence of response solutions in the resonant regime. Within the damped response theory formalism, RIXS moments are expressed as the sum over all electronic states of the system [sum-over-states (SOS) expressions]. By invoking resonance arguments, this expression can be reduced to a few terms, an approximation commonly exploited for the interpretation of computed cross sections. We present an alternative approach: a rigorous formalism for deriving a simple molecular orbital picture of the RIXS process from many-body calculations using the damped response theory. In practical implementations, the SOS expressions of RIXS moments are recast in terms of matrix elements between the zero-order wave functions and first-order frequency-dependent response wave functions of the initial and final states such that the RIXS moments can be evaluated using complex response one-particle transition density matrices (1PTDMs). Visualization of these 1PTDMs connects the RIXS process with the changes in electronic density. We demonstrate that the real and imaginary components of the response 1PTDMs can be interpreted as contributions of the undamped off-resonance and damped near-resonance SOS terms, respectively. By analyzing these 1PTDMs in terms of natural transition orbitals, we derive a rigorous, black-box mapping of the RIXS process into a molecular orbital picture. We illustrate the utility of the new tool by analyzing RIXS transitions in the OH radical, benzene, para-nitroaniline, and 4-amino-4′-nitrostilbene. These examples highlight the significance of both the near-resonance and off-resonance channels.

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I. INTRODUCTION

Resonant inelastic x-ray scattering (RIXS) is a two-photon process, wherein a resonant x-ray photon is absorbed and another x-ray photon of lower energy is emitted; thus, it can be described as the resonant Raman scattering of an x-ray photon. RIXS is a coherent process, which involves photoexcitation of a core electron to a virtual core-excited state and simultaneous filling of this core hole by radiative decay of a valence electron, as shown in Fig. 1. Thus, the overall transition is from the ground state to a valence excited state, and the difference in the photon energies equals the energy gap between the initial and the final states of the system.
and to detect transient species in ultrafast reactions in complex environments.\cite{21}

Theoretical modeling of RIXS spectra is critical for connecting the measured RIXS spectra with the electronic structure of the molecule. Ultimately, the mechanistic interpretation of a spectrum hinges on our ability to describe the underlying process in terms of transitions between molecular orbitals.

The orbital picture of one-photon UV-visible (UV-vis), XAS, and XES transitions can be extracted from many-body wave functions by using reduced quantities, such as one-particle transition density matrices (1PTDMs) and natural transition orbitals (NTOs).\cite{18,19,20} 1PTDMs contain essential information about electronic transitions needed to compute the observables (e.g., cross sections). NTOs, computed by the singular value decomposition (SVD) of 1PTDMs, provide the most compact representation of the transition in terms of the hole and particle states. In contrast to wave-function amplitudes, NTOs are invariant with respect to all allowed orbital rotations, which makes them insensitive to the basis-set choice. Since 1PTDMs and NTOs are directly mapped to the experimental observables, they provide a rigorous and robust framework for wave-function analysis.

The concept of NTOs has been generalized to two-photon absorption (2PA) transitions, enabling the analysis of the corresponding response 1PTDMs and characteristic 2PA virtual states;\cite{21} to non-Hermitian quantum mechanics, enabling the analysis of the complex-valued 1PTDMs and transitions involving states in the continuum;\cite{22} and to spinless 1PTDMs, enabling the analysis of tensorial properties (spin–orbit couplings) and spin-forbidden transitions.\cite{23} Here, we extend the concept of NTOs to RIXS transition moments.

The main challenge in interpreting the RIXS process in terms of molecular orbitals stems from its nonlinear (two-photon) nature. Because of it, the scattering moments are given by cumbersome sum-over-states (SOS) expressions\cite{24–26} and not by matrix elements between the initial and final states, as in the case of UV-vis, XAS, and XES transitions. This dependence on all electronic states of the system makes the analysis of RIXS moments more difficult than the analysis of one-photon moments (matrix elements of the dipole operator between the initial and final states). Furthermore, the RIXS moments are complex-valued and tensors of rank two (3 × 3 matrices), in contrast to the one-dimensional one-photon moments, which are real-valued vectors with components along the three Cartesian coordinates.

Because of its resonant nature, the qualitative picture of the RIXS transition is traditionally derived using approximate few-state models—in particular, a three-state model—involving few near-resonant core-excited states along with the initial and final states. In a few-state model, the orbitals involved in the transitions from the initial state to different intermediate states and from these intermediate states to the final state are computed and stitched together to construct the orbital picture of the RIXS process. For example, in the three-state model, the virtual state (see Fig. 1) of the two-photon RIXS process corresponds to the core-excited state for which the XAS peak is resonant with the incoming photon’s energy. Although being physically justified, such an approach involves arbitrariness and is prone to potential loss of accuracy, because it is not always easy to identify the important intermediate states that need to be included in these few-state models. In this approach, the orbital character of the virtual state of the RIXS process is determined by the (somewhat arbitrary) choice of the intermediate states picked in the few-state model. The loss of accuracy can occur when off-resonance channels make non-negligible contributions to the RIXS cross sections.

