CORRECTION OF FINITE SIZE ERRORS IN MANY-BODY ELECTRONIC STRUCTURE CALCULATIONS

Hendra Kwee

Palembang, South Sumatra, Indonesia

Master of Science, College of William and Mary, 2002 Bachelor of Science, Institut Teknologi Bandung, 2001

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Department of Physics

The College of William and Mary

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Hendra Kwee

Approved by the Committee, October 2007

Committee Chair Professor Henry Krakauer, Physics The College of William and Mary

Assistant Professor Joshua Erlich, Physics The College of William and Mary

Professor Kenneth Petzinger, Physics The College of William and Mary

Associate Professor Shiwei Zhang, Physics The College of William and Mary

Professor Robert Vold, Applied Science The College of William and Mary

ABSTRACT PAGE

Electronic structure calculations using simulation cells for extended systems typically incorporate periodic boundary conditions as an attempt to mimic the real system with a practically infinite number of particles. Periodic boundary conditions introduce unphysical constraints that give rise to finite-size errors. In mean-field type calculations, the infinite size limit is achieved by simple quadrature in the Brillouin zone using a finite number of **k**-points. Many-body electronic structure calculations with explicit two-particle interactions cannot avail themselves of this simplification. Direct extrapolation is computationally costly while size correction with less accurate methods is frequently not sufficiently accurate. The Hartree-Fock method neglects the correlation energy, while the conventional density functional theory (DFT) uses the infinite-size limit of the exchange correlation function. Here we present a new finite-size exchange correlation function designed to be used in DFT calculations to give more accurate estimates of the finite-size errors. Applications of the method are presented, including the P_2 molecule, fcc silicon, bcc sodium and BiScO₃ perovskite. The method is shown to deliver rapidly convergent sizecorrections.

Dedicated to my mother Heryawaty and the memory of my father Johnny Kwee.

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CORRECTION OF FINITE SIZE ERRORS IN MANY-BODY ELECTRONIC STRUCTURE CALCULATIONS

CHAPTER 1

Introduction

In today's world, almost everyone uses electronic devices whose development is based on our knowledge about the microscopic structure of materials. As science develops, deeper understanding of electronic structure of material drives material designs as major needs of human beings. The behavior of electronic devices, ranging from simple resistors to complicated integrated circuits, depends on the structure of atoms bound together by electromagnetic interactions governed by quantum mechanics (QM).

In QM, the evolution of a system is described by the Schrödinger equation, whose Hamiltonian consists of one-body terms and two-body terms. One-body terms such as kinetic energy of electrons and electron-ion interaction are easy to deal with, while two-body terms arising from electron-electron interaction are difficult.

The Hartree-Fock (HF) theory and the density-functional theory (DFT) are two important methods that are used to model the electron-electron interactions. Both methods treat the electron-electron interaction as a collection of independent electrons moving in self-consistent fields. These approaches are known as mean-field approximations. HF theory is an approximate theory by construction, so it only gives accurate results for certain systems. On the other hand, DFT is an exact theory. However in its applications, certain approximations are incorporated into calculations which limit its accuracy.

Many-body methods, like Quantum Monte Carlo (QMC) methods [1], that treat electron-electron interactions explicitly are more accurate than mean-field methods but they are also more expensive. QMC methods calculations include the correlation energy that is not captured by the HF method, and is only approximately included in different approximations of DFT methods.

All of these methods use a finite number of electrons in their simulations and introduce finite-size (FS) errors [2, 3]. The standard method of reducing these errors is to apply periodic boundary conditions (PBC). Important FS errors still remain and they are usually comparable to other systematic or statistical errors. The "finitesize error" in mean-field type calculations for a perfect crystal arises from error in the Brillouin zone (BZ) integration. It can be driven to zero by increasing the number of **k**-points used in the integration. This quadrature error can be viewed as a FS error because increasing a simulation cell is equivalent to adding more **k**-points in the BZ. A careful choice of a single **k**-point or a set of **k**-points can decrease this one-body FS error. Because similar errors also appears in many-body calculations, the onebody FS error in many-body calculations can largely be corrected with mean-field type calculations like DFT.

However, there are other errors in many-body calculations [2, 3]. The coulomb interaction in calculations with PBC is given as the Ewald interaction. The Ewald interaction is a model periodic function such that the sum of interaction between all pairs of particles within one cell reproduces exactly the same energy per particle of the identical real system. In a perfect crystal, the density is truly periodic and therefore the Ewald interaction gives a good description of the classical Coulomb or Hartree energy. However, the exchange correlation (XC) hole is also forced to be periodic in simulations with PBC. This unphysical approximation is particularly inaccurate when the simulation cell is small. This two-body FS error is more difficult to correct. Kohn-Sham DFT calculations do not have this error, since the XC energy is evaluated using standard functional that has been extrapolated to the infinite-size limit. Therefore, the conventional DFT calculations cannot be used as a correction of the two-body FS error in many-body method calculations.

In this thesis, I report studies of these FS corrections [3]. The one-body FS error can be corrected with conventional DFT methods and it is a well-known correction in solid state calculations. We construct a new finite-size-DFT that is used to estimate the two-body FS error. This new FS DFT uses a FS exchange-correlation function to approximately include the two-body FS error in DFT calculations. Applications of the method to the P_2 molecule (in supercells with periodic boundary conditions), to semiconductor bulk silicon, to sodium metal and to perovskite BiScO₃ indicates that the methods remove most of the FS errors, accelerating convergence toward results for the infinite-size system.

The rest of this thesis is organized as follows.

In Chapter 2, I give a summary of several electronic structure methods. The objective of the chapter is to provide a general overview of the many-body problem and the methods for its approximate solutions like Hartree-Fock (HF) and density functional theory (DFT). Many-body methods like configuration interaction (CI) and quantum Monte Carlo (QMC) are briefly discussed.

In Chapter 3, I review the auxiliary field Quantum Monte Carlo (AFQMC) method. This method is used to obtain all many-body results in this thesis. Here, I discuss its use with a planewave basis and also the formalism of the second-quantized form of the many-body Hamiltonian. Review of the ground state projection is also covered in this chapter.

In Chapter 4, I present one simple application of the AFQMC method to the

interacting electron gas (jellium) system. Jellium calculations are used to construct the finite-size exchange-correlation function. The HF solution of infinite-size jellium system is discussed here together with the definition of the correlation energy. I also present calculations on the cutoff energy dependence of the jellium correlation energy. The details data of this cutoff energy dependence are reported in Appendix B.

In Chapter 5, I construct finite-size exchange-correlation function based on a fit to the jellium results. Existing correction schemes are also discussed.

In Chapter 6, I present several applications of the new correction schemes. The first application is the size convergence study of the energy of the P_2 molecule, using supercells and periodic boundary conditions. While the uncorrected QMC energy converges slowly to the infinite-size limit, the new corrections improve the energy convergence significantly. The second application is to fcc silicon, where corrections are applied to previously obtained results for silicon supercells. The results show that our corrections are better than existing methods, and greatly improve size convergence. The next application is to metallic bcc sodium. Many QMC calculations, each with different **k**-point, are used to address the "open shell" problem in metallic calculations. The corrected cohesive energies are in excellent agreement with the experimental value. The last application is to well-depth calculations of BiScO₃ perovskite. The corrected well-depths of QMC are in good agreement with the well-depths calculated with the DFT method, indicating that the DFT well-depths are reliable.

Chapter 7 summarizes our results and comments on the future prospects of this research.

CHAPTER 2

Electronic Structure Methods

2.1 Introduction

The non-relativistic time-independent Schrödinger equation is given by

$$\hat{H}|\Psi\rangle = E|\Psi\rangle,\tag{2.1}$$

where \hat{H} is the Hamiltonian operator for a system of nuclei and electrons at positions \mathbf{d}_{α} and \mathbf{r}_{i} , respectively. In Hartree atomic units, the Hamiltonian for N electrons and $N_{\rm a}$ nuclei is

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_{i}^{2} - \sum_{\alpha=1}^{N_{a}} \frac{1}{2M_{\alpha}} \nabla_{\alpha}^{2} - \sum_{i=1}^{N} \sum_{\alpha=1}^{N_{a}} \frac{Z_{\alpha}}{|\mathbf{r}_{i} - \mathbf{d}_{\alpha}|} + \frac{1}{2} \sum_{i=1}^{N} \sum_{j\neq i}^{N} \frac{1}{r_{ij}} + \frac{1}{2} \sum_{\alpha=1}^{N_{a}} \sum_{\beta\neq\alpha}^{N_{a}} \frac{Z_{\alpha}Z_{\beta}}{d_{\alpha\beta}},$$
(2.2)

where M_{α} is the mass of nucleus α , and Z_{α} is the atomic number of nucleus α . The first term in right hand side of Eq. (2.2) is the operator for kinetic energy of the electrons; the second term is the operator for kinetic energy of the nuclei; the third term represents the interaction between the nuclei and electrons; the fourth and the fifth terms represent the repulsion between electrons and between nuclei, respectively. The factor one half in the last two terms is needed to compensate the double counting of the sum.

Fig. 2.1 illustrates this configuration. The distance between the *i*-th electron and α -th nucleus is $|\mathbf{r}_i - \mathbf{d}_{\alpha}|$; the distance between the *i*-th and *j*-th electron is $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$; and the distance between the α -th nucleus and the β -th nucleus is $d_{\alpha\beta} = |\mathbf{d}_{\alpha} - \mathbf{d}_{\beta}|$.



FIG. 2.1: Illustration of a quantum mechanical system. The positions of Nuclei and electrons are shown by vector position \mathbf{d}_{α} and \mathbf{r}_{i} , respectively. i, j are indexes for electrons and α, β are indexes for nuclei.

Since the nuclei are much heavier than electrons, they move much more slowly, hence, to a good approximation, one can neglect the kinetic energy of these nuclei. This is the Born-Oppenheimer approximation [4]. Using the approximation, Eq. (2.2) is simplified to an electronic hamiltonian:

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_{i}^{2} - \sum_{i=1}^{N} \sum_{\alpha=1}^{N_{a}} \frac{Z_{\alpha}}{|\mathbf{r}_{i} - \mathbf{d}_{\alpha}|} + \frac{1}{2} \sum_{i=1}^{N} \sum_{j\neq i}^{N} \frac{1}{r_{ij}}.$$
(2.3)

Within this approximation, the last term in Eq. (2.2) becomes a constant, and therefore it does not have effect on the electronic eigenstate. This ion-ion interaction will be added to the eigenenergy of Eq. (2.3) to obtain the total energy of the system. The Schrödinger equation for the wave function, $\Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \dots, \mathbf{r}_N s_N)$, of N electrons subject to the ionic potential of N_a nuclei is given by

$$\sum_{i=1}^{N} \left(-\frac{1}{2} \nabla_i^2 \Psi - \sum_{\alpha=1}^{N_a} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{d}_\alpha|} \Psi \right) + \frac{1}{2} \sum_{\substack{i,j\\i \neq j}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \Psi = E \Psi.$$
(2.4)

This 3N-dimensional partial differential equation is exactly solved only for system with $N = N_{\rm a} = 1$, that is the system of a hydrogen atom.

In this thesis, I use two types of atomic units: Hartree atomic units and Rydberg atomic units. In Hartree units, the universal constants are defined as $4\pi\epsilon_0 = m_e =$ $e = \hbar = 1$, while Rydberg units, they are defined as $4\pi\epsilon_0 = 2m_e = e^2/2 = \hbar = 1$. The Bohr radius a_0 is the unit for length in both units. In Rydberg units, a unit of energy 1 Ry is equal to 13.6056923 eV, while in Hartree units, a unit of energy 1 Ha is equal to 27.2113845 eV.

2.2 Mean-field Type Methods

2.2.1 Hartree-Fock Method

The Hartree-Fock (HF) method [5] approximately solves Eq. (2.4) by restricting the wave function to a single $N \times N$ determinant, known as a Slater determinant, where N is number of electrons. By construction, a Slater determinant satisfies the Pauli principle. A Slater determinant of N electrons with positions \mathbf{r}_i and spins s_i occupying N orbital is given by:

$$\Psi(\mathbf{r}_{1}s_{1}, \mathbf{r}_{2}s_{2}, \dots, \mathbf{r}_{N}s_{N}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_{1}(\mathbf{r}_{1}s_{1}) & \chi_{1}(\mathbf{r}_{2}s_{2}) & \dots & \chi_{1}(\mathbf{r}_{N}s_{N}) \\ \chi_{2}(\mathbf{r}_{1}s_{1}) & \chi_{2}(\mathbf{r}_{2}s_{2}) & \dots & \chi_{2}(\mathbf{r}_{N}s_{N}) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_{N}(\mathbf{r}_{1}s_{1}) & \chi_{N}(\mathbf{r}_{2}s_{2}) & \dots & \chi_{N}(\mathbf{r}_{N}s_{N}) \end{vmatrix}, \quad (2.5)$$

where a single particle wavefunction $\chi_i(\mathbf{r}_j s_j)$ is given by the product of a spatial part $\varphi(\mathbf{r}_j)$ and a spin part $\eta(s_j)$, i.e. $\chi_i(\mathbf{r}_j s_j) = \varphi_i(\mathbf{r}_j)\eta_i(s_j)$.

The expectation value of the Hamiltonian with respect to this wave function is given by

$$\langle \Psi | H | \Psi \rangle = \sum_{i} \int d\mathbf{r} \varphi_{i}^{*}(\mathbf{r}) \left(-\frac{1}{2} \nabla^{2} + V_{\text{ion}}(\mathbf{r}) \right) \varphi_{i}(\mathbf{r})$$

$$+ \frac{1}{2} \sum_{i,j} \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} |\varphi_{i}(\mathbf{r})|^{2} |\varphi_{j}(\mathbf{r}')|^{2}$$

$$- \frac{1}{2} \sum_{i,j} \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \delta_{s_{i},s_{j}} \varphi_{i}^{*}(\mathbf{r}) \varphi_{i}(\mathbf{r}') \varphi_{j}^{*}(\mathbf{r}') \varphi_{j}(\mathbf{r}),$$

$$(2.6)$$

where the orthogonal properties of the spin function $\eta_i(s_j)$ has been used to obtain this equation. The first and second terms are the kinetic energy and the ionic potential energy, respectively. The third and fourth terms are known as the Hartree energy and the exchange energy, both arising from the electron-electron interaction. The antisymmetric property of the wave function gives rise to the exchange term. This term lowers the total energy and physically expresses the Pauli exclusion principle that electrons with same spins may not share the same spatial wave function. Note that the spin dependence only appears in the last term.

Minimizing Eq. (2.6) with respect to the φ_i leads to the HF equations:

$$-\frac{1}{2}\nabla^{2}\varphi_{i}(\mathbf{r}) + V_{\text{ion}}(\mathbf{r})\varphi_{i}(\mathbf{r}) + V_{H}(\mathbf{r})\varphi_{i}(\mathbf{r}) + \int v_{x}(\mathbf{r},\mathbf{r}')\varphi_{i}(\mathbf{r}')d\mathbf{r}' = \epsilon_{i}\varphi_{i}(\mathbf{r}), \quad (2.7)$$

where $V_{ion}(\mathbf{r})$, $V_H(\mathbf{r})$ and $v_x(\mathbf{r}, \mathbf{r'})$ are ionic, Hartree and non-local exchange poten-

tial, respectively,

$$V_{\rm ion}(\mathbf{r}) = -\sum_{\alpha=1}^{N_{\rm a}} \frac{Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|},\tag{2.8}$$

$$V_H(\mathbf{r}) = \sum_j \int d\mathbf{r}' \frac{|\varphi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|},$$
(2.9)

and

$$v_x(\mathbf{r}, \mathbf{r}') = -\sum_j \frac{1}{|\mathbf{r} - \mathbf{r}'|} \varphi_j^*(\mathbf{r}') \varphi_j(\mathbf{r}) \delta_{s_i s_j}.$$
 (2.10)

Eq. (2.7) is solved self-consistently. A guess is made for each φ_i to determinant $V_H(\mathbf{r})$ and $v_x(\mathbf{r}, \mathbf{r}')$ and the differential equation is solved for the new φ_i , repeated the processes iteratively until self-consistency is reached.

The final solution to the Hartree Fock equations is a set of orthonormal HF spin orbitals $\{\chi_i\}$ with orbital eigenenergies $\{\epsilon_i\}$. In the ground state configuration, the N spin orbitals with lowest eigenenergies are occupied. The total number of spin orbitals, occupied and unoccupied spin orbitals, is given by the number of basis functions M, where M must be larger or equal to N, the number of electrons. Using larger number of basis functions M decreases the ground state energy which according to the variational principle, improves the HF ground state. The limit of this improvement is known as the Hartree-Fock limit.

The HF energy can be improved by adding more Slater determinants to lower the total energy of the system. At the limit of an infinite number of Slater determinants, the exact ground state energy is obtained. The difference between this exact ground state energy and the Hartree-Fock ground state energy is known as the correlation energy.

2.2.2 Density Functional Theory

Density functional theory (DFT) approaches the many-body problem from a different direction than HF theory, and includes correlation approximately [6, 7].

Kohn and Sham [8] introduced the idea of an auxiliary noninteracting system with the same density as the real system. This enabled them to express the electron density of the interacting system in terms of the one-electron wave functions of the noninteracting system,

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2, \qquad (2.11)$$

and to write the Hohenberg-Kohn energy functional [6] in the form

$$E[n(\mathbf{r})] = -\frac{1}{2} \sum_{i=1}^{N} \int d\mathbf{r} \varphi_{i}^{*}(\mathbf{r}) \nabla^{2} \varphi_{i}(\mathbf{r}) + \int d\mathbf{r} n(\mathbf{r}) V_{\text{ion}}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n(\mathbf{r})], \qquad (2.12)$$

where the terms on the right-hand side are the kinetic energy of the noninteracting system with electron density $n(\mathbf{r})$, the energy of interaction with the ionic potential, the Hartree energy, and the exchange-correlation energy. Eq. (2.12) can be taken as the definition of the exchange-correlation energy functional $E_{xc}[n(\mathbf{r})]$. It can be proved [6–8] that if the exact universal functional $E_{xc}[n(\mathbf{r})]$ were known, the density that gives the global minimum of the energy in Eq. (2.12) is the ground state density while the energy is the ground state energy. Unfortunately, this function is not known exactly and has to be approximated.

Minimization of Eq. (2.12) with respect to the $\varphi_i(\mathbf{r})$ gives rise to the selfconsistent Kohn-Sham equation,

$$\left(-\frac{1}{2}\nabla^2 + V_{\rm ion}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right)\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r}),\qquad(2.13)$$

where the Hartree potential is

$$V_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},\tag{2.14}$$

and the exchange-correlation potential is given by the functional derivative

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}.$$
(2.15)

This self-consistent equation can be solved iteratively after one chooses an approximation to the exchange-correlation energy.

The simplest and best-known approximation for $E_{xc}[n(\mathbf{r})]$ is the local-density approximation (LDA),

$$E_{xc}^{\text{LDA}}[n(\mathbf{r})] = \int \mathcal{E}_{xc}^{\text{gas}}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r},$$
(2.16)

where $\mathcal{E}_{xc}^{\text{gas}}(n)$ is the exchange-correlation energy per electron in a uniform interacting electron gas of density *n* calculated using quantum Monte Carlo simulations [9, 10]. The superscript "gas" is used to emphasize that the exchange-correlation energy is obtained from interacting electron gas calculations. This superscript will be removed later. LDA treats the non-uniform electron density at **r** as if it were part of a uniform electron gas of constant density $n = n(\mathbf{r})$. This approximation is obviously accurate for a system that has almost uniform density. However even on systems with a strongly inhomogeneous density, applications of LDA work surprisingly well.

Finding better approximations to E_{xc} is an area of active research today. For further discussion, see Refs. [4] and [11].

2.3 Many-body methods

2.3.1 Configuration Interaction

There are numerous many-body methods, and this section focuses on configuration interaction (CI) type methods because they bear a formal relationship to the quantum Monte Carlo (QMC) method used in this thesis. Both methods are based on representation of the many-body wave-function by Slater determinants.

Hartree-Fock theory oversimplifies the many-body problem, restricting the Hilbert space of many-body wave functions to single Slater determinants. One obvious improvement of this method is to enlarge the Hilbert space to multi Slater determinant space. One can include the HF single Slater determinant ground state and the excited configurations created from this ground state. The ground state and all the excited configurations are orthogonal to each other. This approach is known as configuration interaction (CI). It is exact in the limit for a given basis.

In practice, one needs to truncate the infinite number of single-particle basis set that constructs the single Slater determinant to a reasonable finite number of single-particle basis set M (M includes both spatial and spin basis set). Using this truncated basis set, one constructs a single Slater determinant and then creates all the excited states determinants from it. For N electrons, using M basis functions, one needs $\frac{M!}{N!(M-N)!}$ determinants. This procedure, called full CI, is the standard in quantum chemistry to benchmark the accuracy of other methods in small system size calculations.

Even for relatively small systems and minimal basis sets, the number of determinants that must be included in a full CI calculation is extremely large. This exponential wall [7] limits applications of full CI to small systems ($N \approx 20$). Various approximations are introduced to the full CI matrix by truncating the full CI expansion and use only a small fraction of the possible determinants, for example singly and doubly excited CI (SDCI). Another approach to limit the CI expansion is called the multiconfiguration self-consistent field (MCSCF) method. The basic idea of this approach is to optimize not only the expansion coefficients of the Slater determinant orbitals, but also orbitals as well. For a more detailed discussion see Ref. [5].

2.3.2 Quantum Monte Carlo

The Hartree-Fock method neglects electron correlation completely. To include correlation terms, one needs to use a multi determinant space which leads to configuration interaction. However, one will encounter the exponential wall that limits the size of the system that can be simulated. On the other hand, density functional theory includes correlations in an approximate functional. It works well in many cases, but in several properties, one need to get accurate correlation energies.

Quantum Monte Carlo (QMC) methods offer a promising alternative [1]. QMC treats the electron-electron interaction exactly. Its required computer time scales algebraically [12] (as opposed to exponentially in CI) with system size. Rather than explicitly integrating over phase space, Monte Carlo methods sample it.

The first and simplest many-body calculation that employs Monte Carlo techniques is the variational Monte Carlo (VMC) method [13]. As indicated by its name, it optimizes a trial wavefunction to obtain a variational estimate of the ground state

$$E_V = \frac{\int \Psi_T^*(\mathbf{R}) \hat{H} \Psi_T(\mathbf{R}) d\mathbf{R}}{\int \Psi_T^*(\mathbf{R}) \Psi_T(\mathbf{R}) d\mathbf{R}} \ge E_0, \qquad (2.17)$$

where $\Psi_T(\mathbf{R})$ is a trial wavefunction, \hat{H} is the Hamiltonian of the system and E_0 is the ground state energy. This 3N dimensional integral is calculated using the Metropolis Monte Carlo method. Eq. (2.17) is rewritten in the form

$$E_V = \frac{\int |\Psi_T(\mathbf{R})|^2 [\Psi_T(\mathbf{R})^{-1} \hat{H} \Psi_T(\mathbf{R})] d\mathbf{R}}{\int |\Psi_T(\mathbf{R})|^2 d\mathbf{R}},$$
(2.18)

and the Metropolis algorithm is used to sample a set of point $\{\mathbf{R}_m : m = 1, M\}$ from the configuration-space probability density $\mathcal{P}(\mathbf{R}) = |\Psi_T(\mathbf{R})|^2 / \int |\Psi_T(\mathbf{R})|^2 d\mathbf{R}$. At each of these points the "local energy" $E_L(\mathbf{R}) = \Psi_T(\mathbf{R})^{-1} \hat{H} \Psi_T(\mathbf{R})$ is evaluated and the average energy accumulated:

$$E_V = \frac{1}{M} \sum_{m=1}^{M} E_L(\mathbf{R}_m).$$
 (2.19)

The wave function consists of a product of Slater determinant and a Jastrow factor, which enforces exact cups conditions [13].

More accurate quantum Monte Carlo methods are based on projection of the ground state $|\Psi_G\rangle$ of a many-body Hamiltonian \hat{H} from any known trial wave function $|\Psi_T\rangle$ that satisfies $\langle \Psi_T | \Psi_G \rangle \neq 0$,

$$|\Psi_G\rangle \propto \lim_{\beta \to \infty} e^{-\beta \hat{H}} |\Psi_T\rangle.$$
 (2.20)

Different types of QMC methods are distinguished by the way they carry out this projection. Diffusion Monte Carlo (DMC) is based on the similiarity of the imaginary-time many-body Schrödinger equation with the diffusion equation [1]. DMC simulations for fermion systems suffer from the fermion sign problem [14], which arises from the antisymmetric properties of fermion wavefunction. The fixed node approximation [1, 15] controls the problem, yielding the lowest energy for a given many-body nodal surface of the trial wavefunction. Thus the energy is variational, i.e. it will never be lower than the true ground state energy, but the results depend on the quality of the trial wavefunction's nodal surface.

Other Monte Carlo methods such as path-integral QMC, and auxiliary-field QMC may also be used to study interacting many-electron systems. AFQMC will be discussed in more detail in Chapter 3. For a more detail review of DMC methods, see Refs. [1] and [16].

CHAPTER 3

Auxiliary Field Quantum Monte Carlo

The recently developed phaseless auxiliary field quantum Monte Carlo method [17–25] provides an alternative to the DMC method. Like DMC, AFQMC projects the ground state of a many-electron system from a trial wave function. The major difference is the space where the projections work. While DMC methods sample the many-body wave function in real space, AFQMC method samples it in Slater determinant space. This automatically incorporates the antisymmetric requirement of the fermionic wavefunction. AFQMC methods also have a different way to handle the sign problem which has shown promise in reducing the dependence of the systematic errors on the trial wave functions.

The orbitals written in the Slater determinant can be expressed in a variety of single particle basis states (*e.g.* planewaves, Gaussians, etc.) which allows AFQMC to share much of the same computational machinery with DFT and other independent-particle type methods. AFQMC can thus straightforwardly incorporate many of the methodological advances from mean-field methods (such as pseudopotentials and fast Fourier transforms), while systematically improving on mean-field accuracy.

Applications of the method using a planewave basis on a few simple systems [17, 20, 25] as well as more correlated TiO and MnO molecules [23] yielded excellent results. More systematic applications of the phaseless AFQMC method to atoms and molecules have been carried out using Gaussian basis sets. All-electron calculations for first-row systems [22] as well as effective-core potential calculations in post-*d* group elements [21] show excellent agreement with near-exact quantum chemistry results and/or experiment. At the large basis-size limit, the AFQMC results for both types of basis sets are in good agreement with each other and with experimental values [24].

