CHEM 5914 Literature Review and Research Plan – COVER SHEET – Fall 2017

Student's Name	**Karl Pierce**
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Check the correct box. (In MS Word double-click on box and change "default value")

☐	**Outline**. Submit to the Research Director only by September 1st. Respond within 1 week.
☐	**Preliminary Draft**. Submit to Research Director only by September 29th. Response needed by Friday, October 13.
☒	**First Draft**. Submit to Advisory Committee by October 31st. Responses needed by Monday, November 13.
☐	**Final Draft**. Submit to Advisory Committee by December 1st. Responses needed Monday of Exam Week.

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1   Introduction

A grand challenge of theoretical chemistry is to be able to predict accurate properties of chemical systems from the first principles of quantum mechanics. This challenge has many front: solving increasingly large systems at low cost, predicting chemical properties and finding transition structures to name a few. The electronic and nuclear structure of a chemical system is described by a many body differential equation using Hamiltonian mechanics, known as the Schrödinger. Solving this equation, analytically, in its raw form for non-trivial systems is too difficult. To model chemical systems, therefore, requires mathematical approximations starting from the first principles of quantum mechanics which can accurately approximate solutions to the Schrödinger equation. There exists a number of approximate methods such as Hartree Fock, coupled cluster, and density functional theory which calculate approximate solutions in a balance between computational effort and time, accuracy and chemical system size.

Hartree-Fock theory is a mean field approximation which provides a foundation to electronic correlation methods. Hartree-Fock thoery's perturbation based extensions, such as Moller-Plesset theory, can be used to calculate electron correlation of molecules with around 100 atoms. The coupled cluster methods, which are sometimes referred to as the gold standard of electronic structure calculations for their ability to calculate accurate electron correlation energy, require the most computational resources restricting it's calculation ability to molecules with 20-30 atoms. The goal of this research expand the scope of these methods through understanding and manipulation of their computational storage objects, tensors.

In the computation of ab initio quantum mechanics, tensor storage, mutation and contraction are major bottlenecks. The term *curse of dimensionality*, first introduced by Bellman[1] in the field of dynamic programming, refers to the exponential growth in operations required to estimate a function at some accuracy as the number of inputs increases. Using standard, non-decomposed, tensor in the formulation of quantum chemistry calculations is sub-optimal and falls victim to the curse of dimensionality.

2 Ab Initio Many Body Quantum Mechanics

The non-relatavistic physics of electron and nuclei in a stationary state is described by the time-independent Schrödinger equation (SE)

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \tag{1}$$

Where $\hat{H}$ is the Hamiltonian electronic and nuclear energy operator, $|Psi\rangle$, the wavefunction, specifies the state of the system, and E is the corresponding energy of the system. Within the Born-Oppenheimer approximation[2] the problem simplifies to describe electrons in a field of fixed nuclei, with the electronic Hamiltonian defined as:

$$\hat{H}_{\text{elec}} = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}} \tag{2}$$

Where ∇_i^2 is the kinetic energy operator of electron i, $\frac{Z_A}{r_{iA}}$ is the potential energy operator between electron-nuclei pairs, and $\frac{1}{r_{ij}}$ is the potential energy operator of electron-electron pairs. This Hamiltonian solves the electronic Scrödinger equation

$$\hat{H}_{\text{elec}}|\Psi_{\text{elec}}\rangle = E_{\text{elec}}|\Psi_{\text{elec}}\rangle \tag{3}$$

With the electronic wavefunction, Ψ_{elec}, dependent explicitly on the position of electrons and implicitly on the position of the nuclei. Because E_{elec} depends parametrically on the position of the nuclei, the total energy of the system can be calculated as

$$E_{tot} = E_{elec} + \sum_{A=1}^{M}\sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}} \tag{4}$$

Though the full SE, eq. (1), is simplified with the Born-Oppenheimer approximation, it is still too complicated to solve for systems with more than one electron.[2]

2.1 Hartree-Fock

Hartree-Fock (HF) theory[2–4] prescribes Ψ_{elec} as an antisymmetrized product of one particle functions, molecular orbitals (MO), that depend on the coordinate, $x = \{\vec{r}, \omega\}$, which contains spatial, $\vec{r}$, and spin, ω, coordinates. Such an antisymmetrized product is conveniently expressed as a determinant, also known as a Slater determinant:[5,6]

$$\Psi_0(x_1, x_2, ..., x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_N(x_2) \\ \vdots & \vdots & \vdots & \vdots \\ \chi_1(x_N) & \chi_2(x_N) & \cdots & \chi_N(x_N) \end{vmatrix} \tag{5}$$

This mathematical formalism introduces correlation between electrons in the same-spin states, also known as "exchange", though not between opposite-spin states.

The best approximate solution can be found by variational minimization, which provides the HF equations:

$$\hat{f}\chi_i = \varepsilon_i \chi_i \tag{6}$$

Held to the constraint that

$$\langle \chi_i | \chi_j \rangle = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases} \tag{7}$$

$\hat{f}$ the Fock operator is an effective one-electron operator of the form

$$\hat{f}(x_1) = \hat{h}_i(x_1) + \sum_{j \neq i}^{N} \hat{J}_j(x_1) - \hat{K}_j(x_1) \tag{8}$$

where $\hat{h}(x_1)$ is the average kinetic and nuclear attraction energy of a single electron:

$$\hat{h}(x_1) = -\frac{1}{2}\nabla_1^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{1A}} \tag{9}$$

The last two terms in eq. (8) represent the potential energy of the electron-electrons interaction.

$\hat{J}_j$ represents the Coulombic repulsion between two electrons:

$$\hat{J}_j(x_1) = \int \chi_j^*(x_2) \frac{1}{r_{ij}} \chi_j(x_2) dx_2 \tag{10}$$

$\hat{K}_j$, the exchange term, does not have a classical interpretationis direct product of the antisymmetric nature of the single determinant wavefunction:

$$\hat{K}_j(x_1) = \int \chi_j^*(x_2) \frac{1}{r_{ij}} \chi_i(x_2) dx_2 \tag{11}$$

The solution to the HF equation provides a set of orthonormal spin orbitals, $\{\chi_k\}$, each with orbital energy $\{\varepsilon_k\}$. In principle there are infinitely many solutions to eq. (6), though in a finite basis there exists K spatial orbitals giving rise to 2K spin orbitals. The solution to the HF eigenvalue problem provides N occupied and 2K-N unoccupied orbitals.

