The role of Hartree–Fock exchange in the simulation of X-ray absorption spectra: A study of photoexcited \([\text{Fe(bpy)}_3]^{2+}\)

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**A B S T R A C T**

We present a theoretical analysis for the K- and L\textsubscript{2,3}\textsuperscript{-edge static and picosecond X-ray absorption spectra of \([\text{Fe(bpy)}_3]^{2+}\). Simulations of the pre-edge region at the Fe K-edge using time-dependent density functional theory demonstrate the importance of Hartree–Fock exchange within the exchange–correlation functional, especially when describing charge transfer and 1s–3d transitions. This becomes particularly relevant for range separated functionals, for which the incorporation of Hartree–Fock exchange at short range decreases the absolute error in the excitation energy usually observed using TD-DFT. Finally, we compute and interpret the L\textsubscript{2,3}\textsuperscript{-edge spectrum using the Restricted Open-Shell Configuration Interaction Singles method.**

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**1. Introduction**

Advances in the experimental methodologies of time-resolved X-ray absorption spectroscopy (XAS) \cite{1,2} have made it possible to extract information about the evolving geometric and electronic structure of a molecule during a chemical reaction with picosecond \cite{3} to femtosecond \cite{4} resolution. In parallel, a number of theoretical developments led to approaches capable of a quantitative description of both the static and transient spectra. Important in the context of this work is the extension of traditional electronic structure approaches to core–hole excitations \cite{5–8} among which, the most widely used is time dependent density functional theory (TD-DFT).

Here, the linear-response TD-DFT eigenvalue equation \cite{9}, usually within the Tamm–Damcoff approximation (TDA) \cite{10}, is projected onto a manifold of core to valence excitations \cite{7,11}, providing an accurate and simple methodology for computing pre-edge intensities. For all TD-DFT simulations the asymptotic behaviour of the exchange–correlation \((x-c)\) functional as \(r \to \infty\) is important for obtaining an accurate description of the excited states \cite{12,13}. In addition, for core excitations, the potential as \(r \to 0\), i.e. close to the nucleus, also becomes important and has been previously shown also to have the wrong asymptotic behaviour for most functionals \cite{14}. These failures stem from the approximate exchange within the \(x-c\) functionals and are associated with the self interaction error (SIE) \cite{13}. However, while several solutions to the CT problem in TDDFT have been proposed, very little has been done on core-excitations that are post-correlated by applying a constant energy shift to the calculated spectrum \cite{15}.

For core–hole excitations using TDDFT, both the relative separation between the transitions and the absolute error in the excitation signals must be addressed. While the former is the most important, the increasing resolution of static and time-resolved signals means that it is also important to quantify \cite{16} and/or remove the error of the transition energies, and, accordingly the somewhat arbitrary shift applied to the calculated transitions. The use of hybrid functionals can reduce the problem \cite{17}, as the constant fraction of Hartree–Fock exchange (HFX) in the electron repulsion operator partially removes the SIE. However, despite improving the situation for a variety of chemically interesting problems, the residual SIE and the inherent local nature of the \(x-c\) potential means that errors, such as the CT problem, can still remain. Alternatively, an increasingly popular approach is the so-called range separated (RS) functionals, for which the amount of HFX incorporated into the electron repulsion operator is partitioned into short and long-range (SR/LR) components \cite{18}. Mixing a large fraction of HFX into the LR component has a rich history \cite{19,20} and significantly improves the description of CT states. Based on the same idea, it has recently been demonstrated that

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an improvement in the absolute energy of core-level excitations can be obtained by including the large fraction of HFX at SR which reduces the SIE for the localised core orbitals [21,23,22].

