EXTENDING THE CAPABILITIES OF ACCURATE AB INITIO METHODS: NOVEL ALGORITHMS AND MASSIVELY PARALLELIZABLE IMPLEMENTATIONS FOR FEASIBLE CALCULATIONS

By

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To my wife, Sondra
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The most general methods in electronic structure theory, capable of attaining chemical accuracy, are coupled cluster (CC) methods. Unfortunately, the “gold-standard”, CCSD(T), formally scales as $N^7$, where $N$ is the size of the chemical system. Consequently, practical brute force computations with these methods on systems of $O(10)$ atoms is out of the question with the serial programs that have been developed. This wall needs to be overcome to allow feasible calculations for moderately sized chemically relevant systems with high accuracy. In this vein, I present different approaches to tackle this scaling problem.

First, I use an exact, in the limit, method that reduces the computational effort of calculations. Specifically, a formally exact procedure for decoupling the four-component relativistic Dirac equation is implemented, in a general way in the ACESII and ACESIII program packages, and used in conjunction with IP-EOM-CCSD methods to improve core ionization energies.

Another way to overcome the scaling of CC methods is to simply develop new \textit{ab initio} theoretical models that are more computationally tractable. I propose a new method with mean-field cost, $N^4$, that obtains core ionization energies to a high degree of accuracy as opposed to increasing the complexity of IP-EOM-CC methods, which would include the same amount of relaxation as the proposed method in the limit only
with exponential scaling, \( N^N \). Furthermore, the proposed method is unambiguous in describing orbital relaxation effects, the dominant energetic effect in core ionizations of organic molecules. Therefore, a perturbation theory analysis allows quick corrections to the computationally tractable IP-EOM-CCSD method.

The final way to push CC methods further is to use modern computer architecture and parallelize over processors. Equation of motion CC (EOM-CC) methods are implemented in this way to allow benchmark studies on biologically relevant molecules. EOM-CC properties, including dipole, second, and transition moments are implemented in this work, as well as the EOM-CCSD(T) method (and other triples extensions), an analogue of the very successful CCSD(T) method, but for excited states. Gradients for EOM-CCSD theory are implemented as well, paving the way for routine studies of potential energy surfaces and dynamics of excited states within the CC framework.
CHAPTER 1
INTRODUCTION

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

— P. A. M. Dirac, *The Quantum Theory of the Electron*

1.1 *Ab Initio* Quantum Chemistry

Dirac’s famous quote \([1]\) has appeared in numerous textbooks, articles, dissertations, etc., emphasizing the troubling reality of modern quantum chemistry and physics. An *ab initio*, or “from the beginning” exact quantum mechanical description of electrons, the necessary particles for describing chemical bonding, reactivity, properties, excitations, and phenomena in general without experimental input, is an intractable, rather unobtainable, goal. However, all is not lost. Dirac continues,

It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

This assertion carries a little more hope than the previous. In fact, it precisely describes the remarkable efforts made in the name of modern quantum chemistry. Judicious and carefully chosen approximations are made with the goal of predicting experimental results. Approximate *ab initio* methods can probe transient species where experiment can not, provide chemical insight for those experiments that are difficult, dangerous, or even impossible, and can help elucidate complicated experimental data to provide definitive conclusions.

To begin, *ab initio* quantum chemistry is concerned with calculating the distribution of electrons in molecules. The non-relativistic, time-dependent description of quantum
particles, electrons in this case, is governed by the Schrödinger equation

\[ -i \frac{\partial}{\partial t} \Psi(x, t) = \hat{H}(t) \Psi(x, t). \]  

(1–1)

For a time-independent Hamiltonian, \( \hat{H} \), one with no external fields or potentials, the wavefunction describing the particles with coordinates \( x \), is separable as

\[ \Psi(x, t) = \Psi(x) \phi(t). \]  

(1–2)

Inserting this in to Equation (1–1) and performing a separation of variables, yields the time-independent Schrödinger equation for bound energetic states

\[ \hat{H} \Psi(x) = E \Psi(x) \]  

(1–3)

with a phase factor describing the time evolution of the particle given as

\[ \phi(t) = e^{-iEt}. \]  

(1–4)

An experimentally observable value or property \( \langle A \rangle \) is defined by the expectation value of the corresponding Hermitian operator \( \hat{A} \),

\[ \langle A \rangle = \frac{\int dx \ e^{iEt} \Psi(x) \hat{A} \Psi(x) e^{-iEt}}{\int dx \ e^{iEt} \Psi(x) \Psi(x) e^{-iEt}} = \frac{\int dx \ \Psi(x) \hat{A} \Psi(x)}{\int dx \ \Psi(x) \Psi(x)} = \frac{\langle \Psi | \hat{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \]  

(1–5)

Here, for convenience, I use Dirac's "bra-ket" notation [2], where the "bra-ket" \( \langle \Psi | \hat{A} | \Psi \rangle \) is the inner product of the "ket" \( | \Psi \rangle \) vector, defined in the relevant fixed particle infinite dimensional Hilbert space, and the "bra" \( \langle \Psi \), the corresponding linear functional in the dual space. [2] Of primary importance is the ground state energy of a system. Assuming an exact, normalized wavefunction \( (\langle \Psi | \Psi \rangle = 1) \), the non-relativistic energy is given by

\[ E_{\text{exact}} = \langle \Psi | \hat{H} | \Psi \rangle \]  

(1–6)
Since $\hat{H}$ is a hermitian, and therefore positive semi-definite, operator \([3]\), then for any normalized trial wavefunction, $|\tilde{\Psi}\rangle$, the following property holds

$$
\langle \tilde{\Psi} | \hat{H} - E_{\text{exact}} | \tilde{\Psi} \rangle \geq 0
$$

(1–7)

This is the Rayleigh-Ritz variational principle, \([4]\) and provides a rigorous upper-bound to the energy for approximate wavefunctions.

For hydrogen and hydrogenic ions, systems with one electron and one nucleus, \(A\) (with charge \(Z_A\) and mass \(M_A\)), the Hamiltonian is

$$
\hat{H} = -\frac{1}{2} \nabla_1^2 - \frac{1}{2M_A} \nabla_A^2 - \frac{Z_A}{|r_1 - R_A|},
$$

(1–8)

and contains the kinetic energy of the electron and nucleus in the first and second terms, respectively, and the electron-nucleus attractive potential energy. In practice, since the timescale of the electronic redistribution, or movement, is extremely fast compared to the timescale of the movement of the nucleus, like “flies around a cake”, \(^1\) there is no kinetic energy term for the nuclei. This is the basis for the Born-Oppenheimer approximation. In fact, for systems with more than one nuclei, the nucleus - nucleus potential energy between nuclei \(A\) and \(B\), $\hat{V}_{NN}(R) = \sum_{A}^{N_A} \sum_{B \neq A}^{N_B} Z_A Z_B \frac{1}{|r_A - r_B|}$, simply becomes an additive scalar, and is trivial to compute using the predefined charges, \(Z\), and coordinate vectors \(R\). It also is essential for the construction of potential energy surfaces (PES) to obtain critical points such as ground state geometries, transition states, and intermediate structures.

Within the Born-Oppenheimer approximation the hydrogenic Hamiltonian then becomes

$$
\hat{H} = -\frac{1}{2} \nabla_1^2 - \frac{Z_A}{|r_1 - R_A|}.
$$

(1–9)

\(^1\) R. J. Bartlett, private communication, 2007
With this Hamiltonian, Equation (1–3) is exactly soluble with exponentially decaying, one-electron distribution functions, or atomic orbitals.

In general, these atomic orbital functions are products of a polynomial radial function and a spherical harmonic function for the angular part centered, or positioned, at $\mathbf{R}$

$$\psi_{nlm}(\mathbf{r}) = Y_{lm}(\theta, \phi) R_n(r) e^{-\alpha |r - \mathbf{R}|}. \quad (1–10)$$

These exponentially decaying functions in spherical coordinates are called Slater orbitals. In cartesian coordinates, Slater orbitals take the form

$$\psi_{lmn}(\mathbf{r}) = x^l y^m z^n e^{-\alpha |r - \mathbf{R}|}, \quad (1–11)$$

where $\{l, m, n\}$ are no longer the usual quantum numbers, although the principal quantum number is the sum of these exponents. However, for molecular systems, it will be convenient to express these Slater orbitals as a sum over Gaussians,

$$x^l y^m z^n e^{\alpha |r - \mathbf{R}|} \approx \sum_{\nu} d_{\mu\nu} x^l y^m z^n e^{\beta_{\nu} |r - \mathbf{R}|^2} = \chi_{\mu}(\mathbf{r}). \quad (1–12)$$

The set of $\{\chi_{\mu}\}$, or $\{|\mu\rangle\}$, are called “contracted Gaussian functions”. Although these contracted Gaussian functions are smooth at the nucleus, rather than having a cusp, and decay too rapidly farther away from the nucleus, the fitting techniques used to determine the coefficients $d_{\mu\nu}$ and exponents $\beta_{\nu}$ do so to very reasonable accuracy in intermediate ranges. Contracted Gaussian basis functions simplify integral evaluation in molecular systems, as will be shown later.

For a molecular systems comprised of $N_n$ nuclei and $N_e$ electrons, with nucleus $A$ specified by its atomic number, $Z_A$, and atomic mass, $M_A$, the time-independent Hamiltonian, within the Born-Oppenheimer approximation, is

$$\hat{H} = -\sum_i \frac{1}{2} \nabla_i^2 - \sum_i \sum_A \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \sum_i \sum_{j>i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \hat{V}_{NN}(\mathbf{R}). \quad (1–13)$$
The first term correspond to the kinetic energy of the electrons, followed by the attractive nucleus - electron potential energy and the repulsive electron - electron and nucleus - nucleus potential energy terms. By subtracting out the nucleus - nucleus potential energy term, the electronic energy, \( E_{ee} \) is determined via

\[
-\sum_i \frac{1}{2} \nabla_i^2 \sum_A \sum_{i \neq j} \frac{Z_A}{|r_i - r_A|} \sum_j N_e \sum_{i \neq j} \frac{1}{|r_j - r_i|} \right] |\Psi(x)\rangle = E_{ee} |\Psi(x)\rangle. \tag{1–14}
\]

Unfortunately, the last term of Equation (1–14), the electron - electron repulsion term, makes an exact analytical solution impossible. This is known as the electronic structure problem.

However, since \( |\Psi(x)\rangle \) is an abstract vector in Hilbert space, it can be expanded in a complete set of orthogonal basis vectors in that space.

\[
|\Psi(x)\rangle = \sum_i c_i |\Phi_i(x)\rangle. \tag{1–15}
\]

The individual basis vectors, \( |\Phi_i(x)\rangle \), are themselves represented by a finite antisymmetric product of one-electron basis functions called molecular orbitals, \( \{\psi_{pi}(x_i)\} \), as

\[
|\Phi_i(x)\rangle = \frac{1}{\sqrt{N_e! A!}} \prod_p \psi_{pi}(x_i). \tag{1–16}
\]

The antisymmetry of this product function is essential due to the indistinguishability of the electrons as dictated by quantum mechanics. \cite{2} When two particles are switched, the wavefunction must change sign. As an example of Equation (1–16), for a system with two electrons, the wavefunction must have the form

\[
|\Phi(x_1, x_2)\rangle = \frac{1}{\sqrt{2}} (|\psi_1(x_1)\psi_2(x_2)\rangle - |\psi_1(x_2)\psi_2(x_1)\rangle). \tag{1–17}
\]
This can be accomplished by expressing each $| \Phi_I \rangle$ as the determinant of a matrix of molecular orbitals, with each row corresponding to an electron number

$$
| \Phi_I(x) \rangle = \frac{1}{\sqrt{N_e!}} \begin{vmatrix}
\psi_i(x_1) & \psi_j(x_1) & \psi_k(x_1) & \cdots \\
\psi_i(x_2) & \psi_j(x_2) & \psi_k(x_2) & \cdots \\
\psi_i(x_3) & \psi_j(x_3) & \psi_k(x_3) & \cdots \\
\cdots & \cdots & \cdots & \cdots 
\end{vmatrix}
$$

(1–18)

Since swapping rows of a matrix changes the sign of the determinant, antisymmetry is built in to the basis vectors from the beginning.

Another critical result of quantum mechanics that needs to be incorporated in the wavefunction is the $m_s$ quantum number, or spin $\sigma = \{\alpha, \beta\}$, of the electron. In the non-relativistic limit, the spin and spatial components of the molecular orbitals can be decoupled resulting in molecular orbitals as

$$
\psi(x_i) = \phi(r_i) \sigma(i),
$$

(1–19)

with $r_i$ being the $\{x, y, z\}$ cartesian coordinates of the $i^{th}$ electron. This is a rather nice result since it allows molecular orbitals, or distribution function, to be graphed and visualized after spin is integrated out. Although, it is important to note, these orbitals do not correspond to any observable quantity in the laboratory.

It is computationally infeasible to use a complete basis for the set of molecular orbitals $\{\phi_i\}$; instead, a finite basis must be used. The most commonly used basis for molecular systems is an expansion of the aforementioned atomic orbitals (AOs), or contracted Gaussian functions $\{|\mu\rangle\}$, distributed over the system, typically centered on the nuclei of the molecule. There are, of course, other choices for a basis. Finite, real-space grids [5] are gaining wide-spread use for molecules, and for periodic systems, plane waves are necessary because of the periodic boundary conditions. [6]
The molecular orbitals are then expanded as a linear combination of the AOs as
\[ \phi_i(r) = \sum_{\mu} c_{\mu i} \chi_{\mu}(r) \]
\[ |i\rangle = \sum_{\mu} c_{\mu i} |\mu\rangle \]

(1–20)

The electronic energy then of an arbitrary normalized determinant comprised of these orbitals, under the constraint the MOs themselves are normalized, \( \langle i|j \rangle = \delta_{ij} \), is given as
\[ E = \langle \Phi|\hat{H}|\Phi \rangle \]
\[ = \langle \phi_1 \cdots \phi_i \phi_j \cdots \phi_n|\hat{H}|\phi_1 \cdots \phi_i \phi_j \cdots \phi_n \rangle \]
\[ = \sum_{i} h_{ii} + \frac{1}{2} \sum_{ij} \langle \hat{\langle} ij|\hat{\rangle} ij \rangle \]

(1–21)

(1–22)

(1–23)

where
\[ h_{ij} = \langle i|\hat{H}|j \rangle = \langle \phi_i(r_1)| - \frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{|r_1 - R_A|} |\phi_j(r_1)\rangle \]

(1–24)

\[ \langle \hat{\langle} ij|\hat{\rangle} kl \rangle = \langle \hat{\langle} ij|\hat{\rangle} kl \rangle - \langle \hat{\langle} ij|\hat{\rangle} lk \rangle \]

(1–25)

(1–26)

\[ \langle \hat{\langle} ij|\hat{\rangle} kl \rangle = \langle \phi_i(r_1)\phi_j(r_2)| \frac{1}{|r_1 - r_2|} |\phi_k(r_1)\phi_l(r_2)\rangle \]

These formula follow naturally with the orthogonality of the MOs and the proper inclusion of antisymmetry. Since \( \hat{H} \) is a one-electron operator, it acts on one “ket” MO, leaving the rest “untouched” and due to orthogonality of the MOs, can only form the inner product with the corresponding “bra” MO
\[ \langle \hat{\langle} ij|\hat{\rangle} kl \rangle = \langle \hat{\langle} ij|\hat{\rangle} kl \rangle \]

(1–27)

(1–28)

(1–29)

(1–30)
The same follows for the electron-electron repulsion operator, except that the antisymmetric nature of the determinant yields two contributions, the \textit{coulomb} and \textit{exchange} pieces. The exchange piece is purely a quantum mechanical effect arising from the indistinguishability of the electrons.

Since the MOs are linear combinations of AOs, the integrals are actually evaluated in the AO basis and transformed to the MO basis. For example, the two-electron integral in the MO basis is

\begin{equation}
\langle ij | kl \rangle = \sum_{\mu\nu\lambda\sigma} c_{i\mu}^* c_{j\nu}^* \langle \mu\nu | \lambda\sigma \rangle c_{\lambda k} c_{\sigma l}.
\end{equation}

Explicitly, this integral, with \( \phi_\mu, \phi_\nu, \phi_\lambda, \) and \( \phi_\sigma \) centered on nuclei A, B, C, and D, respectively, is

\begin{equation}
\langle \mu\nu | \lambda\sigma \rangle = \int dx dy dz \phi_\mu^A(r_1) \phi_\nu^B(r_2) \phi_\lambda^C(r_1) \phi_\sigma^D(r_2) / |r_1 - r_2|.
\end{equation}

However, since the AOs are contracted Gaussian functions, we can use the well-known Gaussian product theorem to construct a Gaussian centered at \( P \) from two Gaussians centered at A and B, respectively.

\begin{equation}
e^{-\alpha|r_1 - R_A|^2} e^{-\beta|r_1 - R_B|^2} = E_{AB} e^{-\rho|r_1 - R_P|^2}
\end{equation}

where

\begin{equation}
p = \alpha + \beta
\end{equation}

\begin{equation}
P = \frac{\alpha R_A + \beta R_B}{\alpha + \beta}
\end{equation}

\begin{equation}
E_{AB} = e^{-\frac{\alpha\beta}{\alpha + \beta} (R_A - R_B)^2}
\end{equation}

Therefore, the 4-center integral reduces to

\begin{equation}
\int dx dy dz \frac{\phi_\mu^A(r_1) \phi_\nu^B(r_2) \phi_\lambda^C(r_1) \phi_\sigma^D(r_2)}{|r_1 - r_2|} = \int dx dy dz |x_1, y_1, z_1| |x_2, y_2, z_2| \frac{\phi_P^P(r_1) \phi_P^Q(r_2)}{|r_1 - r_2|}.
\end{equation}
With the cartesian polynomial piece of the contracted Gaussian being absorbed in $l(x_i, y_i, z_i)$ as

$$l(x_i, y_i, z_i) = (x_i - A_x)^l(y_i - A_y)^m(z_i - A_z)^n$$ (1–38)

The Slater type orbitals of Equation (1–12) are expanded in Gaussians because of this property. It simplifies the integral evaluation tremendously. There is an associated loss of accuracy as this expansion is incomplete and contains unphysical characteristics at the nucleus. One usually chooses Gaussian basis sets optimized for the particular system under investigation to reduce this error.

There are libraries of these Gaussian basis sets for each atom in the periodic table [7, 8]. Sometimes it is convenient to generate one’s own basis set, optimizing the contraction coefficients and exponents. It is also possible to converge to the complete basis set limit by increasing the Gaussian basis set in careful, predefined ways [9, 10] by adding polarization and/or diffuse functions. For example, excited states of molecules are sometimes very delocalized. Diffuse functions, functions that extend far out from the nucleus, are necessary to accurately describe these Rydberg type, delocalized states. However, these may not be necessary for ionized or cationic systems, since the charge distribution will most likely not be distributed too far from the nucleus. It is an extremely important point, as one would like to capture the most amount of necessary physics, with as little computational effort as possible.

1.2 The Hartree-Fock Mean-Field Approximation

The simplest, non-empirical, ab initio method for computing the electronic energy of molecular systems is the independent particle model (IPM). Specifically, minimizing the electronic energy with respect to the molecular orbitals defines the Hartree-Fock IPM approximation and conceptually corresponds to each electron relaxing in the field generated by the remaining electrons.

We seek a single determinant wavefunction, minimized with respect to the MOs to be the lowest energy solution of Equation (1–23) subject to the constraint that the MOs
remain orthogonal. The Lagrangian
\[ \delta \mathcal{L} = \delta \left[ \sum_i^{N_e} \langle i | \hat{\mathcal{H}} | i \rangle + \frac{1}{2} \sum_{ij}^{N_e} \langle ij | ij \rangle - \epsilon_{ji} \left( \langle i | j \rangle - \delta_{ij} \right) \right], \tag{1–39} \]
follows, with the \( \epsilon_{ji} \) being the undetermined multipliers enforcing the MO orthogonality constraint. This minimization yields the canonical Hartree-Fock equations
\[ \left( -\frac{1}{2} \nabla^2 - \sum_A \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \mathcal{J}_i(\mathbf{r}_1) - \mathcal{K}_i(\mathbf{r}_1) \right) |i\rangle = \epsilon_i |i\rangle \tag{1–40} \]
The coulomb and exchange operators, \( \mathcal{J}(\mathbf{r}) \) and \( \mathcal{K}(\mathbf{r}) \), respectively, are orbital dependent and defined as
\[ \mathcal{J}_i(\mathbf{r}) |i\rangle = \sum_{ij}^{N_e} \int d\mathbf{r}' \frac{\phi_j^*(\mathbf{r}') \phi_i(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} = \int d\mathbf{r}' \frac{\rho(\mathbf{r}',\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \phi_i(\mathbf{r}) \tag{1–41} \]
\[ \mathcal{K}_i(\mathbf{r}) |i\rangle = \sum_{ij}^{N_e} \int d\mathbf{r}' \frac{\phi_j^*(\mathbf{r}') \phi_i(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} = \int d\mathbf{r}' \frac{\rho(\mathbf{r},\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi_i(\mathbf{r}'). \tag{1–42} \]
The coulomb operator justifies the IPM, or mean-field terminology, as it conceptually “smears” out the charge distribution of all other electrons. The exchange operator is written in a more suggestive form to demonstrate its non-local nature, note the interchange of \( \mathbf{r}' \) with \( \mathbf{r} \), and is responsible for the correlation of electrons of parallel spin.

The left hand side of Equation (1–40) is called the Fock operator, written \( \hat{\mathcal{F}}_i \) for orbital \( i \), and is dependent on the orbitals. Left projecting by molecular orbital \( \langle j | \) yields the Fock matrix
\[ \langle j | \hat{\mathcal{F}}_i | i \rangle = \epsilon_i \langle j | i \rangle \tag{1–43} \]
\[ = \epsilon_{ji} \delta_{ij} \tag{1–44} \]
The orbital dependence results in a non-linear equation that begins with an initial guess for the set \{\( |\rho\rangle \)\} and is solved until self-consistency is reached. At first, these coupled integro-differential equations were solved numerically. Numerical approaches are still a subject of interest today [11], since they offer a route to arbitrary precision,
however they do not provide higher energy orthogonal functions for the generation of excited determinants, where an electron in an occupied orbital $|i\rangle$, is replaced by a higher energy virtual orbital $|a\rangle$. A more pragmatic approach, that generates the orthogonal higher energy molecular orbitals, was developed by Roothaan and Hall [12]. As suggested above, the molecular orbitals in Equation (1–40) are expanded in an atomic orbital basis

$$
\sum_{\nu} \hat{f}_i |\nu\rangle c_{\nu} = \epsilon \sum_{\nu} |\nu\rangle c_{\nu}.
$$

(1–45)

Left projection with $|\mu\rangle$ yields the Roothaan-Hall or Hartree-Fock-Roothaan equations

$$
\sum_{\nu} \langle \mu | \hat{f}_i |\nu\rangle c_{\nu} = \epsilon \sum_{\nu} \langle \mu |\nu\rangle c_{\nu}.
$$

(1–46)

$$
\text{FC} = \epsilon \text{SC}
$$

(1–47)

with $S_{\mu\nu} = \langle \mu |\nu\rangle$ being the atomic orbital overlap matrix. Beginning with an initial C vectors, from Hückel’s method, previously defined small basis vectors, localized atomic HF calculations, etc . . . , the Fock matrix is constructed and diagonalized, yielding a new set of vectors, $C'$, which are transformed to eliminate the overlap matrix. This procedure is repeated until a convergence threshold is reached.

The lowest $N_e$ molecular orbitals comprise the Hartree-Fock determinant, $|\Phi_0\rangle$, and excited determinants, $|\Phi_i\rangle$ are formed from the swapping occupied orbitals with the remaining $M = N_{AO} - N_e$ virtual orbitals. These excited determinants form the basis for relaxing the energy further, which will be presented after a detour to an approximate relativistic extension of the one-electron operators in $\hat{f}_i$.

1.2.1 Formal Scaling and Rate-Determining Steps

The construction of the Fock matrix in the AO basis formally scales as $N_{AO}^4$ as can be seen in the construction of the $\hat{J} - \hat{K}$ matrices

$$
\langle \mu | \hat{J} - \hat{K} |\nu\rangle = \sum_{\lambda\sigma} \langle \mu\lambda ||\nu\sigma\rangle D_{\sigma\lambda}
$$

(1–48)
with $D_{\alpha\lambda}$ being the charge density [4] generated from backtransforming the molecular orbitals contained in the operators. Having to loop over the four indices $\{\mu, \nu, \lambda, \sigma\}$ causes the $N_{AO}^4$ scaling. However, this piece of the Fock matrix can be computed in blocks, that can be distributed over processors. As will be shown later, for large basis sets, with a properly parallelizable program and algorithm, this brute force construction of the Fock matrix can cease to be the rate-determining step.

When this happens, the new rate-determining step becomes the serial diagonalization of the Fock matrix to obtain a new set of molecular orbital coefficients. The diagonalization scales as $N_{AO}^3$ and can not be divided into independent blocks of data, hence remains serial. Therefore, the development of techniques that avoid this serial diagonalization are critical to push the field further towards the ab initio treatment of very large molecules with $\mathcal{O}(10,000)$ to $\mathcal{O}(100,000)$ atoms.

1.2.2 Scalar-Relativistic Hamiltonians:

As the nuclear charge increases, an extension to a relativistic framework is necessary. The electron begins to move close to the speed of light and Dirac’s equation

$$\hat{H}_D \phi = E \phi$$

becomes the equation describing the bound energetic states of the electron. The Dirac Hamiltonian is a 4 x 4 matrix and $\phi$ is a four-component spinor. Four-component spinor basis sets must be constructed to represent $\phi$, with the large component kinetically balanced with the small component. [13] This is necessary to avoid variational collapse of the positive energy solutions to bound positronic states, or negative energy solutions, since the energy spectrum contains both positive and negative energy solutions. Also, the mean-field approximation obtained by minimizing the Dirac energy with respect to the four-component basis functions representing $\phi$ is much more costly than the non-relativistic calculation.
To avoid these difficulties, many techniques have been developed that attempt to decouple the large and small components for one-electron operators of the Dirac Hamiltonian. Consequently, very nice expressions are obtained for transformed one-electron operators in the non-relativistic Schrödinger equation - the kinetic energy and nucleus-electron potential energy operators. These transformation techniques are separated to spin free (one component) and spin dependent (two component) additive corrections. The spin free transformations, in general, fit into the existing non-relativistic structure, computer codes included, since the same one-electron operators in $\hat{H}$ are also in $\hat{n}$.

1.3 Including Electron Correlation

1.3.1 Configuration Interaction

Hartree-Fock theory recovers roughly 99% of the total electronic energy of the system. Unfortunately, the remaining 1% is critical to describe systems accurately. As an example, Hartree-Fock can not capture dispersion, or London, forces. It will show no minimum energy structure exists for the methane dimer, where we know in practice, that there is a minimum, albeit a very shallow one. This “missing” energetic contribution is known as electron correlation, and is the sudden, instantaneous interaction of electrons with each other.

Electron correlation can be included by considering all possible replacements of the occupied orbitals in the HF reference determinant with higher energy virtual orbitals. Rigorously, the exact wavefunction in a given basis set $\{\phi_{\rho}\}$ can be described as a linear combination of these excited determinants

$$|\Psi\rangle = c_0|\Phi_0\rangle + \sum_{ia} c_i^a|\Phi_i^a\rangle + \sum_{i<j,a<b} c_{ij}^{ab}|\Phi_{ij}^{ab}\rangle + \cdots. \quad (1-50)$$

$$= \left( c_0 + \hat{C}_1 + \hat{C}_2 + \cdots + \hat{C}_n \right) |\Phi_0\rangle \quad (1-51)$$

$$= \left( 1 + \hat{C} \right) |\Phi_0\rangle \quad (1-52)$$
The leading term, $|\Phi_0\rangle$, is the HF reference determinant, and intermediate normalization, $\langle \Psi | \Phi_0 \rangle = 1$, was used to arrive at Equation (1–52). The remaining terms correspond to single, double, etc. . . excited determinants, where occupied orbital $i$ is replaced by virtual orbital $a$ in the singles, and so on and so forth with a probability (coefficient) of that excitation taking place. This expansion is known as Configuration Interaction (CI), and in the limit of all possible substitutions is the Full CI. It is the best answer in a given basis set, invariant to orbital choice, an upper bound to the exact energy, and rigorously defines the correlation energy as

$$E_{\text{corr}} = E - E_{\text{HF}}$$

(1–53)

with $E$ being the exact non-relativistic electronic energy. However, the cost of performing a Full CI calculation grows exponentially with the size of the basis set, making it only feasible for very small molecular systems with small basis sets. Any truncated CI calculation will inherently contain errors that will grow with the system size as it is not a size extensive method. A size extensive method is one where the energy scales properly with the number of particles; truncated CI does not scale properly with system size.

**Formal scaling.** The Full CI method brings in all the possible determinants that can be generated from the number of electrons occupying each of the molecular orbitals, thus exhausting the space spanned by the finite basis set. In this limit, the choice of orbitals is arbitrary, as all possible combinations are incorporated, and therefore includes all mean-field, or orbital relaxation, and electron correlation effects. The scaling of this method is completely and utterly infeasible so judicious approximations are made via truncating the Full CI expansion to a specific excitation level, [4] state-specific iterative matrix diagonalization routines that avoid complete diagonalization of the Full CI matrix, [4], monte carlo algorithms to seek only the most important determinants, [14] and possibly many others.
When truncated, the number of determinants in the CI matrix is approximately given, with binomial coefficients, as

\[ N_{\text{det}} \sim \left( \begin{array}{c} N_e \\ m \end{array} \right) \left( \begin{array}{c} n_v \\ m \end{array} \right) \sim \frac{1}{(m!)^2} N_e^m n_v^m \]  

(1–54)

with a given excitation level, \( m \), number of electrons, \( N_e \), and number of virtual orbitals unoccupied in the reference determinant, \( n_v \). Even more disastrous for truncated CI methods is the lack of size extensivity. Exploiting the fact that the Hamiltonian contains a two-electron operator yielding a sparse CI matrix can help to reduce the scaling, and applying corrections to reduce size inextensivity can help, but the method still remains computationally unsustainable today.

### 1.3.2 Coupled-Cluster Theory

The Full CI wavefunction can be written in an exponential form as

\[ |\Psi\rangle = \exp \left( \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_N \right) |\Phi_0\rangle \]  

(1–55)

where the \( \hat{T}_n \) excitation operators are have the same form as the CI excitation operators, namely

\[ \hat{T}_1 |\Phi_0\rangle = \sum_{ia} t_i^a |\Phi_i^a\rangle \]
\[ \hat{T}_2 |\Phi_0\rangle = \sum_{i<j,a<b} t_{ij}^{ab} |\Phi_{ij}^{ab}\rangle \]
\[ \hat{T}_N |\Phi_0\rangle = \sum_{i<j<k\ldots,a<b<c\ldots} t_{ijk\ldots}^{abc\ldots} |\Phi_{ijk\ldots}^{abc\ldots}\rangle \]  

(1–56)

(1–57)

With the excitation operators contained in the exponential, products of excitations occur yielding independent higher excitations

\[ \hat{T}_1 \hat{T}_1 |\Phi_0\rangle = \sum_{ia} \sum_{jb} t_i^a t_j^b |\Phi_0\rangle \leftrightarrow |\Phi_{ij}^{ab}\rangle. \]  

(1–58)
This offers rapid convergence to the Full CI energy for any truncation of the $\hat{T}_n$ operators. Truncating at double excitations, $\text{expt}(\hat{T}) = \text{expt}(\hat{T}_1 + \hat{T}_2)$ corresponds to the CCSD model. To demonstrate the fast convergence, the CI coefficients can be decomposed into these cluster amplitudes as

\begin{align*}
\hat{C}_1 &= \hat{T}_1 \\
\hat{C}_2 &= \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 \\
\hat{C}_3 &= \hat{T}_2 \hat{T}_1 + \frac{1}{3!} \hat{T}_1^3 \\
\hat{C}_4 &= \frac{1}{2} \hat{T}_2^2 + \frac{1}{2} \left( \hat{T}_2 \hat{T}_1^2 + \hat{T}_1 \hat{T}_2 \right) + \frac{1}{4!} \hat{T}_1^4
\end{align*}

Truncating to doubles in the CC model incorporates independent higher excitations that CI clearly does not contain in the truncated space. The inclusion of these independent higher excitations makes CC theory size extensive for any truncation. CC theory also has the property of orbital invariance in the occupied-occupied and virtual-virtual spaces and inclusion of higher excitations converges to the Full CI energy.

The Schrödinger equation with the CC ansatz is

\begin{align*}
\hat{H}|\Psi\rangle &= E|\Psi\rangle \\
\hat{H}e^T|\Phi_0\rangle &= E e^T|\Phi_0\rangle.
\end{align*}

Projection onto the reference space defines the CC energy expression

\begin{align*}
\langle \Phi_0|\hat{H}|\Psi\rangle &= E \langle \Phi_0|\Psi\rangle \\
\langle \Phi_0|\hat{H}|\Psi\rangle &= E \\
\langle \Phi_0|\hat{H}e^T|\Phi_0\rangle &= E
\end{align*}

where intermediate normalization was used. Complications arise when attempting to determine the $\hat{T}$ amplitudes. Projecting Equation (1–63) onto the excited determinants
The orthogonality of the excited basis vectors was used to get to Equation (1–70) from Equation (1–69). The energy dependent terms can all be eliminated by a careful analysis of the equations, and restricting the contractions between \( \hat{H} \) and \( \hat{T} \) to only those that are connected.

**Traditional coupled-cluster theory.** A more transparent way to see the removal of the energy in the amplitude equations is to left project Equation (1–63) by \( e^{-\hat{T}^\dagger \hat{H} \hat{T}} \),

\[
e^{-\hat{T}^\dagger \hat{H} \hat{T}} |\Phi_0\rangle = E_{CC} e^{-\hat{T}^\dagger \hat{H} \hat{T}} |\Phi_0\rangle
\]

\[
= E_{CC} |\Phi_0\rangle
\]

This similarity transformation does not change the energy eigenvalue spectrum of \( \hat{H} \) but it does break the hermiticity of the equation, and \( E_{CC} \) is no longer an upper bound to the exact energy. It is still guaranteed to converge to the Full CI energy if no truncation is made. Since the reference determinant is orthogonal to all excited determinants, the amplitude equations become

\[
\langle \Phi_{ijk\ldots} | e^{-\hat{T}^\dagger \hat{H} \hat{T}} |\Phi\rangle = E_{CC} \langle \Phi_{ijk\ldots} |\Phi_0\rangle
\]

\[
= 0.
\]

This is the traditional way the CC equations are solved [15]. Truncation of the \( \hat{T} \) operators defines the projection space, the amplitude equations are solved, and the energy is calculated finally. The new similarity transformed Hamiltonian can be expanded into a series of nested commutators between \( \hat{H} \) and \( \hat{T} \) using the Baker-Campbell-Hausdorff formula [15] leaving only terms that contain contractions.
between $\hat{H}$ and $\hat{T}$, or connected terms

$$e^{-\hat{T}}\hat{H}e^{\hat{T}} = \left(\hat{H}e^{\hat{T}}\right)_C \equiv \bar{H}$$  \hspace{1cm} (1–75)

with the subscript “C” referring to connected terms only. Consequently, we can subtract out the reference energy from the beginning and obtain a direct expression for the correlation energy

$$E_{\text{corr}} = \langle \Phi_0 | \left(\left(\hat{H}e^{\hat{T}}\right)_C - E_0\right) | \Phi_0 \rangle$$  \hspace{1cm} (1–76)

$$= \langle \Phi_0 | \bar{H}_N | \Phi_0 \rangle$$  \hspace{1cm} (1–77)

Due to the presence of excitation operators, $\hat{T}_m$, with a particle rank (or excitation number $m$) greater than 1, the similarity transformed Hamiltonian contains one- and two-body operators, but also three-, four-, and higher body operators

$$\bar{H} = \bar{T}^p_0 + \bar{W}^{pq}_{rs} + \bar{H}_{^{pq}_{rs}} + \bar{V}^{pqrs}_{tuvw} + \cdots,$$  \hspace{1cm} (1–78)

which are formed from the connected tensor contractions between the bare Hamiltonian and the cluster amplitudes. In matrix form, in the basis containing the ground, single, double, triple, etc \ldots (0, S, D, T, \ldots),

$$\begin{bmatrix}
\bar{H}_{00} & \bar{H}_{0S} & \bar{H}_{0D} & \bar{H}_{0T} & \cdots \\
0 & \bar{H}_{SS} & \bar{H}_{SD} & \bar{H}_{ST} & \cdots \\
0 & \bar{H}_{DS} & \bar{H}_{DD} & \bar{H}_{DT} & \cdots \\
0 & \bar{H}_{TS} & \bar{H}_{TD} & \bar{H}_{TT} & \cdots \\
\vdots & \vdots & \vdots & \vdots & \ddots
\end{bmatrix}$$  \hspace{1cm} (1–79)

The $\bar{H}$ matrix is clearly not hermitian and therefore $\bar{W}^{pq}_{rs} \neq \bar{W}^{rs}_{pq}$. This doubles the storage requirements. Also, the three- and higher body matrix elements should never be stored, and are typically not stored, but rather computed on the fly when needed.
Another consequence of the non-hermiticity of $\bar{H}$ is that the functional form has left and right hand biorthogonal eigenvectors which yield the same eigenvalue. Therefore the CC energy functional has the general form

$$E_{CC} = \langle \Phi_0 | L \bar{H} R | \Phi_0 \rangle$$  \hspace{1cm} (1–80)

For the ground state, $L = (1 + \hat{\Lambda})$ and $R = 1$, leaving the ground state energy functional as

$$E_{CC} = \langle \Phi_0 | (1 + \hat{\Lambda}) \bar{H} | \Phi_0 \rangle$$  \hspace{1cm} (1–81)

$$= \langle \Phi_0 | \bar{H} | \Phi_0 \rangle + \langle \Phi_0 | \hat{\Lambda} \bar{H} | \Phi_0 \rangle$$  \hspace{1cm} (1–82)

$$= \langle \Phi_0 | \bar{H} | \Phi_0 \rangle + 0$$  \hspace{1cm} (1–83)

The $\hat{\Lambda}$ operator is a deexcitation operator, similar to the $\hat{T}$ operator; consequently

$$\langle \Phi_0 | \hat{\Lambda} \bar{H} | \Phi_0 \rangle = \langle \Phi_0 | \hat{\Lambda} (P + Q) \bar{H} | \Phi_0 \rangle$$  \hspace{1cm} (1–84)

$$= \langle \Phi_0 | \hat{\Lambda} P \bar{H} | \Phi_0 \rangle + \langle \Phi_0 | \hat{\Lambda} Q \bar{H} | \Phi_0 \rangle$$  \hspace{1cm} (1–85)

$$= \langle \Phi_0 | \hat{\Lambda} | \Phi_0 \rangle \langle \Phi_0 | \bar{H} | \Phi_0 \rangle + \sum_i \langle \Phi_0 | \hat{\Lambda} | \Phi_i \rangle \langle \Phi_i | \bar{H} | \Phi_0 \rangle$$  \hspace{1cm} (1–86)

$$= 0 \cdot \langle \Phi_0 | \bar{H} | \Phi_0 \rangle + \sum_i \langle \Phi_0 | \hat{\Lambda} | \Phi_i \rangle \cdot 0$$  \hspace{1cm} (1–87)

$$= 0.$$  \hspace{1cm} (1–88)

In the above equation, an insertion of a resolution of the identity,

$$1 = P + Q = |\Phi_0 \rangle \langle \Phi_0 | + \sum_i | \Phi_i \rangle \langle \Phi_i |,$$  \hspace{1cm} (1–89)

was performed, where index $i$ corresponds to excited determinants. The second term corresponds to the amplitude equations, which have been shown to be 0. In general, the $P$ and $Q$-spaces can be defined, or partitioned, to suit the problem. This generalized energy functional will be used later for the computation of excited, ionized, and electron
attached states. To compute perturbative triples effects the $P$ and $Q$-spaces will be partitioned differently.

