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Theoretical Study of Momentum Dependent Local-Ansatz Variational Approach to Correlated Electron System

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Doctoral Thesis of Philosophy

**Theoretical Study of Momentum Dependent
Local-Ansatz Variational Approach to Correlated
Electron System**

September 2013

By

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Graduate School of Engineering and Science
University of the Ryukyus**

Supervisor : Professor Yoshiro Kakehashi

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A dissertation submitted to the Graduate School of
Engineering and Science, University of the Ryukyus,
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

**Department of Physics
Graduate School of Engineering and Science
University of the Ryukyus**

Supervisor : Professor Yoshiro Kakehashi

We, the undersigned, hereby, declare that we have read this thesis and we have attended the thesis defense and evaluation meeting. Therefore, we certify that, to the best of our knowledge this thesis is satisfactory to the scope and quality as a thesis for the degree of Doctor of Philosophy in Physics, Graduate School of Engineering and Science, University of the Ryukyus.

THESIS REVIEW & EVALUATION COMMITTEE MEMBERS

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Abstract

We propose in this thesis a local-ansatz wavefunction approach with momentum dependent variational parameters (momentum-dependent local-ansatz = MLA) in order to describe correlated electrons in the ground state. The idea is to choose the best local basis set obtained from the two-particle excited states in the momentum representation by projecting out those states onto the local subspace and by controlling the amplitudes of the excited states in the momentum space. Within a single-site approximation we calculate the ground-state energy and derive a self-consistent equation for the variational parameters by minimizing the energy. We obtain an approximate solution which interpolates between the weak Coulomb interaction limit and the atomic limit. We further developed the theory to obtain the best value of the variational parameter self-consistently.

In order to verify the validity of the MLA, we perform the numerical calculations for the non-half-filled band as well as half-filled band in the Hubbard model on the hypercubic lattice in infinite dimensions. We confirm that the self-consistent scheme significantly improves the correlation energy, the momentum distribution and quasiparticle weight. We also demonstrate that the theory improves the standard variational methods such as the local-ansatz approach (LA) and the Gutzwiller wavefunction approach (GW); the ground-state energy in the MLA is lower than those of the LA and the GW in the weak and intermediate Coulomb interaction regimes. The double occupation number is shown to be suppressed as compared with the LA. Calculated momentum distribution functions show a clear momentum dependence, which is qualitatively different from those of the LA and the GW. We also obtained the critical Coulomb interaction $U_{c2} = 3.40$ at which effective mass of electrons diverges. The value is comparable to the best value $U_{c2} = 4.10$ based on the numerical renormalization group method.

We propose an improved MLA wavefunction which can describe the strong Coulomb interaction regime by modifying the starting wavefunction from the Hartree-Fock (HF) type to an alloy-analogy (AA) type wavefunction. Numerical results based on the half-filled band Hubbard model on the hypercubic lattice in infinite dimensions show that the MLA-AA wavefunction yields the ground-state energy lower than the GW in the strong Coulomb interaction regime. The MLA-AA yields the metal-insulator transition at $U_c = 3.26$. Calculated double occupation number is smaller than the result of the GW in the metallic regime, and is finite in the insulator regime as it should be, while the GW gives the Brinkman-Rice atom. Furthermore, the momentum distribution of MLA-AA shows a momentum-dependence in both the metallic and insulator regions, on the other hand the GW as well as the LA gives the constant value below and above the Fermi level.

Finally, we generalize the variational theory of the MLA by introducing a hybrid (HB) wavefunction as a starting wavefunction, whose potential can flexibly change from the HF type to the AA type by varying a weighting factor from zero to one. The MLA-HB scheme yields the ground-state energy lower than that of the GW in the whole Coulomb interaction regime, and shows the first-order transition at $U_c = 2.81$ from the Fermi liquid to the non-Fermi liquid, indicating the metal-insulator transition. The MLA-HB reduces the double occupancy more effectively than the GW and the LA in the weak U region. The resulting double occupancy jumps at the transition point $U_c = 2.81$, and again monotonically decreases with increasing U . Finally the momentum distribution of MLA-HB shows a distinct momentum dependence, which is qualitatively different from that of the GW.

DEDICATED
TO MY SONS
FARHAN & FARDIN

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The Author

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Chapter 1

Introduction

Electron-electron interactions play an important role in condensed matter physics. In a simple system, they are taken into account as a mean-field potential of an independent-particle system. In the Hartree-Fock (HF) approximation, for example, one replaces the Coulomb interactions between electrons by the Coulomb and exchange potentials for an electron. Solving the one-electron Schrödinger equation and putting electrons one by one from the bottom of the lowest level of one-electron energy eigen values up to the Fermi level according to the Pauli exclusion principle, one can construct the ground state of the system. In solids, the energy eigen values form the so-called energy bands. Because of the formation of band gaps at the Brillouin zone boundary, one can explain the basic properties of metal, semiconductor, and insulator (*i.e.*, band insulator) on the basis of the one-electron picture. The independent-particle approximation seems to be applicable especially to the conduction electrons in simple metals such as the alkali metals (Li, Na, K), and alkaline earth metals (Ca, Sr, Ba). But for the systems containing 3d or 4f unfilled shell, it is known that there are various phenomena which cannot be explained by the independent-particle picture, because the electrons of these systems are considerably localized even in solids, and move in a small area with strong electron-electron interactions.

The cohesive energies of 4d and 5d transition metals, for example, are much greater than in the simple metals and follow a roughly parabolic variation as a function of the d electron filling number. In the 3d transition metals, on the other hand, the parabolic behavior is known to break down, and show a deep minimum at Mn. Friedel pointed out that the parabolic behavior of 4d and 5d series is explained by the band energy gain due to d electrons, while the minimum behavior in the 3d series cannot be explained even if the effects of electron-electron interaction are taken into account by means of the HF approximation. In order to explain the behavior of the cohesive energy of 3d transition metals, one has to take into account the energy which is missing in the HF approximation. The latter is called the correlation energy, and is caused by electron correlations.

Electron correlations also play an important role in the stability of ferromagnetism. The HF approximation overestimates the magnetic energy gain due to spin polarization, because it neglects the spin fluctuations in the residual interactions. This means that the ferromagnetism is artificially stabilized in the HF approximation. If we apply the HF approximation to the real elements, most of the elements in solids are known to show the ferromagnetism. This is not consistent with the experimental data; experimentally there are only several elements showing the ferromagnetism. The spin fluctuations should destroy the most of the ferromagnetic order obtained by the HF approximation when electron correlations are taken into account.

The third example showing the failure of the HF approximation is found in the Curie temperature (T_C) and associated susceptibility. The HF approximation overestimates the magnetic energy

and does not produce the magnetic entropy as found in the Heisenberg model because of the neglect of spin fluctuations. Detailed analysis based on the HF approximation shows that the Curie temperatures are overestimated by a factor of ten (see Table 1.1) and the susceptibility does not follow the Curie-Weiss law above T_C [1, 2]. In order to obtain the right results one has to take into account the spin fluctuations at finite temperatures.

Table 1.1: The Curie temperatures T_C for Fe, Co, and Ni calculated by the HF approximation [1, 2]. The experimental data (Expt.) are shown on the bottom line.

| T_C (K) | Fe | Co | Ni |
|-----------|-------|-------|------|
| HF | 12200 | 12100 | 4940 |
| Expt. | 1040 | 1388 | 630 |

The metal-insulator transition in transition metal oxides is one of the oldest problems of electron correlations. Mott considered the electronic structure of NiO. The material has the NaCl structure, so that the unit cell contains one Ni atom, and one O atom. The electron configuration of the Ni²⁺ (O⁸) atom is given by $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$ ($1s^2 2s^2 2p^4$). The oxygen atoms are considered to form a closed shell in the compound taking electrons from Ni atoms, so that we have $Ni^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$ and $O^{2-} = 1s^2 2s^2 2p^6$. In this case, the Fermi level should be on the d bands according to the band theory. Thus, we can expect a metal because the 5-fold d bands overlap each other in general. This feature has been verified in the band calculations as shown in Fig. 1.1. The experimental data however indicate that NiO is an insulator.

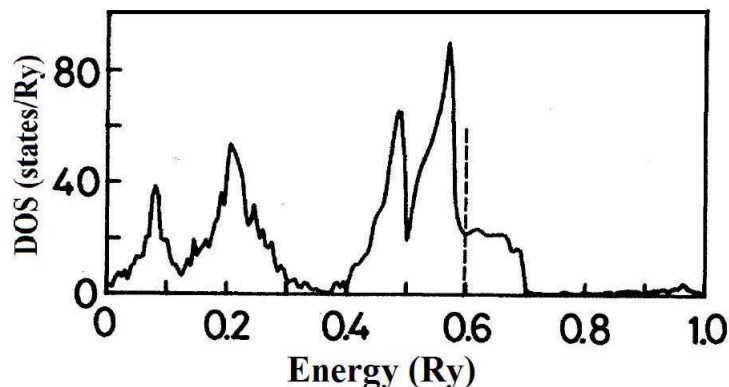


Figure 1.1: Density of states (DOS) of NiO in the paramagnetic state obtained by the band calculation [3]. The vertical dashed line shows the Fermi level.

In order to explain the many-body phenomena mentioned above, various theories of electron correlations have been developed so far. These theories are based on the variational method, the Green function techniques [4], as well as many numerical techniques such as the exact diagonalization method [5] and the Monte-Carlo method [6]. The variational approach is one of the simplest methods among them and has been applied to many systems as a practical tool. Although the variational approach is limited to the ground state, there are various advantages as follows. First, the

method is simple and intuitive, so that one can construct a correlated wavefunction according to a physical picture to the problem. Second, the wavefunction of the correlated state is directly given, so that one can obtain any physical quantity. Third, one could systematically improve the wavefunction by adding the higher-order operators for correlations. Finally, it is possible to perform the first-principle calculation using more realistic Hamiltonian because of its simplicity.

The Gutzwiller wavefunction (GW) is one of the basic wavefunctions, because of its conceptual simplicity and applicability to realistic systems [7, 8, 9]. Assume that the Hamiltonian of the system is given by the single-band Hubbard model which takes into account the on-site Coulomb interaction U on the same orbital. When the Coulomb repulsion U is large, the double occupancy on the same orbital should be suppressed to avoid the energy loss due to the Coulomb repulsion U [10, 11, 12]. The HF wavefunction does not describe such correlations because of the independent motion of electrons. Gutzwiller proposed a trial wavefunction which controls the probability amplitudes of doubly occupied states in the HF wavefunction, by making use of a projection operator $\Pi_i(1 - (1 - g)\hat{n}_{i\uparrow}\hat{n}_{i\downarrow})$. Here $\hat{n}_{i\sigma}$ is the number operator for an electron on site i with spin σ , variational parameter g reduces the amplitudes of doubly occupied states on local orbitals. Stollhoff and Fulde [13, 14, 15] proposed a method called the local-ansatz approach (LA), which is simpler than the GW in treatment. The LA wavefunction takes into account the states created by local two-particle operators such as the residual Coulomb interactions $\{O_i\} = \{\delta\hat{n}_{i\uparrow}\delta\hat{n}_{i\downarrow}\}$. Here $\delta\hat{n}_{i\sigma} = \hat{n}_{i\sigma} - \langle\hat{n}_{i\sigma}\rangle_0$, $\langle\hat{n}_{i\sigma}\rangle_0$ being the average electron number on site i with spin σ in the HF approximation. The theory has been applied to many systems such as molecules, transition metals, polyacetylene, transition metal oxides and semiconductors [16, 17].

Though the GW and the LA are applicable for various correlated electron systems, they are not sufficient for the description of correlations from the weak to the strong interaction regimes. Indeed, the Hilbert space expanded by the local operators is not sufficient to characterize precisely the weakly-correlated states; the LA does not reduce to the second-order perturbation theory in the weak correlation limit. The same difficulty also arises for the GW even in infinite dimensions. Moreover, in the strong Coulomb interaction regime, the GW yields the Brinkman-Rice atom (*i.e.*, no charge fluctuation on an atom) instead of the insulator solid in infinite dimensions [18].

The GW does not take into account exactly the intersite correlations. The variational wavefunction proposed by Jastrow [19] describes the correlations; $|\psi_J\rangle = \exp[\sum_i \sum_j f_{ij} \hat{n}_i \hat{n}_j] |\phi_0\rangle$. Here $|\phi_0\rangle$ represents the ground-state of non-interacting fermions, $f_{ij} = \int d^3x d^3x' |\varphi_i(\mathbf{r})|^2 |\varphi_j(\mathbf{r}')|^2 f(\mathbf{r} - \mathbf{r}')$ is the variational parameters depending on sites i and j , and $\hat{n}_i = \hat{n}_{i\uparrow} + \hat{n}_{i\downarrow}$ is the charge density operator on site i . Note that $\varphi_i(\mathbf{r})$ denotes the atomic wavefunction on site i and the function $f(\mathbf{r} - \mathbf{r}')$ is a variational function of the displacement $\mathbf{r} - \mathbf{r}'$. The wavefunction $|\psi_J\rangle$ describes the intersite long-range density-density correlations. However, the applications are limited to the weakly correlated systems and the low-dimensional systems.

Baeriswyl, on the other hand, proposed a wavefunction called Baeriswyl wavefunction (BW) which accurately describes electron correlations in the strong Coulomb interaction regime [20, 21, 22, 23]. It is constructed by applying a hopping operator \hat{T} onto the atomic wavefunction $|\Psi_\infty\rangle$; $|\Psi_{\text{BW}}\rangle = e^{-\eta\hat{T}}|\Psi_\infty\rangle$. Here $\hat{T} = -\sum_{i,j,\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma}$ is the kinetic energy operator, t_{ij} denotes the transfer integral between sites i and j , $a_{i\sigma}^\dagger$ ($a_{i\sigma}$) being the creation (annihilation) operator for an electron on site i with spin σ . The operator $e^{-\eta\hat{T}}$ with a variational parameter η describes electron hopping from the atomic state and suppresses the configurations with high kinetic energy. The BW describes well the insulator state in the strong correlation regime. However, it is not easy to describe the metallic state from this viewpoint.

The purpose of this thesis is to propose a new local-ansatz wavefunction with momentum de-

pendent variational parameters (MLA) to overcome the difficulties mentioned above, *i.e.*, to obtain the correct results in both the weak and strong U limit, and to interpolate the correlated electron state between the two limits. On the basis of the Hubbard model and the MLA we calculate various physical quantities *i.e.*, the ground state energy, the double occupation number, the momentum distribution as well as the quasiparticle weight, and demonstrate that the MLA overcomes both the GW and the LA.

In the MLA [24, 25, 26], we consider two-particle operators in the momentum space with momentum dependent parameters and project them onto the local orbitals. With use of such local operators $\{\tilde{O}_i\}$, we construct the MLA wavefunction as $|\Psi_{\text{MLA}}\rangle = \prod_i (1 - \tilde{O}_i)|\phi_0\rangle$. Here $|\phi_0\rangle$ is the HF wavefunction and i denotes sites of atoms. The best local basis set is chosen by controlling the variational parameters in the momentum space. Using the variational principle, we determine the momentum-dependent variational parameters. The ground-state energy is obtained analytically from our wavefunction, and agrees with the result of the second-order perturbation theory in the weak interaction limit, and reduces to the correct atomic limit. We demonstrate that the MLA approach much improves the GW as well as the LA in the weak and the intermediate Coulomb interaction regimes.

In order to describe the correlations in the strong Coulomb interaction regime, we propose in the next step an improved MLA wavefunction [27], which starts from the alloy-analogy (AA) wavefunction instead of the HF one. We call the wavefunction the MLA-AA. The concept of the AA approximation can be traced back to Hubbard's original work on electron correlations [12]. He considered that electrons move slowly from site to site in the strong Coulomb interaction regime, so that an electron on a site with (without) opposite-spin electron on the same site feels a potential $\epsilon_0 + U$ (ϵ_0), where ϵ_0 and U denote the atomic level and the on-site Coulomb interaction parameter, respectively. The AA wavefunction is the ground-state wavefunction for an independent-particle Hamiltonian with such two kind of random potentials. We found numerically that the MLA-AA theory describes the strongly correlated regime reasonably, and can go beyond the GW in the strong Coulomb interaction regime.

We propose in the next step a new MLA wavefunction [28] which describes reasonably the whole Coulomb interaction regime on the same footing. We construct a hybrid (HB) wavefunction and make use of it as the starting wavefunction for the MLA. The HB wavefunction is defined by the ground-state of the independent-particle Hamiltonian with a HB potential consisting of the HF potential with a weight $1 - w$ and the AA potential with a weight w , so that the wavefunction can vary from the HF type to the AA one via the new variational parameter w . Hereafter we call the new wavefunction the MLA-HB. On the basis of the numerical results of calculations for the half-filled band Hubbard model, we will clarify the validity of our theory, and demonstrate that the MLA-HB much improves both the GW and the LA, and describes electron correlations from the weak to the strong Coulomb interaction regime.

The dissertation is organized as follows. In the following chapter we describe the single-band Hubbard model to investigate electron correlations in solids and the fundamentals of the HF approximation to the Hubbard model. We also describe the key concept of the variational method and introduce the basic wavefunctions such as the GW as well as the LA. In Chapter 3, we construct the MLA wavefunction on the basis of the HF wavefunction. We obtain the ground-state energy within a single-site approximation (SSA) and derive the self-consistent equation for the momentum-dependent variational parameters. We develop a method to obtain the best value of variational parameters solving the equation. To examine the validity of the MLA wavefunction we present the results of numerical calculations for the half-filled band as well as non-half-filled band

Hubbard model on the hypercubic lattice in infinite dimensions. We verify that the MLA approach improves both the LA and the GW in the weak and the intermediate Coulomb interaction regimes.

The concept of the AA Hamiltonian and the wavefunction are presented in Chapter 4. We describe the correlated MLA-AA wavefunction which starts from the AA wavefunction. We obtain the ground-state energy within the SSA and derive the self-consistent equation for the variational parameters as well as its solution. We present the numerical results for the half-filled band Hubbard model in infinite dimensions. We discuss the ground-state energy, the double occupation number, and the momentum distribution. It is observed that the MLA-AA theory describes the strongly correlated regime reasonably, and thus the MLA-AA + MLA-HF can go beyond the GW in both the weak and the strong Coulomb interaction regimes.

In Chapter 5, we introduce the HB Hamiltonian as well as the HB wavefunction. We will examine the properties of the HB wavefunction, calculating the ground-state energy, the double occupation number and the momentum distribution in infinite dimensions. Next we present the correlated MLA-HB wavefunction which starts from the HB wavefunction. We obtain the ground-state energy within the SSA, and derive the self-consistent equation for the momentum dependent variational parameters and its solution. We present our results of numerical calculations for the half-filled band Hubbard model in infinite dimensions. We discuss the ground-state energy, the double occupation number, the momentum distribution, and the quasiparticle weight as a function of the Coulomb interaction energy parameter. We verify that the MLA-HB approach improves both the GW and the LA in the whole Coulomb interaction regime. In particular, we demonstrate that the momentum distribution calculated by the MLA-HB shows a distinct momentum dependence, and is qualitatively different from those obtained by the GW and the LA which show the constant values below and above the Fermi level. The last Chapter 6 is devoted to summary and discussions. We discuss our numerical results in comparison with other methods. We also discuss the further developments of the theory.

Chapter 2

Hamiltonian and Wavefunction Method

2.1 Hubbard model

The Hubbard model [10, 11] is a basic model Hamiltonian for electrons in solids. It is the simplest model in which electrons hop from site to site with on-site Coulomb repulsion energy. The kinetic energy tends to delocalize electrons, while the on-site Coulomb interaction tends to localize electrons. The model is considered to describe the metal-insulator transition, the magnetism, as well as the superconductivity in the strongly correlated electron system. In this section we derive the Hubbard model from the basic Hamiltonian.

The Hamiltonian of a solid is given in the second quantization as follows:

$$H = \int \sum_{\sigma} \Psi_{\sigma}^{\dagger}(\mathbf{r}) \hat{h} \Psi_{\sigma}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \sum_{\sigma\sigma'} \int \Psi_{\sigma}^{\dagger}(\mathbf{r}) \Psi_{\sigma'}^{\dagger}(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \Psi_{\sigma'}(\mathbf{r}') \Psi_{\sigma}(\mathbf{r}) d\mathbf{r} d\mathbf{r}'. \quad (2.1)$$

Here $\Psi_{\sigma}(\mathbf{r})$ denotes the field operator for the spin σ in the Fock space and \hat{h} is the one electron Hamiltonian. Let us assume that N atoms are condensed and form a solid. When atomic distance is large enough the overlaps of the atomic wavefunction are small and electrons are bound around each atom. Then, one-electron energy eigen-function of solids is considered to be a superposition of eigen-function of each atom. According to the tight-binding approximation, one electron eigen state $\psi_k(\mathbf{r})$ is obtained by the linear combination of local atomic orbitals.

$$\psi_k(\mathbf{r}) = \sum_i \phi_i(\mathbf{r} - \mathbf{R}_i) \langle i|k\rangle. \quad (2.2)$$

Here we considered the electrons in the unfilled shells and assumed one orbital on each atom. $\phi_i(\mathbf{r} - \mathbf{R}_i)$ denotes the atomic orbital of the atom at \mathbf{R}_i .

Therefore, one can expand the field operator $\Psi_{\sigma}(\mathbf{r})$ in the second quantization by means of local orbitals $\{\phi_i\}$, namely,

$$\Psi_{\sigma}(\mathbf{r}) = \sum_k a_{k\sigma} \psi_k(\mathbf{r}) = \sum_i a_{i\sigma} \phi_i(\mathbf{r}), \quad (2.3)$$

$$\Psi_{\sigma}^{\dagger}(\mathbf{r}) = \sum_k a_{k\sigma}^{\dagger} \psi_k^*(\mathbf{r}) = \sum_i a_{i\sigma}^{\dagger} \phi_i^*(\mathbf{r}). \quad (2.4)$$

Here $\{a_{k\sigma}, a_{k'\sigma'}^{\dagger}\} = \delta_{kk'} \delta_{\sigma\sigma'}$, and $\{a_{k\sigma}, a_{k'\sigma'}\} = \{a_{k\sigma}^{\dagger}, a_{k'\sigma'}^{\dagger}\} = 0$. We assume that the local orbitals are orthogonal to each other. Using the orthonormal property of $\{\phi_i\}$, we obtain $a_{i\sigma} =$

$\sum_k a_{k\sigma} \langle i|k \rangle$, $a_{i\sigma}^\dagger = \sum_k a_{k\sigma}^\dagger \langle i|k \rangle^*$. The operators have the same commutation relations as in the case of $\{a_{k\sigma}\}, \{a_{k\sigma}^\dagger\}$. Therefore, $a_{i\sigma}^\dagger (a_{i\sigma})$ denotes the creation (annihilation) operator for an electron on site i with spin σ . Then the quantity $n_{i\sigma} = a_{i\sigma}^\dagger a_{i\sigma}$ expresses the electron density operator on site i for spin σ .

