New Methods for Core-Hole Spectroscopy Based on Coupled Cluster Theory

Megan Simons
msimons@smu.edu

Follow this and additional works at: https://scholar.smu.edu/hum_sci_chemistry_etds

Part of the Computational Chemistry Commons

Recommended Citation
Simons, Megan, "New Methods for Core-Hole Spectroscopy Based on Coupled Cluster Theory" (2023). Chemistry Theses and Dissertations. 36.
https://scholar.smu.edu/hum_sci_chemistry_etds/36

This Dissertation is brought to you for free and open access by the Chemistry at SMU Scholar. It has been accepted for inclusion in Chemistry Theses and Dissertations by an authorized administrator of SMU Scholar. For more information, please visit http://digitalrepository.smu.edu.
NEW METHODS FOR CORE-HOLE SPECTROSCOPY
BASED ON COUPLED CLUSTER THEORY

Approved by:

Dr. Devin Matthews
Assistant Professor, Chemistry

Dr. Doran I.G.B. Raccah
Assistant Professor, Chemistry

Dr. Kevin Brenner
Assistant Professor, Electrical and Computer Engineering
NEW METHODS FOR CORE-HOLE SPECTROSCOPY 
BASED ON COUPLED CLUSTER THEORY

A Dissertation Presented to the Graduate Faculty of the 
Dedman College 
Southern Methodist University 
in 
Partial Fulfillment of the Requirements 
for the degree of 
Doctor of Philosophy 
with a 
Major in Theoretical and Computational Chemistry 
by 
Megan Simons 

B.S., Mathematics and Chemistry, Rhodes College 

May 13, 2023
Copyright (2023)

Megan Simons

All Rights Reserved
ACKNOWLEDGMENTS

I would like to thank Dr. Devin Matthews for being my mentor and advisor for four years. I am forever grateful for the continuous encouragement and guidance I received and support for both my chemistry issues and health issues. This support really shaped my graduate school experience into such a positive one and that really pushed me to continue progressing through a pandemic and various health issues. I would also like to thank the members of the Matthews group for their support and friendship, specifically Tingting Zhao and Dr. Avdhoot Datar. I appreciate their help with all things chemistry and logistical and their support in every aspect of life. I am happy to have been one of the early members of this group and to have seen it flourish into the large and supportive group it is today.

I would like to thank my committee members, Dr. Doran Raccah and Dr. Kevin Brenner, for reading my synopsis and dissertation and more importantly providing valuable feedback and guiding questions after my synopsis presentation. I want to acknowledge the entire faculty and staff in the SMU Chemistry Department. Specifically, I want to mention Dr. Elfi Kraka, department chair, for her mentorship and support during these last four years, Dr. Michael Lattman, graduate program director, for his help on all questions, and Mandy Graham, the departmental assistant, for her assistance on every question and issue I had over the last four years and especially the last two years when I no longer had a Concur account and had to submit all reimbursements through her. I would also like to thank the Center for Research Computing, specifically Dr. Thomas Hagstrom, for the financial support through a fellowship and for fruitful discussion every week on various machine learning problems.

I would like to thank my husband, Ben, for the continuous support throughout the last 5 years. If it were not for you, I would not be at SMU right now. Thank you for telling
me to look at SMU for graduate school and spending your spring break senior year at home so I could come tour SMU and learn more about the program. Thank you for reading this manuscript and your patience as I talk through my research, even if you have no idea what I am talking about. Additionally I would like to thank our dogs, Luna, Felix, Sherman, and Mocha, for the emotional support and hugs during the last half of graduate school.
X-ray absorption spectra (XAS) is a method used to investigate atomic local structure and electronic states. Coupled cluster method is a numerical method used for describing many-body systems and electron correlation in a wavefunction. When equation-of-motion coupled cluster is used in XAS calculations, the ground state is applied to the excitation operator, which excites or ionizes the electron. This causes a large orbital relaxation error, normally ~5 eV, which leads to the need for triple excitations in order to obtain accurate results. This dissertation introduces a coupled cluster method that uses “transition potential” reference orbitals to reduce the orbital relaxation error and help with error cancellation, called transition-potential coupled cluster (TP-CC), that is tested on our 14 small molecule data set. Then, the TP-CC fractional core orbital occupation number is optimized for a specific element and tested on the data set. The results of the optimized core orbital occupation number are utilized in nucleobase x-ray absorption K-edge spectra calculations and compared with experimental data. Another coupled cluster method is introduced to address the issue of orbital relaxation through the addition of triples excitation only in the core ionization potential. The similarity-transformed equation-of-motion coupled cluster (STEOM-CC) method is used, with the additional inclusion of core-valence separation (CVS) and correlation of triple excitations only within the calculation of core ionization energies, called CVS-STEOM-CCSD+cT. Our new method, CVS-STEOM-CCSD+cT is tested on
our data set and compared to previously developed methods. Then, transition moments for CVS-STEOM-CCSD+cT excited states are implemented and tested on our data set. Lastly, tensor hypercontraction for open-shell systems is implemented and tested on molecules such as radicals, bond cleavages, and solvation shells, and the errors are compared to the errors obtained when using closed-shell tensor hypercontraction.
# TABLE OF CONTENTS

LIST OF FIGURES ................................................................. xi

LIST OF TABLES ................................................................. xiii

CHAPTER

1 Introduction ............................................................... 1
   1.1. Overview ............................................................ 1
   1.2. General Introduction .............................................. 2
   1.3. Research Overview ................................................ 4

2 Computational Methods ................................................. 6
   2.1. Quantum Mechanics ................................................. 6
   2.2. Coupled cluster methods .......................................... 10
      2.2.1. Equation of motion (EOM) .................................... 13
      2.2.2. Core valence separation ...................................... 15
      2.2.3. Transition-potential coupled cluster ....................... 16
      2.2.4. Similarity-transformed equation of motion (STEOM) .. 18
      2.2.5. Transition moments ........................................... 21
   2.3. Møller-Plesset Theory ........................................... 29
   2.4. Tensor hypercontraction ......................................... 33

3 Transition-potential coupled cluster (TP-CC) ...................... 35
   3.1. Background ........................................................ 35
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>Results and Discussion</td>
<td>37</td>
</tr>
<tr>
<td>3.3</td>
<td>Summary</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>TP-CC: Optimization of the core occupational number</td>
<td>41</td>
</tr>
<tr>
<td>4.1</td>
<td>Background</td>
<td>41</td>
</tr>
<tr>
<td>4.2</td>
<td>Results and Discussion</td>
<td>42</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Optimizing the core orbital occupation number (lambda)</td>
<td>42</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Comparing x-ray absorption k-edge calculations against experiment</td>
<td>44</td>
</tr>
<tr>
<td>4.3</td>
<td>Summary</td>
<td>46</td>
</tr>
<tr>
<td>5</td>
<td>Similarity-transformed equation of motion coupled cluster (STEOM-CC)</td>
<td>48</td>
</tr>
<tr>
<td>5.1</td>
<td>Background</td>
<td>48</td>
</tr>
<tr>
<td>5.2</td>
<td>Results and Discussion</td>
<td>49</td>
</tr>
<tr>
<td>5.3</td>
<td>Summary</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>STEOM-CC: Transition moments</td>
<td>52</td>
</tr>
<tr>
<td>6.1</td>
<td>Background</td>
<td>52</td>
</tr>
<tr>
<td>6.2</td>
<td>Results and Discussion</td>
<td>53</td>
</tr>
<tr>
<td>6.3</td>
<td>Summary</td>
<td>54</td>
</tr>
<tr>
<td>7</td>
<td>Implementation of open-shell tensor hypercontraction</td>
<td>56</td>
</tr>
<tr>
<td>7.1</td>
<td>Background</td>
<td>56</td>
</tr>
<tr>
<td>7.2</td>
<td>Results and Discussion</td>
<td>57</td>
</tr>
<tr>
<td>7.3</td>
<td>Summary</td>
<td>60</td>
</tr>
</tbody>
</table>
8 Conclusions ......................................................... 62

BIBLIOGRAPHY ....................................................... 63

APPENDIX

A  Paper on transition-potential coupled cluster ......................... 72
B  Paper on optimization of transition-potential coupled cluster ...... 83
C  Paper on similarity-transformed equation-of-motion coupled cluster 94
D  Paper on transition moments for similarity-transformed equation-of-motion coupled cluster ................................................. 102
E  Paper on open shell tensor hypercontraction ............................ 118
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Diagrammatic representation of the wavefunction at the ground state, the electron going from the ground state to the excited state, and the electron going from the ground state to the ionization potential state.</td>
<td>14</td>
</tr>
<tr>
<td>2.2 Brandow diagrams for the connected triples contribution (only for the core orbital) to the STEOM single density matrix. (a) The single loop above the S vertex leads to the 2 in the denominator. (b) The two loops above the S vertex leads to the 4 in the denominator.</td>
<td>28</td>
</tr>
<tr>
<td>3.1 The 14 molecule data set that became our testing data set for every developed method from this project forward. The data set contains all small molecules (6 atoms or less) and all first row elements. This specific set of molecules will be referred to as “the data set” throughout the dissertation. The molecules were optimized using the CCSD(T) method [86, 87] and Dunning’s correlation consistent basis set, cc-pVTZ, [88, 89] which include polarization functions by definition. Then a developmental version of CFOUR was used for all STEOM, EOM, and TP calculations, utilizing the aug-cc-pCVTZ basis set with all electrons correlated, except for water where aug-cc-pCVQZ was used. [89, 90]</td>
<td>38</td>
</tr>
<tr>
<td>3.2 On the left, Gaussian error distributions for absolute core excitation energies. CVS-EOM-CCSD (an iterative method) is represented by a dotted line, CVS-EOM-CCSD* (a perturbative method) is represented by a dashed line, and TP-CCSD methods are represented by solid lines. On the right is an illustration of how the absolute core excitation energies are measured; from the ground state to an excited state (in the figure is an example of an electron being excited from the ground state to the first excited state).</td>
<td>39</td>
</tr>
</tbody>
</table>
4.1 The minimum mean absolute error (in eV) for element-specific k-edge spectra reveals the optimal lambda (core orbital occupation number) for each element. Each curve is for a specific element; nitrogen (orange), carbon (green), oxygen (red), or fluorine (purple) except for the combined element curve (blue). The minimum MAE values for TP-CCSD are compared to the minimum MAE values for EOM-CCSD across various statistics (the numbers are displayed as ratios).

4.2 The nitrogen k-edge spectra for adenine and oxygen k-edge spectra for thymine. The x-ray absorption curves for EOM-CCSD and TP-CCSD methods are compared to experimental curves. Also noted at the top of the graphs are the shifts for each method in order to line up the first computational peak with the first experimental peak (this is done when comparing computational and experimental spectra).

5.1 The core excitation absolute energy errors (in eV) for various coupled cluster methods with respect to CVS-EOM-CCSDT. Our newly developed method, CVS-STEOM-CCSD+cT is emphasized in the middle.

6.1 Error distributions with respect to CVS-EOM-CCSDT for relative oscillator strengths (intensities), displayed as percentages. The equation to calculate oscillator strengths for one state and another state (in our case ground state to excited state) is displayed at the top of the image, with an example of a core excitation energy for HCN under it.

7.1 The 3 molecules we tested for open-shell tensor hypercontraction (plus linear alkanes). Glutathione and 9-propyl-4,11-tridecadienoic acid molecules are presented as ball-and-stick structures; glutathione has the C-C, C-N, and C-S bonds labeled where bond cleavage occurred and 9-propyl-4,11-tridecadienoic acid has arrows pointing to the hydrogens that were “plucked” off the molecule to make it a radical. The 2H-2-azabicyclo[1.1.1]pentane radical is illustrated with a solvation shell and the solvent waters are numbered by center of mass distance from the solute.

7.2 Bond dissociation energy errors of glutathione. (a) Absolute BDE error due to THC. The solid lines indicate homolytic bond cleavage (open-shell) and dashed lines indicate heterolytic bond cleavage (closed-shell). The bond index refers to labeled bonds in Fig. 7.1. (b) Absolute errors in the difference between the homolytic and heterolytic BDEs due to THC. The legend, $-\log(\epsilon)$, represents the parent grid being pruned as done in Ref. [28] (the numerical cutoff can be referred to as the “tolerance”).
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>37</td>
</tr>
</tbody>
</table>

The current theoretical methods used in x-ray absorption spectroscopy calculations are listed, along with their pros and cons.
Dedicated to Ben.
Chapter 1

Introduction

1.1. Overview

This dissertation summarizes my research throughout the four years of my study in the Theoretical and Computational Chemistry department at SMU. Since the beginning, I have studied new methods for x-ray absorption spectroscopy based on coupled cluster methods and the theoretical details of these methods are described in Chapter 2. The new methods that I developed are the transition-potential coupled cluster method—the details are described in Chapter 3, and the similarity-transformed equation-of-motion coupled cluster singles and doubles method with core triples—the details are described in Chapter 5. The TP-CC method was fine-tuned to lower the error by optimizing the fractional occupational core-hole on a element-specific basis and those details can be found in Chapter 4. In addition to excitation energies that are measured when using x-ray spectroscopy, transition moments can be calculated to measure the strength of the interactions between states describing absorption and emission. The transition moment code development and results for EOM-CCSD, STEOM-CCSD, and STEOM-CCSD+cT are described in Chapter 6.

An additional aim of my research included the development of open-shell tensor hyper-contraction methods for MP2 and MP3 methods focusing on interesting molecules, such as bond breaking, radicals, and reactions; a collaboration with Tingting Zhao. The details and results of this work can be found in Chapter 7.
1.2. General Introduction

X-ray absorption spectroscopy (XAS) has been used for many years by experimental chemists to study electronic and molecular structure. [1] Experiments utilizing x-ray absorption spectra can be in the gas phase, solutions, or solids. However, theoretical calculations can utilize XAS to assist in interpreting and predicting spectra of unknown compounds. X-ray techniques are important in addressing the challenges of understanding the structure of complex molecules and understanding the behavior of these molecules. [2, 3] Theoretical chemists have predominantly used density functional theory (DFT) methods for XAS due to their computational efficiency, but these methods are not always very accurate. The inaccuracy is seen when computing a description of the ground state electronic structure [4, 5] due to large self-interaction errors. [3, 6] The large self-interaction errors originate from the inability of approximate density functionals to exactly cancel Coulomb and exchange correlation interactions for all one-electron densities. [7, 8]

Coupled cluster (CC) method is a numerical method used for describing many-body systems and electron correlation in a wave function. CC has an explicit wavefunction, $\lambda$, which is manipulated to excite electrons. [9, 10] In equation of motion coupled cluster theory, the ground state is applied to the excitation operator, which excites or ionizes the electron. [11] In x-ray spectroscopy specifically, coupled cluster goes from the ground state to the excited state. This causes a large orbital relaxation error, normally $\sim 5$ eV. The orbital relaxation error is difficult for the excitation operator to take into account. This necessitates the need for triple excitations in order to obtain accurate results. [12]

Many computational chemists opt to utilize linear response methods, such as equation-of-motion coupled cluster (EOM-CC) methods, due to their success in the description of valence excitations for core-hole states. [10–12] Another linear response method that is utilized is time-dependent density functional theory (TD-DFT), however it has been shown to describe core-hole states rather poorly due to large self-interaction errors. [4, 5, 13] Another method,
the $\Delta$Kohn-Sham method, separately performs semi-variational optimizations of both the ground and core-hole states. [14] It has been shown to accurately reproduce absorption and ionization spectra in many cases but suffers from convergence difficulties and the need to compute transition properties in a non-orthogonal framework. [15–17]

As a compromise between linear-response methods and state-specific orbital optimizations, transition-potential DFT (TP-DFT) can be used. [18–20] TP-DFT works by performing a single calculation with fractional orbital occupation. TP-DFT theoretically works as an approximation to Slater’s Transition State (TS) method. [21] Although TP-DFT improves on methods such as TD-DFT, there remains errors at assigning peak positions and intensities in XAS. Therefore, the accuracy of equation-of-motion coupled cluster (EOM-CC) methods provides a significant motivation for applying EOM-CC to XAS. The additional expense of including triple excitations to achieve accuracy has motivated computational chemists to search for an effective EOM-CC method that can accurately treat core-hole states at a purely singles and doubles level.

Due to the issues plaguing the previously mentioned methods, we proposed a “transition-potential coupled cluster” (TP-CC) method analogous to TP-DFT, with hopes of reducing the orbital relaxation error and helping with error cancellation. Transition-potential coupled cluster applies the ideas of TP-DFT to coupled cluster methods. TP-CC improves the accuracy of energies and oscillator strengths and is computationally efficient.

Equation-of-motion coupled cluster theory can be used for excited (EE-EOM-CC), electron-attached (EA-EOM-CC), and ionized state (IP-EOM-CC) energies. [22, 23] This is possible by taking advantage of the similarity transformation of the Hamiltonian, which guarantees size-extensivity of the excited state total energy. Nooijen et al. proposed an alternative approach to EOM-CC by using a second similarity transformation of the Hamiltonian, followed by diagonalization in a small excitation space. [24, 25] The similarity-transformed equation-of-motion coupled cluster (STEOM-CC) similarity transformation uses the wave function of
a number of ionized and electron-attached states in order to build the transformation. The errors in STEOM-CC are generally smaller than EOM-CC due to the ability of STEOM to accurately compute low lying states, but the errors for the two methods are still comparable. In order to decrease this error, we proposed a method that includes triple excitations in the core ionization potential, STEOM-CCSD+cT (plus core triples). STEOM-CCSD+cT improves the accuracy of energies and oscillator strengths and is more computationally efficient than CVS-EOM-CCSDT.

Tensor hypercontraction (THC) can be applied to any electronic structure method based on the wave function (MP, CC). It is an approximation to help deal with the $O(N^4)$ growth of the electron repulsion integral (ERI) tensor, where $N$ is the number of one-electron basis functions used to represent the electronic wavefunction. THC reduces the 4th order ERI tensor to five matrices, which helps with the storage requirements and the ability to regroup terms. [26–29] It is important to decrease the growth of the ERI as it is a critical part in all electronic structure methods, such as Hartree-Fock (HF) theory to Coupled Cluster (CC) theory. The usual scaling behavior for MP2 and MP3 are $O(N^5)$ and $O(N^6)$, respectively, but can be carried out at the $O(N^4)$ scaling. [26,27] While these advancements for reducing scaling of tensors is important to be able to have computational efficiency, the methods thus far are only for closed-shell molecules (the number of alpha electrons is equal to the number of beta electrons, $n\alpha = n\beta$). The most interesting molecules, such as those involved in reactions and bond breaking, do not have the same number of alpha and beta electrons. These are open-shell molecules and should be studied. We implemented THC code to study open-shell molecules at the MP2 and MP3 level of theory.

1.3. Research Overview

The goal of this research is to improve on existing coupled cluster methods—in both accuracy and computational cost—and to use these coupled cluster methods for x-ray absorption spectroscopy calculations. The research introduced and examined two methods that treat
orbital relaxation for core excited states: the transition-potential couple cluster (TP-CC) method and the similarity transformed equation-of-motion coupled cluster (STEOM-CC) method with triple excitations for only core ionization energies, which is referred to as STEOM-CCSD+cT. The (X)TP-CC methods were further improved by optimizing the core orbital occupation number, $\lambda$, for each K-edge element (carbon, nitrogen, oxygen, fluorine) with the goal of decreasing the remaining errors. Additionally, the accuracy of the TP-CC method is tested by checking its ability to reproduce experimental spectra and compared to EOM-CCSD. While the STEOM-CCSD+cT method was shown to be more accurate for transition energies, the oscillator strengths needed to be computed as they are an important part of the x-ray absorption spectra. Therefore, the oscillator strengths were computed for STEOM-CCSD and STEOM-CCSD+cT. Lastly, open-shell tensor hypercontraction methods at the MP2 and MP3 level of theory were applied to four varying molecules.
2.1. Quantum Mechanics

The theory of quantum mechanics has transformed the development of modern chemistry and paved the way for theoretical chemistry as we know it today. [30–32] While many of the beginning concepts of quantum chemistry were foundational and basic in some manner, monumental advances in computational hardware and computational methods have allowed such methods to be comparable to experimental studies (such as predicting spectra in x-ray spectroscopy [33–35]). This chapter will briefly outline some of those fields of quantum chemistry discussed in this dissertation.

Most of the information in this section comes from knowledge gained in the partial differential equations class I took at Rhodes College (undergraduate), the computational chemistry class I took at Southern Methodist University (graduate), and Ref. [36].

We start with the Schrödinger equation that has both position and space elements for a single non-relativistic particle in one dimension [37],

\[ i\hbar \Psi(x, t) = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t) \right] \Psi(x, t) \]  \hspace{1cm} (2.1)

where \(\Psi(x, t)\) is a wave function with values at each point \(x\) at each time \(t\), \(m\) is the mass of the particle, \(V(x, t)\) is the potential in the environment where the particle exists, \(i\) is the imaginary number, and \(\hbar\) is the reduced Planck constant (Planck’s constant divided by \(2\pi\)). The issue with this Schrödinger equation is that it can only be solved exactly for
hydrogen-like species consisting of one nucleus and one electron and nothing beyond that due to the numerous unknowns. We can get further by utilizing the Born-Oppenheimer approximation [38], which separates the movement of the nuclei from the motion of the electrons. This permits the center of mass of the molecule to be approximated as simply the center of mass for a set of fixed nuclei and allows the molecular Hamiltonian to be used. This form of the Hamiltonian is utilized throughout the computational methods used for calculations.

The time-dependent Schrödinger equation describes the equation with regards to time,

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle$$ \hspace{1cm} (2.2)

where $t$ is time, $|\Psi(t)\rangle$ is the state vector of the quantum system, and $\hat{H}$ is the Hamiltonian operator, an observable, made up of the kinetic and potential energies in the system. An operator applies one or more mathematical acts on a function.

The time-independent Schrödinger equation describes the equation with stationary states and not depending on time explicitly,

$$\hat{H} |\Psi\rangle = E |\Psi\rangle$$ \hspace{1cm} (2.3)

where $E$ is the energy of the system. We define the wavefunction, $|\Psi\rangle$, using the ansatz, which is an assumption about the form of an unknown function (the wave function in our case) which is made in order to facilitate solution of an equation (the time-independent Schrödinger equation in our case), [39]

$$|\Psi\rangle = e^{T}|\Phi\rangle.$$ \hspace{1cm} (2.4)
We insert the above definition into the time-independent equation,

\[ \hat{H} e^T |\Phi\rangle = E e^T |\Phi\rangle \]

and then multiply both sides by \( e^{-T} \) in order to isolate the energy,

\[ e^{-T} \times \hat{H} e^T |\Phi\rangle = E e^T \times e^{-T} |\Phi\rangle. \]

The expression on the left side of the equation to the left of the ansatz gives us \( \tilde{H} \), the singly similarity transformed Hamiltonian used in EOM-CC theory, and the energy with only the ansatz,

\[ \tilde{H} |\Phi\rangle = E |\Phi\rangle. \tag{2.5} \]

The last step to get the energy by itself involves multiplying both sides by an ansatz the bra position, \( \langle \Phi | \) (note: this ansatz can be excited and is not the reference),

\[ \langle \Phi^{ab...} | \tilde{H} |\Phi\rangle = \langle \Phi^{ab...} | E |\Phi\rangle. \]

The energy cannot have one side in the bra-ket notation with an excitation and one with a ground state, so \( \langle \Phi^{ab...}_{ij...} | E |\Phi\rangle \) is equal to 0.
Assessing the expression where both ansatz expressions are not excited,

\[ \langle \Phi | E | \Phi \rangle = \int \Phi^*(r) E \Phi(r) dr \]

\[ E \langle \Phi | \Phi \rangle = \int |\Phi|^2 dr \]

where \( \langle \Phi | \Phi \rangle \) is normalized so it is equal to 1. This leads to the final energy equation,

\[ \langle \Phi | \bar{H} | \Phi \rangle = E. \quad (2.6) \]

The slater determinant describes the wave function for a multi-electron system:

\[ \Psi(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \chi_1(x_1) \chi_2(x_1) \ldots \chi_N(x_1) \chi_1(x_2) \chi_2(x_2) \ldots \chi_N(x_2) \ldots \chi_1(x_N) \chi_2(x_N) \ldots \chi_N(x_N) \quad (2.7) \]

In the determinant above, each electron is associated with each orbital. The Slater determinant is the simplest possible antisymmetric wave function and is used as an approximation to electronic wavefunction in Hartree-Fock theory. The antisymmetry in the wave function comes from the Pauli exclusion principle, which states that two or more identical particles with half-integer spins cannot occupy the same quantum state at the same time (i.e. if one electron has +1/2 spin, then the other electron in the system must have −1/2 spin). \[30, 40\]

In more accurate theories, a linear combination of Slater determinants is needed.
2.2. Coupled cluster methods

Electronic structure theory is used to treat the motion of the electrons in a static field of nuclei, balanced against the repulsive interaction between electrons and their kinetic energy. The issue is that it is nearly impossible to solve for the full electronic wavefunction, therefore approximate theories must be derived to do so. [41, 42] The approximate theory we use in this work is coupled cluster theory, which is a molecular orbital theory. In molecular orbital theory, electrons in a molecule are not assigned to individual chemical bonds between atoms; rather they are treated as moving because of the atomic nuclei in the whole molecule. Utilizing molecular orbital theory in quantum mechanics allows for the spatial and energy properties of electrons to be described as molecular orbitals that surround two or more atoms in a molecule and contain valence electrons between those atoms. [43, 44] Molecular orbital theory approximates the states of bonded electrons, the molecular orbitals, as linear combinations of atomic orbitals. These approximations are made by applying approximate theories, such as DFT or CC, to the Schrödinger equation. [45]

Most of the information in this section comes from Refs. [9, 36, 46, 47].

The coupled cluster method is used to describe many body systems and electron correlation in a wave function. The coupled cluster ground state is characterized by a non-Hermitian similarity transformation of the Hamiltonian during diagonalization, which gives rise to $\tilde{H}$:

$$\tilde{H} = e^{-\hat{T}} He^{\hat{T}}. \tag{2.8}$$

Non-Hermitian is defined as the function not having real energy eigenvalues and it is important to study such systems since there are more open quantum systems than isolated quantum systems. [48] Similarity transformation is a matrix transformation in three dimensions that results in a similarity (when the transformation preserves angles, changes of
Similarity transformations transform objects in space to similar objects. [49] Matrix elements (contains complete set of orbitals) of the transformed function are defined by a transformation matrix and intermediate functions (contains one or more active orbitals). The complete set of orbitals includes the core orbitals, which must always hold two electrons; active orbitals, which are allowed to be fully or partially occupied; and virtual orbitals, which must always hold zero electrons. [50,51]

The transformed Hamiltonian provides the ability to obtain excited states. The Hamiltonian operator is a quantum mechanical operator with energy represented as eigenvalues and the eigenvalues are the possible outcomes of the total energy of a quantum mechanical system. The Hamiltonian expression for coupled cluster systems is a Taylor series expansion and is shown below being truncated at the singles and doubles level,

\[
\hat{H}_N = \sum_{pq} f_{pq} \{ p^\dagger q \} + \frac{1}{4} \sum_{pqrs} v_{pqrs} \{ p^\dagger q^\dagger s r \} \tag{2.9}
\]

where the \( \dagger \) represents a creation operator, which increases the number of particles in a state by one particle, and the indices without \( \dagger \) represent an annihilation operator, which decreases the number of particles in a state by one particle. Creation and annihilation operators act on electronic states. The use of these operators instead of wavefunctions is known as second quantization. Second quantization was introduced by Dirac as an algorithm to express multi-particle quantum operators clearly through the use of creation and annihilation operators to construct and handle the Fock states, which is the sum of a set of Hilbert spaces representing zero particle states, one particle states, two particle states, and so on. [32,52,53] Hilbert spaces are vector spaces equipped with an inner product (e.g. Euclidean vector space consists of three-dimensional vectors equipped with the dot product). [54]
The truncation at the singles and doubles level for coupled cluster allows us to write an expression for the cluster operator, $\hat{T}$, which acts as a pure excitation operator:

$$
\hat{T} = \sum_{ai} t_i^a a_i^\dagger + \frac{1}{4} \sum_{abij} t_{ij}^{ab} b_i^\dagger j_i
$$  \hspace{1cm} \text{(2.10)}

The coupled cluster energy can be expressed using the zeroth order description of the wave function (single determinant) and the transformed Hamiltonian,

$$
E_{CC} = \langle \Phi_0 | \bar{H} | \Phi_0 \rangle.
$$  \hspace{1cm} \text{(2.11)}

The excited determinant, $|P\rangle$, can be written as an expression, made up of singly and doubly excited determinants:

$$
|P\rangle = |S\rangle \oplus |D\rangle
$$  \hspace{1cm} \text{(2.12)}

The ground state coupled cluster energy is expressed as an eigenvalue of $\bar{H}$ with distinct right and left eigenfunctions due to the similarity transformation being non-Hermitian,

$$
\bar{H} \hat{R}(0) |\Phi_0 \rangle = E_{CC} \hat{R}(0) |\Phi_0 \rangle, \hat{R}_0 = 1
$$  \hspace{1cm} \text{(2.13)}

$$
\langle \Phi_0 | \hat{L}(0) \bar{H} = \langle \Phi_0 | \hat{L}(0) E_{CC}, \hat{L}_0 = (1 + \hat{\Lambda}).
$$  \hspace{1cm} \text{(2.14)}
2.2.1. Equation of motion (EOM)

Most of the information in this section comes from Refs. [11, 12, 36].

Computational chemists use equation of motion coupled cluster because it enables treat-
ment of states other than the ground state. Therefore, it is the standard for the computation
of excitation energies. Equation-of-motion coupled cluster method can be defined as the di-
agonalization of the CCSD effective Hamiltonian, where the cluster amplitudes are taken
from the corresponding CCSD ground-state energy calculation, in the space of all singly and
doubly excited determinants. In x-ray spectroscopy specifically, coupled cluster goes from
the ground state to the excited state. This is done by applying the excitation operator to
the ground state, which either excites the electron or ionizes the electron:
Figure 2.1: Diagrammatic representation of the wavefunction at the ground state, the electron going from the ground state to the excited state, and the electron going from the ground state to the ionization potential state.

In Figure 2.1, the wavefunction is defined for the 3 states illustrated. The operator $\hat{R}$ is the excitation operator and it is used to describe the difference between the ground and excited/ionized states. In order to obtain these excited/ionized states, the eigenvalue equation must be solved,

$$\left[ \bar{H}, \hat{R}_1(m) \right] |\Phi_0\rangle = \omega \hat{R}_1(m) |\Phi_0\rangle$$  \hspace{1cm} (2.15)

where $\bar{H}$ is the transformed Hamiltonian, $\hat{R}$ is the excitation operator, and $\omega$ is the vertical excitation energy.

The diagonalization occurs in the singles-singles space, which is the reason for using the singly excited operator. The explicit diagonalization of the transformed Hamiltonian shifted by the ground state energy gives the associated right and left eigenfunctions for the excited state operators (distinct due to the non-Hermitian nature of the similarity transformation),
\[ \hat{R}(m) = \sum_{k=0}^{N} \hat{R}_k(m) \]

\[ = r_0(m) + \sum_{ai} r_i^a(m) a_i^\dagger a_i + \frac{1}{4} \sum_{abij} r_{ij}^{ab}(m) a_i^\dagger a_j^\dagger a_j a_i + \ldots \quad (2.16) \]

\[ \hat{L}(m) = \sum_{k=1}^{n} \hat{L}_k(m) \]

\[ = \sum_{ai} l_i^a(m) a_i^\dagger a_a + \frac{1}{4} \sum_{abij} l_{ij}^{ab}(m) a_i^\dagger a_j^\dagger a_j a_i + \ldots \quad (2.17) \]

The left-hand eigenfunction equations are not explicitly connected, while the connectedness of the right eigenfunction equations allows for a solution purely in terms of \( \hat{R}_1 \) and \( \hat{R}_2 \).