**Variational coupled-cluster theory.** The Schrödinger equation has the property that for any trial wavefunction $|\tilde{\Psi}\rangle$, the energy obtained from the expectation value of the Hamiltonian

$$\frac{\langle \tilde{\Psi}|\hat{H}|\tilde{\Psi}\rangle}{\langle \Psi|\Psi\rangle} = E_0,$$

is necessarily an upper bound the the exact energy obtained from the exact wavefunction.

$$E_0 \geq E$$

This *variational principle* [4] follows from the fact that the Hamiltonian operator is positive semi-definite [3]. This property of the Hamiltonian is lost with the similarity transformation in Equation (1–75), breaking this variational condition. This is not usually a terrible problem, since for problems sufficiently described with a single determinant, the non-variational, or perturbative traditional coupled cluster method converges rapidly to the correct answer.

Keeping this variational condition in CC theory requires

$$E_{\text{VCC}} = \frac{\langle \Phi_0|e^{T\dagger}\hat{H}e^T|\Phi_0\rangle}{\langle \Phi_0|e^{T\dagger}e^T|\Phi_0\rangle}$$

$$= \langle \Phi_0|\left(e^{T\dagger}\hat{H}e^T\right)_c|\Phi_0\rangle,$$

where the numerator was factorized to leave only connected terms. [16] In the limit of no truncation, this is equivalent to the traditional CC method. The connected form of Equation (1–93) does not terminate and must be truncated at judiciously chosen, predefined orders. [17]

Variational CC limited to single substitutions (VCCS) is a special case as it corresponds to Hartree-Fock theory via Thouless’ Theorem. [18, 19] Thouless’ theorem states that the Hartree-Fock ground state determinant can be written as a rotation of any
arbitrary single reference determinant

\[ |\Phi_0\rangle = e^{\hat{T}_1}|\tilde{\Phi}_0\rangle. \]  (1–94)

The Hartree-Fock energy can be written as

\[ E_{HF} = \langle \tilde{\Phi}_0 | \left( e^{\hat{T}_1 \hat{H} e^{\hat{T}_1}} \right) C | \tilde{\Phi}_0 \rangle \]  (1–95)

Recently, a general algorithm for determining the VCCS amplitudes was presented by Simunek and Noga [20]. The central idea, as more detailed equations will be presented in Chapter 2, is to construct the VCCS density as the sum of a reference density and relaxation corrections to it

\[ D(t, t^\dagger)_{pq} = \sum_i \delta_{pi} \delta_{iq} + \langle \tilde{\Phi}_0 | \left( e^{\hat{T}_1 \{ p^\dagger q \} e^{\hat{T}_1}} \right) C | \tilde{\Phi}_0 \rangle. \]  (1–96)

Since the density is a function of the \( t^a \) amplitudes the Fock energy equation can be minimized with respect to the amplitudes as

\[ \frac{\delta E}{\delta t^a} = \sum_{pq} F_{pq} \frac{\delta D(t, t^\dagger)_{qp}}{\delta t^a} = 0. \]  (1–97)

This gives rise to a transformation matrix that enforces the generalized Brillouin condition and yields an updated \( t \) vector that is used to construct the next iteration density matrix.

This is rather nice as it avoids the serial diagonalization of Hartree-Fock theory discussed in the preceding section in favor of very fast matrix multiplications. It does need a sufficiently close starting guess though, which in most cases to date have been lower level Hartree-Fock calculations [20] or a few SCF iterations in the same basis set [21]. The former may not converge in all cases, and the latter only reduces the problem of serial diagonalization, and does not eliminate it.

**Formal scaling.** Typically, the formal scaling of CC methods truncated to excitations of \( m \), is given as \( \sim n^m_o n^{m+2}_v \), with \( n^m_o n^m_v \) storage for the amplitudes. Very
often, in molecular calculations, the number of virtual orbitals is much greater than the number of occupied orbitals. Consequently, the rate-determining step is the virtual MO contraction

\[
\sum_{c,d} \langle ab||cd \rangle t_{ijkl\cdots}^{abcd\cdots} \rightarrow t_{ijkl\cdots}^{abcd\cdots} \quad (1-98)
\]

The fastest algorithms for this contraction are done using the AO basis, where the integrals are computed on-the-fly. The \{c, d\} indices of the \( \hat{T} \) amplitudes are backtransformed and contracted with the AO two-electron integrals. This can be performed with independent blocks of the arrays distributed over processors.

In practical calculations, CCSD performs quite satisfactorily. A perturbative triples extension, CCSD(T), (non-iterative) is considered the “gold-standard” of computational methods, often obtaining very reliable thermochemical quantities of interest in experimental chemistry. This method constructs an approximate \( \hat{T}_3 \) vector from \( \hat{T}_2 \) and the two-electron integrals

\[
t_{ijk}^{abc[2]} = P(a/bc)P(k/ij) \sum_d t_{ij}^{ad}(bc||dk) - P(i/jk)P(c/ab) \sum_l t_{il}^{ab}(cl||jk) \quad (1-99)
\]

with superscript \([2]\) indicating it is a perturbative approximation, and the \( P(p/qr) \) operator defined by its action on an array

\[
P(p/qr)\bigcup(pqr\cdots) = (1 - P(pq) - P(pr))\bigcup(pqr\cdots) = \bigcup(pqr\cdots) - \bigcup(qpr\cdots) - \bigcup(rqp\cdots) \quad (1-100)
\]

As a result, it is often not necessary to go beyond these approximate triple excitations for molecules in the ground state near the equilibrium geometry. This method scales as \( n_o^2n_v^4 + n_v^6n_o^3 \) as evident from the amplitude equation. It can be implemented in a parallelizable way, and represents an economical route towards benchmark accuracy. Any inclusion of higher excitations becomes unfeasible very fast.
1.4 Exploring More Sectors of Fock Space

The previous methods were formulated in the $N$-electron Hilbert space. A generalization of the Hilbert space to include any number of electrons is called Fock space. [22] To begin exploring more sectors of Fock space (electron ionized, attached or excited sectors) a generalization of CC theory is necessary. [15, 23] Rather elegantly, other sectors of Fock space are generated with an operator acting on the ground state wavefunction to create the state of interest. The state of interest, $|\Psi_k\rangle$, is created as

$$|\Psi_k\rangle = \hat{R}_k|\Psi_0\rangle = [|\Psi_k\rangle\langle\Psi_0|] |\Psi_0\rangle \quad (1-101)$$

To determine the exact structure of $\hat{R}$, we begin with the following energy equations

$$\hat{H}|\Psi_0\rangle = \hat{H}e^\dagger|\Phi_0\rangle = E_0 e^\dagger|\Phi_0\rangle \quad (1-102)$$
$$\hat{H}|\Psi_k\rangle = \hat{H}\hat{R}_k|\Psi_0\rangle = \hat{H}\hat{R}_k e^\dagger|\Phi_0\rangle = E_k \hat{R}_k e^\dagger|\Phi_0\rangle \quad (1-103)$$

Left projection with $\exp(-\hat{T})$ followed by commuting $\hat{R}$ with $\hat{T}$ yields

$$\hat{H}|\Psi_0\rangle = E_0|\Phi_0\rangle \quad (1-104)$$
$$\hat{H}|\Psi_k\rangle = \hat{H}\hat{R}_k|\Phi_0\rangle = E_k \hat{R}_k|\Phi_0\rangle \quad (1-105)$$

Finally, multiplying Equation (1–104) on the left with $\hat{R}_k$ and subtracting the two yields

$$\bigl[\hat{H}, \hat{R}_k\bigr]|\Phi_0\rangle = \Delta E_k \hat{R}_k|\Phi_0\rangle \quad (1-106)$$
$$\bigl(\hat{H}\hat{R}_k\bigr)_c|\Phi_0\rangle = \omega_k \hat{R}_k|\Phi_0\rangle \quad (1-107)$$

which is an eigenvalue equation for $\omega_k$ with the eigenvectors, $\hat{R}_k|\Phi_0\rangle$. This formulation is completely general. In fact, the only difference between Equation (1–107) for all states is the sectors of $\hat{H}$ used in the matrix diagonalization. For instance, building $\hat{H}$ in the particle-hole (ph), particle-particle-hole-hole (pphh), etc. . . sectors (ie. singly, doubly, etc. . . ) yields the excitation energy equation of motion coupled cluster method (EE-EOM-CC). [24, 25] Furthermore, the p, pph, . . . and h, phh, . . . , correspond to the
ionization potential (IP-EOM-CC) [24, 26, 27] and electron attachment (EA-EOM-CC) [28, 29] variants. In fact, all sectors are available, allowing the study of multiply ionized and attached states (MI/MA-EOM-CC), [30] however the formal scaling increases by factors of $n^1_o$, $n^1_v$, and $n^1_o n^1_v$ for each additional electron ionization, attachment, and excitation, respectively.

For large molecular systems, the EOM-CC methods are limited to single and double substitutions (EOM-CCSD) for computational tractability. In some cases, triple excitations are necessary to accurately characterize excited state energies. [31–33] These higher excitations can be added perturbatively, similar to the ground state derivation of CCSD(T). [15] This will be explored in detail in Chapter 4.

1.5 Implementation in Robust Computer Codes

*Ab initio* quantum chemistry would be of little use in practical real-world chemical applications without the use of today's powerful computer systems and architectures. The computational requirements of the aforementioned methods are determined by the scaling of the method as a function of the size of the atomic orbital basis set describing the molecular orbitals, the number of electrons in the system, and the corresponding charge and spin multiplicity. Even for the simplest method, the independent-particle model, the requirements can increase rapidly and must be mapped into sufficiently fast and robust computer code. With the development of fast traditional computer processor units (CPU), graphical processing units (GPU), and parallel distribution over these resources, it seems appropriate to modify Dirac's quote as

It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed with sufficient parallelization strategies, which can lead to an explanation of the main features of complex atomic systems while properly distributing data over CPUs and/or GPUs to avoid too much 'direct' computation.

In this vein, a very successful solution to the massive parallelization necessary to describe relevant chemical phenomena with these methods is the ACESIII quantum
chemical software package. [34] ACESIII has been built to allow high-level CC
calculations on $O(100)$ electrons with $O(1,000)$ of basis functions through efficient
parallelization strategies to run on $O(10,000)$ to $O(100,000)$ compute cores, or
processors. [35] Currently, serial, or single processor jobs, are capable of only $O(10)$
of electrons with $O(100)$ basis functions, limiting the applicability of the program to
small molecules in, at best, moderately sized basis sets. The design philosophy is i) to
separate computer science oriented tasks from common quantum chemistry specific
tasks and ii) single floating point numbers are too small a data element to perform work
with or on and blocks of numbers should form the basic element that is passed between
processors and worked with or on.

**Separation of tasks.** To the quantum chemist, certain tasks are performed on
data arrays rather routinely. For example, many of the arrays in the aforementioned
many-body methods are divided by diagonal elements of the Fock operator. These are
called energy denominators. Conveniently, the super instruction architecture (SIA) of
ACESIII can handle these common tasks efficiently and easily through the use of a
*super instruction processor* (SIP). The SIP reads code written in ACESIII homebrew
high-level symbolic super instruction assembly language (SIAL, pronounced "sail"), and
executes super instructions. These are called “super instructions” because, using the
energy denominators as an example, the quantum chemist programs a rather simple
expression

```
PARDO a, i
    GET T1 (a, i)
    EXECUTE ENERGY_DENOMINATOR T1
ENDPARDO a, i
```

read by the SIP. The SIP loads the T1 array in the super instruction “ENERGY_DENOMINATOR”,
determines the block sizes and ranges of the array, and performs the energy denominator
as
\[ T_1(a, i) = \frac{T_1(a, i)}{\epsilon_i - \epsilon_a}. \] (1–108)

All data fetching, MPI message passing, etc . . . are performed “under the hood” allowing the quantum chemist to write very efficient computer code, without being dragged down by some of the more technical aspects of the computer science. In practice though, a hybrid approach generates the most efficient code, and a knowledge of how to write, use, and manipulate the super instructions is very beneficial.

**Distribution of data.** Rather than distributing the following 4 x 4 array of floating point numbers
\[
\begin{bmatrix}
x_{11} & x_{12} & x_{13} & x_{14} \\
x_{21} & x_{22} & x_{23} & x_{24} \\
x_{31} & x_{32} & x_{33} & x_{34} \\
x_{41} & x_{42} & x_{43} & x_{44}
\end{bmatrix}
\] (1–109)

one can distribute the following 2 x 2 array of floating point blocks
\[
\begin{bmatrix}
x_{11} & x_{12} \\
x_{21} & x_{22}
\end{bmatrix}
\] (1–110)
where block indices 1 and 2 contain simple indices \{1, 2\} and \{3, 4\}, respectively, yielding the \( \mathbf{X} \) arrays as

\[
\mathbf{X}_{11} = \begin{pmatrix}
    x_{11} & x_{12} \\
    x_{21} & x_{22}
\end{pmatrix}
\] (1–111)

\[
\mathbf{X}_{12} = \begin{pmatrix}
    x_{13} & x_{14} \\
    x_{23} & x_{24}
\end{pmatrix}
\] (1–112)

\[
\mathbf{X}_{21} = \begin{pmatrix}
    x_{31} & x_{32} \\
    x_{41} & x_{42}
\end{pmatrix}
\] (1–113)

\[
\mathbf{X}_{22} = \begin{pmatrix}
    x_{33} & x_{34} \\
    x_{44} & x_{34}
\end{pmatrix}
\] (1–114)

From the beginning, one already has a blocked space when working with molecular orbitals - occupied, \( \mathbf{O} \), and virtual \( \mathbf{V} \). This automatically forces \( \mathbf{OO} \), \( \mathbf{OV} \), \( \mathbf{VO} \), and \( \mathbf{VV} \) blocks of one-electron operator matrix elements; with a similar structure for two-electron operator matrices. However, when running computations with \( \mathcal{O}(10^2) \) to \( \mathcal{O}(10^3) \) basis functions, it is necessary to further subdivide these blocks to maximize parallelization and reduce the computational time.

For example, the rate determining step for a Hartree-Fock computation is building the Fock matrix, specifically, the \( \hat{J} - \hat{K} \) piece of the Fock operator,

\[
\sum_{\lambda\sigma} V_{\nu\lambda}^\mu P_{\lambda}^\sigma \rightarrow f_{\mu\nu}
\] (1–115)

For simplicity, assume, using 10 basis functions, this piece of the Fock build takes 1 second. With 100 basis functions, the ideal time is then 10,000 seconds, and with 1,000 basis functions the ideal time is 100,000,000 seconds. Now, assuming perfect parallelization, by blocking 100 basis functions in to 10 blocks of 10 basis functions each, distributed perfectly such that each processor is operating on 1 block (100
processors), then ideally, this would take 1 second. The same follows for the 1,000 basis function example.

In practice, however, since quantum chemistry is extremely data intensive (large formal scaling of developed methods), the computations are performed on less than the “ideal” number of processors and each processor has an assortment of independent data blocks. As a measure of performance though, if one doubles the number of CPUs in a computation, one hopes to see a factor of 2 reduction in computing time, and so on and so forth. The ideal limit of an $x$-fold increase in CPUs to an $x$-fold decrease in time is “linear scaling”. Factors including the proximity of processors to one another, the potential imbalance of CPU speed compared to one another, data input (reading) and output (writing) to disk (I/O), and access to memory can play important roles in attaining, or falling short of, linear scaling.

The question then arises as to why not distribute the floating point numbers across as many processors as are available. The aforementioned communication and data/messaging passing factors take considerable time to perform. With poorly written code, or the use of very small data elements, one could be waiting longer for data passing and access rather than actual computation. ACESIII software performs operations with blocks of numbers, and during those operations it is simultaneously passing information to and from CPUs, effectively hiding communication under work. Ideally, block sizes are chosen such that all communication adds “zero” time to the computation. The only time is that of the actual block computing operations themselves. In practice, block sizes are chosen to allow for maximum benefit of this capability.

As a demonstration, the following is psuedo code for a serial computation using Equation (1–115)

\[
\text{DO } \mu = 1, \text{ Number of basis functions} \\
\text{DO } \nu = 1, \text{ Number of basis functions} \\
\text{FOCK } (\mu, \nu) = 0.0
\]
The $O(N^4)$ scaling is seen explicitly. In ACESIII sial code, this is implemented as

```plaintext
PARDO $\mu$, $\nu$, $\lambda$, $\sigma$
  REQUEST $V(\mu,\nu,\lambda,\sigma)$
  GET $P(\lambda,\sigma)$
  $T_{xx}(\mu,\nu) = V(\mu,\nu,\lambda,\sigma) \times P(\lambda,\sigma)$
  FOCK $(\mu,\nu) += T_{xx}(\mu,\nu)$
ENDPARDO $\mu$, $\nu$, $\lambda$, $\sigma$
```

The REQUEST and GET commands correspond to retrieving data stored on disk and in memory, respectively. Each processor is assigned block indices and performs the contraction over this data retrieval as

```plaintext
DO $\mu = \mu_a$, $\mu_b$
DO $\nu = \nu_a$, $\nu_b$
  DO $\lambda = \lambda_a$, $\lambda_b$
  DO $\sigma = \sigma_a$, $\sigma_b$
    $T_{xx}(\mu,\nu) = V(\mu,\nu,\lambda,\sigma) \times P(\lambda,\sigma)$
    FOCK $(\mu,\nu) += T_{xx}(\mu,\nu)$
  ENDDO $\sigma$
  ENDDO $\lambda$
ENDDO $\nu$
```
The indices $\mu_a, \mu_b, \ldots$, are the simple indices contained in the block $\mu$ of size $|\mu_b - \mu_a|$, and each processor has different values for these allowing for the massive parallelizability of ACESIII software.

The programs developed in this work have been implemented with this structure in ACESIII. I demonstrate the performance of the implemented methods with scaling curves, timings, and at times, I let the size of the systems under investigation speak for themselves concerning performance.

1.6 Outline of this Study

In the next three chapters I will discuss accurate \textit{ab initio} techniques used to gain insight into chemical processes. The main focus of this work is the expedient calculation of total energies, properties, and geometries with very high accuracy either through “round-about” methods or direct massively parallelized algorithms. In Chapter 2, I describe a well-known and used formally exact procedure for decoupling the four-component Dirac equation in an order-by-order scheme and the implementation of this Douglas-Kroll-Hess transformation in the ACESII and ACESIII program packages. This transformation allows a significant time savings compared to the full Dirac equation, but until now has not been systematically tested with post Hartree-Fock methods, specifically for core ionizations.

In Chapter 3, I develop a method that captures the independent particle effect of orbital relaxation to infinite order in a direct fashion and apply it specifically to core ionizations, although it can be applied to electron excited and attached states. In contrast, currently, full orbital relaxation can only be incorporated in the Full CI (or Full CC) limit (along with correlation), or by indirect means that are unwieldy to use in practice. The proposed method scales as $N^4$, and is clearly a tremendous benefit over the Full CI, or perturbative approximations with higher excitations in CC theory, although it is state specific.
Having developed and implemented schemes to efficiently obtain the interesting quantities in core ionizations I depart and focus on massively parallel implementations of EOM-CC theory. With the age of serial computing coming to an end, it is critical to the field to push these accurate CC methods further through the use of modern computer architectures. I rederive, in a different light, a perturbative treatment of triple excitations within EE-EOM-CCSD theory and present results on systems current programs can not begin to do in Chapter 4. After finding interesting results for nucleobase systems in DNA, I discuss gradient theory for EOM-CCSD, and discuss the parallel implementation. Scaling curves and demonstrable systems are presented to define the new benchmark of system sizes with CC theory.
CHAPTER 2
DECOUPLING THE DIRAC EQUATION FOR MEAN FIELD COST APPLIED TO CORE IONIZATIONS

2.1 Preliminaries

The mutual relationship that exists between theory and experiment has never been more evident than when electron binding energies, or ionization potentials (IPs), are involved. The orbital picture, or shell model, is the foundation for our conceptual understanding of the electronic structure of atoms and molecules. By approximating the \( N \)-electron wavefunction as a product of double and singly occupied orbitals, for spin restricted and unrestricted systems, one immediately obtains a basis for a quantitative understanding of the ionization process.

Experimentally, principal ionization energies can be measured using X-Ray Photoelectron Spectroscopy (XPS), originally developed by Siegbahn et. al [36, 37] primarily for core orbitals, Ultraviolet Photoelectron Spectroscopy (UPS) techniques for the valence states [38], and even X-ray two-photon photoelectron spectroscopy for double core ionizations [39]. These experiments offer quantitative structural information when paired with a sufficiently accurate theoretical method, and can therefore capture a molecule’s fingerprint, determine the structure of chemical species, and verify proposed mechanisms of chemical reactions [40–45].

How accurate is “sufficiently accurate” [46]? If we consider core electrons, we see chemical shifts of up to 5 eV [26] for electrons in different environments due to the primarily, but not totally, atomic character of the core orbital. This is within the error range of the most accurate and practically useful methods today. Separating the relativistic, relaxation, and correlation contributions will allow a systematic study aimed at revealing the deficiencies of these methods. In this Chapter, I discuss the implementation of the Douglas-Kroll-Hess transformation to study the scalar-relativistic effects in core ionization processes for organic molecules, where spin-orbit is assumed to be small, with CC theory. We also study the breakdown of including only scalar-relativistic
effects for core ionizations in heavy atoms and highly stripped ions with the goal of finding an expedient route towards accurate answers for systems where relativistic effects are non-negligible.

We begin with the equation of motion coupled cluster theory for ionization potentials limited to single and double substitutions (IP-EOM-CCSD) [24–27]. IP-EOM-CCSD is an efficient and accurate method to compute single ionization energies of molecules. It is a direct method, needing only the $N$-electron reference function and corresponding coupled cluster solutions, and applicable to the entire spectrum as a single calculation via diagonalization of $\hat{H}$ (“H-bar”), [15] from traditional CC theory, in the hole and particle-particle-hole sectors defined in Chapter 1.

Many valence ionizations for molecules and ions have been studied and benchmarked with this method, but systematic studies for mid-valence and inner-shell ionizations are far fewer. [29, 47, 48]. The mid-valence region can be notoriously difficult to obtain quantitative accuracy due to the balance needed between correlation, relaxation, and relativistic effects. The inner-shell electrons are also difficult to get correct due to the exceedingly large relaxation and potentially large relativistic effects present as I will show.

IP-EOM-CCSD can incorporate a significant amount of relaxation because of the inclusion of the linear, single excitation operator, $\hat{R}_x$. [29] Of course, the ground state solution is correlated within this framework as well. It can not, however, include relativistic effects. These must be included at the independent particle level of approximation for incorporation into the calculation.

A very successful method that has been used recently to add scalar-relativistic effects is the Douglas-Kroll-Hess (DK) transformation. [49, 50] This transformation seeks to decouple the positive and negative energy solutions of the Dirac equation by block diagonalizing the one-electron operators in an order by order unitary transformation in momentum space. This allows one to focus on the relevant, positive energy solutions.
It also converges rapidly due to large denominators present in momentum space. [49] Interestingly, the first-order transformation drastically overestimates the scalar-relativistic effects, the second-order transformation then over-shoots the exact scalar-relativistic effects, the third-order transformation brings the energetics on track, and the fourth and fifth-order transformations essentially irons out the wrinkles, converging the potential. This result is rather well-known, [50–52] and is the reason I implemented the DK transformation to fifth-order, even though there are infinite order techniques for exact decoupling. [53]

For total energies of highly charged one-electron ions, the fifth-order scalar-relativistic DK transformation provides quantitative accuracy compared to using the full Dirac Hamiltonian for systems up to $Z = 100$. [49] These are excellent test systems because there are no spin-orbit effects and in principle, will converge to the exact Dirac limit, as they have no two-electron term, which is ignored in the DK transformation.

To really test the limits of the fifth-order DK transformation with respect to total energies, Wolf and Reiher [49] have applied the the fifth-order method to many electron atoms including neutral and singly charged silver, $\text{Ag}^0$ and $\text{Ag}^+$, and neutral and singly charged gold, $\text{Au}^0$ and $\text{Au}^+$. These systems demonstrate the effectiveness of the DK method since they contain non-negligible spin-orbit effects, due to their size and nuclear charge, and contain more than one electron. The different properties of gold as compared to silver, including its characteristic shiny color, is actually due to relativistic effects, and therefore is a great fundamental test for approximate relativistic methods. For the silver systems, the fifth-order DK transformation very accurately reproduced the total energy compared to full 4-component Dirac-Fock-Coulomb calculations for the neutral and cation. The non-relativistic energy for $\text{Ag}^0$ is roughly 117 a.u. in error! The HOMO energy of the neutral silver atom was compared to the computed ionization energy $\omega = E(\text{Ag}^+) - E(\text{Ag}^0)$ and shown to be very consistent, being in error by only 0.1 eV. The non-relativistic total energy of $\text{Au}^0$ was in error of the fully relativistic result
by 1,174 a.u. The scalar-relativistic effects reduced that error to 27 a.u. The difference between the Koopmans' value and the $\Delta E$ value for the ionization energy is only 0.3 eV.

Clearly, the DK transformation provides an excellent starting point for correlated calculations, in particular IP-EOM-CCSD. Recently, these two methods have been merged, [54, 55] to compute the valence ionization energies of systems containing heavy atoms. Benchmark results, agreement with experiment under 1 kcal mol$^{-1}$, were obtained for the valence ionization energies under investigation after including spin-orbit effects. This is not surprising when one looks at the valence ionization energies obtained by Wolf and Reiher for silver and gold. [49]. However, application to core ionization energies is non-existent.

There are studies concerning the core ionization energies of molecules, [39, 56, 57] however, these employ different Hamiltonians including scalar-relativistic effects and use different methods, most notably propagator methods, to compute the core IP. By examining the convergence of the DK potential, we definitively benchmark the scalar-relativistic effects in the core IPs of organic molecules and demonstrate they are necessary to obtain accurate energies. We also apply the IP-EOM-CCSD/DK method to increasingly heavy noble gases to determine its breaking point. Our final test is on highly stripped ions, which are relevant in plasma research. [58]

### 2.2 Theory

The relativistic extension of the Schrödinger equation was realized by Dirac [1] in attempting to treat both space and time symmetrically using Einstein's relation [2]

$$H = \left( c^2 p^2 + m^2 c^2 \right)^{1/2}$$

(2–1)
By writing the expression in the square root as a perfect square, we can obtain a Hamiltonian that is linear in space and time

\[ \hat{H}_D = c \alpha \cdot p + (\beta - 1)mc^2 \]  
\[ = \begin{pmatrix} mc^2 I_2 & c \sigma \cdot p \\ c \sigma \cdot p & -mc^2 I_2 \end{pmatrix} \]  

where \( I_2 \) is a 2 x 2 identity matrix and \( \sigma \) are the Pauli spin matrices \( \{\sigma_x, \sigma_y, \sigma_z\} \)

\[ \sigma = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \hat{x} + \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \hat{y} + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \hat{z} \]

The Dirac Hamiltonian, \( \hat{H}_D \), is a 4 x 4 matrix and, consequently, acts on a four-component (4-component) Lorentz spinor, \( \phi \), with upper \( (\phi^L) \) and lower \( (\phi^S) \), for large (positive) and small (negative) components, respectively. By adding the electron-nucleus coulomb potential, \( \hat{V} \), the one-electron Dirac equation is

\[ \begin{pmatrix} (\hat{V} + mc^2)I_2 & c \sigma \cdot p \\ c \sigma \cdot p & (\hat{V} - mc^2)I_2 \end{pmatrix} \begin{pmatrix} \phi^L \\ \phi^S \end{pmatrix} = E \begin{pmatrix} \phi^L \\ \phi^S \end{pmatrix} \]  

For large molecular systems, the Dirac equation becomes computational infeasible. The goal then, is to decouple the large and small components to obtain relativistic effects with standard mean-field scaling

\[ \hat{H}_{bd} = U \hat{H}_D U^\dagger = \begin{pmatrix} h_+ & 0 \\ 0 & h_- \end{pmatrix} \]  

By defining a matrix \( X \) that relates the large component to the small component,

\[ \phi^S = X \phi^L \]
then the unitary matrix can be written
\[
U = U(X) = \begin{pmatrix}
(1 + X^\dagger X)^{-1/2} & (1 + X^\dagger X)^{-1/2}X^\dagger \\
(1 + XX^\dagger)^{-1/2}X & (1 + XX^\dagger)^{-1/2}
\end{pmatrix}
\] (2–8)

and the upper diagonal block of the Dirac Hamiltonian is given as
\[
h_+ = \frac{1}{\sqrt{1 + X^\dagger X}} \left( V + c \sigma \cdot p X + X^\dagger c \sigma \cdot p + X^\dagger (V - mc^2) X \right) \frac{1}{\sqrt{1 + X^\dagger X}}
\] (2–9)

However, an analytical energy-independent \( X \) matrix is not known. Consequently, a few techniques have been developed that attempt to solve for this. Numerical procedures have been implemented by Barysz, Sadlej, and Sniders (BSS transformation) [59, 60] with some success. Though, an analytical expression is more desirable. In that spirit, zeroth and first order regular approximations (ZORA and FORA) have been derived and implemented [61] and extended to infinite order (IORA) generalizations by Dyall and Lenthe [62]. These methods expand \( X \) in Equation (2–7) in powers of \( 1/c \), creating an effective Hamiltonian matrix. [63] In the limit, these methods are not exact and have associated error. In practice, however, the ZORA and FORA methods perform quite satisfactory after scaling the total energy expressions. [61, 64–66]

Another way to block-diagonalize the Dirac Hamiltonian is to choose a suitable unitary transformation order-by-order
\[
\hat{H}_{bd} = U\hat{H}_D U^\dagger
\] (2–10)
\[
= \cdots U_4^\dagger U_3^\dagger U_2^\dagger U_1^\dagger \hat{H}_D U_0 U_1 U_2 U_3 U_4 \cdots
\] (2–11)
\[
= \begin{pmatrix}
h_+ & 0 \\
0 & h_-
\end{pmatrix}.
\] (2–12)
The most general parameterization for $U_i$ can be written as a power series of an anti-hermitian operator $W$,

$$U_i = U_i(W_i) = a_{i,0}1 + \sum_{k=1}^{\infty} a_{i,k}W_i^k.$$  \hfill(2–13)

Then, the $n$-th order transformed Hamiltonian is given as

$$\hat{H}_n = U_{n-1}^i\hat{H}_{n-1}U_{n-1}$$ \hfill(2–14)

$$= \left[a_{(n-1),0}1 + \sum_{k=1}^{\infty} a_{(n-1),k}W_{n-1}^k\right]\hat{H}_{n-1}\left[a_{(n-1),0}1 + \sum_{k=1}^{\infty} a_{(n-1),k}W_{n-1}^k\right]$$ \hfill(2–15)

The zeroth-order transformation is the free-particle Foldy-Wouthuysen (fpFW) transformation [67], which is well-behaved and exact for free electrons. The zeroth order fpFW transformation matrix is [49]

$$U_0 = A_p(1 + \beta R_p)$$ \hfill(2–16)

with

$$A_p = \sqrt{\frac{E_p + mc^2}{2E_p}}, \quad E_p = \sqrt{p^2c^2 + m^2c^4}$$ \hfill(2–17)

$$R_p = \frac{c\alpha \cdot p}{E_p + mc^2} = R_p\alpha \cdot p.$$ \hfill(2–18)

This yields the first-order block-diagonalized Hamiltonian as

$$\hat{H}_1 = (\beta E_p - mc^2) + (A_p(V + R_p VR_p)A_p) + (\beta A_p[R_p, V]A_p),$$ \hfill(2–19)

with the last two terms corresponding to a diagonal ($D_1$) and off-diagonal ($O_1$) form, respectively with subscript $i$ denoting the order in $V$, the electron-nucleus potential. Note that the second term is actually

$$A_p(V + R_p VR_p)A_p = A_p(V + R_p \alpha \cdot p \alpha \cdot p R_p)A_p$$ \hfill(2–20)
and therefore requires AO integrals of the form

\[ \langle p \cdot Vp \rangle = \langle \phi_\mu | p \cdot Vp | \phi_\nu \rangle \] (2–21)

\[ = \langle p\phi_\mu | V | p\phi_\nu \rangle \] (2–22)

\[ = \langle \nabla \phi_\mu | V | \nabla \phi_\nu \rangle , \] (2–23)

or second derivative type integrals of the nucleus-electron potential energy. Note that these expressions are well-defined in momentum \((p\)-) space. The unitary transformation matrix is obtained by diagonalizing the kinetic energy AO integrals, yielding a diagonal representation for \( E_p \). Consequently, the transformation is performed in \( p \)-space, and back transformed to real space afterwards.

The DK transformation is the stepwise elimination of this lowest order in \( V \)
off-diagonal piece via a series of unitary transformations

\[ \mathcal{O}_1 = \beta A_p [R_p, V] A_p . \] (2–24)

As a brief aside, we can rewrite Equation (2–19) in a more transparent form, separating terms in orders of \( 1/c \),

\[ \hat{H}_1 = ( (\beta - 1)mc^2 ) + \left( V + \beta \frac{p^2}{2m} \right) + \left( -\beta \frac{p^4}{8m^3c^4} - [\alpha \cdot p, [\alpha \cdot p, V]] \right) . \] (2–25)

The first two terms of this FW expansion correspond to the rest energy of the electron and the non-relativistic result, respectively. The Darwin, mass-velocity, and spin-orbit coupling terms are contained in the last term, which can be recast to show this as

\[ \frac{1}{8m^2c^2} (\Delta V) - \beta \frac{p^4}{8m^3c^2} + \frac{1}{4m^2c^2} \Sigma \cdot [(\nabla V) \times p] , \] (2–26)

with \( \Sigma \) being the 4-component extension of the aforementioned Pauli matrices.
To remove this off-diagonal potential, $U$ is parameterized in the following way

$$
\hat{H}_{bd} = U\hat{H}_D U^\dagger = \cdots U_4^\dagger U_3^\dagger U_2^\dagger U_1^\dagger \hat{H}_1 U_1 U_2 U_3 U_4 \cdots
$$

(2–27)

$$
= \sum_i^\infty D_i
$$

(2–28)

$$
= \sum_i^\infty \begin{pmatrix} D_{i+} & 0 \\ 0 & D_{i-} \end{pmatrix} = \sum_i^\infty \begin{pmatrix} D_{i+}^{sf} + D_{i+}^{sd} & 0 \\ 0 & D_{i-}^{sf} + D_{i-}^{sd} \end{pmatrix}
$$

(2–29)

The spin free (one component) and spin dependent terms (two component) have been separated in the last term of Equation (2–29). We will focus only on the spin free terms, the scalar-relativistic piece, as this is what has been implemented.

