Generalized single excitation configuration interaction: an investigation into the impact of the inclusion of non-orthogonality on the calculation of core-excited states

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In this paper, we investigate different non-orthogonal generalizations of the configuration interaction with single substitutions (CIS) method for the calculation of core-excited states. Fully non-orthogonal CIS (NOCIS) has been described previously for singlets and doublets and this paper reports the extension to triplet molecules. In addition to NOCIS, we present a novel method, 1C-NOCIS(1C-NOCIS), for open-shell molecules which is intermediate between NOCIS and the static exchange approximation (STEX). We explore this hierarchy of spin-pure methods for singlet, doublet, and triplet molecules and conclude that, while NOCIS provides the best results and preserves the spatial symmetry of the wavefunction, 1C-NOCIS retains much of the accuracy of NOCIS at a dramatically reduced cost. For molecules with closed-shell ground states, STEX and 1C-NOCIS are identical.

I. INTRODUCTION

X-ray absorption spectroscopy (XAS) is a growing area of study with great potential, due in large part to its element specificity and sensitivity to chemical environment^{1,2}. As synchrotron radiation becomes more accessible, XAS becomes increasingly powerful and able to study more systems. In addition to synchrotron-based experiments, smaller XAS set-ups are also now being used in time-resolved experiments³. Therefore, the identification of characteristic peaks is of increasing importance. This is especially true for species with an open-shell ground state, and experimentalists face the difficult job of assigning peaks and identifying the source of peak shifts⁴. At the same time, sensitivity to environment suggests that XAS may be a powerful reporter on excited states and even electron dynamics. Theoretical calculations with a good balance of efficiency and accuracy can greatly facilitate the task of assigning XAS spectra.

There are many different approaches to calculations of core-excited states. Early methods used multiple scattering X_α ⁵ and transition potential calculations⁶, but since then ab-initio quantum methods have dominated the field. Currently, the common methods used for core excitations are time-dependent density functional theory (TDDFT)⁷⁻¹², Δ -SCF and Δ -DFT¹³, equation of motion coupled-cluster methods¹⁴⁻²⁴, algebraic diagrammatic construction (ADC) methods²⁵⁻³¹, and configuration interaction singles (CIS)³²⁻³⁴. The general benefits and pitfalls of all these methods have been discussed elsewhere^{8,17,30}, but we would like to focus on multi-state, spin-pure, wavefunction-based methods that are cheaper than ADC and CC methods. To do so, we first look at the static exchange (STEX) method³⁵⁻³⁷, which has been around for some time. The specific theory will be discussed more later, but of particular relevance is that in molecules with multiple equivalent atoms (eg. the two O 1s k-edges in CO₂) STEX considers the coupling between non-orthogonal determinants to be negligible. This allows for a more efficient calculation.

A natural extension of STEX is to include the coupling between non-orthogonal configurations, which we have termed non-orthogonal configuration interaction singles (NOCIS)³⁸⁻⁴⁰. The theory is discussed in Section II. The inclusion of this coupling can be especially important for computing XAS spectra of doublet molecules⁴⁰ and in this work we reiterate this point and show that it is similarly important for triplet molecules.

The purpose of this paper is to explore the impact of the coupling between non-orthogonal

determinants on the calculation of core-excited states. To do so, we investigate the difference between the fully non-orthogonal method (NOCIS), a method that includes partial non-orthogonality (1C-NOCIS), and a fully orthogonal method (STEX) on molecules with singlet, doublet, and triplet ground states. The theory and implementation of 1C-NOCIS and of NOCIS for molecules with a triplet ground state has not been previously reported. We found that while NOCIS is the most accurate and has the advantage of not breaking spatial symmetry, the 1C-NOCIS method provides the best cost to benefit ratio for computing core-excited states, retaining some important aspects of non-orthogonality at a greatly reduced cost. We also demonstrate the practicality of 1C-NOCIS by computing XAS spectra of some medium-sized open-shell molecules.