The Hamiltonian with use of localized orbitals is obtained by substituting the field operator $\Psi_\sigma(\mathbf{r})$ in Eqs. (2.3) and (2.4) into Eq. (2.1).

$$H = H_0 + H_I, \quad (2.5)$$

$$H_0 = \sum_{ij\sigma\sigma'} \langle i|\hat{h}|j \rangle a_{i\sigma}^\dagger a_{j\sigma'}, \quad (2.6)$$

$$H_I = \frac{1}{2} \sum_{i_1, i_2, i_3, i_4, \sigma, \sigma'} \left\langle i_1 i_2 \left| \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \right| i_3 i_4 \right\rangle a_{i_1\sigma}^\dagger a_{i_2\sigma'}^\dagger a_{i_3\sigma'} a_{i_4\sigma}. \quad (2.7)$$

The matrix element in the Hamiltonian H_0 is given by $\langle i|\hat{h}|j \rangle = (\mathbf{H})_{ij} = \epsilon_0 \delta_{ij} + t_{ij}(1 - \delta_{ij})$. Here ϵ_0 is the atomic level, t_{ij} is the transfer integral between sites i and j . Therefore, the non-interacting part H_0 is given by

$$H_0 = \sum_{i\sigma} \epsilon_0 n_{i\sigma} + \sum_i \sum_{j \neq i} \sum_{\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma}. \quad (2.8)$$

In the interaction part H_I , the intra-atomic Coulomb integral ($i_1 = i_2 = i_3 = i_4$) should be much larger than the others. Therefore, we only take into account the intra-atomic Coulomb interaction.

$$U_i = \left\langle ii \left| \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \right| ii \right\rangle = \int d\mathbf{r} d\mathbf{r}' \frac{e^2 \phi_i^*(\mathbf{r} - \mathbf{R}_i) \phi_i^*(\mathbf{r}' - \mathbf{R}_i) \phi_i(\mathbf{r}' - \mathbf{R}_i) \phi_i(\mathbf{r} - \mathbf{R}_i)}{|\mathbf{r} - \mathbf{r}'|}. \quad (2.9)$$

This is called the intra-atomic Coulomb energy parameter. The interaction part of the Hamiltonian H_I is then written as

$$H_I = \sum_i U_i n_{i\uparrow} n_{i\downarrow}. \quad (2.10)$$

Therefore, the Hamiltonian for many-electron system with use of the local orbitals is given as follows:

$$H = H_0 + H_I = \sum_{i\sigma} \epsilon_0 n_{i\sigma} + \sum_{ij\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}. \quad (2.11)$$

The Hamiltonian (2.11) is known as the Hubbard model, and was proposed by Gutzwiller and Hubbard independently [7, 8, 9, 10, 11]. The first term describes the atomic energy. The second term is the kinetic energy describing electrons hopping between nearest-neighbor sites i and j . The third term is the on-site Coulomb interaction energy, it goes through all the sites and adds an energy U if the site is doubly occupied. We adopt in the following the Hubbard model for the description of correlated electrons in solid.

2.2 $U = 0$ and $t = 0$ in the Hubbard model

Let us consider first the atomic limit of the Hubbard model to clarify its basic nature. For an atom, we have 4 atomic states: the empty state ($n_\uparrow = 0, n_\downarrow = 0$), the single electron states ($n_\uparrow = 1, n_\downarrow = 0$) and ($n_\uparrow = 0, n_\downarrow = 1$), and the doubly occupied state ($n_\uparrow = 1, n_\downarrow = 1$). Associated energies are given as $0, \epsilon_0, \epsilon_0,$ and $2\epsilon_0 + U$, respectively. In the atomic limit for a solid where $t_{ij} = 0$, electron number n_i on each atom is no longer constant, though the total number of electrons N is given; $N = \sum_{i\sigma} n_{i\sigma}$. The eigenstates are given by $|\Psi\rangle = |\{n_{i\sigma}\}\rangle$, i.e., a set of the electron numbers with spin σ on site i . The eigenenergy for the state is given by

$$E(\{n_{i\sigma}\}) = \sum_i (\epsilon_0 n_i + U n_{i\uparrow} n_{i\downarrow}). \quad (2.12)$$

It should be noted that the energy of the system increases by U when the number of doubly occupied states D is increased by one. The ground-state energy E_0 of the atomic limit is obtained by minimizing the energy with respect to the number of double occupancy in solids. Assume that the number of lattice points is given by L . when $N < L$, the ground-state energy is obtained as $E_0 = \epsilon_0 N$ by choosing $D = 0$. Magnetic moments on sites with an electron are active in this case as shown in Fig. 2.1. Because there are $L!/N!(L-N)!$ electron configurations on the L lattice points, the ground state is $[2^N L!/N!(L-N)!]$ -fold degenerate.

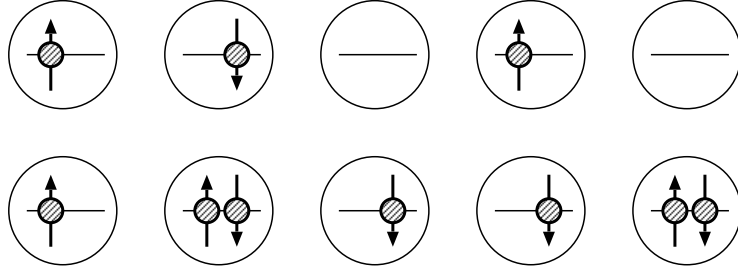


Figure 2.1: Electron configurations for less than half-filling (upper figure) and for more than half-filling (lower figure) in the atomic limit

At the half filling, all the atoms are occupied by an electron so that spin degrees of freedom by 2^N remain; the degenerated wave functions are given by $|1s_{1z} 1s_{2z} 1s_{3z} \cdots\rangle$ when the wave function $|\{n_{i\sigma}\}\rangle$ is written as $|n_1 s_{1z} n_2 s_{2z} n_3 s_{3z} \cdots\rangle$ by using the charge $n_i = n_{i\uparrow} + n_{i\downarrow}$ and the spin $s_{iz} = (n_{i\uparrow} - n_{i\downarrow})/2$.

When the electron number N is larger than L , it is no longer possible to keep $D = 0$; the minimum value of D is given by $D = N - L$. The ground state energy is then given by $E_0 = \epsilon_0 N + U(N - L)$. The ground state is $[2^{2L-N} L!/(2L - N)!(N - L)!]$ -fold degenerate because there are $L!/(2L - N)!(N - L)!$ configurations for choosing $2L - N (< L)$ sites with the single electron from L lattice sites and there are 2^{2L-N} spin degrees of freedom for each configuration. Note that the spins on $2L - N$ sites are active in this case.

When there is no Coulomb interaction ($U = 0$), on the other hand, electrons are generally itinerant. The Hamiltonian is given as

$$H = \sum_{ij\sigma} (\mathbf{H}_0)_{ij} a_{i\sigma}^\dagger a_{j\sigma}. \quad (2.13)$$

Here $(\mathbf{H}_0)_{ij} = \epsilon_0 \delta_{ij} + t_{ij}(1 - \delta_{ij})$. The noninteracting Hamiltonian is diagonalized by a unitary transformation $a_{i\sigma} = \sum_k a_{k\sigma} \langle i|k \rangle$ ($a_{i\sigma}^\dagger = \sum_k a_{k\sigma}^\dagger \langle i|k \rangle^*$) so that

$$H = \sum_{k\sigma} \epsilon_k n_{k\sigma} , \quad (2.14)$$

where $\epsilon_k = \sum_{ij} \langle k|i \rangle (\mathbf{H}_0)_{ij} \langle j|k \rangle$ is an eigenvalue for the tight-binding one-electron Hamiltonian matrix \mathbf{H}_0 , and the set $\{\langle j|k \rangle\}$ ($j = 1, \dots, L$) is the eigen vector for ϵ_k .

The eigen states for noninteracting Hamiltonian H are given by $|\Psi\rangle = |\{n_{k\sigma}\}\rangle$, i.e., a set of electrons with momentum \mathbf{k} and spin σ . The eigenenergy is given by

$$E(\{n_{k\sigma}\}) = \sum_{k\sigma} \epsilon_k n_{k\sigma} , \quad (2.15)$$

where the c-number $n_{k\sigma}$ takes on the value of 0 or 1. The ground state is obtained by putting electrons on the energy levels from the bottom to the Fermi level ϵ_F according to the Pauli principle,

$$|\phi_0\rangle = \left[\prod_{k\sigma}^{\epsilon_k < \epsilon_F} a_{k\sigma}^\dagger \right] |0\rangle , \quad (2.16)$$

so that the ground-state energy is given by

$$E_0(\{n_{k\sigma}\}) = \sum_{k\sigma}^{\epsilon_k < \epsilon_F} \epsilon_k . \quad (2.17)$$

Alternatively, defining the density of states per atom per spin as

$$\rho(\epsilon) = \frac{1}{L} \sum_k \delta(\epsilon - \epsilon_k) , \quad (2.18)$$

we can express the ground-state energy per atom as

$$E_0 = 2 \int_{-\infty}^{\epsilon_F} \epsilon \rho(\epsilon) d\epsilon . \quad (2.19)$$

A non-interacting electron system is in general metallic unless the electrons in the atom form a closed shell. The electrons in such systems are mobile. This is because one can add an electron at the energy level just above the Fermi level by applying infinitesimal electric field. Note that spins of itinerant electrons are also mobile.

We may expect that there is a transition from metal to insulator at half filling when the intra-atomic Coulomb interaction is increased. Assume that there is a band for a non-interacting system whose band width is W . The center of the gravity of the noninteracting band is assumed to be located at ϵ_0 . When the Coulomb interaction U is increased, each atom tends to be occupied by one electron, and electron hopping to neighboring sites tends to be suppressed in order to reduce the on-site Coulomb interaction energy. In the strongly correlated region, an electron should have potential $\epsilon_0 + U$ on a site having an opposite-spin electron because of the increment of the Coulomb interaction energy due to double occupation, while an electron has a potential ϵ_0 on an empty site. We then expect one more band with the band width of order of W around $\epsilon_0 + U$. The density of states as excitation spectrum is expected to split into two bands at $U_c \sim W$ (see Fig. 2.2). The

formation of a gap at the Fermi level implies the existence of an insulator. The insulating state therefore may be realized by the electron correlations when

$$U > W. \quad (2.20)$$

This is Hubbard's alloy-analogy picture to the metal-insulator transition [12]. The metal-insulator transition due to electron correlations as mentioned above is commonly known as the Mott transition. The split bands are named the upper and lower Hubbard bands, respectively. The insulator caused by the electron correlations is referred as the Mott insulator.

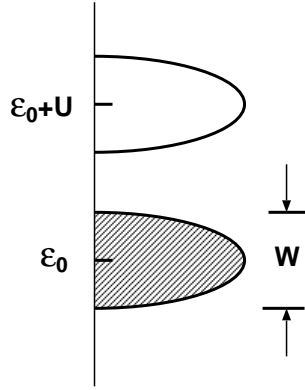


Figure 2.2: The upper and lower Hubbard bands created by on-site Coulomb interaction U

2.3 Hartree-Fock approximation

Although the Hubbard model is a simple model Hamiltonian, it involves a difficulty in solving the many-electron problem inherent in the on-site Coulomb interaction. Thus, approximate methods have been employed to discuss the physics involved in the Hamiltonian. In this section, we make an independent-particle approximation called the Hartree-Fock (HF) approximation, and derive the effective Hamiltonian.

We can rewrite the interaction part of Eq. (2.11) as follows:

$$n_{i\uparrow}n_{i\downarrow} = n_{i\uparrow}\langle n_{i\downarrow} \rangle_0 + n_{i\downarrow}\langle n_{i\uparrow} \rangle_0 - \langle n_{i\uparrow} \rangle_0\langle n_{i\downarrow} \rangle_0 + \delta n_{i\uparrow}\delta n_{i\downarrow}. \quad (2.21)$$

Here $\delta n_{i\sigma} = n_{i\sigma} - \langle n_{i\sigma} \rangle_0$, $\langle \sim \rangle_0$ denotes an average with respect to a wavefunction ϕ_0 for non-interacting electrons: $\langle \phi_0 | (\sim) | \phi_0 \rangle$. $\delta n_{i\uparrow}\delta n_{i\downarrow}$ is the fluctuation of local charge on the same site. In the HF approximation we neglect the fluctuation term, and replace the original Hamiltonian H with an effective Hamiltonian H_{HF} for independent-particle system.

$$H_{\text{HF}} = \sum_{i\sigma} (\epsilon_0 + U\langle n_{i-\sigma} \rangle_0) n_{i\sigma} + \sum_{ij\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} - \sum_i U\langle n_{i\uparrow} \rangle_0\langle n_{i\downarrow} \rangle_0. \quad (2.22)$$

The potential in the first term on the r.h.s. doubly counts the Coulomb interaction. Therefore, the last term $\sum_i U\langle n_{i\uparrow} \rangle_0\langle n_{i\downarrow} \rangle_0$ is subtracted to avoid the double counting of the interaction energy. The wavefunction ϕ_0 is chosen to be the ground-state of the HF Hamiltonian H_{HF} .

The original Hamiltonian (2.11) is then expressed by the HF Hamiltonian and the residual interaction.

$$H = H_{\text{HF}} + U \sum_i O_i . \quad (2.23)$$

Here $O_i = \delta n_{i\uparrow} \delta n_{i\downarrow}$.

The HF approximation is applicable to the system with small Coulomb interaction U because the first-order correction to the HF energy vanishes *i.e.*, $\Delta E = \langle \phi_0 | H_1 | \phi_0 \rangle = 0$. The theory obeys the variational principle. The energy in the HF theory always yields an upper bound for the exact ground-state energy E_0 *i.e.*,

$$\langle \phi_0 | H | \phi_0 \rangle = \langle \phi_0 | H_{\text{HF}} | \phi_0 \rangle \geq E_0 . \quad (2.24)$$

It gives the physical results that follow any conservation laws. The HF theory generally tends to overestimate the symmetry breaking in the Hubbard model since correlations between the electrons are totally ignored. Therefore, the HF theory cannot provide us with a quantitative understanding of the ferromagnetism and the metal-insulator transition as discussed in the introduction.

2.4 Variational wavefunction method

One should take into account electron correlations because the HF ground-state energy is overestimated as we have mentioned in the introduction. We describe in this subsection the variational method to determine approximately the ground-state energy and the wavefunction for correlated electrons.

The variational principle is based on the fact that for any (arbitrary) trial function $|\psi\rangle$ we choose, the energy E is always larger than the exact energy E_0 :

$$E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_0 . \quad (2.25)$$

To verify this, the trial wavefunction can formally be expanded in terms of the exact eigen states of \hat{H} :

$$|\psi\rangle = \sum_n c_n |\phi_n\rangle, \quad (2.26)$$

with

$$H |\phi_n\rangle = E_n |\phi_n\rangle . \quad (2.27)$$

Since $|\psi\rangle$ is normalized; $\langle \psi | \psi \rangle = \sum_n |c_n|^2 = 1$. Therefore the expectation value of H for the function $|\psi\rangle$ is given by

$$\begin{aligned} E = \langle H \rangle &= \left\langle \sum_m c_m \phi_m | H | \sum_n c_n \phi_n \right\rangle \\ &= \sum_m \sum_n c_m^* c_n E_n \langle \phi_m | \phi_n \rangle = \sum_n E_n |c_n|^2 . \end{aligned} \quad (2.28)$$

The ground-state energy is, by definition, the smallest eigenvalue, thus, $E_n \geq E_0$. Then we obtain

$$E \geq E_0 , \quad (2.29)$$

which proves Eq. (2.25).

The equality condition occurs only when $|\psi\rangle$ is proportional to the true ground state $|\psi_0\rangle$. The variational equation is written as follows.

$$\delta E[\psi] = 0. \quad (2.30)$$

If $|\psi\rangle$ depends on parameter α , $E[\psi]$ also depends on α . The variational ansatz (2.30) enables us to vary α so as to minimize $E[\psi]$. The minimum value of $E[\psi]$ provides us with an upper limit for the true energy of the system.

The Gutzwiller wavefunction and the Local-Ansatz wavefunction are popular as a basic wavefunction in correlated electron calculations because of their simplicity and analytic character. In the following subsections we will give a brief outline of these wavefunctions.

2.4.1 Gutzwiller wavefunction

Let us consider the wavefunction for the Hubbard Hamiltonian. The Coulomb interaction reduces the double occupancy on the same site to avoid the energy loss. Taking into account this point Gutzwiller [7, 8, 9] proposed a trial wavefunction so-called Gutzwiller wavefunction (GW).

$$|\Psi_{\text{GW}}\rangle = \left[\prod_i (1 - (1 - g)n_{i\uparrow}n_{i\downarrow}) \right] |\phi_0\rangle. \quad (2.31)$$

Here $n_{i\sigma}$ is the number operator for electron on site i with spin σ . The wavefunction describes on-site electron correlations by making use of a projection operator $n_{i\uparrow}n_{i\downarrow}$ onto the HF state $|\phi_0\rangle$. The variational parameter g ($0 \leq g \leq 1$) has to be determined variationally by minimizing the energy. It controls the amplitudes of the doubly occupied state in the HF approximation. When the variational parameter $g = 1$, the state corresponds to an uncorrelated state; on the other hand, $g = 0$ state corresponds to the atomic state in which all the doubly occupied states have been removed from the HF wavefunction.

The total energy for the GW is given as follows (see Appendix A).

$$E(g) = \sum_{\sigma} q_{\sigma} \left(\sum_k^{N_{\sigma}} \epsilon_k \right) + UD. \quad (2.32)$$

Here the band narrowing factor q_{σ} is given as

$$q_{\sigma} = \frac{\left(\sqrt{(N_{\sigma} - D)(L - N + D)} + \sqrt{D(N_{-\sigma} - D)} \right)^2}{N_{\sigma}(L - N_{\sigma})}. \quad (2.33)$$

N_{σ} denotes the total electron number for the spin σ , D is the number of doubly occupied sites, and L denotes the number of lattice points.

In the non-magnetic state at half-filling ($N = L$), the energy per site is simplified as follows.

$$\epsilon(g) = -q|\epsilon_b| + Ud. \quad (2.34)$$

Here

$$q = 16 \left(\frac{1}{2} - d \right) d, \quad (2.35)$$

$$g = \frac{d}{\frac{1}{2} - d}, \quad (2.36)$$

and $d = D/L$ denotes the double occupation number per site. ϵ_b is the band energy per site, and is given by the non-interacting density of states per atom and per spin $\rho(\epsilon) = L^{-1} \sum_k \delta(\epsilon - \epsilon_k)$ as follows.

$$\epsilon_b = 2 \int_{-\infty}^0 \epsilon \rho(\epsilon) d\epsilon. \quad (2.37)$$

Minimizing the energy (2.34) with respect to g (i.e., d), we obtain

$$q = 1 - \frac{U^2}{U_c^2}, \quad (2.38)$$

$$d = \frac{1}{4} \left(1 - \frac{U}{U_c} \right), \quad (2.39)$$

and

$$g = \frac{1 - \frac{U}{U_c}}{1 + \frac{U}{U_c}}. \quad (2.40)$$

Here $U_c = 8|\epsilon_b|$ is a critical Coulomb interaction at which q and d vanish. The ground-state energy is given by

$$\epsilon(g) = -\frac{1}{8} U_c \left(1 - \frac{U}{U_c} \right)^2. \quad (2.41)$$

When $U > U_c$, there is another solution: $g = 0$ or $d = 0$ which yields the minimum energy $\epsilon(g) = 0$. Note that electrons are completely localized at $U = U_c$; $q = d = 0$. This implies that metal-insulator transition occurs at $U = U_c$. This is known as the Brinkman-Rice transition [18].

It is obvious that the GW is exact both in the small Coulomb interactions limit ($U \rightarrow 0$), and in atomic limit ($U \rightarrow \infty$). In spite of the simplicity the GW (2.31) is known to describe various aspects of the strongly correlated electrons. However, it does not yield the correct weak Coulomb interaction regime even in infinite dimensions.

2.4.2 Local-ansatz wavefunction

The GW yields a physical picture for correlated electrons and has been applied to many problems in the strongly correlated electron systems. However it was not so easy to apply the method to the realistic Hamiltonian. An alternative approach which is simpler in treatment and applicable to the realistic Hamiltonian was proposed by Stollhoff and Fulde [13, 14, 15]. It is known as the local-ansatz (LA) wavefunction.

In the LA the Hilbert space for the correlated electrons is expanded by the local operators such as the residual Coulomb interactions $\{O_i\} = \{\delta n_{i\downarrow} \delta n_{i\uparrow}\}$ so that the wavefunction can describe the weak Coulomb interaction regime. The ansatz for the Hubbard model is written as

$$|\Psi_{\text{LA}}\rangle = \left[\prod_i (1 - \eta_{\text{LA}} O_i) \right] |\phi_0\rangle. \quad (2.42)$$

Here η_{LA} is the variational parameter as the amplitudes of the basis set expanded by $\{O_i\}$.

The variational energy is expressed as

$$E = \langle \phi_0 | H | \phi_0 \rangle + E_c . \quad (2.43)$$

The energy E_c denotes the correlation energy which cannot be described by the HF approximation. In the single-site approximation, the correlation energy per atom is given by

$$\epsilon_c = \frac{-2\eta_{\text{LA}} \langle O_i \tilde{H} \rangle_0 + \eta_{\text{LA}}^2 \langle O_i \tilde{H} O_i \rangle_0}{1 + \eta_{\text{LA}}^2 \langle O_i^2 \rangle_0} . \quad (2.44)$$

Minimizing the energy ϵ_c with respect to the η_{LA} , we obtain

$$\eta_{\text{LA}} = \frac{-\langle O_i \tilde{H} O_i \rangle_0 + \sqrt{\langle O_i \tilde{H} O_i \rangle_0^2 + 4 \langle O_i \tilde{H} \rangle_0^2 \langle O_i^2 \rangle_0}}{2 \langle O_i \tilde{H} \rangle_0 \langle O_i^2 \rangle_0} . \quad (2.45)$$

Each element in the variational parameter and the correlation energy is given as follows.

$$\langle O_i \tilde{H} O_i \rangle_0 = \langle O_i \tilde{H}_0 O_i \rangle_0 + U \langle O_i^3 \rangle_0 , \quad (2.46)$$

$$\langle O_i \tilde{H}_0 O_i \rangle_0 = \sum_{\sigma} \langle n_{i-\sigma} \rangle_0 (1 - \langle n_{i-\sigma} \rangle_0) \left[\langle n_{i-\sigma} \rangle_0 \int d\epsilon \epsilon \rho_{i\sigma}(\epsilon) - \int d\epsilon \epsilon \rho_{i\sigma}(\epsilon) \right] , \quad (2.47)$$

$$\langle O_i^3 \rangle_0 = \langle O_i^2 \rangle_0 (1 - 2 \langle n_{i\uparrow} \rangle_0) (1 - 2 \langle n_{i\downarrow} \rangle_0) , \quad (2.48)$$

$$\langle O_i \tilde{H} \rangle_0 = U \langle O_i^2 \rangle_0 , \quad (2.49)$$

$$\langle O_i^2 \rangle_0 = \langle n_{i\uparrow} \rangle_0 (1 - \langle n_{i\uparrow} \rangle_0) \langle n_{i\downarrow} \rangle_0 (1 - \langle n_{i\downarrow} \rangle_0) . \quad (2.50)$$

Here $\langle n_{i\sigma} \rangle_0$ is the average electron number on site i with spin σ . $\rho_{i\sigma}(\epsilon)$ is the density of states for the one electron energy eigenvalues for the non-interacting system. $f(\epsilon)$ is the Fermi distribution function at zero temperature.

