



# Calculation of near-edge X-ray absorption fine structure with the CIS(D) method

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## ABSTRACT

We report an investigation into the calculation of near-edge X-ray absorption fine structure with the CIS(D) method. Core excitation energies computed with time-dependent density functional theory using standard exchange–correlation functionals are systematically underestimated. CIS(D) predicts core excitation energies that are closer to experiment. However, excitation energies for Rydberg states are too low with respect to valence states, and for some systems spectra that are qualitatively incorrect are obtained. A scaled opposite spin only approach is proposed that reduces the error in the computed core excitation energies, and results in spectra that are in good agreement with experiment.

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## 1. Introduction

Near-edge X-ray absorption fine structure (NEXAFS) is a powerful technique that provides information about the structure and bonding of materials [1]. With advances in the intensity and resolution available with synchrotron sources, the application of NEXAFS is likely to grow. Despite this interest, theoretical calculations of NEXAFS are relatively uncommon in comparison with the more familiar ultra-violet (UV) spectroscopy. There are several approaches to computing NEXAFS spectra. These include multiple scattering  $X_\alpha$  methods [2], static exchange (STEX) [3] and transition potential calculations [4] and  $\Delta$ Hartree–Fock (HF) self-consistent field approaches, and these methods have provided a foundation for analysing and interpreting a wealth of experimental data.

Within density functional theory (DFT), a  $\Delta$ Kohn–Sham self-consistent field approach can provide accurate core-excitation energies. In this method, the core excited state is computed by imposing a constraint of a single occupancy of a core orbital within the self-consistent field calculation to prevent the variational collapse. Since the calculation of NEXAFS spectra often comprises a large number of core-excited states, performing individual Kohn–Sham calculations for all the required states can be arduous. More recently, NEXAFS spectra have been computed using time-dependent density functional theory (TDDFT) [5–9]. With TDDFT core excited states can be computed efficiently by restricting the single excitation space to include only excitations from a subset of (core) orbitals [5,9]. More recently, a resonant converged complex polarization propagator method has been implemented [10], and applied to study NEXAFS [11,12]. While the computed spectral profile is often in good agreement with experiment, the predicted excitation energies are much too low compared with experiment.

The amount by which the excitation energies are underestimated increases with the nuclear charge of the atomic centers on which the core orbitals are localised. This source of this error is associated with the approximate exchange within the exchange–correlation functionals. To correct for this error, exchange correlation functionals with varying fractions of HF exchange [13,14] and a self-interaction correction [15] have been introduced.

CIS(D) is a second-order perturbative approximation to CCSD, based on a single excitation configuration interaction (CIS) Refs. [16,17], and can be considered an excited state analogue to MP2. For valence excited states, CIS(D) often provides similar accuracy to TDDFT. However, since CIS(D) comprises exact HF exchange, superior performance to TDDFT for NEXAFS spectra would be anticipated. In this Letter, we investigate the performance of the CIS(D) method for the calculation of core-excitation energies and NEXAFS spectra.

## 2. Computational details

Comprehensive accounts of the CIS method can be found elsewhere [18], and only a brief overview is given here. The CIS wavefunction can be expressed as

$$\Phi_{\text{CIS}} = \sum_{ia} b_i^a \Phi_i^a \quad (1)$$

Excitation energies and expansion coefficients ( $b_i^a$ ) are obtained from the eigenvalue equation

$$\mathbf{A}\mathbf{X} = \omega\mathbf{X} \quad (2)$$

where  $\omega$  is the diagonal matrix of excitation energies,  $\mathbf{X}$  the matrix of expansion coefficients, and the elements of  $\mathbf{A}$  are given by

$$A_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + (ia||jb) \quad (3)$$

$\epsilon_a$  and  $\epsilon_i$  are orbital energies and  $(ia||jb)$  are the two-electron integrals

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$$(ia||jb) = \int \int \frac{\phi_i(\mathbf{r})\phi_a(\mathbf{r})\phi_j(\mathbf{r}')\phi_b(\mathbf{r}') - \phi_i(\mathbf{r})\phi_j(\mathbf{r})\phi_a(\mathbf{r}')\phi_b(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (4)$$

The matrix **A** is diagonalized using the iterative method of Davidson [19]. While efficient for low-lying states, this approach is inefficient for core-excited states, which are very high in energy. This results in the computation of core excitation energies being computational prohibitive. A solution to this problem is to perform the CIS calculation within the subspace of single excitations involving excitations from the relevant core orbital(s). The following equation is solved [5,20]

$$\bar{\mathbf{A}}\mathbf{X} = \omega\mathbf{X} \quad (5)$$

where

$$\bar{\mathbf{A}} = A_{ia,jb} \quad (6)$$

and {i} denotes a subset of the occupied orbitals. Within TDDFT, we have used an analogous approach to study the NEXAFS [9] and electronic spectroscopy of molecules on surfaces [21,22] and in solution [23].