II. THEORY

A. NOCIS

The motivation for NOCIS is the desire to improve on CIS while still maintaining a reasonably low computational scaling. It does so by including orbital relaxation, which CIS neglects altogether, and the non-orthogonal interaction between multiple core-hole references, such as the O 1s orbitals in O₂.

A brief overview of the NOCIS algorithm is as follows: after a ground-state orbital optimization, a Maximum Overlap Method (MOM)⁴¹ or a Square Gradient Minimization (SGM)⁴² calculation is done for an ionization from each localized core orbital of interest. This introduces orbital relaxation, and also renders the excited states non-orthogonal to the ground state. The Hamiltonian, overlap, and total spin squared matrices are constructed using the Slater-Condon rules for matrix elements between determinants which share a common set of orbitals and NOCI for the remaining matrix elements⁴³. Finally, the generalized eigenvalue problem is solved.

NOCIS is spin-pure, size consistent, and maintains spatial symmetry. Like CIS, NOCIS produces excited states with the same m_s as the reference but potentially with larger total spin. For example, performing NOCIS on a molecule with a singlet ground state will produce both singlet and triplet excited states. In previous papers^{38,40}, we implemented NOCIS for molecules with singlet and doublet ground states. We provide a brief summary of these

FIG. 1. A visual of the Hamiltonian matrices for each method for a two-reference doublet molecule (i.e. containing two atoms of a target element). The peach components are computed with orthogonal Slater-Condon rules, the blue elements are obtained with NOCI from the ionized determinants, and the green elements are obtained with NOCI from the determinants that are excited into the open-shell orbital. The gray elements are zero.

methods here.

Singlet NOCIS has the following wavefunction:

$$|\Psi_{NOCIS}\rangle = \sum_{i=1}^R \sum_{a=1}^V \mathbf{t}_i^a (1 - \hat{\mathbf{P}}) [\hat{a}_a^\dagger \hat{a}_i \pm \hat{a}_{\bar{a}}^\dagger \hat{a}_{\bar{i}}] |\Phi_i\rangle \quad (1)$$

In singlet NOCIS, the wavefunction is constructed from R different core-ionized determinants corresponding to core electron removal from each identical atom of interest and ROHF optimization of those cation determinants, our $|\Phi_i\rangle$. Alpha and beta electrons are then added into each of the V virtual orbitals (different for each cation determinant), and the resulting core-excited configuration is projected against the closed-shell ground state determinant to

ensure that the core-excited states are strongly orthogonal to the ground state.

In doublet NOCIS, we begin to have to contend with ground-state open-shell orbitals in order to fully consider all possible single excitations. This involves the addition of another reference, which we term DS, indicating an excitation from a doubly occupied (D) core orbital to a singly-occupied (S) valence orbital.

$$|\Psi_{NOCIS}\rangle = \sum_{i=1}^R \sum_{a=1}^V (1 - \hat{\mathbf{P}}) \left(t_i^a [a_a^\dagger a_i] + t_i^{\bar{a}} [a_{\bar{a}}^\dagger a_{\bar{i}}] + t_{ik}^{\bar{a}a} [a_k^\dagger a_{\bar{i}} a_a^\dagger a_k] \right) |\Phi_i\rangle + \sum_{i=1}^R t_i^k (1 - \hat{\mathbf{P}}) [a_k^\dagger a_{\bar{i}}] |\Phi_i^k\rangle \quad (2)$$

There are a few changes of note when contrasting doublet and singlet NOCIS. The first is within the space of the original reference, $|\Phi_i\rangle$. In order to maintain spin-purity, we now feature an excitation that can be considered a double excitation, which is an XCIS-type extension⁴⁴, and moves us beyond the space of purely single excitations. Additionally, we can see the DS reference separately optimized, with k being the ground-state open-shell orbital. Because of this, the second and first terms are mutually non-orthogonal, which introduces additional non-orthogonality to our matrices.