Both set of eigenfunctions equations are necessary to calculate properties, such as transition moments. The singly ionized and electron-attached states are formed through excitation operators (only the right-hand side is below),

\[ \hat{R}_{IP}(m) = \sum_{k=1}^{N} \hat{R}_{IP,k}(m) = \sum_{i} r_i(m) a_i + \frac{1}{2} \sum_{aij} r_{ij}^a(m) a_i^\dagger a_j a_i + \ldots \quad (2.18) \]

\[ \hat{R}_{EA}(m) = \sum_{k=1}^{N} \hat{R}_{EA,k}(m) = \sum_{a} r_i^a(m) a_i^\dagger a_a + \frac{1}{2} \sum_{abi} r_{ij}^{ab}(m) a_i^\dagger a_b a_i + \ldots \quad (2.19) \]

2.2.2. Core valence separation

Most of the information in this section comes from Refs. [36, 55–57], with Cederbaum and Schrimer introducing the technique and applied to EOM-CC by Coriani and Koch.
Core-valence separation approximation consists of removing all excitations that do not involve at least one core orbital from the excitation manifold when computing core level spectra. Removing all excitations from the manifold fixes the convergence problems EOM-CC encounters when applied to core excited and core ionized states.

In CVS-EOM-CC, the amplitudes which correspond to purely valence excitations are explicitly zeroed. This leaves only components involving one or more core orbitals (indicated by capital roman letters in figure and equation below). The core-valence separation (CVS) scheme allows one to extend standard methods for excited and ionized states to the core-level states. In this approach, the excitations involving core electrons are decoupled from the rest of the configurational space.

The excitation operator utilizing CVS can be written as:

\[ \hat{R}_{CVS} = \sum_{aI} r^a_I(m) a^\dagger_I a_I + \frac{1}{2} \sum_{ablj} r^{ab}_{lj}(m) a^\dagger_a a^\dagger_b a_j a_I + \frac{1}{4} \sum_{ablI} r^{ab}_{lI}(m) a^\dagger_a a^\dagger_b a_I a_I + \ldots \] (2.20)

For STEOM-CCSD excited states, CVS can be applied in two places—giving rise to CVS-STEOM-CCSD for excited states:

1. Selection of the active space must include the core orbital and when solving for these core ionization wavefunctions, CVS is necessary to stabilize convergence

2. Solution of the eigenvalue equations may also use CVS in defining the single excitation operator, \( \hat{R}_1 \), in order to accelerate computation

2.2.3. Transition-potential coupled cluster
Time-dependent density functional theory (TD-DFT) is an alternative to time-dependent quantum mechanics, where the difference is its basic variable is the one-body electron density, \( n(r,t) \). Transition-potential density functional theory (TP-DFT) is an alternative to TD-DFT that uses Kohn-Sham eigenvalue differences, \( \Delta E = \epsilon_v - \epsilon_c \) where the difference is between core orbitals and valence orbitals. This approach uses Kohn-Sham orbital eigenvalue differences to approximate core-level excitation energies, based on a Kohn-Sham calculation with partial occupations of the orbitals involved in the transitions. [59,60]

The orbital relaxation error, the main problem we are trying to address, refers to the changes in the Fock operator and Hartree-Fock orbitals when changing the number of electrons in the system and it comes from an approximation where the orbitals of only one of the molecules is used to describe both of the species in a system, which is not necessarily true. [61]

The transition potential method is an approximation to Slater’s transition state (TS) method. Slater’s transition state method enables computational chemists to calculate excitation energies by using an artificial state that is halfway between the ground state of an atom and an excited state. Starting with transition-potential density functional theory (TP-DFT) as it is a compromise between linear-response methods and state-specific orbital optimizations. It works by performing a single calculation with a fractional orbital occupation. TP-DFT improves on TD-DFT, but in TP-DFT there are still errors at assigning peak positions and intensities in XAS. The process for deriving a fractional orbital occupation for TP-DFT is as follows:

\[
\omega_{IP,\Delta DFT} = E_{DFT}(n_{1s} = 0) - E_{DFT}(n_{1s} = 1)
\]
\[ = \int_1^0 \frac{\partial E_{DFT}(n_{1s} = \lambda)}{\partial \lambda} d\lambda \text{(by the Fundamental Theorem of Calculus)} \]

\[ = -\int_0^1 \epsilon_{1s}(n_{1s} = \lambda) d\lambda \text{ (by Janak’s Theorem)} \]

\[ \approx -\epsilon_{1s}(n_{1s} = 0.5) \text{ (by the Trapezoidal Rule)} \]

This fractional orbital occupation formulation is used in coupled cluster theory and presented in Chapter 3.

2.2.4. Similarity-transformed equation of motion (STEOM)

Most of the information in this section comes from Refs. [24, 25].

Similarity transformed equation-of-motion coupled cluster theory (STEOM-CC) is an alternative approach to equation-of-motion coupled cluster theory for excited states. STEOM-CC starts with a second similarity transformation of the Hamiltonian,

\[ \hat{G} = \left\{ e^{S^+ + S^-} \right\}_N^{-1} \hat{H} \left\{ e^{S^+ + S^-} \right\}_N \quad (2.21) \]

\[ \hat{G} = \sum_{pq} g_{pq} a^\dagger_p a_q + \frac{1}{4} \sum_{pqrst} g_{pqrst} a^\dagger_p a^\dagger_q a_s a_r + \ldots \quad (2.22) \]

The transformed Hamiltonian assumes a block form where the singles are mostly decoupled, but not fully because pieces of the singles come from the non-active space. The \( S_1 \) amplitudes are not necessary for the solution of the STEOMEE-CC equations as they simply
cause rotations within the singles excitation space, and hence a diagonalization within the full singles space is unchanged. In fact, diagonalization within the full rather than the active singles space is desirable as the portion of the solution falling outside the active space serves as a measure of active space insufficiency.

The transformation operator \( \hat{S} \) has components in both the electron-attached (or \((1,0)\)) and ionized (or \((0,1)\)) sectors of the Fock space,

\[
\hat{S} = \hat{S}^+ + \hat{S}^-,
\]  

\[
\hat{S}^+ = \sum_k \hat{S}^+_k = \sum_{ae} s_{ae}^a a^\dagger_e + \frac{1}{2} \sum_{abej} s_{abej}^a b^\dagger_e a^\dagger_j a_e + \cdots,
\]  

\[
\hat{S}^- = \sum_k \hat{S}^-_k = \sum_{im} s_{im}^m a^\dagger_m a_i + \frac{1}{2} \sum_{ijmb} s_{ijmb}^m b^\dagger_m a^\dagger_j a_i + \cdots,
\]

where \( e \) and \( m \) are associated with sets of \( n_{v;\text{act}} \) active virtual and \( n_{o;\text{act}} \) active occupied orbitals (transformed back to the canonical MO space). The equations that determine the amplitudes of \( \hat{S} \) are obtained by equating the corresponding elements of \( \hat{G} \) to zero, which gives

\[
g_{mi'} = g_{a'e} = 0, \quad g_{abej} = g_{mbij} = 0.
\]  

The transformation amplitudes \( \hat{S}^\pm \) may also be obtained by renormalization of a set of solutions of the EOMIP-CC and EOMEA-CC equations,
\begin{equation}
S_{ji}^{bm} = - \sum_{\kappa\lambda=1}^{n_{\text{act}}} r_{ji}^b(\lambda)(U_{\kappa}^{-1})_{\lambda\kappa}\delta_{\kappa m} \tag{2.27}
\end{equation}

\begin{equation}
S_{je}^{ba} = \sum_{\kappa\lambda=1}^{n_{\text{act}}} r_{j}^{ba}(U_{\kappa}^{-1})_{\lambda\kappa}\delta_{\kappa e} \tag{2.28}
\end{equation}

The matrices $U_{\pm}$ are the transformation matrices and diagonalize the STEOM effective Hamiltonian, which are derived from the single excitation parts of the ionization potential (IP) and electron-attached (EA) solutions,

\begin{equation}
(U_{\kappa})_{\lambda\kappa} = \sum_{n} \delta_{\kappa n} r_n(\lambda) \tag{2.29}
\end{equation}

\begin{equation}
(U_{\pm})_{\kappa\lambda} = \sum_{f} \delta_{\kappa f} r_{f}(\lambda). \tag{2.30}
\end{equation}

The excited states are obtained by solving the eigenvalue equations,

\begin{equation}
[\hat{G}, \hat{R}_1(m)]|\Phi_0\rangle = \omega_m \hat{R}_1(m)|\Phi_0\rangle. \tag{2.31}
\end{equation}

The left-hand eigenvalue equations require a solution in the full singles and doubles space, although computation of properties and transition strengths can be simplified by a perturbative (first order) approximation of $\hat{L}_2$; the equation and usage for transition moments is in subsection 2.2.5.

In order to account for the orbital relaxation error in STEOMEE-CC, a method was created that includes the triple excitations only in the EOMIP-CC solutions for STEOMEE-
CC, called STEOM-CCSD+cT ("singles and doubles plus core triples") and this modification introduces an additional transformation operator $\hat{S}_3$,

$$S^{c_bm}_{kji} = - \sum_{\kappa\lambda=1}^{n_{O,\text{act}}} t^{c_k}_{j\lambda}(\lambda) (U^{-1})^{\lambda\kappa}_{\kappa m} \delta_{km}, \quad (2.32)$$

where at least one of $ijk$ must be an active core orbital, and $\kappa\lambda$ refer to the $n_{O,\text{act}}$ active core orbitals. Since STEOMEE-CC only requires elements of $\hat{G}$ the only modifications necessary to the formation of the twice-transformed Hamiltonian are,

$$g^m_i \leftarrow S^{c_bm}_{kji} \langle jk \| bc \rangle,$$

$$g^{ma}_{ei} \leftarrow -S^{abm}_{ijk} \langle jk \| bc \rangle.$$

### 2.2.5. Transition moments

Matrix elements of $\hat{G}$, denoted $g$, are defined over the complete set of orbitals and intermediates $u$ contain one or more active labels. The equations below were obtained using diagrammatic techniques based on Goldstone convention and are adapted from those presented in Ref. [25]. The indices with bars over them are spin-adapted. Spin-adapted is when both $\alpha$ and $\beta$ spin are taken into account, essentially making the expression "spin-free". [62]

In all of the equations below, $\delta$ is the transformation matrix.
One particle elements:

**hole-hole elements**

\[
 u_{mi} = \sum_{ne} F_{ne} R_{ni}^e - \sum_{noe} W_{ei}^{no} R_{no}^e + \frac{1}{2} \sum_{noe} W_{ej}^{no} R_{noi}^f 
\]

(2.33)

\[
 g_{mi} = f_{mi} - \sum_n \delta_{nm} u_{ni} 
\]

(2.34)

**particle-particle elements**

\[
 u_{ea} = \sum_{mf} F_{mf} R_{m}^{fa} + \sum_{mgf} W_{mg}^{ma} R_{m}^{fg} + \frac{1}{2} \sum_{mgfn} W_{mg}^{mn} R_{m}^{fa} 
\]

(2.35)

\[
 g_{ea} = f_{ea} + \sum_f \delta_{fe} u_{fa} 
\]

(2.36)

**hole-particle elements**

\[
 u_{ei} = \sum_{mfg} W_{m}^{mi} R_{m}^{fg} 
\]

(2.37)

\[
 u_{am} = - \sum_{noe} W_{e}^{no} R_{no}^e 
\]

(2.38)

\[
 g_{em} = f_{em} + \sum_n \delta_{nm} u_{en} + \sum_f \delta_{fe} u_{fm} 
\]

(2.39)
particle-hole elements

\[ g_{me} = f_{me} = 0 \text{ (comes from CCSD equations)} \] (2.40)

Two-particle matrix elements:

hole-hole-hole-particle elements

\[ u_{ajim} = \sum_{en} \left( W^{in}_{ae} R^{e}_{nj} - W^{in}_{ea} R^{e}_{jn} \right) \] (2.41)

\[ u_{ijke} = \sum_{fg} W^{ij}_{fg} R^{f}_{k} \] (2.42)

\[ g_{mnie} = f_{mnie} - \sum_{o} \left( \delta^{om} u^{ei}_{no} + \delta^{on} u^{ei}_{om} \right) + \sum_{f} \delta^{fe} u^{mn}_{if} \] (2.43)

particle-hole-particle-particle elements

\[ u_{ajeb} = \sum_{jn} \left( \frac{1}{2} W^{jb}_{nj} R^{fa}_{ne} - W^{jb}_{jn} R^{fa}_{ne} \right) \] (2.44)

\[ u_{ambc} = \sum_{no} W^{no}_{bc} R^{a}_{no} \] (2.45)

\[ g_{amef} = f_{amef} + \sum_{g} \left( \delta^{ge} u^{am}_{gf} + \delta^{af} u^{am}_{eg} \right) - \sum_{n} \delta^{am} u^{an}_{ef} \] (2.46)
particle-hole-particle-hole elements

\[ u_{jaei} = \sum_{f} \left( f_{fi} R_{fj}^{bf} + f_{fi} R_{fj}^{fb} \right) + \sum_{fg} \left( W_{fg}^{ni} R_{jg}^{fg} + W_{fg}^{ni} R_{jg}^{fg} \right) \]
\[ + \sum_{fn} \left( -W_{fn}^{n} R_{jn}^{bf} + W_{fn}^{n} R_{jn}^{fb} \right) + \sum_{fn} \left( W_{fn}^{n} R_{jn}^{fb} + W_{fn}^{n} R_{jn}^{fb} \right) \]  (2.47)

\[ u_{mabi} = -\sum_{n} \left( f_{an} R_{jn}^{nb} + f_{an} R_{jn}^{nb} \right) + \sum_{no} \left( W_{no}^{jo} R_{jno}^{nb} + W_{no}^{jo} R_{jno}^{nb} \right) \]
\[ + \sum_{nf} \left( -W_{a}^{n} R_{jn}^{f} + W_{a}^{n} R_{jn}^{f} \right) \]  (2.48)

\[ u_{maei} = \sum_{f} \left( u_{fm}^{bf} R_{fj}^{bf} + u_{fm}^{bf} R_{fj}^{fb} \right) + \sum_{fn} \left( -u_{fn}^{bf} R_{jn}^{bf} + u_{fn}^{bf} R_{jn}^{bf} \right) \]
\[ - \sum_{n} \left( u_{en} R_{jn}^{bf} + u_{en} R_{jn}^{bf} \right) + \sum_{no} \left( u_{je}^{bf} R_{jno}^{bf} + u_{je}^{bf} R_{jno}^{bf} \right) \]  (2.49)

\[ g_{maei} = f_{maei} + \sum_{e} \left( \delta^{e} a_{e}^{bf} u_{eb}^{bf} + \delta^{e} a_{e}^{bf} u_{eb}^{bf} \right) - \sum_{m} \left( \delta^{m} a_{m}^{bf} u_{mb}^{bf} + \delta^{m} a_{m}^{bf} u_{mb}^{bf} \right) - \sum_{em} \left( \delta^{e} \delta^{m} u_{mb}^{bf} + \delta^{e} \delta^{m} u_{mb}^{bf} \right) \]  (2.50)

There is an approximation made that the doubles-doubles block is diagonal, where the diagonal consists of Hartree-Fock orbital energies–the same as second-order perturbation theory. Following Nooijen, this is a perturbative approximation for the left hand STEOM states (\( \hat{L}_{2}(\kappa) \)) consistent through first-order:
\[ \begin{align*}
\tilde{l}_{ab}^\kappa = \frac{1 + P_{ai}^{bj}}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b + \omega_\kappa} \left( \sum_e l_e^\kappa (ab||ej) - \sum_m l_m^\kappa (ij||mb) \right) \tag{2.51} \end{align*} \]

where \( P_{bj}^{ai} \) exchanges the labels \( ai \) and \( bj \) in the expression and \( \omega_\kappa \) is the excited state at state \( \kappa \). Due to the last term in the previous equation, the left-hand STEOM vectors are not explicitly connected, therefore STEOM properties calculated as biorthogonal expectation values are not fully connected either.

Transition moments are calculated as expectation values, \( \langle \hat{O} \rangle \), which are determined in STEOM by:

\[ \langle L|\{e^{\hat{S}_2}\}^{-1}e^{-\hat{T}\{a_p^\dagger a_q\}}e^{\hat{T}\{e^{\hat{S}_2}\}}|R\rangle \tag{2.52} \]

\[ = \langle L|\{e^{\hat{S}_2}\}^{-1}\hat{O}\{e^{\hat{S}_2}\}|R\rangle. \tag{2.53} \]

Using biorthogonal expectation values, such as in EOM-CC, allows for the evaluation of other properties besides the energy,

\[ \hat{Q} = \{e^{\hat{S}_2}\}^{-1}\hat{O}\{e^{\hat{S}_2}\} \tag{2.54} \]

\[ \{e^{\hat{S}_2}\}\hat{Q} = \hat{O}\{e^{\hat{S}_2}\}. \tag{2.55} \]

The transition moments can be written as left- and right-hand states (these are explicit equations for \( \hat{Q} \)). In the equations below, \( \tilde{L} \) and \( \tilde{R} \) are the modified wavefunction.
\langle \tilde{L} | = \langle L | (1 - \hat{S}_2) \tag{2.56} \\
\\n| \tilde{R} \rangle = (1 + \hat{S}_2 + \left\{ \frac{1}{2} \hat{S}_2^2 \right\}) | R \rangle \tag{2.57}

The transition moment property above can be evaluated as,

\langle \tilde{L} | \hat{O} | \tilde{R} \rangle, \tag{2.58}

which allows to obtain properties as in the CI-like approximation to EE-EOM-CCSD. In the right-hand state equation, the \( \left\{ \frac{1}{2} \hat{S}_2^2 \right\} \) term leads to an implicit triples correction (because it needs \( L_2 \) and \( R_1 \) contributions).

The transition moments presented in the next chapters are measured as oscillator strengths and are computed using the simpler and accurate expectation value formalism; below is the expression for an excitation from state \( \kappa \) to state \( \lambda \):

\[ f_{\kappa \rightarrow \lambda} = \frac{2m_e(\omega_\lambda - \omega_\kappa)}{3\hbar^2} \sum_{\alpha=x,y,z} \langle \tilde{\Psi}_\kappa | \hat{\mu}_\alpha | \Psi_\lambda \rangle \langle \tilde{\Psi}_\lambda | \hat{\mu}_\alpha | \Psi_\kappa \rangle \tag{2.59} \]

Due to the non-hermitian nature of EOM-CC and STEOM-CC, \( \langle \tilde{\Psi}_\kappa | \) and \( \Psi_\kappa \rangle \) are distinct. Taking the modified wavefunctions above for \( \tilde{L} \) and \( \tilde{R} \), they can be represented in CVS-STEOMEE-CCSD+cT as,

\[ \langle \tilde{\Psi}_\kappa | = \langle 0 | \tilde{L}(\kappa)(1 - \hat{S}_2)e^{-T} \tag{2.60} \]
\[ |\Psi_\kappa \rangle = e^{\hat{T}} (1 + \hat{S}_2 + \frac{1}{2} \hat{S}_2^2 + \hat{S}_3^-) \hat{R}(\kappa) |0\rangle \]  

(2.61)

where \( |0\rangle \) is the normal Hartree-Fock reference determinant. The addition of the core triples in CVS-STEOMEE-CCSD+cT then leads to the additional term in the transition dipole moment between states \( \kappa \) and \( \lambda \),

\[
\mu^{\kappa\lambda}_{\alpha}(cT) = \langle 0 | \hat{L}_2(\kappa) \hat{\mu}_\alpha \hat{S}_3^- \hat{R}_1(\lambda) |0\rangle = \sum_{ai} D^{\kappa\lambda}_{ai}(cT) \mu_{ai;\alpha} 
\]

(2.62)

\[
D^{\kappa\lambda}_{ai}(cT) = \langle 0 | \hat{L}_2(\kappa) \{ a_i^\dagger a_i \} \hat{S}_3^- \hat{R}_1(\lambda) |0\rangle = -\frac{1}{2} \sum_{efmno} t^{ef}_{na}(\kappa) s^{afm}_{ion} t^{e}_{m}(\lambda) - \frac{1}{4} \sum_{efmno} t^{ef}_{na}(\kappa) s^{efm}_{na} t^{e}_{m}(\lambda) 
\]

(2.63)

The core triples contribution to the density matrix can be represented visually as Brandow diagrams (anti-symmetrized Goldstone diagrams):

Brandow diagrams (anti-symmetrized Goldstone diagrams) are used to illustrate the different contributions to the STEOM equation. In Figure 1 the connected triples contributions for the core orbital are depicted. The diagram can be broken up into S, L, and R tensors with indices depicted by the arrows. A linear combination of tensors can be used to simplify the equations needed for the doubles and triples contributions to STEOM transition moments.
Figure 2.2: Brandow diagrams for the connected triples contribution (only for the core orbital) to the STEOM single density matrix. (a) The single loop above the S vertex leads to the 2 in the denominator. (b) The two loops above the S vertex leads to the 4 in the denominator.
2.3. Møller-Plesset Theory

Most of the information in this section comes from Refs. [63–66].

Perturbation theory works by finding an approximate solution to a problem, which starts from the exact solution of a related and simpler problem. The theory works by breaking the problem into “solvable” and “perturbative” parts. The solution is expressed as a power series broken into two parts: the first term is the known solution to the solvable problem and the second part (and successive terms) in the series at higher powers usually become smaller.

\[ A = A_0 + \epsilon A_1 + \epsilon^2 A_2 + \ldots \]  \hspace{1cm} (2.64)

An approximate perturbation solution is obtained by truncating the series, usually by keeping only the first two terms, the solution to the known problem and the first order perturbation correction. [67–69] In our case, we truncate at the second order perturbation correction for MP2 and truncate at the third order perturbation correction for MP3. Møller–Plesset perturbation theory uses a small perturbation to add electron correlation effects and improve on the Hartree-Fock method so the exact Hamiltonian operator can be written as,

\[ H = H_0 + \lambda V \]  \hspace{1cm} (2.65)

where \( V \) is the small perturbation and \( \lambda \) is a dimensionless parameter that controls the size of the perturbation. Expanding the exact wavefunction and energy in terms of the Hartree-Fock wavefunction and energy gives,

\[ \Psi = \Psi_0 + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \lambda^3 \Psi^{(3)} + \ldots \]  \hspace{1cm} (2.66)
\[ E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \ldots \] (2.67)

Then, these expansions can be substituted into the Schrödinger equation and \( \lambda \) terms are canceled on both sides according to the exponent,

\[ H_0 \Psi_0 = E^{(0)} \Psi_0 \] (2.68)

\[ H_0 \Psi^{(1)} + V \Psi_0 = E^{(0)} \Psi^{(1)} + E^{(1)} \Psi_0 \] (2.69)

\[ H_0 \Psi^{(2)} + V \Psi^{(1)} = E^{(0)} \Psi^{(2)} + E^{(1)} \Psi^{(1)} + E^{(2)} \Psi_0 \] (2.70)

and so on for as many levels of excitation energies are needed. Multiplying each of the above equations by \( \Psi_0 \) and integrating over all space yields the energy for MPn:

\[ E^{(0)} = \langle \Psi_0 | H_0 | \Psi_0 \rangle \] (2.71)

\[ E^{(1)} = \langle \Psi_0 | V | \Psi_0 \rangle \] (2.72)

\[ E^{(2)} = \langle \Psi_0 | V | \Psi^{(1)} \rangle \] (2.73)

This gives the Hartree-Fock energy,
\[ E_0 = \langle \Psi_0 | H_0 + V | \Psi_0 \rangle \] (2.74)

which is the sum of the zeroth-order and first-order energies

\[ E_0 = E^{(0)} + E^{(1)} \] (2.75)

Then the remaining terms can be written as the correlation energy,

\[ E_{\text{corr}} = E^{(2)}_0 + E^{(3)}_0 + E^{(4)}_0 + \ldots \] (2.76)

where the first term is the MP2 energy and the second term is the MP3 energy. The MP2 and MP3 energies are defined as,

\[ E_{\text{MP}2} = E_{\text{MP}2a} = \frac{1}{2} \sum_{abij} \frac{(g_{ab}^{ij} - g_{ba}^{ij}) g_{ij}^{ab}}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \] (2.77)

\[ E_{\text{MP}3} = E_{\text{MP}3a} = \frac{1}{2} \sum_{abijkl} \frac{(g_{ab}^{ij} - g_{ba}^{ij}) g_{kl}^{ab} g_{ij}^{ab}}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k + \varepsilon_l - \varepsilon_a - \varepsilon_b)} \]

\[ + \frac{1}{2} \sum_{abcidij} \frac{(g_{ab}^{ij} - g_{ba}^{ij}) g_{cd}^{ab} g_{ij}^{cd}}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_c - \varepsilon_d)} + \sum_{abckj} \frac{(g_{ab}^{ij} - g_{ba}^{ij}) (g_{ck}^{ab} - g_{kc}^{ab}) (g_{ik}^{ac} - g_{ki}^{ac})}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_k - \varepsilon_a - \varepsilon_c)} \] (2.78)

The more common formulation of these energies uses the second-quantized representation of the Hamiltonian, defined in Section 2.2. The two representations are connected by the
The fact that \( v_{rs}^{pq} = g_{rs}^{pq} - g_{rs}^{qp} = g_{rs}^{pq} - g_{sr}^{pq} \). The first-order and second-order perturbed double excitation amplitudes are defined by,

\[

c[n]_{ij}^{ab} = \tilde{c}[n]_{ij}^{ab} - \tilde{c}[n]_{ji}^{ab} = \tilde{c}[n]_{ij}^{ab} - \tilde{c}[n]_{ij}^{ba} \quad (2.79)
\]

\[

c[1]_{ij}^{ab} = \frac{g_{ij}^{ab}}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \quad (2.80)
\]

\[

c[2]_{ij}^{ab} = \sum_{kl} g_{ij}^{kl} \tilde{c}[1]_{kl}^{bc} + \sum_{cd} g_{cd}^{ab} \tilde{c}[1]_{ij}^{cd} + \sum_{ek} (g_{jk}^{ck} - g_{ka}^{jk})(\tilde{c}[1]_{ik}^{ac} - \tilde{c}[1]_{kl}^{ac}) \quad (2.81)
\]

In all of the equations written above with energy denominators, there is an issue of inseparability, and the approach of "Laplace denominators" is used \([70,71]\),

\[
\frac{1}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} = - \int_0^\infty e^{(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)t} dt \quad (2.82)
\]

\[
\approx - \sum_{\lambda=1}^L w_{\lambda} e^{(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)\lambda} \quad (2.83)
\]

\[
= \sum_{\lambda=1}^L \tau_{\lambda}^i r_{\lambda}^j \quad (2.84)
\]

where \( L \) is the number of Laplace quadrature points. In this work we use the quadrature developed by Braess and Hackbusch \([72]\) and a sufficient number of quadrature points to evaluate \( 1/x \) to a relative accuracy of \( 10^{-8} \) (approximately 9 points).
2.4. Tensor hypercontraction

The LS-THC form of the ERI is,

\[(pr|qs) \equiv g_{rs}^{pq} \approx \sum_{RS} (X^{(pr)}_{p})^R R V_{RS} (X^{(qs)}_{q})^S S (X^{(qs)}_{s})^S \]  \hspace{1cm} (2.85)

where the \(X\) matrices are the collocation matrices determined by evaluation of the spatial molecular orbitals \(\psi_p\) at a particular set of grid points \(X_p^R = \psi_p(r_R)\). Superscripts in equations are specific to sets of “pruned” grid points; the pruning process is specific to the occupation of the pair of molecular orbitals, leading to separate occupied-occupied (\(X \equiv X^{(ij)}\)), mixed virtual-occupied (\(\tilde{X} \equiv X^{(ai)} \equiv X^{(ia)}\)), or virtual-virtual (\(\tilde{\tilde{X}} \equiv X^{(ab)}\)) collocation matrices. These three cases are further classified by the spin of the molecular orbitals which leads to six collocation matrices for open-shell LS-THC-MP3. The final matrix \(V\) is the core matrix and is evaluated by the least squares fitting of either the exact ERI tensor or an approximation. In the work presented in Chapter 7, density fitting is utilized in order to maintain an overall scaling of \(\mathcal{O}(N^4)\). All terms used in the core matrix, as well as the core matrix are defined below,

\[V_{RS} = \text{argmin}_{V_{RS}} \frac{1}{2} \sum_{pqrs} (g_{rs}^{pq} - \sum_{RS} (X^{(pr)}_{p})^R R V_{RS} (X^{(qs)}_{q})^S S (X^{(qs)}_{s})^S)^2 \] \hspace{1cm} (2.86)

\[V_{RS} = \sum_{R'S'} (S_{RR'}^{(pr)})^{-1} E_{R'S'} (S_{SS'}^{(qs)})^{-1} \] \hspace{1cm} (2.87)

\[\tilde{g}_{rs}^{pq} = \sum_{JK} (pr|J)(J|K)^{-1}(K|qs) \] \hspace{1cm} (2.88)
\[ E_{RS} = \sum_{pqrs} (X^{(pr)})_p^R (X^{(pr)})_r^R S_{qs}^{pr} (X^{(qs)})_q^S (X^{(qs)})_s^S \] (2.89)

\[ S_{RS}^{(pq)} = \sum_{pq} (X^{(pq)})_p^R (X^{(pq)})_q^R (X^{(pq)})_p^S (X^{(pq)})_q^S \] (2.90)

With collocation matrices, there are as many as 6 distinct metric matrices \( S \) and due to the possible combination of each of these six electron distributions, there are as many as 21 different core matrices, \( V \), and fitting matrices, \( E \). 13 of these matrices are used in open-shell LS-THC-MP3.
3.1. Background

The results of this work are published in Ref. [73] (Appendix A), therefore a short overview is given here.

X-ray absorption spectroscopy is an example of an inner shell spectroscopy; inner shell meaning that an x-ray interacts primarily with a deep-core electron rather than with a valence electron (an electron in the outer shell of an atom) and spectroscopy is measuring some aspect of the interaction changing as a function of photon energy (the electron is absorbing energy in this study). [74,75] The process of x-ray absorption spectroscopy works as such:

1. An incoming photon interacts with a deep-core electron (normally an electron at the ground state–1s)
2. The deep-core electron is excited for a K-edge spectrum
3. The deep-core electron is promoted to some unoccupied state above the Fermi energy (the energy difference between the highest and lowest occupied single-particle states in a quantum system), dissipates away, and leaves behind a core-hole

For theoretical calculations, the measurement consists of a “dipole focused” transition of an electron in a deep-core state into an unoccupied state (normally the lowest unoccupied molecular orbital, or LUMO) computed by integrating between these two states. There
is an issue with computing this integral because even though representing the deep-core state is relatively easy using quantum mechanics, representing the unoccupied state is much more difficult. This is where theoretical chemists come in—testing out methods that accurately represent both states and reproduces the structure and properties (energy, vibrational frequency, oscillator strengths) well. [1–3, 74, 75] Many theoretical chemists utilize density functional theory (DFT) for computational chemistry problems involving the ground state, and time-dependent density functional theory (TD-DFT) extends the concepts of DFT to excited states. In Table 3.1, the current methods used in x-ray absorption spectroscopy are presented.

The orbital relaxation error, the main problem we are trying to address, refers to the changes in the Fock operator and Hartree-Fock orbitals when changing the number of electrons in the system and it comes from an approximation where the orbitals of only one of the molecules is used to describe both of the species in a system, which is not necessarily true. [61] We wanted to address this error by using a coupled cluster method at the singles and doubles level, with a better accuracy than CVS-EOM-CCSD but a lower computational cost than CVS-EOM-CCSDT or CVS-EOM-CCSD*. Therefore, we applied TP-DFT ideas to coupled cluster theory and chose the fractional core occupational number as \( \lambda = 1/2 \) because of the integral in Section 2.2.3 that ends with an approximation by the trapezoidal rule. We applied our transition-potential method to the fourteen small molecules shown in Figure 3.1 for x-ray absorption spectroscopy (XAS) k-edge calculations.

The aim of this publication was to develop a method that combined the concepts of transition-potential and coupled cluster methods and to test this new method against previously researched methods that have shown to be computationally accurate.
Table 3.1: The current theoretical methods used in x-ray absorption spectroscopy calculations are listed, along with their pros and cons.

