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

Student's Name	**Karl Pierce**
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Student's Email Address	Kmp5@vt.edu
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☐	**Outline**. Submit to the Research Director only by September 1^{st}. 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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Function	Name	Department	Email
Chair	Edward Valeev	CHEM	valeev76@vt.edu
Co-Chair (if you have one)			
Member	T. Daniel Crawford	CHEM	crawdad@vt.edu
Member	Nicholas Mayhall	CHEM	nmayhall@vt.edu
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1 Introduction

The goal of theoretical chemistry is to further develop mathematics and computational algorithms to predict the accurate properties of chemical systems using the quantum mechanical nature of electrons. Achieving this goal will push computational analysis to the forefront of investigative research in chemistry reducing the time required to find a chemical for a specific application. To successfully predict properties of chemicals and reactions, accuracy to an extremely small degree is required in computational chemistry[1] To model chemical systems, physics casts them into a many-body integro-differential equation known as the many-body Schrödinger equation. This equation, in its raw form, is much too difficult to solve analytically. Therefore, it is the task of theoretical chemistry is to provide an approximate framework which preserves the physical nature and accuracy of the exact model. There exists a number of methods applicable to different systems depending on the user's interest to balance computational effort and time, accuracy, and chemical system size.

The gold standard in computational chemistry are the coupled cluster methods which are typically used to calculate ground state calculations but require the most computational resources and time. Hartree-Fock and its perturbation based extensions such as Moller-Plesset methods can recover some electron correlation and can be extended to molecules with around 100 atoms. Other methods such as density functional theory and semi-empirical methods based on classical mechanics can solve even larger molecules though their accuracy can be poor.

Computational analysis using any one of these methods requires the storage and computation of many index vectors known as tensors. Tensor storage, manipulation and contraction make up the majority of the bottleneck in the calculation of ab initio quantum chemistry. In the world of mathematics this is known as the curse of dimensionality. Though it also known that as dimensionality of tensor storage increases so does sparsity in the full representation of such tensors. Quantum chemistry has developed methods in order to take advantage of the underlying structure of these tensors, such as projected atomic orbitals, pair natural orbitals and density fitting. In general these methods reduce computational effort by arbitrarily reducing dimension using some canonical matrix decomposition. The area of utilizing tensor decomposition in the realm of these physical approximations is sparsely investigated with only the recent introduction of tensor hypercontraction. Using fast tensor decomposition of physical variables over modern computational architectures can provide data compression without loss of information. Additionally, as theoretical chemistry pushes to calculate systems to analytical levels of accuracy, such as introduction of explicitly correlated methods, algorithms with extremely large computational scaling factors have developed. Utilizing the form of tensor decompositions new algorithms can be developed which reduce exponential scaling factors by separating subspaces spanned in the tensor space.

2 Ab Initio Many Body Quantum Mechanics

The first task of quantum chemistry is to formulate mathematics that can describe molecular systems through the physics of non-relativistic electrons and nuclei. This is accomplished through Hamiltonian mechanics acting on a set of functions, a basis, dubbed the Schrödinger equation(SE).

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

The time-independent SE the full Hamiltonian is formed in the lens of electrostatic interactions of electrons and nuclei. This formulation brings about the first approximation in quantum mechanics, the Born-Oppenheimer approximation.[2] Because of the difference in mass between nuclei and electrons, there is a disparity in their relative motion. Thus one can decide to gauge the full problem in the realm of either a fixed nuclear field with point charge electron coordinates or an average field of electronic charge with nuclei embedded within. To be consistent with the mathematic formulation of electronic structure theory this paper will only consider the problem of explicit electrons coordinate systems with fixed nuclear position. The approximation allows one to neglect the kinetic energy of nuclei and consider nuclear-nuclear repulsion as a constant. What is left is the N-body electronic Hamiltonian

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

The first term in this expression is the kinetic energy operator applied to N electrons, the second is the potential energy operator between electron-nuclei pairs and the final term is the potential energy operator of electron-electron pairs. This Hamiltonian can be used to solve the electronic Scrödinger equation

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

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 multi variable partial differential SE defined above 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

Though it may not be possible to analytically solve the SE for an arbitrary number of electrons, it is able to exactly solve the differential for one electron. The idea of solving the SE in a basis of N-tuple single electron functions is the fundamental basis for an approximate solution, known as Hartree-Fock (HF) theory.[2–4] This approximation implies that one can express the electronic wavefunction, Ψ_{elec}, as an antisymmetric product of one electron functions, molecular orbitals (MO), that depend on the coordinate, $x = \{\vec{r}, \omega\}$, which contains spacial, $\vec{r}$, and spin, ω, coordinates. Formally the antisymmetric wavefunction is constructed using a Slater determinant[5,6]

$$\Psi_0(x_1, x_2, ..., x_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \dots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \dots & \chi_k(x_2) \\ \vdots & \vdots & \vdots & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \dots & \chi_k(x_N) \end{vmatrix} \tag{5}$$

This mathematical formalism introduces exchange correlation to electrons characterized by the same spin variable. Though electrons of opposite spin are a simple uncorrelated product of one another.

