DEVELOPMENT OF NEW QUANTUM METHODS FOR MATERIALS SCIENCE

By

MATTHEW STRASBERG

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This work is dedicated to the future recipients or victims of any of my engineering blunders. Unfortunately, this will not provide the solace you desperately deserve, but may it stand as a testament that at one point I knew what I was doing.
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Fracture is a fundamentally multi-scale process involving bond breaking which cascades to bulk phenomena. Connecting this quantum process to known engineering phenomena is limited by the quality of quantum theory and availability of appropriate experimental observables. New theory is developed to provide a correlated orbital framework which extends the concept of density functional theory to include exact kinetic energy and exact exchange, leaving electron correlation as the only unknown. Improved versions of second-order many-body perturbation theory are presented as an ab initio approach to quantum material science.
The Role of Computational Materials Science in Understanding Fracture of Brittle Materials

The basis of modern fracture mechanics considers the confounding effect of a stress applied to a crack in a continuum material. This is described by the stress intensity factor ($K_I$), a function of stress and crack size. Fracture occurs when $K_I$ reaches a critical value $K_{IC}$, a material property referred to as fracture toughness. Functionally, this is convenient for engineering design since one property, fracture toughness, encompasses all the mechanisms that occur during fracture. But this formulation is only partially supported by theory, namely extensions of the Griffiths Energy Consideration. Griffiths approach models crack growth as the creation of two new free surfaces. When the energy put into the system by an applied load equals the energy needed to create two free surfaces, the crack will propagate and the material fractures [1]. This approach yields the necessary stress for fracture as a function of crack length, but ignores the atomic processes involved. This deterministic view of fracture, yielding only conditions for failure, is symptomatic of fracture theories and leaves many unanswered questions. How does a crack propagate? Why is a fracture surface rough? Is it possible to predict fracture toughness from material structure?

Fracture experiments cannot answer these questions directly due to the speed and scale at which bond breaking occurs. Furthermore, simulations of fracture with molecular dynamics are severely limited by size, time of simulation, and description of bond breaking. This hints at a fundamental question of the viability of computational modeling for fracture. Without matching physical experiments, modeling to determine material properties is only suggestive not predictive. In other words, due to the self-contained nature of atomic simulations, simulations of fracture lack the transparency to extrapolate to the macroscopic scale.
The missing link is a property that can be detected quantitatively in both simulations and physical experiments. Not by coincidence, one of the unaddressed attributes of fracture, the roughness of the fracture surface, is suspected to transverse these scales in a predictable manner. Roughness is a measure of the deviations from a two-dimensional surface, or some partial dimension greater than 2-D. This partial dimension (or fractal dimension) is a fractal construct that exhibits self-affinity. In theory these fractal patterns seen macroscopically on the fracture surface extend to the atomic scale [2]. Exploiting this property has the potential to revise fracture mechanics and increase the relevance of quantum modeling in material science.

Furthermore, the fractal dimension has been demonstrated to be quantitatively related to the fracture toughness, providing a measurable connection between crack propagation and resistance to fracture [3]. This implies that the fracture path is dependent on the arrangement of atoms and strength of the bonds connecting them. Based on this premise, a simulation that produces a fracture surface with the same fractal dimension and same fracture toughness as an experimental analog can be taken as a demonstrative fracture event allowing for a detailed analysis of crack propagation. This would expand the practical applications of fracture theory to materials that are not adequately handled by stress intensity factor consideration or whose small size invalidates any continuum based model. If the fractal dimension can be quantitatively related to bond strength or even the sequence in which bonds break, then the fracture toughness of a material can be predicted purely from a simulation. The incentive is a framework to determine the fracture toughness of new materials without actually fabricating them.

To this end, there are several experimental and computational questions that need to be answered all related to the ability to determine the validity of a computational study of fracture relative to experiment. Fracture is a fundamentally multi-scale problem, a global stress induces a local stress causing individual atoms to dissociate which
transcends to multiple atoms dissociating simultaneously leading to a very dynamic fracture process that spans the atomic to the macroscopic. It may be eventually possible to capture all these processes in a single computational method, but this is not the case at the moment. A pragmatic approach would be to separate a fracture event into constitutive processes which are handled by tailored methods. This approach would require experiments designed for the limitations of computational simulations and corresponding quantitative experimental measurements. Fractography provides a set of such measurements, while not an all inclusive set, it is a necessary set.

Fractography is the study and analysis of fracture surfaces with a distinct emphasis on topographic characterization. This includes a mix of qualitative and quantitative techniques capable of identifying the cause and origin of failure, failure strength, fracture toughness, influence of environment, and quality of processing among other information useful for failure analysis. [4] Independent of type of material, brittle fracture surfaces show characteristic mirror, mist, and hackle patterns that emanate from the origin of failure. These features are a fingerprint left by the crack front as it propagates through the material. These features have a size dependence that increases farther from the origin that is a result of the release of strain energy during fracture. The mirror is a macroscopically smooth region which leads into the mist region which is identified by visible perturbations to the surface. As the crack continues to propagate, the hackle region of significantly larger features emerges. These features have been experimentally shown to exhibit self-similarity and scale invariance [5–7]. It was discovered that these features on the surface exhibit a measurable fractal statistic that correlates with the toughness of the material [8]. Further experimentation revealed a fundamental relationship with the fracture toughness ($K_{IC}$) of a material and the measurable fractal dimensional increment ($D^*$) of the fracture surface [3, 9, 10]:

$$K_{IC} = E \sqrt{a_0 D^*},$$  

(1–1)
where $E$ is the Young's modulus and $a_0$ is a parameter related to the scale of the fracture process. The fractal dimension can be measured experimentally by analyzing cross-sections of contours of the fracture surface [11] or area analysis with atomic force microscopy [2, 12]. The parameter $a_0$ cannot be directly experimentally determined, but is calculated from the above equation. Studies of fracture of single crystal silicon determine $a_0$ to be on the order of 5-10 Å depending on the direction of loading [10, 13]. Their results show a strong correlation between $a_0$ and the lattice parameters of the diamond cubic unit cell for silicon. This relationship was tested with semi-empirical quantum mechanic techniques on characteristic units of different materials; for example 3-, 4-, 5-, and 6-member rings were used as an analogy for silica glass [14]. These structures were pulled apart to simulate a fracture process, from this the effective crack extension was measured. This measurement showed good agreement (84% correlation) with experimentally determined $a_0$ values.

The fractal dimensional increment ($D^*$) and $a_0$ are two experimental parameters at two different length scales, a surface (≈millions of atoms) and a local cluster respectively, that determine the fracture toughness, identify the manner of crack propagation, and provide a means to analyze how local bonding influences macroscopic fracture. Determining either computationally is a significant challenge. Such calculations can be carried out, but their validity is currently hard to qualify. And this is because bond breaking, especially of large clusters, is still a hard and sometimes unsolvable problem even with the most rigorous quantum calculations let alone molecular dynamics. Multi-reference quantum mechanical methods are making great strides to this end [15, 16], but these methods are not accessible to material science due to computational cost. The more affordable second-order perturbation theory (MBPT2), while ab initio, at times lacks the necessarily quality. The next few chapters will propose improved versions of MBPT2 in order to develop a practical quantum method for studying bond
breaking in material science with the intent this will eventually be an approach to study fracture.

**Validity of Density Functional Theory**

Density functional theory (DFT) is a local approach to quantum chemistry in which the energy of a system is determined as a function of the electronic density rather than the wavefunction. The validity of using the density as a variable is proven by the Hohenberg-Kohn theorems, which states that there is a direct relationship between the external potential of a system and the electronic density [17]. Moreover, given a fixed number of electrons in the system, the external potential defines a unique ground state density up to an additive constant. This allows for a variational like procedure to exist for DFT. However, the electronic energy has no known form as a functional of the electronic density and the density of system maps back to the wavefunction in a one to many manner [18]. In other words, there is no framework for a systematically improvable density guaranteed to converge to the correct result.

Practical approaches to handle this problem have been developed, namely Kohn-Sham DFT (KS-DFT) [19]. KS-DFT proposes that the N-electron density can be defined by N spin-orbitals allowing for a compact functional form for the density:

\[ \rho(r) = \sum_{i} \phi_i(r)^2. \]  

(1–2)

The electronic energy is given by

\[ E[\rho] = T[\rho] + J[\rho] + E_{xc}[\rho] + \int \nabla_{ext}(r) \rho(r) dr \]  

(1–3)

where \( T \) is the kinetic energy, \( J \) is the Coulomb energy, \( \nabla_{ext} \) is the external potential, and \( E_{xc} \) is an unknown energy functional used to define the exchange and correlation energies. The main advantages of KS-DFT are that the kinetic energy can be defined as the kinetic energy of a single Slater determinant comprised of the KS orbitals and
the functional derivative with respect to the density is readily determined [18]. This just leaves the $E_{xc}$ term to be determined.

However, the KS-density can never achieve the exact result due to the limited mathematical representation. By choosing the density to be comprised of $N$ orthogonal orbitals, the density is equivalent of the trace of the one-matrix of a single determinant. While this can be a good approximation, the exact one-matrix cannot be defined by a single Slater determinant meaning the exact density cannot be defined by only $N$ orbitals. In other words, the exact density exists in a mathematical space of dimension $M$ greater then $N$, while KS-DFT projects the density only onto $N$ dimensions. Practically, this means the energy functionals have to be falsified in order to give energies that approach the exact result. This is akin to a semi-empirical approach. If the kinetic energy is defined by a local operator instead of the non-local operator, the approach becomes completely classical. Alternatively, if the orbitals are non-orthogonal, the functional form of the KS-density can produce the exact density.
Foundations of Optimized Effective Potential

The optimized effective potential (OEP) framework provides a tool to optimize the many-body electron correlation problem from an orbital perspective using a central potential [20]. This approach has shown success in determining exchange and correlation potentials from wavefunction theory, a crucial requirement for determining the density from an orbital expression. Conventional Kohn-Sham (KS) density functional theory (DFT) suffers from the self-interaction error, a direct result of attempting to express the exchange energy in terms of the density. This error cascades into the determination of correlation functionals which must compensate for the inadequate handling of the exchange. This error transcends the KS orbital eigenvalue equations resulting in orbital eigenvalues that have limited physical relevance and struggle to satisfy the HOMO condition [18, 21, 22]. Within the density framework, OEP approaches act to alleviate the self-interaction error by a least squares type fitting to the non-local exchange; this helps to restore the separation between exchange and correlation representations [23–26]. The OEP framework allows the flexibility for the correlation energy to be defined from wave function theory, density functional theory, density matrix functional theory, or other orbital dependent energy functionals.

Taking an ab initio approach, the second-order many-body perturbation theory (MBPT) energy expression has been used to define OEP-MBPT2 [27, 28]. This approach has successfully provided qualitatively meaningful orbital potentials and quantitative accurate total energies. The total energy, being a second-order expression, is of second-order quality. However, by selecting orbitals and orbital eigenvalues from a local potential as the choice for zeroth order Hamiltonian ($H_0$) causes deviation in the total energy. This deviation is minor and neither a consistent improvement or worsening to total energy relative to the purely ab initio coupled cluster results[28]. This occurs for
two reasons: 1) selecting the local OEP orbital eigenvalues as $H_0$ propagates any errors of the local formulation into higher order terms and 2) the designation of the occupied and virtual spaces are defined by the local orbital eigenvalue equation. To address the first issue, the complementary ab initio DFT approach provides an equivalent frame to OEP-MBPT2, but with a modified $H_0$ to use the semi-canonical Fock operator [29–31]. To the second point, experimenting with mixing in non-local exchange shows improved consistency of the total energy, but suggests there are errors in the correlation potential due to the forced localization [32].

Forcing the OEP framework to produce a non-local potential will address these inconsistencies while maintaining the efficacy of the approach. The use of a local potential in OEP provides a systematic way to improve DFT while working within the known theorems of DFT. Extending to a non-local potential, does not violate any principles of DFT but provides extra flexibility. Gilbert demonstrated that the Hohenberg-Kohn theorems are valid for non-local potentials allowing for the total energy to be expressed as a functional of the one-particle reduced density matrix ($\gamma$) [33]. A parallel constrained search proof exists for an idempotent $\gamma$, a one-matrix composed of the same number of orbitals as electrons, as does exist for the KS density [34].

A simplified derivation of the local OEP procedure will be demonstrated along with connection to ab initio DFT. This derivation will be extended to provide a non-local variant. A second-order potential for both the local and non-local case will be constructed.