<table>
<thead>
<tr>
<th>Method</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>TD-DFT [5, 76–79]</td>
<td>Computationally efficient</td>
<td>Self-interaction errors when computing description of ground state</td>
</tr>
<tr>
<td>EOM-CC [10–12]</td>
<td>Success in description of valence excitations for core-hole states</td>
<td>Large orbital relaxation error, typically 1-3 eV and up to 5 eV</td>
</tr>
<tr>
<td>TP-DFT [18–20, 59]</td>
<td>Compromise between linear-response methods and state-specific orbital optimizations</td>
<td>Errors remain when assigning peak positions and intensities in XAS</td>
</tr>
<tr>
<td>ΔKohn-Sham [14, 20]</td>
<td>Accurately reproduces absorption and ionization spectra</td>
<td>Suffers from convergence difficulties</td>
</tr>
</tbody>
</table>

### 3.2. Results and Discussion

The optimized geometries were used in Psi4 and CFOUR calculations. [80, 81] For any (X)TP-CCSD calculations a Psi4 plugin [82] was used to generate fractional core-hole or core-excited orbitals, using the B3LYP functional [83] and exciting or ionizing $\lambda/2$ electrons of each spin in the selected core orbital. For XTP-CCSD calculations the partially ionized electron is placed in the lowest unoccupied molecular orbital (LUMO). All methods tested were compared to CVS-EOM-CCSDT, which serves as our benchmark, due to the method being shown to reproduce experimental core excitation energies typically within 100 meV [84] and core ionization potentials similarly. [85]

The TP-CCSD and XTP-CCSD [21] methods were compared to CVS-EOM-CCSDT for excitation energies and oscillator strengths. In the figures below (adopted from Ref. [73]), we wanted to focus on 3 methods: CVS-EOM-CCSD, the coupled cluster method popularly used for x-ray spectroscopy calculations; CVS-EOM-CCSD*, a coupled cluster
method that includes triples not perturbably—the cheapest way to have triples—and what we call our aspirational yardstick [91]; and TP-CCSD, the method we developed in this project.

The statistic measured in Figure 3.2 is the core excitation absolute energies, which is when the electron is going from the ground state to an excited state. The distribution for TP-CCSD(1/2) has a similar shape to CVS-EOM-CCSD*, but with a slightly smaller average error. XTP-CCSD(1/2) has a smaller average error in comparison with TP-CCSD(1/2), to about 0.1 eV, but has about twice the standard deviation of CCSD*. This shows for this statistic that all of our newly developed transition potential coupled cluster methods have a decreased average error and standard deviation in comparison to CVS-EOM-CCSD. Additionally, it is shown that TP-CCSD(1/2) performs similarly to CVS-EOM-CCSD* in terms of average error and standard deviation.
Figure 3.2: On the left, Gaussian error distributions for absolute core excitation energies. CVS-EOM-CCSD (an iterative method) is represented by a dotted line, CVS-EOM-CCSD* (a perturbative method) is represented by a dashed line, and TP-CCSD methods are represented by solid lines. On the right is an illustration of how the absolute core excitation energies are measured; from the ground state to an excited state (in the figure is an example of an electron being excited from the ground state to the first excited state).

The oscillator strengths play an important role in assigning the correct peaks in x-ray spectra. The deviation from the CVS-EOM-CCSDT method was calculated for each method tested, just as described in the figure above. The full results of the deviations can be found in the published paper. Similar to absolute excitation energies, (X)TP-CCSD methods improve on the EOM-CCSD method for absolute oscillator strengths. Additionally, similar to relative excitation energies, (X)TP-CCSD methods improve on the EOM-CCSD method for relative oscillator strengths. The standard deviation for (X)TP-CCSD(1/2) methods is approximately 3x smaller than the standard deviation for EOM-CCSD. It is important to obtain accurate oscillator strengths to properly predict x-ray spectra for Rydberg and valence states.
3.3. Summary

In summary, the (X)TP-CCSD method performs more accurately than the CVS-EOM-CCSD method at every statistic in terms of average error and standard deviation. We can conclude that TP-CCSD(1/2) is the best method of the new methods we developed as it has a comparable error and standard deviation to our aspirational yardstick, CVS-EOM-CCSD*, at every statistic measured. It is important that a “good” method has a balance in representing the description of valence and Rydberg states, and unfortunately we found that XTP-CCSD loses that balance. We found that TP-CCSD(1/2) is about as accurate for core-excited states as CCSD is for valence states, only having deviations from CCSDT within a few tenths of an eV. Ultimately, the TP-CCSD(1/2) method was found to improve on CCSD and account for essentially all of the orbital relaxation energy error, while having the same computational cost as CCSD. This work provides a new computationally efficient and accurate transition-potential method that combines the idea of a fractional occupational of a core-hole orbital with the well-established coupled cluster methods.

This work is published in Journal of Chemical Physics (2021) titled:

*Transition-potential coupled cluster* (see Appendix A).
Chapter 4
TP-CC: Optimization of the core occupational number

4.1. Background

The results of this work are published in Ref. [92] (Appendix B), therefore a short overview is given here.

There are five nucleobases that make up part of the nucleotide, which are building blocks for DNA. These building blocks are heavily studied as they are important for the synthesis of anti-cancer drugs and for the development of polymerase chain reactions. [93,94] In order to properly study those nucleobases, an assurance of the correct geometry and characteristics needs to happen. One of the ways to check the geometry is through experimental spectra, which is normally very effective. However, modeling is an emerging practice in computational chemistry and online structures need to be available for this purpose. Therefore, computational x-ray techniques are important in addressing the challenges of understanding the structure of various molecules and understanding the behavior of these molecules.

In x-ray absorption spectroscopy, the k-absorption edge refers to the sudden increase in the absorption when the energy of the x-ray is just above the binding energy of the innermost electron shell of the atoms interacting with the photons. [1,95,96] The binding energies and the k-edge are specific to each element. In our first paper on TP-CC we calculated all elemental k-edges using $\lambda = 1/2$ or $\lambda = 1/4$. We realized the generic treatment of calculating k-edges for different elements was leading to an increase in errors and with this in mind, we wanted to optimize our fractional core occupational number from our first paper on TP-CC.
The aim of this publication was to fine tune our method for element-specific k-edges that combined the concepts of transition-potential and coupled cluster methods and to compare our optimized method to the standard method, EOM-CCSD, and to experimental spectra of nucleobases.

4.2. Results and Discussion

The results and discussion are broken into two parts: our work on optimizing lambda and our work testing the optimized lambda for k-edge spectra calculations for adenine and thymine.

4.2.1. Optimizing the core orbital occupation number (lambda)

The 5 different statistics were all measured in electronvolts with respect to CVS-EOM-CCSDT, just as they were in Chapter 3.2. They are core absolute excitation energies, core absolute ionization energies, core relative excitation energies, absolute oscillator strengths, and relative oscillator strengths. The absolute oscillator strengths are defined as analogous to the absolute excitation and ionization energy deviations as a function of lambda. The relative oscillator strengths are represented as percentages and defined as separately normalizing the spectrum of each edge such that the most intense transition has unit strength. The minima in the curves tell us the optimal lambda value for specific elements and for the combined elements. The core absolute excitation energies and core absolute ionization energies for both TP-CCSD and XTP-CCSD had patterns where obvious minima appeared. The core relative excitation energies had no trend and much more variation than absolute curve distributions, but the overall errors are smaller than absolute statistics. We found that this was due to the cancellation of errors between the excitation and ionization energy calculations. Although there is a lack of trend in the curves, there is still a strong difference in optimizing lambda rather than the initial choice of 1/2 from our first paper. [73] For example, we found the
optimal value in the TP-CCSD distribution for carbon to be 0.350 and for nitrogen to be 0.375. We found the absolute and relative oscillator strengths had no trend and much more variation than the other statistics. The minimum MAE is much more varied, but the error is smaller than absolute statistics. For the oscillator strengths, we had issues with convergence for either the ground-state CCSD or EOM-CCSD equations, therefore we had to omit several data points for $\lambda = 0.725$ and $\lambda = 0.750$. We do not believe there is a clear solution to fixing the convergence issues we faced.
Figure 4.1: The minimum mean absolute error (in eV) for element-specific k-edge spectra reveals the optimal lambda (core orbital occupation number) for each element. Each curve is for a specific element; nitrogen (orange), carbon (green), oxygen (red), or fluorine (purple) except for the combined element curve (blue). The minimum MAE values for TP-CCSD are compared to the minimum MAE values for EOM-CCSD across various statistics (the numbers are displayed as ratios).

The ratios in the figure above are for TP-CCSD because we found that TP-CCSD(\(\lambda\)) had smaller errors for every statistic, every element, and every lambda compared to XTP-CCSD(\(\lambda\)). The ratio of the CVS-EOM-CCSD error to the best value obtained by TP-CCSD is presented. The combined TP-CCSD MAEs used for comparison are chosen based on the minimum of the “combined” curve for each statistic. Figure 4.1 shows that the best TP-CCSD value is the smallest error (minimum of the curve) obtained for each error statistic. The worst ratio value, symbolized by a dark red color, is 4.9. This means that TP-CCSD only reduced the error by a factor of 4.9 in comparison to EOM-CCSD. The best ratio value, symbolized by a dark green color, is 34.4. From these results, we can see that TP-CCSD is capable of reducing the errors in every statistic compared to CVS-EOM-CCSD. Since TP-CCSD incurs nearly zero additional computational cost, we concluded that TP-CCSD is highly preferable for x-ray spectroscopy calculations.

4.2.2. Comparing x-ray absorption k-edge calculations against experiment

We wanted to test our TP-CCSD method with the optimized core occupational number for molecules that were slightly increased in size and are useful in biological applications.
We computed the x-ray absorption spectroscopy carbon, nitrogen, and oxygen k-edges for adenine and thymine and compared TP-CCSD, EOM-CCSD, and experimental gas-phase data. [97] The molecular geometries for adenine and thymine were taken from Ref. [98], which were optimized at the M06-2X/aug-cc-pVTZ level. [89,90,99] X-ray absorption spectra were computed in the same way as for our previous TP-CCSD calculations, utilizing a combination of Psi4 for TP calculations and CFOUR for EOM and TP calculations, but we used the 6-311++G** basis set to save on computational cost. [100–103] This basis set has shown to be quite accurate for its size. [84]

We observed with all spectra for adenine and thymine, two of which are shown in Figure 4.2, that CCSD methods were good at reproducing valence curves, but not the Rydberg region. We believe this can be fixed by adding additional diffuse functions to the basis set. In every spectra, we observed that TP-CCSD has a lower shift and reproduced relative curves well, especially when it came to reproducing small characteristics that CCSD cannot. We saw that the carbon K-edge for both adenine and thymine had an advantage of TP-CCSD over EOM-CCSD due to the clear separation between intense valence transitions and weak Rydberg transitions. In all five k-edge spectra, EOM-CCSD required a larger shift than TP-CCSD. This demonstrates that TP-CCSD reduces the overall energy shifts required to match the experimental spectra, in comparison with EOM-CCSD, while also improving the relative positions and intensities of several peaks. Additionally, TP-CCSD can provide improvements in the valence energy structure of the spectrum compared to EOM-CCSD. Although TP-CCSD reproduce the k-edge spectra well, there is room for improvement in reproducing the Rydberg region. Therefore, we concluded that in the Rydberg region adding additional diffuse functions is necessary to increase accuracy.
Figure 4.2: The nitrogen k-edge spectra for adenine and oxygen k-edge spectra for thymine. The x-ray absorption curves for EOM-CCSD and TP-CCSD methods are compared to experimental curves. Also noted at the top of the graphs are the shifts for each method in order to line up the first computational peak with the first experimental peak (this is done when comparing computational and experimental spectra).

4.3. Summary

In summary, (X)TP-CCSD(\(\lambda\)) needs an element-specific core occupational number. For every statistic, the mean absolute error graphs have a specific lambda where the error is at a minimum and it is different for a specific element. The MAE distributions show a clear minimum and the element-specific minimum are smaller than the combined minimum. Additionally, the minimum MAE values for TP-CCSD perform better every time in comparison to EOM-CCSD. For absolute core excitation and ionization energy calculations, as well as relative excitation energy calculations, there is a noticeable difference in choosing element specific lambda values rather than a single value. There is a significant increase in accuracy seen with element-specific choices, especially with the absolute core energy calculations. We concluded from observing the graphs that the oscillator strengths are less dependent on a specific value of lambda compared to the excitation and ionization energies. As the accuracy of the oscillator strengths does not have a strong correlation with the choice of lambda, we utilized optimal values (the minimum MAE value) of lambda from core relative excitation excitation energies. We chose optimal lambda values from relative shifts because they are
more important than absolute energy errors, for instance when assigning experimental spectra. We were able to optimize our method to have a specific core occupational number, $\lambda$, for specific elements, which lead to a decreased error and an increase in reproducibility of x-ray absorption spectra.

This work is published in Molecular Physics (2022) titled:

*Transition-potential coupled cluster II: Optimisation of the core orbital occupation number* (see Appendix B).
Similarity-transformed equation of motion coupled cluster (STEOM-CC)

5.1. Background

The results of this work are published in Ref. [104] (Appendix C), therefore a short overview is given here.

Similarity-transformed equation of motion coupled cluster theory is an alternative to EOM-CC theory, where the Hamiltonian is second similarity transformed and then used in a diagonalization in the singles-singles excitation space. Since the transformation involves utilization of the singles-singles excitation space, it can be said that the active singly excited electrons are separated from the doubly excited electrons, much as the ground state coupled cluster equations separate the reference orbital from singly and doubly excited electrons. This separation leads to a restricted active space. In similarity-transformed equation of motion coupled cluster (STEOM-CC) theory, the second similarity transformation captures the dynamical correlation of all low-lying excited states by calculating many valence eigenvalues simultaneously at the beginning of the calculation. The eigenvalue in the STEOM transformed Hamiltonian is not different than the EOM eigenvalue in the EOM transformed Hamiltonian, but the approach just described allows for a more efficient computational cost. [24, 25, 105]

Many computational chemists research new methods or means to decrease the error stemming from orbital relaxation. We developed a method that includes the triple excitations only in the EOMIP-CC solutions for STEOMEE-CC, called STEOM-CCSD+cT ("singles and doubles plus core triples"), and believe it to be sufficient to account for orbital relaxation in STEOMEE-CC. This belief comes from the fact that the ionization part of the similarity
transformation provides all of the necessary dynamical correlation for the occupied orbitals. Calculations utilizing core IPs are exciting the core electron to the ionization potential, opposed to the normal valence electron. We chose to calculate triple excitations in the core because core electrons are better for decreasing error coming from orbital relaxation. This is because of the screening effect, which is the reduction of the force of attraction of the nucleus on the outermost valence electrons due to the presence of the inner shell electrons.

The aim of this publication was to introduce a method that does not address orbital relaxation through direct dynamical correlation of the excited state through EOM-CC, but rather a STEOM-CC method that addresses orbital relaxation through a better description of the core-hole (by including triple excitations in the core ionization potential).

5.2. Results and Discussion

In this study the “data set”, shown in Figure 3.1, was used for transition energy calculations for all methods. We chose to use violin plots to illustrate error distributions in this project rather than Gaussian curves because violin plots show the entire distribution of the data, rather than one peak. The violin plots have these statistics: the median (white dot), the interquartile range (the thick black bar), the rest of the distribution (thin black line), and the outliers (part of the violin plot after the thin black line ends) for each method. Wider sections of the violin plot represent a higher probability of the distribution having the given value, while the skinnier sections represent a lower probability.

Error distributions for absolute core excitation energies are shown in Figure 5.1. It is clear from this figure that both “purely singles and doubles" methods, CCSD and STEOM-CCSD, are prone to large errors in absolute vertical core excitation energies, with errors around 3 eV. TP-CCSD(1/2), CCSD*, and STEOM-CCSD+cT all improve the errors significantly, with errors less than 1 eV.
While there are a few cases that are challenging electronic structures for STEOM-CCSD+cT, the overall pre-edge structure is maintained well except for these single gaps. These cases include $CH_2$, where the gap between the excitation into the lone pair and the Rydberg states is overestimated and the flourine k-edges of $HOF$ and $H_2NF$ where the gap between the mixed $\sigma^*/3s$ excitation and the remaining excitations is underestimated. Noticeably, the large errors for $\pi^*$ valence states present in STEOM-CCSD are almost entirely eliminated in STEOM-CCSD+cT due to the improved description of the core-hole.

### 5.3. Summary

Our new CVS-STEOMEE-CCSD+cT method reduces errors in absolute vertical core excitation energies by a factor of $\sim 5$ compared to CVS-EOMEE-CCSD and also improves errors in relative excitation spectra to less than 0.5 eV, except for the challenging cases of $CH_2$ and fluorine K-edges with valence–Rydberg mixing. The addition of triple excitations only affects the core ionization calculation, which results in a small increase in computational
effort compared to the standard CVS-EOM-CCSD. However, the large increase in accuracy outweighs the small increase in computational cost.

This work is published in Journal of Chemical Theory and Computation (2022) titled:

Accurate Core-Excited States via Inclusion of Core Triple Excitations in Similarity-Transformed Equation-of-Motion Theory (see Appendix C).
Chapter 6
STEOM-CC: Transition moments

6.1. Background

The results of this work have been submitted and the full details are available in Ref. [106] (Appendix D), therefore a short overview is given here.

Our work in Chapter 5 showed that our newly developed STEOM-CCSD+cT method was computationally efficient and accurate for excited energies. However, there are more excited state properties that are helpful in studying and identifying complex molecules, including oscillator strengths, dipole moments, and vibrational frequencies. Our focus is on oscillator strengths, which indicate the probability of a given transition from the ground state to an excited state occurring and can be measured through observed intensities. [78,79] Oscillator strengths can be helpful in converting an adiabatic basis, where the off-diagonal terms are the nuclear kinetic energy, into a diabatic basis, where the off-diagonal terms are turned into the potential energy term. This happens when two potential energy surfaces come very close together leading to coupling of the nuclear and electronic coordinates and the nuclear kinetic energy becomes too large and difficult to handle, so converting makes it much easier to handle. [107,108] In our case, oscillator strengths are useful in x-ray absorption spectra for assigning peaks in experimental spectra and comparing peak heights to determine accuracy of calculated oscillator strengths. [1,3] Many theoretical chemists utilize TD-DFT for calculating excitation energies and excited state properties, but as mentioned in Chapter 2 there are some self-interaction errors when computing the ground state energy. [76,109,110]
This has lead us to explore how accurately coupled cluster methods can describe oscillator strengths since these methods can calculate excited energies well. Our goal with this work was to implement the transition moment code for all aspects of CVS-STEOMEE-CCSD and create and implement the transition moment code for CVS-STEOMEE-CCSD+cT.

6.2. Results and Discussion

In this study the “data set”, shown in Figure 3.1, was used to calculate oscillator strengths for core states to excited states.

We tested two STEOM-CCSD+cT methods; one where the triples were not called in the density code, but called in the energy code (labeled (a) in Figure 6.1) and one where the triples are called in both the density code and in the energy code (labeled (b)). STEOM-CCSD+cT(b) was called the “direct” triples contribution because of the modification of $\hat{G}$ by adding $\hat{S}_3^{-}$. When we measure relative oscillator strengths we normalize all k-edge spectra, which allows for us to look at the spectra on “equal-foothing” and keep the relative importance of each peak in the specific k-edge spectrum. We noticed an interesting pattern in the two STEOM-CCSD+cT methods; the “absolute” intensities differed but the “relative” intensities did not differ. Our findings are supported by those observed by Nooijen and Bartlett [24] for their implicit “triples” contribution: there was a significant effect on the transition energy but an almost negligible effect on the oscillator strengths.

All of the STEOM methods have difficulty describing the absolute oscillator strengths of $\pi^*$ and $\sigma^*$ core-to-valence excited states, which lead to an increase in positive absolute errors. The difficulty also leads to a consistent over-estimation of both valence and Rydberg intensities in x-ray spectra, which helps STEOM-CCSD+cT eliminate the large errors for $\pi^*$ and $\sigma^*$ valence states present in both EOM-CCSD and STEOM-CCSD. We observed that the errors for STEOM-CCSD+cT were mostly contained to two problematic molecules, $H_3CF$ and $H_3COH$. Even including these issues, STEOM-CCSD+cT results in a 2.4x reduction in
Figure 6.1: Error distributions with respect to CVS-EOM-CCSDT for relative oscillator strengths (intensities), displayed as percentages. The equation to calculate oscillator strengths for one state and another state (in our case ground state to excited state) is displayed at the top of the image, with an example of a core-excitation energy for HCN under it.

standard deviation compared to EOM-CCSD and over a 1.8x reduction in standard deviation compared to STEOM-CCSD.

6.3. Summary

In summary, this work presents the implementation of transition moments for STEOM-CCSD+cT. We investigated how well this method estimates transition moments in comparison to full CVS-EOM-CCSDT as the benchmark.

The overall improvement of the TP-CCSD(1/2) and STEOM-CCSD+cT intensities is due to the improved description of the core-hole for differing reasons. In TP-CCSD the improvement is due to the inclusion of the fractional occupation in the core-hole which creates a cancellation of errors between the ground and core-excited states. In STEOM-CCSD+cT the improvement is due to the inclusion of explicit triple excitations in the
core ionization potential cancellation, which leads to an improved relaxation of the core hole. All STEOM-CCSD methods are able to calculate an improved ratio of Rydberg intensities to valence intensities, which helps decrease the overall error. Since we have the full picture now with calculated excited state energies and oscillator strengths and STEOM-CCSD+cT performed well for both properties in comparison to (ST)EOM-CCSD methods, we can come to a full conclusion of our developed STEOM method. We recommend the use of the CVS-STEOM-CCSD+cT method for core-hole spectroscopy calculations due to its ability to treat core and valence states on an even footing and to accurately predict relative oscillator strengths and transition core-excitation energies.

This work is under review at the Journal of Chemical Theory and Computation titled:

*Transition moments for STEOM-CCSD with Core Triples* (see Appendix D).
7.1. Background

The results of this work have been submitted and the full details are available in Ref. [111] (Appendix E), therefore a short overview is given here.

Previous to this work being done, the only tensor hypercontraction code implementation was for closed-shell molecules. This means that the number of alpha and beta electrons (spin electrons) are the same and that there are zero unpaired electrons in all occupied spin orbitals. While many molecules are closed-shell, many interesting and commonly occurring molecules, such as molecular ions, radicals, and reactions, do not have the same number of $\alpha$ and $\beta$ electrons. Such molecules are important to study to advance and develop fields such as organic catalysis [112], environmental and health studies [113], green chemistry [114], and photochemistry [115,116]. Open-shell systems typically refer to free radicals that have multiple low-lying electronic states, which complicate the spectroscopy and reaction dynamics of open-shell systems. It is monumental to study the characterization of open-shell species in order to understand their chemical reactivity in complex environments. [117] Thus, it is necessary to develop accurate quantum chemistry methods to assist the experimental studies in understanding the reaction profiles and intermediates. [118, 119] Molecules such as glutathione and 9-propyl-4,11-tridecadienoic acid are useful for environmental and health applications. Glutathione is a tripeptide comprised of three amino acids (cysteine, glutamic acid, and glycine) and acts as an antioxidant in mammalian tissue. [120] 9-propyl-4,11-tridecadienoic acid is not a naturally occurring molecule, but the structure is very similar to conjugated linoleic acid (CLA), which is a type of fat. [121] 9-propyl-4,11-tridecadienoic acid
is of interest as it contains a long hydrocarbon chain, a beta carbon, primary and tertiary carbons, carboxylic acid and propyl functional groups, and double bonds between carbons.

Complexity arising due to the presence of high-order tensors is well known as a bottleneck in wavefunction-based quantum chemical methods. These high-order tensors lead to an exponential scaling for computational cost as system size increases. As the essential component of all electronic structure methods, the electron repulsion integral (ERI) tensor [122,123] has been chosen by many computational chemists to investigate the reduction of cost and scaling, while maintaining accuracy.

The aim of this publication was to develop tensor hypercontraction methods for open-shell molecules and compare errors for the open-shell THC method to closed-shell THC.

7.2. Results and Discussion

In the project involving tensor hypercontraction, we investigated the molecules in Figure 7.1 with labels where bond breaking and plucking of hydrogens to create radicals occurred. We wanted to investigate the changes in errors due to conformation changes of 9-propyl-4,11-tridecadienoic acid, so 24 conformations were generated using Frog2 software [124]. The open-shell tensor hypercontraction results for these molecules were compared to closed-shell tensor hypercontraction, which was shown to have small errors in previous work. [28,29] Only one graph comparison of the results we obtained are shown here; to see all results for all molecules see Ref. [111].
Figure 7.1: The 3 molecules we tested for open-shell tensor hypercontraction (plus linear alkanes). Glutathione and 9-propyl-4,11-tridecadienoic acid molecules are presented as ball-and-stick structures; glutathione has the C-C, C-N, and C-S bonds labeled where bond cleavage occurred and 9-propyl-4,11-tridecadienoic acid has arrows pointing to the hydrogens that were “plucked” off the molecule to make it a radical. The 2H-2-azabicyclo[1.1.1]pentane radical is illustrated with a solvation shell and the solvent waters are numbered by center of mass distance from the solute.

For each bond cleavage, we calculate both a homolytic and a heterolytic cleavage, and use whichever results in more stable products to calculate the bond dissociation energy. When looking at Figure 7.2(a), it is seen that the error is mainly from the large fragments. For example, the bond cleavage occurring at F and the bond cleavage occurring at L shows that the radical stability of both bond breaking fragments are similar. However, the bond breaking at L results in two large fragments which in turn results in a larger cleavage energy error than F. The error comes almost equally from both fragments when the bond at L is broken (absolute energy errors are 0.31 kcal/mol and 0.48 kcal/mol for the smaller and the larger fragments respectively), while when the bond at F is broken, the error is mostly from the large fragment (absolute energy errors are 0.16 kcal/mol and 0.69 kcal/mol for the smaller and the larger fragments respectively).
Figure 7.2: Bond dissociation energy errors of glutathione. (a) Absolute BDE error due to THC. The solid lines indicate homolytic bond cleavage (open-shell) and dashed lines indicate heterolytic bond cleavage (closed-shell). The bond index refers to labeled bonds in Fig. 7.1. (b) Absolute errors in the difference between the homolytic and heterolytic BDEs due to THC. The legend, $-\log(\varepsilon)$, represents the parent grid being pruned as done in Ref. [28] (the numerical cutoff can be referred to as the “tolerance”).
It is also important to examine the correlation of the errors with the various fragment’s stability (radical, anion, or cation). The fragment pairs are more stable with smaller errors. A good example would be the bond breaking at bond B and bond C, both are cleaving a $\text{COOH}\cdot$ or a $\text{COOH}^-$ from the rest of the glutathione molecule. While in the case of the bond breaking at B, there is a resonance effect which results in the radicals being more stable. Similarly, when the stability is small between radicals pairs and anion/cation pairs, the error differences are also smaller. In bond cleavage cases at bond A and bond D, the heterolytic bond breaking pair is more stable than the homolytic bond breaking pair, thus the heterolytic bond cleavage energy error is much smaller.

The error in the difference between the homolytic and heterolytic BDEs ($\Delta BDE$) were also computed and are depicted in Figure 7.2(b). Across the various bonds, errors for this measurement are somewhat lower than for the BDEs themselves. This indicates a reliable error cancellation between the open-shell and closed-shell LS-THC calculations on similar systems.

### 7.3. Summary

In summary, this work presents the implementation of open-shell tensor hypercontraction for MP2 and MP3 methods and compares them to closed-shell.

Similar to the RHF implementation, the LS-THC-MPn errors scale linearly with system size. We found errors for LS-THC-MP2a to be essentially negligible, while errors in LS-THC-MP3b are dominated by the MP2b contribution. The remaining errors in the LS-THC-MP3b contribution are reasonably small with a double-zeta basis set. Reliable error cancellation is evident in almost all calculations of energy differences. We observe that the greatest degree of error cancellation occurs when the systems have resulting fragments that are unequally distributed in size. We also conclude that error cancellations potentially occur when more stable products are produced. The error of the open-shell LS-THC-MPn methods
is not dependent on the specific nature of the chemical structure and type of molecular interactions. To conclude, the errors produced for open-shell systems are highly similar to the errors produced for chemically similar closed-shell systems.

This work is under review at the Journal of Chemical Theory and Computation titled:

*Open-shell tensor hypercontraction* (see Appendix E).
Chapter 8

Conclusions

The newly developed coupled cluster methods, TP-CCSD and STEOM-CCSD+cT, allow for accurate and computationally efficient results. The methods can be used to reproduce experimental x-ray absorption spectra since both transition moments and oscillaor strengths were shown to be accurate. TP-CCSD is element-specific and specific core orbital occupation numbers allow the mean absolute errors to be at their minimum. These methods decrease the orbital relaxation error that arises from the wavefunction going from the ground state to the excited state and can be utilized in a variety of x-ray applications. The ability for such methods to accurately reproduce x-ray spectra is crucial in comparing to experiment and being able to identify unknown compounds.

The newly developed open-shell THC method also allows for computationally efficient results. Applying tensor hypercontraction to high level tensor is crucial in reducing the computational cost to a scale comparably to other methods. The molecules studied using the open-shell THC method are important due to their application to green chemistry and environmental/health studies.

The motivation for developing the coupled cluster and THC methods is very specific and different on a small scale level. However, the big picture comes down to developing highly accurate and computationally efficient methods for various applications.
BIBLIOGRAPHY


[33] D. Hait and M. Head-Gordon, *Highly accurate prediction of core spectra of molecules at density functional theory cost: Attaining sub-electronvolt error from a restricted open-shell kohnâ€as ham approach*, *Journal of Physical Chemistry Letters* **11** (2020) 775–786. 6


65


66


[75] “The international x-ray absorption society.” 35, 36


[95] F. Frati, M. O. Hunault and F. M. deGroot, Oxygen k-edge x-ray absorption spectra, *Chemical Reviews* 120 (2020) 4056–4110. 41


[106] M. Simons and D. A. Matthews, Transition moments for steom-ccsd with core triples, 2304.06583. 52


69


70
APPENDIX A

Paper on transition-potential coupled cluster

Transition-potential coupled cluster

Cite as: J. Chem. Phys. 154, 014106 (2021); https://doi.org/10.1063/5.0036631
Submitted: 06 November 2020. Accepted: 13 December 2020. Published Online: 05 January 2021

Megan Simons, and Devin A. Matthews

ARTICLES YOU MAY BE INTERESTED IN

Toward chemical accuracy at low computational cost: Density-functional theory with σ-functionals for the correlation energy
The Journal of Chemical Physics 154, 014104 (2021); https://doi.org/10.1063/5.0026849

Fully variational incremental CASSCF
The Journal of Chemical Physics 154, 014105 (2021); https://doi.org/10.1063/5.0031208

Coupled-cluster techniques for computational chemistry: The CFOUR program package
The Journal of Chemical Physics 152, 214108 (2020); https://doi.org/10.1063/5.0004837
Transition-potential coupled cluster

ABSTRACT

The problem of orbital relaxation in computational core-hole spectroscopies, including x-ray absorption and x-ray photoionization, has long plagued linear response approaches, including equation-of-motion coupled cluster with singles and doubles (EOM-CCSD). Instead of addressing this problem by including additional electron correlation, we propose an explicit treatment of orbital relaxation via the use of “transition potential” reference orbitals, leading to a transition-potential coupled cluster (TP-CC) family of methods. One member of this family, in particular, TP-CCSD(\(\frac{1}{2}\))A, is found to essentially eliminate the orbital relaxation error and achieve the same level of accuracy for the core-hole spectra as is typically expected of EOM-CCSD in the valence region. These results show that very accurate x-ray absorption spectra for molecules with first-row atoms can be computed at a cost essentially the same as that for EOM-CCSD.

I. INTRODUCTION

The use of x-ray spectroscopies has long been a mainstay in the study of the structure and composition of ordered materials. More recently, x-ray ionization, absorption, and (inelastic) scattering have been applied to molecular systems, both in solution and in the gas phase.\(^1\)\(^2\)\(^3\)\(^4\)\(^5\) Coupled cluster linear response [LR-CC\(^6\)-\(^8\) or equivalently equation-of-motion coupled cluster (EOM-CC\(^9\)-\(^12\))] techniques are a natural method to apply to such “core-ionized” and “core-excited” (collectively “core-hole”) states, given their immense success in the description of valence excitations. Linear response based on density functional theory (TD-DFT)\(^10\) has been shown to describe core-hole states rather poorly because of large self-interaction errors.\(^11\)

Several density functionals have been tuned to reproduce x-ray absorption spectra at the expense of a quantitative description of the ground state electronic structure,\(^12\)-\(^14\) while range-separated functionals also somewhat decrease the self-interaction error.\(^15\)\(^16\)\(^17\) Alternatively, the \(\Delta\)Kohn–Sham method, which separately performs (quasi-)variational optimizations of both the ground and core-hole states, has been shown to accurately reproduce absorption and ionization spectra in many cases but suffers from convergence difficulties and the need to compute transition properties in a non-orthogonal framework.\(^18\)-\(^20\) As a compromise, the family of “transition-potential” DFT (TP-DFT) methods\(^21\)-\(^22\) eschews both linear-response and state-specific orbital optimization by performing a single calculation with fractional orbital occupation and is strongly motivated theoretically as an approximation to Slater’s Transition State (TS) method.