In this work we have also implemented the extension of NOCIS to molecules with triplet ground states. As with doublet NOCIS, triplet NOCIS once again expands the number of configurations necessary to maintain spin-purity for the $m_s = +1$ state. This includes an additional reference for the second singly-occupied ground-state orbital. These excitations are visualized in Figure 2. The triplet NOCIS wavefunction is as follows:

$$|\Psi_{NOCIS}\rangle = \sum_{i=1}^R \sum_{a=1}^V (1 - \hat{\mathbf{P}}) \left(t_i^a [a_a^\dagger a_i] + t_i^{\bar{a}} [a_{\bar{a}}^\dagger a_{\bar{i}}] + t_{ij}^{\bar{a}a} [a_j^\dagger a_{\bar{i}} a_a^\dagger a_j] + t_{ik}^{\bar{a}a} [a_k^\dagger a_{\bar{i}} a_a^\dagger a_k] \right) |\Phi_i\rangle \\ + \sum_{i=1}^R t_i^j (1 - \hat{\mathbf{P}}) [a_j^\dagger a_{\bar{i}}] |\Phi_i^j\rangle + \sum_{i=1}^R t_i^k (1 - \hat{\mathbf{P}}) [a_k^\dagger a_{\bar{i}}] |\Phi_i^k\rangle \quad (3)$$

B. Static Exchange

In the simplest form of STEX³⁵, one computes excitation energies by diagonalizing the virtual space of a Fock matrix for the ionized system. This method is especially attractive for computing x-ray spectra^{36,45} for the same reasons as NOCIS: it achieves systematically improvable, high-quality results in a lower-scaling way than methods such as ADC or EOM-CC.

FIG. 2. All potential triplet core-excitations for spin-completeness. i is a core orbital, j and k are the singly-occupied ground-state orbitals, and a is a virtual orbital. Three different sets of optimized orbitals are employed: core ionized orbitals for the core-to-virtual excitations and a specifically optimized set for each core-to-singly occupied configuration (DS 1 and DS 2 above).

When using STEX on multiple core-ionized states as done, for example, by Ågren et al.⁴⁵, the underlying assumptions are that the coupling between non-orthogonal determinants is negligible, and that all excited determinants can be formed from the core-ionized state. In this way, STEX can be considered to be an approximation to NOCIS.

In our implementation of STEX, we follow an algorithm very similar to NOCIS. Our ground-state calculation includes the Boys localization of the reference orbitals before the MOM/SGM calculation. However, as can be seen in Figure 1, we form the DS reference from the core-ionized reference, instead of optimizing it separately. This renders the DS state orthogonal to the rest of the core-excitations from that particular atom. After the matrix build, we project the orthogonal matrix blocks against the ground state (contrasted with NOCIS, where the whole matrix is projected against the ground state), and solve the eigenvalue problem. Because the basis of excited determinants is not orthogonal to the ground state, NOCI is required to compute the oscillator strengths³⁷. We also explored a method (referred to as STEX + Single Reference in Figure 1) where we separately optimized the DS reference as in NOCIS, but ignored the coupling between the resulting non-orthogonal determinants.

Like NOCIS, STEX is spin-pure and size-consistent. However, due to the de-coupling of the references, STEX calculations break the spatial symmetry of the final states, which can slightly skew the results (see Section III).

C. One-Center NOCIS

To explore the effect of different types of non-orthogonality, we introduce another approximate method, one-center NOCIS (1C-NOCIS), which is an intermediate between NOCIS and STEx. The "DS" determinants are separately optimized as in NOCIS, but the coupling between non-orthogonal determinants with core holes on different centers is ignored. This is depicted in Figure 1, and NOCI is used to compute the remaining matrix elements between non-orthogonal determinants. 1C-NOCIS constructs the orthogonal Slater-Condon components of the matrices, and then performs NOCI to obtain the relevant non-orthogonal components. The diagonal blocks are then projected against the ground state.

