EOM-CC Methods with Approximate Triple Excitations for NEXAFS and XPS

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Abstract
A number of iterative and perturbative approximations to the full equation-of-motion coupled cluster method with single, double, and triple excitations (EOM-CCSDT) are evaluated in the context of calculating the K-edge core-excitation and core-ionization energies of several small molecules. Several of these methods are found to accurately reproduce the full EOM-CCSDT energies well, in particular the EOM-CCSD* method which, when using the core-valence separation (CVS) ansatz, scales rigorously with the sixth power of molecular size. The EOM-CCSDR(3) method, which has been used previously to include triples effects in a cost-effective manner was found to perform rather poorly, although the precise cause has not been determined. These results highlight that very accurate NEXAFS and XPS spectra for molecules with first-row atoms can be computed at a cost not much larger than that for EOM-CCSD.

KEYWORDS
Coupled cluster; NEXAFS; XPS; excited states

1. Introduction
The use of X-rays to investigate the structure and dynamics of molecules and materials is long established [1-4], but recent advances in X-ray sources, particular free-electron lasers, have initiated a renaissance in X-ray absorption (NEXAFS, XPS) and emission/scattering (XES/RIXS) applications [5–9]. Computationally, a number of techniques are available to simulate X-ray spectra with varying levels of fidelity and computational cost [10, 11], including DFT-based approaches such as time-dependent DFT (TD-DFT) [12, 13], ∆DFT (∆KS) [14, 15], and transition-potential DFT (TP-DFT) [16, 17, 18], as well as algebraic diagrammatic construction (ADC) methods [19, 20]. More recently, there has been an increased interest in applying advanced wavefunction-based electronic structure methods, in particular equation-of-motion coupled cluster (EOM-CC) theory [21, 22] to the X-ray regime [23, 24].

Such applications are not without difficulties, however. Importantly, the embedding of X-ray absorption resonances deep in the valence continuum leads to severe convergence issues; initial studies utilizing energy-windowing [25], damped response [26, 27], or Lanczos-based [28] solvers have given way to the core-valence separation [29, 30], introduced to EOM-CC by Coriani and Koch [31]. This approximation has proven highly

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resilient and accurate, and has enabled routine use of EOM-CC in X-ray calculations. Just as important, though, is the issue of orbital relaxation. As the presence of the core hole in the excited (or ionized) state leads to severe contraction of the valence orbitals, the ground state orbitals prove to be a poor reference. EOM-CC corrects for orbital relaxation via electron correlation, but three-electron correlation (e.g. the EOM-CCSDT method [43]) is necessary to fully account for such a large relaxation effect [39, 40]. The full EOM-CCSDT method is much too expensive for routine calculations or indeed for any calculation of molecules beyond a handful of atoms due to its steep scaling with molecular size. Instead, one may opt to include the effect of triple excitations in an approximate fashion, using either an iterative [46–48] or a perturbative [47, 49–52] model.

At present, calculations beyond the CCSD level are rather sparsely represented in the literature; perhaps the best example is the use of the EOM-CCSDR(3) method [49] in the work of Coriani et al [30, 31]. In this article, we show that several computationally efficient approximations to full EOM-CCSDT are effective in recovering nearly all of the residual orbital relaxation energy (i.e. the relaxation not incorporated in EOM-CCSD).

2. Theory

2.1. Core-Valence Separated Equation-of-Motion Coupled Cluster

The equation-of-motion coupled cluster (EOM-CC) approach [25–28] computes the excitation energy \( \omega_{EE} \) as the eigenvalue of a transformed Hamiltonian (EOMEE-CC),

\[
\omega_{EE} \hat{R}_{EE} | \Phi_0 \rangle = [\hat{H}, \hat{R}_{EE}] | \Phi_0 \rangle = \hat{H}_o \hat{R}_{EE} | \Phi_0 \rangle
\]

\[
\hat{R}_{EE} = \hat{R}_0 + \hat{R}_1 + \hat{R}_2 + \cdots
\]

\[
= r_0 + \sum_{i} r_i^a a_i^a + \frac{1}{4} \sum_{abij} r_{ij}^{ab} a_i^a a_j^b + \cdots
\]

where \( | \Phi_0 \rangle \) is the reference determinant (usually Hartree-Fock) and \( \hat{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}} \) is the coupled cluster transformed Hamiltonian. The “open” transformed Hamiltonian \( \hat{H}_o = \hat{H} - \langle 0 | \hat{H} | 0 \rangle \). Following the usual convention, occupied orbitals are denoted by \( ijk \ldots \) while virtual orbitals are denoted by \( abc \ldots \). The \( \hat{T} \) operator is the well-known cluster operator which is determined by the ground state coupled cluster equations,