Here, we overcome these challenges using a novel approach of deriving the mechanistic details of the RIXS transitions by means of NTOs computed directly from the complex-valued damped response 1PTDMs that enter the expressions of RIXS moments. This leads to a rigorous and black-box procedure of mapping the computed scattering moments into molecular orbitals. In contrast to traditional approaches, our scheme does not invoke arbitrary truncation of the SOS expressions and is orbital invariant. We discuss the meaning of the real and the imaginary components of these 1PTDMs and the corresponding NTOs by analyzing RIXS transitions in the OH radical, benzene, para-nitroaniline (pNA), and 4-amino-4′-nitrostilbene (4A4NS). The pNA and 4A4NS examples illustrate the importance of off-resonance RIXS channels and highlight the advantages of fully analytic calculation and analysis of the RIXS moments over approximate treatments by few-state models. We also illustrate how a quantitative metric for the extent of delocalization of electronic density during the RIXS transition can be computed using these response 1PTDMs. While this approach builds upon our prior work on 2PA transitions,\cite{27} the novelty lies in the interpretation of complex-valued RIXS 1PTDMs (and their NTOs) instead of the real-valued 2PA 1PTDMs.

II. THEORY

The RIXS scattering moments are given by the Kramers–Heisenberg–Dirac formula as SOS expressions.\cite{28,29}
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The real components of these terms are smaller than the imaginary contribution of the SOS terms that have $|\Omega| > 0$. The poles due to resonances into the complex plane. The impact of this imaginary phenomenological (damping) parameter $\epsilon$ brings the poles into resonance and reduces the imaginary part of the RIXS moment; however, the error introduced due to truncation is difficult to evaluate a priori. Nevertheless, many studies employ such truncations for computing the RIXS moments and other nonlinear properties. An alternative, more rigorous strategy involves recasting the SOS expressions into a closed form using damped response theory. By doing so, one circumvents the need to compute the wave functions and energies of all electronic states. Instead, only a handful of response amplitudes need to be computed.

Most theoretical formulations for calculating RIXS moments use empirical non-zero inverse lifetimes for all states, which are finite ($\epsilon_k > 0$). In contrast, cluster methods, this is not the case.21–23 $\epsilon_n$ is the inverse lifetime parameter for state $n$. If the lifetimes of all states are infinite ($\epsilon_n = 0$), in the case of RIXS, at least for one state $k$, the denominator in the SOS term is zero ($\Omega_{\rm bg} - \omega_1 = 0$). In other words, the RIXS moments have first-order poles at $\Omega_{\rm bg}$. In practice, this means that attempts to calculate RIXS moments assuming infinite lifetimes of excited states encounter divergent solutions.

Most theoretical formulations for calculating RIXS moments use empirical non-zero inverse lifetimes for all states, which are assumed to have the same nonzero value $\epsilon$. The introduction of this imaginary phenomenological (damping) parameter $\epsilon$ brings the poles due to resonances into the complex plane. The impact of introducing $\epsilon$ on individual SOS terms depends on whether $|\Omega_{\rm bg} - \omega_1| < \epsilon$ or $|\Omega_{\rm bg} - \omega_1| > \epsilon$, as shown in Fig. 2. The contribution of the SOS terms that have $|\Omega_{\rm bg} - \omega_1| < \epsilon$ (nearly resonant SOS terms) is dominated by their imaginary components. The real components of these terms are smaller than the imaginary components. In particular, for the SOS terms with $|\Omega_{\rm bg} - \omega_1| = 0$, the real components are zero and the imaginary components equal $\langle \Psi_n | \mu^I | \Psi_{\mu^I} \rangle = 0$ (or $\langle \Psi_n | \mu^I | \Psi_{\mu^I} \rangle = 0$), thus, the absolute contribution of each of these SOS terms is effectively damped from infinity to a finite value by virtue of $\epsilon$. On the other hand, the real components are larger than the imaginary ones for the SOS terms for which $|\Omega_{\rm bg} - \omega_1| > \epsilon$. In short, the damping puts the near-resonance and off-resonance contributions in the imaginary and real components of the RIXS moments, respectively.

Computing the full set of electronic states for calculating the RIXS moments via Eqs. (1) and (2) is obviously impractical. Only, an approximated (truncated) SOS can provide a qualitatively correct value of the RIXS moment; however, the error introduced due to truncation is difficult to evaluate a priori. Nevertheless, many studies employ such truncations for computing the RIXS moments and other nonlinear properties. An alternative, more rigorous strategy involves recasting the SOS expressions into a closed form using damped response theory. By doing so, one circumvents the need to compute the wave functions and energies of all electronic states. Instead, only a handful of response wave functions need to be computed.
The squares of \( \sigma \) can be interpreted as the weights of the descriptor. \( \phi \) and \( \psi \) describe excitonic wave functions for a one-photon transition, and \( \psi_{\text{exc}} \) is the sum of exciton's wave functions for a one-photon transition. The excitonic wave functions are computed iteratively by solving the following equation:

\[
\begin{align*}
(H - E_k - \omega_{1k} + i\epsilon)\chi_k = (\Phi_k|\epsilon, \rho|\Psi) \\
X_k = (H - E_k + \omega_{1k} + i\epsilon)\chi_k = (\Phi_k|\epsilon, \rho|\Psi),
\end{align*}
\]

These exciton descriptors facilitate the assignment of the transitions in terms of valence, Rydberg, or charge-transfer character. 2,2,3,16

