Nuclear dynamical correlation effects in X-ray spectroscopy from a time-domain perspective

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To date X-ray spectroscopy has become a routine tool that can reveal highly local and element-specific information on the electronic structure of atoms in complex environments. Here, we focus on nuclear dynamical effects in X-ray spectra and develop a rigorous time-correlation method employing ground state molecular dynamics simulations. The importance of nuclear correlation phenomena is demonstrated by comparison against the results from the conventional sampling approach for gas phase water. In contrast to the first-order absorption, second-order resonant inelastic scattering spectra exhibit pronounced fingerprints of nuclear motions. The developed methodology does not depend on the accompanying electronic structure method in principle as well as on the spectral range and, thus, can be applied to, e.g., UV and X-ray photo-electron and Auger spectroscopies.

The central message of this Letter is that nuclear correlation effects are essential for X-ray spectroscopy. We exemplify this on oxygen K-edge spectra of a typical and highly relevant system: gas phase water, by comparison against the results of the aforementioned sampling approach. Importantly, only RIXS, being a second order process, appears sensitive to them, much like non-linear optical spectra provide more detailed insight into the underlying dynamical processes [14,15].

Introduction. Constant increase of spectral resolution and rapid development of various spectroscopies, covering broad energy ranges from radio frequencies to extra hard radiation, opens new horizons for a molecular scientist to investigate more and more intricate and delicate phenomena. When it comes to obtaining highly local and element-specific information on the electronic structure, X-ray spectroscopies stand out [1]. Popular variants include first order X-ray absorption spectra (XAS) and second order resonant inelastic X-ray scattering (RIXS) techniques. The former focuses on the electronic transitions where a core electron is excited to the manifold of unoccupied molecular orbitals (MOs), whereas the latter detects the emission signal resulting from the refill of a core-hole by electrons occupying valence MOs. Although X-ray spectroscopy usually targets electronic transitions, the vibrational ones as well as the accompanying nuclear dynamics have recently received growing attention [2-9]. Remarkably, the RIXS spectra of liquid water and alcohols initiated active ongoing debates in the last decade [10-12], with controversial interpretations, among others involving different aspects of nuclear dynamics [13].

Conventionally, electronic spectra are obtained via single point electronic structure calculations combined with models such as the multi-mode Brownian oscillator one to include broadening on phenomenological level [13]. A big step forward is to sample nuclear distributions in the phase space via molecular dynamics (MD) methods [15-17], leading to a more realistic description of conformational and environmental effects [15,21], although lacking information about correlated nuclear motion. Here, we propose an approach to theoretical calculations of XAS and RIXS spectra based on time-correlation functions obtained from the time evolution provided by electronic ground state MD simulations, analogous to infrared and UV/Vis spectroscopies [14,17,22,25].

\[ \mathcal{X}(\Omega) = \frac{1}{T} \sum_{g,f} \left( \hat{M}^g_f(\omega_{fg} - \Omega) \hat{M}^f_g(\Omega - \omega_{fg}) \right) \]  

(1)
\[ \mathcal{R}(\Omega, \omega) = \frac{1}{T} \sum_{g,f,i,j} \left\langle \int_{-\infty}^{\infty} d\omega_1 \hat{M}_g^f (\omega_1 - \omega) \hat{M}_j^i \left( \omega \right) \right\rangle \]

and

\[ \int_{-\infty}^{\infty} d\omega_2 \hat{M}_g^f (\omega_2) \Delta_i(-\omega_2)\hat{M}_j^i (\omega - \omega_2 - \omega_{ig}) \]

Here, inversed hats denote the Fourier-transformed quantities and the “dressed” transition dipole moments read

\[ \hat{M}_g^f (t, 0) := D_g^f (t) \exp \left[ \int_0^t d\tau U_{f,g} (\tau) \right] \]

\[ \hat{M}_g^i (t, 0) := W_g (t) D_g^i (t) \exp \left[ \int_0^t d\tau U_{f,g} (\tau) \right] \]

where \( D_g^f \) are the transition dipole moments from \( |g\rangle \) to \( |f\rangle \) time-evolved with respect to the Hamilton function of the electronic ground state. The gap fluctuation reads \( U_{f,g} (\tau) := \Delta E_{f,g} (\tau) - \omega_{fg} \), where \( \Delta E_{f,g} \) is the electronic energy gap and \( \omega_{fg} := 1/T \int_0^T d\tau \Delta E_{f,g} (\tau) \) is the mean transition frequency averaged over a trajectory of length \( T \). Further \( \Delta_i (\omega) := 1/(2\pi) \sqrt{\Gamma_j/\pi(\Gamma_j + |\omega|)} \) is the damping function in frequency domain, with \( \Gamma_j \) being the lifetime broadening of the intermediate state \( |j\rangle \). The lifetimes are thus allowed for by means of a simple phenomenological model accounting for the Auger decay. Additionally, the spectra are convoluted with the Gaussian of width \( \sigma \) along the \( \Omega \)-axis, responsible for the bandwidth of the excitation pulse. Finally, the weighting function

\[ W_g (t) := e^{-\Delta E_{f,g}(t)/kT} \left\langle \sum_{f} e^{-\Delta E_{f,g}(0)/kT} \right\rangle \]

with \( \langle \ldots \rangle \) here and in Eqs. \[12\] standing for the classical canonical average with respect to the Hamilton function of the ground state, \( H_0 \), see Fig. \[1\]. Note that for the present case of gas phase water, there is only one initial state \( |g\rangle \) that coincides with the ground state \( |0\rangle \). We note in passing that Eqs. \[12\] can be derived starting from the Fermi’s Golden rule and the Kramers-Heisenberg expression, respectively.