Exact one one particle functions of the SE are described as Slater type orbitals Unfortunately, numerical differentiation and integration as well as finding distinct functional solutions to the HF equations using Slater type orbitals provides a formidable challenge. In order to produce a simplified solution one expands MO basis functions into M atomic orbital (AO) basis functions

$$\chi_i = \sum_{\mu}^{M} C_{i\mu} \phi_\mu(x) \tag{12}$$

where $C_{i\mu}$ are expansion coefficients and ϕ_μ are typically atom centered functions. Applying eq. (12) to eq. (6) produces what is known as the Hartree-Fock-Roothaan matrix equation[7,8]

$$\mathbf{FC} = \mathbf{SC}\varepsilon \tag{13}$$

$\mathbf{C}$ is the transformation matrix from eq. (12), $\mathbf{S}$ is the overlap of two AO's

$$S_{\mu v} = \int \phi_\mu^*(x_1) \phi_v(x_1) dx_1 \tag{14}$$

and elements of the Fock matrix, $\mathbf{F}$, are

$$F_{\mu\nu} = \int \phi_\mu(x_1)\hat{f}(x_1)\phi_\nu(x_1) \tag{15}$$

The Fock matrix terms can also be expanded with respect to the operators defined in eqs. (9)–(11):

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\text{occ}}\sum_{\rho\sigma} C_{\rho i}C_{\sigma i}\langle\mu\rho||\nu\sigma\rangle \tag{16}$$

where

$$\langle\mu\rho||\nu\sigma\rangle = \langle\mu\rho|\nu\sigma\rangle - \langle\mu\rho|\sigma\nu\rangle \tag{17}$$

is the antisymmetrized difference of the coulomb and exchange terms with

$$\langle\mu\rho|\nu\sigma\rangle = (\mu\nu|\rho\sigma) = \int\int \phi_\mu^*(x_1)\phi_\rho^*(x_2)\frac{1}{r_{12}}\phi_\nu(x_1)\phi_\sigma(x_2)dx_1dx_2 \tag{18}$$

in physicist and chemist notation, respectively. Roothaan's equation eq. (13) specifies HF as a system of non-linear equations and must be solved iteratively to optimize expansion coefficients in a self-consistent-field (SCF) procedure. Evaluation of the Fock matrix is the most expensive step of HF with asymptotic scaling of $\mathscr{O}(N^4)$ which can be reduced to $\mathscr{O}(N^2 \cdot ln N)$ by employing integral screening using the Schwartz inequality[9] for large systems where N is the number of electrons and a storage requirement of $\mathscr{O}(N^4)$.

2.2 Electronic Correlation Methods

Electron correlation is a product of: the antisymmetry of the wavefunction due to the fermionic statistics of electrons, fermi correlation, discussed previously, and due to the Coulombic (spin-independent) repulsion between two electrons, coulomb Correlation.[10] HF does cannot recover electron correlation beyond fermi correlation. Because HF theory relies on the independent particle model, it does not consider electron-electron repulsion explicitly but as a field effect. Correlation energy, as defined by Löwdin,[11] is

$$E_{\text{corr}} = \mathscr{E}_0 - E_{\text{HF}} \tag{19}$$

Where $\mathscr{E}_0$ is the exact non-relativistic energy and E_{HF} is energy recovered at the HF limit. This definition is imprecise; it may be more useful to define E_{corr} as an observable of some quantum mechanical operator acting on a wavefunction:

$$\Psi_{\text{exact}} = \Psi_{\text{HF}} + \Psi_{\text{corr}} \tag{20}$$

where Ψ_{corr} is orthogonal to Ψ_{HF} and encapsulates all correlation not captured by HF.[12] Though correlation energy only contributes a very small portion to the total energy, these corrections are necessary in the accurate calculation of molecular properties and prediction of reactions. Outlined in the following are standard methods to systematically calculate correlation energy.

2.2.1 Many Body Perturbation Theory

Many Body Perturbation Theory (MBPT) was first developed in 1957[13] to study the energy of nuclear matter. Not until 1968 was the it applied to ab initio quantum chemistry.[14,15] The formulation presented will follow the Moller-Plesset (MPn) definition of MBPT, where n is the perturbative order correction. MBPT is not variational, the solution recovered from an approximation is lower bounded by the exact energy, but is size consistent. For a method to be size consistent it must be able to calculate the energy of two elements, separated by infinite distant to be the sum of its individual parts.

$$E_{r=\infty}(AB) = E(A) + E(B) \tag{21}$$

Starting with an eigenvalue problem

$$\hat{H}|\Phi\rangle = E|\Phi\rangle \tag{22}$$

one can expand the eigenvalue operator

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)} \tag{23}$$

$\hat{H}^{(0)}$, the zeroth order operator, is assumed to closely approximate the exact Hamiltonian and $\hat{H}^{(1)}$ is the perturbative, first order correction to the zeroth order problem. Perturbative expansion of the eq. (22) with eq. (23) provides the following expression:

$$\hat{H}^{(0)}|\Phi^{(n)}\rangle + \hat{H}^{(1)}|\Phi^{(n-1)}\rangle = \sum_{i=0}^{n} E^{(i)}|\Phi^{(n-i)}\rangle \tag{24}$$

MPn theory assumes

$$\hat{H}^{(0)} = \sum_{i=1}^{N} \hat{f}(i) = \sum_{i=1}^{N} \hat{h}(i) + \hat{J}(i) - \hat{K}(i) \tag{25}$$

and defines the first order correction as

$$\hat{H}^{(1)} = \hat{H}_{elec} - \hat{H}^{(0)} = \sum_{i<j} \frac{1}{r_{ij}} - \sum_{i}(\hat{J}(i) - \hat{K}(i)) \tag{26}$$

MPn theory typically focuses on solving second order correction, MP2, assuming that the wavefuntion the of HF minimization. With this wavefuntion first order corrections are zero by Brillouin theorem.[16] Substituting eqs. (25) and (26) into eq. (24) one finds

$$\langle\Phi^{(0)}|\hat{H}^{(0)}|\Phi^{(0)}\rangle = \sum_{i=1}^{N} \varepsilon_i = E^{(0)} \tag{27}$$

where $\Phi^0 = \Psi_0$ the lowest energy HF reference state

$$\langle\Phi^{(0)}|\hat{H}^{(1)}|\Phi^{(1)}\rangle = \langle\Phi^{(0)}|(\hat{H}_{elec} - \hat{H}^{(0)})|\Phi^{(1)}\rangle = E^{(2)} \tag{28}$$

Where ε_i are the HF orbital energy coefficients. $\Phi^{(1)}$ is expanded in terms of eigenvectors of $\hat{H}^{(0)}$. Slater-Condon rules[2] determine $|\Phi^{(1)}\rangle$ must be from the set of double excited reference state determinant, $|\Psi_{ab}^{ij}\rangle$. Where terms of the form $|\Psi_{abc...}^{ijk...}\rangle$ are created by replacing HF MO χ_i in the set N occupied orbital with an orbital χ_a from the next set of 2K-N unoccupied orbitals and so on. This provides the expansion

$$|\Phi^{(1)}\rangle = \frac{1}{4} \sum_{ijab} t_{ab}^{ij}|\Psi_{ab}^{ij}\rangle \tag{29}$$