The description of exciton’s wave function for a one-photon transition is the most concise in terms of NTOs, which are computed by means of unitary orbital transformations. 2,2,14,16,17 This is achieved by the singular value decomposition (SVD) of the 1PTDM as follows:

\[
\begin{align*}
\Sigma &= UV^T, \\
\psi_k(r) &= \sum_q V_{qk}\phi_q(r), \\
\psi_{\text{exc}}(r) &= \sum_q U_{qk}\phi_q(r).
\end{align*}
\]

where the \( \Sigma \) is the diagonal matrix of singular values, \( \sigma \), and matrices \( V \) and \( U \) contain the hole and particle NTOs according to

\[
\begin{align*}
\|\psi_k\|^2 &= \sum_q V_{qk}^2, \\
\|\psi_{\text{exc}}\|^2 &= \sum_q U_{qk}^2.
\end{align*}
\]

The squares of \(\sigma\) can be interpreted as the weights of the respective NTO pair when divided by the square of the Frobenius norm of \(\psi\),

\[
\begin{align*}
\sum_k \sigma_k^2 &= \sum_k \sigma_k^2, \\
\sum_k \sigma_k^2 &= \sum_k \sigma_k^2.
\end{align*}
\]
In the analyses below, we report such normalized singular values,

\[ \sigma_k = \frac{\sigma_k}{\| y \|}, \]

which are equivalent to using normalized 1PTDMs in the wavefunction analysis.

The SVD procedure removes the arbitrariness associated with the orbital choice. Since only a handful of \( \sigma_k \)'s are non-negligible, the NTO representation enables the most compact molecular orbital representation of any transition, including transitions between multi-configurational correlated wave functions. In terms of NTOs, the exciton’s wave function for a one-photon transition is given by

\[ \psi_{\text{exc}}(r_0, r_e) = \sum_{k} \sigma_k \psi_k(r_e) \psi_k^*(r_0). \]

In contrast to the real-valued exciton’s wave functions and 1PTDMs for one-photon and two-photon absorption processes,\textsuperscript{12,13,16,17} the exciton’s wave function and response 1PTDMs for the RIXS process are complex because the response wave functions become complex within the damped response theory formalism. Below, we explain how to interpret these complex 1PTDMs.

Rewriting the response 1PTDM in Eq. (26), we obtain

\[ \psi_{\text{exc}}^{c,x}(r_0, r_e) = \sum_{pq} \psi_{pq}^{c,x,\text{Re}}(r_e) \psi_{pq}^{c,x,\text{Re}}(r_0) + i \sum_{pq} \psi_{pq}^{c,x,\text{Im}}(r_e) \psi_{pq}^{c,x,\text{Im}}(r_0). \]

Since the real and imaginary components of the RIXS scattering moments accumulate the off-resonance and near-resonance SO terms, respectively, the corresponding real and imaginary response 1PTDMs provide the cumulative orbital information of these off-resonance and near-resonance terms. We reformulate Eq. (28) to

\[ \psi_{\text{exc}}^{c,x}(r_0, r_e) = \sum_{k} \sigma_k \psi_k(r_e) \psi_k^*(r_0) \]

by performing SVD on the real and imaginary response 1PTDMs separately, so that two sets of real NTOs \( \{ \psi_k^{\text{Re}}(r_e), \psi_k^{\text{Re}}(r_0) \} \) and \( \{ \psi_k^{\text{Im}}(r_e), \psi_k^{\text{Im}}(r_0) \} \) are obtained and used for visualization and interpretation.

The relative significance of the off-resonance and near-resonance terms for a given RIXS moment can be estimated from the norms of the real and imaginary response 1PTDMs, \( \| y^{c,x,\text{Re}} \| \) and \( \| y^{c,x,\text{Im}} \| \). For example, if \( v^{\text{Re}} = \| y^{c,x,\text{Re}} \| / \| y^{c,x,\text{Im}} \| \approx 1 \) or \( v^{\text{Re}} = \| y^{c,x,\text{Im}} \| / \| y^{c,x,\text{Re}} \| \approx 0 \), the corresponding \( x \) component of the exciton’s wave function can be approximated by just the imaginary near-resonance contributions. Similarly, the relative significance of the off-resonance and near-resonance terms for the overall RIXS transition can be estimated using the norms of response 1PTDMs along the three Cartesian coordinates. For example, if \( \psi_{\text{Re}} = \| y^{c,x,\text{Re}} \| + \| y^{c,x,\text{Im}} \| \approx 1 \) or \( \psi_{\text{Im}} = \| y^{c,x,\text{Re}} \| + \| y^{c,x,\text{Im}} \| \approx 0 \), where \( \psi_{\text{Re}} = \psi_{\text{Re}}^{\text{Re}} + \psi_{\text{Re}}^{\text{Im}} + \psi_{\text{Im}}^{\text{Re}} + \psi_{\text{Im}}^{\text{Im}} \approx 0 \), and \( \psi_{\text{Im}} = \| y^{c,x,\text{Re}} \| + \| y^{c,x,\text{Im}} \| \approx 0 \), then the RIXS transition has predominant contributions from near-resonance channels. In the discussion that follows, we drop the index \( c \) in \( y^{c,x,\text{Re}} \) and \( y^{c,x,\text{Im}} \) for brevity.

\[ \sum_{\text{Re}} \| y^{c,x,\text{Re}} \| \approx 0, \quad \sum_{\text{Im}} \| y^{c,x,\text{Im}} \| \approx 0. \]