**Local OEP Through Second-Order**

OEP approach provides a framework to optimize an energy expression that is given as a functional of a set orbitals. This eliminates the need for an explicitly determined wavefunction. By placing an emphasis on orbitals rather the density, density matrices, or the wavefunction any energy expression constructed from any combination of these
three quantities can be treated in an equivalent framework. This is achieved by coupling an orbital eigenvalue equation and the many-body energy expression through a functional derivative with respect to a one-particle potential $\hat{u}(r)$. The orbital eigenvalue equation is given by:

$$\langle \phi_q | \hat{g} | \phi_p \rangle = \langle \phi_q | (\hat{h} + \hat{u}) | \phi_p \rangle = \epsilon_p \delta_{qp}$$ (2–1)

Where $\hat{u}(r)$ is local and $\hat{h}$ is the kinetic energy operator and external potential. Indexes $i, j, k, ...$ will indicate occupied orbitals; $a, b, c, ...$ will indicate virtual orbitals; $p, q, r, ...$ are generic indexes representing any orbital. In the context of DFT, this would refer to the KS equation with the first $N$ orbitals defining the density $\rho(r)$.

$$\rho(r) = \sum_i N \langle i | \delta(r, r') | i \rangle = \sum_i \phi_i(r)^* \phi_i(r)$$ (2–2)

The KS equation is determined by imposing the energy be a minimum with respect to the density.

$$\frac{\delta E[\rho(r)]}{\delta \rho(r)} = 0$$ (2–3)

This functional derivative defines $\hat{u}(r)$ and thus the orbitals, which then define the density and total energy. OEP imposes a more general condition, that the energy is stationary with respect to the potential $\hat{u}(r)$

$$\frac{\delta E(\{\phi\}, \{\epsilon\})}{\delta \hat{u}(r)} = 0,$$ (2–4)

where $E$ is the energy of the system. The dependence on $\hat{u}(r)$ is not explicit in $E$, so the chain rule is applied with functional derivatives over all orbitals and the orbital eigenvalues:

$$\sum_p \int dr' \left\{ \frac{\delta E}{\delta \phi_p(r')} \frac{\delta \phi_p(r)}{\delta \hat{u}(r)} + \text{c.c.} \right\} + \sum_p \frac{\delta E}{\delta \epsilon_p} \frac{\delta \epsilon_p}{\delta \hat{u}(r)} = 0.$$ (2–5)
First order uncoupled perturbed Hartree-Fock (UPHF) is used to define the functional derivatives \( \frac{\delta \rho_p(r')}{\delta \hat{u}(r)} \) and \( \frac{\delta \epsilon_p}{\delta \hat{u}(r)} \). The first-order UPHF equations is given as:

\[
(\hat{g} - \epsilon_p) \delta \phi_p + (\delta \hat{u} - \delta \epsilon_p) \phi_p = 0 \tag{2–6}
\]

The variation of orbital \( \phi_p \) induced by variation in \( \hat{u} \) is determined by projecting by orbital \( \phi_{q \neq p} \):

\[
\delta \phi_p(r') = \sum_{q \neq p} C_{pq} \phi_q(r') = \sum_{q \neq p} \frac{\langle \phi_p | \delta \hat{u}(r) | \phi_i \rangle}{\epsilon_i - \epsilon_p} \phi_p(r') \tag{2–7}
\]

The variation in the eigenvalue \( \delta \epsilon_p \) is given by:

\[
\delta \epsilon_p = \langle p | \hat{u}(r) | p \rangle \tag{2–8}
\]

The functional derivatives are determined from the above expressions:

\[
\frac{\delta \phi_p(r')}{\delta \hat{u}(r)} = \sum_{q \neq p} \frac{\phi_q^*(r) \phi_p(r)}{\epsilon_p - \epsilon_q} \phi_q(r')
\]

\[
\frac{\delta \epsilon_p(r')}{\delta \hat{u}(r)} = \phi_p^*(r) \phi_p(r) \tag{2–9}
\]

Inserting the above expressions into the OEP condition in Equation 2–5, we obtain

\[
\frac{\delta E(\{\phi\}, \{\epsilon\})}{\delta \hat{u}(r)} = \sum_{p,q \neq p} \int dr \left\{ \frac{\phi_q^*(r) \phi_p(r) \phi_q(r')}{\epsilon_p - \epsilon_q} \frac{\delta E}{\delta \phi_p(r')} + \frac{\phi_p^*(r) \phi_q(r) \phi_q^*(r')}{\epsilon_p - \epsilon_q} \frac{\delta E}{\delta \phi_p^*(r')} \right\}
\]

\[
+ \sum_p \phi_p^*(r) \phi_p(r) \frac{\delta E}{\delta \phi_p^*(r')}
\]

The total energy is a sum of the kinetic energy \( (E_T) \), the nuclear-nuclear and the nuclear-electron \( (E_{Ne}) \), and the electron-electron interaction \( (V_{ee}) \). As with KS theory, the kinetic energy of the system and the nuclear-electron interaction is defined by the N occupied orbitals.

\[
E_T + E_{Ne} = \sum_i \langle i | -\frac{1}{2} \nabla^2 + v_{\text{ext}} | i \rangle = \sum_i \langle i | \hat{h} | i \rangle \tag{2–11}
\]
The functional derivative of this part of the energy only exists in the occupied-virtual orbital space due to the dependence on only occupied orbitals and the cancellation of occupied-occupied terms in the functional derivative.

\[
\frac{\delta (E_T + E_{Ne})}{\delta \hat{u}(r)} = \sum_{i,a} \left\{ \frac{\phi_a^*(r)\phi_i(r)}{\epsilon_i - \epsilon_a} \langle i | \hat{h} | a \rangle + \text{c.c.} \right\} \tag{2-12}
\]

Manipulating the OEP orbital Equation 2–1 allows the above equation to be used to impose an explicit dependence on \( \hat{u}(r) \). Specifically, inserting the relation \( \langle i | \hat{h} | a \rangle = -\langle i | \hat{u} | a \rangle \) into the above functional derivative

\[
\frac{\delta (E_T + E_{Ne})}{\delta u(r)} = -\sum_{i,a} \left\{ \phi_a^*(r)\phi_i(r) \langle i | \hat{u} | a \rangle + \text{c.c.} \right\} \tag{2-13}
\]

The term preceding \( \hat{u}(r') \) is the KS linear response function or the density-density response function, which will be noted as \( X(r, r') \).

\[
X(r, r') = \sum_{i,a} \left\{ \frac{\phi_a^*(r)\phi_i(r)\phi_a^*(r')\phi_i(r')}{\epsilon_i - \epsilon_a} + \frac{\phi_a^*(r)\phi_a(r)\phi_a^*(r')\phi_a(r')}{\epsilon_i - \epsilon_a} \right\} \tag{2-14}
\]

Since the stationary condition insists the functional derivative of the total energy is zero, the functional derivative of electron-electron contribution to the energy is equal to the negative of the functional derivative of \( E_T + E_{Ne} \). Thus, a framework to define \( \hat{u}(r) \) is established.

\[
\hat{u}(r') = \int dr' X^{-1}(r, r') \sum_{p,q \neq p} \left\{ \phi_q^*(r)\phi_p(r) \phi_q(r') \phi_p(r') \frac{\delta V_{ee}}{\delta \phi_p(r')} + \text{c.c.} \right\} \tag{2-15}
\]

\[
X(r, r') \text{ and its inverse can be expressed nominally in an expansion of orthonormal auxiliary Gaussian functions } g_p(r),
\]

\[
X(r, r') = \sum_{pq} (X)_{qp} g_q(r)g_p(r') \tag{2-16}
\]
\[
X^{-1}(r, r') = \sum_{pq} (X^{-1})_{qp} g_q(r) g_p(r')
\]  
(2–17)

where \((X^{-1})_{qp}\) is determined by singular value decomposition of \(X(r, r')\). Similarly, \(\hat{u}\) is determined by expanding it in the same basis:

\[
\hat{u}(r') = \sum_p c_p g_p(r')
\]  
(2–18)

Whatever choice is made for \(V_{ee}\) defines the OEP potential \(\hat{u}(r)\). This can include any DFT functional, a DMFT functional, or in this case the electron correlation through second-order perturbation theory (MBPT2).

**OEP-MBPT(2)**

There are two choices for the zeroth order Hamiltonian \((H_0)\). First is a self-consistent formulation where \(H_0\) is the sum of orbital eigenvalues from the OEP condition. The other choice is to use the sum of the Fock orbital eigenvalues. These are not equivalent choices; selecting the Fock orbitals and eigenvalues constitutes a correction from Fock orbitals and results in a different functional derivative; this detail will be discussed later. The derivation will progress assuming \(H_0\) is comprised of OEP eigenvalues.

\[
V_{ee}^{\text{OEP-MBPT2}} = \frac{1}{2} \sum_{ij} \langle ij|ij \rangle + \sum_{ia} \frac{\langle i|f|a \rangle \langle a|f|i \rangle}{\Delta_i^a} + \frac{1}{4} \sum_{iabj} \frac{\langle ij|ab \rangle \langle ab|ij \rangle}{\Delta_{ij}^{ab}}
\]  
(2–19)
where $\Delta_i^g = \epsilon_i - \epsilon_a$ and $\Delta_{ij}^{ab} = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b$. The functional derivative of $V_{ee}^{OEP-MBPT2}$ is given by:

$$
\sum_{p \neq q} \int dr \left\{ \frac{\phi_p^*(r)\phi_q(r)\phi_q^*(r')}{\epsilon_p - \epsilon_q} \frac{\delta V_{ee}}{\delta \phi_p^*(r')} + c.c. \right\}
= \sum_{i,a} \frac{\phi_i^*(r)\phi_a(r)}{\epsilon_i - \epsilon_a} \left\{ \sum_j \langle aj || ij \rangle + \sum_b \frac{\langle a||bf \rangle \langle bf || i \rangle}{\Delta_i^b} + \sum_{jb} \frac{\langle ja||bi \rangle \langle bi || f \rangle}{\Delta_j^b} \right.
+ \sum_{jb} \frac{\langle jf || ba \rangle \langle ba || j \rangle}{\Delta_j^b} + \frac{1}{2} \sum_{jbc} \frac{\langle aj || bc \rangle \langle bc || ij \rangle}{\Delta_j^{bc}} + \sum_i \frac{\langle ai || fj \rangle \langle fj || i \rangle}{\Delta_i^a} \\
+ \frac{1}{2} \sum_{jk} \frac{\langle jk || ib \rangle \langle ab || jk \rangle}{\Delta_j^{ab}} \right\} + c.c. \tag{2-20}
$$

And the derivative with respect to the orbital eigenvalues:

$$
\sum_p \phi_p^*(r)\phi_p(r) \frac{\delta V_{ee}}{\delta \epsilon_p} = - \sum_i \phi_i^*(r)\phi_i(r) \left\{ \sum_a \frac{\langle i|af \rangle \langle af || i \rangle}{(\epsilon_i - \epsilon_a)^2} + \frac{1}{2} \sum_{jab} \frac{\langle ij || ab \rangle \langle ab || ij \rangle}{(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^2} \right\} \\
+ \sum_a \phi_a^*(r)\phi_a(r) \left\{ \sum_i \frac{\langle i|af \rangle \langle af || i \rangle}{(\epsilon_i - \epsilon_a)^2} + \frac{1}{2} \sum_{ijb} \frac{\langle ij || ab \rangle \langle ab || ij \rangle}{(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^2} \right\} \tag{2-21}
$$
Collecting terms of the above two equations defines \( \hat{u}(r') \) through second order:

\[
\hat{u}(r') = \int dr' X^{-1}(r, r') \sum_{i,a} \frac{\phi_i^*(r) \phi_a(r)}{\epsilon_i - \epsilon_a} \times
\]

\[
\left\{ \sum_j \langle aj| i jj \rangle + \sum_b \frac{\langle a f| b \rangle \langle b f| i \rangle}{\Delta_i^b} + \sum_{jb} \frac{\langle ja| b \rangle \langle b f| j \rangle}{\Delta_j^b} + \sum_{jb} \frac{\langle jf| b \rangle \langle ba| ji \rangle}{\Delta_j^b} \right. \\
+ \frac{1}{2} \sum_{jbc} \frac{\langle aj| bc \rangle \langle bc| i jj \rangle}{\Delta_{ij}^{bc}} + \sum_j \frac{\langle af| j \rangle \langle j f| i \rangle}{\Delta_j^a} + \frac{1}{2} \sum_{jkb} \frac{\langle jk| ib \rangle \langle ab| jk \rangle}{\Delta_{jk}^{ab}} \right\} + c.c. \\
- \int dr' X^{-1}(r, r') \sum_i \phi_i^*(r) \phi_i(r) \left\{ \sum_a \frac{\langle i f| a \rangle \langle a f| i \rangle}{(\epsilon_i - \epsilon_a)^2} + \frac{1}{2} \sum_{jab} \frac{\langle ij| ab \rangle \langle ab| ij \rangle}{(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^2} \right\} \\
+ \int dr' X^{-1}(r, r') \sum_a \phi_a^*(r) \phi_a(r) \left\{ \sum_i \frac{\langle i f| a \rangle \langle a f| i \rangle}{(\epsilon_i - \epsilon_a)^2} + \frac{1}{2} \sum_{jab} \frac{\langle ij| ab \rangle \langle ab| ij \rangle}{(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^2} \right\}
\]
(2–22)

Once \( \hat{u}(r) \) is determined, the matrix elements \( \langle p| g| q \rangle \) can be determined allowing for new definition of orbitals and orbital eigenvalues. This, in turn, defines a new \( H_0 \) allowing for an iterative determination of \( \hat{u}(r) \) and the orbitals.