In this thesis, I use a planewave basis set to calculate energies of different atoms, molecules and solids. While the use of a localized basis set such as Gaussian is favorable for atomic/molecular systems, it is straightforward to implement the planewave basis on an extended system with periodic boundary conditions. A planewave basis set also has several other advantages. It provides an unbiased representation of the wave function, since its convergence is determined by just a single parameter, the planewave kinetic-energy cutoff $E_{\rm cut}$. It is also algorithmically simple to implement and can be made very efficient with fast Fourier transform techniques as in DFT methods. The use of pseudopotentials to remove highly localized core electron states keeps the planewave basis tractable.

3.1 Conventions

In this section, I introduce some conventions that will be used in all of this chapter and also through out all of this thesis. These conventions follow closely the conventions in Ref. [26] and is meant to be for general cases, but many examples will be given for the AFQMC planewave basis code that was used in this thesis.

- N: number of total electrons. In more general cases, N_{σ} is a number of electrons with spin σ ($\sigma = \uparrow$ or \downarrow).
- M: number of single-electron basis states. In our case, this is the number of planewaves that have kinetic energy lower than $E_{\rm cut}$. Typically $M \gg N_{\alpha}$ for planewave.
- $|\chi_i\rangle$: the *i*th single-particle basis (i = 1, 2, ..., M). In our case, this will be planewave basis.
- c_i^{\dagger} and c_i : creation and annihilation operators for an electron in state $|\chi_i\rangle$, i.e. $\langle \mathbf{r} | c_i^{\dagger} | 0 \rangle = \frac{1}{\Omega^{1/2}} e^{i(\mathbf{k} + \mathbf{G}_i) \cdot \mathbf{r}}$. They satisfy the usual anticommutation relation

$$c_i^{\dagger}c_j + c_jc_i^{\dagger} = \delta_{ij}, \qquad (3.1a)$$

$$c_i^{\dagger}c_j^{\dagger} + c_j^{\dagger}c_i^{\dagger} = 0, \qquad (3.1b)$$

$$c_i c_j + c_j c_i = 0. aga{3.1c}$$

 $n_i \equiv c_i^\dagger c_i$ is the corresponding number operator.

• $|\varphi_i\rangle$: A single particle orbital is expressed as

$$|\varphi_i\rangle = \sum_j \varphi_{j,i} |\chi_j\rangle.$$
(3.2)

• $|\phi\rangle$: An N-electron Slater determinant

$$|\phi\rangle = \frac{1}{N!} \mathcal{A} |\varphi_1 \varphi_2 \dots \varphi_N\rangle, \qquad (3.3)$$

where \mathcal{A} is an antisymmetric operator.

• $\hat{\varphi}_i^{\dagger}$: orbital creator operator. It creates particles in i^{th} orbital from M basis states

$$\hat{\varphi}_i^{\dagger} = \sum_j^M \varphi_{j,i} c_j^{\dagger}. \tag{3.4}$$

With this definition, a Slater determinant is given by

$$|\phi\rangle = \hat{\varphi}_1^{\dagger} \hat{\varphi}_2^{\dagger} \dots \hat{\varphi}_N^{\dagger} |0\rangle.$$
(3.5)

• The N-particle Slater determinant is completely specified by the $M \times N$ matrix Φ :

$$\Phi \equiv \begin{pmatrix}
\varphi_{1,1} & \varphi_{1,2} & \dots & \varphi_{1,N} \\
\varphi_{2,1} & \varphi_{2,2} & \dots & \varphi_{2,N} \\
\vdots & \vdots & & \vdots \\
\varphi_{M,1} & \varphi_{M,2} & \dots & \varphi_{M,N}
\end{pmatrix},$$
(3.6)

where M is the number of basis functions. Each column of the matrix represents an orbital.

|Ψ⟩ is a many-body wave function which is not necessarily a single Slater determinant. In the AFQMC method, a many-body wave function is given as a stochastic sum over many Slater determinants.

There are several properties of Slater determinants that are useful in applications [26].

• For any Slater determinants $|\phi\rangle$ and $|\phi'\rangle$, the overlap between them is given by

$$\langle \phi | \phi' \rangle = \det \left(\Phi^{\dagger} \Phi' \right).$$
 (3.7)

• An operation of any Slater determinant by any operator \hat{B} of the form

$$\hat{B} = \exp\left(\sum_{ij} c_i^{\dagger} U_{ij} c_j\right) \tag{3.8}$$

will lead to another Slater determinant [27]:

$$\hat{B}|\phi\rangle = \hat{\phi}_1^{\prime\dagger} \hat{\phi}_2^{\prime\dagger} \dots \hat{\phi}_N^{\prime\dagger}|0\rangle \equiv |\phi'\rangle, \qquad (3.9)$$

with $\hat{\phi}_m^{\dagger} = \sum_j c_j^{\dagger} \varphi_{jm}^{\dagger}$ and $\Phi' \equiv e^U \Phi$, where U is a square matrix whose elements are given by U_{ij} . Therefore $B \equiv e^U$ is also a square matrix of size $M \times M$. Algebraically, the operation of \hat{B} on $|\phi\rangle$ is simply a matrix multiplication involving matrix $M \times M$ and matrix $M \times N$.

• The single-particle Green function $G_{ij} \equiv \langle c_i^{\dagger} c_j \rangle$ is given by [28]

$$G_{ij} \equiv \frac{\langle \phi | c_i^{\dagger} c_j | \phi' \rangle}{\langle \phi | \phi' \rangle} = \left[\Phi' \left(\Phi^{\dagger} \Phi' \right)^{-1} \Phi^{\dagger} \right]_{ji}.$$
 (3.10)

• The two-particle Green function $G_{ijkl} \equiv \langle c_i^{\dagger} c_j^{\dagger} c_k c_l \rangle$ is given by [25]

$$G_{ijkl} \equiv \frac{\langle \phi | c_i^{\dagger} c_j^{\dagger} c_k c_l | \phi' \rangle}{\langle \phi | \phi' \rangle} = G_{li} G_{kj} - G_{ki} G_{lj}.$$
(3.11)

3.2 Planewave Basis

Periodic boundary conditions (PBC) are easily incorporated using a planewave basis. According to Bloch's theorem [29], every single particle electronic wave function in a periodic solid can be written as the product of a planewave times a function with periodicity of the Bravais lattice:

$$\varphi_i(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{i,\mathbf{k}}(\mathbf{r}). \tag{3.12}$$

A vector \mathbf{k} determines a choice of one particular PBC of a system. A periodic function can be expanded in a planewave basis whose wave vectors are reciprocal lattice vector of the crystal:

$$u_{i,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{k}+\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{R}},\tag{3.13}$$

where the reciprocal lattice vector **G** are defined by $\mathbf{G}.\mathbf{R} = 2\pi m$ for all **R** in a Bravais lattice defined by the simulation cell, and *m* is an integer. A simulation cell of volume Ω can be a primitive cell or a supercell consists of several primitive cells. Any single particle wave function given in the form of Eq. (3.12) can be written as

$$\varphi_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}},\tag{3.14}$$

so that a planewave basis $|\mathbf{k} + \mathbf{G}\rangle$ is defined in real space as

$$\langle \mathbf{r} | \mathbf{k} + \mathbf{G} \rangle \equiv \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}}.$$
 (3.15)

The orthogonality of conditions are given by

$$\langle \mathbf{q} | \mathbf{q}' \rangle = \frac{1}{\Omega} \int_{\Omega} d^3 \mathbf{r} e^{-i(\mathbf{q}' - \mathbf{q}) \cdot \mathbf{r}} = \delta_{\mathbf{q}, \mathbf{q}'}, \qquad (3.16)$$

and

$$\langle \mathbf{r} | \mathbf{r}' \rangle = \frac{1}{\Omega} \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} = \delta(\mathbf{r} - \mathbf{r}'),$$
 (3.17)

where $\mathbf{q} \equiv \mathbf{k} + \mathbf{G}$ here.

The planewave basis defined by Eq. (3.15) spans to infinity. This is not practical for computer simulation. In practice, we will consider only **G** vectors whose kinetic energies $\frac{1}{2}(\mathbf{k} + \mathbf{G})^2$ are smaller than or equal to a given cutoff energy E_{cut} . This defines the **G**-space that we will work in. Correspondingly, the real space is taken to be the Fourier space of the **G**-space.

3.3 Hamiltonian

The hamiltonian within Born-Oppenheimer approximation is given by

$$\hat{H} = \hat{K} + \hat{V}_{ei} + \hat{V}_{ee} + V_{ii} \tag{3.18}$$

For a given **k**-point, the kinetic energy is given in the second quantized form by [17, 25]:

$$\hat{K} = \frac{1}{2} \sum_{\mathbf{G},\lambda} (\mathbf{k} + \mathbf{G})^2 c^{\dagger}_{\mathbf{k} + \mathbf{G},\lambda} c_{\mathbf{k} + \mathbf{G},\lambda}, \qquad (3.19)$$
where λ is a spin of an electron.

The other terms are the Coulomb interaction terms. For system consists of $N_{\rm a}$ ions and N electrons, the total interactions are given by [2]

$$U = \sum_{i=1}^{N} \sum_{\alpha=1}^{N_{a}} Z_{\alpha} \psi(\mathbf{r}_{i}, \mathbf{d}_{\alpha}) + \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1\\j\neq i}}^{N} \psi(\mathbf{r}_{i}, \mathbf{r}_{j}) + \frac{N\xi}{2} + \frac{1}{2} \sum_{\alpha=1}^{N_{a}} \sum_{\substack{j=1\\\beta\neq\alpha}}^{N_{a}} \psi(\mathbf{d}_{\alpha}, \mathbf{d}_{\beta}) + \frac{\xi}{2} \sum_{\alpha=1}^{N_{a}} Z_{\alpha}^{2}.$$
(3.20)

where the interaction potential $\psi(\mathbf{r}, \mathbf{r}')$ is a modified Coulomb potential that incorporates the periodic boundary condition and ξ is the self-energy term. The representation of this modified Coulomb potential in Fourier space is $\frac{1}{|\mathbf{G}-\mathbf{G}'|^2}$, which is the same with the Fourier representation of the original Coulomb potential.

The first term in Eq. (3.20) is the electron-ion interaction. Here we use a norm conserving LDA Kleinman-Bylander (KB) nonlocal pseudopotential [30, 31]. The pseudopotential models the interaction between valence electrons and atomic core (atomic nuclei and core electrons), so the number of electrons that are involved in calculations is significantly reduced. In second quantized formalism, these pseudopotentials can be written as

$$\hat{V}_{ei} = \sum_{\mathbf{G},\mathbf{G}'} \tilde{V}^{\text{loc}}(\mathbf{G} - \mathbf{G}') c^{\dagger}_{\mathbf{k}+\mathbf{G}} c_{\mathbf{k}+\mathbf{G}'} + \sum_{\mathbf{G},\mathbf{G}'} \tilde{V}^{\text{nl}}(\mathbf{k} + \mathbf{G}, \mathbf{k} + \mathbf{G}') c^{\dagger}_{\mathbf{k}+\mathbf{G}} c_{\mathbf{k}+\mathbf{G}'}, \quad (3.21)$$

where $V^{\text{loc}}(\mathbf{G} - \mathbf{G}')$ and $V^{\text{nl}}(\mathbf{k} + \mathbf{G}, \mathbf{k} + \mathbf{G}')$ are the matrix element of local and nonlocal potential as described in Appendix A. Now the local part can be rewritten as follows:

$$\hat{V}_{ei}^{\text{loc}} = \frac{1}{2} \sum_{\mathbf{Q}\neq 0} \tilde{V}^{\text{loc}}(\mathbf{Q}) [\hat{\rho}(\mathbf{Q}) + \hat{\rho}^{\dagger}(\mathbf{Q})] + N V^{\text{loc}}(0), \qquad (3.22)$$

where N is the number of electrons. The last term is just a constant and it excludes the $\mathbf{Q} = 0$ divergent term coming from long range Coulomb interaction. The onebody density operator $\hat{\rho}(\mathbf{Q})$ is given by

$$\hat{\rho}(\mathbf{Q}) \equiv \sum_{\mathbf{G},\lambda} c^{\dagger}_{\mathbf{k}+\mathbf{G}+\mathbf{Q},\lambda} c_{\mathbf{k}+\mathbf{G},\lambda} \theta \left(E_{\text{cut}} - |\mathbf{k}+\mathbf{G}+\mathbf{Q}|^2/2 \right).$$
(3.23)

The step function ensures that $(\mathbf{k} + \mathbf{G} + \mathbf{Q})$ lies within planewave basis and the summation over spin $(\lambda = 1, 2)$ has been made explicit.

The second term in Eq. (3.20) is the electron-electron interaction. This term is a two-body term. The matrix element is given by

$$\langle \mathbf{k} + \mathbf{G}_{i}, \lambda_{i}; \mathbf{k} + \mathbf{G}_{j}, \lambda_{j} | \hat{V}^{\text{ee}} | \mathbf{k} + \mathbf{G}_{k}, \lambda_{k}; \mathbf{k} + \mathbf{G}_{l}, \lambda_{l} \rangle$$
$$= \delta_{\lambda_{i}, \lambda_{k}} \delta_{\lambda_{j}, \lambda_{l}} \delta_{\mathbf{G}_{i} + \mathbf{G}_{j}, \mathbf{G}_{k} + \mathbf{G}_{l}} \frac{1}{2\Omega} \frac{4\pi}{\left(\mathbf{G}_{i} - \mathbf{G}_{k}\right)^{2}}.$$
 (3.24)

In second quantized formalism, the electron-electron interaction is given as

$$\hat{V}^{\text{ee}} = \sum_{\mathbf{G}_{i},\lambda_{i}} \sum_{\mathbf{G}_{j},\lambda_{j}} \sum_{\mathbf{G}_{k},\lambda_{k}} \sum_{\mathbf{G}_{l},\lambda_{l}} \delta_{\lambda_{i},\lambda_{k}} \delta_{\lambda_{j},\lambda_{l}} \delta_{\mathbf{G}_{i}+\mathbf{G}_{j},\mathbf{G}_{k}+\mathbf{G}_{l}} \frac{1}{2\Omega} \frac{4\pi}{\left(\mathbf{G}_{i}-\mathbf{G}_{k}\right)^{2}} c_{\mathbf{k}+\mathbf{G}_{i},\lambda_{i}}^{\dagger} c_{\mathbf{k}+\mathbf{G}_{j},\lambda_{j}}^{\dagger} c_{\mathbf{k}+\mathbf{G}_{l},\lambda_{l}} c_{\mathbf{k}+\mathbf{G}_{k},\lambda_{k}}.$$
 (3.25)

The primed summation indicates that the $\mathbf{G}_i = \mathbf{G}_k$ singular term is excluded due to charge neutrality. The change of variables

$$\mathbf{G}_{i} = \mathbf{G} + \mathbf{Q},$$

$$\mathbf{G}_{j} = \mathbf{G}' - \mathbf{Q},$$

$$\mathbf{G}_{k} = \mathbf{G},$$

(3.26)

$$\mathbf{G}_l = \mathbf{G}',$$

guarantees that $\mathbf{G}_i + \mathbf{G}_j = \mathbf{G}_k + \mathbf{G}_l$. Using these new variables, Eq. (3.25) becomes

$$\hat{V}^{\text{ee}} = \sum_{\lambda_i,\lambda_j} \sum_{\substack{\mathbf{G},\mathbf{G}',\mathbf{Q}\\\mathbf{Q}\neq 0}} \frac{1}{2\Omega} \frac{4\pi}{\mathbf{Q}^2} c^{\dagger}_{\mathbf{k}+\mathbf{G}+\mathbf{Q},\lambda_i} c^{\dagger}_{\mathbf{k}+\mathbf{G}'-\mathbf{Q},\lambda_j} c_{\mathbf{k}+\mathbf{G}',\lambda_j} c_{\mathbf{k}+\mathbf{G},\lambda_i}.$$
(3.27)

Using the commutation relations, Eq. (3.27) can be written as

$$\hat{V}^{\text{ee}} = \sum_{\lambda_i,\lambda_j} \sum_{\substack{\mathbf{G},\mathbf{G}',\mathbf{Q}\\\mathbf{Q}\neq0}} \frac{1}{2\Omega} \frac{4\pi}{\mathbf{Q}^2} c^{\dagger}_{\mathbf{k}+\mathbf{G}+\mathbf{Q},\lambda_i} c_{\mathbf{k}+\mathbf{G},\lambda_i} c^{\dagger}_{\mathbf{k}+\mathbf{G}'-\mathbf{Q},\lambda_j} c_{\mathbf{k}+\mathbf{G}',\lambda_j} - \frac{1}{2\Omega} \sum_{\lambda_i} \sum_{\mathbf{G}} \sum_{\mathbf{Q}\neq0} \frac{4\pi}{\mathbf{Q}^2} c^{\dagger}_{\mathbf{k}+\mathbf{G},\lambda_i} c_{\mathbf{k}+\mathbf{G},\lambda_i}.$$
(3.28)

The first term can be simplified by using definition of $\rho(\mathbf{Q})$ in Eq. (3.23). Note that the sum over \mathbf{Q} in second term has \mathbf{G} dependence and therefore cannot be simplified further. Let rewrite this term in original variable $\mathbf{Q} = \mathbf{G}_i - \mathbf{G}_k$, and since \mathbf{G}_i is just a dummy index, this summation can be written as

$$\hat{V}^{\text{ee}} = \frac{1}{2\Omega} \sum_{\mathbf{Q}\neq 0} \frac{4\pi}{\mathbf{Q}^2} \rho(\mathbf{Q}) \rho^{\dagger}(\mathbf{Q}) - \frac{1}{2\Omega} \sum_{\lambda} \sum_{\substack{\mathbf{G},\mathbf{G}'\\\mathbf{G}\neq\mathbf{G}'}} \frac{4\pi}{(\mathbf{G}-\mathbf{G}')^2} c^{\dagger}_{\mathbf{k}+\mathbf{G},\lambda} c_{\mathbf{k}+\mathbf{G},\lambda}.$$
 (3.29)

If rearrangement of the terms in Eq. (3.28) is done differently, the electron-electron terms can be written in the same form as Eq. (3.29) except that the term $\rho(\mathbf{Q})\rho^{\dagger}(\mathbf{Q})$ is flipped into $\rho^{\dagger}(\mathbf{Q})\rho(\mathbf{Q})$.

The third term in Eq. (3.20) is the interaction term between electrons with their own images. This constant $\frac{N\xi}{2}$ term goes to zero as the simulation cell increases. The fourth and fifth terms of Eq. (3.20) are the nuclei-nuclei interaction and nuclei with they own images interaction, respectively. These terms are also constant.

In second quantization language, all terms in the Hamiltonian can be regrouped into constants, one-body parts and two-body parts. The Hamiltonian is rewritten as follow:

$$\hat{H} = H^{(0)} + \hat{H}^{(1)} + \hat{H}^{(2)} \tag{3.30}$$

$$H^{(0)} = NV^{\rm loc}(0) + \frac{1}{2}N\xi + \frac{1}{2}\sum_{\alpha=1}^{M}\sum_{\substack{\beta=1\\\beta\neq\alpha}}^{M}\psi\left(\mathbf{d}_{\alpha},\mathbf{d}_{\beta}\right) + \frac{\xi}{2}\sum_{\alpha=1}^{M}Z_{\alpha}^{2}.$$
 (3.31)

$$\hat{H}^{(1)} = \frac{1}{2} \sum_{\mathbf{G},\lambda} (\mathbf{k} + \mathbf{G})^2 c^{\dagger}_{\mathbf{k} + \mathbf{G},\lambda} c_{\mathbf{k} + \mathbf{G},\lambda} + \frac{1}{2} \sum_{\mathbf{Q} \neq 0} \tilde{V}^{\text{loc}}(\mathbf{Q}) [\hat{\rho}(\mathbf{Q}) + \hat{\rho}^{\dagger}(\mathbf{Q})] + \sum_{\mathbf{G},\mathbf{G}'} \tilde{V}^{\text{nl}}(\mathbf{k} + \mathbf{G}, \mathbf{k} + \mathbf{G}') c^{\dagger}_{\mathbf{k} + \mathbf{G}} c_{\mathbf{k} + \mathbf{G}'} - \frac{1}{2\Omega} \sum_{\lambda} \sum_{\substack{\mathbf{G},\mathbf{G}'\\\mathbf{G} \neq \mathbf{G}'}} \frac{4\pi}{(\mathbf{G} - \mathbf{G}')^2} c^{\dagger}_{\mathbf{k} + \mathbf{G},\lambda} c_{\mathbf{k} + \mathbf{G},\lambda}.$$
(3.32)

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$$\hat{H}^{(2)} = \frac{1}{2\Omega} \sum_{\mathbf{Q}\neq 0} \frac{4\pi}{\mathbf{Q}^2} \rho(\mathbf{Q}) \rho^{\dagger}(\mathbf{Q}).$$
(3.33)

The two-body terms can be written in more symmetric way as follow:

$$\hat{H}^{(2)} = \sum_{\mathbf{Q}\neq 0} \frac{\pi}{\Omega \mathbf{Q}^2} \left[\rho(\mathbf{Q}) \rho^{\dagger}(\mathbf{Q}) + \rho^{\dagger}(\mathbf{Q}) \rho(\mathbf{Q}) \right].$$
(3.34)

Hermitian operators $\hat{A}(\mathbf{Q})$ and $\hat{B}(\mathbf{Q})$ are defined as

$$\hat{A}(\mathbf{Q}) \equiv \sqrt{\frac{2\pi}{\Omega \mathbf{Q}^2}} \left[\hat{\rho}(\mathbf{Q} + \hat{\rho}^{\dagger}(\mathbf{Q})) \right], \qquad (3.35)$$

$$\hat{B}(\mathbf{Q}) \equiv i \sqrt{\frac{2\pi}{\Omega \mathbf{Q}^2}} \left[\hat{\rho}(\mathbf{Q} - \hat{\rho}^{\dagger}(\mathbf{Q})) \right], \qquad (3.36)$$

so that the two-body operator can be written as a sum of quadratic operator:

$$\hat{H}^{(2)} = \frac{1}{4} \sum_{\mathbf{Q} \neq 0} \left[\hat{A}^2(\mathbf{Q}) + \hat{B}^2(\mathbf{Q}) \right].$$
(3.37)

3.4 Ground-State Projection

The ground state $|\Psi_0\rangle$ of a Hamiltonian \hat{H} is obtained from an imaginary time projection of a trial wave function $|\Psi_T\rangle$:

$$\lim_{n \to \infty} \left(e^{-\Delta \tau (\hat{H} - E_0)} \right)^n |\Psi_T\rangle = |\Psi_0\rangle, \qquad (3.38)$$

where E_0 is an estimate of the lowest eigenenergy of Hamiltonian \hat{H} . This projection works provided $\langle \Psi_T | \Psi_0 \rangle \neq 0$. In present applications, $|\Psi_T\rangle$ is a single Slater determinant obtained from a mean-field calculation, although including more Slater determinants are sometimes used in other applications. With a choice of small $\Delta \tau$, it is safe to separate the one-body and the two-body terms in the Hamiltonian using the Trotter-Suzuki decomposition [32, 33]:

$$\exp(-\Delta\tau\hat{H}) = \exp(-\Delta\tau[\hat{H}_1 + \hat{H}_2])$$

$$= \exp(-\frac{1}{2}\Delta\tau\hat{H}_1)\exp(\Delta\tau\hat{H}_2)\exp(-\frac{1}{2}\Delta\tau\hat{H}_1) + \mathcal{O}(\Delta\tau^3),$$
(3.39)

where an error of order $\Delta \tau^3$ is introduced. As mentioned in Sec. 3.1, an application of the one-body propagator $\exp(-\frac{1}{2}\Delta\tau\hat{H}_1)$ on a single Slater determinant $|\phi\rangle$ leads to another single Slater determinant $|\phi'\rangle = \exp(-\frac{1}{2}\Delta\tau\hat{H}_1)|\phi\rangle$. The two-body propagator in the form of square of one-body propagators can be transformed into one-body propagator using the Hubbard-Stratonovich transformation [34, 35],

$$\exp\left(-\frac{1}{2}\Delta\tau\sum_{i}\lambda_{i}\hat{b}_{i}^{2}\right) = \int\left(\prod_{i}\frac{d\sigma_{i}}{\sqrt{2\pi}}\right)\exp\left[\sum_{i}\left(-\frac{1}{2}\sigma_{i}^{2} + \sigma_{i}\sqrt{-\Delta\tau\lambda_{i}}\hat{b}_{i}\right)\right].$$
(3.40)

This can be written more compactly as,

$$e^{-\Delta\tau\hat{H}^{(2)}} = \left(\frac{1}{\sqrt{2\pi}}\right)^{\dim(\sigma)} \int d\sigma e^{-\frac{1}{2}\sigma\cdot\sigma} e^{\sqrt{\Delta\tau}\sigma\cdot\hat{\mathbf{v}}},\tag{3.41}$$

where we introduce a vector $\sigma \equiv \{\sigma_i\}$, whose dimensionality dim (σ) , is the number of all possible **Q**-vectors satisfying $\mathbf{Q} = \mathbf{G} - \mathbf{G}'$. Vectors **G** and **G'** are the reciprocal lattice vector whose kinetic energy smaller than E_{cut} . The operator $\hat{\mathbf{v}} \equiv \{\sqrt{-\lambda_i}\hat{b}_i\}$ are given by the $i\hat{A}(\mathbf{Q})$ or $i\hat{B}(\mathbf{Q})$ one-body operator, since all the $\lambda_i = 1$ in the planewave case.

In the original applications of the AFQMC method [36, 37], the multidimensional integrations are calculated with a Metropolis algorithm. While in our AFQMC simulation [14, 17, 26], we use importance-sampling transformation to turn the projection into a branching random walk in an over-complete Slater determinant space. The important sampling improves the quality of the random walk by providing a guidance for the walker based on the projected overlap with trial wave function. More importantly, it also allows the imposition of a constraint to control the phase problem.

The phase problem arises from the fact that the projection operators cannot be made all real, or in other word the λ_i is not negative. As the random walk proceeds, the orbitals

$$|\phi'\rangle \leftarrow \exp(\sqrt{\Delta\tau}\sigma \cdot \hat{\mathbf{v}})|\phi\rangle$$
 (3.42)

gain complex phases, which make the stochastic representation of the ground state $|\Psi_0\rangle$ become dominated by noise. This phase problem is similar to the well-known sign problem [14], but it is more severe because, instead of $+|\phi\rangle$ and $-|\phi\rangle$ symmetry, there are now an infinite set $\{e^{i\theta}|\phi\rangle, \theta \in [0, 2\phi)\}$, among which the Monte Carlo sampling cannot distinguish.