Following the notation Wolf et. al [49], the spin-free DK$_n$ (up to $n = 5$) Hamiltonians are given as

$$
D_{2+}^{sf} = \frac{1}{2}[W_1, O_1]
$$

(2–30)

$$
D_{3+}^{sf} = \frac{1}{2}[W_1, [W_1, D_1]]
$$

(2–31)

$$
D_{4+}^{sf} = \frac{1}{8}[W_1, [W_1, [W_1, O_1]]] + \frac{1}{2}[W_2, [W_1, D_1]]
$$

(2–32)

$$
D_{5+}^{sf} = \frac{1}{2}[W_2, [W_2, D_1]] + \frac{1}{2}[W_2, [W_1, [W_1, O_1]]]
+ \frac{1}{2}[W_2, W_1 O_1 W_1] - \frac{1}{8}[W_1^2, [W_1^2, D_1]] + 0.14644661[[W_2, W_1^3], D_0]
$$

(2–33)

with, transparent for programming,

$$
D_0 = \beta E_p - mc^2
$$

(2–34)

$$
D_1(i, j) = A_i V_{ij} A_j + A_i R_j V_{ij} R_j A_j
$$

(2–35)

$$
W_1(i, j) = \beta \frac{O_1(i, j)}{E_i + E_j}
$$

(2–36)

$$
W_2(i, j) = \beta \frac{W_1(i, k) D_1(k, j) - D_1(i, k) W_1(k, j)}{E_i + E_k}
$$

(2–37)

The procedure then, is to diagonalize the kinetic energy AO integrals, transform the $\langle p \cdot V p \rangle$ integrals, compute $E_p$, $A_p$, and $R_p$, and construct the DK Hamiltonians (in
$p$-space) up to the desired order. Following its construction, the DK Hamiltonian is back transformed with the kinetic energy eigenvectors, resulting in the coordinate space representation of the scalar-relativistic Hamiltonian.

With no transformation of the electron-electron potential term, the final electronic DK Hamiltonian, up to order $n$, is

$$\hat{H}_{DKn} = \hat{T}_{DKn} + \hat{V}_{Ne}^{DKn} + \hat{V}_{ee}, \quad (2-38)$$

with the corresponding Fock operator

$$\hat{F} = \hat{T}_{DKn} + \hat{V}_{Ne}^{DKn} + J(r_1) - K(r_1). \quad (2-39)$$

Since the transformed quantities are independent of the orbitals, they only need to be computed once and stored at the beginning of the SCF procedure. When performing post-SCF computations, no changes need to be made to the code, since the MO coefficients and orbital energies are determined with the DK Hamiltonian (ie. the form of the Hamiltonian is unchanged, only the individual elements of the matrix are different).

### 2.3 Implementation

The DK transformation was implemented up to fifth order as a library and therefore is incorporated in the ACESII and ACESIII program packages. The DK main driver needs only the atomic orbital kinetic energy, nucleus - electron potential energy, and the DK specific $p \cdot Vp$ integrals, the corresponding array sizes (number of basis functions), and sufficient scratch space on input. The $p \cdot Vp$ integrals were implemented in the $vmol$ integral package.

In ACESII, the DK transformation has been implemented taking full advantage of the Abelian point group symmetry available in the program. Essentially, each irreducible representation of the one-electron hamiltonian is transformed to the desired order. ACESIII, however, does not include Abelian point group symmetry in its structure, so the entire integral arrays are transformed in one call. This is not really a problem since the
integral arrays are already stored statically on every processor and only have dimension of \( N_{AO} \times N_{AO} \). Since the transformation is a series of matrix multiplications, the scaling is always smaller than that of the SCF or correlated method and effectively adds no time to the computation.

The contraction coefficients and exponents for current general available basis sets \([7, 8]\) are optimized using non-relativistic methods. Consequently, these contracted basis sets are, at best, ill-suited to be applied with the DK transformation and either need to be reoptimized or uncontracted. Therefore, the pre-processing program, \( xjoda \), was modified with a new keyword to read in general contracted Gaussian basis functions, and uncontract them for the calculation. This is actually beneficial for the calculation for more than the aforementioned reasons. Contracted Gaussians typically contain large exponent primitives to represent Slater orbitals near the nucleus, and are “freed” when uncontracted to more accurately describe the region near the nucleus \([68]\) (i.e. more pronounced localization of core electrons near the nucleus). Also, it generates more functions to describe the molecular system, which are optimized during the SCF procedure.

### 2.4 Results and Discussion

For consistency the family of basis sets chosen for the investigated systems are the “Well-Tempered Basis sets” (WTBS) of Huzinaga \( et. \ al \) \([69, 70]\) These basis sets contain many primitives and are therefore sufficiently large enough to provide definitive results. They also contain very large exponent primitive functions to more accurately describe the region where relativistic effects are largest.

#### 2.4.1 Organic Molecules

The average scalar-relativistic stabilization gained with the DK potential for the different methods are shown in Figure 2-1. These are total energy differences to highlight the effect of the transformed potential on various methods to compute the correlation energy. The stabilization is relatively uniform across the tested correlated
methods, indicating the separability of the relativistic and correlation effects. In other words, the correlation energy is the same for the non-relativistic and relativistic potentials (for CCSD and beyond), even though the orbitals are very different.

Calculations were also performed with the uncontracted triple-$\zeta$ basis set, which does not include very tight primitive functions. This demonstrates the need for very tight basis functions near the nucleus, which are not included the cc-pCVTZ basis set. On average, this basis set overshoots the scalar-relativistic corrections as shown in Figure 2-1.

The DK transformation does not correct all core ionization potentials unidirectionally. A few select molecules are shown in Figure 2-2. There appears to be no a priori way to systematically determine when this would occur. Of the few that are destabilized, all but ammonia are organic compounds with a single oxygen - carbon monoxide, formaldehyde, and methanol. However, dimethylether (CH$_3$-O-CH$_3$) contains one oxygen and is stabilized, breaking this trend, and of course ammonia does not fit either.

The direct IP-EOM-CCSD ionization energy is, on average, always improved with a converged DK potential compared to experimental values, demonstrated in Figure 2-3. This is very encouraging as direct methods are more practical than their indirect analogues, and the DK method does not change the computational effort for these calculations. The indirect analogue, $\Delta E_{CCSD}$, though much better than IP-EOM-CCSD for reasons discussed in Chapter 3, is on average marginally worse with the DK5 potential.

### 2.4.2 Noble Gases

**Argon.** Argon is a good, simple starting point to assess the accuracy of IP-EOM-CCSD with a DK potential for neutral systems. There are three totally symmetric $m_s = 0$ shells and one experimentally detectable spin split $m_s = 1$ to $m_s = 1/2, 3/2$ shell. Direct comparison to experiment at the valence ($2p$) level is possible since the spin-orbit splitting between $2p_{1/2}$ and $2p_{3/2}$ is negligible. [71] Also, relativistic effects should be noticeable for the total energy and core orbital energies.
The convergence of the DK potential to fifth order for the SCF and correlation energies, Koopmans energy, and correlation contribution obtained with IP-EOM-CCSD is shown in Table 2-1. The potential is converged by third order, and therefore unambiguously demonstrates the utility of IP-EOM-CCSD. Clearly, the DK potential is necessary at the SCF level, stabilizing the non-relativistic result by 58.6 eV. The usual trend for the DK transformation is seen, first order overshoots the SCF, second order brings it back, and third order is essentially converged. The core orbital energies, where the transformed potential has the greatest impact, behaves the same way. Note that the sign is changed, since the ionization potentials are reported, rather than the orbital energies. The transformed potential has little effect on the correlated portion of the calculation with CCSD. The Koopmans’ ionization potentials, in particular the core, vary significantly from DK0 to DK1, and non-negligibly from DK1 to DK2, but the correlation energy and correlation contribution to the IP are essentially converged at first order.

Comparison of the ionization potentials with experiment are presented in Table 2-2. Koopmans’ IPs are presented to show the orbital shifts at each order in the transformed potential, which can be drastic as demonstrated in Table 2-1. Agreement with experiment is quite good with IP-EOM-CCSD for the entire spectrum at any order. This indicates that argon may not be the best example to study the limits of this computational combination. The valence level, though, worsens when including scalar-relativistic effects. We seem to be removing a source of fortuitous error cancellation between relaxation, correlation, and relativity for the valence shell.

Koopmans theorem is approximately 10 eV too high over the experimental $2p_{1/2}$ shell in the mid-valence region, but is remedied with IP-EOM-CCSD. It brings the IP within the range of the spin-orbit splitting from experiment. For the $2s$ electrons, the non-relativistic result is 1 eV closer to experiment than DK5; though this seems to be a lack of error cancellation between relativistic and relaxation effects, the latter not being described as fully. Relaxation and correlation in the $1s$ level alone is not sufficient to
quantitatively describe the ionization, though the DK5 result is not much better. The DK0 and DK5 result differ from experiment by 7.0 eV and 5.7 eV, respectively, showing a small improvement with a DK potential.

**Krypton.** The convergence of the DK potential up to fifth order for krypton is shown in Table 2-3. The same trends are seen for krypton as for argon except convergence is reached by fourth order. Only the valence $4p$ shell is converged with no relativistic effects. The remaining Koopmans’ IPs change drastically at lower orders and the SCF energy is stabilized by 986 eV at convergence. Again we see that the correlation energy and contribution to the IPs are less sensitive to the order of the potential, and are converged after first order for the mid-valence to valence shells, and second order for the core $s$ electrons.

Comparison with experiment is shown in Table 2-4. The Koopmans’ values are shown because the orbital shift caused by the DK potential is the driver for qualitative accuracy. The non-relativistic Koopmans’ and IP-EOM-CCSD result for the core orbital, where relativity should be most important, differ from experiment by 175.6 eV and 216.4 eV, respectively. The IP-EOM-CCSD result moves in the wrong direction. At fifth order, the two differ from experiment by $−78.7$ eV and $−29.6$ eV respectively. It seems the IP-EOM-CCSD relaxes the orbital of interest, and therefore requires an appropriate initial state, one incorporating the relativistic stabilization of the inner-shell electrons.

Effectively, all ionization energies obtained from IP-EOM-CCSD improve with a DK reference. The valence level is unchanged and the IP for mid-valence split levels either moves into or remains within the range of the splitting. The improvement is not near quantitative accuracy though, and suggests more accurate results can be obtained by incorporating relativity in the ionized state. Although, it is evident that the DK potential is necessary for the IP to begin approaching experimental values.

**Xenon.** The convergence of the DK total energies and orbital energies for xenon are shown in Table 2-5. Relativistic effects are seen to be very large for this system, and
the DK convergence behaves the same way as in argon and krytpon. We cannot say with certainty that the SCF energy and core orbital energies are converged at fifth order. The total correlation energy is converged at first order but the correlation contributions to the ionization energies converge much more slowly due to the amount of relaxation for each core ionization.

The non-relativistic and IP-EOM-CCSD ionization energy for the $1s$ core electron differ from experiment by $1245$ eV and $1307.32$ eV, respectively, shown in Table 2-6. Using the fifth order DK potential, they differ by $-164.1$ eV and $-98.0$ eV, respectively. Again we see that IP-EOM-CCSD simply incorporates missing relaxation for the ionization of interest and the DK potential is needed to shift the IP, causing it to change sign compared to experiment so IP-EOM-CCSD can bring it closer to experiment, rather than farther away.

Clearly, for xenon, the ionization energies for the core electrons are far from the truth, indicating a breakdown of the IP-EOM-CCSD/DK combination. They are orders of magnitude closer to experiment, though, and begin to move towards providing qualitative results.

The IP-EOM-CCSD/DK results provide qualitative accuracy for the mid-valence region. Again, the results move into the correct range, between the splitting, when the non-relativistic results fail to do so.

### 2.4.3 Highly Stripped Ions

Since the nuclear charge for highly stripped ions is large, the Partridge family of basis sets [72] was used to first assess the quality of the WTBS used. The Partridge family of basis sets are completely uncontracted, have very tight primitive functions, and increase in size, which helps determine whether the basis set is converged. The results for helium like ions and beryllium like ions are shown in Table 2-7 and Table 2-8, respectively. For all cases, even the largest nuclear charge, there is very little difference
between the IPs as a function of the basis set size. Since the WTBS contains more functions, the system should be very adequately described with it.

Results with the larger WTBS for highly stripped He-like ions are shown in Table 2-9. These systems were studied because they are two-electron systems, where IP-EOM-CCSD is equivalent to full configuration interaction (FCI), and there are no spin-orbit effects in the occupied levels. Near quantitative agreement with the best theoretical estimate (within $\sim 1$ eV), including QED effects, [73] is obtained up to an ionization energy of around 5,000 eV, though the higher nuclear charge results are drastically improved and very qualitative over the non-relativistic result. The non-relativistic and fifth order results for nuclear charge $Z = 20$ differ from the best theoretical estimate by 24.1 eV and $-1.2$ eV, respectively. For nuclear charge $Z = 30$, the two differ by 132 eV and $-4.6$ eV, respectively, demonstrating the need for the DK potential. For a computationally tractable method, the IP-EOM-CCSD with a DK5 potential is exceedingly good for these systems.

Results with the larger WTBS for Be-like ions, where IP-EOM-CCSD is not equivalent to Full CI, but spin-orbit is also not an issue for the occupied electrons, are shown in Table 2-10. Again we see, where the core electrons are up to 5,000 eV, excellent agreement with experiment and the best theoretical estimate. [74] When the core electron IP is much larger, the DK potential still provides very good qualitative results. For the core ionization of Ni$^{24+}$, the non-relativistic result differs from the best theoretical estimate by 149.2 eV, where as the DK5 result differs by 5.39 eV. Similar results are obtained for Zn$^{26+}$, where the non-relativistic and DK5 results differ from the best estimate by 187 eV and 6.9 eV, respectively. Interestingly, for these two Be-like ions, the $1s^2 2s$ DK5 ionization energy, well below 5,000 eV, differ from experiment by $-2.5$ eV and $-8.1$ eV, respectively. There appears to be consistent error in the spectrum for systems with very high energy core electrons, though using the DK potential provides results orders of magnitude better than not using one. Perhaps, these high energy
systems indicate, not necessarily a breakdown, but the insufficient relativistic treatment of the ionized state. Though, this provides a very efficient route towards the near quantitative study of plasmas.

2.5 Conclusions

IP-EOM-CCSD calculations with DK reference potentials have been systematically studied and proposed as a means to obtain near quantitative accuracy for highly stripped ions and a correct qualitative description of ionization energies for systems with electrons moving near the speed of light. Calculations on highly stripped ions demonstrate that for systems with orbital energies up to 5,000 eV quantitative results are obtainable. Even when the orbital energies become extremely large in magnitude, very good qualitative results are obtained.

For neutral systems with heavy atoms, despite the IP-EOM-CCSD/DK combination not being quantitatively accurate, it is necessary for even a qualitative description of the ionization process. The DK potential shifts all the orbital energies, except for the outermost valence shell, in the direction needed for IP-EOM-CCSD to appropriately relax and correlate the ionization.
Figure 2-1. Average difference in total ionization energies between DK5 and DK0 for different methods in eV. The negative average unsigned difference is reported for direct comparison to the average difference.

Figure 2-2. Difference between DK5 and DK0 total ionization energies with different methods for a subset of molecules in eV.

Figure 2-3. Average error of different DK potentials and methods compared to experiment in eV.
Table 2-1. Convergence of SCF and correlated methods with respect to Douglas-Kroll-Hess orders for Argon. Energy units are in eV. The WTBS is employed.

<table>
<thead>
<tr>
<th></th>
<th>DK1-DK0</th>
<th>DK2-DK1</th>
<th>DK3-DK2</th>
<th>DK4-DK3</th>
<th>DK5-DK4</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCF energy</td>
<td>-58.695</td>
<td>9.330</td>
<td>-0.127</td>
<td>0.004</td>
<td>0.000</td>
</tr>
<tr>
<td>Total corr.</td>
<td>-0.074</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>3p SCF</td>
<td>-0.024</td>
<td>0.005</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>3p corr.</td>
<td>-0.001</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>3s SCF</td>
<td>0.278</td>
<td>-0.033</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>3s corr.</td>
<td>-0.017</td>
<td>0.002</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>2p SCF</td>
<td>0.033</td>
<td>0.047</td>
<td>-0.001</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>2p corr.</td>
<td>-0.033</td>
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</tr>
<tr>
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<td>-0.317</td>
<td>0.004</td>
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<tr>
<td>2s corr.</td>
<td>-0.934</td>
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<td>-0.002</td>
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<td>0.000</td>
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<tr>
<td>1s SCF</td>
<td>17.046</td>
<td>-4.056</td>
<td>0.055</td>
<td>-0.002</td>
<td>0.000</td>
</tr>
<tr>
<td>1s corr.</td>
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<td>0.019</td>
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</table>
Table 2-2. Ionization potentials (in eV) of Argon using different Douglas-Kroll-Hess references with the WTBS.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Theor. Est.</th>
<th>IP-EOM-CCSD</th>
<th>Koopmans</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>DK0</td>
<td>DK1</td>
</tr>
<tr>
<td>3p_{1/2}</td>
<td>15.12</td>
<td>15.09</td>
<td>15.10</td>
</tr>
<tr>
<td>3s_{1/2}</td>
<td>29.31</td>
<td>33.50</td>
<td>33.47</td>
</tr>
<tr>
<td>2p_{3/2}</td>
<td>248.47</td>
<td>249.87</td>
<td>249.91</td>
</tr>
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<td>2p_{1/2}</td>
<td>250.56</td>
<td>249.87</td>
<td>249.87</td>
</tr>
<tr>
<td>2s_{1/2}</td>
<td>324.36</td>
<td>325.36</td>
<td>327.10</td>
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<tr>
<td>1s_{1/2}</td>
<td>3206.07</td>
<td>3199.07</td>
<td>3215.77</td>
</tr>
</tbody>
</table>

* Best theoretical estimate from Ref [71]
Table 2-3. Convergence of SCF and correlated methods with respect to Douglas-Kroll-Hess orders for Krypton. Energy units are in eV. The WTBS is employed.

<table>
<thead>
<tr>
<th></th>
<th>DK1-DK0</th>
<th>DK2-DK1</th>
<th>DK3-DK2</th>
<th>DK4-DK3</th>
<th>DK5-DK4</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCF energy</td>
<td>-1209.283</td>
<td>229.906</td>
<td>-6.704</td>
<td>0.449</td>
<td>-0.084</td>
</tr>
<tr>
<td>Total corr.</td>
<td>-0.531</td>
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<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>4p SCF</td>
<td>-0.048</td>
<td>0.021</td>
<td>-0.001</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>4p corr.</td>
<td>0.009</td>
<td>-0.003</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>4s SCF</td>
<td>1.098</td>
<td>-0.165</td>
<td>0.005</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>4s corr.</td>
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<td>-0.001</td>
<td>0.000</td>
<td>0.000</td>
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<tr>
<td>3d SCF</td>
<td>-2.225</td>
<td>0.118</td>
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<td>0.000</td>
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<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>3p SCF</td>
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<td>0.146</td>
<td>-0.004</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>3p corr.</td>
<td>-1.435</td>
<td>-0.020</td>
<td>0.001</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>3s SCF</td>
<td>11.596</td>
<td>-1.548</td>
<td>0.046</td>
<td>-0.003</td>
<td>0.001</td>
</tr>
<tr>
<td>3s corr.</td>
<td>-3.245</td>
<td>0.606</td>
<td>-0.023</td>
<td>0.002</td>
<td>0.000</td>
</tr>
<tr>
<td>2p SCF</td>
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<td>0.707</td>
<td>-0.021</td>
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<td>0.000</td>
</tr>
<tr>
<td>2p corr.</td>
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<tr>
<td>2s SCF</td>
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<td>0.004</td>
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<tr>
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<td>0.000</td>
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<td>2.905</td>
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<td>0.036</td>
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<tr>
<td>1s corr.</td>
<td>-4.992</td>
<td>0.787</td>
<td>-0.045</td>
<td>0.003</td>
<td>-0.001</td>
</tr>
</tbody>
</table>
Table 2-4. Ionization potentials (in eV) of Krypton using different Douglas-Kroll-Hess references with the WTBS.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Theor. Est.</th>
<th>IP-EOM-CCSD</th>
<th>Koopmans</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>DK0</td>
<td>DK1</td>
</tr>
<tr>
<td>4p(_{1/2})</td>
<td>14.64</td>
<td>27.40</td>
<td>26.94</td>
</tr>
<tr>
<td>3s(_{1/2})</td>
<td>93.72</td>
<td>94.91</td>
<td>95.94</td>
</tr>
<tr>
<td>3d(_{5/2})</td>
<td>214.40</td>
<td>222.21</td>
<td>219.04</td>
</tr>
<tr>
<td>3d(_{3/2})</td>
<td>292.79</td>
<td>290.62</td>
<td>298.97</td>
</tr>
<tr>
<td>2p(_{3/2})</td>
<td>1678.40</td>
<td>1730.92</td>
<td>1687.38</td>
</tr>
<tr>
<td>1s(_{1/2})</td>
<td>14325.98</td>
<td>14109.60</td>
<td>14452.14</td>
</tr>
</tbody>
</table>

\(^{a}\) Best theoretical estimate from Ref [71]
Table 2-5. Convergence of SCF and correlated methods with respect to Douglas-Kroll-Hess orders for Xenon. Energy units are in eV. The WTBS is employed.

<table>
<thead>
<tr>
<th></th>
<th>DK1-DK0</th>
<th>DK2-DK1</th>
<th>DK3-DK2</th>
<th>DK4-DK3</th>
<th>DK5-DK4</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCF energy</td>
<td>-7186.941</td>
<td>1490.375</td>
<td>-65.416</td>
<td>6.578</td>
<td>-1.965</td>
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<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>5p SCF</td>
<td>-0.067</td>
<td>0.045</td>
<td>-0.002</td>
<td>0.000</td>
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<tr>
<td>5p corr.</td>
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<td>0.017</td>
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<td>0.001</td>
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<td>0.000</td>
</tr>
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<td>0.000</td>
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<tr>
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<td>0.001</td>
<td>0.000</td>
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<tr>
<td>4p corr.</td>
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<td>0.000</td>
</tr>
<tr>
<td>4s SCF</td>
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<td>-2.715</td>
<td>0.123</td>
<td>-0.013</td>
<td>0.004</td>
</tr>
<tr>
<td>4s corr.</td>
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<td>-8.776</td>
<td>-0.072</td>
<td>0.007</td>
<td>0.082</td>
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<tr>
<td>3d SCF</td>
<td>-11.333</td>
<td>0.837</td>
<td>-0.038</td>
<td>0.004</td>
<td>-0.001</td>
</tr>
<tr>
<td>3d corr.</td>
<td>-0.070</td>
<td>-0.008</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>3p SCF</td>
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<td>0.004</td>
<td>-0.001</td>
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<tr>
<td>3p corr.</td>
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<td>0.001</td>
</tr>
<tr>
<td>3s SCF</td>
<td>89.194</td>
<td>-13.067</td>
<td>0.591</td>
<td>-0.061</td>
<td>0.018</td>
</tr>
<tr>
<td>3s corr.</td>
<td>-1.205</td>
<td>0.406</td>
<td>-0.291</td>
<td>0.032</td>
<td>-0.009</td>
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<tr>
<td>2p SCF</td>
<td>96.302</td>
<td>3.402</td>
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<td>0.016</td>
<td>-0.005</td>
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<tr>
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<td>-0.003</td>
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<td>0.258</td>
<td>-0.407</td>
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</table>
Table 2-6. Ionization potentials (in eV) of Xenon using different Douglas-Kroll-Hess references in the WTBS.

<table>
<thead>
<tr>
<th>Orbital</th>
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<th>DK0</th>
<th>DK1</th>
<th>DK2</th>
<th>DK3</th>
<th>DK4</th>
<th>DK5</th>
<th>DK0</th>
<th>DK1</th>
<th>DK2</th>
<th>DK3</th>
<th>DK4</th>
<th>DK5</th>
</tr>
</thead>
<tbody>
<tr>
<td>5p(_{1/2})</td>
<td>13.39</td>
<td>12.24</td>
<td>24.04</td>
<td>23.77</td>
<td>23.78</td>
<td>23.78</td>
<td>23.78</td>
<td>25.70</td>
<td>27.83</td>
<td>27.46</td>
<td>27.48</td>
<td>27.48</td>
<td>27.48</td>
</tr>
<tr>
<td>5s(_{1/2})</td>
<td>23.29</td>
<td>22.24</td>
<td>24.04</td>
<td>23.77</td>
<td>23.78</td>
<td>23.78</td>
<td>23.78</td>
<td>25.70</td>
<td>27.83</td>
<td>27.46</td>
<td>27.48</td>
<td>27.48</td>
<td>27.48</td>
</tr>
<tr>
<td>4d(_{5/2})</td>
<td>67.51</td>
<td>70.40</td>
<td>67.35</td>
<td>67.53</td>
<td>67.52</td>
<td>67.53</td>
<td>67.53</td>
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<td>72.35</td>
<td>72.54</td>
<td>72.54</td>
<td>72.54</td>
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<td>67.35</td>
<td>67.53</td>
<td>67.52</td>
<td>67.53</td>
<td>67.53</td>
<td>75.59</td>
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<td>72.55</td>
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<td>160.92</td>
<td>160.92</td>
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<td>166.87</td>
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<td>166.86</td>
<td>166.86</td>
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<tr>
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<td>218.99</td>
<td>219.04</td>
<td>219.04</td>
<td>219.13</td>
<td>213.78</td>
<td>231.93</td>
<td>229.21</td>
<td>229.33</td>
<td>229.32</td>
<td>229.33</td>
</tr>
<tr>
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<td>213.20</td>
<td>208.86</td>
<td>230.48</td>
<td>218.99</td>
<td>219.04</td>
<td>219.04</td>
<td>219.13</td>
<td>213.78</td>
<td>231.93</td>
<td>229.21</td>
<td>229.33</td>
<td>229.32</td>
<td>229.33</td>
</tr>
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<td>692.82</td>
<td>681.42</td>
<td>682.25</td>
<td>682.21</td>
<td>682.21</td>
<td>682.21</td>
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<td>699.40</td>
<td>700.23</td>
<td>700.20</td>
<td>700.20</td>
<td>700.20</td>
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<tr>
<td>3d(_{3/2})</td>
<td>688.99</td>
<td>710.73</td>
<td>692.82</td>
<td>682.25</td>
<td>682.21</td>
<td>682.21</td>
<td>682.21</td>
<td>710.73</td>
<td>699.40</td>
<td>700.23</td>
<td>700.20</td>
<td>700.20</td>
<td>700.20</td>
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<td>966.68</td>
<td>966.68</td>
<td>966.68</td>
<td>958.43</td>
<td>980.41</td>
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<td>981.27</td>
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<td>1162.77</td>
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<td>1150.31</td>
<td>1150.39</td>
<td>1093.24</td>
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<td>1169.95</td>
<td>1169.89</td>
<td>1169.91</td>
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</tr>
<tr>
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<td>1148.87</td>
<td>1074.78</td>
<td>1162.77</td>
<td>1150.11</td>
<td>1150.31</td>
<td>1150.39</td>
<td>1093.24</td>
<td>1182.43</td>
<td>1169.36</td>
<td>1169.95</td>
<td>1169.89</td>
<td>1169.91</td>
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</tr>
<tr>
<td>2p(_{3/2})</td>
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<td>4799.60</td>
<td>4893.45</td>
<td>4897.07</td>
<td>4895.62</td>
<td>4895.62</td>
<td>4837.71</td>
<td>4934.01</td>
<td>4937.41</td>
<td>4937.26</td>
<td>4937.27</td>
<td>4937.27</td>
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</tr>
<tr>
<td>2p(_{1/2})</td>
<td>5107.58</td>
<td>4999.60</td>
<td>4893.45</td>
<td>4897.07</td>
<td>4895.62</td>
<td>4895.62</td>
<td>4837.71</td>
<td>4934.01</td>
<td>4937.41</td>
<td>4937.26</td>
<td>4937.27</td>
<td>4937.27</td>
<td></td>
</tr>
<tr>
<td>2s(_{1/2})</td>
<td>5453.44</td>
<td>5115.09</td>
<td>5534.64</td>
<td>5466.15</td>
<td>5469.05</td>
<td>5468.75</td>
<td>5468.84</td>
<td>5152.21</td>
<td>5569.97</td>
<td>5503.55</td>
<td>5506.54</td>
<td>5506.23</td>
<td>5506.32</td>
</tr>
<tr>
<td>1s(_{1/2})</td>
<td>34562.83</td>
<td>33255.51</td>
<td>35278.88</td>
<td>34634.94</td>
<td>34662.70</td>
<td>34659.96</td>
<td>34660.78</td>
<td>33317.57</td>
<td>35344.96</td>
<td>34700.77</td>
<td>34728.93</td>
<td>34726.11</td>
<td>34726.96</td>
</tr>
</tbody>
</table>

\(^a\) Best theoretical estimate from Ref [71]
Table 2-7. Ionization potentials of helium-like ions with IP-EOM-CCSD/DK in Partridge basis sets. The relativistic column corresponds to the DK5 potential. All values are in eV.

<table>
<thead>
<tr>
<th>Z</th>
<th>Basis set</th>
<th>Relativistic</th>
<th>Non-relativistic</th>
<th>Theor. est. a</th>
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a Best theoretical estimate from Ref. [75]
Table 2-8. Ionization potentials of beryllium-like ions with IP-EOM-CCSD/DK in Partridge basis sets. The relativistic column corresponds to the DK5 potential. All values are in eV.

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Table 2-9. Ionization potentials (in eV) of helium-like ions using IP-EOM-CCSD with different Douglas-Kroll-Hess references. The WTBS is employed and all values are in eV.

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\*a Best theoretical estimate from Ref. [76]
\*b Ref. [76]
Table 2-10. Ionization potentials (in eV) of beryllium-like ions using IP-EOM-CCSD with different Douglas-Kroll-Hess references in the WTBS.

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a Best theoretical estimate from Ref [76]

b Ref. [76]
 CHAPTER 3
AN UNTRADITIONAL APPROACH TO CORE IONIZATION ENERGIES

3.1 Preliminaries

In Chapter 2 the scalar-relativistic energetic effects in core ionizations were systematically studied and shown to be non-negligible but easy to obtain in an efficient manner with the DKH transformation. In this chapter a method will be developed that includes relaxation effects to infinite order at a mean-field computational cost. Furthermore, the structure of this method lends itself nicely to an order-by-order analysis of relaxation, and allows one to compute the relaxation energy to any order. This is critical, since I will show that the large source of error in IP-EOM-CCSD is due to higher order relaxation effects.

Because relaxation is so large for core ionizations, as compared to correlation, the best approach is to separate these contributions and solve for them independently. [77] Numerous theoretical models have been developed in this vein, but practical methods are only consistent to second order in relaxation. For example, if we define the relaxation energy to infinite order, \( \Delta \omega^R_k \), as

\[
\Delta \omega^R_k = \epsilon_k - (E^{SCF}_{k}(N-1) - E^{SCF}(N))
\]

where \( \epsilon_k \) is the \( k \)th occupied-orbital energy for the \( N \) electron system, and \( E^{SCF}_{k}(N-1) \) and \( E^{SCF}(N) \) are the \( (N-1) \) and \( N \)-electron SCF energies, respectively, then an approach such as the Transition Operator Method (TOM) originally developed by Slater [78] and further developed by Pickup, Goscinski, and Purvis [79] is correct through second order only and still contains considerable error compared to experiment. However, Ortiz et. al have obtained very reasonable results for core ionizations using the TOM wavefunction as the starting point for Electron Propagator (EP) computations. [80] However, the TOM wavefunction corresponds to a fictitious system
where the ionized orbital is occupied by half an electron and also yields a determinant that is comprised of orbitals that differ from the $N$-electron reference determinant.

More direct methods that attempt to obtain relaxation with correlation order by order are Greens functions methods. [81–87] and their relativistic extensions [56, 88]. These methods are a viable approach to compute the IPs directly and account for relaxation and correlation; however, there are some difficulties associated with them. The methods are only inexpensive at low orders of perturbation theory, are energy dependent, and it is difficult to know if the perturbation series converges.

For comparison, one can examine the EP techniques against various infinite order equation of motion coupled-cluster (EOM-CC) methods [89–91], sometimes called Coupled Cluster Green’s Functions. [92] Such EOM-CC methods decouple the ionization and electron attachment terms in the one-particle Green’s Functions thus offering a more attractive theory where infinite-order effects enable it to exceed the accuracy of most EP techniques. Unfortunately, EOM-CCSD is, on average, 1 to 3 eV in error for core IPs compared to experiment. I will present evidence that this is due primarily to the linear treatment of relaxation (single excitations) in the ionized state, as opposed to the full exponential treatment of singles in the ground state CC solution. Inclusion of higher excitations, which in the limit yield the Full-CI result, will obviously reduce the error, but comes at a higher and impractical computational price.

Of course, one can move away from these direct methods and compute the IP indirectly as

$$\omega_k = E_k(N - 1) - E(N)$$

$$= [E_{k}^{SCF}(N - 1) + \Delta E_k(N - 1)] - [E_{k}^{SCF}(N) + \Delta E(N)]$$

$$= [E_{k}^{SCF}(N - 1) - E_{k}^{SCF}(N)] + [\Delta E_k(N - 1) - \Delta E(N)]$$

$$= \Delta E_{k}^{SCF} + \Delta E_{k}^{corr}$$

$$= \omega_{k}^{relax} + \Delta \omega_{k}^{corr}$$

(3–2)

(3–3)

(3–4)

(3–5)

(3–6)
This rigorously defines relaxation energy to infinite order in an independent-particle way defining the $\Delta E_{\text{SCF}}$ method. By computing the energy of the $(N - 1)$-electron system, one can incorporate relaxation to infinite order at the SCF level. Also, any amount of correlation, according to the method, can be computed for both states. This ideally separates the relaxation from the correlation and can provide very accurate core IPs. [46, 77, 93] However, converging the SCF for the core hole state can be tedious and difficult, since variational collapse of the wavefunction is hard to avoid. The correlated computation can also be fraught with convergence issues. In the specific case of CC theory, the highly nonlinear equations of CC theory are not even guaranteed to converge to the correct solution, though this seldom happens in careful application.

Essentially, the problem at hand for these indirect methods is the adequate and efficient solution for the $(N - 1)$-electron system. Therefore, our objective is to separate relaxation from correlation and compute it directly, efficiently, and accurately. Since the dominant contribution for a core ionization of an organic molecule is the relaxation, we present a “Direct $\Delta E_{\text{SCF}}$” procedure (named IP-VCCS) and determine this quantity to infinite order at the cost of an SCF computation. This method is built in the $N$-electron molecular orbital basis, thus removing the requirement to optimize the orbitals for the $(N - 1)$-electron state, and converges extremely well. In fact, the present method allows one to obtain the $(N - 1)$-determinant as a simple rotation of the $N$-electron one if one seeks the ionized determinant. An exact equivalence requires one to change the orbital occupation, however, although this can be avoided to a very good approximation - and this is presented as well.

The present method can localize the core electrons on symmetry equivalent atoms, necessary for molecules with symmetric centers [94–99]. It does so a priori and thus avoids the need for a stability analysis, which would have to find the broken symmetry solutions of lower energy. It also appears not to suffer from spin contamination, which is present and problematic in the traditional SCF method.
Furthermore, I demonstrate that IP-EOM-CCSD is consistent to second order only in relaxation. Consequently, I evaluate a third-order relaxation correction that can be added to the IP-EOM-CCSD ionization energy. Unfortunately, tack on perturbative corrections such as these do not yield a wavefunction, making the computation of properties and oscillator strengths ill-defined.

3.2 Theory

3.2.1 Direct $\Delta E_{SCF}$ Realized Through Variational CCS

The basic idea of the “Direct $\Delta E_{SCF}$” method is the construction, and solution, of a connected wave operator, which creates the $(N-1)$-determinant from the $N$-electron one using Thouless’ theorem [18]. Thouless’ theorem states that any arbitrary determinant can be rotated to the Hartree-Fock determinant for the state of interest via $e^{\hat{T}_1}$ as

$$|\Phi_k\rangle = \Omega_k |\Phi_0\rangle$$

$$= (e^{\hat{T}_1 k}) e^{\hat{T}_1'} |\tilde{0}\rangle$$

with

$$\hat{T}_1 = \sum_{ai} t^a_i \{ a^i \}$$

and orbital indices with $i, j, k, \ldots, a, b, c, \ldots, p, q, r, \ldots$ corresponding to occupied, virtual, and arbitrary orbitals, respectively, referenced to the $N$-electron vacuum.