To obtain the analytic expression of various physical quantities in half-filled band Hubbard model, we consider the hypercubic lattice with Gaussian density of states $\rho(\epsilon) = (1/\sqrt{\pi}) \exp(-\epsilon^2)$. The correlation energy per atom for the LA is written as

$$E_c = \frac{-\frac{U}{2} \frac{\eta_{\text{LA}}}{4} + \frac{4}{\sqrt{\pi}} \left(\frac{\eta_{\text{LA}}}{4} \right)^2}{1 + \left(\frac{\eta_{\text{LA}}}{4} \right)^2} . \quad (2.51)$$

Here the variational parameter η_{LA} is defined by

$$\eta_{\text{LA}} = \frac{-\frac{1}{\sqrt{\pi}} + \sqrt{\frac{1}{\pi} + \frac{U^2}{16}}}{\frac{U}{32}} . \quad (2.52)$$

The double occupation is given by

$$\langle n_{i\uparrow}n_{i\downarrow} \rangle = \frac{1}{2} \left(\frac{1}{2} - \frac{\eta_{\text{LA}}/4}{1 + (\eta_{\text{LA}}/4)^2} \right). \quad (2.53)$$

The analytic expression of momentum distribution is defined as follows.

$$\langle n_{k\sigma} \rangle = \frac{1}{2}(1 + Z)f(\epsilon_{k\sigma}) + \frac{1}{2}(1 - Z)(1 - f(\epsilon_{k\sigma})). \quad (2.54)$$

Here $f(\epsilon_{k\sigma})$ is the Fermi distribution function and the Z is the quasiparticle weight. It is written as follows.

$$Z = \frac{1 - 3\eta_{\text{LA}}^2/16}{1 + \eta_{\text{LA}}^2/16}. \quad (2.55)$$

The Hilbert space expanded by the operators $\{O_i\}$ is not sufficient to characterize exactly the weakly correlated region. It does not reduce to the second-order perturbation theory in the weak correlation limit.

Chapter 3

Momentum Dependent Local-Ansatz Approach with Hartree-Fock Wavefunction

As we have emphasized in the previous chapter, the LA does not reduce to the second-order perturbation theory in the weak correlation limit. The same difficulty also arises for the GW even in infinite dimensions. To remove the difficulty in the weak Coulomb interaction regime and to improve the correlated states in the intermediate Coulomb interaction regime, we introduce in this chapter a local-ansatz wavefunction with momentum-dependent variational parameters, and demonstrate that the new approach much improves the LA as well as the GW in the weak and the intermediate Coulomb interaction regimes.

3.1 Construction of momentum dependent local-ansatz wavefunction

Let us expand the LA wavefunction with respect to the Coulomb interaction U to examine the behavior in the weak Coulomb interaction limit.

$$|\Psi_{\text{LA}}\rangle = |\psi_0\rangle + |\psi_1\rangle_{\text{LA}} + \dots, \quad (3.1)$$

with

$$|\psi_1\rangle_{\text{LA}} = - \sum_i \eta_{\text{LA}} O_i |\phi_0\rangle. \quad (3.2)$$

We can rewrite the term $O_i = \delta n_{i\downarrow} \delta n_{i\uparrow}$ using the relations $a_{i\sigma} = \sum_k a_{k\sigma} \langle i|k\rangle$ and $a_{i\sigma}^\dagger = \sum_k a_{k\sigma}^\dagger \langle k|i\rangle$ as follows:

$$O_i = \delta n_{i\downarrow} \delta n_{i\uparrow} = \sum_{k_1 k'_1 k_2 k'_2} \langle k'_1|i\rangle \langle i|k_1\rangle \langle k'_2|i\rangle \langle i|k_2\rangle \delta(a_{k'_2\downarrow}^\dagger a_{k_2\downarrow}) \delta(a_{k'_1\uparrow}^\dagger a_{k_1\uparrow}). \quad (3.3)$$

Therefore,

$$|\psi_1\rangle_{\text{LA}} = - \sum_i \sum_{k_1 k'_1 k_2 k'_2} \langle k'_1|i\rangle \langle i|k_1\rangle \langle k'_2|i\rangle \langle i|k_2\rangle \eta_{\text{LA}} \delta(a_{k'_2\downarrow}^\dagger a_{k_2\downarrow}) \delta(a_{k'_1\uparrow}^\dagger a_{k_1\uparrow}) |\phi_0\rangle. \quad (3.4)$$

Here $\langle i|k\rangle = \exp(-i\mathbf{k} \cdot \mathbf{R}_i) / \sqrt{N}$ is an overlap integral between the localized orbital and the Bloch state with momentum \mathbf{k} , \mathbf{R}_i denotes the atomic position, N is the number of sites and $\delta(a_{k'_\sigma}^\dagger a_{k\sigma}) = a_{k'_\sigma}^\dagger a_{k\sigma} - \langle a_{k'_\sigma}^\dagger a_{k\sigma} \rangle_0$.

Finally, we obtain the expanded form of the LA wavefunction in the weak Coulomb interaction limit as follows:

$$|\Psi_{\text{LA}}\rangle = |\psi_0\rangle - \sum_i \sum_{k_1 k'_1 k_2 k'_2} \langle k'_1|i\rangle \langle i|k_1\rangle \langle k'_2|i\rangle \langle i|k_2\rangle \eta_{\text{LA}} \delta(a_{k'_2\downarrow}^\dagger a_{k_2\downarrow}) \delta(a_{k'_1\uparrow}^\dagger a_{k_1\uparrow}) |\phi_0\rangle. \quad (3.5)$$

The above expression does not agree with the result of the perturbation theory.

To clarify the wavefunction in the correct weak Coulomb interaction limit, we start from the HF wavefunction $|\phi_0\rangle$ and expand the the ground-state wavefunction $|\psi\rangle$ using the Rayleigh-Schrödinger perturbation theory as follows.

$$|\Psi\rangle = |\phi_0\rangle + |\psi_1\rangle + \dots, \quad (3.6)$$

$$|\psi_1\rangle = - \sum_i \sum_{k_1 k'_1 k_2 k'_2} \langle k'_1|i\rangle \langle i|k_1\rangle \langle k'_2|i\rangle \langle i|k_2\rangle \eta_{k'_2 k_2 k'_1 k_1}^{(0)} \delta(a_{k'_2\downarrow}^\dagger a_{k_2\downarrow}) \delta(a_{k'_1\uparrow}^\dagger a_{k_1\uparrow}) |\phi_0\rangle, \quad (3.7)$$

$$\eta_{k'_2 k_2 k'_1 k_1}^{(0)} = -U \lim_{z \rightarrow 0} \frac{\tilde{f}_{k'_2 k_2 k'_1 k_1}}{z - \epsilon_{k'_1\uparrow} - \epsilon_{k_1\uparrow} - \epsilon_{k'_2\downarrow} + \epsilon_{k_2\downarrow}}. \quad (3.8)$$

Here $\tilde{f}_{k'_2 k_2 k'_1 k_1}$ is a Fermi factor of two-particle excitations defined by $\tilde{f}_{k'_2 k_2 k'_1 k_1} = f(\tilde{\epsilon}_{k_1\uparrow})(1 - f(\tilde{\epsilon}_{k'_1\uparrow}))f(\tilde{\epsilon}_{k_2\downarrow})(1 - f(\tilde{\epsilon}_{k'_2\downarrow}))$, $f(\epsilon)$ is the Fermi distribution function at zero temperature, and $\tilde{\epsilon}_{k\sigma} = \epsilon_{k\sigma} - \mu$. μ is the Fermi level. $\epsilon_{k\sigma}$ is the HF one-electron energy eigenvalue given by $\epsilon_{k\sigma} = \epsilon_0 + U\langle n_{i-\sigma} \rangle_0 + \epsilon_k - \sigma h$, ϵ_k being the Fourier transform of t_{ij} .

Equation (3.7) compared with Eq. (3.4) manifests that one has to take into account the momentum dependence of the variational parameters to obtain the exact result in the weak Coulomb interaction limit. We therefore propose the following wavefunction with momentum-dependent variational parameters $\{\eta_{k'_2 k_2 k'_1 k_1}\}$.

$$|\Psi\rangle = \prod_i (1 - \tilde{O}_i) |\phi_0\rangle, \quad (3.9)$$

$$\tilde{O}_i = \sum_{k_1 k_2 k'_1 k'_2} \langle k'_1|i\rangle \langle i|k_1\rangle \langle k'_2|i\rangle \langle i|k_2\rangle \eta_{k'_2 k_2 k'_1 k_1} \delta(a_{k'_2\downarrow}^\dagger a_{k_2\downarrow}) \delta(a_{k'_1\uparrow}^\dagger a_{k_1\uparrow}). \quad (3.10)$$

We call the new form of Eq. (3.9) the momentum-dependent local ansatz (MLA) [24, 25, 26]. The operator \tilde{O}_i is still localized on site i because of the projection $\langle k'_1|i\rangle \langle i|k_1\rangle \langle k'_2|i\rangle \langle i|k_2\rangle$. It should be noted that $\tilde{O}_i^\dagger \neq \tilde{O}_i$ and $\tilde{O}_i \tilde{O}_j \neq \tilde{O}_j \tilde{O}_i$ ($i \neq j$) in general. These properties do not cause any problem when we make a single-site approximation (SSA). The wavefunction $|\Psi\rangle$ reduces to $|\Psi_{\text{LA}}\rangle$ when $\{\eta_{k'_2 k_2 k'_1 k_1}\}$ become momentum-independent.

3.2 The ground-state energy

We have to determine the variational parameters on the basis of the variational principle in order to determine the wavefunction. The correlation energy E_c is defined by the difference between the exact ground-state energy and the HF one as follows.

$$E_c = \langle H \rangle - \langle H \rangle_0 = \frac{\langle \Psi | \tilde{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (3.11)$$

Here $\tilde{H} = \hat{H} - \langle H \rangle_0$. Although it is not easy to calculate the correlation energy with use of the new wavefunction (3.9), one can obtain the expression for the energy within the single-site approximation (SSA).

3.2.1 Single-site approximation (SSA)

We generalize here the problem to calculate the correlation energy, and consider the average of a physical quantity A with respect to the correlated wavefunction (3.9).

$$\langle \tilde{A} \rangle = \frac{\langle \Psi | \tilde{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{A_N}{B_N}. \quad (3.12)$$

Here $\tilde{A} = \hat{A} - \langle A \rangle_0$, $\langle \sim \rangle_0$ being the average with respect to the HF wavefunction. A_N and B_N are defined as follows:

$$A_N = \left\langle \left[\prod_i (1 - \tilde{O}_i^\dagger) \right] \tilde{A} \left[\prod_i (1 - \tilde{O}_i) \right] \right\rangle_0, \quad (3.13)$$

$$B_N = \left\langle \left[\prod_i (1 - \tilde{O}_i^\dagger) \right] \left[\prod_i (1 - \tilde{O}_i) \right] \right\rangle_0. \quad (3.14)$$

Expanding B_N with respect to site 1, we obtain

$$\begin{aligned} B_N = B_{N-1}^{(1)} & - \left\langle \tilde{O}_1^\dagger \left[\prod_i^{(1)} (1 - \tilde{O}_i^\dagger) \right] \left[\prod_i^{(1)} (1 - \tilde{O}_i) \right] \right\rangle_0 \\ & - \left\langle \left[\prod_i^{(1)} (1 - \tilde{O}_i^\dagger) \right] \tilde{O}_1 \left[\prod_i^{(1)} (1 - \tilde{O}_i) \right] \right\rangle_0 \\ & + \left\langle \tilde{O}_1^\dagger \left[\prod_i^{(1)} (1 - \tilde{O}_i^\dagger) \right] \tilde{O}_1 \left[\prod_i^{(1)} (1 - \tilde{O}_i) \right] \right\rangle_0, \end{aligned} \quad (3.15)$$

and

$$B_{N-1}^{(1)} = \left\langle \left[\prod_i^{(1)} (1 - \tilde{O}_i^\dagger) \right] \left[\prod_i^{(1)} (1 - \tilde{O}_i) \right] \right\rangle_0. \quad (3.16)$$

Here the product $\prod_i^{(1)}$ means the product with respect to all sites excluding site 1.

When we calculate B_N using the Wick theorem (see appendix B), we neglect the contractions between different sites. This is a SSA and then Eq. (3.15) is expressed as

$$B_N = \langle (1 - \tilde{O}_1^\dagger) (1 - \tilde{O}_1) \rangle_0 B_{N-1}^{(1)}. \quad (3.17)$$

We can make the same approximation for A_N . In this case, there are two-types of terms, the terms in which the operator \tilde{O}_1 is contracted to \tilde{A} and the other terms with \tilde{O}_1 contracted to the operators \tilde{O}_i ($i \neq 1$). We have then

$$A_N = \langle (1 - \tilde{O}_1^\dagger) \tilde{A} (1 - \tilde{O}_1) \rangle_0 B_{N-1}^{(1)} + \langle (1 - \tilde{O}_1^\dagger) (1 - \tilde{O}_1) \rangle_0 A_{N-1}^{(1)}, \quad (3.18)$$

and

$$A_{N-1}^{(1)} = \left\langle \left[\prod_i^{(1)} (1 - \tilde{O}_i^\dagger) \right] \tilde{A} \left[\prod_i^{(1)} (1 - \tilde{O}_i) \right] \right\rangle_0. \quad (3.19)$$

Successive application of the recursive relations (3.17) and (3.18) leads to

$$A_N = \sum_i \langle (1 - \tilde{O}_i^\dagger) \tilde{A} (1 - \tilde{O}_i) \rangle_0 B_{N-1}^{(i)}, \quad (3.20)$$

$$B_N = \langle (1 - \tilde{O}_i^\dagger) (1 - \tilde{O}_i) \rangle_0 B_{N-1}^{(i)} = \prod_i \langle (1 - \tilde{O}_i^\dagger) (1 - \tilde{O}_i) \rangle_0. \quad (3.21)$$

Taking the ratio A_N/B_N , we obtain.

$$\langle \tilde{A} \rangle = \sum_i \frac{\langle (1 - \tilde{O}_i^\dagger) \tilde{A} (1 - \tilde{O}_i) \rangle_0}{\langle (1 - \tilde{O}_i^\dagger) (1 - \tilde{O}_i) \rangle_0}. \quad (3.22)$$

This is the general expression for an operator A in the SSA.

3.2.2 Correlation energy

The expression of the correlation energy per atom ϵ_c is obtained analytically by making use of the formula (3.22).

$$\epsilon_c = \frac{\langle (1 - \tilde{O}_i^\dagger) \tilde{H} (1 - \tilde{O}_i) \rangle_0}{\langle (1 - \tilde{O}_i^\dagger) (1 - \tilde{O}_i) \rangle_0}. \quad (3.23)$$

We consider all the sites are equivalent to each other. Since $\langle \tilde{H} \rangle_0 = 0$, and $\langle \tilde{O}_i^\dagger \rangle_0 = \langle \tilde{O}_i \rangle_0 = 0$, the correlation energy is given as follows,

$$\epsilon_c = \frac{-\langle \tilde{O}_i^\dagger \tilde{H} \rangle_0 - \langle \tilde{H} \tilde{O}_i \rangle_0 + \langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0}. \quad (3.24)$$

Each term in the correlation energy (3.24) can be calculated by making use of the Wick theorem (see Appendix B) as follows.

$$\langle \tilde{H} \tilde{O}_i \rangle_0 = U \sum_{k_1 k_2 k'_1 k'_2} \langle k'_1 | i \rangle \langle i | k_1 \rangle \langle k'_2 | i \rangle \langle i | k_2 \rangle \sum_j \langle k_1 | j \rangle \langle j | k'_1 \rangle \langle k_2 | j \rangle \langle j | k'_2 \rangle \eta_{k'_2 k_2 k'_1 k_1} \tilde{f}_{k'_2 k_2 k'_1 k_1}, \quad (3.25)$$

$$\langle \tilde{O}_i^\dagger \tilde{H} \rangle_0 = \langle \tilde{H} \tilde{O}_i \rangle_0^*, \quad (3.26)$$

$$\begin{aligned} \langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_0 &= \sum_{k_1 k_2 k'_1 k'_2} \langle i | k'_1 \rangle \langle k_1 | i \rangle \langle i | k'_2 \rangle \langle k_2 | i \rangle \eta_{k'_2 k_2 k'_1 k_1}^* \tilde{f}_{k'_2 k_2 k'_1 k_1} \sum_{k_3 k_4 k'_3 k'_4} \langle k'_3 | i \rangle \langle i | k_3 \rangle \langle k'_4 | i \rangle \langle i | k_4 \rangle \\ &\times \left(\Delta E_{k'_2 k_2 k'_1 k_1} \delta_{k_1 k_3} \delta_{k'_1 k'_3} \delta_{k_2 k_4} \delta_{k'_2 k'_4} + U_{k'_2 k_2 k'_1 k_1 k'_4 k_4 k'_3 k_3} \right) \eta_{k'_4 k_4 k'_3 k_3}, \end{aligned} \quad (3.27)$$

$$\begin{aligned}
U_{k'_2 k_2 k'_1 k_1 k'_4 k_4 k'_3 k_3} &= U \sum_j [\langle j|k_1\rangle \langle k_3|j\rangle f(\tilde{\epsilon}_{k_3\uparrow}) \delta_{k'_1 k'_3} - \langle k'_1|j\rangle \langle j|k'_3\rangle [1 - f(\tilde{\epsilon}_{k'_3\uparrow})] \delta_{k_1 k_3}] \\
&\quad \times [\langle j|k_2\rangle \langle k_4|j\rangle f(\tilde{\epsilon}_{k_4\downarrow}) \delta_{k'_2 k'_4} - \langle k'_2|j\rangle \langle j|k'_4\rangle [1 - f(\tilde{\epsilon}_{k'_4\downarrow})] \delta_{k_2 k_4}] , \quad (3.28)
\end{aligned}$$

$$\langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0 = \frac{1}{N^4} \sum_{k_1 k_2 k'_1 k'_2} |\eta_{k'_2 k_2 k'_1 k_1}|^2 \tilde{f}_{k'_2 k_2 k'_1 k_1} . \quad (3.29)$$

Here $\Delta E_{k'_2 k_2 k'_1 k_1} = \epsilon_{k'_2\downarrow} - \epsilon_{k_2\downarrow} + \epsilon_{k'_1\uparrow} - \epsilon_{k_1\uparrow}$ is the two particle excitation energy.

The above expressions (3.25) and (3.28) contain nonlocal terms in the summation over j (*i.e.*, \sum_j). We thus make additional SSA called the $R=0$ approximation [29, 30]. For example, we have in Eq. (3.25)

$$\sum_j \langle k'_1|i\rangle \langle i|k_1\rangle \langle k'_2|i\rangle \langle i|k_2\rangle \langle k_1|j\rangle \langle j|k'_1\rangle \langle k_2|j\rangle \langle j|k'_2\rangle = \frac{1}{N^4} \sum_j e^{i(k_1+k_2-k'_1-k'_2)(R_j-R_i)} , \quad (3.30)$$

and only take into account the local term ($j = i$), in the $R=0$ approximation. Within the approximation, $\langle \tilde{H} \tilde{O}_i \rangle_0 = \langle \tilde{O}_i^\dagger \tilde{H} \rangle_0^*$ and $\langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_0$ reduce as follows:

$$\langle \tilde{H} \tilde{O}_i \rangle_0 = \frac{U}{N^4} \sum_{k_1 k_2 k'_1 k'_2} \tilde{f}_{k'_2 k_2 k'_1 k_1} \eta_{k'_2 k_2 k'_1 k_1} , \quad (3.31)$$

$$\begin{aligned}
\langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_0 &= \frac{1}{N^4} \sum_{k_1 k_2 k'_1 k'_2} \tilde{f}_{k'_2 k_2 k'_1 k_1} \eta_{k'_2 k_2 k'_1 k_1}^* \left[\Delta E_{k'_2 k_2 k'_1 k_1} \eta_{k'_2 k_2 k'_1 k_1} \right. \\
&\quad + \frac{U}{N^2} \left\{ \sum_{k_3 k_4} f(\tilde{\epsilon}_{k_3\uparrow}) f(\tilde{\epsilon}_{k_4\downarrow}) \eta_{k'_2 k_4 k'_1 k_3} - \sum_{k_3 k'_4} f(\tilde{\epsilon}_{k_3\uparrow}) [1 - f(\tilde{\epsilon}_{k'_4\downarrow})] \eta_{k'_4 k_2 k'_1 k_3} \right. \\
&\quad \left. \left. - \sum_{k'_3 k_4} [1 - f(\tilde{\epsilon}_{k'_3\uparrow})] f(\tilde{\epsilon}_{k_4\downarrow}) \eta_{k'_2 k_4 k'_3 k_1} + \sum_{k'_3 k'_4} [1 - f(\tilde{\epsilon}_{k'_3\uparrow})] [1 - f(\tilde{\epsilon}_{k'_4\downarrow})] \eta_{k'_4 k_2 k'_3 k_1} \right\} \right] . \quad (3.32)
\end{aligned}$$

3.3 Determination of variational parameters $\eta_{k'_2 k_2 k'_1 k_1}$

Variational parameters $\{\eta_{k'_2 k_2 k'_1 k_1}\}$ are obtained by minimizing the correlation energy ϵ_c , *i.e.*, Eq. (3.24) with Eqs. (3.29), (3.31), and (3.32). The self-consistent equations for $\{\eta_{k'_2 k_2 k'_1 k_1}\}$ in the SSA are given as follows.

$$\begin{aligned}
&(\Delta E_{k'_2 k_2 k'_1 k_1} - \epsilon_c) \eta_{k'_2 k_2 k'_1 k_1} \\
&+ \frac{U}{N^2} \left[\sum_{k_3 k_4} f(\tilde{\epsilon}_{k_3\uparrow}) f(\tilde{\epsilon}_{k_4\downarrow}) \eta_{k'_2 k_4 k'_1 k_3} - \sum_{k_3 k'_4} f(\tilde{\epsilon}_{k_3\uparrow}) (1 - f(\tilde{\epsilon}_{k'_4\downarrow})) \eta_{k'_4 k_2 k'_1 k_3} \right. \\
&\left. - \sum_{k'_3 k_4} (1 - f(\tilde{\epsilon}_{k'_3\uparrow})) f(\tilde{\epsilon}_{k_4\downarrow}) \eta_{k'_2 k_4 k'_3 k_1} + \sum_{k'_3 k'_4} (1 - f(\tilde{\epsilon}_{k'_3\uparrow})) (1 - f(\tilde{\epsilon}_{k'_4\downarrow})) \eta_{k'_4 k_2 k'_3 k_1} \right] = U . \quad (3.33)
\end{aligned}$$

It should be noted that the variational parameters $\{\eta_{k_2'k_2k_1'k_1}\}$ in Eq. (3.33) vanish when $U \rightarrow 0$, i.e., $\eta_{k_2'k_2k_1'k_1} \sim O(U)$. Thus in the weak U limit, one can omit the second term on the l.h.s. (left-hand-side). We then obtain the solution in the weak U limit as

$$\eta_{k_2'k_2k_1'k_1} = \frac{U}{\Delta E_{k_2'k_2k_1'k_1}}. \quad (3.34)$$

In the atomic limit the transfer integrals t_{ij} disappear, and one electron energy eigenvalue ϵ_k becomes k -independent, ϵ_0 . Thus, $\Delta E_{k_2'k_2k_1'k_1}$ vanishes. In this limit we can drop the k dependence of $\eta_{k_2'k_2k_1'k_1}$, i.e., $\eta_{k_2'k_2k_1'k_1} \rightarrow \eta$. Then, we find a k -independent solution being identical with the LA.

$$\eta = \frac{-\langle O_i \tilde{H} O_i \rangle_0 + \sqrt{\langle O_i \tilde{H} O_i \rangle_0^2 + 4\langle O_i \tilde{H} \rangle_0^2 \langle O_i^2 \rangle_0}}{2\langle O_i \tilde{H} \rangle_0 \langle O_i^2 \rangle_0}. \quad (3.35)$$

It is not easy to find the solution of Eq. (3.33) for the intermediate strength of Coulomb interaction U . We therefore propose an approximate solution in the following subsections, which interpolates between the weak and the atomic limits.