While TP-DFT has been successful in many cases, errors in both peak positions and intensities remain that can prevent a firm assignment of the spectrum in some cases. EOM-CC has been shown to smoothly and rapidly reduce errors as the excitation level and basis set quality are increased; in particular, inclusion of triple excitations and the use of an augmented triple-zeta basis set (possibly with the addition of explicit Rydberg basis functions) is sufficient for accuracy of better than 0.1 eV (when relativistic effects are included) in absolute energies.\(^26\)-\(^27\) The inclusion of triple excitations is particularly crucial as the orbital relaxation effects for core-hole states are exceptionally large. We have recently shown that a perturbative treatment of triple excitations in the excited state (EOM-CCSD\(^3\)) is sufficient to reproduce the effect of full triple excitations to high accuracy.\(^28\) Even so, the additional expense of triple excitations, especially considering that such an effect is not typically required in valence calculations at a similar level of accuracy, motivates the search for an effective EOM-CC method that can accurately treat core-hole states at a purely singles and doubles level.

In this paper, we present a potential candidate method, transition-potential coupled cluster (TP-CC), that blends the best features of both TP-DFT and EOM-CC in order to fulfill the need for an economical and yet accurate EOM-CC method for treating core-hole states.
II. THEORETICAL METHODS

A. Equation-of-motion coupled cluster theory

Equation-of-motion coupled cluster,\textsuperscript{2–5} as well as the closely related linear response coupled cluster theory,\textsuperscript{6–8} starts with an exponential parameterization of the ground state,

\[
E_{\text{EOM-CC}} = \langle 0 | e^{-\hat{H}} | \bar{N} \rangle,
\]

\[
= \langle 0 | \hat{H} | 0 \rangle, \tag{1}
\]

\[
\hat{H} = \langle \bar{N} | \hat{H} | \bar{N} \rangle,
\]

\[
= \langle 0 | \hat{P} | \bar{N} \rangle,
\]

\[
= \langle 0 | \hat{P} | \hat{H} | 0 \rangle, \tag{2}
\]

where the cluster operator \( \hat{T} \) is a pure excitation operator and \(| \bar{N} \rangle \) and \(| \bar{P} \rangle \) denote the reference determinant and set of excited determinants, respectively. Practical coupled cluster calculations require a truncation of the cluster operator and the set of excited determinants, in this work, a truncation at the level of single and double excitations (CCSD) is adopted. This leads to the following definitions of \( \hat{T} \) and \(| \bar{P} \rangle \), as well as the standard definition of the normal-ordered Hamiltonian \( \hat{H}_N \):

\[
\hat{H}_N = \sum_{pq} v_{pq} \bar{P}^a_{pq} (\bar{P}^a_{pq})^\dagger,
\]

\[
\hat{T} = \sum_{ai} t_{ai}^a \bar{P}^a_{ai} + \frac{1}{4} \sum_{abij} \bar{P}^a_{abij} \bar{P}^{b\dagger}_{ij}, \tag{3}
\]

\[
\bar{P} = |S\rangle \otimes |D\rangle
\]

\[
= (a^\dagger \bar{P}_{0} | 0 \rangle) \otimes (a^\dagger \bar{P}_{0} | 0 \rangle). \tag{4}
\]

We use the standard notations: \( pqr \) refer to creation/annihilation operators of arbitrary spin-orbitals, while \( ab \) refer specifically to virtual spin-orbitals and \( ij \) refer to occupied spin-orbitals (with respect to \(|0\rangle \)). Braces denote normal ordering; note that \( \hat{T} \) is implicitly normal ordered.

From this ground state, the \( m \)th excited state is parameterized by a linear excitation operator \( \hat{R}_m \), a right eigenvector of the similarity-transformed Hamiltonian \( \hat{H} \), and the corresponding excitation energy \( \omega_m \) is determined as the corresponding eigenvalue,

\[
\omega_m \hat{R}_m | 0 \rangle = (\hat{H} - E_{\text{EOM-CC}}) \hat{R}_m | 0 \rangle = [\hat{H}, \hat{R}_m] | 0 \rangle,
\]

\[
\hat{R}_m = r_0 + \sum_{ai} r_{ai}^a i + \frac{1}{4} \sum_{abij} r_{abij}^a b^\dagger j. \tag{5}
\]

The excitation energies obtained with EOM-CC are precisely equal to the poles of the linear response function of the coupled cluster ground state (LR-CC). These two theories only disagree in the definition of transition properties such as oscillator strengths.\textsuperscript{9} In the length gauge, the EOM-CC dipole oscillator strength is given as an expectation value of the dipole operator,

\[
\omega_m (\text{EOM-CC}) = \frac{2m_e \omega_m}{3h^2} \sum_{a,c,y,z} M_{m,ac}, \tag{6}
\]

\[
M_{m,ac} = \langle 0 | \bar{L}_y \hat{R}_m | 0 \rangle \langle 0 | \hat{L}_y \hat{R}_m | 0 \rangle, \tag{7}
\]

where \( \hat{L}_y = e^{-\phi_0} \hat{L}_y e^{\phi_0} \) and \( \hat{L}_y \) is the electronic dipole moment operator along the \( \alpha \) Cartesian axis. Because \( \hat{H} \) is non-Hermitian, it has distinct left eigenvectors \( \hat{L}_0 \). The ground state eigenvectors are \( \hat{L}_0 = 1 \) and \( \hat{L}_0 = (1 + \hat{A}) \), with \( \hat{A} \) being the usual coupled cluster amplitude response operator. In the linear response formalism, the square transition moments \( M_{m,ac} \) are computed from the residue of the corresponding pole in the response function. This gives rise to an additional term that incorporates the response of the excitation amplitudes \( r \) to the electric field. In most circumstances, this additional contribution is very small and can be safely neglected, and we do so in this work.

In contrast to the DFT linear response (TD-DFT) formalism,\textsuperscript{10} correlation of the excited state, which includes orbital relaxation effects, is explicitly included in the excitation operator \( \hat{R}_m \), while in TD-DFT, the exchange–correlation functional must account for such effects. For core-hole states, the stark difference in length scales between valence and core-hole correlation effects leads to large self-interaction errors (SIEs) that fail to cancel between ground and excited states. An explanation of these errors in terms of orbital relaxation is also useful, as the ground state Kohn–Sham orbitals that define the model system fail to sufficiently approximate the core-hole state. While EOM-CC explicitly accounts for such effects, an accurate treatment of them requires sufficient correlation in \( \hat{R}_m \), which is only present at the triple excitation level.

When applied to core-excited and core-ionized states, which are, in fact, resonances embedded in the valence ionization continuum, EOM-CC typically encounters convergence problems. One solution to this problem is the core-valence separation (CVS),\textsuperscript{11} first introduced by Cederbaum and Schirmer\textsuperscript{12–15} and adapted to EOM-CC by Coriani and Koch.\textsuperscript{16–18} In this approach, pure valence excitations or ionizations are excluded from the linear response manifold, which both restores convergence and eliminates spurious couplings to the (badly) discretized continuum determinants.\textsuperscript{19} All EOM-CC methods considered here use the CVS.

B. Transition-potential density functional theory

The TP-DFT theory\textsuperscript{20–25} is an approximation to Slater’s Transition State (TS) method, which, in turn, is ultimately derived from \( \Delta \text{Kohn–Sham} \) (or \( \Delta \text{DFT} \)). In the latter approach, separate DFT calculations are performed for the initial and final states, and the resulting energies are simply subtracted,

\[
\omega_{\text{KS}} = E_f - E_i, \tag{8}
\]

Given a suitable homotopy that connects the orbitals of the initial and final states by a continuous parameter \( \lambda \) (with \( \lambda = 0 \) in the initial state and \( \lambda = 1 \) in the final state), the energy difference can be written as

\[
\omega_{\text{KS}} = \int_0^1 d\lambda \frac{\partial E}{\partial \lambda}. \tag{9}
\]

Now, assume that the initial and final states differ only by a single excitation, that is, we can identify a (spin-)orbital \( \phi_0 \) that has an occupation \( n_0 = 1 \) in the initial state and \( 0 \) in the final state, and another orbital \( \phi_2 \) that has occupation \( n_2 = 0 \) in the initial state and one in the final state, while all other orbitals have the same
occupation (1 or 0) in both states. Note that the actual (spatial) orbitals need not be the same in both states, but only that they can be uniquely identified via the homotopy. Thus,
\[
\frac{dE(\lambda)}{d\lambda} = \frac{\partial E(\lambda)}{\partial n_1} \frac{\partial n_1}{d\lambda} + \frac{\partial E(\lambda)}{\partial n_2} \frac{\partial n_2}{d\lambda}
\]
\[
= -\frac{\partial E(\lambda)}{\partial n_1} + \frac{\partial E(\lambda)}{\partial n_2},
\]
(12)
We assume that \( \lambda \) is defined such that \( n_1 = 1 - \lambda \) and \( n_2 = \lambda \). Janak’s theorem then provides the necessary partial derivatives \( \partial E/\partial n_i = \epsilon_i \) from which we can arrive at
\[
\omega_{\Delta KS} = \int_0^1 [\epsilon_2(\lambda) - \epsilon_1(\lambda)] d\lambda
\]
\[
= \epsilon_2(1/2) - \epsilon_1(1/2),
\]
(13)
where the second step is Slater’s TS, which is the first-order approximation to the exact energy difference (the mid-point rule).

The TS method typically provides a good estimate of the excitation energies, even for core-hole states, but is complicated by the need to converge a half-electron state (with \( n_1 = n_2 = 1/2 \)), especially with regard to the partial occupation of the virtual orbital. In a sufficiently diffuse basis set, typical methods to converge such a state, e.g., using the maximum overlap method, are prone to failure. For high-quality \( \Delta KS \) calculations, more elaborate methods such as orthogonality-constrained DFT or constrained variational excited state optimization can be employed. Instead, the transition-potential (TP) approach further approximates TS by setting the virtual orbital occupation to zero, i.e., \( \omega_{\Delta KS} = \epsilon_2(n_1 = 1/2, n_2 = 0) - \epsilon_1(n_1 = 1/2, n_2 = 0) \). The advantages of TP over TS are (1) the half-electron state [in this case, a half-core-hole (HCH) state] can be more reliably converged, and (2) the same half-electron state may be used for excitations to any virtual orbital. In the context of x-ray absorption spectroscopy [XAS, specifically near-edge x-ray absorption fine structure spectroscopy (NEXAFS)], this means that the entire spectrum due to excitation of a particular core orbital may be obtained in a single calculation.

The selection of a half-electron state is derived via simple one-point approximation of the energy difference integral, but it can also be rationalized from an error cancellation perspective. In TD-DFT, the ground state can be considered well-described (i.e., described as orthogonal to the excited state) due to excitation of a particular core orbital may be obtained from the HF orbitals are variationally optimized; while CC is not variational, arbitrary changes to the orbitals also typically raise the CC energy. This should be especially true for highly non-optimal orbitals that include core relaxation. Second, the explicit inclusion of core relaxation should stabilize the final core-excited or core-ionized state at the CCSD level in a similar manner as the inclusion of triple excitations. This stabilization effect is expected to increase in proportion to the amount of explicit relaxation included in the orbitals.

The first effect is, in isolation, a degradation in the physical description of the ground state. However, since the increase in energy of the ground state has the same effect on the vertical energy differences as a lowering of the final state, both effects of substituting the orbitals in practice act in concert. Therefore, there should be some set of partially relaxed orbitals that combines partial destabilization of the ground state with partial stabilization of the excited state that, combined, reproduce the full orbital relaxation effect but at the CCSD level. To this end, we have defined a family of “transition-potential coupled cluster” (TP-CC) methods, which vary in two ways. First, the choice of how much relaxation to include in the orbitals is parameterized by \( \lambda \) as in Sec. II B. Second, the particular orbitals are obtained from a fractional-occupation SCF (here B3LYP) calculation with either a partial core hole (as in TP-DFT) or a partial core excitation to a virtual orbital (which we call XTP as in Ref. 25). These TP-CCSD(\( \lambda \)) and XTP-CCSD(\( \lambda \)) methods, apart from the non-standard choice of orbitals, are simply standard CVS-EOM-CCSD calculations. EOM-CC is normally orbital-invariant, but the CVS introduces a slight non-invariance similar to when a core orbital is frozen in the correlated calculation. The numerical effect of this non-invariance should be very small and will be bounded by the CVS error, which is already quite small. As with TP-DFT, the issue of symmetry-equivalent centers could be handled.

\[ f_{1 \rightarrow 2}(\text{TP-DFT}) = \frac{2m_e(\epsilon_2 - \epsilon_1)}{3\hbar^2} \sum_{a=x,y,z} M_{1 \rightarrow 2,a}, \]
(14)
\[ M_{1 \rightarrow 2,a} = 2\langle \phi_2 | \mu_a | \phi_1 \rangle^2, \]
(15)
by core orbital localization. In addition, one could maintain the delocalized core orbitals and divide the fractional hole among them. We purposefully avoid such molecules in this work in order to more fully explore such options in further research.

III. COMPUTATIONAL DETAILS

The (X)TP-CCSD(\lambda) methods were implemented via a combination of the Psi4\textsuperscript{32} (v1.3.2) and CFOUR\textsuperscript{33} program packages. A private development version of CFOUR was used, but the same results should be obtainable with the public v2.1. Specifically, we utilized the PSIXAS plugin\textsuperscript{24} for Psi4 to generate fractional core-hole or core-excited orbitals, using the B3LYP functional and ionizing or exciting \lambda/2 electrons of each spin in the selected core orbital. Excited electrons were promoted to the LUMO in each case. We modified the PSIXAS plugin to produce basis set (GENBAS) and molecular orbital (OLDMOS) files suitable for use in CFOUR. We also modified the CFOUR symmetry analysis code to prevent any reorientation or translation of the molecule in order to exactly match Psi4’s reference frame. In CFOUR, the reference orbitals were first reoccupied in the standard Aufbau ordering. Since the resulting determinant is clearly not a Hartree–Fock solution, we included the NON–HF = ON keyword in the CFOUR input file and also requested semicanonicalization of the orbitals. Then, a standard CVS-EOM-CCSD calculation is performed, including all non-Hartree–Fock terms. Oscillator strengths were calculated using the expectation value formalism described above.

The test set consisted of all s principal core ionizations and four core excitations (for each 1s orbital) of H\textsubscript{2}O, CO, HCN, HF, HOF, HNO, CH\textsubscript{2}, CH\textsubscript{3}, NH\textsubscript{3}, H\textsubscript{2}CF H\textsubscript{2}COH, H\textsubscript{2}CO, H\textsubscript{2}CNH, and H\textsubscript{2}NF. The core excitations were selected as those for which we could reliably converge all methods tested, which typically consisted of the first four excitations of dominant single excitation character. Double excitations were specifically avoided as EOM-CCSD is known to describe them quite poorly even in the valence case. All calculations utilized the aug-cc-pCVTZ basis set with all electrons correlated, except for H\textsubscript{2}O where aug-cc-pCVQZ was used. In order to avoid complications due to missing relativistic effects, basis set incompleteness (particularly for Rydberg core excitations), geometric effects, and data quality and availability, which would all be a concern when comparing directly to experimental data, we have used full CVS-EOM-CCSDT as a benchmark. Carbone et al.\textsuperscript{26} showed that CCSDT is typically within 100 meV of the experimental (vertical) core excitation energies, while Liu et al.\textsuperscript{25} showed similar results for core ionization potentials. In addition to CVS-EOM-CCSD, TP-CCSD(\lambda/2), TP-CCSD(\lambda/4), XTP-CCSD(\lambda/2), and XTP-CCSD(\lambda/4) values, we have also expanded the CVS-EOM-CCSD\textsuperscript{\lambda} results from Ref. 26 to encompass the larger test set used here. These results are included as an “aspirational yardstick” since that method was previously found to reproduce the full CVS-EOM-CCSDT results rather well.

IV. RESULTS AND DISCUSSION

In the following discussion, the “shortened” names of the CVS-EOM methods will be used, e.g., CCSDT = CVS-EOM-CCSDT. The distribution of “absolute” (i.e., unmodified vertical) excitation energy deviations from CCSDT are depicted in Fig. 1. The absolute energy deviation for a method X is calculated as \(E(X) - E(\text{CCSDT})\), where \(E\) is a vertical core excitation energy or core ionization potential. The “relative” excitation energy deviations are depicted in Fig. 2. These deviations are determined from excitation energies adjusted such that the lowest excitation energy for each edge is equal to 0 (this is essentially a shift of the entire spectrum; note that the shift is different for each method and is applied before computing the deviations). One relative core excitation out of four is trivially zero.

![Figure 1](image1.png)

**FIG. 1.** Normal error distributions for core excitation energies. Iterative EOM-CC methods are denoted by dotted lines, perturbative EOM-CC methods are denoted by dashed lines, and TP-CC methods are denoted by solid lines.

![Figure 2](image2.png)

**FIG. 2.** Normal error distributions for core excitation relative values. Iterative EOM-CC methods are denoted by dotted lines, perturbative EOM-CC methods are denoted by dashed lines, and TP-CC methods are denoted by solid lines.
after adjustment; these values are not included in the statistics. Since
the methods should make similar errors in the ionization potential
energies and excitation energies, the relative errors should be smaller
due to error cancellation. A similar shift is commonly applied when
comparing to experimental data. Finally, the distribution of com-
puted ionization potentials is depicted in Fig. 3. In each figure, the
distribution of the energy deviations is fit to a Gaussian (normal
distribution).

A. CCSD and CCSD∗

As reported in previous studies,27,28,31,35 CCSD systematically
overestimates all core excitation energies. The large orbital relaxa-
tion energy is challenging for a purely linear response method
due to the localized nature of the core hole, and absolute errors of
1–3 eV remain at the CCSD level. In comparison, EOM-CCSD typ-
ically reproduces EOM-CC3 vertical valence excitation energies to
within 0.3 eV.26 A simple triples correction to the excited (core-hole)
state only (CCSD∗) nearly eliminates the deviation with respect to
CCSDT, indicating that the leading high-order correlation effects
in the upper state (which correspond to orbital relaxation) are the
primary source of error. Residual errors in CCSD∗ are potentially
indicative of the improvement in the correlation of both the ground
and excited states and are of a similar magnitude to triples effects
in valence excitations, and so the CCSD∗ values likely represent a “best
estimate” of the effect of orbital relaxation alone.

B. TP-CCSD(1/2) and XTP-CCSD(1/2)

The choice of λ = 1/2 can be expected to be a reasonable first-
order estimate of the optimal error-cancellation point for TP-CC
methods. Note that while a half-core-hole is provably optimal as a
single-point approximation in the TS- and TP-DFT methods, there

is no such formal argument for TP-CC. Nonetheless, these calcu-
lations show significantly better agreement with CCSDT in compari-
son to the CCSD calculations with standard Hartree–Fock orbitals.
The absolute error distributions can be seen in Fig. 1, where the
distribution for TP-CCSD(1/2) has a similar shape to CCSD∗ but
with slightly smaller average error. XTP-CCSD(1/2) reduces the aver-
age error even more, to below 0.1 eV, but exhibits approximately
twice the variability of CCSD∗. Figure 2 shows the relative error
distribution, where the distribution for XTP-CCSD(1/2) is almost
identical to CCSD∗ but again with a slightly lower average error.
XTP-CCSD(1/2) provides similar statistical deviations, although the
standard deviation is slightly increased over both TP-CCSD(1/2)
and CCSD∗. Similarly to the absolute excitation energies, both TP-
CCSD(1/2) and XTP-CCSD(1/2) show an improvement over CCSD
for core ionization potentials, with XTP-CCSD(1/2) again showing
a smaller average error but larger standard deviation in compar-
ison with TP-CCSD(1/2). The ionization potential distribution for
these methods is shown in Fig. 3. CCSD∗ and TP-CCSD(1/2) have
very similar distributions, but TP-CCSD(1/2) does not attain quite
as small a standard deviation. As with excitation energies, evalu-
ating relative ionization energies, specifically ionization “chemical
shifts” relative to a standard, may further reduce the average and
standard deviation of the error.

Both TP-CC methods significantly improve on CCSD and, for
shifted spectra, account for essentially all of the orbital relaxation
energy (using CCSD∗ as a yardstick). Additionally, the improve-
ment when considering shifted rather than absolute spectra shows
that TP-CC additionally benefits from error cancellation within the
spectrum. While CCSD also displays the same benefit, there are still
residual errors as large as 1 eV, while TP-CC maintains deviation
from full CCSDT within 0.3 eV, closely matching the performance
of CCSD in the valence region. The XTP-CC variant was intro-
duced with the idea that the use of a neutral reference state for
determining the orbitals should balance a tendency toward over-
contraction that might be expected from a fractionally charged sys-
tem. On the other hand, in analogy with Slater’s TS method, we
would expect TP-CCSD(1/2) to be the better choice for ionization
potentials. However, at λ = 1/2, it does not seem to be the case that
XTP-CCSD(1/2) is superior for core-excited states. Upon a closer
investigation of the individual data (see the supplementary mate-
rial), it can be seen that XTP-CC does, in fact, slightly improve the
description of valence resonances (e.g., 1s → π∗) but slightly worsens
the description of Rydberg states (the standard deviation is increased
by ∼80%, although the mean error is actually reduced). Rydberg
states are less sensitive to correlation, and a balanced description
of valence and Rydberg states is a hallmark of a “good” method. XTP-
CC, where the fractional electron is placed in the LUMO, which is
typically a valence anti-bonding orbital, seems to lose this balance.

The simple choice of λ = 1/2 seems to do a remarkably good
job of almost entirely eliminating the orbital relaxation error for
both core excitation energies and core ionization potentials. How-
ever, a finer tuning of the λ parameter may further decrease either
the average error or variability (standard deviation) of the method.
In particular, TP-CCSD(1/2) seems to slightly underestimate abso-
lute energies, while CCSD overestimates, indicating that a slightly
smaller value of λ might offer further improvement. While it would
be impractical to tune λ for each individual system (and largely
defeat the purpose of an ab initio method like EOM-CC), a close

![FIG. 3 Normal error distributions for core ionization energies. Iterative EOM-CC methods are denoted by dotted lines, perturbative EOM-CC methods are denoted by dashed lines, and TP-CC methods are denoted by solid lines.](image-url)
inspection of the results shows that, for example, the standard deviation of the core excitation energies does increase monotonically on going from C to F. While this, to some extent, reflects the increase in energy scale, it may also indicate that different elements require slightly different optimal \( \lambda \) values. We will explore optimization of \( \lambda \) in a future publication, but for now, it seems that \( \lambda = \frac{1}{2} \) is a good default value.

### C. TP-CCSD(\(\frac{1}{4}\)) and XTP-CCSD(\(\frac{1}{4}\))

In addition to \( \lambda = \frac{1}{2} \), we also tried \( \lambda = \frac{1}{4}, \lambda = \frac{3}{4}, \) and even \( \lambda = 1 \) TP-CC calculations in order to understand the tradeoff between ground state destabilization and final state stabilization. The latter two choices resulted in a lack of convergence of the ground state coupled cluster equations in all cases. This is not surprising, given that the choice of very different reference orbitals will induce large cluster amplitudes. In the case of \( \lambda = 1 \), we would even expect \( \hat{T}_i \) amplitudes on the order of 1, which would completely destabilize the (truncated) coupled cluster procedure. While \( \lambda = \frac{1}{2} \) is clearly a good choice for TP-CC, it is worthwhile to also examine \( \lambda = \frac{1}{4} \).

The absolute excitation energy distributions (Fig. 1) for TP-CCSD(\(\frac{1}{4}\)) and XTP-CCSD(\(\frac{1}{4}\)) sit nicely between those of CCSD and CCSD* (\(\langle X \rangle\)TP-CCSD(\(\frac{3}{4}\)), both in terms of average error as well as standard deviation. This shows that there is still some error cancellation between the initial and final state effects, although the cancellation is incomplete. The relationship of XTP-CCSD(\(\frac{1}{4}\)) to TP-CCSD(\(\frac{1}{4}\)) seems to mirror that of XTP-CCSD(\(\frac{1}{4}\)) and TP-CCSD(\(\frac{3}{4}\)), with the former in each case having a slightly higher standard deviation. Moving to relative excitation energies (Fig. 2) shows a very similar situation, as does looking at ionization energies (Fig. 3). In each case, XTP-CCSD(\(\frac{1}{4}\)) performs slightly worse than its TP-CCSD(\(\frac{1}{4}\)) counterpart. In contrast to \( \lambda = \frac{1}{2} \), where XTP-CC did, in fact, decrease the average error for valence and even Rydberg states (although it simultaneously increased the standard deviation of the latter), the average errors for all states increase by \(~0.1\) eV in XTP-CCSD(\(\frac{1}{4}\)) compared to TP-CCSD(\(\frac{1}{4}\)). The standard deviations are also slightly higher across the board, although only very slightly unlike with XTP-CCSD(\(\frac{1}{4}\)). Although we have only sampled \( \lambda = \frac{1}{4} \) and \( \lambda = \frac{1}{2} \) thus far, it seems that the error cancellation properties of TP-CC vary in fairly direct proportion with the fraction of electron ionized in the core orbital.

### D. Oscillator strengths

Because TP-CC is, computationally, identical to a standard EOM-CC calculation, it is simple to compute oscillator strengths, here in the expectation value formalism. We have also added full EOM-CCSDT transition properties in the development version of CFOUR, and so, we can benchmark the effect of transition-potential orbitals on this important property. EOM-CCSD*, as a perturbative correction to EOM-CCSD, does not provide corrected oscillator strengths. The absolute deviations in the dimensionless oscillator strengths, defined in analogy to the absolute excitation and ionization energy deviations, are depicted statistically in Fig. 4. In addition, we have computed the deviations for relative oscillator strengths, which have been normalized separately for each spectrum such that the most intense transition has unit strength; the statistics for these relative deviations are depicted in Fig. 5 as percentages.
shows a rather different effect. Here, the deviations represent the normalized deviation, with the most intense peak set at unity. This measure was chosen rather than relative intensity changes for each peak because in the latter case, large relative changes of very weak transitions (which are ultimately much less important to the overall assignment) would dominate the statistics. Instead, a spectrum-wide normalization, such as the spectrum-wide energy shift in Fig. 2, puts all spectra on an equal footing while preserving the relative importance of each peak in the spectrum. In this case, we can see that the improvement of the TP-CC methods over CCSD is even more pronounced, with a 3–4 factor reduction in standard deviation and essentially zero average deviation. Interestingly, XTP-CCSD(\frac{1}{2}) now performs very slightly better than TP-CCSD(\frac{1}{2}).

The significant improvement of TP-CC oscillator strengths over CCSD is very encouraging, as obtaining the correct relative intensities is often nearly as important to fully assigning a spectrum as the transition energies. While the calculations here do not include the necessary diffuse orbitals in order to directly compare the Rydberg states to experiment, it is most likely that the improved performance of TP-CC will prove important for properly predicting Rydberg spectra, in addition to the usually more intense valence peaks. The improvement of the TP-CC oscillator strengths also suggests that other one-electron properties, such as multipole moments, may also be improved relative to CCSD, although this is beyond the scope of the current study.

### E. Statistical analysis

In Secs. IV A–IV D, it is assumed that the deviations in each category (absolute/relative excitation energies, ionization potentials, and absolute/relative oscillator strengths) represent a normal distribution. In order to test this assumption, we have constructed normal quantile–quantile (Q–Q) plots. In this approach, all observations (deviations) within a category are sorted and then plotted against the inverse cumulative normal distribution (ICDF) for a set of uniformly distributed probability values. For the ith sorted observation out of n (starting with 1), the probability value $p_i = \frac{i - 0.5}{n}$ is input to the ICDF $Q(p) = \sqrt{2}\text{erf}^{-1}(2p - 1)$ to obtain the value to plot against. For a true normal distribution, the Q–Q plot is a straight line; thus, we perform a linear regression and report the $R^2$ values as the “normality” scores. These values, in addition to estimated skewness and excess kurtosis of the distributions are given in Table I.

The distributions for absolute excitation energy deviations are all highly normal, with at most a slight skew toward positive deviations. Moving to relative excitation energies shows additional deviations from normality. The most pronounced deviation is for XTP-CCSD(\frac{1}{2}), which exhibits a significant positive skew, but also a large excess kurtosis, indicating a sharp distribution, but with a long tail of outliers toward the positive end. The excess kurtosis for CVS-EOM-CCSD* is also somewhat positive, while CVS-EOM-CCSD* has a

### Table I. Statistical measures measuring deviations from a normal distribution. Significant deviations from normality are highlighted.

<table>
<thead>
<tr>
<th>Category</th>
<th>Absolute excitation energies (n = 92)</th>
<th>Relative excitation energies (n = 69)</th>
<th>Ionization potentials (n = 23)</th>
<th>Absolute oscillator strengths (n = 90)</th>
<th>Relative oscillator strengths (n = 67)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CVS-EOM-CCSD</td>
<td>0.97</td>
<td>0.97</td>
<td>0.95</td>
<td>0.90</td>
<td>0.59</td>
</tr>
<tr>
<td>CVS-EOM-CCSD*</td>
<td>0.97</td>
<td>0.94</td>
<td>0.96</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>TP-CCSD(\frac{1}{2})</td>
<td>0.99</td>
<td>0.98</td>
<td>0.97</td>
<td>0.73</td>
<td>0.77</td>
</tr>
<tr>
<td>XTP-CCSD(\frac{1}{2})</td>
<td>0.98</td>
<td>0.88</td>
<td>0.95</td>
<td>0.72</td>
<td>0.80</td>
</tr>
<tr>
<td>TP-CCSD(\frac{1}{4})</td>
<td>0.95</td>
<td>0.94</td>
<td>0.93</td>
<td>0.87</td>
<td>0.59</td>
</tr>
<tr>
<td>XTP-CCSD(\frac{1}{4})</td>
<td>0.96</td>
<td>0.96</td>
<td>0.96</td>
<td>0.88</td>
<td>0.60</td>
</tr>
</tbody>
</table>

#### Estimated skewness values for each distribution

<table>
<thead>
<tr>
<th>Category</th>
<th>Absolute excitation energies (n = 92)</th>
<th>Relative excitation energies (n = 69)</th>
<th>Ionization potentials (n = 23)</th>
<th>Absolute oscillator strengths (n = 90)</th>
<th>Relative oscillator strengths (n = 67)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CVS-EOM-CCSD</td>
<td>0.33</td>
<td>0.12</td>
<td>0.24</td>
<td>0.90</td>
<td>3.39</td>
</tr>
<tr>
<td>CVS-EOM-CCSD*</td>
<td>0.24</td>
<td>0.69</td>
<td>–0.58</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>TP-CCSD(\frac{1}{2})</td>
<td>0.26</td>
<td>0.42</td>
<td>0.52</td>
<td>1.94</td>
<td>–0.97</td>
</tr>
<tr>
<td>XTP-CCSD(\frac{1}{2})</td>
<td>0.29</td>
<td>1.62</td>
<td>0.48</td>
<td>1.97</td>
<td>–0.05</td>
</tr>
<tr>
<td>TP-CCSD(\frac{1}{4})</td>
<td>0.74</td>
<td>–0.42</td>
<td>0.50</td>
<td>1.21</td>
<td>2.29</td>
</tr>
<tr>
<td>XTP-CCSD(\frac{1}{4})</td>
<td>0.69</td>
<td>–0.59</td>
<td>0.55</td>
<td>1.14</td>
<td>2.34</td>
</tr>
</tbody>
</table>

#### Estimated excess kurtosis values for each distribution

<table>
<thead>
<tr>
<th>Category</th>
<th>Absolute excitation energies (n = 92)</th>
<th>Relative excitation energies (n = 69)</th>
<th>Ionization potentials (n = 23)</th>
<th>Absolute oscillator strengths (n = 90)</th>
<th>Relative oscillator strengths (n = 67)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CVS-EOM-CCSD</td>
<td>–0.48</td>
<td>–0.87</td>
<td>–1.19</td>
<td>–0.04</td>
<td>15.40</td>
</tr>
<tr>
<td>CVS-EOM-CCSD*</td>
<td>0.59</td>
<td>1.02</td>
<td>–0.18</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>TP-CCSD(\frac{1}{2})</td>
<td>–0.33</td>
<td>0.42</td>
<td>0.56</td>
<td>3.20</td>
<td>10.43</td>
</tr>
<tr>
<td>XTP-CCSD(\frac{1}{2})</td>
<td>–0.77</td>
<td>1.62</td>
<td>–0.83</td>
<td>3.28</td>
<td>9.21</td>
</tr>
<tr>
<td>TP-CCSD(\frac{1}{4})</td>
<td>–0.27</td>
<td>–0.42</td>
<td>–1.03</td>
<td>0.91</td>
<td>15.30</td>
</tr>
<tr>
<td>XTP-CCSD(\frac{1}{4})</td>
<td>–0.13</td>
<td>–0.59</td>
<td>–0.63</td>
<td>0.68</td>
<td>16.08</td>
</tr>
</tbody>
</table>
fairly negative excess kurtosis, indicating a more flattened distribution. Despite a more tightly peaked distribution for XTP-CCSD(\(\lambda/2\)), the long positive tail is concerning for routine application; a similar effect is seen in the larger maximum errors for XTP-CCSD(\(\lambda/2\)) compared to TP-CCSD(\(\lambda/2\)). The ionization potential distributions are almost all flattened [with the exception of TP-CCSD(\(\lambda/2\))], with excess kurtosis ranging from \(-0.63\) to \(-1.19\) (essentially a uniform distribution). The distributions are slightly skewed (positively, except for CVS-EOM-CCSD\(^\dagger\)), but it seems clear that a normal distribution is sufficient for capturing the overall improvement of the TP-CC methods.