Generally, CIS excitation energies are in poor agreement with experiment. This problem was addressed by Head-Gordon et al., who introduced the CIS(D) method [16,17]. The CIS(D) method incorporates a perturbative doubles correction to the CIS excitation energies, and yields a significant improvement in the agreement with experiment. The CIS(D) correction to the excitation energy for a state with CIS excitation energy  $\omega$  is

$$\omega^{\text{CIS(D)}} = -\frac{1}{4} \sum_{ijab} \frac{(u_{ij}^{ab})^2}{A_{ij}^{ab} - \omega} + \sum_{ia} b_i^a v_i^a \quad (7)$$

where

$$A_{ij}^{ab} = \varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j \quad (8)$$

$$u_{ij}^{ab} = \sum_c [(ab||cj)b_i^c - (ab||ci)b_j^c] + \sum_k [(ka||ij)b_k^b - (kb||ij)b_k^a] \quad (9)$$

$$v_i^a = \frac{1}{2} \sum_{jkb} (jk||bc)(b_i^a a_{jk}^{ca} + b_j^a a_{ik}^{cb} + 2b_k^b a_{ik}^{ac}) \quad (10)$$

and  $a_{ij}^{ab}$  are the MP2 amplitudes

$$a_{ij}^{ab} = -\frac{(ij||ab)}{A_{ij}^{ab}} \quad (11)$$

The first term in Eq. (7) is termed the 'direct' contribution and accounts for electron correlation effects of the electron involved in the excitation, while the second 'indirect' term accounts for electron correlation effects between pairs of electrons not involved in the excitation [24].

Recently, Rhee and Head-Gordon reported a resolution of the identity (RI) implementation of CIS(D) in addition to spin component scaled and scaled opposite spin versions of CIS(D), denoted SCS-CIS(D) and SOS-CIS(D), respectively [24]. SCS-CIS(D) is an extension of the SCS-MP2 method [25,26], where the opposite and same spin components of the energy are scaled separately. Within SCS-CIS(D) the excitation energy can be considered as

$$\omega^{\text{SCS-CIS(D)}} = c_U^{\text{OS}} w_U^{\text{OS}} + c_T^{\text{OS}} w_T^{\text{OS}} + c_U^{\text{SS}} w_U^{\text{SS}} + c_T^{\text{SS}} w_T^{\text{SS}} \quad (12)$$

where OS and SS denote opposite and same spin, and  $w_U$  and  $w_T$  are the direct and indirect terms of Eq. (7), respectively. For SOS-CIS(D), only the opposite spin components of Eq. (12) are considered. After optimizing the parameters according to experimental data, an improved performance compared to CIS(D) was obtained.

The accuracy of the theoretical methods is assessed based on computed core excitation energies of 54 core excited states. These