\[
\langle \Phi_{0ij...} | \hat{H}_o | \Phi_0 \rangle = 0
\]

\[
\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots
\]

\[
= \sum_{i} t_i^a a_i^a + \frac{1}{4} \sum_{abij} t_{ij}^{ab} a_i^a a_j^b a_i
\]
where $\langle \Phi_{i\ldots j\ldots} |$ is an excited determinant. EOM-CC is also applicable to ionization energies $\omega_{IP}$ (EOMIP-CC) through the use of a non-number conserving operator,

$$
\omega_{IP} \hat{R}_{IP} |\Phi_0\rangle = \hat{H}_o \hat{R}_{IP} |\Phi_0\rangle \\
\hat{R}_{IP} = \hat{R}_1 + \hat{R}_2 + \cdots \\
= \sum_i r_i a_i + \frac{1}{2} \sum_{ij} r_{ij} a_i^\dagger a_j a_i + \cdots
$$

The truncation of the $\hat{T}$ operator along with an equivalent truncation of the $\hat{R}$ (EE or IP) operators defines a particular canonical EOM-CC method. For example, the truncation $\hat{T} = \hat{T}_1 + \hat{T}_2$ and $\hat{R} = \hat{R}_1 + \hat{R}_2$ gives EOM-CCSD (note that $\hat{R}_0$ does not enter the excitation energy equations due to the fact that the coupled cluster equations have been solved).

The core-valence separation (CVS) \cite{34, 44} is a technique that decouples the core excitation or ionization spectrum from the valence continuum. As core states are resonances embedded in the valence continuum, the core-valence separation allows for direct calculations as if the core states were bound and avoid complications from convergence problems and unphysical couplings \cite{39}. The CVS has been shown to introduce negligible error on the computed excitation and ionization energies for first-row atoms \cite{34, 39}. In the context of EOM-CC, the CVS is equivalent to the restriction that only operators in $\hat{R}_{EE}$ and $\hat{R}_{IP}$ that contain at least one core orbital index are retained. In the present calculations, we also require that this core orbital index corresponds to only the selected atomic number. For example, a CVS-EOM-CC calculation of the oxygen K-edge in CO would neglect operators with only valence or C 1$s$ occupied indices. This requirement is added to separate higher K edges from the core ionization continuum of a lower-energy edge. In larger molecules, it would also be possible to require that only core orbitals of one or a small number of symmetry-unique atoms are included in the core-valence separation. Since such core orbitals are highly localized, this is expected to be a very good approximation, and in theory dramatically reduces the number of excitation or ionization operators needed.

### 2.2. Methods with Approximate Triple Excitations

The EOMEE-CCSDT method \cite{45} canonically scales as $O(n^8)$ in both the ground state and excited state calculations. EOMIP-CCSDT reduces the scaling for the excited state to $O(n^7)$ but has the same ground state cost. For applications on realistic molecules, then, an approximation to the triples excitations that reduces the scaling down to $O(n^5)$ or better yet to $O(n^6)$ is highly desirable. As triples effects are important for reaching sub-eV accuracy for core-excited and core-ionized states (see \cite{39, 40} and the results in this work), such an approximation is critical for accurate calculations. The approximations assessed here span two different approaches: iterative approximations and non-iterative (perturbative) approximations.

The iterative approximations share the common feature that they neglect one or more terms in the transformed Hamiltonian $\hat{H}_o$. For example, the EOM-CCSDT-3 method \cite{48} includes all terms except those that scale as $O(n^8)$, or equivalently the terms of the form $\langle T | \hat{W} | T \rangle$ where $| T \rangle$ represents the triple excitation manifold and $\hat{W}$ is the two-particle part of $\hat{H}_o$. Importantly, these methods apply the same approximation of the transformed Hamiltonian in the ground state and excited state calculations.
This ensures that the EOM-CC excitation energies are equivalent to the linear response coupled cluster (LR-CC) poles of the ground state wavefunction. The iterative approximations used here are EOM-CCSDT-1 [47], -CCSDT-3, and -CC3 [10]. The related EOM-CCSDT-1b and -CCSDT-2 methods are not expected to provide any additional insights into the behavior of such methods for X-ray spectroscopy.