The best approximate solution can be found by variationally minimizing the Rayleigh quotient

$$E_0 = \frac{\langle \Psi_0 | \hat{H}_{elec} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} \tag{6}$$

held to the constraint that

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

and where the bracket notation implies the Hilbert space inner product. The inner product $\langle \Psi_o | \hat{H}_{elec} | \Psi_0 \rangle$ is a set of eigenvalue integro-differential equation over all space, the HF equations, with each element defined as

$$\hat{f}\chi_i = \varepsilon_i \chi_i \tag{8}$$

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

$$\hat{f}(x_1) = \hat{h}_i(x_1) + \sum_{j \neq i}^{N} \hat{J}_j(x_1) - \hat{K}_j(x_1) \tag{9}$$

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

$$\hat{h}(x_1) = -\frac{1}{2}\nabla_1^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{1A}} \tag{10}$$

The last two terms in eq. (9) represent the potential energy of the electron-electrons interaction. $\hat{J}_j$ represents the Coulombic repulsion between two electrons

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

$\hat{K}_j$, the exchange term, does not have a classical representation as the previous terms do and is direct product of the antisymmetric nature of the single determinant wavefunction

$$\hat{K}_j(x_1) = \int \chi_j^*(x_2)\frac{1}{r_{ij}}\chi_i(x_2)dx_2 \tag{12}$$

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. (8), 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.

The solutions of the Hydrogen atom define one electron orbital functions, $\{\chi_k\}$, exactly as Slater type orbitals. Unfortunately, numerical differentiation, integration and 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

$$\chi_i = \sum_{\mu}^{M} C_{i\mu}\phi_\mu(x) \tag{13}$$

where ϕ_μ are typically atom centered functions. Applying eq. (13) to eq. (8) produces what is known as the Hartree-Fock-Roothaan matrix equation[7,8]

$$\mathbf{FC} = \mathbf{SC}\varepsilon \tag{14}$$

C is the transformation matrix from eq. (13), **S** is the overlap of two AO's

$$S_{\mu\nu} = \int \phi_\mu^*(x_1)\phi_\nu(x_1)dx_1 \tag{15}$$

and elements of the Fock matrix, **F**, are

$$F_{\mu\nu} = \int \phi_\mu(x_1)\hat{f}(x_1)\phi_\nu(x_1) \tag{16}$$

The Fock matrix terms can also be expanded with respect to the operators defined in eqs. (10)–(12):

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{occ}\sum_{\rho\sigma} C_{\rho i}C_{\sigma i}\langle\mu\rho||\nu\sigma\rangle \tag{17}$$

where

$$\langle \mu\rho || \nu\sigma \rangle = \langle \mu\rho | \nu\sigma \rangle - \langle \mu\rho | \sigma\nu \rangle \tag{18}$$

is the antisymmetrized difference of the coulomb and exchange terms with

$$\langle \mu\rho | \nu\sigma \rangle = (\mu\nu | \rho\sigma) = \int\int \phi_\mu^*(x_1)\phi_\rho^*(x_2)\frac{1}{r_{12}}\phi_\nu(x_1)\phi_\sigma(x_2)dx_1dx_2 \tag{19}$$

in physicist and chemist notation, respectively. Roothaan's equation eq. (14) 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. Computationally evaluation of the Fock matrix is the most expensive step of HF with asymptotic scaling of $\mathscr{O}(N^4)$ or $\mathscr{O}(N^2(lnN)^2)$ for large systems where N is the number of electrons and a storage requirement of $\mathscr{O}(N^4)$.

2.2 Electronic Correlation Methods

Correlation is a concept of probability. Two variables are considered independent if the joint probability of the variables is a product of each variables probability; $p(x,y) = p(x) \times p(y)$ where $p(\cdot)$ is a probability function. Otherwise, the two variables are said to be correlated.[9] Electron correlation develops from properties of fermions and Coulombic repulsion between electronic charges. HF does cannot recover electron correlation beyond the fermionic description. The wavefunction in HF theory relies on the independent particle model, by definition this is an uncorrelated description as it does not consider electron-electron repulsion explicitly but as field effect. Correlation energy, as defined by Löwdin,[10] is

$$E_{corr} = \mathscr{E}_0 - E_{HF} \tag{20}$$

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 think of E_{corr} as an observable of some quantum mechanical operator acting on wavefunction with the form:

$$\Psi_{exact} = \Psi_{HF} + \Psi_{corr} \tag{21}$$

where Ψ_{corr} is orthogonal to Ψ_{HF} and encapsulates all correlation not captured by HF.[11] Though correlation energy only contributes a very small portion to the total energy, these corrections are extremely necessary in the accurate calculation of molecular properties and prediction of reactions. Outlined to follow are a methods that allow theoretical chemistry to systematically calculate correlation energy.

2.2.1 Many Body Perturbation Theory

Many Body Perturbation Theory (MBPT) was first developed in 1957[12] to study the energy of nuclear matter. Not until 1968 was the it applied to ab initio quantum chemistry.[13,14] Though there are many formulations of MBPT, two of the most well known being Rayleigh-Schrödinger[15] and Moller-Plesset,[16,17] all methods are developed from the same principles. 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.

$$E_{r=\infty}(AB) = E(A) + E(B) \tag{22}$$

Starting with an eigenvalue problem

$$\hat{H}|\Phi\rangle = E|\Phi\rangle \tag{23}$$

one can expand the eigenvalue operator

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)} \tag{24}$$

$\hat{H}^{(0)}$, 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. One can then expand the wavefunction and energy

$$|\Phi\rangle = |\Phi^{(0)}\rangle + \lambda|\Phi^{(1)}\rangle + \lambda^2|\Phi^{(2)}\rangle + \dots \tag{25}$$

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots \tag{26}$$

Applying these expansions to eq. (23) and accumulating terms of a single order, λ^n, one finds

$$\hat{H}^{(0)}|\Phi^{(n)}\rangle + \hat{H}^{(1)}|\Phi^{(n-1)}\rangle = \sum_{i=0}^{n} E^{(i)}|\Phi^{(n-i)}\rangle \tag{27}$$