III. COMPUTATIONAL DETAILS

Using the existing infrastructure of the libwfa library\textsuperscript{15} for wave-function analysis,\textsuperscript{12,13,16} we implemented the calculations of the NTOs for RIXS 1PTDMs in the Q-Chem package.\textsuperscript{36,37} Below, we illustrate the utility of this orbital analysis for the RIXS transitions in the OH radical, benzene, \textit{para}-nitroaniline, and 4-amino-4-nitrostilbene. In all calculations, we employ the recently developed implementation\textsuperscript{22} of RIXS calculations within the fc-CVS-EOM-EE-CCSD framework.\textsuperscript{28} For the OH radical, benzene, and pNA, we use the 6-311(2+,+)G** basis set with the uncontracted core functions.\textsuperscript{29} For the OH radical, we use the experimental bond length of 0.9697 Å. We use the geometries from Refs. 17 and 22 for benzene and pNA, respectively. For 4A4NS, we use the B3LYP/6-311G** optimized geometry and the 6-31+G* basis set with the uncontracted core functions\textsuperscript{29} for XAS, XES, and RIXS calculations. The relevant Cartesian coordinates are provided in the supplementary material. The phenomenological damping parameter \( \epsilon \) was set to 0.005 (OH), 0.01 (benzene and pNA), and 0.03 (4A4NS).

We use Q-Chem’s symmetry notations throughout this paper (more details can be found in Refs. 17 and 22 and at http://iopenshell.usc.edu/resources/howto/symmetry/). We use the \( C_{2v} \) symmetry group for OH and pNA, \( D_{2h} \) symmetry group for benzene, and \( C_{s} \) symmetry group for 4A4NS. The NTOs and canonical MOs were visualized with Gabedit\textsuperscript{30} and IQMol,\textsuperscript{31} respectively.

IV. RESULTS AND DISCUSSION

A. Wave-function analysis of RIXS transition in OH

In the OH radical, the \( \pi \) orbital is singly occupied (see Fig. 3), so the lowest resonant x-ray absorption involves the excitation of the 1s\textsubscript{0} electron to fill the valence \( \pi \) hole.\textsuperscript{28} This is shown by the NTO analysis of the XB\textsubscript{2} \( \rightarrow \) c1A\textsubscript{1} transition presented in Fig. 4 and the supplementary material. Here and below, the prefix “c” denotes a core-excited state or a core orbital.

The lowest valence excited state is the 1A\textsubscript{1} state at 4.15 eV. Within the three-state model, the XB\textsubscript{2} \( \rightarrow \) c1A\textsubscript{1} RIXS transition, with the incoming photon’s energy tuned at the XB\textsubscript{2} \( \rightarrow \) c1A\textsubscript{1} resonance, entails x-ray absorption from the ground state to the c1A\textsubscript{1} state and

\[ \pi_x \]

\[ \pi_y \]

\[ \sigma_z \]

\[ 2s \]

\[ 1s \]

\[ \text{FIG. 3. Molecular orbitals and ground-state electronic configuration of the OH radical.} \]
FIG. 4. NTO analysis of the XB$_2 \rightarrow 1A_1$ RIXS transition in the OH radical. Comparison of important NTO pairs computed separately for the x-ray absorption (XB$_2 \rightarrow c1A_1$) and x-ray emission (c1A$_1 \rightarrow 1A_1$) transitions with the NTO pairs computed from the RIXS 1PTDMs show that the three-state model is appropriate for this transition.

x-ray emission from the c1A$_1$ state to the final valence 1A$_1$ state. This transition is the dominant inelastic feature in the RIXS spectrum of aqueous OH.$^8$ The NTO analysis for the c1A$_1 \rightarrow 1A_1$ emission, which is shown in Fig. 4, indicates $\sigma_z \rightarrow 1s$ character. Based on this three-state model, one can now identify the $\sigma_z \rightarrow 1s \rightarrow \pi_y$ orbital channel as the dominant pathway in the XB$_2 \rightarrow 1A_1$ RIXS transition.

Let us now compare this approximate analysis based on the three-state model with the NTO analysis of the RIXS 1PTDMs. In the analytic RIXS calculations, we find that the imaginary $M^{\ast\ast}$ components—and thus the near-resonance orbital channels—are dominant for the XB$_2 \rightarrow 1A_1$ RIXS transition and, therefore, have the dominant contribution to the cross section. The RIXS 1PTDMs corresponding to the imaginary $M^{\ast\ast}_{x'y'}$ and $M^{\ast\ast}_{x'z}$ components are the $\gamma_{y',\text{Im}}$ and $\gamma_{z,\text{Im}}$ 1PTDMs, respectively. The detailed NTO analyses of these RIXS 1PTDMs are given in the supplementary material.