For singlet NOCIS, 1C-NOCIS is the same as STEx, since there are no open-shell ground-state orbitals. As can be seen in Figure 1, for a doublet ground state this results in a column of matrix elements that must be computed using NOCI. For triplet molecules there are two such columns corresponding to the two open-shell orbitals of the ground state. It is easy to imagine how this could be generalized as the number of ground-state open-shell orbitals increases.

The main advantages of 1C-NOCIS are twofold: first, it is substantially cheaper than NOCIS and so enables the treatment of larger systems. Second, and in contrast to STEx, it allows the DS states to relax separately, which we will show to be important.

D. Computational Implementation

The code for NOCIS, 1C-NOCIS, and STEx is implemented in a development version of Q-Chem 5.0⁴⁶ utilizing the Armadillo linear algebra library⁴⁷. The NOCI code is a further modified version of the code developed by Sundstrom⁴⁸ and adapted by Oosterbaan et al.³⁸. NOCIS scales as $\frac{1}{2}A(A-1)V^2N^2$, where A is the number of atoms of interest, V is the number of virtual orbitals, and N is the number of basis functions. 1C-NOCIS and STEx scale as AVN^2 , which is a substantial improvement.

III. RESULTS

All geometries are obtained from NIST's Computational Chemistry Comparison and Benchmark Database⁴⁹, which are optimized using B3LYP⁵⁰⁻⁵² in the Def2-TZVPD basis

set⁵³, except those in the Larger Cases section, which are optimized in Q-Chem using the same basis set and functional. Single-reference molecules are defined as molecules with only one equivalent atom (eg. the O K-edge in CO). Multi-reference molecules have more than one of the same atom of interest (eg. the O K-edge in CO₂), and thus result in larger matrix dimensions and a further introduction of non-orthogonality.

A. Benchmarks

For singlet molecules with single references, NOCIS, 1C-NOCIS, and STEX methods are identical. Additionally, 1C-NOCIS and STEX are identical for all singlet ground-state molecules. Thus, for singlet molecules we compare NOCIS and 1C-NOCIS/STEX for multi-reference molecules. The results can be seen in Table 1.

The outcome of this is quite clear: while the NOCIS results are always lower in energy, the 1C-NOCIS/STEX results are very close to or the same as the NOCIS numbers, and in all cases are the same up to one decimal place, which is enough to identify a potential XAS K-edge. Thus, we conclude that multi-reference singlet molecules have a low degree of configuration interaction between configurations corresponding to core excitations from different atoms, and 1C-NOCIS/STEX is a more efficient way to obtain reasonably accurate results.

For doublet molecules with single references, 1C-NOCIS and NOCIS are identical. For multi-reference cases, the 1C-NOCIS matrices take the form of diagonal blocks as seen in Figure 1. This dramatic reduction of NOCI calculations provides a substantial speedup in computation time. The comparison results in the 6-31G^{54,55} and cc-pCVDZ⁵⁶ basis sets can be seen in Tables 2 and 3, respectively. We saw that in general, the STEX-NOCIS differences increased with the increase in basis set size.

There are a few items of note in these results. The first is that the NOCIS-STEX differences are markedly larger for doublet molecules than for singlet ones. This is due to the fact that the DS reference state is not optimized alone, and is instead formed from the core-ionized reference. In previous work⁴⁰, we found that doing this substantially decreased the accuracy of our results, and that far more accurate results could be obtained by separately optimizing the DS reference. A more accurate DS determinant obtained from a separate orbital optimization has a large impact, as the DS reference is usually lower in energy than