MPn theory assumes

$$\hat{H}^{(0)} = \sum_{i=1}^{N} \hat{f}(i) = \sum_{i=1}^{N} \hat{h}(i) + \hat{J}(i) - \hat{K}(i) \tag{28}$$

and defines the first order correction as

$$\hat{H}^{(1)} = \hat{H}_{elec} - \hat{H}^{(0)} = \sum_{i<j} \frac{1}{r_{ij}} - \sum_{i} (\hat{J}(i) - \hat{K}(i)) \tag{29}$$

MPn theory typically focuses on solving second order correction, MP2; first order corrections are zero by Brillouin theorem.[18] Substituting eqs. (28) and (29) into eq. (27) one finds

$$\langle\Phi^{(0)}|\hat{H}^{(0)}|\Phi^{(0)}\rangle = \sum_{i=1}^{N} \varepsilon_i = E^{(0)} \tag{30}$$

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

$$\langle\Phi^{(0)}|\hat{H}^{(1)}|\Phi^{(1)}\rangle = \langle\Phi^{(0)}|(\hat{H}_{elec} - \hat{H}^{(0)})|\Phi^{(1)}\rangle = E^{(2)} \tag{31}$$

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 $|\Psi_{abc\dots}^{ijk\dots}\rangle$ 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

$$|\Phi^{(1)}\rangle = \frac{1}{4}\sum_{ijab} t_{ab}^{ij}|\Psi_{ab}^{ij}\rangle \tag{32}$$

projecting eq. (32) onto the first order energy equation, one can find the coefficient t_{ab}^{ij} then solve the second order energy equation

$$E^{(2)} = \frac{1}{4}\sum_{ijab} \frac{\langle ij||ab\rangle}{\varepsilon(i)+\varepsilon(j)-\varepsilon(a)-\varepsilon(b)} \tag{33}$$

The term $\langle ij||ab\rangle$ from eq. (19) has been transformed by

$$\langle ij||ab\rangle = \sum_{\mu\nu\rho\sigma} C_{\mu i}C_{\nu j}C_{\rho a}C_{\sigma b}\langle \mu\nu||\rho\sigma\rangle \tag{34}$$

This transformation is the most computationally rigorous step of MP2 scaling as $\mathscr{O}(N^5)$ with a storage requirement of $\mathscr{O}(N^4)$. Efforts to eliminate the transformation using the Laplace transformation (LT) 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.[1,2] CI methods diagonalize the N-electron hamiltonian in terms of Ψ_{exact}. This can be achieved by expanding Ψ_{corr} as a linear combination of all possible N-tuply excited slater determinants

$$|\Psi_{exact}\rangle = C_0|\Psi_0\rangle + \sum_{ia} C_a^i|\Psi_a^i\rangle + \sum_{\substack{i<j\\a<b}} C_{ab}^{ij}|\Psi_{ab}^{ij}\rangle + \sum_{\substack{i<j<k\\a<b<c}} C_{abc}^{ijk}|\Psi_{abc}^{ijk}\rangle + \dots \tag{35}$$

In an infinite basis this expansion provides an equality to Ψ_{exact}. Though, 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 determinants in the exact wavefunction expansion. The exact wavefunction is not normalized though it does have intermediate normalization[2] defined as

$$\langle\Psi_0|\Psi_{exact}\rangle = 1 \tag{36}$$

Applying SE and substituting eq. (20), one finds

$$(\hat{H}_{elec} - E_{HF})|\Psi_{exact}\rangle = (\mathscr{E}_0 - E_{HF})|\Psi_{exact}\rangle = E_{corr}|\Psi_{exact}\rangle \tag{37}$$

Using intermediate normalization one can project eq. (37) by the HF reference wavefunction and find

$$\langle\Psi_0|(\hat{H}_{elec} - E_{HF})|\Psi_{exact}\rangle = E_{corr}\langle\Psi_0|\Psi_{exact}\rangle = E_{corr} \tag{38}$$

then substituting eq. (35) one finds

$$\langle\Psi_0|(\hat{H}_{elec} - E_{HF})|\Psi_{exact}\rangle = \langle\Psi_0|(\hat{H}_{elec} - E_{HF})|\Psi_0\rangle + \sum_{\substack{i<j\\a<b}} C_{ab}^{ij}\langle\Psi_0|\hat{H}_{elec}|\Psi_{ab}^{ij}\rangle + \dots \tag{39}$$

by Slater-Condon rules one finds

$$\sum_{\substack{i<j\\a<b}} C_{ab}^{ij}\langle\Psi_0|(\hat{H}_{elec})|\Psi_{ab}^{ij}\rangle = E_{corr} \tag{40}$$

To resolve C_{ab}^{ij} it is necessary to project excited determinants onto eq. (37)

$$\begin{aligned}\langle\Psi_{ab}^{ij}|(\hat{H}_{elec} - E_{HF})|\Psi_{exact}\rangle = \langle\Psi_{ab}^{ij}|(\hat{H}_{elec})|\Psi_0\rangle + \sum_{\substack{k\\c}} C_c^k\langle\Psi_{ab}^{ij}|(\hat{H}_{elec})|\Psi_c^k\rangle \\ + \sum_{\substack{k<l\\c<d}} C_{cd}^{kl}\langle\Psi_{cd}^{kl}|(\hat{H}_{elec} - E_{HF})|\Psi_{ab}^{ij}\rangle + \dots \\ = C_{ab}^{ij}E_{corr}\end{aligned} \tag{41}$$

eq. (41) exemplifies how solving the CI energy equation requires one to iteratively 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 $\mathscr{O}(N^6)$ and storage requirement of $\mathscr{O}(N^4)$. Any truncation to the full-CI method eliminates the size-consistency of CI methods. Additionally, truncated CI is not size-extensive, meaning the energy calculated by truncated CI methods do not scale linearly with number of electrons, N; CI is variational.