Substituting eq. (29) into eq. (24), one can resolve weighting coefficient t_{ab}^{ij} and solve the second order energy equation. In the canonical HF molecular orbital basis one finds:

$$E^{(2)} = \frac{1}{4} \sum_{ijab} \frac{\langle ij||ab \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \tag{30}$$

The term $\langle ij||ab \rangle$ can be obtained from eq. (18) using the transformation

$$\langle ij||ab \rangle = \sum_{\mu\nu\rho\sigma} C_{\mu i} C_{\nu j} C_{\rho a} C_{\sigma b} \langle \mu\nu||\rho\sigma \rangle \tag{31}$$

where $C_{\mu i}$ are eigenvectors of the Fock operator. This transformation is the most computationally rigorous step of MP2 scaling as $\mathcal{O}(N^5)$ with a storage requirement of $\mathcal{O}(N^4)$. Efforts to eliminate the transformation using Laplace transformation (LT) methods will be discussed in detail in the research section. Currently, LT-MP2's efficient reduction in computational cost has only been observed with sufficiently large molecules, more than 200 atoms.

2.2.2 Configuration Interaction

Configuration Interaction (CI) method is an application of the Ritz method of linear variations to the electronic wavefunction.[2,17] CI methods diagonalize the N-electron hamiltonian applied to eq. (20), where Ψ_{corr} is expressed as all possible excited state slater determinants

$$|\Psi_{exact}\rangle = C_0|\Psi_0\rangle + \sum_{ia} C_a^i |\Psi_a^i\rangle + \sum_{\substack{i<j \\ a<b}} C_{ab}^{ij} |\Psi_{ab}^{ij}\rangle + \sum_{\substack{i<j<k \\ a<b<c}} C_{abc}^{ijk} |\Psi_{abc}^{ijk}\rangle + \dots \tag{32}$$

In an infinite basis this expansion is exact In a finite basis there exists $\binom{N}{2K}^2$ terms and the expansion is approximate. The coefficients C express the weighting of each slater determinant in the expansion. The exact wavefunction is not normalized though it does have intermediate normalization[2] defined as

$$\langle \Psi_0 | \Psi_{exact} \rangle = 1 \tag{33}$$

Applying SE and substituting eq. (19), one can find the expression of the correlated energy in terms of a HF reference determinant as

$$\sum_{\substack{i<j \\ a<b}} C_{ab}^{ij} \langle \Psi_0 | (\hat{H}_{elec}) | \Psi_{ab}^{ij} \rangle = E_{\text{corr}} \tag{34}$$

To resolve C_{ab}^{ij} it is necessary to solve the expression:

$$\langle \Psi_{ab}^{ij} | (\hat{H}_{\text{elec}} - E_{HF}) | \Psi_{\text{exact}} \rangle = \langle \Psi_{ab}^{ij} | (\hat{H}_{\text{elec}}) | \Psi_0 \rangle + \sum_{\substack{k \\ c}} C_c^k \langle \Psi_{ab}^{ij} | (\hat{H}_{\text{elec}}) | \Psi_c^k \rangle$$

$$+ \sum_{\substack{k<l \\ c<d}} C_{cd}^{kl} \langle \Psi_{cd}^{kl} | (\hat{H}_{\text{elec}} - E_{HF}) | \Psi_{ab}^{ij} \rangle + \dots \tag{35}$$

$$= C_{ab}^{ij} E_{\text{corr}}$$

it is obvious from eq. (35), solving for C_{ab}^{ij} in terms of eq. (20) requires one to solve $\binom{N}{2K}$ coupled equations One can reduce the full-CI correlation energy calculation by truncating the set of CI coefficients, for example CI singles and doubles (CISD). The CISD formulation has computational scaling of $\mathcal{O}(N^6)$ and storage requirement of $\mathcal{O}(N^4)$. Any truncation to the full-CI wavefunction eliminates the size-consistency and size-extensiveness of the method. To be size-extensive a method must scale linearly with number of electrons, N.

2.2.3 Coupled Cluster Theory

Since its development in the 1960's by Čížek and Paldus[18–20] Coupled Cluster (CC) theory has become the most reliable method used for accurate approximations of atomic and molecular properties.[21] Coupled Cluster theory is established on the exponential expression of the wavefunction

$$| \Psi_{\text{exact}} \rangle = e^{\hat{T}} | \Phi \rangle \tag{36}$$

A power series expansion of the expression provides the following equation

$$e^{\hat{T}} | \Phi \rangle = (1 + \hat{T} + \frac{1}{2!} \hat{T}^2 + \frac{1}{3!} \hat{T}^3 + \dots) | \Phi \rangle \tag{37}$$

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Where $\hat{T}$ is the cluster operator of the form

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + ... + \hat{T}_N \tag{38}$$

the nth order cluster operator has the form

$$\hat{T}_n = \left(\frac{1}{n!}\right)^2 \sum_{ij...,ab...} t_{ij...}^{ab...} a_a^\dagger a_b^\dagger ... a_j a_i \tag{39}$$

where a_i and $a_a^\dagger$ are second-quantization operators: a_i deletes an orbital ϕ_i and $a_a^\dagger$ inserts an orbital ϕ_a from the determinant which the operators act upon, χ_l.[21,22] Inclusion of all cluster operators in the expression of eq. (38) recovers the exact wavefunction, though full-CC calculations are unmanageable for non-trivial systems. Therefore the cluster operator, $\hat{T}$ is truncated at some excitation level; most commonly the cluster operator is truncated to include only single and double cluster operators (CCSD).

$$\hat{T} = \hat{T}_1 + \hat{T}_2 \tag{40}$$

Therefore one defines

$$|\Psi_{CC}\rangle = e^{\hat{T}}|\Psi_0\rangle \tag{41}$$

with intermediate normalization, $\langle\Psi_0|\Psi_{CC}\rangle = 1$. The Hamiltonian is projected onto by $e^{-\hat{T}}$ allowing one to simplify the energy expression using the Cambell-Baker-Hausdorff formula[21] and find

$$E_{CC} = \langle\Psi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Psi_0\rangle \tag{42}$$

$$0 = \langle\Psi_i^a|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Psi_0\rangle \tag{43}$$

$$0 = \langle\Psi_{ij}^{ab}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Psi_0\rangle \tag{44}$$

where

$$E_{CC} = E_0 + E_{corr} \tag{45}$$

eqs. (43) and (44) provide a set on nonlinear equations which must be solved iteratively to provide the single and double cluster amplitudes, t_i^a and t_{ij}^{ab}. Coupled Cluster theory is not variational but is size-consistent and size-extensive. CCSD scales as $\mathscr{O}(N^6)$ and inclusion of the triple cluster operator (CCSDT) increases scaling to $\mathscr{O}(N^8)$ [23,24] with storage requirements of $\mathscr{O}(N^4)$ and $\mathscr{O}(N^6)$, respectively. Chemists have developed a way around this problem by applying perturbation theory to CC to include the triples operator. [21] This approach scales as $\mathscr{O}(N^7)$ and is considered quantum chemistry's gold standard.

