INVESTIGATIONS INTO MOLECULAR DIMERS VIA MONTE CARLO MANY-BODY METHODS

BY

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UNDERGRADUATE THESIS

Submitted to the Department of Chemistry in the College of Liberal Arts and Sciences as part of an undergraduate research program.

University of Illinois at Urbana-Champaign, 2020

Urbana, Illinois

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Chapter 1

Introduction

This chapter aims to introduce the reader to the basic mathematical and quantum-mechanical topics needed to achieve a full understanding of the topics presented in this thesis. This chapter borrows heavily from the textbook written by Szabo and Ostlund, and material discussed in this chapter cites it as a reference unless otherwise noted. [1]

Section 1.1 introduces the mathematical concepts and conventions used throughout the text. It assumes at the very least a basic knowledge of multivariable calculus, applied linear algebra, and the quantum mechanics encountered in an introductory semester of physical chemistry. Section 1.2 posits the many-body electronic problem, the central subject of computational chemistry. Section 1.3 describes the Hartree-Fock approximation, arguably the most important first approximation to solutions of the many-body electronic problem. Sections 1.4 and 1.5 then describe post-Hartree-Fock methods, which expand upon and refine the Hartree-Fock approximation to provide more accurate results. In particular, perturbation theory is discussed in greater detail due to its relevance to the subject of this thesis, the MC-MP2 method.

1.1 Mathematical Review

1.1.1 Dirac Notation

Throughout the field of quantum mechanics, *Dirac's bra-ket notation* is widely used to express complex functions and their corresponding inner products, and greatly lessens the burden associated with their notation. It also elegantly encapsules the relationship between functions and vectors.

Any single-valued, continuous, square-integrable function $a(x)$ on some complex interval can be described as a vector lying in *Hilbert space*, an abstract inner product space that extends the concept of Euclidean space to an infinite number of dimensions. The intuition behind this one-to-one correspondence between certain functions and infinite-dimensional vectors is best left to its own section (see Appendix TBD).

$a(x)$ is represented as a *ket* vector living in a Hilbert space termed ket space, and is denoted as follows.

$$a(x) \equiv |a\rangle \tag{1.1}$$

Its complex conjugate, $a(x)^*$, is represented as a *bra* vector living in the dual (or, more descriptively, adjoint) space of ket space, and is denoted as

$$a(x)^* \equiv \langle a| = |a\rangle^\dagger, \tag{1.2}$$

where the dagger denotes the adjoint. Observe that the inner product between any two functions $a(x)$, $b(x)$ then becomes

$$\int a(x)^* b(x)\, \mathrm{d}x = \int \langle a|\, |b\rangle\ \mathrm{d}x \equiv \langle a|b\rangle, \tag{1.3}$$

which is exactly analogous to the definition of an inner product for vectors.

Physical quantity	Atomic unit	Value in SI units
Length	Bohr radius	$a_0 = 5.291772 \times 10^{-11}$ m
Mass	Electron mass	$m_e = 9.109383 \times 10^{-31}$ kg
Charge	Electron charge	$e = 1.602176 \times 10^{-19}$ C
Energy	Hartree	$\frac{\hbar^2}{m_e a_0^2} = 4.359744 \times 10^{-18}$ J
Momentum	Reduced Planck's constant	$\hbar = 1.054571817 \times 10^{-34}$ J $\cdot$ s

Table 1.1: Table of atomic units and their conversion to SI units.

1.1.2 Atomic Units

Atomic units arise from dropping the mathematical constants (e.g. h, π, etc.) in each term of the Schrödinger equation. For instance, the Schrödinger equation of atomic hydrogen,

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right)\Psi = E\Psi, \tag{1.4}$$

reduces to the form

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r} \right)\Psi = E\Psi \tag{1.5}$$

in atomic units. A brief summary of atomic units and their conversion factors has been tabulated in Table 1.1 for the reader's convenience. All subsequent equations hereafter will be derived in terms of these atomic units.

1.1.3 Electronic Orbitals

This thesis will be primarily concerned with *electronic* wavefunctions describing the dynamics of the electrons in a molecular system, rather than considering the total wavefunction describing the nuclei. The reasoning for doing so is outlined in Section 1.2.

The electronic wavefunction for a single electron is defined as a *spatial orbital*, and is denoted by $\psi(\boldsymbol{r})$, where $\boldsymbol{r}$ represents a vector containing the x, y, z spatial coordinates of the electron. The spatial orbital fully defines the spatial distribution of a single electron. We furthermore define the *spin orbital* $\chi(\boldsymbol{x})$ as

$$\chi_j(\boldsymbol{x}) = \begin{cases} \psi_i(\boldsymbol{r})\alpha(\omega) & \text{if } j = 2i - 1, \\ \psi_i(\boldsymbol{r})\beta(\omega) & \text{if } j = 2i, \end{cases} \tag{1.6}$$

where $\boldsymbol{x}$ is a four-vector containing the three spatial coordinates (i.e. the components of $\boldsymbol{r}$) and the additional spin coordinate ω. Here, $\alpha(\omega), \beta(\omega)$ are any two arbitrary orthogonal functions of some arbitrary spin coordinate ω, and represent the electron having $m_s = \pm\frac{1}{2}$ respectively. Thus, the spin orbital also distinguishes between electrons that may have the same spatial distribution, but have different spins. An example of this is the singlet ground state of molecular hydrogen, where the electrons occupy the same spatial 1s molecular orbital (MO), but have opposing spins. Thus, the two electrons are said to occupy separate spin orbitals.

It is now worth mentioning the conventions for indexing the spatial and spin orbitals. Typically, the number of electrons in a system is represented by N, while the total number of possible spatial orbitals (not just the occupied ones) is given by K, where $K \geq \frac{N}{2}$. Thus, the total number of spin orbitals is given by $2K$, directly following from equation 1.6. This convention will be followed throughout the rest of this thesis.

1.1.4 Hartree Products

The full Hamiltonian of a molecular system includes two-body interactions that complicate derivation of the solutions. However, if the Hamiltonian can be approximated as a series of one-electron interactions, e.g.

$$\hat{\mathcal{H}} \approx \sum_i^N \hat{h}(\boldsymbol{r}_i), \tag{1.7}$$

where $\hat{h}(\boldsymbol{r}_i)$ is a one-electron Hamiltonian that *approximates* the contribution of the ith electron to the total energy, e.g. by somehow averaging the contribution of other electrons out (c.f. Section 1.3).

Given this approximation, if the series of one-electron Hamiltonians is solved

for all i, and the spin orbitals $\{\chi_j\}$ are known to satisfy the relation

$$\hat{h}(\boldsymbol{r}_i)\chi_j(\boldsymbol{x}_i) = \epsilon_j \chi_j(\boldsymbol{x}_i), \tag{1.8}$$

then it can be shown that the corresponding *approximate* total electronic wavefunction Ψ, the eigenfunction satisfying equation 1.7, is given by the *Hartree product*

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) = \chi_i(\boldsymbol{x}_1)\chi_j(\boldsymbol{x}_2)\ldots\chi_k(\boldsymbol{x}_N), \tag{1.9}$$

with a corresponding eigenvalue

$$E = \epsilon_i + \epsilon_j + \cdots + \epsilon_k. \tag{1.10}$$

Note that the Hartree product approximates any possible state of the molecular system, not just the ground state, hence the unusual indexing of the spin orbitals in equation 1.9. i, j, k need not satisfy any relation other than that they are distinct and less than or equal to $2K$, and thus the Hartree product can represent the either the ground state or any arbitrary excited state. This makes Hartree products useful first approximations to the true nature of the total electronic wavefunction.