2.2.3 Coupled Cluster Thoery

Since its development in the 1960's by Čív̌ek and Paldus [19–21] Coupled Cluster (CC) theory has become the most reliable method used for accurate approximations of atomic and molecular properties. [22] The foundation of CC theory is based on exponential expression of the wavefunction

$$|\Psi_{exact}\rangle = e^{\hat{T}}|\Phi\rangle \tag{42}$$

A power series expansion of the expression provides the following equation

$$e^{\hat{T}}|\Phi\rangle = (1+\hat{T}+\frac{1}{2!}\hat{T}^2+\frac{1}{3!}\hat{T}^3+...)|\Phi\rangle \tag{43}$$

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

$$\hat{T} = \hat{T}_1+\hat{T}_2+\hat{T}_3+...+\hat{T}_N \tag{44}$$

the nth order cluster operator has the form

$$\hat{T}_n = \left(\frac{1}{n!}\right)^2 \sum_{ij...,ab...}^{n} t_{ij...}^{ab...} a_a^\dagger a_b^\dagger \dots a_j a_i \tag{45}$$

where a_i and $a_a^\dagger$ are the 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_I. [22,23] By including all cluster operators in the expression of $\hat{T}$ one can form the exact wavefunction, though the number of terms and the computational scaling factor becomes quickly unmanageable. To deal with this problem the cluster operator, $\hat{T}$ is truncated. The derivation to follow will restrict the problem to the single and double cluster operators (CCSD)

$$\hat{T} = \hat{T}_1 + \hat{T}_2 \tag{46}$$

Therefore one defines

$$|\Psi_{CC}\rangle = e^{\hat{T}}|\Psi_0\rangle \tag{47}$$

with intermediate normalization, $\langle\Psi_0|\Psi_{CC}\rangle = 1$. Left projecting the SE by $e^{-\hat{T}}$ allows one to simplify the energy expression using the Cambell-Baker-Hausdorff formula[22] and find

$$E_{CC} = \langle\Psi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Psi_0\rangle \tag{48}$$

$$0 = \langle\Psi_i^a|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Psi_0\rangle \tag{49}$$

$$0 = \langle\Psi_{ij}^{ab}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Psi_0\rangle \tag{50}$$

where

$$E_{CC} = E_0 + E_{corr} \tag{51}$$

eqs. (49) and (50) 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 $\mathscr{O}(N^8)$[24,25] 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.[22] This approach scales as $\mathscr{O}(N^7)$ and is considered quantum chemistries gold standard.

2.3 Explicitly Correlated Methods

Within quantum chemistries most accurate approximations one finds the largest contribution to error is the basis set error. In the wavefunction framework established above basis set error contributions have very slow convergence and fails to fully recreate the electron cusp condition thus requiring large basis sets. To exemplify, HF theory considers an average electronic field, correlated electrons probability is constant no matter the position of one relative to another. In truth electron-electron probability is a function of distance and angle in some sphere, see figure 1.Corrections to HF theory are known as Coulombic correlation.

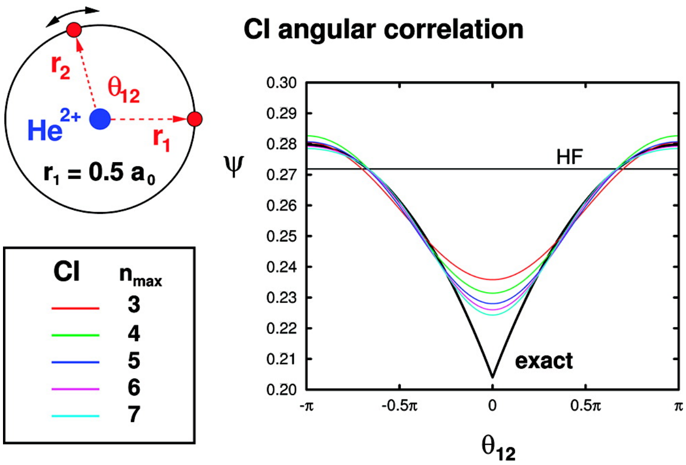

Figure 1: Electron-electron cusp condition for a Heliums ground state wavefunction with both electrons on the same circle of $.5a_0$ using a CI based wavefunction with increasing basis size with maximum principle quantum number, n_{max}.[26]

To accurately calculate Coulombic correlation energy it is necessary to generate a new wavefunction expression that is explicitly dependent on inter-electronic distances. Kato's cusp condition[27] comes from realizing there exists a first-order derivative discontinuity at the Coulombic type singularity[26] which leads to the coalescence condition

$$\left.\frac{\partial \Psi}{\partial r_{12}}\right|_{r_{12}=0} = -\frac{1}{2}\Psi(r_{12}=0) \tag{52}$$