**Table 1**  
Core excited states studied

Molecule	Excitation
CO	C(1s) → π*, C(1s) → 3s, C(1s) → 3p <sub>π</sub> , C(1s) → 3p <sub>σ</sub> O(1s) → π*, O(1s) → 3s, O(1s) → 3p <sub>π</sub>
H <sub>2</sub> CO	C(1s) → π*, C(1s) → 3s <sub>a1</sub> , C(1s) → 3p <sub>b2</sub> , C(1s) → 3p <sub>b1</sub> O(1s) → π*, O(1s) → 3s <sub>a1</sub> , O(1s) → 3p <sub>a1</sub>
CO <sub>2</sub>	C(1s) → π*, C(1s) → 3s, C(1s) → 3p
CH <sub>4</sub>	C(1s) → 3s, C(1s) → 3p
C <sub>2</sub> H <sub>2</sub>	C(1s) → π*, C(1s) → 3s <sub>σ</sub> , C(1s) → 3p <sub>π</sub> , C(1s) → 3p <sub>σ</sub>
C <sub>2</sub> H <sub>4</sub>	C(1s) → π*, C(1s) → 3s <sub>σ</sub>
N <sub>2</sub>	N(1s) → π*, N(1s) → 3s, N(1s) → 3p <sub>π</sub> , N(1s) → 3p <sub>σ</sub>
N <sub>2</sub> O	N <sub>f</sub> (1s) → π*, N <sub>f</sub> (1s) → 3s, N <sub>f</sub> (1s) → 3p, N <sub>c</sub> (1s) → π*, N <sub>c</sub> (1s) → 3s, N <sub>c</sub> (1s) → 3p
SiH <sub>4</sub>	Si(1s) → σ*, Si(2p) → σ*
H <sub>2</sub> S	S(1s) → σ*, S(1s) → 4p, S(1p) → σ*, S(1p) → 4s
SO <sub>2</sub>	S(1s) → π*, S(1s) → 4p, S(2p) → π*, S(2p) → 4s
PH <sub>3</sub>	P(1s) → σ*, P(2p) → σ*
HCl	Cl(1s) → σ*, Cl(1s) → 4p <sub>π</sub> , Cl(2p) → σ*, Cl(2p) → 4p <sub>π</sub>
Cl <sub>2</sub>	Cl(1s) → σ <sub>u</sub> *, Cl(1s) → 4p, Cl(2p) → σ <sub>g</sub> *

states are drawn from the following molecules CO, H<sub>2</sub>CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, N<sub>2</sub>, N<sub>2</sub>O, SiH<sub>4</sub>, H<sub>2</sub>S, SO<sub>2</sub>, PH<sub>3</sub>, HCl and Cl<sub>2</sub>, and a list of the excitations included is shown in Table 1. For first row elements, excitations from the 1s orbital are considered, while 1s and 2p excitations are included for the second row elements. All structures were optimized at the MP2/cc-pVTZ level of theory. The RI-CIS(D) implementation of CIS(D) was used, and excitation energies were computed for a range of basis sets together with the auxiliary basis set of aug-cc-pVTZ [27]. All these calculations were performed with the Q-CHEM software package [28]. Relativity has the effect of lowering the energy of core orbitals. In the calculation of core excitation energies, these effects are significant. In this work, the effect of relativity was estimated from the lowering of the core orbital energy between non-relativistic and relativistic HF/cc-pCVTZ calculations, with the relativistic effects computed with the Douglas-Kroll-Hess Hamiltonian [29]. For these calculations, the MOLPRO software package [30] was used.

### 3. Results and discussion

The lowering in energy of the core orbital due to relativistic effects is found to be 0.10 eV for the carbon 1s orbital in CO, H<sub>2</sub>CO, C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>, and 0.11 eV in CO<sub>2</sub> and CH<sub>4</sub>. For the nitrogen 1s orbital, values of 0.20, 0.19 and 0.22 eV are found for N<sub>2</sub>, and the end (N<sub>f</sub>) and central (N<sub>c</sub>) nitrogen atoms in N<sub>2</sub>O. For the oxygen 1s orbital, a value of 0.37 eV for CO and H<sub>2</sub>CO is obtained. For the 1s orbitals of the second row elements, values of 3.44, 4.60, 5.90, 5.90, 7.88 and 7.99 eV are found for SiH<sub>4</sub>, PH<sub>3</sub>, H<sub>2</sub>S, SO<sub>2</sub>, Cl<sub>2</sub> and HCl, respectively. Similarly, for the 2p orbitals, values of 0.63, 0.88, 1.18, 1.18, 1.58 and 1.60 eV are found. As expected, this effect increases with the nuclear charge of the atom on which the core orbital is localised. Furthermore, this effect shows a weak dependence on the molecule in which the atom is located.

Table 2 shows the mean absolute error in the computed CIS(D) core excitation energies with a range of augmented core/valence basis sets [31,32] for the full set of 54 core excited states, and incorporating the correction due to relativity. For the largest basis set, aug-cc-pCVQZ, the mean absolute error in the computed excitation energies is found to be 2.6 eV. This error is similar for the first and second row molecules, and does not change significantly with the smaller basis sets aug-cc-pCVTZ and aug-cc-pCVDZ. The magnitude of this error shows that CIS(D) does not have the systematic large underestimation of the excitation energy observed with TDDFT [9,13,14], and an average error of about 2.5 eV is relatively good. However, closer inspection of the computed core excitation energies reveals severe problems with the predicted spectra.