1.1.5 Slater Determinants

However, even forgiving the fact that the Hartree product is an approximation to the total electronic wavefunction, there exists a fundamental failure of the Hartree product in its ability to describe real quantum systems. Namely, it does not treat electrons as fermions, which necessarily satisfy the Pauli exclusion principle. The Pauli exclusion principle in turn requires that all electronic wavefunctions must be antisymmetric with respect to exchange, i.e.

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_i, \ldots, \boldsymbol{x}_j, \ldots, \boldsymbol{x}_N)$$
$$= -\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_j, \ldots, \boldsymbol{x}_i, \ldots, \boldsymbol{x}_N). \quad (1.11)$$

Because of the commutativity of simple multiplication, the Hartree product does not satisfy this relation, and thus is not a satisfactory description of the electronic wavefunction. Instead, there must exist a more complex relationship between the total electronic wavefunction and the one-electron spin orbitals satisfying equation 1.7. One method of antisymmetrizing the total electronic wavefunction is to represent it as a normalized determinant of a matrix of spin orbitals, where the ith row and jth column contain the spin orbital $\chi_j(\boldsymbol{x}_i)$, i.e.

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(\boldsymbol{x}_1) & \chi_j(\boldsymbol{x}_1) & \cdots & \chi_k(\boldsymbol{x}_1) \\ \chi_i(\boldsymbol{x}_2) & \chi_j(\boldsymbol{x}_2) & \cdots & \chi_k(\boldsymbol{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(\boldsymbol{x}_N) & \chi_j(\boldsymbol{x}_N) & \cdots & \chi_k(\boldsymbol{x}_N) \end{vmatrix}. \quad (1.12)$$

Equation 1.12 defines the *Slater determinant*, and is the antisymmetrized total electronic wavefunction of a N-electron system. The antisymmetry property of the Slater determinant can be verified by noting that the interchange of any two electrons is equivalent to interchanging two rows in the determinant. The interchange of any two rows or columns of a determinant reverses the sign. This is made especially apparent in the *Leibniz formula for determinants*,

$$|A| = \sum_{\sigma \in S_n} \text{sgn}(\sigma) \prod_i^n A_{\sigma(i),i}, \quad (1.13)$$

where σ is an arbitrary permutation in the set of all $n!$ possible permutations S_n, and $\text{sgn}(\sigma)$ is the signature of the permutation, which is equal to unity and reverses sign following each single interchange of indices.

1.2 The Many-body Electronic Problem

Given the mathematical review in the preceding section, one is now in a position to discuss the many-body electronic problem and the computational difficulty involved in its solution. The central interest of electronic structure theory is the determination of solutions to the non-relativistic, time-independent Schrödinger equation

$$\hat{\mathcal{H}} \left| \Psi(\{\boldsymbol{r_i}\}, \{\boldsymbol{R_I}\}) \right\rangle = E \left| \Psi \right\rangle \tag{1.14}$$

where $\left| \Psi \right\rangle$ is an exact wavefunction for the molecular system, describing both the nuclei and electrons simultaneously, and E is the corresponding energy of $\left| \Psi \right\rangle$. The Hamiltonian is in turn given by the relation

$$\hat{\mathcal{H}} = -\sum_i^n \frac{1}{2}\nabla_i^2 - \sum_I^N \frac{1}{2}\nabla_I^2 - \sum_i^n \sum_I^N \frac{Z_I}{r_{iI}} + \sum_i^n \sum_{j>i}^n \frac{1}{r_{ij}} + \sum_I^N \sum_{J>I}^N \frac{Z_I Z_J}{r_{AB}}. \tag{1.15}$$

Here, lowercase indices index over the n electrons, while uppercase indices index over the N nuclei. Z_I represents the charge of a given nucleus I, and r has the usual definition of being the distance between any two pairs of coordinates. A closer observation reveals the intuition summarized in the above equation. The first and second terms denote the kinetic energy of the electrons and nuclei respectively, while the third, fourth, and fifth terms denote Coulomb attraction and repulsion within the molecular system.

As written above, equation 1.14 is an extraordinarily involved $3(n + N)$-dimensional non-linear partial differential equation (PDE), with no analytical solution known for molecular systems larger than hydrogen. Furthermore, the eigenvalues and eigenfunctions of equation 1.14 are seldom desired. Nuclear coordinates are typically already known via experimental techniques such as X-ray diffraction. The computational chemist wishes to determine purely the electronic component of the wavefunction and its corresponding eigenvalues,

both of which collectively govern pertinent chemical properties such as polarizability, polarity, reactivity, and optical spectra.

Thus, further approximations must be made to simplify equations 1.14 and 1.15 and isolate the many-body electronic problem.

1.2.1 Non-relativistic Approximation

It is worth mentioning that the written form of 1.15 already encompasses the non-relativistic approximation, which neglects special relativistic effects electrons experience with sufficiently high linear and angular momenta [2, 3]. While this effect is especially significant for heavy atoms such as transition and post-transition metals (see the seminal reviews of Pyykkö and coworkers [4, 5, 6]), it typically results in little error for organic systems such as those investigated hereonafter, and thus can be neglected.

1.2.2 Born-Oppenheimer Approximation

Nuclei are orders of magnitude more massive than electrons, and thus experience different time scales of motion, i.e. nuclei move far more slowly than electrons given the same momentum. In the context of the many-body electronic problem, this implies that nuclei can be essentially regarded as fixed points in space, and can be treated as given parameters to the problem. In other words, the problem is said to depend on the nuclear coordinates *parametrically* rather than explicitly. This does not imply that electron-nuclei interactions neglected, but rather that the interactions are *de-coupled* from one another, and that one-body nuclear interactions treated as constants and two-body electron-nuclei interactions are treated as one-body interactions.

Thus, the nuclear terms (the second and fifth terms of equation 1.15) can be dropped and treated as added constants to the final energy of the molecular state. These dropped nuclear terms include the translational, vibrational, and rotational energies of the molecule. Equations 1.14 and 1.15 reduce to

$$\hat{\mathcal{H}} \left| \Psi(\{\boldsymbol{r_i}\}; \{\boldsymbol{R_I}\}) \right\rangle = E \left| \Psi \right\rangle, \tag{1.16}$$

where $\left| \Psi \right\rangle$, E now represent the *electronic* wavefunction and its corresponding energy, and

$$\hat{\mathcal{H}} = -\sum_i^n \frac{1}{2} \nabla_i^2 - \sum_i^n \sum_I^N \frac{Z_I}{r_{iI}} + \sum_i^n \sum_{j>i}^n \frac{1}{r_{ij}}. \tag{1.17}$$

1.2.3 Statement of the Problem

The many-body electronic problem is summarized in equations 1.16 and 1.17, and can be made explicit as follows: *given a set of nuclear coordinates $\{R_I\}$, what are the corresponding wavefunctions and energies which satisfy the electronic Schrödinger equation?*

No general method has been devised to directly solve the many-body electronic problem. Even with the drastic simplification conferred by the non-relativistic approximation, and the $3N$ fewer degrees of freedom resulting from the Born-Oppenheimer approximation, equation 1.16 remains a $3n$-dimensional non-linear PDE with no analytical solution. The subsequent sections in this chapter detail further approximations one can make to arrive at numerical solutions to the many-body electronic problem.

