QUANTUM MONTE CARLO STUDY OF CORRELATED ELECTRONIC SYSTEMS

BY

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DISSERTATION

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Abstract

Describing correlated electron systems has been a major challenge in computational condensed-matter physics. Quantum Monte Carlo, a powerful computational tool for the study of correlated systems, solves electron correlation problems explicitly. It has been taken as a benchmark method for understanding the correlated systems. Instead of making approximations to Hamiltonian, QMC methods work with the wave functions, and the computational cost scales well with the system size. With the development of parallel computing, QMC calculations on large systems are becoming more and more feasible.

We have investigated two correlated systems with highly accurate fixed node QMC techniques. The first system is a correlated hydrogen model system near the metal to insulator transition. We have successfully identified the transition point by calculating spin and charge properties and analyzing the low energy Hilbert space. The second one is a strongly correlated Fe/O system. Calculations on the Fe atoms, O atoms, and FeO molecules are conducted with multiple highly accurate many-body techniques. The source of errors has been disentangled by comparing the results of the many body techniques with the experimental results. For the Fe and O atoms, the calculated properties coincide well with previous experimental results. For the basis-based techniques, the performance is mainly limited by the basis set. The calculated equilibrium bond length, excitation energy and vibrational frequency of the FeO molecules are also in close agreement with the known values from previous experiments.
To Zhangyang and my parents.
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Chapter 1

Introduction

1.1 Correlated systems

Correlated materials are a wide class of compounds, in which the electronic correlations play an important role in their behaviors and properties. For example, in strongly correlated transition metal materials, the electron interactions give rise to a large penalty for double occupancy of the orbitals, spins on the atoms tend to align ("Hund’s rule"), and there is a competition between the covalent and ionic bonding. These properties allow the strongly correlated transition metal materials to form diverse bonding patterns and magnetic orderings, which makes the transition metals promising for technological applications, such as magnetic refrigeration techniques, catalytic materials, high-temperature superconductivity, and colossal magnetoresistance. Under the profound effect of correlations on materials, the correlated materials exhibit some of the most intriguing phenomena. Also because of the complexity of their electronic structure, describing their physical behavior is challenging.

In principle, if we could solve the Schrödinger equation for a given system, we would be able to compute all of its properties. However, except in special cases, it is computationally intractable to solve the Schrödinger equation exactly for a system with more than around 50 fermions. As a consequence, many approximations have been developed to investigate correlated quantum systems.

There is a selection of different methods with tradeoffs between computational cost and accuracy. DFT is standard and packaged but has serious problems with its accuracy when strong correlations are present. Meanwhile, computers are getting faster, and methods based on many-body wave functions are becoming tractable for systems of size relevant for materials. We would like to investigate these higher accuracy methods in challenging and relevant situations to assess the path forward.

For my first project, I have investigated a correlated model system near the metal to insulator transition, where many spectacular phenomena occur. For example, high-temperature superconductivity, where the materials behave like superconductor at an unusually high temperature; colossal magnetoresistance, where the system properties are very sensitive to the changes of magnetic field; and the magnetocaloric effect,
where the temperature of the magnetic materials are varied by applying a magnetic field.

For my second project, I have investigated a correlated realistic system, FeO. We collaborated with other groups working on many-body techniques to analyze the source of errors and investigate how well we can understand the strongly correlated systems with cutting-edge numerical techniques.

The numerical techniques for correlated systems and the projects I worked on, as well as the code I implemented to facilitate highly automated calculation are briefly discussed in this thesis.

1.2 Outline

The dissertation is laid out as follows:

• Chapter 2 is focused on numerical methods that have been developed to describe correlated systems. The tight binding and Hubbard model are discussed in this section. The introduction on numerical methods covers Hartree Fock, quantum chemistry, Kohn-Sham DFT, GW approximation and quantum Monte Carlo methods.

• Chapter 3 introduces the code I have implemented to improve the output format of QWalk and convert the PySCF output to the QWalk input, which enabled the work presented here, as well as other researchers’ work.

• Chapter 4 describes our study of the metal-insulator transition on hydrogen system with a honeycomb lattice structure, which is one of the simplest strongly correlated systems with the Coulomb interaction. We implemented reptation, diffusion, and variational Monte Carlo methods to investigate the mixed estimator error and the fixed node error.

• Chapter 5 introduces the properties of transition metals, and the current experimental and numerical studies that have been done for several interesting transition metal materials, including FeO monoxides, iron complexes, and FeSe superconductors. Their interesting properties, and the performance of numerical techniques are presented in this chapter.

• Chapter 6 is focused on our benchmark calculations of Fe/O systems. The implemented techniques include FN-DMC, FCI-QMC, AF-QMC, DMRG, GW, MCSCF, HF and MRCI+Q. To make sure that all these techniques agree with each other and the pseudopotential and basis sets work as expected, we started from iron and oxygen atomic systems. For larger system, the one we picked out in particular is FeO molecule. We compared the calculated energy with experimental results to analyze the source of errors. We found that for the small systems like O atom, the error is small as well as the variance...
between different techniques. However, for the larger systems, like Fe atom and FeO molecule, the errors are much larger.

- Finally, the projects I worked on during my graduate study and the accomplishments I have achieved are summarized in Chapter 7.

1.3 Accomplishments

This section describes problems and their resolutions accomplished in my Ph.D. work.

- **Code implementation**

  I have implemented the code to convert the PySCF output to the QWalk input and added JSON output option to QWalk, which contributed to our highly automated calculation package autogen.

- **Identify the metal to insulator transition in hydrogen honeycomb lattice**

  We have implemented fixed node Monte Carlo methods, and calculated the energies for different lattice constants and spin states, i.e. the spin unpolarized state and the Néel state. Order parameters, including compressibility, double occupation, spin-spin correlation, spin structure factor and staggered moment are calculated. The transition point is successfully identified by fitting of the energy as a function of order parameters.

- **Benchmark calculation of Fe/O systems**

  We have focused on analyzing the source of errors in these highly accurate techniques. The fixed-node diffusion Monte Carlo is implemented for the atomic systems, i.e. the Fe and O atoms, as well as the FeO molecule systems. Both of the ground and the excited states are investigated and compared. Energies are calculated to compare with the previous experiments. For FeO molecule, the bond length is also varied to find the equilibrium bond length, which has been verified by experiments. The source and scale of errors are disentangled and identified by comparing these techniques as well as with experiments. We find that for a small system, like Fe, it is easy to get a good agreement on different techniques, and the errors are small. But for larger systems, such as Fe atom and FeO molecule, the states are difficult to simulate, and the errors are much larger.

  In summary, this thesis is focused on studying the correlated systems with quantum Monte Carlo methods and exploring the computational limit of many-body quantum systems and its accuracy. I have also contributed to the development of the software for highly automative calculations in order to properly assess the errors.
Chapter 2

Numerical methods for strongly correlated systems

The complex physical phenomena in condensed matter systems arise from the interactions between particles, i.e., electron-electron interaction, electron-ion interaction and ion-ion interaction. If we can model and compute these interactions accurately, we would understand all the properties of this system. In this chapter, I give an overview of models and numerical methods developed for solving correlated systems.

First principle computational approaches are those methods that start from the many-body Schrödinger equation of the interactions,

\[ i\hbar \frac{\partial}{\partial t} \langle \Psi(t) \rangle = \hat{H} \langle \Psi(t) \rangle, \]

(2.1)

\[ \hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \nabla_i^2 - \frac{\hbar^2}{2M} \sum_{l=1}^{L} \nabla_l^2 - \sum_{i,l} \frac{Z_l e^2}{|r_i - R_l|} + \sum_{i,j} \frac{e^2}{|r_i - r_j|} + \sum_{l,l'} \frac{Z_l Z_{l'} e^2}{|R_l - R_{l'}|}, \]

(2.2)

where the lowercase letters are electron indexes, and uppercase letters refer to ions. The first two terms are the kinetic energy of electrons and ions respectively; the third term is the electron-ion interaction, the last two terms are the electron-electron interaction and the ion-ion interaction. If we could solve this differential equation, we would understand all the properties of this system. However, because of the sign problem and the “curse of dimensionality”, solving this many body differential equation is very difficult; for example, a 3D system with N electrons, if we write the many-body wave function on a basis of size M, then the number of Slater determinants is proportional to \( e^{kN} \) \((k > 0)\). Hence, for systems with a large number of electrons, exact calculation is impossible, except in very special circumstances where the sign problem is removable. Various approximations and simplifications are developed to approach the exact results. Basically, they can be classified into two different groups, one making approximations for Hamiltonian, another for wave functions. I will introduce both of them in the following sections.
2.1 Effective Hamiltonian for correlated system

2.1.1 Tight binding model

The tight-binding approximation is one of the simplest models to reduce the complexity of the many-body Schrödinger equation. It assumes that the electrons are independent and considers the interaction of the electron with nuclei and other electrons in an averaged way. The wave function is then approximated as a linear combination of atomic orbitals (LCAO), which are the eigenfunctions of an isolated single atom Hamiltonian \[10, 11\]. If we express the Hamiltonian in the second quantized formalism, the formula is

\[
\hat{H} = -t \sum_{\langle i,j \rangle, \sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + h.c.),
\]

where \(i, j\) are electron indexes and \(\sigma\) refers to spin, \(c_{i,\sigma}^\dagger\) and \(c_{i,\sigma}\) are the creation and annihilation operators, \(t\) indicates the electron hopping between sites\[11, 12, 13\].

The tight binding model can model the band structure of the semiconductor, such as graphene \[14\]. Combined with density functional theory, the density functional tight binding (DFBT) method is widely used for large system calculations \[15, 16\] and pre-screening for more time-consuming DFT calculation in structure searches\[17, 18\]. However, typically the parameters are empirical, and due to its simplicity, the tight binding model has low accuracy in describing correlated systems.

2.1.2 Hubbard model

The Hubbard model improves the tight binding model by adding a repulsion interaction term to the Hamiltonian, and it assumes that the electrons on different sites do not have interaction. For a finite lattice, the Hamiltonian is

\[
\hat{H} = -t \sum_{\langle i,j \rangle, \sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + h.c.) + U \sum_{i=1}^{N} n_{i\uparrow} n_{i\downarrow},
\]

where \(U\) is on-site interaction term, \(\langle i,j \rangle\) represents the summation of nearest neighbors, \(n_{i\sigma}\) is the electron density operator at site \(i\) with spin \(\sigma\) \[19, 20, 21\]. The state of a system is controlled by the ratio of \(U/t\), when \(U \gg t\), electrons barely hop from one site to another, and the repulsion interaction between electrons with different spin is strong, which means electrons are localized and the system is in an insulating state; while \(t \gg U\), the hopping interaction overwhelms the electron interaction, which means electrons are moving freely and the system is in a metallic state.

Despite the simplicity, the Hubbard model provides the insight to the states with the magnetic order,
including metal, insulator and more complicated states like superconductivity\cite{22,23,24} and itinerant ferromagnet \cite{25,26}. Particularly, by modeling the hopping \( t \) and onsite interaction \( U \), Hubbard model contains a correlated metal-insulator transition in its phase diagram. Therefore, it has been studied by numerical techniques. For example, the quantum Monte Carlo method identified the nonmagnetic semi-metal to antiferromagnetic insulator transition of Hubbard model in the 2D Honeycomb lattice at zero temperature and half-filling \cite{27,28}. Sorella’s paper \cite{29} on much larger clusters with QMC technique proved that this SM to AFMI transition is continuous and there is no evidence for the existence of spin liquid phase between those two phases.

### 2.2 Ab-initio methods

Although these effective models qualitatively capture certain microscopic phenomena and describe some specific states, such as the Mott-insulator transition, some other details are ignored. In real applications, we want to get a more accurate description and may be interested in those ignored details. Ab-initio simulation, which includes all the details of the system by starting from the real Hamiltonian, is needed.

Solving the full Hamiltonian (Eq.\ref{eq:full_hamiltonian}) is very difficult. However, the time scale of electrons’ motion is so small compared with the motion of ions that we can take ions as static. Based on this fact, the Born-Oppenheimer approximation\cite{30} assumes that the motion of electrons and ions are separable. The Hamiltonian can then be simplified as the dynamics of electrons,

\[
\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{int}},
\]

(2.6)

which contains the kinetic energies of electrons, the potential energies originate from the electron-nuclei interaction and the electron-electron interaction.

Although this approximation simplifies the equation to a large extent, due to the complexity of the third term, Eq.\ref{eq:full_hamiltonian} is still difficult to be solved exactly. Different ab-initio techniques have different approaches to further simplify Eq.\ref{eq:full_hamiltonian}. In the following, I will give a brief overview of several widely used methods: mean field theory, quantum chemistry and density functional theory. Quantum Monte Carlo techniques will be introduced in the next section.
2.2.1 Mean field theory: Hartree Fock

The Hartree Fock approximation is a mean field method and almost always the starting point of the quantum chemistry methods. It simplifies Eq. 2.5 by ignoring all the electron correlations except those required by Pauli principle \[31\]. As a result, the simplest \(N\)-electron wave function meets this requirement (without spin-orbit interaction) is an anti-symmetrized \(N\times N\) Slater determinant, which changes sign when two particles are exchanged.

\[
\Phi(r_1, r_1, \ldots, r_i, \ldots, r_j, \ldots, r_N) = -\Phi(r_1, r_1, \ldots, r_j, \ldots, r_i, \ldots, r_N).
\] (2.7)

The exact formula of the wave function is

\[
\Phi(R_N) = \frac{1}{\sqrt{N!}} \left| \begin{array}{cccc}
\phi_1(r_1) & \phi_1(r_2) & \phi_1(r_3) & \cdots & \phi_1(r_N) \\
\phi_2(r_1) & \phi_2(r_2) & \phi_2(r_3) & \cdots & \phi_2(r_N) \\
\phi_3(r_1) & \phi_3(r_2) & \phi_3(r_3) & \cdots & \phi_3(r_N) \\
\cdots & \cdots & \cdots & \cdots & \cdots \\
\phi_N(r_1) & \phi_N(r_2) & \phi_N(r_3) & \cdots & \phi_N(r_N) 
\end{array} \right|, \quad (2.8)
\]

where, \(\phi_i(r)\) is called single-particle spin-orbital, which is a linear combination of atomic orbitals, \(\sum_j c^{(i)}_{j} \chi_j(r)\), here \(\chi_i(r)\) is the atomic orbital and \(c^{(i)}_{j}\) is the MO coefficient. Then, system energy is the expectation value of Hamiltonian Eq. 2.6 which has an integral formula \[32\],

\[
E = \langle \Phi | \hat{H} | \Phi \rangle = \sum_i \int dr \psi^*_i(r) \left[ -\frac{1}{2} \nabla^2 + V_{ext}(r) \right] \psi_i(r) + \frac{1}{2} \sum_{i,j} \int dr dr' \psi^*_i(r) \psi^*_j(r') \frac{1}{|r - r'|} \psi_i(r) \psi_j(r') - \frac{1}{2} \sum_{i,j} \int dr dr' \psi^*_i(r) \psi^*_j(r') \frac{1}{|r - r'|} \psi_j(r) \psi_i(r). \quad (2.9)
\]

The determinant Eq. 2.8 is not the exact ground state wave function, but it can be used as the starting trial wave function, and the ground state wave function is achieved by minimizing the total energy Eq. 2.9 with respect to the orbitals \(\phi_i\). This optimization leads to the following Hartree-Fock equation \[32\],

\[
c_i \psi_i(r) = \left( -\frac{1}{2} \nabla^2 + V_{ext}(r) \right) \psi_i(r) + \sum_j \int dr' \frac{\psi_j^*(r')}{|r - r'|} \psi_i(r) - \sum_j \int dr' \psi_j^*(r') \psi_i(r') \frac{1}{|r - r'|} \psi_j(r). \quad (2.10)
\]
The first term is the one body term; the second is the Hartree term, which comes from the mean-field Coulomb interaction, the third term is the exchange term originated from the Pauli exclusion principle, which keeps the electrons with the same spin apart. Eq. 2.10 can be solved exactly in a given basis and end up with the optimized orbital $\psi_\sigma^i$ with eigenvalue $\epsilon_\sigma^i$.