One assumes the new form of the exact wavefunction is

$$\Psi_{exact}(r_1, r_2, \ldots) = \Phi(r_{12})\Psi(R_{12}) \tag{53}$$

Where $R_{12} \equiv \frac{r_1+r_2}{2}$ and $r_{12} \equiv r_1 - r_2$ and the form of Φr_{12} is chosen such that it satisfies the coalescence condition

$$\Phi(r_{12}) = R(r_{12})\Theta(\Omega_{12}) \tag{54}$$

The angular function, $\Theta(\Omega_{12})$, is represented by the spherical harmonics, Y_{lm}, and the radial function, $R(r_{12})$ is determined using approximate solutions to the two-electron radial SE

$$\left(-\frac{1}{2r_{12}^2}\frac{\partial}{\partial r_{12}}r_{12}^2\frac{\partial}{\partial r_{12}}+\frac{l(l+1)}{2r_{12}^2}+\frac{1}{r_{12}}+\mathscr{O}(r_{12}^0)\right)R(r_{12})=0 \tag{55}$$

Solving this differential with appropriate ansätz provides the approximate solution

$$\Psi(r_1,r_2,\dots)\approx r_{12}^l\sum_{m=-l}^{l}\left(1+\frac{r_{12}}{2(l+1)}+\mathscr{O}(r_{12}^2)\right)Y_{lm}(\Omega_{12})\Phi(R_{12},\dots) \tag{56}$$

Initial attempts to develop a wavefunction explicitly dependent on two electron coordinates by Hartree[3,28] and Hylleras[29] 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.[11] These more usable functions have allowed F12/R12 to develop as a computational tool. In the next sections I will discuss the use of F12/R12 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. (32) and the explicitly correlated geminal functions.

$$|\Psi_{MP2-R12}\rangle=|\Phi_{MP}^{(1)}\rangle+\sum_{\substack{i<j\\x<y}}t_{xy}^{ij}|\Psi_{xy}^{ij}\rangle \tag{57}$$

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

$$|\Psi_{xy}^{ij}\rangle=\frac{1}{2}\bar{R}_{xy}^{\alpha\beta}\tilde{a}_{ij}^{\alpha\beta}|\Psi_0\rangle \tag{58}$$

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:

$$R_{xy}^{\alpha\beta}=\langle\alpha\beta|\hat{Q}_{12}f(r_{12})|xy\rangle \tag{59}$$

The most common choice for $\hat{Q}_{12}$, proposed by Valeev[30]

$$\hat{Q}_{12} = (1-\hat{O}_1)(1-\hat{O}_2) - \hat{V}_1\hat{V}_2 \tag{60}$$

Other choices have also been considered.[31,32]

Doubly excited coefficients, t, can be resolved by minimizing a Hylleraas functional of the MP2 energy

$$H^{(2)}(\Phi^{(1)}) = \langle\Phi^{(1)}|\hat{H}_0 - E_0|\Phi^{(1)}\rangle + 2\langle\Phi^{(1)}|\hat{H}|\Phi^{(0)}\rangle \tag{61}$$

using a modified one-step inversion of the zeroth Hamiltonian. After solving for these coefficients $E_{\text{MP2-R21}}$ is

$$E_{\text{MP2-R12}} = \langle\Phi^{(0)}|\hat{H}^{(1)}|\Phi^{1}\rangle = E^{(2)}_{MP2} + E^{(2)}_{R12} \tag{62}$$

The integrals of $E^{(2)}_{R12}$ can be solved analytically if the correlation factor, $f(r_{12})$, is Gaussian.[33] The terms in $E^{(2)}_{R12}$ do require approximations to calculated quickly and accurately such as Density fitting, discussed later.[11]

2.3.2 Explicitly Correlated CC R12 method

It is necessary to apply R12 methods to CC in order to achieve the theories full potential because MP2-R12 has limited chemical framework.[11] CC-R12 extends the standard CC cluster operator, $\hat{T}$, to include R12 geminal operator, $f(r_{12})$.[34,35] For example the CCSD-R12 wavefunction has the form

$$|\Psi_{exact}\rangle = e^{\hat{T}}|\Psi_0\rangle \tag{63}$$

Where $\hat{T}$ has the form

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{R} \tag{64}$$

The operators $\hat{T}_1$ and $\hat{T}_2$ are defined using equation (45) and $\hat{R}$ is defined as

$$\hat{R} = \frac{1}{(2!)^3} t^{xy}_{ij} \bar{R}^{\alpha\beta}_{xy} \tilde{a}^{ij}_{\alpha\beta} \tag{65}$$

where $\bar{R}^{\alpha\beta}_{xy}$ is the conjugate matrix element of the explicitly correlated factor defined in equation (59). 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 $\tilde{\gamma}^{xy}_{ij}$

$$|\Psi^{xy}_{ij}\rangle \equiv \tilde{\gamma}^{xy}_{ij}|\Psi_0\rangle = \frac{1}{2!}\bar{R}^{\alpha\beta}_{xy}\tilde{a}^{ij}_{\alpha\beta} \tag{66}$$

This creates an additional projection term

$$\langle\Psi^{xy}_{ij}|e^{\hat{T}}\hat{H}e^{\hat{T}}|\Psi_0\rangle = 0 \tag{67}$$

Though this additional amplitude equation does have small store dimension, $\mathscr{O}(o^4)$ 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 $\mathscr{O}(N^6)$ with direct computation of an intermediate each iteration.[11]

3 Tensor Algebra Methods to Reduce Computational Complexity in Quantum Chemistry

A tensor is a multidimensional array; an N-th order tensor can considered as a outer 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.[36] Tensors are naturally applied 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, $t^{ij\ldots}_{ab\ldots}$, can be expressed as higher-order tensor whose order depends on the number of indices's. This extension therefore means as number of electrons increase, there is an exponential increase in the amount of storage and computational processing required to solve a given problem. This problem is referred to as the "curse of dimensionality" To overcome this curse requires one to discover the underlying structure in data to reduce storage requirements and to redesign algorithms to scale with the structure of the data.