The phaseless AFQMC method is used to control the phase problem in an approximate manner, using a trial wave function [17, 25]. The method uses a complex importance sampling function, the overlap $\langle \Phi_T | \phi \rangle$, to construct phaseless random walkers, $|\phi\rangle/\langle\Psi_T | \phi\rangle$. The ground state is then represented as a stochastic sum of walkers

$$|\Psi_0\rangle = \sum_{\phi} w_{\phi} \frac{|\phi\rangle}{\langle \Psi_T |\phi\rangle},\tag{3.43}$$

where w_{ϕ} is a weight of phaseless walker,

$$w_{\phi} = \exp\left[-\Delta\tau \frac{\langle \Psi_T | \hat{H} | \phi \rangle}{\langle \Psi_T | \phi \rangle}\right] \equiv \exp[-\Delta\tau E_L(\phi)], \qquad (3.44)$$

and $E_L(\phi)$ is a local energy of a walker.

The ground state energy calculated within mixed estimate is given by

$$E_0 = \frac{\langle \Psi_T | \hat{H} | \Psi_0 \rangle}{\langle \Psi_T | \Psi_0 \rangle} = \lim_{\beta \to 0} \frac{\langle \Psi_T | \hat{H} e^{-\beta \hat{H}} | \Psi_T \rangle}{\langle \Psi_T | e^{-\beta \hat{H}} | \Psi_T \rangle}.$$
(3.45)

In the stochastic representation, the ground state energy is given by

$$E_0^{\rm MC} = \frac{\sum_{\phi} w_{\phi} E_L(\phi)}{\sum_{\phi} w_{\phi}}.$$
 (3.46)

Detail discussion on the implementation of the phaseless AFQMC can be found at Refs. [17, 18, 22].

CHAPTER 4

Jellium

The homogeneous electron liquid¹, known as jellium, is the simplest realistic model of interacting electrons in extended systems, yet it can provide valuable insights into more complex systems [4]. This discussion will be restricted to non-spin polarized jellium.

The local density approximation (LDA) of density functional theory (DFT) uses the exchange correlation energy of jellium to describe realistic systems. There is no a priori reason to believe that this will work well [39] but many applications show that, in fact, this is often a good approximation, except for systems where the correlation energy plays an important role in the physical properties.

In the jellium model, interacting electrons are allowed to move in a non-responsive uniform positive neutralizing background charge. The Hamiltonian of the N electron system of volume Ω , with $N/\Omega = n$ is given by

$$\hat{H} = -\frac{1}{2} \sum_{i}^{N} \nabla_{i}^{2} + \left[\frac{1}{2} \sum_{i \neq j}^{N} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} - \frac{1}{2} \int d^{3}r d^{3}r' \frac{n^{2}}{|\mathbf{r} - \mathbf{r}'|} \right],$$
(4.1)

¹The term *electron liquid* is used to emphasize the electron-electron interaction, as opposed to *electron gas* that used in the independent electron model [38]. Sometimes, the term *interacting electron gas* or simply *jellium* are also used.

where Hartree atomic units ($\hbar = m_e = e = 4\pi\epsilon_0 = 1$) are used, so that lengths are given in unit of the Bohr radius a_0 . The last term arises from the interaction between the electrons with the positive background and the self energy of the background with itself and divergent long-wavelength Coulomb interaction terms eventually drop out due to charge neutrality [40] as the volume $\Omega \to \infty$.

The whole system is parametrized only by the density of the electrons, characterized by the average separation r_s of the electrons in the system :

$$\frac{4}{3}\pi r_s^3 \frac{N}{\Omega} = 1.$$
(4.2)

It is useful to write equation (4.1) in terms of scaled coordinates $\tilde{\mathbf{r}}=\mathbf{r}/r_s$, instead of atomic units (where \mathbf{r} is in unit of a_0),

$$\hat{H} = \left(\frac{1}{r_s}\right)^2 \sum_{i} \left[\frac{1}{2}\nabla_i^2 + \frac{1}{2}r_s\left(\sum_{j\neq i}\frac{1}{|\tilde{\mathbf{r}}_i - \tilde{\mathbf{r}}_j|} - \frac{3}{4\pi}\int\frac{d^3\tilde{\mathbf{r}}}{|\tilde{\mathbf{r}}|}\right)\right].$$
(4.3)

Eq. (4.3) shows that in the high density limit $(r_s \to 0)$ the kinetic energy term is dominant while for the low density limit $(r_s \to \infty)$ the potential energy term is dominant.

In practice, calculations are performed on a finite-size simulation cell with a finite number of electrons, incorporating periodic boundary conditions, keeping the same density as the infinite system's density. Properties of the infinite-size limit are obtained through extrapolation [9, 41], which will be discussed in Chapter 5.

The chapter is organized as follows. First I will discuss Hartree-Fock (HF) solutions to the infinite-size limit of jellium system and define the correlation energy. Benchmark AFQMC calculations for several densities and numbers of electrons will be discussed. Finally, I will discuss convergence with respect to the (planewave) basis.

4.1 Hartree-Fock Solution to the Infinite-Size-Limit of Jellium System

The HF equation for a jellium system is given by [29]

$$-\frac{1}{2}\nabla^{2}\varphi_{i}(\mathbf{r}) - \sum_{j}\int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|}\varphi_{j}^{*}(\mathbf{r}')\varphi_{i}(\mathbf{r}')\varphi_{j}(\mathbf{r})\delta_{s_{i}s_{j}} = \epsilon_{i}\varphi_{i}(\mathbf{r}).$$
(4.4)

The solution to the equations is

$$\varphi_i(\mathbf{r}) = \left(\frac{e^{i\mathbf{k}_i \cdot \mathbf{r}}}{\sqrt{\Omega}}\right) \times \text{spin function},$$
(4.5)

in which each wave vector less than Fermi momentum k_F occurs twice in the Slater determinant. The infinite-size limit $\Omega \to \infty$ will be taken at the end of the calculations. The relation between number of electrons N, Fermi momentum k_F and simulation cell size $\Omega = L^3$ is given by

$$N = 2\frac{\frac{4}{3}\pi k_F^3}{\left(\frac{2\pi}{L}\right)^3}.$$
(4.6)

The factor of two is included to take into account the fact that each state is occupied by spin up and spin down electrons. The relation between Fermi momentum and density is

$$k_F = \left(\frac{9\pi}{4}\right)^{\frac{1}{3}} \frac{1}{r_s}.$$
(4.7)

The single particle eigenenergies of the system are given by

$$\epsilon(\mathbf{k}) = \frac{k^2}{2} - \frac{2}{\pi} k_F F\left(\frac{k}{k_F}\right),\tag{4.8}$$

where

$$F(x) = \frac{1}{2} + \frac{1 - x^2}{4x} \ln \left| \frac{1 + x}{1 - x} \right|.$$
(4.9)

The first term is the kinetic energy term and the second term is the exchange term.

$$E_K = 2\sum_{k < k_F} \frac{k^2}{2}.$$
(4.10)

In the limit $\Omega \to \infty$, this summation can be evaluated as integral to obtain

$$\frac{E_K^{\infty}}{N} \equiv \mathcal{E}_K^{\infty} = \frac{3}{10} k_F^2$$

$$= \frac{3}{5} \epsilon_F.$$
(4.11)

Similarly, the exchange energy is given by [29],

$$E_x = -\frac{k_F}{\pi} \sum_{k < k_F} \left[1 + \frac{k_F^2 - k^2}{2kk_F} \ln \left| \frac{k_F + k}{k_F - k} \right| \right], \tag{4.12}$$

and converting the sum into an integration, the exchange energy per particle is given by

$$\frac{E_x^{\infty}}{N} \equiv \mathcal{E}_x^{\infty} = -\frac{3}{4\pi}k_F.$$
(4.13)

The total HF energy per particle is then given by

$$\mathcal{E}_{HF}^{\infty}(r_s) \equiv \frac{E_{HF}^{\infty}(r_s)}{N}$$

$$= \frac{3}{10} \left(\frac{9\pi}{4}\right)^{\frac{2}{3}} \frac{1}{r_s^2} - \frac{3}{4\pi} \left(\frac{9\pi}{4}\right)^{\frac{1}{3}} \frac{1}{r_s}$$

$$= \frac{1.10495}{r_s^2} - \frac{0.458165}{r_s}.$$
(4.14)

This energy could also be obtained using perturbation theory. In high density (i.e., small r_s/a_0), the kinetic energy is the 0th order energy, and the exchange energy is the 1st order energy correction. The remaining terms in the series are called the correlation energy [40] which is defined as the energy difference between the true total energy and the HF energy

$$\mathcal{E}_c^{\infty}(r_s) = \mathcal{E}^{\infty}(r_s) - \mathcal{E}_{HF}^{\infty}(r_s).$$
(4.15)

The asymptotic expansion for correlation energy of high density jellium $(r_s \ll 1)$ is given by

$$\mathcal{E}_c^{\infty}(r_s) = \frac{1}{\pi^2} (1 - \ln(2)) \ln(r_s) - 0.048 + 0.0020 r_s \ln(r_s) - 0.0116 r_s.$$
(4.16)

The first and second terms were calculated by Gell-Mann and Brueckner (1957) [42] and the other two terms are from a fit by Perdew and Zunger (1981) [10] to diffusion Monte Carlo results of Ceperley and Alder (1980) [9].

4.2 Several Simple AFQMC Test Calculations

In this section, we describe several preliminary AFQMC calculations of jellium. AFQMC calculations will be used to monitor the accuracy of finite-size fits to $\mathcal{E}_c(r_s, L)$ in Chapter 5. Calculations were first performed on an unpolarized 14 electron closed shell (all degenerate states underneath the Fermi surface are filled) system for $r_s = 4.0$ (cubic box of size 15.54 Bohr).

Table 4.1 shows good agreement between our results and previous results [43, 44]. The highest cutoff energy $E_{\rm cut}$ of the plane wave basis used in my calculations was 25 Ry. This accurately describes electron scattering due to correlation effects (the HF Fermi energy $E_F \sim 0.16$ Ry). The momentum distribution of electrons given in Ref. [45] is negligible for electron with $E > 4E_F$. Calculations using the smaller cutoff energy of 2 Ry ($\sim 12E_F$) give a similar result, consistent with our expectations.

Next we benchmark systems with larger number of electrons for several densities. Table 4.2 shows the energy per particle of 54 electron systems with r_s between 1 and 20. At each calculation we use cutoff energy about or larger than $12E_F$. The results are compared with calculations using diffusion Monte Carlo [46], and they are in good agreement. For $r_s = 20$, there is the discrepancy of about 6%. This dis-

TABLE 4.1: Correlation energy per electron of jellium with number of electrons N = 14. The average distance of the electrons r_s is 4.0. The results are compared with other AFQMC calculations (see Ref. [43] and also see discussion on Ref. [44]). All quantities are in Rydberg atomic unit.

	$E_{\rm cut}$	E	\mathcal{E}_c
AFQMC	25.0	-2.262 ± 0.005	-0.0445 ± 0.0003
AFQMC	2.0	-2.275 ± 0.004	-0.0454 ± 0.0003
AFQMC from ref [43]	1.31	-2.27 ± 0.04	-0.045 ± 0.003
AFQMC from ref [43]	1.96	-2.34 ± 0.06	-0.050 ± 0.004
AFQMC from ref [44]	~ 3	-2.28 ± 0.08	-0.046 ± 0.006
GFMC from ref [43]		-2.297 ± 0.006	-0.0470 ± 0.0004

TABLE 4.2: Energy per electron of jellium with number of electrons N = 54. L is the size of the cubic box. The error of the calculation is given in the last digit. All quantities are in the Rydberg atomic unit

L	r_s	$E_{\rm cut}$	E_F	AFQMC Energy	DMC energy
6.09	1	40.0	3.19	1.0591(2)	1.0597(1)
30.46	5	4.0	0.128	-0.1546(4)	-0.15810(1)
60.93	10	0.4	3.19×10^{-2}	-0.1057(6)	-0.10888(1)
121.86	20	0.1	7.98×10^{-3}	-0.0601(4)	-0.06408(1)

crepancy might come from the fact that the basis that we used is not large enough for this low density system. More careful and systematic studies are needed to eliminate possible small errors (time-step, cutoff, etc) for an accurate and unbiased comparison between AFQMC and DMC. However, this low density region is not important in generating finite-size exchange-correlation functional, since AFQMC jellium results will only be used as a guide in our parametrization, we will not pursue such calculations at greater details.

4.3 Cutoff Energy Dependence of Jellium Correlation Energy

As required by the Pauli exclusive principle, the number of basis functions has to be at least equal to the number of electrons. Therefore the correlation energy is zero when $E_{\text{cut}} = E_F$. Figures 4.1 - 4.5 show the convergence with respect to E_{cut} for the range $1 \le r_s \le 5$, most important in realistic systems. Appendix B tabulates these results.

As E_{cut} increases, more of the correlation energy is captured, eventually converging to a value $\mathcal{E}_c(r_s, L)$, which depends only on the density and system size. As seen in figures 4.1 - 4.5, for $E_{\text{cut}} \sim 9E_F$, the error in the correlation energy is smaller than the statistical errors. As anticipating our finite-size fits, the open circles at the end of each curve are the FS correlation energy obtained from the functional given in Table 5.2. This will be further discussed in Chapter 5.

The first derivative in figures 4.1 - 4.5 is seen to decrease in the low cutoff energy region. For example, the correlation energies for N = 10 (the red curves in figures. 4.1 - 4.5) are seen to be curved down. Further studies indicate that this behavior also occurs for larger N, but at even lower cutoff energies. This finitesize effect decreases as the number of particles increases to infinity. In this limit, the correlation energies are expected behave monotonously in both the value and first derivative. It would be useful to construct correlation energy functional that depends on cutoff energy in the infinite-size limit $\mathcal{E}_c(r_s, E_{\rm cut})$. Such a functional would be useful for obtaining a finite-basis correction on many-body calculations. Further studies are needed to establish these corrections.



FIG. 4.1: The correlation energy of jellium system at density $r_s = 1$ as a function of cutoff energy.

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FIG. 4.2: The correlation energy of jellium system at density $r_s=2$ as a function of cutoff energy



FIG. 4.3: The correlation energy of jellium system at density $r_s = 3$ as a function of cutoff energy.

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FIG. 4.4: The correlation energy of jellium system at density $r_s = 4$ as a function of cutoff energy.



FIG. 4.5: The correlation energy of jellium system at density $r_s = 5$ as a function of cutoff energy.

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CHAPTER 5

Finite Size Effects

Realistic many-body calculations for extended systems are needed to accurately treat systems where the otherwise successful density functional theory (DFT) approach fails. These include high-temperature superconductors, transition metal oxides, and systems where accurate treatments of bond-breaking or bond-stretching are required. Effective single-particle methods such as DFT or Hartree Fock (HF) routinely exploit Bloch's theorem in calculations for extended systems. In crystalline materials, the cost of the calculations depends on the number of atoms in the periodic simulation cell, and the macroscopic limit is achieved by a simple quadrature in the Brillouin zone (BZ), using a finite number of **k**-points. Many-body methods with explicit two-particle interactions cannot avail themselves of this simplification. Instead calculations must be performed using increasingly larger simulation cells (supercells), extrapolating the results to infinite size. Finite size (FS) corrections from large one-body contributions (kinetic energy, Hartree energy, etc.), which arise from the downfolding of **k**-points into the smaller supercell Brillouin zone, can be easily incorporated using auxiliary HF or DFT supercell calculations, and these can accelerate size convergence [47]. Residual finite-size (FS) errors in many state-ofthe-art many-body calculations are usually still large and often more significant than other statistical and systematic errors. In this chapter, I introduce a new method [3] that is specifically designed to approximately include two-body FS corrections in DFT calculations, through the use of FS exchange correlation functions. These corrections accelerate the size convergence and reduce the dependence on the size of the simulation cell.

The origin of the FS error is first explained, followed by a discussion of existing correction methods using DFT and HF. FS effects in jellium are discussed next, reviewing the extrapolation to the infinite-size limit. A reverse engineered FS exchange correlation function is then generated and a parametrization for this FS XC function is given.

5.1 Origin of Finite Size Errors

In mean-field type calculations, such as DFT, FS errors effectively arise from the discrete quadratures used to approximate Brillouin-zone integrations. The infinite limit can be obtained in two ways. The first and more efficient way is to increase the number of \mathbf{k} -points sampled in the BZ, using the primitive simulation cell. In this method, the cost of the calculations grow linearly with the number of \mathbf{k} -points. The second way is to increase the size of the simulation cell using only a single or small number of \mathbf{k} -points. This method is more expensive, since it increases both the number of particles and the number of basis functions needed. In many-body calculations, the infinite-size limit can only be achieved using the second approach. Typically several many-body calculations, each at different \mathbf{k} -point, representing a particular choice of periodic boundary conditions (PBC) [see Eq. (3.12)], are averaged to further reduce size effects.

The nature of the FS errors in many-body calculations is different from mean-



FIG. 5.1: Finite size simulation cell for 3 types of systems. The top panel (a) uses periodic boundary conditions for an isolated atomic or molecular calculation. The FS effect arises from spurious interactions of a molecule with its own images. The middle panel (b) shows the model for jellium. Jellium with a certain density r_s is modeled with a simulation cell of any volume Ω containing N electrons where Ω and N are chosen so that $4\pi r_s^3/3 = \Omega/N$. The bottom panel (c) illustrates periodic boundary conditions applied in simulations of a solid. All images of an electron are correlated to the electron in the simulation cell. The size of the simulation cell that can be used in calculations is discrete; being an integer multiple of the primitive cell.

field type calculations. Using DFT calculations to estimate the many-body FS errors does not eliminate all of the FS error. In many-body calculations the long range Coulomb interaction induces correlations between electrons at large distances and these are not captured at the mean field level. Fully reproducing these long range interactions requires large simulation cells. FS simulation cells in PBC effectively use a modified form of the interaction which introduces errors.

Fig. 5.1 illustrates this FS error in three different types of systems.

a. FS errors in atomic/molecular systems with PBC:

It is sometimes convenient to model an isolated atom or molecule using PBC. As a result, interactions with fake images are present. Increasing the simulation cell size eventually removes this error. The cost of increasing the size of the supercell in this atomic/molecular system is lower than for the solid, since only the size of the basis increases, while the number of particles remains constant.

b. FS errors in jellium:

Jellium consists of electrons with uniform density n in the presence of a classical constant positive background. In a simulation with PBC, this system is modeled with a fixed number of electron N in a simulation cell of volume Ω , such that $N/\Omega = n$. As the number of N and volume Ω increases, the system approaches the infinite-size limit. As in the case of solids, increasing the size of simulation cell also increases both the number of particles and the number of basis functions. By definition, the DFT energy of infinite jellium is exactly equal to the manybody value for the infinite size system. We wish to construct a FS DFT exchange correlation function that is equal to the many-body function for finite-size jellium.

c. FS error in solids:

In simulations with PBC, artificial periodicity is enforced on the many-body wave function, which introduces FS errors.

5.2 Existing Correction Methods

The XC energy density $\mathcal{E}_{xc}(n)$ of DFT is most often obtained from interpolation, over a range of densities n, of quantum Monte Carlo (QMC) calculations of the homogeneous interacting electron gas [9, 10, 41]. A key point is that the QMC results, which are obtained with PBC, have been *extrapolated to infinite supercell size* for each density n. This is the correct choice for DFT applications to extended systems, where Bloch's theorem will be used to reach infinite system size.

This choice is not ideal, however, if one seeks to obtain FS corrections from the LDA. Fig. 5.2 shows the FS error for fcc bulk silicon calculated with diffusion Monte Carlo (DMC) [47], LDA and with DMC corrected by LDA. The system size for n=1 to 5 corresponds to $N_{\rm ion} = 2$, 16, 54, 128 and 250 atoms, respectively. The FS error is determined by assuming that the largest system n = 5 is at the infinitesize limit. All the calculations were done using a single **k**-point, the **L**-point in the fcc BZ [48, 49]. The DMC energy is seen to have a different size dependence than the LDA. DMC approaches the infinite-size limit from below, while the LDA energy approaches from above. The size effect actually increases for LDA-corrected DMC.

FS errors can be separated into one-body and two-body FS errors. Sometimes these errors are referred to as the independent-particle finite size error and the Coulomb finite-size error [47], respectively. The one-body FS error is controlled by \mathbf{k} -point convergence and is also present in LDA calculations. As mentioned, these errors are quadrature errors and can be systematically reduced by using more \mathbf{k} points in the BZ integration [50]. The use of certain quadrature grids can accelerate this convergence (so-called special \mathbf{k} -point grid [51]), and the same is true in manybody calculations [48, 49]. In many-body calculations, this is done by averaging over \mathbf{k} -points, using twisted average boundary conditions (TABC) [52]. There is very little loss of efficiency with TABC, since the average over \mathbf{k} -points also reduces



FIG. 5.2: The size dependence of silicon bulk with respect to the system size. Tabulated DMC data is provided by courtesy of Paul Kent (similar to Fig. 2 and 4 in Ref. [47]). The largest cell with size of n = 5, corresponding to $N_{\rm a} = 250$ atoms is assumed to be the infinite-size limit. The DMC energies approach the infinite-size limit from below, while the LDA energies approach it from above. The LDA corrected DMC energies are seen to have larger FS errors.

statistical errors. Further discussion is presented in Chapter 6.

The remaining two-body FS error is more difficult to correct. This error is the residual error after the usual LDA corrections remove most of the FS errors in the kinetic energy, electron-ion interaction energy and the classical electron-electron Hartree energy. The residual error is due to FS effects in the exchange-correlation energy. The effective electrostatic Ewald interaction between particles in the simulation cell is responsible. Expanding the Ewald interaction $\Psi(\mathbf{r})$ about zero separation [1, 2, 47, 53] gives

$$\psi(\mathbf{r}) = \frac{1}{r} + \cos + \frac{2\pi}{3\Omega} \mathbf{r}^T \cdot \mathbf{D} \cdot \mathbf{r} + \mathcal{O}\left(\frac{r^4}{\Omega^{5/3}}\right), \qquad (5.1)$$

where Ω is the volume of the simulation cell, and the tensor **D** depends on the shape

of the simulation cell (for a cubic cell, \mathbf{D} is an identity matrix). The second-order and higher-order terms arise from the imposed periodicity in the Ewald interaction. It introduces a size dependent contribution to the exchange-correlation energy. Some attempts to fix it include modifying the Ewald interaction to a model periodic Coulomb interaction [47]. Corrections based on the random phase approximation in the long wave length limit [54] have also been used. Applying the first method requires repeating the simulations with the modified interaction, while the second method requires calculation of structure factors within the many-body simulations.

The approach that we have developed can be motivated by considering a FS correction scheme using the HF method. The HF method also uses the Ewald interaction to model the Coulomb interactions for finite simulation cells. It thus uses the same FS exchange as in a many-body calculation. The HF method, however, does not include the correlation energy, and therefore it tends to give too large a correction, because the HF exchange hole is significantly different from the screened XC hole of the many-body system [47].

Our new proposed correction approximates the two-body FS error in DFT calculations using a FS version of the exchange and correlation functional. The FS corrections are then obtained by performing parallel LDA calculations with a FS modification of the XC function. Our FS XC function $\mathcal{E}_{xc}(r_s, L)$, derived from finite-size QMC calculations, will be seen to provide a better correction scheme. In tests reported in Chapter 6, $\mathcal{E}_{xc}(r_s, L)$, which has explicit size dependence, is constructed within cubic supercells, but we find that it also provides good FS corrections for simulation cells with other shapes. Using this scheme, a two-body FS correction is obtained from the difference between the DFT energy calculated using the $\mathcal{E}_{xc}(r_s, L)$ function and that calculated using the infinite-size XC function, $\mathcal{E}_{xc}^{\infty}(r_s)$. These corrections are post processing corrections that can be applied to any previously obtained many-body results, without having to repeat expensive calculations. This

correction scheme is obviously exact by construction in the limit of a homogeneous system.

5.3 Finite Size Jellium Energy

5.3.1 Overview of Extrapolation Scheme

We wish to obtain expressions for the exchange-correlation energy functional $\mathcal{E}_{xc}(r_s, L) = \mathcal{E}_x(r_s, L) + \mathcal{E}_c(r_s, L)$. We recall that the total ground state energy of jellium is given by

$$\mathcal{E}(r_s, L) = \mathcal{E}_K(r_s, L) + \mathcal{E}_{xc}(r_s, L), \qquad (5.2)$$

and the Hartree-Fock energy is given by

$$\mathcal{E}_{HF}(r_s, L) = \mathcal{E}_K(r_s, L) + \mathcal{E}_x(r_s, L)$$

= $\mathcal{E}(r_s, L) - \mathcal{E}_c(r_s, L).$ (5.3)

To obtain $\mathcal{E}(r_s, L)$, we use published diffusion Monte Carlo (DMC) results. Ceperley and Alder [9] calculated jellium DMC energies for many densities n and sizes of simulation cells. They presented a fit of the total energy per particle [9, 55, 56],

$$\mathcal{E}(r_s, L) = \mathcal{E}^{\infty}(r_s) + B_1(r_s)\Delta\mathcal{E}_K(r_s, L) + B_2(r_s)\frac{1}{N},$$
(5.4)

to obtain the extrapolated infinite-size limit $\mathcal{E}^{\infty}(r_s)$ at a given density, where $4\pi r_s^3/3 = L^3/N = 1/n$ and $\Delta \mathcal{E}_K(r_s, L)$ is the kinetic energy finite size correction. The inputs to the extrapolation in Eq. (5.4) are $\mathcal{E}(r_s, L)$ and $\Delta \mathcal{E}_K(r_s, L)$ for N electrons in the supercell of size L. $\Delta \mathcal{E}_K(r_s, L)$ is given by $\mathcal{E}_K(r_s, L) - \mathcal{E}_K^{\infty}(r_s)$ [Eq. (5.3) and Eq. (4.11)]. As indicated, the fitting parameters $\mathcal{E}^{\infty}(r_s)$, $B_1(r_s)$ and $B_2(r_s)$ depend only on the density. All of the size-dependent quantities in Eq. (5.4) were obtained using Gamma point ($\mathbf{k} = 0$) calculations in large supercells. In this work, we wish to obtain expression for $\mathcal{E}(r_s, L)$ for arbitrary r_s and L, using fits to the discrete tabulated DMC results entering into Eq. (5.4). To achieve this, we require $\mathcal{E}^{\infty}(r_s)$, $B_1(r_s)$, $B_2(r_s)$ and $\Delta \mathcal{E}_K(r_s, L)$ for arbitrary r_s and L. The parameters $B_1(r_s)$ and $B_2(r_s)$ were tabulated by Kwon, Ceperley and Martin [57] for a few values of r_s . We fitted these values to obtain a continuous representation of these functions,

$$B_1(r_s) = b_{11} + b_{12} \cdot r_s^{\frac{1}{2}} + b_{13} \cdot r_s + b_{14} \cdot r_s^{\frac{3}{2}}, \qquad (5.5)$$

and

$$B_2(r_s) = \frac{b_{21}}{r_s^{1/2}} + \frac{b_{22}}{r_s} + \frac{b_{23}}{r_s^{3/2}} + \frac{b_{24}}{r_s^2}$$
(5.6)



FIG. 5.3: The parameters $B_1(r_s)$ and $B_2(r_s)$. The data is taken from Kwon, Ceperley and Martin's DMC calculations [57].