3.3.1 Interpolating solution of $\eta_{k_2'k_2k_1'k_1}$

In this subsection we consider an approximate solution which interpolates between the weak and the atomic limits. We do not make any approximation to the first term with $\Delta E_{k_2'k_2k_1'k_1}$, because it is mandatory to describe exactly the weak Coulomb interaction regime. As we have mentioned before, the second term on the l.h.s. of Eq. (3.33) does not affect the solution in the weakly correlated limit. Therefore we approximate the variational parameters $\{\eta_{k_2'k_2k_1'k_1}\}$ in the second term with a momentum-independent parameter η , which is suitable in the atomic region. The self-consistent equation (3.33) then reduces as follows.

$$(\Delta E_{k_2'k_2k_1'k_1} - \epsilon_c) \eta_{k_2'k_2k_1'k_1} + U[\eta(1 - 2\langle n_{i\uparrow} \rangle_0)(1 - 2\langle n_{i\downarrow} \rangle_0)] = U. \quad (3.36)$$

We have then an interpolate solution as follows.

$$\eta_{k_2'k_2k_1'k_1} = \frac{U[1 - \eta(1 - 2\langle n_{i\uparrow} \rangle_0)(1 - 2\langle n_{i\downarrow} \rangle_0)]}{\Delta E_{k_2'k_2k_1'k_1} - \epsilon_c}. \quad (3.37)$$

Here $\Delta E_{k_2'k_2k_1'k_1}$ in the denominator is the two particle excitation energy given by $\Delta E_{k_2'k_2k_1'k_1} = \epsilon_{k_2'\downarrow} - \epsilon_{k_2\downarrow} + \epsilon_{k_1'\uparrow} - \epsilon_{k_1\uparrow}$, and ϵ_c is the correlation energy per atom (3.24):

$$\epsilon_c = \frac{-\langle \tilde{O}_i^\dagger \tilde{H} \rangle_0 - \langle \tilde{H} \tilde{O}_i \rangle_0 + \langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle}, \quad (3.38)$$

The best value of η should be determined variationally as will be discussed, but we might make use of that in the LA in a simpler version of numerical calculations and might adopt the correlation energy in the LA for ϵ_c as well. We call this the non-self-consistent MLA [24] in the followings.

3.3.2 Best choice of η

The best value of η , however, should be determined variationally in general. In this subsection we further develop the theory in which η is determined best. According to the variational principle, the ground-state energy E_0 satisfies the following inequality.

$$E_0 \leq E[\Psi] = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (3.39)$$

Here Ψ is a trial wavefunction.

In the MLA, we choose the wavefunction $\Psi = \Psi(\{\eta_{k'_2 k_2 k'_1 k_1}\})$ and the corresponding energy $E(\{\eta_{k'_2 k_2 k'_1 k_1}\})$ satisfies the inequality $E_0 \leq E(\{\eta_{k'_2 k_2 k'_1 k_1}\})$. For the stationary values $\eta_{k'_2 k_2 k'_1 k_1}^*$, we have

$$E_0 \leq E(\{\eta_{k'_2 k_2 k'_1 k_1}^*\}) \leq E(\{\eta_{k'_2 k_2 k'_1 k_1}\}). \quad (3.40)$$

In the previous calculations of non-selfconsistent MLA [24], we obtained an approximate $\eta_{k'_2 k_2 k'_1 k_1}^*$ (3.37);

$$\eta_{k'_2 k_2 k'_1 k_1}(\tilde{\eta}, \epsilon_c) = \frac{U \tilde{\eta}}{\Delta E_{k'_2 k_2 k'_1 k_1} - \epsilon_c}. \quad (3.41)$$

Here

$$\tilde{\eta} = 1 - \eta(1 - 2\langle n_{i\uparrow} \rangle_0)(1 - 2\langle n_{i\downarrow} \rangle_0). \quad (3.42)$$

When we adopt the form (3.41) as a trial set of amplitudes, we have an inequality as

$$\langle E_0 \rangle \leq E(\{\eta_{k'_2 k_2 k'_1 k_1}^*\}) \leq E(\{\eta_{k'_2 k_2 k'_1 k_1}(\tilde{\eta}, \epsilon_c)\}). \quad (3.43)$$

The above relation implies that the best $\tilde{\eta}$ is again determined from the stationary condition of the trial energy $E(\{\eta_{k'_2 k_2 k'_1 k_1}(\tilde{\eta}, \epsilon_c)\})$. Because ϵ_c should satisfy the stationary condition $\delta \epsilon_c = 0$ for the value $\tilde{\eta}^*$, $\tilde{\eta}^*$ is determined by the following condition

$$\left[\frac{\partial \epsilon(\{\eta_{k'_2 k_2 k'_1 k_1}(\tilde{\eta}, \epsilon_c)\})}{\partial \tilde{\eta}} \right]_{\epsilon_c} = 0. \quad (3.44)$$

The self-consistent equation is obtained from Eq.(3.44) in the same way as in Eq. (3.33)

$$\begin{aligned} & \frac{1}{N^4} \sum_{k_1 k'_1 k_2 k'_2} \tilde{f}_{k'_2 k_2 k'_1 k_1} \frac{\partial \eta_{k'_2 k_2 k'_1 k_1}}{\partial \tilde{\eta}} (\Delta E_{k'_2 k_2 k'_1 k_1} - \epsilon_c) \eta_{k'_2 k_2 k'_1 k_1} \\ & + \frac{U}{N^6} \sum_{k_1 k'_1 k_2 k'_2} \tilde{f}_{k'_2 k_2 k'_1 k_1} \frac{\partial \eta_{k'_2 k_2 k'_1 k_1}}{\partial \tilde{\eta}} \left\{ \sum_{k_3 k_4} f(\tilde{\epsilon}_{k_3 \uparrow}) f(\tilde{\epsilon}_{k_4 \downarrow}) \eta_{k'_2 k_4 k'_1 k_3} \right. \\ & - \sum_{k'_3 k_4} [1 - f(\tilde{\epsilon}_{k'_3 \uparrow})] f(\tilde{\epsilon}_{k_4 \downarrow}) \eta_{k'_2 k_4 k'_3 k_1} - \sum_{k_3 k'_4} f(\tilde{\epsilon}_{k_3 \uparrow}) [1 - f(\tilde{\epsilon}_{k'_4 \downarrow})] \eta_{k'_4 k_2 k'_1 k_3} \\ & \left. + \sum_{k'_3 k'_4} [1 - f(\tilde{\epsilon}_{k'_3 \uparrow})] [1 - f(\tilde{\epsilon}_{k'_4 \downarrow})] \eta_{k'_4 k_2 k'_3 k_1} \right\} = \frac{U}{N^4} \sum_{k_1 k'_1 k_2 k'_2} \tilde{f}_{k'_2 k_2 k'_1 k_1} \frac{\partial \eta_{k'_2 k_2 k'_1 k_1}}{\partial \tilde{\eta}}. \end{aligned} \quad (3.45)$$

Here $\partial \eta_{k'_2 k_2 k'_1 k_1} / \partial \tilde{\eta}$ is obtained from Eq. (3.41) as

$$\frac{\partial \eta_{k'_2 k_2 k'_1 k_1}}{\partial \tilde{\eta}} = \frac{U}{\Delta E_{k'_2 k_2 k'_1 k_1} - \epsilon_c}. \quad (3.46)$$

Substituting the above expression into the self-consistent equation (3.45), we obtain

$$\tilde{\eta} = \frac{1}{1 + \frac{UC}{D}}. \quad (3.47)$$

Here

$$\begin{aligned} C = & \frac{1}{N^6} \sum_{k_1 k'_1 k_2 k'_2} \frac{\tilde{f}_{k'_2 k_2 k'_1 k_1}}{(\Delta E_{k'_2 k_2 k'_1 k_1} - \epsilon_c)} \\ & \times \left\{ \sum_{k_3 k_4} \frac{f(\tilde{\epsilon}_{k_3 \uparrow}) f(\tilde{\epsilon}_{k_4 \downarrow})}{(\Delta E_{k'_2 k_4 k'_1 k_3} - \epsilon_c)} - \sum_{k'_3 k'_4} \frac{[1 - f(\tilde{\epsilon}_{k'_3 \uparrow})] f(\tilde{\epsilon}_{k_4 \downarrow})}{(\Delta E_{k'_2 k_4 k'_3 k_1} - \epsilon_c)} \right. \\ & \left. - \sum_{k_3 k'_4} \frac{f(\tilde{\epsilon}_{k_3 \uparrow}) [1 - f(\tilde{\epsilon}_{k'_4 \downarrow})]}{(\Delta E_{k'_4 k_2 k'_1 k_3} - \epsilon_c)} + \sum_{k'_3 k'_4} \frac{[1 - f(\tilde{\epsilon}_{k'_3 \uparrow})] [1 - f(\tilde{\epsilon}_{k'_4 \downarrow})]}{(\Delta E_{k'_4 k_2 k'_3 k_1} - \epsilon_c)} \right\}, \end{aligned} \quad (3.48)$$

and

$$D = \frac{1}{N^4} \sum_{k_1 k'_1 k_2 k'_2} \frac{\tilde{f}_{k'_2 k_2 k'_1 k_1}}{(\Delta E_{k'_2 k_2 k'_1 k_1} - \epsilon_c)}. \quad (3.49)$$

In the energy representation, each term is expressed as follows:

$$\begin{aligned} C = & \int \frac{\left[\prod_{n=1}^6 d\epsilon_n \right] \left[\prod_{n=1}^6 \rho(\epsilon_n) \right] f(\tilde{\epsilon}_{1 \uparrow}) [1 - f(\tilde{\epsilon}_{2 \uparrow})] f(\tilde{\epsilon}_{3 \downarrow}) [1 - f(\tilde{\epsilon}_{4 \downarrow})] f(\tilde{\epsilon}_{5 \uparrow}) f(\tilde{\epsilon}_{6 \downarrow})}{(\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c)(\epsilon_4 - \epsilon_6 + \epsilon_2 - \epsilon_5 - \epsilon_c)} \\ & - \int \frac{\left[\prod_{n=1}^6 d\epsilon_n \right] \left[\prod_{n=1}^6 \rho(\epsilon_n) \right] f(\tilde{\epsilon}_{1 \uparrow}) [1 - f(\tilde{\epsilon}_{2 \uparrow})] f(\tilde{\epsilon}_{3 \downarrow}) [1 - f(\tilde{\epsilon}_{4 \downarrow})] [1 - f(\tilde{\epsilon}_{5 \uparrow})] f(\tilde{\epsilon}_{6 \downarrow})}{(\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c)(\epsilon_4 - \epsilon_6 + \epsilon_5 - \epsilon_1 - \epsilon_c)} \\ & - \int \frac{\left[\prod_{n=1}^6 d\epsilon_n \right] \left[\prod_{n=1}^6 \rho(\epsilon_n) \right] f(\tilde{\epsilon}_{1 \uparrow}) [1 - f(\tilde{\epsilon}_{2 \uparrow})] f(\tilde{\epsilon}_{3 \downarrow}) [1 - f(\tilde{\epsilon}_{4 \downarrow})] f(\tilde{\epsilon}_{5 \uparrow}) [1 - f(\tilde{\epsilon}_{6 \downarrow})]}{(\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c)(\epsilon_6 - \epsilon_3 + \epsilon_2 - \epsilon_5 - \epsilon_c)} \\ & + \int \frac{\left[\prod_{n=1}^6 d\epsilon_n \right] \left[\prod_{n=1}^6 \rho(\epsilon_n) \right] f(\tilde{\epsilon}_{1 \uparrow}) [1 - f(\tilde{\epsilon}_{2 \uparrow})] f(\tilde{\epsilon}_{3 \downarrow}) [1 - f(\tilde{\epsilon}_{4 \downarrow})] [1 - f(\tilde{\epsilon}_{5 \uparrow})] [1 - f(\tilde{\epsilon}_{6 \downarrow})]}{(\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c)(\epsilon_6 - \epsilon_3 + \epsilon_5 - \epsilon_1 - \epsilon_c)}, \end{aligned} \quad (3.50)$$

and

$$D = \int \frac{\left[\prod_{n=1}^4 d\epsilon_n \right] \left[\prod_{n=1}^4 \rho(\epsilon_n) \right] f(\tilde{\epsilon}_{1 \uparrow}) [1 - f(\tilde{\epsilon}_{2 \uparrow})] f(\tilde{\epsilon}_{3 \downarrow}) [1 - f(\tilde{\epsilon}_{4 \downarrow})]}{\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c}. \quad (3.51)$$

Here $\tilde{\epsilon}_{n\sigma} = \epsilon_n + \tilde{\epsilon}_\sigma$ and $\tilde{\epsilon}_\sigma = \epsilon_0 + U \langle n_{-\sigma} \rangle_0 - \mu$ is the atomic level measured from the chemical potential, and $\rho(\epsilon)$ is the density of states for the one-electron energy eigenvalues for the non-interacting system t_{ij} .

It should be noted that the self-consistent solution (3.47) is also obtained by solving approximately the original self-consistent Eq.(3.33). In order to do this, first we divide the both sides of Eq.(3.33) by $(\Delta E_{k'_2 k_2 k'_1 k_1} - \epsilon_c)$, substitute the form (3.41), and we obtain Eq. (3.47) after taking

the average with respect to $k_1 k'_1 k_2 k'_2$ with a weight $\tilde{f}_{k'_2 k_2 k'_1 k_1}$. The variational principles on $\tilde{\eta}$ tell us that such a solution should be the best among possible approximate solutions. We also note that an approximate form (3.42), which was obtained in the non-self-consistent case [24], is derived from the solution (3.47). In fact, we rewrite Eq. (3.47) as $\tilde{\eta} = 1 - U\tilde{\eta}C/D$. By replacing the approximate form (3.41) in the expression of $U\tilde{\eta}C$ with the momentum independent value η , we reach Eq. (3.42).

The expression C given by Eq. (3.50) consists of the multiple integrals up to the 6-folds. One can reduce these integrals up to the 2-folds using the Laplace transform [31]. The Laplace transform can significantly reduce the number of integrals in the physical quantities which appear in our variational theory. It is written as follows:

$$\frac{1}{z - \epsilon_4 + \epsilon_3 - \epsilon_2 + \epsilon_1 + \epsilon_c} = -i \int_0^\infty dt e^{i(z - \epsilon_4 + \epsilon_3 - \epsilon_2 + \epsilon_1 + \epsilon_c)t}. \quad (3.52)$$

Here $z = \omega + i\delta$, and δ is an infinitesimal positive number.

The term D in Eq. (3.51) is written as follows:

$$\begin{aligned} D &= \int \frac{\left[\prod_{n=1}^4 d\epsilon_n \right] \left[\prod_{n=1}^4 \rho(\epsilon_n) \right] f(\tilde{\epsilon}_{1\uparrow}) [1 - f(\tilde{\epsilon}_{2\uparrow})] f(\tilde{\epsilon}_{3\downarrow}) [1 - f(\tilde{\epsilon}_{4\downarrow})]}{(\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c)} \\ &= -\lim_{z \rightarrow 0} \int \frac{\left[\prod_{n=1}^4 d\epsilon_n \right] \left[\prod_{n=1}^4 \rho(\epsilon_n) \right] f(\tilde{\epsilon}_{1\uparrow}) [1 - f(\tilde{\epsilon}_{2\uparrow})] f(\tilde{\epsilon}_{3\downarrow}) [1 - f(\tilde{\epsilon}_{4\downarrow})]}{(z - \epsilon_4 + \epsilon_3 - \epsilon_2 + \epsilon_1 + \epsilon_c)}. \end{aligned} \quad (3.53)$$

Now using the relation of the Laplace transform (3.52), we obtain

$$\begin{aligned} D &= -i \lim_{z \rightarrow 0} \int_0^\infty dt e^{(z + \epsilon_c)t} \int d\epsilon_1 e^{i\epsilon_1 t} \rho(\epsilon_1) f(\tilde{\epsilon}_{1\uparrow}) \\ &\quad \times \int d\epsilon_2 e^{-i\epsilon_2 t} \rho(\epsilon_2) [1 - f(\tilde{\epsilon}_{2\uparrow})] \int d\epsilon_3 e^{i\epsilon_3 t} \rho(\epsilon_3) f(\tilde{\epsilon}_{3\downarrow}) \\ &\quad \times \int d\epsilon_4 e^{-i\epsilon_4 t} \rho(\epsilon_4) [1 - f(\tilde{\epsilon}_{4\downarrow})] \\ &= -i \int_0^\infty dt e^{i\epsilon_c t} a_\uparrow(-t) b_\uparrow(t) a_\downarrow(-t) b_\downarrow(t). \end{aligned} \quad (3.54)$$

Here

$$a_\sigma(t) = \int d\epsilon \rho(\epsilon) f(\epsilon + \tilde{\epsilon}_\sigma) e^{-i\epsilon t}, \quad (3.55)$$

$$b_\sigma(t) = \int d\epsilon \rho(\epsilon) [1 - f(\epsilon + \tilde{\epsilon}_\sigma)] e^{-i\epsilon t}. \quad (3.56)$$

The 4-fold integrals of D in Eq. (3.51) reduce to the 1-fold integral in Eq. (3.54).

In the same way, we can perform the Laplace transform of the element C (Eq.(3.50)) as follows

$$\begin{aligned} C &= -\int_0^\infty dt dt' e^{i\epsilon_c(t+t')} [a_\uparrow(-t) b_\uparrow(t+t') a_\downarrow(-t) b_\downarrow(t+t') a_\uparrow(-t') a_\downarrow(-t') \\ &\quad - a_\uparrow(-t-t') b_\uparrow(t) a_\downarrow(-t) b_\downarrow(t+t') b_\uparrow(t') a_\downarrow(-t') \\ &\quad - a_\uparrow(-t) b_\uparrow(t+t') a_\downarrow(-t-t') b_\downarrow(t) a_\uparrow(-t') b_\downarrow(t') \\ &\quad + a_\uparrow(-t-t') b_\uparrow(t) a_\downarrow(-t-t') b_\downarrow(t) b_\uparrow(t') b_\downarrow(t')]. \end{aligned} \quad (3.57)$$

3.4 Various physical quantities

3.4.1 Correlation energy ϵ_c

The ground-state correlation energy (3.24) per atom in the SSA is given by

$$\epsilon_c = \frac{-\langle \tilde{O}_i^\dagger \tilde{H} \rangle_0 - \langle \tilde{H} \tilde{O}_i \rangle_0 + \langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0}. \quad (3.58)$$

The ground-state correlation energy is obtained by substituting the variational parameters (3.41) into Eq. (3.58). Each element in the energy is given as follows.

$$\begin{aligned} \langle \tilde{H} \tilde{O}_i \rangle_0 &= \langle \tilde{O}_i^\dagger \tilde{H} \rangle_0^* \\ &= U^2 \tilde{\eta} \int \frac{\left[\prod_{n=1}^4 d\epsilon_n \right] \left[\prod_{n=1}^4 \rho(\epsilon_n) \right] f(\tilde{\epsilon}_{1\uparrow}) [1 - f(\tilde{\epsilon}_{2\uparrow})] f(\tilde{\epsilon}_{3\downarrow}) [1 - f(\tilde{\epsilon}_{4\downarrow})]}{\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c}, \end{aligned} \quad (3.59)$$

$$\langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_0 = \langle \tilde{O}_i^\dagger \tilde{H}_0 \tilde{O}_i \rangle_0 + U \langle \tilde{O}_i^\dagger O_i \tilde{O}_i \rangle_0, \quad (3.60)$$

$$\begin{aligned} \langle \tilde{O}_i^\dagger \tilde{H}_0 \tilde{O}_i \rangle_0 &= U^2 \tilde{\eta}^2 \int \frac{\left[\prod_{n=1}^4 d\epsilon_n \right] \left[\prod_{n=1}^4 \rho(\epsilon_n) \right] f(\tilde{\epsilon}_{1\uparrow}) [1 - f(\tilde{\epsilon}_{2\uparrow})] f(\tilde{\epsilon}_{3\downarrow}) [1 - f(\tilde{\epsilon}_{4\downarrow})]}{(\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c)^2 (\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1)^{-1}}, \end{aligned} \quad (3.61)$$

$$\begin{aligned} \langle \tilde{O}_i^\dagger O_i \tilde{O}_i \rangle_0 &= U^2 \tilde{\eta}^2 \int \frac{\left[\prod_{n=1}^4 d\epsilon_n \right] \left[\prod_{n=1}^4 \rho(\epsilon_n) \right] f(\tilde{\epsilon}_{1\uparrow}) [1 - f(\tilde{\epsilon}_{2\uparrow})] f(\tilde{\epsilon}_{3\downarrow}) [1 - f(\tilde{\epsilon}_{4\downarrow})]}{(\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c)^2} \\ &\quad \times \left[\int \frac{\left[\prod_{n=5}^6 d\epsilon_n \right] \left[\prod_{n=5}^6 \rho(\epsilon_n) \right] f(\tilde{\epsilon}_{5\uparrow}) f(\tilde{\epsilon}_{6\downarrow})}{(\epsilon_4 - \epsilon_6 + \epsilon_2 - \epsilon_5 - \epsilon_c)} \right. \\ &\quad - \int \frac{\left[\prod_{n=5}^6 d\epsilon_n \right] \left[\prod_{n=5}^6 \rho(\epsilon_n) \right] f(\tilde{\epsilon}_{5\uparrow}) [1 - f(\tilde{\epsilon}_{6\downarrow})]}{(\epsilon_6 - \epsilon_3 + \epsilon_2 - \epsilon_5 - \epsilon_c)} \\ &\quad - \int \frac{\left[\prod_{n=5}^6 d\epsilon_n \right] \left[\prod_{n=5}^6 \rho(\epsilon_n) \right] [1 - f(\tilde{\epsilon}_{5\uparrow})] f(\tilde{\epsilon}_{6\downarrow})}{(\epsilon_4 - \epsilon_6 + \epsilon_5 - \epsilon_1 - \epsilon_c)} \\ &\quad \left. + \int \frac{\left[\prod_{n=5}^6 d\epsilon_n \right] \left[\prod_{n=5}^6 \rho(\epsilon_n) \right] [1 - f(\tilde{\epsilon}_{5\uparrow})] [1 - f(\tilde{\epsilon}_{6\downarrow})]}{(\epsilon_6 - \epsilon_3 + \epsilon_5 - \epsilon_1 - \epsilon_c)} \right], \end{aligned} \quad (3.62)$$

$$\langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0 = U^2 \tilde{\eta}^2 \int \frac{\left[\prod_{n=1}^4 d\epsilon_n \right] \left[\prod_{n=1}^4 \rho(\epsilon_n) \right] f(\tilde{\epsilon}_{1\uparrow}) [1 - f(\tilde{\epsilon}_{2\uparrow})] f(\tilde{\epsilon}_{3\downarrow}) [1 - f(\tilde{\epsilon}_{4\downarrow})]}{(\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c)^2}. \quad (3.63)$$

It should be noted that $\tilde{\eta}$ in Eq. (3.47) is given as a function of ϵ_c , and ϵ_c in Eq. (3.24) depends on $\tilde{\eta}$ and ϵ_c . Therefore, both equations have to be solved self-consistently. To determine the best value of $\tilde{\eta}$, we start from ϵ_c in the LA for example, and calculate $\tilde{\eta}$ according to Eq. (3.47). Next we calculate various elements $\langle \tilde{H}\tilde{O}_i \rangle_0$, $\langle \tilde{O}_i^\dagger \tilde{H} \rangle_0^*$, $\langle \tilde{O}_i^\dagger \tilde{H}\tilde{O}_i \rangle_0$, and $\langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0$ which are given by Eqs. (3.59), (3.60), and (3.63), respectively. Using these values we calculate ϵ_c again according to Eq. (3.24). We repeat this cycle until the self-consistency of ϵ_c and $\tilde{\eta}$ is achieved. We call this scheme the self-consistent MLA [25].