Molecule	NOCIS	STEX/1C-NOCIS	STEX/1C-NOCIS
	6-31g/cc-pCVDZ	6-31g	cc-pCVDZ
N ₂ N(1s)	404.529/403.134	0.013	0.016
F ₂ F(1s)	685.485/684.528	0.015	0.015
C ₂ H ₂ C(1s)	289.747/288.452	0.023	0.025
C ₂ H ₄ C(1s)	288.677/287.544	0.005	0.006
C ₂ H ₆ C(1s)	292.135/290.049	0.006	0.006
CO ₂ O(1s)	538.045/537.212	0.000	0.000
C ₃ H ₈ C(1s)	292.135/290.101	0.001	0.001
C ₃ H ₆ C(1s)	288.984/287.869	0.000	0.000
C ₃ H ₄ ^a C(1s)	289.597/288.442	0.000	0.001
C ₃ H ₄ ^b C(1s)	290.097/288.823	0.003	0.005
MSE		0.007	0.008
RMSE		0.010	0.011

^a allene

^b propyne

TABLE I. A comparison of NOCIS singlet K-edge energies and 1C-NOCIS/STEX K-edge differences in the 6-31g^{54,55} and cc-pCVDZ⁵⁶ basis sets. Mean signed error (MSE) and root mean square error (RMSE) are included. For singlet molecules, 1C-NOCIS and STEX are identical.

a core-to-virtual excitation, and would be expected to play a large role in core excitations. This is further borne out in cases where the DS state does not play a large role in the K-edge due to symmetry, such as the NO O 1s K-edge. In this case, the K-edge is not a DS excitation, and NOCIS and STEX results are identical.

1C-NOCIS provides a significant improvement over STEX, with its error relative to NOCIS being an order of magnitude smaller. This data also exposes a second item of note: some of these numbers are lower than the NOCIS results. This can be explained by realizing that both STEX and 1C-NOCIS break spatial symmetry. STEX and 1C-NOCIS do not allow localized states to mix.

In sum, for doublet molecules, 1C-NOCIS provides a relatively substantial increase in

Molecule	NOCIS	STEX	1C-NOCIS
HO ₂ O(1s)	531.710	1.179	0.000
N ₂ ⁺ N(1s)	397.679	0.341	-0.031
C ₂ H ₃ C(1s)	285.601	0.493	0.000
NO N(1s)	403.316	0.946	0
NO O(1s)	534.956	0.000	0
NO ₂ N(1s)	404.610	0.842	0
NO ₂ O(1s)	532.775	0.966	0.001
OH O(1s)	529.833	1.654	0
CH ₃ C(1s)	284.967	1.036	0
CN C(1s)	283.797	0.076	0
CN N(1s)	396.910	0.706	0
HCO C(1s)	288.470	0.697	0
HCO O(1s)	534.023	0.504	0
N ₂ O ⁺ O(1s)	531.955	1.148	0
CO ₂ ⁺ C(1s)	292.651	0.000	0
CO ₂ ⁺ O(1s)	530.433	0.955	-0.001
MSE		0.721	-0.002
RMSE		0.850	0.007

TABLE II. A comparison of NOCIS doublet K-edge energies and STEX K-edge and 1C-NOCIS differences in the 6-31g^{54,55} basis set. Mean signed error (MSE) and root mean square error (RMSE) are included.

accuracy for a reasonable computational cost, which can be especially valuable when potential molecules of interest to experimentalists have K-edges that are very close in energy. If accurate spatial symmetry is desired, the only option of these three methods is NOCIS.

