HU, SHUMING. Approximations and Effectiveness of QMC and Other Electronic Structure Methods in Molecules and Solids. (Under the direction of Lubos Mitas.)

Accompanying the development of methodologies and computer technology, first-principle electronic structure calculations are gaining a stronger foothold as well as wider applicability in predicting material properties. We examined and compared fundamental approximations made in different electronic structure methods like Hartree-Fock (HF), Density Functional Theory (DFT) and quantum Monte Carlo (QMC). Some of their boundaries and effectiveness are analyzed through both simple systems as well as real world materials.

Thorium monoxide’s energy and electric properties were studied using HF and subsequently QMC. Thorium dioxide crystal (thoria)’s various electric properties in normal phase were studied using DFT and energetics of phase transition were studied using both DFT and QMC. This is the first attempt of QMC calculations on actinide materials known to the author.

Calculations on manganese oxides are not only benchmarks but also serving the purpose of illustrating QMC method’s variational property for checking and potentially optimizing DFT exchange-correlation functional parameters.

Last but not least, nodal shapes, topologies and fixed-node errors were analyzed for simple atomic and molecular systems, as fixed-node biases are the most important yet elusive errors for QMC. Mathematical quantity “nodal domain average” was proposed to aid the analysis of fixed-node error.
Approximations and Effectiveness of QMC and Other Electronic Structure Methods in Molecules and Solids

by
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DEDICATION

To my parents.
Come up to meet you
Tell you I’m sorry
You don’t know how lovely you are
I had to find you
Tell you I need you
Tell you I set you apart
Tell me your secrets
And ask me your questions
Oh let’s go back to the start
Running in circles; coming up tails
Heads on a silence apart

Nobody said it was easy
It’s such a shame for us to part
Nobody said it was easy
No one ever said it would be this hard
Oh take me back to the start

I was just guessing at numbers and figures
Pulling your puzzles apart
Questions of science; science and progress
Do not speak as loud as my heart

Tell me you love me
Come back and haunt me
Oh and I rush to the start
Running in circles, chasing our tails
Coming back as we are

Nobody said it was easy
Oh it’s such a shame for us to part
Nobody said it was easy
No one ever said it would be so hard
I’m going back to the start

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Coldplay “The Scientist” lyrics
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Chapter 1  Introduction to Electronic Structure Calculation

Electrons and nuclei are the fundamental particles that determine the nature of the matter of our everyday world: atoms, molecules, condensed matter, artificial and biological material. Even life itself can be viewed as an “emergent” behavior and a “meta-stable” state of these fundamental particles.

Understanding of the behavior of electrons holds the key to understanding material properties and development and application of new materials. However, correctly describing their behavior needs the language of quantum mechanics.

Fundamental ideas of quantum mechanics were formulated and developed in the first half of the 20th century. The theory, unintuitive to many, has demonstrated a surprising accuracy and predictive power.

With the help of quantum mechanics, we can see how electrons form the “quantum glue” that holds together nuclei in molecules and materials and how their quantum states determine the vast array of electrical, optical, magnetic and behavioral properties of materials.

One of the most basic and key mathematical tools in quantum mechanics is non-relativistic Schrödinger’s Equation, whose solutions, i.e. many-body wave functions, are explicit mathematical descriptions of quantum states. However, finding these solutions
or even approximating these solutions correctly for various circumstances\(^1\) ranks among the
greatest challenges of theoretical physics.

Some of the standard approaches to the solution will be briefly described in following
chapters.

\(^1\) Sometimes in order get the approximate solution, people modified Schrodinger’s equation or
devised an “effective” equation to begin with; often the effective equation is designed to retain all
the important physical meaning.
Non-relativistic Schrödinger equation

The form of the Schrödinger equation depends on the physical situation. The most general form is:

**Time-dependent Schrödinger equation**

\[ i\hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi \]

This equation describes the evolution of many-body quantum state \( \Psi \) for system with Hamiltonian \( \hat{H} \).

If \( \Psi(R) \) is an eigenstate of \( \hat{H} \) with eigenvalue \( E \), where \( R \) are spatial coordinates of particles, then solution \( \Psi(R)e^{-i\frac{E}{\hbar}t} \) satisfies the equation. The time-dependent piece could be separated out as a simple “oscillating” factor. Since any quantum state could be seen as a linear superposition of energy eigenstates, the dynamics of the system could be known in theory if we have all the eigenstates available. To find \( \hat{H} \) eigenstates, we have:

**Stationary Schrödinger equation**

\[ E \Psi = \hat{H} \Psi \]

However, finding all the eigenstates has been proven to be difficult except for simplest cases (like non-interacting Hamiltonians). People could argue that in most cases, it is near impossible to know exactly and check all the solutions.

For a generic interacting Hamiltonian, total energy grows linearly with system size while number of states/solutions \( \Psi \) grows exponentially. This means average energy spacing between states become exponentially small, implying the time needed to experimentally
resolve these energy differences becomes exponentially large. For a 200 electron system, range of total energy for all eigenstates is about the magnitude of $200 \, \text{eV}$, while the total number of eigenstates is, say, about $2^{200}$; the average energy difference between two states $\frac{200\text{eV}}{2^{200}} \approx 10^{-58} \text{eV}$; the time needed to resolve this difference $\approx \frac{\hbar}{200\text{eV}/2^{200}} \approx 5.288529 \times 10^{42} \text{ seconds} \approx 1.2 \times 10^{25} \times \text{universe age (\sim 14 Gyr )}$. This means even if we could find all the solutions, it would be impossible to check all of them in experiments. Therefore, for solutions of explicit many-body wave function, we want to focus on the ground state and low-lying excitations first which provide the easiest access and sometimes most valuable and interesting information on quantum phenomenon.\(^2\)

Another important observation is that quite often the wave function in chemical environment $\Psi(R_e, R_n)$, $R_e$ being coordinates of electrons, $R_n$ being coordinates of nuclei/ions\(^3\), can be separated into a product of electronic and nuclear wave function, since

---

\(^2\) For an ensemble of excited states, techniques that don’t involve explicit many-body wave functions are preferred, for example, Path Integral Monte Carlo.

\(^3\) To avoid confusion with concepts in nuclear physics, we sometimes call nuclei ions as they are bare ions when we strip an atom of all its electrons. In the following text, we’ll use these two words interchangeably. In practice, we use ECP (effective core potential)/Pseudopotential very often to reduce computation demand, where nuclei and closed-shell core electrons will be modeled by ECP. In this case we only partially strip the atom to get an ion core.
nuclei are much heavier than electrons (details will be discussed in the next section). This enables us to focus on the electronic part and nuclear part separately. This separation is called Born-Oppenheimer approximation.

**Born-Oppenheimer Approximation**

If we write \( \Psi(R_e, R_n) = \Psi_e(R_e, R_n) \Psi_n(R_n) \), and *ignore kinetic energy operator of ions* on \( \Psi_e \), the Schrodinger equation can be broken apart:

\[
\hat{H} \Psi = (\hat{H}_e + \hat{T}_n) \Psi = (\hat{H}_e \Psi_e + \Psi_e \hat{T}_n) \Psi_n = \Psi_e [\hat{T}_n + E_e(R_n)] \Psi_n(R_n)
\]

where \( \hat{T}_n \) is kinetic energy operator for nuclei, \( \hat{H}_e \) contains all the rest like kinetic energy for electrons, ion-electron potential energy, ion-ion potential energy and electron-electron interaction, \( \Psi_e \) is an eigenvector of \( \hat{H}_e \) with eigenvalue \( E_e \).

Thus we end up with two equations to solve, one for electrons and one for nuclei, \( R_n \) are fixed in the former and \( R_e \) don’t appear in the latter:

\[
\hat{H}_e(R_n) \Psi_e = E_e(R_n) \Psi_e
\]

\[
[\hat{T}_n + E(R_n)] \Psi_n = E \Psi_n
\]

Notice the dependence of \( \hat{H}_e \) on \( R_n \) through ion-electron potential and ion-ion potential, naturally implies the dependence of eigenvalue \( E_e \) on \( R_n \). In practice, one might vary these positions \( R_n \) in small steps and repeatedly solving the electronic Schrödinger equation to obtain \( E_e \) as a function of \( R_n \).
$E_e(R_n)$, with all the information about electrons in the system, enters the nuclear equation as an potential energy for nuclei and is commonly referred to as PES(Potential Energy Surface) from nuclei’s point of view\(^4\). Now one can proceed to solve for the motion of nuclei, which for small molecules often involves translation and several vibrational and rotational modes.

It can be shown that Born-Oppenheimer approximation is valid whenever PESs, obtained from solutions of electronic Schrodinger equation $\hat{H}_e \psi^k_e = E^k_e \psi^k_e$ are well separated:

$$E^0_e(R_n) \ll E^1_e(R_n) \ll E^2_e(R_n) \ll \cdots \forall R_n$$

In order to show this, first we recognize that true solution to the original equation can always be expanded in terms of $\psi^k_e$:

$$\Psi = \sum_k \psi^k_n(R_n) \psi^k_e(R_e, R_n)$$

Also in the basis of $\psi^k_e$, it is easy to see $\hat{H}$ would take on matrix form

$$H_{kk'} = E^k_e \delta_{kk'} + \hat{T}_{kk'}$$, where $\hat{T}_{kk'} = \langle \psi^k_e | \hat{T}_n | \psi^{k'}_e \rangle$

\(^4\) Because this procedure of recomputing the electronic wave functions as a function of an infinitesimally changing geometry of ions is reminiscent of the conditions for the adiabatic theorem, this manner of obtaining a PES is often referred to as the adiabatic approximation and the PES itself is called an adiabatic surface.
\( R_n \) appears in all terms so it is omitted here and in the following derivation; expectation \( \langle \rangle \) is understood to be taken over \( R_e \).

Notice that \( \hat{T}_{kk'} \) is an operator that can still act on \( \psi_n^{k'} \), as

\[
\hat{T}_n = \sum_i \frac{P_i^2}{2M_i} \quad I \in \text{nuclei}
\]

\[
\hat{T}_{kk'} = \langle \psi_e^k | \psi_e^{k'} \rangle \hat{n} + \sum_i \frac{1}{M_i} \langle \psi_e^k | P_i | \psi_e^{k'} \rangle \cdot P_i + \langle \psi_e^k | (\hat{n} | \psi_e^{k'}) \rangle
\]

\[
= \delta_{kk'} \hat{n} + \sum_i \frac{1}{M_i} \langle \psi_e^k | P_i | \psi_e^{k'} \rangle \cdot P_i + \langle \psi_e^k | (\hat{n} | \psi_e^{k'}) \rangle
\]

Now we see Born-Oppenheimer approximation is essentially only keeping the first term here and ignoring the last two, which is valid when they are small.

First we know that when \( k = k' \) \( \langle \psi_e^k | P_i | \psi_e^k \rangle = 0 \) if we assume non-degeneracy of \( \psi_e^k \) and time-reversal symmetry of our Hamiltonian; this could easily be shown by the properties of time-reversion operator directly or by showing that \( \psi_e^k \) can be expressed as real wave function in this case, so that \( \langle \psi_e^k | P_i | \psi_e^k \rangle = (\text{some constant}) \times \nabla_{r_I} \langle \psi_e^k | \psi_e^k \rangle = 0 \), as normalization is a constant.

When \( k \neq k' \)

\[
\langle \psi_e^k | P_i | \psi_e^{k'} \rangle = \frac{\langle \psi_e^k | [P_i, \hat{H}_e] | \psi_e^{k'} \rangle}{E_e^{k'} - E_e^k}
\]

The numerator

\[
\langle \psi_e^k | [P_i, \hat{H}_e] | \psi_e^{k'} \rangle = -i\hbar \sum_j Z_I \langle \psi_e^k \left| \frac{r_{Ij}}{r_{Ij}^3} \right| \psi_e^{k'} \rangle, j \in \text{electrons}, \quad r_{Ij} = r_I - r_j
\]
is proportional to the Coulomb force on nucleus $I$ from joint electronic distribution $\rho_e$ shown below.

$$F_I = -Z_I \int \frac{\rho_e(r')}{|r_I - r'|^3} (r_I - r') \, dr'$$

$$\rho_e(r') = \langle \Psi_e^k | \hat{\rho}(r') | \Psi_e^{k'} \rangle$$

$$= \sum_j \int \delta(r_j - r') \psi_e^{k'}(R_n, r_1, r_2, ..., r_n) \cdot \psi_e^{k'}(R_n, r_1, r_2, ..., r_n) \prod_s dr_s$$

Dot product between $\Psi_e^k$ and $\Psi_e^{k'}$ would sum over possible spin dimensions.

Notice $\int \rho_e(r') \, dr' = 0$ due to orthogonality of $\Psi_e^k$ and $\Psi_e^{k'}$.

One can also notice that if both $\Psi_e^k$ and $\Psi_e^{k'}$ are expressed as a linear combination of determinants of single-particle orbitals, then only pairs of determinants, one from each wave function, that are different by at most one single-particle orbital would survive as the density operator in $\rho_e$ is an one-particle operator and can be rewritten using a single pair of creation and annihilation operators.

$$\rho_e(r) = \sum_\sigma \langle \Psi_e^k | \hat{\rho}_\sigma (r) \psi_\sigma (r) | \Psi_e^{k'} \rangle = \sum_{i,j,\sigma} \langle \Psi_e^k | c_{i,\sigma}^+ c_{j,\sigma} | \Psi_e^{k'} \rangle \phi_{i,\sigma}^*(r) \phi_{j,\sigma}(r)$$

, where $\phi_{i,\sigma}(i \in \text{integers, } \sigma \in \text{spin labels})$ are single-particle orbitals.

Using $F_{I,kk'}$ to denote this force on nucleus $I$ from joint density of $\Psi_e^k$ and $\Psi_e^{k'}$, we have
\[ \hat{T}_{kk'} = \delta_{kk'} \hat{T}_n + (1 - \delta_{kk'}) \sum_i \frac{i\hbar}{M_l} \frac{F_{I,kk'}}{E^{k'}_e - E^k_e} \cdot P_I + \sum_{I, k'' \neq k \text{ or } k'} \frac{(i\hbar)^2}{2M_I} \frac{F_{I,kkk''}}{E^{k''}_e - E^k_e} \]

\[ \cdot \frac{F_{I,kkk'}}{E^{k'}_e - E^{k''}_e} \]

If we define Hermitian operator \( P_{I,e} \) (off-diagonal impetus on nucleus \( I \)) by its matrix elements in \( \Psi^k_e \) basis as

\[
(P_{I,e})_{kk'} = \begin{cases} 
    i\hbar \frac{F_{I,kk'}}{E^{k'}_e - E^k_e}, & k \neq k' \\
    0, & k = k'
\end{cases}
\]

we can write

\[ \hat{T}_n = \sum_I \frac{(P_{I,n} + P_{I,e})^2}{2M_I} \]

Operator \( P_{I,n} \), same as \( P_I \) in \( \hat{T}_{kk'} \), would not act on electronic wave function as all that has been absorbed into \( P_{I,e} \). We see \( P_{I,e} \) and \( P_{I,n} \) are in effect nothing but \( P_I \) in the Hilbert space of electron wave function and ion wave function respectively.

Since all \( |F_I| \) are finite, we see that, if \( |E^{k'}_e - E^k_e| \gg 1 \forall k \neq k' \), the last two terms in \( \hat{T}_{kk'} \) expression can be duly dropped, or equivalently speaking, \( P_{I,e} \)'s contribution to \( \hat{T}_n \) can be neglected.

However, PESs could be very close to or sometimes even crossing each other at some \( R_n \). In these cases, we are forced to consider the coupling of different electronic eigenstates due to nuclear kinetic energy operator. One way to continue following current approach is to
diagonalize $\hat{A}_{kk'}$ properly in dimensions no less than the number of PESs close to each other.

One situation of particular interest and importance is when $R_n$ are at equilibrium positions in a crystal environment. Then displacements of lattice sites from $R_n$, if assumed to be small, will only increase $E(R_n)$ in the second order of $\delta R_n$. In this case, it is well known that the lattice oscillations can be decomposed into normal modes that can be characterized by phonons, i.e., Hamiltonian $\hat{H}_n + E(R_n)$ is equivalent to

$$\frac{1}{2M_I} (\sum_k P_k^+ P_k + M_I^2 \omega^2(k) Q_k^+ Q_k),$$

where $P_k = \frac{1}{\sqrt{N}} \sum_i P_I e^{-i k \cdot r_I}$, $Q_k = \frac{1}{\sqrt{N}} \sum_i \delta r_I e^{-i k \cdot r_I}$, $k$ lies in the first Brillouin Zone and $N$ is the total number of ions (We have assumed that there’s a single kind of ions here with mass $M_I$, which can be easily generalized to multiple ones with a proper choice of basis. We have also suppressed the label for polarization. You can think that we only focus on longitudinal modes of vibrations here as an example).

In this case, ignoring coupling/off-diagonal terms for kinetic energy operator, motions of ions are well known to be phonons with frequencies $\omega_k$, $k$ being the wavevector. Starting with these electronic states (ones we solved from periodic potential provided by fixed ions) and phonon states, we can calculate the effect of their coupling as perturbation if their effect is assumed to be small albeit non-zero. Another way to look at the problem from time-dependent perturbation point of view is that if there are transitions between electronic eigenstates and phonon states as a result of the coupling term in the
Hamiltonian, the adiabatic approximation which lies at the heart of Born-Oppenheimer approximation breaks down.

However, in practical calculation of electron-phonon coupling, people always start with a simpler and also more intuitive Hamiltonian (Bloch 1928):

$$\sum_{\text{i} \in \text{ions}} \sum_{\text{j} \in \text{electrons}} \delta r_i \cdot \nabla r_i U_n (r_j - r_i)$$

$U_n$ stands for ion-electron potential energy here being Coulomb potential; $\delta r_i$ acts on the wavefunction of ions while the rest acts on the electronic wavefunction. We’ll refer to this form as Bloch potential.

This looks different from our coupling term, and we usually think this change in ion-electron potential energy should have been included in PES thus well captured in Born-Oppenheimer approximation. But the truth is that this coincides with PES only to the first order of $\delta r_i$ and the counter-intuitive bit is that this generates the same first order electron-phonon scattering probability as the second term in our $\hat{T}_{k,k'}$ expression:

The matrix representation (in electronic eigenstates $n, m$; we switched $k, k'$ to $n, m$ to avoid confusion with wavevector $k$) of the Bloch potential is

$$\sum_{k,k',l} - i k \frac{1}{\sqrt{N}} Q_k e^{i k \cdot r_l} \frac{1}{\sqrt{N}} U_{k'} e^{-i k' \cdot r_l} \int dr \ e^{i k' \cdot r} \langle n | \hat{\rho} (r) | m \rangle$$

$$= - i \sum_{k} k \sqrt{\frac{\hbar}{2 M_i \omega_k}} (a_k + a_k^+) U_k \langle n | \hat{\rho}_k^+ | m \rangle$$

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, where $\hat{\rho}_k^+ = \int dr \ e^{ikr} \hat{\rho}(r)$, would transfer electron to a state with additional momentum $k$, which is obvious in plane wave representation, as $\hat{\rho}(r) = \frac{1}{V} \sum_{p,p'} c_p^+(r) c_p(r) e^{i(p-p')r}$ shows $\hat{\rho}_k^+ = \sum_p c_{p+k}^+ c_p$. Notice that conservation of total momentum of electrons and phonons (up to a reciprocal lattice vector of course as $|n\rangle$ and $|m\rangle$ are many-body Bloch states) is apparent here.

Similarly, we can express our coupling term

$$
\sum_i \frac{i\hbar}{M_i} \frac{F_{i, nm}}{E_e^m - E_e^n} \cdot P_i = \sum_i \frac{-i\hbar}{M_i(E_e^m - E_e^n)} P_i \cdot \int dr \ \nabla_r U_n(r - r_i) \langle n | \hat{\rho}(r) | m \rangle
$$

$$
= -\frac{i\hbar}{M_i(E_e^m - E_e^n)} \sum_k P_k^+ (-ik U_k \langle n | \hat{\rho}_k^+ | m \rangle)
$$

$$
= -\frac{i\hbar}{M_i(E_e^m - E_e^n)} \sum_k (-i) \sqrt{\frac{h M_i \omega_k}{2}} (a_k - a_{-k}^+) (-ik U_k \langle n | \hat{\rho}_k^+ | m \rangle)
$$

$$
= -i \sum_k \sqrt{\frac{\hbar}{2M_i \omega_k}} \left( a_k \frac{\hbar \omega_k}{E_e^m - E_e^n} + a_{-k}^+ \frac{\hbar \omega_k}{E_e^m - E_e^n} \right) U_k \langle n | \hat{\rho}_k^+ | m \rangle
$$

Notice that this is exactly the same as Bloch potential if energy conservation is satisfied, i.e., when a phonon of energy $\hbar \omega_k$ gets destroyed, electronic states must gain the same amount of energy $(E_e^m - E_e^n = \hbar \omega_k)$ and similarly for the creation of a phonon.

To the first order of perturbation, the only non-zero contribution to coupling is coming from degenerate states, because the expectation value of same state vanishes as both $F_i$.
and \( \mathbf{P}_i \) are destroying or creating different states. Degeneracy in total energy of the system means the total energy of electron and phonon states must be conserved. Therefore, the second term in our \( \hat{T}_n \) expression has the same effect as electron-phonon coupling of Bloch potential to the first order. The last term in our \( \hat{T}_n \) expression, \( \frac{p_{i,e}^2}{2M_i} \) is not only small but often has very weak to little dependence on \( \mathbf{r}_i \), so can be safely ignored (J.M.Ziman, 1960).

Electron-phonon coupling has many consequences. Probably the most familiar one is the scattering of electrons by phonons, which is an important cause of resistance in metals. A second consequence is the absorption of phonons by the electrons, which offers a mechanism for the attenuation of a sound wave, or, in higher order, for thermal resistance in metals. Two other closely related renormalization effect, typical manifest of interactions, are the dressing of electron as a quasiparticle (called polaron) due to interaction with phonon cloud, which is responsible for the colossal magneto-resistance effect in manganite, and vice versa as electron gas could be polarized by motion of ions, which in turn changes the effective interaction among ions and hence changes the characteristic phonon frequency.

We’ll not go into the application of electron-phonon coupling here. But we should always caution ourselves whether it is safe to neglect it. We see that one sufficient, but maybe not necessary, condition is that energy spacing between electronic eigenstates are way larger than possible phonon energy \( \hbar \omega_k \), whose average value is around \( kT \). So in general this requires \(|E^n_e - E^m_e| \gg kT \ \forall \ n, m\); also we should not forget zero-point vibrational energy.
which exists, as its name implies, at zero temperature. One clear exception to this condition
is metal at room temperature, as it is zero gap material.

In the following pages of this chapter, we’ll assume Born-Oppenheimer approximation is
valid and focus on the electronic equation with $R_n$ fixed, or more generally, a non-
relativistic Schrodinger equation with Hamiltonian for identical particles in the form:

$$H = \sum_i \left( \frac{p_i^2}{2m} + v_{ext}(r_i) \right) + \sum_{i<j} v(r_{ij})$$

We’ll drop hat notation on operators as they should be clear from context.

Symbol $v$ denotes interaction among particles while $v_{ext}$ is the external potential felt by
individual particle.
Chapter 2  Hartree-Fock Method

We know how to solve the Schrödinger equation if Hamiltonian is non-interacting, i.e. one that only contains one-body terms:

\[ H_0 = \sum_i \left( \frac{p_i^2}{2m} + v_{ext}(r_i) \right) \]

In this approximation the eigenstates of \( H_0 \) may be written as the product of single-particle wave functions, each of which satisfies the equation (\( \hbar = 1 \))

\[ \left( -\frac{\nabla^2}{2m} + v_{ext}(r) \right) \phi_k(r) = \varepsilon_k \phi_k(r) \]

If we can approximate electron-electron interaction by some effective \( v_{ext}(r) \), then the problem reduces to an independent-particle one. However, the proper choice of \( v_{ext} \) to best represent the effects of electron-electron interaction is a subtle problem. Or theoretically speaking, it is downright impossible because the very fact that independent-particle solutions are products of single-particle wave functions means behaviors of particles are not correlated as they should. However, it is valid to ask how we can do this in a way that is least unreasonable. In this thesis, we’ll call using products of a set of single-particle orbitals to describe many-body states independent particle approximation.