Conceptually, $e^{\hat{T}_1'} |\tilde{0}\rangle$ represents the $N$ electron ground state HF determinant, $|\Phi_0\rangle$ and $e^{\hat{T}_1 k}$ represents $\Omega_k$, the wave operator responsible for rotating the $N$-electron determinant to the $(N-1)$-electron HF determinant for the $k^{th}$ ionized state. By using the $N$-electron HF determinant, $|\Phi_0\rangle$, as $|\tilde{0}\rangle$, then $\hat{T}_1' = 0$, and we are left with

$$|\Phi_k\rangle = \Omega_k |\Phi_0\rangle = (e^{\hat{T}_1 k}) |\Phi_0\rangle$$

with the corresponding energy equation

$$E_k = \frac{\langle \Phi_0 | k^i e^{\hat{T}_1} He^{\hat{T}_1} k | \Phi_0 \rangle}{\langle \Phi_0 | k^i e^{\hat{T}_1} e^{\hat{T}_1'} k | \Phi_0 \rangle}$$

(3–11)
and one particle density matrix

\[
[D(k)]_a^p = \frac{\langle \Phi_0 | k^\dagger e^{\tilde{T}_1} p^\dagger q e^{\tilde{T}_1} k | \Phi_0 \rangle}{\langle \Phi_0 | k^\dagger e^{\tilde{T}_1} e^{\tilde{T}_1} k | \Phi_0 \rangle}
\]

(3–12)

\[
= \sum_i \langle \Phi_0 | k^\dagger p^\dagger q k | \Phi_0 \rangle \delta_i^p \delta_i^q + \langle \Phi_0 | (k^\dagger e^{\tilde{T}_1} \{ p^\dagger q \} e^{\tilde{T}_1} k) c | \Phi_0 \rangle
\]

(3–13)

Equations (3–11) and (3–12) are variants of a variational coupled cluster with singles (VCCS) model. The VCCS equations were analytically solved by Noga et. al. [20] The second term of equation (3–13), due to the connected property of the exponential, can be recast as

\[
\langle \Phi_0 | (k^\dagger e^{\tilde{T}_1} \{ p^\dagger q \} e^{\tilde{T}_1} k) c | \Phi_0 \rangle = \langle \Phi_0 | k^\dagger \left( e^{\tilde{T}_1} \right)_L \{ p^\dagger q \} k | \Phi_0 \rangle c
\]

(3–14)

\[
= \sum_{rs} X_s^r \langle \Phi_0 | k^\dagger \{ r^\dagger s \} \{ p^\dagger q \} k | \Phi_0 \rangle
\]

(3–15)

with the \( X \) matrix being a geometric sum involving \( \tilde{T}_1 \) and can be computed to arbitrary precision. [20]

Our goal now is to include the \( k \) dependence so as not to change the reference determinant. A simple evaluation of the matrix elements of equation (3–13) with equation (3–15) using second quantized algebra techniques yields the following

\[
[D(k)]_a^p = \sum_i \delta_i^p \delta_i^q - \delta_i^p \delta_k^q + X_q^p (1 + \delta_k^{p_{eocc}} - \delta_k^{q_{evert}}) - X_q^{p_{eocc}} X_k^{q_{eocc}} - X_k^{p_{evert}} X_q^{q_{evert}}
\]

(3–16)

\[
= \sum_i \delta_i^p \delta_i^q + [\tilde{X}(k)]_a^p
\]

(3–17)

Where the reference density is easily extracted as \( \sum_i \delta_i^p \delta_i^q \) and the rest, being the correction due to ionization, are terms treating \( k \) as a virtual orbital. This is most easily
seen in matrix form

\[
\tilde{X}(k) = \begin{bmatrix}
X_{oo} & X_{ok} & X_{ov} \\
X_{ko} & X_{kk} & X_{kv} \\
X_{vo} & X_{vk} & X_{vv}
\end{bmatrix}
\]  

(3–18)

where o, k, and v correspond to the occupied, ionized, and virtual spaces respectively.

Thus we arrive at a practical working point for the “Direct $\Delta E_{SCF}$” method. We will omit the explicit dependence of the density on $k$ to simplify the expressions. To solve for $\hat{t}_1$, we first form the density matrix. By using the geometric series nature of the density matrix built from $\hat{t}_1$, we can write the occupied-occupied block of the density matrix as

\[
D_{ij}^{(m+1)} = \delta_{ij} + \sum_l D_{il}^{(m)} \left( \sum_a t_{al} t_{lj} \right)
\]  

(3–19)

The remaining blocks of the density matrix are computed with the occupied-occupied block as

\[
\begin{align*}
D_{ia} &= \sum_j t_{ja} D_{ij} \\
D_{ai} &= \sum_j D_{ji} t_{ja} \\
D_{ab} &= \sum_j D_{ja} t_{bj}
\end{align*}
\]  

(3–20–22)

By making the expectation value of the density matrix with the Fock operator stationary with respect to the $t_{ia}^a$ amplitudes,

\[
\sum_{pq} F_{pq}^p \frac{D_{pq}^a}{\partial t_{ia}^a} = 0
\]  

(3–23)

one obtains a transformation matrix, $Q$, that transforms the Fock matrix at each iteration closer to the Fock matrix for the $N - 1$ electron system through the density dependent $\hat{J} - \hat{K}$ operator of the Fock matrix.

\[
\tilde{F} = Q^T F Q
\]  

(3–24)
where

\[ Q^i_j = \delta^i_j + \left[ \tilde{X}(k) \right]^i_j \]  \hspace{1cm} (3–25)  
\[ Q^a_i = - \left[ \tilde{X}(k) \right]^a_i \]  \hspace{1cm} (3–26)  
\[ Q^a_i = \left[ \tilde{X}(k) \right]^a_i \]  \hspace{1cm} (3–27)  
\[ Q^a_b = \delta^a_b - \left[ \tilde{X}(k) \right]^a_b \]  \hspace{1cm} (3–28)  

Computationally, the Fock matrix is constructed from the obtained density. This Fock matrix is then transformed with \( \mathbf{Q} \) to generate a new Fock matrix, one which approaches satisfying the Brillouin condition. This avoids diagonalization of the Fock matrix, and also allows one to remain in the \( N \)-particle basis. Once the transformed Fock matrix is obtained, one can update the \( \hat{T}_1 \) amplitudes using

\[ t^{a(m+1)}_i = t^{a(m)}_i + \frac{E^{a(m)}_{F_i}}{\epsilon_i - \epsilon_a} \]  \hspace{1cm} (3–29)  

It is easily seen that the total \( N - 1 \)-Hartree-Fock energy can be computed at every step, using the Fock matrix, \( \tilde{F} \), constructed from the current density as

\[ E_{SCF}^{N-1} = \sum_{pq} \left( h^p_q + F^p_q + \left[ \tilde{G}(k) \right]^p_q \right) \left[ D(k) \right]^q_p \]  \hspace{1cm} (3–30)  

However, if we expand the Fock operator and density matrix

\[ E_{SCF}^{N-1} = \sum_{pq} \left( h^p_q + F^p_q + \left[ \tilde{G}(k) \right]^p_q \right) \left( \sum_i \delta^p_i \delta^q_i + \left[ \tilde{X}(k) \right]^q_p \right) \]  \hspace{1cm} (3–31)  
\[ = E_{SCF}^{N} + \epsilon_k + \sum_{pq} \left( h^p_q + \sum_{j \neq k} \langle pj || qj \rangle + \sum_{rs} \langle pr || qs \rangle \left[ \tilde{X}(k) \right]^s_r \right) \left[ \tilde{X}(k) \right]^q_p \]  \hspace{1cm} (3–32)  

one immediately sees the implicit Hartree-Fock energy for the \( N \)-electron state, Koopmans’ theorem, and the relaxation correction to Koopmans’ theorem. Subtracting
\( E_{SCF}^N \) from both sides yields the “Direct \( \Delta E_{SCF} \)” ionization energy,

\[
\omega_k = \epsilon_k + \sum_{pq} \left( h_p^0 + \sum_{j \neq k} \langle pj||qj \rangle + \sum_{rs} \langle pr||qs \rangle [\tilde{X}(k)]_r^s [\tilde{X}(k)]_p^q \right) (3-33)
\]

Comparing this to Equation (3–1), we see the direct and complete expression for relaxation is recovered with this energy expression. This method will be named IP-VCCS-E, where the “E” corresponds to an exact formulation compared to \( \Delta E_{SCF} \).

It must be mentioned at this point that exact equivalence to the \( \Delta E_{SCF} \) method is obtained when \( k \) is treated as a virtual orbital. This is easily seen via the \( \hat{T}_1 \) operator, where it excites occupied electrons in the determinant to virtual orbitals, thus facilitating relaxation. However, if \( k \) is not a virtual orbital index, then \( \hat{T}_1 \) cannot excite in to it. This affects the occupation number of the determinant, but it does not affect the orbital basis. Still, it is more desirable to work in the same orbital basis and occupation, i.e. in the same Hilbert space. To that end, an excellent approximation can be made, which removes the need to change occupation. If one allows no coupling between the ionized orbitals and the rest - a sudden ionization - then one can work in the same Hilbert space throughout the computation. By eliminating the coupling terms, and consequently prohibiting a possible variational collapse, the correction matrix, \( \tilde{X}(k) \), becomes

\[
\left[ \tilde{X}(k) \right]_q^p = -\delta_k^p \delta_q^k + X_q^p, \quad (3-34)
\]

or in matrix form

\[
\tilde{X}(k) = \begin{bmatrix}
X_{oo} - \delta_{ok} \delta_{ko} & X_{ov} \\
X_{vo} & X_{vv}
\end{bmatrix} \quad (3-35)
\]

This approximate formulation will be abbreviated as IP-VCCS.

The equations are identical for electron attached states, except that the \( k \) dependent occupied correction, becomes a \( c \) dependent virtual addition, \( \left[ \tilde{X}(c) \right]_q^p \equiv +\delta_c^p \delta_q^c + X_q^p \). This method can presumably work well for core excited states as well, where the correction is \( \left[ \tilde{X}(k, c) \right]_q^p \equiv +\delta_c^p \delta_q^c - \delta_k^p \delta_q^k + X_q^p \), although correlation will be necessary.
for the electron attachment process in the core excitation, since the attachments usually occur in, or near, the LUMO energy region.

### 3.2.2 Third-Order Relaxation Correction

IP-EOM-CCSD includes infinite order effects due to relaxation and correlation and performs very well for valence ionizations; however, it shows some deficiencies in the core region [29] owing to the large relaxation effects accompanying core ionization. [39, 100] The ionized state is created with a linear operator

\[
\hat{R}_k = \sum_k r_k \{ \hat{k} \} + \sum_{iak} r_{ik}^a \{ \hat{a}^\dagger \hat{i} \hat{k} \} \tag{3–36}
\]

with the second term creating the hole state, followed by single substitutions, (relaxation). One wonders if adding quadratic, cubic, . . . , would incorporate the necessary relaxation to obtain truly quantitative results.

In that vein, we recast the previously derived relaxation operator, \( \Omega_{relax} \), as a function of \( \hat{S}_1 \) instead of \( \hat{T}_1 \) (so as not to confuse it with the ground state CC amplitudes)

\[
\Omega_{relax} = e^{\hat{S}_1} \{ \hat{k} \}. \tag{3–37}
\]

Truncation of \( \Omega_{relax} \) to linear terms is an approximation of Eq. (3–36). With this, we can write the fully relaxed energy for the \( k^{th} \) ionized state as [101]

\[
E_k = \langle 0 | \hat{R}_k \hat{H}_N \Omega_r | 0 \rangle / \langle 0 | \Omega_r | 0 \rangle \tag{3–38}
\]

\[
= \langle 0 | \left( \{ \hat{k}^\dagger \} e^{\hat{S}_1} \hat{H}_N e^{\hat{S}_1} \{ \hat{k} \} \right) C | 0 \rangle \tag{3–39}
\]

The fully relaxed energy expression for IP-VCCS, or any VCCS method, is

\[
E_k = \frac{1}{2} \sum_{pq} (h_{pq} + \tilde{r}_{pq}) \tilde{D}_{qp} \tag{3–40}
\]
where $\bar{f}_{pq}$ and $\bar{D}_{qp}$ are the complete fock operator and density matrix, respectively, as functions of $\{\hat{S}_1^t, \hat{S}_1\}$. This allows us to expand in orders of perturbation theory as

$$E_k^{(0)} + E_k^{(1)} + \cdots + E_k^{(n)} = \frac{1}{2} \left( \bar{f}_{pq}^{(0)} + \bar{f}_{pq}^{(0)} + \bar{f}_{pq}^{(1)} + \cdots + \bar{f}_{pq}^{(n)} \right) \left( \bar{D}_{qp}^{(0)} + \bar{D}_{qp}^{(1)} + \cdots + \bar{D}_{qp}^{(n)} \right)$$  \hspace{1cm} (3–41)

With $D_{qp}^{(0)} = \sum_i \delta_{qi} \delta_{ip} - \delta_{qk} \delta_{kp}$, the zeroth order energy is simply Koopmans’ approximation,

$$E_k^{(0)} = E(N) - \epsilon_k$$  \hspace{1cm} (3–42)

By comparison, IP-EOM-CCS, the direct analogue of this zeroth order analysis, yields Koopmans’ approximation also. Consequently, since IP-EOM-CCSD contains the linear ionization operator, (ie. consistent to second order in relaxation in the density in our analysis of IP-VCCS), we can evaluate a third-order relaxation correction as

$$\Delta E_k^{(3)} = \frac{1}{2} \sum_{pq} \left[ \left( \bar{f}_{pq}^{(0)} + \bar{f}_{pq}^{(0)} \right) \bar{D}_{qp}^{(3)} + \bar{f}_{pq}^{(1)} \bar{D}_{qp}^{(2)} + \bar{f}_{pq}^{(2)} \bar{D}_{qp}^{(1)} + \bar{f}_{pq}^{(3)} \bar{D}_{qp}^{(0)} \right]$$  \hspace{1cm} (3–43)

that can be added to any IP-EOM-CCSD computation, with

$$D_{qp}^{(1)} = D_{ai}^{(1)} + D_{ia}^{(1)} = s_i^a + s_a^i$$  \hspace{1cm} (3–44)

$$D_{qp}^{(2)} = D_{ij}^{(2)} + D_{ab}^{(2)} + c.c. = \sum_d s_i^d s_j^d + \sum_l s_i^a s_l^b + \text{c.c.}$$  \hspace{1cm} (3–45)

$$D_{qp}^{(3)} = D_{ai}^{(3)} + D_{ia}^{(3)} = \sum_{ld} s_i^a s_d^l s_l^d + \sum_{dl} s_i^d s_l^d s_l^a$$  \hspace{1cm} (3–46)

and the corresponding $f_{pq}^{(n)} \equiv f_{pq}[D^{(n)}]$.

### 3.2.3 Relaxation with $\Delta E_{\text{CC}}$ Methods

To analyze the errors in IP-EOM-CCSD we compare against ionization potentials obtained indirectly by total energy differences

$$\omega_k = E_k - E_0$$  \hspace{1cm} (3–47)

We test two methods, one where the reference ionized state, $|\Phi_k\rangle$, is variationally optimized, yielding fully relaxed orbitals, before performing a CCSD correlated
calculation. This will be labeled the $\Delta E_{\text{relaxed}}^{\text{CCSD}}$ method. As referenced in 2, a more
direct comparison with IP-EOM-CCSD can be made with the $\Delta E_{\text{non-relaxed}}^{\text{CCSD}}$ method. The
reference ionized state is left as a Koopmans’ determinant, thus generating a quasi-RHF (QRHF) reference [46, 102] used in the correlated CCSD calculation. This has the advantage that the same orbitals used in this method are used in IP-EOM-CCSD, and a more direct analysis of relaxation and correlation is therefore possible. Although, the same line of reasoning to obtain corrections to IP-EOM-CCSD can not be used with this $\Delta E_{\text{non-relaxed}}^{\text{CCSD}}$ approach. In the limit of full substitutions, all relaxation will be included, but there exists no practical way to compare truncated variational versus truncated traditional coupled cluster approaches. [103, 104]

3.3 Implementation

The ACESII program package [105] was used to compute the core ionization energies with the $\Delta E_{\text{relaxed}}^{\text{CCSD}}$, $\Delta E_{\text{non-relaxed}}^{\text{CCSD}}$, $\Delta E_{\text{CCSDT}}$, and IP-EOM-CCSD methods. The IP-VCCS algorithm [101] was implemented in the massively parallelizable program package, ACESII [34], along with the third-order energy correction. The correlation consistent polarized core-valence double and triple-$\zeta$ basis sets were used in the calculations.

For the IP-VCCS method for molecules with symmetry equivalent centers, the ground state $N$-electron determinant was computed with a traditional Hartree-Fock algorithm, yielding symmetric, delocalized orbitals. A linear combination was then made with the $\sigma_g$ and $\sigma_u$ orbitals that localized them on equivalent centers. The IP-VCCS algorithm was then applied to these reference determinants to determine the core IP, which matched broken symmetry SCF computations on the $(N - 1)$-electron states.

3.4 Results and Discussion

3.4.1 IP-VCCS

Example molecules are taken from the G2 test set; the geometries are unmodified. For orthoaminophenol, the geometry is optimized using second-order many-body
perturbation theory [15] with the augmented correlation-consistent double-ζ basis set [106]. The optimized structure is shown in Figure 3-1. This molecule is chosen because of the recent interest in its core ionization spectrum [57].

The $\Delta E_{SCF}$ calculations, where both the $N$ and $(N-1)$-states are variationally optimized, are performed with the ACESII program package [105] for reasons that will be mentioned later. The exact, compared to $\Delta E_{SCF}$, calculation with the $(N-1)$ occupation (IP-VCCS-E) and the approximate (IP-VCCS) calculations are performed with the ACESIII program package [34]. The correlation-consistent core-valence family of basis sets [106] are employed, up to the quadruple-ζ level.

Results obtained with IP-VCCS-E for the single core IPs of small molecules are shown in Table 3-1 for a subset of molecules. Exact agreement with $\Delta E_{SCF}$ results are obtained, as required, though the results are reported to three decimal places for readability. The method converges smoothly and rapidly, exhibiting no signs of possible variational collapse for these systems.

However, since the change in occupation number is an undesirable feature of this theory, as one would like to describe the ground, excited, ionized, and attached states equally and consistently. Results of the sudden approximation, IP-VCCS are shown in Table 3-2. We see excellent agreement for single IPs compared to the exact analogue within this approximation. The average absolute errors for the double and triple-ζ basis sets are 0.007 eV and 0.008 eV, respectively.

The comparison of convergence between $\Delta E_{SCF}$ and IP-VCCS is presented in Figure 3-3. Although this is a rather unfair comparison, as the $\Delta E_{SCF}$ computations are performed with computational symmetry in ACESII [105] and the Direct $\Delta E_{SCF}$ computations are performed in $C_1$ symmetry in ACESIII [34]. Also, for the $\Delta E_{SCF}$, up to 25 histories are stored for the DIIS algorithm, whereas only 5 histories are stored in the Direct $\Delta E_{SCF}$ routine. And, since the $E_{k}^{SCF}$ computation is extremely susceptible to variational collapse, at every iteration, the occupation numbers had to be reread and
the maximum overlap method of Ref. [107] is used to help avoid any collapse. Even with these precautions, only two-thirds of the test set converged using the conventional $\Delta E_{SCF}$ procedure, compared to 100% convergence with IP-VCCS. Taking all this into account, it is rather remarkable that the direct method only differs, on average (including ozone) by a factor of 1.4. In fact, since such poor convergence is experienced for the $\Delta E_{SCF}$ method using the double and triple-$\zeta$ basis sets, we performed the direct calculation using the quadruple-$\zeta$ basis set and maintained excellent convergence.

Results for the extension of IP-VCCS to double core ionization potentials for the orthoaminophenol molecule are shown in Table 3-3. For the single core ionization energies on oxygen and nitrogen very good agreement, again, is obtained compared to $\Delta E_{SCF}$; providing more evidence for the utility of the approach. The double core ionization potentials, however, are roughly $\sim 0.3$ eV off from the $\Delta E_{SCF}$ method for ionizations on the same center, but only $0.03$ eV off for the ionizations in nitrogen and oxygen. Of course the IP obtained with the approximate method is always less than the exact value (assuming there is no spin contamination), due to the constraint on the ionized orbital, but even for the worst case of $0.3$ eV, this is under 1% of the relaxation energy. Obviously, any perturbative corrections to correct the ionization energies should quickly recover this lack of relaxation, and therefore the method is still quite useful and powerful for double core ionizations.

**Spin contamination.** Interestingly, for propene this method differs from the $\Delta E_{SCF}$ result by $\sim 0.1$ eV, as presented in Table 3-5. This apparent peculiarity is due to moderate spin contamination for the traditional $\Delta E_{SCF}$. For propene, the spin multiplicity for the $E_{k}^{HF}$ state is 2.24, compared to the expected doublet. Great care is taken in trying to converge to the doublet core hole state for the $E_{k}^{HF}$, demonstrating the difficulty in obtaining a proper reference function for these calculations. Consequently, this very nicely illustrates the power and utility of the IP-VCCS method, which maintains
proper spin symmetry throughout the computation, due to the exponential ansatz, and reproduces results very close to experiment.

**Broken spatial symmetry.** It is a well know result that for molecules with symmetry equivalent centers, the core orbitals have to be localized on each center, thus breaking the point group symmetry of the wavefunction. [94–99] For $\Delta E_{SCF}$ calculations, a stability analysis is performed, which determines if there are lower energy solutions, and rotates the orbitals accordingly to converge to this solution. This requires the second derivatives of the SCF wavefunction.

The core orbitals, being essentially atomic, are rather easy to localize from the beginning though as

$$1s_{A/B} = 1\sigma_g \pm 1\sigma_u,$$

with symmetric centers $A$ and $B$. Comparison between the symmetry constrained and symmetry broken solutions are shown in Table 3-4. The broken symmetry solutions are also equal to the ones obtained with the $\Delta E_{SCF}$ method. Even though the symmetry breaking ruins the quality of the wavefunction, the energy is much closer to the exact energy due to the variational principle.

### 3.4.2 Third-Order Correction to IP-EOM-CCSD

The comparisons of a given method using double-$\zeta$ and triple-$\zeta$ quality basis sets to experimental values are shown in Table 3-6 and Table 3-7, respectively. Koopmans’ values are listed for comparison purposes, since these values are completely unrelaxed IPs. Also unreliable are the $\Delta E_{CCSD}^{\text{relaxed}}$ results, evident using both basis sets. Since this method is very impractical to use due to poor convergence in the SCF and CCSD equations, we will focus on the more promising $\Delta E_{CCSD}^{\text{non-relaxed}}$, IP-VCCS, and IP-EOM-CCSD methods to obtain relaxed and correlated core IPs.

Somewhat deceiving is the very good agreement with experiment obtained with IP-VCCS and the double-$\zeta$ basis set. Although, completely relaxed, there appears to be a fortuitous cancellation of error between the incomplete basis set description
and correlation effects, which becomes apparent when examining the triple-ζ results for IP-VCCS. In fact, the correlated analog of IP-VCCS, the $\Delta E_{\text{CCSD}}^{\text{non-relaxed}}$ method, performs poorly using the double-ζ basis set, being approximately 2.1 eV in error, but then performs quite satisfactorily for the triple-ζ basis set, with $\sim 0.3$ eV average error. The increase in the size of the basis set, combined with the accurate description of correlation begins to provide quantitative results. Also, it does not seem necessary to break point group symmetry for molecules with symmetry equivalent centers when performing a $\Delta E_{\text{CCSD}}^{\text{non-relaxed}}$ computation. It is necessary, though, for IP-VCCS computations.

The effects of triple substitutions on the core IPs of select molecules are shown in Table 3.5. This test set is rather small, but supports the hypothesis that higher substitutions will converge very slowly to the Full CI result since the core is not a strongly correlated region. Therefore, relaxation is the dominant remaining effect. Comparing Koopmans’ value with IP-VCCS yields the infinite order relaxation energy and comparing a fully correlated $\Delta E_{\text{CCSD}}^{\text{non-relaxed}}$ with one where the ionized orbital is frozen yields the correlation and relaxation energy. These contributions are shown for a subset of molecules in Figure 3-2. For molecules with no symmetry equivalent centers, the contributions from $\Delta E_{\text{CCSD}}^{\text{non-relaxed}}$ are always below those of the total relaxation energy. This strongly suggests that the $\Delta E_{\text{CCSD}}^{\text{non-relaxed}}$ is missing a very small amount of relaxation energy. The relaxation energy is almost exactly half of the contributions from $\Delta E_{\text{CCSD}}^{\text{non-relaxed}}$ for molecules with symmetry equivalent centers. This simply demonstrates the need to break symmetry for these types of molecules, and localize the ionized orbital to one center, rather than half on both orbitals in an SCF procedure.

The direct analogue of $\Delta E_{\text{CCSD}}^{\text{non-relaxed}}$, IP-EOM-CCSD, is systematically below the experimental values, on average of 3.41 eV and 1.78 eV for the double-ζ and triple-ζ basis sets, respectively. The agreement is better with the larger basis set, but appears to converge slowly to the experimental value. If triple substitutions are not important for the
\( \Delta E_{CC} \) methods, then it follows they are not important within the IP-EOM-CC framework. Therefore, the major difference between IP-EOM-CCSD and \( \Delta E_{\text{non-relaxed}}^{\text{CCSD}} \) is the inclusion of \( \tilde{T}_1 \) in a linear ansatz, versus the exponential ansatz, and consequently, the products of single substitutions which incorporate relaxation to infinite order.

Having established that the major error in \( \Delta E_{\text{non-relaxed}}^{\text{CCSD}} \) and IP-EOM-CCSD methods is the lack of higher order relaxation effects, we demonstrate the increase in accuracy by adding a direct, consistent, third-order energy correction to IP-EOM-CCSD in Table 3-9. For molecules with symmetry equivalent centers, both the symmetry constrained and symmetry broken results are reported. Even though the symmetry broken solutions use a reference function different than the one used in the IP-EOM-CCSD computation, the energy correction yields more accurate results compared to the symmetry constrained results. On average, the error compared to experiment, with a triple-\( \zeta \) basis set, decreases from 1.83 eV to 0.04 eV, and the average unsigned error decreases from 1.83 eV to 1.01 eV. For such a simple correction, the results are much more quantitative.

### 3.5 Conclusions and Outlook

A new direct method for electron ionized, attached, and excited states has been tested for core ionizations. The IP-VCCS-E faithfully reproduces the \( \Delta E_{\text{SCF}} \) result and the approximate IP-VCCS reproduces the exact result to better than 0.01 eV on average for cc-pCVDZ and cc-pCVTZ basis sets. Therefore, the single particle perturbation, orbital relaxation, is described to infinite order directly.

Interestingly, though not surprisingly, this offers a very attractive route towards determining core excitation energies. For example, if the fully relaxed, core ionized Hamiltonian can be described as

\[
\tilde{H}_k = \left( k^\dagger e^{T_1} H e^{T_1} k \right)
\] (3–49)

then, the correlated core ionized Hamiltonian can be written as

\[
\tilde{H}_k = \left( \tilde{H}_k e^{T_2} \right).
\] (3–50)
This is obviously an analogue of $\tilde{H}$ (H-bar) from CC theory [15], limited to doubles (CCD), but specific to a chosen core ionized state, and standard EOM-CC methods can be applied to compute the electron attached portion, complete with correlation.

$$\left( \tilde{H}_k R^c \right)_c |0\rangle = \omega_k^c R^c |0\rangle; \; \forall c$$  \hfill (3–51)

Future work will address computing transition moments. This would provide a seamless route towards the extremely difficult problem of core excitation spectra.

A relaxation energy correction based on a third-order analysis of the ionized state density matrix between IP-VCCS and IP-EOM-CCSD has been developed and applied to core ionization energies. The errors in IP-EOM-CCSD for core ionizations have also been demonstrated by comparing it with $\Delta E_{CCSD}^{\text{non-relaxed}}$ and IP-VCCS. For molecules with symmetry equivalent centers, very good agreement with experiment is obtained by computing the correction from the symmetry broken reference function. The average error in IP-EOM-CCSD, due essentially to missing higher order relaxation effects decreases from 1.83 eV to 0.04 eV, and the average unsigned error decreases from 1.83 eV to 1.01 eV. Even higher order corrections can be derived and implemented and future work is aimed in this direction.
Figure 3-1. Ground state geometry of orthoaminophenol molecule.

Figure 3-2. Contributions to core IP using $\Delta E^\text{non-relaxed}_{\text{CCSD}}$ (correlation and relaxation) and IP-VCCS (relaxation) with cc-pCVDZ basis set.

Figure 3-3. Demonstration of convergence of IP-VCCS.
Table 3-1. Comparison between the exact VCCS method (IP-VCCS-E) and the $\Delta E_{SCF}$ method for core IPs of different molecules with different basis sets. All values are in eV.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>cc-pCVDZ $\Delta E_{SCF}$</th>
<th>IP-VCCS-E</th>
<th>cc-pCVTZ $\Delta E_{SCF}$</th>
<th>IP-VCCS-E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>297.989</td>
<td>297.989</td>
<td>297.476</td>
<td>297.476</td>
</tr>
<tr>
<td>Methane</td>
<td>291.577</td>
<td>291.577</td>
<td>290.612</td>
<td>290.612</td>
</tr>
<tr>
<td>Cyanogen</td>
<td>418.355</td>
<td>418.355</td>
<td>417.698</td>
<td>417.698</td>
</tr>
<tr>
<td>Fluorine</td>
<td>709.573</td>
<td>709.573</td>
<td>708.781</td>
<td>708.781</td>
</tr>
<tr>
<td>Formic acid</td>
<td>540.987</td>
<td>540.987</td>
<td>539.890</td>
<td>539.890</td>
</tr>
<tr>
<td>Hydrogen cyanide</td>
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<td>407.337</td>
<td>406.098</td>
<td>406.098</td>
</tr>
<tr>
<td>Ketene</td>
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<td>540.146</td>
<td>538.901</td>
<td>538.901</td>
</tr>
<tr>
<td>Nitrogen</td>
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<td>420.186</td>
<td>419.555</td>
<td>419.555</td>
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<tr>
<td>Ozone</td>
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<td>547.511</td>
<td>546.624</td>
<td>546.624</td>
</tr>
<tr>
<td>Vinyl fluoride</td>
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<td>692.957</td>
<td>691.624</td>
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</table>
Table 3-2. Comparison between the $\Delta E_{SCF}$ and the approximate direct $\Delta E_{SCF}$ method for the core IP of different molecules using different basis sets. All values are in eV.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>cc-pCVDZ $\Delta E_{SCF}$</th>
<th>cc-pCVDZ Direct $\Delta E_{SCF}$</th>
<th>cc-pCVTZ $\Delta E_{SCF}$</th>
<th>cc-pCVTZ Direct $\Delta E_{SCF}$</th>
<th>cc-pCVQZ $\Delta E_{SCF}$</th>
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<tr>
<td>Acetaldehyde</td>
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<td>538.324</td>
<td>537.120</td>
<td>537.020</td>
<td>537.020</td>
<td></td>
</tr>
<tr>
<td>Acetylene</td>
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<td>298.914</td>
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<td>297.987</td>
<td>297.476</td>
<td>297.473</td>
<td>297.442</td>
<td></td>
</tr>
<tr>
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<td>704.986</td>
<td>704.368</td>
<td>704.365</td>
<td>704.301</td>
<td></td>
</tr>
<tr>
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<td>291.567</td>
<td>290.612</td>
<td>290.599</td>
<td>290.540</td>
<td></td>
</tr>
<tr>
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<td>541.204</td>
<td>541.080</td>
<td></td>
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<tr>
<td>Cyanogen</td>
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<td>418.355</td>
<td>417.698</td>
<td>417.697</td>
<td>417.642</td>
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<td>298.982</td>
<td>298.957</td>
<td></td>
</tr>
<tr>
<td>Fluorine</td>
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<td>709.570</td>
<td>708.781</td>
<td>708.778</td>
<td>708.656</td>
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</tr>
<tr>
<td>Formaldehyde</td>
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<td>539.108</td>
<td>537.940</td>
<td>537.925</td>
<td>537.827</td>
<td></td>
</tr>
<tr>
<td>Formic acid</td>
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<td>540.975</td>
<td>539.890</td>
<td>539.875</td>
<td>539.777</td>
<td></td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
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<td>551.742</td>
<td>551.228</td>
<td>551.225</td>
<td>551.172</td>
<td></td>
</tr>
<tr>
<td>Hydrazine</td>
<td>414.853</td>
<td>414.851</td>
<td>414.409</td>
<td>414.406</td>
<td>414.396</td>
<td></td>
</tr>
<tr>
<td>Ketene</td>
<td>540.146</td>
<td>540.133</td>
<td>538.901</td>
<td>538.885</td>
<td>538.776</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>539.071</td>
<td>539.059</td>
<td>537.971</td>
<td>537.956</td>
<td>537.871</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>420.186</td>
<td>420.184</td>
<td>419.555</td>
<td>419.552</td>
<td>419.510</td>
<td></td>
</tr>
<tr>
<td>Nitromethane</td>
<td>551.044</td>
<td>551.043</td>
<td>550.535</td>
<td>550.534</td>
<td>550.494</td>
<td></td>
</tr>
<tr>
<td>Ozone</td>
<td>547.511</td>
<td>547.499</td>
<td>546.624</td>
<td>546.611</td>
<td>555.368</td>
<td></td>
</tr>
<tr>
<td>Oxirane</td>
<td>538.529</td>
<td>538.517</td>
<td>537.422</td>
<td>537.406</td>
<td>537.306</td>
<td></td>
</tr>
<tr>
<td>Vinyl fluoride</td>
<td>692.957</td>
<td>692.945</td>
<td>691.624</td>
<td>691.608</td>
<td>691.489</td>
<td></td>
</tr>
</tbody>
</table>

Average difference  -0.007  -0.008  
Average unsigned difference  0.007  0.008

Table 3-3. Comparison between the IP-VCCS-E and the IP-VCCS methods for designated core IPs of orthoaminophenol using the cc-pVQZ basis set. All values are in eV. The cc-pCVQZ basis set is employed.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E_{SCF}$</th>
<th>IP-VCCS-E</th>
<th>IP-VCCS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doublet single IPs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>538.232</td>
<td>538.232</td>
<td>538.217</td>
</tr>
<tr>
<td>N</td>
<td>404.594</td>
<td>404.594</td>
<td>404.580</td>
</tr>
<tr>
<td>Singlet double IPs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OO</td>
<td>1165.763</td>
<td>1165.763</td>
<td>1165.425</td>
</tr>
<tr>
<td>NN</td>
<td>887.152</td>
<td>887.152</td>
<td>886.830</td>
</tr>
<tr>
<td>NO</td>
<td>947.592</td>
<td>947.592</td>
<td>947.563</td>
</tr>
</tbody>
</table>
Table 3-4. Difference of different symmetry reference results from experiment using IP-VCCS. All values are in eV. The cc-pCVTZ basis set is used in all calculations.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Symbol</th>
<th>Koopmans</th>
<th>Symmetry constrained</th>
<th>Broken symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>HC≡CH</td>
<td>-14.91</td>
<td>-7.82</td>
<td>0.36</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>O=C=O</td>
<td>-20.80</td>
<td>-11.26</td>
<td>0.66</td>
</tr>
<tr>
<td>Fluorine</td>
<td>F-F</td>
<td>-22.46</td>
<td>-12.09</td>
<td>2.18</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N≡N</td>
<td>-17.18</td>
<td>-9.73</td>
<td>0.47</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O=O</td>
<td>-18.15</td>
<td>-8.08</td>
<td>2.94</td>
</tr>
</tbody>
</table>

Table 3-5. Comparison between the $\Delta E_{\text{SCF}}$ and IP-VCCS method for the core IP for propene, which exhibits strong spin contamination in the traditional $E_k^{\text{HF}}$ (in parenthesis) computation. All values in eV.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Exp.$^a$</th>
<th>cc-pCVDZ</th>
<th>cc-pCVTZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propene</td>
<td>290.68</td>
<td>291.178</td>
<td>290.208</td>
</tr>
</tbody>
</table>

$^a$ Ref. [108]

Table 3-6. Differences of the given method with the cc-pCVDZ basis set from experimental values. All values are in eV.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Symbol</th>
<th>Koopmans</th>
<th>IP-VCCS</th>
<th>$\Delta E_{\text{EOM-CCSD}}$</th>
<th>$\Delta E_{\text{relaxedCCSD}}$</th>
<th>$\Delta E_{\text{non-relaxedCCSD}}$</th>
<th>IP-EOM-CCSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>CH$_3$CN</td>
<td>-18.37</td>
<td>-0.55</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>-3.27</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH$_3$</td>
<td>-17.22</td>
<td>-0.56</td>
<td>-2.61</td>
<td>1.42</td>
<td>-2.64</td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>CH$_4$</td>
<td>-14.39</td>
<td>-0.74</td>
<td>-2.53</td>
<td>-1.27</td>
<td>-2.36</td>
<td></td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>CO</td>
<td>-19.94</td>
<td>0.04</td>
<td>-3.10</td>
<td>-1.66</td>
<td>-3.42</td>
<td></td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>H$_2$C=O</td>
<td>-20.44</td>
<td>0.36</td>
<td>-14.41</td>
<td>-5.29</td>
<td>-3.55</td>
<td></td>
</tr>
<tr>
<td>Furan</td>
<td>C$_2$H$_4$O</td>
<td>-21.78</td>
<td>-0.49</td>
<td>...</td>
<td>...</td>
<td>-4.43</td>
<td></td>
</tr>
<tr>
<td>Hydrogen cyanide</td>
<td>HCN</td>
<td>-18.43</td>
<td>-0.98</td>
<td>-3.18</td>
<td>-2.08</td>
<td>-3.48</td>
<td></td>
</tr>
<tr>
<td>Hydrogen fluoride</td>
<td>HF</td>
<td>-20.87</td>
<td>0.07</td>
<td>-2.61</td>
<td>-1.58</td>
<td>-3.03</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>CH$_3$OH</td>
<td>-20.09</td>
<td>0.04</td>
<td>...</td>
<td>-1.47</td>
<td>-3.16</td>
<td></td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>N$_2$O</td>
<td>-20.87</td>
<td>-0.27</td>
<td>-1.14</td>
<td>0.07</td>
<td>-3.99</td>
<td></td>
</tr>
<tr>
<td>Nitrogen trifluoride</td>
<td>NF$_3$</td>
<td>-23.98</td>
<td>-0.77</td>
<td>...</td>
<td>...</td>
<td>-5.07</td>
<td></td>
</tr>
<tr>
<td>Pyrrole</td>
<td>C$_2$H$_4$N</td>
<td>-18.59</td>
<td>-0.40</td>
<td>...</td>
<td>...</td>
<td>-3.34</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>H$_2$O</td>
<td>-19.45</td>
<td>-0.24</td>
<td>...</td>
<td>...</td>
<td>-2.92</td>
<td></td>
</tr>
<tr>
<td>Acetylene</td>
<td>HC≡CH</td>
<td>-15.12</td>
<td>-8.46</td>
<td>-5.8 (0.80)</td>
<td>8.47 (-3.23)</td>
<td>-2.42</td>
<td></td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>O=C=O</td>
<td>-20.87</td>
<td>-11.86</td>
<td>-11.58</td>
<td>12.70</td>
<td>-3.58</td>
<td></td>
</tr>
<tr>
<td>Fluorine</td>
<td>F-F</td>
<td>-22.57</td>
<td>-12.88</td>
<td>14.48 (-2.42)</td>
<td>-2.09</td>
<td>-3.63</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N≡N</td>
<td>-17.27</td>
<td>-10.36</td>
<td>10.14 (-3.70)</td>
<td>2.66</td>
<td>-2.88</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>O=O</td>
<td>-20.62</td>
<td>-8.70</td>
<td>10.22 (-3.11)</td>
<td>-1.02</td>
<td>-3.46</td>
<td></td>
</tr>
</tbody>
</table>

Average signed error -19.49 -0.34 (-0.30) 2.20 (-3.82) -2.11 -3.41
Average unsigned error 19.49 0.42 (0.49) 4.75 (3.82) 2.12 3.41

$^a$ Parenthetical numbers refer to broken symmetry solutions
$^b$ Values for symmetry equivalent centers are not included in the averages
Table 3-7. Difference of a given method with the cc-pCVTZ basis set from experimental values. All values are in eV.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Symbol</th>
<th>Koopmans</th>
<th>IP-VCCS (^{a,b} )</th>
<th>( \Delta E_{relaxed}^{\text{CCSD}} )</th>
<th>( \Delta E_{non-relaxed}^{\text{CCSD}} )</th>
<th>IP-EOM-CCSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>NH(_3)</td>
<td>-17.16</td>
<td>0.47</td>
<td>-1.46</td>
<td>0.21</td>
<td>-1.30</td>
</tr>
<tr>
<td>Methane</td>
<td>CH(_4)</td>
<td>-14.12</td>
<td>0.23</td>
<td>...</td>
<td>0.17</td>
<td>-1.17</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>CO</td>
<td>-19.84</td>
<td>1.28</td>
<td>-1.45</td>
<td>0.35</td>
<td>-1.63</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>H(_2)C=O</td>
<td>-20.39</td>
<td>1.54</td>
<td>...</td>
<td>...</td>
<td>-1.82</td>
</tr>
<tr>
<td>Hydrogen cyanide</td>
<td>HCN</td>
<td>-18.28</td>
<td>0.26</td>
<td>...</td>
<td>...</td>
<td>-2.00</td>
</tr>
<tr>
<td>Hydrogen fluoride</td>
<td>HF</td>
<td>-21.09</td>
<td>1.35</td>
<td>-1.17</td>
<td>0.47</td>
<td>-1.20</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH(_3)OH</td>
<td>-20.15</td>
<td>1.14</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>N(_2)O</td>
<td>-20.84</td>
<td>0.91</td>
<td>...</td>
<td>...</td>
<td>-2.29</td>
</tr>
<tr>
<td>Nitrogen trifluoride</td>
<td>NF(_3)</td>
<td>-23.86</td>
<td>0.64</td>
<td>...</td>
<td>...</td>
<td>-3.37</td>
</tr>
<tr>
<td>Water</td>
<td>H(_2)O</td>
<td>-19.57</td>
<td>0.86</td>
<td>-1.42</td>
<td>0.27</td>
<td>-1.35</td>
</tr>
<tr>
<td>Acetylene</td>
<td>HC≡CH</td>
<td>-14.91</td>
<td>-7.82 (0.36)</td>
<td>-7.71</td>
<td>-1.06</td>
<td>-1.60</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>O=C=O</td>
<td>-20.80</td>
<td>-11.26 (0.66)</td>
<td>-11.72</td>
<td>-1.83</td>
<td>-2.18</td>
</tr>
<tr>
<td>Fluorine</td>
<td>F(_2)</td>
<td>-22.46</td>
<td>-12.09 (2.18)</td>
<td>-14.04</td>
<td>-1.14</td>
<td>-1.65</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N≡N</td>
<td>-17.18</td>
<td>-9.73 (0.47)</td>
<td>-9.39</td>
<td>-1.20</td>
<td>-1.44</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O=O</td>
<td>-18.15</td>
<td>-8.08 (2.94)</td>
<td>-9.49</td>
<td>0.60</td>
<td>-1.88</td>
</tr>
</tbody>
</table>

Average signed error: -19.25 -0.87 (1.02) -6.43 -0.32 -1.78
Average unsigned error: 19.25 0.87 (1.02) 6.43 0.73 1.78

\(^{a}\) Parenthetical numbers refer to broken symmetry solutions

\(^{b}\) Values for symmetry equivalent centers are not taken.