**Table 2**  
Mean absolute errors in the computed core excitation energies

Method	Mean absolute error (eV)
CIS(D)/aug-cc-pCVQZ	2.6
CIS(D)/aug-cc-pCVTZ	2.5
CIS(D)/aug-cc-pCVDZ	2.7
cSOS-CIS(D)/aug-cc-pCVQZ	1.2
cSOS-CIS(D)/aug-cc-pCVTZ	1.2
cSOS-CIS(D)/aug-cc-pCVDZ	2.3

**Table 3**  
Computed excitation energies including relativistic correction with the error in parenthesis in eV for first row atoms

Excitation	Expt.	CIS(D)/aug-cc-pCVQZ	cSOS-CIS(D)/aug-cc-pCVQZ
CO C(1s) → π*	287.4	289.9 (+2.5)	287.7 (+0.3)
CO C(1s) → 3s	292.4	295.1 (+2.7)	294.9 (+2.5)
CO C(1s) → 3p <sub>π</sub>	293.3	294.7 (+1.5)	295.5 (+2.2)
CO C(1s) → 3p <sub>σ</sub>	293.5	295.0 (+1.5)	295.5 (+2.0)
CO O(1s) → π*	534.2	533.7 (−0.5)	532.8 (−1.4)
CO O(1s) → 3s	538.9	533.1 (−5.8)	536.2 (−2.7)
CO O(1s) → 3p <sub>π</sub>	539.9	531.7 (−8.2)	535.9 (−4.0)
H <sub>2</sub> CO C(1s) → π*	286.0	288.8 (+2.8)	286.6 (+0.6)
H <sub>2</sub> CO C(1s) → 3s <sub>a1</sub>	290.2	293.5 (+3.3)	292.9 (+2.7)
H <sub>2</sub> CO C(1s) → 3p <sub>b2</sub>	291.3	295.1 (+3.8)	294.1 (+2.8)
H <sub>2</sub> CO C(1s) → 3p <sub>b1</sub>	291.7	292.4 (+0.7)	293.3 (+1.6)
H <sub>2</sub> CO O(1s) → π*	530.8	531.8 (+1.0)	529.6 (−1.2)
H <sub>2</sub> CO O(1s) → 3s <sub>a1</sub>	535.4	530.5 (−4.9)	533.6 (−1.4)
H <sub>2</sub> CO O(1s) → 3p <sub>a1</sub>	536.3	531.7 (−4.6)	534.4 (−1.9)
CO <sub>2</sub> C(1s) → π*	290.8	293.8 (+3.0)	291.1 (+0.3)
CO <sub>2</sub> C(1s) → 3s	292.7	295.6 (+2.9)	294.4 (+1.7)
CO <sub>2</sub> C(1s) → 3p	295.0	296.6 (+1.6)	297.2 (+2.2)
CH <sub>4</sub> C(1s) → 3s	287.1	287.7 (+0.7)	287.8 (+0.8)
CH <sub>4</sub> C(1s) → 3p	288.0	288.3 (+0.3)	289.2 (+1.2)
C <sub>2</sub> H <sub>2</sub> C(1s) → π*	285.8	288.5 (+2.7)	286.8 (+1.0)
C <sub>2</sub> H <sub>2</sub> C(1s) → 3s <sub>σ</sub>	287.7	290.3 (+2.6)	289.9 (+2.2)
C <sub>2</sub> H <sub>2</sub> C(1s) → 3p <sub>π</sub>	288.7	287.9 (−0.8)	289.1 (+0.4)
C <sub>2</sub> H <sub>2</sub> C(1s) → 3s <sub>σ</sub>	288.8	287.5 (−1.3)	288.7 (−0.1)
N <sub>2</sub> N(1s) → π*	401.0	403.2 (+2.2)	401.0 (0.0)
N <sub>2</sub> N(1s) → 3s	406.2	405.8 (−0.4)	407.0 (+0.8)
N <sub>2</sub> N(1s) → 3p <sub>π</sub>	407.1	404.4 (−2.7)	406.7 (−0.4)
N <sub>2</sub> N(1s) → 3p <sub>σ</sub>	407.3	403.5 (−3.8)	406.2 (−1.1)
N <sub>2</sub> O N <sub>f</sub> (1s) → π*	401.1	403.4 (+2.3)	400.7 (−0.4)
N <sub>2</sub> O N <sub>f</sub> (1s) → 3s	404.0	405.1 (+1.1)	405.2 (+1.2)
N <sub>2</sub> O N <sub>f</sub> (1s) → 3p	405.9	402.6 (−3.3)	405.3 (−0.6)
N <sub>2</sub> O N <sub>c</sub> (1s) → π*	404.8	407.4 (+2.6)	404.7 (−0.1)
N <sub>2</sub> O N <sub>c</sub> (1s) → 3s	407.5	410.1 (+2.6)	409.4 (+1.9)
N <sub>2</sub> O N <sub>c</sub> (1s) → 3p	407.8	407.5 (−0.3)	410.1 (+2.4)