We’ll illustrate the idea using electrons, which are also the main focus of current thesis, as an example.
To begin with, \( v_{ext} \) should incorporate, at least approximately, the fact that electrons feel the electric fields of all other electrons. If we treat the remaining electrons as a smooth distribution of charge with charge density \( \rho \), the potential energy of given electron in their field would be

\[
V(r) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}
\]

Furthermore, if we insisted on an independent electron picture, ground state \( \rho \) can be easily expressed as

\[
\rho(r) = \sum_{\sigma} \langle \psi_\sigma^+(r) \psi_\sigma(r) \rangle = \sum_{i,j,\sigma} \langle c_{i,\sigma}^+ c_{j,\sigma} \rangle \phi_{i,\sigma}(r) \phi_{j,\sigma}(r) = \sum_{i,\sigma} \langle n_{i,\sigma} \rangle |\phi_{i,\sigma}(r)|^2
\]

where \( n_{i,\sigma} \) are number operators and \( \langle n_{i,\sigma} \rangle \) are current occupation numbers (1 for occupied and 0 for unoccupied).

By adding this \( V(r) \) to \( v_{ext} \) that originally only contains contribution from ions, we arrive at a set of self-consistent equations:

\[
\left[-\frac{\nabla^2}{2m} + V_{ion}(r)\right] \phi_{i,\sigma}(r) + \sum_{j,\sigma'} \int d\mathbf{r}' \langle n_{i,\sigma'} \rangle \frac{|\phi_{j,\sigma'}(r')|^2}{|\mathbf{r} - \mathbf{r}'|} \phi_{i,\sigma}(r) = \varepsilon_{i,\sigma} \phi_{i,\sigma}(r)
\]

This set of equations is known as **Hartree equations**. We call these non-linear equations self-consistent as the problem (Hamiltonian) is dependent on the solution \( \phi_i \) so that its solution has to be self-consistent. And in practice, it is often solved by iteration. Since the potential/field is generated from solutions of previous iteration, this kind of methods are called SCF (self-consistent field) methods. The iterations terminate whenever the
differences between two solutions of adjacent iterations is smaller than certain preset
threshold that deemed accurate enough for the situation.

The Hartree equations have a fundamental inadequacy that might not evident from the
simple derivation above. The defect emerges if we return to the original Hamiltonian and
cast it into the equivalent variational form. It becomes apparent when we can compare the
expectation of interaction in original Hamiltonian and our Hartree approximation.

Electron-electron interaction in second quantized form:

$$\frac{1}{2} \sum_{\sigma, \sigma'} \int \! dr dr' \psi^+_\sigma(r) \psi^+_{\sigma'}(r') \frac{1}{|r-r'|} \psi_{\sigma'}(r') \psi_\sigma(r)$$

Electron-electron interaction in Hartree approximation:

$$\frac{1}{2} \sum_{\sigma, \sigma'} \int \! dr dr' \langle \psi^+_\sigma(r) \psi_\sigma(r) \rangle \frac{1}{|r-r'|} \langle \psi^+_{\sigma'}(r') \psi_{\sigma'}(r') \rangle$$

Even with the assumption of independent particle approximation (that our many-body state
is a simple product of single-particle states $|\Psi\rangle = \prod_i c^+_{i\sigma_i} |0\rangle$, $c^+_{i\sigma_i}$ being the corresponding
creation operator for spin orbital $\phi_{i\sigma}$; we don’t construct spin eigenstates here), the
expectation of true Coulomb interaction is not just what we have in Hartree approximation,
which can be clearly seen from two-body density matrix:

$$\rho_2(r, r') = \sum_{\sigma, \sigma'} \langle \Psi| \psi^+_\sigma(r) \psi^+_\sigma(r') \psi_{\sigma'}(r') \psi_{\sigma}(r) |\Psi\rangle$$

$$= \sum_{\sigma, \sigma'} \left( \langle \psi^+_\sigma(r) \psi_\sigma(r) \rangle \langle \psi^+_\sigma(r') \psi_{\sigma'}(r') \rangle - \langle \psi^+_\sigma(r) \psi_{\sigma'}(r') \rangle \langle \psi^+_\sigma(r') \psi_\sigma(r) \rangle \right)$$
\[
\sum_{\sigma, \sigma'} (\psi_\sigma^+(r) \psi_\sigma(r))(\psi_{\sigma'}^+(r') \psi_{\sigma'}(r')) - \sum_{\sigma} (\psi_\sigma^+(r) \psi_\sigma(r))(\psi_{\sigma'}^+(r') \psi_{\sigma'}(r'))
\]

\[
= \rho(r)\rho(r') - \sum_{\sigma} |\rho_\sigma(r, r')|^2
\]

Expectation is understood to be taken over \(|\Psi\rangle\). The first step is from the observation that, when sandwiched between \(|0\rangle\), two sets of \(\psi\) and \(\psi^+\) have to pair with two orbitals \(c_{i,\sigma_i}^+, c_{i,\sigma_i}, c_{j,\sigma_j}^+, c_{j,\sigma_j}\) in \(\Psi\). If there is an even number of crossings among these four pairings we could find it in the first term of the 2\(^{nd}\) line, while others (odd number of crossing gives an extra negative sign) could be found it in the second term of the 2\(^{nd}\) line.

Notice that possible situation for \(i = j\) and \(\sigma_i = \sigma_j\) the same contribution will be made to the two terms in subtraction so that we recover the original expression. We see that even with independent particle approximation, two-body density is not a simple product of two one-body densities when two interacting electrons share the same spin \((\sigma = \sigma')\). The first term which is a product of two densities leads to the energy term we have in Hartree approximation. This energy called Hartree energy. The second term, associated with off-diagonal one-body density matrix, when integrated with Coulomb potential over space gives so called exchange energy. More explicitly,

\[
U_{\text{Hartree}} = \frac{1}{2} \int drdr' \frac{\rho(r)\rho(r')}{|r - r'|}
\]

\[
U_{\text{exchange}} = -\frac{1}{2} \int drdr' \sum_{\sigma} \frac{|\rho_\sigma(r, r')|^2}{|r - r'|}
\]

\(U_{\text{exchange}}\) depends on \(|\Psi\rangle\) or, in our case, \(\phi_s\) through \(\rho_\sigma(r, r')\)
\[ \rho_\sigma(r, r') = \langle \psi_\sigma^+(r') \psi_\sigma(r) \rangle = \sum_{i,j,\sigma} (c_{i,\sigma}^+ c_{j,\sigma}) \phi_{i,\sigma}^*(r') \phi_{j,\sigma}(r) = \sum_{i,\sigma} (n_{i,\sigma}) \phi_{i,\sigma}(r) \phi_{i,\sigma}^*(r') \]

Therefore, the exact variational evaluation of electron-electron interaction for our \( \Psi \)
contains not only \( U_{\text{Hartree}} \) but also \( U_{\text{exchange}} \). Thus to find the best \( \Psi \) within independent
particle approximation, i.e. the set of occupied orbitals, we only have to minimize total
energy with both \( U_{\text{Hartree}} \) and \( U_{\text{exchange}} \) included. With the help of derivatives

\[
\frac{\delta U_{\text{Hartree}}}{\delta \phi_{i,\sigma}^*(r)} = \int dr' \frac{\rho(r')}{|r-r'|} \phi_{i,\sigma}(r) = \sum_{j,\sigma'} \int dr' \langle n_{j,\sigma'} \rangle \frac{|\phi_{j,\sigma'}(r')|^2}{|r-r'|} \phi_{i,\sigma}(r)
\]

\[
\frac{\delta U_{\text{exchange}}}{\delta \phi_{i,\sigma}^*(r)} = -\int dr' \frac{\rho_\sigma(r', r)}{|r-r'|} \phi_{i,\sigma}(r') = -\sum_{j} \int dr' \langle n_{j,\sigma} \rangle \frac{\phi_{j,\sigma}(r) \phi_{j,\sigma}^*(r')}{|r-r'|} \phi_{i,\sigma}(r')
\]

, we can minimize \( \langle \Psi | H | \Psi \rangle \) with constrains \( \int dr \phi_{i,\sigma}^*(r) \phi_{i,\sigma}(r) = 1 \forall i, \sigma \).

We arrive at a set of equations for \( \phi_i \)

\[
\left[ -\frac{\nabla^2}{2m} + V_{\text{ion}}(r) \right] \phi_{i,\sigma}(r) + \sum_{j,\sigma'} \int dr' \langle n_{j,\sigma'} \rangle \frac{|\phi_{j,\sigma'}(r')|^2}{|r-r'|} \phi_{i,\sigma}(r)
\]

\[ -\sum_{j} \int dr' \langle n_{j,\sigma} \rangle \frac{\phi_{j,\sigma}(r) \phi_{j,\sigma}^*(r')}{|r-r'|} \phi_{i,\sigma}(r) = \epsilon_i \phi_{i,\sigma}(r) \]

Eigenvalues \( \epsilon_i \) are Lagrange multipliers during minimization and they resemble single-
particle energies. Their physical meaning will be clarified shortly afterwards.

Notice that the exchange term can be simply obtained from the Hartree term (when \( \sigma = \sigma' \))
by exchanging \( i \) and \( j \) for \( \phi_{j,\sigma}(r') \phi_{i,\sigma}(r) \). This set of SCF equations is called \textbf{Hartree-Fock}
equations. The operator we defined here is called Fock operator, which is our new effective
Hamiltonian \( \sum_{i,\sigma} \epsilon_i \sigma_i^+ \sigma_i \).
We can drop all the spin labels if we don’t distinguish between orbitals [and their eigenvalues] of different spin, just be careful that once we dropped the spin label the occupation number in Hartree term would be 2 for doubly occupied orbitals while exchange term is always counting occupation with the same spin. This is called Restricted Hartree-Fock. The method in which we accommodate different orbitals for different spins is named Unrestricted Hartree-Fock.

Total energy of Hartree-Fock method could be calculated after the iterations converged. If we simply added up \( \varepsilon_{i,\sigma} \), we would have counted electron-electron interaction twice. Therefore,

\[
E_{\text{total}} = \sum_{i,\sigma} \langle n_{i,\sigma} \rangle \varepsilon_{i,\sigma} - U_{\text{Hartree}} - U_{\text{exchange}}
\]

Notice that if we take away one electron (in orbital \( i \) with spin \( \sigma \)) from the system, without changing orbitals,

\[
\Delta \rho(r) = -|\phi_{i,\sigma}(r)|^2
\]

\[
\Delta \rho_\sigma(r, r') = -\phi_{i,\sigma}(r) \phi_{i,\sigma}^*(r')
\]

\[
\Delta \varepsilon_{j,\sigma'} = \int dr dr' \Delta \rho(r) \frac{|\phi_{j,\sigma'}(r')|^2}{|r - r'|} - \delta_{\sigma,\sigma'} \int dr dr' \Delta \rho_\sigma(r, r') \phi_{j,\sigma}(r) \phi_{j,\sigma}(r')
\]

Notice when \( j = i, \sigma = \sigma' \), \( \Delta \varepsilon_{j,\sigma'} = 0 \) as expected for self-interaction is cancelled out in Hartree-Fock.

\[
\sum_{j,\sigma'} \langle n_{j,\sigma'} \rangle \Delta \varepsilon_{j,\sigma'} = \int dr dr' \frac{\Delta \rho(r) \rho(r')}{|r - r'|} - \int dr dr' \frac{\Delta \rho_\sigma(r, r') \rho_\sigma(r', r)}{|r - r'|}
\]
\[ = \Delta U_{Hartree} + \Delta U_{exchange} \]

Therefore,

\[ \Delta E_{total} = -\varepsilon_{i,\sigma} + \sum_{j,\sigma'} \langle n_{j,\sigma'} \rangle \Delta \varepsilon_{j,\sigma'} - \Delta U_{Hartree} - \Delta U_{exchange} \]

\[ = -\varepsilon_{i,\sigma} \]

Similarly if we add an electron on a certain spin orbital, the total energy would increase by an amount equal to the eigenvalue of that spin orbital. This is known as Koopmans’ Theorem. We see that Lagrange multipliers \( \varepsilon_{i,\sigma} \) do bear meanings of single-particle energies; they are the correct ionization, affinity energies to the first order (as orbitals are fixed) within Hartree-Fock approximation.
Hartree-Fock for HEG

Planewaves are the well-known solutions to non-interacting homogeneous electron gas, as they are eigenstates of kinetic energy operator. As a matter of fact, it is straightforward to show they are also Hartree-Fock eigenstates.

First, let’s look at the effective Hamiltonian with Hartree-Fock approximation

\[
H_{HF} = \sum_{k,\sigma} t_k c_{k,\sigma}^+ c_{k,\sigma}
\]

\[
- \frac{1}{2} \sum_{k, k', q, \sigma} V_q \left[ \langle c_{k+q, \sigma}^+ c_{k'+q, \sigma} \rangle c_{k', \sigma}^+ c_{k, \sigma}^+ + c_{k+q, \sigma}^+ c_{k'+q, \sigma}^\prime \langle c_{k'+q, \sigma}^\prime c_{k, \sigma} \rangle
\]

\[
- \langle c_{k+q, \sigma}^+ c_{k'+q, \sigma} \rangle \langle c_{k'+q, \sigma}^\prime c_{k, \sigma} \rangle \right]
\]

where \( c_{k, \sigma}^+ \) creates a planewave with wavenumber \( k \) and spin \( \sigma \), \( t_k \) being its kinetic energy, first term includes all kinetic energy, second term describes exchange and Hartree potential is zero due to uniform positive charge background, which is almost always introduced in HEG systems to cancel charges of electrons so that average charge density is zero\(^5\). We have also used conservation of momentum to simplify the expression.

\( V_q \) is the Fourier transform of Coulomb potential by \( q \)

\( ^5 For non-homogenous periodic systems, uniform background charges are often introduced as well, so that at least \( \langle \hat{\rho}_{k=0} \rangle \) vanishes. \)
\[ V_q = \frac{1}{V^2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} e^{-iq(\mathbf{r}_1 - \mathbf{r}_2)} = \frac{1}{V} \int d\mathbf{r} \frac{1}{r} e^{-iqr} = \frac{4\pi}{Vq^2} \]

Since \( V_q = V_{-q} \), which is a natural result if the interaction potential is symmetric, we can write \( H_{HF} \) as

\[
H_{HF} = \sum_{k,\sigma} t_k c_{k,\sigma}^+ c_{k,\sigma} - \sum_{k,q,\sigma} V_q \langle c_{k+q,\sigma}^+ c_{k+q,\sigma}^+ \rangle c_{k,\sigma}^+ c_{k,\sigma} \\
+ \frac{1}{2} \sum_{k,q,\sigma} V_q \langle c_{k+q,\sigma}^+ c_{k+q,\sigma}^+ \rangle \langle c_{k,\sigma}^+ c_{k,\sigma} \rangle
\]

Notice that for \( |\Psi\rangle = \Pi_{k,\sigma} c_{k,\sigma}^+ |0\rangle \), \( \langle c_{k+q,\sigma}^+ c_{k+q,\sigma}^+ \rangle = \delta_{k,k'} n_{k+q} \), so that \( H_{HF} \) reduces to

\[
H_{HF} = \sum_{k,\sigma} t_k c_{k,\sigma}^+ c_{k,\sigma} - \sum_{k,q,\sigma} V_q \langle c_{k+q,\sigma}^+ c_{k+q,\sigma}^+ \rangle c_{k,\sigma}^+ c_{k,\sigma} \\
+ \frac{1}{2} \sum_{k,q,\sigma} V_q \langle c_{k+q,\sigma}^+ c_{k+q,\sigma}^+ \rangle \langle c_{k,\sigma}^+ c_{k,\sigma} \rangle
\]

It is easy to see now \( |\Psi\rangle \) here is also eigenstates of \( H_{HF} \), so that self-consistency is achieved.

However, for a general system, eigenstates of non-interacting Hamiltonian won’t be Hartree-Fock eigenstates

\[
H_{HF} = \sum_{i,\sigma} \varepsilon_{i,\sigma} c_{i,\sigma}^+ c_{i,\sigma} \\
+ \frac{1}{2} \sum_{i,j,k,l,\sigma,\sigma'} V_{ijkl\sigma\sigma'} [ (c_{i,\sigma'}^+ c_{j,\sigma'}) c_{k,\sigma}^+ c_{k,\sigma} + c_{i,\sigma'}^+ c_{l,\sigma'}^+ c_{j,\sigma} c_{k,\sigma} ] \\
- \delta_{\sigma,\sigma'} (c_{i,\sigma}^+ c_{k,\sigma}) c_{j,\sigma} c_{l,\sigma} - \delta_{\sigma,\sigma'} c_{i,\sigma} c_{k,\sigma} (c_{j,\sigma}^+ c_{l,\sigma}) + \text{Const.}
\]
where the constant term is \(-U_{\text{Hartree}} - U_{\text{exchange}}\) correcting double counting, \(c^+_{i,\sigma}\) creates an electron occupying non-interacting eigenstates \(\phi_{i,\sigma}\) with eigenvalue \(\varepsilon_{i,\sigma}\)

\[
V_{ijkl\sigma\sigma'} = \int dr_1 dr_2 \phi_{i,\sigma'}^*(r_1)\phi_{i,\sigma'}(r_1) \frac{1}{|r_1 - r_2|} \phi_{j,\sigma'}(r_2)\phi_{k,\sigma}(r_2)
\]

Potential \(V_{ijkl\sigma\sigma'}\) is in general non-zero, comparing it to HEG, where all \(\phi_{i,\sigma}\) are planewaves

\[
V_{k+q,k',+q',k\sigma\sigma'} = \frac{1}{V^2} \int dr_1 dr_2 e^{-i(k+q) r_1 + i k r_1} \frac{1}{|r_1 - r_2|} e^{-i k' r_2 + i (k'+q') r_2}
\]

\[
= \frac{\delta_{q,q'}}{V} \int dr \frac{1}{|r|} e^{-iqr} = \delta_{q,q'} V_q
\]

which shows the conservation of momentum explicitly. As a direct consequence of this only terms like \(V_q (c^+_{k+q,\sigma} c^{+\dagger}_{k'+q,\sigma}) c^+_{k',\sigma} c_{k,\sigma}\) would survive and it’s trivial to see that \(k = k'\) when \(k + q = k' + q\). This means self-consistency is automatically achieved for planewave states.

However, in the generic case, \(V_{ijkl\sigma\sigma'}\) places no such constraint between \(i, j, k, l\), so that there’s no guarantee that only diagonal terms would appear. For example, terms with \(j \neq l\) and \(i = k\) don’t necessarily vanish and non-diagonal terms in \(\phi_{i,\sigma}\) basis like \(V_{ijkl\sigma\sigma'} \delta_{\sigma,\sigma'} (c^+_{i,\sigma} c_{k,\sigma}) c^+_{j,\sigma} c_{l,\sigma}\) mean that \(\phi_{i,\sigma}\)'s are not eigenstates of Fock operator.

Therefore, the physical moral behind non-interacting eigenstates remain eigenstates in the interacting case for HEG (single-particle picture; we are not talking about total momentum of many-particle state here) is simple and clear: Momentum is a good quantum number for a single particle in non-interacting HEG. Coulomb interaction conserves total momentum so
that momentum is still a good quantum number for single-particle states after we switch on
the interaction between particles, assuming Hartree-Fock approximation.

Now let’s move forward with the calculation Hartree-Fock Hamiltonian for HEG. To write it
in terms of Hartree-Fock eigenvalues,

\[ H_{HF} = \sum_{k, \sigma} \varepsilon_k c_{k, \sigma}^+ c_{k, \sigma} - U_{\text{exchange}} \]

\[ \varepsilon_k = t_k - \sum_q V_q \langle c_{k+q, \sigma}^+ c_{k+q, \sigma} \rangle \]

At zero temperature, \( \langle c_{k+q, \sigma}^+ c_{k+q, \sigma} \rangle = \Theta(k_F - |k + q|) \), \( k_F \) being fermion wave vector, so that

\[ \varepsilon_k = \frac{k^2}{2} - \frac{V}{(2\pi)^3} \int \frac{4\pi}{Vq^2} \Theta(k_F - |k + q|) \, dq \]

\[ = \frac{k^2}{2} - \frac{1}{(2\pi)^3} \left[ \int_0^{k_F-k} dq \, 16\pi^2 + \int_{k_F-k}^{k+k_F} dq \, \int_0^{k_F-k} d\theta \sin(\theta) 8\pi^2 \right] \]

\[ = \frac{k^2}{2} - \frac{2}{\pi} (k_F - k) + \frac{1}{\pi} \int_{k_F-k}^{k+k_F} dq \int_0^1 \arccos \left( \frac{k_F^2 - k^2 - q^2}{2kq} \right) \, dx \]

\[ = \frac{k^2}{2} - \frac{k_F}{\pi} \left( 1 + \frac{k_F^2 - k^2}{2kq} \ln \left| \frac{k + k_F}{k - k_F} \right| \right) \]

Even though we used condition \( k \leq k_F \) in the second step, it is straightforward to show that
the result for \( k > k_F \) has exactly the same form. So this formula applies to both occupied
and unoccupied states. Exchange potential for occupied states changes from \( -\frac{2k_F}{\pi} \) to \( -\frac{k_F}{\pi} \)
as \( k \) changes from 0 to \( k_F \).
The calculation for Total Energy of HEG system as ground-state eigenvalue of $H_{HF}$ follows easily.
\[ E_{HF} = 2 \sum_{k} \left[ \frac{k^2}{2} - \frac{k_F}{\pi} \left( 1 + \frac{k_F^2 - k^2}{2kk_F} \ln \left| \frac{k + k_F}{k - k_F} \right| \right) \right] - U_{exchange} \]

\[ = 2 \sum_{k} \left[ \frac{k^2}{2} - \frac{k_F}{2\pi} \left( 1 + \frac{k_F^2 - k^2}{2kk_F} \ln \left| \frac{k + k_F}{k - k_F} \right| \right) \right] \]

\[ = \frac{2V}{(2\pi)^3} \int_{0}^{k_F} d\xi 4\pi k^2 \left[ \frac{k^2}{2} - \frac{k_F}{2\pi} \left( 1 + \frac{k_F^2 - k^2}{2kk_F} \ln \left| \frac{k + k_F}{k - k_F} \right| \right) \right] \]

\[ = \frac{2V}{(2\pi)^3} 4\pi \left[ \frac{1}{2} \frac{k_F^5}{5} + \frac{k_F^4}{2\pi} \int_{0}^{1} x^2 F(x) \right] \]

\[ = \frac{2V}{(2\pi)^3} \frac{4}{3} \pi k_F^3 \left[ \frac{3}{5} \frac{k_F^2}{2} - \frac{3}{4\pi} k_F \right] = N \left( \frac{3}{5} \varepsilon_F - \frac{3}{4\pi} k_F \right) \]

\[ \frac{3}{5} N \varepsilon_F \] is the total energy for free electron gas; the correction to it is exchange energy.

Hartree-Fock exchange energy is the same as first-order perturbation of Coulomb interaction on free electron gas, since Hartree-Fock eigenstates coincide with non-interacting eigenstates. In literature, energy per particle is often shown as an expression of average inter-particle distance \( r_s \)

\[ \frac{4}{3} \pi r_s^3 = \frac{V}{N} = \frac{(2\pi)^3}{3\pi k_F^3} \]

\[ E_{HF} = \frac{1}{2} \left( \frac{2.2099}{r_s^2} - \frac{0.91633}{r_s} \right) \]

This can be shown to be exact in the high density \( (r_s \to 0) \) limit. It might seem first to be counterintuitive. Nevertheless, it’s true that at zero temperature fermions behave more like free particles at high density. At very low densities, they form Wigner Crystals (Drummond, Radnai, Trail, Towler, & Needs, 2004).
One alarming feature of the Hartree-Fock spectrum is that \( \frac{d \epsilon_k}{dk} |_{k=k_F} \rightarrow +\infty \). This means density of states at Fermi wavevector is 0, i.e. there’s an infinitesimal gap for HEG, which is unphysical as we know the system should be metallic. The divergence of the derivative can be traced back to

\[
\int dq V_q \sim \int dq \frac{1}{q} = \ln |\frac{k+k_F}{k-k_F}|.
\]

Had \( V_q \) been \( \frac{1}{V} \frac{4\pi}{q^2 + \alpha^2} \), which is the Fourier transform for screened Coulomb (Yukawa) potential \( e^{-\alpha r} \),

\[
\int dq V_q \sim \int dq \frac{q}{q^2 + \alpha^2} \approx \ln |\frac{(k+k_F)^2 + \alpha^2}{(k-k_F)^2 + \alpha^2}| \text{ so there wouldn’t be this divergence. Screening is probably the first thing one should think of when considering correlation of electrons.}
\]
Chapter 3 Density Functional Theory

Density functional theory (DFT) is a powerful, formally exact theory. In the formulation of Kohn-Sham DFT (Kohn & Sham, 1965), it tries to use a non-interacting model to mimic the behavior of many-body system so it shares some similarities with Hartree-Fock. But instead of having effectively a non-interaction wavefunction like Hartree-Fock, its non-interacting system aims to produce the same density distribution as the many-body system, for ground-state properties of the electronic system is uniquely determined by density according to Hohenberg-Kohn Theorem (Hohenberg & Kohn, 1964). DFT has come to prominence as a method potentially capable of very accurate results at low cost. In practice, approximations are required to implement the theory, as the exact mapping between density and ground-state property like energy is unknown. The next small section is the derivation of Hohenberg-Kohn theorem. Instead of the original derivation of Hohenberg and Kohn, which was based upon “reduction ad absurdum”, we follow the “constrained search” approach of Levy (Levy, 1979).