Based on different restrictions on orbital occupation and pairing, the Hartree Fock methods can be classified into three types,

- **Restricted closed shell Hartree Fock (RHF):** All electrons are paired in molecular orbitals, and the paired electrons only differ in spin functions.

- **Restricted open-shell Hartree Fock (ROHF):** The number of spin up electron and spin down electron are not required to be equal.

- **Unrestricted closed shell Hartree Fock (UHF):** Spin up and down electrons are not required to occupy the same set of orbitals, which means the spatial part wavefunction of the $\alpha$(up) and the $\beta$(down) electrons can be different.

Hartree Fock gets the best single Slater determinant wave function; it’s often able to account for $\sim 99\%$ of the total energy of atoms, molecules and solids. It has been applied to the molecular calculations as well as calculating crystal properties, such as cohesive energy and band gap \[33, 34, 35\]. However, the remaining $\sim 1\%$ is essential in describing chemical phenomena. For example, 50\% of the binding energy for nitrogen molecules comes from correlation energy, which is 0.5\% of the total energy\[2\]; the bonding energies and bond distances of the transition metal diatomic molecules and complexes are also highly related to electron correlation\[36\].

The energy that the Hartree Fock approximation neglects is the electron correlation energy between opposite spins, which is defined as

$$E_{corr} = E_{exact} - E_{HF}$$

(2.11)

This correlation comes from two sources; the first is the dynamic correlation, which originates from the limitation that the HF model ignores the real interactions between electrons, and the electrons are treated as interacting with the averaged field created by other electrons; another source is the static correlation, which arises from the insufficient description of the many-body system with a single Slater determinant. The boundary between the dynamic correlation and the static correlation is poorly defined, when the static correlation is fixed, the dynamic correlation may be fixed also. One way to ameliorate this limitation
is by calculating with UHF. By allowing electrons with opposite spin to have different spatial functions, UHF takes the correlation between unpaired electrons and paired electrons into account, therefore giving realistic density\cite{37, 38, 39}. However, because of the spin contamination, the wave function is no longer the eigenfunction of the spin operator $\hat{S}^2$.

Let’s illustrate the failure of mean field theory with a simple system, $H_2$, where there are two ions and two electrons. The Hamiltonian is

$$\hat{H} = -t(c_1^\dagger c_2 + c_2^\dagger c_1) + U \sum_i n_i^\uparrow n_i^\downarrow. \quad (2.12)$$

If we allow symmetry breaking, the orbital function on each site is

$$\phi_1 = a|1\rangle + b|2\rangle, \quad \phi_2 = b|1\rangle + a|2\rangle \quad (2.13)$$

Then the mean field ground state wave function is

$$\Psi_{MF} = \phi_1 \phi_2 = ab(|11\rangle + |22\rangle) + a^2|12\rangle + b^2|21\rangle. \quad (2.14)$$

On the other hand, the Heitler-London wave function is

$$\Psi_{HL} = \frac{a}{\sqrt{2}}(|11\rangle + |22\rangle) + \frac{b}{\sqrt{2}}(|12\rangle + |21\rangle),$$

$$a^2 + b^2 = 1,$$

where $a$ and $b$ are two parameters restricted by normalization.

The energies calculated with these two different wave functions are shown in Fig. \ref{fig:energies}, where we fixed $U/t$ as three different values, and plot energy as a function of $a^2$. The upper and lower plots correspond to mean field energy and Heitler London energy respectively. We then plot the value of $a^2$ that minimizes energy for a specific $U/t$, and plot it in Fig. \ref{fig:transition}. The red curve is for the Heitler London wave function, the blue one is for the mean field. As we can see, in the mean-field plot, there’s an abrupt transition, while in Heitler-London, the curve is smooth. This means that the mean-field result is fundamentally wrong. The Heitler-London wave function gives a reasonable result, however, for more complex systems, the construction of Heitler-London wave function is difficult.
Figure 2.1: Energy vs. $a^2$ for Heitler-London and UHF wave functions for a 2-site Hubbard model. Here we evaluated with three different $U/t$. The upper plot is for mean field wave function, and the lower one is for Heitler-London wave function.

Figure 2.2: $a^2$ vs. $U/t$. $a^2$ is the value that minimizes the ground state energy. Blue curve is for mean field model, red curve is for Heitler-London model.
2.2.2 Quantum Chemistry methods

Another approach to include the electron correlation is by including multiple Slater determinants. The variational quantum chemistry methods: configuration interaction, coupled cluster, and multi-configuration self-consistent field theory are all based on multiple Slater determinants.

Configuration interaction (CI)

Electron configuration is defined as the orbital occupation of electrons. If there are \( M \) atomic orbitals and \( N \) electrons, the electrons always first occupy the lowest \( N \) orbitals, these orbitals are called occupied orbitals, the remaining \( M-N \) orbitals are called virtual orbitals. Hartree Fock is a single configuration treatment; it returns us the configuration of electrons that occupying the lowest \( N \) orbitals. In configuration interaction methods, we create more configurations by exciting one or more electrons from occupied orbitals to virtual orbitals. For example, in the water molecule, with the basis set VDZ, there are \( M = 13 \) orbitals and \( N = 10 \) electrons. The Hartree Fock configuration, i.e., ground state configuration, is \((2222200000000)\), the singly excited configuration could be: \((2222110000000)\), \((2221101000000)\), \((2221001000000)\) e.t.c. By exciting the electrons into virtual orbitals, a better description of correlated electrons is achieved.

In the full configuration interaction (FCI) method (also called exact diagonalization), all possible configurations are mixed together to get a better approximation of wave function,

\[
|\Phi_{\text{FCI}}\rangle = |\Phi_0\rangle + \sum_i c_i^a |\Phi_i^a\rangle + \sum_{ij} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \sum_{ijk} c_{ijk}^{abc} |\Phi_{ijk}^{abc}\rangle + \cdots,
\]

where \( \Phi_0 \) is the configuration generated from Hartree Fock calculation; \( \Phi_{ij}^{ab} \) represents the configuration that electrons in orbital \( i \) and \( j \) are excited to orbital \( a \) and \( b \); \( c_{ij}^{ab} \) are the coefficients that need to be optimized in the variational calculation. If we write Eq. 2.15 into an operator formula, we get

\[
|\Phi_{\text{FCI}}\rangle = \hat{C}|\Phi_0\rangle, \quad \hat{C} = 1 + \sum_p \hat{C}_p.
\]

The FCI excludes all the other errors and leads to the exact energy and wave function described by a given basis set. According to Weyl's formula, the size of FCI space for a system with \( M \) orbitals and \( N \) electrons is

\[
d(N,S,M) = \frac{2S + 1}{M + 1} \left( \frac{M + 1}{N/2 - S} \right) \left( \frac{M + 1}{N/2 + S + 1} \right),
\]

where \( S \) is the total spin of the \( N \)-electron system. It increases dramatically as the number of orbitals
increases. For example, \( \text{H}_2\text{O} \) with the VDZ basis set \((M = 13)\), the size of FCI space is 0.4 million; this number will increase to 30 million for the VTZ basis set \((M = 19)\) \[40\]. The computational cost is extremely high for large basis sets and large systems. Therefore, FCI could only be used in calculating relatively small electron systems.

There are several approaches to reduce the complexity. One way is freezing the core and only using the orbitals of the valence shell, or we can delete some high-energy virtual orbitals, which cannot be occupied by electrons. Another method that makes the configuration interaction method more practical is truncated CI, which truncates the number of excitations to a given level. For example, the complexity of CID (with only D excitation) and CISD (with single and double excitations) are \( O(M^6) \) when \( M \) basis orbitals are involved; the number for CISDT and CISDTQ are \( O(M^8) \) and \( O(M^{10}) \) respectively. Hence, the computational cost of the truncated CI is significantly lower than FCI; it yields an upper bound of energy for electron systems, but it is not size consistent.

CI achieves a significant advance in calculating small molecules, such as \( \text{H}_2\text{O}, \text{F}^- \) \[45, 46\]. It effectively takes a large portion of correlation interactions into consideration. In the calculation of helium atoms with four configurations, 88% of the correlation is recovered and the importance of the angular electron correlation is underlined\[47\]. 89% of correlation energy for \( \text{LiH} \) is recovered with only 45 configurations\[48\]. With the development of parallel computing, huge FCI benchmark calculations have been conducted in recent years. For example, the calculations of \( \text{N}_2 \) molecule\[49\], \( \text{CN} \) anion\[50\], \( \text{BN} \)\[51\], \( \text{AlN} \) and \( \text{C}_2 \)\[52\], are all based on more than a billion Slater determinants, which would not be possible without advanced computational resources and parallel computing algorithms.

Coupled Cluster Theory

The coupled cluster method is similar to configuration interaction method, which is size consistent. Full coupled cluster (FCC) and FCI both lead to exact energy and wave function within the basis set. The difference between them is that coupled cluster has an exponential form

\[
|\Phi_{\text{CC}}\rangle = \hat{C}|\Phi_0\rangle = \exp(\hat{T})|\Phi_0\rangle, \tag{2.18}
\]

where \( \hat{T} \) is defined as

\[
\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_n \tag{2.19}
\]
with

\[ \hat{T}_1 |\Phi_0\rangle = \sum_{i,\alpha} t^\alpha_i |\Phi^\alpha_i\rangle \]
\[ \hat{T}_2 |\Phi_0\rangle = \sum_{i>j, a>b} t^\alpha_{ij} |\Phi^\alpha_{ij}\rangle \]
\[ \hat{T}_3 |\Phi_0\rangle = \sum_{i>j>k, a>b>c} t^{abc}_{ijk} |\Phi^{abc}_{ijk}\rangle \]  \hspace{1cm} (2.20)

\[ \hat{T}_n \] representing the linear combination of all configurations with \( n \) electron excitations, which is the \( n \) electrons correlation effect. Expanding the exponential form into polynomial form, we end up with a large number of nonlinear cluster terms

\[ |\Phi_{CC}\rangle = \exp(\hat{T})|\Phi_0\rangle \]
\[ = (1 + \hat{T} + \hat{T}^2/2 + \hat{T}^3/3! + \cdots)|\Phi_0\rangle. \]  \hspace{1cm} (2.22)

These nonlinear terms introduce the product of clusters such as \( \hat{T}_1 \hat{T}_2 \) and \( \hat{T}_2 \hat{T}_2 \), which are called disconnected operators. They represent the different types of correlation, for example, \( \hat{T}_1 \hat{T}_2 \) describes the correlation from the orbital rotation, \( \hat{T}_2 \hat{T}_2 \) is the pair-pair correlation [40].

The CI operators are a combination of connected and disconnected coupled cluster operators,

\[ \hat{C}_1 = \hat{T}_1 \]
\[ \hat{C}_2 = \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 \]
\[ \hat{C}_3 = \hat{T}_3 + \hat{T}_1 \hat{T}_2 + \frac{1}{3!} \hat{T}_1^3 \]
\[ \hat{C}_4 = \hat{T}_4 + \frac{1}{2} \hat{T}_2^2 + \hat{T}_1 \hat{T}_2 + \frac{1}{4!} \hat{T}_1^4. \]  \hspace{1cm} (2.23)

From this decomposition, we can foresee which type of correlation effect is more important [40]. In contrast to CI methods, CC coefficients cannot be variationally optimized efficiently. It use a similarity transformed Hamiltonian \( \hat{H}^T = \exp(-\hat{T}) \hat{H} \exp(\hat{T}) \), and the fact that

\[ \langle HF | \exp(-\hat{T}) \hat{H} \exp(\hat{T}) | HF \rangle = E \]
\[ \langle \mu | \exp(-\hat{T}) \hat{H} \exp(\hat{T}) | HF \rangle = 0. \]  \hspace{1cm} (2.24)
where $\mu$ is the determinant with excitation \cite{53}. The optimization starts from

$$\Omega(t) = \langle \mu | \exp(-\hat{T})\hat{H} \exp(\hat{T}) | HF \rangle$$

with an arbitrary set of amplitudes $t$, then expand around the current best guess $t^n$

$$\Omega(t) = \Omega^0(t^n) + \frac{\partial \Omega^1(t^n)}{\partial t} \Delta t + \cdots,$$

the amplitudes are improved with Newton’s method,

$$t^{n+1} = t^n + \Delta t$$

$$\Omega^1(t^n) \Delta t^n = -\Omega^0(t^n) \ [53].$$

One of the advantages of CC is that truncated CC is size extensive, for example the wave function of CCD is

$$|\Phi_{CCD}\rangle = \exp(\hat{T}_2)|\Phi_0\rangle = (1 + \hat{T}_2 + \frac{1}{2!}\hat{T}_2^2 + \frac{1}{3!}\hat{T}_2^3 + \cdots)|\Phi_0\rangle,$$

which guarantees that the energy calculated with truncated CC scales linearly with the number $N$ of the electrons\cite{53,55}. Due to the size extensivity of coupled cluster and the fact that the contribution of connected four electron correlation is very small ($\approx 1\%$), the CCSD(T) has become a golden standard for quantum chemistry\cite{56} and been widely used in describing not only molecules but also periodic systems and transition metals.

**Multi-configurational self-consistent field**

The multi-configurational self-consistent field (MCSCF) is another post-HF method that is developed to deal with the problems that a single Slater determinant can not describe. The MCSCF is quite similar to CI methods. The wave functions are written in CI form as a linear combination of Slater determinants; the CI coefficients are optimized variationally by minimizing the energy. The difference between MCSCF and CI is that the orbitals are also determined by minimizing the CI energy of MCSCF wave function, instead of minimizing the energy of Slater determinants.
The MCSCF wave function is written as

$$\Psi_{mcscf} = \sum c_I \phi_I$$  \hspace{1cm} (2.29)

where $\phi_I$ is the Slater determinant which is selected by the user to be included in MCSCF wave function. A common way to select the Slater determinants is defining an "active" space and select all the combination of configurations in this active space, which is called the complete active space self-consistent field (CASSCF)\[57\]. The energy is then

$$E = \sum_{IJ} c_I c^*_J H_{IJ}$$  \hspace{1cm} (2.30)

where $H_{IJ} = \langle \phi_I | \hat{H} | \phi_J \rangle$. $H_{IJ}$ can be written as one or two-electron integrals; we end up with the formula

$$E = \sum_{pq} h_{pq} \gamma_{pq} + \frac{1}{2} \sum_{pqrs} \Gamma_{pqrs} \langle pq | rs \rangle$$  \hspace{1cm} (2.31)

where $p, q, r, s$ represent the orbitals. $\gamma_{pq}$ and $\Gamma_{pqrs}$ are one-body and two-body density matrices, defined as

$$\gamma_{pq} = \sum_{IJ} c^*_I c_J \gamma_{IJ}^{pq}, \hspace{1cm} \Gamma_{pqrs} = \sum_{IJ} c^*_I c_J \Gamma_{pqrs}^{IJ}$$

$$\gamma_{IJ}^{pq} = \langle \phi_I | \hat{E}_{pq} | \phi_J \rangle, \hspace{1cm} \Gamma_{pqrs}^{IJ} = \langle \phi_I | \hat{E}_{pq} \hat{E}_{rs} - \delta_{qr} \hat{E}_{ps} | \phi_J \rangle,$$

$\hat{E}_{pq}$ is written in terms of creation and annihilation operators

$$\hat{E}_{pq} = a^\dagger_{pq} a_{pq} + a^\dagger_{p\beta} a_{q\bar{\beta}}.$$  \hspace{1cm} (2.32)

As a result, the total CI energy is written in terms of orbitals and CI coefficients.

The normal calculation procedure has three steps: First, select the active space with a subset of occupied and virtual orbitals from HF results. Then, optimize the total energy with the SCF process, and calculate the electron structure in this active space exactly. After that, we rotate the occupied, active and virtual space to minimized energy. The last two steps are repeated until they converge (SCF part).
2.2.3 Kohn-Sham DFT based methods

Methods based on configuration space, such as, configuration interaction and coupled cluster, have a great demand for the computational resource, and calculation can only be performed for small systems. Density functional theory (DFT) provides an alternative approach, which is less accurate, but time efficient and takes the electron correlation into account.