Experimental data from Refs. [33–40].

Tables 3 and 4 show the computed CIS(D)/aug-cc-pCVQZ excitation energies with the values from experiment. For a number of molecules, the Rydberg bands are computed to lie below a low-lying valence band, which is qualitatively incorrect compared to experiment. This is shown by the molecules H<sub>2</sub>CO, C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub>S in particular. More generally, for most molecules studied the Rydberg state excitation energies are underestimated. Hence, while TDDFT predicts ‘correct spectra in the wrong place’, CIS(D) gives ‘incorrect spectra in the right place’.

In calculations of UV spectra, the underestimation of Rydberg state excitation energies with CIS(D) has been noted to be a generic problem. CIS(D) can be viewed as a low-order truncated solution to linear response coupled cluster theory, and the poor results for Rydberg states has been associated with an unbalanced treatment of Rydberg and valence states [24]. This problem was addressed by adopting SCS-CIS(D) and SOS-CIS(D) approaches [24]. Optimizing the coefficients in Eq. (12) to reproduce excitation energies from experiment resulted in an improved performance. The application of this parameterization to core excited is not successful since a damping factor was also introduced. This results in the omission

**Table 4**  
Computed excitation energies including relativistic correction with the error in parenthesis in eV for second row atoms

Excitation	Expt.	CIS(D)/aug-cc-pCVQZ	cSOS-CIS(D)/aug-cc-pCVQZ
SiH <sub>4</sub> Si(1s) → σ*	1842.5	1840.4 (−2.1)	1842.8 (+0.3)
SiH <sub>4</sub> Si(2p) → σ*	102.8	105.0 (+2.2)	102.9 (+0.1)
H <sub>2</sub> S S(1s) → σ*	2473.1	2470.4 (−2.7)	2472.5 (−0.6)
H <sub>2</sub> S S(1s) → 4p	2476.3	2469.9 (−6.4)	2474.9 (−1.4)
H <sub>2</sub> S S(1p) → σ*	164.5	167.3 (+2.8)	164.8 (+0.3)
H <sub>2</sub> S S(1p) → 4s	166.5	167.6 (+1.1)	165.6 (−0.9)
SO <sub>2</sub> S(1s) → π*	2473.8	2471.4 (−2.4)	2472.0 (−1.8)
SO <sub>2</sub> S(1s) → 4p	2478.4	2476.0 (−2.4)	2477.7 (−0.7)
SO <sub>2</sub> S(2p) → π*	164.4	167.5 (+3.1)	163.6 (−0.8)
SO <sub>2</sub> S(2p) → 4s	171.3	172.2 (+0.9)	169.4 (−1.9)
PH <sub>3</sub> P(1s) → σ*	2145.8	2143.9 (−1.9)	2146.1 (+0.3)
PH <sub>3</sub> P(2p) → σ*	132.3	134.4 (+2.1)	132.1 (−0.2)
HCl Cl(1s) → σ*	2823.9	2821.3 (−2.6)	2823.6 (−0.3)
HCl Cl(1s) → 4p <sub>π</sub>	2827.8	2823.2 (−4.6)	2819.6 (−0.3)
HCl Cl(2p) → σ*	201.0	204.2 (+3.2)	201.7 (+0.7)
HCl Cl(2p) → 4p <sub>π</sub>	204.6	205.5 (+0.9)	204.6 (0.0)
Cl <sub>2</sub> Cl(1s) → σ <sub>u</sub> *	2821.3	2818.7 (−2.6)	2820.8 (−1.1)
Cl <sub>2</sub> Cl(1s) → 4p	2828.5	2824.4 (−4.2)	2828.8 (+0.3)
Cl <sub>2</sub> Cl(2p) → σ <sub>u</sub> *	198.7	201.3 (+2.6)	198.3 (−0.4)