1.3 The Hartree-Fock Approximation

1.3.1 Physicists' Notation

Prior to further discussion, it is worth mentioning a notational shorthand for one-electron and two-electron Coulomb integrals that are so commonly encountered in further derivation of Hartree-Fock methods. This notation is known as *physicists' notation*. For the one-electron case,

$$\langle a|h|b \rangle = \int \chi_a^*(\boldsymbol{x}_i) h(\boldsymbol{r}_i) \chi_b(\boldsymbol{x}_i) \, \mathrm{d}x_i, \tag{1.18}$$

and for the two-electron case,

$$\langle ab|cd\rangle = \iint \chi_a^*(\boldsymbol{x}_i)\chi_b^*(\boldsymbol{x}_j)\frac{1}{r_{ij}}\chi_c(\boldsymbol{x}_i)\chi_d(\boldsymbol{x}_j)\,\mathrm{d}\boldsymbol{x}_i\,\mathrm{d}\boldsymbol{x}_j. \qquad (1.19)$$

It is implied that during integration, spin orbitals lying left of the central separator are transformed to their corresponding complex conjugates, and are functions of $\boldsymbol{x}_i, \boldsymbol{x}_j$ respectively. Spin orbitals lying to the right are similarly defined, but are left unaffected during integration.

One can furthermore define the *anti-symmetrized* two-electron Coulomb integration in physicists' notation through the addition of an additional vertical separator as follows.

$$\langle ab|\,|cd\rangle = \langle ab|cd\rangle - \langle ab|dc\rangle. \qquad (1.20)$$

1.3.2   The Hartree-Fock Equations

The most troublesome aspect of the many-body electronic problem is the two-body Coulomb interaction which makes it inseparable. However, to approximate the two-body Coulomb interaction that a single electron experiences, one could compute an average potential generated from all other electrons, thus simplifying the many-body electronic problem.

The *Hartree-Fock (HF) approximation* achieves this by decomposing the N-electron Schrödinger equation detailed in equations 1.16 and 1.17 into N one-electron *Hartree-Fock equations*, which satisfy the relation

$$
\begin{aligned}
\hat{f}(\boldsymbol{x}_i)\chi_a(\boldsymbol{x}_i) &= \hat{h}(\boldsymbol{x}_i)\chi_a(\boldsymbol{x}_i) \\
&+ \sum_{b\neq a}^{2K}\left[\int |\chi_b(\boldsymbol{x}_j)|^2\frac{1}{r_{ij}}\,\mathrm{d}\boldsymbol{x}_j\right]\chi_a(\boldsymbol{x}_i) \\
&- \sum_{b\neq a}^{2K}\left[\int \chi_b^*(\boldsymbol{x}_j)\chi_a(\boldsymbol{x}_j)\frac{1}{r_{ij}}\,\mathrm{d}\boldsymbol{x}_j\right]\chi_b(\boldsymbol{x}_i) \\
&= \epsilon_a\chi_a(\boldsymbol{x}_i)
\end{aligned}
\qquad (1.21)
$$

for all occupied spin orbitals, where $\hat{f}(\boldsymbol{x}_i)$ is termed the *Fock operator*, ϵ_a is the energy of the spin orbital χ_a occupied by electron i, K is the number of given spatial basis functions, and $\hat{h}(\boldsymbol{x}_i)$ is the simplified one-electron Hamiltonian

$$\hat{h}(\boldsymbol{x}_i) = -\frac{1}{2}\nabla_i^2 - \sum_I^M \frac{Z_I}{r_{iI}}, \qquad (1.22)$$

given M nuclei.

The seemingly complicated integro-differential Hartree-Fock equations in equation 1.21 can be decomposed term-by-term to assess the intuition behind the expression. The bracketed quantity in the second term can be interpreted as a *mean-field Coulomb operator*, which computes the average potential by the ith electron generated by an electron occupying the bth spin orbital. This can be made explicit in the expression

$$\hat{J}_b(\boldsymbol{x}_i) = \int |\chi_b(\boldsymbol{x}_j)|^2 \frac{1}{r_{ij}} \, \mathrm{d}\boldsymbol{x}_j. \qquad (1.23)$$

The third term in equation 1.21 can also be written in terms of a new operator known as the *exchange operator*, though this does not have a simple classical interpretation as did the mean-field Coulomb operator, and arises purely from the antisymmetric nature of the wavefunction as expressed by the Slater determinant. The action of the exchange operator on a spin orbital is given by the equation

$$\hat{K}_b(\boldsymbol{x}_i)\chi_a(\boldsymbol{x}_i) = \left[\int \chi_b^*(\boldsymbol{x}_j) \frac{1}{r_{ij}} \chi_a(\boldsymbol{x}_j) \, \mathrm{d}\boldsymbol{x}_j \right] \chi_b(\boldsymbol{x}_i). \qquad (1.24)$$

An ad-hoc justification for the presence of this term in the Hartree-Fock equations is to account for the lower energy of systems of parallel spins, a quantum-mechanical phenomenon known as *exchange correlation*. This process can be rationalized by noting that electrons with parallel spins have an inherently lower probability of being near each other because of Pauli exclusion, and thus experience less classical Coulomb repulsion between one another, lowering

the energy of the system.

Given the Coulomb and exchange operators, the Hartree-Fock equations can be re-written as

$$\hat{f}(\boldsymbol{x}_i)\chi_a(\boldsymbol{x}_i) = \left[h(\boldsymbol{x}_i) + \sum_{b \neq a}^{2K} \hat{J}_b(\boldsymbol{x}_i) - \sum_{b \neq a}^{2K} \hat{K}_b(\boldsymbol{x}_i) \right] \chi_a(\boldsymbol{x}_i) = \epsilon_a \chi_a(\boldsymbol{x}_i). \quad (1.25)$$

1.3.3 The Self-Consistent Field Method

The Hartree-Fock equations expressed in equation 1.25 still present with immense computational difficulty, in that the Fock operator depends on the eigenfunctions themselves. Thus, the Hartree-Fock equations are *pseudo-eigenvalue problems*, as the operator itself depends on the solutions obtained from the operator, and can only be solved iteratively. Nevertheless, there at least exists a clear method for solving this problem, dubbed the *self-consistent field method* (SCF method). The general theoretical procedure is as follows.

1. Assuming one has already been given a molecule (i.e. the set of nuclear coordinates, atomic numbers, and number of electrons), one must provide a basis set of spatial *atomic orbitals* (AOs). Many different basis sets are available in the literature for varying applications, and it is to the chemists' discretion which to use.