2.3 Explicitly Correlated Methods

Within quantum chemistries most accurate approximations one finds basis set error as the largest contribution to total error. In the wavefunction framework established above basis set error contributions are slow to converge and fails to fully recreate the electron cusp condition. Extremely accurate calculations therefore requiring large basis sets. HF theory considers an average electronic field, i.e. electron probability relative to other electrons is constant. In truth electron-electron probability is a function of distance and angle on a sphere, see figure 1.
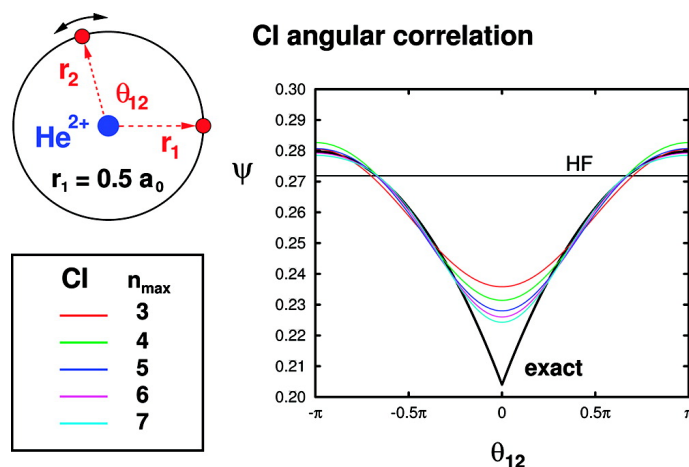
Figure 1: The electron-electron cusp condition for a He ground state CI based wavefunction with both electrons a circle of .5 a_0 using a basis with maximum principle quantum number, n_{max}. [25]

To accurately calculate the Coulombic correlation energy it is necessary to generate a new wavefunction expression that is explicitly dependent on inter-electronic distances. Kato's cusp condition [26] comes from realizing there exists a first-order derivative discontinuity at the

Coulombic type singularity[25] which leads to the coalescence condition

$$\left.\frac{\partial \Psi}{\partial r_{12}}\right|_{r_{12}=0} = \frac{1}{2}\Psi(r_{12}=0) \tag{46}$$

Using this condition, one can construct the new R12 wavefunction as:

$$\Psi(r_1, r_2, \ldots) \approx r_{12}^l \sum_{m=-l}^{l}\left(1 + \frac{r_{12}}{2(l+1)} + \mathcal{O}(r_{12}^2)\right)Y_{lm}(\Omega_{12})\Phi(R_{12}, \ldots) \tag{47}$$

Where $R_{12} \equiv \frac{r_1 + r_2}{2}$ and $r_{12} \equiv r_1 - r_2$ and Y_{lm} is the spherical harmonics. Initial attempts to develop a wavefunction explicitly dependent on two electron coordinates by Hartree[3,27] and Hylleras[28] did not satisfy the cusp condition thus functional representations were not effective. Incorporation of cusp condition has allowed the introduction of functions such as Hylleraas-CI, explicitly correlated Gaussian, and many body Gaussian geminal type.[12] These more functions have allowed R12/F12 methods to develop as functional computational tools. In the next sections I will discuss the use of R12/F12 in MP2 and CC methods.

2.3.1 Explicitly Correlated MP2-R12 method

The difference between MP2 and MP2-R12 methods is in the definition of the first order wavefunction. MP2-R12's first order wavefunction includes eq. (29) and the explicitly correlated geminal functions.

$$|\Psi_{\text{MP2-R12}}\rangle = |\Phi_{\text{MP}}^{(1)}\rangle + \sum_{\substack{i<j \\ x<y}} t_{xy}^{ij}|\Psi_{xy}^{ij}\rangle \tag{48}$$

Where the geminal basis function are quasi-double excitations with respect to the HF reference, $|\Psi_0\rangle$

$$|\Psi_{xy}^{ij}\rangle = \frac{1}{2}\bar{R}_{xy}^{\alpha\beta}\tilde{a}_{ij}^{\alpha\beta}|\Psi_0\rangle \tag{49}$$

Where $\tilde{a}_{ij}^{\alpha\beta}$ is normal ordered with respect $|\Psi_0\rangle$, string of creation and annihilation operators that produce a doubly excited state $|\Psi_{\alpha\beta}^{ij}\rangle$ and $\bar{R}_{xy}^{\alpha\beta}$ are matrix elements of the explicitly correlated factor, $f(r_{12})$ projected by a function, $\hat{Q}_{12}$, which ensure orthogonality of the excited geminal functions:

$$R_{xy}^{\alpha\beta} = \langle\alpha\beta|\hat{Q}_{12}f(r_{12})|xy\rangle \tag{50}$$

The most common choice for $\hat{Q}_{12}$, proposed by Valeev[29]

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2) - \hat{V}_1 \hat{V}_2 \tag{51}$$

Other choices have also been considered.[30,31] The MP2-R12 energy expression is now:

$$E_{\text{MP2-R12}} = \langle \Phi^{(0)} | \hat{H}^{(1)} | \Phi^1 \rangle = E_{\text{MP2}}^{(2)} + E_{\text{R12}}^{(2)} \tag{52}$$

The integrals of $E_{\text{R12}}^{(2)}$ can be solved analytically if the correlation factor, $f(r_{12})$, is Gaussian.[32] The terms in $E_{\text{R12}}^{(2)}$ do require approximations to calculated quickly and accurately such as Density fitting, discussed later.[12]

2.3.2 Explicitly Correlated CC-R12 method

Because MP2-R12 has a limited chemical framework, it is necessary to apply R12 wavefunctions to CC theory.[12] CC-R12 extends the standard CC cluster operator, $\hat{T}$, to include R12 geminal operator, $f(r_{12})$.[33,34] For example the CCSD-R12 wavefunction has the form

$$|\Psi_{\text{exact}}\rangle = e^{\hat{T}} |\Psi_0\rangle \tag{53}$$

Where $\hat{T}$ has the form

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{R} \tag{54}$$

The operators $\hat{T}_1$ and $\hat{T}_2$ are defined using eq. (39) and $\hat{R}$ is defined as

$$\hat{R} = \frac{1}{(2!)^3} t_{ij}^{xy} \bar{R}_{xy}^{\alpha\beta} \tilde{a}_{\alpha\beta}^{ij} \tag{55}$$

where $\bar{R}_{xy}^{\alpha\beta}$ is the conjugate matrix element of the explicitly correlated factor defined in eq. (50). The energy and amplitudes of the CC equation are found in the same fashion described in section 2.2.3 with the added projection of excited geminal functions using the operator $\tilde{\gamma}_{ij}^{xy}$

$$|\Psi_{ij}^{xy}\rangle \equiv \tilde{\gamma}_{ij}^{xy} |\Psi_0\rangle = \frac{1}{2!} \bar{R}_{xy}^{\alpha\beta} \tilde{a}_{\alpha\beta}^{ij} \tag{56}$$