By inspecting the norms of the imaginary RIXS 1PTDMs and of the respective $\omega$DMs, we note that only the first terms in Eqs. (13) and (14) provide significant contributions. Thus, the NTOs of the full imaginary RIXS 1PTDMs can be explained by interpreting these imaginary $\omega$DMs. The first imaginary $\omega$DM in Eq. (13) reflects the transition from the "virtual" $X_g$ state (first-order response ground state) to the final state, and so the NTO pairs correspond to the transition that fills the core hole (emission). Complementary to this orbital transition, the NTO pairs from the first imaginary $\omega$DM in Eq. (14) reflect the transition from the $X_f$ "virtual" state (first-order perturbed final state) to the initial state, i.e., the reverse of core-hole formation in the absorption step. By joining these two sets of NTOs together, the orbital picture of the RIXS transition is constructed. For the XB$_2 \rightarrow 1A_1$ RIXS transition, each set consists of one dominant NTO pair (see the supplementary material). The analysis of $\gamma_{y',\text{Im}}$ identifies the $\sigma_z$ hole and 1s particle NTOs; the analysis of $\gamma_{z,\text{Im}}$ identifies the $\pi_y$ hole and 1s particle NTOs. Using the norms of response 1PTDMs, we obtain $\Upsilon_{\text{Im}} = 1.00$ for this transition. Thus, the dominant RIXS channel is resonant and given by $\sigma_z \rightarrow 1s \rightarrow \pi_y$ with its $1s \rightarrow \pi_y$ excitation and $\sigma_z \rightarrow 1s$ de-excitation components. This is consistent with the three-state model described above, indicating that for this RIXS transition, the three-state model provides a good approximation to the full SOS expression.

B. Wave-function analysis of RIXS transitions in benzene

Figure 5 shows the occupied molecular orbitals of benzene. The six 1s$_C$ core orbitals form six nearly degenerate delocalized molecular orbitals. Depending on the symmetry of the target orbital, different core orbitals are active in the XAS transitions.$^{22}$ The relevant virtual molecular orbitals (not shown) are doubly degenerate $\pi^*_{LUMO}$ and diffuse $s$ and $p$ Rydberg orbitals.

The two dominant features in the XAS spectrum of benzene$^{43–50}$ are peak A and peak B at 285.97 eV and 287.80 eV.

FIG. 5. Molecular orbitals and ground-state electronic configuration of benzene.
respectively [theoretical values\textsuperscript{22} computed with fc-CVS-EOM-EE-CCSD/uC-6-311(2+,+)G\textsuperscript{**}]. When the incoming photon’s energy is tuned to the peak-A resonance, the dominant inelastic feature is the energy-loss peak at 10.67 eV, characterized by equal contributions from the degenerate \(X_A \rightarrow 13B_{2g} \) and \(X_A \rightarrow 12B_{3g} \) transitions. In contrast, when the incoming photon’s energy is tuned to the peak-B resonance, the dominant inelastic feature is the energy-loss peak at 6.45 eV, characterized by equal contributions from the degenerate \(X_A \rightarrow 1B_{2g} \) and \(X_A \rightarrow 1B_{3g} \) transitions. Below, we show the NTO analysis of only the \(X_A \rightarrow 13B_{2g} \) and \(X_A \rightarrow 1B_{2g} \) transitions with incoming photon energies tuned at peak-A and peak-B resonances, respectively. The NTO analyses for the two transitions are similar, except for the differences in symmetry labels of the orbitals.

The NTO analysis for the dark one-photon \(X_A \rightarrow 13B_{2g} \) transition (given in the supplementary material) suggests that this valence transition is made up of two orbital transitions: \(b_{2u} \rightarrow a_u \) and \(b_{3u} \rightarrow b_{1u} \). Similarly, the NTO analysis of XAS peak A (\(X_A \rightarrow c_{2B_{1u}} \)) transition in Fig. 6 shows two dominant orbital transitions: \(c_{b_{1g}} \rightarrow a_u \) and\( c_{a_{g}} \rightarrow b_{1u} \). Similarly, the NTO analysis of the \(c_{2B_{1u}} \rightarrow 13B_{2g} \) x-ray emission shows two dominant orbital transitions: \(b_{2u} \rightarrow b_{1g} \) and \(b_{3u} \rightarrow c_{a_{g}} \). Based on these analyses, the three-state model for the \(X_A \rightarrow 13B_{2g} \) RIXS transition identifies two important orbital channels: \(b_{2u} \rightarrow b_{1g} \) and \(b_{3u} \rightarrow c_{a_{g}} \rightarrow b_{1u} \). Based on these analyses, the three-state model is adequate for this RIXS transition. Both orbital channels provide dominant contributions.

The NTO analysis of the \(1A_g \rightarrow 1B_{2g} \) RIXS transition in benzene. Comparison of important NTO pairs computed separately for the x-ray absorption (\(1A_g \rightarrow c_{2B_{3u}} \)) and x-ray emission (\(c_{2B_{3u}} \rightarrow 1B_{2g} \)) transitions with the NTO pairs computed from the RIXS 1PTDMs shows that the three-state model is adequate for this RIXS transition. Orbital channel 1 provides dominant contributions.
from the $b_{3u}$ orbital to the $2a_u$ orbital and from the $b_{3u}$ orbital to the $4b_{1u}$ orbital, respectively. This orbital analysis of the RIXS 1PTDMs is consistent with the approximate analysis from the three-state model.

