PSIXAS: A Psi4 plugin for efficient simulations of X-ray absorption spectra based on the transition-potential and Δ-Kohn–Sham method

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Abstract
Near edge X-ray absorption fine structure (NEXAFS) spectra and their pump-probe extension (PP-NEXAFS) offer insights into valence- and core-excited states. We present PSIXAS, a recent implementation for simulating NEXAFS and PP-NEXAFS spectra by means of the transition-potential and the Δ-Kohn–Sham method. The approach is implemented in form of a software plugin for the Psi4 code, which provides access to a wide selection of basis sets as well as density functionals. We briefly outline the theoretical foundation and the key aspects of the plugin. Then, we use the plugin to simulate PP-NEXAFS spectra of thymine, a system already investigated by others and us. It is found that larger, extended basis sets are needed to obtain more accurate absolute resonance positions. We further demonstrate that, in contrast to ordinary NEXAFS simulations, where the choice of the density functional plays a minor role for the shape of the spectrum, for PP-NEXAFS simulations the choice of the density functional is important. Especially hybrid functionals (which could not be used straightforwardly before to simulate PP-NEXAFS spectra) and their amount of "Hartree-Fock like" exact exchange affects relative resonance positions in the spectrum.

KEYWORDS
transition-potential method, X-ray absorption, X-ray absorption spectroscopy, Δ-Kohn–Sham

1 | INTRODUCTION

X-ray absorption spectroscopy (XAS) is a powerful analytical tool to investigate molecules in the gas phase or adsorbed on surfaces, where an X-ray photon is used to promote the system into a core-excited state. In a one-electron picture, these states are characterized by a core hole, that is, an empty core orbital close to a nucleus that results from the excitation of a core electron into an unoccupied valence orbital. A Near Edge X-ray Absorption Fine Structure spectrum (NEXAFS) is obtained if the absorption cross section is measured as a function of the photon energy.[1] If the core excitation occurs after a valence excitation, so-called pump-probe- or transient NEXAFS (PP-NEXAFS) spectra can be measured.[2–5]

For organic molecules containing N, C or O atoms, one is usually interested in the K-edge, meaning that a 1s electron is excited by an X-ray photon. Because core electron binding energies of different elements in a molecule are energetically well separated, it is possible to probe only a specific element in the molecule. In addition, if atoms of the same element have a different chemical environment, it is even possible to probe specific sites in the molecule. Therefore, NEXAFS and PP-NEXAFS can be element- and site-specific.

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The interpretation of complex experimental spectra can be improved by quantum chemical calculations. A comprehensive review of X-ray absorption simulation techniques has been published recently by Norman and Dreuw. Briefly, one possible choice is to use wave function based methods like coupled-cluster (CC), symmetry adapted cluster configuration interaction (SAC-CI), or the algebraic-diagramatic construction (ADC) method. In general, all of these methods are accurate and reliable. A drawback, however, is the unfavorable scaling of computational costs with respect to the system size. Therefore, only small to medium-sized molecules can be investigated. Alternatively, density functional theory can be used to simulate NEXAFS and PP-NEXAFS spectra. One way is to use techniques based on time dependent density functional theory, another one uses the so-called transition-potential approach in combination with the Kohn–Sham (KS) method. This approach has been successfully used by us and other authors to simulate NEXAFS absorptions of various systems. Recently, we proposed and extension of this method to calculate also PP-NEXAFS spectra.

In this paper, we present a software plugin for the Psi4 quantum chemistry program to calculate primarily NEXAFS and PP-NEXAFS phenomena using the transition-potential and KS techniques. Besides the core functionality to calculate X-ray absorption phenomena, the plugin offers a user-friendly input, a multicore parallelization and access to a large number of basis sets, generalized gradient, hybrid, meta and long-range corrected functionals, and an easy to use interface to visualize the resulting orbitals and spectra. Because of these features, we hope that this software plugin may be of use for other theoreticians or even for experimental researchers working in this field. We may note that other programs like CP2K and StoBe are also able to simulate ordinary NEXAFS spectra within the TP-DFT/KS approach. However, to the best of our knowledge, it is either not possible or rather cumbersome to calculate PP-NEXAFS using these programs. In addition, using hybrid, meta and long-range corrected functionals to simulate PP-NEXAFS spectra is a unique feature of PSIXAS.