2. Generate the Fock operator using the given basis set.

3. The generated Fock operator to solve for the new eigenvalues and new eigenvectors, which are closer approximations to the true eigenvalues and eigenvectors of the Fock operator. The new eigenvectors are linear combinations of the AOs, and are termed *molecular orbitals* (MOs).

4. Repeat steps 2 and 3 until the eigenvalues and eigenvectors reach sufficient convergence.

Ideally, this provides a set of MOs defined in terms of the AO basis, with

a corresponding set of eigenvalues. Of course, this by no means provides a practical implementation of the HF method. In practice, implementation of the HF method is complicated by issues such as non-orthogonal basis functions, and requires inclusion of more sophisticated techniques in numerical linear algebra such as diagonalization and unitary transformations. This work will not discuss such techniques, as its primary intent is to illustrate developments in MC-MP2 theory, and will treat obtained HF energies and orbitals as givens. Nevertheless, MP2 builds off of the theoretical foundations laid out by the HF method, and it is instructive to learn the fundamentals of the HF method as to improve upon its results via MP2 theory.

1.4 Post-Hartree-Fock Methods

Post-Hartree-Fock methods are computational methods aimed at achieving more accurate solutions to the many-body electronic problem than those obtained via the HF method. Each of these methods corrects for one (of multiple) approximations made during solution of the HF equations. One such method, second-order many-body perturbation theory (MP2), is the central topic of this thesis, and is discussed in its own subsequent section. This section aims at discussing alternative post-Hartree-Fock methods and their various shortcomings as motivations for further development of MP2 theory.

1.4.1 Configuration Interaction

In the HF method, the ground state N-electron total electronic wavefunction is evaluated as the Slater determinant of N single-electron eigenfunctions of the Fock operator. This incomplete, approximate representation of the total electronic wavefunction necessarily over-estimates the ground state energy, per the variational principle.

To achieve a finer upper bound to the ground state energy, one can include contributions from other Slater determinants formed from the N electrons all $2K$

spin orbitals, not just those lowest in in energy. This requires the computation of

$$\binom{2K}{N} = \frac{2K!}{N!(2K-N)!} \tag{1.26}$$

Slater determinants. Thus, the *method of configuration interaction (CI)* aims at solving the variational problem

$$\Psi = c_o \left| \Psi_0 \right\rangle + \sum_a \sum_r c_a^r \left| \Psi_a^r \right\rangle + \sum_a \sum_{b>a} \sum_r \sum_{r>s} c_{ab}^{rs} \left| \Psi_{ab}^{rs} \right\rangle + \cdots , \tag{1.27}$$

with the second term representing a summation over all singly-excited Slater determinants, the third term representing a summation over all doubly-excited Slater determinants, and so on. Needless to say, solution of this variational problem for all possible Slater determinants (full CI) is extraordinarily computationally complex as the number of Slater determinants required grows on the order of $2K!$. A full CI calculation of just molecular nitrogen using the ANO basis (4s3p1d) requires 9.68×10^9 Slater determinants. [7]

With full CI being prohibitively expensive, an alternative is to truncate the above variational problem past the doubly-excited Slater determinants in equation 1.27, in a procedure known as singly and doubly excited CI (SDCI). Alternatively, one can choose to vary the spin orbitals within the Slater determinant simultaneously while varying the set of coefficients to counteract the error introduced via truncation, in a procedure known as multiconfiguration self-consistent-field (MCSCF).

However, truncated CI also suffers from a serious failure in that it fails to be *size-consistent*, i.e. its energy fails to scale with N given N interacting systems. In fact, its variational estimate of the energy tends towards zero in the limit $N \to \infty$. For investigations into molecular dimers (such as the ones discussed in this thesis) or larger systems such as crystals, this shortcoming is fatal. An investigation of why this is true in the general case of truncated CI

is rather involved and well beyond the scope of this text. Nevertheless, a brief mention of this shortcoming, in conjunction with the computational cost of CI methods in general, is enough to rationalize the relative scarcity of CI methods in computational chemistry today.

1.4.2 Pair and Coupled Pair Theories

Pair and coupled pair theories are a broad family of methods that essentially provide size-consistent approximations to the full CI method. This includes the independent electron pair approximation (IEPA) and the coupled cluster (CC) method. Of these theories, the CC method is the most competitive. A specific instance of the CC method, CCSD(T) (coupled cluster single double triple) provides some of the most highly accurate results available in computational chemistry. [8, 9, 10, 11]

Thus, CC methods serve as a competitive benchmark for correlation energies obtained using the MC-MP2 method discussed in this thesis. However, its computational cost scaling makes it prohibitively expensive for very large systems. Thus, further development of post-Hartree-Fock methods are still needed to analyze very large molecular systems.

1.5 Perturbation Theory

Perturbation theory is a theory encompassing a broad range of methods in computational physics and chemistry aimed at improving approximations to complex systems by constructing the application of successive refinements known as to the eigenvalues and eigenfunctions of the approximate system. Here, the two most pertinent examples to the many-body electronic structure problem are discussed.

1.5.1 Rayleigh-Schrödinger Perturbation Theory

Suppose one is already given the eigenfunctions and eigenvalues of an *approximate* Hamiltonian $\hat{\mathcal{H}}_0$, which relates to the full Hamiltonian $\hat{\mathcal{H}}$ through the addition of *perturbation* $\hat{V}$, i.e.

$$\hat{\mathcal{H}} \left| \Psi_i \right\rangle = (\hat{\mathcal{H}}_0 + \lambda \hat{V}) \left| \Psi_i \right\rangle = E_i \left| \Psi_i \right\rangle \tag{1.28}$$

where λ is equal to unity, and used purely to keep track of terms for future derivation. Next, let the eigenfunctions and eigenvalues of $\hat{\mathcal{H}}$ be expanded into a power series relation with respect to its approximated counterparts.

$$E_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \cdots \tag{1.29}$$

$$\left| \Psi_i \right\rangle = \left| \Psi_i^{(0)} \right\rangle + \lambda \left| \Psi_i^{(1)} \right\rangle + \lambda^2 \left| \Psi_i^{(2)} \right\rangle + \cdots \tag{1.30}$$

where the superscripts represent the successively finer corrections to the energy and wavefunction. For instance, $E_i^{(2)}$ represents the second-order correction to the ith energy. This expansion of the eigenvalues and eigenfunctions into a sum of successive corrections to their zeroth-order approximations is *Rayleigh-Schrödinger perturbation theory* (RSPT). To simplify this discussion, the expressions for third and higher-order perturbations will not be discussed, for their expressions are exceedingly cumbersome, and serve little purpose in the discussion of the MC-MP2 method, a variant of second-order perturbation theory.