DFT based on Hohenberg-Kohn (HK) theorem, which has the following statements:

- Given the ground state electron density \( n_0(r) \), the non-degenerate ground state (GS) wave function \( \Phi_0 \) can be uniquely determined, which means \( \Phi_0 \) is a functional of \( n_0(r) \).

\[
\Phi_0(r_1, r_2, \ldots, r_N) = \Phi_0[n_0(r)],
\]

(2.33)

where \( n(r) \) is

\[
n(r) = N \int d^3 r_2 \int d^3 r_3 \ldots \int d^3 r_N \Phi^*(r, r_2, \ldots, r_N) \Phi(r, r_2, \ldots, r_N).
\]

(2.34)

Since the observations are defined as expectation value,

\[
O_0 = \langle \Phi_0[n_0(r)] | \hat{O} | \Phi_0[n_0(r)] \rangle = O_0[n(r)],
\]

(2.35)

the observations are also a functional of density, which means as long as we know the ground state density, we would be able to identify all the properties of this system.

- The ground state energy is the lower bound of energy calculated with any other density \( n' \),

\[
E_0 = E_0[n_0] = \langle \phi_0[n_0] | \hat{H} | \phi_0[n_0] \rangle < E[n'],
\]

(2.36)

which is the variational property of density functional theory. When minimizing the energy, the restriction \( \int d^3 r n(r) = N \) is used as a Lagrange multiplier,

\[
\frac{\delta (E[n] - \mu N)}{\delta n(r)} = 0, \quad N = \int d^3 r n(r),
\]

(2.37)

which leads to

\[
\frac{\delta E[n]}{\delta n(r)} = \mu,
\]

(2.38)
where $\mu$ is the chemical potential.

- The $\hat{T}$ and $\hat{V}_{\text{int}}$ in Eq. 2.6 are universal for all systems. The external potential with a given $v(r)$ is non-universal but simple.

$$V_{\text{ext}} = \sum_i v(r_i) = \sum_{i,I} Z_I e^2 |r_i - R_I|$$

$$V_{\text{ext}} = \int d^3r n(r)v(r).$$

When the system is specified ($v(r)$ is specified), we would be able to know $\hat{V}_{\text{ext}}$ explicitly.

Therefore, the energy can be written as a function of density $n(r)$,

$$E_v[n] = T[n] + V_{\text{int}}[n] + \int d^3r n(r)v(r). \quad (2.39)$$

When we have reliable approximations of the universal terms $T[n]$ and $V_{\text{int}}[n]$, the ground state can be achieved by minimizing $E_v[n]$ with respect to $n(r)$.[59]

Theoretically, one would be able to calculate all the observables with $n(r)$. For example, by letting $v(r)$ as a function of lattice constant $a$, we can calculate molecular geometries, unit cell volumes, compressibility, phonon spectra and bulk moduli. Dissociation energy and ionization energy can also be identified by comparing the constituent system energy with the energy of the system with one electron more or less. However, in practice, reliable approximation of $T[n]$ and $V_{\text{int}}[n]$ are hard to identify; on the other hand, minimizing energy is a tough numerical work[59].

The development of the Kohn-Sham approach settles these problems by working with single-particle orbital wave functions rather than the particle density, which makes DFT formally like single-particle theory with correlation included via the so-called exchange-correlation functional. The kinetic functional $T[n]$ of interacting electrons is decomposed into an interacting part and a non-interacting part

$$T[n] = T_s[n] + T_c[n], \quad (2.40)$$

where $s$ and $c$ stand for "single particle" and "correlation". In the single particle picture, $T_s[n]$ is the sum of individual kinetic energies, which could be written in terms of single-particle orbitals $\phi_i(r)$,

$$T_s[n] = -\frac{\hbar^2}{2m} \sum_i N \int d^3r \phi^*_i(r) \nabla^2 \phi_i(r). \quad (2.41)$$
Therefore, we can write $T_s[n] = T_s[\{\phi_i[n]\}]$, which means $T_s$ fully depends on single particle wave functions. The internal potential is approximated as Hartree energy, which is the electrostatic interaction energy of the charge distribution $n(r)$,

$$U_H[n(r)] = \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(r)n(r')}{|r - r'|}. \quad (2.42)$$

Hence, the exact energy is written as

$$E[n] = T[\{\phi_i[n]\}] + U_H[n] + E_{xc}[n] + V_{ext}[n] \quad (2.43)$$

here $E_{xc}[n] = (T[n] - T_s[n]) + (U[n] - U_H[n])$ is the exchange-correlation functional, which includes the many-body electron interactions that are not covered in $T_s$ and $U_H$. Normally, $E_{xc}$ is decomposed into $E_x + E_c$, $E_c$ comes from correlation and $E_x$ is the exchange term due to Pauli principle. For a single Slater determinant wavefunction, the exchange term can be represented explicitly in single particle orbitals as

$$E_x[\{\phi_i[n]\}] = -\frac{e^2}{2} \sum_{jk} \int d^3r \int d^3r' \frac{\phi_j^*(r)\phi_k^*(r')\phi_j(r')\phi_k(r)}{|r - r'|}. \quad (2.44)$$

Taking the derivative of energy with respect to $n(r)$, we get

$$\frac{\delta E[n]}{\delta n(r)} = \frac{\delta T[n]}{\delta n(r)} + \frac{\delta V_{ext}[n]}{\delta n(r)} + \frac{\delta U_H[n]}{\delta n(r)} + \frac{\delta E_{xc}[n]}{\delta n(r)} = \frac{\delta T_s[n]}{\delta n(r)} + v(r) + v_H(r) + v_{xc}(r), \quad (2.45)$$

here $v(r)$ is the external potential, $v_H(r)$ is the Hartree potential, and $v_{xc}(r)$ can be identified once the approximation for $E_{xc}$ is made. If we replace the last three potential terms with effective potential $v_{eff}(r)$, the problem of minimizing energy is replaced by solving the noninteracting Schrödinger equation

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + v_{eff}(r)\right] \phi_i(r) = \epsilon_i \phi_i(r),$$

$$v_{eff}(r, \{\phi_i\}) = v(r) + v_H(r, \{\phi_i\}) + v_{xc}(r, \{\phi_i\}). \quad (2.46)$$

Then, the density can be calculated with these orbital functions

$$n(r) = n_s(r) = \sum_{i=1}^{N} f_i|\phi_i(r)|^2. \quad (2.47)$$

The procedure for solving this problem is called the ”self-consistency cycle”. After the approximation for the exchange-correlation functional is made, we start with an initial guess of $n(r)$ and calculate the corresponding
\(u_s(r)\), then get \(\phi_i\) by solving the differential equation Eq. 2.46, a new density is evaluated with Eq. 2.47. Repeat this process until it converges.

The most widely used approximation for the exchange-correlation functional is the local-density approximation (LDA) [61, 62].

\[
E_{xc}[n] \approx E_{xc}^{LDA}[n] = \int d^3r e_{xc}^{hom}(n(r))
\]

(2.48)

where \(e_{xc}^{hom} = e_x^{hom} + e_c^{hom}\) is the exchange-correlation energy of homogenous gas. The exchange term is known as

\[
e_{xc}^{hom}(n) = -\frac{3e^2}{4} \left(\frac{3}{\pi}\right)^{1/3}n^{4/3},
\]

(2.49)

the correlation energy is approximated from quantum Monte Carlo calculations for electron liquid [63, 64, 65, 66]. The LDA is accurate when the electron density is almost uniform, it also achieves great success when applying for systems that are very different with homogenous gas, such as surfaces and molecules. In the situation where the LDA is not accurate, generalized gradient approximation (GGA), which approximates \(e_{xc}\) as a nonlinear function of \(n(r)\) and \(|\nabla n(r)|\), improves the LDA results [67, 68, 69]. Another widely used functional is hybrid functional, which blends a portion of exact exchange functional from HF with the rest of exchange-correlation functional from other approximations [70]. For example, the exchange-correlation energy from the PBE\(_x\) functional is

\[
E_{xc}^{PBE} = pE_x^{HF} + (1-p)E_{xc}^{PBE} + E_c^{PBE}
\]

(2.50)

In spite of the low accuracy compared to configuration interaction, coupled cluster and quantum Monte Carlo methods, DFT is less computationally demanding, so it has broad applications, for example, QMC methods often use DFT to generate trial wave functions.

### 2.2.4 GW approximation

Density functional theory is time efficient and gives relatively good results for ground state quantities. But for some systems (for example, the s-p, d and f systems), the widely used LDA approximation suffers from serious discrepancies for band gap problems. It overestimates the bandwidth of Na for 10 – 20% [71] and Ni for \(\sim 30\%\) [72, 73]; the band gaps in semiconductor systems like, Si, GaAs are underestimated [74]; also for the transition metal oxides, LDA underestimate the band gaps to very small values [75, 76, 77] as well.
Figure 2.3: Fundamental gaps of sp compounds from LDA (squares) and GW. Figure from reference [1]. LDA can not evaluate the band gap correctly. GW methods improves the results for band gap.

as the magnetic moments [78, 79], in some cases, gives the totally wrong results for band gaps [80]. Other examples are shown in Fig. 2.3.

The GW approximation is another efficient method that improves LDA and is feasible for large molecules and atoms calculations. It addresses the band gap problems in LDA with perturbation theory. According to Green function theory [81], the equation for calculating the single-particle excitation energy and quasiparticle energy is

\[
\left[ -\frac{1}{2} \nabla^2(r) + V^H(r) \right] \Psi_i(r) + \int d^3r' \Sigma(r, r'; E_i) \Psi_i(r') = E_i \Psi_i(r). \tag{2.51}
\]

The self-energy \( \Sigma \) contains both the correlation and exchange energies. In the Hartree Fock approximation, the exchange potential is written as

\[
\Sigma^x(r, r', t - t') = iG(r, r', t - t')v(r - r')\delta(t - t'). \tag{2.52}
\]

The GW approximation is quite similar to the Hartree Fock approximation [82, 83]: except that it replaces the bare Coulomb interaction \( v \) by a screened interaction \( W \).

\[
\Sigma(1, 2) = iG(1, 2)W(1, 2). \tag{2.53}
\]
After Fourier transform, we get

\[ \Sigma(r, r', \omega) = \frac{i}{2\pi} \int d\omega' G(r, r', \omega + \omega') W(r, r', \omega'), \quad (2.54) \]

where \( W \) is the interaction between electrons in a polarizable medium,

\[ W(r, r') = \frac{e^2}{4\pi\varepsilon_0} \int dr'' \frac{\varepsilon^{-1}(r, r', \omega)}{|r'' - r'|}, \quad (2.55) \]

thus, the GW approximation includes both the exchange and correlation interaction. If we take GWA as a perturbation of LDA, the \( G \) term can be guessed from the Kohn-Sham wave function,

\[ G(r, r', \omega) = \sum_i \frac{\Psi_{KS}^*(r')\Psi_{KS}(r)}{\omega - \epsilon_{KS}^i \pm i\eta}, \quad (2.56) \]

then we get the final energy

\[ \epsilon_{GW}^i = \epsilon_{LDA}^i + Z_i \langle \Psi_{LDA}^i | \Sigma_{xc}(\epsilon_{LDA}^i) - v_{LDA}^i | \Psi_{LDA}^i \rangle, \quad (2.57) \]

where \( Z_i = 1/(1 - \partial \Sigma_{xc}/\partial \epsilon) \). The calculation is implemented as follows:

- Get \( \Psi_{LDA}^i \) and \( \epsilon_{LDA}^i \) from density functional theory.
- Calculate \( W \) and \( G \) from Eq. 2.56 and Eq. 2.55 respectively, get \( \Sigma^{GW} \).
- Calculate \( \Psi_{GW}^i \) and \( \epsilon_{GW}^i \) with Eq. 2.57 If self consistent, return the eigenvalues and eigenfunctions. If not, repeat the last two steps.

The GW approximation gets better band gap than LDA as shown in Fig. 2.3; nonetheless, the calculation cost is much heavier, other technical approximations like \( G_0W_0 \), are developed to improve the efficiency \[84\].

### 2.3 Quantum Monte Carlo methods

Quantum Monte Carlo methods work with wave functions and are closely related to Monte Carlo methods used in statistics. There are many QMC methods, for example, the auxiliary-field quantum Monte Carlo (AFQMC) \[85\] \[86\] \[87\] and path integral quantum Monte Carlo (PIQMC) \[88\] \[89\] \[90\], which could be used to compute expectation values of interacting many-electron system in finite and high temperature; full configuration interaction quantum Monte Carlo (FCIQMC) \[91\], which involves a stochastic sampling of Slater determinant space; variational Monte Carlo (VMC), based on the variational property and Metropolis
algorithm; diffusion Monte Carlo (DMC), which is a stochastic projection process to project out ground state wave function. In this section, I will briefly present the basic concepts of these techniques.

### 2.3.1 Monte Carlo and Metropolis algorithm

#### Monte Carlo methods

The Monte Carlo method is a broad class of methods that obtain numerical results by repeatedly sampling the random numbers. One important numerical problem that Monte Carlo methods solved is computing the multi-dimensional integral. The advantage of Monte Carlo methods is that the statistical error in the value of integral does not depend on the dimension, and decreases as the square root of the number of sampling points. This property is based on the central limit theorem\[92\].

Suppose we have a $3N$ dimensional vector $\mathbf{R} = (r_1, r_2, \cdots, r_N)$, which has a probability distribution $P(\mathbf{R})$. Therefore, the integral of $P(\mathbf{R})$ in the space of $\mathbf{R}$ is

$$\int d\mathbf{R} P(\mathbf{R}) = 1,$$

(2.58)

with $P(\mathbf{R}) > 0$. Let’s consider a square-integrable function $f(\mathbf{R}) = f(r_1, r_2, \cdots, r_N)$, where $\mathbf{R}$ has probability distribution $P(\mathbf{R})$. Then the mean $\mu_f$ and variance $\sigma_f^2$ of $f$ are given by

$$\mu_f = \int d\mathbf{R} f(\mathbf{R}) P(\mathbf{R}) = \int d^N \mathbf{r} f(r_1, r_2, \cdots, r_N) P(r_1, r_2, \cdots, r_N),$$

$$\sigma_f = \int d\mathbf{R} (f(\mathbf{R}) - \mu_f)^2 P(\mathbf{R}).$$

The central limit theorem states that, for a set of mutually independent vector $\{\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_M\}$, which has distribution function $P(\mathbf{R})$, the new random number $I_f$ defined as

$$I_f = \frac{f(\mathbf{R}_1) + f(\mathbf{R}_2) + \cdots + f(\mathbf{R}_N)}{M}$$

(2.59)

is normally distributed with mean $\mu_f$ and standard derivation $\sigma_f/\sqrt{M}$. Therefore, when the number of samples goes to infinity, $I_f$ converges to the integral of $f(\mathbf{R}) P(\mathbf{R})$, which is the mean of $f(\mathbf{R})$ with respect to $P(\mathbf{R})$. Meanwhile, the error decrease as $1/\sqrt{M}$, regardless of the dimension of integral and the choice of $P(\mathbf{R})$. Consequently, Monte Carlo is more efficient in calculating multi-dimensional integrals compared with conventional quadrature methods.
Metropolis algorithm

The Metropolis algorithm is used to generate samples from an arbitrary distribution, for which direct sampling is impossible. It generates an initial configuration $R$, which is a random walker. Then a move to a new configuration $R'$ is proposed based on the probability density function $T(R \rightarrow R')$. This move is accepted with probability

$$
\rho(R \rightarrow R') = \min \left( 1, \frac{T(R \rightarrow R') P(R')}{T(R' \rightarrow R) P(R)} \right).
$$

(2.60)

When it reaches the equilibrium state, the walkers are distributed according to a specific distribution, and the number of walkers moving from $dR$ to $dR'$ is equal to the number that moving in the opposite direction.

The probability that a walker at $R$ will move to $R'$ is $dR' \rho(R \rightarrow R') T(R \rightarrow R')$, therefore, in the equilibrium state, with the detailed balance, we get

$$
n(R) \rho(R \rightarrow R') T(R \rightarrow R') dR' = n(R') \rho(R' \rightarrow R) T(R' \rightarrow R) dR.
$$

(2.61)

We know that the ratio of acceptance probabilities for those moves is

$$
\frac{\rho(R \rightarrow R')}{\rho(R' \rightarrow R)} = \frac{T(R \rightarrow R') P(R')}{T(R' \rightarrow R) P(R)}
$$

(2.62)

it follows that

$$
\frac{n(R)}{n(R')} = \frac{P(R)}{P(R')}
$$

(2.63)

which means the equilibrium distribution is proportional to our target distribution $P(R)$.