The fits are shown in Fig. 5.3, and the fitting parameters are given in Table 5.1.

TABLE 5.1: The parameters in the $B_1(r_s)$ and $B_2(r_s)$. All parameters are given in Rydberg atomic unit

i	1	2	3	4
b_{1i}	0.980309	0.140501	-0.026359	0.0015489
b_{2i}	0.048587	-0.365285	-0.989827	0.146525

In the infinite size limit, the total energy per particle is given by

$$\mathcal{E}^{\infty}(r_s) = \mathcal{E}^{\infty}_{HF}(r_s) + \mathcal{E}^{\infty}_c(r_s), \qquad (5.7)$$

where $\mathcal{E}_{HF}^{\infty}(r_s)$ is given by Eq. (4.14) [40]

$$\mathcal{E}_{HF}^{\infty} = \frac{b_0}{r_s^2} + \frac{a_0}{r_s},\tag{5.8}$$

where $b_0 \approx 1.105$ Ha and $a_0 \approx -0.458$ Ha.

Several fits to the DMC data for $\mathcal{E}_c^{\infty}(r_s)$ have been published (see Perdew and Zunger [10]; Perdew and Wang [58]; and Vosko, Wilk and Nusair [59]). In this work, we use the parametrization from Perdew and Zunger (PZ),

$$\mathcal{E}_{c}^{\infty} = \begin{cases} c_{1} \ln r_{s} + c_{2} + c_{3} r_{s} \ln r_{s} + c_{4} r_{s} & r_{s} < 1, \\ \frac{c_{5}}{1 + c_{6} \sqrt{r_{s}} + c_{7} r_{s}} & r_{s} \ge 1. \end{cases}$$
(5.9)

The next section describes the finite-size behavior of $\mathcal{E}_K(r_s, L)$ and $\mathcal{E}_x(r_s, L)$.

5.3.2 Hartree-Fock Energy of Jellium

In the HF approximation, the ground state of jellium is simply described by a N-electron Slater determinant constructed by filling up the N lowest energy planewave states. The HF ground state energy per particle of an unpolarized jellium simulation cell containing N electrons for a given \mathbf{k} -point is given by [2]

$$\mathcal{E}_{HF}(r_s, L, \mathbf{k}) = \frac{2}{N} \sum_{\mathbf{G} \text{ occ.}} \frac{1}{2} (\mathbf{k} + \mathbf{G})^2 + \frac{\xi}{2} - \frac{1}{N} \sum_{\mathbf{G} \text{ occ.}} \sum_{\substack{\mathbf{G}' \text{ occ.} \\ \mathbf{G} \neq \mathbf{G}'}} \frac{4\pi}{\Omega |\mathbf{G} - \mathbf{G}'|^2}$$

$$= \mathcal{E}_K(r_s, L, \mathbf{k}) + \mathcal{E}_x(r_s, L, \mathbf{k}),$$
(5.10)

where the first term is the kinetic energy,

$$\mathcal{E}_{K}(r_{s}, L, \mathbf{k}) \equiv \frac{2}{N} \sum_{\mathbf{G} \text{ occ.}} \frac{1}{2} (\mathbf{k} + \mathbf{G})^{2}, \qquad (5.11)$$

while the second and last terms are the self interaction and HF exchange energies, respectively,

$$\mathcal{E}_x(r_s, L, \mathbf{k}) \equiv \frac{\xi}{2} - \frac{1}{N} \sum_{\mathbf{G} \text{ occ. } \mathbf{G}' \text{ occ.} \atop \mathbf{G} \neq \mathbf{G}'} \frac{4\pi}{\Omega |\mathbf{G} - \mathbf{G}'|^2}.$$
(5.12)

The sums are over the N/2 occupied **G**-states. The FS HF energy per electron will be defined as the average over many TABC (**k**-points) as

$$\mathcal{E}_{HF}(r_s, L) = \left\langle \mathcal{E}_{HF}(r_s, L, \mathbf{k}) \right\rangle_{\mathbf{k}}.$$
(5.13)

The Hartree-Fock FS kinetic energy per particle is obtained from the average over many **k**-points (up to 100,000 **k**-points in the low density region and \sim 10,000 in the high density region). The exchange energy per particle is found to have weaker **k**-point dependence, so it is averaged over a smaller number of **k**-points (the energy difference between averaging over 20 and 100 **k**-points is only a few mHa).

As shown by Eq. (5.10), the HF kinetic and interaction energy obey simple scaling relations

$$\mathcal{E}_K(r_s, L) = \frac{\tilde{\mathcal{E}}_K(N)}{L^2},\tag{5.14}$$

and

$$\mathcal{E}_x(r_s, L) = \frac{\widetilde{\mathcal{E}}_x(N)}{L},\tag{5.15}$$

where $\widetilde{\mathcal{E}}_{K}(N)$ and $\widetilde{\mathcal{E}}_{x}(N)$ depend only on the number of electrons N in the supercell. Note that N is fully determined by the ratio L/r_s . The size dependence in the HF energy per particle is given by [41]

$$\mathcal{E}_{HF}(r_s, L) = \mathcal{E}_{HF}^{\infty}(r_s) + \Delta \mathcal{E}_K(r_s, L) + \Delta \mathcal{E}_x(r_s, L)$$
(5.16)

where the scaling relations can be used to express the error in the kinetic energy as

$$\Delta \mathcal{E}_K(r_s, L) \equiv \frac{\Delta t(N)}{r_s^2}$$

= $\mathcal{E}_K(r_s, L) - \mathcal{E}_K^{\infty}(r_s),$ (5.17)

and the error in the interaction energy as

$$\Delta \mathcal{E}_x(r_s, L) \equiv \frac{\Delta v(N)}{r_s}$$

= $\mathcal{E}_x(r_s, L) - \mathcal{E}_x^{\infty}(r_s).$ (5.18)

Fig. 5.4 shows that Δt_N is an oscillating function of N with an envelope which decays like 1/N, while Δv_N is always negative and decays smoothly like $N^{-2/3}$ [41].

5.4 Fitting the FS Exchange Correlation functional

The exchange functional is defined as the interaction energy in Hartree-Fock calculations of jellium systems. Fig. 5.4 indicates that the leading term in the finite-size exchange energy per particle $\mathcal{E}_x(r_s, L)$ is $\mathcal{E}_x^{\infty}(r_s)$ and $\operatorname{cons.}/(r_s N^{\frac{2}{3}})$. The last term can be simplified to be $\operatorname{cons.}'r_s/L^2$. To improve the fitting, a next higher order is added to this fitting, with a constraint that this additional term follow the simple scaling relation in Eq. (5.15):

$$\mathcal{E}_x(r_s, L) = \frac{a_0}{r_s} + \frac{a_1 r_s}{L^2} + \frac{a_2 r_s^2}{L^3},\tag{5.19}$$

where the first term is the infinite-size limit $\mathcal{E}_x^{\infty}(r_s)$. Note that this fitting function increases as the density decreases. For fixed L, however, the expression becomes



FIG. 5.4: The size dependence of jellium energies within the HF method. The top figure shows the size dependence of the kinetic energy. $\Delta t(N)$ is an oscillatory function with an envelop that decays as 1/N. The lower figure shows the size dependence of the potential energy. $\Delta v(N)$ decays smoothly as $1/N^{2/3}$. Both $\Delta t(N)$ and $\Delta v(N)$ are obtained from averaging over many **k**-points.

ill-defined when the number of particles N < 2, or equivalently the average distance between electrons $r_s > R_2 \equiv r_s(N = 2)$, since the exchange is ill-defined when N < 2.

At N = 2, the HF exchange energy is zero by definition and the only contribution to the exchange functional is just the self-energy term ξ . The exchange functional for $r_s > R_2$ is defined as

$$\mathcal{E}_x(r_s > R_2, L) \equiv \tilde{\xi} = \frac{a_3}{L}.$$
(5.20)

where $\tilde{\xi}$ differs from ξ due to the fitting of a_1 and a_2 in Eq. (5.19), and a_3 is defined

using continuity:

$$a_3 = a_0 \left(\frac{8\pi}{3}\right)^{\frac{1}{3}} + a_1 \left(\frac{3}{8\pi}\right)^{\frac{1}{3}} + a_2 \left(\frac{3}{8\pi}\right)^{\frac{2}{3}}.$$
 (5.21)

For solid applications, we ignore the ill-defined nature of $\mathcal{E}_x(r_s, L)$ in the low density region since this is rarely sampled in practice in the FS DFT calculations. For atomic/molecular applications, we quench the exchange functional in the low density region as

$$\mathcal{E}_x(r_s > R_2, L) = \frac{a_4 L^5}{r_s^6}.$$
(5.22)

This choice forces $\mathcal{E}_x(r_s, L)$ to quickly decay to zero in the low density region so that it does not produce slowly convergent artificial 1/L contributions. It also follows the right scaling relation in Eq. (5.15). We will show in Chapter 6 that the function provides good correction for a molecule on PBC. The value of a_4 is chosen such that the exchange potential $v_x(r_s) = d(\rho \mathcal{E}_x)/d\rho$ is continuous

$$a_4 = \frac{4}{9} \left(\frac{3}{8\pi}\right)^{\frac{5}{3}} a_0 + \frac{2}{9} \left(\frac{3}{8\pi}\right)^{\frac{7}{3}} a_1 + \frac{1}{9} \left(\frac{3}{8\pi}\right)^{\frac{8}{3}} a_2.$$
(5.23)

For many solid applications, the use of either the first form or the second form of the exchange energy functional makes little difference. The effect is noticeable only in particularly small systems, where the number of electrons involved in the simulation is only around N = 2. As the simulation cell size increases (more electrons are used in the simulation), $R_2 = \left(\frac{4\pi V}{3 2}\right)^{1/3}$ increases and quickly becomes larger than r_s .

The fitting of the jellium correlation energy involves a more complicated procedure. Figures 5.5 and 5.6 show correlation energy per electron for system of sizes L = 7.533 - 18.0 Bohr. The solid black squares represent my calculated AFQMC correlation energy per particles, while the solid small red circles represent the correlation energy calculated using the extrapolation scheme in Eq. (5.4). The figures show that the extrapolation scheme works well for the high density region (large number of electrons), but is not accurate in the low density region (small number of electrons). These results are not surprising, since the asymptotic expression in Eq. (5.4) is obtained from QMC simulations with large number of electrons. The more accurate fit (solid line) is described below.

We express the correlation energy per particle in the following form

$$\mathcal{E}_{c}(L, r_{s}) = \begin{cases} \mathcal{E}_{c}^{\infty}(r_{s}) - \frac{a_{1}}{L^{2}}r_{s} + \frac{g(r_{s})}{L^{3}} & r_{s} < R_{h} \\ h(r_{s}) & R_{h} < r_{s} < R_{l} \\ 0 & R_{l} < r_{s} \end{cases}$$
(5.24)

where the $\mathcal{E}_c^{\infty}(r_s)$ is the correlation energy per particle for infinite-size jellium at density r_s [Eq. (5.9)], and the $-a_1r_s/L^2$ factor exactly cancels the corresponding term in $\mathcal{E}_x(r_s, L)$ [Eq. (5.19)], since $\mathcal{E}_{xc}(r_s, L)$ should converge as $1/L^3$. Note that there is no L dependence in $g(r_s)$, which makes this function universal for all (cubic) simulation cell sizes. R_h and R_l are defined below.

The function $g(r_s)$ is fitted (to Eq. 5.4 for $r_s < R_h$) to the following form

$$g(r_s) = d_1 \ln r_s + d_2 r_s + d_3 r_s^{\frac{3}{2}} + d_4 r_s^2.$$
(5.25)

The $g(r_s)$ plot is given in Fig. 5.7. As indicated in the figure, the values of $g(r_s)$ obtained from extrapolation are good only for large numbers of particle (small r_s). For small number of particles ($N \leq 12$), the QMC calculated energies are higher than the energies calculated with the extrapolation.

For the low density region, $r_s \ge R_l$ where $R_l = r_s(N = 0.5)$, the correlation is set to be zero. In the intermediate density region, $R_h \le r_s \le R_l$ where $R_h \equiv r_s(N = 12) = L \cdot \left(\frac{3}{48\pi}\right)^{1/3}$, the correlation energy per particle is given as a polynomial $h(r_s)$

$$h(r_s) = e_1 + e_2 r_s + e_3 r_s^2 + e_4 r_s^3.$$
(5.26)



FIG. 5.5: Comparison of the QMC, extrapolation (Eq. (5.4)), and fitting function (see Table. 5.2) for jellium system inside cubic boxes of size L=7.533 Bohr up to 10.259 Bohr.



FIG. 5.6: Comparison of the QMC, extrapolation (Eq. (5.4)), and fitting function (see Table. 5.2) for jellium system inside cubic boxes of size L=10.722 Bohr up to 18.000 Bohr.



FIG. 5.7: Comparison of $g(r_s)$ obtained from extrapolation and QMC calculations. The extrapolation values are only accurate for large number of particles, as indicated by good agreement between QMC values and extrapolation values. For small number of particles, QMC values of $g(r_s)$ differ from the extrapolation curve, which break down.

The parameter e_1 , e_2 , e_3 and e_4 are completely determined from continuity conditions at R_l and R_h ,

$$e_{i} = \frac{e_{1i}}{L^{i}} \mathcal{E}_{c}(R_{h}, L) + \frac{e_{2i}}{L^{i-1}} \left. \frac{d\mathcal{E}_{c}(r_{s}, L)}{dr_{s}} \right|_{r_{s}=R_{h}},$$
(5.27)

where $\mathcal{E}_c(R_h, L)$ and $\frac{d\mathcal{E}_c(r_s, L)}{dr_s}|_{r_s=R_h}$ are the value and the first derivative of correlation energy per particle in the high density region.

Detail of the FS exchange correlation functions are summarized in Table 5.2 and the parameter values are presented in Table 5.3. Figures 5.5 and 5.6 show that the fitting function (solid line) well describes both the high and low density regions. It matches both the present AFQMC results as well as the extrapolation results [eq. (5.4)] in the high density region. The calculations shown in Figures 5.5 and 5.6 cover a range of supercell sizes from $(7.5 \text{ Bohr})^3$ to $(18 \text{ Bohr})^3$.

The final FS exchange and correlation energy per particle are shown for several

function	form	region
$\mathcal{E}_x(r_s,L)$	$\frac{a_0}{r_s} + \frac{a_1 r_s}{L^2} + \frac{a_2 r_s^2}{L^3} f(r_s, L)$	$r_s \le R_2$ $R_2 < r_s$
$f(r_s, L)$	$\frac{\frac{a_3}{L}}{\frac{a_4L^5}{r_s^6}}$	for solid systems for atomic/molecular system
$R_2(L)$	$L \cdot \left(\frac{3}{8\pi}\right)^{\frac{1}{3}}$	
$\mathcal{E}^{\infty}_{x}(r_{s})$	$\frac{a_0}{r_s}$	all region
$\mathcal{E}_c(r_s,L)$	$ \begin{array}{l} \mathcal{E}_c^{\infty}(r_s) - \frac{a_1 r_s}{L^2} + \frac{g(r_s)}{L^3} \\ h(r_s, L) \\ 0 \end{array} $	$r_s \le R_h$ $R_h < r_s \le R_l$ $R_l < r_s$
$g(r_s)$	$d_1 r_s \ln r_s + d_2 r_s + d_3 r_s^{\frac{3}{2}} + d_4 r_s^2$	
$h(r_s)$	$e_1 + e_2 r_s + e_3 r_s^2 + e_4 r_s^3$	
e_i	$\frac{e_{1i}}{L^i}\mathcal{E}_c(R_h,L) + \frac{e_{2i}}{L^{i-1}} \left. \frac{d\mathcal{E}_c(r_s,L)}{dr_s} \right _{r_s = R_h}$	
$R_h(L)$	$L \cdot \left(\frac{3}{48\pi}\right)^{\frac{1}{3}}$	
$R_l(L)$	$L \cdot \left(\frac{3}{4\pi}\right)^{\frac{1}{3}}$	
$\mathcal{E}_c^{\infty}(r_s)$	$\frac{c_1 \ln r_s + c_2 + c_3 r_s \ln r_s + c_4 r_s}{\frac{c_5}{1 + c_6 \sqrt{r_s} + c_7 r_s}}$	$\begin{array}{l} r_s \leq 1 \\ 1 < r_s \end{array}$

TABLE 5.2: Summary of the FS exchange and correlation functions

parameter	value	parameter	value
a_0	-0.9163	d_1	0.1182
a_1	-2.2037	d_2	1.1656
a_2	0.4710	d_3	-5.2884
a_3	-2.8373	d_4	-1.1233
a_4	-0.0150	e_{11}	-0.1436
c_1	0.0622	e_{12}	9.5439
C_2	-0.096	e_{13}	-23.7164
C_3	0.0040	e_{14}	15.0215
C_4	-0.0232	e_{21}	-0.6348
C_5	-0.2846	e_{22}	3.9673
c_6	1.0529	e_{23}	-7.0343
C_7	0.3334	e_{24}	3.8352

TABLE 5.3: Numerical values of parameters used in Table. 5.2. All parameters are given in Rydberg atomic unit.

simulation cell sizes in Fig. 5.8. The FS exchange energies approach the infinitesize limit from below, while the FS correlation energies approach it from above. This is the reason why the HF method gives too large a correction, since it does not include the correlation energy. In the exchange functional (top panel of Fig. 5.8) the dashed line represents the choice of the low density ($r_s > R_2$) for atomic/molecular systems with PBC [Eq. (5.22)] and the dot-dashed line represents the low density choice [Eq. (5.20)] for solids. As the simulation cell size increases, R_2 [visualized by the discontinuity in Fig. 5.8] moves to lower densities, where it makes smaller and smaller contributions.


FIG. 5.8: The FS exchange and correlation energy per particles for several simulation cell sizes. The top figure shows the exchange energy per particle. The dashed line represents the choice in the low density $(r_s < R_2)$ region for atomic/molecular system [Eq. (5.22)]; R_2 visualized by discontinuity, which moves to lower densities with increasing L. In crystalline systems, the contribution from $r_s > R_2$ is negligible for any reasonable size L, and we use a constant $\mathcal{E}_x(R_2, L)$ to make \mathcal{E}_x continuous. The dot-dashed line represents the choice for solids. The bottom figure show the correlation energy per particle. Note the change of scale.

CHAPTER 6

Applications of Finite Size Correction

In this chapter, applications of the new size-correction method are presented on several types of systems. After discussing some technical details on how to use the FS XC function, I will report applications on the P_2 molecule, bulk fcc silicon, metallic bulk bcc sodium, and perovskite structure BiScO₃.

6.1 Correction Scheme

The infinite-size limit of a many-body calculation is obtained from the FS manybody calculations after applying one-body and two-body FS corrections,

$$E^{\infty} = E(\Omega) + \Delta E^{1-b}(\Omega) + \Delta E^{2-b}(\Omega), \qquad (6.1)$$

where Ω is the volume of the simulation cell. The FS dependence on the simulation cell size and shape is shown as a function of Ω only, where $\Omega = L^3$, which is approximate except for cubic cells. We will return to this later in this chapter. The approach in Eq. (6.1) is valid if the one-body FS error is well separated from the two-body FS error. The FS corrections are calculated from the difference of DFT energies which are obtained with the the ABINIT code [60–62]. The XC functional of the ABINIT code has been modified in order to calculate a FS version of DFT energies, $E_{\rm DFT}^L$.

The one-body FS correction is defined as

$$\Delta E^{1-b}(\Omega, \mathbf{k}) \equiv E_{\text{DFT}}^{\infty}(\Omega, \text{dense-}\mathbf{k}) - E_{\text{DFT}}^{\infty}(\Omega, \mathbf{k}), \qquad (6.2)$$

where the superscript " ∞ " in the DFT energy refers to the infinite-size limit XC function (for example the Perdew-Zunger functional [10]). The term "dense-**k**" refers to the use of a highly converged dense **k**-point grid based on the Monkhorst-Pack scheme [50], while "**k**" refers to either a single special **k**-point or a TABC over a set of **k**-points.

Fig. 6.1 shows the **k**-point dependence of the QMC energies and DFT energies for two bulk solids: bcc sodium (left panels) and fcc silicon (right panels). The error bars on the QMC energies are from the Monte Carlo statistical error. Larger-scale fluctuations due to the one-body FS errors are evident.

Strong **k**-point dependence is seen in both the QMC and DFT calculations, but they are correlated. The standard deviation σ of the QMC and DFT energy for bcc sodium with L = 16.2 Bohr are about 2.1 eV and 1.7 eV, respectively. After the DFT corrections, the standard deviation of energy is just about 0.48 eV. If only the one-body error were present, difference in energies ($E_{\text{QMC}} - E_{\text{DFT}}$) should be independent of **k**-point ($\sigma = 0$). For any given FS supercell, the one-body FS error can be further reduced by averaging over the **k**-points (TABC). However, in nonmetallic case, the **k**-point averaging is less important, since the **k**-point dependence is weaker. The silicon energies shown in the right panels indicate that the corrected energies have smaller **k**-point dependence. The standard deviation σ of QMC, DFT and (QMC-DFT) energies for silicon bulk system of size L = 10.3 Bohr are 2.99



FIG. 6.1: The QMC, DFT and difference (QMC-DFT) energies of sodium (left panels) and silicon (right panels) bulk. The sodium calculations are done with 16 atom supercells using 50 random **k**-points. The silicon calculations are done with 8 atom supercells using 5 **k**-points. There are 3 lattice constants in each plot, expressed in terms of the experimental lattice constant L_0 . Notice the change of scale in the bottom panels.

eV, 3.04 eV, and 0.12 eV, respectively. These results confirm that the one-body FS error in many-body calculations can be largely removed through the use of one-body FS corrections obtained from DFT calculations.

A way to further reduce the one-body FS error is to introduce a fitting parameter $a(\Omega)$,

$$\Delta \widetilde{E}^{1-b}(\Omega, \mathbf{k}_i) = a(\Omega) \cdot \Delta E^{1-b}(\Omega, \mathbf{k}_i).$$
(6.3)

The parameter $a(\Omega)$ plays a similar role to the parameter $B_1(r_s)$ in Eq. (5.4). The one-body FS effect in many-body calculations is not precisely equal to the FS effect in mean-field type calculations. From several tests, the one-body FS error in manybody calculations seems somewhat larger than one-body FS in DFT calculations. Fig. 6.2 shows the modified results with the parameter $a(\Omega)$. The parameter is chosen such that the variance of the energy difference $(E_{\text{QMC}} - a(\Omega) \cdot E_{\text{DFT}})$ is minimized. The average of QMC energies of sodium 16 atom supercell is slightly modified after the new corrections, but the variance (σ^2) of it decreases more. We see that the optimal value of $a(\Omega)$ is larger than 1, consistent with the value of $B_1(r_s)$ in jellium. This additional correction scheme is not used in the calculations reported in this thesis.

Figures 6.1 and 6.2 show that one-body FS effect in QMC can be much reduced by applying a correction obtained from DFT calculations. The two-body FS errors can be corrected separately. The two-body FS correction is defined as

$$\Delta E^{2-b}(\Omega, \mathbf{k}_i) \equiv E^{\infty}_{\text{DFT}}(\Omega, \mathbf{k}_i) - E^{L}_{\text{DFT}}(\Omega, \mathbf{k}_i).$$
(6.4)

The last term, $E_{\text{DFT}}^{L}(\Omega, \mathbf{k}_{i})$, is the FS DFT energy, that is obtained from DFT calculations using FS XC functional defined in Table 5.2. The superscript "L" indicates that the FS XC function $\mathcal{E}_{xc}(r_{s}, L)$ should be used. The actual value of L is chosen as $L = \Omega^{1/3}$. For cubic simulations, this is exact, but we will show that



FIG. 6.2: Alternative correction for one-body FS error. The top panel shows the QMC energies of 16 atom supercells for bcc Na after the corrections using Eq. (6.2), the bottom panel shows the QMC energies after the corrections using Eq. (6.3). Each panel shows results for three lattice constants. The value of $a(\Omega)$ varies from 1.17 to 1.33. The energy fluctuations using the alternative correction method in bottom figure are smaller than in the top figure.

this gives good corrections even for non-cubic cells. Fig. 6.3 shows the two-body FS corrections for 16 atom supercell bcc sodium. The 1-body FS effects in DFT calculations are almost exactly identical to the ones in FS DFT, resulting in a two-body correction that has virtually no \mathbf{k} -point dependence. The fluctuations are in the order of few meV. This is to be compared with the size of the total correction which is of the order of a few eV. This further confirms the separability of the one-body and two-body FS errors.

In practice, the corrected many-body energies are obtained from

$$E_{\text{QMC}}^{\infty} = \frac{1}{N_k} \sum_{i}^{N_k} \left(E_{\text{QMC}}(\Omega, \mathbf{k}_i) - E_{\text{DFT}}^L(\Omega, \mathbf{k}_i) \right) + E_{\text{DFT}}^{\infty}(\Omega, \text{dense-}\mathbf{k}).$$
(6.5)



FIG. 6.3: The energies of DFT (top panel) and FS DFT (middle panel) calculated for 50 random \mathbf{k} -points. The 3 curves in each panel are the energies for 3 lattice constants. The bottom panel shows the two-body FS correction, as defined in Eq. (6.4).

This twist averaging over **k**-point is efficient for stochastic method like QMC, since the averaging also helps reduce the statistical noise [52]. As shown before, while the fluctuations of $E_{\text{QMC}}(\Omega, \mathbf{k}_i)$ and $E_{\text{DFT}}(\Omega, \mathbf{k}_i)$ are individually large, the difference has a smaller variance. It is therefore better to average over the difference to reduce statistical error. The last term $E_{\text{DFT}}^{\infty}(V, \text{dense-k})$ is **k**-point independent, and can therefore be obtained from any supercell. To reduce the computational cost, we simply use the primitive cell to obtain this term. Eq. (6.5) can be rewritten by adding and subtracting a $E_{\text{DFT}}^{\infty}(\Omega, \mathbf{k}_i)$,

$$E_{\text{QMC}}^{\infty} = \frac{1}{N_k} \sum_{i}^{N_k} \left(E_{\text{QMC}}(\Omega, \mathbf{k}_i) - E_{\text{DFT}}^{\infty}(\Omega, \mathbf{k}_i) \right) + \frac{1}{N_k} \sum_{i}^{N_k} \left(E_{\text{DFT}}^{\infty}(\Omega, \mathbf{k}_i) - E_{\text{DFT}}^{L}(\Omega, \mathbf{k}_i) \right) + E_{\text{DFT}}^{\infty}(\Omega, \text{dense-}\mathbf{k}).$$
(6.6)

If the second term in Eq. (6.6) is neglected, this is just the one-body corrected QMC energy (with TBC). The major advantage of the one-body FS correction is that it reduces energy fluctuations due to **k**-point sampling, while the two-body FS correction improves physical properties of the system, such as the equilibrium lattice constant and the bulk modulus.