**Computational details.** The MD simulations have been performed using GROMACS ver. 4.6.5 \[27\] employing the anharmonic qSPC/Fw water model with a Morse O–H potential \[28\]. A set of 140 uncorrelated initial conditions has been sampled from an NVT MD run at 300 K further serving as starting points for NVE trajectories. The trajectories have been 0.5ps long with a timestep of 0.5fs, yielding a spectral resolution of \( \approx 8\)meV. The electronic Schrödinger equation for each MD snapshot has been solved via ground state density functional theory with the PBE functional \[29\] using ORCA ver. 3.0.3 \[30\]. The def-QZVPP basis set \[31\] together with (5s5p)/(1s1p) generally contracted Rydberg functions on oxygen have been used. Such a small Rydberg basis does not allow one to reproduce the high-energy tail of the absorption spectrum \[32\], but enables the description of the lowest states just above the core-excitation threshold. The energies of the valence and core-excited states have been approximated by the differences of the respective Kohn-Sham orbital energies; the corresponding dipole transition moments have been calculated with respect to these orbitals \[33\], which is known to yield a reasonable compromise between accuracy and efficiency \[2\] \[32\] \[33\]. To preserve the continuous time evolution of the dressed dipoles, the entire manifold of relevant electronic levels has been traced along the MD trajectories in a fully-automated manner. The excitation Gaussian linewidth and the uniform Lorentzian lifetime broadening have been chosen as \( \sigma = 0.05\)eV and \( \Gamma = 0.25\)fs\(^{-1}\), respectively. The data have been averaged...
over the molecular orientations assuming the orthogonality of e and u, which corresponds to a typical experimental setup, and the spectra have been shifted globally by 24.8 eV such that the peak structure roughly matches the experimental data\([26]\). Note that both the sampling and time-correlation approaches employ the same datasets for the consistency of comparison. For further computational details see Supplement.

**Results.** The fingerprints of nuclear correlations are revealed by comparing the spectra obtained via the sampling and correlation approaches. The XAS amplitudes, Fig. 2, are in fairly good agreement with the experimental data\([26]\) shown with the dashed line. We would like to stress that we do not aim at quantitative reproducing the inelastic features shown in panels (a) and (b) in Fig. 4. In particular the sidebands for peaks at 510.5 eV and 526.4 eV are coupled to the bending vibrational mode having the frequency of \(\approx 1500\ \text{cm}^{-1}\).

Second, the sampling approach exhibits higher intensity of the elastic peak (panel (c)) and lower intensities of the inelastic ones with respect to the correlation method although both techniques employ the same statistics. The origin of the differences in intensities can be mainly traced back to the complex exponential of the gap fluctuations in the dressed transition dipoles, see Eq. (3), as will be shown in detail elsewhere. We believe that this makes RIXS spectra more sensitive to nuclear dynamical correlation effects, since the expression in Eq. (2) contains energy gap fluctuations between different pairs of electronic states. In contrast, the absorption spectrum, Eq. (1), depends only on the initial-final gap fluctuations.
Conclusions and Outlook. The simulation protocol allowing for nuclear dynamical phenomena in X-ray spectra has been developed. This rigorously derived method intrinsically exploits molecular dynamics in the electronic ground state together with a phenomenological dephasing model for core-excited states. As a word of caution, using the latter model leaves cases that exhibit intricate large-amplitude dynamics in the excited state, e.g., ultrafast dissociation outside reach. Still, this technique does provide an improvement to the description of nuclear dynamical effects in X-ray spectra. Importantly, these effects have been demonstrated to be essential for X-ray spectroscopy via the comparison against the conventional sampling approach results for gas phase water. Especially RIXS, being a two-photon process, has turned out to be a sensitive technique for the effects in question. In contrast, XAS, being a one-photon process, exhibits no traces of the underlying nuclear dynamics. Interestingly, static (sampling) and dynamic (correlation) nuclear phenomena have been disentangled from each other experimentally, employing RIXS with excitation pulses strongly detuned from the resonance. Thus, a theoretical prediction of fine nuclear effects is expected to stimulate respective high-resolution experiments.

Remarkably, the developed methodology is rather universal and does not conceptually depend on the accompanying electronic structure method. Further, a similar strategy can be applied to the related photon-in/electron-out techniques, such as photo-electron and Auger spectroscopies as well as to other spectral ranges, e.g., UV/Vis. We believe that these developments are especially important in view of the recently suggested non-linear X-ray techniques that are foreseen to be even more informative and sensitive than the conventional X-ray techniques.

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