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This creates an additional projection term

$$\langle \Psi_{ij}^{xy} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_0 \rangle = 0 \tag{57}$$

Though this additional amplitude equation does have small store dimension, $\mathscr{O}(o^4)$, where o is the number of occupied states, the computational complexity to implement CCSD-R12 is much greater than CCSD and MP2-R12, with CCSD-R12 scaling as $\mathscr{O}(N^8)$ with storage requirement of $\mathscr{O}(N^6)$. Scaling can be reduced to $\mathscr{O}(N^6)$ by computing an intermediate directly each iteration.[12]

3 Tensor Algebra Methods to Reduce Computational Complexity in Quantum Chemistry

A tensor is a multidimensional array; an N-th order tensor is an element of the tensor product of N vector spaces. A first order tensor is an array, a second order tensor is a matrix and tensor of order three or higher is referred to as a higher-order tensor.[35] Tensors are naturally applied to single reference quantum mechanics: operators such as **F** can be expressed in terms of two electron coordinate products and form second order tensors while other operators and amplitudes such as the coulomb repulsion operator, $\hat{J}$, and the cluster operator amplitudes, $t_{ab...}^{ij...}$, can be expressed as higher-order tensor. Using tensor's as storage devices creates a problem, known as the "curse of dimensionality", where storage and computational processing required to solve a problem scale exponentially with dimension. To overcome this curse requires one to discover the underlying structure in ones data allowing one to reduce storage requirements and to redesign algorithms to scale with the structure of the data.

The goal of any tensor decomposition is to reduce the complexity of a tensor via the underlying form of ones data. The result of a tensor decomposition provide information on the relative importance and weighting of individual vector spaces. Direct methods to compute second order, matrix decompositions such as the singular value (SVD), lower-upper (LU), and Jordan decomposition, have been around for quite some time. Though, interests to decom-

pose higher order tensors didn't develop until 1927 with Hitchcock's idea of a tensor to be a polyadic sum of products[36,37] and later Cattells's idea of a multi-way model in 1944.[38,39] These ideas would later be used to develop canonical product(CP) (CANDECOMP/PARAFAC canonical decomposition / parallel factor decomposition)[40,41] and Tucker decompositions.[42] In order to apply ab initio quantum mechanics to larger systems and circumvent the "curse of dimensionality" it is necessary to take advantage of matrix and higher order tensor decomposition approximations and to redesign canonical algorithms using tensors in decomposed form. To follow are theoretical chemist's current tools to approximate and reduce the complexity of large systems while preserving accuracy.

3.1   Cholesky Decomposition

The Cholesky decomposition (CD) was first applied to quantum chemistry and specifically the two electron integral (TEI) tensor in 1977 by Beeble and Linderberg[43] when the authors realized that, coupled with the positive definite nature of the integrals values, one could to reorder the higher-order tensor into a lower order object and perform a matrix decomposition. What makes the CD special is that it can remove small and zero eigenvalues without calculating the entire matrix, providing computational savings. CD has been in conjunction with two electron geminal implementation, derivative integrals and more recently has been applied to large scale TEI decomposition.[44]

CD works by using a partial (LU) decomposition of any two electron tensor recast into a symmetric positive definite matrix

$$M_{\mu\nu,\gamma\sigma} = \int \int \rho_{\mu\nu}(r_1)\hat{M}(r_1,r_2)\rho_{\gamma\sigma}dr_1dr_2 \equiv (\rho_{\mu\nu}|\rho_{\gamma\sigma}) \qquad (58)$$

where $\rho_{\mu\nu} = \phi_\mu\phi_\nu$ is an orbital density product and $\hat{M}(r_1,r_2)$ is some two electron operator. The goal of the CD is to express M as

$$M = BB^T \qquad (59)$$

This expression can be approximated to some extent, γ, with elements of M expressed as

$$M_{\mu\nu,\gamma\sigma} \approx \sum_{p=1}^{P} B_{\mu\nu}^{P} B_{\gamma\sigma}^{P} = \sum_{p=1}^{P} (\rho_{\mu\nu}|B_p)(B_p|\rho_{\gamma\sigma})$$
$$= \sum_{pq} (\rho_{\mu\nu}|b_p)(\hat{M}(r_1,r_2)^{-1})_{pq}(b_q|\rho_{\gamma\sigma}) \tag{60}$$

where P is the rank of the decomposition which depends on γ. A comprehensive CD algorithm is presented by Epifanovsky et al[45] which can be used to find optimal Cholesky basis, b_p, for a given $\hat{M}(r_1,r_2)$

3.2 Density Fitting

Density fitting (DF) is an specific application of CD where a canonical optimized Cholesky basis is used to decompose the TEI tensor into two order three tensors. The roots of DF have been grounded in Coulomb[46,47] and Exchange[48] fitting in Hartree-Fock and has been applied to MP2,[49] CCSD(T)[50] and even explicitly correlated methods.[51] The derivation of DF to proceed will be based on equations presented by Werner et al.[52] The goal of DF is to decompose the TEI tensor

$$\langle \mu\gamma|\nu\sigma \rangle = (\mu\nu|\gamma\sigma) = \int \frac{\phi_\mu(r_1)\phi_\nu(r_1)\phi_\gamma(r_2)\phi_\sigma(r_2)}{r_{12}} dr_1 dr_2$$
$$= \int \frac{\rho_{\mu\nu}(r_1)\rho_{\gamma\sigma}(r_2)}{r_{12}} dr_1 dr_2 \tag{61}$$

one electron densities, $\rho_{\mu\nu}(r) = \phi_\mu(r)\phi_\nu(r)$, can then be approximated as

$$\bar{\rho}_{\mu\nu}(r) = \sum_{A}^{N_{\text{fit}}} d_A^{\mu\nu} \chi_A(r) \tag{62}$$

where $\chi_A(r)$ are fitting basis functions and expansion coefficients, $d_A^{\mu\nu}$, are expressed as

$$d_B^{\mu\nu} = \sum_{B} (\mu\nu|A)[J^{-1}]_{AB} \tag{63}$$

where

$$(\mu\nu|A) = \int dr_1 \int dr_2 \frac{\phi_\mu(r_1)\phi_\nu(r_1)\chi_A(r_2)}{r_{12}} \tag{64}$$

The term J is chosen to be some metric, here it is defined as the coulomb metric[53,54]

$$J_{AB} = \int dr_1 \int dr_2 \frac{\chi_A(r_1)\chi_B(r_2)}{r_{12}} \tag{65}$$

other metrics have been proposed[55] and though they are less accurate, these metrics are computed more quickly than the Coulomb metric.