Hohenberg-Kohn Theorem (Density Variational Principle)

According to variational principle, ground state energy can be expressed as

\[ E = \min_{\Psi} \langle \Psi | H | \Psi \rangle \]

where \( \Psi \) are chosen from all normalized, antisymmetric \( N \)-particle wavefunctions.
We can now separate the minimization into two steps. First we minimize over wavefunctions that yield a given density $n(r)^6$

$$\min_{\Psi \to n} \langle \Psi | H | \Psi \rangle = \min_{\Psi \to n} \langle \Psi | T + V_{ee} | \Psi \rangle + \int d^3r \ v(r)n(r)$$

Then we define the universal functional

$$F[n] = \min_{\Psi \to n} \langle \Psi | T + V_{ee} | \Psi \rangle$$

Finally we minimize over all $N$-electron densities $n(r)$:

$$E = \min_n E_v[n]$$

$$= \min_n \left\{ F[n] + \int d^3r \ v(r)n(r) \right\}$$

, where $v(r)$ is held fixed during the minimization. The minimizing density is then the ground-state density.

The constraint of fixed particle number $N$ can be handled formally through introduction of a Lagrange multiplier $\mu$:

$$\delta \left\{ F[n] + \int d^3r \ v(r)n(r) - \mu \int d^3r \ n(r) \right\} = 0$$

, which leads to

---

$^6$ This is one-body density $(\psi^+(r)\psi(r))$, diagonal part of one-body density matrix. We use $n(r)$ instead of $\rho(r)$ here following conventions in DFT.
\[ v(r) = \mu - \frac{\delta F}{\delta n(r)} \]

, where \( \mu \) is to be adjusted until total conservation of particle number is satisfied \( \int d^3r \, n(r) = N \)

This equation shows that the external potential \( v(r) \) is uniquely determined by the ground state density. The functional \( F[n] \), minimized kinetic energy and electron-electron interaction for a given density, applies to all densities \( n(r) \) which are “\( N \)-representable”, i.e., coming from an antisymmetric \( N \)-electron wavefunction. The functional derivative \( \frac{\delta F}{\delta n(r)} \)

is defined for all densities which are “\( v \)-representable”, i.e., come from antisymmetric \( N \)-electron ground-state wavefunctions for some choice of external potential \( v(r) \).\(^7\)

It is straightforward to generalize the derivation for spin-density functional theory: just replace the constraint of fixed \( n \) by that of fixed \( n^\uparrow \) and \( n^\downarrow \). There are two practical reasons to do so:

(1) This extension is required when the external potential is spin-dependent, for instance if there’s an external magnetic field. (If this field not only couples to electron spin but also current density, then we must resort to a current-density functional theory).

\(^7\) We’ll not delve into the discussion of \( v \)-representability in this thesis. Interested readers referred to Density Functional Theory, An Advanced Course(Dreizler, 2011)
Even when external potential is spin-independent, we may still be interested in physical magnetization (arising from exchange effect).

**Kohn-Sham DFT**

For a system of non-interacting electrons, $V_{ee}$ vanishes so $F[n]$ reduces to

$$T_s[n] = \min_{\Psi \rightarrow n} \langle \Psi | T | \Psi \rangle$$

Even though we can search over all antisymmetric $N$-electron wavefunctions, the minimizing wavefunction for a given density will be a non-interacting wavefunction (a single Slater determinant) for some external potential $V_s$ such that

$$\frac{\delta T_s}{\delta n(r)} + v_s(r) = \mu$$

, the Kohn-Sham potential $v_s(r)$ is a functional of $n(r)$. If there were any difference between $\mu$ and $\mu_s$, the chemical potentials for interacting and non-interacting systems of the same density, it could be absorbed into $v_s(r)$.

Now we define the exchange-correlation energy $E_{xc}[n]$ by

$$F[n] = T_s[n] + U_{Hartree}[n] + E_{xc}[n]$$

, where $U[n]$ is the usual Hartree energy $\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(r)n(r')}{|\mathbf{r} - \mathbf{r}'|}$. Then our Kohn-Sham potential has to be

$$v_s(r) = v(r) + \frac{\delta U_{Hartree}[n]}{\delta n(r)} + \frac{\delta E_{xc}[n]}{\delta n(r)}$$
\[
= v(r) + v_{\text{Hartree}}(r) + v_{\text{xc}}(r)
\]

The Kohn-Sham method treats \( T_s[n] \) exactly, leaving only \( E_{xc}[n] \) to be approximated. This makes good sense, for several reasons:

1. We can guarantee \( N \)-representability of \( n(r) \) and \( v \)-representibility for the trivial case.

2. \( T_s[n] \) is typically a very large part of the energy, while \( E_{xc}[n] \) is a smaller part.

3. \( T_s[n] \) is largely responsible for density oscillations of the shell structure and Friedel types, which are accurately described by the Kohn-Sham method.

4. \( E_{xc}[n] \) is somewhat better suited to the local and semi-local approximations than \( T_s[n] \).

The price to be paid for these benefits is the appearance of orbitals. If we had a very accurate approximation for \( T_s[n] \) directly in terms of \( n \), we could dispense with the orbitals and solve directly for \( n(r) \).

Once we know how to form Kohn-Sham potential from density, we can immediately obtain a set of self-consistent equations since we can solve for the eigenvectors (orbitals) from which we can compute the density for the next iteration. This set of equations is known as Kohn-Sham equations through which we can solve for Kohn-Sham orbitals.

\[
\left[ -\frac{1}{2} \nabla^2 + v(r) + v_{\text{Hartree}}([n]; r) + v_{\text{xc}}^\sigma([n_\uparrow, n_\downarrow]; r) \right] \phi_{l,\sigma}(r) = \epsilon_{l,\sigma} \phi_{l,\sigma}(r)
\]
We have made the potential’s functional dependence on density explicit and also
generalized the framework to be spin-dependent (the constraint \( \int d^3r \ n(r) = N \) is still on
total density \( n(r) = n_\uparrow(r) + n_\downarrow(r) \)).

The self-consistence process can be illustrated by the simple flow chart below.

\[
\begin{align*}
n(r) &\rightarrow v_s(r) \rightarrow \phi_{l.s} \\
\text{occupation} &
\end{align*}
\]

The total energy of the system can be expressed as

\[
E = \sum_{i,\sigma} \epsilon_{i,\sigma} \langle c_{i,\sigma}^+ c_{i,\sigma} \rangle - U_{\text{Hartree}}[n] - \sum_\sigma \int d^3r \ n_\sigma(r) v_{\text{xc}}^\sigma ([n_\uparrow, n_\downarrow]; r) + E_{\text{xc}}[n_\uparrow, n_\downarrow]
\]

Hartree energy has been subtracted due to double counting and all exchange-correlation
part of energy in the sum of eigenvalues has been replaced by the correct \( E_{\text{xc}} \).

Once we have a good approximation of exchange-correlation functional \( E_{\text{xc}} \), we can use
Kohn-Sham equations to solve our system at relatively low computational cost compared to
methods of quantum chemistry.

**Approximations for Exchange-Correlation Functional**

The local spin density (LSD) approximation (Kohn & Sham, 1965) is among the earliest
attempts at approximating \( E_{\text{xc}} \) and it has long been popular in solid state physics.

\[
E_{\text{xc}}^{\text{LSD}}[n_\uparrow, n_\downarrow] = \int d^3r \ n(r) e_{\text{xc}}(n_\uparrow(r), n_\downarrow(r))
\]
, where \( e_{xc}(n_\uparrow, n_\downarrow) \) is the known exchange-correlation energy per particle for homogeneous electron gas with uniform spin densities \( n_\uparrow, n_\downarrow \).

Many functionals belong to the category of generalized gradient approximation (GGA)(Becke, 1986, 1988; Lee, Yang, & Parr, 1988; Perdew, 1985; Perdew, 1986; Perdew, Burke, & Ernzerhof, 1996; Perdew, Ruzsinszky, et al., 2008; Perdew & Yue, 1986; Wu & Cohen, 2006). They have the form

\[
E_{xc}^{GGA}[n \uparrow, n \downarrow] = \int d^3r \ f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow)
\]

This is a kind of simple extension of LSD, more widely used in quantum chemistry (e.g. gives much better atomization energies), but LSD remains the most popular way to do electronic-structure calculations in solid state physics. Table 1 and Table 2 provide a summary of typical errors for LSD and GGA.

The “third-rung” of this “Jacob’s ladder” in exchange-correlation functional approximations are called meta-GGA (Tao, Perdew, Staroverov, & Scuseria, 2003) which has the general form

\[
E_{xc}^{meta-GGA}[n \uparrow, n \downarrow] = \int d^3r \ f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow, \tau_\uparrow, \tau_\downarrow)
\]

\[
\tau_\sigma = \sum_{i \in \text{occupied}} \left| \frac{1}{2} \nabla \phi_{i,\sigma}(r) \right|^2
\]

Notice that what have been introduced here are merely general mathematical structure (the more general the mathematical form the higher up in “Jacob’s ladder”). Real performance usually varies from functional to functional.
Readers should be reminded that Hartree-Fock (introduced in the previous section) treats exchange exactly, but neglects correlation completely. While the Hartree-Fock total energy is an upper bound to the true ground-state total energy, the LSD and GGA energies are not.
Table 1 Typical errors with LSD and GGA approximations

<table>
<thead>
<tr>
<th>Property</th>
<th>LSD</th>
<th>GGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex(exchange)</td>
<td>5% (not negative enough)</td>
<td>0.5%</td>
</tr>
<tr>
<td>Ec(correlation)</td>
<td>100% (too negative)</td>
<td>5%</td>
</tr>
<tr>
<td>bond length</td>
<td>1% (too short)</td>
<td>1% (too long)</td>
</tr>
<tr>
<td>structure</td>
<td>overly favors close packing</td>
<td>more correct</td>
</tr>
<tr>
<td>energy barrier</td>
<td>100% (too low)</td>
<td>30% (too low)</td>
</tr>
</tbody>
</table>

Table 2 Mean absolute error of the atomization energies

MAE are for 20 molecules From reference (Perdew, Burke, et al., 1996)

<table>
<thead>
<tr>
<th>Approximation</th>
<th>Mean absolute error (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unrestricted Hartree-Fock</td>
<td>3.1 (underbinding)</td>
</tr>
<tr>
<td>LSD</td>
<td>1.3 (overbinding)</td>
</tr>
<tr>
<td>GGA</td>
<td>0.3 (mostly overbinding)</td>
</tr>
<tr>
<td>desired “chemical accuracy”</td>
<td>0.05</td>
</tr>
</tbody>
</table>

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Coupling-Constant Integration

Following our definition of exchange-correlation functional

\[ E_{xc}[n] = F[n] - T_s[n] - U_{Hartree}[n] \]

\[ = \langle \Psi_\lambda | T + \lambda V_{ee} | \Psi_\lambda \rangle_{\lambda=1} - \langle \Psi_\lambda | T + \lambda V_{ee} | \Psi_\lambda \rangle_{\lambda=0} - U_{Hartree}[n] \]

where we have introduced coupling constant \( \lambda \) (\( 0 \leq \lambda \leq 1 \)) and \( \Psi_\lambda \) is the wavefunction that produces the correct density \( n(r) \) while minimizes \( T + \lambda V_{ee} \).

Since \( \Psi_\lambda \) is the variational wavefunction within our constraint

\[ \langle \Psi_\lambda | T + \lambda V_{ee} | \Psi_\lambda \rangle \leq \langle \Psi_{\lambda'} | T + \lambda V_{ee} | \Psi_{\lambda'} \rangle_{\lambda' \neq \lambda} \implies \frac{d}{d\lambda} \langle \Psi_{\lambda'} | T + \lambda V_{ee} | \Psi_{\lambda'} \rangle_{\lambda'=\lambda} = 0 \]

We can use Hellman-Feynman Theorem to simplify

\[ E_{xc}[n] = \int_0^1 d\lambda \frac{d}{d\lambda} \langle \Psi_\lambda | T + \lambda V_{ee} | \Psi_\lambda \rangle - U_{Hartree}[n] \]

\[ = \int_0^1 d\lambda \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle - U_{Hartree}[n] \]

This equation “looks like” a potential energy; the kinetic energy contribution to \( E_{xc} \) has been subsumed by the coupling-constant integration. We should remember, of course, that only \( \lambda = 1 \) is real or physical. The Kohn-Sham system at \( \lambda = 0 \), and all the intermediate values of \( \lambda \), are convenient mathematical constructs.

Now kinetic energy operators are conveniently out of way, we can write the whole expression in terms various density distributions and Coulomb interaction.

\[ E_{xc}[n] = \frac{1}{2} \int d^3r' d^3r \frac{n(r)\rho_{xc}(r,r')}{|r-r'|} \]

\( \rho_{xc} \) is \( \lambda \) averaged exchange-correlation hole \( \rho_{xc}^3 \) corresponding to \( \Psi_\lambda \) (\( \rho_{xc} = \int_0^1 d\lambda \rho_{xc}^3 \)).
And exchange-correlation hole is defined such that

\[ \rho_2(r, r') = n(r)(\rho_{xc}(r, r') + n(r')) \]

Since \( \rho_2(r, r') \) is the two body density define earlier \( \rho_2(r, r') = \langle \psi^+(r)\psi^+(r')\psi(r')\psi(r) \rangle \), we can see that \( \rho_{xc}(r, r') + n(r') \) is the conditional density distribution given one particle is already at \( r \). \( \rho_{xc} \) is simply the difference between this conditional density and \( n(r') \). \( n(r') \) is chosen as a reference, for without the effect of exchange and correlation, particle distribution will be uncorrelated hence \( \rho_2(r, r') = n(r)n(r') \) and \( \rho_{xc} = 0 \).

It is easy to see \( \rho_{xc}(r, r') \) integrates to \(-1\) over \( r' \) for a system with fixed number of particles.

To see this, we can integrate both sides over \( r' \).

\[
\int \rho_2(r, r') \, d^3r' = (N - 1)(\psi^+(r)\psi(r)) = (N - 1) \, n(r)
\]

\[
\int d^3r' \, n(r)[\rho_{xc}(r, r') + n(r')] = n(r) \left[ \int d^3r' \, \rho_{xc}(r, r') + N \right]
\]

Equating both sides, we see

\[
\int d^3r' \, \rho_{xc}(r, r') = -1
\]

Exchange correlation hole conveniently offers intuitive picture of exchange-correlation effects as “exclusion” of particles at \( r' \) given the presence of a particle at \( r \).

\( \rho_{xc}^3 \) is the exchange-correlation hole of system with interaction coupling strength \( \lambda \) \( (H = T + \lambda V_{ee}) \)

\[
E_{xc}^3[n_1, n_1] = \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle - U_{Hartree}[n]
\]
\[
\frac{1}{2} \int d^3r' d^3r \ \frac{n(r) \rho_{xc}^2(r, r')}{|r - r'|}
\]

The knowledge of \( \overline{\rho_{xc}} \) (\( \lambda \) averaged) would uniquely determine exchange-correlation energy density

\[
e_{xc}(r) = \frac{1}{2} \int d^3r' \overline{\rho_{xc}(r, r')} \frac{|r - r'|}{|r - r'|}
\]

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

However, accurate description of exchange-correlation hole is not a mathematically necessary condition to have a working \( E_{xc} \). For example, in an inhomogeneous system exact \( \rho_{xc} \) would have various kinds of different shapes (anisotropic), but only the spherically averaged one would matter to \( E_{xc} \) as Coulomb interaction is isotropic i.e. we only need

\[
\int_{|r' - r| = constant} \frac{d^2r'}{4\pi|r - r'|^2} \rho_{xc}(r, r')
\]

to be correct. For this reason, one often drops the vector notation for second-electron coordinates and uses a scalar to indicate the distance between two particles like \( u = |r - r'| \) and use \( \rho_{xc}(r, u) \) to denote the spherically averaged value.

Therefore, normalization for \( \rho_{xc} \) amounts to the second moment of hole density

\[
\int du \ 4\pi u^2 \rho_{xc}(r, u) = -1
\]

, and \( e_{xc}(r) \) is nothing other than the first moment of hole density.

\[
e(r) = \frac{1}{2} \int du \ 4\pi u^2 \frac{\rho_{xc}(r, u)}{u} = \int du \ 2\pi u \rho_{xc}(r, u)
\]

Thus, if the exact exchange-correlation hole is not too extended, the approximation can't be too wrong.
There are also several other reasons why local/semilocal functionals work surprisingly reasonable for a wide range of systems including accurate on-top exchange-correlation hole $\rho_{xc}(r, r)$ (not only the value but also the right electron-electron cusp condition, i.e. correct $\frac{d}{du}\rho_{xc}(r, u)_{u=0}$)(Burke, Perdew, & Ernzerhof, 1998), system average effects, the cancellation of errors in exchange energy (not negative enough) and correlation energy (too negative)(Hood, Chou, Williamson, Rajagopal, & Needs, 1998) etc.

**Hybrid Functionals**

Nevertheless, there are situations where local/semilocal functionals produce significant errors. Closer examination reveals that in some regions the usual cancellation of the error in exchange energy and correlation energy doesn’t work very well. In these places, non-locality is unveiled and exchange could dominate correlation, e.g. one-electron, rapidly varying and non-uniform high density regions.

Different schemes of mixing exact exchange globally have been proposed (Becke, 1993; Lee et al., 1988; Perdew, Emzerhof, & Burke, 1996). The starting theoretical point is using linear interpolation of $\lambda = 0$ and $\lambda = 1$ to approximate coupling-constant integration for exchange-correlation functional ($\lambda = 0$ corresponds to exact exchange and $\lambda = 1$ corresponds to traditional local/semilocal functional).

$$E_{xc} = a E_{xc}^{\lambda=0} + (1 - a)E_{xc}^{\lambda=1} \quad (0 \leq a \leq 1)$$

Notice that for $\lambda = 0$, $\Psi_{\lambda}$ is Kohn-Sham wavefunction and $E_{xc}^{\lambda=0}$ is the exact exchange.

Thus, $\rho_{xc}^{\lambda=0}$ is nothing but exact exchange hole in this case. We’ll simply label it $\rho_x$. Using
similar expressions we derived in Hartree-Fock (only difference being we have Kohn-Sham orbitals instead of Hartree-Fock orbitals here), it’s easy to verify that \( \rho_x(r, r') \) integrates to 1 over \( r' \).

\[
\rho_\sigma(r, r') = \langle \psi_\sigma^+(r') \psi_\sigma(r) \rangle = \sum_i \langle n_{i,\sigma} \rangle \phi_{i,\sigma}(r) \phi_{i,\sigma}^*(r')
\]

\[
\int d^3r' \rho_x(r, r') = \int d^3r' \sum_\sigma \frac{-|\rho_\sigma(r, r')|^2}{n(r)} = \sum_\sigma -\frac{|\langle n_{i,\sigma} \rangle \phi_{i,\sigma}(r)|^2}{n(r)} = -1
\]

However, the presence of fractional charge (0 < \( \langle n_{i,\sigma} \rangle < 1 \)) would make the integral different from −1.

Open systems with fluctuating charges or calculations of chemical reaction barrier which usually involves stretched bonds require special attention and extra caution.

The most common form now is only to mix exact exchange with semilocal exchange, while leaving semilocal correlation unchanged.

\[
E_{xc} = a E_x + (1 - a) E_{xsl} + E_{csl}
\]

We used \( E_x \) for exact exchange, and \( E_{xsl} \) for semilocal exchange and \( E_{csl} \) for semilocal correlation. \( E_{xsl} + E_{csl} \) is the standard LSD, GGA or meta-GGA exchange-correlation functional. The calculation of exact exchange \( E_x \) is generally more demanding as we have to take into account the extended exchange hole which often has long tails, while semilocal energies are more readily available given the local density information. Choosing the mixing parameter \( a \) is a delicate matter. While semilocal approximations (\( a = 0 \)) typically overestimate atomization energies of molecules and underestimate the energy barriers to
chemical reactions, the use of exact or Hartree-Fock exchange \((a = 1)\) makes opposite errors. Fitting this mixing to atomization energies often gives \(a \approx 0.2\), while the reaction barrier heights typically require \(a \approx 0.5\) (Perdew, Staroverov, Tao, & Scuseria, 2008). The smallness of \(a\) indicates that semilocal exchange is more compatible with semilocal correlation than is the exact. We’ll in later chapters append one of our papers of quantum Monte Carlo validation of \(a\) value for transition metal oxide system.

Rewriting it using full exact exchange as first term

\[
E_{xc} = E_x + (1 - a) (E_x^{sl} - E_x) + E_c^{sl}
\]

This way, we can identify the rest of terms (2\(^{nd}\) and 3\(^{rd}\)) as correlation. Nonetheless, the 2\(^{nd}\) term has long range component while the 3\(^{rd}\) term is semilocal. Thus we hope to capture non-local part of correlation like static or near-degeneracy correlation by the 2\(^{nd}\) term and semilocal dynamic correlation by the 3\(^{rd}\) term. One could also change the design of a global constant \(a\) to a position dependent function \(a(r)\), which would have different value depending on the behavior of corresponding local density(Perdew, Staroverov, et al., 2008).

Screened hybrid functionals are also quite popular for solid-state calculations(Heyd, Scuseria, & Ernzerhof, 2003; Paier et al., 2006). In screened hybrid functionals, the exact exchange is screened at large distances, effectively giving a hybrid functional only at short range and GGA behavior at long range. However, the optimal screening length chosen could be different from system to system.

Primary functionals used in this thesis would be PBE(GGA) (Perdew, Burke, et al., 1996) and PBEh(hybrid-GGA). When we use PBEh, we can vary the mixing of exact exchange. PBE0
(Perdew, Emzerhof, et al., 1996) is PBE with 25% mixing of exact exchange. The number 0 simply means it has none empirical parameters and $a = 25\%$ was derived from first principle.
QMC (Quantum Monte Carlo) and DMC (diffusion Monte Carlo)

Monte Carlo methods are a broad class of computational algorithms that rely on stochastic process to obtain numerical results. Here we focus on the kind of Monte Carlo methods used for numerical integration.

Deterministic numerical integration algorithms work well in a small number of dimensions, but run into problems when the functions need to be integrated have many variables. The number of function evaluations needed increases rapidly with the number of dimensions. For example, if 10 evaluations provide adequate accuracy in one dimension, the $10^{100}$ points are needed for 100 dimensions—far too many to be computed. This is called the curse of dimensionality. For 3-d physical systems, each particle has 3 degrees of freedom thus the system’s dimension would scale as $3N$, $N$ being the number of particles in the system. Thus any deterministic numerical integration on top of any function that is an explicit many-body description of the system is not manageable.

Monte Carlo methods provide a way out of this exponential increase in computation time. As long as the function in question can be viewed as a well-behaved probability distribution function, it can be estimated by randomly selecting points in higher dimensional space according to the probability distribution function, and taking average of samples or some continuous function of sampled values. By central limit theorem or the delta method, the
average will tend to a Gaussian distribution with dispersion proportional to \( \frac{1}{\sqrt{N_s}} \)—i.e., quadrupling the number of samples halves the error, regardless of the number of dimensions.

Using Monte Carlo for integration is the essence of VMC (variational Monte Carlo) for it is nothing but calculating expectations like

\[
\langle \Psi^\dagger | H | \Psi^\dagger \rangle = \frac{\int dR \, \Psi^\dagger(R) \, H \, \Psi(R)}{\int dR \, \Psi^\dagger(R) \, \Psi(R)}
\]

Energy, the Hamiltonian expectation, is the most often calculated quantity though other observables can be evaluated as well. It is so named due to variational principle —i.e., whatever trial wavefunction \( \langle \Psi^\dagger \rangle \) we used, the result will be an upper bound to the true exact ground state energy. The implementation is also straightforward: we generate walkers (samples) according to probability distribution function \( \frac{|\Psi(R)|^2}{\sqrt{\int dR \, |\Psi(R)|^2}} \) while the quantity to sample is \( \frac{H \, \Psi(R)}{\Psi(R)} \), which is often referred to local energy. It is easy to see the final average will be the expectation we sought after.