2.3.2 Variational Monte Carlo

Variational Monte Carlo (VMC) method is a combination of variational principle and the Metropolis algorithm[93,94]. It calculates the variational energy associated with trial wave function $\Psi_T$ and Hamiltonian $\hat{H}$, which is the upper bound of the exact ground state energy $E_0$,

$$
E = \frac{\langle \hat{H} \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} = \frac{\int \Psi_T^*(R) \hat{H} \Psi_T(R) dR}{\int \Psi_T^*(R) \Psi_T(R) dR} > E_0.
$$

(2.64)
In VMC, the energy formula is rewritten as

\[
E = \frac{\int |\Psi_T(R)|^2 [\Psi_T(R)^{-1} \hat{H} \Psi_T(R)] dR}{\int |\Psi_T(R)|^2 dR}.
\]  

(2.65)

The Metropolis algorithm is used to sample a set of random numbers \( R_1, R_2, \cdots, R_M \) that have probability distribution \( \frac{|\Psi_T(R)|^2}{\int |\Psi_T(R)|^2 dR} \). The expectation value of energy is evaluated as

\[
E = \frac{1}{M} \sum_{i=1}^{M} E_L,
\]

\[
E_L(R) = \Psi_T(R)^{-1} \hat{H} \Psi_T(R),
\]

here \( E_L \) is called local energy. To get stable and reliable energy results, the trial wave function should meet several basic conditions. \( \Psi_T \) and \( \nabla \Psi_T \) must be continuous, the integral \( \int \Psi_T^* \Psi_T \) and \( \int \Psi_T^* \hat{H} \Psi_T \) must exist, and to ensure finite variance, \( \int \Psi_T^* \hat{H}^2 \Psi_T \) must exist.

Usually, VMC starts with a set of random walkers that have an initial distribution, a trial move is proposed with the Metropolis algorithm, and energy is calculated. The walks keep moving until energy converges. The trial moves are usually sampled from a Gaussian distribution centered at the original positions plus a drift term. To keep the acceptance rate roughly at 50%, the variance of the Gaussian distribution is adjusted. Except for energy, we can also choose to minimize the variance of local energy,

\[
\sigma_{VMC}^2 = \langle E_L^2 \rangle - \langle E_L \rangle^2,
\]  

(2.66)

or the linear combination of energy and variance

\[
C[\Psi_T] = \alpha E_{VMC} + (1 - \alpha) \sigma_{VMC}^2.
\]  

(2.67)

The errors of VMC basically come from two sources. One source is the statistical errors due to the finite sampling of the distribution. Another is the systematic error caused by the approximation made to the trial wave functions. According to the central limit theorem, the statistical error is proportional to \( \sqrt{\text{Var}(E_L)/M} \). The variance of local energy \( E_L \) depends on the sampling distribution. In the limit that \( \Psi_T \) is the exact ground state wave function, \( E_L \) is exact, and the variance is zero, as well as the systematic error. Therefore, the efficiency of VMC depends greatly on the trial wave function.

In practice, the most widely used trial wave function for electron systems is the Slater-Jastrow type wave
function. The formula is written as

$$\Psi(\mathbf{R}) = e^{J(\mathbf{R})} \sum_i D_i(\mathbf{R})D_{i\dagger}(\mathbf{R}),$$

(2.68)

here, $D_{i\dagger}(\mathbf{R})$ is the Slater determinant for spin up electrons, which usually comes from density functional theory, $J(\mathbf{R})$ is the Jastrow factor with a general formula

$$J(\mathbf{R}) = \sum_{i\alpha} c_k^n a_k(r_{i\alpha}) + \sum_{ij} c_k^e b_k(r_{ij}) + \sum_{ij\alpha} c_{klim}^e [a_k(r_{i\alpha})a_l(r_{j\alpha}) + a_k(r_{j\alpha})a_l(r_{i\alpha})]b_m(r_{ij}),$$

(2.69)

where $i$ and $j$ are electron indexes, $\alpha$ is the nuclei index, $r_{ij}$ and $r_{i\alpha}$ are the electron-electron distance and electron-nuclei distance respectively, $a_k(r_{i\alpha})$ is electron-nuclei interaction and $b_k(r_{ij})$ is electron-electron interaction. The two-body term in the Jastrow factor takes the electron correlation into consideration and prevents the superposition of electrons, therefore reducing electron interaction energy. During the VMC calculation, the parameters in the Jastrow factor are optimized.

### 2.3.3 Diffusion Monte Carlo

Diffusion Monte Carlo (DMC) is a stochastic projection method that projects out the ground state by acting the imaginary-time projector $\exp[-\tau \hat{H}]$ repeatedly on a trial wave function $\Psi_T$. The imaginary-time Schrödinger equation is

$$-\frac{\partial}{\partial \tau} \Psi(\mathbf{R}, \tau) = (\hat{H} - E_T)\Psi(\mathbf{R}, \tau).$$

(2.70)

If we apply the projection operator to a trial wave function that has non-zero overlap with ground state wave function, the lowest energy state will be projected out as $\tau \to \infty$,

$$\lim_{\tau \to \infty} \langle \Psi(\tau) \rangle = \lim_{\tau \to \infty} \sum_i e^{(E_i - E_T)\tau} \langle \Psi_i | \Psi \rangle \langle \Psi | \Psi_i \rangle$$

$$= \lim_{\tau \to \infty} e^{(E_0 - E_T)\tau} \langle \Psi_0 | \Psi_T \rangle.$$

(2.71)

The deduction from the first line to the second line in Eq. 2.71 comes from the fact that the excited states energies are higher than the ground state, $E_i > E_0$ ($i > 0$), hence, the corresponding terms decay exponentially faster than the ground state. By adjusting $E_T \approx E_0$, we end up with

$$\lim_{\tau \to \infty} \langle \Psi(\tau) \rangle \propto \langle \Psi_0 \rangle.$$
This is the main concept of diffusion Monte Carlo and other methods that depend on the Green function.

Let’s illustrate the exact algorithm with the Green function,

\[
G(R \leftarrow R', t) = \langle R \mid \exp[-t(\hat{H} - E_T)]\mid R' \rangle = \sum_i \Psi^*(R) \exp[-t(\hat{H}(R) - E_T)]\Psi(R). \quad (2.73)
\]

It satisfies the same differential equation Eq. 2.70 as the wave function. If we only consider the kinetic energy for \(3N\)-dimensional space, this differential equation describes the diffusion stochastic process, and the Green function has a Gaussian expression with a variance \(\tau\),

\[
G(R \rightarrow R', \tau) = (2\pi\tau)^{-3N/2} \exp\left[\frac{-|R - R'|^2}{2\tau}\right]. \quad (2.74)
\]

Then if we add the potential energy to the Hamiltonian, using the approximation of the Trotter-Suzuki formula

\[
\exp[-\tau(\hat{A} + \hat{B})] = \exp(-\tau\hat{B}/2) \exp(-\tau\hat{A}) \exp(-\tau\hat{B}/2) + \mathcal{O}(\tau^3) \quad (2.75)
\]

the Green function can be approximated by

\[
G(R \rightarrow R', \tau) = \langle \Psi(R) \mid e^{-\tau(T+V-E_T)} \mid \Psi(R') \rangle \\
\approx e^{-\tau(V(R') - E_T)/2} \langle \Psi(R) \mid e^{-\tau\hat{T}} \mid \Psi(R') \rangle e^{-\tau(V(R') - E_T)/2} \\
= (2\pi\tau)^{-3N/2} \exp\left[\frac{-|R - R'|^2}{2\tau}\right] \exp[-\tau(V(R') + R' - 2E_T)/2]. \quad (2.76)
\]

This green function is interpreted as transition probability density of walkers that moving from \(R\) to \(R'\), which can be simulated by the stochastic process. The influence of the factor

\[
P = \exp[-\tau(V(R') + V(R') - 2E_T)/2] \quad (2.77)
\]

can be reflected by the birth/death algorithm, in which \(P\) determines the number of walkers that survive to the next step.

The explicit process is shown as follows,

- Propose a move from \(R\) to \(R'\), which is sampled from a Gaussian probability distribution.
- If \(P < 1\), accept this evolution with probability \(P\); if \(P \geq 1\), accept this move, and create another walker with probability \(P - 1\) at the same position.
Figure 2.4: Illustration of the evolution of walkers in the case of single particle in 1D potential well (figure from [2]). The walkers start from a random distribution, after the evolution, the density of walkers at low potential energy region is higher than that in high potential energy region.

It’s evident that in the regions with a high potential, $P$ is small, and the walkers would likely to disappear, and at the low potential regions, the walkers will survive and proliferate. The parameter $E_T$ is adjusted during the process to make sure the total number of walkers are stable. For the case of a single particle in a one-dimensional potential well, the evolution of walkers is illustrated in Fig. 2.4.

**Fermion sign problem and fixed node approximation**

In the previous discussion, we assume that the electron wave function is positive everywhere, therefore, we can treat the wave function as a probability density. This works for the ground state of Boson systems. However, for the fermion systems, there are both positive and negative wave function regions; therefore the wave function is no longer a probability density. This problem is the famous fermion sign problem [96]. The fixed node approximation [97, 98, 99, 100] is developed to resolve this problem. The basic idea of the fixed node approximation is fixing the nodal surface of the initial trial wave function during the stochastic process, which means walkers are not allowed to across the nodes, the nodal surfaces are treated as surfaces with an infinite potential wall, and the lowest energy state is produced within each pocket independently. Fig. 2.5 is a slice of nodal surfaces for two-dimensional electron gas (plot from [3]). If the nodal surface is exact, the
Figure 2.5: A slice of nodal surfaces for two dimensional electron gas with 321 electrons (from [3]). The slice is defined by freezing 160 electron, which is the circles in the plot, and allow the other electrons free to move.

The algorithm for FN-DMC can be extended from normal DMC algorithm easily. The only difference is that, after proposing a move, the sign of the trial wave function is checked and the walker is deleted if the wave function changes sign. However, this simple algorithm is not time efficient, mainly because of the fluctuation of renormalization factor $P$ in Eq. 2.77. The importance sampling transformation [101, 102, 99] improves the efficiency. Instead of directly sampling the wave function, it uses a “guide” wave function $\Psi_T$ to generate the probability distribution $f(R, \tau) = \Psi(R, \tau)\Psi_T(R, \tau)$. The differential equation for $f$ is

$$-\partial_t f(R, \tau) = -\frac{1}{2} \nabla^2 f(R, \tau) + \nabla \cdot [v_D(R)f(R, \tau)] + [E_L(R) - E_T]f(R, \tau), \tag{2.78}$$

where, $v_D(R) = \Psi_T(R)^{-1}\nabla \Psi_T(R)$ is the drift velocity. The corresponding Green function formula is

$$G(R \rightarrow R', \tau) \approx G_D(R \rightarrow R', \tau) G_B(R \rightarrow R', \tau) \tag{2.79}$$

with

$$G_D(R \rightarrow R', \tau) = (2\pi\tau)^{-3N/2} \exp\left[-\frac{[R' - R - \tau v_D(R)]^2}{2\tau}\right] \tag{2.80}$$
and
\[ G_B(R \to R', \tau) = e^{-\tau[E_L(R) + E_L(R') - 2E_T]/2} \quad (2.81) \]

where \( E_L = \Psi_T^{-1} \hat{H} \Psi_T \) is the local energy. Compared with Eq. 2.76, the renormalization factor with importance sampling now contains local energy instead of potential energy. Normally the local energy is close to ground state energy, which is a constant; therefore, the fluctuation is reduced. In addition, the diffusion term of the new Green function involves the drift velocity \( v_D \), which enhances the density of walkers in the region with high \( \Psi_T \), because \( v_D \) pushes walkers to the direction where \( |\Psi_T| \) is increasing. The importance sampling also helps with fixed node constraint, because when the walkers approach the nodal surfaces, the drift velocity will drag them away.

The acceptance probability with importance sampling is then defined as
\[ P(R \to R') = \min \{ 1, \frac{G(R \to R', \tau)\Psi_T^2(R')}{G(R' \to R, \tau)\Psi_T^2(R)} \} = \min \{ 1, \frac{G_D(R \to R', \tau)\Psi_T^2(R')}{G_D(R' \to R, \tau)\Psi_T^2(R)} \}. \quad (2.82) \]

The simulation procedure is
(1), Sample a set of walkers with distribution \( \Psi_T^2 \).
(2), Evaluate drift velocity \( v_D \), and propose a move to \( R' \), which defined as
\[ R' = R + \chi + \tau v_D(R). \quad (2.83) \]

Check whether the wave function changes sign. If yes, move the walker back to original position.
(3), Accept the move with probability defined in Eq. 2.82.
(4), For each walker, the number of copies that will continue in the evolution is
\[ M = \text{Int}(k + e^{-(E_L(R) + E_L(R') - 2E_T)/2}) \quad (2.84) \]

(5) Evaluate the interested quantities by averaging over the walkers.
(6) Repeat the steps 2-6, until reaching the equilibration stage, where the error bars of the quantities are sufficiently small.
The quantities are evaluated with mixed estimator, for example, the energy is

\[
E = \lim_{\tau \to \infty} \frac{\langle e^{-\tau \hat{H}/2} \Psi_T | \hat{H} | e^{-\tau \hat{H}/2} \Psi_T \rangle}{\langle e^{-\tau \hat{H}/2} \Psi_T | e^{-\tau \hat{H}/2} \Psi_T \rangle}
= \lim_{\tau \to \infty} \frac{\langle e^{-\tau \hat{H}} \Psi_T | \hat{H} | \Psi_T \rangle}{\langle e^{-\tau \hat{H}} \Psi_T | \Psi_T \rangle}
= \frac{\langle \Psi_0 | \hat{H} | \Psi_T \rangle}{\langle \Psi_0 | \Psi_T \rangle}
= \frac{1}{M} \sum_m E_L(R_m).
\]

(2.85)

The errors of quantities that do not commute with Hamiltonian have the scale of \(|\Psi_T - \Psi_0|\). One approach to reducing the error is combining the mixed estimator with the variational estimator,

\[
\langle \hat{A} \rangle = 2\langle \Psi | \hat{A} | \Psi_T \rangle - \langle \Psi_T | \hat{A} | \Psi_T \rangle + \mathcal{O}(|\Psi - \Psi_T|^2)
= 2\langle \hat{A} \rangle_{DMC} - \langle \hat{A} \rangle_{VMC} + \mathcal{O}(|\Psi - \Psi_T|^2),
\]

(2.86)

which reduces the error to second order. Therefore, FNDMC only makes approximation on the nodal surfaces and has no restriction on the wave functions within the pockets, and the error is much smaller than VMC.

### 2.3.4 Reptation Monte Carlo

The accuracy of the mixed estimator is determined both by the trial wave function and the fixed node approximation, which makes the evaluation of operators that do not commute with the Hamiltonian less accurate. Reptation Monte Carlo (RMC) \cite{103,104} gets rid of mixed estimator error as well as population bias by propagating both forward and backward. In RMC, the configuration is no longer a single electron configuration \(R\); it is instead a “reptile” that links \(L+1\) electron configurations together \(x = \{R_0 R_2 \ldots R_L\}\). The distribution RMC simulates is

\[
F(x) = \Psi_T(R_0) G(R_0, R_1, \tau) \ldots G(R_{L-1}, R_L, \tau) \Psi_T(R_L).
\]

(2.87)

Therefore, when \(L \to \infty\), at \(R_0\), the Green function \(G(R_{i-1}, R_i, \tau)\) can be viewed as acting on \(\Psi_T(R_L)\), and we get the distribution \(\Psi_T(R_0) \Psi_0(R_0)\). The Green function is symmetric with respect to changing the position of the two coordinates. At \(R_L\), using the same rule, we get the distribution is \(\Psi_0(R_L) \Psi_T(R_L)\). We can further split the formula into two parts; one part acts on \(\Psi_T(R_0)\), another part acts on \(\Psi_T(R_L)\),
then we get

\[
F_{L/2}(x) = G(R_{L/2}, R_{L/2-1}, \tau) \ldots G(R_1, R_0, \tau) \Psi_T(R_0)
\]

\[
G(R_{L/2+1}, R_{L/2+2}, \tau) \ldots G(R_{L-1}, R_L, \tau) \Psi_T(R_L)
\]

\[
= \Psi_0^2(R_{L/2}),
\]  

(2.88)

and the distribution at the center $R_{L/2}$ is $\Psi_0(R_{L/2})\Psi_0(R_{L/2})$, which is the pure ground state distribution.