The distributions for oscillator strength deviations are much more non-normal. In particular, the relative oscillator strengths exhibit extremely large excess kurtosis, suggesting much more sharply peaked distributions that the standard deviation in Fig. 5 would seem to indicate, with long tails in both directions [more to the positive for CVS-EOM-CCSD and (X)TP-CCSD(\(\lambda/4\))]. The primary outliers seem to be the fluorine edge of CH\(_3\)F as well as the oxygen edge of CH\(_3\)OH. In the former case, the most intense peak in the most calculated spectra is a Rydberg 3p transition; inclusion of additional diffuse basis functions would likely decrease the intensity of this and the other Rydberg peaks and so should lead to better overall accuracy. The absolute oscillator strengths are somewhat more well-behaved but still with significant tails to the positive side.

V. CONCLUSIONS AND FUTURE WORK

Core ionization and core excitation energies for a variety of small molecules were calculated with several "traditional" equation-of-motion coupled cluster methods: CVS-EOM-CCSD, CVS-EOM-CCSD\(^\dagger\), and CVS-EOM-CCSDT, as well as with a range of proposed transition-potential coupled cluster methods, (X)TP-CCSD(\(\lambda/4\)), in which a fractionally ionized or fractionally excited reference state is employed. In comparison to full CVS-EOM-CCSDT, TP-CCSD(\(\lambda/2\)) seems to account for essentially all of the orbital relaxation energy. CVS-EOM-CCSD\(^\dagger\) was used as an "aspirational yardstick" in this study, as previous work showed that a simple non-iterative triples correction in the final state was able to account for the relaxation error, and TP-CCSD(\(\lambda/4\)) indeed achieves similar statistical error measures. The XTP-CC variant, in which the fractional core electron is promoted to the LUMO, does not measurably improve on TP-CC, despite expectations that a neutral reference state should provide more balanced orbitals (especially virtual orbitals). TP-CCSD(\(\lambda/4\)) was also tested and has intermediate performance between CCSD and TP-CCSD(\(\lambda/2\)), while TP-CCSD(\(\lambda/4\)) and TP-CCSD(1) calculations were seen to diverge.

Overall, TP-CCSD(\(\lambda/2\)) is about as accurate for core-excited states as EOM-CCSD is for valence states, with deviations from full CVS-EOM-CCSDT within a few tenths of an eV. TP-CCSD intensities are also much improved over CVS-EOM-CCSD, and in particular, considering normalized spectra, the reduction in deviations is between threefold and fourfold. The ability of a relatively simple modification of “vanilla” CVS-EOM-CCSD, using only non-standard reference orbitals, to accurately predict core ionization and core excitation energies is an exciting prospect, especially as the computational cost of TP-CCSD is essentially the same as CVS-EOM-CCSD and scales rigorously with the system size \(n\) as \(\Theta(n^3)\).

While this study looks at only a few choices of \(\lambda\) (the fraction of an electron to remove from the core orbital), it would be interesting to pursue optimizing \(\lambda\), possibly in an element-specific manner. In addition, B3LYP orbitals are used here in order to capture some effect of electron correlation on the fractionally occupied reference state. In future work, we plan to assess the use of plain Hartree–Fock orbitals, which would allow for a simpler native implementation in CFOUR. Additionally, we are interested in applying TP-CCSD to the case of transient x-ray absorption (tr-NEXAFS, alternatively UV pump/x-ray probe or PP-NEXAFS); the ability of the TP orbitals to simultaneously describe valence excitations is of highest importance. Finally, the application of TP-CCSD to larger molecules and direct comparison with experimental spectra is necessary to fully explore the potential benefits of our proposed method.

SUPPLEMENTARY MATERIAL

An electronic supplementary material file is available as an Excel file (.xlsx). This file contains the employed molecular geometries and basis sets and the complete results, comprising absolute and relative excitation energies, ionization potentials, and oscillator strengths, as well as computed normal distributions and statistical measures.

ACKNOWLEDGMENTS

This work was supported by a generous start-up grant from Southern Methodist University. All calculations were performed on the ManeFrame II computing system at SMU. We would also like to thank Dr. Christopher Ehlerl for his work on PSIXAS, which made this project possible.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

REFERENCES

The Journal of Chemical Physics


Appendix B

Paper on optimization of transition-potential coupled cluster

Transition-potential coupled cluster II: optimisation of the core orbital occupation number

Megan Simons & Devin A. Matthews

To cite this article: Megan Simons & Devin A. Matthews (2022): Transition-potential coupled cluster II: optimisation of the core orbital occupation number, Molecular Physics, DOI: 10.1080/00268976.2022.2088421

To link to this article: https://doi.org/10.1080/00268976.2022.2088421

View supplementary material

Published online: 16 Jun 2022.

Submit your article to this journal

View related articles

View Crossmark data
Transition-potential coupled cluster II: optimisation of the core orbital occupation number

Megan Simons and Devin A. Matthews
Southern Methodist University, Dallas, TX, USA

ABSTRACT
The issue of orbital relaxation in computational core-hole spectroscopy, specifically x-ray absorption, has been a major problem for methods such as equation-of-motion coupled cluster with singles and doubles (EOM-CCSD). The transition-potential coupled cluster (TP-CC) method is utilised to address this problem by including an explicit treatment of orbital relaxation via the use of reference orbitals with a fractional core occupation number. The value of the fractional occupation parameter $\lambda$ was optimised for both TP-CCSD and XTP-CCSD methods in an element-specific manner due to the differences in atomic charge and energy scale. Additionally, TP-CCSD calculations using the optimised parameters were performed for the K-edge absorption spectra of gas-phase adenine and thymine. TP-CCSD reproduces the valence region well and requires smaller overall energy shifts in comparison to EOM-CCSD, while also improving on the relative position and intensities of several absorption peaks.

1. Introduction
X-ray absorption spectroscopy (XAS) has been used for many years by experimental chemists to study electronic and molecular structure [1–3], but theoretical calculations can often assist in interpreting spectra as well as predicting spectra of unknown compounds. X-ray techniques are important in addressing the challenges of understanding the structure of complex molecules and understanding the behaviour of these molecules. Historically, theoretical chemists have predominately used density functional theory (DFT) methods for XAS [4–6]. However, techniques such as Transition-Potential DFT (TP-DFT) improve on TD-DFT [7–11], and the systematic improvability of equation-of-motion coupled cluster (EOM-CC) [12–15] methods provides a significant motivation for applying EOM-CC to XAS.

TP-DFT [16–18] directly addresses the problem of orbital relaxation which plagues even EOM-CC theory by construction a fractionally-occupied reference state. On the other hand, within the EOM-CC framework the inclusion of two-electron excitations in the excited state response operator ($\hat{R}$ vector) allows EOM-CC to recover much of the relaxation error, and triple excitations are sufficient to fully overcome this problem [19,20]. However, the combination of fairly large residual errors of as much as 1–3 eV at the doubles level and the excessive computational cost of triple excitations calls for a novel solution.
We recently introduced a Transition-Potential Coupled Cluster (TP-CC) method [21] in analogy to TP-DFT, in hopes of reducing the orbital relaxation error. This method utilises the best parts of TP-DFT and EOM-CC and was able to successfully reduce errors in both the absolute and relative (i.e. empirically shifted) transition energies and intensities. This improvement comes about due to a cancellation of errors between the destabilised ground state and stabilised core-hole state which counterbalance the overestimation of core excitation energies at the singles and doubles level. The precise point of cancellation depends on the orbitals used, however, with the total number of core electrons removed from the core orbital, \( \lambda \), as the controlling parameter. In this previous work, which we will refer to as Paper I, we tested only \( \lambda = 1/2 \) (in analogy to TP-DFT) and \( \lambda = 1/4 \). Unlike TP-DFT, though, there is no theoretical basis for such an a priori choice in TP-CC and in fact other values may produce superior results. Additionally, the optimal value of \( \lambda \) may vary in an element-specific manner due to the differences in atomic charge and energy scale.

In this work, we systematically investigate the optimal \( \lambda \) parameter as a function of element for molecules containing first-row elements CNOF, and finally apply TP-CC with the optimised parameters to the example of the nitrogen, oxygen, and carbon K-edge spectra of gas-phase nucleobases.

2. Transition-potential coupled cluster

Equation-of-motion coupled cluster (or equivalently coupled cluster linear response) theory [12,14,15,22–24] computes excitation energies as eigenvalues of the transformed Hamiltonian, \( \hat{H} \),

\[
E_{CC} = \langle 0 | \hat{H} | 0 \rangle \\
0 = \langle P | \hat{H} | 0 \rangle \\
\omega_m(P|\hat{R}_m|0) = \langle P|\hat{H},\hat{R}_m|0\rangle
\]

from which we can also easily incorporate the ground state with excitation energy \( \omega_0 = 0 \) and response vector (right-hand eigenvector) \( \hat{R}_0 = 1 \). In EOM-CCSD the excitation space \( \langle P \rangle \) is restricted to singly- and doubly-excited determinants. Transition intensities (oscillator strengths) are formally computed as residues of the excitation poles, but we adopt the simpler and typically very accurate expectation value formalism,

\[
f_m^{(EOM-CC)} = \frac{2m_e\omega_m}{3\hbar^2} \sum_{\alpha=x,y,z} M_{m,\alpha} \\
M_{m,\alpha} = \langle 0 | \hat{L}_0 \mu_\alpha \hat{R}_m | 0 \rangle \langle 0 | \hat{L}_m \mu_\alpha \hat{R}_0 | 0 \rangle
\]

where \( \mu_\alpha \) is the similarity-transformed electronic dipole moment operator along the \( \alpha \) Cartesian axis and \( \hat{L}_m \) are the left-hand eigenvectors of \( \hat{H} \).

In order to address the issue of orbital relaxation, we adopt a non-standard reference state. We are motivated by TP-DFT theory [17,18,25,26], which is an approximation to Slater’s Transition State (TS) method, which in turn is ultimately derived from ΔKohn-Sham (or ΔDFT) [16,27–30]. Essentially, TP-DFT allows one to approximate a direct energy difference between two states differing by the excitation of an electron from one orbital to another, by an orbital energy difference obtained with a fractional occupation,

\[
\omega_{\Delta KS} = E_f - E_i \\
= \int_0^1 [\epsilon_2(\lambda) - \epsilon_1(\lambda)] d\lambda \\
\approx [\epsilon_2(1/2) - \epsilon_1(1/2)] \\
= \omega_{TP-DFT}
\]

The choice of a half-electron occupation is justified by the trapezoidal rule of numerical integration. In TP-CCSD, we also compute a fractionally-occupied reference determinant (using a constrained variational optimisation), but then reoccupy the orbitals according to the Aufbau principle for use in a non-Hartree–Fock EOM-CCSD calculation. While standard EOM-CCSD typically overestimates core-hole excitation and ionisation energies by 1–3 eV [19,21], TP-CCSD largely corrects this error by combining a partial destabilisation of the ground state due to the use of non-HF orbitals and a partial stabilisation of the core-hole state due to the explicit inclusion of core-hole relaxation. The balance between these effects is controlled by the \( \lambda \) parameter as defined in (6), defining a family of methods TP-CCSD(\( \lambda \)). Note however that in order to maintain a spin-restricted reference state we de-occupy both the \( \alpha \) and \( \beta \) core orbitals by \( \lambda/2 \) electrons each. Importantly, this guarantees that the excited state is a spin eigenfunction. We also defined an XTP-CC class of methods which differ by promoting electrons from the core to the LUMO instead of ionising them. This maintains a charge-neutrality while optimising the orbitals and also includes some stabilisation of the LUMO (often a \( \pi^* \) orbital).

In Paper I we showed that TP-CCSD (1/2) was highly effective in reducing errors in both transition energies and intensities relative to EOM-CCSD. However, \( \lambda = 1/2 \) is by no means guaranteed to provide the lowest errors. In fact, we expect the optimal value of \( \lambda \) to vary depending on the atomic number, as the size of the orbital relaxation error grows with energy scale and hence atomic charge. As TP-CCSD is essentially a
'normal' EOM-CCSD calculation with a different choice of orbitals, both the calculation of core-hole states via the core-valence separation (CVS) [31] and the calculation of transition intensities are identical to EOM-CCSD. We use the CVS for all EOM-CC and TP-CC calculations in this work. We adopt the original formulation from Coriani and Koch and included core–valence correlation in both the ground and excited states.

3. Computational details

The (X)TP-CCSD(\(\lambda\)) methods were implemented via a combination of the Psi4 [32] and CFOUR [33] programme packages. We used a locally-modified version of the PSIXAS plugin [34] for Psi4 to generate fractional core-hole or core-excited orbitals at the B3LYP level of theory.

The test set used and methodology are the same as in Paper I, except where noted below. The test set consisted of all 1s principal core ionisations and four core excitations (for each 1s orbital) of H\(_2\)O, CO, HCN, HF, HOF, HNO, CH\(_2\), CH\(_4\), NH\(_3\), H\(_3\)CF, H\(_3\)COH, H\(_2\)CO, H\(_2\)CNH, and H\(_2\)NF. All calculations utilised the aug-cc-pCVTZ basis set with all electrons correlated, except for H\(_2\)O where aug-cc-pCVQZ was used. We performed calculations with values of \(\lambda\) from 0.25 to 0.75 in steps of 0.025 (21 points total). We use the same full CVS-EOM-CCSDT benchmark as in Paper I, except in the calculations of nucleobase spectra where we compare to experimental data. In the latter case, we include an estimate of relativistic effects as +0.38 eV for the oxygen K-edge, +0.21 eV for the nitrogen K-edge, and +0.10 eV for the carbon K-edge. The relativistic contributions are very weakly-dependent on the chemical environment for first-row K-edges [19]. Note that in Paper I we selected four excited states for each edge on the basis of dominant single-excitation character and non-negligible oscillator strengths. This is critical as doubly-excited states are poorly treated at the singles and doubles level. We changed a small number of state selections in this work to avoid states which mix strongly with doubly-excited states for some values of \(\lambda\), although certain unavoidable crossings remain (see Section 4.2).

Variation of errors across the test set are quantified by computing the mean absolute error (MAE) across the entire test set, except for a small number of calculations which did not converge for large values of \(\lambda\). The full data set is available in the electronic Supporting Information file.

4. Results and discussion

4.1. Excitation and ionisation energies

The distribution of 'absolute' (i.e. unmodified vertical) excitation energy deviations from CVS-EOM-CCSDT is depicted in Figure 1. The MAE distribution of computed ionisation potentials is depicted in Figure 2. Finally, the MAE distribution of 'relative' excitation energies is depicted in Figure 3. The relative deviations are determined from excitation energies measured from the corresponding ionisation edge (this is essentially a shift of the entire spectrum – note that the shift is method- and \(\lambda\)-dependent, and is applied before computing the MAE). Since each method should make similar errors in the ionisation potential energies and excitation energies, the relative errors should be smaller due to error cancellation. A similar shift is commonly applied when comparing to experimental data.

In Paper I, the choice of \(\lambda = 1/2\) was shown to be a reasonable first-order estimate of the optimal error-cancellation point for TP-CC methods. From Figures 1 and 2 we can see that there is indeed a fairly sharp minimum in the mean absolute energy as \(\lambda\) is varied, with somewhat sharper minima for TP-CCSD than for XTP-CCSD. However, in many cases the optimal \(\lambda\) value is

![Figure 1](image-url). TP-CCSD (left) and XTP-CCSD (right) mean absolute error distributions for absolute (vertical) core excitation energies. Errors specific to the K-edges of elements C–F are reported separately, and a combined MAE value is also included.
Figure 2. TP-CCSD (left) and XTP-CCSD (right) mean absolute error distributions for absolute (vertical) core ionisation energies. Errors specific to the K-edges of elements C–F are reported separately, and a combined MAE value is also included.

Figure 3. TP-CCSD (left) and XTP-CCSD (right) mean absolute error distributions for relative core excitation energies (see text). Errors specific to the K-edges of elements C–F are reported separately, and a combined MAE value is also included.

significantly different from 0.5. For example, the optimal value for nitrogen 1s excitations with TP-CCSD is approximately 0.425, while the best value for oxygen 1s excitations with XTP-CCSD is approximately 0.575. The optimal value of $\lambda$ also depends strongly on the atomic number of the 1s core orbital. Looking at the ‘combined’ MAEs shows that the blindly-averaged results do not, in many cases, obtain errors as low as when considering elements independently nor predict the best value of $\lambda$ for any particular edge. Due to the sharpness of the error distributions, the simple choice of $\lambda = 1/2$ may result in errors twice as large or more compared to a ‘tuned’ value. While we do not advocate optimising the value of $\lambda$ for any specific spectrum, it does seem clear that large accuracy gains can be obtained by making a more informed and element-specific choice of the $\lambda$ parameter.

The relative excitation energies, owing to a significant cancellation of errors between the excitation and ionisation energy calculations, do not show a clear trend with atomic number, although individual MAEs are significantly lower than for absolute energies. As with excitation energies, evaluating relative ionisation energies, specifically ionisation ‘chemical shifts’ [35] relative to a standard species, may similarly reduce the ionisation potential errors. Despite the lack of overall trends, there is still a strong effect of atomic number on the optimal value of $\lambda$. In fact, the deviation of the optimal value from our previous choice of 0.5 is even more pronounced, with carbon and nitrogen K-edges benefiting most from a value of $\lambda$ as low as 0.35. The combined TP-CCSD relative excitation energy results do show that a ‘global’ choice of 0.425 results in fairly good treatment regardless of atomic number, with error increasing over the optimal $\lambda$ values by only 20% or so. However, choosing slightly better element-specific values of $\lambda$ is trivial to do and results in the best predictions of core excitation spectra. We will defer choosing a recommended set of $\lambda$ values until Section 4.2.

Splitting up the test set based on the atomic edge (C 1s through F 1s) reveals several interesting patterns in the absolute excitation and ionisation energy results. Firstly, the errors at low values of $\lambda$ (and similarly in standard CVS-EOM-CCSD) are strongly dependent on atomic number and increase proportionally. This reflects the increasing energy scale of the 1s orbital energies. Additionally, the optimal value of $\lambda$ for TP-CCSD increases with increasing atomic number. This indicates that a larger amount of core-hole character must be included in
the reference orbitals in order to cancel out the orbital relaxation error. As the orbital relaxation contribution increases along with the absolute energy scale, this trend is not unexpected. However, this trend is completely reversed in the XTP-CCSD results, with the optimal value of $\lambda$ now decreasing with atomic number. As XTP-CC places a fractional electron into the LUMO, this must indicate a stronger stabilisation of the LUMO with atomic number. This may derive from the increasing electronegativity of the elements along the first row of the periodic table, which alters the shape (in particular the polarisation) of the LUMO, which is typically a $\pi^*$ orbital. These clear trends disappear in the case of relative excitation energies due to cancellation of the overall trends in the absolute energies.

The deviations corresponding to Figures 1–5 for standard CVS-EOM-CCSD are reproduced in Table 1, which of course do not depend on a $\lambda$ parameter. For ease of comparison, we have included the ratio of the CVS-EOM-CCSD MAEs to the best TP-CCSD values (i.e. the minima of the curves in the figures) in parentheses. From these results, we can see that TP-CCSD is easily capable of reducing the size of the orbital relaxation error in vertical core-excitation and core-ionisation energies by approximately a factor of 15 (and as high as a factor of 22) compared to a standard EOM calculation. Given that TP-CCSD incurs nearly zero additional computational cost, it seems that TP-CCSD is highly preferable for routine calculations. Errors in relative excitation energies (intra-edge) are also significantly reduced by a factor of 5–8. This leads to errors in the line positions of approximately 100 meV, which is on par with or smaller than the typical instrument broadening. Equally as important as the line positions, the errors oscillator strengths (either relative or absolute, discussed in more detail in Section 4.2) are also reduced by at least a factor of 15 compared to CVS-EOM-CCSD. Relative oscillator strengths are correct in TP-CCSD to within 2–3% (compared to our CVS-EOM-CCSDT reference), which enables a significantly more reliable basis for experimental assignment.

4.2. Oscillator strengths

Because TP-CC is computationally identical to a standard EOM-CC calculation apart from the choice of orbitals, it is simple to compute oscillator strengths using the expectation value formalism. By extension, it is also trivial to compute other important excited state properties such as excited state dipole moment, natural transition orbitals, and extent of diffusion ($\langle r^2 \rangle$ values).
We calculated dimensionless oscillator strengths for all transitions and compared to benchmark CVS-EOM-CCSDT values from Paper I. The mean absolute deviations in the oscillator strengths, defined in analogy to the absolute excitation and ionisation energy deviations, are depicted in Figure 4 as a function of $\lambda$. In addition, we have computed the mean absolute deviations of relative oscillator strengths. In this case we separately normalised the spectrum of each edge such that the most intense transition has unit strength; the statistics for these relative deviations are depicted in Figure 5 as percentages.

Due to a lack of convergence of either the ground-state CCSD or EOM-CCSD equations, several data points are not available for $\lambda = 0.725$ and $\lambda = 0.75$. These data points were omitted from the MAE statistics, but the effect is clearly discernible in Figures 4 and 5 due to the large variations in oscillator strengths across the test set. Additionally, an irregularity in the nitrogen 1s MAE curves is clearly visible, with a sharp local maximum near $\lambda = 0.3$. This is due to mixing with a dark doubly-excited state near this value of $\lambda$, which is not present in the reference CVS-EOM-CCSDT calculations.

Both MAE distributions for absolute and relative oscillator strengths have broad and rather unstructured minima, with the exception of the carbon K-edges. Additionally, the smaller overall MAE for fluorine can probably be attributed to the low number of data points for fluorine containing molecules. While an extension of the test set to better represent fluorine K-edge could improve the statistical relevance of the MAE curves, it seems clear that, in general, the oscillator strengths are less dependent on a specific value of $\lambda$ compared to the excitation and ionisation energies. The increase in error for the ‘worst’ value of $\lambda$ tested compared to the optimal value is less than a factor of 2 in all cases. Additionally, any ‘reasonable’ value of $\lambda$ leads to a significantly reduced error, as demonstrated in Table 1. While we did not systematically examine $0 < \lambda < 0.25$, the disconnect between the shallowness of the MAE curves in the $0.25 \leq \lambda \leq 0.75$ region and the large reduction of error relative to CVS-EOM-CCSD (equivalent to $\lambda = 0$) necessitates a ‘bathtub’-like shape of the MAE curve, with a sharp decrease at low values of $\lambda$ followed by a relatively flat region.

Because the accuracy of the oscillator strengths depends only weakly on the choice of $\lambda$, and because both the absolute and relative errors are very low in any case, we base our recommended values of $\lambda$ on the minimum MAE points in Figure 3. The absolute energy errors are typically less important than the relative shifts, for example when assigning experimental spectra. The recommended values for both TP- and XTP-CCSD calculations are presented in Table 2.

### 4.3. K-edge absorption spectra: canonical nucleobases

As an additional benchmark, we computed carbon, nitrogen, and oxygen K-edge spectra of adenine (9H) and thymine using TP-CCSD and the recommended values of $\lambda$ (Table 2), and compared the simulated absorption spectra to available experimental gas-phase data [36] and standard CVS-EOM-CCSD calculations. The x-ray absorption spectra of these systems were previously studied by Vidal et al. using the fc-CVS-EOMEE-CCSD method [37]. The molecular geometries were taken from Ref. [38], which are optimised at the M06-2X/aug-cc-pVTZ level. Vertical x-ray absorption spectra were computed the same way as our previous TP-CCSD calculations, utilising a combination Psi4 and CFOUR, but we used the more economical 6-311++G** basis set. This basis set has shown to be quite accurate for its size [19], although we did not decontract the core orbital(s) as suggested in Ref. [39].

The final spectra are obtained by summing spectra from separate calculations restricted to each C 1s, O 1s,
or N 1s orbital in turn. Because of the orbital-specific nature of the CVS, a similar procedure must be followed in typical CVS-EOM-CC implementations, although the development version of CFOUR supports mixing multiple edges in a standard CVS-EOM-CC calculation. The calculation of each edge included the lowest 10 excited states. We apply Lorentzian broadening with a half-width half-maximum of 0.2 eV in all cases. The excited state energies are shifted so that the first peak in the computational spectra lines up with the first peak in the experimental spectra, as is customary. The shifts reported for each computational spectra are the raw shift of the curve minus the estimated relativistic effects for each K-edge.

The N 1s XAS spectrum of adenine (Figure 6, top) is characterised by three prominent bands. The first peak at 399.5 eV is composed of three valence transitions (1s → $\pi^*$). TP-CCSD and CCSD both reproduce this peak well, with TP-CCSD requiring half of the shift required by EOM-CCSD. The second, broader peak at 402.1 eV arises from a number of transitions. TP-CCSD improves on the separation between this peak and the main pre-edge peak, while also clearly reproducing the smaller features between 401 and 401.5 eV and providing a clear and unambiguous assignment of these subtle transitions. The third peak at 403.3 eV is of primarily Rydberg transitions, and neither method reproduces the position of this peak well, although TP-CCSD improves on EOM-CCSD by approximately 0.5 eV. In this region, the insufficiency of the basis set is the main limiting factor, and adding additional diffuse functions is necessary to more accurately place the Rydberg transitions. The corresponding C 1s XAS spectrum (Figure 6, bottom) has a relatively simpler structure dominated by three valence peaks. Both TP-CCSD and EOM-CCSD reproduce the relative positions of these peaks well, although the TP-CCSD relative
intensities are distinctly improved compared to EOM-CCSD. The largest energy change from EOM-CCSD to TP-CCSD is in the weaker transitions appearing at ∼286.5 and ∼286.6 eV. In the EOM-CCSD spectrum, these transitions are nearly degenerate with the stronger transitions. Again, neither method reproduces the very weak Rydberg region of the spectrum well. For the carbon K-edge, EOM-CCSD requires a shift of −1.8 eV which is reduced to −1.15 eV in TP-CCSD. This reduction in absolute energy error is more modest compared to the EOM-CCSDT benchmark. This observation, paired with the poor performance in the Rydberg region points to the basis set as the main limiting factor. However, the close correlation of TP-CCSD to the full EOM-CCSDT indicates strongly that calculations with larger basis sets could provide further improvements over the current results. We are currently working on improving the efficiency and scalability of our implementation in order to enable such precise applications.

The nitrogen, carbon, and oxygen K-edge spectra of thymine (Figure 7) show similar results, with the valence region reproduced well, the Rydberg transitions still somewhat poorly represented due to basis set insufficiency, and overall smaller shifts required for TP-CCSD by about a factor of two. However, the carbon K-edge (Figure 7, middle) shows some additional advantage of TP-CCSD over EOM-CCSD. As with adenine, the spectrum shows a clear separation between intense valence transitions and weak Rydberg transitions. However, TP-CCSD almost exactly reproduces the positions of the four valence peaks, spanning energies from 285 eV to almost 290 eV, while EOM-CCSD still exhibits residual errors as high as 0.3 eV. This demonstrates the TP-CCSD, in addition to reducing absolute energy errors and improving relative intensities, can still provide improvements in the valence energy structure of the spectrum compared to EOM-CCSD.

5. Conclusions

Core excitation and ionisation energies were calculated for a group of small molecules using transition-potential coupled cluster [(X)TP-CCSD(λ)] methods with a variety of fractional core-hole occupations (with \( n_{1s\sigma} = n_{1s\sigma} = 1 - \lambda/2 \)). Our previous work [21] showed that TP-CCSD(1/2) was as accurate for core-excited states as EOM-CCSD for valence states, with deviations from CVS-EOM-CCSDT within a few tenths of an eV. In this work, we optimised \( \lambda \) in an element-specific manner to identify the ‘best’ core-hole fraction for K-edges of carbon, nitrogen, oxygen, and fluorine. We used the mean absolute error in comparison to full CVS-EOM-CCSDT and identified clear minima in the MAE curves for both absolute and relative energy errors, while errors in oscillator strengths did not clearly favour a particular value of \( \lambda \). We found that an element-specific choice of the \( \lambda \) parameter leads to the best accuracy (summarised in Table 2), although a generic value of \( \lambda = 0.425 \) for TP-CCSD or \( \lambda = 0.525 \) for XTP-CCSD is almost as accurate.

We then used TP-CCSD with our recommended element-specific \( \lambda \) values, in combination with the more economical 6-311++G** basis set for calculating the C, N, and O K-edge absorption spectra of adenine and thymine, for which gas-phase experimental data is available. TP-CCSD was found to systematically reduce the overall energy shifts required to match the experimental spectra, in comparison to CVS-EOM-CCSD, while also improving the relative positions and/or intensities of several peaks. In the Rydberg region, the insufficiency of the basis set is the main limiting factor and adding additional diffuse functions is necessary to increase accuracy. However, the close correlation of TP-CCSD to the full CVS-EOM-CCSDT shows that calculations with larger basis sets could provide further improvements over the current results. We are currently working on improving the efficiency and scalability of our implementation in order to enable such precise applications.

Acknowledgments

MS is supported by an SMU Center for Research Computing Graduate Fellowship. All calculations were performed on the ManeFrame II computing system at SMU.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was supported in part by the US National Science Foundation under grant OAC-2003931.

ORCID

Megan Simons  http://orcid.org/0000-0001-9457-7019
Devin A. Matthews  http://orcid.org/0000-0003-2795-5483

References

APPENDIX C

Paper on similarity-transformed equation-of-motion coupled cluster

Accurate Core-Excited States via Inclusion of Core Triple Excitations in Similarity-Transformed Equation-of-Motion Theory

Megan Simons* and Devin A. Matthews

ABSTRACT: The phenomenon of orbital relaxation upon excitation of core electrons is a major problem in the linear-response treatment of core-hole spectroscopies. Rather than addressing relaxation through direct dynamical correlation of the excited state via equation-of-motion coupled cluster theory (EOM-CC), we extend the alternative similarity-transformed equation-of-motion coupled cluster theory (STEOMEE-CC) by including the core–valence separation (CVS) and correlation of triple excitations only within the calculation of core ionization energies. This new method, CVS-STEOMEE-CCSD+cT, significantly improves on CVS-EOMEE-CCSD and unmodified CVS-STEOMEE-CCSD when compared to full CVS-EOM-CCSDT for K-edge core-excitation energies of a set of small molecules. The improvement in both absolute and relative (shifted) peak positions is nearly as good as that for transition-potential coupled cluster (TP-CC), which includes an explicit treatment of orbital relaxation, and CVS-EOMEE-CCSD*, which includes a perturbative treatment of triple excitations.