Since two-body FS correction was shown to have little \mathbf{k} -point dependence, it can be obtained by using sampling over only a few \mathbf{k} -points or by just using a single calculation with a dense \mathbf{k} -point grid,

$$\Delta E^{2-b}(\Omega) = E^{\infty}_{\text{DFT}}(\Omega, \text{dense-}\mathbf{k}) - E^{L}_{\text{DFT}}(\Omega, \text{dense-}\mathbf{k}).$$
(6.7)

As before, this quantity can be calculated using the primitive cell with the proper XC function. In this case, the notation is as follows: the superscript L refers to the size of the supercell whose FS $\mathcal{E}_{xc}(r_s, L)$ is used, while Ω is the volume of the primitive cell.

6.2 P_2 Molecule

The first application presented here is for the ground state energy of the P_2 molecule, using supercells and periodic boundary condition. The FS effect of this system is illustrated in plot a. of Fig. 5.1. Here the FS correction is defined as

$$E^{\infty}_{\mathbf{QMC}} = E_{\mathrm{QMC}}(\Omega, \Gamma) + \left[E^{\infty}_{\mathrm{DFT}}(\Omega \to \infty, \Gamma) - E^{L}_{\mathrm{DFT}}(\Omega, \Gamma) \right], \qquad (6.8)$$

since all calculations were done using only the Γ -point ($\mathbf{k} = 0$). This choice is reasonable for an atom or a molecule inside a large supercell calculation. The infinite-size limit of DFT energy $E_{\text{DFT}}^{\infty}(\Omega \to \infty, \Gamma)$ is obtained by direct extrapolation using very large simulation cells and the specific boundary condition (\mathbf{k} -points) has little effect.



FIG. 6.4: The QMC energy of the P_2 molecule using supercells and periodic boundary condition. The dashed and dotted lines are the DFT energies calculated with the infinitesize XC function and the FS XC function, respectively. The blue solid line with circles is the QMC energy. The the dashed line with boxes and the dotted lines with diamonds are the QMC energy after correction with the infinite-size limit and FS DFT XC function, respectively. The inset shows the same energy plotted with respect to $1/\Omega$.

The core states of the P atom are represented with a norm conserving pseudopotential generated using OPIUM [30]. Calculations of the P₂ molecule at experimental equilibrium bondlength of 3.578 Bohr were performed for cubic supercells of size $(7 \text{ Bohr})^3$ to $(18 \text{ Bohr})^3$ using auxiliary field quantum Monte Carlo (AFQMC) [17]. Fig. 6.4 shows the energies calculated with QMC, DFT^{∞} and DFT^{FS}. The superscript " ∞ " in DFT^{∞} indicated that the infinite-size limit XC function is used. DFT^{∞} yields the conventional correction

$$\Delta \text{DFT}^{\infty} = E_{\text{DFT}}^{\infty}(\Omega \to \infty, \Gamma) - E_{\text{DFT}}^{\infty}(\Omega, \Gamma), \qquad (6.9)$$

while DFT^{FS} is used to calculate the new FS XC correction

$$\Delta DFT^{FS} = E^{\infty}_{DFT}(\Omega \to \infty, \Gamma) - E^{L}_{DFT}(\Omega, \Gamma).$$
(6.10)

As seen in Fig. 6.4, the conventional DFT^{∞} energy converges very rapidly to the infinite limit. The energy at (18 Bohr)³ differs from its infinite-size limit by less then 4 meV. By contrast the QMC error is 310 meV, and the slow convergence of the DFT-corrected-QMC energy (QMC + ΔDFT^{∞}) is evident. DFT^{FS}, however, shows similar size convergence to QMC, yielding a better correction scheme. With these corrections, the corrected energy has an error of about 34 ± 91 meV at the size of (18 Bohr)³. The inset in Fig. 6.4 shows that the QMC energy corrected with the new scheme gives not only a more linear-curve as a function of $1/\Omega$, but also has a smaller slope. Accurate extrapolation to infinite-size is thus possible.

6.3 Fcc Silicon

Fcc silicon has the diamond structure with 2 atoms per primitive unit cell, located at the origin and at $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$ in reduced coordinates. Here I apply the new FS correction on previously published DMC results [47] and show that the new correction accelerates the size convergence [3]. The pseudopotential used is different from that in the DMC calculations. We used multiple pseudopotentials to ensure that the FS correction are independent of the choice of pseudopotential. The DMC calculations were for $n \times n \times n$ supercells of the primitive (non-cubic) cell. Nevertheless, the new correction significantly improves the convergence, indicating that the correction also works with non-cubic simulation cells. Finally, I will present results for the equilibrium lattice constant, bulk modulus and cohesive energy. These properties are calculated for supercells with number of atom equal to 8 and 16 using AFQMC. We calculated the FS correction of fcc bulk silicon using 4 different pseudopotentials, described in Table 6.1. Table 6.2 shows the results of the pseudopotential

TABLE 6.1: The pseudopotentials that are used to test the dependence of the two-body FS correction on pseudopotentials. The first three pseudopotentials were obtained from the OPIUM code [30], and the fourth one is the Goedecker-Teter-Hutter pseudopotential [63]. r_c is the cut-off radius of the pseudopotential in Bohr.

	Pseudopotential	$E_{\rm cut}(Ry)$
1	OPIUM $r_c(3s) = r_s(3p)3 = 2.20, r_s(3d) = 2.5$	12.25
2	OPIUM $r_c(3s) = r_s(3p) = r_s(3d) = 2.08$	25.0
3	OPIUM $r_c(3s) = r_s(3p) = r_s(3d) = 1.60$	42.5
4	HGH	80.0

tests. The pseudopotential results are in good agreement with each other. The first pseudopotential is a slightly too soft (has a small cutoff energy $E_{\rm cut}$), and therefore has underestimated the bulk modulus. Overall, the pseudopotential results are in good agreement with our all-electron LAPW method results, and also with results calculated by Holzwarth *et.al.* [64]. These results suggest that the present pseudopotentials are reliable.

As discussed in the previous section, the two-body FS correction can be obtained from any \mathbf{k} -point, since it has weak \mathbf{k} -dependence. Here we calculated the two-body corrections using dense grids within the primitive cell

$$\Delta E^{2-b}(\Omega) = E^{\infty}_{\text{DFT}}(\Omega_0, \text{dense-}\mathbf{k}) - E^L_{\text{DFT}}(\Omega_0, \text{dense-}\mathbf{k}), \qquad (6.11)$$

where $L = \Omega^{1/3}$, Ω is the volume of the many-body calculation to be corrected and Ω_0 is the volume of the primitive cell. Table 6.3 shows the correction for number of atoms from $N_{\rm ion} = 2$ to 250. If these two-body corrections are calculated using Eq. (6.6), with a single **k**-point, the differences between it and the result of Eq. (6.11) are only about 30 meV for $N_{\rm ion}=2$ and about 1 meV for $N_{\rm ion}=8$. The variance σ^2

	Lattice	Bulk	Cohesive
	constant (Bohr)	modulus (GPa)	energy $(eV)[a]$
This work			
Pseudopotential 1	10.175	93	5.33
Pseudopotential 2	10.180	95	5.33
Pseudopotential 3	10.170	97	5.36
Pseudopotential 4	10.171	96	5.33
LAPW	10.214	97	5.19
Ref. [64]			
Pseudopotential	10.186	98	—
LAPW	10.223	98	_
experiment [65]	10.261	99	4.63

TABLE 6.2: Several physical properties calculated with the four pseudopotentials in Table. 6.1. The results are compared with our own all electron LAPW results and with the pseudopotential and LAPW calculations from Ref. [64].

[a] Cohesive energies from Ref. [64] are not shown, since they used a non-spin-polarized Si atom

due to the different pseudopotential is very small. We also note that the two-body correction is essentially linear versus $1/N_{ion}$ (see the inset in Fig. 6.5 below).

The raw DMC energies were calculated by Kent *et al.* [47] for system sizes of n = 1, 2, 3, 4, and 5, corresponding to $N_{\rm ion} = 2, 16, 54, 128$, and 250 atoms. These calculations only used single **k**-point, (the **L**-point). Fig. 6.5 shows the raw DMC energies, together with the energies after one-body and two-body corrections. Also shown are results using a modified periodic Coulomb (MPC) interaction [47] (see also discussion in section 5.2). The one-body correction ΔE^{1-b} has an opposite direction (approaching infinite-size limit from above) and therefore increases the FS error. For the smallest system, it increases the error by more than 50%, but for larger systems (n=3) the one body correction is essentially zero (less than 10 meV). The MPC improves the energies by about 0.44 eV for smallest simulation cell n = 1, while for n = 3, the improvement is only 11 meV. The new FS correction improves

L			pseudopotential			
N	(Bohr)	supercell	1	2	3	4
2	6.4638494	fcc	2.7429	2.7357	2.7381	2.7343
8	10.2607213	cubic	0.7117	0.7101	0.7106	0.7098
16	12.9276988	fcc	0.3568	0.3560	0.3563	0.3559
54	19.3915481	fcc	0.1057	0.1055	0.1056	0.1054
64	20.5214426	cubic	0.0892	0.0890	0.0891	0.0890
128	25.8553975	fcc	0.0446	0.0445	0.0445	0.0445
216	30.7821639	cubic	0.0264	0.0264	0.0264	0.0264
250	32.3192469	fcc	0.0228	0.0228	0.0228	0.0228

TABLE 6.3: The two-body correction for 4 pseudopotentials (in eV). $N_{\rm a}$ is the number of atoms. The parameter L indicates the effective volume of the cell $L = \Omega^{1/3}$ (in Bohr). Results are shown for fcc and cubic supercells.



FIG. 6.5: Total energy per atom of silicon as a function of simulation cell size n. The vertical axis is defined as $\Delta E \equiv E(N_{\rm a}) - E^{\infty}$. The black circles represent the raw energies (DMC), the one-body corrected energies are given by red squares. The fully corrected energies are shown by blue triangles. MPC energies, calculated by Kent *et al.* [47], are shown as the green diamonds. The inset show the volume dependence of two-body FS error. Both cubic and fcc results lie on the same linear curve.

the energy about 1.45 eV for the smallest cell n = 1, and still give a correction of 96 meV for system size of n = 3. The overall size corrections are systematically improved.

Next we calculate the equilibrium lattice constant, bulk modulus and cohesive energy of silicon. The AFQMC method was used for the rest of fcc silicon applications. The pseudopotential used here is the second pseudopotential in Table 6.1 with $E_{\rm cut}$ of 25 Ry. The silicon atomic energy is needed to calculate the cohesive energy of the crystal. Fig. 6.6 shows results of atomic calculations inside supercell of sizes (14 Bohr)³ to (20 Bohr)³ with PBC. The infinite-size limit is obtained through the extrapolation. The FS correction can not yet be applied here, because it was designed for non-spin-polarized systems. A linear fit yields an extrapolated atomic energy of -103.33 ± 0.02 eV.



FIG. 6.6: The silicon atom total energy for simulation cell of sizes $(14 \text{ Bohr})^3$ to $(20 \text{ Bohr})^3$. The FS correction can not be applied to this atom because silicon atom has a spin polarization due to two spin up electrons at orbital 2p. The infinite-size limit is obtained through extrapolation.

Convergence of the total energy is shown in Fig. 6.7. The total energy of silicon bulk has already well converged at $E_{\rm cut} = 25$ Ry for both DFT and QMC calculations.



FIG. 6.7: Convergence of the total energy of an 8 atom Si supercell for 3 lattice constants, calculated using DFT (left panel) and QMC (right panel). At $E_{\rm cut} = 25$ Ry, the energy has already reached convergence.

The Trotter error, which arises from neglecting higher order terms when the imaginary time propagator $e^{-\Delta \tau \hat{H}}$ is decomposed into one-body and two-body operators in Eq. (3.39), is shown in Fig. 6.8. The total energy of an 8 atom Si supercell calculated with $\Delta \tau = 0.04$ (in Rydberg atomic unit) is in good agreement with the energy calculated with $\Delta \tau = 0.01$. This result suggests that the Trotter error of calculations using $\Delta \tau = 0.01$ is already smaller than statistical errors.

Table 6.4 shows the equilibrium lattice constant, bulk modulus and cohesive energy of the Si. The QMC energy shown in Fig. 6.9 were fit to Murnaghan's



FIG. 6.8: Trotter error for 8 atom supercell of silicon bulk for 3 lattice constants. Rydberg atomic unit is used in this figure. The production calculations are done using $\Delta \tau = 0.01$.

equations [66] to obtain these physical properties,

$$E = E_0 + \frac{3}{2}\Omega_0 B_0 \left[\frac{3}{4} (1+2\delta) \left(\frac{\Omega_0}{\Omega} \right)^{4/3} - \frac{\delta}{2} \left(\frac{\Omega_0}{\Omega} \right)^2 -\frac{3}{2} (1+\delta) \left(\frac{\Omega_0}{\Omega} \right)^{2/3} + \frac{1}{2} \left(\delta + \frac{3}{2} \right) \right],$$
(6.12)

where Ω_0 is the equilibrium volume, B_0 is the zero-pressure bulk modulus, $\delta = (3 - 3B'_0/4)$ and B'_0 is the derivative of bulk modulus with respect to pressure at zero pressure. In the applications, we simply fit the data to equivalent equation

$$E = E_0 + \frac{E_1}{\Omega^{2/3}} + \frac{E_2}{\Omega^{4/3}} + \frac{E_3}{\Omega^2},$$
(6.13)

and the equilibrium lattice constant is determined by the lattice constant that minimize the energy (indicated by black arrows in Fig. 6.9) and the bulk modulus is determined by $B = \Omega \cdot \frac{\partial^2 E}{\partial \Omega^2}$ at equilibrium lattice constant. Cohesive energy is the energy per atom needed to decompose the solid into atoms (indicated as the dashed arrows in Fig. 6.9).



FIG. 6.9: The energy of fcc silicon bulk as a function of lattice constant. The calculations are done using 8 atom cubical supercell. The solid black arrows indicate the positions of the equilibrium lattice constant for different methods of calculations. The QMC energies (black circles) and QMC + ΔE^{1-b} energies (red boxes) are almost identical, as also indicated by the size of one-body ΔE^{1-b} FS correction in lower panel.

The 8 atom supercell is a cubic cell while the 16 atom supercell is the $2 \times 2 \times 2$ fcc supercell (i.e. 8 fcc primitive cells, each with 2 atoms). QMC calculations obtained from averaging over several **k**-point site are shown in Table 6.4. The **k**-point sets TBC 2 and TBC 4 in the table refer to the twist-averaged boundary condition [52] based on $2 \times 2 \times 2$ and $4 \times 4 \times 4$ Mankhorst-Pack [50] **k**-point grids. The first set consists of only single **k**-point: $\mathbf{k} = \frac{1}{4}\mathbf{G}_1 + \frac{1}{4}\mathbf{G}_2 + \frac{1}{4}\mathbf{G}_3$ (can be written as $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$) which is also the Baldereschi point [51]. The second set consist of 4 **k**-points: $(\frac{1}{8}\frac{1}{8}\frac{1}{8})$, $(\frac{3}{8}\frac{1}{8}\frac{1}{8})$, $(\frac{3}{8}\frac{3}{8}\frac{1}{8})$ and $(\frac{3}{8}\frac{3}{8}\frac{3}{8})$. The **L**-point is given by $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. For 16 atoms system, the TBC 2 consist of two **k**-points: $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$ and $(-\frac{1}{4}\frac{1}{4}\frac{1}{4})$.

The one-body FS correction (dashed black line in lower panel of Fig. 6.9) is very small and it has an opposite sign from the total FS error. The energies that were obtained after this correction $E_{\rm QMC} + \Delta E^{1-b}$ are almost identical to the uncorrected

TABLE 6.4: The equilibrium lattice constant, bulk modulus and cohesive energy of silicon bulk. $N_{\rm a}$ is the number of atoms used in calculations. TBC 2 and TBC 4 are twist-averaged boundary condition [52] based on $2 \times 2 \times 2$ and $4 \times 4 \times 4$ Mankhorst-Pack [50] **k**-point grids, respectively. $\Delta E = \Delta E^{1-b} + \Delta E^{2-b}$. The cohesive energies contain a correction for the zero-point energy of the solid of $E_{\rm ZPE}$ =0.06 eV per atom.

	N	k -point	lattice	bulk	cohesive
			constant (Bohr)	modulus (GPa)	energy (eV)
QMC	8	TBC 2	10.01 ± 0.03	112 ± 4	5.59 ± 0.06
QMC	8	TBC 4	9.96 ± 0.02	103 ± 4	5.66 ± 0.04
$QMC + \Delta E^{1-b}$	8	TBC 2	10.00 ± 0.03	112 ± 4	5.68 ± 0.06
$QMC + \Delta E^{1-b}$	8	TBC 4	9.96 ± 0.02	113 ± 4	5.66 ± 0.04
$QMC + \Delta E$	8	TBC 2	10.10 ± 0.03	102 ± 6	4.97 ± 0.06
$QMC + \Delta E$	8	TBC 4	10.06 ± 0.02	100 ± 4	4.95 ± 0.03
QMC	16	$\mathbf{L} ext{-point}$	10.10 ± 0.03	106 ± 3	5.33 ± 0.04
$QMC + \Delta E^{1-b}$	16	$\mathbf{L} ext{-point}$	10.08 ± 0.03	106 ± 3	5.41 ± 0.04
$QMC + \Delta E$	16	$\mathbf{L} ext{-point}$	10.13 ± 0.03	103 ± 3	5.05 ± 0.04
QMC	16	TBC 2			5.47 ± 0.02
$QMC + \Delta E^{1-b}$	16	TBC 2			5.47 ± 0.02
$QMC + \Delta E$	16	TBC 2			5.12 ± 0.02
DMC [67]	432	1 k-point	10.278 ± 0.005	103 ± 7	4.62 ± 0.01
exp. $[68, 69]$			10.261	99	4.62 ± 0.08

energy E_{QMC} and therefore all physical properties of these two sets of calculations are almost identical as reported in Table 6.4. The two-body FS correction (red solid line in the lower panel of Fig. 6.9) is much larger than the one-body FS correction, decreasing as the lattice constant increases, opposite to the one-body FS correction. This two-body correction improves all physical properties.

The size corrected physical properties still have some discrepancies with respect to the experimental data (a little more than 1% for the lattice constant and about 7% for the cohesive energy). Based on Fig. 6.5, there are still FS error of about 0.2 eV per atom at supercell of 8 atom. These errors might responsible for the discrepancy of the size corrected properties and experimental values. DMC results [67] have better agreement with experimental measurements, but the size of the system is much larger. It used the simulation cell of size 27 times larger than the largest system used in these calculations.

6.4 Bcc Sodium

Bcc sodium has one atom per primitive unit cell. However in our calculations, we studied cubic simulation cells with 2, 16 and 54 atoms. Since sodium is a conductor with a half-filled band, it is necessary to used dense **k**-point sampling to get accurate energies. For DFT calculations, we have used a $12 \times 12 \times 12$ Monkhorst-Pack [50] **k**-point grid. For QMC, 396, 50, and 4 random **k**-points are used for the 2, 16 and 54 atom supercell, respectively. Those **k**-points are randomly sampled in reciprocal space in order to address the "open-shell" problem, which is a one-body effect. Since metals have partially filled bands, there can be some ambiguity in filling degenerate states at high symmetry **k**-points. Randomly selected **k**-points (boundary condition) eliminates the possibility of degenerate orbitals, and therefore alleviates the "open-shell" problem.

The sodium atom is represented by an OPIUM pseudopotential with reference configuration [Ne] $3s^1$ and with cutoff radius of 2.5 Bohr for all s, p and d angular momentum channels. The kinetic energy cutoff for all calculations is 16 Ry. The atomic energy of this pseudopotential is easy to obtain. There is no 2-body term in this single-electron system, and therefore there is no need to perform a Hubbard-Stratonovich transformation and Monte Carlo sampling, which simply leads to a total energy with no Monte Carlo statistical noise. Fig. 6.10 shows the energy of the sodium atom versus inverse volume. The infinite-size limit that has been obtained through extrapolation is -0.389024 ± 0.000017 Ry = -5.29294 ± 0.00023 eV.

The above "large core" pseudopotential neglects the semicore states. DFT calculations show, however, that the effects of semicore states are not significant



FIG. 6.10: The sodium atom total energy for simulation cell of sizes $(24 \text{ Bohr})^3$ to $(50 \text{ Bohr})^3$. These QMC energies do not have Monte Carlo statistical error. The infinite-size limit is obtained through extrapolation.

on the cohesive energy. All-electron calculations with LDA [70] give a cohesive energy of 1.20 eV, while our LDA calculations using a large core pseudopotential give a cohesive energy of 1.21 eV. On the other hand, the lattice constant and bulk modulus have a stronger dependence on the neglected semicore states. Table 6.5 shows the effects of semicore states in the equilibrium lattice constant and bulk modulus. Including the semicore states in LDA calculations increases the lattice constant by about 0.1 Bohr, while it decreases by about the same amount in a GGA calculation. However, including semicore states increases both the LDA and GGA bulk modulus. Because of the error from excluding the semicore states, our final infinite-size limit of the lattice constant and bulk modulus are not expected to agree with he experimental values.

Including semicore states improves the properties of the system, but it increases

TABLE 6.5: The equilibrium lattice constant and bulk modulus of solid sodium calculated with DFT. Calculations with and without semicore states are shown as well as all-electron LAPW calculations. To gauge the effects of the semicore states, we have used 2 types of exchange correlation function: the local density functional (LDA) and generalized gradient approximation (GGA).

	lattice	bulk
	constant (Bohr)	modulus (GPa)
HGH pseudopotential [63], LD	A	
without semicore states	7.54	8.9
with semicore states	7.65	9.3
OPIUM pseudopotential, LDA		
without semicore states	7.54	8.9
with semicore states	7.64	9.3
OPIUM pseudopotential, GGA	A	
without semicore states	8.02	7.1
with semicore states	7.92	7.9
LAPW, LDA [71]	7.65	9.2
Experiment	7.98	7.3

the computational cost significantly. The OPIUM pseudopotential with semicore states has a kinetic energy cutoff of 115 Ha, while the large-core OPIUM pseudopotential only has a kinetic energy cutoff of 8 Ha. For the HGH pseudopotential, the pseudopotential with semicore states requires extremely high cutoff of 250 Ha. In our applications here, we want to demonstrate that the new FS correction will accelerate the convergence of the physical properties. Comparison with experimental cohesive energy is valid but not for the equilibrium lattice constant and bulk modulus.

The top panel of Fig. 6.11 shows the equation of state of sodium bulk for 16 and 54 atom supercells. For each supercell, there are two set of data shown, one set (dashed line) is the QMC energies that have been corrected with one-body



FIG. 6.11: top: Total energy per atom for bcc sodium bulk. The black line and dashed line are the one-body-corrected and full-corrected energy per atom of sodium simulations using 16 atoms. The red line and dashed-dotted line are for the 54 atoms. The arrows indicate positions of equilibrium lattice constants. bottom: the one-body and two-body correction as a function of lattice constant.

FS correction, and the other one is the fully-corrected QMC energies (solid line). The two-body correction improves the predicted equilibrium lattice constant, as indicated by the black arrows. It also improves the bulk modulus and the cohesive energy of the bulk (see Table 6.6).

The bottom panel of Fig. 6.11 show the one-body and two-body corrections as a function of lattice constant. As in fcc silicon, the two-body FS corrections are much larger than one-body FS correction and they approach zero from above as the volume of the simulation cells increase. Even for the system of 128 atoms, the two-body FS correction still give a correction of 19 meV at the experimental lattice constant of 7.98 Bohr.

The uncorrected lattice constant, bulk modulus, and cohesive energy have large

	lattice	bulk	cohesive
	constant (Bohr)	modulus (GPa)	energy (eV)
2 atoms, 99 random k -p	oints		
QMC	7.05 ± 0.14	13 ± 6	2.050 ± 0.035
$QMC + \Delta E^{1-b}$	6.992 ± 0.004	14.2 ± 0.2	2.141 ± 0.002
$QMC + \Delta E$	7.620 ± 0.006	8.66 ± 0.06	1.124 ± 0.002
16 atoms, 50 random ${\bf k}\text{-}$	points		
QMC	7.44 ± 0.05	9.8 ± 1.1	1.264 ± 0.014
$QMC + \Delta E^{1-b}$	7.417 ± 0.013	9.9 ± 0.3	1.287 ± 0.004
$QMC + \Delta E$	7.514 ± 0.014	9.16 ± 0.22	1.135 ± 0.004
54 atoms, 4 random \mathbf{k} -p	oints		
QMC	7.54 ± 0.05	9.0 ± 0.8	1.184 ± 0.009
$QMC + \Delta E^{1-b}$	7.54 ± 0.03	8.97 ± 0.3	1.189 ± 0.010
$QMC + \Delta E$	7.57 ± 0.03	8.79 ± 0.24	1.143 ± 0.010
54 atoms, 10 random ${\bf k}\text{-}$	points		
QMC			1.197 ± 0.009
$QMC + \Delta E^{1-b}$			1.201 ± 0.006
$QMC + \Delta E$			1.155 ± 0.002
DMC (512 atoms) [70]			1.0221 ± 0.0003
Experiment	7.98	7.3	1.13

TABLE 6.6: The equilibrium lattice constant, bulk modulus and cohesive energy of sodium bulk. All the cohesive energy contain a correction for the zero-point energy of the solid of $E_{\text{ZPE}}=0.0145$ eV per atom.

errors for both 2 and 16 atoms supercell calculations. The one-body FS correction mostly just reduces the statistical error, but does not improve the value of the physical properties, in many cases the one-body FS correction even increases the discrepancy from the infinite-size limit value. All the fully-corrected properties for these three supercells are in good agreement with each other, which indicates that the FS correction is converging rapidly to the correct infinite-size limits.

The cohesive energy calculated by Maezono *et.al.* [70] using model periodic Coulomb (MPC) [2, 47, 53] included the one-body correction. It also included a two-body core polarization potential (CPP) to compensate for the neglect of the semicore states. The CPP slightly improves the cohesive energy from 0.9910(5) to 1.0221(5) eV (the numbers in the brackets are the error in the last digit). Their 512 atom supercell calculations give a cohesive energy with an error of about 0.11 eV, while our series of calculations using much smaller supercell of 2, 16 and 54 atoms give consistent cohesive energies in excellent agreement with the experimental value.

6.5 Perovskite BiScO₃

Perovskite structure based materials exhibit a wide range of technologically important properties such as high T_c superconductors, ferroelectricity and multiferroic instabilities. The basic chemical formula unit is the ABO₃ cubic structure, where the A and B are cations of different sizes (for example PbTiO₃ and BiScO₃), the A atom is located at the corner of the cell, the B atom is at the center, with oxygen atoms at the face centers as the six nearest neighbor of the B atom for an octahedral cage.