Hence, for the operators that do not commute with Hamiltonian, we evaluate them with the center distribution, $\langle O \rangle = \langle O(R_{L/2}) \rangle$ if $O$ is local. The energy is evaluated with distributions at the ends, $E = (E_L(R_0) + E_L(R_L))/2$.

The practical implementation in QWalk has following steps:

- Sample $R_0$ with the distribution $\Psi_T\Psi_T$.

- Sample the configurations in the path $x = \{R_0, R_2, \ldots, R_L\}$ one by one by applying only the diffusion part of the Green function with importance sampling. Keep the memory of the previous steps during sampling, and we get a whole set of reptiles.

- We can move both forward and backward. Suppose we decide to move forward, then, we generate another configuration $S$ with importance-sampled diffusion Green function, and we get a new reptile $y = \{R_1, R_2, \ldots, S\}$. The new step is accepted with the Metropolis algorithm,

\[
P(x \to y) = \min \left(1, \frac{F(y)T(y \to x)}{F(x)T(x \to y)} \right),
\]  

(2.89)

where $T(x \to y)$ is the transfer probability of generating the new point, which is $\tilde{G}_D(R_L \to S, \tau)$. If we substitute the $F$ with Eq. 2.87 and cancel the same part, we get

\[
\frac{F(y)}{F(x)} = \frac{\Psi_T(R_1)G(R_L, S, \tau)\Psi_T(S)}{\Psi_T(R_0)G(R_0, R_1, \tau)\Psi_T(R_L)}
\]  

(2.90)

With the importance sampling, the diffusion part of the green function is approximated as

\[
\tilde{G}_D(R \to R', \tau)\tilde{G}_D(R \to R', \tau) \approx \frac{\Psi_T(R')G(R, R', \tau)/\Psi_T(R)}{\Psi_T(R)G_B(R \to R', \tau)}
\]  

(2.91)
Then we end up with

\[
P(x \to y) = \min \left(1, \frac{\exp(-\tau(E_L(R_L) + E_L(S))/2)}{\exp(-\tau(E_L(R_0) + E_L(R_1))/2)} \right),
\]

(2.92)

We decide to accept or reject this new move with probability \(P(x \to y)\).

- Repeat sampling process, until we get enough sampling.

If we choose a direction to propagate at each step, it may take a long time to update a reptile when the length \(L\) is large, which means the correlation time is long. The bounce algorithm [106] improves the efficiency on a large scale by keeping moving in one direction, and change direction when the proposed move is rejected. It has been proved that the bounce algorithm can generate the distribution \(F(x)\). In practice, we should choose an appropriate projection length \(L\) with the tradeoff between calculation efficiency and accuracy. If it is too long, it takes a longer time to update the path, however, when it is too short, the evaluated quantities are not converged.

### 2.3.5 Auxiliary-Field quantum Monte Carlo (AFQMC)

Auxiliary-Field quantum Monte Carlo (AFQMC) is another ground state quantum Monte Carlo method based on the projection operator,

\[
|\Psi_0\rangle \propto \lim_{\tau \to \infty} e^{-\tau \hat{H}} |\Psi_T\rangle
\]

(2.93)

AFQMC method is similar to FNDMC, the difference is that AFQMC works in the second quantized representation in an auxiliary field[107], FNDMC works in first quantized representation and configuration space[108 2].

The Hamiltonian

\[
\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ci} + \hat{V}_{ii}
\]

(2.94)

is represented in the second quantized form with plane-wave basis \(\langle r | G \rangle = \langle r | c_G^{\dagger} | 0 \rangle = \frac{1}{\Omega} e^{iG_k \cdot r}\), where \(G_k\) is the reciprocal lattice vector, and \(\Omega\) is the volume of the simulation cell. Each term in Eq. 2.94 can be
expressed as

\[ \hat{T} = \frac{1}{2} \sum_{G,\sigma} G^2 c_{G,\sigma}^{\dagger} c_{G,\sigma}, \]

\[ \hat{V}_{ei} = \sum_{i\neq j} V_{\text{local}}(G_i - G_j) c_i^{\dagger} c_j + \sum_{i=j} V_{\text{nonlocal}}(G_i, G_j) c_i^{\dagger} c_j, \]

\[ \hat{V}_{ee} = \frac{1}{2\Omega} \sum_{Q \neq 0} \frac{4\pi}{|Q|^2} \rho^{\dagger}(Q) \rho(Q) - \frac{1}{2\Omega} \sum_{\sigma} \sum_{i,j} \frac{4\pi}{|G_i - G_j|^2} c_{G_i,\sigma}^{\dagger} c_{G_i,\sigma} \]

The Hamiltonian is then separated into the sum of the first and second quantized terms \( \tilde{H} = \tilde{H}_1 + \tilde{H}_2 \).

where

\[ \tilde{H}_2 = \frac{1}{2\Omega} \sum_{Q \neq 0} \frac{4\pi}{|Q|^2} \hat{\rho}^{\dagger}(Q) \hat{\rho}(Q) \] (2.96)

is the two-body propagator and \( \tilde{H}_1 \) is the one-body propagator that includes the remaining terms \([109]\).

Through the Hubbard-Stratonovich transformation \([110, 111]\), the two-body propagator is transformed into a high-dimensional integral of one-body propagator over an auxiliary field, written as

\[ e^{-\Delta \tau \tilde{H}_2} = \left( \frac{1}{\sqrt{2\pi}} \right)^{D_x} \int d\sigma e^{-(1/2)\sigma \sigma} e^{\sqrt{\Delta \tau} \sigma \cdot \hat{v}}, \] (2.97)

here \( \sigma \) is a vector of the auxiliary field, and \( D_x \) is the number of possible \( Q \) vector, the operator \( \hat{v} \) is a linear combination of propagator \( \hat{\rho}^{\dagger}(Q) \) and \( \hat{\rho}(Q) \). In the AFQMC random walk, the initial Slater determinant is generated with DFT or other methods, and the operator \( e^{-\tau \tilde{H}} \) is then applied to the Slater determinant until it projects out the ground state. Therefore, each step in the random walk is a matrix multiplication.

### 2.3.6 Full configuration interaction quantum Monte Carlo (FCIQMC)

Full configuration interaction quantum Monte Carlo (FCIQMC) is a combination of stochastic techniques and full configuration interaction\([112, 113]\). It minimizes the energy with respect to sampled FCI wave function expansion.

Here we briefly introduce the semi-stochastic FCIQMC, which reduces the stochastic error bars for a given amount of computational effort, and improves the efficiency on a large scale. The initial trial wave function is simply a linear combination of all Slater determinants that constructed with single-particle orbitals that
span the space

\[ |\Psi_T\rangle = \sum_i c_i |D_i\rangle, \]  

(2.98)

and the wave function is represented by a set of walkers with signed weights and resides on a particular many-electron basis. The projection operator in FCIQMC is defined as

\[ \hat{P} = 1 - \Delta \tau (\hat{H} - S), \]  

(2.99)

where \( S \) is the energy offset that used to control the population of walkers and \( \Delta \tau \) is the time step. The projection operator can also be expanded with the chosen basis set as,

\[ \hat{P} = \sum_{i,j} P_{ij} |i\rangle \langle j|. \]  

(2.100)

In semi-stochastic FCIQMC, the basis set is divided into the deterministic part and the remaining. So does the projection operator,

\[ \hat{P} = \hat{P}^D + \hat{P}^S, \]  

(2.101)

where \( \hat{P}^D \) is a deterministic operator \( \hat{P}^D = \sum_{i \in D,j \in D} P_{ij} |i\rangle \langle j| \) expanded with deterministic basis set, and \( \hat{P}^S \) is the remainder. The \( \hat{P}^D \) operator is applied to the wave function as a matrix multiplication, and \( \hat{P}^S \) is applied with stochastic spawning [113].

One of the most important properties of FCIQMC is that no prior knowledge of wave function is needed. Furthermore, FCIQMC is time efficient, because it finds the correct linear combination of Slater determinants without performing any explicit diagonalization, or similar time-consuming numerical procedure.

2.3.7 Comparison of VMC, DMC and RMC

In this section, I will give a comparison of error sources and accuracy of VMC, DMC and RMC introduced in the previous sections. As shown in Table 2.1 the VMC method is based on the variational principle. It optimizes the parameters in the Slater-Jastrow trial wave function. The expectation values are evaluated with the trial wave function. Hence, the error is proportional to the error of the trial wave function. The advantage of the VMC method is that it’s easy to implement and time efficient. VMC is able to recover 80% of correlation energy. Therefore, VMC is usually used as a preprocessor to optimize the trial wave function.
FNDMC and FNRMC are all based on stochastic projection, which projects out the ground state wave function from the trial wave function by applying the projection operator repeatedly. The difference between RMC and DMC is that the configuration in DMC is a set of walkers’ coordinates, the final distribution is a mixed distribution $\Psi_0 \Psi_T$, and the interested quantities are calculated with mixed estimator; the configuration for RMC is a set of reptiles with pure distribution $\Psi_0 \Psi_0$ in the middle and does not have mixed estimator error. Both RMC and DMC have achieved great success in strongly correlated systems, such as transition metals.

Table 2.1: Comparison of quantum Monte Carlo methods

<table>
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<th>Methods</th>
<th>Basic concept</th>
<th>Accuracy</th>
<th>Error sources</th>
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<td>Variational principle</td>
<td>$O(</td>
<td>\Psi_T - \Psi_0</td>
<td>)$</td>
</tr>
<tr>
<td>FNDMC</td>
<td>Variational principle, stochastic projection</td>
<td>$O(</td>
<td>\Psi_T - \Psi_0</td>
<td>)$ for operators do not commute with Hamiltonian</td>
</tr>
<tr>
<td>FNRMC</td>
<td>Variational principle stochastic projection</td>
<td>Depends on nodal surfaces</td>
<td>Fixed node error, time step bias</td>
<td>$\langle \Psi_0</td>
</tr>
</tbody>
</table>

2.4 Conclusion

In this Chapter, I introduce several widely used techniques for many-body systems. Hartree Fock method assumes the electrons are not correlated, and wave function can be represented with a Slater determinant. Therefore, HF does not include the correlation energies. Post-HF methods, like configuration interaction and coupled cluster, take correlation into consideration by including more than one Slater determinants in the wave function and express Hamiltonian with a basis of Slater determinants. Post-HF can be used to describe both ground state and excited states. However, the computational cost for these methods increases dramatically with the number of Slater determinants. Density functional theory reduces the complexity based on the Hohenberg-Kohn (HK) theorem, which states that the ground state wave function can be determined by the electron density. In this way, DFT reduces the high-particle problem to a one-dimensional problem. The accuracy of DFT depends highly on the approximation of exchange-correlation functional. Instead of making approximations to the Hamiltonian, QMC methods make approximations to the wave function. VMC method is able to recover 80% of correlation and normally used as an optimization process for projection methods. FNDMC, FNRMC, and AFQMC are all projection methods that project out the
ground state wave function from the initial trial wave function. FCIQMC expands the wave function with Slater determinant basis and optimizes the coefficients with random walk. QMC methods are widely used in the calculation of strongly correlated systems and have achieved great successes.

It’s still an open question which technique is the most appropriate in describing a specific system. There are tradeoffs between the computational efficiency and accuracy. If we want a qualitative understanding with low computational cost, DFT is the most suitable method. However, if our goal is achieving highly accurate results, we should explore the wave function techniques, like QMC. Furthermore, with the development of computational resources, reducing the computational cost for wave function techniques is promising.
Chapter 3

Code development for highly automated QMC calculations

3.1 JSON output option of QWalk

QWalk only has text output format, which is inconvenient for read and store. JSON format is more feasible for data collection, especially when many different properties are calculated together. It stores the information in an organized and easy to read manner by implementing the dictionary structure. The following is a sample of the JSON data format,

```json
{
   "label":"vmc",
   "total blocks":5,
   "reblocking":1,
   "warmup blocks":0,
   "properties":{
      "total_energy":{
         "value":-44.41525297,
         "error":0.01533841556,
         "sigma":2.444884847
      },
      "kinetic":{
         "value":31.91396161,
         "error":0.1509705153,
         "sigma":7.297900056
      },
      "potential":{
         "value":81.04407048,
         "error":0.154418257,
```
"sigma": [9.499204722]
},
"nonlocal": {
"value": [4.714855894],
"error": [0.1391727248],
"sigma": [6.092385123]
},
"weight": {
"value": [1],
"error": [0],
"sigma": [0]
},
"EKT": {
"nmo": 16,
"states": [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16],
"normalization": {
"value": [0.06270772658, 0.0619802673, 0.0621343695, 0.0620494216, 0.06293089614, 0.06197488142, 0.0628536, 0.0622545121, 0.06242922159, 0.06210304351, 0.06266751864, 0.06231992245, 0.06267771454, 0.06251599316, 0.06389767548, 0.06250323597],
"error": [0.0004292224666, 0.0005461775922, 0.0005915938263, 0.0003560693443, 0.0003759552907, 0.000271760467, 0.0006658785704, 0.0004728720846, 0.0002082414704, 0.0005992611147, 0.0003451181987, 0.0003715926014, 0.0007304559884, 0.001028953731, 0.0001197905564, 0.0007535315837]
}
}

I implemented the JSON format output option in the QWalk code, which is helpful to the highly automated calculation package autogen developed by our group to set up bulks of PySCF, CRYSTAL, and QMC jobs, check the process and collect the output.
3.2 The interface between PySCF and QWalk

PySCF is a lightweight and efficient quantum chemistry calculation platform implemented with Python. It includes the Hartree Fock, DFT, MCSCF, coupled cluster and so on. The Hamiltonian in the code is flexible and able to be modified. Therefore, PySCF is used to generate multiple initial trial wave functions for QMC calculations in our group. I contributed to the code that converts the PySCF output wave function to the input trial wave function of QWalk.

Five files are needed for the QWalk inputs.

- **System file:** Contains the Hamiltonian and boundary conditions of the simulated system. There are two types of boundary condition: *MOLECULE*, which indicates the system is a molecule with open boundary condition; *PERIODIC*, which defines a bulk material with periodic or twisted boundary condition. The pseudopotential information is also stored in this file.

- **Orbital file:** Contains the molecule orbital coefficients. The molecule orbitals are evaluated with \( \phi_i(r) = \sum_j c_{ij} b_j(r) \), where \( b_j \) is the basis. There are two sections in this file, the first section is a table with headers: MO (indicates \( i \) in the function), AO (basis set label on a given center, i.e. \( b_j \)), Center, Coefficient number. The second section is the coefficient values \( c_{ij} \).

- **Basis file:** Stores basis set used in the QMC calculation.

- **Slater file:** Saves the Slater determinant wave function information. The Slater determinant is defined by several sections with keywords, *ORBITALS*, *DETWT* and *STATES*. *ORBITALS* includes the information that defines the orbitals, it contains the paths of basis and orbital files, and the number of included orbitals. *DETWT* is a list of the weights for determinants. *STATES* lists the molecular orbital occupation, the occupation of spin-up electrons goes first and followed by spin-down. If more than one determinants are included, we continue to list the occupations of other determinants.

- **Jastrow file:** Contains the Jastrow correlation factor of the trial wave function. It includes three types of interaction, electron-electron \( (\sum_{i\alpha} \sum_k c_k a_k(r_{i\alpha})) \), electron-ion \( (\sum_{ij} \sum_k c_k b_k(r_{ij})) \) and electron-electron-ion \( (\sum_{\alpha ij} \sum_{klm} c_{klm} (a_k(r_{i\alpha})a_l(r_{j\alpha}) + a_k(r_{j\alpha})a_l(r_{i\alpha})b_k(r_{ij})) \). Each interaction is written in one section. If only electron-electron interaction and electron-ion interaction are included, then the Jastrow factor is classified as the two-body Jastrow factor. If the electron-electron-ion interaction is also involved, then it belongs to the three-body Jastrow factor.