Our walkers walk in many-body space of dimension \( 3N \), and are guaranteed to follow the aforementioned probability distribution function of trial wavefunction by Metropolis Algorithm. To improve the efficiency (acceptance) of Metropolis Algorithm, we added drift \( \nabla \ln |\Psi^\dagger(R)| \) to the proposition of walker movement just as Importance sampling in DMC (Diffusion Monte Carlo).

DMC is evaluating “mixed” expectations like
\[
\lim_{\tau \to \infty} \frac{\langle \Psi_T | H e^{-H \tau} | \Psi_T \rangle}{\langle \Psi_T | e^{-H \tau} | \Psi_T \rangle} = \lim_{\tau \to \infty} \frac{\int d \mathbf{R} \, \Psi_T^*(\mathbf{R}) \, H \, e^{-H \tau} \Psi_T(\mathbf{R})}{\int d \mathbf{R} \, \Psi_T^*(\mathbf{R}) \, e^{-H \tau} \Psi_T(\mathbf{R})}
\]

Operator \(e^{-H \tau}\) will project out the ground state of \(H\) from our trial wavefunction given \(\tau\) is large enough.

Notice that DMC is what we call a mixed estimator for ordinary observables (it could be observable \(A\) instead of \(H\) sandwiched between states). But mixed estimate won’t bother us for the evaluation of \(H\) as the ground state \(e^{-H \tau}\) projects out is, of course, an eigenstate of \(H\).

For an arbitrary observable \(A\), denoting the projected ground state by \(\Psi_0\), it is easy to see we can extrapolate to a pure estimate of \(\Psi_0\) for

\[
\langle \Psi_0 | A | \Psi_0 \rangle = 2 \text{Re} \langle \Psi_0 | A | \Psi_T \rangle - \langle \Psi_T | A | \Psi_T \rangle + \langle \delta \Psi | A | \delta \Psi \rangle
\]

\[
= 2 \text{Re} \, A_{DMC} + A_{VMC} + O(\delta \Psi^2)
\]

\[
\delta \Psi = \Psi_0 - \Psi_T
\]

If we estimate \(\langle \Psi_0 | A | \Psi_0 \rangle\) by \(A_{DMC} + (A_{DMC} - A_{VMC})(\text{assuming } A_{DMC} \text{ to be real})\), we have an error only to the second order in the difference of trial and projected wavefunctions\(^8\).

Efficiently realizing the projection operator \(e^{-H \tau}\) is at the core of DMC method. First we can notice that \(\Psi(\tau) = e^{-H \tau} \Psi_T\) satisfies equation

---

\(^8\) This is the method of extrapolation we used for calculating static structure factor in this thesis.
\[-\frac{\partial \Psi(\tau)}{\partial \tau} = H\Psi(\tau) = (T + V)\Psi(\tau)\]

This equation can be viewed as time-dependent Schrödinger’s equation \(i\frac{\partial \Psi}{\partial \tau} = H\Psi\) transformed by substitution \(\tau = it\). Thus \(\tau\) is called imaginary time and equation above is quite often referred to as imaginary time Schrödinger’s equation. If potential energy \(V = 0\), there are only Laplacian operators on the right hand side, one readily recognizes equation to be a diffusion equation, i.e. if \(\Psi_T\) is a positive function we can find \(\Psi_T\) stochastically through a diffusion process whose initial walker positions represent \(\Psi_T\). One simple step forward to include \(V\) is to branch the walkers at each diffusion time step by weight \(e^{-V\tau_0}\), \(\tau_0\) being the imaginary time step size. This is only correct to the first order of \(\tau_0\) for in general \(T\) and \(V\) don’t commute with each other and to the second order of \(\tau_0\)

\[
e^{-H\tau_0} \approx e^{-T\tau_0} e^{-V\tau_0} e^{-\frac{1}{2}[T,V]\tau_0^2}
\]

If we choose a time step small enough, this works for simple system like 1-d Harmonic system. But for real systems it quickly gets out of hand due to large fluctuations of \(e^{-V\tau_0}\).

Fluctuations of this sort can be greatly reduced if we can use some information from our trial wavefunction \(\Psi_T\) as leverage. If there exists a probability distribution function \(f(R,\tau) = \Psi(R,\tau)\Psi_T(R)\), it must satisfy equation

\[\]

\(^9\text{This error is often referred to as time-step error in literature.}\)
\[-\frac{\partial f}{\partial \tau} = -\Psi_T \frac{\partial \Psi(\tau)}{\partial \tau} = \Psi_T H \Psi(\tau) = \Psi_T H \Psi_T^{-1} f\]

Let's see if we can do some algebraic gymnastics so that $\Psi_T H \Psi_T^{-1}$'s action on $f$ can be directly implemented:

\[
\Psi_T H \Psi_T^{-1} f = \Psi_T \left( -\frac{1}{2} \nabla^2 + V \right) \Psi(\tau)
\]

\[
= -\frac{1}{2} \left[ \nabla^2 f - \frac{\nabla^2 \Psi_T}{\Psi_T} f - 2 \nabla \cdot (\Psi(\tau) \nabla \Psi_T) + 2 \Psi(\tau) \nabla^2 \Psi_T \right] + V f
\]

\[
= -\frac{1}{2} \nabla^2 f + \nabla \cdot \left( \frac{\nabla \Psi_T}{\Psi_T} f \right) + \left( -\frac{1}{2} \frac{\nabla^2 \Psi_T}{\Psi_T} + V \right) f
\]

We have represented kinetic energy operator $T$ as $-\frac{1}{2} \nabla^2$ (where $\nabla$ is understood to be $\sum_{i=1}^{N} \nabla_i^2$). So we have

\[-\frac{\partial f}{\partial \tau} = -\frac{1}{2} \nabla^2 f + \nabla \cdot (v f) + E_L f\]

\[v(R) = \frac{\nabla \Psi_T(R)}{\Psi_T(R)}\]

\[E_L(R) = \frac{H \Psi_T(R)}{\Psi_T(R)} = -\frac{1}{2} \frac{\nabla^2 \Psi_T}{\Psi_T} + V\]

Without local energy $E_L$, this is immediately recognized to be Fokker-Planck equation which describes particle diffusion process with drift velocity $v$. The local energy term can realized
through branching $e^{-E_L(R)\tau_0}$. But this time $E_L(R)$ has much smaller variance for different $R$, for we usually construct reasonable and accurate trial wavefunctions to start with (our trial wavefunctions are based on Hatree-Fock orbitals or DFT Kohn-Sham orbitals in this thesis). If our trial wavefunction already represents Hamiltonian eigenstate, then $E_L(R)$ is constant (eigenvalue). This method is called importance sampling. When $\tau \to \infty$, we’ll have $f(R) = \Psi_0(R)\Psi_T(R)$, average of local energy $E_L(R)$ under this distribution would be the expectation we are after.

$$\frac{\int f(R)E_L(R)dR}{\int f(R)dR} = \frac{\int \Psi_0\Psi_T \frac{H\Psi_T}{\Psi_T} dR}{\int \Psi_0\Psi_T dR} = \frac{\int \Psi_0H\Psi_TdR}{\int \Psi_0\Psi_T dR}$$

10 This would, again, introduce time-step error. But it is smaller this time due to smaller variance of local energy $E_L(R)$. Metropolis Algorithm is also used in DMC to reduce time-step error. (Umrigar, Nightingale, & Runge, 1993)

Also the actual branching weight implemented is $e^{\left[\frac{E_L(R)+E_L(R')}{z} - E_{ref}\right]}$, $R$ and $R'$ are walker positions of two consecutive steps while reference energy is chosen to maintain a stable total population. For discussion of population control bias, please see reference (Jaron & David).

11 The time it needs to equilibrate is inverse proportional to energy difference between ground state and next excited state component in the trial wavefunction.
Mixed estimates of other observables follow similarly.

In fact our current implementations of VMC and DMC share very similar structure of dynamics (walker movement). Mostly diffusion and drift are realized through sampling a Gaussian distribution\(^\text{12}\)

\[
T(R \rightarrow R') = \frac{1}{\sqrt{2\pi \tau_0}} e^{\frac{(R' - R - v \tau_0)^2}{2 \tau_0}}
\]

One can easily verify this is the Green’s function \(G(R', R, \tau_0) = \Psi_T(R') \langle R' | e^{-H \tau_0} | R \rangle \Psi_T^{-1}(R)\) when \(E_L(R) = 0\).

The main difference between VMC and DMC dynamics is that we can choose a large time step in VMC since we are merely sampling \(|\Psi_T|^2\) in VMC and Metropolis Algorithm can guarantee detailed balance. We often choose \(\tau_0\) to be large enough so acceptance is around 50%. In fact, VMC is very robust and acceptance in the range of 20% to 80% all gives reasonable result. In DMC, we have to choose a very small time step to reduce time-

\(^{12}\) Gaussian random numbers are generated from uniform random numbers via the polar form of Box-Muller transformation.

\(^{13}\) In practice, we use one electron update, i.e. only one electron’s coordinates are different in a single proposition \(R - R' = r_i - r'_i\) and we \(i\) iterates through all electrons in the program.
step error. This is one of reasons that DMC calculations are much more expensive than VMC calculations. For all-electron DMC calculations, the dynamics are different when walkers have electron positions close to nucleus: we sample exponential functions that satisfy the correct electron-nucleus cusp condition for radial movement instead of gaussians. This can significantly reduce time-step errors in these scenarios. Please see reference (Umrigar et al., 1993) for details.

**Trial Wavefunction and Fixed-Node Approximation**

Cautious readers might have paid special attention to the constraint $f(R) = \Psi(R)\Psi_T(R)$ being non-negative for all $R^{14}$. Wavefunctions in quantum mechanics are generally complex. Presence of time-reversal symmetry (like the absence of magnetic field for example) means wavefunctions can be written as real functions. Even then, electronic wavefunctions in general (barring the case of one electron under some circumstances) cannot be non-negative as electrons are fermions. When two fermions exchange coordinates with each other, the wavefunction has to switch sign. Thus $f(R) \geq 0$ means $\Psi(R)$ and $\Psi_T(R)$ have to share the same sign i.e. they share the same nodes.

---

$^{14}$ Release node methods require $f = \Psi\Psi_G$, where $\Psi_G$ is called guiding function and it is everywhere positive but it could be different from trial wavefunction $\Psi_T$. 

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(where wavefunction value vanishes)\textsuperscript{15}. Therefore, the wavefunction for our projected ground state $\Psi_0$ will be the ground state within nodal constraint. So it will have a higher energy than the true/exact ground state. The difference between FN-DMC (Fixed-Node DMC) energy and true ground state energy is called Fixed-Node Error.

Now we understand importance sampling in this case more than just uses trial wavefunction $\Psi_T$ to reduce variance, it inherits the nodes from $\Psi_T$. Therefore, the quality of $\Psi_T$ is of crucial importance. The most often used $\Psi_T$ has form

$$\Psi_T(R) = e^{J(R)}\Psi_A(R)$$

where $e^{J(R)}$ is referred to as Jastrow factor which is symmetric under exchange (it is positive everywhere) and $\Psi_A$ is the antisymmetric wavefunction that has forms like Slater determinants or linear combination of Slater determinants often seen in quantum chemistry. If our Hamiltonian $H$ does not explicitly involve spin, a trick called “spin assignment” can often be performed. We can divide all electrons in $R$ into $R_\uparrow$ and $R_\downarrow$ so that our trial wavefunction can be written as

$$\Psi_T(R) = e^{J(R_\uparrow, R_\downarrow)} \sum_i c_i Det_i^\uparrow [R_\uparrow] Det_i^\downarrow [R_\downarrow]$$

\textsuperscript{15} In fact, for electrons near the nodes, drift will always be pointing away from the nodes. Hence when time step is small enough, our walkers won’t cross the nodes imposed by trial wavefunction.
Without Jastrow, picking out one spin component (spin assignment) of $\Psi_A(R)$ (linear combination of determinants of spin orbitals that are assumed to be spin eigenstates) would give the same result as the original wavefunction for observables not dependent on spin. The reason is $\Psi_A$ could always be decomposed into spin components orthogonal to each other. When evaluating expectation of non-spin-dependent observables, there’s no mixing among these spin components and they all make the same contribution hence they are all equivalent and we can simply pick out one component to represent them all. With the presence of Jastrow, however, spin assignment could introduce spin contamination (Huang, Filippi, & Umrigar, 1998). But this contamination is often evaluated to be very small and our DMC result should in theory not depend on Jastrow factor (it does not affect nodes). In practice we almost always use spin-assigned Jastrow for easiness of expressing electron-electron cusp condition and evaluating such Jastrow factors. Electron-electron cusp condition (Kato, 1957) is often expressed in the center-of-mass frame of these two electrons ($\vec{r} = \frac{r_i + r_j}{2}, r_{ij} = r_i - r_j$)

For like spins

$$\frac{\partial \Psi_T}{\partial r_{ij}}|_{r_{ij}=0} = \frac{1}{2} \Psi_T|_{r_{ij}=0}$$

For unlike spins

$$\frac{\partial \Psi_T}{\partial r_{ij}}|_{r_{ij}=0} = \frac{1}{4} \Psi_T|_{r_{ij}=0}$$

$$n_{ij} = |r_i - r_j|$$
\[ \Psi_T(r_{ij}) = \frac{1}{4\pi} \int \Omega_{|r_{ij}|=r_{ij}} \Psi_T(\vec{r}, r_{ij}) \]

For our spin assigned Jastrow, this translates to

\[ \frac{\partial J(r_{ij})}{\partial r_{ij}} \bigg|_{r_{ij}=0} = \begin{cases} \frac{1}{2} & (\sigma_i = \sigma_j) \\ \frac{1}{4} & (\sigma_i \neq \sigma_j) \end{cases} \]

This is often the starting point for constructing Jastrow factors.

Jastrow is often written as the sum of one-body (electron-nucleus), two-body (electron-electron) and three-body (electron-electron-nucleus) terms.

\[ J(\{r_{ij}\}, \{r_{ii}\}, \{r_{ji}\}) = \sum_{i,l} \chi_i(r_{ii}) + \sum_{i\neq j} u(r_{ij}) + \sum_{i\neq j,l} w_l(r_{ij}, r_{il}, r_{jl}) \]

We have already identified \( u(r) \) to have non-zero derivative at \( r = 0 \). In our implementation all other functions have zero derivatives at \( r_{il} = 0 \) or \( r_{ij} = 0 \). Thus for all-electron calculations \( \Psi_A \) has to satisfy electron-nucleus cusp condition and for pseudopotential calculations \( \Psi_A \) should also have zero cusps.

Jastrow factor is a very compact form to capture a large amount of correlation and we generally optimize the parameters we have in the Jastrow factor to reduce the variance of local energy of our trial wavefunction. Quite often, with our form of Jastrow, the variance would go down by more than a factor of 4 after optimization.

Nevertheless, the result of our DMC energy calculations should not depend on Jastrow factor, if you don’t consider statistics (fluctuations, errorbars and population control
biases). The only part of our wavefunction that imposes nodal constraint under FN-DMC
is $\Psi_A$. To find a $\Psi_A$ with accurate nodes is a formidable task. The most common used $\Psi_A$ has
form

$$\Psi_A = Det^\uparrow[\mathbf{R}_1] Det^\downarrow[\mathbf{R}_1]$$

$$Det^\uparrow[\mathbf{R}_1] = Det[\phi_1^\uparrow(\mathbf{r}_1), \phi_2^\uparrow(\mathbf{r}_2), ... \phi_n^\uparrow(\mathbf{r}_n)]$$

$$Det^\downarrow[\mathbf{R}_1] = Det[\phi_1^\downarrow(\mathbf{r}_1), \phi_2^\downarrow(\mathbf{r}_2), ... \phi_n^\downarrow(\mathbf{r}_n)]$$

A determinant is an antisymmetrized sum of products of the orbitals within. This often
corresponds to Hartree-Fock wavefunction. We often say our trial wavefunction has
Hartree-Fock nodes. Orbitals for spin-up and spin-down electrons are different if they are
from unrestricted Hartree-Fock calculation. If orbitals are obtained from DFT calculations,
we have effectively a Slater determinant of Kohn-Sham orbitals, which is not a good
wavefunction by itself. But they sometimes provide good nodes and that’s all we need.
Ewald Interaction and Finite-Size Error

When simulating infinite periodic systems or finite systems subject to periodic boundary conditions, it is not possible to use the usual $\frac{1}{r}$ form of the Coulomb interaction as in the case of molecular systems because the sums over images of the simulation cell do not converge absolutely due to the long range nature of Coulomb interaction. The standard solution to this problem is to replace the Coulomb interaction by the Ewald interaction, which effectively arranges components of Coulomb interaction in the sum in a certain order to achieve fast convergence. And it achieved this by finding out the components whose sum converges very fast in reciprocal space and real space respectively and adding these two sums finally.

Ewald interaction enforces exact periodicity in all electronic densities and potentials. It may be used all kinds of solid state calculations as it lessens size variation of total energy per particle compared to most schemes using truncated sum of Coulomb interaction. We only show its explicit expression here because we want to demonstrate its implementation and understand its finite-size error (due to finite size of the simulation cell) in QMC.

Static structure factor can be defined (dimensionless) as

$$S(r, r') = \frac{V}{N} \langle [\hat{\rho}(r) - \rho(r)][\hat{\rho}(r') - \rho(r')] \rangle$$

$$= \frac{V}{N} \langle [\hat{\rho}(r)\hat{\rho}(r')] - \rho(r)\rho(r') \rangle$$
We immediately recognize that the first term can be expressed in terms of two-body/pair density

\[
\langle \hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}') \rangle = \langle \psi^+(\mathbf{r})\psi(\mathbf{r})\psi^+(\mathbf{r}')\psi(\mathbf{r}') \rangle
\]

\[
= \langle \psi^+(\mathbf{r})\psi^+(\mathbf{r}')\psi(\mathbf{r}')\psi(\mathbf{r}) \rangle + \langle \psi^+(\mathbf{r})[\psi(\mathbf{r}),\psi^+(\mathbf{r}')]\psi(\mathbf{r}') \rangle
\]

\[
= \rho_2(\mathbf{r}, \mathbf{r}') + \langle \psi^+(\mathbf{r})[\psi(\mathbf{r}),\psi^+(\mathbf{r}')]\psi(\mathbf{r}') \rangle
\]

\[
= \rho_2(\mathbf{r}, \mathbf{r}') + \rho(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')
\]

Dirac delta function here is understood to be periodic with respect to simulation cell.

This can also be shown if we look at states as many-body wavefunctions with the usual position representation of fixed number of particles as in our Monte Carlo program.

\[
\hat{\rho}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)
\]

\[
\rho_2(\mathbf{r}, \mathbf{r}') = \langle \sum_{i\neq j} \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{r}' - \mathbf{r}_j) \rangle
\]

\[
= \langle \sum_{i,j} \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{r}' - \mathbf{r}_j) \rangle - \langle \sum_{i=j} \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{r}' - \mathbf{r}_j) \rangle
\]

\[
= \langle \hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}') \rangle - \rho(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')
\]

Thus pair density and hence exchange-correlation hole can be expressed in terms of static structure factor

\[
\rho_2(\mathbf{r}, \mathbf{r}') = \frac{N}{V} S(\mathbf{r}, \mathbf{r}') + \rho(\mathbf{r})\rho(\mathbf{r}') - \rho(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')
\]

\[
\rho(\mathbf{r})\rho_{xc}(\mathbf{r}, \mathbf{r}') = \frac{N}{V} S(\mathbf{r}, \mathbf{r}') - \rho(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')
\]

Integrating over both sides with respect to \( \mathbf{r}' \), we have again
\[
\int d^3r' \rho_{xc}(r, r') = -1
\]

The translationally averaged (or system averaged) static structure factor is defined as

\[
S(r') = \frac{1}{V} \int d^3r S(r, r + r')
\]

\[
= \frac{1}{N} \int d^3r \left[ \langle \hat{\rho}(r)\hat{\rho}(r + r') \rangle - \rho(r)\rho(r + r') \right]
\]

The integration is carried out over the entire simulation cell. This quantity has periodicity of the simulation cell and we can expand it as Fourier series of reciprocal lattice vectors of simulation cell. Integrating both sides with \( e^{-i\mathbf{G}_s \cdot r'} \) over \( r' \), we have

\[
S(\mathbf{G}_s) = \int d^3r' S(r') e^{-i\mathbf{G}_s \cdot r'}
\]

\[
= \frac{1}{N} \int d^3r \sum_{\mathbf{G}_s', \mathbf{G}_s''} \frac{1}{\sqrt{V}} \left[ \langle \hat{\rho}^*(\mathbf{G}_s')\hat{\rho}^*(\mathbf{G}_s'') \rangle - \rho^*(\mathbf{G}_s')\rho(\mathbf{G}_s'') \right] e^{-i\mathbf{G}_s'r} e^{i\mathbf{G}_s'\cdot(r + r')} e^{-i\mathbf{G}_s'r'}
\]

\[
= \frac{1}{N} \int d^3r \sum_{\mathbf{G}_s} \frac{1}{V} \left[ \langle \hat{\rho}^*(\mathbf{G}_s')\hat{\rho}(\mathbf{G}_s) \rangle - \rho^*(\mathbf{G}_s')\rho(\mathbf{G}_s) \right] e^{i(\mathbf{G}_s - \mathbf{G}_s') \cdot r}
\]

\[
= \frac{1}{N} \left[ \langle \hat{\rho}^*(\mathbf{G}_s)\hat{\rho}(\mathbf{G}_s) \rangle - \rho^*(\mathbf{G}_s)\rho(\mathbf{G}_s) \right]
\]

\[
\hat{\rho}(\mathbf{G}_s) = \int d^3r \hat{\rho}(r) e^{-i\mathbf{G}_s \cdot r} = \int d^3r \sum_i \delta(\mathbf{r} - \mathbf{r}_i) e^{-i\mathbf{G}_s \cdot \mathbf{r}_i} = \sum_i e^{-i\mathbf{G}_s \cdot \mathbf{r}_i}
\]

This can be readily evaluated by our Monte Carlo program. Notice that \( S(\mathbf{G}_s) \rightarrow 0 \) as \( \mathbf{G}_s \rightarrow 0 \) and \( S(\mathbf{G}_s) \rightarrow 1 \) as \( \mathbf{G}_s \rightarrow \infty \).
When $G_s \notin \{G_p\}$, second term in $S(G_s)$ expression vanishes (no one-body contribution).

When $G_s \in \{G_p\}$, one-body density contributions are subtracted so that Bragg peaks wouldn’t show up.