Next, let equations 1.29 and 1.30 be substituted into the perturbation expansion 1.28. Gathering the zeroth, first, and second order terms corresponding to $1, \lambda, \lambda^2$ respectively, one finds

$$\hat{\mathcal{H}}_0 \, |\Psi_i^{(0)}\rangle = E_i^{(0)} \, |\Psi_i^{(0)}\rangle \tag{1.31}$$

$$\hat{\mathcal{H}}_0 \, |\Psi_i^{(1)}\rangle + \hat{V} \, |\Psi_i^{(0)}\rangle = E_i^{(0)} \, |\Psi_i^{(1)}\rangle + E_i^{(1)} \, |\Psi_i^{(0)}\rangle \tag{1.32}$$

$$\hat{\mathcal{H}}_0 \, |\Psi_i^{(2)}\rangle + \hat{V} \, |\Psi_i^{(1)}\rangle = E_i^{(0)} \, |\Psi_i^{(2)}\rangle + E_i^{(1)} \, |\Psi_i^{(1)}\rangle + E_i^{(2)} \, |\Psi_i^{(0)}\rangle . \tag{1.33}$$

Further simplification of the above expressions by taking advantage of the orthogonality and completeness of the set $\{|\Psi_i^{(0)}\rangle\}$ results in the following expressions for the zeroth, first, and second-order energies.

$$E_i^{(0)} = \langle\Psi_i^{(0)}|\hat{\mathcal{H}}_0|\Psi_i^{(0)}\rangle \tag{1.34}$$

$$E_i^{(1)} = \langle\Psi_i^{(0)}|\hat{V}|\Psi_i^{(0)}\rangle \tag{1.35}$$

$$E_i^{(2)} = \sum_{j\neq i} \frac{\langle\Psi_i^{(0)}|\hat{V}|\Psi_j^{(0)}\rangle \langle\Psi_j^{(0)}|\hat{V}|\Psi_i^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}} . \tag{1.36}$$

1.5.2 Many-body Perturbation Theory

Application of RSPT to the many-body electronic problem is termed *many-body perturbation theory* (MBPT), and aims at improving the approximate energies and wavefunctions obtained by the HF method. In MBPT, a two-body perturbation, which removes the mean-field approximation and replaces it with the two-electron Coulomb operator, is applied to the Hartree-Fock operator. This can be explicit as follows.

$$\hat{\mathcal{H}}_0 = \sum_i \hat{f}(\boldsymbol{x}_i) = \sum_i \left[\hat{h}(\boldsymbol{x}_i) + \hat{v}^{\text{HF}}(\boldsymbol{x}_i)\right], \tag{1.37}$$

$$\hat{V} = \sum_i \sum_{j>i} \frac{1}{r_{ij}} - \sum_i \hat{v}^{\text{HF}}(\boldsymbol{x}_i). \tag{1.38}$$

The second-order MBPT (termed *MP2*) energy expression can then be derived using the second-order RSPT energy expression in 1.36 through substitu-

tion into equatoin 1.28 and simplification of two-electron integrals. The rules for simplifying such integrals are given in Appendix TBD. It turns out that only doubly-excited determinants contribute to the MP2 correction, and the final expression for a *closed-shell system* (with no unpaired electrons in any spatial orbital) is given by the relation

$$E^{(2)} = \sum_{a,b}^{\text{occ}} \sum_{r,s}^{\text{vir}} \left[\frac{2 \langle ab|rs \rangle \langle rs|ab \rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} - \frac{\langle ab|rs \rangle \langle rs|ba \rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \right], \qquad (1.39)$$

where a, b sum over the occupied spatial orbitals and r, s sum over the unoccupied spatial orbitals, appropriately termed *virtual orbitals*. For future reference, it is useful to separate the summation in equation 1.39 into two separate summations containing the first and second terms, and denote them as "direct" and "exchange" energies respectively, i.e.

$$\begin{aligned} E^{(2)} &= \sum_{a,b}^{\text{occ}} \sum_{r,s}^{\text{vir}} \frac{2 \langle ab|rs \rangle \langle rs|ab \rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} - \sum_{a,b}^{\text{occ}} \sum_{r,s}^{\text{vir}} \frac{\langle ab|rs \rangle \langle rs|ba \rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \\ &= E^{(2)}_{\text{direct}} + E^{(2)}_{\text{exchange}}. \end{aligned} \qquad (1.40)$$

1.5.3 Computational Complexity of MP2

Despite being a size-consistent alternative to CI methods, kth order MBPT methods suffer from a high computational cost scaling similar to that of the coupled cluster methods. The computational complexity is bounded by $O(n^{k+3})$, where n is some measure proportional to the size of molecular system (e.g. number of basis sets) [12, 13]. Interestingly, the bottleneck of the traditional (hereafter termed *direct*) MP2 algorithm is not the evaluation of the two-electron integrals, but rather the transformation of the integral of basis AOs to the integral of MOs using coefficient matrices desired in equation 1.39, i.e.

$$\langle pq|rs \rangle = \sum_{\kappa} \sum_{\lambda} \sum_{\mu} \sum_{\nu} C_p^{\kappa*} C_q^{\lambda*} C_r^{\mu} C_s^{\nu} \langle \kappa\lambda|\mu\nu \rangle, \qquad (1.41)$$

where p, q, r, s denote arbitrary MOs that are linear combinations of the basis AOs $\kappa, \lambda, \mu, \nu$ related by the transformation matrices $C_p^\kappa, C_q^\lambda, C_r^\mu, C_s^\nu$ generated by the HF method.

Despite this transformation being costly to execute each iteration, it is usually still more rapid than pre-computing and storing the integrals, and then loading the integrals from memory. This is especially true for parallel supercomputing applications, where interprocess communication is costly. Furthermore, not many integrals are reused in MP2 energy expression, and thus memory I/O is even more inefficient with respect to computing the transformation in equation 1.41 each iteration.

To understand why this may be so, it is helpful to consider the following analogy. The scaled time difference between one CPU cycle (assuming a 3 GHz CPU) and loading from DIMM RAM is the difference equivalent to the difference between one second and four minutes [14]. If the number of MO integrals is too large to be stored in DIMM RAM, the computational cost is drastically worse; the scaled time requirement (again, given a CPU cycle is one second) of loading from external memory is anywhere between 4 days for SSDs to 9 months for HDDs. Thus, in the case of MP2 methods, the AO-MO transformation in equation 1.41 is a painful but necessary step.

To enhance the applicability of MBPT methods, specifically MP2, more sophisticated, parallelized implementations of MBPT methods are needed. The next chapter will discuss the MC-MP2 method forwarded by the Hirata group, and its relevance towards obtaining solutions to the many-body electronic problem for very large systems.

Chapter 2

The MC-MP2 Method I: Theory

2.1 Monte Carlo Integration

Suppose one wishes to evaluate a multi-dimensional integral on some *finite* interval L,

$$I = \int f(\boldsymbol{x}) \, \mathrm{d}\boldsymbol{x}, \qquad (2.1)$$

where $\boldsymbol{x}$ is high in dimensionality (e.g. 10-dimensional). Quadrature rules become an increasingly poor choice as the dimensionality of the system increases, as the number of integrand evaluations scales with respect to $O(n^d)$, where n is the number of points selected for the quadrature rule, and d is the dimensionality of the system. In this case, even a primitive 5-point quadrature rule, insufficient to provide accuracy for anything but simple functions on a small interval, requires $5^{10} = 9,765,625$ integrand evaluations.

Thus, one seeks a method of integration that converges independently of the number of dimensions involved in the problem. This is of particular relevance to the many-body electronic structure problem; the MP2 energy correction in

equation 1.39 requires evaluation of two 6-dimensional integrals.