In the following, we will briefly outline the theoretical foundations to calculate NEXAFS and PP-NEXAFS spectra, followed by details about the implementation. Then, we revisit the thymine molecule and analyze the importance of larger basis sets with higher angular momentum basis functions and the impact of hybrid, meta and long-range corrected density functionals on the shape of the PP-NEXAFS spectrum. Finally, we conclude our work and give an outlook.

2 | METHODS

As we will outline below, the simulation of NEXAFS and PP-NEXAFS spectra within the TP-DFT/KS approach requires self-consistent Kohn–Sham solutions with orbital occupation patterns different from the ground state. The most important occupation patterns for this work are shown in Figure 1. In the following two sections, we will briefly summarize the approach. For more detailed descriptions, we refer the reader to the original publications.

### 2.1 Ordinary NEXAFS simulations

Within the TP-DFT method, the NEXAFS cross section is calculated by using the Golden Rule expression

\[
\sigma_{\text{GS}}(\omega) = \sum_i \sigma_{\text{GS}}^i(\omega) = C \alpha \sum_i \sum_f \left| \langle \psi_f | \xi | \psi_i \rangle \right|^2 \delta (\epsilon_i - \epsilon_f - \hbar \omega). \tag{1}
\]

Here, \( \sigma_{\text{GS}}^i(\omega) \) is the contribution of an excitation center \( i \), \( C \) is a constant, \( \hbar \omega \) the excitation energy, \( \xi \) is the polarization of the incoming light, \( \psi_i \) represents the initial state for excitation center \( i \) (see below), \( \psi_f \) are all possible final states. \( \epsilon_i \) and \( \epsilon_f \) correspond to initial and final state energies. The \( -\langle \psi_f | \xi | \psi_i \rangle \) are the transition dipole moments with \( \xi = (x, y, z)^T \). The \( \delta \)-functions in Equation (1) are usually replaced by Gaussians with finite width (see below).

The initial and final states and energies correspond to the solutions of a self-consistent Kohn–Sham calculation for a transition-potential state. This is an artificial, auxiliary state where the core orbital of excitation center \( i \) is occupied by only half an electron. Such a state can be seen as a compromise between the ground state, where the core orbital is fully occupied, and the final states where the core orbital is empty. The Kohn–Sham eigenvectors and \( \epsilon \)-values \( (\psi_i, \epsilon_i \) and \( \psi_f, \epsilon_f \) are then used to calculate the NEXAFS cross section for one excitation center \( i \). The main advantage of this approach is that all possible final states are obtained in one calculation. The orbital occupation pattern of the transition-potential state is schematically shown in Figure 1 (denoted as \( \sigma_{\text{GS}}^i(\omega) \)).

The final spectrum is usually further corrected by shifting the whole spectrum to the first core excitation energy

\[
\Delta \epsilon_1 = \epsilon_{\text{ce}}^1 - \epsilon_{\text{gs}}.
\]

Here, \( \epsilon_{\text{gs}} \) is the ground state energy and \( \epsilon_{\text{ce}}^i \) is the first core excited state, that is, where one electron is fully removed from the

![Figure 1: Orbital occupation schemes used to simulate NEXAFS and PP-NEXAFS spectra within the TP-DFT and KS approach. The left three panels (framed in blue) correspond to the calculation of ground state NEXAFS spectra, while the three occupation patterns on the right (framed in red) are used to calculate PP-NEXAFS spectra. The index \( i \) labels the excitation center, where the core hole is created. [Color figure can be viewed at wileyonlinelibrary.com]
core orbital and placed into the lowest, former empty, valence orbital. The occupation patterns that are used to find self-consistent solutions are shown in Figure 1 (denoted as $E_{ee}$ and $E_{ca}$).

Finally, if multiple excitation centers are present, the overall spectrum is obtained by summing over the NEXAFS absorptions of all excitation centers as shown in Equation (1).