In a similar way, we can do translational averages for pair density and exchange-correlation hole and find their Fourier component

$$
\rho_2(r') = \frac{N}{V} S(r') + \frac{1}{V} \int d^3r \rho(r) \rho(r + r') - \frac{N}{V} \delta(r')
$$

$$
\rho_2(G_s) = \frac{N}{V} [S(G_s) - 1] + \frac{1}{V} \rho^*(G_s) \rho(G_s)
$$

$$
\frac{1}{V} \int d^3r \ \rho(r) \rho_{xc}(r, r + r') = \frac{N}{V} [S(r') - \delta(r')]
$$

If we define system averaged exchange-correlation hole (only this average will affect total energy of the system) as

$$
\rho_{xc}^{av}(r') = \frac{1}{N} \int d^3r \ \rho(r) \rho_{xc}(r, r + r')
$$

Then the last two equations about $\rho_{xc}$ actually defines $\rho_{xc}^{av}$ in terms of static structure factor

$$
\rho_{xc}^{av}(r') = S(r') - \delta(r')
$$

$$
\rho_{xc}^{av}(G_s) = S(G_s) - 1
$$

With these quantities’ $G_s$ component, we can have a look at the relation between interaction potential energy evaluated as a Ewald sum and simulation cell size which determines the density of our $G_s$ grid.

$$
\langle V_E \rangle = \frac{N v_M}{2} + \frac{1}{2} \int_V \int_V \rho_2(r, r') v_E(r - r') \ d^3r \ d^3r'
$$
\[
\begin{align*}
&= \frac{N\nu_M}{2} + \frac{1}{2} \int \rho(r)\rho_{xc}(r, r') v_E(r - r') \, d^3r \, d^3r' + \frac{1}{2} \int \rho(r)\rho(r') v_E(r - r') \, d^3r \, d^3r' \\
&= \frac{1}{2} \int \rho(r)\rho_{xc}(r, r') [v_E(r - r') - \nu_M] \, d^3r \, d^3r' + \frac{1}{2} \int \rho(r)\rho(r') v_E(r - r') \, d^3r \, d^3r'
\end{align*}
\]

Substitute \( r' \) with \( r + r' \)

\[
\langle V_E \rangle = \frac{1}{2} \int \rho(r)\rho_{xc}(r, r + r') [v_E(r') - \nu_M] \, d^3r \, d^3r' + \frac{1}{2} \int \rho(r)\rho(r + r') v_E(r') \, d^3r \, d^3r'
\]

\[
= \frac{N\nu_M}{2} + \frac{1}{2} \sum \rho_{xc}(G_s) \frac{e^{iG_s r}}{V} v_E(G_s') \frac{e^{iG_s' r}}{V} \, d^3r' \\
+ \frac{1}{2} \sum \rho^*(G_s) \rho(G_s) \frac{e^{iG_s r}}{V} v_E(G_s') \frac{e^{iG_s' r}}{V} \, d^3r'
\]

\[
= \frac{N\nu_M}{2} + \frac{1}{2V} \sum \rho_{xc}(G_s) v_E(G_s) + \frac{1}{2V} \sum \rho^*(G_s) \rho(G_s) v_E(G_s)
\]

\[
= \frac{N\nu_M}{2} + \frac{1}{2V} \sum [S(G_s) - 1] v_E(G_s) + \frac{1}{2V} \sum \rho^*(G_p) \rho(G_p) v_E(G_p)
\]

Hartree term (last one) vanishes unless \( G_s \in \{ G_p \} \). Assuming charge density and the Fourier components of the static structure factor converge rapidly with system size and noticing that \( \nu_M \) tends to 0 as system size tends to infinity, \( \nu_M \) and the discretization error from the second term dominates finite-size error as for an infinite system the summation becomes an integral. For in the infinite size limit Ewald potential \( (v_E) \) reduces to Coulomb potential \( (v_c) \)

\[
\Delta V_E \approx \frac{N}{2} \left[ \frac{1}{(2\pi)^3} \int d^3k \ v_c(k) [S(k) - 1] - \frac{V}{N} \sum [S(G_s) - 1] v_E(G_s) - \nu_M \right]
\]
The sum and the integral converge as $S(k)$ quickly goes to 1 as $k$ increases. Also note that

$$v_M \approx \frac{1}{V} \sum_{G_s \neq 0} \frac{4\pi \exp(-\epsilon G_s^2)}{G_s^2} - \frac{1}{\sqrt{\pi \epsilon}}$$

$$= \frac{1}{V} \sum_{G_s \neq 0} \frac{4\pi \exp(-\epsilon G_s^2)}{G_s^2} - \frac{1}{(2\pi)^3} \int d^3k \frac{4\pi \exp(-\epsilon k^2)}{k^2}$$

So we can write

$$\Delta V_E \approx \frac{N}{2} \left[ \frac{1}{(2\pi)^3} \int d^3k \ v_c(k) S(k)e^{-\epsilon k^2} - \frac{1}{V} \sum_{G_s \neq 0} v_E(G_s)S(G_s)e^{-\epsilon G_s^2} \right]$$

The leading error is coming from $k = 0$ for the absence for $G_s = 0$ component in the second term and we can estimate this leading error by

$$\frac{N}{2} \frac{1}{(2\pi)^3} \int_{\Omega} d^3k \frac{4\pi}{k^2} S(k)$$

The integration is carried over domain $\Omega$ centered on origin with volume $\frac{(2\pi)^3}{V}$ and we have substituted $4\pi/k^2$ for $v_c(k)$.

For calculations in this thesis, we used such a correction. Change in the energy per particle is

$$\frac{1}{4\pi^2} \int_{\Omega} d^3k \ \frac{S(k)}{|k|^2}$$

, where $S(k)$ values are extrapolated from $S(G_s)$ values obtained from our Monte Carlo simulation.
Chapter 5  Electronic Structure Calculations of Thorium Oxides

Besides uranium and plutonium, thorium is also an important nuclear material. Thorium metal and its compounds have been widely investigated both experimentally and theoretically since metal thorium was discovered in 1828. Among thorium compounds, thorium dioxide $\text{ThO}_2$, which is a stable diamagnetic transparent insulating solid, has attracted special attention. In addition to its usage as nuclear fuel material, thorium dioxide has also been used as a solid-state electrolyte. In particular, due to its prominent hardness, $\text{ThO}_2$ has potential interest as an optical component material and laser host. Despite the interest, calculation of actinides and related material using QMC method has not been done before due to special difficulties dealing with $f$ electrons. But just like the way people tried to overcome the difficulties existed with $d$ electron calculations, it is not unlikely that a flurry of serious theoretical and computational attempts will be made for compounds involving last-row elements on the periodic table in the near future. With the enhancement of computer technology (we are entering the era of exascale computing), QMC methods will more than likely be deployed to obtain accurate results for these material

Thorium and related material provide a unique opportunity for us to try out and benchmark our methods for it contains no valence $f$ electrons. As a first attempt, we used relativistic
pseudopotential to remove all core electrons up to the 5th shell. With 12 electrons \((6s^26p^66d^27s^2)\) for each thorium atom, QMC calculation is more manageable.

**ThO (Thorium Monoxide molecule)**

We began our investigation with the calculation of ground state \(^{1}\Sigma^+\) properties of ThO (thorium oxide) molecule. ThO molecule belongs to a few actinide molecules well characterized both experimentally and theoretically. It has been nominated as one of the favorable molecular candidates for the search of electronic dipole moment owing to particularly high effective electric field acting on its electrons and the existence of metastable state \(^3\Delta\) convenient for spectroscopic investigations. Very recently, a detailed proposal for such experiments and some preliminary results have been published. Based on the polarization of ThO by an external electric field, the proposed experiments require accurate and detailed information on the molecular electric properties. However, little is known about them even for the ground state \(^{1}\Sigma^+\) of the molecule. Accurate experiments have been carried out for the measurement of bond length and dissociation energy.

We used the standard Slater-Jastrow form of wavefunction for this molecule. Stuttgart Relativistic Large Core ECP (effective core potential) and accompanying Gaussian basis set from EMSL basis set exchange (Feller, 1996) have been used for Th atom. Burkatzki-Filippi-Dolg energy-consistent ECP and accompanying v5z basis (Burkatzki, Filippi, & Dolg, 2007) set have been used for O atom. Hartree-Fock orbitals obtained from GAMESS RHF (Restricted Hartree Fock) calculation were used to form the Slater determinant. There are 12 valence
electrons for Th atom and 6 valence electrons for O atom, i.e. 9 spin-up electrons and 9 spin-down electrons. Our spin-assigned wavefunction is composed of Jastrow factor, a 12x12 determinant for spin-up electrons and another 12x12 determinant for spin-down electrons. VMC and DMC total energy compared with Hartree Fock is shown in the graph below.

Figure 2 ThO Dissociation Curve

We can see that VMC recovers a large part of correlation. Energy gain compared to Hartree-Fock in VMC is due to optimized Jastrow factor in VMC. If you pay close attention to VMC points, you’ll notice that they tend to jump around the Morse curve a little bit. The reasons are twofold:
(1) Optimization of parameters in Jastrow factor is a highly non-linear process. One can refer to Michal Bajdich’s thesis (Bajdich, 2007) to see the form of Jastrow factors and optimization technique (Levenberg-Marquart Algorithm) used in our research group. The optimization process might result in relatively large differences in wavefunctions for different configurations.

(2) QMC is a stochastic method. Calculated results are statistical averages which will fluctuate around expectation value. The errorbars that come with the averages are confidence intervals. Typical errorbars calculated in our programs are 66% confidence intervals. Times these errorbars by a factor of 1.96 then you’ll get 95% confidence interval. Errorbars in this thesis if not shown otherwise are smaller than symbol size in the plot.

DMC energies on the other hand should not depend on Jastrow in theory if one neglects the small differences from pseudopotential evaluation (projections used in locality approximation). One can always obtain a strict upper bound for nonlocal pseudopotential energy in DMC using a special Green function method called T-moves. Nonetheless, if VMC wavefunctions really have poor qualities, DMC energies might have relatively large statistical biases.
A more detailed graph of DMC dissociation energy is shown in Figure 3.

![Graph showing DMC dissociation curve](image)

**Figure 3 ThO DMC dissociation curve**

Summary of Morse potential $M(r) = c - d + d\left[1 - e^{-a(r-r_e)}\right]^2$ from Hartree-Fock, VMC and DMC data can be seen in Table 3.

<table>
<thead>
<tr>
<th>Morse Potential</th>
<th>$c$</th>
<th>$d$</th>
<th>$c - d$</th>
<th>$a$</th>
<th>$r_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>$-50.7191$</td>
<td>$0.449454$</td>
<td>$-51.168554$</td>
<td>$1.46921$</td>
<td>$1.80866$</td>
</tr>
<tr>
<td>VMC</td>
<td>$-51.2557$</td>
<td>$0.446802$</td>
<td>$-51.702502$</td>
<td>$1.4647$</td>
<td>$1.81712$</td>
</tr>
<tr>
<td>DMC</td>
<td>$-51.4721$</td>
<td>$0.383118$</td>
<td>$-51.855218$</td>
<td>$1.51437$</td>
<td>$1.8205$</td>
</tr>
</tbody>
</table>
The dissociation limit taken from Morse curve fit has to be taken with a pinch of salt, for Monte Carlo averages don’t exactly lie perfectly on the curve for reasons explained before and also that the fit is not taking into account of errorbars from Monte Carlo calculations. However, one could clearly see Hartree-Fock is not producing consistent dissociation limit while DMC is. The lowest DMC number is $-51.8544(9)$, in range of Morse curve bottom. Dissociation energy estimated by DMC is $0.353(2)$ Hartree, i.e. $9.6(5)$ eV. This is consistent with zero point energy corrected binding energy $9$ eV estimated from experiments.

Equilibrium bond length is reported to be $1.84$ Å.

Due to interests in ThO’s peculiar electric properties, it’s natural to include dipole in our calculation. Dipole moment can be easily obtained in QMC programs by averaging electron coordinates from all walkers, which adds little to existing routines for calculating energy. The caveat is that, since dipole moment does not commute with Hamiltonian, we have only mixed estimates from DMC.

Mixed estimates and extrapolated DMC pure estimates of dipole moments are shown in the graph below. Since DMC dipoles are mixed estimates, they’ll have a lot more dependence...
on the quality of trial wavefunctions than DMC energies. One can clearly see the
fluctuations of DMC numbers below.

![Figure 4 Dipole Moment of ThO.](image)

Both atoms are on z axis, which is pointing towards O atom.

All electron RCCSD(T) curve is from reference (Buchachenko, 2010) and it's valid only for the region from 1.5Å to 2.3Å.

RCCSD(T) calculation referenced here is a polynomial curve fit by original author for all
electron RCCSD(T) numbers from 1.5Å to 2.3Å using segmented contraction of aug-cc-pVQZ
basis with additional two sets of spdfg for Th atom and aug-cc-pVQZ basis for O
atom (Buchachenko, 2010).
One can also calculate particle and potential energy densities from QMC methods. Simply divide the space into a grid of tiny boxes, then use walkers to count the occurrences of particles in each box or count one-body or two-body potential energy associated with a single electron within that tiny box. Finally divide the value for each box by the total number of total samples.

What is shown below is a 2-d slice (through z axis, i.e. the axis of Th and O nucleus) of two-body potential energy density from DMC calculation.

![Figure 5 two-body energy density for ThO molecule.](image)

Th is on the left, O is on the right.

Every color in the graph above represents a value range about 1e-6. Resolution (the side length of our tiny boxes) is 0.02. This means every color represent energy density value range of \( \frac{1e^{-6}}{0.02^3} = 0.125 \). A rough visual estimate of thickness of a single colored ring is on the order of 0.1Å. This would imply a local electric field on the order

\[
\text{of } \frac{0.125 \text{ Hartree}}{1 \text{ electron charge } \times 0.1 \text{Å}} = 3.4 \text{ GV/cm, point towards Th nucleus } (\hat{z}) \text{. Electric field caused by nucleus in the bonding region can be easily estimated by } \frac{Z_1}{r_1^2} \hat{z} - \frac{Z_2}{r_2^2} \hat{z} (Z_1 = 12, Z_2 = 6) \text{ as}
\]
our nuclei are screened by core electrons and we ignore the effect of core polarization here, \( r_1 \approx 0.6 \text{Å}, r_2 \approx 1.295 \text{Å} \) ) to be around 42.8 GV/cm in \( \hat{z} \) direction. Thus the net local electric field for the point we picked is about 39.4 GV/cm. Of course this visual inspection and back-of-envelope calculation is not meant to be quantitatively correct. But it gives an estimate of the order of magnitude. CCSD(T) calculation of electric field is reported to be 104 GV/cm (Meyer & Bohn, 2008). Huge magnitude of internal electric field of ThO molecule has been used to help set the newest upper limit of electron dipole moment (Vutha et al., 2010).

**ThO\(_2\) Crystal (Thorium Dioxide)**

For ThO\(_2\) crystal calculation, we have used again Slater-Jastrow form of trial wavefunction where the orbitals in the slater determinant were obtained from DFT calculations. DFT calculations were performed with the same pseudopotentials and basis sets as in ThO molecule calculation\(^{16}\). The main code used for DFT calculation is CRYSTAL09 (Dovesi et al., 2005).

\(^{16}\) For Th atom, the Gaussian basis sets that come with Stuttgart RLC ECP has been truncated for the crystal calculation. All gaussians with exponents small than 0.1 or with spherical symmetries higher than \( f \) have been removed. Similar truncation has also been applied on the basis sets for O atom.
All calculations have been performed for the two phases that have been observed in experiments. At ambient pressure, ThO₂ crystallizes in the fluorite structure with space group $Fm\overline{3}m$ (No. 225) (Figure 6). Starting at about 35GPa, ThO₂ undergoes a phase transition to the orthorhombic structure of cotunnite ($PbCl₂$) type with space group $Pnma$ (No. 62) (Idiri, Le Bihan, Heathman, & Rebizant, 2004)(see Figure 7. It’s a bit harder to visualize the structure of this phase, so we have to pictures here with different highlights). Since the primitive cell for cotunnite phase is significantly bigger than fluorite phase, we used a smaller k-point mesh in DFT calculations. A 9x9x9 Monkhorst pack k-mesh has been used for primitive cell fluorite phase DFT calculations while a 4x4x4 Monkhorst pack k-mesh has been used for primitive cell cotunnite phase DFT calculations.

![Figure 6 Crystal structure of ThO₂. Fluorite phase ($Fm\overline{3}m$) at normal pressure.](image)
Both PBE and PBE0 correctly predict ThO$_2$ to be insulating but they report different in band gap as expected. Below is a plot of PBE DOS (density of states). Band gap is calculated to be 4.228 eV. Atomic symmetry projected DOS can also be seen in the plot. Valence band is mostly a mixing contribution from Th $d$ and O $p$. Th $6d$ and $5f$ are largely unoccupied and they dominate conduction band characteristic. The underestimation of band gap compared with experimental value of 5.9 eV (Evans, Barton, Clemens, & Allred, 2006) typical of GGA exchange-correlation functional.
Figure 8 Total and partial (atomic symmetry projected) DOS.

This is from FP-LAPW calculation in Wien2k. O p component here is from one atom only.

PBE0 produces a band gap of 7.27 eV, which is closer to what was observed in experiments. Their charge distribution all show the material to be strongly ionic and weakly covalent.

Charge distribution on [110] plane of fluorite (\(\text{Fm}\overline{3}m\)) phase thoria from our PBE calculation at lattice constant 5.62Å can be seen in Figure 9. Color range/scale is shown on the left. The density increases as red gradually turns to violet. 10 isovalue contour lines ranging from 0.01 \(au\) to 0.5 \(au\) with logarithmic (10 based) spacing have been drawn. Large blue circles are Th atoms while small blue and purple circles are O atoms. Red is for value below 0.02 \(au\). The red color and blue color in center of Th and O atoms are due to employment of pseudopotentials.
Figure 9 Electron Charge distribution on [110] plane of fluorite thoria.

Density values are in atomic units (e/\text{bohr}^3). Big circles are Th atoms. Small circles are O atoms.

One can immediately notice the empty region in between Th atoms. The ionic feature of the crystal is fairly obvious with Th atoms being donors and O atoms being acceptors. The relative weak covalent bonding between Th and O atoms is evident from the relative low density in the bonding region. The distance between Th atom and O atom on the graph
is 2.4335 Å. Band structure of fluorite phase thoria from our PBE calculation is shown in

Figure 10 Band structure of $Fm\overline{3}m$ phase ThO$_2$ calculated using PBE functional.

Figure 10. HOMO and LUMO are colored red and blue respectively.

There are 12 valence electrons coming from Th atom ($6s^26p^66d^27s^2$) and 6 electrons coming from each O atom ($2s^22p^4$). So a total of 24 electrons in the primitive cell means 12 bands will be occupied. Only 6 of those are shown in the band structure plot as Th $6s^26p^6$ and O $2s^2$ form 6 very low lying bands (the band coming from Th $6s$ is the
lowest and it’s almost entirely flat). 6 valence bands shown here occupy an energy range of about 0.15 Hartree (4.08 eV, smaller than band gap). They in fact are mainly formed by O $p$ atomic orbitals. 8 conduction bands shown are mainly formed by Th $f$ and $d$ atomic orbitals. This can be seen more straightforwardly in total DOS (Density of States) and atomic orbital projected DOS plot (Figure 11). If we add Th $f$, $d$, and O $p$ contributions (first 3 graphs) together we recover total DOS in this energy range. Thus we see the usual $s$ — $p$ covalent mixing in typical metal oxides is absent here (Th $6s$ is too low and $7s$ is too high to mix with O $2p$ orbital). Th $f$ and $d$ dominate the 8 conduction bands shown here. These 8 conduction bands are rather narrow as well.
Figure 11 DOS for $Fm\bar{3}m$ phase ThO$_2$ from PBE calculation.

The first three are DOS projected onto Th $f$, $d$ and O $p$ respectively; the last is total DOS. Each grid interval along y axis stands for 50 states/Hartree.
However, this material with relatively simple chemistry has some desired electric properties. Thoria and Ti-doped thoria were being considered as potential candidates for high-k material in MOSFET (metal–oxide–semiconductor field effect transistor) due to their high low frequency dielectric constant, thermal stability on semiconductors and small leakage current and band offsets when interfacing with semiconductors (Dutta & Waghmare, 2008; Evans & Allred, 2006).

We started an optical dielectric constant calculation using standard finite-field approach. A small electric field is applied along z-axis ([100] direction) (the dielectric tensor will be diagonal and x y z directions are equivalent due to cubic symmetry). DFT calculations follows to find the new electronic wavefunction. Then we calculate the response field from induced macroscopic electron charge distribution by Poisson equation (Macroscopic charge distribution is obtained by averaging over the original primitive cell. If no external field is applied, this is 0 as our cell is neutral.) Since the response field is always opposite to the original applied field. The net field will be smaller than the applied field. We find the dielectric constant by dividing the applied field with net field, which is always larger than 1.
The supercell has a height 8 times of conventional cell lattice constant (5.62 Å). Tics on x-axis are multiples of conventional cell lattice constant. PBE functionals are used.

In practical calculations, external potential has to be made periodic. We chose a saw-tooth form of electric potential whose gradient gives an alternating electric field (square wave form) (Figure 12). As a result, we’ll adopt a larger simulation cell (a supercell that accommodates an entire period of external potential in z direction). The larger the supercell is along z direction, the more accurate the result.
Table 5 Dielectric Constant of ThO$_2$ along [100] direction.

Row labels are different applied field strength. Column labels are the ratio of supercell height over conventional cell lattice constant.

<table>
<thead>
<tr>
<th></th>
<th>2</th>
<th>4</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>3.1518517509</td>
<td>3.9253755269</td>
<td>4.6220348041</td>
</tr>
<tr>
<td>0.0005</td>
<td>3.1041929382</td>
<td>4.6286148645</td>
<td>4.6943315291</td>
</tr>
<tr>
<td>0.0004</td>
<td>3.1030608725</td>
<td>4.6232652152</td>
<td>4.7006843929</td>
</tr>
</tbody>
</table>

Our results for different supercell size and different applied fields can be seen in Table 5.

Besides a numerical approach, Coupled Perturbative Hartree Fock (CPHF) (Ferrero, Rerat, Orlando, & Dovesi, 2008), a method for evaluating analytical derivates in this case, gives a high-frequency dielectric constant of 4.598. This method has converged beyond the third digit at k mesh of 12x12x12.

To calculate static dielectric constant, contribution from lattice dynamics has to be accounted for. Thus we calculated Born effective charge tensors and phonons/vibrations at $\Gamma$ point. Born effective charges were calculated using Berry phase approach and vibrations modes were calculated through a numerical approach (force constants, hessians of potential energy surface, were calculated as finite differences of forces on ions, which could be calculated analytically thanks to Hellman-Feymann Theorem) (Pascale et al., 2004).

Three atoms in the primitive unit cells give rise to 9 vibration modes:

- 3 acoustic modes with zero frequency at $\Gamma$ point.
- 3 optical modes where 2 O atoms move against Th atom ($\omega = 273.4529$ cm$^{-1}$).
• 3 optical modes where Th atom is held steady while 2 O atoms move against each other \( (\omega = 431.25 \text{ cm}^{-1}) \).

Combine these results and after adding electronic contribution to dielectric constant, we have a total static dielectric constant of 20.00816.

The large difference between static dielectric constant and electric dielectric constant has the same origin as splitting of longitudinal and transverse modes of the set of vibration modes \( (296.977 \text{ cm}^{-1}) \) where Th atoms and O atoms move against each other: the material is fairly ionic/polar so that vibrations of cations and anions against each other create macroscopic electric field that will in turn be coupled to ionic motion and polarize the ions.

The frequency of this longitudinal optical mode will be lifted to \( \omega_{LO} = (273.452 + 296.977) \text{ cm}^{-1} = 570.4299 \text{ cm}^{-1} \).

An interesting relation here is that

\[
\frac{\varepsilon_0}{\varepsilon_\infty} = \frac{20.00816}{4.598} \approx 4.35 \approx \left(\frac{\omega_{LO}}{\omega_{TO}}\right)^2 = \frac{(570.4299)^2}{(273.4529)^2}
\]

This relation is expected to hold for ionic crystals with cubic symmetry (Cochran & Cowley, 1962).

Experimentally observed \( \varepsilon_\infty \) and \( \varepsilon_0 \) are 4.30(5) and 18.9(4) (Axe & Pettit, 1966), which are smaller than our PBE results. This is not surprising considering PBE’s underestimation of band gap.
We found a similar chemical environment for cotunnite phase \( (Pnma) \) thoria. Charge density plots in Figure 13 and Figure 14 show an even more ionic bonding picture compared to fluorite phase.

**Figure 13** Electron density 2d map sliced through 3 inequivalent atoms in \( Pnma \) phase primitive cell.

**Figure 14** Electron density 2d map in a 4-atom plane in \( Pnma \) phase primitive cell.
Also relative to fluorite phase, there are significantly less vacuum charge regions and the structure is more close-packed.

![Figure 15 DFT Cohesive Energy per formula unit (ThO₂) in Rydberg.](image)

**Figure 15 DFT Cohesive Energy per formula unit (ThO₂) in Rydberg.**

X-axis is the cell volume for conventional cell, i.e. the volume for 4 formula units (4ThO₂).

Cohesive energies (per formula unit) for both phases can be seen above from both PBE and PBE0 calculations. Atomic positions in the cell were fully relaxed from PBE calculations.

Fractional coordinates of Th and O atom in $Fm\bar{3}m$ phase are relatively trivial

\[
\text{Th } 0.0 \ 0.0 \ 0.0,0 \ 0.25 \ 0.25 \ 0.25
\]

Fractional coordinates for 3 inequivalent atoms in $Pnma$ phase:

\[
\text{Th } 0.25 \ 0.25 \ 0.111,0 \ 0.142 \ 0.25 \ 0.431,0 \ 0.472 \ 0.75 \ 0.328
\]
For $Pnma$ phase, we also fix the relative ratio of three lattice constants, so that when we vary the volume there is only one degree of freedom.

$$a/b/c = 6.1446/3.7590/7.1820$$

Transition pressures are accordingly estimated to be 26 $GPa$ from PBE and 23 $GPa$ from PBE0. We used PBE0 orbitals to construct our trial wavefunctions. The reason we used PBE0 orbitals instead of PBE orbitals is similar to the MnO case. We carried out primitive cell calculations with different mixings of exact exchange and DMC energies were lowest when mixing is around 20%-30%. Since DMC method is a variational method (providing strict upper bounds), we are confident these are the best percentage for mixing global exact exchange.