**Selecting Fock Operator as \( H_0 \)**

The OEP procedure can be framed as a correction from the Fock operator and corresponding Fock orbitals. This achieved by selecting \( H_0 \) as the Fock operator; for simplicity semi-canonical Fock orbitals will be selected giving \( H_0 \) as the diagonal Fock elements:

\[
H_0 = \sum_p \langle p| f| p \rangle = \sum_p \tilde{\epsilon}_p.
\]
(2–23)

This choice of \( H_0 \) causes the OEP procedure to behave only as an orbital optimization with each iteration determining an improved set of semi-canonical Fock orbitals and an
perturbing potential $\hat{u}(r)$. The OEP orbital equation is no longer an eigenvalue equation:

$$\langle i|g|j \rangle = \epsilon_{ij}$$
$$\langle a|g|b \rangle = \epsilon_{ab}$$
$$\langle i|g|a \rangle = \langle a|g|i \rangle = 0$$ (2–24)

While the energy is still optimized with respect to $\hat{u}(r)$, the functional derivatives in the chain rule have to be modified. The relevant UPHF equation is given by:

$$(f - \tilde{\epsilon}_p)\delta \phi_p + (\delta u - \delta \tilde{\epsilon}_p)\phi_p = 0$$ (2–25)

where $\tilde{\epsilon}_p$ is the diagonal element from the Fock matrix.

$$\frac{\delta \phi_p(r')}{\delta u(r)} = \sum_{q \neq p} \frac{\phi_q^*(r)\phi_p(r)}{\epsilon_p - \epsilon_q} \phi_q(r')$$
$$\frac{\delta \tilde{\epsilon}_p(r')}{\delta u(r)} = \phi_p^*(r)\phi_p(r)$$ (2–26)

From here, the derivation of $\hat{u}(r)$ proceeds in the same manner as before, just with the modified denominators $\tilde{\epsilon}_p$ corresponding to the diagonal elements of the Fock operator. This variant maintains more of the non-local quality as all elements in the energy expression are coming from non-local operators with the exception of the separation of the occupied and virtual orbitals. This scheme is called OEP-MBPT(2)SC in order to differentiate it from the definition of OEP-MBPT(2) presented in the previous section.

**ab initio DFT**

An alternative formulation of the OEP framework is impose conditions directly on the corrections to the density. Specifically, that corrections to the KS density, $\delta \rho$, are zero. This is a local natural orbital condition. The corrections to the density can be determined through double perturbation theory with the second perturbation operator
being the density operator, \( \hat{\rho}(r, r') \). The first order correction is given by:

\[
\delta \rho^{(1)} = \langle 0 | \delta R_0 V | 0 \rangle + \langle 0 | VR_0 \delta | 0 \rangle
\]

\[
= \sum_{ia} \frac{\phi^*_i(r) \phi_a(r)}{\Delta_i^a} \langle a | f | i \rangle + \text{c.c.}
\]

\[
= \sum_{ia} \frac{\phi^*_i(r) \phi_a(r)}{\Delta_i^a} \langle a | h | i \rangle + \sum_{ia} \frac{\phi^*_i(r) \phi_a(r)}{\Delta_i^a} \sum_j \langle aj || ij \rangle + \text{c.c.
} (2-27)
\]

\[
= - \sum_{ia} \frac{\phi^*_i(r) \phi_a(r) \phi^*_a(r') \phi_i(r')}{\Delta_i^a} u(r') + \sum_{ia} \left\{ \frac{\phi^*_i(r) \phi_a(r)}{\Delta_i^a} \sum_j \langle aj || ij \rangle + \text{c.c.} \right\}
\]

From here, \( \hat{u}(r') \) can be determined in the same manner as with the OEP case by setting the correction to the density to zero.

\[
\delta \rho(r) = \delta \rho^{(1)}(r) + \delta \rho^{(2)}(r) + \cdots = 0
\]

(2–28)

Rearranging terms gives:

\[
u(r') = \int drX^{-1}(r, r') \sum_{ia} \left\{ \frac{\phi^*_i(r) \phi_a(r)}{\Delta_i^a} \sum_j \langle aj || ij \rangle + \text{c.c.} \right\} + \int drX^{-1}(r, r') [\delta \rho^{(2)}(r) + \cdots]
\]

(2–29)

The second order correction to the density is given by:

\[
\delta \rho^{(2)} = \langle 0 | \delta R_0 VR_0 V | 0 \rangle + \langle 0 | VR_0 \delta R_0 V | 0 \rangle + \langle 0 | VR_0 VR_0 \delta | 0 \rangle
\]

(2–30)

The first and last terms in \( \delta \rho^{(2)} \) are the adjoint of each other, with \( \langle 0 | \delta R_0 VR_0 V | 0 \rangle \) given by:

\[
\langle 0 | \delta R_0 VR_0 V | 0 \rangle = \sum_{i,a} \frac{\phi^*_i(r) \phi_a(r)}{\epsilon_i - \epsilon_a} \left\{ \sum_b \frac{\langle af | b \rangle \langle b | f i \rangle}{\Delta_i^b} + \sum_{jb} \frac{\langle ja | b \rangle \langle b | f j \rangle}{\Delta_j^b} + \sum_{jb} \frac{\langle jf | b \rangle \langle ba | ji \rangle}{\Delta_j^{ab}} 
\right\}
\]

\[
+ \frac{1}{2} \sum_{jbc} \frac{\langle aj || bc \rangle \langle bc | ij \rangle}{\Delta_i^{bc}} + \sum_j \frac{\langle af | j \rangle \langle j | f i \rangle}{\Delta_i^a} + \frac{1}{2} \sum_{jkb} \frac{\langle jk || ib \rangle \langle ab | jk \rangle}{\Delta_j^{ab}}
\]

(2–31)
The second term is given by:

$$\langle 0 | VR_0^\dagger | 0 \rangle = \sum_{i,a} \phi_i^\dagger(r) \phi_a(r) \sum_{jb} \frac{\langle j | f | b \rangle \langle ba | ji \rangle}{\Delta_i^a \Delta_j^b} + \text{c.c.}$$

$$- \sum_i \phi_i^\dagger(r) \phi_i(r) \left\{ \sum_a \frac{\langle i | f | a \rangle \langle a | f | i \rangle}{(\epsilon_i - \epsilon_a)^2} + \frac{1}{2} \sum_{jab} \frac{\langle ij | ab \rangle \langle ab | ij \rangle}{(\epsilon_{ij} + \epsilon_j - \epsilon_a - \epsilon_b)^2} \right\}$$

$$+ \sum_a \phi_a^\dagger(r) \phi_a(r) \left\{ \sum_i \frac{\langle i | f | a \rangle \langle a | f | i \rangle}{(\epsilon_i - \epsilon_a)^2} + \frac{1}{2} \sum_{jab} \frac{\langle ij | ab \rangle \langle ab | ij \rangle}{(\epsilon_{ij} + \epsilon_j - \epsilon_a - \epsilon_b)^2} \right\}$$

One simplification can be made by combining certain terms in $$\langle 0 | VR_0^\dagger \delta R_0 V | 0 \rangle$$ and $$\langle 0 | VR_0^\dagger \delta R_0 V | 0 \rangle$$:

$$\sum_{i,a} \phi_i^\dagger(r) \phi_a(r) \sum_{jb} \left\{ \frac{\langle j | f | b \rangle \langle ba | ji \rangle}{\Delta_i^a \Delta_j^b} + \frac{\langle ji | ab \rangle \langle ab | ij \rangle}{\Delta_i^a \Delta_j^b} \right\}$$

$$= \sum_{i,a} \phi_i^\dagger(r) \phi_a(r) \sum_{jb} \left\{ \frac{\langle j | f | b \rangle \langle ba | ji \rangle (\Delta_j^b + \Delta_i^a)}{\Delta_i^a \Delta_j^b} \right\}$$

$$= \sum_{i,a} \phi_i^\dagger(r) \phi_a(r) \sum_{jb} \left\{ \frac{\langle ji | ab \rangle \langle ab | ij \rangle}{\Delta_j^b} \right\}$$

Comparing the terms from the above expressions to the OEP Equations 2–22 shows that they are exactly the same. This is a completely independent formulation of exactly the same equations, with same flexibility regarding the choice of $$H_0$$. This demonstrates that the OEP optimization is the equivalent to a stationary density condition. This is not coincidental. The functional derivative with respect to $$\hat{u}(r)$$ is defined using the chain rule and first order UPHF. UPHF is an orbital perturbation on top on an orbital equation, which is built into the OEP framework implicitly. In other words, this is an optimization of a perturbing operator in a double perturbation framework [35]. If we define the following perturbations:

$$V = H - H_0$$

$$U = \hat{u}(r)$$

(2–32)
It has been demonstrated that an optimal expression for the external perturbation can be determined by minimizing the mixed perturbation expression, $\langle \psi | U | \psi \rangle$ [36, 37]. This is a first order perturbation with respect to $U$ and any choice of of order in $V$; orders in $U$ will be noted with a subscript and orders in $V$ will noted with a superscript. The stationary condition through second-order in $V$ is given by

$$\frac{\delta(E_1^1 + E_1^2)}{\delta \hat{u}(r)} = \frac{\delta}{\delta \hat{u}(r)} \{ \langle 0 | U R_0 V | 0 \rangle + \langle 0 | V R_0 U | 0 \rangle + \langle 0 | U R_0 V R_0 V | 0 \rangle \\ + \langle 0 | V R_0 U R_0 V | 0 \rangle + \langle 0 | V R_0 V R_0 U | 0 \rangle \}$$

(2–35)

The perturbation $U$ will produce terms of the form $\langle p | u | q \rangle$ with a corresponding denominator. The function derivative of $\langle p | u | q \rangle$ with respect to $\hat{u}(r)$ is $\phi_p \ast (r) \phi_q (r)$. The result is identical to the ab initio DFT equations. The connection between ab initio DFT and ab initio versions of OEP has been discussed previously, but in terms of modified functional derivative diagrams [38].

An additional note, the derivative with respect to the orbital eigenvalues is not adding correlation but is an occupation number correction. Removing these terms will not change the converged result for $\langle \hat{u}(r') \rangle$ as these terms must sum to zero in order to preserve the number of electrons in the density.

**Using OEP to Build a Non-Local Potential**

The local variant of OEP has significant utility as both an orbital optimization scheme and fitting scheme to translate non-local functions into local functions for use with DFT. The fitting from non-local to local allows for a much improved treatment of exchange than in conventional DFT functions. This addresses the self-interaction error that plagued the development of functionals and convolutes the definition of orbitals and their orbital eigenvalues. However, as discussed by Nesbet, forcing exchange to be local causes quantitative errors producing a higher energy than the Hartree-Fock case. For example, with the neon atom the error is about 2 milliHartrees with the OEP energy
consistently higher in energy than the HF energy (not considering correlation) [39]. This is not surprising, HF is an energy from variationally optimized wavefunction while the OEP energy is from local fitting of that energy expression. Additionally, in order to determine the local potential the inverse of the density response, \(X^{-1}(r, r')\), must be determined through a singular value decomposition [25, 27, 40]. This procedure can cause the convergence of \(\hat{u}(r)\) to be challenging. Both these issues can be alleviated by insisting on a non-local potential \(\hat{u}(r, r')\) instead. This can be extended further to force \(\hat{u}(r, r')\) to be a correction to the Fock operator. The non-local OEP orbital equation is given by:

\[
\langle \phi_q | n\hat{g} | \phi_p \rangle = \langle \phi_q | (\hat{f} + \hat{u}) | \phi_p \rangle = \epsilon_p \delta_{qp}
\]

(2–36)

The non-local OEP condition, with the chain rule, is now:

\[
\frac{\delta E(\{\phi\}, \{\epsilon\})}{\delta \hat{u}(r, r')} = 0 = \sum_p \int dr'' \left\{ \frac{\delta E}{\delta \phi_p(r'')} \frac{\delta \phi_p(r'')}{\delta \hat{u}(r, r')} + c.c. \right\} + \sum_p \frac{\delta E}{\delta \epsilon_p} \frac{\delta \epsilon_p}{\delta \hat{u}(r, r')}
\]

(2–37)

This requires a new definition of the functional derivatives with respect to \(\hat{u}(r, r')\). These are still determined from first-order UPHF.