Experimental data from Refs. [41–46].

of the CIS excitation energy from the denominator of the direct term in Eq. (7). Core excitation energies are much larger than valence excitation energies, and their absence leads to a large error in the computed value. To find a version of CIS(D) that is applicable to core-excited states, we have adopted an opposite spin only formalism.

$$\omega^{\text{SOS-CIS(D)}} = c_U^{\text{OS}} w_U^{\text{OS}} + c_T^{\text{OS}} w_T^{\text{OS}} \quad (13)$$

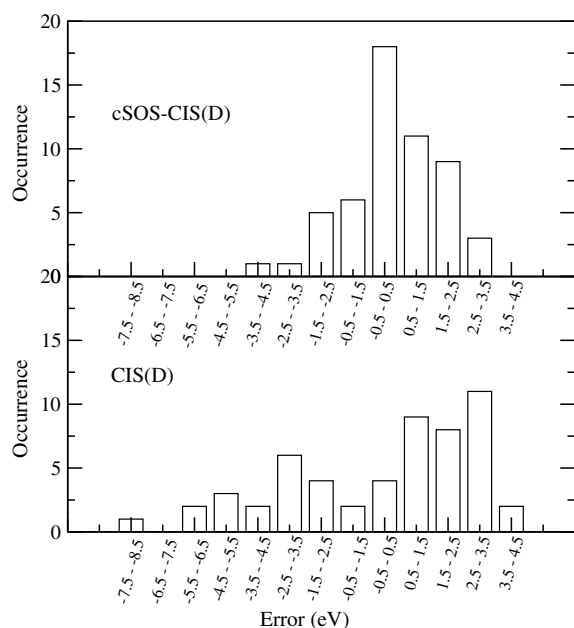
For the core-excited states studied, the direct term is negative, leading to a lowering of the CIS excitation energy, while the indirect term is positive. We have observed that including only the direct term, can lead to a significant improvement in the calculated core excitation energies. This is denoted cSOS-CIS(D), and can be expressed as

$$\omega^{\text{cSOS-CIS(D)}} = c_U^{\text{OS}} w_U^{\text{OS}} \quad (14)$$

with the parameter  $c_U^{\text{OS}}$  determined to be 1.42 from optimization of the core excitation energies of all the states in Table 1 with aug-cc-pCVTZ and aug-cc-pCVQZ basis sets.

Mean absolute errors computed with cSOS-CIS(D) with augmented core/valence basis sets are also shown in Table 2. The mean absolute error for the aug-cc-pCVQZ and aug-cc-pCVTZ basis sets are reduced to 1.2 eV. This error is large in comparison with the error in calculation of UV spectra, where an average error of about 0.3 eV can be achieved. However, when expressed as a percentage of the excitation energies, an error of 1.2 eV corresponds to 0.002%, which is very low. For the aug-cc-pCVQZ basis set, errors of 1.5 eV and 0.7 eV for first and second row atoms, respectively. This represents a significant reduction in the error compared to standard CIS(D) calculations. For cSOS-CIS(D) with the aug-cc-pCVDZ basis set, there is a significant increase in the observed error. However, the error remains lower than for CIS(D). In general, sSOS-CIS(D)/aug-cc-pCVDZ are too high and can be improved by a larger  $c_U^{\text{OS}}$  coefficient. However, it is not desirable to have many parameterizations that are dependent on the basis set. It would also be possible to optimize the method by reintroducing the indirect term and optimizing both  $c_U^{\text{OS}}$  and  $c_T^{\text{OS}}$  coefficients. However, our preliminary studies indicate that this would not lead to a large increase in accuracy, and the including only the direct term leads to a reduction in the computational cost [24].