Various terms of correlation energy ϵ_c in Eq. (3.24) are expressed by means of the Laplace transform as follows:

$$\langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0 = -U^2 \tilde{\eta}^2 \int_0^\infty dt dt' e^{i\epsilon_c(t+t')} a_\uparrow(-t-t') b_\uparrow(t+t') a_\downarrow(-t-t') b_\downarrow(t+t') , \quad (3.64)$$

$$\langle \tilde{H}\tilde{O}_i \rangle_0 = \langle \tilde{O}_i^\dagger \tilde{H} \rangle_0^* = iU^2 \tilde{\eta} \int_0^\infty dt e^{i\epsilon_c t} a_\uparrow(-t) a_\downarrow(-t) b_\uparrow(t) b_\downarrow(t) , \quad (3.65)$$

$$\begin{aligned} \langle \tilde{O}_i^\dagger \tilde{H}_0 \tilde{O}_i \rangle_0 = & -U^2 \tilde{\eta}^2 \int_0^\infty dt dt' e^{i\epsilon_c(t+t')} [a_\uparrow(-t-t') b_\uparrow(t+t') a_\downarrow(-t-t') b_{1\downarrow}(t+t') \\ & - a_\uparrow(-t-t') b_\uparrow(t+t') a_{1\downarrow}(-t-t') b_\downarrow(t+t') \\ & + a_\uparrow(-t-t') b_{1\uparrow}(t+t') a_\downarrow(-t-t') b_\downarrow(t+t') \\ & - a_{1\uparrow}(-t-t') b_\uparrow(t+t') a_\downarrow(-t-t') b_\downarrow(t+t')] , \end{aligned} \quad (3.66)$$

$$\begin{aligned} \langle \tilde{O}_i^\dagger O_i \tilde{O}_i \rangle_0 = & -U^2 \tilde{\eta}^2 \int_0^\infty dt dt' e^{i\epsilon_c(t+t')} [a_\uparrow(-t) b_\uparrow(t+t') a_\downarrow(-t) b_\downarrow(t+t') a_\uparrow(-t') a_\downarrow(-t') \\ & - a_\uparrow(-t) b_\uparrow(t+t') a_\downarrow(-t-t') b_\downarrow(t) a_\uparrow(-t') b_\downarrow(t') \\ & - a_\uparrow(-t-t') b_\uparrow(t) a_\downarrow(-t) b_\downarrow(t+t') b_\uparrow(t') a_\downarrow(-t') \\ & + a_\uparrow(-t-t') b_\uparrow(t) a_\downarrow(-t-t') b_\downarrow(t) b_\uparrow(t') b_\downarrow(t')] . \end{aligned} \quad (3.67)$$

Here

$$a_{1\sigma}(t) = \int d\epsilon \rho(\epsilon) f(\epsilon + \tilde{\epsilon}_\sigma) \epsilon e^{-i\epsilon t} , \quad (3.68)$$

$$b_{1\sigma}(t) = \int d\epsilon \rho(\epsilon) [(1 - f(\epsilon + \tilde{\epsilon}_\sigma))] \epsilon e^{-i\epsilon t} . \quad (3.69)$$

3.4.2 Electron number $\langle n_i \rangle$

In order to obtain the expectation value of any physical quantity, we may use the Feynman-Hellmann theorem. It relates the derivative of the total energy with respect to a parameter, to the expectation value of the derivative of the Hamiltonian with respect to the same parameter.

Consider a system with Hamiltonian $H(\lambda)$ that depends on some parameter λ . Let $\Psi(\lambda)$ be an eigenfunction of $H(\lambda)$ with an eigenvalue $E(\lambda)$.

$$H(\lambda)\Psi(\lambda) = E(\lambda)\Psi(\lambda). \quad (3.70)$$

We start from the relation.

$$E(\lambda) = \langle \Psi(\lambda) | H(\lambda) | \Psi(\lambda) \rangle. \quad (3.71)$$

Differentiating both sides with respect to λ yields

$$\frac{\partial E}{\partial \lambda} = \left\langle \frac{\partial \Psi(\lambda)}{\partial \lambda} | H(\lambda) | \Psi(\lambda) \right\rangle + \langle \Psi(\lambda) | \frac{\partial H(\lambda)}{\partial \lambda} | \Psi(\lambda) \rangle + \langle \Psi(\lambda) | H(\lambda) | \frac{\partial \Psi(\lambda)}{\partial \lambda} \rangle. \quad (3.72)$$

Generally, $H(\lambda)$ is the Hermite operator. Therefore,

$$\begin{aligned} \frac{\partial E}{\partial \lambda} &= E(\lambda) \left\langle \frac{\partial \Psi(\lambda)}{\partial \lambda} | \Psi(\lambda) \right\rangle + \langle \Psi(\lambda) | \frac{\partial H(\lambda)}{\partial \lambda} | \Psi(\lambda) \rangle + E(\lambda) \left\langle \Psi(\lambda) | \frac{\partial \Psi(\lambda)}{\partial \lambda} \right\rangle \\ &= \langle \Psi(\lambda) | \frac{\partial H(\lambda)}{\partial \lambda} | \Psi(\lambda) \rangle + E(\lambda) \left[\left\langle \frac{\partial \Psi(\lambda)}{\partial \lambda} | \Psi(\lambda) \right\rangle + \left\langle \Psi(\lambda) | \frac{\partial \Psi(\lambda)}{\partial \lambda} \right\rangle \right]. \end{aligned} \quad (3.73)$$

Since $|\Psi(\lambda)\rangle$ is assumed to be normalized, we have from the normalization condition, $\langle \Psi(\lambda) | \Psi(\lambda) \rangle = 1$, the following identity.

$$\left\langle \frac{\partial \Psi(\lambda)}{\partial \lambda} | \Psi(\lambda) \right\rangle + \left\langle \Psi(\lambda) | \frac{\partial \Psi(\lambda)}{\partial \lambda} \right\rangle = \frac{\partial(1)}{\partial \lambda} = 0. \quad (3.74)$$

Hence, the second term on the r.h.s. of Eq. (3.73) vanishes, and we reach

$$\frac{\partial E(\lambda)}{\partial \lambda} = \langle \Psi(\lambda) | \frac{\partial H(\lambda)}{\partial \lambda} | \Psi(\lambda) \rangle. \quad (3.75)$$

The above relation is called the Feynman-Hellmann theorem [32, 33].

The average electron number is obtained by making use of Feynman-Hellmann theorem (3.75) on the Hubbard model (2.11).

$$\frac{\partial \langle H \rangle}{\partial \epsilon_0} = \langle \hat{\Psi} | \frac{\partial H}{\partial \epsilon_0} | \hat{\Psi} \rangle = \sum_{\sigma} \langle n_{i\sigma} \rangle. \quad (3.76)$$

Here $\langle n_i \rangle = \sum_{\sigma} \langle n_{i\sigma} \rangle$ is the average electron number on site i . In the above expression we adopt the normalized variational wavefunction $|\Psi\rangle$. Then the l.h.s. of the above equation is given as

$$\frac{\partial \langle H \rangle_{\text{MLA}}}{\partial \epsilon_0} = \langle \hat{\Psi} | \frac{\partial H}{\partial \epsilon_0} | \hat{\Psi} \rangle_{\text{MLA}} = \langle \phi | \frac{\partial H}{\partial \epsilon_0} | \phi \rangle + \frac{\langle \Psi | \left(\frac{\partial H}{\partial \epsilon_0} - \langle \phi | \frac{\partial H}{\partial \epsilon_0} | \phi \rangle \right) | \Psi \rangle_{\text{MLA}}}{\langle \Psi | \Psi \rangle_{\text{MLA}}}, \quad (3.77)$$

or

$$\frac{\partial \langle H \rangle_{\text{MLA}}}{\partial \epsilon_0} = \left[\frac{\partial \langle \phi | H | \phi \rangle}{\partial \epsilon_0} \right]_v + N \left[\frac{\partial \epsilon_c}{\partial \epsilon_0} \right]_{v,\eta}. \quad (3.78)$$

Here, v is the potential energy of one electron, $[A]_v$ means that the change of A via potential v in the HF wavefunction $|\phi\rangle$ should be neglected. $[A]_{v,\eta}$ implies that there is no change of A via v and η . Therefore, the relation (3.76) reduces to the following formula.

$$\langle n_i \rangle = \left[\frac{\partial \langle \phi | H | \phi \rangle}{\partial \epsilon_0} \right]_v + N \left[\frac{\partial \epsilon_c}{\partial \epsilon_0} \right]_{v,\eta}. \quad (3.79)$$

To calculate the r.h.s. of the above equation, we separate the energy into the HF energy and the correlation energy part *i.e.*, $\langle H \rangle = \langle H \rangle_0 + N\epsilon_c$. The HF energy is given by $\langle H \rangle_0 = \langle \phi | H_0 | \phi \rangle -$

$\sum_i U_i \langle n_{i\uparrow} \rangle_0 \langle n_{i\downarrow} \rangle_0$. Here $H_0 = \sum_i (\epsilon_0 + U_i \langle n_{i-\sigma} \rangle_0) n_{i\sigma} + \sum_{ij\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma}$, is the HF Hamiltonian as an independent particle.

The first term on the r.h.s. of Eq. (3.79) is calculated as

$$\left[\frac{\partial \langle \phi | H | \phi \rangle_{LA}}{\partial \epsilon_0} \right]_v = \langle \phi | \frac{\partial H}{\partial \epsilon_0} | \phi \rangle = \langle n_i \rangle_0. \quad (3.80)$$

The correlation energy per atom (3.24) is given by

$$N \epsilon_c = \sum_i \frac{-\langle \tilde{O}_i^\dagger \tilde{H} \rangle_0 - \langle \tilde{H} \tilde{O}_i \rangle_0 + \langle \tilde{O}_i \tilde{H} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0}. \quad (3.81)$$

Thus, we have

$$N \left[\frac{\partial \epsilon_c}{\partial \epsilon_0} \right]_{v,\eta} = \frac{- \left[\frac{\partial \langle \tilde{O}_i^\dagger \tilde{H} \rangle_0}{\partial \epsilon_0} \right]_v - \left[\frac{\partial \langle \tilde{H} \tilde{O}_i \rangle_0}{\partial \epsilon_0} \right]_v + \left[\frac{\partial \langle \tilde{O}_i \tilde{H} \tilde{O}_i \rangle_0}{\partial \epsilon_0} \right]_v}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0}. \quad (3.82)$$

Here $\langle \tilde{H} \tilde{O}_i \rangle_0 = \langle \tilde{H}_0 \tilde{O}_i \rangle_0 + U_i \langle O_i \tilde{O}_i \rangle_0$. Using the Wick theorem (see Appendix B), we calculate $\langle \tilde{H}_0 \tilde{O}_i \rangle_0$ as $\langle \tilde{H}_0 \tilde{O}_i \rangle_0 = \langle \tilde{O}_i^\dagger \tilde{H}_0 \rangle_0 = 0$. Therefore, the first two terms of the numerator on the r.h.s. of Eq. (3.82) vanish and the third term is written as

$$\langle \tilde{O}_i \tilde{H} \tilde{O}_i \rangle_0 = \langle \tilde{O}_i^\dagger \tilde{H}_0 \tilde{O}_i \rangle_0 + U \langle \tilde{O}_i^\dagger O_i \tilde{O}_i \rangle_0. \quad (3.83)$$

The second term on the r.h.s. of the above equation does not explicitly include ϵ_0 . Hence, there is no need to differentiate this term with respect to ϵ_0 . The derivative of the first term with respect to ϵ_0 gives

$$\frac{\partial \langle \tilde{O}_i^\dagger \tilde{H}_0 \tilde{O}_i \rangle_0}{\partial \epsilon_0} = \langle \tilde{O}_i^\dagger \sum_\sigma \tilde{n}_{i\sigma} \tilde{O}_i \rangle_0, \quad (3.84)$$

and thus

$$\frac{\partial \langle \tilde{O}_i \tilde{H} \tilde{O}_i \rangle_0}{\partial \epsilon_0} = \langle \tilde{O}_i^\dagger \sum_\sigma \tilde{n}_{i\sigma} \tilde{O}_i \rangle_0. \quad (3.85)$$

Hence Eq. (3.82) becomes

$$N \left[\frac{\partial \epsilon_c}{\partial \epsilon_0} \right]_{v,\eta} = \frac{\sum_\sigma \langle \tilde{O}_i^\dagger \tilde{n}_{i\sigma} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0}. \quad (3.86)$$

The final expression for the average electron number is obtained by using Eqs. (3.79), (3.80) and (3.86).

$$\langle n_i \rangle = \langle n_i \rangle_0 + \frac{\sum_\sigma \langle \tilde{O}_i^\dagger \tilde{n}_{i\sigma} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0}. \quad (3.87)$$

Here $\langle n_i \rangle_0$ is the HF term, and $\sum_\sigma \langle \tilde{O}_i^\dagger \tilde{n}_{i\sigma} \tilde{O}_i \rangle_0$ denotes the correlation contribution.

The term $\langle \tilde{O}_i^\dagger \tilde{n}_{i\sigma} \tilde{O}_i \rangle_0$ can be written by means of energy representation as follows.

$$\begin{aligned} & \langle \tilde{O}_i^\dagger \tilde{n}_{i\sigma} \tilde{O}_i \rangle_0 \\ &= U^2 \tilde{\eta}^2 \int \frac{\left[\prod_{n=1}^5 d\epsilon_n \right] \left[\prod_{n=1}^5 \rho(\epsilon_n) \right] f(\tilde{\epsilon}_{1-\sigma}) [1 - f(\tilde{\epsilon}_{2-\sigma})] f(\tilde{\epsilon}_{3\sigma}) [1 - f(\tilde{\epsilon}_{4\sigma})]}{(\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c)^2} \\ & \quad \times \left[\frac{[1 - f(\tilde{\epsilon}_{5\sigma})]}{(\epsilon_5 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c)} - \frac{f(\tilde{\epsilon}_{5\sigma})}{(\epsilon_4 - \epsilon_5 + \epsilon_2 - \epsilon_1 - \epsilon_c)} \right], \end{aligned} \quad (3.88)$$

After the Laplace transform, we obtain

$$\begin{aligned} \langle \tilde{O}_i^\dagger \tilde{n}_{i\sigma} \tilde{O}_i \rangle_0 &= -U^2 \tilde{\eta}^2 \int_0^\infty dt dt' e^{i\epsilon_c(t+t')} [a_{-\sigma}(-t-t') b_{-\sigma}(t+t') a_\sigma(-t-t') b_\sigma(t) b_\sigma(t') \\ & \quad - a_{-\sigma}(-t-t') b_{-\sigma}(t+t') a_\sigma(-t) b_\sigma(t+t') a_\sigma(t')]. \end{aligned} \quad (3.89)$$

Another quantity $\langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0$ in Eq. (3.87) is given by Eq. (3.63).

3.4.3 Momentum distribution $\langle n_{k\sigma} \rangle$

Momentum distribution function $\langle n_{k\sigma} \rangle$ represents a distribution of electrons in the momentum space. The ground state energy for normalized wavefunction Ψ is

$$\langle H \rangle = \langle \hat{\Psi} | (H_0 + \sum_i U_i O_i) | \hat{\Psi} \rangle. \quad (3.90)$$

In the momentum representation, the Hamiltonian H is expressed as.

$$H = \sum_{k\sigma} \epsilon_{k\sigma} n_{k\sigma} + \sum_i U O_i, \quad (3.91)$$

$$H_0 = \sum_{k\sigma} (\epsilon_0 - \sigma h + U \langle n_{i-\sigma} \rangle_0) n_{k\sigma} + \sum_{k\sigma} \epsilon_k n_{k\sigma}. \quad (3.92)$$

Here $\epsilon_{k\sigma} \equiv \epsilon_k - \sigma h + U \langle n_{i-\sigma} \rangle_0$.

By making use of the Feynman-Hellmann theorem (3.75), we obtain

$$\langle n_{k\sigma} \rangle = \langle \hat{\Psi} | \frac{\partial H}{\partial \epsilon_{k\sigma}} | \hat{\Psi} \rangle = \frac{\partial \langle H \rangle}{\partial \epsilon_{k\sigma}}. \quad (3.93)$$

We calculate for the variational wavefunction the derivative on the r.h.s. of Eq. (3.93).

$$\frac{\partial \langle H \rangle_{\text{MLA}}}{\partial \epsilon_{k\sigma}} = \langle \hat{\Psi} | \frac{\partial H}{\partial \epsilon_{k\sigma}} | \hat{\Psi} \rangle_{\text{MLA}} = \langle \phi | \frac{\partial H}{\partial \epsilon_{k\sigma}} | \phi \rangle + \frac{\langle \Psi | (\frac{\partial H}{\partial \epsilon_{k\sigma}} - \langle \phi | \frac{\partial H}{\partial \epsilon_{k\sigma}} | \phi \rangle) | \Psi \rangle_{\text{MLA}}}{\langle \Psi | \Psi \rangle_{\text{MLA}}}, \quad (3.94)$$

or

$$\frac{\partial \langle H \rangle_{\text{MLA}}}{\partial \epsilon_{k\sigma}} = \left[\frac{\partial \langle \phi | H | \phi \rangle}{\partial \epsilon_{k\sigma}} \right]_v + N \left[\frac{\partial \epsilon_c}{\partial \epsilon_{k\sigma}} \right]_{v,\eta}. \quad (3.95)$$

Here v is the potential energy of the one particle state. Therefore,

$$\langle n_{k\sigma} \rangle = \left[\frac{\partial \langle \phi | H | \phi \rangle}{\partial \epsilon_{k\sigma}} \right]_v + N \left[\frac{\partial \epsilon_c}{\partial \epsilon_{k\sigma}} \right]_{v,\eta}. \quad (3.96)$$

The Hamiltonian is divided into the HF energy and the correlation energy part: $\langle H \rangle = \langle H \rangle_0 + N\epsilon_c$. The HF part is given by $\langle H \rangle_0 = \sum_{k\sigma} \epsilon_{k\sigma} \langle n_{k\sigma} \rangle_0 - \sum_i U_i \langle n_{i\uparrow} \rangle_0 \langle n_{i\downarrow} \rangle_0$. Hence

$$\left[\frac{\partial \langle \phi | H | \phi \rangle}{\partial \epsilon_{k\sigma}} \right]_v = \langle \phi | \frac{\partial H}{\partial \epsilon_{k\sigma}} | \phi \rangle = \langle n_{k\sigma} \rangle_0. \quad (3.97)$$

The correlation part in Eq. (3.96) is given by

$$N \left[\frac{\partial \epsilon_c}{\partial \epsilon_{k\sigma}} \right]_{v,\eta} = \frac{- \left[\frac{\partial \langle \tilde{O}_i^\dagger \tilde{H} \rangle_0}{\partial \epsilon_{k\sigma}} \right]_v - \left[\frac{\partial \langle \tilde{H} \tilde{O}_i \rangle_0}{\partial \epsilon_{k\sigma}} \right]_v + \left[\frac{\partial \langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_0}{\partial \epsilon_{k\sigma}} \right]_v}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0}. \quad (3.98)$$

The 1st- and 2nd-term of the numerator on the r.h.s. are given as $\langle \tilde{H} \tilde{O}_i \rangle_0 = \langle \tilde{O}_i^\dagger \tilde{H} \rangle_0^* = U \langle O_i \tilde{O}_i \rangle$. Since $U \langle O_i \tilde{O}_i \rangle$ is independent of $\epsilon_{k\sigma}$, both the terms vanish. The third term on the r.h.s. of Eq. (3.98) is given as $\langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_0 = \langle \tilde{O}_i^\dagger \tilde{H}_0 \tilde{O}_i \rangle_0 + U_i \langle \tilde{O}_i^\dagger O_i \tilde{O}_i \rangle_0$. Since $U_i \langle \tilde{O}_i^\dagger O_i \tilde{O}_i \rangle_0$ is independent of $\epsilon_{k\sigma}$, we can ignore the differentiation of it with respect to $\epsilon_{k\sigma}$. Therefore

$$\left[\frac{\partial \langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_0}{\partial \epsilon_{k\sigma}} \right]_v = \left[\langle \tilde{O}_i^\dagger \frac{\partial \tilde{H}}{\partial \epsilon_{k\sigma}} \tilde{O}_i \rangle_0 \right]_v = \langle \tilde{O}_i^\dagger \delta n_{k\sigma} \tilde{O}_i \rangle_0. \quad (3.99)$$

Here $\tilde{H}_0 = \sum_{k\sigma} \epsilon_{k\sigma} \delta n_{k\sigma}$ and $\delta n_{k\sigma} = n_{k\sigma} - \langle n_{k\sigma} \rangle_0$. Equation (3.98) is therefore written as follows.

$$N \left[\frac{\partial \epsilon_c}{\partial \epsilon_{k\sigma}} \right]_{v,\eta} = \sum_i \frac{\langle \tilde{O}_i^\dagger \tilde{n}_{k\sigma} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0}. \quad (3.100)$$

We obtain the expression of $\langle n_{k\sigma} \rangle$ using Eqs. (3.96), (3.97), and (3.100) as follows.

$$\langle n_{k\sigma} \rangle = \langle n_{k\sigma} \rangle_0 + \sum_i \frac{\langle \tilde{O}_i^\dagger \tilde{n}_{k\sigma} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0}. \quad (3.101)$$

Since $\langle \tilde{O}_i^\dagger \tilde{n}_{k\sigma} \tilde{O}_i \rangle_0$ should be independent of site i for a system with one atom per unit cell, we have $\sum_i \langle \tilde{O}_i^\dagger \tilde{n}_{k\sigma} \tilde{O}_i \rangle_0 = N \langle \tilde{O}_i^\dagger \tilde{n}_{k\sigma} \tilde{O}_i \rangle_0$, N being the total number of sites. Finally, we obtain the expression of the momentum distribution $\langle n_{k\sigma} \rangle$ as follows.

$$\langle n_{k\sigma} \rangle = \langle n_{k\sigma} \rangle_0 + \frac{N \langle \tilde{O}_i^\dagger \tilde{n}_{k\sigma} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0}. \quad (3.102)$$

The momentum distribution function consists of the HF term $\langle n_{k\sigma} \rangle_0$ and correlation contribution $N \langle \tilde{O}_i^\dagger \tilde{n}_{k\sigma} \tilde{O}_i \rangle_0$.