To reduce FSE (Finite Size Error), 10 twist averages (simulation cell $k$ points centered at $\Gamma$ point in Irreducible Brillouin Zone) have been used for all fluorite phase calculations. 8 twist averages have been used for all cotunnite phase calculations. To reduce FSE due to overestimation of exchange-correlation energy in Ewald interaction, corrections based on static structure factor $S(k)$, as detailed in the previous chapter, have been applied. An example of calculated static structure factor is shown in Figure 16. Notice the data shown are at $k \in \{G_s\}$, where $G_s$ are reciprocal lattice vectors. Therefore the larger the size of simulation cell one could afford, the more accurate one is at estimating $k \rightarrow 0$ behavior of $S(k)$, which is the main contribution to exchange-correlation FSE correction.
Static structure factor for ThO$_2$.

\[ S(k) = \frac{1}{N}[(\bar{\rho}_k\bar{\rho}_{-k}) - (\bar{\rho}_k)(\bar{\rho}_{-k})]. \]

Shown data are obtained from \( Fm\bar{3}m \) phase conventional cell calculation. Standard pure DMC estimator extrapolation has been performed.

The analytical behavior of \( S(k) \sim k^2 \) near \( k = 0 \) is well known. So we then fit our data to expression \( S(k) = 1 - \exp(-a k^2 - b k^3) \) via \( a, b \). As shown in the previous chapter, we integrate \( S(k) \) over a domain \( \Omega \) size of the first Brillouin Zone centered at origin to estimate FSE.

\[ \frac{1}{4\pi^2} \int_{\Omega} d^3k \frac{S(k)}{k^2} \]

This number is then added to the total energy per particle.

An example of extrapolation to infinite cell size and \( S(k) \) correction is shown in Figure 17.

We can see \( S(k) \) correction accounts for more than 70% of FSE in this case.
Cohesive energies calculated from DMC after FSE correction are shown in Figure 17. The curve for normal pressure phase \((Fm\overline{3}m)\) is almost identical to that from PBE results. However, there is a significant difference between DMC and PBE results for high pressure phase \((Pnma)\). Transition pressure is lower from DMC estimation \((\sim 17.7 \text{ GPa})\)
relative to PBE estimation (~ 26 GPa). In experiments, \textit{Pnma} phase starts to appear at around 35 GPa (Idiri et al., 2004).

Experimental cohesive energy could be deduced from enthalpies of formations listed in Table 6 (J.D. Cox, 1989). Zero point vibrational energy (ZPVE) included cohesive energy is related to $H_0$ (enthalpy of formation at 0K) as following

$$E_c = H_0(\text{ThO}_2) - H_0(\text{Th}) - 2H_0(0)$$

$$= [(-1226.4 - 10.560) - (602 - 6.197) - 2 \times (249.18 - 6.725)](\pm 9.725) \text{kJ/mol}$$

$$= -2317.673(\pm 9.725) \text{kJ/mol} = -0.88275(370) \text{ au pfu} = -1.7655(74) \text{ Ry pfu}$$

ZPVE is relatively small due to the heaviness of Th atoms. From our PBE calculations for conventional cell this is estimated to be 0.005588 Hartree per formula unit. Thus ZPVE adjusted cohesive energy is -0.88834(370) Hartree per formula unit or -1.7767(7) Rydberg per formula unit. Our best estimate of this number from PBE and DMC are -1.7769 and -1.7817(7) respectively.

\textbf{Table 6 Enthalpies of formation for ThO}_2

\textbf{Numbers are in unit kJ/mol.}

<table>
<thead>
<tr>
<th>Substance</th>
<th>Phase</th>
<th>$H^o (295.18K)$</th>
<th>$H^o(295.18K) - H^o(0K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ThO$_2$</td>
<td>Crystal</td>
<td>-1226.4 ± 3.5</td>
<td>10.560 ± 0.020</td>
</tr>
<tr>
<td>O</td>
<td>Gas</td>
<td>249.18 ± 0.10</td>
<td>6.725 ± 0.001</td>
</tr>
<tr>
<td>Th</td>
<td>Gas</td>
<td>602 ± 6</td>
<td>6.197 ± 0.003</td>
</tr>
</tbody>
</table>
Figure 18 DMC Cohesive Energy per formula unit (ThO₂) in Rydberg. PBE curves are also shown here as reference. DMC numbers are FSE (finite size error) corrected. X-axis is the cell volume for conventional cell, i.e. the volume for 4 formula units (4ThO₂).
Chapter 6  DMC as an Accurate Variational Tool

DMC (Diffusion Monte Carlo) benchmark calculations in history served as Rosetta stone for modern electronic structure calculations. Heavy computational costs have been paid to evaluate and improve (projecting out ground state) explicit many-body wave functions in DMC in order to gain highly accurate results. One of the hallmark features of this approach is that energy benchmarks in DMC in theory are strict upper bounds for true ground-state energies even if they are not the exact. This means the energies we calculate in DMC are expectation values satisfying variational principle of quantum mechanics. This can be explained in simple terms as following

\[ E_{DMC} = \frac{\langle \Psi_T | H | \Psi_{DMC} \rangle}{\langle \Psi_T | \Psi_{DMC} \rangle} = \frac{\langle \Psi_{DMC} | H | \Psi_{DMC} \rangle}{\langle \Psi_{DMC} | \Psi_{DMC} \rangle} \geq \frac{\langle \Psi_0 | H | \Psi_0 \rangle}{\langle \Psi_T | \Psi_0 \rangle} = E_0 \]

Where \( \Psi_{DMC} \) is the ground state projected out by DMC process and \( \Psi_0 \) is the true ground state and \( E_0 \) is the true ground-state energy. Equality \((a)\) holds because \( \Psi_{DMC} \) is an eigenstate of \( H \). Inequality \((b)\) holds due to variational principle or more specifically \( \Psi_{DMC} \), being the eigenstate of \( H \) subject to “artificial” boundary conditions (nodes inherited from \( \Psi_T \) due to fixed-node approximation), will have a higher energy than the true ground state in general and will attain the true ground-state energy if the boundary conditions (nodes from \( \Psi_T \)) are exact. But this explanation is rather “handwaving” in nature can only serve as a guide for intuition as mathematically speaking boundary conditions are part of
the Hamiltonian. The exact mathematical proof can be found in the appendix of reference (Moskowitz, Schmidt, Lee, & Kalos, 1982).

In practice this means that the only uncontrollable error in DMC, fixed-node error, can only increase the result energy (it only has one sign), while all other kind of errors like statistical errors, finite-size errors, errors from pseudopotential evaluations can be controlled (Hennig et al., 2010). In DMC calculations if careful controlled “experiments” have been carried out to estimate various kinds of controllable errors then all the rest of the error, if any, is due to fixed-node approximation.

The magnitude of fixed-node error, as the result of fixed-node approximation, is a measure of the quality of fermion nodes of our trial wavefunctions. Therefore, the method provides a “fair ground” for testing various kinds of trial wavefunctions in that whichever has the lowest fixed-node error “wins”. Or equivalently speaking, once all controllable errors have been ruled out, whichever trial wavefunction attains the lowest DMC total energy is the most desirable candidate for true ground-state wavefunction.

It is exactly this variational property that enables us to try out wavefunctions from different sources. Our Slater wavefunctions often consists of orbitals from Hartree-Fock or DFT calculations. It is also this property that allows us optimize trial wavefunctions to our will as we often optimize parameters in our Jastrow factor to best capture correlation effect in a specific system and we sometimes even optimize the weights for determinants or configuration state functions from CI wavefunctions.
Our picture is simple and clear: we are evaluating expectation values of true Hamiltonian with different trial wavefuntions, no matter what sources they are from or they are optimized or not. In theory, no matter what the trial wavefunctions are, these are all legitimate calculations. As we improve our trial wavefunctions (the quality of their nodes), we should lower our DMC total energies.

Take Kohn-Sham orbitals from DFT calculations as an example. Kohn-Sham orbitals are designed in DFT to produce the correct many-body ground state density while they themselves only correspond to solutions of a fictitious non-interacting system. In our calculations, however, we form Slater determinant out of occupied Kohn-Sham orbitals as part of our trial wavefunction. The determinant itself has no designed physical meaning according to DFT theory. But from the perspective of DMC, this is just another mathematically constructed trial wavefunction. And we sometimes find these determinants attain lower DMC total energies than determinants formed from Hartree-Fock orbitals, which would attest to their superior nodal qualities and partially explains somewhat surprising success of many DFT calculations (echoing the meaning of Kohn-Sham orbitals and their eigenvalues). This has to be discussed on a case-by-case basis of course.

What is included in the following is our DMC study of orbitals from DFT with hybrid exchange-correlation functionals (Kolorenč, Hu, & Mitas, 2010). We demonstrated that for a certain percentage mixing of global exact exchange DMC calculations yield the lowest total energy. This is the only approach we know that does not rely on perturbation or excited
states (as DFT is a ground-state theory) to verify a certain mixing parameter for hybrid exchange-correlation functional.
Wave functions for quantum Monte Carlo calculations in solids: Orbitals from density functional theory with hybrid exchange-correlation functionals

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We investigate how the fixed-node diffusion Monte Carlo energy of solids depends on single-particle orbitals used in Slater-Jastrow wave functions. We demonstrate that the dependence can be significant, in particular in the case of 3d transition-metal compounds, which we adopt as examples. We illustrate how exchange-correlation functionals with variable exact-exchange component can be exploited to reduce the fixed-node errors. On the basis of these results we argue that the fixed-node quantum Monte Carlo provides a variational approach for optimization of effective single-particle Hamiltonians with parameters.

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I. INTRODUCTION

Steady increase in supercomputer performance over the last three decades stimulates development of very accurate electronic-structure methodologies that provide detailed understanding of ever larger and more complex systems. Diffusion Monte Carlo (DMC) method1,2 is one of the prime examples of these advanced many-body approaches. It uses a stochastic process to refine a given many-body wave function \( \langle \psi_f \rangle \), toward the actual ground-state solution \( \langle \psi_g \rangle \). The asymmetry of the wave function with respect to fermionic degrees of freedom is usually maintained by imposing the so-called fixed-node condition. In practice, it means that the nodal surface (the subset of configuration space where the many-body wave function vanishes) is restricted to be the same as in the initial guess \( \langle \psi_f \rangle \) throughout the entire stochastic simulation. The basic premise is that high accuracy is achieved even when relatively simple functional forms are employed for \( \langle \psi_f \rangle \).

The impact of the fixed-node approximation has been intensively studied in few-electron atoms and molecules as well as in homogeneous systems, where the performance of the DMC method with increasing accuracy of the trial wave function \( \langle \psi_f \rangle \) is relatively well mapped out.3,4 Applications to solids are not nearly as numerous, and hence the influence of the fixed-node condition in crystalline settings is much less examined. Evaluation of bulk properties necessarily involves extrapolation to the thermodynamic limit, which decreases the amount of computational resources available for exploration of rather subtle fixed-node errors. Consequently, only the simplest trial wave functions, having the Slater-Jastrow form, are typically employed. These wave functions have nodal surfaces defined by single-particle orbitals, and therefore they correspond to mean-field nodes. The subject of our study are the fixed-node errors associated with such trial functions when they are applied to simple transition-metal oxides in crystalline phases.

II. FIXED-NODE DIFFUSION MONTE CARLO METHOD

The fixed-node diffusion Monte Carlo method calculates expectation values of quantum-mechanical operators in the ground state (as well as in certain excited states) of a many-body Hamiltonian \( \hat{H} \). The DMC wave function is found by a projection,

\[
\langle \psi_d \rangle = \lim_{\tau \to \infty} e^{-\tau \hat{H}} \langle \psi_f \rangle, \tag{1a}
\]

that gradually increases the weight of the lowest-energy eigenstate of \( \hat{H} \) relative to all other states admitted in some initially guessed wave function \( \langle \psi_f \rangle \). Building on similarity between the Schrödinger and the diffusion equations, the projection is realized with the aid of a classical stochastic process. The outcome of this simulation is a set of \( 3N \)-dimensional samples \( \{R\}_i \) distributed according to a probability density \( \mathcal{P}(R) = \langle \psi_d \rangle(R) \langle \psi_d \rangle(R) / \langle \psi_f \rangle(R) \langle \psi_f \rangle(R) \). Here \( R = (r_1, r_2, \ldots, r_N) \) denotes coordinates of all \( N \) electrons comprising the investigated quantum system. The Hamiltonian \( \hat{H} \) is assumed to be spin independent, which prevents any spin-flip processes to occur in Eq. (1a), and hence the spins do not enter the simulations as dynamical variables. The probabilistic interpretation of \( \mathcal{P}(R) \) is possible only if it is a positive quantity. In the case of fermions, the projection as written in Eq. (1a) does not fulfill this requirement, which must therefore be prescribed in the form of an additional condition

\[
\langle \psi_f \rangle(R) \langle \psi_f \rangle(R) / \langle \psi_f \rangle(R) \langle \psi_f \rangle(R) = 0. \tag{1b}
\]

This step introduces the so-called fixed-node approximation since the projection cannot reach the true ground state \( \langle \psi_g \rangle \) if the fermionic nodes of the trial wave function \( \langle \psi_f \rangle \) differ from (a priori unknown) nodes of the desired ground state. Our primary aim is to explore the impact of this fixed-node approximation for a particular functional form of the trial wave function.

The set of \( N \) samples \( \{R\}_i \) acquired as a result of a DMC simulation can be directly used to calculate the so-called mixed estimates of the quantum-mechanical expectation values,
\[
\langle \Psi_2 | \hat{A} | \Psi_2 \rangle = \int dR \left( \frac{\Psi_2(R)}{\langle \Psi_2 | \Psi_2 \rangle} \right) \left( \frac{\hat{A} \Psi_2(R)}{\langle \Psi_2 | \Psi_2 \rangle} \right) 
\]
\[
= \sum_{i=1}^{N} \left( \frac{\hat{A} \Psi_2(R_i)}{\Psi_2(R_i)} \right) + O(N^{-1/2}).
\]

If the operator \(\hat{A}\) commutes with the Hamiltonian, the mixed estimate equals the desired quantum-mechanical expectation value, \(\langle \Psi_2 | \hat{A} | \Psi_2 \rangle = \langle \Psi_2 | \hat{A} | \Psi_2 \rangle = \langle \Psi_2 | \hat{A} | \Psi_2 \rangle = \langle \Psi_2 | \Psi_2 \rangle = E_0\). In general, however, there is an error proportional to the difference between \(\Psi_2\) and \(\Psi_2\) that can be reduced to the next order using the following extrapolation: \(^2\)

\[
\left( \begin{array}{c}
\langle \Psi_2 | \hat{A} | \Psi_2 \rangle \\
\langle \Psi_2 | \Psi_2 \rangle
\end{array} \right) = \left( \begin{array}{c}
\langle \Psi_2 | \hat{A} | \Psi_2 \rangle \\
\langle \Psi_2 | \Psi_2 \rangle
\end{array} \right) + O\left( \frac{\Psi_2}{\sqrt{\langle \Psi_2 | \Psi_2 \rangle}} \right)^2.
\]

The expectation value \(\langle \Psi_2 | \hat{A} | \Psi_2 \rangle = \langle \Psi_2 | \Psi_2 \rangle \) is evaluated by straightforward Monte Carlo integration and it is referred to as the estimate of the variational Monte Carlo (VMC) method.

### III. TRIAL WAVE FUNCTIONS

We employ trial wave functions having the Slater-Jastrow functional form, which is an antisymmetrized product of single-particle orbitals (Slater determinant) multiplied by a correlation factor that is symmetric with respect to pair-electron exchanges. We can write

\[
\psi_j(R) = \det(\phi_i) \det(\phi_i) e^{i H X},
\]

where \(\phi_i\) and \(\phi_i\) are spatial parts of single-particle orbitals that correspond to spin-up, respectively, spin-down electronic states. The vector \(X = (x_1, x_2, \ldots, x_N)\) encompasses positions of all \(M\) ions in the lattice. The expression in Eq. (4) represents only a spatial component of the trial wave function corresponding to one particular spin configuration, where electrons with labels \(1, \ldots, N\) are in the spin-up state and electrons with labels \(N+1, \ldots, N\) are in the spin-down state. We can use this simplified form with fixed spin states instead of the full wave function as long as neither the Hamiltonian nor any other operator, expectation value of which we intend to calculate, depend on electron spins. \(^3\) The applications we consider involve only cases with zero total spin, i.e., \(N\) is an even number and \(N_1 = N_2 = N/2\).

The Jastrow correlation factor we use,

\[
J(R, X) = \sum_{ij} f(x_i - x_j) + \sum_{ij} g(x_i - x_j),
\]

contains one- and two-body terms, \(g\) and \(f\), that are parametrized in the same way as in Ref. 9. This correlation factor improves efficiency of the Monte Carlo sampling and accuracy of general expectation values calculated according to Eq. (3). Quality of the DMC total energy \(E_0\) depends solely on the accuracy of the nodal surface that is, given the functional form of Eq. (4), completely determined by the single-particle orbitals \(\psi_i, \psi_i\). Ideally, these orbitals would be parametrized by an expansion in a saturated basis with the expansion coefficients varied to minimize the DMC total energy. Unfortunately, the stochastic noise and the computational demands of the DMC method make this route extremely inefficient in practice except, perhaps, in the case of the simplest few-electron systems.

A more feasible alternative is to skip the DMC projection, Eq. (1a), and optimize the orbitals \(\langle \phi_i, \phi_i \rangle\) with respect to a simpler quantity \(E_0\). For instance, the variational Monte Carlo methodology can be utilized to minimize the variational energy \(E_V = \langle \psi_0 | \hat{H} | \psi_0 \rangle / \langle \psi_0 | \psi_0 \rangle\). The VMC optimization of one-particle orbitals was successfully employed for atoms and small molecules of the first-row atoms \(^6, ^7\) but the method is still too demanding for applications to solids. It is also not completely robust since an improvement of the variational energy does not automatically guarantee an improvement of the fixed-node energy due to the limited parametric freedom of the trial wave function \(\langle \Psi_2 | \Psi_2 \rangle\). This issue is even more pronounced when the wave functions are not optimized with respect to the VMC energy but with respect to another quantity, such as the energy variance.

To avoid the large number of variational parameters needed to describe the single-particle orbitals, another family of methods has been proposed. The orbitals in the Slater-Jastrow wave function are found as solutions to self-consistent-field (SCF) equations that represent a generalization of the Hartree-Fock (HF) theory to the presence of the Jastrow correlation factor. \(^1, ^3, ^4\) These methods were tested in atoms as well as in solids within the VMC framework. \(^1, ^2, ^5\) Unfortunately, the wave functions derived in this way did not lead to lower DMC energies compared to wave functions with orbitals from the Hartree-Fock theory or from the local-density approximation (LDA). \(^1, ^2, ^5\) Taking into account our results presented below it seems likely that the lack of observed improvements in the fermionic nodal surfaces stems from the fact that only applications to weakly correlated systems with just \(s\) and \(p\) valence electrons were considered so far.

In this paper, we also use SCF equations as a means to construct the one-particle orbitals but the parametric dependence of these equations is introduced without any relation to the actual Jastrow factor. The self-consistent-field equations in question are Kohn-Sham equations corresponding to the hybrid exchange-correlation functional PBE1, \(^7, ^9\)

\[
E_{xc}^{PBE1} = w E_x + (1 - w) E_x^{PBE} + E_x^{PBE}.
\]

Here \(E_x^{PBE}\) and \(E_x^{PBE}\) are exchange and correlation parts of the PBE formula \(^8\) of the generalized gradient approximation (GGA), and \(E_x\) is the exchange functional from the Hartree-Fock theory evaluated with Kohn-Sham orbitals. The weight \(w\) is in the range \(0 \leq w \leq 1\) and serves as a variational parameter with respect to which the fixed-node DMC energy is minimized.

In the transition-metal oxides we study, it is understood that exchange in GGA is underestimated \(^1\) whereas the “exact” exchange from the Hartree-Fock theory overestimates the real exchange mechanism as any screening effects are
neglected. The hybrid density-functional theory (DFT) provides an interpolating scheme between these two extremes. There are numerous examples in the literature illustrating that reasonable agreement between its predictions and experimental observations can be achieved.

Arguably, the single parameter introduced to the one-particle orbitals represents only relatively constrained variational freedom compared to the approaches mentioned above. On the other hand, the simplicity of the parameter space allows for direct optimization of the fixed-node DMC total energy, and therefore the variations in the fermionic nodal structure can be directly quantified. Initial applications of this strategy to molecules and in a more elementary form also to solids were reported previously. In the following sections, we perform the DMC optimization for two compounds, MnO and FeO, and systematically analyze the variational freedom available within this method in crystalline environments. Preliminary data leading to the results presented here were shown in Ref. 30.

IV. THERMODYNAMIC LIMIT

Crystals in our simulations are represented by periodically repeated simulation cells of a finite size, in which the Coulomb interaction energy is evaluated with the aid of the Ewald formula. To calculate bulk quantities, one has to perform an extrapolation to the thermodynamic limit (infinite crystal volume). Our main objective, however, is to compare energies obtained for different trial wave functions in a given simulation cell with fixed volume, and hence the size extrapolation seems redundant. Indeed, the leading-order term of the finite-size errors related to the long-range character of the Coulomb interaction is a function of the average charge density alone. Variation in single-particle orbitals does not change this quantity, and these finite-size errors are therefore mostly irrelevant for our wave-function optimization since they cancel out.

The Coulomb interaction is not the only cause of finite-size biases in calculations performed in finite simulation cells. There is another source of nonvanishing surface terms that appear even if no two-body interaction is present in the Hamiltonian. These can be brought to light as follows: the statement "periodically repeated simulation cells" used above refers to observable quantities and does not fully specify the boundary condition for the phase of the wave function. In the language of single-particle description of solids, different boundary conditions compatible with periodicity of observables correspond to simulations being done at different k points. Averaging over all k points from the first Brillouin zone removes the dependence of the computed quantities on the boundary conditions and in the case of non-interacting particles it is equivalent to performing the thermodynamic limit. For Hamiltonians with particle-particle interactions this correspondence is not exact but a very substantial reduction in finite-size errors is observed nevertheless.

Comparison of trial wave functions at a single k point is certainly a valid approach. On the other hand, variation in the exchange-correlation functional in the Kohn-Sham equations modifies the resulting band structure in a generally non-trivial k-dependent manner, see, for instance, Ref. 24 for illustration. As a result, the minimization of the total energy calculated at a single k point does not necessarily lead to the same optimal weight w as does the minimization of the k-averaged total energy. Since the latter is arguably a better approximation of the thermodynamic limit, which is what we are ultimately interested in, we work with the k-averaged quantities.

V. MnO AT AMBIENT CONDITIONS

We start our investigations with manganese monoxide at experimental equilibrium volume, V = 21.7 Å³/MnO. Calculations are performed for two lattice structures, both with antiferromagnetic (AFM) ordering of magnetic Mn atoms: B1 (symmetry group P3m1, the so-called AFM-II state) and B8 (symmetry group P3m1). The former phase is the low-temperature ground-state structure at atmospheric pressure and the latter is a phase stable at high pressures. Since all states investigated in this paper are antiferromagnetic, we will often leave out this attribute.

Data were collected in simulation cells containing 16 atoms (eight Mn and eight O). Atomic cores were replaced by Hartree-Fock norm-conserving pseudopotentials within the so-called localization approximation. Helium core was excluded from oxygen atoms and neon core from manganese atoms, which left 168 valence and conduction electrons explicitly included in the simulations. The Monte Carlo calculations were performed with CRYSTAL09 (Ref. 39) and the single-particle orbitals were prepared in CRYSTAL09. In both codes, the orbitals were expanded in a Gaussian basis, completeness of which was verified against a converged basis of linearized augmented plane waves as implemented in the Wien2k code. The basis-set benchmarks were performed within DFT using the PW91 exchange-correlation functional. The Jastrow factor, Eq. (5), was optimized for the exact-exchange weight w = 0.1 at the P point employing a mixture of 95% VMC energy and 5% variance as a cost function. The resulting correlation factor (one for each simulation cell) was then used for all values of the weight w at all k points without further reoptimization. Several tests (see the Appendix for one of them) indicated that independent optimization of the Jastrow factor for each weight and at every k point would not change the final results within the targeted statistical precision.