This allows one to express the TEI as

$$(\mu\nu|\gamma\sigma) = \sum_B d_B^{\mu\nu}(B|\gamma\sigma) = \sum_{AB}(\mu\nu|A)[J^{-1}]_{AB}(B|\gamma\sigma) \tag{66}$$

transforming $J^{-1} = J^{-1/2}J^{-1/2}$ allows one to store the TEI as two order three tensors, reducing storage requirements from $\mathcal{O}(N^4)$ to $\mathcal{O}(N^2 \cdot N_{fit}) \approx \mathcal{O}(N^3)$; N_{fit} typically scales linearly with basis set. Using DF Reduced scaling algorithms to calculate values such as the HF Coulomb term, $\hat{J}$, and AO to MO integral transformations et al have been developed.

To further reduce scaling of DF one can choose to use a subset of the full auxiliary basis. Original construction of subsets was developed using distance based domains. Unfortunately, this led to discontinuities on the potential energy surface. Recently it has been shown that a better auxiliary subset includes, for a given density, $\rho_{\mu_a\nu_b}$, fitting functions on either center a or b, $|A_{(ab)})$; referred to as concentric atomic density fitting (CADF). This idea combined with localization methods and inclusion of exact semi-diagonal terms has been shown to reduce complexity in the calculation and storage of the coulomb, $\hat{J}$, and exchange term, $\hat{K}$, in HF by Hollman et al[56]
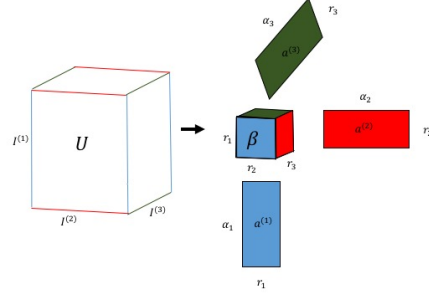
3.3 Direct Tensor Decomposition methods

Matrix decomposition methods are straightforward and refer to the transformation to some canonical matrix product representation. The extensions of decompositions to higher order tensors is not simple. The rank of a tensor is defined as the smallest number of rank one tensors that generate the tensor as its sum, where a rank one tensor is defined as

$$X = a^{(1)} \otimes a^{(2)} \otimes \cdots \otimes a^{(N)} \tag{67}$$

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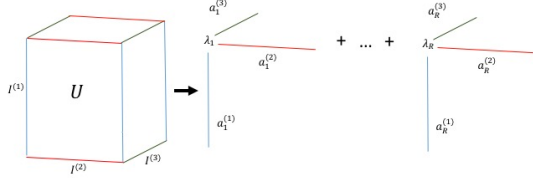
Figure 2: Representation of CP format   **Figure 3:** Representation of Tucker format

where

$$X \in \mathbb{R}^{I_1 I_2 \ldots I_N}$$

$$a^{(1)} \in \mathbb{R}^{I_1}, \quad a^{(2)} \in \mathbb{R}^{I_2}, \quad \ldots, \quad a^{(N)} \in \mathbb{R}^{(N)}$$

(68)

and a rank R tensor, U, can be defined in either the canonical format (CP)

$$U = \sum_{r=1}^{R} \lambda_r a_r^{(1)} \otimes a_r^{(2)} \otimes \cdots \otimes a_r^{(N)} \quad \lambda_r \in \mathbb{R}$$

(69)

where λ is the normalization of the normalized vectors $a_i^{(l)}$ and one can then define a factor matrix as

$$A^{(l)} = [a_1^{(l)}, \ldots a_r^{(l)}] \quad l \in \{1, 2, \ldots, N\}$$

(70)

such that

$$A \in \mathbb{R}^{I_l R}$$

(71)

Or U can be defined in the Tucker format (also referred to as the higher order singular value decomposition, HOSVD), where each factor matrix is not required to have the same rank, R,

$$U = \sum_{\alpha_1}^{r_1} \cdots \sum_{\alpha_N}^{r_N} \beta_{\alpha_1 \ldots \alpha_N} a_{\alpha_1}^{(1)} \otimes \cdots \otimes a_{\alpha_N}^{(N)}$$

(72)

where $\{a_{\alpha_i}^{(l)}\}$ is a set of R_l orthonormal vectors and $\beta \in \mathbb{R}^{r_1, r_2, \ldots r_n}$ is the Tucker core tensor. Figure's 2 and 3 depict diagrammatically the CP and Tucker format

Unlike matrix decompositions, there are no concise method to calculate the rank of a tensor, solving the rank is an NP hard problem.[57] Though there are many schemes which can solve for

the approximate rank of a tensor, T, by iteratively minimizing a series of non-linear equations[35]

$$\|T - U\| < \varepsilon \tag{73}$$

where $\mathscr{U}$ is defined using canonical or Tucker format.

Historically, the Tucker decomposition is linked to complete active-space self-consistent field (CASSCF) method,[58] where the decomposition of excitation amplitudes yields optimized orbitals and the CP decomposition can be linked to full CI[59] (FCI) where methods such as perfect pairing approach can be considered rank one tensor approximations to the FCI tensor. Applications of the CP decomposition to FCI recently resurfaced.[60,61] Today, there is an effort to make use of the tensor element sparsity that naturally occurs as dimension increases to decompose tensors in canonical ab initio methods. In work presented by Benedikt et al,[62–65] post-HF operator and amplitude tensors are decomposed to compute MP2 and CCD using CP format for example

$$(\mu\nu|\rho\sigma) = \sum_r^R \chi_r^{(\mu)} \otimes \chi_r^{(\nu)} \otimes \chi_r^{(\rho)} \otimes \chi_r^{(\sigma)} \tag{74}$$

Using this form the authors developed equations to preserve decomposed form and rank. These methods allow for reduced complexity in storage with out significant trade-off in accuracy. In this form efforts to compute a single index contraction between two tensors of order d and f with dimension of each order N decomposed to rank R_1 and R_2 are reduced from scaling as $\mathscr{O}(N^{d+f-1})$ to $\mathscr{O}(N \cdot R_1 * R_2)$. Unfortunately, finding the optimal rank and CP decomposition of tensors, such as the TEI, is non-trivial and costly and tensor contractions increases storage requirements, though it is possible to perform decompositions to reduce the contracted tensor rank. Therefore, implementation of CP decomposed post-HF methods are not yet desirable. Efforts to implement a fast tensor compression algorithm to reduce the effort of computing the CP decomposition will be discussed in the research sections.