Table 3-8. Comparison of CCSDT with CCSD and IP-EOM-CCSD using the cc-pCVDZ basis set. All values are in eV.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( \Delta E_{non-relaxed}^{\text{CCSDT}} )</th>
<th>( \Delta E_{non-relaxed}^{\text{CCSD}} )</th>
<th>IP-EOM-CCSD</th>
<th>Exp.(^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>407.02</td>
<td>406.99</td>
<td>408.21</td>
<td>405.57</td>
</tr>
<tr>
<td>Fluorine</td>
<td>699.16</td>
<td>699.78</td>
<td>700.32</td>
<td>696.69</td>
</tr>
<tr>
<td>Hydrogen fluoride</td>
<td>695.68</td>
<td>695.76</td>
<td>697.21</td>
<td>694.18</td>
</tr>
<tr>
<td>Water</td>
<td>541.30</td>
<td>541.34</td>
<td>542.72</td>
<td>539.79</td>
</tr>
</tbody>
</table>

\(^{a}\) Ref. [108]
Table 3-9. Comparison of IP-EOM-CCSD and third order corrected IP-EOM-CCSD with experiment\textsuperscript{a}. All values are in eV.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>IP-EOM-CCSD</th>
<th>IP-EOM-CCSD+VCCS(3)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>-2.22</td>
<td>1.05</td>
</tr>
<tr>
<td>Acetylene</td>
<td>-1.56</td>
<td>-1.37</td>
</tr>
<tr>
<td>Ammonia</td>
<td>-1.34</td>
<td>0.45</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>-2.09</td>
<td>-1.87</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>-2.03</td>
<td>0.31</td>
</tr>
<tr>
<td>Carbonyl fluoride</td>
<td>-2.11</td>
<td>-1.87</td>
</tr>
<tr>
<td>Cyanogen</td>
<td>-2.06</td>
<td>-0.64</td>
</tr>
<tr>
<td>Difluoromonoxide</td>
<td>-3.14</td>
<td>-1.37</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>-1.87</td>
<td>1.40</td>
</tr>
<tr>
<td>Formic acid</td>
<td>-2.00</td>
<td>0.18</td>
</tr>
<tr>
<td>Hydrogen cyanide</td>
<td>-2.23</td>
<td>3.70</td>
</tr>
<tr>
<td>Hydrogen fluoride</td>
<td>-1.07</td>
<td>0.48</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>-0.66</td>
<td>-0.47</td>
</tr>
<tr>
<td>Ketene</td>
<td>-2.36</td>
<td>0.94</td>
</tr>
<tr>
<td>Methane</td>
<td>-1.21</td>
<td>0.33</td>
</tr>
<tr>
<td>Methylamine</td>
<td>-1.38</td>
<td>0.48</td>
</tr>
<tr>
<td>Ozone</td>
<td>-2.87</td>
<td>1.65</td>
</tr>
<tr>
<td>Oxirane</td>
<td>-2.00</td>
<td>0.56</td>
</tr>
<tr>
<td>Tetrafluoroethene</td>
<td>-1.97</td>
<td>-1.96</td>
</tr>
<tr>
<td>Trifluoromethane</td>
<td>-1.77</td>
<td>-1.58</td>
</tr>
<tr>
<td>Water</td>
<td>-1.45</td>
<td>0.33</td>
</tr>
<tr>
<td>Ethane</td>
<td>-1.21</td>
<td>-0.97 (-0.21)</td>
</tr>
<tr>
<td>Fluorine</td>
<td>-1.67</td>
<td>-1.57 (0.46)</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>-1.35</td>
<td>-1.10 (-0.17)</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>-1.37</td>
<td>-1.23 (1.13)</td>
</tr>
<tr>
<td>Oxygen</td>
<td>-2.59</td>
<td>-2.46 (-0.50)</td>
</tr>
<tr>
<td>Avg. error</td>
<td>-1.83</td>
<td>-0.25 (0.04)</td>
</tr>
<tr>
<td>Avg. unsigned error</td>
<td>1.83</td>
<td>1.17 (1.01)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Ref. [108]

\textsuperscript{b} Parenthetical numbers refer to broken symmetry solution for the third-order correction.
4.1 Preliminaries

The results presented in Chapters 2 and 3 demonstrate successful approaches for quantities of chemical interest with only mean-field scaling. In contrast, adding higher excitations in CI or CC theory will guarantee the right answer in the limit, but at drastic increases in computational cost. However, for molecules well described by a single reference, CCSD performs satisfactorily, and CCSD with perturbative triples (CCSD(T)) is considered the “gold-standard”; each with $n^2_0 n^6_o$ and $n^3_o n^4_v$ formal scaling respectively. Therefore, pushing these methods forward, to perform calculations on moderately sized molecules, still remains an area of intense research. [34, 35]

Making use of modern supercomputers, equipped with $O(1,000)$ to $O(100,000)$ of compute cores and shared memory on compute nodes is the logical (and necessary) route towards this goal. The ACESIII program package [34] has been designed, very efficiently, with this capability and thus offers a very attractive environment for the massive parallelization of coupled cluster algorithms. In fact, many recent studies have been performed on systems of demonstrable size with coupled cluster methods. [109–112]

However, a new programming paradigm requires new codes for well-established methods, but with a different mindset as to how the data should actually be distributed. One such example with ACESIII, is that the integral package at the beginning, although extremely efficient, only computed the necessary integrals for total energies (kinetic energy, nucleus-electron attraction, electron-electron repulsion, and AO overlap integrals), [113] and was rather limited in applicability due to the lack of property integrals for observables. Consequently, following the blocked design philosophy of Focke [113], arbitrary order moment integrals ($x^p y^q z^r$) integrals and arbitrary derivatives of these integrals were implemented in the integral package. This opened the door for
routine property analysis for the massively parallel MBPT(2) and CCSD programs that already existed, given that the ground state densities are computed for each method.

Similarly, only the right hand eigenvector solutions of $\bar{H}$ were programmed in ACESIII, [110] allowing only the calculation of excitation energies, with no information about the strength of the transition in the spectrum, the avenue for scanning the excited state potential energy surface, or even extremely high accuracy with perturbative triples, all of which need the left hand eigenvector. In fact, in the demonstrable performance paper by Kus [110], the excitation energies of the cytosine-hydroxyl adduct are given by the EE-EOM-CCSD method, and the line intensities are given at the CIS level of theory.

The goal then of this chapter is to extend the massively parallel ground state capabilities of ACESIII to excited states, using the equation of motion coupled cluster methodology. Specifically, one would like a general program for oscillator strengths, or line intensities for UV spectra, benchmark accuracy for excitation energies, given by the EE-EOM-CCSD(T) method, and the ability to scan and characterize critical points on a potential energy surface.

**Simulating ultra-violet spectra.** Theoretically determined excitation energies are necessary to aide experimental spectra, and do so with the accurate assignments of the states by computing the corresponding line intensity, or oscillator strength. In fact, the controversy concerning the structure of water clusters [114–116] points directly to the need of accurate excitation energies and oscillator strengths. Saykally et. al [116] argue that the theoretical methods used to simulate the spectra of structures obtained by Zwier and Shin [114, 115] could generate any number for an oscillator strength, and therefore are not precise enough to provide the quantitative detail necessary.

Since serial EOM-CCSD programs are not able to be used on systems of more than $\sim 10$ heavy atoms in modest sized basis sets, studies of larger water clusters are not possible without a massively parallel implementation. Furthermore, obtaining oscillator strengths requires the solution of the left hand eigenvector of $\bar{H}$, which raises
the computational cost by a factor of 2. In the limit, though, \( \hat{L}_k = \hat{R}_k^\dagger \). Therefore, for any truncation of the EOM-CC equations (where \( \hat{L}_k \neq \hat{R}_k^\dagger \)), one can write

\[
\hat{L}_k = \hat{R}_k^\dagger + \left( \hat{L}_k - \hat{R}_k^\dagger \right) = \hat{R}_k^\dagger + \delta \hat{L}_k, \tag{4-1}
\]

and assume that the second term is negligible. Then, \( \hat{R}_k^\dagger \) represents a good approximation to \( \hat{L}_k \). This would save this factor of 2 in the computation of oscillator strengths. This approximation is tested with the goal of accurate and precise results with half the computational cost.

**Benchmark excitation energies.** Of primary importance to biological systems are the nucleobase and sugar extended networks of DNA. \([117–120]\). The nucleobases include chromophores, and consequently easily accessible excited states, which is a subject of intense computational research. \([121–128]\) Due to the size of these systems, mostly lower level approaches such as CASPT2, TDDFT, MCSCF, and CC2 have been used to examine the vertical excitation spectrum. These methods typically have large, less systematic error compared to EE-EOM-CCSD and EE-EOM-CCSD(T). \([117]\) However, understanding the spectral properties of DNA and RNA requires the accurate calculations on nucleobase dimers, hydrated nucleobases, and nucleoside systems, rather than the nucleobase monomers.

For ground states dominated by a single reference wave function, CC limited to single and double substitutions with a noniterative perturbative treatment of triples (CCSD(T)) \([129, 130]\) is known as the “gold standard” of theoretical methods for finite molecular systems. The CCSD(T) method has been extended to include factorized quadruples effects (CCSD(TQ_r)) \([131, 132]\) and has been formulated using the completely renormalized variants of Piecuch \textit{et al.} \([133, 134]\) Also, a whole perturbative hierarchy on the CC ground state, convergent to the Full CI limit, has been developed, beginning with the CCSD(2) method of Gwaltney \textit{et al.} \([135–137]\) and extended to higher order corrections in the cluster operators and perturbation truncations, \( m \) and
n, respectively \((\text{CC}(m)\text{PT}(n))\) by Hirata et al. [138] Also related as approximations to traditional CC theory are the linear response \(\text{CC} n\) family of methods of Christiansen, Koch, and Jørgensen [139–141]

Similarly, successful noniterative perturbative approaches can be extended to excited states via EOM-CC methodology. Akin to the ground state, completely renormalized variants of Piecuch et al. [142–148] have been developed for excited states (including EOM-CCSD(T), EOM-CCSD(T)\(_L\), r-EOM-CCSD(T)). However, these methods are either not size consistent or not invariant to orbital rotations by virtue of using of Epstein-Nesbet energy denominators. [149, 150] A noniterative perturbative approximation to CC3, [139, 140] named CCSDR(3), [151, 152] performs quite satisfactorily compared to CC3. [153] The \((\text{CC}(m)\text{PT}(n))\) hierarchy of Hirata et al. [138] have been extended for excited states in a similar fashion and denoted EOM-CC\((m)\text{PT}(n)\). [33, 154, 155] This hierarchy converges to the Full CI limit, but incurs severe formal scaling bottlenecks as \(m\) and \(n\) are increased. The specific EOM-CC(2)PT(2)\(_T\) variant is formally equivalent, for the excited state, as the EOM-CCSD(\(\tilde{T}\)) method of Watts and Bartlett. [31, 156] though there is some ambiguity in the treatment of the ground state for the latter method. [33] Taking the leading order terms in the two-electron perturbation, \(\hat{\mathcal{W}}\), of EOM-CCSD(\(\tilde{T}\)) gives the EOM-CCSD(T) method [157] for excited states, an analogue of the CCSD(T) for ground states.

We note that in the original derivation [156] given by Watts for the EOM-CCSD(\(\tilde{T}\)) method, further approximations, on top of defining the orders of the complete \(\hat{R}_k\) and \(\hat{L}_k\) eigenvectors, are made based on order arguments concerning the excitation energy itself (ie. \(\omega_{\text{CCSDT}}\) being replaced by \(\omega_{\text{CCSD}}\)) and it coupled with the perturbative overlap term \((\omega_{\text{CCSDT}}(\hat{L}_k|\hat{R}_k))\). However, these replacements are never needed, since all these terms cancel with a careful examination of the amplitude equations and a properly partitioned Hamiltonian. Furthermore, the order-by-order analysis and rederivation given by Gwaltney et al. [31] contains an \(\omega_{\text{CCSD}}\) dependence in the denominator, and this is
removed by a suitably partitioned Hamiltonian. We partition the similarity transformed Hamiltonian of CC theory, $\bar{H}$ in a similar spirit to Stanton and Gauss’ partitioning scheme [158–160] to arrive at the EOM-CCSD($\bar{T}$) energy expression and amplitude equations with no approximation other than the limitation to triple substitutions in the $Q$-space. A simple Löwdin type partitioning [161] is also applied, analogous to Stanton’s analysis of CCSD(T) [162] and extension by Stanton and Crawford [163], which bolsters the presented derivation. Furthermore, one can take the lead terms in $\hat{V}$ to arrive at EOM-CCSD(T) or one can perform a Møller-Plesset [164] type partitioning of $\bar{H}$, [158–160, 162, 163] transparent with Löwdin partitioning, to arrive at the EOM-CCSD(T) fourth order correction to the excitation energy.

These noniterative perturbative triples methods have mostly been tested on small prototypical systems. Recently, a robust test set consisting of over 24 molecules and over 120 excited states has been proposed and used in assessing the accuracy of TDDFT and MRCI methods [165] as well as CASPT2, CC2, EOM-CCSD, and CC3 methods [166]. This test set was also used for benchmarking the perturbative CCSDR(3) method compared to its iterative analogue, CC3. [153] One wonders how well any of these other perturbative methods would perform over this wide variety of chromophores.

In that vein, the EOM-CCSD($\bar{T}$) and EOM-CCSD(T) are rederived in a different light, implemented in a massively parallel way, and compared against the formally robust EOM-CCSDT-3 method [31, 156] with the aforementioned test set. For completeness, the CCSDR(3) and CC3 methods, which are linear response analogues of the former methods, are compared against EOM-CCSDT-3.

In a rather interesting turn of events, the EE-EOM-CCSD(T), having been shown to have less satisfactory performance for excited states compared to the remarkable performance of CCSD(T) for ground states [33] for small molecules essentially reproduces the iterative and robust EE-EOM-CCSDT-3 method for the larger nucleobase
systems for all types of transitions. [117] Also, the EE-EOM-CCSD(\(\bar{T}\)) method, which performed remarkably well for a class of systems [32] performs far less satisfactorily for general transitions of a variety of organic molecules, [167] typically overshooting the correct triples energy.

As a result, since the EE-EOM-CCSD(T) method is a factor of 2 faster than the EE-EOM-CCSD(\(\bar{T}\)) variant and more accurate over a wide-ranging test set, this is the method of choice for benchmarking the excited states of the nucleobase systems. Since this method also follows from the energy functional, the \(\hat{L}_k = \hat{R}_k^\dagger\) is tested to seek significant time savings. Along with a new derivation and massively parallel implementation, benchmark results are presented for microhydrated cytosine, cytidine, guanosine, and the Watson-Crick cytosine-guanine base pair.

**Characterizing the potential energy surface.** The accurate and feasible characterization of ground and excited state potential energy surfaces of chemically relevant systems is one of the most important research topics in modern quantum chemical methods. The EE-EOM-CCSD method is considered a “black-box” method, capable of high accuracy, and retains the opportunity for systematic corrections. However, there are currently only serial implementations of the EE-EOM-CCSD gradients, greatly limiting the applicability of the method to small systems. A massively parallel implementation is necessary to tackle larger systems.

Specifically, questions remain about the relaxation mechanisms along the potential energy surface of DNA and RNA after absorption of ultra-violet light. [117, 168]. Lower level methods, including semi-empirical [169–173] and CASSCF, [168, 174–176] MR-CIS, [168, 177], and TDDFT [169, 178, 179] molecular dynamics have been used, and without an accurate account of the relative energies of the involved electronic states, the picture obtained can be quite unreliable. [112].

Therefore, the massively parallel implementation of the EE-EOM-CCSD gradients are given, with demonstrable scaling curves. The sizes of the systems also speak for the
applicability of the code. I demonstrate the performance on the nucleobases cytosine, guanine, thymine, and adenine, as well as the cytosine-guanine stacked dimer. This allows the routine use of EE-EOM-CCSD theory for accurate scanning of potential energy surfaces of chemically relevant molecules.

Analyzing the ground and excited state densities and the difference between the two is essential for a deeper understanding of the involved transitions and the electronic redistribution. To this end, the densities and density differences are computed and stored on disk, in a *molden* [180] readable format.

### 4.2 General Theory

In EOM-CC methods, the Hamiltonian that is diagonalized in the appropriate sector of Fock space, $\hat{H}$, is not hermitian, having both left and right eigenvectors. These are chosen to be biorthogonal

$$
\delta_{kl} = \langle \tilde{\Psi}_k | \Psi_l \rangle = \langle \Phi_0 | \hat{L}_k \hat{R}_l | \Phi_0 \rangle 
$$

yielding the CC energy functional

$$
E_k = \langle \Phi_0 | \hat{L}_k \hat{H} \hat{R}_k | \Phi_0 \rangle. 
$$

When the CC equations are limited to single and double substitutions only, the $\hat{L}_k$ and $\hat{R}_k$ eigenvectors have the form

$$
\hat{R}_k | \Phi_0 \rangle = (r_0 + \hat{R}_{1k} + \hat{R}_{2k}) | \Phi_0 \rangle = r_0 | \Phi_0 \rangle + \sum_i r_i^a | \Phi_i^a \rangle + \frac{1}{4} \sum_{iab} r_{ij}^a | \Phi_{ij}^{ab} \rangle 
$$

$$
\langle \Phi_0 | \hat{L}_k = \langle \Phi_0 | (l_0 + \hat{L}_{1k} + \hat{L}_{2k}) = \langle \Phi_0 | l_0 + \sum_i \langle \Phi_i^a | l_i^a \rangle + \frac{1}{4} \sum_{iab} \langle \Phi_{ij}^{ab} | l_{ij}^{ab} \rangle. 
$$

Note the linear vectors resemble a CI ansatz, where the $r_0$ term is necessary to describe excited states of the same symmetry as the ground state; $l_0$ is zero by construction for all excited states ($l_0 = 1$ for the ground state). [15]
The CC functional of Equation (4–3) satisfies the generalized Hellman-Feynman property, [15] since linear variations in the \( \hat{L}_k \) and \( \hat{R}_k \) eigenvectors is zero, and sets up a suitable perturbation parameterization at the EOM-CCSD level with the \( P \)-space defined by the ground, singly, and doubly excited determinants \( P = \{ |\Phi_0\rangle, |\Phi_i^s\rangle, |\Phi_i^{ab}\rangle \} \) and the \( Q \)-space containing higher excited determinants. Consequently, properties, including transition moments and oscillator strengths, can be computed with little computational effort, and perturbative corrections due to higher excitations can be computed as well for benchmark quality singly excited states. Also, the functional can be differentiated with respect to geometrical perturbations allowing the computation of gradients and critical points on a potential energy surface.

### 4.3 Expectation Value Form for One-Electron Properties

The expectation value of any linear operator in EOM-CC theory is

\[
\theta = \langle \Phi_0 | \hat{L}_k \theta \hat{R}_k | \Phi_0 \rangle \tag{4–6}
\]

\[
= \text{Tr} [ \theta \rho ] \tag{4–7}
\]

with \( \theta \) being the matrix representation of the operator in the molecular orbital basis, and the reduced \( n \)-particle density matrix, \( \rho \), given by

\[
\rho_{pq...rs} = \langle \Phi_0 | \hat{L}_k \left( \{ p^\dagger q^\dagger ... sr \} e^\dagger \right)_c \hat{R}_k | \Phi_0 \rangle \tag{4–8}
\]
The reduced 1-particle density matrix is particularly simple, given in einstein notation [25] as

\[
\rho_{ij} = -r_0 \left( \frac{\mu^j_{c} \epsilon^i_{l} + \frac{1}{2} \mu^j_{cd} \epsilon^i_{ik}}{l_{c} \epsilon^i_{l} - \frac{1}{2} \mu^j_{cd} \epsilon^i_{ik}} \right) - \frac{1}{2} \mu^j_{cd} \epsilon^i_{ik}
\]

(4–9)

\[
\rho_{ab} = -r_0 \left( l^a_{b} \epsilon^a_{c} + \frac{1}{2} l^a_{cd} \epsilon^a_{ik} \right) + \frac{1}{2} r^a_{i} \epsilon^a_{ik}
\]

(4–10)

\[
\rho_{ia} = r_0 l^i_{a} + \frac{1}{2} l^i_{ac} \epsilon^a_{ki}
\]

(4–11)

\[
\rho_{ai} = r_0 \left( l^i_{c} \left( \epsilon^a_{ki} - \epsilon^a_{ci} \right) + \frac{1}{2} \left( t^a_{cd} \epsilon^i_{l} + t^a_{cd} \epsilon^i_{cd} \right) \epsilon^a_{cl} + \epsilon^i_{a} \right)
\]

\[
+ l^i_{c} \left( r^a_{ic} - \epsilon^a_{ci} \right) + \frac{1}{2} l^i_{cd} \left( t^a_{ci} - \epsilon^a_{ci} \right) r^a_{ci}
\]

\[
- \frac{1}{2} l^i_{cd} \left( t^a_{cd} \epsilon^a_{ci} + t^a_{cd} \epsilon^a_{cd} \right) - \frac{1}{2} l^i_{cd} \left( t^a_{cd} \epsilon^a_{ci} + t^a_{cd} \epsilon^a_{cd} \right)
\]

(4–12)

and is the only necessary quantity for a given one-electron property. In practice, suitable intermediates are formed, or factorization is performed, that can be chosen to reduce disk space requirements or increase parallelizability. As an example, it would be unwise to program the \( t^a_{cd} \epsilon^a_{ci} \) piece of Equation (4–12) as an intermediate. The storage requirements would be \( n_0^3 n_\psi^3 \) and the resulting tensor contraction with \( l^i_{cd} \) would scale the same, or roughly \( N^6 \). Rather, the intermediate \( l^i_{cd} t^a_{cd} \) is formed in an \( n_0^2 n_\psi^3 \) contraction step with only \( n_0^2 n_\psi^2 \) storage (if stored) and then contracted with \( t^a_{cd} \) in a simple \( n_0 n_\psi^2 \) contraction step.

However, one has the choice to compute the intermediates ahead of time and store them in memory or on disk, or compute the intermediates on the fly. In a serial program, the intermediates are generally computed on the fly and used immediately after, thus avoiding the storage. This can hurt a parallel program. In pseudo code, the on the fly contraction is

\[
\text{PARDO a, c}
\]
\[ Y_c^a = 0.0 \]

\begin{verbatim}
DO k
  DO l
    DO d
      REQUEST \[ l_{cd}^{kl} \]
      REQUEST \[ t_{kl}^{ad} \]
      \[ Y_c^a = Y_c^a + l_{cd}^{kl} \cdot t_{kl}^{ad} \]
    ENDDO d
  ENDDO l
ENDDO k

DO i
  GET \[ t_i^c \]
  \[ X_i^a = Y_c^a \cdot t_i^c \]
  \[ \rho_i^{a+} = X_i^a \]
ENDDO i
ENDPARDO a, c
\end{verbatim}

This implementation only parallelizes over blocks \( a \) and \( c \) and worse, requests data in the innermost loop. The “better” way to perform this contraction, to demonstrate with pseudo code,

\begin{verbatim}
PARDO d, k, l, c
  REQUEST \[ l_{cd}^{kl} \]
  DO a
    REQUEST \[ t_{kl}^{ad} \]
    PUT \[ Y_c^a + = Y_c^a + l_{cd}^{kl} \cdot t_{kl}^{ad} \]
  ENDDO a
ENDPARDO d, k, l, c
\end{verbatim}
EXECUTE SIP_BARRIER

PARDO i, a, c
GET Y^a_c
GET t^c_i
X^a_i = Y^a_c \cdot t^c_i
\rho^a_i + = X^a_i
ENDPARDO i, a, c

In the above, the intermediate Y is formed, parallelized over 4 indices, and stored in memory. Once all blocks of Y have been computed and stored (at the SIP_BARRIER), a simple, completely parallelized contraction is performed to compute the contribution to the density. The intermediate array can subsequently be destroyed, so the block of memory is freed and able to be used again.

Of particular importance in excited state calculations is transition moments and the corresponding oscillator strengths. Since \( \hat{H} \) has left and right eigenvectors, left and right transition moments (\( \theta_{0k} \) and \( \theta_{k0} \), respectively) are computed for the dipole strength, \( D \), as

\[
D = \langle \Phi_0 | \hat{L}_0 \hat{\mu} \hat{R}_k | \Phi_0 \rangle \langle \Phi_0 | \hat{L}_k \hat{\mu} \hat{R}_0 | \Phi_0 \rangle
\]

\[= \text{Tr} [\mu \rho_{0k}] \text{Tr} [\mu \rho_{k0}]
\]

\[= \theta_{0k} \theta_{k0},\]

which is used to compute the oscillator strength, or line intensity \( f \), as

\[
 f = \frac{2}{3} \omega_k D.
\]

The EE-EOM-CCSD method has been very successful in determining excitation energies and computing the corresponding oscillator strengths. [25] However, this
expectation value formula requires the solution of $\hat{R}_k$ and $\hat{L}_k$, which raises the computational effort by a factor of two. It would be nice if this effort could be reduced. In that vein, we experimented with replacing $\hat{L}_k$ by $\hat{R}_k^\dagger$ to compute the density and properties. This can be justified by noting that in the limit of Full CI or CC, $\hat{L}_k = \hat{R}_k$. We test the hypothesis that the left eigenvector should be well represented by the right eigenvector, truncating at the singles and doubles level.

4.3.1 Implementation

The eigenvalue equation to determine the left hand eigenvector was implemented in ACESIII. The $\hat{R}$ eigenvectors are used as initial guesses, reducing the number of iterations, on average, needed to converge the diagonalization algorithm. The largest contribution ($\sim n_o^2 \ n_v^4$)

$$\frac{1}{2} \sum_{cd} \langle ab||cd\rangle \ l^l_{cd} \rightarrow l^l_{ab}$$

is computed directly by backtransforming the virtual indices of the $\hat{L}_k$ amplitude array and contracting with two-electron AO integrals generated on-the-fly. This increases scalability, as the $\langle ab||cd\rangle$ integral arrays are so large, and would need to be read off disk every iteration. It reduces disk storage and performs significantly better than the “indirect” algorithm [110] at the cost of more floating point operations.

Intermediates were formed at the cost of storage due to the large gain in parallelization. Not only because the computation of each intermediate is more efficiently parallelized, but the intermediates can be computed independently from each other, giving further gains in performance. After all the independent intermediates are computed, they are used in the final contractions to form the density, and immediately deleted to restore space.

The EOM-CCSD density code was implemented in a general way to allow the use of $\hat{L}_k$ or $\hat{R}_k^\dagger$ amplitudes. In fact, since the computational time of computing the density is small, when using appropriate intermediates, in comparison to the right or left EOM computation, after computing the right and left hand side, the properties are computed
with the $\hat{R}_k^\dagger$ approximation and $\hat{L}_k$ eigenvector, respectively. Meaning, if only the right hand code is run, then the oscillator strengths correspond to the $\hat{R}_k^\dagger$ approximation.

**Blocked moment integrals.** The $x^p$, $y^q$, and $z^r$ integrals necessary for calculating the dipole and transition moments, for any level of theory (provided a density matrix is computed), were implemented in the ACESIII program package making use of its block structure. This was done in the most general way to allow the computation of arbitrary moment integrals.

A quick description can be given starting with a general moment integral centered at C between two AOs centered at A and B

$$\langle \phi_\mu | M(\mu) | \phi_\nu \rangle = \int d\mathbf{r}_1 \phi^A_{\alpha.l_a,m_a,n_a}(\mathbf{r}_1) M^C_{s,t,u}(\mu) \phi^B_{\beta.l_b,m_b,n_b}(\mathbf{r}_1)$$  \hspace{1cm} (4–18)

with

$$\phi^A_{\alpha.l_a,m_a,n_a}(\mathbf{r}_1) = (x - A_x)^{l_a}(y - A_y)^{m_a}(z - A_z)^{n_a} e^{-p|\mathbf{r}_1 - \mathbf{R}_A|^2}$$  \hspace{1cm} (4–19)

$$\phi^B_{\beta.l_b,m_b,n_b}(\mathbf{r}_1) = (x - B_x)^{l_b}(y - B_y)^{m_b}(z - B_z)^{n_b} e^{-p|\mathbf{r}_1 - \mathbf{R}_B|^2}$$  \hspace{1cm} (4–20)

$$M^C_{s,t,u}(\mu) = (x - C_x)^s(y - C_y)^t(z - C_z)^u$$  \hspace{1cm} (4–21)

Focusing on one cartesian coordinate, since they are separable, we can rewrite the moment integral as

$$\langle \phi_\mu | M(\mu) | \phi_\nu \rangle = \int d\mathbf{r}_1 \phi^A_{\alpha,a}(\mathbf{r}_1) M^C_{a}(\mu) \phi^B_{\beta,b}(\mathbf{r}_1)$$  \hspace{1cm} (4–22)

$$= \int d\mathbf{r}_1 M^C_{a}(\mu) \phi^P_{p,a,b}(\mathbf{r}_1)$$  \hspace{1cm} (4–23)

$$= \int d\mathbf{r}_1 \phi^P_{p,a,b,s}(\mathbf{r}_1)$$  \hspace{1cm} (4–24)

with the modified overlap Gaussian given as

$$\phi^P_{p,a,b,s}(\mathbf{r}_1) = (x - A_x)^a(x - B_x)^b(x - C_x)^s e^{-p|\mathbf{r}_1 - \mathbf{R}_P|^2}$$  \hspace{1cm} (4–25)
With this form, it is clear that the integrals reduce to modified overlap integrals. Since the ACESIII program package contains a very efficient integral package with overlap integrals, [113] and arbitrary derivative overlap integrals, the necessary modifications were made to incorporate moment integrals to any power and arbitrary derivative moment integrals to any power. This implementation greatly increased the applicability of ACESIII, and given these integrals yield chemical properties, resulted in a greater chemical understanding, of DNA nucleobases and complexes [110, 112, 117] and large chemical explosive compounds. [111]

4.3.2 Results and Discussion

Various biologically relevant molecules in an assortment of basis sets formed the test set to examine using the right hand EOM eigenvector, \( \hat{R}_k^\dagger \), in place of the true left hand eigenvector, \( \hat{L}_k \) for computing oscillator strengths. Included in this are the four nucleobases (adenine, cytosine, thymine, and guanine) with augmented double-\( \zeta \) and triple-\( \zeta \) basis sets, the nucleosides cytidine and guanosine in an augmented double-\( \zeta \) basis set, hydrated cytosine molecules with augmented double-\( \zeta \) basis sets and two Watson-Crick base pairs, adenine-thymine and cytosine-guanine in Ahlrichs’ triple-\( \zeta \) basis set [181]. The lowest eleven or twelve roots are computed at the EOM level resulting in a test set of 187 excited states. The deviation of the total oscillator strengths compared to the formally correct expectation value formula is shown in Figure 4-1. The bright states are separated from the dark states since on average, they appear to differ more significantly from the dark states. Most dark states have an intensity under \( 10^{-3} \), and this approximation faithfully captures this. Also, since the magnitude of the bright states in relation to each other is the important quantity, the minor deviations seen for them are relatively insignificant. On average, the bright and dark states differ from the exact by 0.003 and 0.0003 units, respectively.

Further analysis with small molecules used \( \hat{\Lambda} = \hat{T}^\dagger \) to explore more time savings. This also performed exceptionally well as demonstrated in Table 4.6. A skewed structure
of ammonia was used since it has $C_1$ symmetry, and the approximate oscillator strengths are in almost perfect agreement with the exact ones. The lambda equations are relatively fast to solve, compared to the EOM equations, possibly making this approximation unnecessary. Nevertheless, it does save a factor of 2 in the ground state calculation.

This degree of accuracy demonstrates quality of the CC wavefunction. In the limit of the exact Full CI result, the left and right hand eigenvectors are equivalent. Therefore, this accurate description of the oscillator strengths reflects the fast convergence property of CC, or in other words, it illustrates that $\hat{R}_k^l \approx \hat{L}_k$ at the CCSD level. More notably, with confidence, one can completely neglect the left hand EOM equations if seeking the oscillator strengths and first-order properties alone. This saves a factor of 2 in the excited state calculations, with no approximations made to the excitation energy itself.