2.2 | Pump-probe NEXAFS simulations

In contrast to an ordinary NEXAFS experiment, where all molecules are excited from the electronic ground state, in a pump-probe experiment a certain fraction of molecules is pre-excited (pump) to a valence excited state before the X-ray absorption (probe) takes place. Further, a delay between pump and probe pulse allows the system to relax via internal conversion or intersystem crossing to other states which may be initially optically dark or spin forbidden. These states can then be probed by X-ray.

The PP-NEXAFS spectrum is therefore given by a weighted sum

$$\sigma_{\text{PP-NEXAFS}}(\omega) = p \sum_{\mu} \sigma_{\mu}^{\prime}(\omega) + (1 - p) \sum_{\mu} \sigma_{\mu}^{\prime}\omega(\omega),$$

where $p$ represents the aforementioned fraction of pre-excited molecules. $\sigma_{\mu}^{\prime}(\omega)$ is the cross section for the X-ray absorption that takes place at excitation center $i$ for a valence excited molecule. The occupation pattern used to calculate the transition-potential state is shown in Figure 1 ($\sigma_{\mu}^{\prime}(\omega)$) and the spectrum is calculated according to Equation (1). In addition, a second energy correction is used to shift the spectrum to the lowest-energy transition

$$\Delta E^{\prime} = E_{ca}^{\prime} - E_{ve},$$

where $E_{ve}$ is the energy of the valence excited state and its orbital occupation pattern is depicted in Figure 1 (denoted $E_{ve}$ and $E_{ca}$).

3 | IMPLEMENTATION DETAILS

Before we discuss the details of the implementation, it is worth to list the capabilities a program should have to successfully calculate NEXAFS and PP-NEXAFS spectra. A program needs to:

1. Perform ordinary unrestricted ground state Kohn–Sham calculations.
2. Localize core orbitals, if degenerate.
3. Perform a nonground state unrestricted Kohn–Sham calculation for an arbitrary occupation pattern.
4. Be able to maintain the occupation pattern during the self-consistent field (SCF) procedure.
5. Offer flexibility to control the SCF convergence.
6. Calculate transition dipole matrix elements to obtain the spectrum.
7. Printout the orbitals for postprocessing.

As mentioned before, we chose to write a Python plugin for the Psi4 program. The main advantage is that the plugin can make use of the comprehensive software infrastructure of Psi4 and its Python bindings. For example, typical tasks like user input validation, basis set assignment, the construction of the exchange-correlation functional, the calculation of two electron integrals, the calculation of one-electron matrices and many more are done by using Psi4 capabilities. This allows us to focus efficiently on the algorithms without spending too much time on technical issues. Another example project that makes use of this approach is the Psi4NumPy project, which also inspired the development of PSIXAS.

It is therefore straightforward to implement an ordinary unrestricted Kohn–Sham algorithm using the Psi4 capabilities. The program can use all pre- and user-defined basis sets. All standard LDA, GGA, hybrid, meta, range-separated, and user-defined exchange-correlation functionals (including Hartree-Fock) can be used. Double-hybrid functionals are not supported. To control the convergence behavior, we use density mixing and a direct inversion of the iterative subspace (DIIS) algorithm. To increase performance and decrease hardware requirements, we chose as default the density-fitting (RUK approximation) algorithm, but all other Psi4 options can also be used in the usual way. Once the calculation has converged, the orbitals are written for user inspection in the Mol3den format and for restart/localization purposes in a NumPy format. Then, the core orbitals can be localized (in case they are degenerate), using the Pipek-Mezey algorithm.