\[
\frac{\delta \phi_p(r'')}{\delta \hat{u}(r, r')} = \sum_{q \neq p} \frac{\phi_q^*(r) \phi_p(r')}{\epsilon_p - \epsilon_q} \phi_q(r'')
\]

\[
\frac{\delta \epsilon_p(r')}{\delta \hat{u}(r)} = \phi_p^*(r) \phi_p(r')
\]

(2–38)

This is the same definition implicitly used in the work by Pernal to determine effective potentials in natural orbital functional theory [41]. Inserting the above expression into Equation 2–37.

\[
\frac{\delta E(\{\phi\}, \{\epsilon\})}{\delta \hat{u}(r, r')} = \sum_{p,q \neq p} \int dr'' \left\{ \frac{\phi_q^*(r) \phi_p(r') \phi_q(r'')}{\epsilon_p - \epsilon_q} \frac{\delta E}{\delta \phi_p(r'')} + \frac{\phi_p^*(r) \phi_q(r') \phi_q^*(r'')}{\epsilon_p - \epsilon_q} \frac{\delta E}{\delta \phi_p(r'')} \right\} + \sum_p \phi_p^*(r) \phi_p(r') \frac{\delta E}{\delta \epsilon_p}
\]

(2–39)
Looking at the occupied-occupied portion of the derivative:

\[
\sum_{i,j \neq i} \int dr'' \left\{ \frac{\phi_j^+(r) \phi_i^+(r') \phi_j(r'')}{\epsilon_i - \epsilon_j} \frac{\delta E}{\delta \phi_i(r'')} + \frac{\phi_j^+(r) \phi_i^+(r') \phi_j^+(r'')}{\epsilon_j - \epsilon_i} \frac{\delta E}{\delta \phi_j^+(r'')} \right\}
\]

\[
= \sum_{i,j \neq i} \frac{\phi_j^+(r) \phi_i^+(r')}{\epsilon_i - \epsilon_j} \int dr'' \left\{ \frac{\delta E}{\delta \phi_j(r'')} \phi_j(r'') - \frac{\delta E}{\delta \phi_j^+(r'')} \phi_j^+(r'') \right\} \tag{2–40}
\]

The unfortunate lesson learned from local derivation is that occupied-occupied and virtual-virtual portions of these functional derivatives respectively cancel out as the ab initio many-body energy (the HF energy plus any level of correlation) is invariant to occupied-occupied (OO) and virtual-virtual (VV) orbital rotations.

\[
\int dr'' \left\{ \frac{\delta E}{\delta \phi_j(r'')} \phi_j(r'') - \frac{\delta E}{\delta \phi_j^+(r'')} \phi_j^+(r'') \right\} = 0 \tag{2–41}
\]

\[
\int dr'' \left\{ \frac{\delta E}{\delta \phi_a(r'')} \phi_b(r'') - \frac{\delta E}{\delta \phi_a^+(r'')} \phi_b^+(r'') \right\} = 0
\]

In other words, only the occupied-virtual (OV) and virtual-occupied (VO) terms persist for any ab initio definition of the many-body energy,

Furthermore, the derivative with respect to orbital eigenvalues only indicates a change in the occupation number and is irrelevant to the derivation of potential. The non-local OEP condition is then given by:

\[
\frac{\delta E}{\delta u(r, r')} = \sum_{i,a} \frac{\phi_i^+(r) \phi_a^+(r')}{\epsilon_i - \epsilon_a} \int dr'' \left\{ \frac{\delta E}{\delta \phi^+_a(r'')} \phi_a^+(r') - \frac{\delta E}{\delta \phi^+_a(r'')} \phi_a(r') \right\} + c.c. \tag{2–42}
\]

An important property of non-local functional derivative, in contrast to the local version, is that every term \(\phi_i^+(r) \phi_a^+(r')\) is linearly independent. This can be shown by integrating by a specific \(\phi_i(r) \phi_a^+(r')\), which means each integral in the sum must be zero.

\[
\int dr'' \left\{ \frac{\delta E}{\delta \phi^+_i(r'')} \phi_a^+(r') - \frac{\delta E}{\delta \phi^+_a(r'')} \phi_i^+(r') \right\} = 0 \tag{2–43}
\]
This bypasses the need for a density-response or density-matrix response operator and removes the dependence on $X^{-1}(r, r')$. The many-body energy is given by:

$$E = \sum_i \langle i|\hat{h}|i \rangle + \frac{1}{2} \sum_{ij} \langle ij||ij \rangle + E_c$$  \hspace{1cm} (2\text{-}44)$$

where $E_c$ is the correlation energy. Inserting this definition into the integral expression above:

$$\int dr'' \left\{ \frac{\delta E}{\delta \phi_i^*(r'')} \phi_a(r'') - \frac{\delta E}{\delta \phi_a(r'')} \phi_i(r'') \right\} = 0$$

$$= \langle a|h|i \rangle + \sum_j \langle aj||ij \rangle + \int dr'' \left\{ \frac{\delta E_c}{\delta \phi_i^*(r'')} \phi_a(r'') - \frac{\delta E_c}{\delta \phi_a(r'')} \phi_i(r'') \right\}$$  \hspace{1cm} (2\text{-}45)$$

Using the OEP orbital Equation 2–36, it can be shown that $\langle a|h|i \rangle = -\langle a|u|i \rangle + \sum_j \langle aj||ij \rangle$. Using this relation produces a definition for $\langle a|u|i \rangle$:

$$\langle a|u|i \rangle = \int dr'' \left\{ \frac{\delta E_c}{\delta \phi_i^*(r'')} \phi_a(r'') - \frac{\delta E_c}{\delta \phi_a(r'')} \phi_i(r'') \right\}$$  \hspace{1cm} (2\text{-}46)$$

The expression for $\langle a|u|i \rangle$ through second is given by:

$$\langle a|u|i \rangle = \sum_b \frac{\langle a|f|b \rangle \langle b|f|i \rangle}{\Delta_b^f} + \sum_{jb} \frac{\langle ja||bj \rangle \langle b|f|j \rangle}{\Delta_j^b} + \sum_{jb} \frac{\langle j|f|b \rangle \langle ba||ji \rangle}{\Delta_j^b}$$

$$+ \frac{1}{2} \sum_{jbc} \frac{\langle aj||bc \rangle \langle bc||ij \rangle}{\Delta_j^{bc}} + \sum_j \frac{\langle a|f|j \rangle \langle j|f|i \rangle}{\Delta_j^a} + \frac{1}{2} \sum_{jkb} \frac{\langle jk||ib \rangle \langle ab||jk \rangle}{\Delta_j^{ab}}$$  \hspace{1cm} (2\text{-}47)$$

The above expression can be derived using double perturbation theory in the same manner as in the ab inito DFT approach by replacing the density operator ($\hat{\delta}$) with the one-matrix operator ($\hat{\gamma}_{pq} = |q\rangle \langle p|$). This is purely an alternative derivation that allows for the use of diagrammatic perturbation theory instead of functional derivatives, but results in the same potential. Unfortunately neither approach provides a prescription to define a correlated potential in the occupied-occupied space or the virtual-virtual space. At this point, what has be derived is a natural orbital second-order which produces an orbital optimized second-order energy (OO-MBPT2).
Complementary Approaches to Improving Orbital Eigenvalues

There are limited advantages to defining a potential \( \hat{u}(r, r') \) in the OO or VV spaces. Rotations in these spaces have no effect on the total energy. There are two equally valid justifications for this rotation: 1) the semi-canonical Fock rotation which forces the OO and VV blocks of the Fock matrix to be diagonal and 2) the diagonal one-matrix condition. The aim is to provide a correction to the eigenvalues beyond HF, to this end the semi-canonical rotation is preferred. The work of Pernal determines \( \langle p|u|p \rangle \) by taking the functional derivative with respect to the occupation number.

\[
\langle p|u|p \rangle = \frac{\delta E_c}{\delta n_i} \tag{2–48}
\]

There is no explicit dependence on occupation number in MBPT approaches. Efforts have been made to introduce a dependence on occupation number in the wavefunction framework, which has shown some success for determining ionization potentials and electron attachments \([42]\). Instead, an equivalent approach to considering occupation number will be used that extends the functional derivative with respect to the orbitals using \( \langle p|u|p \rangle \) as a Lagrangian multiplier:

\[
\langle p|u|p \rangle = \int dr \frac{\delta E_c}{\delta \phi_p^*(r)} \phi_p(r) = \int dr \frac{\delta E_c}{\delta \phi_p(r)} \phi_p(r) \tag{2–49}
\]

Inserting the second-order energy expression gives corrections to the orbital eigenvalues:

\[
\langle i|u|i \rangle = \sum_a \frac{\langle i|f|b \rangle\langle b|f|i \rangle}{\Delta_i^b} + \frac{1}{2} \sum_{jbc} \frac{\langle ij|bc \rangle\langle bc|i \rangle}{\Delta_i^{bc}} \\
+ \sum_{jb} \frac{\langle j|f|b \rangle\langle bi|j \rangle}{\Delta_j^b} + \sum_{jb} \frac{\langle ji|bf \rangle\langle b|f|i \rangle}{\Delta_j^b} \tag{2–50}
\]

\[
\langle a|u|a \rangle = \sum_j \frac{\langle a|f|j \rangle\langle j|f|a \rangle}{\Delta_j^a} + \frac{1}{2} \sum_{jkb} \frac{\langle jk|ab \rangle\langle ab|jk \rangle}{\Delta_{jk}^{ab}}
\]

The first two terms in both expressions are correlation terms while the last two terms in \( \langle i|u|i \rangle \) are corrections to \( J \) and \( K \) or coupled perturbed HF terms. The double excitation
terms in the above expression match double excitation corrections from the fractional occupation framework [42]. These are diagonal pieces of the one-electron portion of the second-order correlated Hamiltonian, \( \hat{F}_l^{(2)} \). As result, as much of \( \hat{F}_l^{(2)} \) as possible is being put in the one-particle operator \( \hat{g} \).

Again, \( H_0 \) can be selected as the Fock operator (OO-MBPT2) or can include this correction to the orbital eigenvalues creating an augmented second-order (A-MBPT2).
CHAPTER 3
DEVELOPMENT OF A HIGHLY-CORRELATED WAVE-FUNCTION BASED THEORY FOR MATERIALS SCIENCE

Foundations of Correlated Orbital Theory

The purpose of Correlated Orbital Theory (COT) is to provide a single-particle framework for routine and accurate quantum calculations. The utility of single-particle equations has already been demonstrated by the wide success of DFT, specifically Kohn-Sham DFT (KS-DFT) [19]. KS-DFT relies on a two level formulation: 1) a many-body energy given as a functional of the electronic density and 2) the non-interacting orbital equation which is determined by a functional derivative of the energy with respect to an assumed functional form of the density [18]. This structure of a many-body energy linked to a single-particle formulation persists in any orbital based quantum method. With DFT, however, the many-body energy is undetermined and cannot guarantee convergence to the correct answer. While this is not a overwhelming deficiency, it does hinder the predictability of the method.

Quantum simulations of materials are dominated by density functional theory (DFT) and semi-empirical methods. Density matrix functional theory has emerged as a legitimate alternative to DFT. New approaches include corrected-Hartree Fock [43], Geminal Functional Theory [44], Natural Orbital Functional Theory [45, 46], and Density Cumulant Functional Theory [47] to name few. Second-order perturbation theory (MBPT2) is gaining an increased importance in materials science due the relative high accuracy for the given computational effort [48–50]. MBPT2 can be viewed as a linear type ansatz to the many-body wavefunction which can be functionalized through manipulation of orbitals and $H_0$. Despite the long history of the method (the paper by Møllet and Plesset was published in 1934 [51]), there is still significant flexibility for creating an improved MBPT2 suitable for the predictive study of materials and molecules.
Orbital optimization has been explored extensively in quantum chemistry with the purpose of either improving the quality of results or speed of the calculation. Various orbital optimization schemes exist from different variants of Hartree-Fock [52], optimization of the virtual space [53], energy minimization [54, 55], improved properties [56], reduced computational cost [57], and improved convergence [58] among other motivations. Brueckner orbitals correspond to maximum overlap condition with the exact wavefunction [59]. These orbitals can be obtained through an optimization of $T_1$ or indirectly through direct manipulation of the one-particle density matrix, called the Brueckner-Hartree-Fock method [59, 60]. A Brueckner-Kohn-Sham scheme has been proposed to capitalize on the physical relevance of Brueckner orbitals and the corresponding quality in treatment of properties [61]. Orbitals are determined from an effective potential derived through an energy minimization of an infinite-order energy expectation. The result is a Kohn-Sham like eigenvalue equation resulting in Brueckner orbitals, which then are inserted into a standard DFT functional.