The acquired dependence of the DMC total energies on the exact-exchange weight w is plotted in Fig. 1. Each energy value shown in the picture represents an average over eight k points. Such average made within DFT differs from the converged integral over the first Brillouin zone of the simulation cell by less than the statistical error bars plotted in the figure. Quadratic functions fitted through the DMC data using the least-squares method lead to the optimal values of the weight w listed in Table I. Drop of the total energy from the pure PW91 orbitals (w=PW1) to the minimum is ≈ 0.15 eV/MnO, and from the Hartree-Fock orbitals (w=HFE1) it is ≈ 0.2 eV/MnO. The dependence of the fixed-node DMC total energy on the admixture of the exact
exchange is weaker in the MnO solid than in the MnO molecule, where the gain from the Hartree-Fock to hybrid DFT orbitals was observed as large as 0.6 eV. We attribute this difference to a greater freedom of charge density to adapt in the molecule than in the constrained solid-state environment.

The data collected so far can be utilized to evaluate quantities of direct physical interest. The difference between the optimized total energies provides a measure of relative stability of the investigated phases at the given volume. We find that the B1 structure is lower in energy than the B8 structure by $0.27 \pm 0.01$ eV/MnO. The cohesive energy $E_{\text{coh}}$ of MnO can also be estimated. To this end, energies of isolated Mn and O atoms need to be calculated, and the crystalline total energy has to be extrapolated to the infinite volume. We provide details of these steps in the Appendix. In the end, we obtain $E_{\text{coh}} = 9.29 \pm 0.04$ eV that is in good agreement with the value 9.5 eV derived from experimental formation enthalpies. Our result differs from the earlier DMC estimates by 0.40 eV, whose seemingly better agreement with experiment is fortuitous and originates in underestimation of the finite-size effects. The prior calculations were done in smaller simulation cells and only at a single $k$ point.

**TABLE I.** Exact-exchange weight $w$ leading to minimal DMC total energies of several phases of MnO and FeO solids.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase</th>
<th>$V$ (Å$^3$/XO)</th>
<th>$w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO</td>
<td>B1 AFM-II</td>
<td>21.7</td>
<td>0.30 ± 0.01</td>
</tr>
<tr>
<td>MnO</td>
<td>B8 AFM</td>
<td>21.7</td>
<td>0.33 ± 0.01</td>
</tr>
<tr>
<td>FeO</td>
<td>B1 AFM-II</td>
<td>20.4</td>
<td>0.25 ± 0.02</td>
</tr>
<tr>
<td>FeO</td>
<td>B1 AFM-II</td>
<td>17.3</td>
<td>0.214 ± 0.006</td>
</tr>
<tr>
<td>FeO</td>
<td>IB8 AFM</td>
<td>17.0</td>
<td>0.156 ± 0.003</td>
</tr>
</tbody>
</table>

**VIS. LARGE SIMULATION CELLS NECESSARY?**

It was argued in Sec. IV that $k$-point averaging should remove nearly all finite-size biases relevant to the optimization of single-particle orbitals performed at a fixed volume. It would certainly be beneficial if one could find the optimal exact-exchange weight in a small simulation cell and only then proceed with production runs in large cells.

To explore this possibility we have repeated the optimization procedure in the primitive cell of the B1 AFM-II structure, which contains only four atoms (two Mn and two O). All other parameters were kept unchanged, except the number of $k$ points employed in the averaging had to be substantially increased—from 8 to 125—to achieve comparable convergence. The necessity to enlarge the set of considered $k$ points introduces an extra technical complication since trial wave functions corresponding to the majority of these $k$ points are complex valued. Consequently, we replace the fixed-node DMC method with its natural generalization, the so-called fixed-phase DMC. The fixed-phase condition reduces to the fixed-node condition for real-valued trial wave functions.

The $w$ dependence of the DMC total energy calculated in the small simulation cell (Fig. 2) is similar but not completely identical to the behavior observed in the larger cell. The minimum is shifted to a slightly lower weight $w$ and the $E(w)$ curve raises a little slower with $w$ decreasing toward the pure PBE-GGA. It is plausible to assume that these differences are a fingerprint of the residual Coulomb finite-size effects.

**VII. COMPRESSED FeO**

Finally, we turn our attention to iron oxide subject to high pressures. We revisit our earlier study of the phase transition from the B1 AFM-II phase, stable at atmospheric pressure, to
the iB8 AFM structure (space group $P6_3/m2$), which the fixed-node DMC simulations predicted as stable above approximately 65 GPa. Calculations leading to this estimate used single-particle orbitals provided by the PBE1$_{w=0.2}$ functional. This choice was based on prior investigations and on a preliminary version of the results we present here. In the following, we analyze in detail how appropriate the PBE1$_{w=0.2}$ orbitals are in this case and how sensitive the transition pressure is to variations in single-particle orbitals in the Slater-Jastrow trial wave function.

We return to simulation cells containing 16 atoms, partly because the orbital optimization appears more robust in larger cells (Sec. VI) and partly because we already acquired some data in the 16-atom cells in the course of our earlier investigations. The pseudopotential used for oxygen atoms is identical as in the MnO calculations (Secs. V and VI), the pseudopotential employed for iron atoms has the same origin as the manganese pseudopotential and again removes only non-core electrons. The variational parameters in the Jastrow factor were found following the procedure described in Sec. V, except that the optimization was performed with the PBE1$_{w=0.2}$ orbitals.

The optimal values for the exact-exchange weight $w$ in FeO are listed in Table I for experimental equilibrium volume $V=20.4$ Å$^3$/FeO as well as for two compressed states. The optimal proportion of the exact exchange decreases with compression, which is an expected phenomenon—the role of screening increases as the bands widen and a larger fraction of $d$ electrons participates in chemical bonding.

In contrast to MnO, where B1 and B8 phases displayed very similar behavior, the two investigated structures of FeO differ noticeably at comparable volumes. Detailed data for compressed FeO are shown in Fig. 3 to highlight the differences. Like in Sec. V, each total energy is obtained as an average over eight $k$ points. To facilitate comparison with our previous study, energies corresponding to the PBE1$_{w=0.2}$ orbitals are used as a reference. It can be seen that $w=0.2$ indeed represents a reasonable compromise value, since corresponding DMC energies lie within error bars from the true minima.

In the case of the iB8 phase, the $E(w)$ data are well described by a quadratic function. In the B1 phase, on the other hand, the functional dependence is asymmetric around the minimum and a quadratic function does not provide a satisfactory fit. To locate the minimum for Table I, we used an alternative fitting function $E(w) = (a + bw + cw^2)/(d + w)$, which characterizes the calculated energies much better. Figure 3 shows that the energy rises rather fast when the exchange-correlation functional approaches the pure PBE-GGA. It does not come as a surprise since the Kohn-Sham spectrum is metallic in the limit $w=0$, which is also in accordance with experimental facts. All other phases investigated here (FeO iB8 and both MnO phases) are insulating for all values of the weight $w$, and hence even orbitals close to the PBE-GGA provide reasonable trial wave functions.

The different behavior of the DMC total energies in the B1 and iB8 structures causes the pressure of the transition between these two phases to depend on the used orbitals. To roughly estimate the variation in the transition pressure, we assume that the energy-volume equations of state of the respective phases only rigidly shift along the energy axis when the exchange weight is varied. The equations of state corresponding to the PBE1$_{w=0.2}$ orbitals were calculated in Ref. 48 and the corresponding shifts can be extracted from Fig. 3. When, for instance, the PBE1$_{w=0.2}$ orbitals are used, the iB8 phase is raised in energy by approximately 0.1 eV compared to the B1 structure, which leads to the transition pressure increased to $\sim 85$ GPa. When the PBE1$_{w=0.05}$ orbitals are utilized, the iB8 phase is lowered by approximately 0.2 eV, which corresponds to the transition pressure of only 30 GPa. Evidently, the B1 to iB8 transition pressure is quite sensitive to the choice of the single-particle orbitals. Of course, the DMC method provides a definite prediction as long as the exchange weight is individually optimized in each phase. The pressure 65±5 GPa derived in Ref. 48 remains valid as the actual DMC estimate for the B1 to iB8 transition pressure since the energies obtained with the PBE1$_{w=0.2}$ orbitals lie within error bars from the minimal energies (Fig. 3).

VIII. OPTIMIZATION OF EFFECTIVE HAMILTONIANS

The optimization of not only the variational wave function but also of the effective one-particle Hamiltonian can be considered in a broader context. The upper-bound property of the fixed-node approximation offers a new opportunity for finding optimal values of any parameters of such Hamiltonians in a consistent and well-defined manner. For example, in DFT+$U$ methods, the Hubbard parameter $U$ as well as the form of the double counting terms could be optimized in a similar way as the exact-exchange weight in the presented calculations. The optimized Hamiltonian can subsequently be utilized for further calculations. We illustrate this on the
density of states of the iron oxide shown as a function of the exact-exchange weight in Fig. 4. Note that for PBE1_{ω=0.5}, that is, for the functional that we used as optimal for the calculations of the equation of state, the single-particle spectrum exhibits a reasonable value of the gap of about 2.9 eV, which is much closer to the experimental value (≈2.4 eV, Ref. 49) than either pure GGA or pure Hartree-Fock limits. The key observation is that although the Hamiltonian was optimized in the ground state, the excitations are clearly improved as well.

In a more general sense, one could consider effective Hamiltonians with more parameters and/or with more elaborated content beyond the one-particle form, such as explicit treatment of particle pairs, for example. The idea of employing the fixed-node DMC method could be of importance for such constructions as the most accurate and explicitly variational method available at present.

IX. CONCLUSIONS

We have found that single-particle orbitals in Slater-Jastrow wave functions represent a non-trivial variational parameters for fermionic nodes in 3d transition-metal compounds. When these orbitals are generated with the aid of an exchange-correlation functional with variable admixture of the exact exchange, the corresponding fixed-node DMC energies differ by several tenths of an electron-volts per transition-metal atom. These variations can translate to substantial quantitative changes in the phase diagram as demonstrated in the case of iron oxide. Consequently, some form of orbital optimization should be performed in order to confidently predict relative stability of different crystal structures and the location of corresponding phase transitions.

The optimal amount of the exact exchange providing minimal DMC energies depends on the particular compound and on the specific structural phase but it is generally close to the value ω=1/4 deduced from comparison of the hybrid density-functional theory to the Möller-Plesset perturbation expansion. The corresponding functional PBE1_{ω=0.5} is commonly denoted as PBE0 where “0” emphasizes that the exact exchange is incorporated without introducing any extra empirical parameters. It is noteworthy that our calculations arrive in the vicinity of this functional despite using a method that has no obvious relation to the mentioned perturbative arguments. Our quantum Monte Carlo simulations provide yet another confirmation that the hybrid DFT indeed provides an improved picture of the investigated compounds compared to more conventional exchange-correlation functionals (LDA and GGA).

ACKNOWLEDGMENTS

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APPENDIX: COHESIVE ENERGY OF MnO

We have calculated DMC energies of the MnO crystal in three simulation cells containing 16, 24, and 32 atoms. The results obtained with the optimal PBE1_{ω=0.5} orbitals are plotted in Fig. 5. Despite reoptimization of the Jastrow factor for these orbitals, the result for the 16-atom simulation cell is practically indistinguishable from the total energy shown in Fig. 1 that was obtained with the correlation factor corresponding to the PBE1_{ω=0.5} orbitals. This observation indicates that the localization approximation, which represents the only mechanism for the Jastrow factor to influence the
The static structure factor \( S(k) \) entering the expression is defined as \( S(k) \equiv \langle |\psi_0\rangle |\alpha_k| |\psi_0\rangle / N \) with \( \alpha_k \) standing for a Fourier component of the electron density. The integral in Eq. (A1) runs over a domain \( D \) centered around \( k=0 \) and having volume \( 8\pi^2/\Omega \), where \( \Omega \) is volume of the simulation cell. The structure factor \( S(k) \) is evaluated along the DMC simulation at a discrete set of points and then extrapolated toward \( k=0 \). We show this extrapolation for the present case in Fig. 6, where we compare mixed and extrapolated DMC estimates, Eqs. (2) and (3). The small-momentum behavior of \( S(k) \) is found to be \( \sim k^2 \) for the mixed estimate and \( \sim k^{1.6} \) for the extrapolated one. This variance originates in a limited quality of our trial wave functions at large distances between electrons—the Jastrow factor we use is restricted to zero for interelectron separations larger than the Wigner-Seitz radius, and hence the correct long-range asymptotics cannot be fully captured. At the end, this deficiency is irrelevant since the prediction of the extrapolated estimate is sufficiently close to the exact asymptotics \( \sim k^2 \) that translates to \( \Delta E_{\text{ER}} \sim 1/N \). The total energies corrected according to Eq. (A1) are shown in Fig. 5 together with the pure Ewald data. The correction reduces the finite-size errors by 75%.

For calculations of individual atoms, we utilize the same form of the trial wave function as we did in solids in order to stay within the same level of theoretical description. Single-particle orbitals for atomic calculations were obtained using GAMESS code. Fixed-node DMC energies for the manganese atom corresponding to several choices of orbitals are listed in Table II. The difference between Hartree-Fock and PBE1-w0.5 orbitals is negligible for our purposes since it is smaller than the statistical error bar achieved for the energy of the bulk crystal.

Variation in single-particle orbitals in the trial wave function for the oxygen atom does not lead to any appreciable differences of DMC energies. To evaluate the cohesion of MnO, we use the result quoted in Ref. 52, \( E_D = -15.8421 \pm 0.0002 \) hartree.

### Table II. Fixed-node DMC total energy of isolated Mn atom calculated using several sets of single-particle orbitals.

<table>
<thead>
<tr>
<th>Single-particle orbitals</th>
<th>( E ) (hartree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Restricted open-shell HF</td>
<td>-104.0133 ± 0.0006</td>
</tr>
<tr>
<td>Unrestricted HF</td>
<td>-104.0185 ± 0.0005</td>
</tr>
<tr>
<td>Unrestricted PBE1-w0.5</td>
<td>-104.0192 ± 0.0002</td>
</tr>
</tbody>
</table>

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6 On leave from Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, CZ-18221 Prague 8, Czech Republic.
8 B. L. Hammond, W. A. Lester, Jr., and P. I. Reynolds, Monte Carlo Methods In Ab Initio Quantum Chemistry (World Scientific, Singapore, 1994).
(2003).
38 Y. Lee (private communication); see also Y. Lee, P. R. C. Kent, M. D. Towler, R. J. Needs, and G. Rajapopal, Phys. Rev. B 62, 13347 (2000) for large core version of these pseudopotentials.
46 The 125 k points sample the whole Brillouin zone, they fold into 19 in the irreducible wedge of the Brillouin zone.
Chapter 7  Fermion Nodes

As shown in the previous chapter, the qualities of fermion nodes of trial wavefunctions \( \{ \mathbf{R} | \Psi_T(\mathbf{R}) = 0 \} \) are crucial to the accuracy of fixed-node diffusion Monte Carlo (FN-DMC) results. However, it is rather difficult to improve nodal qualities or even estimate them prior to DMC calculations. In fact, the fermion sign problem associated with fermion nodes is one of the most profound challenges in quantum simulations of fermionic systems by stochastic methods such as quantum Monte Carlo (QMC). In the context of wavefunction formulation, fermion sign problem arises from requirement that many-body wavefunction has to be anti-symmetric with respect to exchange of two fermions, which runs counter to the design of stochastic methods where positive definite probability distribution functions are needed.

In DMC, fixed-node approximation is a clever trick to circumvent the fermion sign problem by replacing anti-symmetry requirement with boundary conditions. In practice, walkers are restricted from crossing the nodes, which is equivalent to focusing in one nodal domain of the trial wavefunction (a connected domain of configuration space \( \{ \mathbf{R} \} \) where trial wavefunction has the same sign) while infinite potential barriers are introduced to prevent nodal crossing. The whole configuration space can be partitioned into equivalent nodal domains related by symmetry according to tiling property (Ceperley, 1991). So only one nodal domain is needed in FN-DMC in theory. We sample all nodal nodal domains only for practical and statistical purposes. If the nodes of trial wavefunctions are correct, then we...
will have essentially the correct boundaries to work with in DMC. If not, we will inherit artificial boundary conditions from trial wavefunctions hence the existence of fixed-node error. FN-DMC calculations which use Hartree-Fock (HF) or DFT orbitals to form trial wavefunctions typically provide about 95% of the correlation energy in real systems such as molecules, clusters, and solids (Foulkes, Mitas, Needs, & Rajagopal, 2001) leaving fixed-node error to be around 5% of correlation energy.

To overcome the intractable nature of fixed-node error, we think a closer look at the nodes of typical trial wavefunctions and a detailed study of nodal properties of the exact wavefunctions would be most helpful. First, considering the topology of nodal domains, it has long been conjectured that true fermionic ground state only has two nodal domains. Ground state of spin-polarized non-interacting system has been proved to have only two nodal domains (Mitas, 2006). Spin-unpolarized non-interacting states will have multiple nodal domains but interaction has been observed to reduce the number of nodal domains to two. A clear demonstration of this is Beryllium atom (Rasch, 2012).

In the first part of this chapter, we continue our investigation and comparison of Hartree-Fock and exact nodes for simple systems (or HF like nodes, meaning we have HF like single configuration wavefunction while the orbitals could have different origins such as DFT calculations).

First, we observed the collapse of nodal domains once we introduced correlation into HF wavefunction for quartet \( ^4S(1s^2s^3s) \) state:
\[ \Psi_{HF} = \text{det}[\psi_{1s}(r_1), \psi_{2s}(r_2), \psi_{3s}(r_3)] \]

\[ \Psi_{HF} = 0 \] whenever \( r_i = r_j \ \forall \ i \neq j \). Therefore each permutation of \( r_1, r_2, r_3 \) would place the configuration in a distinct nodal domain (so this is analogous to a 1D case), meaning that there are 6 nodal domains (3! is the number of permutations) for \( \Psi_{HF} \). This can be visualized in Figure 19.

![Figure 19](image)

**Figure 19** \([^4S(1s2s3s)]\) HF nodes.

x, y, z axis for the left pic are \( r_1, r_2, r_3 \) respectively. The picture on the right is showing the cross section of nodes in plane \( r_1 + r_2 + r_3 = 1 \), z-axis being a dummy axis.

Three nodal planes are \( r_1 = r_2, r_2 = r_3 \) and \( r_1 = r_3 \).

However, if we build a wavefunction that contains some angular correlation:

\[ \Psi_{corr} = \Psi_{HF} + c \left\{ \text{det}[\psi_{1s}(r_1), \psi_{2p_x}(r_2), \psi_{3p_x}(r_3)] + \text{det}[\psi_{1s}(r_1), \psi_{2p_y}(r_2), \psi_{3p_y}(r_3)] \right\} \\
+ \text{det}[\psi_{1s}(r_1), \psi_{2p_z}(r_2), \psi_{3p_z}(r_3)] \right\} \\
= \Psi_{HF} + c \left\{ \text{det}[\psi_{1s}(r_1), \rho_{2p}(r_2)x_2, \rho_{3p}(r_3)x_3] + \text{det}[\psi_{1s}(r_1), \rho_{2p}(r_2)y_2, \rho_{3p}(r_3)y_3] \right\} \\
+ \text{det}[\psi_{1s}(r_1), \rho_{2p}(r_2)z_2, \rho_{3p}(r_3)z_3] \right\} \\
\]
Where $c$ is a variational parameter and $\rho$ is simply the radial part of the corresponding orbital. The correlated wavefunction not only depends on $r_1, r_2$ and $r_3$, but also their relative angles. Therefore we can trace out the change of cross section shown in Figure 19 by using certain angular dependence as the third dimension.

For illustration purpose, we use the angle $\theta$ between electron as shown in Figure 20, orbitals corresponding for a Harmonic well to construct the wavefunction and $c = 0.01$.

\[ r_1, r_2 \text{ and } r_3 \text{ are chosen to be on the same plane, where } r_1 \perp r_3 \text{ and the angle between } r_1 \text{ and } r_2 \text{ is } \theta. \]

The nodes we traced out in this subspace can be seen in Figure 21.

\[ \text{Figure 20 Relative positions of electrons.} \]

\[ \text{Figure 21 Nodal domains have been reduced to two after the introduction of angular correlation.} \]

The picture on the left is for $\Psi_{\text{corr}}$ and the picture on the right is for $\Psi_{\text{HF}}$. Z-axis is show $\theta$ from 0 to $\pi/2$. 

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Notice two saddle points in the picture for nodes of $\Psi_{corr}$. Every other domain from the original 6 nodal domains of $\Psi_{HF}$ now connects to each other from above or under the saddle points. The result is that $\Psi_{corr}$ has only two nodal domains. We observe similar results with orbitals from Coloumb potential (both hydrogenic orbitals and real Hartree-Fock orbitals) (A.H. Kulahlioglu, 2013).

The lesson here is similar to the Beryllium case. This change in topology is due to added configurations without which it wouldn’t be possible no matter what kind of orbitals are used in the single configuration construction. Even though this is a hand-picked low symmetry high-spin case, it shows the qualitative deficiency of single configuration widely used in mean-field methods. We mentioned in the previous chapter that sometimes single Slater determinant formed with DFT orbitals give reasonable nodes verified by DMC can serve as a partial justification for the meaning of DFT orbitals. This would be a counterexample: it shows the topological difference between single configuration and exact wavefunctions. Single determinant with the right orbitals might be able produce the correct density for many-body ground state. But it could be far off in other aspects. Therefore, one should always be cautious when using DFT orbitals to calculate properties beyond those purely dependent on ground-state density.

The subspace we chose above is convenient due to the special symmetry of the system. In most other cases, one electron scan (3D) would be a convenient choice. As a matter of fact, we have one-electron update for proposition of walker movement in our implementation of
FN-DMC. Thus, one-electron scan of nodes could be a natural choice echoing the nodal boundaries the walkers perceive during the run of the program.

The system we focused on next has 4 electrons, nitrogen valence configuration. This particular choice is not random. It is a natural continuation to our studies which revealed the characteristics responsible for the differences of fixed-node errors between first row and second row atoms (Rasch, 2012). A brief recap here is in order.

It begins with the fact that first row atoms have generally multiple times larger fixed-node error compared to second row atoms in our pseudopotential calculations even though they have similar electronic shell structure (number of valence electrons are the same if both atoms are in the same column, like N and P atoms both have five electrons in the calculation as core electrons are pseudized). Then it was revealed that it was non-monotonicity in the ratio of radial orbitals that contributed to the increase fixed-node error for the first row atom. This characteristic could also be demonstrated through fixed-node error of Ne atom with two different pseudopotential (Table 7). Both ECP BFD (Burkatzki et al., 2007) and ECP TN (Trail & Needs, 2005) are norm-conserving pseudopotentials that remove two $1s$ electrons. This is analogous to the difference in fixed-node error between N and P atom (Table 8). In all DMC calculations here, Hartree-Fock orbitals are used to construct trial wavefunctions.
Table 7 Fixed-node error for Ne atom.

\( E_{exact} \) are \( CCSD[T] \) results. \( E_{error} = E_{exact} - E_{DMC} \). All numbers are absolute values.

<table>
<thead>
<tr>
<th></th>
<th>( E_{exact} )</th>
<th>( E_{DMC} )</th>
<th>( E_{error} ) in ( E_{correlation} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECP TN</td>
<td>34.91280800</td>
<td>34.9031(2)</td>
<td>0.0097(2) ( \approx 3% )</td>
</tr>
<tr>
<td></td>
<td>0.31847536</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ECP BFD</td>
<td>35.02753445</td>
<td>35.0241(3)</td>
<td>0.0034(3) ( \approx 1% )</td>
</tr>
<tr>
<td></td>
<td>0.31847536</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 8 Fixed-node error for N and P atom.

<table>
<thead>
<tr>
<th></th>
<th>( E_{exact} )</th>
<th>( E_{DMC} )</th>
<th>( E_{error} ) in ( E_{correlation} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>N (ECP BFD)</td>
<td>9.79973109</td>
<td>9.7908(2)</td>
<td>0.0088(2) ( \approx 6.7% )</td>
</tr>
<tr>
<td></td>
<td>0.13135479</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P (ECP BFD)</td>
<td>6.47624878</td>
<td>6.4752(2)</td>
<td>.0010(2) ( \approx 1% )</td>
</tr>
<tr>
<td></td>
<td>0.11614013</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The differences can be explained in terms of ratio of radial atomic orbitals seen in Figure 22.