One such method is *Monte Carlo integration* (MC integration), which involves simply computing an average of the integrand of randomly selected points on L. The *estimator*, $\hat{I}$, thus satisfies the property

$$I \approx \hat{I}(N) = \frac{1}{N} \sum_{i=1}^{N} f({}^{i}\boldsymbol{x}), \tag{2.2}$$

where ${}^{i}\boldsymbol{x}$ is the nth randomly chosen value of $\boldsymbol{x}$ on the interval L. Because the number of integrand evaluations N can be chosen prior to MC integration, this method is independent of the dimensionality of the problem. Given the same number of iterations, the error in MC integration converges more rapidly than any other quadrature rule for high-dimensional problems.

Furthermore, because $\boldsymbol{x}$ is treated as a random variable during MC integration, the *standard error of the integral* converges with respect to $1/N$, and obeys the relation

$$^{N}s = \sqrt{\frac{\sigma^2}{N-1}}, \tag{2.3}$$

where σ^2 can be obtained from its definition,

$$\sigma^2 = \mathrm{E}[(X-\mu)^2] = \int (f(\boldsymbol{x}) - I)^2 \, \mathrm{d}\boldsymbol{x}. \tag{2.4}$$

The main drawback of the MC integration is the slow rate of convergence, as exhibited by equation 2.3. To reduce the uncertainty by a factor of 10, the number of iterations must be increased by a factor of 100. If the uncertainty is already high due to the nature of the integrand or the chosen weight function (discussed later), then MC integration may not exhibit sufficient convergence in any reasonable amount of time. Such practical concerns regarding variance reduction are addressed in the next chapter.

For now, let us focus on deriving a method with which to apply MC integration to the many-body electronic problem, specifically the calculation of

the second-order MP2 energy expression in equation 1.39. The next step is to determine how one should proceed with evaluating an integral over an *infinite* interval.

2.1.1 Importance Sampling

Clearly, one cannot sample an infinite interval in a finite amount of time. Thus, a method of accurately sampling points to evaluate an integral over an infinite interval is needed. To do so, one begins by introducing a well-chosen *weight function* $\omega(\boldsymbol{x})$, such that

$$I = \int \frac{f(\boldsymbol{x})}{\omega(\boldsymbol{x})} \omega(\boldsymbol{x}) \, \mathrm{d}\boldsymbol{x} = \mathrm{E} \left[\frac{f(\boldsymbol{x})}{\omega(\boldsymbol{x})} \right]_{\boldsymbol{x} \sim \omega(\boldsymbol{x})}, \tag{2.5}$$

where the notation to the right of the bracket implies $\boldsymbol{x}$ is sampled according to the weight function $\omega(\boldsymbol{x})$. Given this new function, the estimator then satisfies the relation

$$\hat{I}(N) = \frac{1}{N} \sum_{i=1}^{N} \frac{f(^i\boldsymbol{x})}{\omega(^i\boldsymbol{x})} \tag{2.6}$$

where $^i\boldsymbol{x}$ is similarly sampled according to the weight function $\omega(\boldsymbol{x})$. This weighted estimator in equation 2.6 is guaranteed to converge to the original integral of interest in equation 2.1, provided the weight function satisfies the following properties. [15]

- $\omega(\boldsymbol{x})$ has a normalized probability density function (PDF) which satisfies the property

$$\int \omega(\boldsymbol{x}) \, \mathrm{d}\boldsymbol{x} = 1. \tag{2.7}$$

- $\omega(\boldsymbol{x})$ is always greater than 0, and thus does not alter the sign of the integral.

- $\omega(\boldsymbol{x})$ has a slower rate of decay than $f(\boldsymbol{x})$ as it vanishes for large magnitudes of $\boldsymbol{x}$.

- $\omega(\boldsymbol{x})$ satisfies the property

$$\left| \frac{f(\boldsymbol{x})}{\omega(\boldsymbol{x})} \right| < \infty \tag{2.8}$$

except at a countable, finite number of points. In other words, the weighted integral should not diverge.

Another property $\omega(\boldsymbol{x})$ must satisfy, specific to the evaluation of the integrals in the MP2 energy expression, is that it must share the same singularities as $f(\boldsymbol{x})$. In other words, it should diverge at points where $f(\boldsymbol{x})$ diverges. This is important because in the expression for $E^{(2)}$, the two-electron integrals are undefined if r_{12} or r_{34} are zero, and thus the weight function should not sample from such points.

The weight function not only allows one to sample an infinite interval by using a weighted PDF that decays as $|\boldsymbol{x}| \to \infty$, but also lessens uncertainty in the estimate of I. Observe that the variance of equation 2.6 is given by the relation

$$\sigma^2 = \int \left(\frac{f(\boldsymbol{x})}{\omega(\boldsymbol{x})} - I \right)^2 \omega(\boldsymbol{x}) \, \mathrm{d}\boldsymbol{x} = \int \frac{f(\boldsymbol{x})^2}{\omega(\boldsymbol{x})} \, \mathrm{d}\boldsymbol{x} - I^2, \tag{2.9}$$

and that a well-chosen weight function that satisfies the expression

$$\omega(\boldsymbol{x}) \approx \frac{f(\boldsymbol{x})}{I} \tag{2.10}$$

minimizes the variance. However, since I is unknown, it is best to search for a weight function that behaves like $f(\boldsymbol{x})$ everywhere, but is easier to evaluate.

2.1.2 Inverse Transform Sampling

2.2 Laplace Transform Formalism

MC integration thus seems highly applicable to the many-body electronic problem, and the evaluation of the 6-dimensional two-electron integrals of the MBPT

energy corrections. However, the MP2 energy expression as written in equation 1.39 cannot be directly evaluated because of the denominator. This section will investigate the problem of separability, the additional transformations needed to bring about an MC-integrable MP2 energy expression, originally forwarded by Willow and colleagues in the Hirata group [16, 17].

2.2.1 Separability of the MP2 Energy

It is unfortunate that the modern convention for denoting indices over the occupied and virtual MOs is different from the one used by Szabo and Ostlund. For convenience, the MP2 energy is reprinted below with the different indices.

$$
\begin{aligned}
E^{(2)} &= \sum_{i,j}^{\text{occ}} \sum_{a,b}^{\text{vir}} \frac{2 \langle ij|ab \rangle \langle ab|ij \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} - \sum_{a,b}^{\text{occ}} \sum_{r,s}^{\text{vir}} \frac{\langle ij|ab \rangle \langle ab|ji \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \\
&= E^{(2)}_{\text{direct}} + E^{(2)}_{\text{exchange}},
\end{aligned}
\tag{2.11}
$$

where i, j and a, b sum over all occupied and virtual orbitals, respectively. MC integration, because it is an inherently stochastic method that introduces uncertainty, is not suitable for evaluating sums of many integrals, as the error becomes especially tedious and intractable, and the estimate of the MP2 energy would be lost. The objective is to somehow represent this summation into a single, 12-dimensional integral that can be evaluated by MC integration.