Other attempts have been made to construct an exact SCF theory which connects an independent-particle model to a many-body formulation. Originally develop to study nuclear interactions, a series to two particle potentials were developed from scattering theory [62, 63]. However, these theories never reached a practical implementation. More successful has been attempts to determine ionization potentials (IP) and electron affinities (EA) from one-particle SCF like procedures. Natural transition orbitals derive a potential for correlated orbitals corresponding to IP’s and EA’s through commutator relations [64]. This is equivalent to the Extended-Hartree-Fock procedure [65, 66]. Similar procedures have been used to obtain IP’s from density matrices manipulations [67].

In connection to the total wavefunction, one-particle operators have limited value as the exact wavefunction is invariant to orbital rotations. However, the relevancy of orbitals and their eigenvalues is increased at low orders of perturbation theory. Koopmans’
Theorem indicates that the orbital eigenvalues from the Hartree-Fock procedure provide good estimates to IP’s and EA’s. When the Fock operator is used as the zeroth order Hamiltonian, $H_0$, in a perturbative expansion, differences of these eigenvalues serve as weights in the wavefunction. It has been shown that modifying these values can lead to improved convergence or implicit higher order terms [68, 69]. The role of $H_0$ and what comprises a criterion for goodness has been discussed with no clear conclusion [70]. This is the crucial connection between a developing an accurate one-particle operator and the many-body energy. To this end, by mimicking Koopmans’ theorem, COT aims to provide a physically significant choice for $H_0$ while not deviating far from the success of standard Hartree-Fock based perturbations.

The additional benefit developing COT based on MBPT2 is the ease of property calculations. Coupled-cluster theory is non-hermitian which complicates the determination of density matrices and properties [71]. Perturbation theory, alternatively, while hermitian is limited through order-by-order expansions and requires significantly more effort to approach the quality of CC results. Furthermore, studies in $\Lambda$SCCS(T) show that imposing some hermitian character is beneficial to exploring potential energy surfaces, especially instances of bond breaking [72]. COT-MBPT2 provides a hermitian framework established through second-order perturbation theory, but also folds in some infinite order quality through the modification of $H_0$.

**Goals and Structure of COT**

COT, in the present formulation, is completely ab initio producing a many-body energy that traverses from HF theory to CC theory [73–75]. In this structure a single-particle theory is established systematically in a wavefunction framework. Additionally, the correlated orbitals are constructed to correspond to physical observables with orbital energies equal to ionization potentials and electron affinities, a constraint unique to COT. This is in great contrast to DFT, where the orbitals correspond
to a non-physical, non-interacting system in order to capture the correct kinetic energy. Eventually this can be expanded upon to utilize known physics from other aspects of wavefunction theory, many-body Green’s functions, or even density functional theory. The connection between COT and electron propagator approaches has been previously discussed [73] as well as a detailed comparison to the second order Dyson self-energy [75].

Hartree-Fock (HF) theory can be cast as a zeroth order, or uncorrelated, COT. Correlation is added to the Fock operator as a correlation potential. This maintains the simplicity of the iterative determination of orbitals and eigenvalues as utilized in HF theory. The HF wavefunction is designed assuming electrons form a shell structure of orthonormal orbitals arranged in a fermionic system. That is to say, for a system of N electrons, the wavefunction is a single Slater determinant comprised of N orbitals. The interaction of the wavefunction with the electronic Hamiltonian (assuming the Born-Oppenheimer approximate form [76]) can be optimized with the variational principle providing an upper bound to the energy of the system. This optimization process consists of minimizing the energy with respect to orbital shape yielding a variationally optimum wavefunction, a mean-field operator \( \hat{f} \), a set of orbitals \( \{ \phi_p \} \), and orbital energies \( \{ \epsilon_p \} \) that correspond to ionization potentials and electron affinities according to Koopmans’ Theorem [52].

\[
\hat{f}\phi_p = \epsilon_p \phi_p \tag{3–1}
\]

HF theory assumes that every orbital interacts with a mean-field from the other N-1 electrons and, thus, lacks correlation. Nevertheless, HF provides a convenient framework to extend to higher-order methods, specifically the orbital structure that is crucial to many-body perturbation theory, coupled-cluster theory, and configuration iteration methods. The utility of the orbital structure stems from inherent compression of information from the high dimensionality of the total wavefunction to a small set of
one-electron orbitals that interact with this high dimensional system. To this end, HF is too crude as the mean-field approximation eliminates all dimensionality associated with correlation. COT uses an orbital optimization procedure with a correlation potential based on many-body perturbation theory and and Fock-Space theory resulting in a new system of orbital eigenvalue equations:

\[ \hat{g}_{\text{COT}}(\{\epsilon\})\phi_p = [\hat{\mathcal{F}} + \hat{V}_c(\{\epsilon\})]\phi_p = \epsilon_p\phi_p \]  

(3–2)

**An Implicit Potential From Orbital Optimizations**

COT involves an iterative update of both orbitals and orbital energies, whose convergence indicates the completion of the calculation. This is achieved by integrating multiple wavefunction techniques to define orbital rotations in three respective blocks: occupied-occupied (OO), occupied-virtual (OV/VO), and the virtual-virtual (VV). Occupied orbitals will be indexed with a character \(i, j, k, \ldots\) and virtual orbitals will be similarly indexed with \(a, b, c, \ldots\). The procedure starts with a current definition of the orbitals and their energies; at the first iteration these are Fock orbitals and energies. Minimization the HF energy imposes the condition that there is no interaction between occupied and virtual orbitals across the Fock operator, also called the Brillouin-Brueckner condition\[77\]. In other words, Fock orbitals are defined by an OV rotation which imposes:

\[ \langle a|\hat{f}|i\rangle = 0. \]  

(3–3)

This OV condition will be mimicked for the correlated definition of orbitals and the COT operator, \(\hat{g}\). That is to say:

\[ \langle a|\hat{g}|i\rangle = 0. \]  

(3–4)

For the second-order implementation of COT, which will be referred to as COT-MBPT2, the total energy is the second order MBPT2 energy with COT-MBPT2
orbitals and eigenvalues.

\[ E_{COT-MBPT2} = \langle 0 | H_0 | 0 \rangle + \langle 0 | V | 0 \rangle + \langle 0 | V | 1 \rangle \]

\[ = \sum_i \langle i | h | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | ij \rangle + \sum_{ia} \frac{\langle ij | a | a | ij \rangle}{\epsilon_i - \epsilon_a} + \frac{1}{4} \sum_{ijab} \langle ij | ab | ab | ij \rangle \tag{3-5} \]

The above expression is obtained by Raleigh-Schrödinger Perturbation Theory where the electronic Hamiltonian is split into a zeroth order Hamiltonian and perturbation:

\[ H = H_0 + V \tag{3-6} \]

\( H_0 \) is selected to be the COT operator, \( g = f + v_c \), which at the first iteration is the Fock operator. The perturbation, \( V \), then adjusts with each successive update of \( g \) and hence \( H_0 \).

The energy can be reformulated into an immediately identifiable Hermitian form, namely the Hylleraas second-order functional. By optimizing with respect to orbital choice, the OV orbital rotation can defined. The Hylleraas functional is given by:

\[ E^{(2)} = \langle 1 | V - E^{(1)} | 0 \rangle + \langle 0 | V - E^{(1)} | 1 \rangle + \langle 1 | H_0 - E^{(0)} | 1 \rangle. \tag{3-7} \]

In the COT framework, emphasis is put on the optimization of the orbitals as a means to influence the total wavefunction. As a result, functional form for the first-order correction to the wavefunction is assumed and only the orbitals are varied. The first-order wavefunction is given by:

\[ |1\rangle = (\hat{T}_1^{(1)} + \hat{T}_2^{(1)}) |0\rangle \tag{3-8} \]

where \( \hat{T}_1^{(1)} + \hat{T}_2^{(1)} \) are first-order excitation operators taking the reference determinant to all single excitations \( \hat{T}_1^{(1)} \) and double excitations \( \hat{T}_2^{(1)} \) respectively. These are determined by the first-order generalized many-body perturbation theory (GMBPT) expressions [78]:

\[ \langle a | (E_0 - H_0) \hat{T}_1^{(1)} | 0 \rangle = \langle a | V | 0 \rangle \tag{3-9} \]
\[ \langle a | (E_0 - H_0) \hat{T}_2^{(1)} | b \rangle = \langle a | \hat{V} | b \rangle \]  

(3–10)

Inserting \( T_1 \) and \( T_2 \) into the energy functional gives the expressions:

\[
E_2 = \langle 0 | (\hat{T}_1^{(1)} + \hat{T}_2^{(1)}) \dagger \hat{V} | 0 \rangle + \langle 0 | \hat{V} (\hat{T}_1^{(1)} + \hat{T}_2^{(1)}) | 0 \rangle \\
+ \langle 0 | (\hat{T}_1^{(1)} + \hat{T}_2^{(1)}) \dagger (H_0 - E^{(0)}) (\hat{T}_1^{(1)} + \hat{T}_2^{(1)}) | 0 \rangle.
\]  

(3–11)

This is not a interesting result at second-order as the correlated Hamiltonian without modification is expressly Hermitian with \( T^{(1)}\dagger \) equal to the transpose of \( T^{(1)} \). However, this discussion is introduced for the sake of deriving the OO and VV blocks of the \( g \) operator since this expression is no longer Hermitian for the N-1 and N+1 spaces. For the rest of the derivation, the standard expression for \( E_2 \) will be used:

\[
E_2 = \langle 0 | \hat{V} (\hat{T}_1^{(1)} + \hat{T}_2^{(1)}) | 0 \rangle
\]  

(3–12)

The OV and VO blocks of the \( g \) operator are defined by an minimization of the energy with respect to the zeroth-order wavefunction. Since the energy expression is Hermitian, optimizing the left-hand projection of the zeroth order wavefunction implies that its complex conjugate is optimized as well. The variation of the energy with respect to the zeroth-order wavefunction can be manifested by an orbital optimization through a unitary optimization, namely a Brueckner rotation:

\[
\delta (E_0 + E_1 + E_2) = \frac{\partial}{\partial \tau_i^a} \sum_{ia} \langle 0 | e^{\tau_i^a} [H + V \hat{T}^{(1)}] | 0 \rangle_L
\]  

(3–13)

This is an iterative procedure in which \( \tau \) is re-evaluated after each orbital rotation. In the limit of near convergence, the exponential can be expressed as a linear operator:

\[
0 = \frac{\partial}{\partial \tau_i^a} \langle 0 | (1 + \tau_i^a) [H + V \hat{T}^{(1)}] | 0 \rangle_L
\]

\[
= \langle a | V + V \hat{T}^{(1)} | 0 \rangle_L
\]  

(3–14)

The above expression define a relation between \( T_1 \) at first and second-order, \( T_1^{(1)} + T_1^{(2)} = 0 \). This is the second-order Brueckner condition. The second-order expression for \( T_1 \) is
given by:

\[ \langle \alpha | V \hat{T}^{(1)} | 0 \rangle = \langle \alpha | (E_0 - H_0) T_1^{(2)} | 0 \rangle \]  (3–15)

The VO rotation matrix is the negative transpose of the OV rotation matrix as dictated by orthogonality constraints. Since the total energy is invariant to rotations within the OO and VV blocks, these spaces are rigorously determined by the OV block. At second order, this is rotation is equivalent to non-local OEP rotation. The OO and VV rotations will be defined by IP and EA problems respectively; this is handled by the Bloch equation.