To calculate transition-potential, core-excited and valence-excited states, we implemented a nonground state Kohn–Sham algorithm that is able to maintain a user-defined occupation pattern during the self-consistent field procedure. If for example, $|\psi_{\gamma}\rangle$ and $|f_{\gamma}\rangle$ with $\gamma \equiv \alpha$ or $\beta$ are the Kohn–Sham orbitals and occupation numbers, the electron density is given by

$$\rho(\omega) = \sum_{\gamma=1}^{K} |f_{\gamma}\rangle |\psi_{\gamma}\rangle^2 + \sum_{\gamma=1}^{K} |\psi_{\gamma}\rangle |f_{\gamma}\rangle^2,$$

where $K$ is the number of basis functions/molecular orbitals. The orbital indices, orbital spins and orbital occupation numbers are defined with respect to the ground state solution, where $f_{1}, f_{2}, ..., f_{N}$ are equal to one, and $f_{N+1}, ..., f_{K}$ are zero ($N_{\gamma}$ is the number of alpha/beta electrons). Then, for the nonground state calculation the $|f_{\gamma}\rangle$ can take any values between zero and one. In addition, an overlap criterion can be applied to find the orbitals during the self-consistent field procedure in case the energetic order changes. For example, if in the beginning of the calculation the orbital $|\psi_{\alpha,0}\rangle$ is chosen to have a different occupation number, its overlap during the SCF with the current set of orbitals $|\psi_{\mu}\rangle$ can be calculated by

$$p_{\gamma}^{\mu} = \langle |\psi_{\alpha,0}\rangle |\psi_{\mu}\rangle\rangle$$

and

$$p_{\gamma}^{\mu} = \sum_{\mu} \sum_{\gamma} c_{\gamma,0}^{\mu} S_{\mu,\gamma} C_{\gamma,\alpha},$$

where $c_{\gamma,0}^{\mu}$ and $C_{\gamma,\alpha}$ are the coefficients for the basis set expansion $|\psi_{\alpha,0}\rangle = \sum_{\gamma} c_{\gamma,0}^{\mu}|\phi_{\gamma}\rangle$ and $S_{\mu,\gamma} = \langle \psi_{\mu} | \phi_{\gamma}\rangle$ is the overlap matrix for the basis functions $|\phi_{\gamma}\rangle$. The second index (0 or $n$) refers to the 0-th (initial) or
n-th SCF step. Then the occupation number of that orbital having the largest overlap with the initial one is modified. This approach has some similarities with the so-called maximum-overlap-method (MOM) by Gilbert et al.\cite{gilbert1973} and its alternative, the initial-maximum-overlap-method (IMOM) by Barca et al.\cite{barca1983} For both methods all occupied orbitals in SCF step n are those with the maximum overlap with the orbitals of the preceding n-1 step (MOM) or the orbitals of the initial guess (IMOM). Our implementation is different, as we use the overlap criterion for a subset of user-defined orbitals, while the rest is found by the aufbau principle.

Finally, one can choose orbitals to be frozen during the SCF. If the orbital with index \( j \) should be frozen, its off-diagonal elements in the Kohn–Sham matrix (\( F_{ij}^{KS} \)) are set to zero in each step of the SCF

\[
F_{ij}^{KS} = 0 \quad \text{and} \quad F_{ji}^{KS} = 0, \quad \text{for} \quad i \neq j.
\]

Here, \( F_{ij}^{KS} = \langle \psi_i | \hat{F}_{KS} | \psi_j \rangle \) is the Kohn–Sham matrix in the basis of the molecular orbitals, with \( f_{KS} \) being the Kohn–Sham operator. In addition to damping and DIIS techniques, we have found that energetically shifting the virtual orbitals is helpful in some cases.\cite{ehlert2018} Similar to the ground state Kohn–Sham procedure, orbitals are written for visualization and restart purposes. Once the transition-potential states are obtained in a self-consistent way, our program calculates and exports the transition dipole moments which can be used to calculate the absorption cross section.

In addition to using the self-consistent transition state orbitals, it is also possible to use a the double basis technique as done by Ågren et al.,\cite{agren2004,agren2006} in case a better description of Rydberg and continuum states is required. Here, the basis set at the center where the core excitation takes place is augmented with a set of diffuse s, p, and d basis functions as used in StoBe\cite{stobe2008} and Erkale.\cite{erkale2009} The Kohn–Sham matrix is then once diagonalized in this new basis and the resulting molecular orbitals are used to calculate the transition dipole moments.