As in the doublet case, for triplet molecules with with single references, 1C-NOCIS and NOCIS are identical. The comparison results in the 6-31g^{54,55} and cc-pCVDZ⁵⁶ basis sets can be seen in Tables 4 and 5, respectively. Our results are largely consistent with the results from doublets: with the addition of another DS excitation, the difference between NOCIS

Molecule	NOCIS	STEX	1C-NOCIS
HO ₂ O(1s)	530.136	1.204	0.000
N ₂ ⁺ N(1s)	395.902	0.518	-0.033
C ₂ H ₃ C(1s)	283.927	1.300	0.089
NO N(1s)	401.735	0.593	0
NO O(1s)	533.820	0.000	0
NO ₂ N(1s)	403.254	0.883	0
NO ₂ O(1s)	531.334	1.006	0.001
OH O(1s)	528.211	1.593	0
CH ₃ C(1s)	283.813	0.964	0
CN C(1s)	281.619	0.779	0
CN N(1s)	394.547	0.697	0
HCO C(1s)	286.939	0.670	0
HCO O(1s)	532.454	0.479	0
N ₂ O ⁺ O(1s)	530.079	1.238	0
CO ₂ ⁺ C(1s)	291.915	0.000	0
CO ₂ ⁺ O(1s)	528.454	1.066	-0.001
MSE		0.812	0.004
RMSE		0.917	0.024

TABLE III. A comparison of NOCIS doublet K-edge energies and STEX K-edge and 1C-NOCIS differences in the cc-pCVDZ⁵⁶ basis set. Mean signed error (MSE) and root mean square error (RMSE) are included.

and STEX further increases.

When exploring the STEX + single reference implementation for doublet and triplet molecules, we found that it improved on STEX, but remained about 0.1 eV on average higher than 1C-NOCIS at a comparable cost. This is consistent with our expectation that the addition of the singly-occupied orbital reference would improve the results. This is effectively a Δ -SCF calculation using the DS-optimized determinant, and this method may not be suitable for higher excitations as there is no mixing between the DS state and the

Molecule	NOCIS	STEX	1C-NOCIS
O ₂ O(1s)	532.784	1.146	0.027
CH ₂ C(1s)	285.274	0.864	0
NH N(1s)	399.233	1.225	0
CH ₃ N C(1s)	288.983	0.892	0
CH ₃ N N(1s)	408.604	0.752	0
HCF C(1s)	286.762	2.027	0
HCF F(1s)	688.240	0.534	0
HCCl C(1s)	293.396	0.756	0
F ₂ C C(1s)	287.956	0.971	0
F ₂ C F(1s)	687.485	0.622	0.000
Cl ₂ C C(1s)	295.463	0.532	0
MSE		0.938	0.002
RMSE		1.022	0.008

TABLE IV. A comparison of NOCIS triplet K-edge energies and STEX K-edge and 1C-NOCIS differences in the 6-31g basis set. Mean signed error (MSE) and root mean square error (RMSE) are included.

other core-to-valence determinants.

B. Applications

1. *TEMPO*

FIG. 3. TEMPO

With the significantly decreased computational time of 1C-NOCIS, we are now able to

Molecule	NOCIS	STEX	1C-NOCIS
O ₂ O(1s)	531.433	1.209	0.015
CH ₂ C(1s)	283.751	0.832	0
NH N(1s)	397.628	1.174	0
CH ₃ N C(1s)	287.837	0.971	0
CH ₃ N N(1s)	406.610	0.762	0
HCF C(1s)	285.292	1.254	0
HCF F(1s)	686.801	0.626	0
HCCl C(1s)	291.137	1.138	0
F ₂ C C(1s)	286.134	1.011	0
F ₂ C F(1s)	686.130	0.744	0.000
Cl ₂ C C(1s)	293.674	0.576	0
MSE		0.936	0.001
RMSE		0.964	0.004

TABLE V. A comparison of NOCIS triplet K-edge energies and STEX K-edge and 1C-NOCIS differences in the cc-pCVDZ⁵⁶ basis set. Mean signed error (MSE) and root mean square error (RMSE) are included.

generate K-edges for larger molecules. As an example, we look at (2,2,6,6-tetramethylpiperidin-1-yl)oxyl, more pithily known as TEMPO. TEMPO and its fellow free radicals are widely used in fields such as biochemistry and paramagnetic resonance spectroscopy, and may show promise for future use in medicine and organic synthesis⁵⁷. With nine carbons, one nitrogen, and one oxygen, TEMPO is an ideal test for 1C-NOCIS.