There is a considerable improvement in the predicted excitation energies for the Rydberg states. This is illustrated in Fig. 1, which shows the distribution of errors in the computed excitation ener-



**Fig. 1.** Distribution of errors in the computed core excitation energies. Lower panel – CIS(D), top panel – cSOS-CIS(D).

gies. For CIS(D), there is a broad distribution of errors, with some large negative errors corresponding to Rydberg states. For cSOS-CIS(D), the error distribution is much narrower and is peaked at an error of less than 0.5 eV. The cSOS-CIS(D)/aug-cc-pCVQZ excitation energies are also shown in Tables 3 and 4. The resulting spectra are in better agreement with experiment, and the excitation energies for the difficult molecules  $\text{H}_2\text{CO}$ ,  $\text{C}_2\text{H}_2$  and  $\text{H}_2\text{S}$  are much improved. As mentioned earlier, CIS(D) provides an unbalanced treatment of valence and Rydberg states. For core-excited states, this manifests itself in the indirect term which is much larger for the valence states than for the Rydberg states. Since this contribution is positive, it has the effect of increasing the excitation energy of the valence states compared to the Rydberg states. This is offset by the direct term which is negative. However, the magnitude of this term is larger for the Rydberg states. Consequently, both terms result in a lowering of the Rydberg states relative to the valence

states. By including just the direct term reduces the lowering of the Rydberg states relative to the valence states and results in a more balanced treatment.

Fig. 2 shows experimental and computed cSOS-CIS(D) NEXAFS spectra for three molecules not included in the original data set. In general, the theoretical spectra do reproduce the experimental features. For butadiene, the calculations predict the pattern of the experimental bands well, but are a little too high in energy. For ethane, the low energy features are reproduced, but again are a little too high in energy. The discrepancy in these computed core excitation energies is consistent with the average error of approximately 1 eV. For  $\text{CS}_2$ , the broad band at 2470 eV is predicted well, with the weaker band at higher energy found to be a little too high.

#### 4. Conclusions

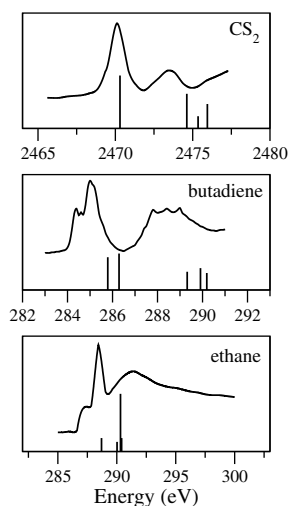
Core excitation energies computed with TDDFT show a large underestimation, which increases with the nuclear charge of the relevant atoms. Consequently, while the spectra are often correct, they need to be shifted in energy to match experiment. The origin of this error is associated with the approximate local exchange used in most exchange–correlation functionals. CIS(D) provides a natural alternative approach that avoids this problem. Core excitation energies computed with CIS(D) do not show a systematic underestimation, but the predicted spectra are often qualitatively incorrect with the Rydberg states predicted to lie too low in energy. Adopting a scaled spin only formalism, denoted cSOS-CIS(D), in which only the direct contribution to the excitation energy is retained, results in a much improved agreement with experiment. Overall, the computed NEXAFS spectra represent an improvement over standard CIS(D) calculations, and provide a reliable basis for interpreting experimental spectra. CIS(D) scales computationally as  $N^5$ , where  $N$  is the size of the system, and is more expensive than TDDFT. Recent advances in CIS(D) have reduced the cost of CIS(D) calculations [24], and the cSOS-CIS(D) formalism used in this work scales as  $N^4$ , which is competitive with TDDFT and can be applied to large systems. There remains an average error of over 1 eV in the computed core excitation energies. This is larger than level of accuracy achieved with calculations of valence excited states. Ultimately, it is desirable for a similar level of accuracy to be obtained for core excited states. The errors observed with the CIS(D) method are naturally corrected by the equations of motion coupled cluster (EOM-CCSD) approach. The calculation of core excited states using EOM-CCSD should provide accurate core-excitation energies within a formalism that is parameter free. We are currently implementing such an approach.

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**Fig. 2.** Experimental (bold line) and computed cSOS-CIS(D) (stick representation) NEXAFS spectra. Experimental data adapted from Refs. [47] for ethane, [48] for butadiene and [49] for  $\text{CS}_2$ .

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