In this work, we perform an analysis of the static and picosecond X-ray absorption spectra of the spin crossover complex [Fe(bpy)3]2+ [24] at both the K- [25,26] and L2/3-edges [27,28]. Using the B3LYP functional we demonstrate that HFX is critical for obtaining the correct spectral shape. The short-range corrected (SRC) functional [22] shows that a high proportion of HFX close to the nucleus significantly reduces the error of the transition energies, while retaining a good description of the low spin spectrum. Finally, using a combined DFT and restricted open-shell configuration interaction method (DFT/ROCIS) [29–32], we calculate the L2/3-edge of the low- and high-spin states and demonstrate not only good agreement between experiment and theory, but also the connection between the features appearing in the K- and L2/3-edge spectra.

2. Methods

2.1. Theoretical and computations

Throughout this work we use the low spin (LS) and high spin (HS) structures of [Fe(bpy)3]2+ optimised by EXAFS [26]. The simulations using the BLYP and B3LYP functionals were performed using ORCA [29], while those using the SRC functional [22] were performed using Q-Chem [33]. A TZVP basis set was used throughout and the TD-DFT equations were solved for 50 states, within the TDA. For both functionals the calculated spectra have been corrected for scalar relativistic effects computed with the Douglas–Kroll–Hess Hamiltonian [34]. They were then shifted so that the 1s → Metal–Ligand Charge Transfer (MLCT) transition is aligned with the second feature of the experimental spectrum. This shift correlates with the error in the absolute excitation energy and is summarised in Table 1. The transient spectrum is calculated by subtracting ground state spectrum from the high-spin spectrum and scaling by the photoysis yield which, in close agreement with previous experiments, is 0.65 [35].

The Exr for B3LYP [36] is well known and expressed:

\[
Exr = c_1E_{c\text{LDA}} + c_2E_{c\text{BS}} + c_3E_{c\text{HF}} + c_4E_{c\text{HFX}} + (1 - c_4)c_5E_{c\text{VWN}}. \tag{1}
\]

where \(E_{c\text{LDA}}\) is the Slater exchange, \(E_{c\text{BS}}\) is Becke’s gradient correction for the exchange [37], \(E_{c\text{HF}}\) is the HFX energy, \(E_{c\text{HFX}}\) [38] and \(E_{c\text{VWN}}\) [39] are the correlation energies and the parameters are \(c_1 = 0.80, c_2 = 0.72, c_3 = 0.20\) and \(c_4 = 0.81\). \(c_5\) dictates the amount of HFX incorporated into the functional, therefore the changes discussed below related only to this parameter.

| Table 1 | The experimental and calculated (as a function of HFX), AEexr, i.e., the energy difference between the ground state and lowest quintet states. \(^*\) The core-level excitation energy error. The units for both AEexr and the excitation error are eV.
|---------|---------|---------|--------|
| HFX | AEexr | Error \(\text{Exr}\)
| SR (%) | LR (%) | Error (eV) |
|____ | ____ | ____ | ____ |
| Expt | 0.43–0.73 [44] | – | – |
| BLYP | – | 1.58 | 94.7 |
| B3LYP | – | 1.21 | 66.8 |
| SRC | – | 0.85 | 62.2 |
| – | 0.52 | 57.0 |
| – | 0.21 | 51.9 |
| – | 0.57 | 0.7 |
| – | 0.34 | –0.2 |
| – | 0.11 | –1.0 |
| – | –0.05 | –1.8 |

For the SRC, the principal difference is the partitioning of the electron repulsion into SR and LR components using:

\[
\frac{1}{r_{12}} = \frac{1}{c_{\text{SR}}} \text{erfc}\left(\frac{\gamma_{\text{SR}} r_{12}}{r_{12}}\right) - \frac{1}{c_{\text{LR}}} \text{erfc}\left(\frac{\gamma_{\text{LR}} r_{12}}{r_{12}}\right) + \frac{1}{c_{\text{LR}}} \text{erf}\left(\frac{\gamma_{\text{LR}} r_{12}}{r_{12}}\right) - \frac{1}{c_{\text{SR}}} \text{erf}\left(\frac{\gamma_{\text{SR}} r_{12}}{r_{12}}\right)
\]

(2)

Here, \(\gamma_{\text{SR}}\) is the HFX energy, \(\gamma_{\text{LR}}\) are the error function kernel parameters which are set to 2.20a_0^{-1} and 1.80a_0^{-1}, respectively throughout.