1. INTRODUCTION

Coupled cluster (CC) theory is one of the most powerful methods for treating dynamical correlation in molecules and is capable of computing highly accurate ground state energies of small molecules. Beyond the ground state, coupled cluster has been extended to excited states via the time-dependent linear-response formalism,\(^1,2\) the closely related equation-of-motion approach,\(^3,4\) and other approaches, such as the symmetry-adapted cluster technique.\(^5,6\) Equation-of-motion coupled-cluster (EOM-CC) theory can be used for excited (EE-EOM-CC), electron-attached (EA-EOM-CC), and ionized state (IP-EOM-CC) energies, as well as multiply ionized or attached states and even spin-flip excitations (SF-EOM-CC).\(^7,8\) EOM-CC is able to do this by taking advantage of the similarity transformation of the Hamiltonian, which guarantees size-extensivity of the excited state total energy (although excitation energies are not in general size-consistent with respect to charge separation). While the ground state CC wave function is single reference, the configuration interaction (CI)-like nature of the EOM-CC wave function can capture significant multireference character of excited states.\(^9,10\)

Nooijen et al. proposed an alternative approach to EOM-CC of using a second similarity transformation of the Hamiltonian, followed by diagonalization in a small (CI singles (CIS)-like) excitation space.\(^11,12\) In this similarity-transformed equation of motion coupled cluster (STEOM-CC) theory, the second similarity transformation simultaneously captures the dynamical correlation of all low-lying excited states. In comparison, EOM-CC determines the wave function for a single excited state and incorporates dynamical correlation effects via explicit inclusion of higher excitations in the excited state wave function. The STEOM-CC similarity transformation uses the wave functions of a number of ionized and electron-attached states in order to build the transformation. This transformation can be viewed as decoupling the “active” single-electron excitations from the double excitations, much as the ground state coupled cluster equations decouple the reference from single and double excitations. Thus, while STEOM-CC obtains the excited state energies by diagonalization only in the space of single excitations, it achieves an accuracy much greater than that of CIS or EOM-CCS.

Both EOMEE-CCSD and STEOMEE-CCSD have been highly successful at describing valence excited states of predominately single-excitation character, but some modifications to the theory are necessary for application in the X-ray regime. X-ray excited states, necessary for simulating spectra such as near-edge X-ray absorption fine structure (NEXAFS), X-ray emission spectroscopy (XES), and resonant inelastic X-ray scattering (RIXS),\(^13,14\) are not bound states but are resonances embedded deep in the valence continuum. For
EOM-CC, the core–valence separation (CVS) approach of Coriani and Koch,16 has been highly successful, although it is also possible to employ other techniques such as damped response,17 complex scaling/complex absorption potential,18–20 etc. However, the CVS does not address the other major issue encountered in the X-ray regime: orbital relaxation. Due to the presence of a core hole in the excited state wave function, the valence orbitals undergo considerable contraction and rotation. CVS-EOMEE-CCSD incompletely captures this effect and hence overestimates core vertical excitation energies by 1–3 eV (vide infra). The addition of triple excitations, either full CVS-EOMEE-CCSDT21 or an approximate treatment of triples,22 is necessary to fully treat the relaxation effects within standard EOM-CC theory.

The CVS can be ported from EOM-CC to STEOM-CC in a relatively straightforward manner.23 However, STEOM-CC also offers an alternative approach to the orbital relaxation issue. Here we propose a modification of CVS-STEOMEE-CCSD that efficiently and accurately treats orbital relaxation for core excited states, which we dub CVS-STEOMEE-CCSD+CT. This method compares favorably with standard CVS-(ST)-EOM-CCSD, and achieves similar performance compared to an approximate inclusion of triples (CVS-EOMEE-CCSD+), as well as to an explicit inclusion of relaxation effects in the reference via TP-CCSD.24

2. THEORETICAL METHODS

2.1. EOM-CC. The coupled ground state25 is characterized by a non-Hermitian similarity transformation of the Hamiltonian, which decouples the reference from the space of excited determinants,

\[ \hat{H} = e^{-\hat{T} \hat{H} \hat{T}} \]

(1)

\[ \hat{T} = \sum_{k=1}^{N} \hat{T}_k = \sum_{i} t^a_i a_i^\dagger + \frac{1}{4} \sum_{abij} t^{ab}_{ij} a_i^\dagger a_j^\dagger a_i a_j + \ldots \]

(2)

\[ \langle \Phi_0 | \hat{T} | \Phi_0 \rangle = E_{\text{CC}} \]

(3)

\[ \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = 0, \quad 0 < k \leq N \]

(4)

where \(|\Phi_0\rangle\) is a zeroth order description of the wave function (single determinant) and \(|\Phi_k^a, a_i \rangle\) are the \(k\)th excited determinants. In EOM-CCSD, the CC equations are solved in the space of single and double excitations, and hence \(N = 2\).

The transformed Hamiltonian, \(\hat{H}\), defined via the cluster operators \(\hat{T}_k\), provides the means to obtain excited states as well. The ground state coupled cluster energy is an eigenvalue of \(\hat{H}\) with distinct right and left eigenfunctions due to the non-Hermitian nature of the similarity transformation,

\[ \hat{H} \hat{\rho}(0)|\Phi_0\rangle = E_{\text{CC}} \hat{\rho}(0)|\Phi_0\rangle, \quad \hat{\rho}(0) = \hat{1} \]

(5)

\[ \langle \Phi_0 | \hat{H}| \hat{L}(0) | \Phi_0 \rangle = \langle \Phi_0 | \hat{L}(0) | E_{\text{CC}} \rangle \quad \hat{L}(0) = \hat{1} + \hat{A} \]

(6)

Explicit diagonalization of the transformed Hamiltonian, shifted by the ground state energy, yields the vertical excitation energies \(\omega_i\) and their associated right and left eigenfunctions,\(^6\)

\[ (\hat{H} - E_{\text{CC}}) \hat{\rho}(m)|\Phi_0\rangle = [\hat{H}, \hat{\rho}(m)]|\Phi_0\rangle = \omega_i \hat{\rho}(m)|\Phi_0\rangle \]

(7)

Note that the left-hand eigenfunction equations are not explicitly connected. The connectedness of the right eigenfunction equations allows for a solution purely in terms of \(\hat{R}_1\) and \(\hat{R}_2\). Only one set of eigenfunctions is necessary to obtain the energy, although both are necessary in order to calculate properties (including transition properties) and analytic gradients.26,27 We will use \(\hat{R}(m)\) and \(\hat{L}(m)\) to refer to generic EOM-CC excitation and de-excitation operators or a subscript EE to refer specifically to the EOMEE-CC amplitudes. STEOMEE-CC additionally requires singly ionized and electron-attached states, which are formed via the application of non-number-conserving excitation operators (here only for the right-hand side),

\[ \hat{R}_{ip}(m) = \sum_{k=1}^{N} \hat{R}_{ip,k}(m) \]

(8)

\[ \hat{R}_{iA}(m) = \sum_{k=1}^{N} \hat{R}_{iA,k}(m) \]

(9)

\[ \hat{R}(m) = \sum_{a} r(a) a_i^\dagger a_i + \frac{1}{4} \sum_{abij} r^{ab}(a) a_i^\dagger a_j^\dagger a_i a_j + \ldots \]

(10)

2.2. STEOM-CC. Similarity transformed equation-of-motion coupled cluster theory14 starts with the definition of the transformed Hamiltonian, \(\hat{G}\),

\[ \{ \epsilon^\dagger \} \hat{G} = \hat{H} \{ \epsilon^\dagger \} \]

(11)

\[ \hat{G} = \sum_{pq} g_{pq} a_i^\dagger a_p + \frac{1}{4} \sum_{pqrs} g_{pqrs} a_i^\dagger a_p a_q a_r + \ldots \]

(12)

where the braces denote operator normal ordering (essentially, this ensures that \(\{ \epsilon^\dagger \}\) has no internal contractions). The transformation operator \(\hat{S}\) has components in both the electron-attached \([0, 1]\) and ionized \([1, 0]\) sectors of Fock space,

\[ \hat{S} = \hat{S}^+ + \hat{S}^- \]

(13)

\[ \hat{S}^+ = \sum_{k} \hat{S}^+_k = \sum_{i} s_{ia} a_i^\dagger + \frac{1}{2} \sum_{abij} s_{abij} a_i^\dagger a_j^\dagger a_i a_j + \ldots \]

(14)

\[ \hat{S}^- = \sum_{k} \hat{S}^-_k = \sum_{im} s_{mi} a_i a_m^\dagger + \frac{1}{2} \sum_{ijmb} s_{ijmb} a_i a_m^\dagger a_j a_m + \ldots \]

(15)
where $e$ and $m$ are associated with sets of $n_{v;act}$ active virtual and $n_{o;act}$ active occupied orbitals (transformed back to the canonical MO space).

As noted by Nooijen and Bartlett,14 the $\hat{S}_1$ amplitudes are not necessary for the solution of the STEOMEE-CC equations as they simply cause rotations within the singles excitation space, and hence a diagonalization within the full singles space is invariant. In fact, diagonalization within the full rather than the active singles space is desirable as the portion of the solution falling outside the active space serves as a measure of active space insufficiency.14

The transformation amplitudes $\hat{S}^\pm$ may be easily obtained by renormalization of a set of solutions of the EOMIP-CC and EOMEEA-CC equations,

$$ S^h_{\nu} = -\sum_{\kappa l=1}^{n_{v;act}} r^\nu_{\kappa l}(U_-^{-1})_{\nu l} \delta_{\nu m} \tag{18} $$

$$ S^a_{\mu} = \sum_{\kappa l=1}^{n_{o;act}} r^a_{\mu l}(U_+^{-1})_{\mu l} \delta_{\mu a} \tag{19} $$

where the extra minus sign for the IP coefficients comes from the contraction over the hole line $\lambda$ in eq 18. The matrices $U_\pm$ are the transformation matrices, which diagonalize the STEOM effective Hamiltonian. They are derived from the single excitation parts of the IP and EA solutions,

$$ (U_-)_{\nu l} = \sum_{\kappa} \delta_{\nu \kappa} r^\nu_{\kappa l} \tag{20} $$

$$ (U_+)_{\mu l} = \sum_{\kappa} \delta_{\mu \kappa} r^a_{\mu l} \tag{21} $$

In eqs 18–21, the factor $\delta_{\nu \kappa}$ indicates that the active orbitals (indexed by $\kappa$) are simply a subset of the canonical molecular orbitals (indexed by $p$), typically those orbitals within a small energy range around the Fermi level. The solutions, $\hat{R}_{IP/EA}(\lambda)$, typically correspond to principal ionizations from and electron attachments to these active orbitals. The active orbitals may also be chosen as linear combinations of molecular orbitals,23,28 with the proper transformation matrix replacing the Kronecker delta.

The excited states are obtained by solving the eigenvalue equations,

$$ [\hat{G}, \hat{R}(m)|\Phi_\nu > = \omega_m \hat{R}(m)|\Phi_0 > \tag{22} $$

The left-hand eigenvalue equations formally require a solution in the full singles and doubles space, although computation of properties and transition strengths can be simplified by a perturbative approximation of $L_\nu$.14

2.3. Core Excited States. The direct calculation of core excited states, even for the 1s orbitals of first row elements with energies on the order of 100–500 eV, is fraught with difficulties. Standard EOMEE-CC calculations are difficult or impossible to converge, and even when convergence is achieved, the energies may be contaminated by spurious couplings to high-lying valence excited determinants which form an unphysical discretization of the valence continuum.29

As a remedy to this problem, Coriani and Koch16 adapted the core–valence separation scheme first introduced by Cederbaum, Domcke, and Schirmer30 to EOM-CC. In CVS-EOM-CC, amplitudes that correspond to purely valence excitations are explicitly zeroed. This leaves only components involving one or more core orbitals (indicated by capital Roman letters),

$$ \hat{R}_{CVS} = \sum_{a \ell} r^a_{\ell}(m)a^{\dagger}_{\ell}a_{\ell} + \frac{1}{2} \sum_{a b \ell j} r^{a b}_{\ell j}(m)a^{\dagger}_{a \ell}a^{\dagger}_{b \ell}a_{j}a_{\ell} + \ldots \tag{23} $$

This formulation eliminates all core–valence couplings and recovers the core-excited states as bound solutions. A number of variations on this basic theme exist, such as including only one or a small number of symmetry-related core orbitals in the “core” set and treating the rest as valence,21 solving the ground state equations in the frozen-core approximation,24 etc. In this work, we target a single core orbital in each calculation and define $\hat{R}$ as in eq 23, with an all-electron solution of the ground state. Note that we purposefully avoid test molecules with symmetric nuclei as these cases require either treating the symmetric and antisymmetric core molecular orbitals equally or breaking the symmetry via orbital localization.

Within STEOMEE-CCSD, the CVS can be applied in two places, giving rise to CVS-STEOMEE-CCSD. First, the selection of the active space must include the core orbital(s) of interest, and when solving for these core ionization wavefunctions, the CVS is necessary to stabilize convergence. Second, the solution of the eigenvalue equations in eqs 22 may also use the CVS in defining the excitation operator $\hat{R}$, in order to accelerate the computation. Note that if only one core orbital is included in the CVS treatment, then the diagonalization step scales as $O(n_v^2 n_a^2)$, whereas $n_v$ is the number of virtual orbitals. The application of the CVS to the $\hat{R}_{IP}$ operator does not induce a similar restriction on the $\hat{S}^\pm$ operator. Because this operator contains information from both valence and core ionized wave functions, it must necessarily span the full molecular orbital space. The combined valence and core nature of $\hat{S}^\pm$ also allows for the simultaneous and balanced determination of core and valence excitation energies.4 In principle, it may be possible to construct an $\hat{S}^\pm$ and hence $\hat{G}$ operator using only core ionization wave functions if no valence excitations are desired. We have not explored this possibility as the valence IP solutions are rarely a bottleneck in practice.

The CVS eliminates most convergence issues and recovers excitation energies that are systematically improvable toward the experimental value with increasing basis set size and level of excitation.21,32 However, at the singles and doubles level, large errors, which are attributable to the significant orbital relaxation from the ground to the excited core-hole state, remain. We previously introduced the transition-potential coupled cluster (TP-CC) method,24 which accounts for orbital relaxation explicitly by performing the calculation with molecular orbitals optimized for a fractional core hole. Instead, the STEOMEE-CC approach offers an alternative.

The ionization part of the similarity transformation, defined by the solution of the standard EOMIP-CC equations, provides all of the necessary dynamical correlation for the occupied orbitals. Then, since the inclusion of triple excitations in EOMEE-CC provides a necessary level of correlation to account for core-hole orbital relaxation, we propose that inclusion of triple excitations only in the EOMIP-CC solutions is sufficient to account for orbital relaxation in STEOMEE-CC.
This modification introduces an additional transformation operator, $S_3$,

$$S_{ij}^{\text{clm}} = -\sum_{\kappa \lambda = 1}^{n_{\text{O,act}}} t_{ij}^{\kappa \lambda}(U^{-1})_{\lambda \delta} \delta_{\delta m}$$

where at least one of $ijk$ must be an active core orbital and $\kappa \lambda$ refer to the $n_{\text{O,act}}$ active core orbitals. Since STEOMEE-CC only requires elements of $\hat{G}$ with at most two lines at the top and bottom, diagrammatically, the only modifications necessary to the formation of the twice-transformed Hamiltonian are

$$\delta_{im}^m \leftarrow S_{ij}^{\text{clm}}(jkl | bc)$$

$$S_{ij}^{\text{ma}} \leftarrow -S_{ij}^{\text{alm}}(jkl | bc)$$

The diagonalization step proceeds exactly the same as in unmodified CVS-STEOM-CCSD. We denote this new method as CVS-STEOMEE-CCSD+$cT$ (“singles and doubles plus core triples”). For a single core orbital, the solution of the CVS-EOMIP-CCSDT equations scales as $O(n_e^2 n_v^4)$, which is the same as the ground state CCSD equations. Also note that the connectivity of the EOMIP-CCSDT equations is preserved even without including triple excitations in the ground state.

Although we expect CVS-STEOMEE-CCSD+$cT$ to be similar in overall accuracy to the existing CVS-EOM-CCSD* and TP-CCSD(1/2) methods, there are several advantages to CVS-STEOMEE-CCSD+$cT$ over these alternatives. First, CVS-STEOMEE-CCSD+$cT$ is more computationally efficient than CVS-EOM-CCSD* as triple excitations are only included in the ionization potential calculations and not in the excitation energy calculation. In the case of CVS-EOM-CCSD*, the triple excitation contributions must also be included for each excitation, while for CVS-STEOMEE-CCSD+$cT$ these contributions are only included once for each core orbital, irrespective of the number of excitations sought from that orbital. Second while we may expect CVS-STEOMEE-CCSD+$cT$ and TP-CCSD(1/2) to incur similar overall computational costs, a TP-CCSD calculation is inherently specific to one core orbital/edge, as the reference orbitals must be specifically optimized. In CVS-STEOMEE-CCSD+$cT$, the reference orbitals are the standard canonical orbitals, and importantly, the valence excitations obtained are almost precisely the same as within standard STEOM-CCSD (except for a very small core orbital contribution). We expect this property to be important for the calculation of excited state X-ray spectra, for example, for transient X-ray absorption spectroscopy (XAS). A final important advantage of STEOM-CC in general is that a large number of excitations can be calculated without significantly raising computational cost or memory consumption.

### 3. COMPUTATIONAL DETAILS

CVS-STEOMEE-CCSD and CVS-STEOMEE-CCSD+$cT$ were implemented in a development version of the CFOUR program package. In all cases, we included all canonical orbitals with orbital energies between $-20$ and $+10$ eV as active orbitals. A single core orbital was included in the CVS treatment and STEOM principal IP solution in each calculation. We observed only very small (a few tens of millielectronvolts) changes upon expansion of the active space.

The test set consisted of four vertical core excitation energies from each 1s core orbital of H$_2$, CH$_4$, NH$_3$, H$_2$CF, H$_2$COH, H$_2$CO, H$_2$CNH, and H$_2$NF. This includes a total of 94 vertical excitation energies. The core excitations were selected as those for which we could reliably converge all methods tested, which typically consisted of the first four excitations of dominant single excitation character. All calculations utilized the aug-cc-pCVTZ basis set with all electrons correlated, except for H$_2$O where aug-cc-pCVQZ was used. In order to avoid complications due to missing relativistic effects, basis set incompleteness (particularly for Rydberg core excitations), geometric effects, and data quality and availability, which would all be a concern when comparing directly to experimental data, we have used full CVS-EOM-CCSDT as a benchmark, as in previous work.

### 4. RESULTS AND DISCUSSION

In the following discussion and in Figures 1 and 2, the “shortened” names of the CVS-EOM methods will be used, for example, CCSD = CVS-EOM-CCSD, with the exception of TP-CCSD(1/2). The distribution of “absolute” (i.e., unmodified vertical) excitation energy deviations from CCSDT are depicted in Figure 1. The absolute energy deviation for a method $X$ is calculated as $E(X) - E(\text{CCSDT})$ where $E$ is a vertical core excitation energy. The “relative” excitation energy deviations are depicted in Figure 2. These deviations are determined in two ways, (a) from excitation energies measured relative to the lowest excitation energy in each edge, $E_{\text{rel}}(X) = E(X) - E_{\text{ref}}(X)$, and (b) from excitation energies measured downward from the ionization edge, $E_{\text{rel}}(X) = IP(X) - E(X)$, and then deviations are computed as before. In the former case, the first excitation energy (which has zero relative error by definition) is not included in the distribution. The use of the ionization edge or excitation onset as a reference causes a shift of the entire spectrum, which is method- and molecule-specific. Note that the core ionization potentials for CVS-STEOMEE-CCSD are identical to EOMIP-CCSD, while those for CVS-STEOMEE-CCSD+$cT$ are the same as “EOMIP-CCSD(2,3)” that is, EOMIP-CC with a CCSD ground state and an EOMIP-CCSDT ionized state.

From Figure 1, it is clear that both “purely singles and doubles” methods, CCSD and STEOM-CCSD, are prone to large errors in absolute vertical core excitation energies. In the

![Figure 1: Error distributions with respect to CVS-EOM-CCSDT for absolute vertical core excitation energies.](https://doi.org/10.1021/acs.jctc.2c00268)
case of CCSD, errors are as large as 3 eV but uniformly positive, reflecting the tendency of orbital relaxation to lower the excitation energies. STEOM-CCSD errors cover a slightly larger range, with a few states predicted too low, but overall the performance of the two methods is similar. The remaining methods, TP-CCSD(1/2) (which includes explicit orbital relaxation), CCSD* (which includes explicit triple excitations in the excited state), and our new method STEOM-CCSD+cT, all improve significantly, lowering absolute errors to less than 1 eV and less than 0.5 eV in the typical case.

On the other hand, Figure 2 represents a more useful picture of error characteristics by including a shift of the spectrum for each ionization edge. Since such a shift is almost always applied when comparing to experimental spectra, these error distributions reflect the remaining errors that directly affect the structure of the pre-edge region. Large errors here (larger than the experimental line widths of ~0.3 eV) can lead to errors in assignment and analysis of experimental spectra. Errors for CCSD and STEOM-CCSD are indeed reduced, although observed deviations from CCSDT cover almost 1.5 eV for CCSD and 2.5 eV for STEOM-CCSD. Here we note that STEOM-CCSD does indeed display noticeably worse performance compared to CCSD, with the larger number of outliers (almost all valence \( \pi^* \) states) significantly stretching the error distribution. This effect is particularly striking in Figure 2b where the otherwise nicely compact error distribution of STEOM-CCSD is ruined by large positive errors for such valence states (here, a positive error indicates that the valence states lie too low or, conversely, that the Rydberg series lies too high). TP-CCSD(1/2) and CCSD* essentially achieve the goal of relative errors in the range of 0.3 eV for both types of relative error.

Errors for STEOM-CCSD+cT relative to the ionization edge (Figure 2b) show a fairly compact distribution but an overall downward shift of ~0.3 eV for the entire excitation spectrum. This may be due to imbalance in the level of correlation of the core ionization potential, which now includes full triples, and the excitation spectrum, which derives largely from the valence electron affinity calculation, which remains purely singles and doubles. An approximate treatment of triples in the core ionization potential calculation would further speed up the calculation and also possibly correct for this excessive gap. When results are compared to the lowest excitation energy (Figure 2a), STEOM-CCSD+cT displays a compact distribution flanked by two outlying wings. The positive wing is essentially entirely due to CH2, where the gap between the excitation into the lone pair and the Rydberg states is overestimated by 0.6 eV. The negative wing is dominated by the fluorine K-edges of HOF and H2NF, where the gap between the mixed \( \sigma^* / 3s \) excitation and the remaining excitations is underestimated by 0.4–0.5 eV. While these cases represent challenging electronic structures for STEOM-CCSD+cT, the overall pre-edge structure is maintained well except for these single gaps. Noticeably, the large errors for \( \pi^* \) valence states present in STEOM-CCSD are almost entirely eliminated in STEOM-CCSD+cT due to the improved description of the core-hole.

5. CONCLUSIONS AND FUTURE WORK

The problem of orbital relaxation is central to the accurate computation of core-hole spectra. While our previous work focused on an explicit inclusion of core relaxation via the use of orbitals optimized for fractional core occupation, here we show that a simple modification of similarity-transformed equation-of-motion theory can similarly address this important problem. With full CVS-EOM-CCSDT as a benchmark, our new CVS-STEOMEE-CCSD+cT method reduces errors in absolute vertical core excitation energies by a factor of ~5 compared to CVS-EOMEE-CCSD and also improves errors in preshifted excitation spectra to less than 0.5 eV, except for the challenging cases of CH2 and fluorine K-edges with valence–Rydberg mixing. The addition of triple excitations only affects the core ionization calculation and scales as \( O(n_a n_b n_c) \) for \( n_a \) active core, \( n_b \) occupied, and \( n_c \) virtual orbitals. This results in a modest increase in computational effort compared to standard CVS-EOM-CCSD, since the solution of the electron-attachment problem is typically the main bottleneck in STEOM-CC other than the ground state.
We are currently implementing CVS-STEOM-CC excited state and transition properties, which require little additional development over the standard theory.\(^1\)\(^2\) Importantly, the inclusion of triple excitations in the core ionization potential calculation does not directly enter the computation of these properties. However, inclusion of triple excitations should indirectly improve the quality of the transition moments. We are currently working on implementing these properties. In another vein, the approximate inclusion of triple excitations equation-of-motion theory will be treated core and valence states on an even footing, and its proven computational efficiency.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jctc.2c00268.

Employed molecular geometries and basis sets and the complete results, comprising absolute and relative excitation energies and ionization potentials (XLSX)

**AUTHOR INFORMATION**

**Corresponding Author**

Megan Simons − Department of Chemistry, Southern Methodist University, Dallas, Texas 75275, United States; orcid.org/0000-0001-9457-7019; Email: msimons@smu.edu

**Author**

Devin A. Matthews − Department of Chemistry, Southern Methodist University, Dallas, Texas 75275, United States; orcid.org/0000-0003-2795-5483

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acs.jctc.2c00268

**Notes**

The authors declare no competing financial interest. The data that supports the findings of this study are available within the article and its Supporting Information.

**ACKNOWLEDGMENTS**

The authors thank Prof. Marcel Nooijen for inspiring us to work on triple excitations in STEOM-CC theory and for several fruitful discussions. This work was supported in part by the US National Science Foundation under Grant OAC-2003931. M.S. is supported by an SMU Center for Research Computing Graduate Fellowship. All calculations were performed on the ManeFrame II computing system at SMU.

**ADDITIONAL NOTE**

“The ground state, IP or EA, and \( \hat{G} \) computations may be shared, although separate diagonalization steps are still necessary as the core and valence wave functions are not strictly orthogonal and have different structure. The diagonalizations are computational very inexpensive, however.

**REFERENCES**


APPENDIX D

Paper on transition moments for similarity-transformed equation-of-motion coupled cluster

Under review at Journal of Chemical Theory and Computation.
Transition moments for STEOM-CCSD with core triples

Megan Simons* and Devin A. Matthews

Department of Chemistry, Southern Methodist University, Dallas, TX 75275, USA

E-mail: msimons@smu.edu

Abstract

Similarity transformed equation-of-motion coupled cluster theory (STEOM-CC) is an alternative approach to equation-of-motion coupled cluster theory for excited states (EOMEE-CC) which uses a second similarity transformation of the Hamiltonian, followed by diagonalization in a small (CI singles-like) excitation space, even when single and double excitations are included in the transformation. In addition to vertical excitation energies, transition moments measure the strength of the interactions between states determining absorption, emission, and other processes. In STEOM-CCSD, transition moments are calculated in a straight-forward manner as biorthogonal expectation values using both the left- and right-hand solutions, with the main difference from EOMEE-CC being the inclusion of the transformation operator. We recently developed an extension of STEOM-CCSD to core excitations, CVS-STEOM-CCSD+cT, which includes triple excitations and the well-known core-valence separation for the core ionization potential calculations. In this work, we derived transition moments for core-excited states with core triple excitations, including both ground-to-core-excited and valence-to-core-excited transitions. The improvement of the computed transition moments of the CVS-STEOM-CCSD+cT method is compared to standard CVS-STEOMEE-CCSD and CVS-EOMEE-CCSD for our previously published small molecule benchmark set.
1 Introduction

A fundamental objective of electronic structure theory is to describe the properties of the ground state. While this does create a partial picture, it is important to describe the many transition properties for molecules being excited from the ground state to an excited state or from one excited state to another. Excited state energies, and to some extent geometries, are easily benchmarked and can be compared against various experimental or theoretical references. However, this is not the case for other properties, such as oscillator strengths, dipole moments, and vibrational frequencies.1,2 The need for formally-derived transition properties, especially between two excited states, is incredibly important to study experimental spectra and theoretical methods such as time-resolved x-ray spectroscopy, x-ray absorption and emission, and non-adiabatic coupling. In x-ray absorption spectroscopy, computed oscillator strengths aid in the assignment of peaks in experimental spectra.3,4 The focus on transition moments allows for insight on the strength of the interactions between states governing absorption, emission, and other processes. Oscillator strengths, $f$, indicate the probability of a given transition from the ground state to an excited state occurring and can be measured through observed intensities.1,5

Many theoretical chemists utilize density functional theory (DFT) for computational chemistry problems involving the ground state, and time-dependent density functional theory (TD-DFT) extends the concepts of DFT to excited states.6,7 TD-DFT has become popular for calculating excitation energies and excited state properties due to its ability to be accurate, yet computationally efficient.1,5 However, there are self-interaction errors when computing the description of the ground state.2,8 Other methods used for calculating excited state properties include equation-of-motion coupled cluster (EOM-CC) theory9–11 and transition-potential density functional theory (TP-DFT).12–14 Even though EOM-CC, particularly when used with the core-valence separation technique,15 has success in describing valence excitations for core-hole states, there are still large orbital relaxation errors up to 5 eV and there is a large computation cost for each excited state. TP-DFT is a compro-
mise between linear-response methods and state-specific orbital optimizations, but errors remain when assigning peak positions and intensities in x-ray absorption spectra.\textsuperscript{13,14,16} We recently introduced a transition-potential coupled cluster (TP-CC) method that combines the concepts of coupled cluster theory and TP-DFT in order to reduce the orbital relaxation error present in EOM-CCSD.\textsuperscript{17,18} We also explored similarity-transformed equation of motion coupled cluster (STEOM-CC) theory, (originally proposed by Nooijen and Bartlett\textsuperscript{19,20}) an alternative to EOM-CC theory, for excitation energies for XAS and introduced a CVS-STEOM-CCSD+cT method that includes triple excitations only in the core ionized potential to account for the orbital relaxation present in STEOMEE-CC methods.\textsuperscript{21}

In this paper we present a comparison of oscillator strengths for CVS-EOM-CCSDT, TP-CCSD(1/2), and CVS-(ST)EOM-CCSD methods. Additionally, we present the implementation and calculation of oscillator strengths for CVS-STEOM-CCSD+cT, which has an explicit triples contribution only for the core orbital(s).

2 Theoretical Methods

The details of the CVS-STEOMEE-CCSD+cT method are available in our previous publication,\textsuperscript{21} while the theory of transition moments in similarity-transformed equation-of-motion coupled cluster was developed by Nooijen in his original publications.\textsuperscript{20} Here we briefly recap the important features of the core triples and their effect on the computed STEOM transition moments.

In STEOMEE-CCSD+cT,\textsuperscript{21} the relaxation effects of the core hole are accounted for by including triple excitations in the solution of the core ionization potential equations via CVS-EOMIP-CCSDT.\textsuperscript{22} This results in a three-body transformation operator which is derived
from the triples amplitudes of the core EOMIP solution,

\[ \hat{S}_3^- = \frac{1}{12} \sum_{ijkmbc} s_{cbm}^{ijk} a_m^\dagger a_k^\dagger a_b^\dagger a_j a_i \]  

(1)

\[ s_{cbm}^{ijk} = - \sum_{\kappa \lambda = 1}^n r_{cb}^{ij}(\lambda)(U_{\lambda}^{-1})_{\kappa \lambda} \delta_{\lambda m} \]  

(2)

where \( m \) and at least one of \( ijk \) must be an active core orbital. Formally, we consider \( r_{cb}^{ij} = 0 \) for valence or inactive core ionized states. The addition of this transformation operator modified the form of the twice-transformed Hamiltonian, \( \hat{G} \), and the resulting STEOM eigenstates. In our implementation we also employ the core-valence separation in the diagonalization of the singles-singles block of \( \hat{G} \), but the effect of this approximation on the energies should be very small given the lack of coupling to high-lying doubly-excited valence determinants.