We introduced a set of keywords to provide sufficient flexibility and to control the flow of the program. All keywords and their options are listed in Table 1. The first eight keywords are used to control the overall behavior of the program. Here, the aforementioned ground and nonground state Kohn–Sham calculations can be selected (using the MODE keyword). For the latter, the options to specify an orbital occupation pattern, activate the overlap criterion and/or freeze

| Keyword | Type       | Options                        | Description                                                                 | Default |
|---------|------------|--------------------------------|-----------------------------------------------------------------------------|---------|
| PREFIX  | String     |                                | Defines the prefix for filenames                                            | KS      |
| MODE    | String     | [GS, LOC, EX, SPEC]            | Defines what calculations should be run                                      | GS      |
| ORBS    | List of integers | [Oi]; i = 1..N | Defines the indices of orbitals to be modified                             | -       |
| OCCS    | List of float | [fi]; i = 1..N     | Defines the occupation numbers                                              | -       |
| SPIN    | List of chars | [si]; i = 1..N; s ∈ {a, b} | Defines the spins of the orbitals                                            | -       |
| OVL     | List of chars | [OVL_i]; i = 1..N; OVL_i ∈ {T, F} | OVL_i defines if overlap criterion is applied for orbital O_i               | -       |
| FREEZE  | List of chars | [FRZ_i]; i = 1..N; FRZ_i ∈ {T, F} | FRZ_i defines if orbital O_i should be frozen                              | -       |
| USE_AUG | Bool       | True/False                    | Use the double basis formalism                                              | False   |
| E_GS_CONV | Double     | X                              | Sets energy convergence criteria for the GS calculation                       | 1.0E–8  |
| E_EX_CONV | Double     | X                              | Sets energy convergence criteria for the EX calculation                      | 1.0E–6  |
| D_GS_CONV | Double     | X                              | Sets density convergence criteria for the GS calculation                      | 1.0E–6  |
| D_EX_CONV | Double     | X                              | Sets density convergence criteria for the EX calculation                      | 1.0E–4  |
| DAMP    | Double     | X                              | Sets the amount of density mixing                                           | 0.8     |
| MAXITER | Integer    | X                              | Sets the maximum number of SC iterations                                    | 100     |
| VSHIFT  | Double     | X                              | Sets the shift applied to virtual eigenvalues [eV]                          | 0.0     |
| DIIS_MODE | String   | [CDIIS, ADIIS + CDIIS]         | Sets the version of DIIS that should be used                               | ADIIS + CDIIS |
| DIIS_LEN | Integer    | X                              | Length of the DIIS vectors                                                 | 6       |
| DIIS_EPS | Double     | X                              | Sets the energy threshold when to start DIIS [Ha]                           | 0.1     |
| LOC_SUB | List of integers | [Li]; i = 1..M | Defines a subset of orbitals to be localized                              | -       |

Note: The keywords in the upper part of table control the general program behavior. Below are the keywords used to control the self-consistent field convergence behavior and the localization algorithm.
individual orbitals are provided. In the lower part of the table, the keywords that control the SCF convergence and the localization algorithm can be found.

4 | RESULTS AND DISCUSSION

4.1 | A PP-NEXAFS example

In the following, we present the results of a PP-NEXAFS simulation applied to the O-K edge of thymine, which was recently investigated by us.\textsuperscript{[39]} For this system experimental spectra and simulations based on the correlated coupled cluster method exist.\textsuperscript{[14]} The experimental peak positions will serve as reference for the simulations. The molecule and the labels for the two oxygens are shown in Figure 2.

The characteristics of the resonances in the NEXAFS and PP-NEXAFS simulations have been already discussed in detail in Ehlert et al.\textsuperscript{[39]} Very briefly, the ground state O-K NEXAFS spectrum of thymine exhibits two resonances, each the results of an oxygen 1\textit{s} \rightarrow \pi^* excitation. The pump-probe (\textit{n} \pi^*)-NEXAFS spectrum has two additional resonances which can be assigned to O 1\textit{s} \rightarrow \textit{n} transitions, where the O2 1\textit{s} \rightarrow \textit{n} resonance is significantly more intense (the O1 1\textit{s} \rightarrow \textit{n} resonance will be neglected in the following).