The goal of a decomposition is to reduce the complexity of a tensor utilizing the underlying form of data in a tensor. 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, LU, and Jordan decomposition, have been around for quite some time. Though, interests to decompose higher order tensors didn't develop until 1927 with Hitchcock's idea of a tensor to be a polyadic sum of products[37,38] and later Cattells's idea of a multi-way model in 1944.[39,40] These ideas would later be used to develop canonical product(CP) (CANDECOMP/PARAFAC canonical decomposition / parallel factor decomposition)[41,42] and Tucker decompositions.[43] 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[44] 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.[45]

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

$$M_{\mu\nu,\gamma\sigma} = \int\int \rho_{\mu\nu}(r_1)\hat{M}(r_1,r_2)\rho_{\gamma\sigma}dr_1dr_2 \equiv (\rho_{\mu\nu}|\rho_{\gamma\sigma}) \tag{68}$$

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. With the goal of expressing

$$M = BB^T \tag{69}$$

This expression can be approximated to some decomposition threshold, γ, therefore elements of M can be expressed as

$$\begin{aligned} M_{\mu\nu,\gamma\sigma} \approx \sum_{p=1}^{P} B_{\mu\nu}^{P} B_{\gamma\sigma}^{P} &= \sum_{p=1}^{P} (\rho_{\mu\nu}|B_p)(B_p|\rho_{\gamma\sigma}) \\ &= \sum_{pq} (\rho_{\mu\nu}|b_p)(\hat{M}(r_1, r_2)^{-1})_{pq}(b_q|\rho_{\gamma\sigma}) \end{aligned} \tag{70}$$

where P is the rank of the decomposition which depends on γ. A comprehensive CD algorithm is presented by Epifanovsky et al[46] 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 third order tensors. The roots of DF have been grounded in Coulomb[47,48] and Exchange[49] fitting in Hartree-Fock and has been applied to MP2,[50] CCSD(T)[51] and even explicitly correlated methods.[52] The derivation of DF to proceed will be based on equations presented by Werner et al.[53] The goal of DF is to decompose the TEI tensor

$$\begin{aligned} \langle \mu\gamma|\nu\sigma\rangle = (\mu\nu|\gamma\sigma) &= \int \frac{\phi_\mu(r_1)\phi_\nu(r_1)\phi_\gamma(r_2)\phi_\sigma(r_2)}{r_{12}} dr_1 dr_2 \\ &= \int \frac{\rho_{\mu\nu}(r_1)\rho_{\gamma\sigma}(r_2)}{r_{12}} dr_1 dr_2 \end{aligned} \tag{71}$$

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

$$\bar{\rho_{\mu\nu}}(r) = \sum_{A}^{N_{fit}} d_A^{\mu\nu} \chi_A(r) \tag{72}$$

where $\chi_A(r)$ are fitting basis functions and expansion coefficients, $d_A^{\mu\nu}$, can be found by minimizing the functional

$$\Delta_{\mu\nu} = \int dr_1 \int dr_2 \frac{(\rho_{\mu\nu}(r_1) - \bar{\rho}_{\mu\nu}(r_1)) - (\rho_{\mu\nu}(r_2) - \bar{\rho}_{\mu\nu}(r_2))}{r_{12}} \tag{73}$$

which provides

$$d_B^{\mu\nu} = \sum_B (\mu\nu|A)[J^{-1}]_{AB} \tag{74}$$

where

$$(\mu\nu|A) = \int dr_1 \int dr_2 \frac{\phi_\mu(r_1)\phi_\nu(r_1)\chi_A(r_2)}{r_{12}} \tag{75}$$

The term J is chosen to be some metric, here it is defined as the coulomb metric[54,55]

$$J_{AB} = \int dr_1 \int dr_2 \frac{\chi_A(r_1)\chi_B(r_2)}{r_{12}} \tag{76}$$

other metrics have been proposed[56] and though they are less accurate, these metrics are computed more quickly than the Coulomb metric.

This allows one to express the TEI as

$$(\mu\nu|\gamma\sigma) = \sum_B d_B^{\mu\nu}(B|\gamma\sigma) = \sum_{AB} (\mu\nu|A)[J^{-1}]_{AB}(B|\gamma\sigma) \tag{77}$$

transforming $J^{-1} = J^{-1/2}J^{-1/2}$ allows one to store the TEI as two third order tensors, reducing storage requirements from $\mathscr{O}(N^4)$ to $\mathscr{O}(N^2 \cdot N_{fit}) \approx \mathscr{O}(N^3)$; N_{fit} typically scales linearly with basis set. Additionally one finds reduction in computational effort in calculations such as the Coulomb term, $\hat{J}$, in HF and transforming integrals from the AOs to MOs in MP2 calculations. To further reduce the complexity and storage of DF one can choose to use only a subset of the given auxiliary basis. Original construction of subsets was based on distance based domains. Unfortunately this led to discontinuities on the potential energy surface. Recently it has been shown that a better method is to only include fitting functions for a density,$\rho_{\mu\nu}$, where μ and ν are centered on the same point. This method is referred to as Concentric Atomic Density Fitting. This idea combined with a localization method and inclusion of exact semi-diagonal terms to reduce complexity in calculation and storage of the coulomb, $\hat{J}$, and exchange term, $\hat{K}$ in HF by Hollman et al[57]