### 4.4 Perturbative Triples for Accurate Energies.

The $P$-space for EE-EOM-CCSD is spanned by the reference determinant with a projector, $|0\rangle\langle 0|$ and the $Q$-space is spanned by the singly, $|S\rangle$, and doubly, $|D\rangle$, excited determinants with a projector

$$Q = |S\rangle\langle S| + |D\rangle\langle D|$$

$$= \sum_{ia} |\Phi_i^a\rangle\langle \Phi_i^a| + \frac{1}{4} \sum_{ijab} |\Phi_{ij}^{ab}\rangle\langle \Phi_{ij}^{ab}|$$

This partitions the Hamiltonian, $\tilde{H}$, explicitly as

$$\tilde{H} = \begin{bmatrix} \tilde{H}_{PP} & \tilde{H}_{PQ} \\ \tilde{H}_{QP} & \tilde{H}_{QQ} \end{bmatrix} = \begin{bmatrix} 0 & \tilde{H}_{0S} & \tilde{H}_{0D} \\ 0 & \tilde{H}_{SS} & \tilde{H}_{SD} \\ 0 & \tilde{H}_{DS} & \tilde{H}_{DD} \end{bmatrix},$$

clearly indicating that only the $Q$-space of $\tilde{H}$ needs to be diagonalized. This is critical when examining perturbative triples corrections to EE-EOM-CCSD.
It will be useful to define the following quantities used in the perturbative triples correction to EE-EOM-CCSD. We will redefine the $P$-space to be spanned by the ground, singly, and doubly excited determinants with a projector

$$P = |0\rangle\langle 0| + |S\rangle\langle S| + |D\rangle\langle D|$$

(4–29)

$$= |\Phi_0\rangle\langle \Phi_0| + \sum_{ia} |\Phi_{i}^a\rangle\langle \Phi_{i}^a| + \frac{1}{4} \sum_{ijab} |\Phi_{ij}^{ab}\rangle\langle \Phi_{ij}^{ab}|$$

(4–30)

and the $Q$-space will be limited to triples, $Q \equiv Q_3 = \frac{1}{36} \sum_{ijk} \sum_{abc} |\Phi_{ijk}^{abc}\rangle\langle \Phi_{ijk}^{abc}|$. The complete similarity transformed Hamiltonian, $\bar{H}$, is partitioned in the $P$- and $Q$-spaces as

$$\bar{H} = (P + Q) \bar{H}(P + Q)$$

(4–31)

$$= \bar{H}_{PP} + \bar{H}_{PQ} + \bar{H}_{QP} + \bar{H}_{QQ}.$$  

(4–32)

and partitioned in orders as

$$\bar{H} = \bar{H}^{(0)} + \bar{W}^{(1)}$$

(4–33)

with the zeroth order Hamiltonian

$$\bar{H}^{(0)} = P\bar{H}P + Q(\omega_{\text{CCSD}} + f_{oo} + f_{vv})Q$$

(4–34)

and $\bar{W}^{(1)}$ containing the rest of the $\bar{H}$ matrix in the appropriate spaces. Note that the subscripts are used to reduce clutter. The freedom to include the EE-EOM-CCSD excitation energy, $\omega_{\text{CCSD}}$, and the (semi)canonical occupied-occupied and virtual-virtual Fock matrices, $f_{oo}$ and $f_{vv}$, respectively in the $Q$-space was used, as it will define (and simplify) the resulting energy denominators while maintaining orbital invariance. [33, 182]

This partitioning will define the EE-EOM-CCSD($\bar{T}$) method originally developed by Watts and Bartlett [31] and further examined by Gwaltney et. al [156] with $\bar{H}$ given
explicitly as
\[
\tilde{H} = \begin{bmatrix}
\tilde{H}_{PP} & \tilde{H}_{PQ} \\
\tilde{H}_{QP} & \tilde{H}_{QQ}
\end{bmatrix} = \begin{bmatrix}
0 & \tilde{H}_{0S} & \tilde{H}_{0D} & \tilde{H}_{0T} \\
0 & \tilde{H}_{SS} & \tilde{H}_{SD} & \tilde{H}_{ST} \\
0 & \tilde{H}_{DS} & \tilde{H}_{DD} & \tilde{H}_{DT} \\
\tilde{H}_{T0} & \tilde{H}_{TS} & \tilde{H}_{TD} & \tilde{H}_{TT}
\end{bmatrix}
\] (4–35)

We note in passing that the \(Q_3\)-projections would be zero if the full triples were solved for in the ground state. This has been alluded to by Shiozaki \textit{et. al} \cite{33} where they address the ambiguity of triples in the ground state for this method.

The exact left and right hand eigenvectors up to triples for state \(k\), \(\hat{L}_k\) and \(\hat{R}_k\), are
\[
\langle \Phi_0 | \hat{L}_k = \langle \Phi_0 | \hat{L}_k (P + Q) = \langle \Phi_0 | \hat{L}_P + \langle \Phi_0 | \hat{L}_Q \\
= \langle \Phi_0 | (\hat{L}_{1k} + \hat{L}_{2k}) + \langle \Phi_0 | \hat{L}_{3k} \\
\hat{R}_k | \Phi_0 \rangle = (P + Q) \hat{R}_k | \Phi_0 \rangle = \hat{R}_P | \Phi_0 \rangle + \hat{R}_Q | \Phi_0 \rangle \\
= (r_{0k} + \hat{R}_{1k} + \hat{R}_{2k}) | \Phi_0 \rangle + \hat{R}_{3k} | \Phi_0 \rangle
\] (4–36)

With these definitions, the excitation energy can be written as
\[
\omega_k = \omega = \omega_P + \omega_Q = \omega_{\text{CCSD}} + \omega_Q
\] (4–40)

The starting point for perturbative corrections to the excitation energy is the EE-EOM-CCSD energy functional partitioned with the defined \(P\) and \(Q\)-spaces,
\[
\omega \langle \Phi_0 | \hat{L}_k \hat{R}_k | \Phi_0 \rangle = \langle \Phi_0 | \hat{L}_k \left[ \tilde{H}, \hat{R}_k \right] | \Phi_0 \rangle \\
(\omega_P + \omega_Q) \left( \hat{L}_P \hat{R}_P + \hat{L}_Q \hat{R}_Q \right) = \langle \Phi_0 | \hat{L}_k \left( \tilde{H} \hat{R}_k \right)_C | \Phi_0 \rangle \\
(\omega_P + \omega_Q) \left( \hat{L}_P \hat{R}_P + \hat{L}_Q \hat{R}_Q \right) = \left[ \hat{L}_P \quad \hat{L}_Q \right] \begin{bmatrix}
\tilde{H}_{PP} & \tilde{H}_{PQ} \\
\tilde{H}_{QP} & \tilde{H}_{QQ}
\end{bmatrix} \begin{bmatrix}
\hat{R}_P \\
\hat{R}_Q
\end{bmatrix}
= \hat{L}_P \tilde{H}_{PP} \hat{R}_P + \hat{L}_P \tilde{H}_{PQ} \hat{R}_Q + \hat{L}_Q \tilde{H}_{QP} \hat{R}_P + \hat{L}_Q \tilde{H}_{QQ} \hat{R}_Q
\] (4–41)

\(\omega_P + \omega_Q\) \left( \hat{L}_P \hat{R}_P + \hat{L}_Q \hat{R}_Q \right) = \left[ \hat{L}_P \quad \hat{L}_Q \right] \begin{bmatrix}
\tilde{H}_{PP} & \tilde{H}_{PQ} \\
\tilde{H}_{QP} & \tilde{H}_{QQ}
\end{bmatrix} \begin{bmatrix}
\hat{R}_P \\
\hat{R}_Q
\end{bmatrix}
= \hat{L}_P \tilde{H}_{PP} \hat{R}_P + \hat{L}_P \tilde{H}_{PQ} \hat{R}_Q + \hat{L}_Q \tilde{H}_{QP} \hat{R}_P + \hat{L}_Q \tilde{H}_{QQ} \hat{R}_Q (4–44)
The first terms on the left and right hand side cancel. We are free to subtract $\hat{L}_Q \omega_{CCSD} \hat{R}_Q$ from both sides to remove the second term and therefore arrive at the following expression for the energy correction, using the normalization condition $\langle \Phi_0 | \hat{L}_P \hat{R}_P | \Phi_0 \rangle = 1$,

$$\omega_1 + \omega \langle \Phi_0 | \hat{L}_Q \hat{R}_Q | \Phi_0 \rangle = \langle \Phi_0 | \hat{L}_P \hat{H}_{PQ} \hat{R}_Q + \hat{L}_Q \hat{H}_{QP} \hat{R}_P + \hat{L}_Q (\hat{H}_{QQ} - \omega_{CCSD}) \hat{R}_Q | \Phi_0 \rangle. \quad (4-45)$$

To further simplify, we examine the projected equations for the right hand side

$$Q \omega \hat{R}_k | \Phi_0 \rangle = Q (\hat{H} \hat{R}_k)_C | \Phi_0 \rangle \quad (4-46)$$

$$\left(\omega_{CCSD} + \omega \right) \hat{R}_Q | \Phi_0 \rangle = \left( \hat{H}_{QP} \hat{R}_P \right)_C | \Phi_0 \rangle + \left( \hat{H}_{QQ} \hat{R}_Q \right)_C | \Phi_0 \rangle \quad (4-47)$$

$$\omega \hat{R}_Q | \Phi_0 \rangle = \left( \hat{H}_{QP} \hat{R}_P \right)_C | \Phi_0 \rangle + \left( \hat{H}_{QQ} - \omega_{CCSD} \right) \hat{R}_Q | \Phi_0 \rangle \quad (4-48)$$

Insertion of this final expression in Equation (4–45) simplifies the energy correction (dropping the connected subscript)

$$\omega_1 + \omega \langle \Phi_0 | \hat{L}_Q \hat{R}_Q | \Phi_0 \rangle = \langle \Phi_0 | \hat{L}_P \hat{H}_{PQ} \hat{R}_Q + \omega \hat{L}_Q \hat{R}_Q | \Phi_0 \rangle \quad (4-49)$$

$$\omega = \langle \Phi_0 | \hat{L}_P \hat{H}_{PQ} \hat{R}_Q | \Phi_0 \rangle. \quad (4-50)$$

All that remains is to define $\hat{R}_Q$. To this end, we use the Hamiltonian separated by the defined orders and collect the lowest order correction, in $\tilde{W}^{(1)}$, to $\omega_Q$. Applying this to the amplitude equation (4–48), showing explicitly the orders and triples $Q$-space

$$\omega_3 \hat{R}_Q | \Phi_0 \rangle = \hat{H}_{Q,3P} \hat{R}_P | \Phi_0 \rangle + (\hat{H}_{Q,3} - \omega_{CCSD}) \hat{R}_Q | \Phi_0 \rangle \quad (4-51)$$

$$(\omega_3^{(2)} - \hat{R}_Q^{(0)} + \omega_{CCSD}^{(0)}) \hat{R}_Q^{(1)} | \Phi_0 \rangle = \hat{H}_{Q,3P}^{(1)} \hat{R}_P | \Phi_0 \rangle \quad (4-52)$$

$$(f_{oo} + f_{uv}) \hat{R}_Q^{(1)} | \Phi_0 \rangle = \tilde{W}^{(1)}_{Q,3P} \hat{R}_P | \Phi_0 \rangle \quad (4-53)$$

$$\hat{R}_Q^{(1)} | \Phi_0 \rangle = D_3 \tilde{W}^{(1)}_{Q,3P} \hat{R}_P | \Phi_0 \rangle. \quad (4-54)$$
The energy denominator, $D_3$, using the definitions given in Equation (4–34) is

\[
D_3 = Q_3 \left( \frac{\tilde{H}^{(0)}_{Q_3}}{Q_3} - \omega_{CCSD} \right) Q_3 \tag{4–55}
\]

\[
= Q_3 \left( \omega_{CCSD} + f_\infty + f_{sv} - \omega_{CCSD} \right) Q_3 \tag{4–56}
\]

\[
= \frac{1}{36} \sum_{ijk} \sum_{abc} |\Phi_{ijk}^{abc}\rangle \langle \Phi_{ijk}^{abc}| \epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c \tag{4–57}
\]

The $R_{Q_3}^{(1)}$ is defined explicitly as

\[
Q_4 R_{Q_3}^{(1)} = Q_3 D_3 \left( r_0 \tilde{W}^{(1)} |\Phi_0\rangle + (\tilde{W}^{(1)} R_{1k})_c |\Phi_0\rangle + (\tilde{W}^{(1)} R_{2k})_c |\Phi_0\rangle \right) \tag{4–58}
\]

\[
= Q_3 D_3 \left( (\tilde{W}^{(1)} R_{1k})_c |\Phi_0\rangle + (\tilde{W}^{(1)} R_{2k})_c |\Phi_0\rangle \right) \tag{4–59}
\]

with the second order correction to the EE-EOM-CCSD excitation energy given as

\[
\delta\omega^{(2)} = \langle \Phi_0 | \hat{L}_P \tilde{W}^{(1)}_{PQ_3} \left( (\tilde{W}^{(1)} R_{1k})_c + (\tilde{W}^{(1)} R_{2k})_c \right) |\Phi_0\rangle \tag{4–60}
\]

Since we have limited ourselves to $Q_3$, the correction scales $\sim n_3^2 n_v^4$. Note that the $r_0$ term vanishes, as it is a scalar and cannot be connected to $\tilde{W}$.

We now highlight some of the new features of this derivation. The original derivation given by Watts et al. [31] makes apparent approximations such as replacing $\omega_Q$ ($\omega_{CCSDT-3}$ in their derivation) by $\omega_{CCSD}$ and neglecting the overlap $\langle \Phi_0 | \hat{L}_3k |\Phi_0\rangle$ based on the negligible magnitude of these terms, however, they are seen to be unnecessary with this partitioning. The second derivation, and order-by-order analysis, given by Gwaltney et al. [156] is very similar in spirit to the presented derivation, but still contains the $\omega_{CCSD}$ dependence in the denominator, shown here to vanish.

In fact, a much simpler derivation that highlights these results can be done by using Löwdin partitioning. [161–163] First, we need to express the functional form in a form
that is more easily manipulated,

\[
\omega_k = \langle 0 | \hat{\mathcal{L}}_k [\hat{\mathcal{H}}, \hat{\mathcal{R}}_k] | 0 \rangle
\]

\[
= \langle 0 | \hat{\mathcal{L}}_k \hat{\mathcal{H}} \hat{\mathcal{R}}_k | 0 \rangle - \langle 0 | \hat{\mathcal{L}}_k \hat{\mathcal{R}}_k \hat{\mathcal{H}} | 0 \rangle
\]

\[
= \langle 0 | \hat{\mathcal{L}}_k \hat{\mathcal{H}} \hat{\mathcal{R}}_k | 0 \rangle - \langle 0 | \hat{\mathcal{L}}_k \hat{\mathcal{R}}_k (P + Q_3) \hat{\mathcal{H}} | 0 \rangle
\]

\[
= \langle 0 | \hat{\mathcal{L}}_k \hat{\mathcal{H}} \hat{\mathcal{R}}_k | 0 \rangle - \langle 0 | \hat{\mathcal{L}}_k \hat{\mathcal{R}}_k | Q_3 \rangle \langle Q_3 | \hat{\mathcal{H}} | 0 \rangle
\]

\[
= \langle 0 | \hat{\mathcal{L}}_k (\hat{\mathcal{H}} - E_0) \hat{\mathcal{R}}_k | 0 \rangle - r_0 \langle 0 | \hat{L}_{k3} \hat{W} | 0 \rangle.
\]

Notice that in Equation (4–65) we will be including the \( \hat{H}_{T0} \) block described at the beginning of this section, and we will carry along the scalar, \( -r_0 \langle 0 | \hat{L}_{k3} \hat{W} | 0 \rangle \). With this form, we can perform a Löwdin type partitioning on the disconnected functional in the \( P \)-space as

\[
\omega_{\text{exact}} = \langle \Phi_0 | \hat{L}_P \hat{W}_P | \Phi_0 \rangle + \langle \Phi_0 | \hat{L}_P \hat{H}_{PQ} (\omega_{\text{exact}} - \hat{H}_{QQ})^{-1} \hat{H}_{QP} \hat{P}_P | \Phi_0 \rangle - r_0 \langle 0 | \hat{L}_{k3} \hat{W} | 0 \rangle
\]

The lowest order correction to this expression in the \( Q_3 \)-space, using the predefined definitions of \( \hat{H} \) given in Equation (4–33) and left and right eigenvectors, is

\[
\delta \omega^{(2)} = \langle \Phi_0 | \hat{L}_P \hat{H}_{PQ_3}^{(1)} (\omega_{\text{CCSD}} - \hat{H}_{Q_3Q_3}^{(0)})^{-1} \hat{H}_{Q_3P}^{(1)} \hat{P}_P | \Phi_0 \rangle - r_0 \langle 0 | \hat{L}_{k3} \hat{H} | 0 \rangle
\]

Substitution with the aforementioned Hamiltonian and \( \hat{R}_{Q_3} \) (disconnected) expression yield

\[
\delta \omega^{(2)} = \langle \Phi_0 | \hat{L}_P \hat{W}_{PQ_3}^{(1)} D_3 \hat{W}_{Q_3P}^{(1)} \hat{R}_P | \Phi_0 \rangle - r_0 \langle 0 | \hat{L}_{k3} \hat{H} | 0 \rangle
\]

\[
= \langle \Phi_0 | \hat{L}_P \hat{W}_{PQ_3}^{(1)} \hat{R}_{Q_3} | \Phi_0 \rangle - r_0 \langle 0 | \hat{L}_{k3} \hat{H} | 0 \rangle
\]

\[
= \langle \Phi_0 | \hat{L}_P \hat{W}_{PQ_3}^{(1)} \left( (\hat{W}^{(1)} \hat{R}_{1k})_c + (\hat{W}^{(1)} \hat{R}_{2k})_c \right) | \Phi_0 \rangle
\]

which is identical to Equation (4–60).
This method clearly couples triples with singles via the \( \tilde{W}^{(1)}_{1k} | \Phi_0 \rangle \) contribution, which is assumed to be essential for dominant singly excited states. [31, 32, 156] However, this assumes the higher excited \( Q \)-spaces, specifically the \( Q_4 \) contribution to be negligible. This seems to be a reasonable assumption for small molecules as it approaches the Full CI result for those cases. [31–33, 156]. However, as will be shown later, this approximation always over corrects the excitation energy in the large test set used. The \( Q_4 \left( \tilde{W}^{(1)}_{1k} \right)_C | \Phi_0 \rangle \) contribution is hypothesized to be non-negligible for larger systems due to the similar contribution in the \( Q_3 \)-space \( \tilde{W}^{(1)}_{1k} | \Phi_0 \rangle \). Including this \( Q_4 \) contribution would scale as \( \sim n_e^4 n_v^5 \), making it infeasible for any system of moderate size.

A convenient approximation is to count orders in the two-electron perturbation, \( \tilde{W} \), in Equation (4–45)

\[
\tilde{W} = \sum_{ia} f_{ia} \{ a^\dagger i \} + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \{ p^\dagger q^\dagger sr \} = \tilde{f}_{ov} + \tilde{V},
\]

Doing this removes the \( Q_3 \left( \tilde{W}^{(1)}_{1k} \right)_C | \Phi_0 \rangle \) as it cannot be connected, and yields the perturbed \( \hat{R}_{Q_3} \) vector as

\[
\hat{R}^{(1)}_{Q_3} | \Phi_0 \rangle = D_3 \left( \tilde{W}^{(1)}_{2k} \right)_C | \Phi_0 \rangle
\]

This approximation, named EE-EOM-CCSD(T), performs very satisfactorily, possibly because the unbalanced terms (\( Q_3 \) but not \( Q_4 \)) in EE-EOM-CCSD(\( \tilde{T} \)) are not included. It can also be adapted to computer codes with a ground state CCSD(T) implementation, since the only difference is the \( \hat{R} \) amplitudes replace the \( \hat{T} \) amplitudes and the \( \hat{L} \) amplitudes replace the \( \hat{\Lambda} \) amplitudes in the programmable equations.

There is also no ambiguity with the triples contribution in the ground state with the EE-EOM-CCSD(T) method. This is evident by employing Löwdin’s partitioning again of the energy functional [161–163]

\[
\omega_{\text{exact}} = \langle \Phi_0 | \hat{L} P \tilde{H} P | 0 \rangle + \langle 0 | \hat{L} P \tilde{H} P Q \left( \omega_{\text{exact}} - \tilde{H}_{QQ} \right)^{-1} \tilde{H}_{QP} \hat{P} | \Phi_0 \rangle
\]
with the eigenvectors as defined before, except the Hamiltonian is partitioned as

\[
\bar{H}^{[0]} = P\bar{H}P + Q \left( \omega_{\text{CCSD}} + \hat{\tau}_\infty + \hat{\tau}_w \right) Q
\]

(4–75)

\[
\bar{H}^{[1]} = \hat{\mathcal{W}} + \left[ (\hat{\tau}_\infty + \hat{\tau}_w) \hat{\mathcal{T}}_1 \right]_c + \left[ (\hat{\tau}_\infty + \hat{\tau}_w) \hat{\mathcal{T}}_2 \right]_c
\]

(4–76)

\[
\bar{H}^{[2]} = (\hat{\mathcal{W}} \hat{\mathcal{T}}_1)_c + (\hat{\mathcal{W}} \hat{\mathcal{T}}_2)_c
\]

(4–77)

In this way, we can count *generalized* orders (indicated with brackets) in a Moller-Plesset fashion, \([158–160, 164]\) using \(\hat{\mathcal{W}}\) as perturbation parameter. Meaning, we can use the well known order-by-order expansion in ground state CC theory applied to the excited state.

For the ground state, the lowest order correction with this partitioning, first shown by Stanton \([162, 163]\) and later by Taube, \([182]\) to the energy is given by

\[
E^{[3]} = \langle \Phi_0 | \hat{L}_P \bar{H}^{[1]} | Q_3 \rangle \langle Q_3 | \bar{H}^{[0]} | Q_3 \rangle^{-1} \langle Q_3 | \bar{H}^{[2]} \hat{R}_P | \Phi_0 \rangle + \langle \Phi_0 | \hat{L}_P \bar{H}^{[2]} | Q_3 \rangle \langle Q_3 | \bar{H}^{[0]} | Q_3 \rangle^{-1} \langle Q_3 | \bar{H}^{[1]} \hat{R}_P | \Phi_0 \rangle
\]

(4–78)

However, for excited states the lowest order correction is

\[
E^{[2]} = \langle \Phi_0 | \hat{L}_P \bar{H}^{[1]} | Q_3 \rangle \langle Q_3 | \bar{H}^{[0]} | Q_3 \rangle^{-1} \langle Q_3 | \bar{H}^{[1]} \hat{R}_P | \Phi_0 \rangle
\]

(4–79)

For the ground state, the left and right vectors are defined as

\[
\hat{L}_P = \hat{1} + \hat{\Lambda}
\]

(4–80)

\[
\hat{R}_P = \hat{1}
\]

(4–81)
and consequently, the second term in Equation (4–78) disappears since there is no $Q_3$ projection from $\bar{H}^{[1]}|0\rangle$. This leaves, showing explicit generalized orders in $\hat{W}$,

$$\delta E = \langle \Phi_0 | (\hat{\Lambda}_1^{[1]} + \hat{\Lambda}_2^{[1]}) \hat{W}^{(1)} | Q_3 \rangle D_3 \langle Q_3 | (\hat{W}^{(1)} \hat{T}_2^{[1]} \rangle_c | \Phi_0 \rangle$$  \hspace{1cm} (4–82)

$$= \langle \Phi_0 | \hat{\Lambda}_1^{[1]} \hat{W}^{(1)} + \hat{\Lambda}_2^{[1]} f_{ov}^{(1)} + (\hat{\Lambda}_2^{[1]} \hat{W}^{(1)} \rangle_c | Q_3 \rangle D_3 \langle Q_3 | (\hat{W}^{(1)} \hat{T}_2^{[1]} \rangle_c | \Phi_0 \rangle$$  \hspace{1cm} (4–83)

$$= \frac{1}{36} \sum_{ijk} \sum_{abc} \lambda_{abc}^{ijk} \frac{1}{\epsilon_{ijk}} t_{ijk}^{abc}$$  \hspace{1cm} (4–84)

When going from Equation (4–83) to Equation (4–84), we recognize that the $\hat{\Lambda}$ and $\hat{T}_2$ amplitudes first arise in first-order, and therefore the energy contribution is fourth-order in $\hat{W}$.

For excited states, we use the second-order correction in Equation (4–79) with

$$\hat{L}_P = \hat{L}_{1k} + \hat{L}_{2k}$$  \hspace{1cm} (4–85)

$$\hat{R}_P = r_0 + \hat{R}_{1k} + \hat{R}_{2k}$$  \hspace{1cm} (4–86)

to arrive at

$$E^{[2]} = \langle \Phi_0 | (\hat{L}_{1k} + \hat{L}_{2k}) \bar{H}^{[1]} | Q_3 \rangle D_3 \langle Q_3 | \bar{H}^{[1]} (r_0 + \hat{R}_{1k} + \hat{R}_{2k}) | \Phi_0 \rangle$$  \hspace{1cm} (4–87)

$$= \langle \Phi_0 | (\hat{L}_{1k} + \hat{L}_{2k}) \bar{H}^{[1]} | Q_3 \rangle D_3 \langle Q_3 | \bar{H}^{[1]} \hat{R}_{2k} | \Phi_0 \rangle$$  \hspace{1cm} (4–88)

$$= \langle \Phi_0 | \hat{L}_{1k} \hat{V} + \hat{L}_{2k} f_{ov} + (\hat{L}_{2k} \hat{V})_c | Q_3 \rangle D_3 \langle Q_3 | \hat{W} \hat{R}_{2k} | \Phi_0 \rangle$$  \hspace{1cm} (4–89)

$$= \frac{1}{36} \sum_{ijk} \sum_{abc} \lambda_{abc}^{ijk} \frac{1}{\epsilon_{ijk}} t_{ijk}^{abc}$$  \hspace{1cm} (4–90)

With the $\hat{L}_{3k}$ and $\hat{R}_{3k}$ amplitudes given exactly as in ground state CCSD(T), just with $\hat{R}$ replacing $\hat{T}$ and $\hat{L}$ replacing $\hat{\Lambda}$. With the perturbed Hamiltonian inserted as defined above, this is the expression for the EOM-CCSD(T) correction. The $\omega_k^{CCSD}$ dependence in the denominator is eliminated by the appropriate choice of $\bar{H}^{[0]}$ and the triples in the ground state, $\hat{T}_3$, do not enter when using this Møller-Plesset perturbation expansion of $\bar{H}$, since they would first appear in $\bar{H}^{[2]}$. Furthermore, the expanded space is only $Q_3$, since there can be no connections made to $Q_4$ at this order. Recognizing that the $\hat{L}_P$ and
$\hat{R}_P$ vectors are themselves first-order in $\hat{W}$, and the $\hat{R}_{3k}$ and $\hat{L}_{3k}$ vectors are one order higher, the energy expression is actually fourth-order.

Much akin to the expectation value calculation of properties, it is justifiable to use $\hat{R}_k^\dagger$ in place of $\hat{L}_k$ in the above expressions. Note that this is not true for a linear response treatment, or a derivative of the functional with respect to a perturbation. This will be detailed later, in the gradient section. This replacement would save a factor of two in the EE-EOM-CCSD energy equation and in the triples calculation, since only $Q_3R$ would need to be computed and not $\mathcal{L}Q_3$

4.4.1 Parallelization Strategies for EOM-CCSD(T)

The details of the implementation of the triples corrected excitation energy are important, as the method formally scales as $n_o^3 n_v^4$. The triples method is ideally suited for ACESIII, since the data passing is for arrays of, at most, size $n_o n_v^3$, and the entire time of the computation is spent in the contraction step.

The expression for the correction to the energy is identical for EOM-CCSD(\tilde{T}) and EOM-CCSD(T)

$$\Delta \omega^{[4]} = \sum_{i<j<k} \sum_{a<b<c} l_{ijk}^{[2]} \frac{1}{\epsilon_{abc}^{jk}} \epsilon_{ijk}^{abc} [2]$$

The difference between the methods is in the amplitude equations. In the EOM-CCSD(T) method, they are defined as

$$l_{ijk}^{[2]} = P(a/ bc) P(k/ ij) \sum_e \langle bc | || ek \rangle r_{ij}^{ae} - P(i/ jk) P(c/ ab) \sum_l \langle mc | || jk \rangle r_{im}^{ab}$$

$$l_{abc}^{[2]} = P(a/ bc) P(k/ ij) \sum_e l_{ae}^{ij} \langle ek | || bc \rangle - P(i/ jk) P(c/ ab) \sum_l l_{ab}^{im} \langle jk | || mc \rangle$$

$$+ P(k/ ij) P(c/ ab) \langle ij | || ab \rangle l_{i}^{jk}$$

$$+ P(k/ ij) P(c/ ab) \langle ij | || ab \rangle l_{i}^{jk}$$

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The permutation operators $P(p/qr)$ account for antisymmetrization and are defined by their action on an arbitrary tensor, $X$, as

$$P(p/qr) = (1 - P(pq) - P(pr)) X_{stu...}^{pqr...}$$  \hspace{1cm} (4–94)$$

$$= X_{stu...}^{pqr...} - X_{stu...}^{qpr...} - X_{stu...}^{rpq...}$$  \hspace{1cm} (4–95)$$

For large systems, storing blocks (note the primed quantities) of dimension $n_o' n_v^3 n_o^2$ is not a good strategy for implementation. Instead, one stores blocks of $n_o' n_v^3 n_o^2$, where the occupied squared storage results from simple indices $j$ and $k$. Essentially, the vectors are computed and stored as $r_{ijk}^{ABC}$ (with capital indices referring to blocks of simple indices). Also, all terms resulting from the action of the permutation operator are independent and can be computed separately. Consequently, we can compute all 9 permutations in each triples amplitude at the same time. This is how the EOM-CCSD(T) method was implemented.

The EE-EOM-CCSD($\tilde{T}$) amplitude equations are a bit more tedious. Explicitly, they are given in spin-orbital form, using the aforementioned expansion of $\tilde{H}$, as

$$r_{ijk}^{abc} [2] = (P(i/jk) \sum_d \tilde{I}_{djk}^{abc} r_{ij}^d - P(a/bc) \sum_l \tilde{I}_{ljk}^{lbc} r_{il}^a + \sum_{ld} \tilde{I}_{djk}^{lbc} r_{il}^a)$$

$$+ P(a/bc)P(i/jk) \sum_{ld} \tilde{I}_{djk}^{lbc} r_{il}^a + \frac{1}{2} \sum_{de} \tilde{I}_{djk}^{abc} r_{ik}^d$$

$$+ \frac{1}{2} P(b/ac) \sum_{lm} \tilde{I}_{ijkm}^{lbc} r_{im}^c$$

$$+ (P(a/bc)P(k/ij) \sum_e \tilde{W}_{ek}^{bc} r_{ij}^{ae} - P(i/jk)P(c/ab) \sum_l \tilde{W}_{jk}^{mc} r_{im}^{ab})$$

$$= A + B$$

$$l_{abc}^{ijk} [2] = P(a/bc)P(k/ij) \sum_s \tilde{l}_{ck}^{jblue} \tilde{W}_{bc}^{ek} - P(i/jk)P(c/ab) \sum_l \tilde{l}_{ab} r_{im}^{mc}$$  \hspace{1cm} (4–96)$$

$$+ P(k/ij)P(c/ab)\langle ij||ab\rangle l_{ck}^k + P(k/ij)P(c/ab)l_{ab} l_{ck}^k$$

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The construction of the right hand eigenvector, although intimidating, is only two times more expensive to compute than in the EE-EOM-CCSD(T) variant. Each of the computationally expedient terms, $A$ and $B$, can be programmed as

$$
\delta \hat{R}_{3k} = P(a/bc)P(k/ij) \sum_e Y_{ek}^{bc} X_{ij}^{ae} - P(i/jk)P(c/ab) \sum_l Y_{jk}^{mc} X_{lm}^{ab}
$$

(4–97)

to make use of the pre-existing code. Term $B$ is exactly the same as in the EE-EOM-CCSD(T) variant, with $X \equiv \hat{R}_{2k}$ and the two-electron bare integrals are replaced by $\bar{H}$ integrals, $Y \equiv \bar{W}_2$. The $A$ term can be written with the intermediates, in spin-orbital form,

$$
Y_{ci}^{ab} = \sum_d \bar{W}_{cd}^{ab} r_k^d + P(ab) \sum_{kd} \bar{W}_{cd}^{ak} r_k^{bd} - P(ab) \sum_k \bar{W}_{ci}^{kb} r_k^a - \frac{1}{2} \sum_k t_{ki}^{ab} \sum_{ld} \langle cd||kl \rangle r_l^d - \frac{1}{2} \sum_{kl} (r_{kl}^{ab} + P(kl) P(ab) r_k^a t_{ij}^b) \bar{W}_{ci}^{kl}
$$

(4–98)

$$
Y_{ij}^{ka} = - \sum_l \bar{W}_{ij}^{kl} r_l^a + P(ij) \sum_{ld} \bar{W}_{ld}^{kl} r_j^{ad} - P(ab) \sum_d \bar{W}_{ij}^{ka} r_j^d - \frac{1}{2} \sum_d t_{ij}^{da} \sum_{le} \langle de||kl \rangle r_l^e + \frac{1}{2} \sum_{cd} (r_{ij}^{cd} + P(ij) P(cd) r_i^c t_{ij}^d) \bar{W}_{cd}^{ka}
$$

(4–99)

$$
X_{ij}^{ab} = t_{ij}^{ab}
$$

(4–100)

and use the same code for $B$ and EE-EOM-CCSD(T). This is how the EE-EOM-CCSD($\tilde{T}$) is implemented in ACESIII.

### 4.4.2 Approximating the Left Hand Eigenvector

To test the limits of this left hand approximation, the triples correction was computed with \(\hat{L}_k = \hat{R}_k^\dagger\). Results for the water molecule in an augmented double-\(\zeta\) basis set, are shown in Table 4-2 for five roots. This approximation is quite bad, and in error by about a factor of 2. To determine the source of the error, the triples contribution to the energy was separated into only those coming from \(\hat{L}_{1k} = \hat{R}_{1k}^\dagger\) (singles) and \(\hat{L}_{2k} = \hat{R}_{2k}^\dagger\) (doubles). These results are also shown in Table 4-2. The singles contribution approximation is in excellent agreement with the exact singles result, further supporting the \(\hat{L}_k = \hat{R}_k^\dagger\) approximation for one-electron properties. The doubles contribution, however, differs
significantly (relative to the total triples correction), and is always opposite in sign to
the singles contribution. Consequently, the difference of these two “larger” numbers to
determine the total triples corrections propagates the error further, resulting in the poor
agreement with this approximation.

4.4.3 Comparison of Triples Methods

4.4.3.1 Computational details

The EE-EOM-CCSD(T) and EE-EOM-CCSD($\tilde{T}$) methods were implemented in the
massively parallel program package, ACESIII. [34] The CFOUR [183] program package
was used for the EE-EOM-CCSDT-3 calculations, and has the advantage to run in the
computational point group symmetry. The test set comprised of a subset of the 121
singlet valence states for 24 molecules used in the CCSDR(3) performance studies of
Sauer et. al. [153], due to the expense of EOM-CCSDT-3. All geometries were obtained
from MP2/6-31G* optimizations with the core electrons frozen. The subsequent EOM
calculations were performed with the TZVP basis set [181] with core electrons frozen to
allow direct comparison to CCSDR(3) and CC3 results. [153]

All EOM-CCSD(T) and EOM-CCSD($\tilde{T}$) calculations on the test set were performed
on 256 compute cores using the ARSC machine, Chugach. [184] As a quick demonstration
of timings, the largest calculation, Naphthalene, with 238 basis functions and 24 valence
electrons took only 2.5 hours for the EE-EOM-CCSD(T) and the smallest calculation,
ethene, with 50 basis functions and 6 valence electrons took 6.7 minutes.

More representative timings are demonstrated with cytosine, guanine, and their
corresponding Watson-Crick base pair; the latter chosen to demonstrate the applicability
of the program. The nucleobases - cytosine, adenine, thymine, and guanine - in
aug-cc-pVDZ basis sets [106] were tested over a range of compute cores starting
with 32 and ending with 512 to demonstrate the efficiency and scaling properties. The
parameters for each molecule are shown in Table 4-3, with the block sizes [34] being
kept constant across the CPU range.
4.4.3.2 Results

A correlation plot was constructed for visual demonstration of EOM-CCSD compared to EOM-CCSDT-3 and shown in Figure 4-2. Not surprisingly, triples effects cannot be neglected. [153] The largest deviation with this comparison is from $2^1A_{1g} \pi \rightarrow \pi^*$ state of all-E-hexatriene with a deviation of 0.72 eV. Therefore, we examine the perturbative triples corrected methods.

The correlation plots for the EOM-CC perturbative triples methods compared to EOM-CCSDT-3 are shown in Figure 4-3. The EOM-CCSD($\tilde{T}$), which has been shown to lower EOM-CCSD excitation energies for many states, [31, 32, 156] continues to do so for this test set, overshooting the EOM-CCSDT-3 in essentially all cases, with an average deviation of 0.18 eV, and a maximum deviation of 0.32 eV in the $1^1A''_1 n \rightarrow \pi^*$ excited state of s-triazine. We expect that the contribution of the $Q_4$ space, which has been neglected, would bring the excitation energy closer to that of EOM-CCSDT-3. Although, Shiozaki et. al incorporate the quadruples contribution for small molecules including CH$^+$, C$_2$, and H$_2$CO, and show that the quadruples contribution actually lowers the excitation energy even more. [33] However, those molecules are sufficiently small for broad conclusions, as is witnessed in this study when EOM-CCSD($\tilde{T}$) is performed with larger molecules and the ground state is treated differently between the two methods.