In performing these calculations, the most difficult part of the calculation is converging the open-shell SCF calculations on the core ionized determinants: the MOM algorithm was converging to unphysical state with high energies that, in turn, led to incorrect results based off these determinants. Fortunately, we are able to use the recently developed SGM approach⁴², to obtain the target core-ionized state energies. We used SGM instead of MOM for all our calculations of the C, N, and O K-edges of TEMPO, and the results can be seen in Figure 4.

FIG. 4. A comparison of TEMPO experimental spectra (black)⁵⁷ to open-shell NOCIS spectra for the carbon (green), nitrogen (blue), and oxygen (red) K-edges. Calculated spectra are shifted (C -3.4 eV, N -1.2 eV, O -1.1 eV) and use Gaussian and Lorentzian broadening (.2 G, .25 L for N and O, .1 G, .15 L for C).

Before discussing the results, it is first important to point out some features of the experimental spectra⁵⁷. In the nitrogen spectrum, the second large peak at around 401.5 eV is actually the N₂ peak from the air, and so should not be seen in any calculated spectra. In the oxygen spectrum, the small peak next to the main peak at around 531 eV is the O₂ peak from the air, and should also not be seen in calculated spectra.

As can be seen from the comparisons, 1C-NOCIS agrees very well with the experimental spectra for TEMPO. These results continue to provide encouragement for the use of 1C-NOCIS for use in identifying experimental spectra for doublet radicals.

2. Singlet and Triplet States of MBA

As more NEXAFS spectra are taken, it will become increasingly useful to be able to distinguish between the ground singlet and excited triplet state of a molecule, for example in studying the signatures of electronic dynamics. To this end, we looked at the singlet versus triplet states of 4-mercaptobenzoic acid (MBA), which has been examined using XAS, but only in its solid state⁵⁸.

FIG. 5. 4-mercaptobenzoic acid, singlet geometry.

After optimizing the singlet and triplet state geometries separately, we then performed open-shell NOCIS calculations for the oxygen K-edge, again using the SGM algorithm. The results can be seen in Figure 6.

FIG. 6. A comparison of the 1C-NOCIS spectra for singlet (black) and triplet (red) MBA. Spectra use Gaussian and Lorentzian broadening (.2 G, .25 L).

Triplet MBA has a distinctive lower energy peak that singlet MBA does not, which is a signature that should be useful in identifying the presence of triplet MBA. The nominal final state is the same in the K-edge of both the singlet and triplet species, so the peak shift is

therefore a measure of the singlet-triplet splitting in the ground state. This is promising for the future use of 1C-NOCIS to assist experimentalists in determining the presence of singlet or triplet states of their molecule. This is also important in time-resolved spectroscopy.

IV. CONCLUSIONS

This paper explores the impact of varying levels of inclusion of non-orthogonality on core-excitation calculations, and also presents the implementation of one-center and triplet NOCIS. Overall, we found that the impact of non-orthogonality increased as the number of singly-occupied orbitals increased, but that it had a limited effect on molecules with multiple of the same atom of interest. However, full NOCIS is the only method to retain spatial symmetry, so it is still recommended in cases where this is important.

This motivated the development of an approximation to NOCIS, 1C-NOCIS, which includes non-orthogonality only in regard to the core excitations to singly-occupied ground-state orbitals. 1C-NOCIS dramatically reduces the number of NOCI calculations, the method’s computational bottleneck, and enables the treatment of far larger molecules than full NOCIS. Methods based on open-shell NOCIS provide a very promising framework for core-excited states. Extensions to include dynamical correlation and spin orbit coupling are promising future directions. Already, these methods provide a convenient way to simulate XAS spectra of first-row atoms in concert with experimentalists at an acceptable cost.

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