The L2/3-edge spectra were calculated using the DFT/ROCIS method [30–32]. The equations were solved for 50 excited states and includes spin orbit coupling (SOC) through the quasi-degenerate perturbation theory [41]. In addition, because HF theory represents a poor starting wavefunction for transition metal complexes, open-shell B3LYP Kohn–Sham orbitals, were used as the reference orbitals. Following their calculation the spectra were shifted by 11 eV to match the experiment.

The experimental data for the static and the picosecond XAS experiments has been previously presented in Ref. [35]. The High Energy Resolution Fluorescence Detection (HERFD) spectrum was obtained using the standard setup implemented at the ESRF, Grenoble and has a higher resolution than traditional data acquisition methods owing to the reduced lifetime broadening [42,43]. The L2/3-edge ground state spectrum has been reproduced from Ref. [27] and its transient spectrum from Ref. [28].

3. Results

3.1. Simulating the \(K\)-edge

3.1.1. Excitation energy error

Figures 1 and 2 show the spectra calculated using the B3LYP and SRC functionals, respectively. The corresponding excitation energy errors are summarised in Table 1. The BLYP functional, which in the absence of HFX exhibits the largest SIE, has an error of 94.7 eV, which diminishes by ~30 eV upon inclusion of HFX. This shift, which is largest for 5% HFX points to a non-linear dependence of the excited error vs the proportion of HFX. For the SRC functional, the error is almost completely removed, as a consequence of the much larger percentage of HFX at SR further reducing the inherent SIE of the core electrons. Given that the present range-separated parameters were fitted for 2nd row elements [22] these results demonstrate a good transferability of this approach.

3.1.2. The static spectrum

Figure 1 (upper panel) shows the pre-edge region of the Fe K-edge using the standard X-ray absorption data acquisition procedure (red line) and the HERFD spectrum (black line). The effect of the line sharpening is apparent as the one broad pre-edge feature, previously assigned as 1s→3d [26] is resolved into three distinct features.

The spectrum calculated using the BLYP functional (Figure 1 second panel, 0% HFX) exhibits two features at 7.1145 and
7.1155 keV which have, in order of energy a predominantly MLCT (1s\textsubscript{Fe} \rightarrow \pi_{\text{ligand}}) and 1s\rightarrow 3d character. However, upon inclusion of 5\% HFX the character of the two principal features are exchanged with the lowest transition becoming 1s\rightarrow 3d. The shift of this transition to lower energies relative to the MLCT transition continues as the amount of HFX is increased and the best agreement with experiment is found for between 10–15\% HFX. A similar case was also observed in the study of the manganese K-edge of [Mn(II)(tpa)(NCS)]\textsubscript{2} [45]. Here, the authors attributed the shift of the 1s\rightarrow 3d transition relative to the MLCT transitions to the CT problem within TD-DFT, which lessens by increasing amounts of HFX. For our present complex, although the inclusion of HFX improves the description of CT excitations, it also overestimates the \( t_{2g} \rightarrow e_{g} \) splitting, owing to the neglect of electron correlation in HF theory [46]. The consequence of this is to reduce the energy difference between the LS and HS configurations (\( \Delta E_{\text{el}} \), Table 1) and correspondingly reduce the energy of the 1s\rightarrow 3d (\( e_{g} \)) transition. This effect was not discussed in Ref. [45] due to the stronger ligand field effects of the complexes studied. Reiher et al. [47] have previously shown that the separation between the LS-HS transition energy is underestimated within B3LYP for a range of weak ligand field iron complexes and concluded that 15\% HFX, provides a more accurate representation. Our present results demonstrate that this reparametrisation also holds for the case of core hole spectra and we find that the best agreement with experiment is achieved with
10–15% HFX. In this case, the spectrum exhibits all three 1s→3d ($e_g$) and two MLCT transitions spectral features and the energy separation between them closely matches the experiment.