Perturbative approximations approach the problem from a different direction: instead of approximating the transformed Hamiltonian, they approximate the energy directly, and retain only important terms as determined by some partitioning of the Hamiltonian. The CCSD(T) method is the most well-known perturbative method for the ground state, but unlike the iterative approximations, CCSD(T) provides no approximate wavefunction or transformed Hamiltonian which can be used in the LR-CC or EOM-CC equations. The EOM-CCSD* method [50, 51] was developed in analogy to CCSD(T), but working from the final excited state energy in the perturbation expansion. In order to balance the treatment of triple excitations in the ground and excited states, the EOM-CCSDR(3) [49] and EOM-CCSD(T)(a) [52] methods were introduced. The latter explicitly constructs an approximate transformed Hamiltonian which is used in the excited state calculation, in close analogy to the iterative approximations. However, this requires an iterative calculation of the triples in the excited state, and so the EOM-CCSD(T)(a)* method [52] was also introduced which blends the EOM-CCSD(T)(a) and EOM-CCSD* approaches.

2.3. Scaling Reduction

Almost all of the approximate approaches scale as $O(n^7)$ for the ground state, with the exception of EOM-CCSD*. Of course, the leading-order cost is a one-time correction for EOM-CCSDR(3) and EOM-CCSD(T)(a) (“star” and “no star”), while for the iterative methods this cost must be paid every iteration of the coupled cluster equations. In the excited state, these methods also scale as $O(n^7)$ for valence excitations. Within the CVS, though, we can theoretically restrict the $\hat{R}$ operators to only those allowable (with at least one target core orbital) and reduce the scaling by one order of $n$. In the EOM-CCSD part of the calculation, this scaling reduction has only been recently achieved by Vidal et al. [37] and is not realized in the implementation in this work. However, the restriction of the triples excitations has been implemented. This is made possible by the non-orthogonal spin-adaptation approach [53] used in CFOUR [54], where the triples (and quadruples) amplitudes are stored as a set of “virtual blocks”.

For example, the $\hat{R}_3$ amplitudes are stored as a set of dense tensors $\{r_{abc}\}_{ijk}$, one for each symmetry-unique combination of the occupied orbital indices. Because the occupied indices are already treated separately from the virtuals and take advantage of sparsity due to permutational symmetry, this approach was naturally extensible to the CVS by simply filtering out all $ijk$ indices that do not contain at least one target core orbital. In this way, the scaling of all of the approximate approaches except for EOM-CCSD(T)(a) is reduced to $O(n^6)$ for the excited state calculation, and even for EOM-CCSD(T)(a) the calculation of ionization energies scales as at most $O(n^6)$. The methods used here should then be suitable for molecular sizes in the range that is currently accessible via CCSD(T), CC3, etc., with EOM-CCSD* potentially scalable to even larger systems due to strict $O(n^6)$ scaling.

\[1\] Of course, all of this analysis assumes treatment of core-excited and core-ionized states within the CVS approximation and with only a small number of core orbitals targeted. In the valence case, for example, scaling is not reduced.
3. Computational Approach

In the following benchmarks, EOM-CCSDT is used as the target method, as previous work has shown it to be accurate in comparison to experiment to within about 0.1 eV \cite{39, 40} with the aCVQZ (aug-cc-pCVQZ \cite{55–57}) basis. A limited number of calculations with EOM-CCSDTQ have also shown only small (<0.1 eV) residual correlation effects. Calculations at the EOM-CCSDT level were carried out using a development version of the CFOUR program package \cite{54} on the core ionization energies and the first four (vertical) core excitation energies for each K edge of H$_2$O, CO, NH$_3$, HCN, and C$_2$H$_4$, using the aCVTZ basis set except for H$_2$O which used the aCVQZ basis set. The computational geometries are listed in the Supplemental Information. For ethylene, the average of the nearly-degenerate gerade and ungerade transitions was used. EOM-CCSD, –CCSD*, –CCSDR(3), –CCSD(T)(a)*, –CCSDT-1, –CCSDT-3, and –CC3 calculations with the same basis sets were then performed on this test set. Additionally, EOM-CCSD(T)(a) (with an iterative triples correction for the excited state) was used to calculate all core ionization energies. All EOM calculations utilized the CVS with only a single core orbital targeted, except for C$_2$H$_4$ where molecular symmetry requires that both C$_1s$ orbitals are included in the target space. We also performed direct two-determinant coupled cluster singles and doubles (TD-CCSD \cite{58, 59}) calculations on all core-excited states, as all of these states are well-described as two-determinant open-shell singlets. Most states were accessible at this level of theory, however the 4s and 5s Rydberg states of HCN, CO, and NH$_3$ could not be converged with TD-CCSD. We have also excluded C$_2$H$_4$ from the TD-CCSD treatment as a broken-symmetry localized core-hole SCF solution is required to fully relax the orbitals in this case \cite{38}. The difference between the TD-CCSD energies and the CCSD ground state energy is denoted by $\Delta$CCSD, in analogy with $\Delta$SCF methods.