As in standard equation-of-motion coupled cluster theory, the oscillator strength for excitation from state \( \kappa \) to state \( \lambda \) is computed from non-hermitian transition dipole moments via an expectation value formalism,

\[ f_{\kappa \rightarrow \lambda} = \frac{2m_e(\omega_{\lambda} - \omega_{\kappa})}{3\hbar^2} \sum_{\alpha=x,y,z} \langle \tilde{\Psi}_\kappa | \hat{\mu}_\alpha | \Psi_\lambda \rangle \langle \tilde{\Psi}_\lambda | \hat{\mu}_\alpha | \Psi_\kappa \rangle \]  

(3)

Due to the non-hermitian nature of EOM-CC and STEOM-CC, \( \langle \tilde{\Psi}_\kappa | \) and \( | \Psi_\kappa \rangle \) are distinct. In CVS-STEOMEE-CCSD+cT, these are,

\[ \langle \tilde{\Psi}_\kappa | = \langle 0 | \hat{L}(\kappa)(1 - \hat{S}_2)e^{-\hat{T}} \]  

(4)

\[ | \Psi_\kappa \rangle = e^{\hat{T}}(1 + \hat{S}_2 + \frac{1}{2} \hat{S}_2^2 + \hat{S}_3^-) \hat{R}(\kappa) | 0 \rangle \]  

(5)

where \( | 0 \rangle \) is the (usually Hartree–Fock) reference determinant. The right-hand ground eigenstate is trivially \( \hat{R}(0) = 1 \). The left-hand ground eigenstate is formally an eigenvector of \( \hat{G} \), but here we use an approximation where the standard left-hand (EOM-)CC eigenstate is
used, $\hat{L}(0) = 1 + \hat{\Lambda}$.

The addition of the core triples in CVS-STEOMEE-CCSD+cT then leads to the additional term in the transition dipole moment between states $\kappa$ and $\lambda$,

$$
\mu_{\alpha}^{\kappa \lambda}(cT) = \langle 0 | \hat{L}_2(\kappa) \hat{\mu}_\alpha \hat{S}_3^- \hat{R}_1(\lambda) | 0 \rangle = \sum_{ai} D_{ai}^{\kappa \lambda}(cT) \mu_{ai;\alpha} \tag{6}
$$

$$
D_{ai}^{\kappa \lambda}(cT) = \langle 0 | \hat{L}_2(\kappa) \{ a^\dagger_i a_i \} \hat{S}_3^- \hat{R}_1(\lambda) | 0 \rangle \tag{7}
$$

$$
= -\frac{1}{2} \sum_{efmno} l_{ef}^{ij}(\kappa) s_{ion}^{a} r_{m}^{e}(\lambda) - \frac{1}{4} \sum_{efmno} l_{ef}^{ij}(\kappa) s_{noi}^{e} r_{m}^{a}(\lambda) \tag{8}
$$

Because the addition of $\hat{S}_3^-$ modifies $\hat{G}$ and hence $\hat{L}(\kappa)$ and $\hat{R}(\kappa)$, the transition moments in CVS-STEOMEE-CCSD+cT are already different from those in CVS-STEOMEE-CCSD without considering (6). Thus, we term the contribution arising directly from the inclusion of $\hat{S}_3^-$ in the transition dipole moment expression in (6) as the "direct" triples contribution.

Finally, we note that while $\hat{R}(\kappa)$ consists only of single excitations (and potentially a small contribution from the reference determinant), the left-hand eigenstate $\hat{L}(\kappa)$ formally spans both single and double excitations. The left-hand singles amplitudes may be determined from the singles-singles block of $\hat{G}$ alone, but the doubles amplitudes would require a costly diagonalization in the full singles and double space. Following Nooijen, we use a perturbative approximation for $\hat{L}_2(\kappa)$, although we opt for a simpler approximation which is consistent through first-order,

$$
l_{ab}^{ij}(\kappa) = \frac{1 + P_{ai}^{ab}}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b + \omega_\kappa} \left( \sum_e l_{e}^{i}(\kappa) \langle ab || e \rangle - \sum_m l_{m}^{j}(\kappa) \langle ij || mb \rangle \right) \tag{9}
$$

where $P_{ai}^{ab}$ exchanges the labels $ai$ and $bj$ in the following expression.
3 Computational Details

Transition energy and transition moment calculations for CVS-EOMEE-CCSDT, CVS-EOMEE-CCSD, TP-CCSD(1/2), CVS-STEOMEE-CCSD, and CVS-STEOMEE-CCSD+cT were implemented in a development version of the CFOUR program package. A single core orbital was included in the CVS treatment and STEOM principal IP solution in each calculation.

The test set used and methodology are the same for transition energy and transition moment calculations, as in previous papers. The test set consisted of all 1s principal core ionizations and four vertical core excitation energies from each 1s core orbital of H$_2$O, CO, HCN, HF, HOF, HNO, CH$_2$, CH$_4$, NH$_3$, H$_3$CF, H$_3$COH, H$_2$CO, H$_2$CNH, and H$_2$NF. The core excitations (and oscillator strengths) were selected as those for which we could reliably converge all methods tested, which typically consisted of the first four excitations of dominant single excitation character. All calculations utilized the aug-cc-pCVTZ basis set with all electrons correlated, except for H$_2$O where aug-cc-pCVQZ was used. We have used full CVS-EOM-CCSDT as a benchmark to avoid the complications coming from missing relativistic effects, basis set incompleteness, and geometric effects. The rationale for choosing the benchmark is the same as in previous work.

4 Results and Discussion

In the following discussion and in Figures 1 and 2, the "shortened" names of CVS-EOM methods will be used, for example, STEOM-CCSD = CVS-STEOMEE-CCSD, with the exception of TP-CCSD(1/2). The distribution of "absolute" oscillator strength deviations from CCSDT are depicted in Figure 1. The absolute oscillator strength deviation for a method X is calculated as $f(X) - f(CCSDT)$. The distribution of "relative" oscillator strength deviations from CCSDT are depicted in Figure 2, as percentages. The relative oscillator strength deviation is determined by normalizing each spectrum so that the most intense transition has unit strength.
Figure 1: Error distributions with respect to CVS-EOM-CCSDT for absolute oscillator strengths (intensities).

a Excluding direct core-triples contribution to oscillator strengths.

b Including direct core-triples contribution to oscillator strengths.
Figure 2: Error distributions with respect to CVS-EOM-CCSDT for relative oscillator strengths (intensities).

- Excluding direct core-triples contribution to oscillator strengths.
- Including direct core-triples contribution to oscillator strengths.
As can be seen in Fig. 1, the deviations of absolute oscillator strengths indicates an improvement in the TP-CCSD(1/2) and STEOM-CCSD+cT (as measured by standard deviation) over EOM-CCSD and STEOM-CCSD. STEOM-CCSD exhibits a significant increase in standard deviation and outliers (primarily overestimation of oscillator strength) compared to EOM-CCSD. STEOM-CCSD+cT also exhibits a number of outliers compared to TP-CCSD(1/2) and even to EOM-CCSD. All of the STEOM methods have difficulty describing the absolute oscillator strengths of $\pi^*$ and $\sigma^*$ core-to-valence excited states, with STEOM-CCSD+cT overestimating by an average of $\sim 0.25 \times$. Interestingly, the intensity distributions for all methods have a positive skew in comparison with the EOM-CCSDT benchmark. Direct STEOM-CCSD+cT contributions have a slight effect on the absolute oscillator strengths, leading to a $\sim 10\%$ reduction in standard deviation compared to the STEOM-CCSD+cT calculation when direct core triples are excluded. The standard deviation of the error is reduced by almost $40\%$ compared to STEOM-CCSD without any inclusion of core triples.

Normalization of each spectrum with respect to the most intense peak gives us a different viewpoint since all spectra are "equal" while keeping the relative importance of each peak in each spectrum. It can be seen from Fig. 2 that both "purely singles and doubles" methods, EOM-CCSD and STEOM-CCSD, are prone to large errors in both the positive and negative direction, as large as $75\%$ of the relative peak intensity. It can also be seen that the STEOM-CCSD+cT methods have essentially the same relative intensity error distributions, indicating an almost complete cancellation of the direct effect of core triples between different peaks in the same spectrum. Nooijen and Bartlett\textsuperscript{19} observed a similar effect for the "triples" contribution arising from $\hat{S}_2^2 \hat{R}_1$, where there was a significant effect on the transition energy but an almost negligible effect on the oscillator strengths (from the direct triples contribution—the indirect effect through the solution of the eigenstates was larger). For TP-CCSD(1/2) and STEOM-CCSD+cT, significant outliers are mostly negative (oscillator strength is underestimated). For STEOM-CCSD+cT, the significant errors are confined al-
most entirely to the F and C K-edges of $H_3$CF and the O K-edge of $H_3$COH. Even including these problematic cases, STEOM-CCSD+cT results in a $2.4 \times$ reduction in standard deviation compared to EOM-CCSD and over a $1.8 \times$ reduction in standard deviation compared to STEOM-CCSD.

The large errors for $\pi^*$ and $\sigma^*$ valence states present in both EOM-CCSD and STEOM-CCSD are almost entirely eliminated in the TP-CCSD(1/2) and STEOM-CCSD+cT, in the latter thanks to a consistent over-estimation of both valence and Rydberg intensities in these spectra. It is not clear why both the valence and Rydberg peaks are so consistently overestimated, although there could be a consistent error introduced by the left-hand ground state eigenstate used. Also, despite the over-estimation of the valence excitation oscillator strengths, many Rydberg absolute oscillator strengths are not significantly changed from their EOM-CCSD values. There is not enough data yet to indicate if this indicates a link between EOM-CCSD and the over-estimation effects seen in STEOM-CCSD. The overall improvement of the TP-CCSD(1/2) and STEOM-CCSD+cT intensities is due to the improved description of the core-hole, although in differing ways—in TP-CCSD through the fractional occupation in the core-hole which creates a cancellation of errors between the ground and core-excited states, and in STEOM-CCSD+cT through the improved relaxation of the core hole via the inclusion of explicit triple excitations in the core ionization potential cancellation (note that the ionized wavefunction is utilized in STEOM, and not just the improved ionization energy). Apart from the cases mentioned above, STEOM-CCSD+cT is seen to estimate the oscillator strengths almost as well as TP-CCSD(1/2).

5 Conclusions

Absolute and relative oscillator strengths were calculated for a group of small molecules using various coupled cluster methods, including CVS-EOM-CCSDT, CVS-(ST)EOM-CCSD, TP-CCSD(1/2), and CVS-STEOM-CCSD+cT. Our previous work$^{21}$ showed that the CVS-
STEOM-CCSD+cT method performed well for core-excited state energies and was comparable to TP-CCSD(1/2), which has an explicit inclusion of core relaxation via the molecular orbitals. Here, we investigated how well this method estimates transition moments in comparison to full CVS-EOM-CCSDT as the benchmark. CVS-STEOM-CCSD+cT decreases relative errors in oscillators by over 1.8× in comparison to CVS-(ST)EOM-CCSD. All STEOM-CCSD methods are seen to over-estimate the oscillator strengths for $\pi^*$ and $\sigma^*$ core excitations, but do so consistently, leading to an improved ratio of Rydberg intensity to valence intensity. We recommend the use of the CVS-STEOM-CCSD+cT method for core-hole spectroscopy calculations due to its ability to treat core and valence states on an even footing and to accurately predict relative oscillator strengths and transition energies.

Acknowledgments

The authors would like to thank Prof. Marcel Nooijen for inspiring us to work on triple excitations in STEOM-CC theory. This work was supported in part by the US National Science Foundation under grant CHE-2143725. MS is supported by an SMU Center for Research Computing Graduate Fellowship. All calculations were performed on the ManeFrame II computing system at SMU.

Supplementary Material

An electronic supplementary information file is available as an Excel file (.xlsx). This file contains the raw transition energies and oscillator strengths for each orbital K-edge, as well as the absolute and relative transition energies and the absolute and relative oscillator strengths for each orbital K-edge.
Data Availability

The data that supports the findings of this study are available within the article and its supplementary material.

References


APPENDIX E

Paper on open shell tensor hypercontraction

Open-shell Tensor Hypercontraction

Tingting Zhao,†‡ Megan Simons,†‡ and Devin A. Matthews∗†

†Department of Chemistry, Southern Methodist University, Dallas, TX
‡These authors contributed equally to this work.

E-mail: damathews@smu.edu

Abstract

The extension of least-squares tensor hypercontracted second- and third-order Møller-Plessett perturbation theory (LS-THC-MP2 and LS-THC-MP3) to open-shell systems is an important development due to the scaling reduction afforded by THC and the ubiquity of molecular ions, radicals, and other open-shell reactive species. The complexity of wavefunction-based quantum chemical methods such as Møller-Plessett and coupled cluster theory is reflected in the steep scaling of the computational costs with the molecular size. The least-squares tensor hypercontraction (LS-THC) method is an efficient, single-step factorization for the two-electron integral tensor, but can also be used to factorize the double excitation amplitudes, leading to significant scaling reduction. Here, we extend this promising method to open-shell variants of LS-THC-MP2 and -MP3 using diagrammatic techniques and explicit spin-summation. The accuracy of the resulting methods for open-shell species is benchmarked on standard tests systems such as regular alkanes, as well as realistic systems involving bond breaking, radical stabilization, and other effects. We find that open-shell LS-THC-MPn methods exhibit errors highly comparable to those produced by closed-shell LS-THC-MPn, and are highly insensitive to particular chemical interactions, geometries, or even to moderate spin contamination.
Introduction

Complexity arising due to the presence of high-order tensors is well known as a bottleneck in wavefunction-based quantum chemical methods, leading to steep scaling of computational cost with system size. As the essential component of all electronic structure methods, the 4th-order electron repulsion integral (ERI) tensor, \( g_{pq}^{rs} \equiv (pr|qs) \) (with the latter in chemists’ notation), is the most obvious target for cost and scaling reduction. Many approaches have been developed to tackle the complexity of the ERIs, such as the density fitting (DF) approximation and similar techniques such as the resolution-of-the-identity (RI), Cholesky decomposition (CD), pseudospectral (PS) method, and more recently tensor hypercontraction (THC). Approximations of the wavefunction itself have received less attention, but due to the presence of the 4th-order double excitations amplitude (\( \hat{C}_2 \) or \( \hat{T}_2 \)) which appear in virtually any wavefunction theory, some approximation is necessary to achieve significant reductions in computational scaling.

While a wide range of approximations to the ERIs and/or doubles amplitudes have proven highly successful, the vast majority of these methods have been implemented, tested on, and subsequently applied to closed-shell systems. While closed-shell systems are of vital importance to chemistry as a whole—neutral stable chemical species, both reactants and products, tend to adopt a closed-shell configuration—open-shell species are of equal importance due to the high reactivity and richness of electronic structure exhibited by radical species. Such species are central to a number of chemical fields, such as organic catalysis, environmental and health studies, combustion and alternative fuel chemistry, and photochemistry. Additionally, due to the reactive nature of radical transient intermediates or transition states, they are often difficult to study in the laboratory, requiring more elaborate instrumentation or complicated spectroscopic analysis. Thus, it is necessary to develop quantum chemistry methods to assist the experimental studies of these systems, along with approximation techniques to reduce computational scaling for the study of larger systems.

We are especially interested in the least squares tensor hypercontraction (LS-THC) approximation.
method as an efficient approximation of both the ERI and doubles amplitudes tensors. We and other have previously demonstrated the potential for high accuracy and low scaling ($O(N^4)$, where $N$ is a measure of system size) for closed shell third-order Møller-Plesset perturbation theory (MP3).\textsuperscript{21,39} In LS-THC, the fourth order ERI tensor is approximated as a (hyper)product of five matrices: four collocation matrices, determined by evaluation of the molecular orbitals at a set of grid points, and a core matrix evaluated by least-squares fitting of the canonical ERIs (or ERIs approximated by a second method such as density fitting). In the “MP3a” variant, this approximation is combined with the Laplace transform quadrature technique\textsuperscript{40–43} in order to compute the energy without referencing the doubles amplitudes explicitly. Alternatively, the “MP3b” method invokes an LS-THC factorization of the first-order doubles amplitudes and instead avoids the computational complexity of the Laplace transform quadrature (and a quadratic scaling with the number of quadrature points). Lastly, the “MP3c” and “MP3d” methods directly approximate the second-order doubles amplitudes, using an energy functional form identical to that used for coupled cluster and other more complex methods.\textsuperscript{1,22} This range of interpretations of MP3, as well as the basic building blocks of the MP3 energy (especially the well-known particle–particle ladder, hole–hole ladder, and “ring” terms), make MP3 an ideal stepping stone to more complete theories such as coupled cluster with single and double excitations (CCSD).

In this word, an extension of the LS-THC approach to open-shell MP2 and MP3 energies was developed using a mixed graphical-algebraic technique for deriving the working equations. We have implemented the MP3b variant of LS-THC-MP3, but the techniques developed are immediately applicable to the other MP3 variants as well as to more complex LS-THC methods.

Theory

The following notational conventions are used throughout this work:
• The letters \( pqrs \) denote arbitrary molecular orbitals (MOs).

• The letters \( abcdef \) (\( ijklmn \)) denote virtual (occupied) MOs.

• The letters \( RSTUVWX \) denote grid points.

• The letters \( JK \) denote auxiliary (density fitting) basis functions.

• Where applicable, \( \alpha \) (\( \beta \)) molecular orbitals, pruned grid points, and other quantities are denoted by an overbar (no overbar).

### Least-squares Tensor Hypercontraction

Tensor hypercontraction (LS-THC)\(^{17-20}\) is a method that combines the desirable features of several other factorizations: the representation of electron distributions over a linear-scaling auxiliary basis as in DF/RI/CD methods, the pseudospectral method’s flexibility of factoring exchange terms, the use of least-squares fitting as in DF and alternating least squares-based CP factorizations (although the LS-THC factorization is linear and non-iterative), and finally in the least-squares form a grid-based expansion as in the numerical integration of exchange–correlation functions in density functional theory. The LS-THC form of the ERIs is,

\[
(\text{pr}|\text{qs}) \equiv g_{rs}^{pq} \approx \sum_{RS} (X^{(pr)})_p^R (X^{(pr)})_r^R V_{RS} (X^{(qs)})_q^S (X^{(qs)})_s^S
\]

(1)

The matrices \( X \) are the collocation matrices, determined \textit{a priori} by evaluation of the (spatial) molecular orbitals \( \psi_p \) at a set of grid points \( r_R \): \( X_p^R = \psi_p(r_R) \). Superscripts such as \( (pr) \) in (1) differentiate different sets of “pruned” grid points.\(^20\) The pruning process is specific to the occupation of the pair of molecular orbitals, leading to separate occupied–occupied (\( X \equiv X^{(ij)} \)), mixed virtual–occupied (\( \tilde{X} \equiv X^{(ai)} = X^{(ia)} \)), or virtual–virtual (\( \tilde{\tilde{X}} \equiv X^{(ab)} \)) collocation matrices. These three cases may be further classified by the spin of the associated molecular orbitals (differentiated by an overbar on the MO and grid indices), leading to six unique collocation matrices for open-shell LS-THC-MP3.
The final matrix $V$ is the core matrix, and is evaluated by least squares fitting of either
the exact ERI tensor or some intermediate approximation. In this work we utilize density
fitting in order to maintain an overall scaling of $O(N^4)^{21}$

$$
\tilde{g}_{qs}^{pr} = \sum_{JK} (pr|J)(J|K)^{-1}(K|qs) \\
V_{RS} = \arg\min_{V_{RS}} \frac{1}{2} \sum_{pqrs} \left| \tilde{g}_{qs}^{pr} - \sum_{RS} (X^{(pr)})_p^R (X^{(pr)})_r^R V_{RS} (X^{(qs)})_q^S (X^{(qs)})_s^S \right|^2 \\
E_{RS} = \sum_{pqrs} (X^{(pr)})_p^R (X^{(pr)})_r^R \tilde{g}_{qs}^{pr} (X^{(qs)})_q^S (X^{(qs)})_s^S \\
S_{RS}^{(pq)} = \sum_{pq} (X^{(pq)})_p^R (X^{(pq)})_q^S (X^{(pq)})_p^S (X^{(pq)})_q^S
$$

where in each case a superscript •$^{-1}$ is understood as an element of the matrix inverse rather
than an inverse of the matrix element itself. Note that, as with the collocation matrices,
there are as many as six distinct metric matrices $S$. Due to the possible combination of each
of these six electron distributions, there are as many as 21 different core ($V$) and fitting
($E$) matrices, of which 13 are utilized in open-shell LS-THC-MP3 (assuming a canonical
Hartree–Fock reference for which the single excitation amplitudes can be neglected). In
order to avoid notational clutter, we rely on context to determine which of these 13 core
matrices in intended, unless explicitly specified.

**Canonical Formulation of MP2 and MP3**

In the canonical spin-orbital representation, the MP2 and MP3 energies are defined as,

$$
E_{MP2} = E_{MP2a} = \frac{1}{2} \sum_{abij} \frac{(g_{ij}^{ab} - g_{ib}^{aj})g_{ij}^{ab}}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \\
E_{MP3} = E_{MP3a} = \frac{1}{2} \sum_{abijkl} \frac{(g_{ij}^{ab} - g_{ib}^{aj})g_{ij}^{ab}g_{kl}^{ij}}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}(\varepsilon_k + \varepsilon_l - \varepsilon_a - \varepsilon_b)
$$
Note that the more common formulation of these energies uses the fully second-quantized representation of the Hamiltonian, $\hat{H} = \sum_{pq} f^p_q \{ a^\dagger_p a_q \}_N + \frac{1}{4} \sum_{pqrs} v^p_q \{ a^\dagger_p a^\dagger_q a_s a_r \}_N$, where $\{ \cdot \}_N$ denotes normal-ordering. The two representations are connected by the simple identity $v^p_q = g^p_q - g^q_p = g^p_q - g^q_p$. The first-order and second-order perturbed double excitation amplitudes are most commonly defined by,

$$t^{[n]}_{ij} = \tilde{t}^{[n]}_{ij} - \tilde{t}^{[n]}_{ji}$$  \hspace{1cm} (8)

$$\tilde{t}^{[1]}_{ij} = \frac{g^i_j}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$  \hspace{1cm} (9)

$$\tilde{t}^{[2]}_{ij} = \sum_{kl} g^i_j g^k_l \tilde{t}^{[1]}_{ij} + \sum_{cd} g^a_b \tilde{t}^{[1]}_{cd} + \sum_{ek} \left( g^b_j c^e_k \tilde{t}^{[1]}_{i} - \tilde{t}^{[1]}_{ac} \right) \left( \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b \right)$$  \hspace{1cm} (10)

The representation of $\tilde{t}^{[n]}$ in a non-antisymmetric form is critical in the following derivation, where we also show that such a representation is always well-defined by following a physically-motivated graphical derivation. With these definitions we can write several additional variant forms of the MP2 and MP3 energies, although all variants are mathematically identical when exact ERIs and perturbed amplitudes are used,

$$E_{MP2_b} = \frac{1}{2} \sum_{abij} (g^i_j - g^j_i) \tilde{t}^{[1]}_{ij}$$  \hspace{1cm} (11)

$$E_{MP3_b} = \frac{1}{2} \sum_{abijkl} \left( \tilde{t}^{[1]}_{ij} - \tilde{t}^{[1]}_{ji} \right) \tilde{t}^{[1]}_{kl} + \frac{1}{2} \sum_{abCDij} \left( \tilde{t}^{[1]}_{ij} \tilde{t}^{[1]}_{ab} - \tilde{t}^{[1]}_{ij} \tilde{t}^{[1]}_{ba} \right) g^a_b \tilde{t}^{[1]}_{cd}$$

$$+ \sum_{abCDijk} \left( \tilde{t}^{[1]}_{ij} \tilde{t}^{[1]}_{ab} - \tilde{t}^{[1]}_{ij} \tilde{t}^{[1]}_{ba} \right) (g^b_j c^k_i - g^b_j c^k_i) \left( \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b \right)$$  \hspace{1cm} (12)

$$E_{MP3_c} = \frac{1}{2} \sum_{abij} (g^i_j - g^j_i) \tilde{t}^{[2]}_{ij}$$  \hspace{1cm} (13)
A further variant MP3d is obtained by separating the formation of $\tilde{t}^{[2]}$ into two parts: evaluation of the residual starting with the first-order amplitudes, and division of the residual by the orbital energy differences to obtain the second-order amplitudes. In Ref. 21 we showed that this approach results in a distinct LS-THC-MP3 method with lower cost and nearly-identical numerical error.

Before moving on to the derivation of the LS-THC-MP$n$ approximations, we must deal with the inseparability of the energy denominators present in (6)–(10). A convenient approach is the method of “Laplace denominators”, pioneered by Almlöf and others,\textsuperscript{40,44}

\[
\frac{1}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} = -\int_{0}^{\infty} e^{(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)t} dt \\
\approx -\sum_{\lambda=1}^{L} w_{\lambda} e^{(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)t_{\lambda}} \\
= \sum_{\lambda=1}^{L} \tau_{a}^{\lambda} \tau_{b}^{\lambda} \tau_{i}^{\lambda} \tau_{j}^{\lambda}
\]

(14)

where $L$ is the number of Laplace quadrature points. In this work we use the quadrature developed by Braess and Hackbusch\textsuperscript{45} and a sufficient number of quadrature points to evaluate $1/x$ to a relative accuracy of $10^{-8}$ (approximately 9 points).

**Closed-Shell LS-THC-MP$n$**

The MP2a and MP3a formulations of MP2 and MP3, which are defined solely in terms of integrals and orbital energy denominators, are easily represented in compressed form using tensor hypercontraction. Spin-integration for closed-shell systems is straightforward (see e.g. Ref. 1), and we may exploit the equivalence of the different spin-cases of the integrals,

\[
g_{rs}^{pq} = g_{r\bar{s}}^{pq} = g_{r \bar{s}}^{pq}
\]

(15)
We may then expand the equations in terms of say, \( g_{rs}^{pq} \) alone and then approximate these integrals using the form of (1), while also approximating the energy denominators using (14). This results in the LS-THC-MP2a and LS-THC-MP3a methods,

\[
E_{LS-THC-MP2a} = -\sum_{abij} \sum_{RSTU} \sum_{\lambda=1}^{L} \tau_{i}^{\lambda} \tau_{j}^{\lambda} \left( 2\tilde{X}_{i}^{R} \tilde{X}_{j}^{S} \tilde{X}_{b}^{S} \tilde{X}_{i}^{S} - \tilde{X}_{a}^{R} \tilde{X}_{j}^{R} \tilde{X}_{b}^{S} \tilde{X}_{i}^{S} \right)
\times \tilde{X}_{i}^{T} \tilde{X}_{j}^{U} V_{TU} \tilde{X}_{b}^{U} \tilde{X}_{j}^{T}
\]

(16)

\[
E_{LS-THC-MP3a} = \sum_{abij} \sum_{RSTU} \sum_{\lambda=1}^{L} \tau_{i}^{\lambda} \tau_{j}^{\lambda} \left( 2\tilde{X}_{i}^{R} \tilde{X}_{j}^{S} \tilde{X}_{b}^{S} \tilde{X}_{i}^{S} - \tilde{X}_{a}^{R} \tilde{X}_{j}^{S} \tilde{X}_{b}^{S} \tilde{X}_{i}^{S} \right)
\times \sum_{kl} \sum_{WYX} \sum_{\lambda=1}^{L} \tau_{i}^{\lambda} \tau_{j}^{\lambda} \tilde{X}_{i}^{T} \tilde{X}_{j}^{U} V_{TU} \tilde{X}_{b}^{U} \tilde{X}_{j}^{T}
\]

(17)

The “b” variants are simply obtained by directly approximating the first-order (orbital) doubles amplitudes using THC,

\[
t^{[1]}_{ij} = t^{[1]}_{ij} - t^{[1]}_{ij}
\]

(18)

\[
t^{[1]}_{ij} = t^{[1]}_{ij} \approx \sum_{RS} \tilde{X}_{i}^{R} \tilde{X}_{j}^{R} T^{[1]}_{RS} \tilde{X}_{b}^{S} \tilde{X}_{j}^{S}
\]

(19)

\[
E_{LS-THC-MP2b} = \sum_{abij} \sum_{RSTU} \left( 2\tilde{X}_{i}^{R} \tilde{X}_{j}^{S} \tilde{X}_{b}^{S} \tilde{X}_{i}^{S} - \tilde{X}_{a}^{R} \tilde{X}_{j}^{S} \tilde{X}_{b}^{S} \tilde{X}_{i}^{S} \right)
\times \tilde{X}_{i}^{T} \tilde{X}_{j}^{U} T^{[1]}_{TU} \tilde{X}_{b}^{U} \tilde{X}_{j}^{T}
\]

(20)
\[
E_{LS-THC-MP3b} = \sum \sum \sum_{\text{abij RSTU}} \left( 2\tilde{X}^R_a \tilde{X}^R_i T^{[1]}_{RS} \tilde{X}^S_b \tilde{X}^S_j - \tilde{X}^R_a \tilde{X}^R_j T^{[1]}_{RS} \tilde{X}^S_b \tilde{X}^S_i \right) \\
\times \left[ \sum \sum \sum_{kl WY} X^T_k X^T_i V_{TU} X^U_j X^W_{k,c} T_{WY} \tilde{X}^X_{b,c} \tilde{X}^Y_{i,j} \right. \\
+ \sum \sum \sum_{cd WY} \tilde{X}^T_c X^T_i V_{TU} \tilde{X}^U_j \tilde{X}^W_{d,c} T_{WY} \tilde{X}^X_{b,c} \tilde{X}^Y_{i,j} \right. \\
+ 4 \sum \sum \sum_{ck WY} \tilde{X}^T_c X^T_i V_{TU} \tilde{X}^U_j \tilde{X}^W_{k,c} T_{WY} \tilde{X}^X_{b,c} \tilde{X}^Y_{i,j} \right. \\
- 2 \sum \sum \sum_{ck WY} \tilde{X}^T_c X^T_i V_{TU} \tilde{X}^U_j \tilde{X}^W_{k,c} T_{WY} \tilde{X}^X_{b,c} \tilde{X}^Y_{i,j} \right. \\
- 2 \sum \sum \sum_{ck WY} \tilde{X}^T_c X^T_i V_{TU} \tilde{X}^U_j \tilde{X}^W_{k,c} T_{WY} \tilde{X}^X_{b,c} \tilde{X}^Y_{i,j} \right. \\
\left. \left[ \sum \sum \sum_{cd WY} \tilde{X}^T_c X^T_i V_{TU} \tilde{X}^U_j \tilde{X}^W_{d,c} T_{WY} \tilde{X}^X_{b,c} \tilde{X}^Y_{i,j} \right. \right] \right) (21)
\]

We do not further address the MP3c and MP3d variants and instead focus solely on LS-THC-MP3b.

These equations must be factorized (i.e. parentheses must be inserted to define to order of operations) before we can obtain efficient working equations. Here we adopt the same factorization as in our earlier work.\textsuperscript{21} As an example, consider the “particle-particle ladder” term of LS-THC-MP3b (depicted as the PP\textsubscript{C} and PP\textsubscript{X} diagrams in Fig. 2),

\[
E_{PP} = \sum \sum \left( 2\tilde{X}^R_a \tilde{X}^R_i T^{[1]}_{RS} \tilde{X}^S_b \tilde{X}^S_j - \tilde{X}^R_a \tilde{X}^R_j T^{[1]}_{RS} \tilde{X}^S_b \tilde{X}^S_i \right) \\
\times \left[ \sum \sum \left( \sum \sum \left( \sum \tilde{Q}^{Y}_{a,c} \tilde{X}^S_{i,j} \right) \right) \right. \\
- \sum \sum \left( \sum \sum \left( \sum \tilde{Q}^{Y}_{a,c} \tilde{X}^S_{i,j} \right) \right. \\
\left. \left. \text{Q}_{b,j}^S \right) \tilde{X}^U_{b,j} \right)
\right) (22)
\]

\[
\tilde{P}_{ab}^R = \sum S V_{RS} \tilde{X}^S_a \tilde{X}^S_b (23)
\]
\[ Q_{ai}^R = \sum_S T_{RS}^{[1]} \tilde{X}_a^S \tilde{X}_i^S \]  

(24)

This factorization enables each step to be completed in at most \( O(N^4) \) time, given a linear number of occupied and virtual orbitals as well as grid points. The full working equations for the closed-shell case are given in Ref. 21, and those for the open-shell case are given in the ESI.