The output of PySCF is a text file that includes information of energy, orbital occupation and so on. For the MCSCF calculation, the output also includes the coefficients of Slater determinants. There is a built-in
database in PySCF, in which the basis sets and pseudopotential for each element are stored, as well as some build-in functions to calculate properties such as density matrix.

In the conversion interface, I get the information from PySCF output and write it to the required file (and format) for QWalk. The implementation of each function is shortly illustrated as follows.

• System file: Read the material information such as coordinates, charge, spin, and pseudopotential with PySCF build-in functions. Convert these data into the QWalk defined format and write to the .sys file.

• Orbital file: I first evaluated the ratio of PySCF and QWalk normalization factors, because the orbital normalization in PySCF and QWalk are different. Then read in the coefficients and orbitals from PySCF, and convert them to QMC format by multiplying the evaluated ratio to the PySCF coefficients.

• Basis file: Read the basis data with the built-in PySCF function, convert it to the required format for QMC and write it to the .basis file.

• Slater file: Read in the orbital occupations. If calculated with MCSCF, we also read in the coefficients of all the determinants and convert them to the QMC format.

• Jastrow file: We set the Jastrow factor parameters with experience values, and read the basis cutoff and atom types from the PySCF output. Then, these parameters are optimized in the variance and linear optimization steps.

These modifications make it convenient to perform QMC calculations in an automatic way. The only thing we need to do is setup the calculation by defining the required input parameters. With the automated conversion code, the PySCF output is converted to the QWalk input upon finishing the PySCF calculations. The dictionary property of JSON format makes it straightforward to read and store the results of calculations with different methods (PySCF, VMC, DMC and RMC) in a unit. Additionally, the JSON format makes it feasible to store and analyze the results of thousands of calculations in one file. We used this capability to perform the studies in the rest of this dissertation.
Chapter 4

Metal to insulator transition on hydrogen honeycomb lattice

This chapter based largely on this paper[114].

4.1 Metal to insulator transition, challenges and previous work

Many spectacular phenomena occur near phase transitions of correlated electron systems[115]. For example, high-temperature superconductivity[116, 117, 118], colossal magnetoresistance [119, 120], and the magnetocaloric effect[121, 122, 123]. An emblematic correlated phase transition is the metal to Mott insulator transition (MIT), which is a metal-insulator transition that would not occur in the absence of interactions. Near this transition, the system is neither in the non-interacting limit nor in the strongly interacting limit. Because there is no small parameter near the MIT, it is challenging to describe the system theoretically. Single determinant pictures fail qualitatively in this region of physical space[124, 125, 126]. Exotic states in between the insulator and metal, like the spin liquid state [127, 128, 129], have been proposed in this region based on approximate theories. Whether these states might exist in realistic material systems is still very much an open question because solutions either focus on a very simplified model or make large approximations in the solution of the first principles Hamiltonian.

Exact correlated solutions can be found for the Hubbard model. Sorella and collaborators[29] conducted large-scale unbiased quantum Monte Carlo calculation on the honeycomb lattice. They showed that there is no evidence for the spin liquid phase near the transition between semi-metal and antiferromagnetic insulator. However, this is far from realistic systems since the Hubbard model only includes on-site interactions.

For the full first principles Hamiltonian, there are no exact solutions. There are two broad classes of approaches in this case. The first is density functional theory (DFT) plus corrections, such as LDA+U[120, 129, 131] and LDA+DMFT[132, 133]. While these techniques often offer substantial improvement over the underlying DFT calculations[134, 131, 130], they depend on the starting point, parameter values[135], and have significant uncertainty due to double counting of correlations[136]. The second class consists of many-electron wave function techniques, which have no adjustable parameters but are computationally demanding.
and must approximate the wave function form for efficiency. For extended systems, quantum Monte Carlo (QMC) methods, in particular fixed node diffusion Monte Carlo (FN-DMC) is broadly applied, with recent applications\cite{137, 138} to realistic strongly correlated systems. However, the FN-DMC method suffers from the fixed node error, which has not been explored in depth near the metal-insulator transition for realistic periodic systems.

In this study, we investigate the fixed node error of hydrogen honeycomb lattice using fixed node reptation Monte Carlo (FN-RMC). We chose this system for several reasons. First, it is one of the simplest relatively "realistic" systems with a $1/r$ interaction. Second, since there is only one electron per atom, we expect that the nodal error will be at its minimum in this system. We assess the fixed node error by using nodes from both the metallic and antiferromagnetic insulating mean-field states. We investigated several order parameters to identify the transition order and critical point. The investigated order parameters include compressibility, staggered moment, spin structure factor, double occupancy and spin-spin correlation. To find the most accurate ground state quantities, we performed QMC calculations with multiple starting trial wave functions and find the ground state order parameters by fitting. We identified the scale of fixed node error as well as transition point successfully, and find that the order parameters are strongly correlated.

4.2 Phase transition orders

According to Ehrenfest’s classification scheme\cite{139}, the phase transitions are classified to different orders by the derivative of Gibbs potential. It states that the phase transition from $\alpha$ to $\beta$ state is $n$th order, if

\[
\left( \frac{\partial^m G_\alpha}{\partial T^m} \right)_P = \left( \frac{\partial^m G_\beta}{\partial T^m} \right)_P
\]

\[
\left( \frac{\partial^m G_\alpha}{\partial P^m} \right)_T = \left( \frac{\partial^m G_\beta}{\partial P^m} \right)_T
\]

when $m < n$, and fails when $m = n$.

Normally, the first and second orders are of most importance. The first order phase transition has continuous Gibbs potential, but discontinuous first derivatives of the Gibbs potential, $S = -(\partial G/\partial T)_P$ and $V = (\partial G/\partial P)_T$, across the phase boundary. Hence, we may see phenomena such as a collapse in structure. The second order transition has continuous $V$ and $S$, but discontinuous response functions like, $C_p = -T(\partial^2 G/\partial T^2)_P$, $k_T = -(\partial^2 G/\partial P^2)/V$ and $\beta = (\partial^2 G/\partial P \partial T)/V$. A more general classification of second order transition is that there are singularities in these response function rather than finite discontinuity.
Table 4.1: Order parameters

<table>
<thead>
<tr>
<th>Order parameters</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Local compressibility</td>
<td>$\langle (n_i - \langle n_i \rangle)^2 \rangle$</td>
</tr>
<tr>
<td>Double occupancy</td>
<td>$\langle n_i^\uparrow n_i^\downarrow \rangle$</td>
</tr>
<tr>
<td>Staggered moment</td>
<td>$\langle (S_i - S_j)^2 \rangle$</td>
</tr>
<tr>
<td>Spin spin correlation</td>
<td>$C_s(L_{\text{max}}) = \frac{1}{N_{\text{max}}} \sum_{R, \tau_{\text{max}}} \langle S_R \cdot S_{R+\tau_{\text{max}}} \rangle$</td>
</tr>
<tr>
<td>Spin Structure factor</td>
<td>$S_{\text{AF}} = \frac{1}{N} \langle \sum (S_{r,A} - S_{r,B}) \rangle^2$</td>
</tr>
</tbody>
</table>

Here $n_i$, $n_i^\uparrow$, and $n_i^\downarrow$ are the number of total electrons, the number of spin-up electrons, and the number of spin-down electrons on the $i$-th site respectively. Electrons in the unpolarized UNP state have more freedom than those in the Néel state, producing a larger local compressibility for the unpolarized state.

4.3 Calculation procedure

Our calculation was done in three steps. First, we generated Slater determinants with density functional theory. We then multiplied a Jastrow factor to each Slater determinant and optimized the resulting trial wave functions using the VMC method. Finally, we used these optimized trial wave functions to perform reptation Monte Carlo energy calculations. To reduce the fixed-node error, we generate multiple Slater determinants by varying spin states and exchange-correlation functionals. Density functional theory (DFT) calculations were carried out with the CRYSTAL software suite [140, 141]. QMC calculations were performed with the open source package QWalk [95], using a constant time-step of $0.02\text{Ha}^{-1}$ throughout the RMC projection procedure. We checked smaller time-steps with no change in results. We sampled lattice constants between 2.4\AA and 3.3\AA, with a step size of 0.05\AA. To control the finite size error, we varied the system cell size (2x2, 4x4, 6x6 and 8x8).

To identify the MIT transition points and investigate the behavior around transition region, we calculated several order parameters listed in the following table.

**Compressibility:** Compressibility measures the averaged local charge fluctuation on each site. It is defined as

$$\langle (n_i - \langle n_i \rangle)^2 \rangle = \langle (n_i^\uparrow + n_i^\downarrow - \langle n_i^\uparrow + n_i^\downarrow \rangle)^2 \rangle,$$  \hspace{1cm} (4.2)$$

where, $n_i$, $n_i^\uparrow$, and $n_i^\downarrow$ are the number of total electrons, the number of spin-up electrons, and the number of spin-down electrons on the $i$-th site respectively. Electrons in the unpolarized UNP state have more freedom than those in the Néel state, producing a larger local compressibility for the unpolarized state.

**Double occupancy:** Double occupancy evaluates the probability of two opposite spins occupying one
\[ D = \langle n_i \uparrow n_i \downarrow \rangle. \]  

We expect the double occupancy to decrease with the transformation from spin unpolarized to Néel state.

**Staggered moment:** The staggered moment is the averaged spin difference between nearest neighbors,

\[ \langle (S_i - S_j)^2 \rangle = \langle (n_{i \uparrow} - n_{i \downarrow}) - (n_{j \uparrow} - n_{j \downarrow}) \rangle^2, \]  

where \( i \) and \( j \) indicate nearest neighbors. Because spins are uniformly distributed in the unpolarized state and symmetry-broken in the Néel state, we expect the staggered moment to increase with the lattice constant.

**Spin-spin correlation at maximum distance:**

The spin-spin correlation examines the long range correlation between two symmetry-equivalent sites. The spin-spin correlation order parameter is defined as

\[ C_s(L_{\text{max}}) = \frac{1}{N N_{\tau_{\text{max}}}} \sum_{R, \tau_{\text{max}}} \langle S_R \cdot S_{R+\tau_{\text{max}}} \rangle, \]  

where \( S_R \) is the spin operator at site \( R \), and \( \tau_{\text{max}} \) is a vector that connects two symmetry-equivalent sites with maximum distance in the finite cell. \( N_{\tau_{\text{max}}} \) is the number of \( \tau_{\text{max}} \) vectors.

**Spin structure factor:** The spin structure factor also evaluates long range interactions,

\[ S_{\text{AF}} = \frac{1}{N} \langle \sum_r (S_{r,A} - S_{r,B}) \rangle^2. \]  

Here \( S_{r,A} \) and \( S_{r,B} \) are spin operators on the \( A \) and \( B \) sublattices of unit cell \( r \).

### 4.4 Energies calculations

#### 4.4.1 DFT energy

For small lattice constants, the system is well approximated by a noninteracting model, in which there is no formation of spin moments on the hydrogen atoms. Thus one would expect a high-quality trial function to be a single Slater determinant with no spin polarization, which we generate using the restricted Kohn-Sham technique. We will label this trial wave function UNP, for unpolarized. On the other hand, for large lattice constants, the system becomes an antiferromagnetic Mott insulator\cite{142, 143} with Néel order. An
Figure 4.1: DFT energy vs. lattice constant. Here the vertical axis is the energy difference between Néel state and spin unpolarized state. Lines correspond to different hybridization. The inset plot shows the symmetry breaking point (where the AFM functional produces the Néel state) as a function of hybridization.

appropriate trial wave function for this state is the function in which spin symmetry is broken and the up/down determinants are inequivalent. We term this trial wave function the Néel state.

Depending on the density functional used, the Néel state may not be stable relative to the UNP state. In order to obtain both types of trial function, we used hybrid functionals PBE$_x$ [144, 70], where the functional is given by:

\[ E_{xc} = (1 - p)E_{xc}^{PBE} + pE_{xc}^{HF} + E_{xc}^{PBE}. \] (4.7)

The results of these calculations are shown in Fig 4.1. From a mean-field perspective, one would identify the paramagnetic-antiferromagnetic transition at the point that the Néel state becomes lower in energy. This transition point is very sensitive to the percentage of Hartree-Fock exchange in the density functional, varying by 0.6 Å over a reasonable range of values.

4.4.2 RMC energy and Finite size errors

Optimal reptile length

The length of reptile (number of points in a reptile) plays a very important role in RMC calculation. With the increasing of reptile length, updating the reptile takes longer time, therefore, the correlation time will
Figure 4.2: Reptation Monte Carlo energy vs. reptile length. We fixed the lattice constant and initial trial wave function, and calculated the energy with different reptile length. The plot is fitted with exponential function, the green line is the fitted line. We find that 600 is the smallest length where energy converged.

increase. When the reptile length is too short, the sampled wave function is not close to the ground state. The identification of the best reptile length is needed before calculation. Fig. 4.2 shows the RMC energies vs. reptile length. We fixed the lattice constant as 3.5Å and used the same initial trial wave function. The plot is fitted with an exponential function. At length = 600, the energy converges. Hence, we used length = 600 as our optimal reptile length in the following calculations.

**Finite size error**

After setting the optimal reptile length, we evaluated the finite size error by selecting several specific lattice constants and calculating the RMC energies with different atom numbers N. Fig. 4.3 shows the change of energy with the increase of 1/N, starting from the unit cell containing 32 atoms (cell size 4x4), energy increases linearly with the number of atoms.

Fig. 4.4 illustrates the finite size errors. The left plot is the energy difference between Néel state and UNP state, for specific set of lattice constants and hybridization values, the circles are results for finite size (8x8), and triangles represent infinite size results, which is estimated by linear extrapolation from results of 4x4, 6x6, and 8x8 cell size. The right plot is the difference between infinite size and finite size results (8x8 cell size).

Averaging the values on the right plot, we get the finite size error for a unit cell with 128 atoms (8x8)
Figure 4.3: Energy vs. 1/number of atoms. Energy starts to converge linearly at lattice cell size 4×4 (32 atoms).

Figure 4.4: Left: Energy difference between Néel state and UNP state, the circles are finite size (8×8) results, and the triangles are infinite size results. Right: Energy difference between finite size and infinite size results. Different color corresponds to different set of lattice constant and hybridization.
RMC energies

For each value of the lattice constant, we generated a set of Slater determinants that either have spin moments (Néel) or are paramagnetic (UNP) as shown in section 4.4.1. Fig 4.5 shows the RMC energy vs. lattice constant for each of these trial functions. The RMC energies vary by few meV/atom depending on the orbitals. We mark the lowest energy state of a given type (UNP or Néel) by a line on the graph.

One might think to determine the paramagnetic-antiferromagnetic transition at the point where the fixed node energy of the minimum of each of the two different trial functions crosses; in this case at around 2.8Å. However, there are two issues with this approach. First, the properties of the fixed node wave function are not guaranteed to be the same as the trial function. We have noted several cases, for example, VO$_2$ and FeSe$^{[137, 138]}$, where a trial function from an insulating mean-field solution results in a zero gap in fixed-node diffusion Monte Carlo. Second, there is substantial variation of the fixed node energy even within
the same class of trial function, which leads to uncertainty in the transition point.

### 4.5 Identify the ground state values

Our solution to accurately identify the ground state properties is to compute the energy as a function of order parameters of the correlated wave function. The investigated order parameters are listed in Table. 4.1 and summarized in this section. Fig. 4.6 plots the energy as a function of order parameters. As we observe from this plot, energy looks quadratically correlated with the order parameters. Therefore, we fitted each plot with a polynomial function (degree=2). The heatmap in Fig 4.7 shows the calculated ground state order parameters as a function of lattice spacing. We use blue (red) to denote the lower (higher) energy regions. The ground state order parameters are estimated by minimizing the energy for each curve. The curve overlaying the heatmap depicts the fitted ground state compressibility.