The one-photon $X\Delta g \rightarrow 1B_{2g}$ transition is dark; its NTO analysis given in the supplementary material reveals its dominant HOMO–LUMO character ($b_{2g} \rightarrow a_g$) and a miniscule contribution from the $b_{1u} \rightarrow b_{3u}$ transition. The NTO analysis of XAS peak B transition ($X\Delta g \rightarrow c2B_{3u}$) shown in the supplementary material and Fig. 7 indicates that this core excitation has predominantly $cb_{1u} \rightarrow a_g$ character, with a small contribution from the $ca_g \rightarrow b_{3u}$ transition. The NTO analysis of the $c2B_{3u} \rightarrow 1B_{2g}$ x-ray emission transition has a predominantly $b_{2g} \rightarrow cb_{3u}$ character with a small contribution from the $b_{1u} \rightarrow ca_g$ transition. Thus, within the three-state model, the NTO analyses of the $X\Delta g \rightarrow c2B_{3u}$ x-ray absorption and $c2B_{3u} \rightarrow 1B_{2g}$ x-ray emission identify the orbital character as $b_{2g} \rightarrow cb_{3u} \rightarrow a_g$, with a small contribution from the $b_{1u} \rightarrow ca_g \rightarrow b_{3u}$ channel.

The RIXS moment tensor for the $X\Delta g \rightarrow 1B_{2g}$ transition is dominated by the imaginary component of $M^{zz}$ moments. Here, we perform NTO analyses of the $\gamma^{1im}$ and $\gamma^{2im}$ RIXS 1PTDMs corresponding to the $M^{zz}_{1g}$ and $M^{zz}_{2g}$ components, respectively. The analysis of $\gamma^{1im}$ identifies the $b_{2g} \rightarrow cb_{3u}$ NTO pair as dominant, with a miniscule contribution from the $b_{1u} \rightarrow ca_g$ NTO pair. The analysis of $\gamma^{2im}$ identifies the dominant $a_g \rightarrow cb_{3u}$ NTO pair and a less important $b_{3u} \rightarrow ca_g$ NTO pair. Combining these two analyses, the dominant orbital channel is $b_{2g} \rightarrow cb_{3u} \rightarrow a_g$. We obtain $\gamma^{im} = 0.98$ for this RIXS transition, which is consistent with the analysis from the three-state model discussed above. Similarly, the dominant RIXS channel is resonant and given by $b_{2g} \rightarrow cb_{2u} \rightarrow a_g$ for the $X\Delta g \rightarrow 1B_{2g}$ transition.

C. Wave-function analysis of RIXS transitions in para-nitroaniline

The orbital analysis of the selected RIXS transitions in the OH radical and benzene supports the notion that the dominant orbital channel in RIXS is (nearly) resonant and that three-state models are sufficient for determining the important orbitals involved in the RIXS transition. In this section, we present a counterexample illustrating the limitations of few-core-excited-states models. We consider RIXS transitions in para-nitroaniline (pNA) and show that for this system, the predominant channel driving the electronic density in the course of inelastic scattering may or may not be (nearly) resonant in character.

Figure 8 shows the occupied molecular orbitals of pNA. The special feature of this molecule is that the lowest excited state has strong intramolecular charge-transfer character.41-54 This state corresponds to the lowest fully symmetric $X\Delta_1 \rightarrow 2A_1$ transition with a large oscillator strength ($f = 0.4$). The NTO analysis (provided in the supplementary material) shows that this transition can be described as HOMO–LUMO excitation: $\pi(b_2) \rightarrow \pi^*(b_2)$.

The strong charge-transfer character of this transition ($\Delta\mu = 3.2$ a.u.) has non-trivial consequences on the character of the 2PA transition, as discussed in Ref. 17. Specifically, we have shown that the 2PA moments for the $X\Delta_1 \rightarrow 2A_1$ transition in pNA can be described by the two-state model involving just the initial and final states, in contrast to other 2PA examples involving specific
virtual states giving dominant contributions to the cross sections. Thus, for this transition, the 2PA transition moments are given according to

$$M_{xy}^{\gamma \rightarrow f} \approx - \sum_{n=g,f} \left( \frac{\langle \psi_f | \mu^x | \psi_n \rangle \langle \psi_n | \mu^y | \psi_f \rangle}{\Omega_{ng} - \omega_{1x} - i\epsilon} + \frac{\langle \psi_f | \mu^y | \psi_n \rangle \langle \psi_n | \mu^x | \psi_f \rangle}{\Omega_{ng} - \omega_{2y} - i\epsilon} \right)$$

$$\approx - \langle \psi_f | \mu^y | \psi_n \rangle \langle \psi_n | \mu^x | \psi_f \rangle$$

and

$$M_{f \rightarrow g}^{\gamma \rightarrow \ell} \approx - \sum_{n=g,f} \left( \frac{\langle \psi_g | \mu^x | \psi_n \rangle \langle \psi_n | \mu^y | \psi_g \rangle}{\Omega_{ng} - \omega_{1x} - i\epsilon} + \frac{\langle \psi_g | \mu^y | \psi_n \rangle \langle \psi_n | \mu^x | \psi_g \rangle}{\Omega_{ng} - \omega_{2y} - i\epsilon} \right)$$

$$\approx - \langle \psi_g | \mu^y | \psi_n \rangle \langle \psi_n | \mu^x | \psi_g \rangle$$

Similarly to the one-photon transition, this 2PA transition also has intramolecular charge-transfer character; its large 2PA moments