3.3 Direct Tensor Decomposition methods

In the case of matrices, applications of decomposition methods are straightforward and imply the transformation to some canonical form based on the rank of the matrix. 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

$$X = a^{(1)} \otimes a^{(2)} \otimes \cdots \otimes a^{(N)} \tag{78}$$

where

$$\begin{gathered} X \in \mathbb{R}^{I_1 I_2 \ldots I_N} \\ a^{(1)} \in \mathbb{R}^{I_1}, \quad a^{(2)} \in \mathbb{R}^{I_2}, \quad \ldots, \quad a^{(N)} \in \mathbb{R}^{(N)} \end{gathered} \tag{79}$$

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

$$U = \sum_{r=1}^{R} \lambda_r a_r^{(1)} \otimes a_r^{(2)} \otimes \cdots \otimes a_r^{(N)} \quad \lambda_r \in \mathbb{R} \tag{80}$$

where $a_i^{(l)}$ are normalized vectors and one can then define the factor matrices as $A^{(l)} = [a_1, \ldots a_r] \quad l \in \{1, 2, \ldots, N\}$. Though it is not necessary to require each factor matrix have the same rank therefore one can also define the Tucker format (also refered to as the higher order singular value decomposition, HOSVD)

$$U = \sum_{\alpha_1}^{r_1} \ldots \sum_{\alpha_N}^{r_N} \beta_{\alpha_1 \ldots \alpha_N} a_{\alpha_1}^{(1)} \otimes \cdots \otimes a_{\alpha_N}^{(N)} \tag{81}$$

where $\{a_{\alpha_i}^{(l)}\}$ are a set of orthonormal vectors and $\beta \in \mathbb{R}^{r_1, r_2, \ldots r_n}$ is the Tucker core tensor Unlike matrix decompositions, there are no concise method to calculate the rank of a tensor, solving the rank is an NP hard problem.[58] Though there are many schemes which can solve for the

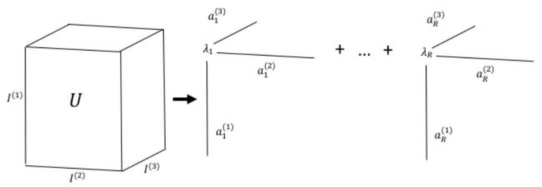

Figure 2: Representation of CP format

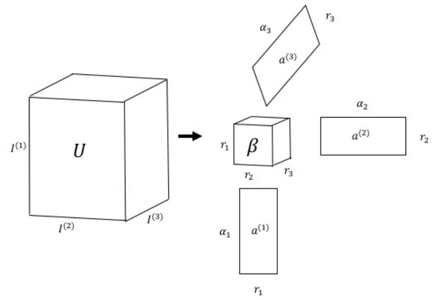

Figure 3: Representation of Tucker format

approximate rank of a tensor, T, by iteratively minimizing a series of non-linear equations[36]

$$\|T - U\| < \varepsilon \tag{82}$$

where $\mathscr{U}$ is defined using canonical or Tucker format. Figure's 2 and 3 depict diagrammatically the CP and Tucker format

Historically, the Tucker decomposition can be linked to complete active-space self-consistent field (CASSCF) method,[59] where excitation amplitude decomposition yields optimized orbitals for each tensor, and the CP decomposition can be linked to full CI[60] (FCI) where methods such as perfect pairing approach can be considered rank one tensor approximations to the FCI tensor. The idea of using CP decomposition for FCI has recently resurfaced.[61,62] Today, there is an effort to make use of element sparsity in higher dimension to decompose tensors in canonical ab initio methods. In work presented by Benedikt et al,[63–66] post-HF operator and amplitude tensors are decomposed to compute MP2 and CCD using CP format for example

$$(\mu\nu|\rho\sigma) = \sum_{r}^{R} \chi_r^{(\mu)} \otimes \chi_r^{(\nu)} \otimes \chi_r^{(\rho)} \otimes \chi_r^{(\sigma)} \tag{83}$$

Using this form the authors developed equations which preserve decomposed form and rank. These methods allow for reduced complexity in storage with out significant trade-off in accuracy and reduce the computational effort to perform any tensor contraction to $K \cdot d \cdot R1 \cdot R2$where K is the number of orbitals, d is the dimension of the tensors, and R1 and R2 are the ranks of each tensor. Unfortunately, finding the CP decomposition for tensors such as the TEI is non-trivial and costly and each tensor contraction increases storage requirements. Therefore, implementation of CP decomposed post-HF methods are not yet desirable.

In work presented by Bell et al[60] truncated HOSVD is employed to decompose the MP2 method T_2 amplitude expression,

$$T_2(i,a,j,b) = \frac{(ia|jb)}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \tag{84}$$

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 $\mathcal{O}(N^5)$.[60]

3.4 Tensor Hypercontraction

Tensor Hypercontraction (THC) was introduced in 2012 by Hohenstein, Parrish and Martinez.[67] 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

$$V_{pqrs} \approx W_{p,\alpha} W_{q,\alpha} X_{\alpha\beta} W_{\beta,r} W_{\beta,s} \tag{85}$$

First the step is to rewritten the FIT aa two index tensor

$$V_{pqrs} = V_{pq,rs} \tag{86}$$

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

$$V_{pq,rs} = U_{pq,r_{SVD}} S_{\lambda,\lambda} V^T_{\lambda,rs} \tag{87}$$

where λ is the rank of the decomposition. Here one may choose to use a truncated SVD or a 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.