The $\Delta$CCSD ionization energies correspond to the difference between an ROCCSD calculation of the core-ionized state and the CCSD ground-state energy. Note that the TD-CCSD and ROCCSD calculations required that the “dangerous denominators” be removed \cite{29, 38} in the present implementation these denominators $\Delta_{ij}$ are identified as those for which $\min(\varepsilon_i, \varepsilon_j) > \min(\varepsilon_a, \varepsilon_b)$. No electrons are frozen in any of these calculations.

4. Results and Discussion

4.1. Ionization Energies

The aggregate results are summarized as normal error distributions in Figure 1, while the full results are available in the Supplementary Information. In this format, the ionization energy error for method $X$, $\omega_{IP}(X) - \omega_{IP}$(CVS-EOM-CCSDT), is modeled by a normal distribution and plotted as a normalized Gaussian function. In the following discussion, the “short” name for each method will be used for brevity, e.g. CVS-EOM-CCSD will be denoted as simply CCSD. The exception is the $\Delta$CCSD method which is not an equation-of-motion approach, and should not be confused with “CCSD”.

From the error distributions, we can see that the most accurate method is CCSD(T)(a), without the perturbative “star” correction. This is not unexpected as this method performs essentially full CCSDT for the excited state, with only the ground state triple excitations being approximated. Because the most important correlation effects for the core hole (orbital relaxation and core hole correlation) occur only in
the excited state, this explains its superior performance. Approximation of the ground state has much less of an effect as the majority of the valence correlation error cancels between the excited and ground states. On the other end of the spectrum, CCSD predicts core ionization energies almost uniformly more than 1 eV above CCSDT. ∆CCSD significantly improves on CCSD as it takes orbital relaxation into account explicitly rather than through correlation in the excited state. In contrast, the iterative triples approximations, with the exception of CCSDT-3, fail to improve the unsystematic error. The 95% confidence interval (CI) for each of these methods is greater than 1.2 eV. CCSDT-3 is an improvement, but only a marginal one as the CI only drops to ~0.7 eV. Finally, the perturbative approximations CCSD* and CCSD(T)(a)* both perform very well, with CIs below 0.3 eV, although the mean error is as large as 0.5 eV. Interestingly, CCSDR(3) is not able to improve on the iterative methods. Because full CCSD(T)(a) scales iteratively as $O(n^7)$ for core excitation calculations, it is really only a viable candidate for core ionization energies. However, its superior performance for absolute ionization energies opens the possibility that it could be used as an internal correction for systematic errors (systematic within the X-ray spectrum of a specific molecular K edge—this is a more powerful correction than a simple rigid shift). To this end, we also defined the “corrected” CCSD* method for core-excited states,

$$\omega_{EE}(\text{CCSD* corr.}) = \omega_{EE}(\text{CCSD*}) + \omega_{IP}(\text{CCSD(T)(a)}) - \omega_{IP}(\text{CCSD*})$$
4.2. Vertical Excitation Energies

Similar normal error distributions for all methods (now replacing CCSD(T)(a) with CCSD* corr.) are given for vertical core excitation energies in Figure 2. The CCSD and $\Delta$CCSD methods perform essentially identically to the ionization energy case (note that while the vertical axis is arbitrary, it is slightly more compressed in this figure). CCSDT-1 and CC3 also show minimal change, performing similarly to CCSD in terms of standard distribution albeit with essentially zero mean error. CCSD* and CCSD(T)(a)* also continue to perform quite well, with CCSDT-3 improving slightly so that it roughly matches the perturbative approximations in accuracy. The corrected CCSD* method also illustrates that the correction from the CCSD(T)(a) ionization energy can remove some systematic errors from CCSD*, as the mean error is shifted to almost zero. Additionally, the standard deviation of the CCSD* error drops slightly, showing that this correction is indeed leading to a more sophisticated error cancellation than a rigid shift. Finally, the most significant change from the ionization energy case is that the error in CCSDR(3) is dramatically improved such that it is essentially indistinguishable from CCSD(T)(a)*.