Figure 2 shows the variation of HFX for the range-separated SRC functional [22] for which the amount of HFX at Sr is kept fixed at 87% and only the LR component is varied. The present implementation approximates the interaction of the X-ray field to the dipole moment and therefore for comparison the dotted lines show the dipole only component of Figure 1. This leads to a loss in oscillator strength for the first (1s→3d) transition, however the pseudo-octahedral geometry of the complex means that 3d/4p mixing is possible and therefore the small dipole contributions (1s→4p) means that the transition strength is not zero. The spectral shape of the two approaches exhibits similar trends, indicating that the large percentage of HFX at short exchange does not have a large effect on the oscillator strengths. The largest difference between the SRC and B3LYP functionals is seen for the energy between the 1s→3d and MLCT transitions, which is larger for the former because, as shown in Table 1, the large HFX at Sr increases $\Delta E_{\text{hl}}$. As a consequence, we find the best agreement with the experimental spectrum is with 5% HFX in the LR component.

These results show that the range-separated SRC functional effectively removes the error in the excitation energies and the need for a post-calculation shift of the spectrum. However, the significant portion of HFX at short exchange affects the transition energies as demonstrated by the shift to lower energies of the 1s→3d transition. Consequently, the portion of HFX at long range has to be reduced to 5%, in contrast to 10–15% found for B3LYP.

### 3.1.3. The transient spectrum

Calculating the transient spectrum represents a more challenging case, because both the relative energies and oscillator strengths must be in excellent agreement with the experiment. The black trace in Figure 3 shows the experimental spectrum in the pre-edge region of the Fe K-edge spectrum of [Fe(bpy)$_3$]$_2^{2+}$ (HS–LS). Despite the larger broadening used (FWHM = 2.5 eV) to match the experimental resolution, we observe significant differences between the transient calculated with the different functionals. The BLYP functional (magenta line), like all of the calculated spectra exhibits a positive feature at ~7.112 keV, in agreement with the experiment, which arises from transitions into the $t_{2g}$ orbitals accessible for the high-spin configuration. However neither of the proceeding

![Figure 3](image)

**Figure 3.** The 50 ps transient (i.e. HS – LS) pre-edge region of the Fe K-edge of [Fe(bpy)$_3$]$^{2+}$. The experiment is the black line, BLYP = magenta, B3LYP (20% HFX) = green, B3LYP (15% HFX) = red and B3LYP (10% HFX) = blue. Each of the calculated spectra have been broadened with a Gaussian function with full width half maximum (FWHM) = 2.5 eV. (For interpretation of the references to colour in this figure caption, the reader is referred to the web version of this article.)

negative (7.114 keV) or positive (7.117 keV) features are reproduced. This is because, as shown in Figure 1 the states are in the wrong order and the MLCT transition which appears between the 1s→3d ($t_{2g}$) and 1s→3d ($e_g$) transitions nullifies the negative feature.

In contrast, the green line shows the transient spectrum calculated using the standard B3LYP functional, i.e. with 20% HFX. Here, the spectrum exhibits the correct profile, although it is too broad and the positive features at 7.112 and 7.117 keV occur slightly too low and high in energy, respectively. This is a consequence of the exaggerated $t_{2g}$–$e_g$ splitting as described previously for the LS spectrum. In agreement with this previous analysis, reducing the amount of HFX to 10% (blue line) improves the spectrum, but the best agreement is found for the spectrum calculated using 15% HFX. As shown in Table 1, this amount of HFX not only remedies the CT excitations, but also yields the correct $\Delta E_{\text{hl}}$, i.e., the energy difference between the low and high spin states.

Finally, for this present study the absence of quadrupole transitions for the SRC functional makes it difficult to obtain a good description of the transient spectrum, highlighting the importance of including them for core hole excitations [48]. In common with the observations of Figure 2, the transient spectrum of SRC was very similar to the dipole only transient spectrum calculated using B3LYP. However, the absence of 1s→3d intensity meant that neither gave good agreement with the experimental transient, and they are therefore not shown.