In work presented by Bell et al[59] truncated HOSVD is employed to decompose the MP2 method T_2 amplitude expression,

$$T_2(i,a,j,b) = \frac{(ia|jb)}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \tag{75}$$

This author showed that HOSVD could reduce storage of T_2 amplitudes for MP2 energy recovery from 85 to 99%. Additionally, they showed that orbital active spaces obtained through the HOSVD coincide with physical intuition based on how the tensor is unfolded, in the first step of the HOSVD algorithm. Though the HOSVD does have some downsides, first HOSVD alone does not provide an optimal basis in terms of energy recovery it must therefore be coupled with other tensor decompositions and the algorithm to compute the HOSVD scales asymptotically as $\mathscr{O}(N^5)$.[59]

3.4 Tensor Hypercontraction

Tensor Hypercontraction (THC) was introduced in 2012 by Hohenstein, Parrish and Martinez.[66] THC can be though of as a tensors decompositions applied to a DF decomposition, though in practice a CD or DF is not required. The THC for the TEI for example can be formulated a number of ways. As an example a TCH on a general four index tensor (FIT) will be derived. THC's goal is to recompose the FIT as a connected product of matrices

$$V_{pqrs} \approx W_{p,\alpha} W_{q,\alpha} X_{\alpha\beta} W_{\beta,r} W_{\beta,s} \tag{76}$$

First the step is to rewrite the FIT as a two index tensor

$$V_{pqrs} = V_{pq,rs} \tag{77}$$

Then using an SVD one can express the two index tensor as

$$V_{pq,rs} = U_{pq,\lambda} S_{\lambda,\lambda} V_{\lambda,rs}^T \tag{78}$$

where λ is the rank of the decomposition, U and V^T are unitary matrices and S is the singular value matrix. Here one may choose to use a truncated SVD or CD or DF. The singular values are then rerepresented as $S = S^{1/2} S^{1/2}$ and multiplied into the left and right singular vectors.

$$V_{pq,rs} = \tilde{U}_{pq,\lambda} \tilde{V}_{\lambda,rs}^T \tag{79}$$

If one uses the CD or DF, a matrix roots of the overlap, $J^{1/2}$ of $J_{\lambda,\lambda}$ must be found to using an eigenvalue decomposition or SVD. Next, a CP decomposition is performed on the three index tensors $\tilde{U}$ and $\tilde{V}$

$$\tilde{U}_{pq,\lambda} = W_{p,\alpha}W_{q,\alpha}W_{\alpha,\lambda}$$
$$\tilde{V}^T_{\lambda,rs} = W_{\lambda,\beta}W_{\beta,r}W_{\beta,s}$$

(80)

where α and β are the rank of the CP decomposition. So far only applications where $\alpha = \beta$ have been studied. Finally the terms $W_{\alpha,\lambda}$ and $W_{\lambda,\beta}$ are contracted and one finds

$$V_{pqrs} = W_{p,\alpha}W_{q,\alpha}X_{\alpha,\beta}W_{\beta,r}W_{\beta,s}$$

(81)

where

$$X_{\alpha,\beta} = W_{\alpha,\lambda}W\lambda,\beta$$

(82)

THC has been used in the field to represent the electron interaction potentials in CC2 methods and to decompose the TEI used to calculate CCSD and FCI energies. In work presented by Hummel et al[67] using THC the scaling of distinguishable CCD or linearlized CCSD from $\mathcal{O}(N^6)$ to $\mathcal{O}(N^5)$ and in work presented by Schutski et al[66] using THC scaling of CCSD was reduced to $\mathcal{O}(N^4)$. Schutski also presents a direct THC method which allows TEI decomposition to scale as $\mathcal{O}(N^5)$ using the SVD or $\mathcal{O}(N^4)$ using a DF scheme while preserving accuracy of ~.5 millihartree .

3.5   Orbital localization methods

A non-obvious method to reduce the complexity of tensors is to define new more compact occupied and unoccupied orbital sets, such is the basis for the projected atomic orbitals (PAO), pair natural orbitals(PNO) and orbital specific virtual (OSV) methods. Conveniently, unitary transformations of the molecular orbital space which do not mix occupied and unoccupied orbitals commute with all observable operators[2] and these transformations can be used in orbital localization correlation (LC) methods. There are many developed orbital localization schemes such as Boys and Pipek-Mezey[68] among others which are utilized by PNO, PAO and OSV methods. In all the following methods MO are optimized using HF, though other optimizations

are possible. Localized occupied MO's (OMO) will be denoted i,j,k and canonical unoccupied MOs (UMO) will be denoted a,b,c, non-canonical UMO's will be denoted r,s,t. All the following methods start by localizing the set of canonical OMO's. Below is a formula to generate a new occupied electron pair specific UMO's

$$|r^{ij}\rangle = \sum_a |a\rangle R^{ij}_{ar} \tag{83}$$

where R^{ij}_{ar} is a pair specific transformation matrix. Using this occupied electron pair specific UMO one can transform the T_1 and T_2 amplitudes

$$t^i_a = \sum_{r \in [ii]} R^{ij}_{ar} t^i_r \tag{84}$$

$$t^{ij}_{ab} = \sum_{r \in [ij]} R^{ij}_{ar} t^{ij}_{rs} R^{ij}_{bs} \tag{85}$$

In this format, correlation amplitudes and residual equations can be redefined and if possible reduced using domain approximations based on occupied electron pair distances.[69] The PAO method works by projecting AO basis functions against the UMO's[70]

$$|r\rangle = \sum_a |a\rangle R_{ar} \tag{86}$$

where

$$R_{ar} = \langle a|\phi_r\rangle \tag{87}$$

This type of localization ensures the unoccupied space be orthogonal to the occupied space, but vectors in the unoccupied space are not orthogonal. PAO implementation has large impact in its implementation in CCSD(T), equation of motion CCSD, and more recently R12 methods by Werner et al.[71] The number of PAOs to obtain accurate recovery of correlation energy (>99%) grows linearly with size of the basis set per atom and domain sizes are asymptotically independent of molecule size.

In PNO methods R_{ar}^{ij} is defined by diagonalizing the MP2-like density matrix[69,72]

$$D^{ij} = \frac{1}{1 + \delta_{ij}} (\tilde{T}^{ij} T^{ij} + \tilde{T}^{ij} T^{ij\dagger}) \tag{88}$$

where

$$T_{ab}^{ij} = \frac{\langle ij|ab \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \tag{89}$$

$$\tilde{T}_{ab}^{ij} = 2T_{ab}^{ij} - T_{ab}^{ji} \tag{90}$$

such that

$$D^{ij} R_r^{ij} = n_r^{ij} R_r^{ij} \tag{91}$$

where n^{ij} is the natural occupation number. Thus PNOs can be expanded in the basis of UMO or vice versa as

$$|r^{ij}\rangle = \sum_a R_{ar}^{ij} |a\rangle \tag{92}$$

$$|a\rangle = \sum_r \bar{R}_{ar}^{ij} |r^{ij}\rangle \tag{93}$$

PNOs for a given pair are orthogonal but PNOs between pairs are non-orthogonal. One can truncate the full set of PNOs using the occupation number as a threshold; it has been found that 30 to 40 PNOs per electron pair can recover 99.9% of canonical correlation energy for a triple-ζ basis set. Unfortunately the number of PNOs scales with the number of pairs so the total number of PNOs might still be too large. To compensate one can also truncate the set of [ij] pairs based on a pair MP2 energy threshold. The PNO methods formal scaling is $\mathscr{O}(N^5)$ though the approximations described above among others have allowed for the development of near linear scaling PNOs in CCSD[71]