The term $N \langle \tilde{O}_i^\dagger \tilde{n}_{k\sigma} \tilde{O}_i \rangle_0$ can be written in the energy representation as follows.

$$\begin{aligned} & N \langle \tilde{O}_i^\dagger \tilde{n}_{k\sigma} \tilde{O}_i \rangle_0 \\ &= U^2 \tilde{\eta}^2 \left[[1 - f(\tilde{\epsilon}_{k\sigma})] \int \frac{\left[\prod_{n=1}^3 d\epsilon_n \right] \left[\prod_{n=1}^3 \rho(\epsilon_n) \right] f(\tilde{\epsilon}_{1-\sigma}) [1 - f(\tilde{\epsilon}_{2-\sigma})] f(\tilde{\epsilon}_{3\sigma})}{(\epsilon_{k\sigma} - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c)^2} \right. \\ & \quad \left. - f(\tilde{\epsilon}_{k\sigma}) \int \frac{\left[\prod_{n=1}^3 d\epsilon_n \right] \left[\prod_{n=1}^3 \rho(\epsilon_n) \right] f(\tilde{\epsilon}_{1-\sigma}) [1 - f(\tilde{\epsilon}_{2-\sigma})] f(\tilde{\epsilon}_{3\sigma})}{(\epsilon_3 - \epsilon_{k\sigma} + \epsilon_2 - \epsilon_1 - \epsilon_c)^2} \right], \end{aligned} \quad (3.103)$$

In the Laplace transform representation, it is given as

$$N\langle\tilde{O}_i^\dagger\tilde{n}_{k\sigma}\tilde{O}_i\rangle_0 = U^2\tilde{\eta}^2\int_0^\infty dt dt' e^{i\epsilon_c(t+t')} a_{-\sigma}(-t-t') b_{-\sigma}(t+t') \\ \times [f(\tilde{\epsilon}_{k\sigma})b_\sigma(t+t')e^{i\epsilon_k(t+t')} - [1-f(\tilde{\epsilon}_{k\sigma})]a_\sigma(-t-t')e^{-i\epsilon_k(t+t')}] . \quad (3.104)$$

Another quantity $\langle\tilde{O}_i^\dagger\tilde{O}_i\rangle_0$ in Eq. (3.102) is given by Eq. (3.63).

3.4.4 Double occupation number $\langle n_{i\uparrow}n_{i\downarrow}\rangle$

The double occupation number $\langle n_{i\uparrow}n_{i\downarrow}\rangle$ denotes the probability of finding doubly-occupied electrons on the same site. In the HF approximation, this is constant irrespective of U . It is obtained by applying the Feynman-Hellmann theorem to the Hubbard model (2.11):

$$\langle n_{i\uparrow}n_{i\downarrow}\rangle = \langle\hat{\Psi}|\frac{\partial H}{\partial U_i}|\hat{\Psi}\rangle = \frac{\partial\langle H\rangle}{\partial U_i} . \quad (3.105)$$

In the case of the MLA,

$$\frac{\partial\langle H\rangle_{\text{MLA}}}{\partial U_i} = \langle\hat{\Psi}|\frac{\partial H}{\partial U_i}|\hat{\Psi}\rangle_{\text{MLA}} = \langle\phi|\frac{\partial H}{\partial U_i}|\phi\rangle + \frac{\langle\Psi|(\frac{\partial H}{\partial U_i} - \langle\phi|\frac{\partial H}{\partial U_i}|\phi\rangle)|\Psi\rangle_{\text{MLA}}}{\langle\Psi|\Psi\rangle_{\text{MLA}}} . \quad (3.106)$$

Therefore,

$$\langle n_{i\uparrow}n_{i\downarrow}\rangle = \left[\frac{\partial\langle\phi|H|\phi\rangle}{\partial U_i}\right]_v + N\left[\frac{\partial\epsilon_c}{\partial U_i}\right]_{v,\eta} . \quad (3.107)$$

Here v represents the potential energy of one electron. The HF energy is given by $\langle H\rangle_0 = \sum_{k\sigma}\epsilon_{k\sigma}\langle n_{k\sigma}\rangle - \sum_i U_i\langle n_{i\uparrow}\rangle_0\langle n_{i\downarrow}\rangle_0$. The first term is given by

$$\left[\frac{\partial\langle\phi|H|\phi\rangle}{\partial U_i}\right]_v = \langle n_{i\uparrow}\rangle_0\langle n_{i\downarrow}\rangle_0 . \quad (3.108)$$

The second term on the r.h.s. of Eq. (3.107) is given by

$$N\left[\frac{\partial\epsilon_c}{\partial U_i}\right]_{v,\eta} = \frac{-\left[\frac{\partial\langle\tilde{O}_i^\dagger\tilde{H}\rangle_0}{\partial U_i}\right]_v - \left[\frac{\partial\langle\tilde{H}\tilde{O}_i\rangle_0}{\partial U_i}\right]_v + \left[\frac{\partial\langle\tilde{O}_i^\dagger\tilde{H}\tilde{O}_i\rangle_0}{\partial U_i}\right]_v}{1 + \langle\tilde{O}_i^\dagger\tilde{O}_i\rangle_0} . \quad (3.109)$$

First, we calculate the 1st-term and 2nd-term on the r.h.s. of the above expression.

$$\langle\tilde{H}\tilde{O}_i\rangle_0 = U_i\langle\tilde{O}_i\tilde{O}_i\rangle = \frac{U}{N^4}\sum_{k_1k'_1k_2k'_2}\tilde{f}_{k'_2k_2k'_1k_1}\eta_{k'_2k_2k'_1k_1} , \quad (3.110)$$

$$\langle\tilde{O}_i^\dagger\tilde{H}\rangle_0 = \langle\tilde{H}\tilde{O}_i\rangle_0^* . \quad (3.111)$$

Therefore,

$$\left[\frac{\partial\langle\tilde{H}\tilde{O}_i\rangle_0}{\partial U_i}\right]_v = \frac{\langle\tilde{H}\tilde{O}_i\rangle_0}{U_i} = \frac{1}{N^4}\sum_{k_1k'_1k_2k'_2}\tilde{f}_{k'_2k_2k'_1k_1}\eta_{k'_2k_2k'_1k_1} , \quad (3.112)$$

$$\left[\frac{\partial \langle \tilde{O}_i^\dagger \tilde{H} \rangle_0}{\partial U_i} \right]_v = \frac{\langle \tilde{O}_i^\dagger \tilde{H} \rangle_0}{U_i} = \frac{1}{N^4} \sum_{k_1 k'_1 k_2 k'_2} \tilde{f}_{k_2 k_2 k'_1 k_1} \eta_{k'_2 k_2 k'_1 k_1}^*. \quad (3.113)$$

In the same way, Eqs. (3.112) and (3.113) can be written as follows.

$$\left[\frac{\partial \langle \tilde{O}_i^\dagger \tilde{H} \rangle_0}{\partial U_i} \right]_v = \frac{\langle \tilde{O}_i^\dagger \tilde{H} \rangle_0}{U_i} = \langle \tilde{O}_i^\dagger O_i \rangle_0, \quad (3.114)$$

$$\left[\frac{\partial \langle \tilde{H} \tilde{O}_i \rangle_0}{\partial U_i} \right]_v = \frac{\langle \tilde{H} \tilde{O}_i \rangle_0}{U_i} = \langle O_i \tilde{O}_i \rangle_0. \quad (3.115)$$

Next, we calculate the third-term on the r.h.s. of Eq. (3.109).

$$\begin{aligned} \left[\frac{\partial \langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_0}{\partial U_i} \right]_v &= \frac{1}{N^6} \sum_{k_1 k_2 k'_1 k'_2} \tilde{f}_{k_2 k_2 k'_1 k_1} \eta_{k'_2 k_2 k'_1 k_1}^* \\ &+ \left[\sum_{k_3 k_4} f(\tilde{\epsilon}_{k_3 \uparrow}) f(\tilde{\epsilon}_{k_4 \downarrow}) \eta_{k'_2 k_4 k'_1 k_3} \right. \\ &- \sum_{k_3 k'_4} f(\tilde{\epsilon}_{k_3 \uparrow}) [1 - f(\tilde{\epsilon}_{k'_4 \downarrow})] \eta_{k'_4 k_2 k'_1 k_3} \\ &- \sum_{k'_3 k_4} [1 - f(\tilde{\epsilon}_{k'_3 \uparrow})] f(\tilde{\epsilon}_{k_4 \downarrow}) \eta_{k'_2 k_4 k'_3 k_1} \\ &\left. + \sum_{k'_3 k'_4} [1 - f(\tilde{\epsilon}_{k'_3 \uparrow})] [1 - f(\tilde{\epsilon}_{k'_4 \downarrow})] \eta_{k'_4 k_2 k'_3 k_1} \right]. \end{aligned} \quad (3.116)$$

Here the Hamiltonian is divided into the HF and the correlation parts.

$$\langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_0 = \langle \tilde{O}_i^\dagger \tilde{H}_0 \tilde{O}_i \rangle_0 + \langle \tilde{O}_i^\dagger \sum_j U_j O_j \tilde{O}_i \rangle_0, \quad (3.117)$$

Therefore,

$$\left[\frac{\partial \langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_0}{\partial U_i} \right]_v = \langle \tilde{O}_i^\dagger \frac{\partial \tilde{H}_0}{\partial U_i} \tilde{O}_i \rangle_0 + \left[\frac{\partial}{\partial U_i} \langle \tilde{O}_i^\dagger \sum_j U_j O_j \tilde{O}_i \rangle_0 \right]_v. \quad (3.118)$$

Using the HF Hamiltonian (3.92), we obtain $\partial \tilde{H}_0 / \partial U_i = \sum_\sigma \langle n_{i-\sigma} \rangle_0 \tilde{n}_{i\sigma}$. Thus,

$$\left[\frac{\partial \langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_0}{\partial U_i} \right]_v = \sum_\sigma \langle n_{i-\sigma} \rangle_0 \langle \tilde{O}_i^\dagger \tilde{n}_{i\sigma} \tilde{O}_i \rangle_0 + \langle \tilde{O}_i^\dagger O_i \tilde{O}_i \rangle_0, \quad (3.119)$$

The correlation contribution in Eq. (3.109) becomes as follows.

$$\left[\frac{\partial \epsilon_c}{\partial U_i} \right]_{v,\eta} = \frac{-\langle \tilde{O}_i^\dagger O_i \rangle_0 - \langle O_i \tilde{O}_i \rangle_0 + \langle \tilde{O}_i^\dagger O_i \tilde{O}_i \rangle_0 + \sum_\sigma \langle n_{i-\sigma} \rangle_0 \langle \tilde{O}_i^\dagger \tilde{n}_{i\sigma} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0}. \quad (3.120)$$

Finally, the double occupation number $\langle n_{i\uparrow} n_{i\downarrow} \rangle$ is obtained from Eqs. (3.107), (3.108), and (3.120) as follows.

$$\begin{aligned} \langle n_{i\uparrow} n_{i\downarrow} \rangle &= \langle n_{i\uparrow} \rangle_0 \langle n_{i\downarrow} \rangle_0 \\ &+ \frac{-\langle \tilde{O}_i^\dagger O_i \rangle_0 - \langle O_i \tilde{O}_i \rangle_0 + \langle \tilde{O}_i^\dagger O_i \tilde{O}_i \rangle_0 + \sum_\sigma \langle n_{i-\sigma} \rangle_0 \langle \tilde{O}_i^\dagger \tilde{n}_{i\sigma} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0}. \end{aligned} \quad (3.121)$$

The expression, $\langle \tilde{O}_i^\dagger O_i \rangle_0 + \langle O_i \tilde{O}_i \rangle_0$ is written in the energy representation as follows.

$$\begin{aligned} & \langle \tilde{O}_i^\dagger O_i \rangle_0 + \langle O_i \tilde{O}_i \rangle_0 \\ &= 2U\tilde{\eta} \int \frac{\left[\prod_{n=1}^4 d\epsilon_n \right] \left[\prod_{n=1}^4 \rho(\epsilon_n) \right] f(\tilde{\epsilon}_{1\uparrow})[1 - f(\tilde{\epsilon}_{2\uparrow})]f(\tilde{\epsilon}_{3\downarrow})[1 - f(\tilde{\epsilon}_{4\downarrow})]}{(\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c)}, \end{aligned} \quad (3.122)$$

In the Laplace transformation, it is given by

$$\langle \tilde{O}_i^\dagger O_i \rangle_0 + \langle O_i \tilde{O}_i \rangle_0 = 2iU\tilde{\eta} \int_0^\infty dt e^{i\epsilon c t} a_\uparrow(-t)b_\uparrow(t)a_\downarrow(-t)b_\downarrow(t). \quad (3.123)$$

The other quantities $\langle \tilde{O}_i^\dagger O_i \tilde{O}_i \rangle_0$, $\langle \tilde{O}_i^\dagger \tilde{n}_{i\sigma} \tilde{O}_i \rangle_0$, and $\langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0$ have been given by Eqs. (3.62), (3.88), and (3.63), respectively.

3.5 Numerical results

We have performed the numerical calculations for the non-half-filled as well as half-filled bands of the Hubbard model in order to examine the validity of the improved scheme of the MLA and the effect of electron correlations. To calculate various physical quantities, we have adopted the hypercubic lattice in infinite dimensions, where the SSA works best. The density of states (DOS) for non-interacting system is given by $\rho(\epsilon) = (1/\sqrt{\pi}) \exp(-\epsilon^2)$ in this case [24](See Appendix C). The energy unit is chosen to be $\int d\epsilon \rho(\epsilon) \epsilon^2 = 1/2$. The external magnetic field h is assumed to be zero.

3.5.1 Effect of the best choice of $\tilde{\eta}$

To calculate various quantities in the MLA, we solved the self-consistent equations (3.24) and (3.47) with use of the Laplace transforms of elements. In this sub-section, we compare the self-consistent results with the non self-consistent ones to clarify the role of the best choice of $\tilde{\eta}$.

Figure 3.1 shows the calculated correlation energy as a function of Coulomb interaction. The correlation energy for the non-selfconsistent MLA gives the lower correlation energy as compared with the LA. The correlation energy for the MLA with the best choice of $\tilde{\eta}$ (*i.e.*, the self-consistent MLA) is lower than that of the non-self-consistent MLA. The results indicate that the self-consistency of $\tilde{\eta}$ is significant for finding the best energy.

In Fig. 3.2 we show an example of the momentum distribution as a function of energy $\epsilon_{k\sigma}$ when electron number per atom (n) is deviated from 1. The MLA with non self-consistent $\tilde{\eta}$ (3.42) shows a bump in the vicinity of the Fermi level, leading to an unphysical result. The MLA with self-consistent $\tilde{\eta}$ yields a significant momentum dependence which shows monotonical decrease of the distribution with increasing $\epsilon_{k\sigma}$.

We have also calculated the quasiparticle weight Z vs. Coulomb interaction energy curves at half-filling. As shown in Fig. 3.3, we find that the best choice of $\tilde{\eta}$ increases Z (*i.e.*, decreases the inverse effective mass), so that the critical Coulomb interaction of the divergence of the effective mass, U_{c2} changes from 3.21 to 3.40. The latter is closer to the numerical renormalization group (NRG) [34] value $U_{c2} = 4.10$, which is believed to be the best at present.

From the above discussions on the results with and without self-consistent $\tilde{\eta}$, it is obvious that self-consistent MLA improves the MLA theory without self-consistent $\tilde{\eta}$. In the following discussions we adopt the MLA with the best choice of $\tilde{\eta}$.

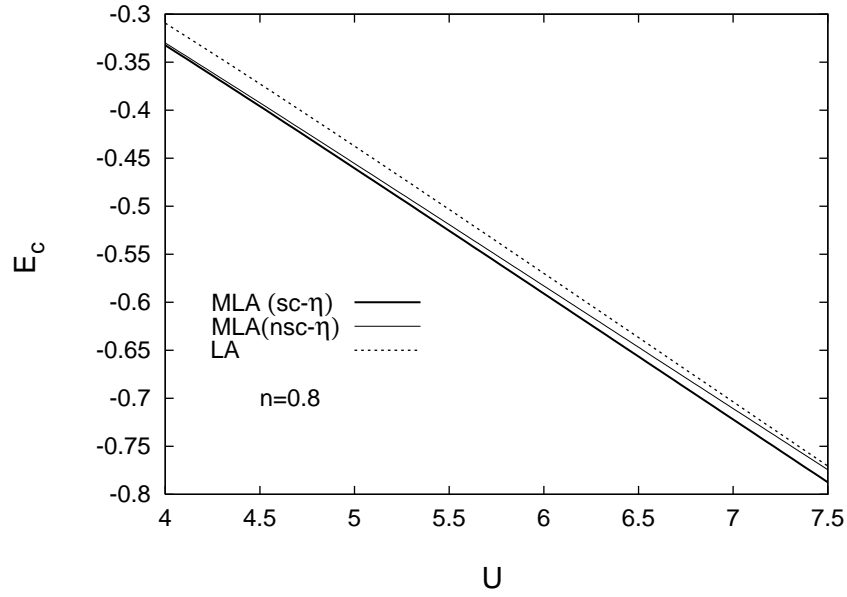


Figure 3.1: The correlation energy E_c vs. Coulomb interaction energy curve for $n = 0.8$. The thick solid curve: the MLA with self-consistent $\tilde{\eta}$, the thin curve: the MLA with non self-consistent $\tilde{\eta}$, and the dashed curve: the LA.

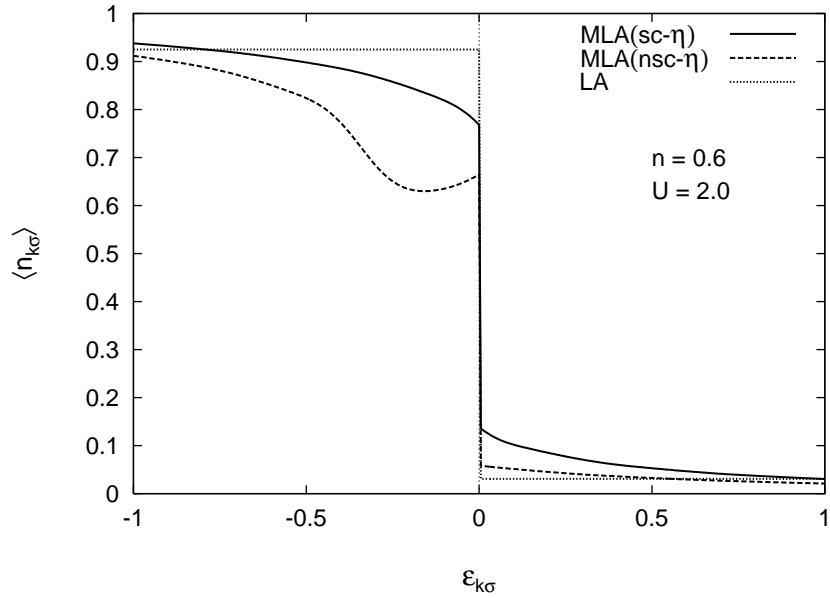


Figure 3.2: The momentum distribution as a function of energy $\epsilon_{k\sigma}$ for various theories with $n = 0.6$ and $U = 2.0$. The solid curve: the MLA with the best choice of $\tilde{\eta}$, the dashed curve: the MLA without the best choice of $\tilde{\eta}$, and the dotted curve: the LA.

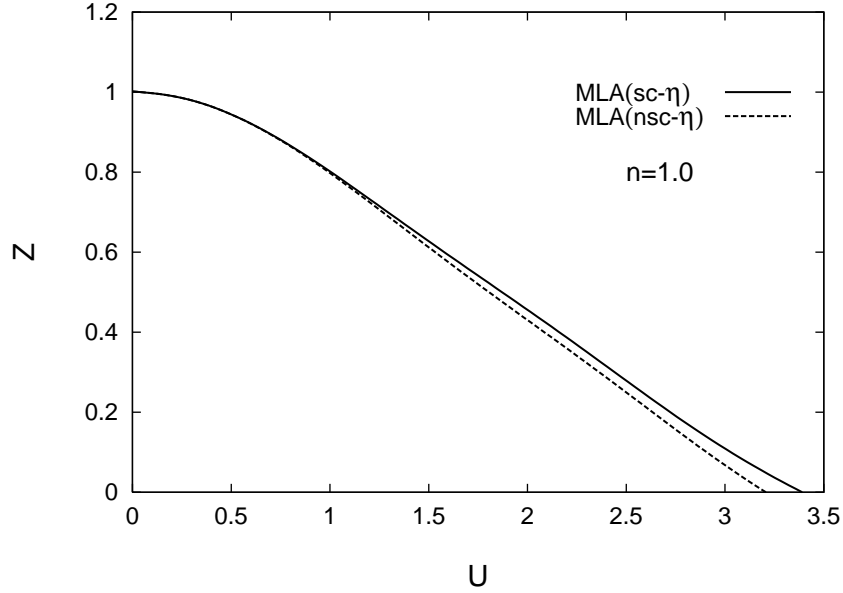


Figure 3.3: Quasiparticle-weight Z vs. Coulomb interaction curves in the MLA with self-consistent $\tilde{\eta}$ (solid curve), and without (dashed curve).