The local compressibility (Fig 4.7(d)) and double occupancy (Fig 4.7(e)) curves are smooth, which indicates a continuous transition. Obvious kinks show up simultaneously around $a \approx 2.75 \text{ Å}$ in the plots of staggered moment (Fig 4.7(a)), spin-spin correlation (Fig 4.7(b)) and spin structure factor (Fig 4.7(c)). This observation reveals a paramagnetic-antiferromagnetic transition at a critical point around $a = 2.75 \text{ Å}$. From Fig 4.1 the transition point identified by DFT calculations varies with the change of exchange-correlation.
Table 4.2: Correlation coefficients between order parameters

<table>
<thead>
<tr>
<th></th>
<th>Staggered moment</th>
<th>Spin structure factor</th>
<th>Spin-spin correlation</th>
<th>Double occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Local compressibility</td>
<td>-0.98781498</td>
<td>-0.97847496</td>
<td>-0.97817482</td>
<td>0.99875347</td>
</tr>
<tr>
<td>Staggered moment</td>
<td>0.99791757</td>
<td></td>
<td>0.99789502</td>
<td>-0.99360847</td>
</tr>
<tr>
<td>Spin structure factor</td>
<td></td>
<td>-0.99360847</td>
<td></td>
<td>0.99985429</td>
</tr>
<tr>
<td>Spin-spin correlation</td>
<td></td>
<td></td>
<td>-0.99360847</td>
<td>0.99985429</td>
</tr>
</tbody>
</table>

functional, so it is difficult to accurately estimate the transition point; our QMC results provide a benchmark for the methods like DFT; it appears that in this case, a hybrid of around 20-30% obtains a transition similar to the QMC result. As can be seen from Fig 4.7(c), the RMC calculation can miss the transition if sufficiently poor trial wave functions are used. We found wave functions that are high in fixed node energy, but have very small spin structure factors.

Fig 4.7 can give some hints as to the nature of the metal-insulator transition. First, the order parameters of the minimum energy wave functions change continuously as we pass through the transition, with no discernible jumps. To the limits of our statistical resolution, the energy also appears to have no first-order kinks. The computed transition thus appears to be second order.

To check for intervening phases, we also evaluated the correlation coefficients between different order parameters, with the result shown in Table 4.2. Fig 4.8 shows the correlation between the staggered moment and the other order parameters. We find that these order parameters are almost perfectly correlated. So it appears that our sampling essentially spans only a one-dimensional path through Hilbert space. We never saw a tendency for the RMC process to move outside this path between metal and antiferromagnetic insulator, which might have happened if there are other phases. While it is possible that there are other intervening phases, the fixed node error would have to be large enough to prevent the RMC process from accessing them.

4.6 Mixed estimation error

To investigate the effect of the projection on the wave function, we evaluated VMC, DMC, and RMC calculations using a trial function made up of orbitals from the PBE functional and no hybrid mixing. The code was allowed to break symmetry to form a Néel state, which happens at around 3 Å, as can be seen in Fig 4.1. There are immediately several things that are interesting to note about these curves presented in Fig 4.9. First is that the local compressibility is decreased for all lattice constants as we move from a Slater determinant to a correlated wave function. This is due to a decrease in double occupancy through short-range correlations. Concurrently with this change, the staggered moment increases, since opposite
spin electrons spend more of their time on separate sites, even in the metallic phase. The long-range order parameters, spin-spin correlation, and spin structure factor, also increase.

At the transition, the Slater determinant has a sharp change in all order parameters (same with what we get for $H_2$ in Fig. 2.2). As the treatment of correlation improves, the transition becomes more smooth, to the point that it is very difficult to resolve in the local compressibility. Given that the orbitals from PBE are not optimal, we can see that the transition point identified using this trial function would be somewhat larger than the optimized wave function presented before, but also somewhat smaller than PBE itself. It thus appears that the projection does correct the trial function in the correct direction, but the fixed node error is large enough to prevent a full relaxation.

4.7 Conclusion

We have used reptation Monte Carlo to study a correlated metal-insulator transition on the honeycomb lattice with $1/r$ interactions. The fixed node approximation affects the computed properties of the fixed node wave function significantly. We addressed this by considering an ensemble of wave functions to map...
Figure 4.8: Other order parameters vs. Staggered moment. The order parameters we investigated are linearly correlated.
Figure 4.9: Order parameters computed with a PBE trial function. Green, blue and red colors represent the results calculated with VMC, DMC and RMC respectively. Grey dots are extrapolated values with Equation 2.86. All statistical uncertainties are much smaller than the symbols.
out the low-energy Hilbert space as a function of the order parameters. We observed a change in magnetic state, which we believe to be indicative of the MIT. It is most likely a second order transition; other methods have noticed the transition [145] and we do observe a change of order parameter from zero to finite. We have provided our data which can be used as a high-quality benchmark for density functional theory development; not just for the energy but also the properties of the wave function.
Chapter 5

Correlated electronic states in transition metal systems

5.1 Properties of transition metal materials

Transition metal elements are those that have partially filled d orbitals and can form one or more stable ions with incompletely filled d orbitals. We have wide contact with transition metals in our daily life. Fe is one of the main components of Earth’s mantle; Ti is widely used in manufacturing lightweight durable products; Cr is used as a protective plating on automotive detailing.

Transition metals have a wide range of oxidation states, for example, Fe has oxidation states with Fe$^{2+}$, Fe$^{3+}$ ions, as well as the less common oxidation state FeO$_4^{2-}$, which has charge 6+ for iron. Mn also has oxidation states with various charges, including Mn$^{2+}$ (+2), Mn$_2$O$_3$ (+3), MnO$_2$ (+4), MnO$_4^{2+}$ (+6) and MnO$_4^{-}$ (+7).

Transition metal oxides exhibit diverse structures and properties, which makes transition metal oxides one of the most interesting classes of solids. They can exhibit both metallic and insulating states\cite{146}. The high temperature superconductivity phase was also discovered for transition metals, for example, cuprate series TlCa$_{1-x}$In$_x$Sr$_2$Cu$_2$O$_{7+\delta}$ have $T_c$ in the range of 60 $-$ 80K\cite{147}. With the change of temperature, pressure, and composition, some of those oxides can also traverse between the metallic and insulating regimes. For example, VO$_2$ undergoes a metal to insulator transition with the change of structure\cite{137} or temperature\cite{148}, La$_{1-x}$Sr$_x$VO$_3$ has this transition with the change of composition\cite{149}, and NiO transfers with a pressure increase.

In addition to the diversity in electronic conduction properties, transition oxides also have diverse magnetic properties. CrO$_2$, La$_{0.5}$Sr$_{0.5}$MnO$_3$ are found to be ferromagnets\cite{150, 151, 152}, and NiO, LaCrO$_3$ are antiferromagnetism\cite{153, 154}.

This diversity comes from electron correlation, which results in a large penalty for double occupancy of the orbitals. Electrons tend to align in spin ("Hund’s rule"), and there is a competition between covalent bonding and ionic bonding. Therefore, it is much easier for highly charged transition metal ions to lose more electrons than normal metal ions. There is a small overlap between transition metals’ d orbital and
Figure 5.1: High spin and low spin states for Fe in FeO crystal.

Among all these transition metal elements, Fe is challenging both in the experiment and numerical calculations. It relates to geological phenomena, such as earthquakes, and has many states of different symmetries due to $d$ orbital configuration. In the following section, I will give a brief review of experimental and numerical studies that have been done on Fe materials.

5.2 Review of experimental and numerical studies on Fe materials

5.2.1 FeO crystal

For the transition metal $d$ electrons, there are often two different spin configurations: high-spin and low-spin states, caused by the $\Delta$ splitting of $d$ orbitals, in which the $d$ orbital is split into two energy levels $e_g$ and $t_{2g}$, where $t_{2g}$ has lower energy. In the high-spin state, both $e_g$ and $t_{2g}$ are occupied; in the low-spin state, only $t_{2g}$ is occupied. For FeO monoxide, the electron occupancy of Fe is $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^6$, for oxygen it is $(1s)^2(2s)^2(2p)^6$. The two spin states of Fe are shown in Fig. 5.1. Under ambient conditions, FeO monoxide is in the high-spin state and has a rocksalt structure (B1) shown in Fig. 5.2.

With the change of pressure and temperature, FeO can exhibit many phases, including metallic, in-
sulating, magnetic phases, and structural phases. A collapse of magnetism in Fe\textsubscript{0.94}O from a high-spin to a low-spin state was observed with Mössbauer spectroscopy by increasing the pressure at temperature \( \leq 300K \) \cite{155}. Based on the measurements, they extrapolated their data to high pressure and argued that the Fe in FeO would be entirely in low spin state at pressure 140GPa \cite{155}. After that, a high-resolution X-ray study of FeO monoxides up to 143GPa at room temperature revealed that it remained a magnetic insulator and the high-spin to low-spin transition was not observed \cite{5}. Based on their study and previous studies with different temperatures and pressures \cite{155, 156, 157}, they presented a new magnetic phase diagram \cite{5} of FeO shown in Fig. 5.3. FeO exhibits many phases, including metallic, insulating, magnetic phases, and structural phases. A collapse of magnetism in Fe\textsubscript{0.94}O from high spin to low spin state was observed with Mössbauer spectroscopy by increasing the pressure at temperature \( \leq 300K \) \cite{155}. Based on their measurement, they extrapolated their data to high pressure and argued that the Fe in FeO would be entirely in low spin state at pressure 140GPa \cite{155}. After that, a high-resolution X-ray study of FeO monoxides up to 143GPa at room temperature revealed that it remains a magnetic insulator and the high-spin to low-spin transition is not observed \cite{5}. Based on their study and previous studies with different temperatures and pressures \cite{155, 156, 157}, they presented a new magnetic phase diagram \cite{5} of FeO shown in Fig. 5.3. The maximum temperature of antiferromagnetic phase was extrapolated to 50GPa. Based on their phase diagram, at very high pressure, the antiferromagnetic phase vanishes, and at high pressure and high temperature, the total magnetic moment of Fe may goes to zero.

The metal to insulator transition and structural transition introduced by the change of temperature and pressure have also been investigated. The situ synchrotron x-ray diffraction measurements of FeO at
Figure 5.3: Magnetic phase diagram of FeO, plot from reference [5]. The maximum temperature of anti-ferromagnetic phase is extrapolated to around 50GPa. At very high pressure, the antiferromagnetic phase vanishes, and at high pressure and high temperature, the total magnetic moment of iron may go to zero.
high temperature and pressure indicated that the insulator to metal transition of FeO at high temperature and pressure is caused by the transition from a rocksalt to a NiAs structure\textsuperscript{158}. However, a measure of electrical conductivity did not agree with these results; they showed that FeO metallizes at 70GPa and 1900K, and it keeps the rocksalt structure \textsuperscript{6}. They also obtained a structural and metal-insulator phase diagram through their measurements, shown in Fig. 5.4. This phase diagram shows that the transition boundary has a negative P-T slope.

The phase diagram of FeO also challenges numerical calculations. The density functional study with GGA in the high-pressure region indicated that FeO is antiferromagnetic with an inverse NiAs (iB8) structure and no magnetic collapse was observed\textsuperscript{159}. An \textit{ab initio} calculation with a band structure method and DMFT revealed a high-spin to low spin transition accompanied by the MIT metal-insulator transition by compressing
the lattice volume above 73GPa\textsuperscript{[160]}. Furthermore, a diffusion quantum Monte Carlo calculation with pseudopotential gives similar results; it showed that, at ambient temperature, FeO undergoes a structural transition from rocksalt to NiAs at pressure 65GPa. The calculated ambient pressure properties are in good agreement with the experiments\textsuperscript{[161]}. To investigate how well can these highly accurate techniques describe FeO and how closely they agree with each other, it is necessary to bring different techniques together, and standardized on certain simulation conditions.

5.2.2 Fe complexes

Fe complexes are another challenging group of materials for both experimental and theoretical studies. Fe complexes exist widely in biological systems, they serve as the catalysts for many chemical and biological reactions \textsuperscript{[162, 163]}. The mechanisms of catalyst reactions depend on the spin states of Fe complexes\textsuperscript{[164, 165]}. The ground spin state and the transition from a high-spin to a low spin state play an important role in determining the reaction rate \textsuperscript{[166, 167]} Therefore, our understanding of the catalyst strongly depends on the study of structures and relative energies of the ground and excited spin states.

A Kohn-sham density functional study calculated the electronic structure of Fe\textsuperscript{2+} ion, gaseous FeO and 14 iron complexes\textsuperscript{[168]}. Seven of these complexes belong to Fe(II) group, five to Fe(III) and two to Fe(IV). Each of the Fe complexes has six ligands coordinated to the metal center. To examine the performance of different density functional approximations, 20 exchange-correlation functionals are used. The calculated spin-splitting energies for Fe\textsuperscript{2+} are compared with the experimental data\textsuperscript{[169]}. For the 14 complexes, the functional PW6B95 successfully predict the ground spin state of all these complexes; B3LYP, MPW1B95 and MN15 get 13 predictions right. The local functionals, OPBE, OLYP, and M06-L, get 12 correct. Some functional like M08-SO and M11-L, do not find the correct ground state \textsuperscript{[168]}.

DMC has been benchmarked for transition metal complexes. DMC calculations on four Fe complexes are compared with DFT methods with exchange-correlation functional LSDA, BP86, B3LYP, PBE0 and BHH\textsuperscript{[170]}. All these exchange-correlation functionals fail quantitatively in evaluating the energy splits between the high-spin and low-spin states. They either underestimate the exchange energy or the multiconfigurational character of the Fe complexes.

5.2.3 FeSe

FeSe is one of the most studied iron-based superconductors. The superconducting phase transition critical temperature depends highly on the pressure. When the pressure is 1.48GPa, the observed onset temperature is as high as 27K \textsuperscript{[171]}. \(T_c\) is found to be 37K at \(\sim 7\)GPa and decreases to 6K when further increasing
the compression to $\sim 14\text{GPa}^{[172]}$. A Se NMR study found a similar tendency and showed that the $T_c$ is around $9K$ when there is no pressure, and increases to $37K$ when pressure is applied$^{[173]}$. Another X-ray experiment explored the phase diagram of FeSe$^{[174]}$. The superconducting phase transition temperature increase from $8.5K$ to $36.7K$ with a pressure of $8.9\text{GPa}$. The transition temperature decreases with the increase of pressure. Another interesting property of FeSe they found is that no static magnetic ordering is observed for the whole phase diagram. At high temperatures, the non-magnetic behavior was observed and the structure transfers to NiAs-type. M. C. Rahn$^{[175]}$ performed power inelastic neutron scattering measurements and revealed a strong paramagnetic fluctuation.

In the numerical calculations of FeSe, due to the strong electron correlation, first principle methods like density functional theory still have difficulty in correctly describing it’s magnetic and structural properties. For example, DFT cannot fully describe the superconductor properties with the change of temperature and does not agree with the experimental results in the calculations of the band structure$^{[176, 177, 178]}$. The LDA+DMFT calculation explained how multi-bond correlations generate an incoherent normal state, which agrees semi-quantitatively with observations$^{[179]}$. The highly accurate diffusion Monte Carlo method was also applied to FeSe and obtained the structural and magnetic properties under pressure, which is found agree with experiments$^{[138]}$.

For all these transition metal materials we have discussed above, there are many imperfect techniques, and we would like to carefully evaluate their errors. A collaboration between different numerical methods is needed.
Chapter 6

Benchmark calculation of Fe/O systems

The objective of this study is to bring together different many-body techniques and work on a correlated electron system which is close to realistic materials. We aim at investigating how well we can solve realistic systems.

Fe/O systems are selected as our candidates, because Fe has many states with different symmetries due to the $d^6$ configuration. In order to simplify the problem, we used a small core pseudopotential. It has been proved that the small core pseudopotential has better performance for the later transition metals, like Fe. We cooperated with other groups who are working on many-body techniques. The groups and techniques are listed in Table 6.1. We built a Github repository to share and analyze the data. The format of data and the investigated states are stated in the Github. We also set up monthly meetings to discuss the progress and make plans.

What we want is to get quantitative agreement of different techniques in the calculation of the target quantities (energy and dipole moment). In order to disentangle the multiple sources of error and account for the error cancellations, we standardized on the basis sets and pseudopotential. We used the BFD pseudopotential and Gaussian basis sets [180, 181] (vtz, vqz, v5z, e.t.c).