![Diagram of X-ray absorption and emission](image)
result from the large one-photon transition dipole moment and the large difference in the dipole moments between the initial and final states. As discussed in Ref. 17, these two quantities are present in the numerators of Eqs. (30) and (31). On the other hand, it is the pole structure (which comes from the denominators) of Eqs. (1) and (2) that imparts the resonant character to a RIXS transition. Thus, one can potentially identify two-photon RIXS transitions involving the $X_A \rightarrow 2A_1$ states in pNA for which both the near-resonance (involving the intermediate core states) and off-resonance (involving the initial and final valence states) orbital channels are important. Below, we provide such an example by considering the $X_A \rightarrow 2A_1$ RIXS transition in pNA for which the incoming photon frequency is tuned to its $C$-edge resonance at 288.01 eV. We compute the $X_A \rightarrow 2A_1$ RIXS cross section using a modified fc-CVS-EOM-EE-CCSD method in which the SOS includes the CVS states plus the initial and the final states, so that the RHS terms in Eqs. (30) and (31) are also incorporated.

The $X_A \rightarrow c6B_2$ core excitation is dark due to symmetry, but it is nearly degenerate with the bright (near-)degenerate $X_A \rightarrow c1A_1$ and $X_A \rightarrow c1B_1$ transitions at 287.96 eV (see the supplementary material). The NTO analysis for $X_A \rightarrow c6B_2$ core excitation given in the supplementary material and Fig. 9 reveals two dominant orbital transitions: $ca_1 \rightarrow b_2$ and $cb_1 \rightarrow a_2$. From the NTO analyses of the $X_A \rightarrow c6B_2$ x-ray absorption and $c6B_2 \rightarrow 2A_1$ x-ray emission, the three-state model suggests that the $b_2 \rightarrow ca_1 \rightarrow b_2$ near-resonance channel should dominate for the $\gamma^{\text{Im}}$ and $\gamma^{\text{Im}}$ 1PTDMs.

For this RIXS transition, the $M^{xx}$, $M^{yy}$, and $M^{zz}$ RIXS moments are comparable. $M^{\text{Im},\text{Im}}$ and $M^{\text{Re},\text{Im}}$ have larger magnitudes, indicating that the near-resonance channels along the $y$ and $x$ axis have the largest contribution. The NTO analyses of $\gamma^{\text{Im}}$ and $\gamma^{\text{Im}}$ RIXS 1PTDMs are given in the supplementary material. The near-resonance mechanism of electronic density transfer in the inelastic scattering obtained from analyzing $\gamma^{\text{Im}}$ and $\gamma^{\text{Im}}$ is not what is expected from the three-state model (Fig. 10); the obtained intermediate core orbitals are a linear combination of the six $1s_C$ molecular orbitals. This reflects that the SOS resonant term with $\Omega_{\text{gy}} = \omega_1$ does not provide the dominant contribution to the RIXS moment. In fact, the damped contributions from other off-resonance terms, which are collected in the $\gamma^{\text{Re}}$ and $\gamma^{\text{Re}}$ 1PTDMs, contribute more than the near-resonance term primarily due to larger transition dipole moments than the ones forming the near-resonance term (i.e., the transition dipole moments for $X_A \rightarrow c6B_2$ and $2A_1 \rightarrow c6B_2$ transitions). The fact that the off-resonance terms are dominant is also reflected in the larger norms of the $\gamma^{\text{Re}}$ and $\gamma^{\text{Re}}$ 1PTDMs than the $\gamma^{\text{Im}}$ and $\gamma^{\text{Im}}$ 1PTDMs ($\nu X_{\text{Im}} = 0.03$). Furthermore, the rms electron–hole distances ($d_{\text{rms}}$) computed for these components of the RIXS transition ($=2.4 \text{Å}$) are smaller than the $3.6 \text{ Å}$ value computed for the one-photon $X_A \rightarrow 2A_1$ transition (see the supplementary material), highlighting the local character of the RIXS transition along the $y$ direction.

Since the $X_A \rightarrow c6B_2$ core excitation is nearly degenerate with $X_A \rightarrow c1A_1$ and $X_A \rightarrow c1B_1$ core excitations, the latter two transitions with larger oscillator strengths open near-resonance orbital channels and impact the imaginary $M^{xx}$ and $M^{yy}$ RIXS moments. As shown in Fig. 9, the $ca_1 \rightarrow a_1$ and $cb_1 \rightarrow b_1$ transitions are important in the $X_A \rightarrow c1A_1$ core excitation and the $ca_1 \rightarrow a_1$ and $ca_1 \rightarrow b_1$ transitions are important in the $X_A \rightarrow c1B_1$ core excitation. These orbital transitions also dominate the NTO analysis of $\gamma^{\text{Re}}$ and $\gamma^{\text{Re}}$ 1PTDMs, consistent with the three-state models constructed with the NTO analyses of these two XAS peaks. Furthermore, the rms electron–hole distances for these 1PTDMs are smaller than the one computed for the one-photon $X_A \rightarrow 2A_1$ transition, indicating that these near-resonance channels are local and confined to the respective active core-hole orbitals.