More recently Yang et al[73] has combined the ideas of pair independent PAOs and pair specific PNOs and proposed an OSV method. In this method R_{ar}^{ij} is found by SVD of the diagonal MP2 pair amplitudes.

$$[R^{i\dagger} T^{ij} R^i]_{rs} = t_r^{ii} \delta rs \tag{94}$$

$$|r^i\rangle = \sum_a |a\rangle Q_a^i r \tag{95}$$

Like PNOs, OSVs of a single OMO are orthogonal but OSVs of different OMO's are non-orthogonal. It has been shown that typically 100 OSVs are required to recover 99.8% of correlation energy, requiring fewer orbitals than both PNO and OSV methods. Construction of OSVs scales as $\mathscr{O}(N^4)$

4 Research Plan

It is apparent from the literature that operators and amplitude expressions in quantum chemistry have some compact format that can be taken advantage of as the dimension of a system increases, ie number of electrons. It is the goal for this research to apply tensor decomposition algorithms, which make use of modern computational architecture, to reduce scaling of correlation methods based on MBPT, CC, and CC-R12 methods. THC is quantum chemistries first step into utilizing the structure of tensor decompositions to reduce storage requirements without arbitrary truncation based on practiced thresholds.CP and Tucker decompositions encode the behavior of every element in a given tensor into a set of vectors with reduced dimension. While truncation methods based on an eigenvalue, occupation number, or diagonal MP2 amplitudes discard information deemed unnecessary. Implementing tensor decompositions, instead of these truncation methods, to reduce storage requirements will allow for data compression without significantly loss of information. Figure 4 and 5, below, show how memory requirements of canonical tensors in quantum chemistry, such as the TEIs, can be significantly reduced with little cost in accuracy. Tensor decompositions will allow for method development in reduced scaling accurate molecular property investigation, where truncation based approaches can significant influence a property's value.

In order to reduce the computational demands of computing the CP decomposition modern mathematics turns to tensor compression. Tensor compression reduces computational bottleneck of large tensor using smaller proxy tensors, which are then used to approximately the CP decomposition. Original methods to compute a tensor compression used the Tucker decomposition.[74,75] However, this approach requires the computation of an expensive singular value decomposition on each mode of a tensor. More recently, mathematicians have found that
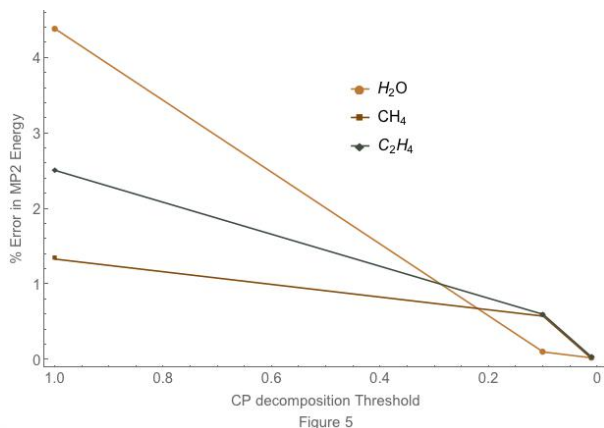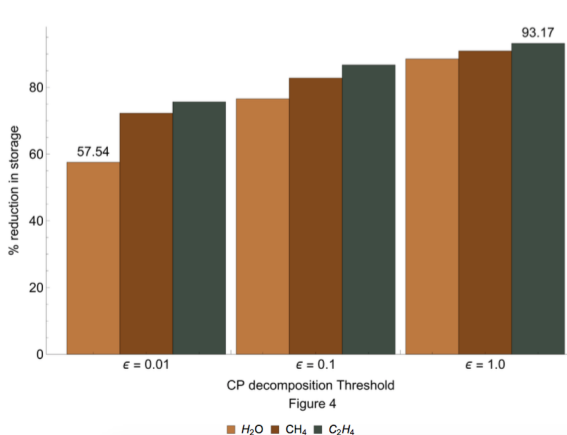
Figure 4: Reduced storage requirements of TEI after CP decomposition
Figure 5: MP2 energy calculated using methods presented by Benedikt et al [62] compared to canonical spin restricted MP2 calculations. Following Benedikt's implementation the HF orbital energy denominator term was decomposed to a CP threshold of $\varepsilon = .01$; Calculations on H_2O and CH_4 were performed using a 6-31G* basis and calculations on C_2H_4 used a 6-31G basis

randomized tensor compression methods can achieve significant computational savings while producing near-optimal approximation quality.[76] Application of these compression methods, to tensors which are too either large to store in fast memory or are slow to converge to their optimal rank, will allow for reduced scale tensor algebra methods to be more reasonably applied to single reference quantum chemistry.

Generally tools in computational chemistry limit the application of methods such as CCSD(T) or CCSD-RI because computational scaling and storage requirements are unmanageably high. These methods do not have a simple prescription to reorder indices's of higher order tensors to apply matrix decomposition. Though, tensor decomposition methods to compress higher order amplitude expressions has not yet been explored by quantum chemistry. An interesting example is the application of CP decomposition to the CADF work presented by Hollman et al.[56] Application of CP decompositions to CADF will decouple electronic indices's from electronic density terms allowing one to calculate more simply HF exchange terms

In work originally presented by Almöf[77] and later Häser Haser1992 it has been shown that the integral transform step of MP2 eq. (31) using a Laplace transform of the denominator term

$$D_{ijab} = \frac{1}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} = \int e^{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)t} dt \tag{96}$$

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from there the exponential term can be factored into the AO wavefuntion

$$|\phi_i\rangle = |\phi_i\rangle e^{-\varepsilon_i t/2} \tag{97}$$

$$|\phi_a\rangle = |\phi_a\rangle e^{\varepsilon_a t/2} \tag{98}$$

Computationally the integral in eq. (96) can be transformed to a finite sum

$$E_{MP2} = \sum_{\alpha}^{\tau} w_\alpha e_2^\alpha \tag{99}$$

e_2^α is the weighted integral form of eq. (31) based on the difference in energy between ε_i or ε_a and ε_F the fermi level. These integrals can be in AO basis or any non-canonical form. Using tensor decomposition methods one can optimize the weighting coefficients and calculate more accurate quadrature points. Laplace transform methods coupled with multiple applications of tensor decompositions to perturbation theories such as CCSD(T) and CCSD(T)-R12, could provide interesting in reducing the storage and computational cost scaling of these calculations

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