Of course, both the ionization and vertical excitation energies computed here are not necessarily the proper observables in the context of X-ray spectroscopy. In XPS, the chemical shift, i.e. the change in core ionization energy from some reference molecule has been shown to be less sensitive to errors in correlation energy. For CVS-EOM-CCSD, Liu et al. [39] found that the mean absolute error decreased by approximative a factor of 5–6 when considering chemical shifts rather than absolute ionization energies, but that the standard deviation only decreased by about 20%. Zheng et al. [38] found
Figure 3. Normal error distributions for core excitation term values. Iterative methods are denoted by solid lines, and perturbative methods by dashed lines. All methods except $\Delta$CCSD are core-valence separated EOM, e.g. "CCSD" = CVS-EOM-CCSD.

similar results for $\Delta$CCSD, while in both studies the addition of triples effects gave essentially the same error statistics for absolute ionization energies and chemical shifts. For core excitations, the absolute energy scale of the spectrum is often irrelevant, and calculated spectra are simply shifted to match either the first excitation peak or the ionization edge of the experimental spectrum. This shifting would be expected to have a similar effect on the error as going from absolute ionization energies to chemical shifts. One slight difference, however, is that the shift commonly applied to excitation energies is edge-specific, while chemical shifts constitute a global rigid shift for each element.

4.3. Term Values

To capture the effect of a system-specific shift on the core excitation energies, we have recomputed normal error distributions based on the error in the excitation term value, that is the difference in energy between the excitation and the corresponding ionization edge. We have used this measure rather than an experimental shift in order to maintain an entirely internally-calibrated theoretical benchmark. The term value normal error distributions are plotted in Figure 3 For CCSD, we can see that the mean error is significantly reduced, indicating that such a shift can indeed reduce the average deviation, but the standard deviation is essentially unchanged. A similar effect is observed for CCSD*, CCSD(T)(a)*, and CCSDT-3 (CCSD* corr. is exactly equal to CCSD* for term values). For CCSDT-1 and CC3 some reduction in mean error is observed as before, but the standard deviation is significantly reduced as well. The most
probably cause is that residual correlation errors (from the triples approximation) in the excited and ionized states almost precisely cancel, while this error does not necessarily cancel between different chemical systems. It should also be noted that the mean errors for these two methods are now the largest among the tested methods. This indicates a “consistent inconsistency” in the correlation treatment of the excited and ionized states, such that the ionization energy is consistently overestimated compared to the excitation energies, along with a high degree of error cancellation. Finally, the CCSDR(3) method shows very odd behavior for term values, with the standard deviation increasing by almost a factor of four compared to the vertical excitation energies. As this method also fared poorly for ionization energies, it seems that unlike CCSDT-1 and CC3 there is no benefit from error cancellation and in fact a degradation of the error inherited from the poor description of ionization. As CCSDR(3) and CCSD(T)(a)* are similar theoretically, it is not clear what the source of this error is, although a closer look at the individual errors shows that CCSDR(3) has trouble describing nitrogen core ionizations in particular.

5. Conclusions

Core ionization and core excitation energies for a variety of small molecules were computed with a selection of both iterative and non-iterative triple excitation methods, as well as with CVS-EOM-CCSD and ΔCCSD which neglect triple excitation effects. Comparison to full CVS-EOM-CCSDT shows that the unsystematic error in CVS-EOM-CCSD can be reduced by a factor of 2-3 by an approximate inclusion of triples effects, while systematic error in excitation energies can be largely eliminated by shifting the spectrum. The ΔCCSD method significantly improves on CVS-EOM-CCSD by taking orbital relaxation into account explicitly, and despite a complete lack of triple excitations, is the most accurate method tested here. Among the approximate triples methods, CVS-EOM-CCSD*, optionally augmented by an ionization energy correction from full CVS-EOM-CCSD(T)(a), is the most accurate method. The iterative CVS-EOM-CCSDT-3 method is also highly accurate, while the similar CVS-EOM-CCSDT-1 and CVS-EOM-CC3 methods are less accurate and in particular seem to consistently underestimate the gap between the excitation spectrum and the ionization edge. The CVS-EOM-CCSDR(3) method, while similar theoretically to other methods tested, does not seem to be suitable for calculating core excitation and ionization energies.

The ability of approximate triples methods to accurately describe soft X-ray spectra is an exciting prospect for highly-accurate spectroscopy in this region, especially as all of the methods tested scale as $\mathcal{O}(n^6)$ for the excited state calculation. In addition, the CVS-EOM-CCSD* method scales rigorously as $\mathcal{O}(n^4)$ including the ground state, and is coincidentally the most accurate EOM method. While the current study focuses only on energetics, it would also be interesting to explore approximate methods for calculating transition strengths. Going beyond energetics also weighs in favor of CVS-EOM-CC approaches over ΔCCSD, as the derivation of analytic properties in the latter would be difficult to say the least, in addition to the difficulty of converging a sufficient number of states with two-determinant coupled cluster.

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