For the $M^{yx}$ RIXS moments, the imaginary components are larger than the respective real components ($\nu X^{\text{Im}} = 0.71$), consistent with larger norm for the $\gamma^{\text{Im}}$ and $\gamma^{\text{Im}}$ 1PTDMs than the respective $\gamma^{\text{Re}}$ and $\gamma^{\text{Re}}$ 1PTDMs (Fig. 11). On the other hand, the real components are larger than the imaginary components for the $M^{xx}$ moment ($\nu X^{\text{Re}} = 0.01$), consistent with the larger norms for $\gamma^{\text{Re}}$ and $\gamma^{\text{Re}}$ 1PTDMs than those for $\gamma^{\text{Im}}$ and $\gamma^{\text{Im}}$ 1PTDMs. The NTO analyses of the $\gamma^{\text{Re}}$ and $\gamma^{\text{Re}}$ 1PTDMs.
show that the $b_2(\pi) \to b_2(\pi^*)$ transition is the significant off-resonance RIXS channel, indicating that this two-photon process has some intramolecular charge-transfer character (Fig. 12). This is further supported by the larger rms electron–hole distances for the $\gamma_{z,\text{Re}}^z$ and $\gamma_{\text{Re}}^\gamma$ 1PTDMs than the other RIXS 1PTDMs and comparable to the rms electron–hole distance for the one-photon $\chi_A \to 2A_1$ transition. This intramolecular $\pi \to \pi^*$ charge-transfer channel is, however, not the dominant off-resonance channel in the overall RIXS process as $\gamma_{\text{Re}}^z < \gamma_{\text{Im}}^\gamma$, even though the overall character of this RIXS transition is not resonant ($\gamma_{\text{Im}}^\gamma = 0.03$).

D. Wave-function analysis of RIXS transitions in 4-amino-4′-nitrostilbene

Similar to pNA, 4-amino-4′-nitrostilbene (4A4NS) is a push–pull chromophore. Its one-photon $\chi_A \to 2A'$ transition has an even larger oscillator strength than the $\chi_{A_1} \to 2A_1$ transition in pNA with strong intramolecular charge-transfer character ($f = 1.22$, $\Delta E = 5.0$ a.u.; see the NTO analysis of this transition in the supplementary material). For this molecule, we pick the $\chi_A \to 2A'$ RIXS transition and the incoming photon frequency that is resonant with its lowest N-edge XAS peak ($\chi_{A'} \to 2A_1$) computed at 404.01 eV. We use the modified fc-CVS-EOM-EE-CCSD method that was used in the pNA example discussed above. For the $\chi_{A'} \to 2A'$ RIXS transition, only the real $M_{z,\text{Re}}$ moments and the real and imaginary $M_{z,\text{Im}}$ moments are important. The NTO analysis in Fig. 13 of the $\gamma_{x,\text{Re}}^x$ and $\gamma_{y,\text{Re}}^y$ RIXS 1PTDMs identifies its dominant off-resonance intramolecular charge-transfer channel ($\nu_{x,\text{Re}} = 1.00$), which also describes the one-photon $\chi_A \to 2A'$ transition. The NTO analyses of the real and imaginary components of $\gamma^x$ and $\gamma^y$ 1PTDMs show similar orbitals (see the supplementary material), with the norms of the real 1PTDMs larger than the imaginary $\nu_{x,\text{Im}} = 0.28$. This indicates that important orbital channels along the z axis are off-resonance, originating from the large numerators in the SOS off-resonance terms, which also dominate the imaginary 1PTDMs. This is not surprising because the lowest N-edge XAS peak (at which the incoming photon energy is tuned) is separated by more than 1 eV from other XAS transitions. Clearly, a few-core-excited-state model would be inadequate for this transition dominated by off-resonance channels—in particular, the intramolecular charge-transfer channel—and $\gamma_{x,\text{Re}}^x = 0.50$. This example provides another illustration of the merits of the analytic approach for characterizing RIXS transitions.

V. CONCLUSION

We presented a novel black-box approach for deriving the molecular orbital picture of RIXS transitions based on the corresponding response 1PTDMs and their NTOs. This is the first example of the generalization of the concept of NTOs to coherent nonlinear x-ray processes. This new tool for analyzing RIXS transitions relies on the rigorous and compact formalism of the response 1PTDMs based on damped response theory. The NTOs computed with this approach facilitate the visualization of RIXS transitions in terms of orbital channels but without crude simplifying assumptions. 1PTDMs are also useful for computing the physical quantities related to the spatial extent of the RIXS transitions such as the average electron–hole separation. This analytic approach is superior to the traditional few-state treatments, which relies on computing few intermediate core-excited states for a qualitative orbital picture of RIXS. The few-state treatment inherently suffers from the arbitrariness of the choice of intermediate states and potential loss of accuracy; it also ignores the coherent nature of RIXS. We demonstrate the utility of the new analysis tool by calculating the orbital picture of RIXS transitions in the OH radical, benzene, pNA, and 4A4NS molecules. The RIXS transitions in the latter two systems have significant contributions from off-resonance orbital channels, which are difficult to capture with the few-state models, illustrating the merits of the rigorous analytic approach for analyzing RIXS transitions. For chromophores in complex environments, ab initio methods augmented
with our analysis tool can help elucidate the role of molecular structure and intermolecular interactions on the RIXS spectra and provide rigorous assignments of the features in experimental RIXS spectra.

SUPPLEMENTARY MATERIAL

See the supplementary material for tabulated NTO analysis for valence absorption, x-ray absorption, x-ray emission, and RIXS transitions; relevant Cartesian coordinates; and basis sets used in our calculations.

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DATA AVAILABILITY

The data that support the findings of this article are available within the article and its supplementary material.

REFERENCES