One can attempt to do this by multiplying the two-electron integrals together, and expand the direct and exchange energies, but the derivation fails at the following step.

$$
\begin{aligned}
E^{(2)}_{\text{direct}} = 2 \sum_{i,j}^{\text{occ}} \sum_{a,b}^{\text{vir}} &\frac{1}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \\
&\times \left[\iiiint \phi_i^*(\boldsymbol{r}_1) \phi_i(\boldsymbol{r}_3) \phi_j^*(\boldsymbol{r}_2) \phi_j(\boldsymbol{r}_4) \phi_a^*(\boldsymbol{r}_3) \phi_a(\boldsymbol{r}_1) \right. \\
&\left. \times \phi_b^*(\boldsymbol{r}_4) \phi_b(\boldsymbol{r}_2) \times \frac{1}{r_{12} r_{34}} \, \mathrm{d}\boldsymbol{r}_1 \, \mathrm{d}\boldsymbol{r}_2 \, \mathrm{d}\boldsymbol{r}_3 \, \mathrm{d}\boldsymbol{r}_4 \right]
\end{aligned}
\tag{2.12}
$$

$$E_{\text{exchange}}^{(2)} = -\sum_{i,j}^{\text{occ}} \sum_{a,b}^{\text{vir}} \frac{1}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$
$$\times \left[\iiiint \phi_i^*(\boldsymbol{r}_1)\phi_i(\boldsymbol{r}_3)\phi_j^*(\boldsymbol{r}_2)\phi_j(\boldsymbol{r}_4)\phi_a^*(\boldsymbol{r}_4)\phi_a(\boldsymbol{r}_1) \right.$$
$$\left. \times \phi_b^*(\boldsymbol{r}_3)\phi_b(\boldsymbol{r}_2) \times \frac{1}{r_{12}r_{34}} \, \mathrm{d}\boldsymbol{r}_1 \, \mathrm{d}\boldsymbol{r}_2 \, \mathrm{d}\boldsymbol{r}_3 \, \mathrm{d}\boldsymbol{r}_4 \right]$$

$$(2.13)$$

The problem is that the summations over occupied and virtual orbitals is *coupled* by the external denominator, and the sum of integrals cannot be represented as an integral of sums (i.e. the summation operators cannot be *interchanged* with the 12-dimensional integral operator). Thus, some transformation of the denominator is required to separate the denominator.

2.2.2 The Laplace Transform

Thankfully, such a mathematical transformation exists. The *Laplace transform* is defined as the transformation

$$\mathcal{L}\{f(\tau)\}(s) \equiv F(s) = \int_0^\infty f(t)e^{-st} \, \mathrm{d}\tau, \qquad (2.14)$$

where τ is typically called *imaginary time* in physics and chemistry. This is especially relevant in solving differential equations as it can transform derivatives and integrals into algebraic expressions [18]. However, its most relevant property for this discussion is its action on denominators. Observe that

$$\mathcal{L}\{1\}(a+b) = \int_0^\infty e^{-(a+b)\tau} \, \mathrm{d}\tau = \frac{1}{a+b}. \qquad (2.15)$$

2.2.3 MP2 Energy in the Laplace Transform

This observation was made by Almlöf, who derived what is now called the *Laplace transform formalism* of MP2 theory [19, 20, 21]. Application of the

Laplace transform to the energy denominator in equation 2.11 results in the transformation

$$
\begin{aligned}
\mathcal{L}\{1\}(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b) &= \int_0^\infty e^{-(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)\tau} \, \mathrm{d}\tau \\
&= -\int_0^\infty e^{\epsilon_i \tau} e^{\epsilon_j \tau} e^{-\epsilon_a \tau} e^{-\epsilon_b \tau} \, \mathrm{d}\tau.
\end{aligned}
\tag{2.16}
$$

Separation of energy terms is thus achieved through such a transformation. Upon multiplying the exponential energy terms into the integrand of 2.11, the terms are finally separable, and the summation can be moved within the integral to yield

$$
\begin{aligned}
E_{\text{direct}}^{(2)} = -2 \int_0^\infty \iiiint \, o(\boldsymbol{r}_1, \boldsymbol{r}_3, \tau) o(\boldsymbol{r}_2, \boldsymbol{r}_4, \tau) v(\boldsymbol{r}_1, \boldsymbol{r}_3) v(\boldsymbol{r}_2, \boldsymbol{r}_4, \tau) \\
\times \frac{1}{r_{12} r_{34}} \, \mathrm{d}\boldsymbol{r}_1 \, \mathrm{d}\boldsymbol{r}_2 \, \mathrm{d}\boldsymbol{r}_3 \, \mathrm{d}\boldsymbol{r}_4 \, \mathrm{d}\tau,
\end{aligned}
\tag{2.17}
$$

and

$$
\begin{aligned}
E_{\text{exchange}}^{(2)} = \int_0^\infty \iiiint \, o(\boldsymbol{r}_1, \boldsymbol{r}_3, \tau) o(\boldsymbol{r}_2, \boldsymbol{r}_4, \tau) v(\boldsymbol{r}_1, \boldsymbol{r}_4) v(\boldsymbol{r}_2, \boldsymbol{r}_3, \tau) \\
\times \frac{1}{r_{12} r_{34}} \, \mathrm{d}\boldsymbol{r}_1 \, \mathrm{d}\boldsymbol{r}_2 \, \mathrm{d}\boldsymbol{r}_3 \, \mathrm{d}\boldsymbol{r}_4 \, \mathrm{d}\tau,
\end{aligned}
\tag{2.18}
$$

where o, v are defined as

$$
o(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_i^{\text{occ}} \phi_i^*(\boldsymbol{r}_1) \phi_i(\boldsymbol{r}_2) e^{\epsilon_k \tau},
\tag{2.19}
$$

$$
v(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_a^{\text{vir}} \phi_a^*(\boldsymbol{r}_1) \phi_a(\boldsymbol{r}_2) e^{-\epsilon_a \tau}.
\tag{2.20}
$$

Finally, combining the MP2 direct and exchange integrals, the MC-integrable

MP2 energy is given by

$$E^{(2)} = \int_0^\infty \iiiint [o(\boldsymbol{r}_1, \boldsymbol{r}_3, \tau) o(\boldsymbol{r}_2, \boldsymbol{r}_4, \tau) v(\boldsymbol{r}_1, \boldsymbol{r}_4) v(\boldsymbol{r}_2, \boldsymbol{r}_3, \tau)$$
$$- 2o(\boldsymbol{r}_1, \boldsymbol{r}_3, \tau) o(\boldsymbol{r}_2, \boldsymbol{r}_4, \tau) v(\boldsymbol{r}_1, \boldsymbol{r}_3) v(\boldsymbol{r}_2, \boldsymbol{r}_4, \tau)] \quad (2.21)$$
$$\times \frac{1}{r_{12} r_{34}} \, \mathrm{d}\boldsymbol{r}_1 \, \mathrm{d}\boldsymbol{r}_2 \, \mathrm{d}\boldsymbol{r}_3 \, \mathrm{d}\boldsymbol{r}_4 \, \mathrm{d}\tau,$$

Thus, at the cost of another integral over imaginary time, one has obtained a 13-dimensional integral that can be integrated through MC integration. However, in practice, only the inner 12-dimensional integral over spatial coordinates should be evaluated using the MC method. The reasoning is twofold:

1. The exponential term is a well-behaved, monotonically decreasing function. Such functions can be evaluated with quadrature rules with high accuracy given few more than 10–20 points. MC integration could require millions of iterations to achieve the same accuracy.