The error of finite system calculation mainly comes from four different sources, which are listed in Table 6.2. For a calculated quantity $Q$, the error is

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Group</th>
<th>institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>FNDMC</td>
<td>Lucas Wagner, Li Chen</td>
<td>UIUC</td>
</tr>
<tr>
<td>AFMQMC</td>
<td>Shiwei Zhang, Mario Motta, Hao Shi</td>
<td>William and Mary</td>
</tr>
<tr>
<td>DMRG</td>
<td>Garnet Chan, Ushnish Ray</td>
<td>Caltech</td>
</tr>
<tr>
<td>FCIQMC</td>
<td>George Booth</td>
<td>King’s College London</td>
</tr>
<tr>
<td>GW</td>
<td>Mark van Schilfgaarde</td>
<td>King’s College London</td>
</tr>
<tr>
<td>GW</td>
<td>Emanuel Gull, Jia Li</td>
<td>UMICH</td>
</tr>
</tbody>
</table>
Table 6.2: Sources of error in numerical calculation

<table>
<thead>
<tr>
<th>Error type</th>
<th>Symbol</th>
<th>Possible values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relativistic / electrodynamic effects</td>
<td>e</td>
<td>D(Dirac equation), S(Schrödinger/Coulomb equation)</td>
</tr>
<tr>
<td>Basis sets</td>
<td>b</td>
<td>vdz, vtz, vqz, v5z, CBS(complete basis set)</td>
</tr>
<tr>
<td>Pseudopotential</td>
<td>p</td>
<td>BFD, AE (all electrons), FC (frozen core)</td>
</tr>
<tr>
<td>Approximation</td>
<td>a</td>
<td>AFQMC, FNDMC, GW, DMRG, FCIQMC, CASCI, CASSCF</td>
</tr>
</tbody>
</table>

\[ Error_Q(m, e, b, p, a) = Q(m, e, b, p, a) - Q(m, D, CBS, AE, -), \]

which is a function of five parameters m, e, b, p and a. Here m is the material system, e, b, p, a are the quantities listed in the table above. Normally, we assume Q(m, D, CBS, AE, -) is same with experimental value. Here we ignore the error that comes from Born-Oppenheimer approximation.

To examine that the pseudopotential and basis sets are working as expected, we started from the simplest systems: Fe atoms and O atoms, then gradually proceeded to molecules. In the following sections, I will present the results we obtained for different systems and states.

6.1 Benchmark calculation of O atom

6.1.1 Definition of benchmark for O atom

We first calculated the small core O atoms, the pseudopotential includes two core electrons. Therefore, the error caused by pseudopotential is very small. The techniques we used include CASSCF, HF, FNQMC, AFQMC, DMRG, FCIQMC, MRCI+Q, CCSD(T) and GW as introduced in Chapter.

The states we calculated are listed in Table 6.3. With the BFD pseudopotential, there are 6 effective electrons outside the core of O atom, which belong to the 2s and 2p orbitals. We investigated four different states, two of them have neutral charge and the rest have charge +1, in which one electron is taken out from the atom. The electron occupations for these four different states are listed in Fig. 6.1. The ground state
for neutral charge atoms is the $^3P$ state, while the one for charge +1 atoms is $^4S$ state.

For fixed node DMC, the calculation process is,

- Generate multiple trial wave functions with the CASSCF, CASCI, DFT, and HF, which are all implemented in PySCF [182]. To get trial wave functions with various nodal surfaces, in the CASSCF and CASCI calculations, the number of frozen core and active space size are varied.

- Add two-body Jastrow factor to the Slater determinants and optimize the wave functions with variational Monte Carlo.

- Take this optimized function as a guiding function for fixed-node DMC, and evaluate the energy and other interested quantities.

- For each trial wave function, extrapolate energies to the values with $\tau = 0$, and take the lowest-energy result afterward.

### 6.1.2 O atom results

The total energies of O are shown in Fig. 6.2. The four plots correspond to the $^4S$, $^2D$, $^3P$ and $^1D$ state from left to right respectively. The y-axis here is the shifted energy, which is the difference between calculated
Figure 6.2: Total energies of O atom calculated with different methods. These four plots correspond to \( ^4S \), \( ^2D \), \( ^3P \) and \(^1D\) from left to right. The x-axis is the different techniques, y-axis is the shifted energy, which is the difference between calculated value and lowest energy. The colors of dots represent different basis sets.

Figure 6.3: Total energies of O atom calculated with different methods (zoomed). Zoomed in the best results.

energy and the minimum value among all these energies. The different color corresponds to different basis set. Since the methods like DMRG, AFQMC, FCIQMC, CCSD(T), MRCI+Q and GW work within a basis, they have to extrapolate the values to the complete basis set. The yellow color dots are extrapolated complete-basis data.

The correlation energies, which is defined as the energy difference between ground state and Hartree Fock energy, are approximately \( E_{\text{cor}}(^4S) \approx 0.15 \), \( E_{\text{cor}}(^2D) \approx 0.2 \), \( E_{\text{cor}}(^3P) \approx 0.2 \) and \( E_{\text{cor}}(^1D) \approx 0.25 \) Hartree.

To compare the highly accurate techniques, we zoom in the plot in Fig. 6.3. The methods FNDMC, DMRG, AFQMC, FCIQMC, CCSD(T) and MRCI+Q give low energies for most of the states, and the variation between those best energy is \( \approx 10mH\). FNDMC works with the complete basis, while the results of other techniques are that for a give basis set. Therefore, the results for complete basis set are expected to be lower, as shown in Fig. 6.4. These basis methods agree with one another at each basis as expected. Fig. 6.5 shows the compression of estimated excitation energies with the experimental values. The y-axis is the energy differences between the ground state and all other states. The high-accuracy techniques mentioned above
Figure 6.4: Total energy of Oxygen vs. basis sets. All these methods agree to within a few mHartree on the total energy. Given these techniques, the main error in solving the Schroedinger equation is the basis set.

agree very well with experimental values, which are shown by pink stars. We can also conclude that, for these basis-based techniques, the main error in solving the Schroedinger equation is the basis set.

6.2 Benchmark calculation for Fe atom

6.2.1 Definition of benchmark for Fe

There are 26 electrons in a Fe atom, with the pseudopotential approximation, 10 electrons are taken as core electrons, and the free electrons occupy the 4s and 3d orbitals. The calculated states are shown in Table 6.4.

Similar to O atoms, two positively charged states (5D is the ground state) and two neutral states (6D is the ground state) are calculated. Although 3F is not the first excited state, we selected this state as one of the target states because it’s the ground state of |S|^2, with s = 1 (i.e., it’s the lowest energy triplet state).

<table>
<thead>
<tr>
<th>Charge state</th>
<th>Spin and angular momentum</th>
<th>Atomic orbital occupation</th>
<th>Shortname</th>
<th>Pseudopotential</th>
<th>Basis sets</th>
<th>Quantities</th>
<th>State type</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1</td>
<td>5D</td>
<td>3d^6 4s</td>
<td>Feplus6D</td>
<td>BFD</td>
<td>vdz, vtz, vqz, v5z, ..., cbs</td>
<td>Energy</td>
<td>Ground state</td>
</tr>
<tr>
<td>+1</td>
<td>4F</td>
<td>3d^7</td>
<td>Feplus4F</td>
<td>BFD</td>
<td>vdz, vtz, vqz, v5z, ..., cbs</td>
<td>Energy</td>
<td>Excited state</td>
</tr>
<tr>
<td>0</td>
<td>5D</td>
<td>3d^6 4s^2</td>
<td>Feneutral5D</td>
<td>BFD</td>
<td>vdz, vtz, vqz, v5z, ..., cbs</td>
<td>Energy</td>
<td>Ground state</td>
</tr>
<tr>
<td>0</td>
<td>3F</td>
<td>3d^7 4s</td>
<td>Feneutral3F</td>
<td>BFD</td>
<td>vdz, vtz, vqz, v5z, ..., cbs</td>
<td>Energy</td>
<td>Excited state</td>
</tr>
</tbody>
</table>
Figure 6.5: Excitation energy vs. basis sets. The vertical axis is the energy difference between the specific state and the ground state.

Figure 6.6: Total energies of Fe atom calculated with different techniques.

6.2.2 Fe atom results

The total energies of these four different states are plotted in Fig[6.6]. By examining the differences between Hartree Fock energies and the lowest energies among all these techniques, the correlation energies are found to be around 0.8 Hartree for all these four different states, which is much larger than that for O atoms. This is due to the involvement of d orbitals in the calculations. Zooming in the high-accuracy results in Fig[6.7] which are FNDMC, DMRG, FCIQMC and AFQMC data, similar to the variance of O atoms, the variance between these methods is $\approx 10\text{mH}$.

Fig. 6.8 shows the dependence of each technique on the basis set. For basis-based techniques, the results are extrapolated to complete basis set limit. Fig. 6.9 is the comparison of expected excitation energies with that from experiments. The FNDMC results coincide with experiments, and the other high-accuracy techniques agree with each other for a given basis set, and are mainly limited by the basis set.
Figure 6.7: Total energies of Fe atom vs. techniques (zoomed). Zoomed in the high-accuracy results.

Figure 6.8: Energy vs. basis set. The solutions of basis-based techniques are mainly limited by the basis set.

Figure 6.9: Excitation energy vs. basis set. The excitation energies are compared with experimental values (pink star). Multiple points for experiment indicate different values of J.
6.3 Error analysis for atom systems

To analyze and disentangle the source of errors, in Fig. 6.10 and Fig. 6.11 we plotted the mean averaged errors, which is the average of errors (comparing with experiments) for the excitation energies. To give a better visualization, we plotted the y-axis with logarithm scale. The grey lines at 25meV is approximately the ‘chemical accuracy’. For O atom calculation, DMRG is taken as the benchmark value for a given Hamiltonian approximation, hence, the mean averaged error of DMRG is the error comes from the approximation made on Hamiltonian, which is about 75meV. The error from solution approximation (10meV as mentioned above) is much smaller than the error from Hamiltonian approximation. It looks like the limiting factor for FNDMC (which lead to the error difference between DMRG and FNDMC) is node error.

For Fe atom calculation, the basis-based methods are not extrapolated to complete basis set, however the high-accuracy methods (DMRG, FCIQMC, AFQMC) agree with each other with each basis set. We are able to compare the FNDMC results with experiments and the error has the scale of 100meV. The limiting factor for accuracy for Fe appears to be spin-orbit effects, which were not included in our original Hamiltonian.

From the above analysis, we can conclude that for the O atom (smaller system), most of these techniques agree with each other as well as the experiments. For larger system, Fe atom, the variance of different techniques is larger. By comparing the mean averaged errors, we can estimate the errors that come from the solution approximation and Hamiltonian approximation. From now on, we will proceed to more complicated molecule systems.

6.4 Benchmark calculation for FeO molecule

6.4.1 Definition of benchmark for FeO

For FeO molecule, we investigated the ground state $^5\Delta$ and the first excited state $^7\Sigma$. We varied the bond length to find the equilibrium bond length which could be used to compare with experimental data. The parameters for calculation are listed in Table 6.5.

<table>
<thead>
<tr>
<th>Charge state</th>
<th>Spin and angular momentum</th>
<th>Shortname</th>
<th>Pseudopotential</th>
<th>Basis sets</th>
<th>Quantities</th>
<th>State type</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1</td>
<td>$^5\Delta$</td>
<td>FeO5Delta</td>
<td>BFD</td>
<td>vdz, vtz, vqz, v5z, ..., cbs</td>
<td>Energy</td>
<td>Ground state</td>
</tr>
<tr>
<td>+1</td>
<td>$^7\Sigma$</td>
<td>FeO7Sigma</td>
<td>BFD</td>
<td>vdz, vtz, vqz, v5z, ..., cbs</td>
<td>Energy</td>
<td>Excited state</td>
</tr>
</tbody>
</table>
Figure 6.10: Mean averaged error vs. basis sets for O atoms. The vertical axis has logarithm scale. The grey dashed line is approximately 'chemical accuracy'.
Figure 6.11: Mean averaged error vs. basis set for Fe atoms. The vertical axis has logarithm scale. The grey dashed line is approximately ‘chemical accuracy’.
6.4.2 FeO molecule results

To find the best trial wave function and reduce the fixed node error, we first calculated with the experimental bond length 3.058 Bohr. In FNDMC calculation, many different trial wave functions are generated with density functional theory (with B3LYP, PBE0, and PBE functional) and CASCI. The results are shown in Fig. 6.12, the x-axis is the method and the y-axis is the energy. The color of dots represents different state. The wave function get from the CASCI calculation(with initial density matrix get from ROKS(B3LYP)) is the one that gives the lowest energy.

We then used this setting to generate the trial wave functions for the other bond lengths, which is in the range of (2.6, 3.6)Bohr. The FNDMC results as well as that from other techniques are shown in Fig. 6.13. Multiple points for a method come from different basis sets. The total energy difference between less accurate methods (like, HF, HF + DMFT and MCSCF) and high accurate methods (FNDMC, FCIQMC, GF2 and MRCI+Q) is large. To compare with the equilibrium bond length from experiments, we fitted the energy.
Figure 6.13: FeO energy vs. bond length. Multiple points for a method are different basis sets. There is a large difference in the predicted total energy between 'less accurate' methods and 'more accurate' methods.

Figure 6.14: Estimated equilibrium bond length vs. basis set. The grey dashed line is the experimental results with Morse potential, which is defined as

\[ V(r) = D\epsilon \left(1 - e^{-\alpha(r-r_e)}\right)^2 \]  

where \( r_e \) is the equilibrium bond length. The fitted equilibrium bond length are shown in Fig. 6.14, where the grey line the experimental value. FNDMC results agree well with experiments; FCIQMC, HF+DMFT and MRCI+Q give close results, although the total energy of HF+DMFT is much higher. The dissociation energies in Fig. 6.15 are also obtained from this fitting. The value from less accurate methods (HF) are much lower than high accurate methods (FCIQMC, FNDMC). In Fig. 6.16 the excitation energies are compared with experimental values, the error is about 200 meV. The difference between high-accuracy and low-accuracy is large. Fig. 6.17 plots the estimated vibrational frequency and experimental value. The
Figure 6.15: Dissociation energy vs. basis set.

Figure 6.16: Excitation energy vs. basis set. The excitation energy is defined as the energy different between $^5\Delta$ and $^7\Sigma$. The grey dashed line is the experimental result.
In conclusion, molecule is more difficult to calculate than atom. High accurate techniques agree with experimental values in the calculation of bond length, excitation energy and vibrational frequency. Development of new basis sets are need to extrapolate to the complete basis limit.
Chapter 7

Summary

In summary, the thesis work focuses on studying the correlated systems with quantum Monte Carlo methods. It mainly includes two projects.

Metal to Mott insulator transition of hydrogen on the honeycomb lattice, which occurs when there are interactions. We selected the hydrogen on honeycomb lattice because it is one of the simplest systems with $1/r$ interaction. There is only one electron on each site, so we can reduce the calculation error to the minimum. The reptation projector Monte Carlo is implemented, which only have fixed node error even for operators that do not commute with Hamiltonian. We investigated the fixed node error and found that it has a significant influence on the properties of fixed node wave functions. We identified the ground state properties by mapping out the low-energy Hilbert space with an ensemble of wave functions and successfully identified the transition point. Based on our calculation, the phase transition is identified as a second-order transition.

Benchmark calculation of Fe/O system. The simulation of transition metal systems is one of the most challenging problems in numerical techniques. Transition metal systems are strongly correlated and have diverse phase and properties. To understand how well can we describe transition metal systems with the most accurate numerical calculations, and identify the sources of error, we bring together multiple different numerical techniques to study the Fe/O systems. The techniques we implemented includes FNDMC, AFQMC, DMRG, FCIQMC, GW, CCSD(T) and MRCI. To disentangle the error, we defined a set of benchmark parameters, like basis set, pseudopotential, and states. Each calculation is based on these definitions. The properties we investigated are total energies and ionization energies. We find that for small atom, like oxygen, the variance between different techniques as well as errors from pseudopotential and the Schrödinger equation are small. For the Fe system, which involves the correlated d orbitals, the calculation is more difficult, the highly accurate methods agree well with experimental values. We successfully disentangled the errors from solution approximation and Hamiltonian approximation. For FeO molecule, the calculated equilibrium bond length and excitation coincide with experiments. The vibrational frequency and dissociation energy are also estimated with compared.
Chapter 8

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