The hypothesis remains that the following substantial term, present in $Q_3$ for this method

$$r_{ijk}^{abc} = \sum_m r_m^a \tilde{H}_{ijk}^{mbc} + \sum_e r_e^e \tilde{H}_{ijk}^{Ebc}$$  \hspace{1cm} (4–101)

cancels with a similar term in $Q_4$

$$r_{ijkl}^{abcd} = \sum_m r_m^a \tilde{V}_{ijkl}^{mbcd} + \sum_e r_e^e \tilde{V}_{ijkl}^{abcd}$$  \hspace{1cm} (4–102)

In fact, excluding this contribution in the EOM-CCSD($\tilde{T}$) computation yields results essentially identical to the EOM-CCSD(T) method. To test this though, means implementing an approximate $\tilde{R}_4$ array. Consequently, the method would scale
\[ \sim n_{\text{occupied}}^4 n_{\text{virtual}}^5, \] whereas the proper inclusion of full triples would only scale as
\[ \sim n_{\text{occupied}}^3 n_{\text{virtual}}^5. \]

The EOM-CCSD(T) method performs quite well for this large test set; better than expected, as mentioned by Shiozaki et al. [33] alluding to earlier studies, [31, 32, 156] and most likely is due to the wide range of molecules in this set. The average absolute deviation is 0.06 eV, within the range of desired accuracy for excited states. The maximum deviation, however is 0.15 eV and is for the \(3^1 A_1 \pi \rightarrow \pi^*\) state of furan. Comparison with CCSDR(3) is insightful, as the largest deviations typically occur in a side-by-side manner. For instance, the largest deviation of CCSDR(3) is for the \(2^1 A_{1g} \pi \rightarrow \pi^*\) state of all-E-hexatriene, the state with largest deviation in EOM-CCSD. The deviations for CCSDR(3) and EOM-CCSD(T) are 0.16 eV and 0.13 eV, respectively. This trend is demonstrated in Figure 4-6. The maximum deviation for each system is plotted for both methods as well as the EOM-CCSD(T) deviation for the root that corresponds to root from CCSDR(3) with maximum deviation, to demonstrate that the excited state roots with maximum deviation are typically the same for each method. The CCSDR(3) method performs slightly better, on average, though both are within the range of accuracy necessary for an accurate description of excited states, but the maximum errors in each typically coincide. The maximum deviations of only five molecules, out of the 24, do not coincide.

The two correlation plots in Figure 4-4 compare the linear response triples methods with EOM-CCSDT-3. There is little difference between the methods, supporting previous work of Sauer et. al [153]. The iterative \(N^7\) CC3 method is too prohibitive to be used for larger systems, so we choose to focus on the perturbative CCSDR(3) correction. The average absolute deviation from EOM-CCSDT-3 is 0.03 eV with a maximum deviation, as mentioned earlier, of 0.16 eV for the \(2^1 A_{1g} \pi \rightarrow \pi^*\) state of all-E-hexatriene. For further detail, a correlation plot for EOM-CCSD(T) compared to CCSDR(3) is shown in Figure 4-5. The absolute average deviation of EOM-CCSD(T)
from CCSDR(3) is 0.08 eV with a maximum deviation of 0.66 eV for the $2^1B_{1u} \pi \rightarrow \pi^*$ state of all-E-octatetraene. However, the CCSDR(3) differs by CC3 for this state by 0.85 eV. The EOM-CCSD(T) differs from CC3 by only 0.19 eV. Sauer et. al recognize that all-E-octatetraene provided a few outliers, but EOM-CCSD(T) does not seem to follow this trend.

With no statistically distinguishable difference between CCSDR(3) and EOM-CCSD(T) over this test set, we discuss the massively parallel performance of the EOM-CCSD(T) method. As this method is computationally equivalent to the ground state $\Lambda$CCSD(T) equations, [162, 163, 182] except that the $\hat{\Lambda}$ and $\hat{T}$ amplitudes are replaced by $\hat{L}_k$ and $\hat{R}_k$ amplitudes, respectively, the existing ground state CCSD(T) code can accommodate this method with minor changes.

To this end, more appropriate test systems that demonstrate the capabilities of ACESIII were chosen for representative timings. These include the cytosine, adenine, and guanine nucleobases, as well as the cytosine-guanine Watson-Crick base pair. The more demonstrable system, the Watson-Crick base pair, timings are shown in Table 4-4, along side the nucleobase building blocks. The final column reports the total time in hours for twelve EOM-CCSD solutions, for the right and left eigenvectors, as well as twelve EOM-CCSD(T) calculations. This is slightly misleading as the calculations are partitioned into the $\alpha\alpha\alpha$ and $\alpha\alpha\beta$ summations, over virtual indices, and computed separately. These two contributions to the EOM-CCSD(T) energy can be computed independently, though the total time for both are reported. Also, the EOM-CCSD(T) energy for all twelve roots were computed separately, with each one taking only a fraction of that total time. In essence, the number of roots and the different summations can be “parallelized” over for significant time savings, and the 368 hours is actually a quite inflated time.

The scaling and efficiency of the code was performed on the four mentioned nucleobases. The efficiency of the total calculations for each system are shown in
Figure 4-7, and the efficiency for just the triples piece is shown in Figure 4-8. The first graph in each figure correspond to the complete calculation. Cytosine and guanine behave as expected - the larger the system, the better the performance across cores - but thymine and adenine exhibit what appears to be super-scaling performance. However, this is an artifact of the chosen block sizes being inadequate for the smaller processor range. To demonstrate this, the average time the processors waited for blocks of data (called block wait time), to then begin floating point operations, across the range, for the total calculation and the triples piece are shown in Figure 4-9. Ideally, the block wait time for the total calculation should resemble that of the triples piece, the larger the molecule, the longer the wait on small numbers of processors. However, the EOM-CCSD equations took longer to converge for adenine, thus inflating the block wait time. On 64 processors, though, an “optimum” amount of the data appears to be residing in memory, yielding lower block wait times and the apparent super-scaling. The efficiencies for the total calculation and triples piece, subtracting out the block wait time, are shown in the second graphs, and exhibit the expected behavior. Note that the triples efficiency does not change, illustrating the nature of iterative portions of the calculation compared to noniterative ones and speaks to the good performance of the triples code.

The scaling curves for the total calculation, with and without block wait time, are shown in Figure 4-10 and the triples curves are shown in Figure 4-11. As the system gets larger, the scaling gets better, as indicated by the graph that does not include the block wait time. This is true for the total calculation and the triples piece, however, again adenine is seen to perform very well only because the block sizes are not optimum for 32 processors and the number of EOM-CCSD iterations is larger than for any other nucleobase.

4.4.4 Application to Nucleobases and Their Complexes

To actually apply the aforementioned approximations for benchmark data sets on biologically relevant molecules, we examined the excited state energies and orderings
of the free nucleobases, hydrated cytosine, cytidine, guanosine, and cytosine-guanine
base pair. The ground state MBPT(2)/aug-cc-pvDZ optimized geometries for the larger
molecules in this benchmark study are shown in Figures 4-12, 4-13, 4-14, and 4-15.

The characterized excited states of the hydrated cytosine structure B with
EOM-CCSD(T) energies are shown in Table 4-5. The excited states do not change
order when micro-hydrated with one water molecule. More importantly, the triples
correction on the free base is essentially unchanged when adding the water molecule.
This is rather nice as it implies the triples correction can be carried over to the complex
from the free nucleobase, offering significant time savings for larger complexes.

The oscillator strengths of the excitations as a function of the number of water
molecules around cytosine are shown in Table 4-6 using the $\hat{R}_k^\dagger$ approximation. The
most intense transition, the third $\pi\pi^*$ transition, in the free nucleobase decreases with
each added water molecule from 0.412 to 0.267. After microsolvated with five waters,
the fourth $\pi\pi^*$ state becomes the most intense transition, growing from 0.180 to 0.557.
The third most intense transition, the second $\pi\pi^*$ transition, is relatively unchanged by
the addition of water molecules. Any lower level parameterized method should reflect
this solvent effect when being developed.

The triples correction for cytidine remains essentially the same as the triples
correction on cytosine as shown in Table 4-7, again suggesting that a triples correction
applied to the free base is sufficient for chemical accuracy. There are more drastic
changes to the transition intensities when adding the sugar. The brightest state, the
third $\pi\pi^*$ transition, is reduced from 0.412 to 0.191, similar to the effect of hydration.
Four dark states, however, become much more intense after the addition of the sugar.
The first $\pi\pi^*$ increases from 0.049 to 0.129, the second $\pi R$ increases from 0.003 to
0.115 with an $n\pi^*$ component responsible for the intensity. The third and fourth $\pi R$, with
a $\pi\pi^*$ component responsible for the transition, increases both from 0.0 to 0.107 and
0.109, respectively.
Guanine remains largely unaffected by the addition of the sugar. Results are shown in Table 4-8. The triples correction on the free base and the sugar, again, remains unchanged. There are also only minor changes to the oscillator strengths in guanosine compared to guanine.

The cytosine-guanine Watson-Crick base pair results are shown in Table 4-9. The excited states are stabilized in this complex as the two lowest excited states of the free bases, cytosine first with an excitation energy of 4.74 eV and guanine second at 4.93 eV, change ordering. The lowest excitation on the base pair is a $\pi\pi^*$ on guanine, with an energy of 4.67 eV, followed by a $\pi\pi^*$ excitation localized on cytosine, with an energy of 4.86 eV. The oscillator strengths remain unchanged, however. This change in ordering reflects the need for benchmark data sets describing these systems. The aforementioned previous studies do not reproduce this ordering in their study.

A charge-transfer state exists. It is the fifth $\pi\pi^*$ state. It would be very interesting to characterize the potential energy surface of this excited state as it would help elucidate the complicated relaxation mechanisms these complexes undergo.

### 4.5 Gradient Theory for Accurate Critical Point Geometries

Recall that the EOM-CC energy functional is given as

$$E_k = \langle 0 | \mathcal{L}_k \tilde{H} \mathcal{R}_k | 0 \rangle$$

$$= \langle 0 | \mathcal{L}_k \left( e^{-\tilde{T} \hat{H} e^{\tilde{T}}} \right) \mathcal{C} \mathcal{R}_k | 0 \rangle$$

(4–103)  

(4–104)
The change in electronic energy with respect to a perturbation, \( \chi \), such as the change in nuclear coordinates, is the following energy derivative

\[
\frac{\partial E_k}{\partial \chi} = \langle 0 | \frac{\partial L_k}{\partial \chi} \bar{H} R_k | 0 \rangle + \langle 0 | L_k \bar{H} \frac{\partial \bar{T}}{\partial \chi} R_k | 0 \rangle \\
- \langle 0 | L_k \frac{\partial \bar{T}}{\partial \chi} \bar{H} R_k | 0 \rangle + \langle 0 | L_k \bar{H} \frac{\partial \bar{T}}{\partial \chi} R_k | 0 \rangle \\
+ \langle 0 | L_k \left( e^{-\bar{T}} \frac{\partial \bar{H}}{\partial \chi} e^{\bar{T}} \right) C R_k | 0 \rangle
\]

\[
= A + B + C + D + E. \hspace{1cm} (4-105)
\]

The first two terms \( (A \text{ and } B) \) vanish as a consequence of the generalized Hellman-Feynman theorem. The third and fourth terms remain since the \( \bar{T} \) amplitudes are not stationary with respect to a perturbation on the excited state and would require the solution for \( 3N \) degrees of freedom for geometrical perturbations. However, inserting a resolution of the identity yields

\[
C + D = -\langle 0 | L_k \frac{\partial \bar{T}}{\partial \chi} (P + Q) \bar{H} R_k | 0 \rangle - \langle 0 | L_k \bar{H}(P + Q) \frac{\partial \bar{T}}{\partial \chi} R_k | 0 \rangle \\
= \omega_k \left( -\langle 0 | L_k \frac{\partial \bar{T}}{\partial \chi} P R_k | 0 \rangle + \langle 0 | L_k P \frac{\partial \bar{T}}{\partial \chi} R_k | 0 \rangle \\
- \langle 0 | L_k \frac{\partial \bar{T}}{\partial \chi} Q \bar{H} R_k | 0 \rangle + \langle 0 | L_k \bar{H} Q \frac{\partial \bar{T}}{\partial \chi} R_k | 0 \rangle \right) \\
= -\langle 0 | L_k \frac{\partial \bar{T}}{\partial \chi} Q \bar{H} R_k | 0 \rangle + \langle 0 | L_k \bar{H} Q \frac{\partial \bar{T}}{\partial \chi} R_k | 0 \rangle \\
= \langle 0 | L_k \bar{H} Q \frac{\partial \bar{T}}{\partial \chi} R_k | 0 \rangle. \hspace{1cm} (4-106)
\]

The \( P \)-space is defined as before

\[
P = |0\rangle \langle 0| + \sum_{ia} |\Phi_i\rangle \langle \Phi_i| + \frac{1}{4} \sum_{jab} |\Phi_{ij}\rangle \langle \Phi_{ij}|
\]

\[
(4-110)
\]
and the $Q$-space contains all higher excited determinants. The following definitions were used

\begin{align}
\omega_k &= \langle 0 | \mathcal{L}_k \hat{H} \mathcal{R}_k | 0 \rangle = \langle 0 | \mathcal{L}_k \mathcal{P} \hat{H} \mathcal{P} \mathcal{R}_k | 0 \rangle \tag{4–111} \\
\mathcal{R}_k &= \mathcal{P} \mathcal{R}_k \tag{4–112} \\
\mathcal{L}_k &= \mathcal{L}_k \mathcal{P} \tag{4–113} \\
0 &= \langle 0 | \mathcal{L}_k \frac{\partial \hat{T}}{\partial \chi} Q = \langle 0 | \mathcal{L}_k Q' = \langle 0 | \mathcal{L}_k Q \tag{4–114}
\end{align}

where the last equality holds because $\partial \hat{T} / \partial \chi$ is strictly an excitation operator, so when acting on the $Q$-space, only $Q$-space determinants can be generated, which $\hat{L}_P$ can not connect to.

Unfortunately, in the present form, Equation (4–109) still requires the solution of $\partial \hat{T} / \partial \chi$ for all $3N$ degrees of freedom. However, we can use the definition of $\mathcal{R}_k$ and the fact that it commutes with $\hat{T}$ and derivatives of $\hat{T}$, to isolate the derivative of the $\hat{T}$ amplitudes

\begin{align}
\langle 0 | \mathcal{L}_k \hat{H} Q \frac{\partial \hat{T}}{\partial \chi} \mathcal{R}_k | 0 \rangle &= \langle 0 | \mathcal{L}_k \hat{H} Q \mathcal{R}_k \frac{\partial \hat{T}}{\partial \chi} | 0 \rangle \\
&= \langle 0 | \mathcal{L}_k \hat{H} Q \mathcal{R}_k \mathcal{P} \frac{\partial \hat{T}}{\partial \chi} | 0 \rangle \\
&= \langle 0 | \Xi \mathcal{P} \frac{\partial \hat{T}}{\partial \chi} | 0 \rangle \tag{4–115}
\end{align}

where the shorthand notation with $\langle 0 | \Xi \mathcal{P} = \langle 0 | \mathcal{L}_k \hat{H} Q \mathcal{R}_k \mathcal{P}$ was used, following the derivation of Stanton et. al. \cite{185} Before giving the explicit spin-orbital programmable equations for Equation (4–117), we examine the derivative of the ground state CC equations to determine a perturbation independent form for the derivative $\hat{T}$ amplitudes.

It will be convenient to recast the $P$-space as

$$P = |0\rangle \langle 0| + |g\rangle \langle g|, \tag{4–118}$$
with \(|g\rangle\langle g|\) containing the space spanned by the singly and double excited determinants. The derivative of the ground state CCSD amplitude equations are then

\[
0 = \frac{\partial}{\partial \chi} \left( \langle g| \bar{H} |0\rangle \right) = \langle g| \bar{H} \frac{\partial \hat{T}}{\partial \chi} |0\rangle - \langle g| \frac{\partial \hat{T}}{\partial \chi} \bar{H} |0\rangle + \langle g| \left( e^{-\hat{T}} \frac{\partial \bar{H}}{\partial \chi} e^{\hat{T}} \right) |0\rangle 
\]

(4–119)

\[
= \langle g| \bar{H} (P + Q) \frac{\partial \hat{T}}{\partial \chi} |0\rangle - \langle g| \frac{\partial \hat{T}}{\partial \chi} (P + Q) \bar{H} |0\rangle + \langle g| \bar{H}^x |0\rangle 
\]

(4–120)

\[
= \langle g| \bar{H} \langle g| \frac{\partial \hat{T}}{\partial \chi} |0\rangle - \Delta E_{\text{CC}} \langle g| \frac{\partial \hat{T}}{\partial \chi} |0\rangle + \langle g| \bar{H}^x |0\rangle 
\]

(4–121)

\[
= \langle g| \bar{H} - \Delta E_{\text{CC}} |g\rangle \langle g| \frac{\partial \hat{T}}{\partial \chi} |0\rangle + \langle g| \bar{H}^x |0\rangle 
\]

(4–122)

\[
= \langle g| \bar{H}_N |g\rangle \langle g| \frac{\partial \hat{T}}{\partial \chi} |0\rangle + \langle g| \bar{H}^x |0\rangle 
\]

(4–123)

\[
= \langle g| \bar{H} \frac{\partial \hat{T}}{\partial \chi} |0\rangle = \langle g| \bar{H}_N |g\rangle^{-1} \langle g| \bar{H}^x |0\rangle 
\]

(4–124)

The derivative \(\hat{T}\) amplitudes are then easily seen to be given by

\[
\langle g| \frac{\partial \hat{T}}{\partial \chi} |0\rangle = \langle g| \bar{H}_N |g\rangle^{-1} \langle g| \bar{H}^x |0\rangle 
\]

(4–125)

It should be noted that to arrive at this expression, the linear \(\hat{T}\) operators, defined to generate single and double excitations only, cannot connect the reference determinant to the triply or higher excited determinants in the \(Q\)-space. Consequently, all \(Q \frac{\partial \hat{T}}{\partial \chi} |0\rangle\) terms are zero. Also, with the \(P\)-space defined in Equation (4–118), the following relations hold

\[
\langle g| \bar{H} P = \langle g| \bar{H} |0\rangle + \langle g| \bar{H} |g\rangle = 0 + \langle g| \bar{H} |g\rangle 
\]

(4–126)

\[
P \bar{H} |0\rangle = \langle 0| \bar{H} |0\rangle + \langle g| \bar{H} |0\rangle = \Delta E_{\text{CC}} + 0. 
\]

(4–127)

The shorthand notation, \(\bar{H}^x \equiv \left( e^{-\hat{T}} \frac{\partial \bar{H}}{\partial \chi} e^{\hat{T}} \right)_C\), was used for the final term to reduce clutter.
Insertion of Equation (4–125) in to Equation (4–117) yields

\[
\langle 0 | \mathcal{L}_k \bar{H} Q \mathcal{R}_k \frac{\partial \hat{T}}{\partial \chi} | 0 \rangle = \langle 0 | \Xi | g \rangle \langle g | \frac{\partial \hat{T}}{\partial \chi} | 0 \rangle
\]

(4–128)

\[
= \langle 0 | \Xi | g \rangle \langle g | \bar{H}_N | g \rangle^{-1} \langle g | \bar{H}^\chi | 0 \rangle
\]

(4–129)

Rather than invert the very large \( \langle g | \bar{H}_N | g \rangle \) matrix, we define the perturbation independent operator \( Z \) as

\[
\langle 0 | Z | g \rangle = \langle 0 | \Xi | g \rangle \langle g | \bar{H}_N | g \rangle^{-1}
\]

(4–130)

and use standard linear algebra techniques to determine \( Z \).

The gradient expression is then, in closed analytical form,

\[
\frac{\partial E_k}{\partial \chi} = \langle 0 | Z \bar{H}^\chi | 0 \rangle + \langle 0 | \mathcal{L}_k \bar{H}^\chi \mathcal{R}_k | 0 \rangle
\]

(4–131)

\[
= \text{Tr}[\rho(Z) \frac{\partial f}{\partial \chi}] + \text{Tr}[\rho(\mathcal{L}_k, \mathcal{R}_k) \frac{\partial f}{\partial \chi}] + \text{Tr}[\Gamma(Z) \frac{\partial V}{\partial \chi}] + \text{Tr}[\Gamma(\mathcal{L}_k, \mathcal{R}_k) \frac{\partial V}{\partial \chi}]
\]

(4–132)

\[
= \sum_{pq} D_{pq} \frac{\partial f_{pq}}{\partial \chi} + \frac{1}{4} \sum_{pqrs} D_{pq}^r \frac{\partial \langle pq || rs \rangle}{\partial \chi}.
\]

(4–133)

This form is convenient, as one can exploit pre-existing ground state CC gradient programs given the one-electron and two-electron density matrices. Instead of the ground state two-particle density matrix

\[
\Gamma_{rs}^{pq} = \langle 0 | (1 + \hat{\Lambda}) \left\{ p^\dagger q^\dagger rs \right\} e^{\hat{T}} C | 0 \rangle,
\]

(4–134)

the \( \hat{\Lambda} \) array is replaced by \( Z + r_0 \hat{L}_k \) for excited state gradients, allowing the use of the ground state code. The ground state CC gradient code in ACESIII has a great track record already. It scales very well and can handle large systems in the massively parallel environment enabling the determination of critical points on potential energy surfaces of larger molecules. However, EE-EOM-CCSD gradients have not been implemented in a robust form in any program capable of scaling to \( \mathcal{O}(10,000) \) to \( \mathcal{O}(100,000) \) processors. Therefore, given the success of the ground state gradient code,
I will focus only on the massively parallel implementation of the presented equations; the formation of $\Xi$ and the one- and two-particle density matrices.

The use of $\hat{R}^\dagger$ in place of $\hat{L}$ is not an option in EE-EOM-CCSD gradients. The first two terms, $A$ and $B$, in the derivative of the energy functional (Equation (4–105)) are zero because of the following

$$I + II = \langle 0 | \frac{\partial L_k}{\partial \chi} \bar{H} R_k | 0 \rangle + \langle 0 | L_k \bar{H} \frac{\partial R_k}{\partial \chi} | 0 \rangle$$

(4–135)

$$= \langle 0 | \frac{\partial L_k}{\partial \chi} (P + Q) \bar{H} R_k | 0 \rangle + \langle 0 | L_k \bar{H}(P + Q) \frac{\partial R_k}{\partial \chi} | 0 \rangle$$

(4–136)

$$= \omega_k \left[ \langle 0 | \frac{\partial L_k}{\partial \chi} R_k | 0 \rangle + \langle 0 | L_k \frac{\partial R}{\partial \chi} | 0 \rangle \right]$$

(4–137)

$$= \omega_k \frac{\partial}{\partial \chi} \left[ \langle 0 | L_k R_k | 0 \rangle \right]$$

(4–138)

$$= \omega_k \frac{\partial}{\partial \chi} [1]$$

(4–139)

$$= 0$$

(4–140)

This simplification is not possible if using $\hat{R}^\dagger$ because $\langle 0 | \hat{R}^\dagger \omega_k \neq \langle 0 | \hat{R}^\dagger \bar{H}$ due to the non-hermiticity of $\bar{H}$.

4.5.1 Implementation

Details for the one-particle density matrix are given in section 4.3. The construction of $\Xi$ and the two-particle density matrix use many of the same intermediates. With the primary goal of parallel performance, these intermediates were formed in an independent step and stored on disk or memory, where appropriate, rather than computed on-the-fly and used immediately. Remember, the latter can hurt parallel performance.

The choice of intermediates is not completely unambiguous. Given the design of ACESIII, the following intermediates specific to the excited state were constructed, in
order, as

\[(L_2 R_2)_{b_i}^a = \sum_{kc} r_{ik}^{ac} l_{cb}^{kj} \]  \hspace{1cm} (4–141)

\[(L_2 T_2)_{b_i}^a = \sum_{kc} t_{ik}^{ac} l_{cb}^{kj} \]  \hspace{1cm} (4–142)

\[(\bar{W} R_2)_{b_i}^b = -\frac{1}{2} \sum_{cd} \bar{W}_{cd}^{bi} r_{jk}^{cd} \]  \hspace{1cm} (4–143)

\[(\bar{W} 1)_{b_i}^a = \sum_{kc} \bar{W}_{ac}^{bk} r_{k}^{c} \]  \hspace{1cm} (4–144)

\[(L_2 R_2)_{i_j}^i = \sum_{cd} l_{cd}^{ij} r_{kl}^{cd} \]  \hspace{1cm} (4–145)

\[(L_2 T_2)_{i_j}^i = \sum_{cd} l_{cd}^{ij} r_{kl}^{cd} \]  \hspace{1cm} (4–146)

\[(\bar{W} 1)_{i_j}^a = \sum_{kc} \bar{W}_{ac}^{ik} r_{k}^{c} \]  \hspace{1cm} (4–147)

\[(\bar{W} 1)_{i_j}^i = \sum_{kc} \bar{W}_{ac}^{ik} r_{k}^{c} \]  \hspace{1cm} (4–148)

\[(L_1 R_2)_{i}^a = \sum_{kc} r_{ik}^{ac} l_{k}^{i} \]  \hspace{1cm} (4–149)

\[(L_2 R_2)_{i}^a = \frac{1}{2} \sum_{kcd} \bar{W}_{cd}^{ak} r_{ik}^{cd} - \frac{1}{2} \sum_{klc} \bar{W}_{kc}^{lk} r_{kl}^{ac} \]  \hspace{1cm} (4–150)

\[(L_2 R_2)_{a}^b = -\frac{1}{2} \sum_{klc} l_{ac}^{i} r_{bc}^{lk} \]  \hspace{1cm} (4–151)

\[(\bar{W} R_2)_{i}^b = -\frac{1}{2} \sum_{klc} \bar{W}_{ac}^{i} r_{bc}^{lk} \]  \hspace{1cm} (4–152)

\[(L_2 R_2)_{i}^i = \frac{1}{2} \sum_{kcd} l_{cd}^{ij} r_{jk}^{cd} \]  \hspace{1cm} (4–153)

\[(\bar{W} R_2)_{i}^i = \frac{1}{2} \sum_{kcd} \bar{W}_{cd}^{ik} r_{jk}^{cd} \]  \hspace{1cm} (4–154)

\[\bar{W} R_2^{i} \]  \hspace{1cm} (4–155)

Note that no intermediates of size \(n_o n_o^3\) are formed. The largest intermediates are of size \(n_c n_k^2\). These are smaller and can consequently be passed between processors faster.

Also, all two-index intermediates were stored in local arrays in memory for faster access.
to these quantities. Given these intermediates, used directly in the formation of \( \Xi \) and
the two-particle density matrix, more intermediates for the latter were constructed as

\[
X_i^j = \sum_c (L_2 R_1)_i^j c t_j^c + (L_2 R_2)_i^j + \sum_c l_i^c r_j^c \tag{4–156}
\]

\[
X_a^b = \sum_k (L_2 R_1)_a^b k t_k^b + (L_2 R_2)_a^b + \sum_k l_a^k r_k^b \tag{4–157}
\]

\[
X_i^a = (L_1 R_2)_i^a - \frac{1}{2} \sum_k t_{i k}^{a} \sum_j l_{i c j}^{k} t_{a j}^c - \frac{1}{2} \sum_k t_{i d k}^{a} \sum_j l_{i c d j}^{k} t_{a j}^c + \frac{1}{2} \sum_k t_{k a}^{d} \sum_c l_{k c d}^{i} t_{a j}^c \tag{4–158}
\]

\[
Y_i^j = \frac{1}{2} \sum_k l_{i k}^{c} t_{c k}^d + \sum_c l_i^c t_j^c \tag{4–159}
\]

\[
Y_a^b = \sum_k l_a^b t_k^b - \frac{1}{2} \sum_k l_{a c}^{k} t_{b k}^c \tag{4–160}
\]

\[
Y_i^a = \sum_k l_{i a}^{c} t_{k c}^d - \frac{1}{2} \sum_k t_{i d k}^{c} \sum_j l_{i c j}^{k} t_{a j}^c - \sum_k t_{k a}^{d} \sum_c l_{k c d}^{i} t_{a j}^c + \frac{1}{2} \sum_k t_{a k}^{d} \sum_c l_{k c d}^{i} t_{a j}^c \tag{4–161}
\]

\[
\tilde{r}_{ij}^{ab} = r_{ij}^{ab} + r_{i j}^a t_{j}^b + t_i^a r_j^b \tag{4–162}
\]

\[
\tilde{r}_{ij}^{ab} = t_{ij}^{ab} + P_{ij} P_{ab} t_i^a t_j^b \tag{4–163}
\]

\[
(L_2 \tilde{r})_{ij}^{k l} = \sum_{cd} l_{i c d}^{k} r_{j}^{c} \tag{4–164}
\]

\[
(L_2 \tilde{r})_{ij}^{k l} = \sum_{cd} l_{i c d}^{k} \tilde{r}_{j}^{c} \tag{4–165}
\]

All of the two-index intermediates are stored locally on each processor, and we avoid
the storage, again, of \( n_o n_a^4 \) or larger four-index quantities. The \( n_o^4 \) arrays are stored
distributed in memory over the processors.
Having defined the intermediates, the $\Xi$ amplitudes are given as

$$
\xi^i_a = \sum_{kcd} (L_2 R_2)^{id}_{ck} W^c_d - \sum_{cd} \bar{W}^{cd}_{dc}(L_2 R_2)^d_c - \sum_{klc} \bar{W}^{lk}_{lc}(L_2 R_2)^c_{ak} + \frac{1}{2} \sum_{klc} l^{ik}_{ac}(R_2 \bar{W})^c_{kl} 
+ \sum_{kc} l^{jk}_{ac}(R_2 \bar{W})^c_{k} + \sum_{kci} \bar{I}^c_{k}(L_2 R_2)^k_{ic} + \frac{1}{4} \sum_{klm} \bar{W}^{kl}_{ml}(R_2 L_2)^m_{kl}
- \sum_{kl} \bar{W}^{kl}_{kl} (R_2 L_2)^k_{a} + \sum_{c} \bar{I}^c_{c}(R_2 \bar{W})^c_{k} + \sum_{k} \bar{I}^k_{c}(R_2 \bar{W})^c_{k} - \sum_{k} I^k_{a}(R_2 \bar{W})^c_{k} + l^i_{a} + \bar{I}^i_{a}
$$

$$
(4\text{-}166)
$$

$$
\xi_{ab}^{ij} = P(ij) P(ab) \sum_{bc} \bar{W}^{kj}_{cb}(L_2 R_2)^k_{ab} + P(\bar{i}) \sum_{c} \bar{W}^{ij}_{ac}(L_2 R_1)^i_{c}
+ P(ij) P(ab) \sum_{kc} l^{ik}_{ac} \left( \sum_{d} r^{d}_{k} \bar{W}^{ij}_{rd} + \sum_{l} r^{l}_{c} \bar{W}^{ij}_{lk} \right) - P(\bar{i}) \sum_{k} \bar{W}^{ij}_{ac}(R_2 L_2)^i_{k}
- P(ij) \sum_{k} l^{ij}_{ab}(R_2 \bar{W})^i_{k} - P(ab) \sum_{c} \bar{W}^{ij}_{cb}(R_2 L_2)^c_{a} - P(\bar{a}) \sum_{c} l^{ij}_{cb}(R_2 \bar{W})^c_{a}
+ P(ab) \sum_{c} l^{ij}_{ab}(R_1 \bar{W})^i_{b} - P(ij) \sum_{k} l^{ik}_{ab}(R_1 \bar{W})^i_{k} + \bar{W}^{ij}_{ab}
+ P(ij) P(ab) l^{ij}_{ab}(R_1 \bar{W})^i_{b} + P(\bar{i}) P(ab) \bar{I}^i_{a}(R_1 L_2)^i_{b} + l^{ij}_{ab} \left( \sum_{kc} r^{c}_{k} \bar{I}^k_{c} + \frac{1}{4} \sum_{klc} \bar{W}^{kl}_{cd} \right)
- P(ab) \sum_{k} \bar{W}^{ij}_{ab}(R_1 L_2)^i_{a} + \frac{1}{4} \sum_{klc} l^{ik}_{ab}(R_2 \bar{W})^i_{kl} + \frac{1}{4} \sum_{klc} \bar{W}^{kl}_{cd}(R_2 L_2)^j_{kl}
- P(ab) \sum_{kc} l^{ik}_{c} \bar{W}^{ij}_{ck} - P(ab) \sum_{kc} l^{ij}_{cb} \bar{I}^k_{c} - P(ij) \sum_{kc} l^{ij}_{c} \bar{W}^{ij}_{ck} - P(\bar{i}) \sum_{k} l^{ij}_{ab} \bar{I}^k_{c}
- \sum_{kcd} l^{ij}_{cd} l^{ik}_{k} \bar{W}^{ij}_{cd} - \sum_{klc} l^{ik}_{ab} l^{ij}_{k} \bar{W}^{ij}_{cl}
(4\text{-}167)
$$

In the equations for $\Xi$, the order of the terms is important, and sheds light on the parallel implementation and performance. For example, the first term in $\xi_{ab}^{ij}$ can be computed, parallelized over $\{a, b, c, k\}$, and the final term is parallelized over $\{i, k, l\}$. The design philosophy was to implement the “fat” loops first and descend to the “skinny” loops in the code. In this way, the most work is distributed first, and so on, to optimize the data flow.
The same philosophy is used in the construction of the two-particle density matrix. The independent blocks of the density matrix is given as

\[
\Gamma_{ij}^{kl} = \frac{1}{2} \sum_{cd} \tilde{r}_{ij}^{cd} l_{cd}^{kl}
\]  

(4–168)

\[
\Gamma_{cd}^{ab} = \frac{1}{2} \sum_{kl} \tilde{r}_{kl}^{ab} l_{cd}^{kl}
\]  

(4–169)

\[
\Gamma_{ka}^{ij} = -\frac{1}{2} \sum_{c} \tilde{r}_{ca}^{ij} r_{k}^{c}
\]  

(4–170)

\[
\Gamma_{ci}^{ab} = \frac{1}{2} \sum_{k} j_{k}^{ab} r_{c}^{k}
\]  

(4–172)

\[
\Gamma_{ab}^{ci} = -\frac{1}{2} \sum_{k} \tilde{r}_{ki}^{ab} l_{c}^{k} - \frac{1}{2} \sum_{kl} \tilde{r}_{kl}^{ab} l_{cd}^{kl} - \frac{1}{2} \sum_{k} j_{k}^{ab} r_{c}^{k} - \frac{1}{2} \sum_{k} \tilde{r}_{ki}^{ab}
\]

\[
- \frac{1}{2} P(ab) \left( (L_2 R_2)^k r_{ij}^a + (L_2 T_2)^k r_{ij}^b \right) + \frac{1}{2} P(ab) \sum_{k} t_{k}^{a} (L_2 R_2)^{kb} c_{i}
\]

\[
+ \frac{1}{2} P(ab) \sum_{k} r_{k}^{a} (L_2 T_2)^{kb} c_{i} + \frac{1}{2} \sum_{k} (L_2 R_2)^{kb} c_{i} r_{k}^{a}
\]  

(4–173)

\[
\Gamma_{bi}^{ia} = \tilde{r}_{bi}^{ia} + (L_2 R_2)^{ib} r_{i}^{a} + (L_2 R_2)^{ib} r_{bi}^{a} + \sum_{k} j_{k}^{bc} (r_{k}^{c} t_{k}^{a} + t_{k}^{c} r_{k}^{a})
\]  

(4–174)
\[ \Gamma_{ij}^{ab} = \tau_{ij}^{ab} + P(ij)P(ab)\left(X_i^a t_j^b + Y_i^a r_j^b\right) + \sum_{kc} \left(t_{ik}^{ac} - t_{ik}^a t_{ik}^c\right)(L_2 R_1)_k^c t_j^b \]

\[ - \frac{1}{2} P(ij) \sum_k \left(t_{kj}^{ab} X_i^k + r_{kj}^{ab} Y_i^k\right) - \frac{1}{2} P(ab) \sum_c \left(t_{ij}^{cb} X_c^a + r_{ij}^{cb} Y_c^a\right) \]

\[ + \frac{1}{4} \sum_{kl} \left((L_2 R_1)_k^i r_{kl}^{ab} + (L_2 R_1)_k^i r_{kl}^{ab}\right) \]

\[ + P(ij)P(ab) \sum_{kc} \left((L_2 R_2)_{ik}^{ac}(t_{kj}^{cb} - 2t_j^c t_k^b) + (L_2 T_2)_{ik}^{ac}(r_{kj}^{cb} - 2(r_j^c t_k^b + t_j^c r_k^b))\right) \]  

The structure of the code then becomes, separating the independent steps in an efficient way,

```
COMPUTE   Ξ   INTERMEDIATES
EXECUTE   BARRIER

COMPUTE   Ξ
EXECUTE   BARRIER

SOLVE FOR  Z  (Ξ = Z\tilde{H})
EXECUTE   BARRIER

COMPUTE   Γ   INTERMEDIATES
EXECUTE   BARRIER

COMPUTE   Γ
EXECUTE   BARRIER

USE EXISTING GROUND STATE GRADIENT CODE

DONE
```
4.5.2 Demonstrable Performance

To test the performance of the code, scaling curves were generated for gradient calculations on adenine, thymine and guanine in an augmented double-$\zeta$ basis set on 256 and 512 processors. These results are shown in Figures 4-16, 4-18, and 4-19. Each gradient calculation is a factor of 1.5 faster within this range processor count. The range was extended for cytosine in an augmented double-$\zeta$ basis set to 512 and 1024 processors. Again, there is a factor of 1.5 speed increase within this range. Most notably, the gradient code was run on 1024 and 2048 processors for the stacked cytosine-guanine complex. This system has 29 atoms, 136 electrons (none were dropped from the correlated calculation), and 527 basis functions. This system also experienced a speed up of 1.5 times when doubling the processor count. The consistency among systems and processor count is very encouraging, since there is no degradation of performance as the system and number of processors gets larger.

4.5.3 Excited State Geometries for Nucleobases

Methods to visualize the orbitals involved in the excitation process as well as the change in density between the ground and excited states are critical for a deeper understanding of the chemistry. Two methods we employ to decipher the orbitals involved in the transition are

1. Large $r_i^a$ weights for specific $a$ and $i$ orbitals are a useful metric.
2. Natural orbitals of the density difference.