3.5.2 MLA in various physical quantities

We present in this section the numerical results on various physical quantities, and discuss the new aspects of the MLA and related effects of electron correlations by comparing the MLA with the LA.

We first represent in Fig. 3.4 the calculated correlation energy per atom as a function of Coulomb interaction U . The energy in the MLA is lower than that of the LA over all Coulomb interaction energy parameters U and electron numbers n . These results imply that the MLA improves the LA. The magnitude of the correlation energy $|\epsilon_c|$ tends to increase with increasing U , because with increasing U the correlation corrections increase as U^2 for small U and cancel the HF energy loss being linear in U for large U . For a fixed value of the Coulomb interaction U , the gain of the correlation energy $|\epsilon_c|$ increases with increasing n , because there is a correlation energy gain at each doubly-occupied site and the number of such sites increases with increasing n .

Figure 3.5 depicts the double occupation number $\langle n_{\uparrow}n_{\downarrow} \rangle$ vs. Coulomb interaction curves for the half-filled case as well as non-half-filled case. In the uncorrelated limit, the double occupancy is the same for both the LA and the MLA and it decreases with increasing Coulomb interaction U because electrons move on the lattice so as to suppress the loss of Coulomb energy due to the double occupation. For the half-filled case, the suppression of the double occupancy is prominent in the intermediate regime of Coulomb interaction. We find that the MLA wavefunction reduces the double occupancy as compared with that of the LA, for the non-half-filled case, in the range $0 < U \lesssim 5$, while in the range $5 \lesssim U$ the double occupancy in the MLA is larger than that of the LA. It implies that the LA with momentum-independent η_{LA} overestimates the itinerant character for weak and intermediate U regions, while it overestimates the atomic character for large U region.

The momentum-distribution function shown in Fig. 3.6 indicates more distinct difference between the LA and the MLA. The distributions in the LA are constant below and above the Fermi level irrespective of U . The same behavior is also found in the GW [7, 8, 9]. The MLA curves

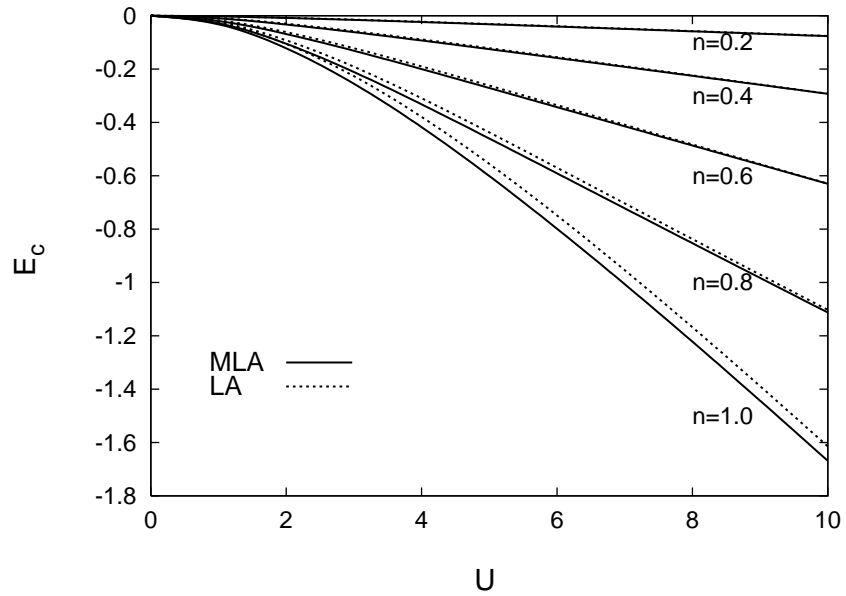


Figure 3.4: The correlation energies E_c vs. Coulomb interaction energy parameter U in the MLA (solid curve) and the LA (dashed curve) for various electron number n .

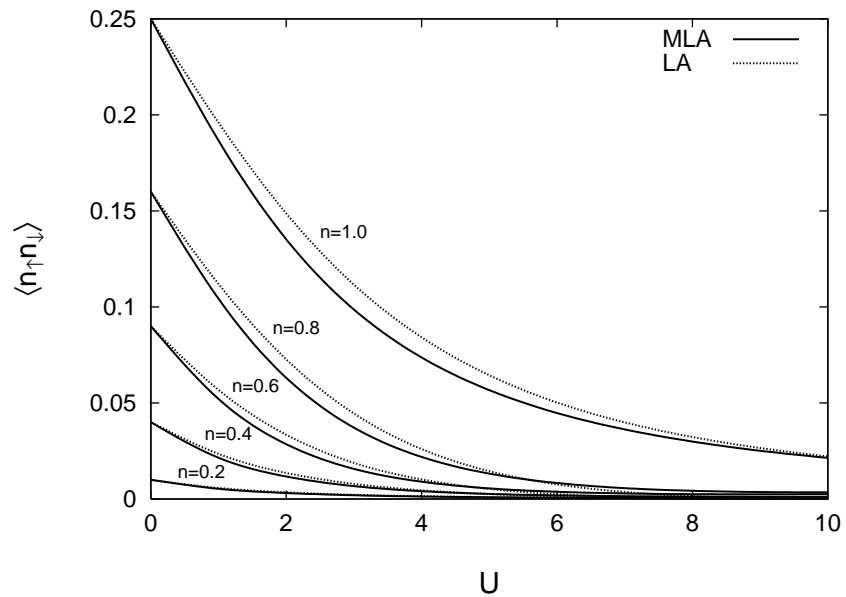


Figure 3.5: The double occupation number $\langle n_{\uparrow}n_{\downarrow} \rangle$ vs. Coulomb interaction energy U curves in the MLA (solid curve) and the LA (dotted curve).

show a monotonical decrease of the distribution with increasing $\epsilon_{k\sigma}$, indicating a distinct momentum dependence of $\langle n_{k\sigma} \rangle$ via energy $\epsilon_{k\sigma}$, which is qualitatively different from both the LA and the GW.

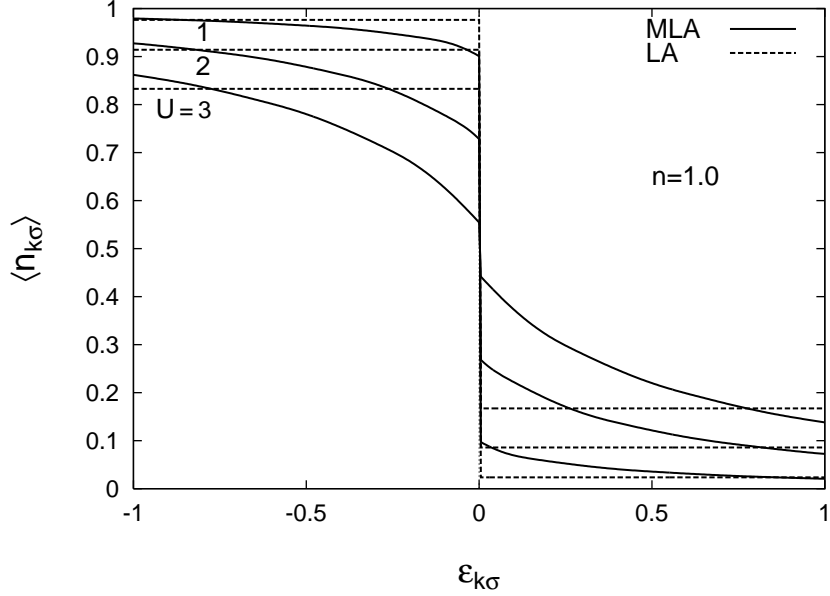


Figure 3.6: The momentum distribution as a function of energy $\epsilon_{k\sigma}$ for various electron number with constant Coulomb interaction energy parameters $U = 3$. The MLA: solid curves, the LA: dashed curves.

The quasiparticle weight Z (*i.e.* the inverse effective mass) is obtained from the jump at the Fermi level in the momentum distribution according to the Fermi liquid theory [35, 36, 37, 38] (see Appendix D). Calculated quasiparticle weight vs Coulomb interaction curves are shown in Fig. 3.7 for the half-filled case. The quasiparticle weight in the LA changes as $Z = (1 - 3\eta_{\text{LA}}^2/16)/(1 + \eta_{\text{LA}}^2/16)$ and vanishes at $U_{c2}(\text{LA}) = 24/\sqrt{3\pi} (= 7.82)$. In the GW [18], the quasiparticle weight changes as $Z = 1 - (U/U_{c2})^2$. The curve in the GW agrees with the LA curve for small U . But it deviates from the LA when U becomes larger, and vanishes at $U_{c2}(\text{GW}) = 8/\sqrt{\pi} (= 4.51)$. It should be noted that the GW curve strongly deviates from the curve in the NRG [34] which is considered to be the best. It is remarkable that the RPT-1 (renormalized perturbation theory with first order approximation to the memory function) is close to the NRG through $U_{c2} = 3.705$. We observe that the critical Coulomb interaction U_{c2} for the self-consistent $\tilde{\eta}$ is 3.40 in the MLA while U_{c2} in the non-self-consistent $\tilde{\eta}$ yields 3.21. The quasiparticle weight in the MLA much improves the LA as seen in Fig.3.7. We note that the wavefunction itself does not show the metal-insulator transition at U_{c2} in the present approximation because the approximate expression of variational parameters (3.37) has no singularity at finite value of U . The values of Z obtained by the LA and the MLA should be regarded as an estimate from the metallic side.

In summary, we have developed a momentum dependent local-ansatz wavefunction approach (MLA) to the correlated electron systems in solids to solve best a self-consistent equation for variational parameters at half-filling as well as non half-filling. With use of the improved variational scheme we performed the numerical calculations for the Hubbard model on the hypercubic lattice in infinite dimensions. We verified that the self-consistent scheme significantly improves the correlation energy and the momentum distribution as compared with the non self-consistent

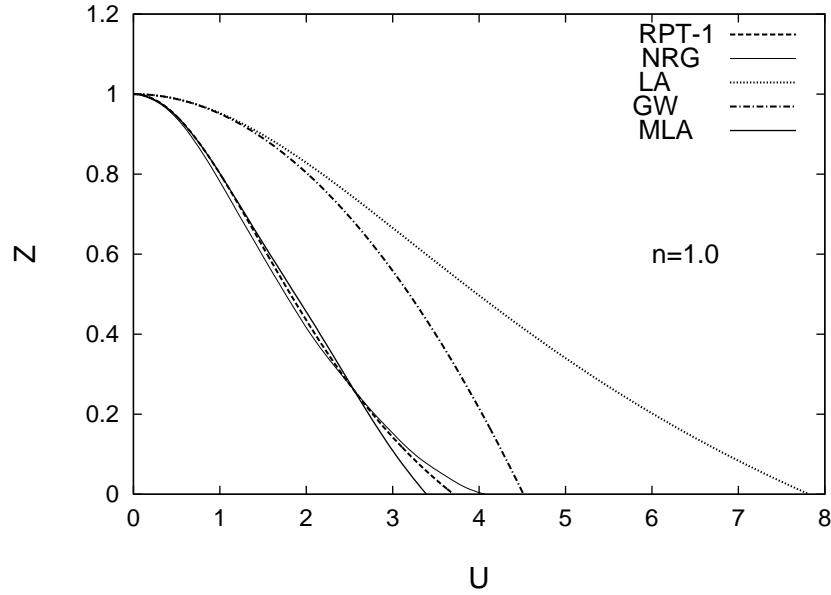


Figure 3.7: Quasiparticle-weight vs. Coulomb interaction curves in various theories. The RPT-1: dashed curve [39], the NRG: thin solid curve [34], the LA: dotted curve, the MLA: solid curve, and the GW: dot-dashed curve.

scheme in the MLA. We also demonstrated that the theory improves the standard variational methods such as the local-ansatz approach (LA) and the Gutzwiller wavefunction approach (GW); the ground-state energy in the MLA is lower than those of the LA and the GW in the weak and intermediate Coulomb interaction regimes. The double occupation number is shown to be suppressed as compared with the LA. Calculated momentum distribution functions show a distinct momentum dependence, which is qualitatively different from those of the LA and the GW.

Chapter 4

Momentum Dependent Local-Ansatz Approach with Alloy-Analogy Wavefunction

As we have mentioned in the previous chapter the MLA wavefunction does suitably describe electron correlations in the weak and the intermediate Coulomb interaction, but it cannot suppress loss of Coulomb repulsion in the strong interaction regime. To improve the difficulty we propose in this chapter a new wavefunction [27] by changing the starting wavefunction from the HF wavefunction to the alloy-analogy (AA) wavefunction which is suitable in the strong Coulomb interaction regime.

4.1 Alloy-analogy wavefunction

The concept of the alloy-analogy Hamiltonian can be traced back to Hubbard's original work on electron correlations [12]. In the strong Coulomb interaction regime, electrons with spin σ move slowly from site to site due to electron correlations, and therefore should feel a potential U instead of the HF average potential $U\langle\hat{n}_{i-\sigma}\rangle_0$, when the opposite spin electron is on the same site. Hubbard regarded this system as an alloy with different random potentials $\epsilon_0 + U$ and ϵ_0 having the concentration $\langle\hat{n}_{i-\sigma}\rangle$ (occupied) and $[1 - \langle\hat{n}_{i-\sigma}\rangle]$ (unoccupied), respectively. Here ϵ_0 denotes the atomic level of electron. This is called the alloy-analogy (AA) approximation (see Fig. 4.1). The AA Hamiltonian is then defined by

$$H_{AA} = \sum_{i\sigma} (\epsilon_0 - \mu + Un_{i-\sigma})\hat{n}_{i\sigma} + \sum_{ij\sigma} t_{ij}a_{i\sigma}^\dagger a_{j\sigma} - U \sum_i (n_{i\uparrow}\langle\hat{n}_{i\downarrow}\rangle_{AA} + n_{i\downarrow}\langle\hat{n}_{i\uparrow}\rangle_{AA}) + U \sum_i \langle\hat{n}_{i\uparrow}\rangle_{AA}\langle\hat{n}_{i\downarrow}\rangle_{AA}. \quad (4.1)$$

Here $\langle\sim\rangle_{AA}$ denotes the AA average $\langle\phi_{AA}|(\sim)|\phi_{AA}\rangle$ with respect to the ground-state wavefunction $|\phi_{AA}\rangle$ of the AA Hamiltonian H_{AA} . Since the motion of electrons with opposite spin are treated to be static in the AA approximation, related operators $\{\hat{n}_{i-\sigma}\}$ are regarded as a random static C number $n_{i-\sigma}$ (0 or 1). Each configuration of $\{n_{i\sigma}\}$ is considered as a snapshot in time development.

The ground-state energy E satisfies the following inequality for any wavefunction $|\phi_{AA}\rangle$.

$$E \leq \langle\phi_{AA}|H|\phi_{AA}\rangle = \langle H_{AA}\rangle_{AA}, \quad (4.2)$$

and thus

$$E \leq \overline{\langle H \rangle}_{AA}. \quad (4.3)$$

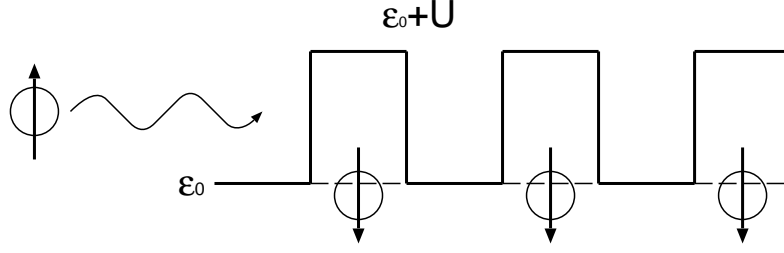


Figure 4.1: Alloy-analogy approximation

Here $\langle H \rangle_{AA} \equiv \langle \phi_{AA} | H | \phi_{AA} \rangle = \langle H_{AA} \rangle_{AA}$ and the upper bar denotes the configurational average. The AA ground-state energy per atom is obtained by taking the configurational average.

$$\overline{\langle H \rangle}_{AA} = n\mu + 2 \int_{-\infty}^0 \epsilon \overline{\rho_{i\sigma}(\epsilon)} d\epsilon + U \overline{\langle \hat{n}_{i\uparrow} \rangle_{AA} \langle \hat{n}_{i\downarrow} \rangle_{AA}} - U (\overline{\langle \hat{n}_{i\uparrow} \rangle_{AA} \langle \hat{n}_{i\downarrow} \rangle_{AA}} + \overline{\langle \hat{n}_{i\downarrow} \rangle_{AA} \langle \hat{n}_{i\uparrow} \rangle_{AA}}). \quad (4.4)$$

Here n is the electron number per atom. $\rho_{i\sigma}(\epsilon)$ is the local density of states (DOS) and is obtained from the one-electron Green function as follows.

$$\rho_{i\sigma}(\epsilon) = -\frac{1}{\pi} \text{Im} G_{ii\sigma}(z). \quad (4.5)$$

The Green function $G_{ii\sigma}(z)$ is defined by

$$G_{ii\sigma}(z) = [(z - \mathbf{H}_\sigma)^{-1}]_{ii}. \quad (4.6)$$

Here $(\mathbf{H}_\sigma)_{ij}$ is the one-electron Hamiltonian matrix for the AA Hamiltonian (4.1), which is defined by

$$(\mathbf{H}_\sigma)_{ij} = \epsilon_{i\sigma} \delta_{ij} + t_{ij} (1 - \delta_{ij}), \quad (4.7)$$

$$\epsilon_{i\sigma} = \epsilon_0 - \mu + U n_{i-\sigma}. \quad (4.8)$$

The average electron number $\langle \hat{n}_{i\sigma} \rangle_{AA}$ for the AA Hamiltonian (4.1) is given as

$$\langle \hat{n}_{i\sigma} \rangle_{AA} = \int f(\epsilon) \rho_{i\sigma}(\epsilon) d\epsilon. \quad (4.9)$$

Here $f(\epsilon)$ denotes the Fermi distribution function.

To obtain the local DOS, we make use of the coherent potential approximation (CPA) [40, 41]. In the CPA, we replace the random potentials at the surrounding sites with coherent potentials $\Sigma_\sigma(z)$. The on-site impurity Green function $G_{ii\sigma}(z)$ is then obtained as follows.

$$G_{ii\sigma}(z) = \frac{1}{F_\sigma(z)^{-1} - \epsilon_{i\sigma} + \Sigma_\sigma(z)}. \quad (4.10)$$

Here $F_\sigma(z)$ is the on-site Green function for the coherent system in which all the random potentials have been replaced by the coherent ones, and is given by

$$F_\sigma(z) = \int \frac{\rho(\epsilon) d\epsilon}{z - \Sigma_\sigma(z) - \epsilon}. \quad (4.11)$$

Here $\rho(\epsilon)$ is the DOS per site for the noninteracting system. The coherent potential $\Sigma_\sigma(z)$ is determined from the self-consistent condition (see Appendix E).

$$\overline{G_{00\sigma}(z)} = F_\sigma(z). \quad (4.12)$$

The configurational average of the impurity Green function is given as

$$\overline{G_{00\sigma}(z)} = \frac{\langle \hat{n}_{-\sigma} \rangle_{AA}}{F_\sigma(z)^{-1} - \epsilon_0 + \mu - U + \Sigma_\sigma(z)} + \frac{1 - \langle \hat{n}_{-\sigma} \rangle_{AA}}{F_\sigma(z)^{-1} - \epsilon_0 + \mu + \Sigma_\sigma(z)} \quad (4.13)$$

The average DOS in the second term on the right hand side (r.h.s.) of Eq. (4.4) is given by

$$\overline{\rho_{i\sigma}(\epsilon)} = -\frac{1}{\pi} \text{Im} \overline{G_{00\sigma}(z)}. \quad (4.14)$$

The double occupation numbers on the r.h.s. of Eq. (4.4) are obtained in the SSA as follows.

$$\overline{\langle \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \rangle_{AA}} = \overline{\langle \hat{n}_{i\uparrow} \rangle_{AA} \langle \hat{n}_{i\downarrow} \rangle_{AA}} = \sum_{\alpha} P_{\alpha} \langle \hat{n}_{\uparrow} \rangle_{\alpha} \langle \hat{n}_{\downarrow} \rangle_{\alpha}. \quad (4.15)$$

Here $\alpha = 00, 10, 01, 11$ denotes the on-site electron number configuration. Alternative notation ν that $\nu = 0$ (empty on a site), $1 \uparrow$ (occupied by an electron with spin \uparrow), $1 \downarrow$ (occupied by an electron with spin \downarrow) and 2 (occupied by 2 electrons) is also useful. In this case, the probability P_{α} for the configuration α is expressed as $P_0, P_{1\uparrow}, P_{1\downarrow}$ and P_2 .

For the empty site *i.e.*, $\alpha = 00$, the expression $\epsilon_{i\sigma}$ in Eq. (4.8) for the up spin (\uparrow) and down spin (\downarrow) state becomes ϵ_0 . Therefore, the term $\langle \hat{n}_{\uparrow} \rangle_{00} \langle \hat{n}_{\downarrow} \rangle_{00}$ in Eq. (4.15) is redefined as $\langle \hat{n}_{\uparrow} \rangle_{\epsilon_0} \langle \hat{n}_{\downarrow} \rangle_{\epsilon_0}$. Similarly, the rest of the terms for $\alpha = 10, 01, 11$ are expressed as $\langle \hat{n}_{\uparrow} \rangle_{\epsilon_0} \langle \hat{n}_{\downarrow} \rangle_{\epsilon_0+U}$, $\langle \hat{n}_{\uparrow} \rangle_{\epsilon_0+U} \langle \hat{n}_{\downarrow} \rangle_{\epsilon_0}$, and $\langle \hat{n}_{\uparrow} \rangle_{\epsilon_0+U} \langle \hat{n}_{\downarrow} \rangle_{\epsilon_0+U}$, respectively. The electron number is then given by

$$\langle \hat{n}_{\sigma} \rangle_{\epsilon_0} = \int f(\epsilon) \rho_{\epsilon_0\sigma}(\epsilon) d\epsilon, \quad (4.16)$$

$$\rho_{\epsilon_0\sigma}(\epsilon) = -\frac{1}{\pi} \text{Im} G_{\epsilon_0\sigma}(z), \quad (4.17)$$

$$G_{\epsilon_0\sigma}(z) = \frac{1}{F_\sigma(z)^{-1} - \epsilon_0 + \mu + \Sigma_\sigma(z)}, \quad (4.18)$$

$$\langle \hat{n}_{\sigma} \rangle_{\epsilon_0+U} = \int f(\epsilon) \rho_{\epsilon_0+U\sigma}(\epsilon) d\epsilon, \quad (4.19)$$

$$\rho_{\epsilon_0+U\sigma}(\epsilon) = -\frac{1}{\pi} \text{Im} G_{\epsilon_0+U\sigma}(z), \quad (4.20)$$

$$G_{\epsilon_0+U\sigma}(z) = \frac{1}{F_\sigma(z)^{-1} - \epsilon_0 + \mu - U + \Sigma_\sigma(z)}. \quad (4.21)$$

Note that $P_0 + P_{1\uparrow} + P_{1\downarrow} + P_2 = 1$, and the probability of finding an electron with spin \uparrow (\downarrow) on a site is given by $P_{\uparrow(\downarrow)} = P_{1\uparrow(1\downarrow)} + P_2$. Three statistical probabilities P_0 , $P_{1\uparrow}$, and $P_{1\downarrow}$ depend on the probability P_2 . In the following, we obtain an approximate expression of P_2 .