In ferroelectric materials such as $BaTiO_3$, the cubic structure is unstable against symmetry lowering distortion. Off-centering along the [0 0 1] direction, for example yields a tetragonal structure, while distortions along the [1 1 1] direction produce a rhombohedral structure. The lower symmetry structures have a net electric dipole moment and the material is said to be ferroelectric.

The perovskite alloys of BiScO₃ with PbTiO₃, (BiScO₃)_{1-x}-(PbTiO₃)_x (BS-PT) exhibit some interesting properties [72, 73]. The piezoelectric properties are comparable to the Pb(Zr_{1-x}Ti_x)O₃ (PZT) and Pb(Zn_{1/3}Nb_{2/3})O₃ (PZN). BS-PT has more robust dielectric and piezoelectric properties over a wider range of temperature, compared with PZT and PZN-PT [72–74]. First-principle studies of the end compound, BiScO₃, by Íñiguez *et.al.* [75] using the LDA indicated an extraordinary large well-depth of about 1 eV, compared with the well-depth of PT of 60 meV in the tetragonal structure. It also has a large c/a = 1.29 strain in the tetragonal



FIG. 6.12: The ABO₃ perovskite structure. Off-centering along the $[0\ 0\ 1]$ axis gives a tetragonal structure, while the off-centering along the diagonal $[1\ 1\ 1]$ yields a rhombohedral structure.

phase compared with 1.05 in tetragonal PT.

The accuracy of this large ferroelectric well-depth are not readily validated by experiment [75], and the corresponding error due to the LDA or GGA (generalized gradient approximation) of DFT is not known. It is known that DFT using LDA tends to systematically underestimate the equilibrium volume of perovskite by about 3% and GGA tends to overcompensate and yields volume of about 3% too large [76]. Our aim is to use quantum Monte Carlo (QMC) calculation to probe this. The end compound BS has a large well-depth, which reduces the required Monte Carlo statistical accuracy.

The QMC calculations use a single Slater determinant trial wavefunction obtain from DFT program ABINIT. Norm-conserving pseudopotential constructed using OPIUM are used to remove the core electrons with a kinetic energy cutoff $E_{\rm cut} = 64$ Ry. For the primitive BiScO₃ unit cell, 44 valence electrons are included: Bi $(5d^{10} 6s^2 6p^3)$, Sc $(3s^2 3p^6 3d^1 4s^2)$, O $(2s^2 2p^4)$. Using the same structural parameters as in Ref. [75] (see Appendix C), our pseudopotentials well-depth results are in good agreement with those in Ref. [75], which used an ultrasoft pseudopotential. Fig. 6.13 shows the well-depths of both structures calculated using OPIUM pseudopotentials. The present tetragonal and rhombohedral well-depths are -1.098 and -1.339 eV, respectively, compared to -1.124 and -1.353 eV in Ref. [75]. To achieve this level of agreement as well as small residual forces, we found it necessary to include a Bi l = 3 pseudopotential. All calculations are with a $6 \times 6 \times 6$ Monkhorst-Pack [50] **k**-point grid.



FIG. 6.13: The tetragonal and rhombohedral ferroelectric instabilities of perovskite $BiScO_3$ calculated with ABINIT using OPIUM pseudopotentials. The positive x axis represent the distortion amplitude along the $[0\ 0\ 1]$ direction, while the negative x axis shows that along the $[1\ 1\ 1]$ direction.

The k-point convergence of the well-depth is shown in Table 6.7. The well-

TABLE 6.7: The one-body size effects in DFT calculations of BiScO₃. There are several set of **k**-points in this table: 3 Monkhorst-Pack **k**-point grid calculations $(2 \times 2 \times 2, 4 \times 4 \times 4, \text{ and } 6 \times 6 \times 6)$, the Γ -point calculation and 2 twist-averaged boundary conditions calculations (based on $2 \times 2 \times 2$ and $4 \times 4 \times 4$ MP **k**-point grids). The well-depth of tetragonal and rhombohedral structures are in eV.

	$\Delta E(T)$	$\Delta E(R)$
MP $2 \times 2 \times 2$	-1.238	-1.601
MP $4 \times 4 \times 4$	-1.092	-1.334
MP $6 \times 6 \times 6$	-1.098	-1.339
Γ -point	-7.531	-4.385
TBC $2 \times 2 \times 2$	-1.238	-1.594
TBC $4 \times 4 \times 4$	-1.067	-1.353

depth calculations using MP $4 \times 4 \times 4$ are already quite converged, with an error on the order of few meV. Using TABC instead yields similar results. Using only the Γ -point yields large one-body FS errors.

The two-body FS corrections (Table 6.8) for non-cubical structures are obtained from the same XC function $\mathcal{E}_{XC}(r_s, L)$ as described in Table 5.2. Since the shapes of both the tetragonal and rhombohedral unit cells are only slightly different from cubic, L is defined as $L = \Omega^{1/3}$. The two-body FS corrections are individually large for the primitive cubic, tetragonal and rhombohedral unit cells, which are small in size. Table 6.8 shows the two-body FS corrections for sequences of 4 supercells corresponding to number of atom of 5, 40, 135 and 320 atoms. The cubic simulation cell is smallest, and therefore has the largest FS error, while the largest rhombohedral cell has the smallest correction. The two-body FS corrections are linear with respect to the inverse of volume for all three structures. Due to cancellation of errors, the two-body correction for the tetragonal and rhombohedral well-depths are much smaller than the energy corrections as shown in Table 6.8 and Fig. 6.14. However the well-depth correction is still large for the primitive cell.

The well-depths calculated with QMC method together with the corrected QMC

TABLE 6.8: The two-body FS corrections for supercells of $BiScO_3$ cubic, tetragonal and rhombohedral structures, together with the corrections for the well-depths. The size n=1,2,3 and 4 correspond to 5, 40, 135 and 320 atom supercells. The corrections are in eV per primitive cell.

\overline{n}	$\Delta E^{2-b}(C)$	$\Delta E^{2-b}(T)$	$\Delta E^{2-b}(R)$	$\Delta E^{2-b}(T-C)$	$\Delta E^{2-b}(R-C)$
1	8.5712	7.9684	7.8801	-0.6028	-0.6911
2	1.0764	1.0066	0.9957	-0.0698	-0.0807
3	0.3189	0.2982	0.2950	-0.0207	-0.0239
4	0.1345	0.1258	0.1245	-0.0087	-0.0101

are given in Table 6.9. The results show that, as expected, the single **k**-point (Γ -point) is not reliable. It has large FS errors, even after the one-body and twobody FS corrections. The one-body FS correction improves the agreement between calculations using the TBC based on $2 \times 2 \times 2$ and $4 \times 4 \times 4$ **k**-point grids, but they still have large FS errors. The full corrected QMC well-depths for both tetragonal and rhombohedral structures are in good agreement with LDA calculated well-depths. These suggest that the LDA calculated well-depths are reliable.

Further technical specifications are given in Appendix C.



FIG. 6.14: The two-body FS corrections for two perovskite structures: tetragonal and rhombohedral as a function of system sizes n. The corrections are given in eV per primitive unit cells. The numbers of atoms $(5n^3)$ for each system sizes are $N_{\rm a} = 5$, 40, 135 and 320. Inset: the two-body FS correction as a function of $1/N_{\rm a}$

TABLE 6.9: The well-depths of $BiScO_3$ calculated with raw QMC, one-body and twobody FS corrections. All the energies are in eV.

	$\Delta E(T)$	$\Delta E(R)$
QMC		
Γ -point	-5.40 ± 0.42	-3.00 ± 0.43
TBC $2 \times 2 \times 2$	-0.42 ± 0.12	-1.60 ± 0.23
TBC $4 \times 4 \times 4$	-0.19 ± 0.19	-0.70 ± 0.17
$QMC + \Delta E^{1-b}$		
$\Gamma ext{-point}$	1.03 ± 0.42	0.05 ± 0.43
TBC $2 \times 2 \times 2$	-0.28 ± 0.12	-1.34 ± 0.23
TBC $4 \times 4 \times 4$	-0.22 ± 0.19	-0.69 ± 0.17
$QMC + \Delta E^{1-b} + \Delta E^{2-b}$		
$\Gamma ext{-point}$	0.45 ± 0.42	-0.63 ± 0.43
TBC $2 \times 2 \times 2$	-0.88 ± 0.12	-2.03 ± 0.23
TBC $4 \times 4 \times 4$	-0.83 ± 0.19	-1.38 ± 0.17
DFT	-1.098	-1.339

CHAPTER 7

Conclusion and Outlook

Realistic many-body calculations for extended systems are needed to accurately treat systems where the otherwise successful density functional theory (DFT) approach fails. Effective single-particle methods such as DFT or Hartree-Fock (HF) routinely exploit Bloch's theorem in calculation for extended systems. In crystalline materials, the cost of the calculation depends only on the number of atoms in the periodic cell while the macroscopic limit is achieved by quadrature in the Brillouin zone, using finite number of **k**-points. Many-body methods, in contrast, cannot avail themselves of this simplification. Instead, calculations must be performed using increasingly larger supercells. Because the Coulomb interactions are long-ranged, finite-size effects tend to persist to large system sizes, making reliable extrapolations impractical.

In state-of-the-art quantum simulations, finite size (FS) errors often can be more significant than the statistical or other systematic errors. Reducing FS errors is thus a key to broader applications of many-body calculations in real materials. Previous attempts have focused on estimating the FS errors internally within the many-body simulation. In this thesis, I introduced an external correction method which is designed to approximately include two-body FS corrections in *finite-size* DFT calculations. The method is simple, and provides post-processing corrections applicable to any previously obtained many-body results. Conceptually, it gives a consistent framework for relating FS effects in many-body and DFT calculations, which is important if the two methods are to be seamlessly interfaced to bridge length scales. The correction method is applied to a model insulator (P_2 in a supercell), to semiconductor bulk silicon, to sodium metal and to perovskite BiScO₃. We find that it consistently removes most of the FS errors, leading to rapid convergence of the many-body results to the infinite system.

The FS correction is constructed for cubic simulation cells, but the correction is shown to be accurate for non-cubic supercells as well, including fcc cells and ferroelectrically distorted cubic cells. The current FS functional is restricted to systems without spin polarization but the extension to include spin polarization should be straightforward. Including polarization will be important in treating solids with magnetic order.

Our tests indicate that the FS correction from the Hartree-Fock method tends to overcorrect the energy. The present DFT FS correction gives much better corrections but they tend to be somewhat too small. Replacing the exchange energy with an orbitally dependent exact exchange functional should be investigated, since it could improve the quality of the correction.

Other possible future work could include further study of the shape dependence of the FS correction for non cubic systems with extreme aspect ratios.

Finally, I have presented calculations of the cutoff energy dependence of the correlation energy. Fitting this data to a function $\mathcal{E}_c(r_s, E_{\text{cut}})$ could be useful for obtaining a finite-basis correction in many-body calculations. The idea is similar to the FS correction of many-body calculations. Further studies are needed to test these ideas.

APPENDIX A

Pseudopotential

The tightly bound core electrons of an atom are fairly insensitive to the chemical environment of the atom. Including the core electrons can be very expensive but has a little effect. The use of a pseudopotential eliminates the core electron states from the spectrum of the valence-only pseudo-Hamiltonian, while retaining an accurate description of valence electron bounding.

Norm conserving Kleinman-Bylander type non local pseudopotentials [31] are used in this thesis. The requirements for a good norm-conserving pseudopotential are given by Hamann, Schlüter and Chiang [77]:

- 1. All-electron and pseudo valence eigenvalues agree for the chosen atomic reference configuration.
- 2. All-electron and pseudo valence wavefunction agree beyond a chosen core radius $r_c. \label{eq:rc}$
- 3. The integrated charge inside a radius r_c from the nucleus for each wavefunction agrees (norm-conservation) with the all-electron value.
- 4. The logarithmic derivatives of all electron and pseudo wavefunction agree at

 r_c (this reproduces the valence electron scattering properties near the reference energy).

5. The first energy derivatives of the logarithmic derivatives of the all-electron and pseudo wavefunctions agrees at r_c .

It is useful to separate the ionic pseudopotential into a local (*l*-independent) part

$$\langle \mathbf{r} | \hat{V}^{\text{loc}} | \mathbf{r}' \rangle = V^{\text{loc}}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}'),$$
 (A.1)

and semi local (*l*-dependent) part.

$$\langle \mathbf{r} | \hat{V}^{\mathrm{nl}} | \mathbf{r}' \rangle = V^{\mathrm{nl}}(\mathbf{r}, \mathbf{r}').$$
 (A.2)

In the following discussion, I describe the applications of the pseudopotential in calculations using periodic boundary condition.

Let first consider the local potential. The local potential is given as a sum over all ion's contributions in a crystal:

$$V^{\rm loc}(\mathbf{r}) = \sum_{\mathbf{R},\alpha} V^{\rm loc}_{\alpha}(|\mathbf{r} - \mathbf{d}_{\alpha} - \mathbf{R}|), \qquad (A.3)$$

where \mathbf{R} is the direct lattice vector, and \mathbf{d}_{α} is the relative position of the α atom in a simulation cell relative to the cell's origin. The sum over \mathbf{R} is an infinite sum, since a crystal is perfectly periodic over all spaces. The matrix element of this local potential in reciprocal space is given by

$$\langle \mathbf{k} + \mathbf{G} | \hat{V}^{\text{loc}} | \mathbf{k} + \mathbf{G}' \rangle = \frac{1}{\mathcal{V}} \sum_{\mathbf{R}, \alpha} \int d^3 \mathbf{r} e^{-i(\mathbf{G} - \mathbf{G}') \cdot \mathbf{r}} V_{\alpha}^{\text{loc}} (\mathbf{r} - \mathbf{d}_{\alpha} - \mathbf{R}).$$
(A.4)

Note that in this expression, there is no \mathbf{k} -vector dependence. Now let us define

 $\mathbf{r}' \equiv \mathbf{r} - \mathbf{d}_{\alpha} - \mathbf{R}$. Then the matrix element becomes

$$\langle \mathbf{k} + \mathbf{G} | \hat{V}^{\text{loc}} | \mathbf{k} + \mathbf{G}' \rangle = \frac{1}{\mathcal{V}} \sum_{\mathbf{R},\alpha} e^{-i(\mathbf{G} - \mathbf{G}') \cdot (\mathbf{d}_{\alpha} + \mathbf{R})} \int d^{3}\mathbf{r}' e^{-i(\mathbf{G} - \mathbf{G}') \cdot \mathbf{r}'} V_{\alpha}^{\text{loc}}(\mathbf{r}')$$
$$= \frac{1}{\Omega} \sum_{\alpha} e^{-i(\mathbf{G} - \mathbf{G}') \cdot \mathbf{d}_{\alpha}} \bar{V}_{\alpha}^{\text{loc}}(\mathbf{G} - \mathbf{G}')$$
$$\equiv \tilde{V}^{\text{loc}}(\mathbf{G} - \mathbf{G}') \tag{A.5}$$

We have used the fact that $e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{R}} = 1$ for any direct lattice vector \mathbf{R} , and that $\mathcal{V}^{-1}\sum_{\mathbf{R}} = \Omega^{-1}$. The terms $\bar{V}^{\text{loc}}_{\alpha}$, defined as

$$\bar{V}_{\alpha}^{\text{loc}}(\mathbf{Q}) = \int d^3 \mathbf{r} e^{-i\mathbf{Q}\cdot\mathbf{r}} V_{\alpha}^{\text{loc}}(\mathbf{r}), \qquad (A.6)$$

are simply the Fourier transform of the local potential. Using the planewave expansion [78]

$$e^{i\mathbf{k}.\mathbf{r}} = 4\pi \sum_{l=0}^{\infty} i^{l} j_{l}(kr) \sum_{m=-l}^{l} Y_{l,m}^{*}(\hat{\mathbf{k}}) Y_{l,m}(\hat{\mathbf{r}}), \qquad (A.7)$$

together with the orthogonality of the spherical harmonic $Y_{l,m}(\theta, \phi)$, Eq. (A.6) can be simplified:

$$\bar{V}_{\alpha}^{\rm loc}(\mathbf{Q}) = 4\pi \int_0^\infty r^2 j_0(Qr) V_{\alpha}(r) dr \tag{A.8}$$

where $j_0(Qr)$ is a spherical Bessel function. This function is obtained directly from pseudopotential code. It is convenient to add and subtract the long range point charge Coulomb potential with effective charge equal to $+Z_{\text{val}}$ so that the local potential has a rapid spatial decay. The point charge term is handle in Fourier space:

$$\int d^3 \mathbf{r} e^{i\mathbf{Q}\cdot\mathbf{r}} \frac{+Z_{\alpha}}{|\mathbf{r}|} = \frac{4\pi Z_{\alpha}}{|\mathbf{Q}|^2}.$$
(A.9)

Due to charge neutrality, the divergent $\mathbf{Q} = 0$ term cancels between electron-ion, electron-electron and ion-ion interactions.

Similarly, the nonlocal pseudopotential is given by:

$$V^{\rm nl} = \sum_{\mathbf{R},\alpha} V^{\rm nl}_{\alpha} (\mathbf{r} - \mathbf{d}_{\alpha} - \mathbf{R}, \mathbf{r}' - \mathbf{d}_{\alpha} - \mathbf{R}).$$
(A.10)

Using the same manipulation as above, the matrix element is given by

$$\langle \mathbf{k} + \mathbf{G} | \hat{V}^{\mathrm{nl}} | \mathbf{k} + \mathbf{G}' \rangle$$

$$= \frac{1}{\mathcal{V}} \int d^3 \mathbf{r} d^3 \mathbf{r}' e^{-i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}} \left(\sum_{\mathbf{R}, \alpha} V_{\alpha}^{\mathrm{nl}} (\mathbf{r} - \mathbf{d}_{\alpha} - \mathbf{R}, \mathbf{r}' - \mathbf{d}_{\alpha} - \mathbf{R}) \right) e^{-i(\mathbf{k} + \mathbf{G}') \cdot \mathbf{r}'}$$

$$= \frac{1}{\Omega} \sum_{\alpha} e^{-i(\mathbf{G} - \mathbf{G}') \cdot \mathbf{d}_{\alpha}} \overline{V}_{\alpha}^{\mathrm{nl}} (\mathbf{k} + \mathbf{G}, \mathbf{k} + \mathbf{G}') \cdot \mathbf{G}'$$

$$= \tilde{V}^{\mathrm{nl}} (\mathbf{k} + \mathbf{G}, \mathbf{k} + \mathbf{G}')$$

$$(A.11)$$

This form is expensive to use in calculations. The Kleinman-Bylander fully non-local pseudopotential [31] is given in the following separate form:

$$\hat{V}_{\alpha}^{\mathrm{nl}} = \sum_{l,m} \frac{|V_{\alpha,l}\varphi_{\alpha,l}^{\mathrm{ps}}Y_{l,m}\rangle\langle Y_{l,m}\varphi_{\alpha,l}^{\mathrm{ps}}V_{\alpha,l}|}{\eta_{\alpha,l}}$$
(A.12)

where

$$\eta_{\alpha,l} = \langle Y_{l,m}\varphi_{\alpha,l}^{\rm ps}|V_{\alpha,l}|\varphi_{\alpha,l}^{\rm ps}Y_{l,m}\rangle.$$
(A.13)

Substitute Eq. (A.12) into Eq. (A.11), we get:

$$\bar{V}_{\alpha}^{\mathrm{nl}}(\mathbf{Q},\mathbf{Q}') = \sum_{l,m} \frac{1}{\eta_{\alpha,l}} \int d^{3}\mathbf{r} e^{-i\mathbf{Q}\cdot\mathbf{r}} V_{\alpha,l}(r) \varphi_{\alpha,l}^{\mathrm{ps}}(r) Y_{l,m}(\hat{\mathbf{r}})$$
$$\int d^{3}\mathbf{r}' e^{-i\mathbf{Q}'\cdot\mathbf{r}'} V_{\alpha,l}(r') \varphi_{\alpha,l}^{\mathrm{ps}}(r') Y_{l,m}(\hat{\mathbf{r}}')$$
(A.14)

Obviously this two integrations are identical and separable. Let evaluate one of them:

$$I(\mathbf{Q}) = \int d^{3}\mathbf{r} e^{-i\mathbf{Q}\cdot\mathbf{r}} V_{\alpha,l}(r)\varphi_{\alpha,l}^{\mathrm{ps}}(r)Y_{l,m}(\hat{\mathbf{r}})$$

$$= 4\pi \sum_{l'} (-i)^{l'} \int r^{2} dr d\Omega j_{l'}(Qr) \sum_{m'=-l'}^{l'} Y_{l',m'}(\hat{\mathbf{Q}})Y_{l',m'}^{*}(\hat{\mathbf{r}})V_{\alpha,l}(r)\varphi_{\alpha,l}^{\mathrm{ps}}(r)Y_{l.m}(\hat{\mathbf{r}})$$

$$= 4\pi (-i)^{l} \int r^{2} dr j_{l}(Qr)V_{\alpha,l}(r)\varphi_{\alpha,l}^{\mathrm{ps}}Y_{l,m}(\hat{\mathbf{Q}})$$
(A.15)

In the last equation, we use the orthogonality of the spherical harmonics. Now let us define:

$$f_{\alpha,l}(Q) = \int r^2 dr j_l(Qr) V_{\alpha,l}(r) \varphi_{\alpha,l}^{\rm ps}.$$
 (A.16)

This function is obtained directly from pseudopotential code. Then Eq. (A.11) can be written as:

$$\langle \mathbf{Q} | \hat{V}^{\mathrm{nl}} | \mathbf{Q}' \rangle = \frac{(4\pi)^2}{\Omega} \sum_{l,m} \frac{1}{\eta_{\alpha,l}} \sum_{\alpha} e^{-i(\mathbf{Q} - \mathbf{Q}') \cdot \mathbf{d}_{\alpha}} f_{\alpha,l}(Q) Y_{l,m}(\hat{\mathbf{Q}}) f_{\alpha,l}(Q') Y_{l,m}(\hat{\mathbf{Q}}'), \quad (A.17)$$

where $\mathbf{Q} = \mathbf{k} + \mathbf{G}$ and $\mathbf{Q}' = \mathbf{k} + \mathbf{G}'$. Defining

$$F_{j}(\mathbf{Q}) \equiv F_{\alpha,l,m}(\mathbf{Q}) \equiv \frac{4\pi}{\sqrt{\Omega}} e^{i\mathbf{Q}\cdot\mathbf{d}_{\alpha}} f_{\alpha,l}(Q) Y_{l,m}^{*}(\hat{\mathbf{Q}}'), \qquad (A.18)$$

the nonlocal matrix element takes a simple separable form:

$$\langle \mathbf{k} + \mathbf{G} | \hat{V}^{\mathrm{nl}} | \mathbf{k} + \mathbf{G}' \rangle = \sum_{j \in \{(\alpha, l, m)\}} \frac{1}{\eta_j} F_j^* (\mathbf{k} + \mathbf{G}) F_j (\mathbf{k} + \mathbf{G}').$$
(A.19)

This is the form used in planewave base DFT calculations and in our planewave AFQMC code.
APPENDIX B

Dependence of the Jellium Correlation Energy on the Cutoff Energy E_{cut}

The jellium system is described in Chapter 4. A series of calculations were performed using AFQMC method in cubic simulation cells with no spin polarization with N electrons. There are total of 25 sets of data for densities of $r_s = 1, 2, 3, 4$, and 5 Bohr. For each density, calculations were performed with N equal to 10, 20, 30, 40 and 50 electrons. Each set was obtained from TABC averages over 20 QMC calculations with different **k**-points [52]. The results of over 5000 calculations are presented in the five tables below.

The cutoff energy is expressed as a function of the Fermi energy (as given by restricted HF). The Fermi momentum is given by Eq. (4.7),

$$k_F = \left(\frac{9\pi}{4}\right)^{\frac{1}{3}} \frac{1}{r_s},\tag{B.1}$$

and the Fermi energy is given by

$$E_F = \frac{\hbar^2 k_F^2}{2m},\tag{B.2}$$

only depends on the density of the system. The relation between the cube edge L, the number of electrons N, and the density r_s is given in Eq. (4.2)

$$L = r_s \left(\frac{4\pi N}{3}\right)^{\frac{1}{3}}.\tag{B.3}$$

The Fermi energy definition given here is for the infinite size limit. In finite size simulations, E_F has a **k**-point dependence. For example, in the system of 54 electrons using the Γ -point, the electrons fill the momentum states $\mathbf{G} = (0,0,0), (1,0,0),$ (1,1,0) and (1,1,1) (and all other states related with these 4 states by symmetry) in units of $\frac{2\pi}{L}$. The electrons with highest energy fill the $\mathbf{G} = (1,1,1)$ state. The Fermi momentum of this electron is $k_F = \sqrt{\left(\frac{2\pi}{L}\right)^2 \left(1^2 + 1^2 + 1^2\right)} = \frac{2\pi}{L} \sqrt{3} = 1.732 \frac{2\pi}{L}$. The Fermi momentum calculated with Eq. (B.1) is $\frac{2\pi}{L} \left(\frac{81}{4\pi}\right)^{1/3} = 1.861 \frac{2\pi}{L}$. In the limit of large simulation cells with a large number of particles, the approximate formula is equal to the exact result. Moreover, the average of Fermi momenta over many **k**-points also tends to the result in Eq. (B.1).

The correlation energy is given as the difference between the total energy and the Hartree-Fock energy. The HF energy is independent of the size of the basis, as long as the basis is large enough to accommodate all electrons. When the basis size exactly accommodate the number of electrons, the HF energy is exactly the same with the AFQMC total energy so the correlation energy is exactly zero in this case.

The list of random \mathbf{k} -points used in the simulations is given in Table B.1. Since the QMC statistical error is much smaller than the error due to \mathbf{k} -point averaging (by approximately two orders of magnitude), the errors reported here are from the \mathbf{k} -point averaging only. The Hartree-Fock energy, by definition, does not have a statistical error, but it still has a \mathbf{k} -point averaging error. As expected, the error in

	k_x	k_y	k_z
1	0.0506	0.1980	0.2700
2	0.1764	0.1229	0.4107
3	0.2489	0.2204	0.0065
4	0.2690	0.4449	0.4921
5	0.2952	0.3266	0.2446
6	0.2011	0.0913	0.3978
$\overline{7}$	0.3071	0.0455	0.0457
8	0.4285	0.2451	0.1115
9	0.4449	0.0281	0.4095
10	0.1301	0.1981	0.2810
11	0.3360	0.0695	0.3170
12	0.1185	0.2152	0.0502
13	0.2379	0.0838	0.2244
14	0.0122	0.3499	0.4420
15	0.2693	0.1890	0.2086
16	0.4659	0.2727	0.4260
17	0.1087	0.4740	0.1011
18	0.2392	0.3505	0.1955
19	0.3802	0.3269	0.1716
20	0.4423	0.3462	0.4634

TABLE B.1: The list of **k**-points used in the simulation in reduced coordinate $\frac{2\pi}{L}(k_x, k_y, k_z)$.