### 3.2. Simulating the $L_{2,3}$-edges

In contrast to the K-edge which can be accurately simulated using the one-electron picture, the $L_{2,3}$-edges usually require a more sophisticated description and in particular a careful treatment of multiplet and spin–orbit coupling effects. Here we use the DFT/ROCIS method implemented within ORCA. Figure 4(a) shows the $L_{2,3}$-edge spectrum of the LS complex [27] (black = experiment and red = theory) and the HS complex (blue). The corresponding experimental transient spectrum (i.e. HS–LS) is shown in Figure 4(b), and is reproduced from Ref. [28].

The calculated LS spectrum is in good agreement with the experiment, and both the $L_2$ and $L_3$ edges exhibit two distinct peaks, separated by ~1.75 eV. The first corresponds to a 2p–3d (45%)+MLCT (55%) (Figure 5) transition, while the smaller shoulder corresponds to higher MLCT transitions, which becomes allowed through a small mixing with the Fe 3d orbitals. The calculated HS spectrum (Figure 4(a), blue line) exhibits a ~2.0 eV shift of the main transition to lower energy. In addition, there is also a small shoulder on the low energy side of the main absorption peak, which corresponds to transitions into the 3d ($t_{2g}$) orbitals, vacant in the HS configuration. The separation of these two features is ~1.7 eV and is in good agreement with the splitting of the d-orbitals in the high spin configuration which is 10Dq = 1.55 eV [28]. Figure 4(b) shows the transient (i.e. HS–LS) $L_{2,3}$-edges for [Fe(bpy)$_3$]$^{2+}$ [28]. The DFT/ROCIS calculations achieve good agreement with the experiment, and demonstrates that the spectrum is dominated by the red shift (2.0 eV) in the spectrum synchronous with the LS to HS transition due to the reduced $t_{2g}$–$e_g$ splitting of the HS complex.

Finally, the availability of high resolution K pre-edge and $L_{2,3}$-edge spectra allows us to make a direct comparison between the features appearing in the two spectra as shown in Figure 5. Such comparisons can be useful in assessing the distribution of the metal p- and d-orbitals throughout the valence orbitals, the magnitude of configuration mixing and for obtaining a more definitive assignment of the spectral features. For the K-edge, the lowest feature (7.113 keV) is 1s→3d transition and is relatively weak because it is dipole forbidden. The transition to the same 3d orbitals from
the 2p core hole corresponds to the strong first (dipole allowed) resonance in the L2/3-edges. However, the transition is shifted to slightly higher energies owing to the configuration mixing with the MLCT transitions (Figure 5) which occurs at slightly higher energy, and corresponds to the second transition in the K pre-edge spectrum. This mixing of the 2p → 3d and MLCT is approximately 50%/50%, but the intensity of the feature is primarily determined by the former (2p → 3d) dipole allowed transition. Finally, the third transition (higher MLCT) in the K-edge correspond to orbitals which have a small amount of 4p mixing and 3d mixing. As a consequence, it is weak in both the K- and L2/3-edge spectra.

4. Conclusions

We have presented computations of the Fe K-edge for [Fe(bpy)_3]^{2+} and demonstrated that 15% HFX within the B3LYP functional, in contrast to the standard 20%, is required to achieve a good description of both the steady state and picosecond X-ray absorption spectrum. However, the absolute excitation energies are still too small and the entire spectrum requires an empirical shift of ~60 eV. Using the SRC functional, we have shown that the incorporation of a significant portion of HFX at short range reduces the error in the absolute absorption spectrum to ~ 1 eV.

The spectral shape is altered slightly, especially for the 1s → 3d transition. However these changes are not large and this work represents an exciting starting point for for the extension of this approach to a wide range of transition metal complexes.

Using the DFT/ROCIS method we have presented simulations of the L2/3-edge of [Fe(bpy)_3]^{2+}. These simulations provide good agreement with the experimental spectra and permit the interpretation in terms of the important molecular orbitals. We have also been able to provide an interpretation of the features arising in both spectra and their relationship with respect to selection rules.

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