The first can become ambiguous if there are a few dominant $r_i^a$ elements. The second is unambiguous in assigning the character of the states since the natural orbitals obtained from the density difference contain a large positive occupation in the ground state orbital and a large negative occupation in the excited state orbital. Therefore, the natural orbitals were generated for the ground and excited states, as well as the density differences, and written to disk in a *Molden* [180] readable format. However, ACESIII (and ACESII) did not have this capability, and it consequently was added.
To demonstrate the practicality of this density difference approach, the difference in electron densities for cytosine, thymine, guanine, and the cytosine-guanine stack are shown in Figures 4-23, 4-25, 4-21, and 4-27, respectively. The right side of the figures indicate the region of space the electron occupied in the ground state, the left side indicates the region of space the electron occupies in the excited state. The geometries are all ground state structures and all excited states are the lowest $\pi\pi^*$ transitions. These figures are shown simply to demonstrate the types of systems that can be routinely studied in a “black-box” manner by the community.

4.6 Conclusions and Outlook

Accurate studies of excited states requires the equation of motion coupled cluster method. Increasing the applicability of this method requires approximations that result in negligible loss of accuracy and the efficient massive parallelization of data across compute cores. In this vein, for accurate oscillator strengths used in deciphering UV spectra, it is sufficient to compute only the right hand eigenvector and use that to compute first-order properties, including transition moments and oscillator strengths. The necessary integrals have been implemented in a block form that allows distribution of basis functions over processors to allow massively parallel calculations with this approximation. There is essentially no loss of accuracy with this method, thus saving a factor of 2 in computer time and resources.

Furthermore, triple substitutions are necessary for accurate excitation energies. The non-iterative EOM-CCSD(T) with no omega shift was tested against the iterative benchmark short of the full triples, EOM-CCDST-3, with excellent performance. The more formally justified EOM-CCSD(\tilde{T}) method performs worse, however, this is attributed to a lack of consistency without the inclusion of the $Q_4$ space in the perturbation. Regardless, the EOM-CCSD(T) method was implemented in a massively parallel way in the ACESIII program package with very encouraging scaling results. The
sizes of the systems studied speak for themselves concerning the performance of the program.

Extremely accurate oscillator strengths and excitation energies have been presented for nucleobases and nucleobase complexes. These data sets can serve to parameterize lower level methods to enable the accurate calculation of DNA and RNA strands. One possible scheme, demonstrated here, is for excitations localized on nucleobases, the triples corrections on the free nucleobase is sufficient to accurately describe the energetics of the complex; provided at least the EOM-CCSD level is performed on the complex.

Gradients for the EOM-CCSD method have been implemented in the massively parallelizable ACESIII program package enabling a very accurate characterization of potential energy surfaces of large molecules. Specifically, excited state geometries have been reported for nucleobases and the cytosine-guanine stacked structure. The programs scales well, allowing the use of $O(10,000)$ processors to study even larger chemically relevant molecules.

Adiabatic excitations are a little more complicated to obtain, as it requires the calculation of the hessian matrix. For the largest system studied here, the hessian can be computed numerically by running gradient calculations on $3(29) - 6 = 81$ different points. Unfortunately, this is a tremendous computational task. Each gradient calculation on 1024 processors takes roughly 20 hours. Each gradient point can be computed independently though, but the available computational resources will still limit these hessian calculations.

Although, the foundation is laid for extensions to gradients for multi-ionized/attached EOM-CCSD methods [30] enabling an efficient route towards routine multi-reference studies. Great care was taken to produce a robust transparent code with the goal of transferability to these extended methods.
Figure 4-1. Error in oscillator strength using $\hat{L}_k = \hat{R}_k^\dagger$ for computing the density in atomic units.

Figure 4-2. Correlation plot for calculated single excited states with CCSD vs. CCSDT-3.

Figure 4-3. Correlation plot for calculated single excited states with EOM-CC methods vs. CCSDT-3. A) corresponds to EOM-CCSD(T), and B) corresponds to EOM-CCSD(T̄).
Figure 4-4. Correlation plot for calculated single excited states with the linear response CC methods vs. CCSDT-3. A) corresponds to CCSDR(3), B) corresponds to CC3.

Figure 4-5. Correlation plot for calculated single excited states with CCSD(T) vs. CCSDR(3).

Figure 4-6. Maximum deviations (errors) from EOM-CCSDT-3 for each system, ordered by increasing basis set size, using the EOM-CCSD(T) and CCSDR(3) methods. For detailed comparison between the two methods, the error in the root obtained with EOM-CCSD(T) corresponding to the root with maximum error using CCSDR(3) is also plotted.
Figure 4-7. Efficiency plots for the complete EOM-CCSD(T) calculation for various nucleobases in an aug-cc-pVDZ basis set over 32 - 512 range of CPUs. A) is the total time, B) does not include the block wait time, the time waiting for data to arrive at a compute core. See text for details on the “over”-efficiency of adenine and thymine.

Figure 4-8. Efficiency plots for the triples piece of the EOM-CCSD(T) calculation for various nucleobases in an aug-cc-pVDZ basis set over 32 - 512 range of CPUs. A) is the total time, B) does not include the block wait time, the time waiting for data to arrive at a compute core.

Figure 4-9. Block wait times for each processor count in the EOM-CCSD(T) calculations. A) is for the total calculation, B) is for the triples piece only. Since adenine block wait on 32 processors is so large, the inset shows the range from 64 to 512 processors.
Figure 4-10. A log-log plot depicting the scaling behavior of the total EOM-CCSD(T) calculation for various nucleobases in an aug-cc-pVDZ basis set. A) is the total time, B) does not include the block wait time, the time waiting for data to arrive at a compute core. Note that the x-axis displays the number of processors, but is actually the log of that number to have equal distances between the different processor counts. The y-axis for each nucleobase was shifted for clarity.

Figure 4-11. Log-log plots depicting the scaling behavior of the triples piece of the EOM-CCSD(T) calculation for various nucleobases in an aug-cc-pVDZ basis set. A) is the total time, B) does not include the block wait time, the time waiting for data to arrive at a compute core. Note that the x-axis displays the number of processors, but is actually the log of that number to have equal distances between the different processor counts. The y-axis for each nucleobase was shifted for clarity.
Figure 4-12. Structure of the microhydrated cytosine clusters optimized at the MP2/aug-cc-pVDZ basis. The structures are separated by the number of waters positioned at sites A, B, or C.
Figure 4-13. MP2/aug-cc-pVDZ optimized structure of cytidine used in this study.

Figure 4-14. MP2/aug-cc-pVDZ optimized structure of guanosine used in this study.

Figure 4-15. MP2/aug-cc-pVDZ optimized structure of guanine-cytosine Watson-Crick pair used in this study.
Figure 4-16. EOM-CCSD gradient scaling curve for Adenine up to 512 processors.

Figure 4-17. EOM-CCSD gradient scaling curve for Cytosine up to 1024 processors.

Figure 4-18. EOM-CCSD gradient scaling curve for Thymine up to 512 processors.
Figure 4-19. EOM-CCSD gradient scaling curve for Guanine up to 512 processors.

Figure 4-20. EOM-CCSD gradient scaling curve for Cytosine Guanine stack up to 2048 processors.
Figure 4-21. Density differences for the lowest $\pi\pi^*$ excitation using EOM-CCSD in an aug-cc-pVDZ basis set on guanine.

Figure 4-22. Comparison of excited vs. ground state geometries in an aug-cc-pVDZ basis set for guanine.

Figure 4-23. Density differences for the lowest $\pi\pi^*$ excitation using EOM-CCSD in an aug-cc-pVDZ basis set on cytosine.
Figure 4-24. Comparison of excited vs. ground state geometries in an aug-cc-pVDZ basis set for cytosine

Figure 4-25. Density differences for the lowest $\pi\pi^*$ excitation using EOM-CCSD in an aug-cc-pVDZ basis set on thymine.

Figure 4-26. Comparison of excited vs. ground state geometries in an aug-cc-pVDZ basis set for thymine
Figure 4-27. Density differences for the lowest $\pi\pi^*$ excitation using EOM-CCSD in an aug-cc-pVDZ basis set on stacked cytosine-guanine.

Figure 4-28. Comparison of excited vs. ground state geometries in an aug-cc-pVDZ basis set for stacked cytosine-guanine.
Table 4-1. Computed oscillator strengths \(^a\) at the EE-EOM-CCSD/aug-cc-pVTZ level of theory with various approximations.

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<th>Molecule</th>
<th>Exc. energy (eV)</th>
<th>EOM osc. str.(^b)</th>
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<td>0.0000</td>
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<td>0.0030</td>
<td>0.0014</td>
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<td>9.12</td>
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<td>0.0256</td>
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<td>Skew ammonia</td>
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<td>0.0740</td>
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<td>7.80</td>
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<td>0.0168</td>
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<td>0.0065</td>
<td>0.0065</td>
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<tr>
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<td>9.19</td>
<td>0.0039</td>
<td>0.0042</td>
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<td>9.24</td>
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<td>0.0092</td>
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<td>9.63</td>
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<td>0.0101</td>
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<td>0.0119</td>
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<tr>
<td></td>
<td>10.50</td>
<td>0.0021</td>
<td>0.0025</td>
<td>0.0004</td>
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<td>10.65</td>
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<td>0.0049</td>
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<td>Water</td>
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<td>7.54</td>
<td>0.0523</td>
<td>0.0544</td>
<td>0.0021</td>
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<td>10.78</td>
<td>0.0027</td>
<td>0.0029</td>
<td>0.0001</td>
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<td>12.87</td>
<td>0.0265</td>
<td>0.0273</td>
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<td>9.92</td>
<td>0.1000</td>
<td>0.1023</td>
<td>0.0023</td>
</tr>
<tr>
<td></td>
<td>11.34</td>
<td>0.0010</td>
<td>0.0011</td>
<td>0.0000</td>
</tr>
<tr>
<td></td>
<td>13.24</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0000</td>
</tr>
<tr>
<td></td>
<td>11.66</td>
<td>0.0188</td>
<td>0.0190</td>
<td>0.0002</td>
</tr>
</tbody>
</table>

\(^a\) Only oscillator strengths greater than \(10^{-4}\) were used in comparison.

\(^b\) Oscillator strength computed using \(L_{\sigma}\) and \(\lambda\) for the left transition density.

\(^c\) Oscillator strength computed using \(R_{\sigma}^{\dagger}\) and \(T_{\pi}^{\dagger}\) for the left transition density.
Table 4-2. Comparison of using $R^T_k$ for $L$ in triples corrections for the water molecule in an aug-cc-pVDZ basis set. All values are in eV. See text for details.

<table>
<thead>
<tr>
<th>$\omega$</th>
<th>$L_k \equiv L_k$</th>
<th>$L_k \equiv R^T_k$</th>
<th>$L_k \equiv L_{1k}$</th>
<th>$L_k \equiv R^T_{1k}$</th>
<th>$L_k \equiv L_{2k}$</th>
<th>$L_k \equiv R^T_{2k}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.64</td>
<td>0.07</td>
<td>0.12</td>
<td>0.44</td>
<td>0.44</td>
<td>-0.36</td>
<td>-0.32</td>
</tr>
<tr>
<td>8.42</td>
<td>0.07</td>
<td>0.12</td>
<td>0.43</td>
<td>0.44</td>
<td>-0.36</td>
<td>-0.32</td>
</tr>
<tr>
<td>9.08</td>
<td>0.07</td>
<td>0.11</td>
<td>0.40</td>
<td>0.40</td>
<td>-0.33</td>
<td>-0.29</td>
</tr>
<tr>
<td>10.60</td>
<td>0.09</td>
<td>0.14</td>
<td>0.45</td>
<td>0.45</td>
<td>-0.36</td>
<td>-0.31</td>
</tr>
<tr>
<td>10.96</td>
<td>0.07</td>
<td>0.12</td>
<td>0.43</td>
<td>0.44</td>
<td>-0.36</td>
<td>-0.32</td>
</tr>
</tbody>
</table>

Table 4-3. Parameters for each nucleobase used to demonstrate performance of EOM-CCSD(T) calculations. Details on block sizes can be found in Ref. [34]

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Electrons a</th>
<th>Basis functions</th>
<th>Atomic orbital</th>
<th>Occupied</th>
<th>Virtual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cytosine</td>
<td>21</td>
<td>229</td>
<td>33</td>
<td>21</td>
<td>30</td>
</tr>
<tr>
<td>Thymine</td>
<td>24</td>
<td>261</td>
<td>33</td>
<td>17</td>
<td>33</td>
</tr>
<tr>
<td>Adenine</td>
<td>25</td>
<td>275</td>
<td>35</td>
<td>18</td>
<td>30</td>
</tr>
<tr>
<td>Guanine</td>
<td>28</td>
<td>298</td>
<td>33</td>
<td>20</td>
<td>33</td>
</tr>
</tbody>
</table>

a The number of valence electrons are reported, since the core electrons were frozen.

Table 4-4. Parameters and timings of the ACESIII calculations on cytosine and guanine and the corresponding Watson-Crick base pair. All calculations employ the aug-cc-pVDZ basis set.

<table>
<thead>
<tr>
<th>System</th>
<th>Number of atoms</th>
<th>Number of val. els.</th>
<th>Number of basis functions</th>
<th>Number of CPUs</th>
<th>Elapsed time (sec)</th>
<th>Total time in hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cytosine</td>
<td>13</td>
<td>42</td>
<td>229</td>
<td>32</td>
<td>515</td>
<td>3694 5843</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>64</td>
<td>323</td>
<td>2179 3080</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>128</td>
<td>210</td>
<td>1292 1722</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>256</td>
<td>155</td>
<td>900 1358</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>512</td>
<td>141</td>
<td>760 1161</td>
</tr>
<tr>
<td>Guanine</td>
<td>16</td>
<td>56</td>
<td>298</td>
<td>32</td>
<td>2157</td>
<td>21178 25900</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>64</td>
<td>1226</td>
<td>10272 13817</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>128</td>
<td>668</td>
<td>4654 7693</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>256</td>
<td>417</td>
<td>2743 4771</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>512</td>
<td>276</td>
<td>1730 3231</td>
</tr>
<tr>
<td>Cytosine-Guanine</td>
<td>29</td>
<td>98</td>
<td>527</td>
<td>512</td>
<td>4310</td>
<td>12360 98000 368</td>
</tr>
</tbody>
</table>

a Timings for construction of $H$ and both the left and right EOM solutions for one excited state
b Timings for one excited state solution.

Total time for all steps including EOM-CCSD(T) considering 12 excited state solutions
Table 4-5. Change of the excitation energies (eV) of cytosine by interaction with water (structure B) calculated at the EOMEE-CCSD and EOMEE-CCSD(T) levels\textsuperscript{a}

<table>
<thead>
<tr>
<th>transition type</th>
<th>assignment</th>
<th>cytosine</th>
<th>cytosine-water (B)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CCSD</td>
<td>CCSD(T)</td>
</tr>
<tr>
<td>1(p(\pi)*)</td>
<td>(\pi \rightarrow \pi^*)</td>
<td>4.94</td>
<td>4.74</td>
</tr>
<tr>
<td>1(n(\pi)*)</td>
<td>(n_N \rightarrow \pi^*)</td>
<td>5.46</td>
<td>5.25</td>
</tr>
<tr>
<td>1((\pi)-(\pi))</td>
<td>(\pi \rightarrow R)</td>
<td>5.56</td>
<td>5.49</td>
</tr>
<tr>
<td>2(p(\pi)*)</td>
<td>(\pi_{-1} \rightarrow \pi^*)</td>
<td>5.86</td>
<td>5.62</td>
</tr>
<tr>
<td>2((\pi)-(\pi))</td>
<td>(\pi_{-1} \rightarrow R)</td>
<td>6.04\textsuperscript{d}</td>
<td>5.91</td>
</tr>
<tr>
<td>2(n(\pi)*)</td>
<td>(n_O \rightarrow 2\pi^*)</td>
<td>6.06\textsuperscript{d}</td>
<td>5.96</td>
</tr>
<tr>
<td>3((\pi)-(\pi))</td>
<td>(\pi \rightarrow R)</td>
<td>6.19</td>
<td>6.08</td>
</tr>
<tr>
<td>3(n(\pi)*)</td>
<td>(n_O \rightarrow \pi^*)</td>
<td>6.34</td>
<td>5.90</td>
</tr>
<tr>
<td>3((\pi)-(\pi))</td>
<td>(\pi \rightarrow 2\pi^*)</td>
<td>6.50</td>
<td>6.35</td>
</tr>
<tr>
<td>4((\pi)-(\pi))</td>
<td>(\pi \rightarrow R)</td>
<td>6.51</td>
<td>6.43</td>
</tr>
<tr>
<td>1(n(\pi))</td>
<td>(n_O, n_N \rightarrow R)</td>
<td>6.70</td>
<td>6.57</td>
</tr>
<tr>
<td>4((\pi)*)</td>
<td>(\pi_{-1} \rightarrow 2\pi^*)</td>
<td>6.88</td>
<td>6.69</td>
</tr>
</tbody>
</table>

\textsuperscript{a}MP2/aug-cc-pVDZ geometry, aug-cc-pVDZ basis. \textsuperscript{b} Change of excitation energy with respect to isolated cytosine. \textsuperscript{c} Difference of the triple shift between monomer and hydrated molecule. \textsuperscript{d} These two states are strongly mixed.
<table>
<thead>
<tr>
<th>type</th>
<th>cytosine</th>
<th>cytosine + water</th>
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<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1(ππ⁺)</td>
<td>4.94 0.049</td>
<td>4.85 0.065</td>
<td>4.88 0.066</td>
<td>4.88 0.079</td>
<td>4.93 0.068</td>
<td>4.93 0.077</td>
<td>4.98 0.086</td>
<td>5.00 0.092</td>
<td>5.09 0.104</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1(nπ⁺)</td>
<td>5.46 0.002</td>
<td>5.42 0.004</td>
<td>5.66 0.001</td>
<td>5.45 0.003</td>
<td>5.75 0.006</td>
<td>5.77 0.002</td>
<td>5.86 0.005</td>
<td>5.90 0.003</td>
<td>5.93 0.014</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1(πR)</td>
<td>5.56 0.004</td>
<td>5.79 0.017</td>
<td>5.64 0.005</td>
<td>5.81 0.014</td>
<td>5.66 0.004</td>
<td>5.85 0.006</td>
<td>5.87 0.005</td>
<td>5.89 0.005</td>
<td>6.01 0.003</td>
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<tr>
<td>2(ππ⁺)</td>
<td>5.86 0.142</td>
<td>5.83 0.130</td>
<td>5.69 0.171</td>
<td>5.85 0.125</td>
<td>5.64 0.182</td>
<td>5.72 0.169</td>
<td>5.68 0.200</td>
<td>5.71 0.181</td>
<td>5.72 0.184</td>
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</tr>
<tr>
<td>2(nπ⁺)</td>
<td>6.04 0.003</td>
<td>6.18 0.011</td>
<td>6.18 0.002</td>
<td>6.21 0.001</td>
<td>6.18 0.002</td>
<td>6.26 0.010</td>
<td>6.27 0.011</td>
<td>6.29 0.016</td>
<td>6.43 0.013</td>
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<td></td>
</tr>
<tr>
<td>2(nR)</td>
<td>6.06 0.006</td>
<td>6.15 0.000</td>
<td>6.04 0.000</td>
<td>6.18 0.014</td>
<td>6.12 0.000</td>
<td>6.28 0.002</td>
<td>6.36 0.005</td>
<td>6.41 0.000</td>
<td>6.64 0.044</td>
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<td></td>
</tr>
<tr>
<td>3(πR)</td>
<td>6.19 0.006</td>
<td>6.44 0.090</td>
<td>6.37 0.015</td>
<td>6.49 0.065</td>
<td>6.42 0.014</td>
<td>6.59 0.003</td>
<td>6.65 0.011</td>
<td>6.66 0.031</td>
<td>6.83 0.004</td>
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</tr>
<tr>
<td>3(nπ⁺)</td>
<td>6.34 0.000</td>
<td>6.40 0.003</td>
<td>6.29 0.000</td>
<td>6.47 0.001</td>
<td>6.39 0.000</td>
<td>6.53 0.000</td>
<td>6.63 0.007</td>
<td>6.71 0.002</td>
<td>7.07 0.007</td>
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</tr>
<tr>
<td>3(nR)</td>
<td>6.50 0.412</td>
<td>6.34 0.414</td>
<td>6.47 0.416</td>
<td>6.31 0.459</td>
<td>6.47 0.377</td>
<td>6.39 0.358</td>
<td>6.38 0.314</td>
<td>6.35 0.286</td>
<td>6.32 0.267</td>
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</tr>
<tr>
<td>4(πR)</td>
<td>6.51 0.005</td>
<td>6.62 0.004</td>
<td>6.61 0.002</td>
<td>6.59 0.003</td>
<td>6.63 0.008</td>
<td>6.67 0.049</td>
<td>6.70 0.097</td>
<td>6.69 0.008</td>
<td>6.87 0.003</td>
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</tr>
<tr>
<td>1(nR)</td>
<td>6.70 0.026</td>
<td>6.80 0.022</td>
<td></td>
<td>6.85 0.026</td>
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</tr>
<tr>
<td>5(πR)</td>
<td>6.82 0.000</td>
<td></td>
<td></td>
<td></td>
<td>7.09 0.006</td>
<td>7.08 0.006</td>
<td>7.10 0.003</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4(ππ⁺)</td>
<td>6.88 0.180</td>
<td>6.81 0.192</td>
<td>6.77 0.224</td>
<td>6.80 0.229</td>
<td>6.69 0.249</td>
<td>6.72 0.297</td>
<td>6.64 0.299</td>
<td>6.63 0.367</td>
<td>6.61 0.557</td>
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</tr>
<tr>
<td>4(nn⁺)</td>
<td>6.87 0.047</td>
<td>6.83 0.017</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.94 0.008</td>
<td></td>
</tr>
</tbody>
</table>

a For orbital based assignment compare with 4-5. b Oscillator strength from right hand vector only; c These two states are strongly mixed.
<table>
<thead>
<tr>
<th>transition</th>
<th>assignment</th>
<th>Cytosine</th>
<th>Cytosine</th>
<th>Cytosine</th>
<th>Cytosine</th>
<th>ΔCCSD</th>
<th>ΔCCSD(T)</th>
<th>ΔΔb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(ππ* )</td>
<td>π → π*</td>
<td>4.94</td>
<td>0.049</td>
<td>4.74</td>
<td>4.84</td>
<td>0.129</td>
<td>4.63</td>
<td>-0.10</td>
</tr>
<tr>
<td>1(nπ* )</td>
<td>nN → π*</td>
<td>5.46</td>
<td>0.002</td>
<td>5.25</td>
<td>5.49</td>
<td>0.006</td>
<td>5.29</td>
<td>0.03</td>
</tr>
<tr>
<td>1(πR )</td>
<td>π → R</td>
<td>5.56</td>
<td>0.004</td>
<td>5.49</td>
<td>5.77</td>
<td>0.009</td>
<td>5.67</td>
<td>0.21</td>
</tr>
<tr>
<td>2(ππ* )</td>
<td>π → R</td>
<td>5.86</td>
<td>0.142</td>
<td>5.62</td>
<td>5.81</td>
<td>0.142</td>
<td>5.58</td>
<td>-0.05</td>
</tr>
<tr>
<td>2(nπ* )</td>
<td>nO → 2π*</td>
<td>6.04</td>
<td>0.003</td>
<td>5.91</td>
<td>6.14</td>
<td>0.115</td>
<td>5.99</td>
<td>0.10</td>
</tr>
<tr>
<td>3(ππ* )</td>
<td>π → 2π*</td>
<td>6.50</td>
<td>0.412</td>
<td>6.35</td>
<td>6.24</td>
<td>0.191</td>
<td>6.12</td>
<td>0.05</td>
</tr>
<tr>
<td>3(πR )</td>
<td>π → R</td>
<td>6.19</td>
<td>0.006</td>
<td>6.08</td>
<td>6.46</td>
<td>0.011</td>
<td>6.34</td>
<td>0.27</td>
</tr>
<tr>
<td>3(nπ* )</td>
<td>nO → π*</td>
<td>6.34</td>
<td>0.000</td>
<td>5.90</td>
<td>6.47</td>
<td>0.008</td>
<td>6.05</td>
<td>0.13</td>
</tr>
<tr>
<td>4(πR )</td>
<td>π → R</td>
<td>6.51</td>
<td>0.005</td>
<td>6.43</td>
<td>6.55</td>
<td>0.107</td>
<td>6.42</td>
<td>0.04</td>
</tr>
<tr>
<td>5(πR )</td>
<td>π → R</td>
<td>6.82</td>
<td>0.000</td>
<td>6.73</td>
<td>6.67</td>
<td>0.101</td>
<td>6.54</td>
<td>-0.15</td>
</tr>
<tr>
<td>1(nR )</td>
<td>nO, nN → R</td>
<td>6.70</td>
<td>0.026</td>
<td>6.57</td>
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<tr>
<td>4(ππ* )</td>
<td>π → 2π*</td>
<td>6.88</td>
<td>0.180</td>
<td>6.68</td>
<td>6.82</td>
<td>0.174</td>
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<td>-0.06</td>
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</table>

a Relative excitation energy with respect to cytosine. b) Difference of the triple shift between monomer and hydrated molecule c) These two states are strongly mixed, essentially a mixture of the two designations. d) These three states are mixed combination of the corresponding cytosine states causing intensity borrowing from the third state. e) There is also a component π → 2π* which introduces oscillator strength in both of these states.
Table 4-8. Excitation energies of the lowest 12 transitions of guanine and guanosine

<table>
<thead>
<tr>
<th>transition type</th>
<th>assignment</th>
<th>Guanine</th>
<th>Guanosine</th>
<th>∆&lt;sub&gt;CCSD&lt;/sub&gt;</th>
<th>∆&lt;sub&gt;CCSD(T)&lt;/sub&gt;</th>
<th>∆&lt;sub&gt;CCSD&lt;/sub&gt;</th>
<th>∆&lt;sub&gt;CCSD(T)&lt;/sub&gt;</th>
<th>∆Δ&lt;sup&gt;b&lt;/sup&gt;</th>
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<tbody>
<tr>
<td>1(πR)</td>
<td>π → R</td>
<td>4.92 0.003</td>
<td>4.81 5.16 0.034</td>
<td>5.03 0.24</td>
<td>0.22</td>
<td>0.02</td>
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<tr>
<td>2(πR)</td>
<td>π → R</td>
<td>5.11 0.114</td>
<td>4.93 5.05 0.125</td>
<td>4.87 -0.06</td>
<td>-0.06</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2(ππ*)</td>
<td>π → π*</td>
<td>5.32 0.005</td>
<td>5.23 5.90 0.006</td>
<td>5.80 0.58</td>
<td>0.57</td>
<td>0.01</td>
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<tr>
<td>1(nπ*)</td>
<td>nO → π*</td>
<td>5.61 0.297</td>
<td>5.43 5.54 0.246</td>
<td>5.36 -0.07</td>
<td>-0.07</td>
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<tr>
<td>3(πR)</td>
<td>π → R</td>
<td>5.65 0.000</td>
<td>5.51 5.56 0.092</td>
<td>5.40 -0.09</td>
<td>-0.11</td>
<td>0.02</td>
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<tr>
<td>4(πR)</td>
<td>π → R</td>
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<td>5.76 5.99 0.001</td>
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<td>0.02</td>
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</tr>
<tr>
<td>5(πR)</td>
<td>π → R</td>
<td>6.01 0.001</td>
<td>5.94 6.17 0.015</td>
<td>6.04 0.16</td>
<td>0.10</td>
<td>0.06</td>
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<tr>
<td>6(πR)</td>
<td>π → R(π)</td>
<td>6.29 0.001</td>
<td>6.22 6.34 0.004</td>
<td>6.20 0.05</td>
<td>-0.02</td>
<td>0.07</td>
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<tr>
<td>3(ππ*)</td>
<td>π → 3π*</td>
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<td>6.24 6.23 0.001</td>
<td>6.10 -0.09</td>
<td>-0.14</td>
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<tr>
<td>2(nπ*)</td>
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<td>6.31 6.39&lt;sup&gt;c&lt;/sup&gt; 0.033</td>
<td>6.22 -0.10</td>
<td>-0.09</td>
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<tr>
<td>7(πR)</td>
<td>π → R</td>
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<td>6.46 6.41 0.016</td>
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<sup>a</sup> Relative excitation energy with respect to guanine. <sup>b</sup> Difference of the triples shift between monomer and hydrated molecule. 
<sup>c</sup> Includes strong Rydberg component.
Table 4-9. Excitation energies (eV) and oscillator strengths of the lowest transitions of cytosine, guanine and their Watson-Crick pair. EOM-CCSD/aug-pVDZ calculations

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<th>Guanine</th>
<th>GC pair</th>
<th>monomers</th>
<th>GC pair</th>
<th>∆∆&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>1(ππ&lt;sup&gt;∗&lt;/sup&gt;)</td>
<td>G&lt;sub&gt;π&lt;/sub&gt; → π&lt;sup&gt;∗&lt;/sup&gt;</td>
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<tr>
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<td>C&lt;sub&gt;π&lt;/sub&gt; → π&lt;sup&gt;∗&lt;/sup&gt;</td>
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<td>0.049</td>
<td>–</td>
<td>–</td>
<td>5.07</td>
<td>0.097</td>
</tr>
<tr>
<td>3(ππ&lt;sup&gt;∗&lt;/sup&gt;)</td>
<td>G&lt;sub&gt;π&lt;/sub&gt; → 2π&lt;sup&gt;∗&lt;/sup&gt;</td>
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<td>–</td>
<td>5.61</td>
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<td>5.86</td>
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<td>0.174</td>
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<tr>
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<td>G&lt;sub&gt;O&lt;/sub&gt; → π&lt;sup&gt;∗&lt;/sup&gt;</td>
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<td>–</td>
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<td>5.91</td>
<td>0.000</td>
</tr>
<tr>
<td>1(π&lt;sup&gt;R&lt;/sup&gt;)</td>
<td>G&lt;sub&gt;π&lt;/sub&gt; → R</td>
<td>–</td>
<td>–</td>
<td>4.92</td>
<td>0.003</td>
<td>4.92</td>
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</tr>
<tr>
<td>2(π&lt;sup&gt;R&lt;/sup&gt;)</td>
<td>G&lt;sub&gt;π&lt;/sub&gt; → R</td>
<td>–</td>
<td>–</td>
<td>5.32</td>
<td>0.005</td>
<td>5.37</td>
<td>0.006</td>
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<tr>
<td>3(π&lt;sup&gt;R&lt;/sup&gt;)</td>
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<td>–</td>
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<tr>
<td>4(π&lt;sup&gt;R&lt;/sup&gt;)</td>
<td>G&lt;sub&gt;π&lt;/sub&gt; → R</td>
<td>–</td>
<td>–</td>
<td>6.01</td>
<td>0.001</td>
<td>5.76&lt;sup&gt;a&lt;/sup&gt;</td>
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</tr>
<tr>
<td>5(π&lt;sup&gt;R&lt;/sup&gt;)</td>
<td>C&lt;sub&gt;π&lt;/sub&gt; → R</td>
<td>5.56</td>
<td>0.004</td>
<td>–</td>
<td>–</td>
<td>5.68</td>
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<sup>a</sup> The natural orbitals corresponding to the hole to have substantial contribution on both cytosine and guanine. <sup>b</sup> Difference of the shift due triples between monomer and GC pair.
CHAPTER 5
CONCLUDING REMARKS

The most accurate electronic structure methods to date, capable of chemical accuracy, quickly hit the wall of applicability due to their large formal scaling. Extending the calculations to include full effects of relativity make the situation more dire. Successful approaches, with the goal of performing accurate calculations on increasingly large molecules, should include a variety of optimization techniques including the development of new, efficient theoretical methods, and exploiting modern computer architectures to speed up calculations. The work presented in this study applies both of these strategies to further push the applicability of coupled cluster theory.

The Douglas-Kroll-Hess transformation is a formally exact procedure that can incorporate all the relativistic information from the Dirac equation in a very computationally efficient manner. It has been tested in conjunction with IP-EOM-CCSD in an attempt to improve theoretically determined core ionization energies to aide in deciphering experimental data. The implementation only includes the scalar-relativistic effects, as I have ignored the spin-dependent terms due to the hard-coded symmetry of the existing quantum chemistry coupled cluster programs. However, it allows near quantitative accuracy for molecules with low nuclear charge and qualitative accuracy for molecules with higher nuclear charge. The inclusion of the spin dependent terms would most likely improve the results towards quantitative accuracy, but is beyond the scope of the present study. In fact, the fifth-order DKH transformation performs with quantitative accuracy for highly stripped ions where spin-orbit effects are not present up to a very high energy threshold of $\sim 5,000$ eV. This enables the efficient study of high energy plasmas, and has been implemented efficiently in the ACESII and ACESIII program packages.

For organic molecules, where relaxation effects are the dominant energetic effects in core ionization energies, a method was developed to compute this relaxation quantity to infinite-order, directly using variational coupled cluster theory. A direct formulation
has been needed since the pioneering work of Bagus et al [186]. This IP-VCCS method converges rapidly, avoids symmetry dilemmas a priori, and reduces spin contamination errors obtained in the traditional, indirect way. It is a completely size extensive method and has only mean-field computational cost. Consequently, the whole ionization spectrum can be obtained with $n_{\text{occ}}N_{\text{AO}}^4$ formal scaling. This method parallelizes very well, as it avoids any serial diagonalization, which is present in a traditional SCF algorithm, and has thus been implemented in the ACESIII program package.

In a departure from core ionization energies, I embark on a mission to offer the very accurate EOM-CC methodology in a massively parallel way. Having implemented the left hand eigenvector solutions in ACESIII, the routine study of properties and transition intensities can be routinely studied on ever larger molecules. With the goal of computational efficiency, even in a massively parallel environment, in mind, using the right hand eigenvectors in place of the left hand eigenvectors provides a quantitative approximation to oscillator strengths, and reduces the computational effort by a factor of 2. Furthermore, one can simply avoid the computation of the $\hat{\Lambda}$ equations of CC theory to obtain near quantitative theoretical line intensities, with no approximation to the excitation energy itself.

In order to obtain more quantitative excitation energies, the noniterative perturbative triples methods, EOM-CCSD(T) and EOM-CCSD(\tilde{T}), have been rederived in a different light via Löwdin partitioning, and implemented in a massively parallel way in ACESIII. I show that the EOM-CCSD(\tilde{T}) method, which should incorporate the quadruples space in the computation, performs less satisfactorily than its first order approximation (in the two-electron perturbation), EOM-CCSD(T). The new derivation highlights the lack of approximations in the EOM-CCSD(T) method, and helps explain its excellent performance compared to EOM-CCSDT-3. The performance of the code is equally good, and is shown to perform better, the larger the system gets.
To explore the excited state potential energy surfaces of large molecules, the EOM-CCSD gradients were implemented in the ACESIII environment. The code shows very good performance across a wide range of processors, enabling the routine study of molecules that are far beyond the reach of serial implementations. I have tested the implementation on biologically relevant molecules, a major focus in this work. This opens the door to adiabatic excitation energies, excited state geometries, transition states along the excited state surface, and even excited state ab initio molecular dynamics. Moreover, the groundwork is laid for the extension of multi-ionized/multi-attached EOM-CC methods for the routine exploration of states dominated by multiple, degenerate, reference determinants.
### Table A-1. Excitation energies of molecules with various CC methods. All values are in eV. The TZVP basis set was used for all methods.

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<th>Molecule</th>
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<th>CCSD(T)</th>
<th>CCSD($\tilde{T}$)</th>
<th>CCSDR(3)</th>
<th>CC3</th>
<th>CCSDT-3</th>
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REFERENCES


[37] K. Siegbahn et al., ESCA Applied to Free Molecules., Amsterdam North Holland,
1969.
(2005).


[184] Chugach is a Cray XE6 with 728 compute nodes each with 2-eight cores, or 16 compute cores per node and 30 GB accessible RAM per node located at the Artic Regional Supercomputing Center.


BIOGRAPHICAL SKETCH

Tom Watson Jr. was born in Providence, Rhode Island in 1985. His sixth grade physical science teacher, Mr. Moore, at Burrillville Middle School was the liveliest teacher there, and as a result he began gravitating towards science. During his time at the Woonsocket High School, pursuing a path specific to medical school, he recalled his fond days in middle school. Thanks to the guidance of Mr. Brown, Mrs. Pierannunzi, and Mrs. Pichette, he forgot about that path and focused on his first academic love, chemistry, of any kind, and attended Rhode Island College (RIC).

His original intentions for teaching and encouraging high school students towards a career in chemistry were very quickly removed upon joining Dr. Génnison de Oliveira’s (Dr. D) computational chemistry research group at RIC, where he played around with basis sets and density functionals (what else can an undergraduate do). Working with, talking with, and running an Olympic Triathlon with Dr. D brought out his passion for quantum chemical research (and disdain for running), with a very specific goal of incorporating it in the undergraduate curriculum, since it is so fundamental to chemistry.

Yearning for a more rigorous and robust way to study chemical systems, he attended the University of Florida to work under the direction of Dr. Rodney J. Bartlett. He further refined his interests towards the development and implementation of new theory with new technologies. He also married his college sweetheart, Sondra Trafford, his first year there, and had his first daughter, Ayla Grace Watson, in his third.

He hopes to be actively involved in using new computational technologies to encourage undergraduate students towards the noble pursuit of advancing science. He hopes to be as encouraging as his mentors to the future generations not yet excited about chemistry.