Instead of discussing the detailed spectrum, we will focus primarily on the new features offered by PSIXAS. This includes the elaboration of larger basis sets with higher angular momentum functions and the use of more advanced density functionals for the simulation of the spectra. In the previous approach,\textsuperscript{[39]} the choice of exchange-correlation functionals was restricted to a limited set of local density and generalized gradient approximations. In addition, basis functions with angular momentum quantum numbers higher than two were neglected.

All spectra are calculated for a geometry, which was optimized using Psi4 and the same functional and basis set as for the PP-NEXAFS calculations. See Appendix and the supporting information for a set of example input files to calculate the PP-NEXAFS-spectrum for B3LYP/def2-SVP (see below). We assume a fraction of $\rho = 13\%$ of pre-excited molecules in a randomly oriented ensemble and use Gaussians with a full width at half maximum (FWHM) of 0.8 eV for the spectra shown in Figure 3 as done in Ehlert et al.\textsuperscript{[39]} For the resonance positions given in Tables 2 and 3, we use the overall spectrum and extracted the corresponding local maxima of the peaks. We may note that relativistic effects are completely neglected in the current approach. As shown in a study by Takahashi and Pettersson\textsuperscript{[57]} these effects are supposed to uniformly shift the O-K spectrum by approximately 0.3 eV toward higher energies.

4.1.1 | Basis set dependence

In Table 2, the basis set dependence of the aforementioned resonance positions is shown. All spectra simulations were done using the B3LYP\textsuperscript{[58,59]} density functional and the Karlsruhe basis sets.\textsuperscript{[60]} In addition to the absolute peak positions, the table also provides relative resonance positions.

From the numbers given in Table 2, one can derive the following conclusions:

1 All resonance positions are red shifted if larger basis sets are used. For example, when going from the double-zeta def2-SVP to the quadruple-zeta def2-QZVPD basis set, all resonance positions are shifted almost uniformly by 2.6 eV. This effect can be assigned to better description of the electron relaxation that follows the creation of the core-hole. For the largest basis set, however, the first two resonance positions are actually below the experimental values.

2 The relative peak positions are not affected by the basis set size.

3 Adding diffuse functions does not change the positions of first resonances in a spectrum. Therefore, the aforementioned double basis

FIGURE 3  (a) Simulated PP-NEXAFS spectra of thymine for BLYP, B3LYP, PBE0, B97-K, and BHANDHLYP as implemented in Psi4 (all calculation with the def2-QZVPD basis set). The vertical blue lines indicate the experimental resonance positions.\textsuperscript{[14]} (b) The same set of simulated PP-NEXAFS spectra as in (a) with the O2 1\textit{s} \rightarrow \pi^* resonance shifted to 0 eV. The experimental value of $-\delta_2$ is indicated by the vertical red line [Color figure can be viewed at wileyonlinelibrary.com]
technique can be omitted here, as the final states of interest do not
have continuum or Rydberg character.

4 For the large basis sets, the peak positions are in good agreement
with the experiment. The main deviations are slightly larger $\delta_1$
values, that is, larger energetic separations of the two $O\,1s \rightarrow \pi^*$
resonances.

5 Basis set convergence is faster if the basis set is decontracted for
the oxygen atoms. Because of the locality of the excitation process,
rapid improvements of resonance positions are obtained if more
basis set flexibility is provided at the corresponding excitation cen-
ters. This can be a reasonable and economic approach especially
for larger systems.
4.1.2 Functional dependence

One additional feature of PSIXAS is the capability to make use of several hybrid, meta and long-range corrected density functionals within the TP-DFT/Δ-KS approach. Especially for the case of PP-NEXAFS spectra, hybrid functionals can play an important role, because of their known influence on the energy gap between the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbital. We use all functionals as implemented through the LibXC library in the Psi4 program. In Table 3, we list the absolute and relative resonance positions as a function of the exchange-correlation functional. The def2-QZVPD basis set has been used for spectra simulations and geometry optimizations, which have been done for each functional. Note, that for HF and BHANDHLYP the energetic order of the O 1s MOs is exchanged compared to all other functionals, which show the same ordering as given in the example inputs (see Appendix).