**Open-Shell LS-THC-MP\(_n\)**

![Goldstone diagrams for the MP2 energy, omitting denominator lines for clarity.](image)

**Figure 1.** Goldstone diagrams for the MP2 energy, omitting denominator lines for clarity.

In the preceding section, we used the non-antisymmetrized doubles amplitudes \( \tilde{t}^{[n]} \). We can justify the validity of such a representation in the open-shell case and utilize it to easily derive open-shell variants of LS-THC-MP\(_n\) methods by utilizing diagrammatic methods.

First, we may recognize each term in (6), (7), and (10), after distribution of the parentheses, as a unique Goldstone diagram.\(^{21}\) These diagrams are reproduced in Figures 1, 2, and 3, respectively. In particular, the diagrams in Figure 3 are easily recognized as the necessary contributions to the closed-shell second-order \( \hat{T} \) amplitudes or, with replacement of the bottom integral vertex by doubles amplitudes, the iterative \( \hat{T}_2 \rightarrow \hat{T}_2 \) contributions in coupled cluster theory. In the closed-shell interpretation, closed loops contribute a factor of 2 and each diagram is symmetrized, leading to the well-known expression,

\[
(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j) \tilde{t}^{[2]}_{ab} = \sum_{ef} g_{ef}^{ab} \tilde{t}^{[1]}_{ij} + \sum_{mn} g_{mn}^{ij} \tilde{t}^{[1]}_{mn} + (1 + P_{ai}^{bj}) \sum_{em} 2g_{ie} g_{mn}^{ij} \tilde{t}^{[1]}_{me}.
\]
where the permutation operator $P_{ai}^{bi}$ exchanges the top labels with those on the bottom in the following expression. Note that in the last term on the right-hand side, the $ij$ orbitals are ordered differently than in the remaining terms. This highlights the rule for Goldstone diagrams that, for orbitals sharing the same “column” in the external vertex (e.g. $ai$ or $bj$), we must be able to follow a continuous loop through the diagram from one label to the other. Thus the “PH$_{XX}$” diagram of Fig. 3 results in such a modified labeling. This choice is discussed further and theoretically motivated below.
Figure 3. Goldstone diagrams for the $\tilde{t}_{ij}^{[2]ab}$ amplitudes, omitting denominator lines for clarity.

For the closed-shell case we may use $\tilde{t}_{ij}^{[2]ab}$ without ambiguity since it is precisely defined as the mixed-spin amplitudes $t_{ij}^{ab}$ due to the relationship between the various spin cases in the closed-shell case. However, in the open-shell case we could instead replace the factor of 2 for closed loops by an explicit summation over spin. In any case, each contraction line along a loop must carry the same spin since contraction implies a spin integral over orthonormal spin functions. Then, we can derive equations for the three distinct spin cases in the spin-unrestricted formalism,

$$
(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)\tilde{t}_{ij}^{[2]ab} = \sum_{ef} g_{ef}^{[1]ef} t_{ij}^{[2]ab} + \sum_{mn} g_{ij}^{[1]mn} t_{ij}^{[1]ab} + (1 + P_{ij}) \left( \sum_{em} g_{ie}^{am} t_{mn}^{[1]eb} \right) \quad (26)
$$

$$
(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)\tilde{t}_{ij}^{[2]ab} = \sum_{ef} g_{ef}^{[1]ef} t_{ij}^{[2]ab} + \sum_{mn} g_{ij}^{[1]mn} t_{ij}^{[1]ab} + \sum_{em} g_{ie}^{am} t_{mn}^{[1]eb} + \sum_{em} g_{ie}^{am} t_{mn}^{[1]eb} \quad (27)
$$
Antisymmetrization of (26) and (28) in accordance with our definition of $i^{[2]ab}_{ij}$ arrives precisely at the standard equations for the second-order amplitudes in a (canonical) unrestricted Hartree–Fock reference. The application of Goldstone diagrams along with explicit spin-summation then gives us a rather simple route to derive the open-shell working equations. The necessary equivalence of these equations with the standard spin-integrated form after antisymmetrization, and that these equations trivially reduce to the one given above in the closed-shell is what we mean by claiming that $i^{[2]}$ is well-defined. As we discuss below, however, these amplitudes and their factorized form are not numerically well-defined, but we can make a consistent choice based on theoretical arguments.

A recursive application of (26)–(28), with additional terms accounting for single excitation amplitudes, provides a route to define non-antisymmetrized amplitudes for methods such as coupled cluster with single and double excitations (CCSD). In the present work, we focus on LS-THC-MP3b, where in fact we only require $i^{[1]}$. These amplitudes are trivially defined in terms of the orbital two-electron integrals,

$$i^{[1]ab}_{ij} = \frac{g_{ij}^{ab}}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \approx \sum_{RS} \tilde{X}_a^R \tilde{X}_i^R T_{RS}^{[1]} \tilde{X}_b^S \tilde{X}_j^S$$  \hspace{1cm} (29)

$$i^{[1]ba}_{ij} = \frac{g_{ij}^{ba}}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \approx \sum_{RS} \tilde{X}_a^R \tilde{X}_i^R T_{RS}^{[1]} \tilde{X}_b^S \tilde{X}_j^S$$  \hspace{1cm} (30)

$$i^{[1]bb}_{ij} = \frac{g_{ij}^{bb}}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \approx \sum_{RS} \tilde{X}_a^R \tilde{X}_i^R T_{RS}^{[1]} \tilde{X}_b^S \tilde{X}_j^S$$  \hspace{1cm} (31)

We note that these chosen definitions, while perhaps obvious given the close relationship of the first-order amplitudes to the integrals, are also derivable using the diagrammatic technique outlined above.
Returning to the issue of relabeling the $ij$ indices in the ring terms, we do note that for the same-spin amplitudes, every term may in fact be written in one of two ways due to the $P(ij)$ [or equivalently $P(ab)$] factor which relates the antisymmetric and non-antisymmetric amplitudes. Thus, we may technically define a large number of equivalent non-antisymmetric amplitudes. However, once a tensor factorization such as THC is applied, these different definitions are no longer equivalent and may incur errors of differing magnitude. In this regard, our specific choice of (26) and (28) is motivated by the physical compressibility (in an information-theoretic sense) of inter-electron interactions. The “same column same loop” rule espoused above allows us to interpret a tensor factorization of the entire diagram as a “recompression” step. In Fig. 4 we conceptually identify regions of each Goldstone diagram with the resulting factors in the THC compressed form: electron pairs will be represented.
by a pair of collocation matrices e.g. $\tilde{X}_a^R \tilde{X}_i^R$ which effect a transformation from molecular orbital to grid space, and pair correlation is represented by the core matrix $T^{[2]}$. The orbital labeling in Fig. 4 demands that the collocation matrices capture some correlation effects leading to “dressed” particle-hole pairs (which contributes to the numerical errors discussed previously by us$^{21}$), while the interaction must capture bare, dressed, and higher-dimensional interactions via a linear-scaling extraction of important features, in a similar spirit to the singular value decomposition and other low-rank decompositions. Switching either the $ij$ or $ab$ labels destroys this clear separation in terms of local (raw or dressed Coulombic) interactions of dressed particle-hole pairs, and instead introduces a picture with more exchange-like interactions. The THC decomposition, like most low-rank decompositions, is not able to effectively capture such non-local interactions.

A final numerical issue for the $\tilde{t}_{ij}^{ab}$ and $\tilde{t}_{ij}^{ab}$ amplitudes are the exclusion principle-violating (EPV) amplitudes which occur when $i = j$ or $a = b$. In the canonical equations these amplitudes cancel after antisymmetrization and do not affect the energy or properties in any way. Thus, we could assign these amplitudes any numerical value. However, when applying the tensor hypercontraction approximation, information from all doubles amplitudes is mixed together to determine the elements of the core matrix $T^{[2]}$ via least-squares fitting. Thus, the EPV amplitudes do potentially contribute to the LS-THC-MP3 energy. We argue that, in order to minimize the impact of EPV amplitudes, we should choose a value for these amplitudes which produces the most accurate THC decomposition of the doubles amplitudes as a whole. This guideline is based on the fact that as the THC decomposition approaches exactness (e.g. as the grid size is increased), the cancellation of the EPV terms, regardless of their numerical value, becomes more complete. This approach is quite different from setting the EPV amplitudes themselves to the smallest possible value (namely, zero). Thus, we suggest to not modify the EPV terms from their definition as obtained using the above diagrammatic approach, e.g. (26)–(28). Because the THC approximation captures the global mathematical structure of the amplitudes (i.e. it is an interpolation), a consistent choice of
EPV and non-EPV terms should provide the most compressible amplitudes. For \( \tilde{t}^{[1]} \), which are the only amplitudes used in LS-THC-MP3b, the proposed choice of the EPV amplitudes also corresponds directly to the “correct” Coulomb self-interaction.

Following the diagrammatic method using Fig. 2 (where we replace the top and bottom Hamiltonian vertices by the first-order amplitudes), followed by THC approximation of the integrals and first-order amplitudes for each spin case, we arrive at equations for open-shell LS-THC-MP3b,

\[
E_{LS-THC-MP3b} = \sum_{abij} \sum_{RS} \left( \tilde{X}_a^R \tilde{X}_i^RT^{[1]}_{RS} \tilde{X}_j^S - \tilde{X}_a^R \tilde{X}_b^RT^{[1]}_{RS} \tilde{X}_j^S \right)
\times \left[ \frac{1}{2} \sum_{kl} \sum_{TUWY} X_k^T X_i^T V_{TU} X_j^U X_a^U \tilde{X}_i^T X_k^T \tilde{X}_{TU} X_b^T X_{TU} \tilde{X}_j^Y \tilde{X}_l^Y 
+ \frac{1}{2} \sum_{cd} \sum_{TUWY} \tilde{X}_a^T \tilde{X}_c^T V_{TU} \tilde{X}_b^U \tilde{X}_d^U \tilde{X}_a^U \tilde{X}_i^T \tilde{X}_k^T \tilde{X}_{TU} \tilde{X}_j^Y \tilde{X}_l^Y 
+ \sum_{ck} \sum_{TUWY} \tilde{X}_a^T \tilde{X}_c^T V_{TU} \tilde{X}_b^U \tilde{X}_j^U \tilde{X}_a^U \tilde{X}_i^T \tilde{X}_k^T \tilde{X}_{TU} \tilde{X}_j^Y \tilde{X}_l^Y 
+ \sum_{cd} \sum_{TUWY} \tilde{X}_a^T \tilde{X}_c^T V_{TU} \tilde{X}_b^U \tilde{X}_d^U \tilde{X}_a^U \tilde{X}_i^T \tilde{X}_k^T \tilde{X}_{TU} \tilde{X}_j^Y \tilde{X}_l^Y 
- \sum_{ck} \sum_{TUWY} \tilde{X}_a^T \tilde{X}_c^T V_{TU} \tilde{X}_b^U \tilde{X}_j^U \tilde{X}_a^U \tilde{X}_i^T \tilde{X}_k^T \tilde{X}_{TU} \tilde{X}_j^Y \tilde{X}_l^Y 
- \sum_{cd} \sum_{TUWY} \tilde{X}_a^T \tilde{X}_c^T V_{TU} \tilde{X}_b^U \tilde{X}_d^U \tilde{X}_a^U \tilde{X}_i^T \tilde{X}_k^T \tilde{X}_{TU} \tilde{X}_j^Y \tilde{X}_l^Y 
+ \sum_{abij} \sum_{RS} \tilde{X}_a^R \tilde{X}_i^RT^{[1]}_{RS} \tilde{X}_j^S \tilde{X}_j^S 
\times \left[ \sum_{kl} \sum_{TUWY} X_k^T X_i^T V_{TU} X_j^U X_a^U \tilde{X}_i^T X_k^T \tilde{X}_{TU} X_b^T X_{TU} \tilde{X}_j^Y \tilde{X}_l^Y 
+ \sum_{cd} \sum_{TUWY} \tilde{X}_a^T \tilde{X}_c^T V_{TU} \tilde{X}_b^U \tilde{X}_d^U \tilde{X}_a^U \tilde{X}_i^T \tilde{X}_k^T \tilde{X}_{TU} \tilde{X}_j^Y \tilde{X}_l^Y 
+ \sum_{ck} \sum_{TUWY} \tilde{X}_a^T \tilde{X}_c^T V_{TU} \tilde{X}_b^U \tilde{X}_j^U \tilde{X}_a^U \tilde{X}_i^T \tilde{X}_k^T \tilde{X}_{TU} \tilde{X}_j^Y \tilde{X}_l^Y \right] 
\right]
\]
\begin{align}
&+ \sum_{\alpha \kappa} \sum_{TUWY} \tilde{X}_T^{\alpha} \tilde{X}_k^{\kappa} V_{TU} \tilde{X}_b^{\alpha} \tilde{X}_j^{\kappa} \tilde{X}_i^{\alpha} \tilde{X}_l^{\kappa} \tilde{X}_a^{\alpha} \tilde{X}_a^{\kappa} \tilde{X}_T^{\alpha} \tilde{X}_k^{\kappa} \\
&- \sum_{\alpha \kappa} \sum_{TUWY} \tilde{X}_T^{\alpha} \tilde{X}_k^{\kappa} V_{TU} \tilde{X}_b^{\alpha} \tilde{X}_j^{\kappa} \tilde{X}_i^{\alpha} \tilde{X}_l^{\kappa} \tilde{X}_a^{\alpha} \tilde{X}_a^{\kappa} \tilde{X}_T^{\alpha} \tilde{X}_k^{\kappa} \\
&- \sum_{\alpha \kappa} \sum_{TUWY} \tilde{X}_T^{\alpha} \tilde{X}_k^{\kappa} V_{TU} \tilde{X}_b^{\alpha} \tilde{X}_j^{\kappa} \tilde{X}_i^{\alpha} \tilde{X}_l^{\kappa} \tilde{X}_a^{\alpha} \tilde{X}_a^{\kappa} \tilde{X}_T^{\alpha} \tilde{X}_k^{\kappa} \\
&- \sum_{\alpha \kappa} \sum_{TUWY} \tilde{X}_T^{\alpha} \tilde{X}_k^{\kappa} V_{TU} \tilde{X}_b^{\alpha} \tilde{X}_j^{\kappa} \tilde{X}_i^{\alpha} \tilde{X}_l^{\kappa} \tilde{X}_a^{\alpha} \tilde{X}_a^{\kappa} \tilde{X}_T^{\alpha} \tilde{X}_k^{\kappa} \\
&+ \sum_{\alpha \kappa} \sum_{TUWY} \tilde{X}_T^{\alpha} \tilde{X}_k^{\kappa} V_{TU} \tilde{X}_b^{\alpha} \tilde{X}_j^{\kappa} \tilde{X}_i^{\alpha} \tilde{X}_l^{\kappa} \tilde{X}_a^{\alpha} \tilde{X}_a^{\kappa} \tilde{X}_T^{\alpha} \tilde{X}_k^{\kappa} \\
&+ \sum_{\alpha \kappa} \sum_{TUWY} \tilde{X}_T^{\alpha} \tilde{X}_k^{\kappa} V_{TU} \tilde{X}_b^{\alpha} \tilde{X}_j^{\kappa} \tilde{X}_i^{\alpha} \tilde{X}_l^{\kappa} \tilde{X}_a^{\alpha} \tilde{X}_a^{\kappa} \tilde{X}_T^{\alpha} \tilde{X}_k^{\kappa} \\
&- \sum_{\alpha \kappa} \sum_{TUWY} \tilde{X}_T^{\alpha} \tilde{X}_k^{\kappa} V_{TU} \tilde{X}_b^{\alpha} \tilde{X}_j^{\kappa} \tilde{X}_i^{\alpha} \tilde{X}_l^{\kappa} \tilde{X}_a^{\alpha} \tilde{X}_a^{\kappa} \tilde{X}_T^{\alpha} \tilde{X}_k^{\kappa} \\
&- \sum_{\alpha \kappa} \sum_{TUWY} \tilde{X}_T^{\alpha} \tilde{X}_k^{\kappa} V_{TU} \tilde{X}_b^{\alpha} \tilde{X}_j^{\kappa} \tilde{X}_i^{\alpha} \tilde{X}_l^{\kappa} \tilde{X}_a^{\alpha} \tilde{X}_a^{\kappa} \tilde{X}_T^{\alpha} \tilde{X}_k^{\kappa} \\
&- \sum_{\alpha \kappa} \sum_{TUWY} \tilde{X}_T^{\alpha} \tilde{X}_k^{\kappa} V_{TU} \tilde{X}_b^{\alpha} \tilde{X}_j^{\kappa} \tilde{X}_i^{\alpha} \tilde{X}_l^{\kappa} \tilde{X}_a^{\alpha} \tilde{X}_a^{\kappa} \tilde{X}_T^{\alpha} \tilde{X}_k^{\kappa}
\end{align}

(32)
These equations bear a striking similarity to those in the closed-shell case, where each open-shell term corresponds exactly to one of the closed-shell terms, except for numerical prefactor and the spin of each electron (loop). We leverage this similarity in our implementation by adding loops over \( \alpha \) and \( \beta \) spins to the closed-shell code, resulting in a highly efficient and maintainable implementation.

Computational Details

![Figure 5. 2H-2-azabicyclo[1.1.1]pentane radical with solvation shell. Solvent waters are numbered by center of mass distance from the solute.](image)

Open-shell LS-THC-MP2a, -MP2b, and -MP3b were implemented in a development version of CFOUR.\footnote{46} We tested the accuracy of these methods on four types of test systems:

1. **Linear alkyl radicals** \((\text{H(CH}_2\text{)}_n^*, \ n=1–10)\): Geometries were optimized at the B3LYP/def2-TZVP level, starting with synthetic structures with \( R_{CC} = 1.54 \text{Å} \), \( R_{CH} = 1.1 \text{Å} \), and tetrahedral angles.
2. **Micro-solvated 2H-2-azabicyclo[1.1.1]pentane radical** (Fig. 5): The aqueous micro-solvation environment and solute radical geometry were determined from a short QM/MM simulation (see ESI for details). Up to the 11 closest water molecules (based on the distance of the water oxygen atom to the closest solute atom) were retained in the THC calculations. Solvation energies were computed without geometry relaxation.
or counterpoise corrections.

3. **Glutathione** (Fig. 6): A gas-phase structure for glutathione (C$_{10}$N$_3$O$_6$SH$_{18}$) was optimized at the B3LYP/def2-TZVP level. Heterolytic and homolytic bond cleavage energies were calculated for each bond indicated in Fig. 6. Isolated bond cleavage fragments were re-optimized at the same level of theory. The fragment charges after heterolytic cleavage were assigned based on the lowest-energy configuration.

4. **9-propyl-4,11-tridecadienoic acid** (Fig. 7): An initial structure was obtained at the same B3LYP/def2-TZVP level, as well as radical and ionic structures produced by removing, in turn, each hydrogen atom indicated in Fig. 7 followed by reoptimization. We also generated 24 distinct conformations using the FRee Online druG conformation generation (FROG) tool. We then removed the tertiary hydrogen (#5) from each conformation and reoptimized using B3LYP/def2-TVZP.

All B3LYP geometry optimizations were performed with Q-Chem. For all THC calculations, we used the cc-pVDZ basis set, density fitting with the cc-pVDZ-RI auxiliary basis set, and SG0 as the parent grid. The parent grid was pruned as in Ref. 20, based on a numerical cutoff $\epsilon$ which was varied from $10^{-1}$ to $10^{-4}$ in each experiment. An unrestricted Hartree–Fock (UHF) reference was used in all cases.

In most cases, spin contamination of the UHF reference was negligible (< 5%), although certain systems (e.g. some radical bond-breaking fragments of glutathione and the vinylic tridecanoic acid radical) exhibit moderate spin contamination, with values of $\langle \hat{S}^2 \rangle$ as high as 0.99. We specifically avoid the use of a restricted open-shell Hartree–Fock (ROHF) reference, as these systems provide a test case for how the THC approximation is affected by spin contamination.
Results

Size-extensivity of the error

Fig. 8. Absolute energy errors for open-shell linear alkyl radicals, H(CH₂)ₙ•. The absolute value of the per-electron error between the THC and corresponding DF-MPₙ calculation is plotted for (a) the total LS-THC-MP₃b correlation energy, which is the sum of (b) the LS-THC-MP₃b third-order correction and (c) the LS-THC-MP₂b correlation energy, and finally (d) the LS-THC-MP₂a correlation energy.

We first examine the error of the THC approximations compared to their density-fitted counterparts for linear alkyl radicals in order to correlate absolute energy errors with system size. Fig. 8 gives the THC error per correlated electron. THC calculations with a range of grid cutoff parameters, ε, were performed in order to examine the dependence of the error with grid size (a smaller ε results in a larger grid and should yield a smaller error). The error per electron quickly reaches an approximately constant value, whether for the total MP₃ correlation energy (Fig. 8a), the MP₂ correlation energy (Fig. 8c,d), or the MP₃ correction
by itself (Fig. 8b). The latter contribution is the most irregular, perhaps due to its smaller magnitude and sensitivity to the virtual-virtual grid represented by \( \tilde{X} \).

Notably, the error for LS-THC-MP2a is much smaller than for LS-THC-MP2b as previously observed in the closed-shell case. As the total LS-THC-MP3b correlation energy includes an LS-THC-MP2b contribution, this error is in fact dominated by the MP2 part, with the MP3 correction error being a minor part for most reasonable choices of \( \epsilon \). In each case, the asymptotic error per electron decreases roughly linearly with respect to \( \epsilon \) (note that the \( \epsilon \) values are chosen on a log scale, and the y-axis is also logarithmic). Certain narrow ranges of \( \epsilon \) significantly depart from this trend, e.g. \( \epsilon \sim 10^{-1.2} \) in Fig. 8a or \( \epsilon \sim 10^{-3.0} \) in Fig. 8d. These irregularities occur due to a sign change in the error.

Typical density-fitting errors for DF-MP3 seem to be approximately 15 \( \mu E_h/e^- \) based on previous experiments.\(^2\) This indicates that the LS-THC-MP2b errors are comparable for \( \epsilon \sim 10^{-3.2} \), or even earlier near \( \epsilon \sim 10^{-2.0} \) if the LS-THC-MP2b contribution is replaced by LS-THC-MP2a. These results confirm the size-extensivity of open-shell LS-THC-MPn as was observed for the closed-shell variant. Typical per-electron errors are also similar for the closed- and open-shell THC methods; e.g. for \( \text{C}_8\text{H}_{18}/\text{C}_8\text{H}_{17}^- \) at \( \epsilon = 10^{-2.4} \) we find errors of 1.0/0.35 \( \mu E_h/e^- \) (MP2a), 102/105 \( \mu E_h/e^- \) (MP2b), and 6.9/8.7 \( \mu E_h/e^- \) (MP3b correction), respectively. We also observe, as for closed-shell THC, a “threshold” effect where convergence of the incremental error to the asymptotic value is only reached for a sufficiently long chain. This effect diminishes with looser cutoff values (smaller grids), suggesting a saturation of the orbital pair space for smaller systems.

**Radical micro-solvation energies**

We next examine the error of the THC approximations for 2H-2-azabicyclo[1.1.1]pentane (ABP) in order to study how an increase in solvation size impacts solvation energy errors. This is an important test given that subsequent solvent waters will contribute very different physical interactions to the total solvation (interaction) energy. For example, the 5th and
Figure 9. Errors in incremental solvation energy for 2H-2-azabicyclo[1.1.1]pentane in an explicit water solvation environment. From 1 to 11 waters are added in the order indicated in Fig. 5. See text for details.

7th waters added (see Fig. 5) interact directly with the radical center, and the 7th water at least forming a hydrogen bond with the amino nitrogen. Other waters interact via weaker electrostatic interactions or van der Waals interactions and instead hydrogen bond with other solvent molecules (e.g. the 6th, 8th, and 9th waters), and some more distant waters do not seem to form any strong interactions, at least with other fragments included in the present calculations (e.g. the 10th and 11th waters). However, the errors due to THC, presented as percentages of the incremental solvation energy,

\[
\% \Delta E_n = \left| 1 - \frac{E_{THC-MP3}(\text{ABP} \cdot (\text{H}_2\text{O})_n) - E_{THC-MP3}(\text{ABP} \cdot (\text{H}_2\text{O})_{n-1})}{E_{DF-MP3}(\text{ABP} \cdot (\text{H}_2\text{O})_n) - E_{DF-MP3}(\text{ABP} \cdot (\text{H}_2\text{O})_{n-1})} \right| \times 100\% \tag{33}
\]

do not show any clear trend with the strength or type of solvent interaction. Rather, the
errors are relatively consistent at moderate cutoff values ($0.001 < \epsilon < 0.01$). At or below $\epsilon = 10^{-2.6}$, errors are consistently less than 5%. The absence of a trend or significant outliers indicates a relative insensitivity of THC-MP3 to different types of interactions, and critically, no bias of the open-shell THC-MP3 method toward or against interactions involving unpaired electrons.

**Bond cleavages and radical stability**

![Figure 10. Bond dissociation energy errors of glutathione. (a) Absolute BDE error due to THC. The solid lines indicate homolytic bond cleavage (open-shell) and dashed lines indicate heterolytic bond cleavage (closed-shell). The bond index refers to labeled bonds in Fig. 6. (b) Absolute errors in the difference between the homolytic and heterolytic BDEs due to THC.](image)

We evaluate the robustness of the THC approximation with respect to various bond cleavage points and charge/spin separation by examining 13 different bond dissociation en-
ergies (BDEs) for the glutathione system (Fig. 6) and 5 different hydrogen atom abstraction (HA) energies for the tridecadienoic acid system (Fig. 7).

We only consider bond breakages in glutathione between backbone C−C or C−N bonds, as well as the C−S bond in the cysteine peptide. For each bond cleavage, we calculate both a homolytic (AB → A• + B•) and a heterolytic (AB → A− + B+ or AB → A+ + B−, whichever results in more stable products) bond dissociation energy.

The homolytic and heterolytic bond dissociation energy errors with respect to standard density fitting calculations are shown in Fig. 10a. Overall, the THC approximation produces an accurate bond cleavage energy (around 1 kcal/mol) for most of the bond-breaking cases at reasonable selections of ε (ε < 0.01). Additionally, the error differences between the homolytic (solid lines) and heterolytic (dashed lines) bond cleavage energy are of similar magnitude for each value of ε, and at tighter thresholds follow the same trend towards lower energies for bonds A, B, and D. These bonds cleave the thiol or other terminal functional groups—because of the “threshold” effect noted above, these bond dissociations result in the lowest total error due to near-saturation of the THC grid for the smaller fragment. The closed-shell calculations result in smaller errors for these three cases, perhaps indicating a slight difference in how quickly the grid saturates in the open- and closed-shell cases. However, “moderate” cutoff values do not show such a trend and instead provide a rather consistent magnitude of error irrespective of the bond being broken.

The error in the difference between the homolytic and heterolytic BDEs (ΔBDE) were also computed and are depicted in Fig. 10b. Across the various bonds, errors for this relative measure are somewhat lower than for the BDEs themselves. This indicates a reliable error cancellation between the open- and closed-shell LS-THC calculations on similar systems (note that the geometries of the products were optimized separately for hetero- and homolytic cleavage).

In Fig. 11, bond dissociation energy errors are shown for H(+•−) abstraction from 9-propyl-4,11-tridecadienoic acid. For the closed-shell products (dashed lines; these are all
Figure 11. Bond dissociation energy errors of 9-propyl-4,11-tridecadienoic acid. (a) Absolute BDE error due to THC. The solid lines indicate homolytic bond cleavage (open-shell) and dashed lines indicate heterolytic bond cleavage (closed-shell). (b) Absolute errors in the difference between the homolytic and heterolytic BDEs due to THC.

cationic with the exception of the carboxylate) there does seem to be a trend which tends to result in lower errors for the more stable cationic products (substituted alkyl radicals and especially doubly-bonded sp\(^2\) cationic centers). This may result from enhanced error cancellation between more similar geometries where re-hybridization is incomplete. The errors for radical open-shell products (solid lines) are more consistent, perhaps again due to reduced rehybridization even in the primary and secondary carbon radicals. Fig. 11b gives the error in the relative energy between the charged and neutral abstraction products. As for glutathione, there is some cancellation of errors for, in particular for the carboxyl and vinyl abstractions where the geometric changes are more similar.
Conformational energy ordering

Figure 12. Errors in the relative energies of 24 conformations 9-propyl-4,11-tridecadienoic acid due to THC. Conformational energy differences are calculated with respect to the lowest energy conformation (index 19), and the remaining conformations are ordered by increasing energy (using the DF-MP3 energies). (a) Errors for open-shell radical conformations. (b) Errors for closed-shell cationic conformations.

Again focusing on 9-propyl-4,11-tridecadienoic acid, we examine the relative energies of 24 distinct conformations of the 9H hydrogen abstraction (open-shell radical) and hydride abstraction (cationic) products. In Fig. 12, the errors in relative conformational energies due to THC are presented for both types of products. While it is clear that there is not a strong correlation of the errors between the neutral radical and charged closed-shell products (c.f. the lack of any distinct trend in the open-shell errors with respect to the closed-shell errors ordered from smallest to largest at $\epsilon = 10^{-4}$). However, both the closed- and open-shell errors seem to span almost identical ranges for each value of $\epsilon$. The smallest and largest errors,
even at a tight tolerance of $\epsilon = 10^{-4}$, seem to span at least an order of magnitude, although there does not seem to be a trend of the size of the error with any chemically-relevant features of the individual conformations. The fact that the smallest errors are significantly lower than observed in, for example, Fig. 10 may then simply indicate fortuitous error cancellation which is not reproducible between the radical and cationic structures. Since the final structures in these cases were optimized independently (despite starting with the same algorithmically-generated guess structure), this is perhaps not surprising.

Conclusions

The LS-THC method has proven to be an efficient approximation of both the ERI and doubles amplitudes tensors with high accuracy and low scaling for closed-shell systems.

Here, LS-THC was implemented for MP2 and MP3 calculations on open-shell systems and was evaluated with various test systems: linear alkyl radicals, a micro-solvated amine radical, heterolytic and homolytic bond cleavages in glutathione, and proton/hydrogen/hydride abstractions as well as conformational differences of 9-propyl-4,11-tridecadienoic acid. A number of trends were observed:

1. Similar to the RHF implementation, the LS-THC-MP$n$ errors scale linearly with system size, after a critical “threshold” molecular size is reached (this effect is diminished for looser cutoff values). Errors for LS-THC-MP2a are essentially negligible, while errors in LS-THC-MP3b are dominated by the MP2b contribution. Remaining errors in only the LS-THC-MP3b contribution are reasonably small with a double-zeta basis set.

2. Reliable error cancellation is evident in almost all calculations of energy differences. The greatest degree of error cancellation occurs when the systems are most chemically similar, resulting fragments are unequally distributed in size, or potentially when more stable products are produced. Errors in relative energies are typically below 1 kcal/mol for moderate cutoff values in the range $\epsilon < 10^{-2}$.
3. The errors produced for open-shell systems are highly similar to the errors produced for chemically similar closed-shell systems. In some cases, error cancellation can also be exploited between open- and closed-shell processes, such as in the relative BDEs of heterolytic and homolytic bond cleavages.

4. The error of the open-shell LS-THC-MP\(n\) methods is highly insensitive to the specific nature of the chemical structure, type of interactions, and even moderately severe spin contamination of the reference wavefunction.

In summary, *open-shell THC seems to be equally as applicable as closed-shell THC*. The diagrammatic method of derivation presented also enables the implementation of open-shell THC methods with little additional effort compared to the closed-shell version, and a highly similar code structure which should enable maintainable, efficient codes.

**Acknowledgements**

This work was supported by the US Department of Energy under grant DOE-SC0022893, and in part by the US National Science Foundation under grant OAC-2003931 and CHE-2143725. MS is supported by an SMU Center for Research Computing Graduate Fellowship. All calculations were performed on the ManeFrame II computing system at SMU.

**Disclosure Statement**

No potential conflict of interest was reported by the authors.

**Supporting Information**

The following electronic supplementary information files are available from the publisher’s website:
• The factorized LS-THC MP3b equations and QM/MM simulation details (.pdf).

• All calculated DF- and LS-THC-MP\textsubscript{n} correlation energies (.xlsx).

• Molecular geometries used for all calculations (.xlsx).

References


(25) Benedikt, U.; Böhm, K.-H.; Auer, A. A. Tensor decomposition in post-Hartree-Fock


Graphical TOC Entry