**Bloch Equation to Define OO and VV Rotations**

The Bloch equation is a generalization of the electronic Hamiltonian which is formulated to directly handle degenerate references as well as changing number of electrons from a fixed reference \([79, 80]\). Of particular interest to COT is the ability to calculate both electronic affinities and ionization potentials with one set of orbitals defined by the neutral reference. This achieved through a wave operator framework in which the exact electronic wavefunction for any system can be represented by an unknown operator \( \Omega \) acting on a known reference function \([81]\):

\[ H \tilde{\Psi}_\alpha = H \Omega \tilde{\Phi}_\alpha = \Omega \tilde{\Phi}_\alpha E_\alpha \]  (3–16)

where \( \tilde{\Psi}_\alpha \) is the exact wavefunction, \( \tilde{\Phi}_\alpha \) is linear combination of reference Slater determinants, and \( E_\alpha \) is the exact energy of the system. The wavefunction \( \tilde{\Psi}_\alpha \) is orthogonal to all other wavefunctions \( \tilde{\Psi}_\beta \) such that projection of \( \Omega \) onto the \( \tilde{\Phi}_\alpha \) uniquely defines \( \tilde{\Psi}_\alpha \). This one-to-one correspondence allows for the orthogonality of the unknown many-body wavefunctions \( \{ \tilde{\Psi} \} \) to manifest in known functions \( \{ \tilde{\Phi} \} \). Each \( \tilde{\Phi}_\alpha \) is a linear combination of reference determinants:

\[ \tilde{\Phi}_\alpha = \sum_\beta C_{\beta\alpha} \Phi_\beta. \]  (3–17)
For the N-1 electron case the set reference determinants are all determinants that
formed by removing one orbital from the ground state reference $|0\rangle$; the N+1 reference is
the set of all determinants with one virtual orbital added. These spaces will be noted by
the following second quantized projection operators:

\[
P^N = |0\rangle \langle 0|
\]

\[
P^{N-1} = \sum_i i|0\rangle \langle 0| i^\dagger
\]

\[
P^{N+1} = \sum_a a^\dagger |0\rangle \langle 0| a
\]

(S3–18)

Since the overlap of wavefunctions with different numbers of electrons is zero, all three
projectors can be combined into a general projector $P$ without altering the rest of the
derivation. The Schrödinger equation becomes

\[
H\Omega P\tilde{\Phi}_\alpha = \Omega P\tilde{\Phi}_\alpha E_\alpha
\]

(S3–19)

There are two unknowns in the wavefunction, the wave operator $\Omega$ and the
coefficients of the reference states $C_{\beta\alpha}$. The wave operator is determined by
perturbative techniques while the coefficients of the reference are determined by
formulating the Bloch equation into an eigenvalue problem, as illustrated by expanding $\tilde{\Phi}_\alpha$:

\[
H\Omega P \sum \Phi_\beta C_{\beta\alpha} = E_\alpha \Omega P \sum \Phi_\beta C_{\beta\alpha}
\]

(S3–20)

Projecting by $P$ on the left produces a reduced space effective Hamiltonian whose
eigenvalues are the energies $E_\alpha$. Since $H_{eff,B}$ is non-Hermitian, the matrix $C$ defines the
right-hand eigenvectors in a bi-orthogonal set. This is the Bloch effective Hamiltonian
which is a similarity transformation of the exact electronic Hamiltonian with the same
eigenvalues [82].

\[
H_{eff,B} = PH\Omega P
\]

(S3–21)
The reference wavefunctions $\tilde{\phi}_\alpha$ are the eigenvectors of the $H_{eff,B}$. The benefit of the Bloch effective Hamiltonian is the ability to determine the electronic energies in a reduced dimension matrix problem rather than the full space of available states. This is achieved through perturbative determination of $\Omega$ and the application of matrix consistency conditions. The use of perturbation theory (or coupled-cluster theory) pushes the effort of treating correlation onto $\Omega$ and allows for a tractable $P$ space rather than requiring a large, CI-like reference space. The matrix consistency conditions impose restraints on $\Omega$ so that the effective Hamiltonian only needs to be defined for the states of interest, the $P$ space.

The complementary space to $P$ will be defined as $Q$ with projector $Q = 1 - P$, which includes all orbital excitations from determinants in the $P$ space. Implicit in the above derivation is the condition that $\Omega Q = 0$ or that there is no attempt to solve for the wavefunctions in the $Q$ space.

Starting from the wave operator equation obscures the mathematics enabling the Bloch equation which is just a similarity transform of the true electronic Hamiltonian with rotation matrix $U$:

\[
U = 1 + Q \Omega P
\]

\[
U^{-1} = 1 - Q \Omega P
\]  

(3–22)

The transformed Hamiltonian is given by:

\[
\tilde{H} = H + HQ \Omega P - Q \Omega PH - Q \Omega PHQ \Omega P
\]

(3–23)

and is shown in Figure 3-1. The each block of $\tilde{H}$ is given by:
Figure 3-1. Similarity transformation for the Bloch effective Hamiltonian allows for $\Omega$ and the correct eigenvalues to be determined though block diagonalization.

$$P \tilde{H}P = PHP + PHQ\Omega P = PH\Omega P$$

$$P \tilde{H}Q = PHQ$$

$$Q \tilde{H}P = QHP + QHQ\Omega P - Q\Omega PHP - Q\Omega PHQ\Omega P$$

$$= QH\Omega P - Q\Omega PHP$$

$$Q \tilde{H}Q = QHQ - Q\Omega PHQ$$

The $P \tilde{H}P$ block is the Bloch effective Hamiltonian. $\Omega$ can be determined by insisting $Q \tilde{H}P = 0$ which block diagonalizes $\tilde{H}$. With $\Omega$ defined, the Bloch effective Hamiltonian is completely determined and, due to the block diagonalization, the eigenvalues are exact.
**Defining Perturbative Order**

The wave operator $\Omega$ is determined by perturbation theory, specifically the Brillouin-Wigner formulation $[83]$. The zeroth-order approximation to $\Omega$ is $P$, the reference state projector. Higher order terms map $P$ states into $Q$ states.

$$\Omega = P + Q\Omega^{(1)} + Q\Omega^{(2)} + ... \quad (3–25)$$

The infinite order realization is Fock-space coupled-cluster (FSCC) where $\Omega$ satisfies an exponential ansatz $[78]$.

$$\Omega = e^S = P + S + \frac{1}{2}S^2 + ... \quad (3–26)$$

The operator $S$ is an excitation operator like $T$ but generalized for any number of electrons and can be separated into operators specific for each case. The part of $S$ that represents the N-electron wavefunction ($S^{[0,0]}$) is the $T$ operator from CC theory, which is determined before the rest of $S$. As such, $T$ can be extracted from the total exponential:

$$\Omega = e^Te^{\Delta S}. \quad (3–27)$$

The rest of the exponential, $e^{\Delta S}$, is defined by the Bloch equation; the N-1 portion is written as ($S^{[0,1]}$) and the N+1 portion is $S^{[1,0]}$. To make the notation universal for both the N-1 and N+1 systems, a general $S$ will be used to stand in for either $S^{[0,1]}$ or $S^{[1,0]}$ (these operators do not interact for the equations below, but this is not generally true for different sectors of Fock Space). We are interested in second-order energies and orbitals which requires $\Omega$ to be determined to first order. By splitting the electronic Hamiltonian into a zeroth-order approximation ($H_0$) and a first-order perturbation ($V$), the Bloch Equation 4–8 can be cast into a perturbative expansion. The first order definition of $\Omega$ is given by the QP block:

$$0 = QH_0Q\Omega^{(1)}P + QVP - Q\Omega^{(1)}PH_{\text{eff}}P \quad (3–28)$$
Before determining $\Omega$ it is convenient to normal order the Bloch equation to simplify the diagrammatic representation.

$$\{H\Omega\} P = H\Omega P - \langle 0 | H \Omega | 0 \rangle$$

$$= H\Omega P - \langle 0 | H(1 + T) | 0 \rangle$$

$$= H\Omega P - (E_0 + E_1 + E_2)$$

(3–29)

The eigenvalues from the normal ordered equations become energy differences—ionization potentials for the $N-1$ system and electron affinities for the $N+1$ states. Normal ordering does not change the definition of $\Omega$, but does simplify the derivation. Constructing a first-order $\Omega$ requires truncation of the exponential form which creates a linear approximation:

$$\Omega^{(0+1)} = 1 + T^{(1)} + S^{(1)}$$

(3–30)

Using this definition, Equation 3–28 becomes

$$0 = Q\{H_0\}\{S^{(1)}\} P + Q\{V\} P - Q\{S^{(1)}\} P\{H_{\text{eff}}\} P$$

(3–31)

Since $P$ is a complete active space, $Q$ is limited to all single excitations from states in $P$. The elements of $S^{(1)}$ are determined iteratively until convergence. The exact form of the equations are readily determined from the diagrammatic representation (Figure 3-2).

![Diagrammatic representation of $\Omega$ determining equations for the (1,0) and (0,1) sectors in skeleton form. The $\times$ represents a $H_0$ interaction and the box is the $H_{\text{eff},B}$ interaction.](image)

Now that $\Omega$ through first order is determined, $H_{\text{eff},B}$ can be defined through second order. From Equation 4–8, $H_{\text{eff},B}$ is the contribution through second order of the PP
The zeroth and first-order expressions just recover the normal ordered Hamiltonian while the second-order expression incorporates the $Q$ space. Expanding $\Omega^{(1)}$ using the linked-diagram theorem \[84\] gives the second order $H_{\text{eff},B}$:

$$PH_{\text{eff},B}^{(2)}P = P\{H_0\}P + P\{V\}P + P\{V\}^{(1)}\Omega$$

$$PH_{\text{eff},B}^{(2)}P = P\{H\}P + P(\{V\} T_1^{(1)}) L P + P(\{V\} T_2^{(1)}) L P + P(\{V\} S_2^{(1)}) L P$$

The $PP$ block effective Hamiltonian through second order is shown diagrammatically in Figure 3-3.

![Diagram](image)

Figure 3-3. Diagrammatic representation of $H_{\text{eff},B}$ equation for the $(1,0)$ and $(0,1)$ sectors in skeleton form. The box represents $H_{\text{eff},B}$.

$H_{\text{eff},B}$ is determined by iteratively updating $\Omega$ and then $H_{\text{eff},B}$ until both converge. This interdependence is a renormalization process inherent to Fock-Space approaches. Once convergence is reached, $H_{\text{eff},B}$ is diagonalized to obtain eigenvalues and eigenvectors or, in the context of COT, orbital energies and orbital rotation matrices. Since $H_{\text{eff},B}$ is manifestly non-Hermitian, the construction of orbitals from the eigenvectors of $H_{\text{eff},B}$ would require a bi-orthogonal set of orbitals. Alternatively, the Bloch equation can be cast into an Hermitian form allowing for one set of orbitals.

**Hermitization**

The original electronic Hamiltonian is Hermitian, but enforcing the exponential ansatz through a similarity transformation causes the resulting effective Hamiltonian to be non-Hermitian. Alternative similarity transformations result in the same eigenvalues.
but distinctly different effective Hamiltonians, the most common of which are: the Bloch
effective Hamiltonian, the Ōkubo effective Hamiltonian (which is the adjoint of the Bloch
effective Hamiltonian), and the canonical Hermitian des Cloizeaux effective Hamiltonian
[82]. The des Cloizeaux effective Hamiltonian is obtained by rotating $H$ by the following
similarity transformation:

$$U = \Omega (\Omega^\dagger \Omega)^{-\frac{1}{2}} P,$$

$$U^{-1} = P (\Omega^\dagger \Omega)^{-\frac{1}{2}} \Omega^\dagger.$$

This produces the des Cloizeaux effective Hamiltonian:

$$H_{\text{eff, } dC} = PU^{-1} H U P$$

$$= P (\Omega^\dagger \Omega)^{-\frac{1}{2}} \Omega^\dagger H \Omega (\Omega^\dagger \Omega)^{-\frac{1}{2}} P. \quad (3–35)$$

This can be iterated like the Bloch equation with each iteration requiring
simultaneous determination of $\Omega^\dagger$ and $\Omega$. Meissner and Nooijen demonstrated that
the des Cloizeaux effective Hamiltonian expression can be formulated as a similarity
transformation acting on the Bloch effective Hamiltonian rather than electronic
Hamiltonian [85].

$$H_{\text{eff, } dC} = P (\Omega^\dagger \Omega)^{\frac{1}{2}} H_{\text{eff, } B} (\Omega^\dagger \Omega)^{-\frac{1}{2}} P. \quad (3–36)$$

This allows for the Hermitization to be imposed after convergence of the Bloch effective
Hamiltonian by a similarity transformation of the Bloch equation. Unfortunately, this
rotation requires finding the inverse of $(\Omega^\dagger \Omega)$, which is not guaranteed to exist.

An alternative Hermitization can be achieved by mimicking Hylleraas variational
approach for the Fock-Space formulation. In traditional perturbation theory, the Hylleraas
equations are derived by projecting the adjoint of the first-order wavefunction onto the
first-order equation, Equation 3–7. This produces an zero term that can be added to
the second order energy. This structure can be reproduced with the Bloch equation by
projecting with $P\Omega^{(1)\dagger}$ onto the equation defining $\Omega^{(1)}$ (Equation 3–28).

$$0 = PS^{(1)\dagger}Q\{H_0\}Q\{S^{(1)}\}P + PS^{(1)\dagger}Q\{V\}P - PS^{(1)\dagger}Q\{S^{(1)}\}P\{H_{eff}\}P$$

(3–37)

Incorporating both this expression and the Hylleraas Variational expression, Equation 3–7, to the second-order Bloch effective Hamiltonian produces a Hermitian second-order effective Hamiltonian:

$$PH_{eff}^{(2)}P = FP + P(VT^{(1)})_LP + P(T^{(1)\dagger}V)_LP + P(T^{(1)\dagger}H_0 T^{(1)})_LP$$

$$+ P(S^{(1)\dagger})_LP + P(S^{(1)\dagger}V)_LP + P(S^{(1)\dagger}H_0 S^{(1)})_LP - P(S^{(1)\dagger}S^{(1)}PH_{eff})_LP$$

(3–38)

A single set of orthonormal orbitals can be determined from this effective Hamiltonian, $H_{eff}$, which is constructed after convergence of the Bloch equation.