HF is correlated with that in QMC, so the correlation energy has a much smaller error. All energies reported here are in Rydberg atomic units.

TABLE B.2: E_{cut} dependence of the total energy E and the correlation energy per particle \mathcal{E}_c of jellium with density of $r_s = 1$ for five choice of N, the numbers of electrons. E_{cut} is in unit of E_F .

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		N = 10, L = 3.47 Bohr			N = 20, L = 4.38 Bohr			
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		$E_{HF} = (11.76 \pm 0.24) \text{ Ry}$			$E_{HF} = (24.30 \pm$	= 0.19) Ry		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$E_{\rm cut}$	E(Ry)	$\mathcal{E}_c(\mathrm{mRy/N})$	$E_{\rm cut}$	$E(\mathrm{Ry})$	$\mathcal{E}_c(\mathrm{mRy/N})$		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.5	11.71 ± 0.24	-5.12 ± 0.84	1.5	24.06 ± 0.17	-11.80 ± 1.31		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.0	11.57 ± 0.24	-18.62 ± 0.86	2.0	23.70 ± 0.18	-30.09 ± 0.91		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.5	11.47 ± 0.24	-28.86 ± 1.01	2.5	23.39 ± 0.17	-45.60 ± 0.78		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3.0	11.39 ± 0.24	-36.63 ± 0.92	3.0	23.21 ± 0.17	-54.48 ± 1.19		
5.0 11.24 ± 0.24 -52.09 ± 0.61 5.0 22.95 ± 0.17 -67.56 ± 1.14 6.0 11.22 ± 0.24 -53.89 ± 0.67 6.0 22.91 ± 0.17 -69.51 ± 1.12 7.0 11.21 ± 0.24 -55.02 ± 0.68 7.0 22.88 ± 0.17 -70.80 ± 1.16 8.0 11.20 ± 0.24 -55.70 ± 0.64 8.0 22.87 ± 0.17 -71.30 ± 1.11 9.0 11.20 ± 0.24 -56.11 ± 0.66 9.0 22.86 ± 0.17 -71.91 ± 1.17 N = 30, L = 5.01 BohrN = 40, L = 5.51 BohrE _{HF} = (36.52 \pm 0.40) RyE _{HF} = (49.14 \pm 0.51) RyE _{Cut} E(Ry) $\mathcal{E}_{c}(mRy/N)$ E _{cut} E(Ry) $\mathcal{E}_{c}(mRy/N)$ 5.34.9 ± 0.42 -51.15 ± 1.13 2.5 46.84 ± 0.50 -57.39 ± 0.76 3.0 34.71 ± 0.41 -60.33 ± 0.77 34.33 ± 0.41 -73.15 ± 0.66 5.0 45.33 ± 0.41 -73.15 ± 0.66 5.0 45.33 ± 0.41 -76.60 ± 0.65 70.342 ± 0.40 -77.55 ± 0.59 $9.34.22 \pm 0.40$ -76.60 ± 0.65 70.342 ± 0.40 -77.55 ± 0.59 $9.34.22 \pm 0.40$ -77.55 ± 0.59 9.0 46.16 ± 0.49 -80.83 ± 0.64 <td co<="" td=""><td>4.0</td><td>11.28 ± 0.24</td><td>-48.16 ± 0.55</td><td>4.0</td><td>23.03 ± 0.16</td><td>-63.61 ± 1.25</td></td>	<td>4.0</td> <td>11.28 ± 0.24</td> <td>-48.16 ± 0.55</td> <td>4.0</td> <td>23.03 ± 0.16</td> <td>-63.61 ± 1.25</td>	4.0	11.28 ± 0.24	-48.16 ± 0.55	4.0	23.03 ± 0.16	-63.61 ± 1.25	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5.0	11.24 ± 0.24	-52.09 ± 0.61	5.0	22.95 ± 0.17	-67.56 ± 1.14		
7.0 11.21 ± 0.24 -55.02 ± 0.68 7.0 22.88 ± 0.17 -70.80 ± 1.16 8.0 11.20 ± 0.24 -55.70 ± 0.64 8.0 22.87 ± 0.17 -71.30 ± 1.11 9.0 11.20 ± 0.24 -56.11 ± 0.66 9.0 22.86 ± 0.17 -71.91 ± 1.17 N = 30, $L = 5.01$ BohrN = 40, $L = 5.51$ Bohr $E_{HF} = (36.52 \pm 0.40)$ Ry $E_{HF} = (49.14 \pm 0.51)$ Ry E_{cut} $E(Ry)$ $\mathcal{E}_c(mRy/N)$ E_{cut} $E(Ry)$ $\mathcal{E}_c(mRy/N)$ 1.5 36.10 ± 0.41 -14.21 ± 0.70 1.5 48.45 ± 0.50 -17.22 ± 0.86 2.0 35.44 ± 0.41 -36.02 ± 0.47 2.0 47.50 ± 0.51 -40.97 ± 0.60 2.5 34.99 ± 0.42 -51.15 ± 1.13 2.5 46.84 ± 0.50 -57.39 ± 0.76 3.0 34.71 ± 0.41 -60.33 ± 0.79 3.0 46.49 ± 0.49 -66.15 ± 0.84 4.0 34.44 ± 0.40 -69.29 ± 0.58 4.0 46.16 ± 0.49 -74.40 ± 0.75 5.0 34.33 ± 0.41 -73.15 ± 0.66 5.0 45.98 ± 0.49 -78.97 ± 0.81 6.0 34.26 ± 0.40 -77.52 ± 0.59 6.0 45.91 ± 0.49 -80.83 ± 0.83 7.0 34.22 ± 0.40 -76.60 ± 0.65 7.0 45.87 ± 0.49 -83.02 ± 0.80 N = 50, $L = 5.94$ Bohr $E_{HF} = (61.90 \pm 0.41)$ Ry $E_{c}(mRy/N)$ $E_{c}(mRy/N)$ $E_{c}(mRy/N)$ 1.5 60.88 ± 0.38 -20.41 ± 0.85 $E_{c}(mRy/N)$ $E_{c}(mRy/N)$ 2.5 58.85 ± 0.38 -69.60	6.0	11.22 ± 0.24	-53.89 ± 0.67	6.0	22.91 ± 0.17	-69.51 ± 1.12		
8.0 11.20 ± 0.24 -55.70 ± 0.64 8.0 22.87 ± 0.17 -71.30 ± 1.11 9.0 11.20 ± 0.24 -56.11 ± 0.66 9.0 22.86 ± 0.17 -71.91 ± 1.17 N = 30, L = 5.01 Bohr N = 40, L = 5.51 Bohr $E_{HF} = (36.52 ± 0.40)$ Ry $E_{HF} = (49.14 ± 0.51)$ Ry E_{cut} $E(Ry)$ $\mathcal{E}_c(mRy/N)$ E_{cut} $E(Ry)$ $\mathcal{E}_c(mRy/N)$ 1.5 36.10 ± 0.41 -14.21 ± 0.70 1.5 48.45 ± 0.50 -17.22 ± 0.86 2.0 35.44 ± 0.41 -36.02 ± 0.47 2.0 47.50 ± 0.51 -40.97 ± 0.60 2.5 34.99 ± 0.42 -51.15 ± 1.13 2.5 46.84 ± 0.50 -57.39 ± 0.76 3.0 34.71 ± 0.41 -60.33 ± 0.79 3.0 46.49 ± 0.49 -66.15 ± 0.84 4.0 34.44 ± 0.40 -69.29 ± 0.58 4.0 46.16 ± 0.49 -74.40 ± 0.75 5.0 34.33 ± 0.41 -73.15 ± 0.66 5.0 45.98 ± 0.49 -88.83 ± 0.83 7.0 34.22 ± 0.40 -76.60 ± 0.65 7.0 45.87 ± 0.49 -82.60 ± 0.83 9.0 34.20 ± 0.40 -77.55 ± 0.59 <t< td=""><td>7.0</td><td>11.21 ± 0.24</td><td>-55.02 ± 0.68</td><td>7.0</td><td>22.88 ± 0.17</td><td>-70.80 ± 1.16</td></t<>	7.0	11.21 ± 0.24	-55.02 ± 0.68	7.0	22.88 ± 0.17	-70.80 ± 1.16		
9.0 11.20 ± 0.24 -56.11 ± 0.66 9.0 22.86 ± 0.17 -71.91 ± 1.17 $N = 30, L = 5.01$ Bohr $N = 40, L = 5.51$ Bohr $E_{HF} = (36.52 \pm 0.40)$ Ry E_{ut} $E(49.14 \pm 0.51)$ Ry E_{cut} $E(Ry)$ $\mathcal{E}_{c}(mRy/N)$ E_{cut} $E(Ry)$ $\mathcal{E}_{c}(mRy/N)$ 1.5 36.10 ± 0.41 -14.21 ± 0.70 1.5 48.45 ± 0.50 -17.22 ± 0.86 2.0 35.44 ± 0.41 -36.02 ± 0.47 2.0 47.50 ± 0.51 -40.97 ± 0.60 2.5 34.99 ± 0.42 -51.15 ± 1.13 2.5 46.84 ± 0.50 -57.39 ± 0.76 3.0 34.71 ± 0.41 -60.33 ± 0.79 3.0 46.49 ± 0.49 -66.15 ± 0.84 4.0 34.44 ± 0.40 -69.29 ± 0.58 4.0 46.16 ± 0.49 -74.40 ± 0.75 5.0 34.33 ± 0.41 -73.15 ± 0.66 5.0 45.98 ± 0.49 -78.97 ± 0.81 6.0 34.26 ± 0.40 -75.49 ± 0.59 6.0 45.91 ± 0.49 -80.83 ± 0.83 7.0 34.22 ± 0.40 -76.60 ± 0.65 7.0 45.87 ± 0.49 -83.02 ± 0.80 $N = 50, L = 5.94$ Bohr $E_{HF} = (61.90 \pm 0.41)$ Ry E_{cut} $E(Ry)$ $\mathcal{E}_{c}(mRy/N)$ 1.5 60.88 ± 0.38 -20.41 ± 0.85 2.0 ± 0.49 -83.02 ± 0.80 $N = 50, L = 5.94$ Bohr $E_{HF} = (61.90 \pm 0.41)$ Ry $E_{HF} = (61.90 \pm 0.41)$ Ry E_{cut} $E(Ry)$ $\mathcal{E}_{c}(mRy/N)$ E_{cut} E_{cut} E_{cut} E_{cut} 0.5 57.8 ± 0.38 -60.97 ± 0.71 3.0 $58.42 \pm $	8.0	11.20 ± 0.24	-55.70 ± 0.64	8.0	22.87 ± 0.17	-71.30 ± 1.11		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	9.0	11.20 ± 0.24	-56.11 ± 0.66	9.0	22.86 ± 0.17	-71.91 ± 1.17		
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		N = 30, L = 5	.01 Bohr		N = 40, L = 5	.51 Bohr		
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		$E_{HF} = (36.52 \pm$	= 0.40) Ry		$E_{HF} = (49.14 \pm$	= 0.51) Ry		
1.5 36.10 ± 0.41 -14.21 ± 0.70 1.5 48.45 ± 0.50 -17.22 ± 0.86 2.0 35.44 ± 0.41 -36.02 ± 0.47 2.0 47.50 ± 0.51 -40.97 ± 0.60 2.5 34.99 ± 0.42 -51.15 ± 1.13 2.5 46.84 ± 0.50 -57.39 ± 0.76 3.0 34.71 ± 0.41 -60.33 ± 0.79 3.0 46.49 ± 0.49 -66.15 ± 0.84 4.0 34.44 ± 0.40 -69.29 ± 0.58 4.0 46.16 ± 0.49 -74.40 ± 0.75 5.0 34.33 ± 0.41 -73.15 ± 0.66 5.0 45.98 ± 0.49 -78.97 ± 0.81 6.0 34.26 ± 0.40 -75.49 ± 0.59 6.0 45.91 ± 0.49 -80.83 ± 0.83 7.0 34.22 ± 0.40 -76.60 ± 0.65 7.0 45.87 ± 0.49 -81.84 ± 0.77 8.0 34.21 ± 0.40 -77.12 ± 0.61 8.0 45.84 ± 0.49 -82.60 ± 0.81 9.0 34.20 ± 0.40 -77.55 ± 0.59 9.0 45.82 ± 0.49 -83.02 ± 0.80 N = 50, L = 5.94 BohrE _{HF} = (61.90 \pm 0.41) RyEE (Ry) \mathcal{E}_c (mRy/N)1.5 60.88 ± 0.38 -20.41 ± 0.85 2.0 59.62 ± 0.41 -45.65 ± 0.39 -45.82 ± 0.49 -83.02 ± 0.80 2.5 58.85 ± 0.38 -60.97 ± 0.71 -60.5 ± 0.78 -66.5 ± 0.78 -66.5 ± 0.78 3.0 57.78 ± 0.38 -82.52 ± 0.70 -66.5 ± 0.78 -78.48 ± 0.64 -77.59 ± 0.38 -86.27 ± 0.69 9.0 57.56 ± 0.38 -86.77 ± 0.69 -96.5 ± 0.75	$E_{\rm cut}$	$E(\mathrm{Ry})$	$\mathcal{E}_c(\mathrm{mRy/N})$	$E_{\rm cut}$	$E(\mathrm{Ry})$	$\mathcal{E}_c(\mathrm{mRy/N})$		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.5	36.10 ± 0.41	-14.21 ± 0.70	1.5	48.45 ± 0.50	-17.22 ± 0.86		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.0	35.44 ± 0.41	-36.02 ± 0.47	2.0	47.50 ± 0.51	-40.97 ± 0.60		
3.0 34.71 ± 0.41 -60.33 ± 0.79 3.0 46.49 ± 0.49 -66.15 ± 0.84 4.0 34.44 ± 0.40 -69.29 ± 0.58 4.0 46.16 ± 0.49 -74.40 ± 0.75 5.0 34.33 ± 0.41 -73.15 ± 0.66 5.0 45.98 ± 0.49 -78.97 ± 0.81 6.0 34.26 ± 0.40 -75.49 ± 0.59 6.0 45.91 ± 0.49 -80.83 ± 0.83 7.0 34.22 ± 0.40 -76.60 ± 0.65 7.0 45.87 ± 0.49 -81.84 ± 0.77 8.0 34.21 ± 0.40 -77.12 ± 0.61 8.0 45.84 ± 0.49 -82.60 ± 0.81 9.0 34.20 ± 0.40 -77.55 ± 0.59 9.0 45.82 ± 0.49 -83.02 ± 0.80 N = $50, L = 5.94$ Bohr $E_{HF} = (61.90 \pm 0.41)$ Ry E_{cut} $E(Ry)$ $\mathcal{E}_c(mRy/N)$ 1.5 60.88 ± 0.38 -20.41 ± 0.85 2.0 59.62 ± 0.41 -45.65 ± 0.39 2.5 58.85 ± 0.38 -60.60 ± 0.76 4.0 57.98 ± 0.38 -78.48 ± 0.64 5.0 57.78 ± 0.38 -82.52 ± 0.70 6.0 57.67 ± 0.38 -85.84 ± 0.68 8.0 57.59 ± 0.38 -86.27 ± 0.69 9.0 57.56 ± 0.38 -86.76 ± 0.65	2.5	34.99 ± 0.42	-51.15 ± 1.13	2.5	46.84 ± 0.50	-57.39 ± 0.76		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3.0	34.71 ± 0.41	-60.33 ± 0.79	3.0	46.49 ± 0.49	-66.15 ± 0.84		
5.0 34.33 ± 0.41 -73.15 ± 0.66 5.0 45.98 ± 0.49 -78.97 ± 0.81 6.0 34.26 ± 0.40 -75.49 ± 0.59 6.0 45.91 ± 0.49 -80.83 ± 0.83 7.0 34.22 ± 0.40 -76.60 ± 0.65 7.0 45.87 ± 0.49 -81.84 ± 0.77 8.0 34.21 ± 0.40 -77.12 ± 0.61 8.0 45.84 ± 0.49 -82.60 ± 0.81 9.0 34.20 ± 0.40 -77.55 ± 0.59 9.0 45.82 ± 0.49 -83.02 ± 0.80 N = 50, $L = 5.94$ Bohr $E_{HF} = (61.90 \pm 0.41)$ Ry E_{cut} $E(Ry)$ $\mathcal{E}_c(mRy/N)$ 1.5 60.88 ± 0.38 -20.41 ± 0.85 2.0 59.62 ± 0.41 -45.65 ± 0.39 2.5 58.85 ± 0.38 -60.97 ± 0.71 3.0 58.42 ± 0.38 -69.60 ± 0.76 4.0 57.98 ± 0.38 -82.52 ± 0.70 6.0 57.67 ± 0.38 -84.56 ± 0.64 7.0 57.61 ± 0.38 -86.27 ± 0.69 9.0 57.56 ± 0.38 -86.76 ± 0.65	4.0	34.44 ± 0.40	-69.29 ± 0.58	4.0	46.16 ± 0.49	-74.40 ± 0.75		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5.0	34.33 ± 0.41	-73.15 ± 0.66	5.0	45.98 ± 0.49	-78.97 ± 0.81		
7.0 34.22 ± 0.40 -76.60 ± 0.65 7.0 45.87 ± 0.49 -81.84 ± 0.77 8.0 34.21 ± 0.40 -77.12 ± 0.61 8.0 45.84 ± 0.49 -82.60 ± 0.81 9.0 34.20 ± 0.40 -77.55 ± 0.59 9.0 45.82 ± 0.49 -83.02 ± 0.80 N = 50, L = 5.94 Bohr $E_{HF} = (61.90 \pm 0.41)$ Ry $E_{HF} = (61.90 \pm 0.41)$ Ry E_{cut} $E(Ry)$ $\mathcal{E}_c(mRy/N)$ 1.5 60.88 ± 0.38 -20.41 ± 0.85 2.0 59.62 ± 0.41 -45.65 ± 0.39 2.5 58.85 ± 0.38 -60.97 ± 0.71 3.0 58.42 ± 0.38 -69.60 ± 0.76 4.0 57.98 ± 0.38 -82.52 ± 0.70 6.0 57.78 ± 0.38 -82.52 ± 0.70 6.0 57.67 ± 0.38 -85.84 ± 0.68 8.0 57.59 ± 0.38 -86.27 ± 0.69 9.0 57.56 ± 0.38 -86.76 ± 0.65	6.0	34.26 ± 0.40	-75.49 ± 0.59	6.0	45.91 ± 0.49	-80.83 ± 0.83		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	7.0	34.22 ± 0.40	-76.60 ± 0.65	7.0	45.87 ± 0.49	-81.84 ± 0.77		
9.0 34.20 ± 0.40 -77.55 ± 0.59 9.0 45.82 ± 0.49 -83.02 ± 0.80 $N = 50, L = 5.94$ Bohr $E_{HF} = (61.90 \pm 0.41)$ Ry $E_{HF} = (61.90 \pm 0.41)$ Ry E_{cut} $E(Ry)$ $\mathcal{E}_c(mRy/N)$ 1.5 60.88 ± 0.38 -20.41 ± 0.85 2.0 59.62 ± 0.41 -45.65 ± 0.39 2.5 58.85 ± 0.38 -60.97 ± 0.71 3.0 58.42 ± 0.38 -69.60 ± 0.76 4.0 57.98 ± 0.38 -78.48 ± 0.64 5.0 57.78 ± 0.38 -82.52 ± 0.70 6.0 57.67 ± 0.38 -85.84 ± 0.68 8.0 57.59 ± 0.38 -86.27 ± 0.69 9.0 57.56 ± 0.38 -86.76 ± 0.65	8.0	34.21 ± 0.40	-77.12 ± 0.61	8.0	45.84 ± 0.49	-82.60 ± 0.81		
$\begin{split} N &= 50, L = 5.94 \text{ Bohr} \\ E_{HF} &= (61.90 \pm 0.41) \text{ Ry} \\ \hline E_{\text{cut}} & E(\text{Ry}) & \mathcal{E}_c(\text{mRy/N}) \\ \hline 1.5 & 60.88 \pm 0.38 & -20.41 \pm 0.85 \\ 2.0 & 59.62 \pm 0.41 & -45.65 \pm 0.39 \\ 2.5 & 58.85 \pm 0.38 & -60.97 \pm 0.71 \\ 3.0 & 58.42 \pm 0.38 & -69.60 \pm 0.76 \\ 4.0 & 57.98 \pm 0.38 & -78.48 \pm 0.64 \\ 5.0 & 57.78 \pm 0.38 & -82.52 \pm 0.70 \\ 6.0 & 57.67 \pm 0.38 & -84.56 \pm 0.64 \\ 7.0 & 57.61 \pm 0.38 & -85.84 \pm 0.68 \\ 8.0 & 57.59 \pm 0.38 & -86.27 \pm 0.69 \\ 9.0 & 57.56 \pm 0.38 & -86.76 \pm 0.65 \\ \end{split}$	9.0	34.20 ± 0.40	-77.55 ± 0.59	9.0	45.82 ± 0.49	-83.02 ± 0.80		
$E_{HF} = (61.90 \pm 0.41) \text{ Ry}$ $E_{\text{cut}} \qquad E(\text{Ry}) \qquad \mathcal{E}_c(\text{mRy/N})$ 1.5 $60.88 \pm 0.38 -20.41 \pm 0.85$ 2.0 $59.62 \pm 0.41 -45.65 \pm 0.39$ 2.5 $58.85 \pm 0.38 -60.97 \pm 0.71$ 3.0 $58.42 \pm 0.38 -69.60 \pm 0.76$ 4.0 $57.98 \pm 0.38 -78.48 \pm 0.64$ 5.0 $57.78 \pm 0.38 -82.52 \pm 0.70$ 6.0 $57.67 \pm 0.38 -84.56 \pm 0.64$ 7.0 $57.61 \pm 0.38 -85.84 \pm 0.68$ 8.0 $57.59 \pm 0.38 -86.27 \pm 0.69$ 9.0 $57.56 \pm 0.38 -86.76 \pm 0.65$		N = 50, L = 5	.94 Bohr					
$E_{\rm cut}$ $E({\rm Ry})$ $\mathcal{E}_c({\rm mRy/N})$ 1.560.88 ± 0.38-20.41 ± 0.852.059.62 ± 0.41-45.65 ± 0.392.558.85 ± 0.38-60.97 ± 0.713.058.42 ± 0.38-69.60 ± 0.764.057.98 ± 0.38-78.48 ± 0.645.057.78 ± 0.38-82.52 ± 0.706.057.67 ± 0.38-84.56 ± 0.647.057.61 ± 0.38-85.84 ± 0.688.057.59 ± 0.38-86.27 ± 0.699.057.56 ± 0.38-86.76 ± 0.65		$E_{HF} = (61.90 \pm$	= 0.41) Ry					
1.5 60.88 ± 0.38 -20.41 ± 0.85 2.0 59.62 ± 0.41 -45.65 ± 0.39 2.5 58.85 ± 0.38 -60.97 ± 0.71 3.0 58.42 ± 0.38 -69.60 ± 0.76 4.0 57.98 ± 0.38 -78.48 ± 0.64 5.0 57.78 ± 0.38 -82.52 ± 0.70 6.0 57.67 ± 0.38 -84.56 ± 0.64 7.0 57.61 ± 0.38 -85.84 ± 0.68 8.0 57.59 ± 0.38 -86.27 ± 0.69 9.0 57.56 ± 0.38 -86.76 ± 0.65	$E_{\rm cut}$	$E(\mathrm{Ry})$	$\mathcal{E}_c(\mathrm{mRy/N})$					
2.0 59.62 ± 0.41 -45.65 ± 0.39 2.5 58.85 ± 0.38 -60.97 ± 0.71 3.0 58.42 ± 0.38 -69.60 ± 0.76 4.0 57.98 ± 0.38 -78.48 ± 0.64 5.0 57.78 ± 0.38 -82.52 ± 0.70 6.0 57.67 ± 0.38 -84.56 ± 0.64 7.0 57.61 ± 0.38 -85.84 ± 0.68 8.0 57.59 ± 0.38 -86.27 ± 0.69 9.0 57.56 ± 0.38 -86.76 ± 0.65	1.5	60.88 ± 0.38	-20.41 ± 0.85					
2.5 58.85 ± 0.38 -60.97 ± 0.71 3.0 58.42 ± 0.38 -69.60 ± 0.76 4.0 57.98 ± 0.38 -78.48 ± 0.64 5.0 57.78 ± 0.38 -82.52 ± 0.70 6.0 57.67 ± 0.38 -84.56 ± 0.64 7.0 57.61 ± 0.38 -85.84 ± 0.68 8.0 57.59 ± 0.38 -86.27 ± 0.69 9.0 57.56 ± 0.38 -86.76 ± 0.65	2.0	59.62 ± 0.41	-45.65 ± 0.39					
3.0 58.42 ± 0.38 -69.60 ± 0.76 4.0 57.98 ± 0.38 -78.48 ± 0.64 5.0 57.78 ± 0.38 -82.52 ± 0.70 6.0 57.67 ± 0.38 -84.56 ± 0.64 7.0 57.61 ± 0.38 -85.84 ± 0.68 8.0 57.59 ± 0.38 -86.27 ± 0.69 9.0 57.56 ± 0.38 -86.76 ± 0.65	2.5	58.85 ± 0.38	-60.97 ± 0.71					
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	3.0	58.42 ± 0.38	-69.60 ± 0.76					
5.0 57.78 ± 0.38 -82.52 ± 0.70 6.0 57.67 ± 0.38 -84.56 ± 0.64 7.0 57.61 ± 0.38 -85.84 ± 0.68 8.0 57.59 ± 0.38 -86.27 ± 0.69 9.0 57.56 ± 0.38 -86.76 ± 0.65	4.0	57.98 ± 0.38	-78.48 ± 0.64					
6.0 57.67 ± 0.38 -84.56 ± 0.64 7.0 57.61 ± 0.38 -85.84 ± 0.68 8.0 57.59 ± 0.38 -86.27 ± 0.69 9.0 57.56 ± 0.38 -86.76 ± 0.65	5.0	57.78 ± 0.38	-82.52 ± 0.70					
7.0 57.61 ± 0.38 -85.84 ± 0.68 8.0 57.59 ± 0.38 -86.27 ± 0.69 9.0 57.56 ± 0.38 -86.76 ± 0.65	6.0	57.67 ± 0.38	-84.56 ± 0.64					
8.0 57.59 ± 0.38 -86.27 ± 0.69 9.0 57.56 ± 0.38 -86.76 ± 0.65	7.0	57.61 ± 0.38	-85.84 ± 0.68					
9.0 57.56 \pm 0.38 -86.76 \pm 0.65	8.0	57.59 ± 0.38	-86.27 ± 0.69					
	9.0	57.56 ± 0.38	-86.76 ± 0.65					