The first observation is that the LDA functionals (SVWN, TETER93 and KSDT) perform rather poor with respect to the absolute resonance positions, while the relative resonance positions are still acceptable. The group of GGA (PBE, BLYP, HCTH120) and pure META (TPSS, RREVTPSS) functionals do better and the absolute resonance positions are all close to the experiment. The relative resonance positions do not change significantly within the group of GGA and pure META functionals. However, when taking a look at functionals that incorporate Hartree-Fock like exchange, namely global hybrid (B3LYPS, B3LYP, PBE0, B97-K, BHANDHLYP), long-range corrected (ωPBE, ωB97X, CAM-B3LYP) and meta-hybrid functionals (TPSSH), one observes that the gaps between O2 1s → n and O2 1s → π* resonances increase depending on the amount of exact exchange used in the functional. This is exactly what one would expect from ground state calculations, where exact exchange shifts occupied orbitals toward lower energies and unoccupied orbitals to higher energies. When going from TPSSH with an exact exchange of 10% to BHANDHLYP with an exact exchange of 50%, the difference between the O2 1s → n and O2 1s → π* resonances increases by 0.6 eV. However, the difference between the resonances arising from the O2 1s → π* and O1 1s → π* is also affected and increases by 0.4 eV, which slightly reduces the agreement with the experiment. Therefore, the amount of exact exchange is a key ingredient to model PP-NEXAFS spectra accurately within the TP-DFT/Δ-KS approach.

These findings are illustrated in Figure 3 for selected global hybrid functionals with different amounts of exact exchange, that is, BLYP, B3LYP, PBE0, B97-K, and BHANDHLYP. In Figure 3a the simulated PP-NEXAFS spectra are given and vertical blue lines indicate the experimental resonance positions. All spectra seem to be rather similar and scatter around the experimental values with acceptable error margins. However, in Figure 3b the same spectra are shown, but this time shifted in a way that the O2 1s → π* resonance is centered around 0 eV. In this graph one can clearly see that δ2, that is, difference between the O2 1s → n and O2 1s → π* resonances, indeed depends on the amount of exact exchange, as stated above. In addition the increase of δ1, that is, the splitting of the two O 1s → π* resonances, as a function of the exchange can be observed. For this selection of functionals, we find that B97-K and BHANDHLYP perform best with respect to relative resonance positions. The latter also provides the best absolute resonance positions compared to the experiment in this group of functionals.

One can also examine the dependence of simulated resonance positions as a function of the amount of exact Hartree-Fock like exchange by constructing user defined functionals. This is shown in Table 4, where we used the BLYP functional as a template to construct four additional functionals with varying ratios of B88 and exact exchange. In order to focus on only one parameter, we calculated the spectra at the minimum geometry of BLYP. Again we find that the energy gap between the O2 1s → n and O2 1s → π* resonances increase with higher admixtures of exact exchange. This is mainly caused by a red shift of the O2 1s → n resonance, which shifts by 0.8 eV from BLYP to BLYP-100. On the other side, the O2 1s → π* resonance is blue shifted by only 0.2 eV. Further, the gap between the two 1s → π* resonances is also slightly affected and increases from 1.4 to 2.2 eV. The best overall resonance positions relative to the experimental values are obtained for BLYP-50 and BLYP-75, again a rather high amount of exact exchange.

Finally, it is worth to discuss a special aspect of long-range corrected density functionals. These functionals treat the exchange interaction between electrons differently for different interelectronic