**Intruder States**

Since COT is reliant on Fock-Space tools, intruder states are a fundamental concern. Intruder states refer to excited states that form near degeneracies with the states in the P space. This results in divergent iterations, the occasional zero denominator, and spurious results that are difficult to detect [86–89]. The issue arise from extracting eigenvalues from a reduced dimensional space problem. The dimensionality is reduced by determining $\Omega$ perturbatively, which uses energy differences as a preconditioning technique. As a result, intruder states are given an artificially high significance because of this preconditioning.

There are several approaches to address the intruder state problem. Approximate approaches such as denominator shifts (Intruder State Avoidance [87]) or neglect of intruder states are efficient, but inaccurate. Intermediate Hamiltonians allow for neutralization of intruder states and exact results by selecting an active space within P [90] or dressing the Hamiltonian [85, 91]. The only drawback, and a minor one at that, is that choosing an active space means that COT would no longer be an all orbital method. The Mixed-Sector Intermediate Hamiltonian, alternatively, increase the P space into
the Q space [92]. Unfortunately, this approach depends on having a sufficiently large auxiliary space added to the P space. A new intermediate Hamiltonian was constructed for this problem, the Canonical-Mixed Sector Intermediate Hamiltonian (CMSIH). CMSIH hybridizes Fock-Space and EOM techniques to allow the treatment of intruder states by adding them to the P space. Adding only the intruder states to the P space allows for an exact determination of Omega and all eigenvalues without the dependence on an increasingly large Q space. Details of this method will be discussed in the next chapter.

**Defining Orbitals from \( H_{\text{eff}} \)**

As previously mentioned, the Bloch equation can be used to define occupied-occupied rotations through the N-1 electron equation and virtual-virtual rotations space through the N+1 equation. To elaborate, diagonalization of the Hermitized \( H_{\text{eff}} \) for the N-1 system produces a set orthogonal eigenvectors which allows for a new definition of occupied orbitals \( \tilde{\phi}_i \). This is possible because the reference functions, \( \Phi_{N-1} \), in the \( P_{N-1} \) space span the set of all determinants with one orbital removed from the N electron reference. The eigenvectors that diagonalize \( H_{\text{eff}} \), \( \tilde{\phi}_{N-1} \), are orthogonal linear combinations of the set of \( \Phi_{N-1} \). To illustrate, the eigenvector \( \tilde{\phi}_i \) is given by

\[
\tilde{\phi}_i = \sum_j C_{ij} |0\rangle
\]  

(3–39)

From this summation, a new orbital \( \tilde{\phi}_i \) can be defined as:

\[
\tilde{\phi}_i = \sum_j C_{ji} \phi_j.
\]  

(3–40)

These orbitals inherit the orthogonality of the N-1 states. This is similarly true for the electron attached states with a rotation over all virtual orbitals. Thus, the eigenvector matrix \( C_{ip} \) defines a unitary transformation of the occupied orbitals. This is similarly true with \( C_{EA} \).
The OV rotation is carried out like a traditional Brueckner orbital rotation where each orbital is updated assuming a linear approximation:

\[ \tilde{\phi}_i = \phi_i + \sum_a t^a_{[(1)+(2)]} \phi_a, \]
\[ \tilde{\phi}_a = \phi_a - \sum_i t^a_{[(1)+(2)]} \phi_i. \]  

(3–41)

With the exception at convergence, the newly updated orbitals are not orthonormal and require a Gram-Schmidt procedure.

While the OO, VV, and OV blocks are discussed and formulated as separate problems, they are inherently interdependent must be updated simultaneously. This is achieved through a single matrix rotation (U) of the molecular orbitals, where U is given by:

\[
U = \begin{bmatrix}
C_{ip} & T^{(1)+(2)}_1 \\
-T^{(1)+(2)}_1 & C_{EA}
\end{bmatrix}
\]

(3–42)

Psuedocode Outline

Convergence of the calculation is achieved when the orbitals and orbital energies become stationary to a desired level of precision. The iterative process involves a macro-iterative procedure with nested micro-iterative steps. The procedure is outlined below.

1. Define \( H_0 = f + v_c \)
2. Perform second-order energy calculation.
   
   (a) Calculate Hartree-Fock Energy
   (b) Build first order \( T_1 \) and \( T_2 \)
   (c) Calculate \( E_2 \)
3. Build second order \( T_1 \)
4. Calculate second-order Ionization Potentials
   (a) Identify intruder states with CMSIH
   (b) Build $S_2^{[0,1]}$ for non-intruder states
   (c) Build and diagonalize the CMSIH intermediate Hamiltonian
   (d) Extract $H_{eff}^{[0,1]}$ and $S_2^{[0,1]}$
   (e) If not converged return to 4.(a)

5. Calculate second-order Electron Affinities
   (a) Identify intruder states with CMSIH
   (b) Build $S_2^{[1,0]}$ for non-intruder states
   (c) Build and diagonalize the CMSIH intermediate Hamiltonian
   (d) Extract $H_{eff}^{[1,0]}$ and $S_2^{[1,0]}$
   (e) If not converged return to 4.(a)

6. Hermitize $H_{eff}^{[0,1]}$ and $H_{eff}^{[1,0]}$
   (a) Build $S_2^{[1,0]}$ and $S_2^{[0,1]}$
   (b) Construct FS-Hylleraas Functional
   (c) Diagonalize to obtain $C_{IP}$ and $C_{IP}$

7. Update orbitals

8. Check for convergence, if not converged return to 1

**COT as an Extendable Tool**

There are two logical extensions that may greatly increase the power of COT. First, modification of the many-body energy expression to fully utilize the COT orbitals. This can be as simple as extending the concept of HF-DFT; using COT orbitals to define a density to be used in a DFT many-body energy expression. Unlike Kohn-Sham orbitals, COT are physical and are motivated from a maximum overlap condition and as a result will not suffer from many of the same problems that DFT orbitals do. In a much more speculative sense, utilizing either tools from Green’s functions or dynamical mean field
theory may greatly increase the usefulness of COT. The second type of extension is the allowance for functionalization at the IP and EA level without trivializing the wavefunction nature of the equations. There are three types of functionals that can be used:

1. Direct functionalization of $H_{\text{eff}}$, specifically adding terms to $PH\Omega P$ such as select higher order terms (LCCD or RPA) or external potentials from DFT or other sources.

2. Coupling functions that manipulate the interaction with $\Omega$. At the moment these are only terms of the type $PHQ$ but they can include a correlation operator.

3. Wavefunction manipulation by adding select higher order terms in the FS expansion to create a better description of $\Omega$.

The primary intent of COT is provide a framework to view quantum chemistry differently that maintains verifiable criteria. In other words, provide a platform for experimental theory that has a more meaningful measure than total energy, namely IP’s and EA’s and their corresponding orbitals. This has been achieved.
The Intruder State Problem

Fock-space coupled-cluster (FSCC) is a powerful tool which uses a wave-operator to describe excited states and states of different particle number from the N-electron ground state correlated Hamiltonian [93, 94]. This allows for extension of coupled-cluster (CC) ground state tools [95–97] to other aspects of chemistry. FSCC constructs an effective Hamiltonian in a reduced dimension model space through a perturbatively determined wave-operator. Energies and corresponding wavefunctions of states in the model space are determined from the effective Hamiltonian. Equation-of-motion CC (EOM-CC), by contrast, produces equivalent results by diagonalizing the correlated Hamiltonian in the entire relevant determinant space [98–102]. The FSCC effective Hamiltonian is a coupled-cluster formulation of the Bloch effective Hamiltonian, a similarity transformation of the electronic Hamiltonian which allows for the reduced dimension description [79–81].

Effective Hamiltonians in general and FSCC specifically suffer from convergence issues related to intruder states or near degeneracies with states in the model space. The issues related to intruder states can be handled with an intermediate Hamiltonian, an extended effective Hamiltonian which exactly describes states in the model space at the cost of approximately treating states in an intermediate reference space [103]. This is achieved through a modified wave-operator of which there are multiple choices [104]. Alternatively, intruder states can be avoided with a dressed Hamiltonian produced by double similarity transformation [85, 91, 105].

Canonical Bloch Equation: the Interconnection Between FSCC and EOM

FSCC refers to the application of an exponential ansatz to the Bloch equation. The Bloch equation utilizes a wave-operator, \( \Omega \), to project a reference state (\( \tilde{\phi}_\alpha \)) to an exact
wavefunction ($\Psi_{\alpha}$).

$$\Psi_{\alpha} = \Omega \Phi_{\alpha} = \sum_{\beta} \Omega C_{\beta \alpha} \Phi_{\beta} \tag{4-1}$$

Each reference state is a linear combination of known reference Slater determinants ($\Phi_{\beta}$). The basis of all possible states can be split into two relevant spaces and corresponding projection operators: $P$ contains all the reference determinants and $Q = 1 - P$ is the complimentary space. The energy of each reference state, the coefficients ($C_{\beta \alpha}$), and the wave-operator ($\Omega$) are all determined by the Bloch equation framework. The Bloch equation is derived through a similarity transformation of the electronic Hamiltonian which yields an effective Hamiltonian that connects the reference functions to many-body energies.

$$P \tilde{H} \tilde{P} \Phi_{\alpha} = P \tilde{H} \Omega P \tilde{P} \Phi_{\alpha} = E_{\alpha} \Phi_{\alpha} \tag{4-2}$$

Manipulation of identity conditions of $\Omega$ allows the Bloch equation to be written in compact form:

$$H \Omega = \Omega H_{\text{eff}}. \tag{4-3}$$

$\Omega$ is a generalized wave-operator which can be cast into an exponential ansatz:

$$\Omega = e^S \tag{4-4}$$

$$S = T + S^{[0,1]} + S^{[0,1]} + ...$$

The coupled-cluster exponential can be extracted from $\Omega$:

$$\Omega = e^T e^{\Delta S} = e^T \tilde{\Omega} \tag{4-5}$$

Projecting Equation 4–3 by $e^{-T}$ yields the FSCC equations:

$$\tilde{H} \tilde{\Omega} = \tilde{\Omega} H_{\text{eff}}. \tag{4-6}$$
The amplitudes of $\Delta S$ are determined by projecting each $Q$ state on the above equation which produces a set of consistency equations.

$$0 = Q\tilde{H}\tilde{\Omega} - Q\tilde{\Omega}H_{\text{eff}}.$$  \hspace{1cm} (4–7)

This is equivalent to block diagonalization the similarity transformed $H$. The similarity transformed $H$ is given by:

$$\tilde{H} = U^{-1}HU$$

$$= PH\Omega P + PHQ + Q(H\Omega - \Omega PH)P + Q(H - \Omega H)Q$$  \hspace{1cm} (4–8)

$$U = \begin{bmatrix} P & 0 \\ Q\Omega P & Q \end{bmatrix} \quad U^{-1} = \begin{bmatrix} P & 0 \\ -Q\Omega P & Q \end{bmatrix}$$

The $PP$ block is $H_{\text{eff}}$ and the $QP$ block defines $\tilde{\Omega}$. This can be recast into an matrix eigenvector form:

$$PU^{-1}HU\bar{C}P = PH_{\text{eff}}PC_P = C_PC_E$$  \hspace{1cm} (4–9)

$$HUC_P = UC_P E_P$$

The above matrix equation is split into configurational spaces $P$ and $Q$ [106, 107].

$$\begin{bmatrix} H_{PP} & H_{PQ} \\ H_{QP} & H_{QQ} \end{bmatrix} \begin{bmatrix} C_P \\ C_P \end{bmatrix} = \begin{bmatrix} C_P \\ C_P \end{bmatrix} E_P$$  \hspace{1cm} (4–10)

Expanding $\Omega$ to its exponential form and projecting by $e^{-T}$ the produces the Canonical Bloch framework [106, 107].

$$\begin{bmatrix} \tilde{H}_{PP} & \tilde{H}_{PQ} \\ \tilde{H}_{QP} & \tilde{H}_{QQ} \end{bmatrix} \begin{bmatrix} C_P \\ \tilde{C}_P \end{bmatrix} = \begin{bmatrix} C_P \\ \tilde{C}_P \end{bmatrix} E_P$$  \hspace{1cm} (4–11)
Partitioning these equations recovers the FSCC equations.

\[
\hat{H}_{PP}C_P + \hat{H}_{PQ}\tilde{C}_P = C_PE_P \\
\hat{H}_{QP}C_P + \hat{H}_{QQ}\tilde{C}_P = \tilde{C}_P E_P
\]  \hspace{1cm} (4–12)

Relabeling eigenvectors as \(R_P = C_P\) and \(R_Q = \tilde{C}_P\) shows that the above equations are the EOM-CC equations [107].

\[
\begin{bmatrix}
\hat{H}_{PP} & \hat{H}_{PQ} \\
\hat{H}_{QP} & \hat{H}_{QQ}
\end{bmatrix}
\begin{bmatrix}
R_P \\
R_Q
\end{bmatrix}
= \begin{bmatrix}
R_P \\
R_Q
\end{bmatrix} E_P
\]  \hspace{1cm} (4–13)

EOM approaches utilize configuration interaction tools with a correlated Hamiltonian (\(\hat{H}\)) rather than the bare Hamiltonian (\(H\)). In this context, besides the perturbation order with respect to defining \(T\) and \(S\), each additional block of \(\hat{H}\) carries an additional order. The following notation will be used where \(\hat{H}^{(N)}\) implies the perturbation order of each block.

\[
\hat{H}^{(N)} = P\hat{H}^{(N)}_{PP}P + Q\hat{H}^{(N-1)}_{QP}P + P\hat{H}^{(N-1)}_{PQ}Q + Q\hat{H}^{(N-2)}_{QQ}Q
\]  \hspace{1cm} (4–14)

The order of \(\tilde{\Omega}\) is ambiguous as the definition is fixed by the choice of \(\hat{H}^{(N)}\). The discussion of order becomes irrelevant in an infinite order CC implementation.