Generally speaking, for the same electronic configuration, the larger the non-monotonicity in the ratio plot, the larger the fixed-node error. Please reference for derivation (Rasch, 2012). But the simple explanation is that when the ratio is monotonic, HF nodes for these atoms only consists of simple type that are constrained by the symmetry of Hamiltonian therefore there’s not much space “to be wrong”. When the ratio is not monotonic, there would be extra fermion nodes that are generally more complex and we can safely assume that HF nodes will deviate more from exact nodes on these occasions. However, we don’t know how much and in what way HF nodes will deviate from exact nodes here.
Radial part of atomic orbitals are defined: 

$$\rho_2s(r) = \psi_{2s}(r), \quad \rho_{2p}(r) = \psi_{2px}(r) x = \psi_{2py}(r) y = \psi_{2pz}(r) z$$

That's why we are now trying to do a comparison of HF nodes and exact nodes for $N$ atom. Out of 5 valence electrons, we fix 4 spin-up electrons and the spin-down electron and scan the nodes by moving the other spin-up electron (whenever the total wavefunction is zero we record the place). Therefore, we obtain a 3D scan of nodes for each configuration of 4 fixed electrons. Exact nodes are obtained by using self-healing wavefunction, which is essentially exact for our purpose.
Table 9 HF nodes vs Exact nodes for N atom.

In all pictures, gray dot is the nucleus, blue dot is the spin-down electron, 3 green dots are 3 spin-up electrons and nodes (yellow/orange surface) are determined by scanning the other spin-up electron. All fixed electrons are drawn connected by a thin line to the nucleus.

<table>
<thead>
<tr>
<th>HF Nodes</th>
<th>Exact Nodes</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image 1" /></td>
<td><img src="image2.png" alt="Image 2" /></td>
</tr>
<tr>
<td><img src="image3.png" alt="Image 3" /></td>
<td><img src="image4.png" alt="Image 4" /></td>
</tr>
</tbody>
</table>

All four picture have the same configuration of 3 fixed spin-up electrons while the first row have the fixed spin-down electron at one location and the second row have it at another location. The nodes cross all spin-up electrons as we are scanning by the other spin-up electron. This is a simple requirement from Pauli Exclusion Principle. All fixed electrons are
drawn connected by a thin line to the nucleus. The thin line connecting spin-up electrons on
the nodal plane generally crosses nodes multiple times. This is related to the non-
monotonicity of orbital ratios we just talked about.

HF nodes are independent of location of spin-down electron as HF wavefunction can be
written as a product of spin-up and spin-down component. This is no longer true for self-
healing wavefunction. As move the spin-down electron, the nodal plane becomes polarized
to different directions and the topology changes in this subspace. Actually, even when the
spin-down electron is far away from other electrons, the self-healing nodal plane is tiled in
different direction compared to HF nodal plane and this can be seen as an effect due to
same spin correlation. But the self-healing nodal plane will be tiled by different angles as we
move the spin-down electron. This is an effect due to different spin correlation. But the
influence of different spin correlation is more important near the change of shape of the
“bubble” and its connection to the “plane” as here it is a relatively high density region.

The mystery is not solved here and more insights are needed to further clarify the situation.
Maybe some quantitative analysis or a mathematical measure of nodal qualities would be
very helpful. We include our definition of nodal domain average(Hu, Rasch, & Mitas, 2012)
here as a stepping stone for others to develop mathematical tools.
Chapter 7

Many-Body Nodal Hypersurface and Domain Averages for Correlated Wave Functions

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We outline the basic notions of nodal hypersurface and domain averages for antisymmetric wave functions. We illustrate their properties, analyze the results for few-electron explicitly solvable cases, and discuss possible further developments.

Quantum Monte Carlo is one of the most effective many-body methodologies for the study of quantum systems. It is based on a combination of analytical insights, robustness of stochastic approaches, and performance of parallel architectures (1–10). The approach has been applied to a variety of challenging problems in electronic structure of atoms, small molecules, clusters, solids, ultracold condensates, and beyond (1–15). The two most commonly used QMC methods are variational Monte Carlo and diffusion Monte Carlo (DMC). Let us briefly recapitulate the basics of the DMC method.

It is straightforward to show that for $t \to \infty$, the operator $\exp(-tH)$ projects out the ground state of a given symmetry from any trial function with nonzero overlap. We assume that the Hamiltonian $H$ is time-reversal symmetric so that the eigenstates can be chosen to be real. This projection is most conveniently carried

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In Advances in Quantum Monte Carlo, Tanaka, S., et al.;

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out by solving the Schrödinger equation in an imaginary time integral form so that the product

\[ f(\vec{R}, t) = \Phi(\vec{R}, t) \Psi(\vec{R}) \]

obeys

\[ f(\vec{R}, t + \tau) = \int G(\vec{R}, \vec{R}', \tau) f(\vec{R}', t) d\vec{R}'. \]

The Green's function is given by

\[ G(\vec{R}, \vec{R}', \tau) = \frac{\Psi^T(\vec{R})}{\Psi^T(\vec{R}')} \left( \frac{e^{-m|\tau|}}{|\vec{R} - \vec{R}'|} \right) \]

where \( \vec{R} = (r_1, \cdots, r_N) \)

denotes positions of \( N \) particles and \( E_\tau \) is an energy offset. In the DMC method, the function \( f(\vec{R}, t) \) is represented by a set of \( 10^2 \text{-} 10^4 \) random walkers (sampling points) in the \( 3N \)-dimensional space of electron configurations. The walkers are propagated for a time slice \( \tau \) by interpreting the Green's function as a transition probability from \( \vec{R} \rightarrow \vec{R}' \). The kernel is known for small \( \tau \), and the large time \( t \) limit is obtained by iterating the propagation. The method is formally exact provided that the boundary conditions, i.e. the fermion nodes of the antisymmetric solution defined as \( \Phi(\vec{R} \rightarrow 0) = 0 \), are known (1, 5, 14).

Unfortunately the antisymmetry does not specify the nodes completely, and currently we have to use approximations. The commonly used fixed-node approximation (14) enforces the nodes of \( f(\vec{R}, t) \) to be identical to the nodes of \( \Psi f(\vec{R}) \) which then implies that

\[ f(\vec{R}, t) \geq 0 \]

everywhere. It is therefore clear that the accuracy of the fixed-node DMC is determined by the quality of the trial wave function nodes. The commonly used form for \( \Psi f \) is the Slater-Jastrow wave function given as

\[ \Psi^T(\vec{R}) = \sum_n d_n \cdot \det^{\uparrow}_{\uparrow}(\{ \varphi_n \}) \cdot \det^{\uparrow}_{\uparrow}(\{ \varphi_p \}) \cdot \exp(U_{\text{cor}}) \]

where \( U_{\text{cor}} \) is the correlation factor explicitly depending on interparticle distances thus describing pair or higher order correlations explicitly. The typical number of Slater determinants is between 1 and \( 10^3 \), and the corresponding weights \( d_n \) are usually estimated in multi-reference Hartree-Fock (HF) or Configuration Interaction (CI) calculations and then re-optimized in the variational framework.
It is quite remarkable that the nodes of such Slater-Jastrow wave functions (often with a single-determinant product only) lead to unexpectedly small errors and that the typical amount of obtained correlation energy in fixed-node DMC is ≈95%. This is true for essentially all systems we have studied: atoms, molecules, clusters and solids (1–15).

The fixed-node approximation is perhaps the single most important unsolved problem which hampers the progress in further improvement of accuracy and efficiency of the QMC calculations. One of the key difficulties is that the fixed-node bias is actually very small on the scale of the total energy. A comparison of the total energy components for a typical electronic structure problem is given in Table I.

Table I. Energy components as percentages of the total energy in Coulombic systems

<table>
<thead>
<tr>
<th>Energy Component</th>
<th>% of $E_{\text{total}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic</td>
<td>100</td>
</tr>
<tr>
<td>Exchange</td>
<td>≈8</td>
</tr>
<tr>
<td>Correlation</td>
<td>≈3</td>
</tr>
<tr>
<td>$\Delta_{\text{FN}}$</td>
<td>≈2</td>
</tr>
</tbody>
</table>

$\Delta_{\text{FN}} = E_{\text{total}} - E_{\text{DMC+HF}}$ is the fixed-node (FN) bias corresponding to the Hartree-Fock nodes.

Considering the typical fluctuations of the DMC energy per stochastic sample (which is of the order of a few percent of the total energy), the node-related “signal” is very weak. Unfortunately a few percent of the correlation energy can influence the energy differences we are interested in.

The optimization methods (despite a number of recent developments) have difficulties picking up the nodal bias signal as it appears buried in the noise which is inherent to the QMC methodology. Recent developments in the nodal optimization using the self-healing method (16) enable the filtering of some of the noise quite effectively, however, the performance of the method has to be tested on more systems. However, this is not the only problem. Another key issue is that our knowledge of the nodal properties is very limited. At present we simply have no clear idea how to improve the nodal hypersurfaces for general cases in an efficient manner (for example, in systems which might require an exponential number of Slater determinants just to describe the correct spin and spatial symmetries).

We simply have to develop other measures which can provide more targeted information about the nodal shapes. It is straightforward to show that the total energy or its components are not selective enough in this respect. Let us consider a few simple illustrations. For example, the two non-interacting two-electron atomic states $^3S(1s2s)$ and $^3P(1s2p)$ have the same total, kinetic, and potential energies, but different nodal shapes. Since the symmetries in this case are different, one might argue that the symmetry should be used to distinguish and, possibly, classify the nodal shapes in this case. Consider another case: non-interacting four-electron

---

atomic states $^1S(1s^22s^2)$ and $^1S(1s^22p^2)$. These degenerate states have the same symmetry, however, the nodes are different, both in topology and in the shape. Clearly, we would like to measure and distinguish the nodes in such cases.

Characterization of the nodes can be of significant interest in another context. Recently, an interesting scenario was suggested for systems in quantum critical point, namely, that the nodes in such a state might exhibit fractal (scale-invariant) character [16]. For this purpose it would be very useful to measure the smoothness of the nodal surfaces.

Let us now consider the stationary Schrödinger equation

$$-rac{1}{2} \nabla_x^2 \Psi(\vec{R}) + V(\vec{R}) \Psi(\vec{R}) = E \Psi(\vec{R}).$$

The exact fermionic eigenstate $\psi$ determines the nodal domains

$$\Omega^+ = \{ \vec{R} ; \Psi(\vec{R}) > 0 \}, \quad \Omega^- = \{ \vec{R} ; \Psi(\vec{R}) < 0 \}$$

and the corresponding node $\partial \Omega$. We integrate the equation over the $\Omega^+$ domain only, and using the Gauss-Stokes-Green theorem we get

$$\int_{\Omega^+} (V(\vec{R}) - E) \Psi(\vec{R}) \, d\vec{R} - \frac{1}{2} \int_{\partial \Omega} \nabla_x \Psi(\vec{R}) \cdot d\vec{S}_x = 0.$$

Similarly, we can integrate over the $\Omega^-$ domain and if we put it together (assuming either free or periodic boundary conditions) then we get

$$\int_{\Omega^+} |\nabla_x \Psi(\vec{R})| \, d\vec{S} + \int_{\Omega^-} |V(\vec{R})| \Psi(\vec{R}) \, d\vec{R} - E \int |\Psi(\vec{R})| \, d\vec{R} = 0.$$

The obtained equation shows that the total energy is given as a sum of kinetic and potential components, which we call nodal (hypersurface) and domain averages (nda, in short). They are defined as follows

$$E_{\text{nda}} = \int_{\Omega^+} |\nabla_x \Psi(\vec{R})| \, d\vec{S} / \int |\Psi(\vec{R})| \, d\vec{R}$$

and

$$E_{\text{nda}} = \int |V(\vec{R})| \Psi(\vec{R}) \, d\vec{R} / \int |\Psi(\vec{R})| \, d\vec{R},$$

so that

$$E = E_{\text{nda}} + E_{\text{nda}}.$$

This derivation and the definitions deserve some comment. First, we tacitly assumed that there is only one positive and one negative nodal domain, however, this generically applies only to fermionic ground states. Generalization to more domains is straightforward: one integrates domain by domain and sums the
results. It therefore applies to any eigenstate including excitations, both fermionic and bosonic (the bosonic ground state is an exception since it is nodeless). It is important that $E_{\text{ext}}^{\text{nda}}$ depends solely on the gradient of the wave function on the node (domain boundary) and not on the wave function values inside the domain. The key idea is that these expressions measure properties of the quantum amplitudes more directly than the expectation values. In fact, the expectations suppress the nodal signal since both the square of the exact eigenstate and also its Laplacian vanish at the node. Note that although the sum of kinetic and potential nda components produces the total energy, the expression has no variational property, i.e. it is not quadratic in the wave functions as is the usual expectation value. It is rather a “one-sided expectation” which enables one to probe the nodal structure as we will show in what follows.

The nda values are not trivial to calculate, and for illustration we will present just a few simple cases. Let us first consider a toy model, an electron in a $2p$ orbital so that the state is $\Psi(r)=Zr$. For the Coulomb potential $V(r)=Z/r$ we have

$$\Psi = z \rho_{2p}(r) = z e^{-r^2/2},$$

and we can write

$$E_{\text{kin}}^{\text{nda}}(2p) = \frac{\int \int r \rho_{2p}(r) r^2 \cos(\theta) \sin(\theta) \, dr \, d\theta}{\int \int \rho_{2p}(r) r^2 \cos(\theta) \sin(\theta) \, dr \, d\theta} = \frac{-Z^2}{6}.$$

Since the node is the plane given by $z=\theta$ and

$$|\nabla \Psi|_z = \rho_{2p}(r),$$

we can easily evaluate the kinetic energy part

$$E_{\text{kin}}^{\text{nda}}(2p) = \frac{\int \int \rho_{2p}(r) \, dx \, dy}{2\pi \int \int \rho_{2p}(r) r \cos(\theta) \sin(\theta) \, dr \, d\theta} = \frac{Z^2}{24}.$$

Note that the integral in the numerator is over the plane while the integration domain of the denominator is the full 3D volume. One can also verify that the sum of the two components gives $E=-Z/8$ as expected.

Cases with more than one particle are much more interesting. We mentioned the two excitations of the He atom, namely $^2S(^1s^2s^2)$ and $^2P(^1s^2p)$, and also the corresponding four-particle singlets $^2S(^1s^2s^2s^2)$ and $^2S(^1s^2s^2p)$). Actually, these are quite nontrivial to calculate even in noninteracting cases. The state $^2S(^1s^2s^2s^2)$ is straightforward but rather involved, and one ends up with numerous integrals. The states with $2p$ orbitals are even more complicated since the node is given by a combination of exponentials and linear functions so that the integration domains become complicated. Therefore for this case we have used Monte Carlo integration. The resulting values are listed in Table II.
Table II. Energy components for two- and four-electron atoms: standard expectations and nda values\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>States</th>
<th>$E_{tot}$</th>
<th>$E_{nuc}$</th>
<th>$E_{Int}$</th>
<th>$E_{Int}^{nuc}$</th>
<th>$E_{tot}^{nda}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1S(1s^2s)$</td>
<td>5/8</td>
<td>5/8</td>
<td>-5/4</td>
<td>10/221</td>
<td>-1185/168</td>
</tr>
<tr>
<td>$^3P(1s^2p)$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1/20 (c)</td>
<td>-27/40 (c)</td>
</tr>
<tr>
<td>$^3S(1s^22s)$</td>
<td>5/4</td>
<td>5/4</td>
<td>-5/2</td>
<td>20/221</td>
<td>-1185/984</td>
</tr>
<tr>
<td>$^3S(1s^22p)$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1/10 (c)</td>
<td>-1185/20 (c)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The energies in au. are proportional to $Z^6$. The results are exact except for the values with the error bars $=1.10^{-3}$ in the brackets.

\textsuperscript{b} The dot means that the value is the same as in the row above.

The values show clearly that one can distinguish the states and the nodes by the nodal and domain averages. For example, the $E_{Int}^{nda}$ differ by more than 10 (0.002)\% between the corresponding degenerate states. Note that if one would consider the interaction, then the two four-electron states would mix. Clearly, the nda components will depend on the mixing and thus reflect the node change under interactions. If fact, there is an optimal mixing which provides the best node within the functional form as shown previously in calculations of the Be atom (17, 18).

It is interesting to analyze another case: two noninteracting electrons in $2p^2$ configuration which can couple into the three states $^3P$, $^1S$, $^3D$. For example, the wave function for the state $^3P(2p^2)$ is given by

$$\Psi(1,2) = \rho_{2p}(r_1)\rho_{2p}(r_2)(x_1y_2 - x_2y_1),$$

and the nda potential energy can be written as

$$E_{pot}^{nda}(2p^2) = 2 \int \int V(r_1)\rho_{2p}(r_1)\rho_{2p}(r_2) |x_1y_2 - x_2y_1| dr_1 dr_2$$

$$- \int \int \rho_{2p}(r_1)\rho_{2p}(r_2) |x_1y_2 - x_2y_1| dr_1 dr_2$$

The integrals can be factored into radial and angular components. Since the angular parts cancel out, we get

$$E_{pot}^{nda}(2p^2) = 2E_{pot}^{nda}(2p).$$

It is perhaps somewhat unexpected that we also get the same result for the other two states $^1S(2p^2)$ and $^1D(2p^2)$, all of which are summarized in Table III.
Table III. Energy components for 2p^2 states for Coulomb potential: standard expectations and nda values

<table>
<thead>
<tr>
<th>States</th>
<th>E_{tot}</th>
<th>E_{des}</th>
<th>E_{pot}</th>
<th>E_{ex}^{nda}</th>
<th>E_{tot}^{nda}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3p, 1S, 1D</td>
<td>-1/4</td>
<td>1/4</td>
<td>-1/2</td>
<td>1/12</td>
<td>-1/3</td>
</tr>
</tbody>
</table>

We therefore conclude that all the components are the same for all three states, although two of them are singlets and one is triplet and also have different spatial symmetries. Note that this is strictly true only for the noninteracting system. This implies that the states might have equivalent nodes, and a little bit of analysis actually shows that. One can find that the node for the 1P state can be described from the perspective of one of the two electrons as the plane defined by the angular momentum axis and the second electron. Similarly, the node of the 1D state looks to one of the electrons as the plane which contains the angular momentum axis and is orthogonal to a plane defined by the second electron and the angular momentum axis. Finally, for 1S states one of the electrons sees a plane which is orthogonal to the position vector of the second electron. In all three cases the node subset is therefore a plane which passes through the origin. Although these are only subsets of the complete 5D node, which is a hyperbolic hypersurface in 6D, the construction enables us to get an insight into their properties. In fact, this shows that there are only two nodal domains in all three cases: the scanning electron is either on one or the other side of the considered plane. Let us further define the equivalency for a set of nodes. By equivalency we mean that the nodes in the given set can be transformed to each other by coordinate transforms which are unitary (the determinant of the transformation matrix is equal to +1 or -1). This includes not only rotations but also reflections around the origin since otherwise the triplet nodes cannot be transformed to the singlet nodes. This can be inspected, for example, by transforming the node of one of the 1D states

\[ \Psi (1,2) = \rho_{3p} (r_1) \rho_{3p} (r_2) (x_1 y_3 + x_3 y_1), \]

to the node of 1P state using the reflection of one coordinate component, say, \( x_2 \rightarrow -x_2 \) (see the wave function above). With some effort one could find that the nodes of the singlets are also equivalent. For this the reader might find it useful to consult our previous papers on related topics of nodal structure and analysis (9).

Note that for two interacting electrons in these states the nda components will not be identical since the e-e Coulomb repulsion will distort the wave function gradients in different ways for different states, and energetically, it will favor the triplet over the singlets.

The previous case of two non-interacting electrons can be further generalized to a given subshell \( l = n-1 \) for any \( n \) and for any possible spin symmetry and occupations up to the maximum \( 2(l+1) \). The energies can be evaluated the same way as above, and it is revealing to explore the quasiclassical limit of the

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nda estimates. Consider the class of atomic (excited) states such that $k$ electrons occupy subshell $l$ with any allowed spatial and spin symmetry. The state is $2S+1L[\phi^k]$ where $k$ is the occupation. One can find:

$$E_{\text{kin}}^{\text{lea}}(k, l) = kZ^2 \frac{l}{2(l + 1)^2(l + 2)}$$

and

$$E_{\text{pot}}^{\text{lea}}(k, l) = -kZ^2 \frac{l}{(l + 1)(l + 2)}$$

so that all the non-interacting nodes for various symmetries are equivalent. By checking out the quasiclassical limit $l \rightarrow \infty$, we find

$$\lim_{l \rightarrow \infty} E_{\text{kin}}^{\text{lea}}(k, l) = \lim_{l \rightarrow \infty} E_{\text{kin}}^{\text{lea}}(k, l)$$

and

$$\lim_{l \rightarrow \infty} E_{\text{pot}}^{\text{lea}}(k, l) = \lim_{l \rightarrow \infty} E_{\text{pot}}^{\text{lea}}(k, l)$$

Clearly, averages over $\eta^2$ and $|\eta|$ become identical since the quantum effects become irrelevant for $l \rightarrow \infty$.

Let us now turn to the case of a system with interactions. Consider the two-particle 3D harmonic problem with the Coulomb interaction. The Hamiltonian is given by

$$H = (P_1^2 + P_2^2)/2 + \alpha^2 (r_1^2 + r_2^2)/2 + g_0/r_{12}$$

where $g_0$ is the interaction strength. For certain values of $g_0$ and $\alpha$, combined with particular symmetry, one can find simple analytical eigenstates. For $g_0=1$ and $\alpha=1/4$, the lowest triplet of P symmetry $^3P(2p)$ is given exactly as (19)

$$\Psi_{\text{exact}} = \Psi_0 (1 + r_{12}/4)$$

where the noninteracting solution $\Psi_0$ (i.e. $g_0=0$) is as usual

$$\Psi_0 = e^{-c_1^2 r_1^2 + c_2^2 r_2^2/2} (z_1 - z_2).$$

The noninteracting energy for this particular state $(n_1=n_2=l_1=0, l_2=l)$ can be expressed as

$$E_0 = (2n_1 + 2n_2 + l_1 + l_2 + 3)\alpha + 4\alpha = 1$$
while the interacting exact eigenvalue is

\[ E_{\text{exact}} = E_0 + 1/4. \]

These analytical solutions are sufficiently simple so that we can evaluate the ndn components for various combinations of Hamiltonians and wave functions.

a. Noninteracting Hamiltonian and Noninteracting Wave Function

It is straightforward to find out that for \( \gamma_0 = 0 \), we get

\[ E_{\text{pot}}^{\text{exact}} = \frac{7\omega}{2} = \frac{7}{8}, \]

and correspondingly

\[ E_{\text{kin}}^{\text{spot}} = \frac{\omega}{2}. \]

b. Interacting Hamiltonian with \( \gamma_0 = 1 \) and the Exact Eigenstat

After making transformation to center of mass and relative coordinates, one can find

\[ E_{\text{pot}}^{\text{spot}} = \frac{7\omega}{2} - \frac{3}{8} \sqrt{\pi} - \frac{1 + \sqrt{\pi}/2}{4 + 3\sqrt{\pi}}, \]

and using the exact result above, we find

\[ E_{\text{kin}}^{\text{spot}} = E - E_{\text{pot}}^{\text{spot}}. \]

c. Interacting Hamiltonian and Noninteracting Wave Function with the Correct Node

It is interesting to find out the estimation energy considering an approximate wave function which has the exact node. Let us first consider the noninteracting wave function. This will give quite a poor estimate since the potential and kinetic energy will be “unbalanced,” but it will still be instructive. Taking \( \gamma_0 \) above, we get

\[ E_{\text{pot}}^{\text{spot}} = \frac{7\omega}{2} + \frac{\sqrt{\pi} \omega}{4}. \]

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and

\[ E_{\text{nda}}^{a} = \frac{\omega}{2} \]

This provides a clear demonstration that the energy obtained as nda sum is not necessarily an upper bound since

\[ E_{\text{nda}}^{ab} + E_{\text{nda}}^{c} \approx \frac{9.77 \ldots \omega}{2} < E_{\text{exact}} = \frac{10\omega}{2}. \]

which gives 1.226 ... vs. the exact value 5/4. Actually, the error is not very large considering how crude the trial state is. The dominant error is the potential part, which comes out lower. This is caused by two effects: the noninteracting value of the exponent in the gausssian is not optimal and a secondary impact comes also from the absence of the correlation. The kinetic energy component is the same as in the noninteracting Hamiltonian, i.e. slightly larger than the exact. This results from the missing exchange hole which affects the gradient of the wave function on the nodal surface. Obviously, these ideas should be explored further and such investigations are currently in progress.

Conclusions

We have introduced the nodal hypersurface and domain averages, dubbed "nda," as a tool for characterization of the nodes of trial wave functions. We have demonstrated their properties on a number of few-particle cases and analyzed implications of these results. For example, we were able to distinguish the nodal differences between degenerate states of the same and different symmetries. These characteristics enabled us to identify the equivalence of nodes in unexpected situations such as between noninteracting singlets and triplets. Clearly, the results show interesting potential and deserve further investigation. The theory can be further explored with much more powerful developments which will be presented elsewhere.

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