	N = 10, L = 6.95 Bohr			N = 20, L = 8.75 Bohr			
	$E_{HF} = (0.233 \pm 0.064) \text{ Ry}$			$E_{HF} = (0.960 \pm 0.057) \text{ Ry}$			
$E_{\rm cut}$	E(Ry)	$\mathcal{E}_c(\mathrm{mRy/N})$	$E_{\rm cut}$	E(Ry)	$\mathcal{E}_c(\mathrm{mRy/N})$		
1.5	0.187 ± 0.063	-4.56 ± 0.74	1.5	0.768 ± 0.043	-9.63 ± 1.01		
2.0	0.068 ± 0.063	-16.48 ± 0.77	2.0	0.470 ± 0.052	-24.49 ± 0.65		
2.5	-0.021 ± 0.061	-25.34 ± 0.79	2.5	0.222 ± 0.051	-36.93 ± 0.49		
3.0	-0.086 ± 0.064	-31.89 ± 0.78	3.0	0.067 ± 0.043	-44.68 ± 0.84		
4.0	-0.188 ± 0.062	-42.10 ± 0.52	4.0	-0.103 ± 0.043	-53.16 ± 0.87		
5.0	-0.222 ± 0.061	-45.45 ± 0.45	5.0	-0.173 ± 0.045	-56.65 ± 0.74		
6.0	-0.237 ± 0.061	-46.97 ± 0.49	6.0	-0.205 ± 0.044	-58.24 ± 0.73		
7.0	-0.246 ± 0.060	-47.88 ± 0.55	7.0	-0.221 ± 0.045	-59.07 ± 0.75		
8.0	-0.251 ± 0.061	-48.36 ± 0.44	8.0	-0.224 ± 0.045	-59.20 ± 0.77		
9.0	-0.251 ± 0.060	-48.38 ± 0.50	9.0	-0.240 ± 0.044	-59.99 ± 0.82		
	N = 30, L = 10	02 Bohr		N = 40, L = 11	.03 Bohr		
	$E_{HF} = (1.624 \pm 0.024)$	0.099) Ry		$E_{HF} = (2.418 \pm$	0.138) Ry		
$E_{\rm cut}$	E(Ry)	$\mathcal{E}_c(\mathrm{mRy/N})$	$E_{\rm cut}$	E(Ry)	$\mathcal{E}_c(\mathrm{mRy/N})$		
1.5	1.282 ± 0.109	-11.41 ± 0.51	1.5	1.885 ± 0.132	-13.34 ± 0.63		
2.0	0.769 ± 0.104	-28.51 ± 0.35	2.0	1.162 ± 0.142	-31.41 ± 0.45		
2.5	0.410 ± 0.114	-40.46 ± 0.85	2.5	0.620 ± 0.132	-44.95 ± 0.48		
3.0	0.161 ± 0.108	-48.76 ± 0.60	3.0	0.320 ± 0.125	-52.46 ± 0.46		
4.0	-0.081 ± 0.103	-56.84 ± 0.38	4.0	0.009 ± 0.128	-60.24 ± 0.42		
5.0	-0.191 ± 0.105	-60.50 ± 0.48	5.0	-0.151 ± 0.127	-64.24 ± 0.45		
6.0	-0.250 ± 0.103	-62.46 ± 0.34	6.0	-0.228 ± 0.123	-66.16 ± 0.56		
7.0	-0.279 ± 0.104	-63.45 ± 0.47	7.0	-0.261 ± 0.123	-66.97 ± 0.48		
8.0	-0.285 ± 0.101	-63.63 ± 0.41	8.0	-0.279 ± 0.125	-67.43 ± 0.49		
9.0	-0.302 ± 0.103	-64.19 ± 0.42	9.0	-0.289 ± 0.123	-67.70 ± 0.50		
	N = 50, L = 11.	.88 Bohr					
	$E_{HF} = (3.262 \pm 0.00)$	0.115) Ry					
$E_{\rm cut}$	$E(\mathrm{Ry})$	$\mathcal{E}_c(\mathrm{mRy/N})$					
1.5	2.492 ± 0.092	-15.42 ± 0.59					
2.0	1.524 ± 0.116	-34.76 ± 0.29					
2.5	0.908 ± 0.101	-47.09 ± 0.39					
3.0	0.543 ± 0.096	-54.39 ± 0.43					
4.0	0.127 ± 0.101	-62.71 ± 0.37					
5.0	-0.075 ± 0.099	-66.75 ± 0.42					
6.0	-0.142 ± 0.099	-68.08 ± 0.41					
7.0	-0.200 ± 0.099	-69.25 ± 0.41					
8.0	-0.223 ± 0.097	-69.72 ± 0.42					
9.0	-0.246 ± 0.100	-70.17 ± 0.38					

TABLE B.3: E_{cut} dependence of the total energy E and the correlation energy per particle \mathcal{E}_c of jellium with density of $r_s = 2$ for five choice of N, the numbers of electrons. E_{cut} is in unit of E_F .

N = 10, L = 10.42 Bohr			N = 20, L = 13.13 Bohr			
$E_{HF} = (-1.099 \pm 0.030) \text{ Rv}$			$E_{HF} = (-1.846 \pm 0.030) \text{ Ry}$			
$E_{\rm cut}$	E(Ry)	$\mathcal{E}_c(\mathrm{mRy/N})$	$E_{\rm cut}$	E(Ry)	$\mathcal{E}_c(\mathrm{mRy/N})$	
1.5	-1.141 ± 0.029	-4.14 ± 0.69	1.5	-2.010 ± 0.018	-8.19 ± 0.86	
2.0	-1.246 ± 0.029	-14.63 ± 0.68	2.0	-2.257 ± 0.026	-20.54 ± 0.53	
2.5	-1.321 ± 0.026	-22.18 ± 0.75	2.5	-2.465 ± 0.025	-30.93 ± 0.41	
3.0	-1.380 ± 0.030	-28.08 ± 0.62	3.0	-2.600 ± 0.019	-37.70 ± 0.67	
4.0	-1.469 ± 0.030	-36.92 ± 0.37	4.0	-2.750 ± 0.019	-45.19 ± 0.64	
5.0	-1.501 ± 0.028	-40.13 ± 0.40	5.0	-2.817 ± 0.022	-48.53 ± 0.51	
6.0	-1.518 ± 0.027	-41.87 ± 0.50	6.0	-2.842 ± 0.021	-49.78 ± 0.56	
7.0	-1.523 ± 0.028	-42.35 ± 0.35	7.0	-2.867 ± 0.017	-51.05 ± 0.72	
8.0	-1.524 ± 0.028	-42.47 ± 0.39	8.0	-2.873 ± 0.020	-51.34 ± 0.61	
9.0	-1.526 ± 0.028	-42.67 ± 0.39	9.0	-2.879 ± 0.020	-51.63 ± 0.60	
	N = 30, L = 15	.03 Bohr		N = 40, L = 16.	.54 Bohr	
1	$E_{HF} = (-2.614 \pm$	0.044) Ry	1	$E_{HF} = (-3.310 \pm$	0.066) Ry	
$E_{\rm cut}$	E(Ry)	$\mathcal{E}_c(\mathrm{mRy/N})$	$E_{\rm cut}$	E(Ry)	$\mathcal{E}_c(\mathrm{mRy/N})$	
1.5	-2.897 ± 0.052	-9.42 ± 0.39	1.5	-3.745 ± 0.061	-10.87 ± 0.48	
2.0	-3.325 ± 0.048	-23.69 ± 0.26	2.0	-4.337 ± 0.070	-25.66 ± 0.35	
2.5	-3.639 ± 0.058	-34.15 ± 0.70	2.5	-4.786 ± 0.066	-36.90 ± 0.29	
3.0	-3.839 ± 0.051	-40.82 ± 0.38	3.0	-5.062 ± 0.057	-43.79 ± 0.33	
4.0	-4.069 ± 0.048	-48.50 ± 0.35	4.0	-5.342 ± 0.062	-50.79 ± 0.30	
5.0	-4.162 ± 0.049	-51.60 ± 0.36	5.0	-5.497 ± 0.058	-54.66 ± 0.32	
6.0	-4.212 ± 0.048	-53.25 ± 0.29	6.0	-5.546 ± 0.058	-55.90 ± 0.33	
7.0	-4.236 ± 0.046	-54.05 ± 0.24	7.0	-5.578 ± 0.059	-56.70 ± 0.29	
8.0	-4.249 ± 0.048	-54.48 ± 0.28	8.0	-5.606 ± 0.061	-57.39 ± 0.33	
9.0	-4.261 ± 0.047	-54.89 ± 0.28	9.0	-5.612 ± 0.055	-57.55 ± 0.37	
	N = 50, L = 17	.82 Bohr				
1	$E_{HF} = (-3.978 \pm$	0.057) Ry				
$E_{\rm cut}$	$E(\mathrm{Ry})$	$\mathcal{E}_c(\mathrm{mRy/N})$				
1.5	-4.602 ± 0.039	-12.48 ± 0.46				
2.0	-5.377 ± 0.061	-27.97 ± 0.21				
2.5	-5.907 ± 0.046	-38.58 ± 0.32				
3.0	-6.245 ± 0.041	-45.33 ± 0.40				
4.0	-6.626 ± 0.049	-52.96 ± 0.28				
5.0	-6.801 ± 0.046	-56.46 ± 0.35				
6.0	-6.877 ± 0.047	-57.97 ± 0.33				
7.0	-6.909 ± 0.048	-58.62 ± 0.26				
8.0	-6.935 ± 0.045	-59.14 ± 0.33				
9.0	-6.938 ± 0.047	-59.20 ± 0.23				

TABLE B.4: E_{cut} dependence of the total energy E and the correlation energy per particle \mathcal{E}_c of jellium with density of $r_s = 3$ for five choice of N, the numbers of electrons. E_{cut} is in unit of E_F .

N = 10, L = 13.89 Bohr			N = 20, L = 17.50 Bohr				
1	$E_{HF} = (-1.295 \pm 0.018) \text{ Ry}$			$E_{HF} = (-2.317 \pm 0.020) \text{ Ry}$			
$E_{\rm cut}$	E(Ry)	$\mathcal{E}_c(\mathrm{mRy/N})$	$E_{\rm cut}$	E(Ry)	$\mathcal{E}_c(\mathrm{mRy/N})$		
1.5	-1.333 ± 0.017	-3.77 ± 0.63	1.5	-2.457 ± 0.011	-7.00 ± 0.69		
2.0	-1.422 ± 0.018	-12.72 ± 0.63	2.0	-2.668 ± 0.016	-17.53 ± 0.46		
2.5	-1.493 ± 0.016	-19.76 ± 0.61	2.5	-2.852 ± 0.018	-26.74 ± 0.28		
3.0	-1.542 ± 0.018	-24.67 ± 0.52	3.0	-2.967 ± 0.013	-32.51 ± 0.49		
4.0	-1.626 ± 0.017	-33.08 ± 0.44	4.0	-3.120 ± 0.011	-40.13 ± 0.57		
5.0	-1.653 ± 0.015	-35.78 ± 0.42	5.0	-3.164 ± 0.014	-42.34 ± 0.42		
6.0	-1.669 ± 0.016	-37.35 ± 0.34	6.0	-3.193 ± 0.015	-43.77 ± 0.39		
7.0	-1.674 ± 0.015	-37.87 ± 0.44	7.0	-3.220 ± 0.012	-45.12 ± 0.48		
8.0	-1.672 ± 0.015	-37.73 ± 0.40	8.0	-3.216 ± 0.013	-44.95 ± 0.47		
9.0	-1.672 ± 0.016	-37.69 ± 0.35	9.0	-3.222 ± 0.013	-45.24 ± 0.47		
	N = 30, L = 20	.04 Bohr		N = 40, L = 22	.05 Bohr		
1	$E_{HF} = (-3.347 \pm$	0.025) Ry	1	$E_{HF} = (-4.329 \pm$	0.039) Ry		
$E_{\rm cut}$	$E(\mathrm{Ry})$	$\mathcal{E}_c(\mathrm{mRy/N})$	$E_{\rm cut}$	$E(\mathrm{Ry})$	$\mathcal{E}_c(\mathrm{mRy/N})$		
1.5	-3.588 ± 0.031	-8.03 ± 0.35	1.5	-4.700 ± 0.037	-9.28 ± 0.37		
2.0	-3.949 ± 0.028	-20.06 ± 0.22	2.0	-5.205 ± 0.044	-21.91 ± 0.28		
2.5	-4.221 ± 0.036	-29.14 ± 0.59	2.5	-5.590 ± 0.041	-31.54 ± 0.31		
3.0	-4.403 ± 0.033	-35.21 ± 0.48	3.0	-5.822 ± 0.036	-37.32 ± 0.27		
4.0	-4.608 ± 0.029	-42.04 ± 0.27	4.0	-6.102 ± 0.037	-44.34 ± 0.32		
5.0	-4.701 ± 0.030	-45.13 ± 0.31	5.0	-6.233 ± 0.035	-47.61 ± 0.28		
6.0	-4.749 ± 0.029	-46.75 ± 0.36	6.0	-6.273 ± 0.033	-48.62 ± 0.26		
7.0	-4.781 ± 0.028	-47.80 ± 0.27	7.0	-6.334 ± 0.035	-50.15 ± 0.23		
8.0	-4.786 ± 0.026	-47.96 ± 0.27	8.0	-6.334 ± 0.035	-50.14 ± 0.30		
9.0	-4.780 ± 0.027	-47.76 ± 0.21	9.0	-6.334 ± 0.031	-50.14 ± 0.33		
	N = 50, L = 23	.75 Bohr					
1	$E_{HF} = (-5.291 \pm$	0.035) Ry					
$E_{\rm cut}$	$E(\mathrm{Ry})$	$\mathcal{E}_c(\mathrm{mRy/N})$					
1.5	-5.814 ± 0.021	-10.46 ± 0.39					
2.0	-6.495 ± 0.040	-24.09 ± 0.22					
2.5	-6.946 ± 0.026	-33.10 ± 0.28					
3.0	-7.237 ± 0.019	-38.92 ± 0.41					
4.0	-7.583 ± 0.032	-45.85 ± 0.32					
5.0	-7.740 ± 0.028	-48.97 ± 0.30					
6.0	-7.806 ± 0.029	-50.29 ± 0.29					
7.0	-7.860 ± 0.031	-51.39 ± 0.22					
8.0	-7.865 ± 0.028	-51.49 ± 0.28					
9.0	-7.868 ± 0.027	-51.55 ± 0.30					

TABLE B.5: E_{cut} dependence of the total energy E and the correlation energy per particle \mathcal{E}_c of jellium with density of $r_s = 4$ for five choice of N, the numbers of electrons. E_{cut} is in unit of E_F .

N = 10, L = 17.36 Bohr			N = 20, L = 21.88 Bohr			
$E_{HF} = (-1.262 \pm 0.012) \text{ Ry}$			$E_{HF} = (-2.301 \pm 0.014) \text{ Ry}$			
$E_{\rm cut}$	$\mathcal{E}_{\rm cut}$ $E({\rm Ry})$ $\mathcal{E}_{c}({\rm mRy/N})$		$E_{\rm cut}$	E(Ry)	$\mathcal{E}_c(\mathrm{mRy/N})$	
1.5	-1.296 ± 0.012	-3.42 ± 0.59	1.5	-2.423 ± 0.008	-6.09 ± 0.60	
2.0	-1.377 ± 0.012	-11.49 ± 0.53	2.0	-2.610 ± 0.013	-15.43 ± 0.37	
2.5	-1.436 ± 0.010	-17.37 ± 0.69	2.5	-2.771 ± 0.014	-23.49 ± 0.26	
3.0	-1.485 ± 0.012	-22.34 ± 0.44	3.0	-2.874 ± 0.010	-28.62 ± 0.36	
4.0	-1.555 ± 0.014	-29.29 ± 0.39	4.0	-3.004 ± 0.008	-35.15 ± 0.47	
5.0	-1.586 ± 0.011	-32.38 ± 0.32	5.0	-3.059 ± 0.011	-37.88 ± 0.36	
6.0	-1.595 ± 0.009	-33.34 ± 0.42	6.0	-3.082 ± 0.010	-39.02 ± 0.44	
7.0	-1.600 ± 0.011	-33.76 ± 0.31	7.0	-3.102 ± 0.011	-40.03 ± 0.34	
8.0	-1.602 ± 0.010	-34.04 ± 0.34	8.0	-3.113 ± 0.009	-40.61 ± 0.40	
9.0	-1.606 ± 0.010	-34.45 ± 0.32	9.0	-3.108 ± 0.010	-40.31 ± 0.42	
	N = 30, L = 25	.04 Bohr		N = 40, L = 27	.56 Bohr	
1	$E_{HF} = (-3.343 \pm$	0.016) Ry	1	$E_{HF} = (-4.349 \pm$	0.027) Ry	
$E_{\rm cut}$	E(Ry)	$\mathcal{E}_c(\mathrm{mRy/N})$	$E_{\rm cut}$	E(Ry)	$\mathcal{E}_c(\mathrm{mRy/N})$	
1.5	-3.552 ± 0.021	-6.95 ± 0.29	1.5	-4.665 ± 0.025	-7.91 ± 0.35	
2.0	-3.869 ± 0.020	-17.54 ± 0.23	2.0	-5.108 ± 0.032	-18.98 ± 0.26	
2.5	-4.115 ± 0.027	-25.72 ± 0.54	2.5	-5.464 ± 0.027	-27.88 ± 0.30	
3.0	-4.282 ± 0.024	-31.30 ± 0.40	3.0	-5.656 ± 0.024	-32.68 ± 0.26	
4.0	-4.468 ± 0.021	-37.49 ± 0.37	4.0	-5.898 ± 0.026	-38.73 ± 0.31	
5.0	-4.547 ± 0.019	-40.13 ± 0.28	5.0	-6.029 ± 0.026	-42.01 ± 0.25	
6.0	-4.594 ± 0.019	-41.69 ± 0.35	6.0	-6.081 ± 0.029	-43.30 ± 0.26	
7.0	-4.625 ± 0.016	-42.73 ± 0.24	7.0	-6.119 ± 0.024	-44.26 ± 0.25	
8.0	-4.633 ± 0.017	-43.00 ± 0.22	8.0	-6.137 ± 0.020	-44.71 ± 0.27	
9.0	-4.633 ± 0.017	-43.01 ± 0.24	9.0	-6.129 ± 0.026	-44.50 ± 0.25	
	N = 50, L = 29	.69 Bohr				
1	$E_{HF} = (-5.340 \pm$	0.025) Ry				
$E_{\rm cut}$	$E(\mathrm{Ry})$	$\mathcal{E}_c(\mathrm{mRy/N})$				
1.5	-5.784 ± 0.014	-8.86 ± 0.32				
2.0	-6.372 ± 0.028	-20.64 ± 0.20				
2.5	-6.785 ± 0.018	-28.89 ± 0.27				
3.0	-7.028 ± 0.017	-33.75 ± 0.37				
4.0	-7.377 ± 0.021	-40.74 ± 0.35				
5.0	-7.526 ± 0.019	-43.70 ± 0.38				
6.0	-7.568 ± 0.022	-44.56 ± 0.32				
7.0	-7.622 ± 0.014	-45.64 ± 0.29				
8.0	-7.654 ± 0.027	-46.27 ± 0.27				
9.0	-7.653 ± 0.019	-46.25 ± 0.25				

TABLE B.6: E_{cut} dependence of the total energy E and the correlation energy per particle \mathcal{E}_c of jellium with density of $r_s = 5$ for five choice of N, the numbers of electrons. E_{cut} is in unit of E_F .

APPENDIX C

Technical Details of the $BiScO_3$ Calculation

TABLE C.1: Structural data of $BiScO_3$ cubic, tetragonal and rhombohedral structure (in unit of Bohr). The reduced coordinates of the tetragonal and rhombohedral structures are given as the difference from the ideal cubic positions. Structures are from Ref. [75].

	cubic	tetragonal	rhombohedral
Real space primitive vector			
R	$\left(\begin{array}{rrrr} a_1 & 0 & 0 \\ 0 & a_1 & 0 \\ 0 & 0 & a_1 \end{array}\right)$	$\left(\begin{array}{rrrr} a_2 & 0 & 0 \\ 0 & a_2 & 0 \\ 0 & 0 & c_2 \end{array}\right)$	$\left(\begin{array}{rrrr} a_3 & b_3 & b_3 \\ b_3 & a_3 & b_3 \\ b_3 & b_3 & a_3 \end{array}\right)$
	$a_1 = 7.533$	$a_2 = 7.11284$ $c_2 = 9.14$	$a_3 = 7.7778225$ $b_3 = 0.0941625$
Reduced c	oordinates of the a	atoms in the prim	itive cell
Bi	(0.0,0.0,0.0)	(0, 0, 0)	$(\delta_{r1},\delta_{r1},\delta_{r1})$
Sc	(0.5,0.5,0.5)	$(0, 0, \delta_{t1})$	$(\delta_{r2},\delta_{r2},\delta_{r2})$
O 1	(0.0,0.5,0.5)	$(0, 0, \delta_{t2})$	$(\delta_{r3},\delta_{r4},\delta_{r4}$)
O 2	(0.5,0.0,0.5)	$(0, 0, \delta_{t2})$	$(\delta_{r4}, \delta_{r3}, \delta_{r4})$
O 3	(0.5,0.5,0.0)	$(0, 0, \delta_{t3})$	$(\delta_{r4}, \delta_{r4}, \delta_{r3})$
		$\delta_{t1} = 0.073$	$\delta_{r1} = 0.0849720646$
		$\delta_{t2} = 0.229$	$\delta_{r2} = 0.0000032952$
		$\delta_{t3} = 0.177$	$\delta_{r3} = -0.0183029402$
			$\delta_{r4} = -0.0547217723$

k-point	w	QMC	DFT	FS DFT
Cubic				
$(0\ 0\ 0)$		-4477.17 ± 0.25	-4485.79	-4494.32
TBC $2 \times 2 \times 2$				
$(1/4 \ 1/4 \ 1/4)$	1	-4488.21 ± 0.07	-4494.02	-4502.58
TBC $4 \times 4 \times 4$				
$(1/8 \ 1/8 \ 1/8)$	1/8	-4483.20 ± 0.34	-4488.94	-4497.49
$(3/8\ 1/8\ 1/8)$	1/8	-4486.08 ± 0.25	-4491.65	-4500.21
$(3/8 \ 3/8 \ 1/8)$	1/8	-4490.66 ± 0.18	-4496.46	-4505.04
$(3/8 \ 3/8 \ 3/8)$	1/8	-4495.16 ± 0.31	-4501.30	-4509.88
Tetragonal				
$(0\ 0\ 0)$		-4482.57 ± 0.34	-4493.32	-4501.26
TBC $2 \times 2 \times 2$				
$(1/4 \ 1/4 \ 1/4)$	1	-4488.64 ± 0.09	-4495.26	-4503.22
TBC $4 \times 4 \times 4$				
$(1/8 \ 1/8 \ 1/8)$	1/8	-4487.37 ± 0.33	-4493.94	-4501.90
$(3/8\ 1/8\ 1/8)$	1/4	-4488.48 ± 0.27	-4494.90	-4502.86
$(3/8 \ 3/8 \ 1/8)$	1/8	-4490.66 ± 0.38	-4496.75	-4504.73
$(1/8 \ 1/8 \ 3/8)$	1/8	-4486.82 ± 0.36	-4493.71	-4501.66
$(3/8\ 1/8\ 3/8)$	1/4	-4489.11 ± 0.33	-4495.60	-4503.56
$(3/8 \ 3/8 \ 3/8)$	1/8	-4490.12 ± 0.23	-4497.71	-4505.69
Rhombohedral				
$(0\ 0\ 0)$		-4480.17 ± 0.36	-4490.18	-4498.03
TBC $2 \times 2 \times 2$				
$(1/4 \ 1/4 \ 1/4)$	1/4	-4489.26 ± 0.08	-4495.57	-4503.43
$(-1/4 \ 1/4 \ 1/4)$	3/4	-4489.99 ± 0.29	-4495.64	-4503.51
TBC $4 \times 4 \times 4$				
$(1/8 \ 1/8 \ 1/8)$	1/32	-4485.52 ± 0.33	-4492.04	-4499.91
$(3/8\ 1/8\ 1/8)$	3/32	-4487.34 ± 0.31	-4494.31	-4502.18
$(-3/8 \ 1/8 \ 1/8)$	3/32	-4488.36 ± 0.37	-4494.24	-4502.11
$(-1/8 \ 1/8 \ 1/8)$	3/32	-4485.70 ± 0.39	-4491.89	-4499.76
$(3/8 \ 3/8 \ 1/8)$	3/32	-4490.86 ± 0.26	-4496.97	-4504.85
$(-3/8 \ 3/8 \ 1/8)$	3/16	-4490.77 ± 0.30	-4497.03	-4504.92
$(-1/8 \ 3/8 \ 1/8)$	3/16	-4487.82 ± 0.38	-4494.30	-4502.17
(-3/8 - 3/8 1/8)	3/32	-4491.03 ± 0.24	-4497.05	-4504.93
$(3/8 \ 3/8 \ 3/8)$	1/32	-4492.62 ± 0.25	-4499.46	-4507.35
$(-3/8 \ 3/8 \ 3/8)$	3/32	-4492.39 ± 0.24	-4499.58	-4507.48

TABLE C.2: Calculated energies of $BiScO_3$ cubic, tetragonal and rhombohedral structures. All energies are given in eV. The **k**-points are given in reduced coordinates. w is the weight of each **k**-point

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VITA

Hendra Kwee

Hendra Kwee was born on August 8, 1979 in Palembang, South Sumatra, Indonesia. He began his formal education in 1985 at Baptist Elementary School in Palembang. In 1991, he entered Xaverius Maria Middle School, and in 1994 he entered Xaverius I High School, both also in Palembang. In the last year of his study, he had the opportunity to represent his country as one of the participants in the XXVIII International Physics Olympiad in Sudbury, Canada and won an Honorable Mention. In the same year, 1997, he started his undergraduate education at Institut Teknology Bandung, in Bandung, West Java, Indonesia. He pursued his interest in science by studying physics. In February 2001 he graduated with Cum Laude honorable mention. Afterward, for the next four months, he worked as a trainer for the Indonesian Physics Olympiad Team. He entered the College of William and Mary in Williamsburg, Virginia in the fall of 2001 to study in the physics graduate program. In the fall of 2002, he joined Dr. Henry Krakauer and Dr. Shiwei Zhang's computational condensed matter physics group. He defended his thesis on the correction of finite size errors in many-body electronic structure calculations on October 30, 2007.