**Canonical Mixed-Sector Intermediate Hamiltonian**

The complementary frameworks of FSCC and EOM-CC can be manipulated to avoid the intruder state problem in FSCC. Intruder states are only problematic in the determination of \(\Omega\) where their effect is demonstrated by divergent amplitudes or over weighted amplitudes which produce spurious results. However, these states are real and do have correct amplitudes that just can’t be determined through traditional FSCC approaches. Alternatively, the EOM-CC structure can be recast to selectively determine the amplitudes for these problematic intruder states. This hybridization of EOM-CC and FSCC will be called the Canonical Mixed-Sector Intermediate Hamiltonian (CMSIH).
The set of all determinants will be split into three spaces: $P$ the standard set of all reference states for the sector of interest, $Z$ the set of intruder states, and $Q' = 1 - P - Z$ the remaining states. The definition of $Q = 1 - P$ will persist. $\tilde{\Omega}$ still maps states in $P$ to excited determinants in both $Q'$ and $Z$.

$$\tilde{\Omega} = P + (Q' + Z)\tilde{\Omega}P \quad (4-15)$$

$\tilde{\Omega}$ is separated into a portion to be determined perturbatively ($Q'\tilde{\Omega}P$) and portion to be determined from the eigenvector coefficients ($C_Z = Z\tilde{\Omega}P\tilde{\Omega}$). The canonical Bloch Equation (4–11) is rewritten to reflect the redefined spaces.

$$\begin{bmatrix}
\hat{H}_{PP}^{(N)} & \hat{H}_{PZ}^{(N-1)} & \hat{H}_{PQ'}^{(N-1)} \\
\hat{H}_{ZP}^{(N-1)} & \hat{H}_{ZZ}^{(N-2)} & \hat{H}_{QZ}^{(N-2)} \\
\hat{H}_{Q'P}^{(N-1)} & \hat{H}_{Q'Z}^{(N-2)} & \hat{H}_{Q'Q'}^{(N-2)}
\end{bmatrix}
\begin{bmatrix} C_P \\ C_Z \\ Q'\tilde{\Omega}P \end{bmatrix} =
\begin{bmatrix} C_P \\ C_Z \\ Q'\tilde{\Omega}P \end{bmatrix} E_P \quad (4–16)$$

The matrix is partitioned into three equations:

$$\begin{align*}
\hat{H}_{PP}^{(N)}C_P &+ \hat{H}_{PZ}^{(N-1)}C_Z + \hat{H}_{PQ'}^{(N-1)}Q'\tilde{\Omega}P = C_P E_P \quad (4–17) \\
\hat{H}_{ZP}^{(N-1)}C_P &+ \hat{H}_{ZZ}^{(N-2)}C_Z + \hat{H}_{QZ}^{(N-2)}Q'\tilde{\Omega}P = C_Z E_P \quad (4–18) \\
\hat{H}_{Q'P}^{(N-1)}C_P &+ \hat{H}_{Q'Z}^{(N-2)}C_Z + \hat{H}_{Q'Q'}^{(N-2)}Q'\tilde{\Omega}P = Q'\tilde{\Omega}P E_P \quad (4–19)
\end{align*}$$

Equations 4–17 and 4–18 form a reduced space effective Hamiltonian, or the CMSIH:

$$H_{CMSIH}^{(N)} = P\tilde{H}^{(N)}(P + Q')\tilde{\Omega}P + Z\tilde{H}^{(N)}(P + Q')\tilde{\Omega}P + P\tilde{H}^{(N)}Z + Z\tilde{H}^{(N)}Z$$

$$= P(\tilde{H}_{PP}^{(N)} + \tilde{H}_{PQ'}^{(N-1)}Q'\tilde{\Omega})P + Z(\tilde{H}_{ZP}^{(N-1)} + \tilde{H}_{QZ}^{(N-2)}Q'\tilde{\Omega})P + P\tilde{H}_{PP}^{(N-1)}Z + Z\tilde{H}_{ZP}^{(N-2)}Z$$

(4–20)
Equation 4–19 defines $Q'\tilde{\Omega}P$:

$$0 = Q'\tilde{H}^{(N)}PC_p + Q'\tilde{H}^{(N)}Z\tilde{P}C_p + Q'\tilde{H}^{(N)}Q'\tilde{P}C_p - Q'\tilde{P}C_pE_P$$

$$= Q'\tilde{H}^{(N)}\tilde{P}C_p - Q'\tilde{P}C_pC_p^\dagger H_{\text{eff},B}^\dagger C_p$$

$$= [Q'\tilde{H}^{(N)}\tilde{P} - Q'\tilde{P}H_{\text{eff},B}^{(N)}]C_p$$

$$= Q'\tilde{H}^{(N)}\tilde{P} - Q'\tilde{P}H_{\text{eff},B}^{(N)}P$$

$$= Q'\tilde{H}_{Q'}^{(N-1)}P + Q'\tilde{H}_{Q'}^{(N-2)}(Z + Q')\tilde{P} - Q'\tilde{P}H_{\text{eff},B}^{(N)}P$$

(4–21)

Only amplitudes corresponding to determinants in $Q'$ are defined by Equation 4–21. However, the amplitudes are defined by their interaction with $H_{\text{eff},B}$ which contains all amplitudes in $\tilde{\Omega}$ not just the $Q'$ ones.

The CMSIH is an iterative procedure that produces exact FSCC eigenvalues, exact eigenvectors, and the exact $H_{\text{eff},B}$. The computational procedure is given as follows:

1. Identify intruder states and define $Z$.
2. Load $S$ amplitudes from previous iteration, holding amplitudes corresponding to states in $Z$ fixed.
4. Build $H_{\text{CMSIH}}$ using Equation 4–20 and newly defined $S$.
5. Diagonalize $H_{\text{CMSIH}}$.
6. Extract $H_{\text{eff},B} = C_pE_PC_p^{-1}$.
7. Extract $Z\tilde{P} = C_ZC_p^{-1}$
8. Check for convergence. If not converged return to 1.

**Identification of Intruder States**

The most robust way to identify an intruder states is a direct analysis of energy denominators that occur in the determination of $\tilde{\Omega}$. Specifically, if the magnitude of a denominator is less than one atomic unit, the corresponding state can be classified...
as an intruder state. This will overestimate the number of intruders and classify non-intruder states as such, but this guarantees success and is the rudimentary approach used in this paper. This criteria can be fined tuned on a case by case basis, but this is not preferred. Effort has been given to the identification of intruder states in the context of multi-reference second-order perturbation theory (MRMP2) [86, 87, 108]. In this context an intruder state can be classified as any determinant that produces a small energy denominator relative a chosen threshold and has a non-negligible contribution to the energy. Such determinants can be subjected to a two-state perturbative analysis to surmise whether each determinant is problematic through the calculation of a representative radius of convergence ($R_c$). States that produce a small $R_c$, formally any radius less than one, will cause a divergent perturbation. This model does not translate directly to the discussion of intruder states in FSCC as MRMP2 is a multi-reference Raleigh-Schrödinger perturbation where only one root is desired. Perhaps a modification of this approach will result in an efficient method to identify all intruder states.

**Comparison with MSIH**

The mixed-sector intermediate Hamiltonian (MSIH) is an another intermediate Hamiltonian that expands the reference space ($P$) to include an intermediate space ($Z$) which includes states from $Q$ [92, 109]. This is achieved through an alternative wave-operator ($R$) and a corresponding modified similarity transformation ($U_R$).

$$R = R + Q'R'P$$

$$U_R = 1 + Q'R'P$$

(4–22)

The amplitudes in $R$ are defined by a set of consistency equations with the convention wave-operator from the Bloch equation, $\Omega$; specifically $R\Omega P = \Omega P$ and $Q'\Omega HRP = Q'HPP$. From these relations, an equation quantifying the difference between $\Omega$ and $R$ can be defined. However, the choice of $Z$ needs to sufficiently large so that $Q'R'P =$
$Q'\Omega P$ causing the working equation so to be determined purely by $\Omega$. The amplitudes of $\Omega$ are given by [92]:

$$Q'\Omega H(P + Q')\Omega P = Q' H(P + Q')\Omega P. \quad (4–23)$$

The MSIH is given by:

$$H_I = PH(P + Q')\Omega P + ZH(P + Q')\Omega P + PHZ + ZHZ. \quad (4–24)$$

There are three primary difference between the CMSIH and the MSIH. First, the amplitude equation for the CMSIH is an exact formulation and does not require an increasingly large $Z$ to obtain exact results. At the correct limit, the MSIH amplitudes converge to the CMSIH amplitudes. The amplitudes from the $Z$ states are absent from Equation 4–23 which prevents correct coupling with these amplitudes leading to the need for a large enough $Z$ space to create a buffer between $P$ and $Q'$, unlike Equation 4–21. Second, the MSIH does not consider the order of the Hamiltonian. This is a minor point as this is not an issue for infinite order FSCC. Lastly, the MSIH does not given correct eigenvectors while the CMSIH does by design.
CHAPTER 5
CONCLUSIONS

Several new approaches to quantum chemistry are derived to establish functionalized second-order perturbation theory as an approach for conducting quantum mechanic calculations for materials science.

A non-local extension to OEP is presented. This removes the inexact treatment of exchange that occurs in local OEP and \textit{ab initio DFT}. This becomes a viable tool for orbital optimization of any density functional or density matrix functional in addition to \textit{ab initio} approaches. A second-order implementation is derived (OO-MBPT2) along with a diagonal correction to the orbital eigenvalues (A-MBPT2). This eigenvalue correction is the diagonal elements of the one-electron part of the correlated effective Hamiltonian, $\hat{H}$. Including this piece of $\hat{H}$ in $H_0$ results in an infinite order effect at second-order. This framework provides a consistent means to provide optimized orbitals and densities for creating hybrid functionals. Additionally, the equivalence of local OEP and \textit{ab initio DFT} is demonstrated through second order perturbation theory.

Similarly, COT provides an orbital optimization based on \textit{ab initio} theory, correlated ionization potentials and electron affinities, and an improved $H_0$ to increase the relevancy of the second order many-body energy. However, the relevance of COT to quantum chemistry is limited relative to its potential. At the moment, the many-body energy is limited to perturbative or coupled-cluster expressions. In other words, despite being an independent formulation with physically important orbitals, the total energy does not break new ground beyond the concept of an improved second order.

The canonical mixed-sector intermediate Hamiltonian is a new form of intermediate Hamiltonian that extends the framework of FSCC to utilize EOM-CC tools. This method allows for determination of all states with $P$ (e.g. when all orbitals active in IP and EA) and their corresponding eigenvectors by extending the model space to include all intruder states. Note, this approach has all the functionality of FSCC and can
isolate individual states or valence states and only requires $Z$ to include intruder states corresponding to states in $P$. Proper identification of intruder states is still needed to refine the determination of $Z$. 
REFERENCES


BIOGRAPHICAL SKETCH

Matthew Strasberg was born in Portland, Oregon. After graduating from Clarkstown High School North in New City, New York, Matthew attended Cornell University. At Cornell, he perused a degree in applied physics with an interest in the mechanical behavior of materials. His experiences at Cornell, combined with research opportunities at Brookhaven National Laboratory and Stanford Linear Accelerator Center, convinced him to pursue a graduate degree in material science. He attended the University of Florida for his graduate studies and this document is a testament that he finished. He received his Ph.D. from the University of Florida in the fall of 2013. Matthew currently alive. To the determinant of the world, this will change eventually. Do not dry your tears with this document.