2. One would need to construct a new weight function to account for the presence of the exponential term, if imaginary time coordinates are to be integrated over via the MC method as well. This unnecessarily complicates evaluation of the integrand and slows convergence.

2.3 The Electronic Importance Function

Because the integral is over an infinite measure, an importance function must be specified for the inner 12-dimensional integral over spatial coordinates in equation 2.21 before the MC method can be applied. The development of such an importance function was forwarded by Willow and colleagues in the Hirata group [16, 17]. The *electronic importance function* is

$$\omega(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4) = \frac{1}{N_g^2} \frac{g(\boldsymbol{r}_1) g(\boldsymbol{r}_2) g(\boldsymbol{r}_3) g(\boldsymbol{r}_4)}{r_{12} r_{34}}, \quad (2.22)$$

where N_g is the normalization constant

$$N_g = \iint \frac{g(\boldsymbol{r}_1)g(\boldsymbol{r}_2)}{r_{12}} \, \mathrm{d}\boldsymbol{r}_1 \, \mathrm{d}\boldsymbol{r}_2, \qquad (2.23)$$

and $g(\boldsymbol{r})$ is the sum of s-type *Gaussian atomic orbitals* (GTOs), each of which are centered on the atoms of system. While this is certainly not the only possible importance function, there are several reasons for why this is a good choice.

- The importance function is computationally efficient. It can be shown that any product of linear combination of Gaussian functions is itself a linear combination of Gaussian functions [22]. This is the *Gaussian product theorem*, and greatly simplifies evaluation of the importance function.

- Related to the preceding point, integrals of linear combinations of GTOs have been extensively studied for the past several decades, as Gaussian functions are common basis AOs in computational chemistry. Thus, calculation of the normalization factor is nearly trivial, for it can be obtained analytically [23].

- The denominator cancels out the singularities of the MP2 energy, namely the $r_{12}r_{34}$ term.

- Using the chosen importance function has been verified to give more rapid convergence than using the electron density spatial distribution as the importance function in existing studies [16].

2.4 Conclusions

The theoretical foundations laid out in this chapter constitute *Monte Carlo second-order MBPT* (MC-MP2), and is the subject of further investigation throughout this thesis.

Chapter 3

The MC-MP2 Method II: Implementation

In the preceding chapter, the theoretical background of the MC-MP2 method was discussed. This chapter focuses on the additional methodology needed for a robust and practical implementation of the MC-MP2 method, and includes discussion of some of my personal contributions to the MC-MP2 method code written by Doran.

3.1 Inverse Sampling

3.2 The Redundant-Walker Algorithm

Unfortunately, direct implementation of the

3.3 The Control Variates Method

3.4 Pseudorandom Number Generation

Pseudorandom number generation is a non-trivial issue in the field of computer science, because truly random numbers are difficult to generate, and are typically limited by hardware I/O. A complete discussion and comparison of random number generation methods is beyond the scope of this text. However, it suffices to mention the general process. *Pseudorandom number generators* (PRNGs) generate a sequence of numbers that approximate sequences generated by truly random processes. However, they are deterministic, and the sequence is entirely dependent on the *seed* provided to the PRNG. The seed value is just a parameter chosen to generate different random sequences each iteration, and is typically chosen from a truly random input, e.g. analog hardware noise. For all subsequent experimental work, the *Mersenne Twister algorithm* is assumed.

3.5 Inverse Transform Sampling

Chapter 4

MC-MP2 Calculations of Selected Dimer Systems

To demonstrate the efficacy of MC-MP2 method I improved upon, the MC-MP2 method was applied to a subset of the S22 data set of interacting dimers [24]; namely the H_2O, CH_4, C_6H_6 (T-shaped), C_6H_6 (parallel–displaced) dimers. The following chapter details the results of this investigation.

4.1   3D Dimer Geometries

For the readers' convenience, this section exhibits the 3D geometries of the dimers chosen for analysis via the MC-MP2 method.

4.2   HF Calculations

For each dimer system, the aug-cc-pVDZ basis set was used for HF and MC-MP2 calculations.
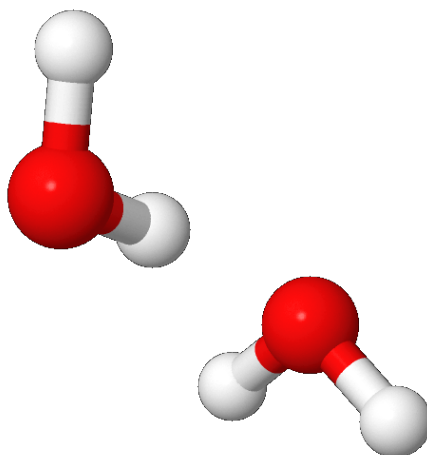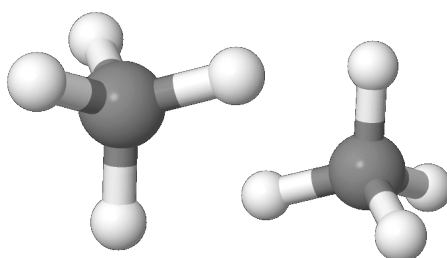
4.3   MP2 Energies

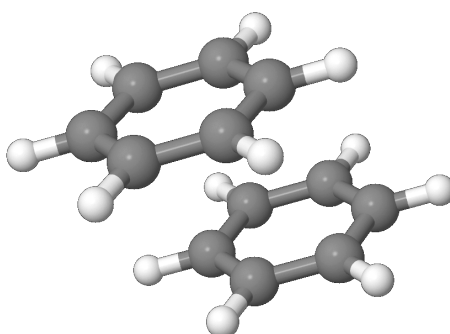Figure 4.1: 3D geometry of H$_2$O dimer.

Figure 4.2: 3D geometry of CH$_4$ dimer.

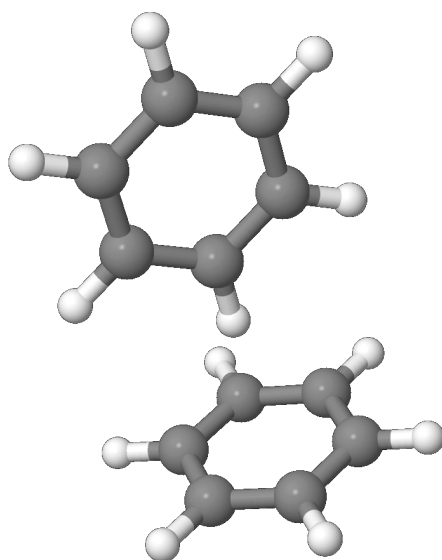Figure 4.3: 3D geometry of C$_6$H$_6$ (parallel–displaced) dimer.

Figure 4.4: 3D geometry of C_6H_6 (T-shaped) dimer.

Chapter 5

Conclusions

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