$$V_{pq,rs} = \tilde{U}_{pq,\lambda} \tilde{V}^T_{\lambda,rs} \tag{88}$$

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 then performed on the three index tensors $\tilde{U}$ and $\tilde{V}$

$$\begin{aligned}\tilde{U}_{pq,\lambda} &= W_{p,\alpha} W_{q,\alpha} W_{\alpha,\lambda} \\ \tilde{V}^T_{\lambda,rs} &= W_{\lambda,\beta} W_{\beta,r} W_{\beta,s}\end{aligned} \tag{89}$$

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

$$V_{pqrs} = U_{p,\alpha} W_{q,\alpha} W_{\alpha,\beta} W_{\beta,r} W_{\beta,s} \tag{90}$$

THC has been used in the field to represent the electron interaction potentials in CC2 methods and to decompose the TEI and calculate CCSD and FCI energies. In work presented by Hummel et al[68] THC was used to reduce the computational 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[67] computational 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 commutes with all observable operators[2] and can be used in orbital localization correlation (LC) methods. There are many developed orbital localization schemes such as Boys and Pipek-Mezey[69] 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. The methods to follow specify some formula to generate a new occupied electron pair specific UMO's

$$|r^{ij}\rangle = \sum_{a} |a\rangle R^{ij}_{ar} \tag{91}$$

where R^{ij}_{ar} is a pair specific transformation matrix. This allows one to transform T_1 and T_2 amplitudes as

$$t^{i}_{a} = \sum_{r\in[ii]} R^{ij}_{ar} t^{i}_{r} \tag{92}$$

$$t^{ij}_{ab} = \sum_{r\in[ij]} R^{ij}_{ar} t^{ij}_{rs} R^{ij}_{bs} \tag{93}$$

In this format, correlation amplitudes and residual equations can be reduced using domain approximations based on electron pair distances.[70] The PAO method works by projecting AO basis functions against the UMO's[71]

$$|r\rangle = \sum_{a} |a\rangle R_{ar} \tag{94}$$

where

$$R_{ar} = \langle a|\phi_r\rangle \tag{95}$$

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) and equation of motion CCSD by Werner et al and more recently R12 methods.[72] 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^{ij}_{ar} is defined by diagonalizing the MP2-like density matrix[70,73]

$$D^{ij} = \frac{1}{1+\delta_{ij}}(\tilde{T}^{ij}T^{ij} + \tilde{T}^{ij}T^{ij^{\dagger}}) \tag{96}$$

where

$$T^{ij}_{ab} = \frac{\langle ij|ab\rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \tag{97}$$

$$\tilde{T}^{ij}_{ab} = 2T^{ij}_{ab} - T^{ji}_{ab} \tag{98}$$

such that

$$D^{ij}R^{ij}_r = n^{ij}_r R^{ij}_r \tag{99}$$

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

$$|r^{ij}\rangle = \sum_a R^{ij}_{ar}|a\rangle \tag{100}$$

$$|a\rangle = \sum_r \bar{R}^{ij}_{ar}|r^{ij}\rangle \tag{101}$$

PNOs for a given pair are orthogonal but PNOs between pairs are non-orthogonal. One can truncate the full set of PNOs taking 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 bsis 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 MP2 based on a pair MP2 energy threshold. The PNO methods formal scaling is $\mathscr{O}(N^5)$ though these approximations among others have introduced near linear scaling of PNOs in CCSD[72]

More recently Yang et al[74] has combined the ideas of pair independent PAOs and pair specific PNOs and proposed an OSV method. In this method R^{ij}_{ar} is found by SVD of the diagonal MP2 pair amplitudes.

$$[R^{i\dagger}T^{ij}R^{i}]_{rs} = t_r^{ii}\delta rs \tag{102}$$

$$|r^i\rangle = \sum_a |a\rangle Q_a^i r \tag{103}$$

Like PNOs, OSVs of a given 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. Computational scaling of OSV construction is $\mathcal{O}(N^4)$

4 Research Plan

It is apparent from the literature that operators and amplitude expressions in quantum chemistry have some low order format that can be taken advantage of as dimensionality increases. It is therefore the goal for this research to apply modern computational architecture scaling tensor decomposition algorithms to reduce scaling of correlation methods based on MBPT, CC and CC-R12 methods. THC is quantum chemistries first step into utilizing structure of tensors to reduce storage requirements without arbitrary truncation based on intrinsics. CP and Tucker decompositions have character from the full set of vectors which span the tensor space, unlike the truncated SVD or eigenvalue decomposition. In PNO and OSV methods virtual set domain truncation is based on either a occupation number or the diagonal MP2 amplitude threshold and rank is reduced by removing information. Changing these rank reduction methods to tensor decompositions would allow for data compression without loss of information. These new rank reductions methods would assist in the calculation of molecular properties where for example loss of even small valued vectors could have large contributions in derivative based response properties.

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.

In work originally presented by Almöf[75] and later Häser Haser1992 it has been shown that the integral transform step of MP2 eq. (34) using a Laplace transform of the denominator term

$$D_{ijab} = \frac{1}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} = \int e^{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)t} dt \tag{104}$$

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

$$|\phi_i\rangle = |\phi_i\rangle e^{\varepsilon_i} t/2 \tag{105}$$

$$|\phi_a\rangle = |\phi_a\rangle e^{\varepsilon_a} t/2 \tag{106}$$

Computationally the integral in eq. (104) can be transformed to a finite sum

$$E_{MP2} = \sum_{\alpha}^{\tau} w_{\alpha} e_2^{\alpha} \tag{107}$$

e_2^{α} is the weighted integral form of eq. (34) 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 weighting coefficients, typically 3 to 4 terms. 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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