| Functional % HF-X | Experiment[14] | O2 1s → n | O2 1s → π* | O1 1s → π* | δ1 | δ2 |
|-------------------|--------------|-----------|------------|------------|----|----|
| User defined      | BLYP         | 0         | 526.5      | 530.9      | 532.3 | 1.4 | 4.4 |
|                   | BLYP-25      | 25        | 526.4      | 531.0      | 532.5 | 1.6 | 4.6 |
|                   | BLYP-50      | 50        | 526.2      | 531.0      | 532.8 | 1.7 | 4.8 |
|                   | BLYP-75      | 75        | 525.9      | 531.1      | 533.1 | 2.0 | 5.1 |
|                   | BLYP-100     | 100       | 525.7      | 531.1      | 533.3 | 2.2 | 5.4 |
|                   | BLYP-150     | 150       | 525.0      | 531.0      | 533.2 | 2.1 | 5.2 |
|                   | BLYP-200     | 200       | 524.5      | 530.9      | 533.1 | 2.0 | 5.1 |
|                   | BLYP-250     | 250       | 524.0      | 530.8      | 533.0 | 2.0 | 5.0 |
|                   | BLYP-300     | 300       | 523.5      | 530.7      | 532.9 | 2.0 | 5.0 |
|                   | BLYP-350     | 350       | 523.0      | 530.6      | 532.8 | 2.0 | 5.0 |
|                   | BLYP-400     | 400       | 522.5      | 530.5      | 532.7 | 2.0 | 5.0 |
|                   | BLYP-450     | 450       | 522.0      | 530.4      | 532.6 | 2.0 | 5.0 |
|                   | BLYP-500     | 500       | 521.5      | 530.3      | 532.5 | 2.0 | 5.0 |

Note: A set of user defined exchange-correlation functionals based on the BLYP functional has been used. All calculations have been done with the def2-QZVPD basis set and at the optimized BLYP geometry. Note, that δ1 and δ2 are calculated in full accuracy before rounding.
5 SUMMARY AND OUTLOOK

In summary, we present a plugin for the Psi4 software package which allows the simulation of NEXAFS and PP-NEXAFS spectra within the TP-DFT/Δ-KS approach. The core capability of the plugin is to find self-consistent nonground state Kohn–Sham solutions for a given occupation pattern. This is accomplished by overlap and freezing techniques. In addition, the plugin provides access to a wide selection of basis sets and LDA, GGA, META, LRC, and hybrid density functionals. Applied to the case of thymine, we find that larger basis sets are needed to provide a better description of electron relaxation effects. As a result, better absolute resonance positions can be obtained, while relative peak positions are not affected. On the other side, the use of functionals that incorporate exact exchange has a direct influence on the relative resonance positions in the PP-NEXAFS spectra. For thymine, best results with respect to relative peak positions have been obtained with the (IP-fitted) ωB97X and BHANDHLYP functionals, the latter having a rather high amount of global exact exchange. It remains to future investigations to find out if these functionals are in general more accurate for PP-NEXAFS simulations, or if the amount exact exchange needs to be adjusted for each individual system.

In the near future, we will focus on expanding the capabilities and functionalities of PSIXAS. On the DFT side, a recent paper by Halt et al.[65] demonstrates good accuracy by using the restricted open-shell Kohn–Sham (ROKS) method in combination with the square gradient minimization.[66] On the side of wave function based methods, we will focus on efficient techniques based on configuration interaction[17] and extend them for PP-NEXAFS spectra.

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SUPPORTING INFORMATION
Additional supporting information may be found online in the Supporting Information section at the end of this article.

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APPENDIX
Example inputs B3LYP/def2-SVP
The following example input files can be found in the supporting online information (⇒ indicates calculated quantities, cf. Figure 1):

1. \( \text{tp-gs-MO-0.txt} \Rightarrow \sigma^{0}_{\sigma}(\omega) \)
2. \( \text{tp-gs-MO-1.txt} \Rightarrow \sigma^{1}_{\sigma}(\omega) \)
3. \( \text{ce-MO-0.txt} \Rightarrow E_{ce}^{0} \)
4. \( \text{ce-MO-1.txt} \Rightarrow E_{ce}^{1} \)
5. \( \text{tp-ve-MO-0.txt} \Rightarrow \phi^{0}_{ve} \)
6. \( \text{tp-ve-MO-1.txt} \Rightarrow \phi^{1}_{ve} \)
7. \( \text{ve.txt} \Rightarrow E_{ve} \)

Further information and the plugin can be found at https://github.com/Masterluke87/psixas