Note that we made the following approximations in the derivation of the AA Hamiltonian.

$$\hat{n}_{i\uparrow}\hat{n}_{i\downarrow} \approx n_{i\uparrow}\hat{n}_{i\downarrow} + n_{i\downarrow}\hat{n}_{i\uparrow} - n_{i\uparrow}n_{i\downarrow}. \quad (4.22)$$

Taking the quantum mechanical average as well as the configurational average of the double occupation number of the above expression, we obtain the probability of the double occupation P_2 ($= \overline{\langle \hat{n}_{i\uparrow}\hat{n}_{i\downarrow} \rangle}$) as follows.

$$P_2 = \overline{n_{i\uparrow}\langle \hat{n}_{i\downarrow} \rangle_{AA}} + \overline{n_{i\downarrow}\langle \hat{n}_{i\uparrow} \rangle_{AA}} - \overline{n_{i\uparrow}n_{i\downarrow}} \quad (4.23)$$

The last term on the r.h.s. of Eq. (4.23) may be regarded as the probability P_2 . Therefore, we obtain

$$P_2 \approx \frac{1}{2}(\overline{n_{i\uparrow}\langle \hat{n}_{i\downarrow} \rangle_{AA}} + \overline{n_{i\downarrow}\langle \hat{n}_{i\uparrow} \rangle_{AA}}). \quad (4.24)$$

The double occupation numbers on the r.h.s. of Eq. (4.4) are obtained in the SSA as follows.

$$\overline{n_{i\uparrow}\langle \hat{n}_{i\downarrow} \rangle_{AA}} + \overline{n_{i\downarrow}\langle \hat{n}_{i\uparrow} \rangle_{AA}} = P_\uparrow\langle \hat{n}_\downarrow \rangle_{\epsilon_0+U} + P_\downarrow\langle \hat{n}_\uparrow \rangle_{\epsilon_0+U} \quad (4.25)$$

The electron number $\langle \hat{n}_\sigma \rangle_{\epsilon_0+U}$ is defined by Eq. (4.19).

The momentum distribution in the AA scheme is given by

$$\overline{\langle \hat{n}_{k\sigma} \rangle_{AA}} = \int f(\epsilon)\rho_{k\sigma}(\epsilon) d\epsilon, \quad (4.26)$$

$$\rho_{k\sigma}(\epsilon) = -\frac{1}{\pi} \text{Im} F_{k\sigma}(z), \quad (4.27)$$

$$F_{k\sigma}(z) = \frac{1}{z - \Sigma_\sigma(z) - \epsilon_k}. \quad (4.28)$$

Here ϵ_k is the eigenvalue of t_{ij} with momentum k .

In summary, in order to determine the AA energy $\overline{\langle H \rangle_{AA}}$ in Eq. (4.4) we first determine the coherent potential Σ_σ self-consistently by using the Eqs. (4.11), (4.12), and (4.13); then calculate the average DOS (Eq. (4.14)) as well as the double occupation number by Eqs. (4.15) and (4.25).

4.2 Local-ansatz + alloy-analogy wavefunction approach with momentum dependent variational parameters

We have constructed the MLA wavefunction in Sec. 3.1, which is given as follows (see Eq. (3.9)).

$$|\Psi_{\text{MLA}}\rangle = \prod_i (1 - \tilde{O}_i)|\phi_0\rangle. \quad (4.29)$$

In the MLA wavefunction we considered the HF wavefunction as a starting wavefunction. The theory can describe electron correlations in the weak and the intermediate Coulomb interaction regimes. Hereafter we refer the wavefunction (4.29) to the MLA-HF wavefunction. The MLA-HF wavefunction is not suitable for the description of strongly-correlated electrons as we discussed in Chap. 3. In order to describe the strong interaction regime we adopt in this section the AA wavefunction $|\phi_{AA}\rangle$ as a starting wavefunction and propose a new ansatz, which we call the MLA-AA wavefunction, as follows.

$$|\Psi_{\text{MLA-AA}}\rangle = \prod_i (1 - \tilde{O}_i) |\phi_{AA}\rangle. \quad (4.30)$$

Note that we introduced modified local operators $\{\tilde{O}_i\}$ with variational parameters $\eta_{\kappa'_2\kappa_2\kappa'_1\kappa_1}$ in the above expression, which is defined as follows.

$$\tilde{O}_i = \sum_{\kappa'_2\kappa_2\kappa'_1\kappa_1} \langle \kappa'_1|i\rangle \langle i|\kappa_1\rangle \langle \kappa'_2|i\rangle \langle i|\kappa_2\rangle \eta_{\kappa'_2\kappa_2\kappa'_1\kappa_1} \delta(a_{\kappa'_2\downarrow}^\dagger a_{\kappa_2\downarrow}) \delta(a_{\kappa'_1\uparrow}^\dagger a_{\kappa_1\uparrow}). \quad (4.31)$$

Here $a_{\kappa\sigma}^\dagger$ and $a_{\kappa\sigma}$ are the creation and annihilation operators which diagonalize the Hamiltonian H_{AA} , and $\delta(a_{\kappa'\sigma}^\dagger a_{\kappa\sigma}) = a_{\kappa'\sigma}^\dagger a_{\kappa\sigma} - \langle a_{\kappa'\sigma}^\dagger a_{\kappa\sigma} \rangle_{AA}$. It should be noted that the MLA-AA wavefunction reduces to the MLA-HF by replacing the random potential $Un_{i-\sigma}$ with the HF one, *i.e.*, $U\langle \phi_0|\hat{n}_{i-\sigma}|\phi_0\rangle$, so that $\Psi_{\text{MLA-AA}}$ and $\Psi_{\text{MLA-HF}}$ might be mutually connected to each other via a suitable parameter which interpolates between the two wavefunctions.

The inequality condition for the ground-state energy E of any wavefunction $|\Psi\rangle$ is written as follows.

$$E \leq \frac{\langle \Psi|H|\Psi\rangle}{\langle \Psi|\Psi\rangle} = \langle H \rangle_{AA} + N\epsilon_c. \quad (4.32)$$

Here $\langle H \rangle_{AA}$ denotes the energy for the AA wavefunction. ϵ_c is the correlation energy per atom defined by

$$N\epsilon_c = \frac{\langle \Psi|\tilde{H}|\Psi\rangle}{\langle \Psi|\Psi\rangle}, \quad (4.33)$$

with $\tilde{H} = H - \langle H \rangle_{AA}$. Since it depends on the electron configuration $\{n_{i\sigma}\}$ via the AA potential, we have to take the configurational average at the end. To determine the variational parameters, we minimize the ground-state energy.

We adopt here the single-site approximation (SSA) to obtain the correlation energy. It is given by using the relation (3.22) as follows.

$$\epsilon_c = \frac{-\langle \tilde{O}_i^\dagger \tilde{H} \rangle_{AA} - \langle \tilde{H} \tilde{O}_i \rangle_{AA} + \langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_{AA}}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_{AA}}. \quad (4.34)$$

Each element in the correlation energy (4.34) can be calculated by making use of Wick's theorem as follows.

$$\langle \tilde{H} \tilde{O}_i \rangle_{AA} = U \sum_{\kappa'_2\kappa_2\kappa'_1\kappa_1} \langle \kappa'_1|i\rangle \langle i|\kappa_1\rangle \langle \kappa'_2|i\rangle \langle i|\kappa_2\rangle \sum_j \langle \kappa_1|j\rangle \langle j|\kappa'_1\rangle \langle \kappa_2|j\rangle \langle j|\kappa'_2\rangle \eta_{\kappa'_2\kappa_2\kappa'_1\kappa_1} \tilde{f}_{\kappa'_2\kappa_2\kappa'_1\kappa_1}, \quad (4.35)$$

$$\langle \tilde{O}_i^\dagger \tilde{H} \rangle_{\text{AA}} = \langle \tilde{H} \tilde{O}_i \rangle_{\text{AA}}^* , \quad (4.36)$$

$$\begin{aligned} \langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_{\text{AA}} = & \sum_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} \langle i | \kappa'_1 \rangle \langle \kappa_1 | i \rangle \langle i | \kappa'_2 \rangle \langle \kappa_2 | i \rangle \eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}^* \tilde{f}_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} \sum_{\kappa'_4 \kappa_4 \kappa'_3 \kappa_3} \langle \kappa'_3 | i \rangle \langle i | \kappa_3 \rangle \langle \kappa'_4 | i \rangle \langle i | \kappa_4 \rangle \\ & \times (\Delta E_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} \delta_{\kappa_1 \kappa_3} \delta_{\kappa'_1 \kappa'_3} \delta_{\kappa_2 \kappa_4} \delta_{\kappa'_2 \kappa'_4} + U_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1 \kappa'_4 \kappa_4 \kappa'_3 \kappa_3}) \eta_{\kappa'_4 \kappa_4 \kappa'_3 \kappa_3} , \end{aligned} \quad (4.37)$$

$$\begin{aligned} U_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1 \kappa'_4 \kappa_4 \kappa'_3 \kappa_3} = & U \sum_j [\langle j | \kappa_1 \rangle \langle \kappa_3 | j \rangle f(\tilde{\epsilon}_{\kappa_3 \uparrow}) \delta_{\kappa'_1 \kappa'_3} - \langle \kappa'_1 | j \rangle \langle j | \kappa'_3 \rangle (1 - f(\tilde{\epsilon}_{\kappa'_3 \uparrow})) \delta_{\kappa_1 \kappa_3}] \\ & \times [\langle j | \kappa_2 \rangle \langle \kappa_4 | j \rangle f(\tilde{\epsilon}_{\kappa_4 \downarrow}) \delta_{\kappa'_2 \kappa'_4} - \langle \kappa'_2 | j \rangle \langle j | \kappa'_4 \rangle (1 - f(\tilde{\epsilon}_{\kappa'_4 \downarrow})) \delta_{\kappa_2 \kappa_4}] , \end{aligned} \quad (4.38)$$

$$\langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_{\text{AA}} = \sum_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} |\langle \kappa'_1 | i \rangle|^2 |\langle \kappa_1 | i \rangle|^2 |\langle \kappa'_2 | i \rangle|^2 |\langle \kappa_2 | i \rangle|^2 |\eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}|^2 \tilde{f}_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} . \quad (4.39)$$

Here $\tilde{f}_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}$ is a Fermi factor of two-particle excitations which is defined by $\tilde{f}_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} = f(\tilde{\epsilon}_{\kappa_1 \uparrow}) (1 - f(\tilde{\epsilon}_{\kappa'_1 \uparrow})) f(\tilde{\epsilon}_{\kappa_2 \downarrow}) (1 - f(\tilde{\epsilon}_{\kappa'_2 \downarrow}))$, $f(\epsilon)$ is the Fermi distribution function at zero temperature, $\tilde{\epsilon}_{\kappa \sigma} = \epsilon_{\kappa \sigma} - \mu$, and $\epsilon_{\kappa \sigma}$ is the one-electron energy eigenvalue for the AA Hamiltonian. Moreover, $\Delta E_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} = \epsilon_{\kappa'_2 \downarrow} - \epsilon_{\kappa_2 \downarrow} + \epsilon_{\kappa'_1 \uparrow} - \epsilon_{\kappa_1 \uparrow}$ is a two-particle excitation energy.

In the correlation energy, the expressions (4.35) and (4.38) contain nonlocal terms via summation over j (*i.e.*, \sum_j). We thus make additional SSA that we only take into account the local term ($j = i$), so that $\langle \tilde{H} \tilde{O}_i \rangle_{\text{AA}} (= \langle \tilde{O}_i^\dagger \tilde{H} \rangle_{\text{AA}}^*)$ and $\langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_{\text{AA}}$ reduce as follows. The procedures are the same as in the MLA-HF presented in Chap. 3.

$$\langle \tilde{H} \tilde{O}_i \rangle_{\text{AA}} = U \sum_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} |\langle \kappa'_1 | i \rangle|^2 |\langle \kappa_1 | i \rangle|^2 |\langle \kappa'_2 | i \rangle|^2 |\langle \kappa_2 | i \rangle|^2 \eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} \tilde{f}_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} , \quad (4.40)$$

$$\begin{aligned} \langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_{\text{AA}} = & \sum_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} |\langle \kappa'_1 | i \rangle|^2 |\langle \kappa_1 | i \rangle|^2 |\langle \kappa'_2 | i \rangle|^2 |\langle \kappa_2 | i \rangle|^2 \\ & \times \eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}^* \tilde{f}_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} \left[\Delta E_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} \eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} \right. \\ & + U \left\{ \sum_{\kappa_3 \kappa_4} |\langle \kappa_3 | i \rangle|^2 |\langle \kappa_4 | i \rangle|^2 f(\tilde{\epsilon}_{\kappa_3 \uparrow}) f(\tilde{\epsilon}_{\kappa_4 \downarrow}) \eta_{\kappa'_2 \kappa_4 \kappa'_1 \kappa_3} \right. \\ & - \sum_{\kappa'_3 \kappa_4} |\langle \kappa'_3 | i \rangle|^2 |\langle \kappa_4 | i \rangle|^2 (1 - f(\tilde{\epsilon}_{\kappa'_3 \uparrow})) f(\tilde{\epsilon}_{\kappa_4 \downarrow}) \eta_{\kappa'_2 \kappa_4 \kappa'_3 \kappa_1} \\ & - \sum_{\kappa_3 \kappa'_4} |\langle \kappa_3 | i \rangle|^2 |\langle \kappa'_4 | i \rangle|^2 f(\tilde{\epsilon}_{\kappa_3 \uparrow}) (1 - f(\tilde{\epsilon}_{\kappa'_4 \downarrow})) \eta_{\kappa'_4 \kappa_2 \kappa'_1 \kappa_3} \\ & \left. \left. + \sum_{\kappa'_3 \kappa'_4} |\langle \kappa'_3 | i \rangle|^2 |\langle \kappa'_4 | i \rangle|^2 (1 - f(\tilde{\epsilon}_{\kappa'_3 \uparrow})) (1 - f(\tilde{\epsilon}_{\kappa'_4 \downarrow})) \eta_{\kappa'_4 \kappa_2 \kappa'_3 \kappa_1} \right\} \right] . \end{aligned} \quad (4.41)$$

The variational parameters $\{\eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}\}$ are obtained by minimizing the correlation energy ϵ_c , *i.e.*, Eq. (4.34) with Eqs. (4.39), (4.40), and (4.41). The self-consistent equations for $\{\eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}\}$

in the SSA are given as follows.

$$\begin{aligned}
& (\Delta E_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} - \epsilon_c) \eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} + U \left[\sum_{\kappa_3 \kappa_4} |\langle \kappa_3 | i \rangle|^2 |\langle \kappa_4 | i \rangle|^2 f(\tilde{\epsilon}_{\kappa_3 \uparrow}) f(\tilde{\epsilon}_{\kappa_4 \downarrow}) \eta_{\kappa'_2 \kappa_4 \kappa'_1 \kappa_3} \right. \\
& - \sum_{\kappa'_3 \kappa_4} |\langle \kappa'_3 | i \rangle|^2 |\langle \kappa_4 | i \rangle|^2 (1 - f(\tilde{\epsilon}_{\kappa'_3 \uparrow})) f(\tilde{\epsilon}_{\kappa_4 \downarrow}) \eta_{\kappa'_2 \kappa_4 \kappa'_3 \kappa_1} \\
& - \sum_{\kappa_3 \kappa'_4} |\langle \kappa_3 | i \rangle|^2 |\langle \kappa'_4 | i \rangle|^2 f(\tilde{\epsilon}_{\kappa_3 \uparrow}) (1 - f(\tilde{\epsilon}_{\kappa'_4 \downarrow})) \eta_{\kappa'_4 \kappa_2 \kappa'_1 \kappa_3} \\
& \left. + \sum_{\kappa'_3 \kappa'_4} |\langle \kappa'_3 | i \rangle|^2 |\langle \kappa'_4 | i \rangle|^2 (1 - f(\tilde{\epsilon}_{\kappa'_3 \uparrow})) (1 - f(\tilde{\epsilon}_{\kappa'_4 \downarrow})) \eta_{\kappa'_4 \kappa_2 \kappa'_3 \kappa_1} \right] = U. \quad (4.42)
\end{aligned}$$

To solve the equation approximately, we make use of the same idea as in the MLA-HF (see Sec. 3.3.1); we obtain the following solution which interpolate between the weak Coulomb interaction limit and the atomic limit.

$$\eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}(\tilde{\eta}, \epsilon_c) = \frac{U \tilde{\eta}}{\Delta E_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} - \epsilon_c}. \quad (4.43)$$

Here $\tilde{\eta} = 1 - \eta(1 - 2\langle \hat{n}_{i\uparrow} \rangle_0)(1 - 2\langle \hat{n}_{i\downarrow} \rangle_0)$.

The ground-state correlation energy is obtained by substituting the variational parameters (4.43) into Eq. (4.34).

$$\begin{aligned}
\langle \tilde{H} \tilde{O}_i \rangle_{AA} &= \langle \tilde{O}_i^\dagger \tilde{H} \rangle_{AA}^* \\
&= U^2 \tilde{\eta} \int \frac{\left[\prod_{n=1}^4 d\epsilon_n \right] \rho_\uparrow(\epsilon_1) \rho_\uparrow(\epsilon_2) \rho_\downarrow(\epsilon_3) \rho_\downarrow(\epsilon_4) f(\epsilon_1) (1 - f(\epsilon_2)) f(\epsilon_3) (1 - f(\epsilon_4))}{\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c}, \quad (4.44)
\end{aligned}$$

$$\langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_{AA} = \langle \tilde{O}_i^\dagger \tilde{H}_0 \tilde{O}_i \rangle_{AA} + U \langle \tilde{O}_i^\dagger O_i \tilde{O}_i \rangle_{AA}, \quad (4.45)$$

$$\langle \tilde{O}_i^\dagger \tilde{H}_0 \tilde{O}_i \rangle_{AA} = U^2 \tilde{\eta}^2 \int \frac{\left[\prod_{n=1}^4 d\epsilon_n \right] \rho_\uparrow(\epsilon_1) \rho_\uparrow(\epsilon_2) \rho_\downarrow(\epsilon_3) \rho_\downarrow(\epsilon_4) f(\epsilon_1) (1 - f(\epsilon_2)) f(\epsilon_3) (1 - f(\epsilon_4))}{(\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1)^{-1} (\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c)^2}, \quad (4.46)$$

$$\begin{aligned}
\langle \tilde{O}_i^\dagger O_i \tilde{O}_i \rangle_{AA} &= U^2 \tilde{\eta}^2 \int \frac{\left[\prod_{n=1}^4 d\epsilon_n \right] \rho_\uparrow(\epsilon_1) \rho_\uparrow(\epsilon_2) \rho_\downarrow(\epsilon_3) \rho_\downarrow(\epsilon_4) f(\epsilon_1) (1 - f(\epsilon_2)) f(\epsilon_3) (1 - f(\epsilon_4))}{\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c} \\
&\quad \times \left[\int \frac{d\epsilon_5 d\epsilon_6 \rho_\uparrow(\epsilon_5) \rho_\downarrow(\epsilon_6) f(\epsilon_5) f(\epsilon_6)}{\epsilon_4 - \epsilon_6 + \epsilon_2 - \epsilon_5 - \epsilon_c} - \int \frac{d\epsilon_5 d\epsilon_6 \rho_\uparrow(\epsilon_5) \rho_\downarrow(\epsilon_6) f(\epsilon_5) (1 - f(\epsilon_6))}{\epsilon_6 - \epsilon_3 + \epsilon_2 - \epsilon_5 - \epsilon_c} \right. \\
&\quad \left. - \int \frac{d\epsilon_5 d\epsilon_6 \rho_\uparrow(\epsilon_5) \rho_\downarrow(\epsilon_6) (1 - f(\epsilon_5)) f(\epsilon_6)}{\epsilon_4 - \epsilon_6 + \epsilon_5 - \epsilon_1 - \epsilon_c} + \int \frac{d\epsilon_5 d\epsilon_6 \rho_\uparrow(\epsilon_5) \rho_\downarrow(\epsilon_6) (1 - f(\epsilon_5)) (1 - f(\epsilon_6))}{\epsilon_6 - \epsilon_3 + \epsilon_5 - \epsilon_1 - \epsilon_c} \right], \quad (4.47)
\end{aligned}$$

$$\langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_{AA} = U^2 \tilde{\eta}^2 \int \frac{\left[\prod_{n=1}^4 d\epsilon_n \right] \rho_\uparrow(\epsilon_1) \rho_\uparrow(\epsilon_2) \rho_\downarrow(\epsilon_3) \rho_\downarrow(\epsilon_4) f(\epsilon_1) (1 - f(\epsilon_2)) f(\epsilon_3) (1 - f(\epsilon_4))}{(\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c)^2}. \quad (4.48)$$

Here $\rho_\sigma(\epsilon)$ is the local DOS for the one-electron energy eigenvalues of the AA Hamiltonian matrix (4.7).

We determine $\tilde{\eta}$ in Eqs. (4.44)-(4.48) variationally using the following variational principle.

$$E \leq \langle H \rangle (\{ \eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}^* \}) \leq \langle H \rangle (\{ \eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}(\tilde{\eta}, \epsilon_c) \}). \quad (4.49)$$

Here $\{ \eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}^* \}$ are the exact solution for the Eq. (4.42). Minimizing the correlation energy with respect to $\tilde{\eta}$ (*i.e.*, $\delta\epsilon_c = 0$), we obtain

$$\tilde{\eta} = \frac{1}{1 + \frac{UC}{D}}. \quad (4.50)$$

Here

$$\begin{aligned} C = & \sum_{\kappa_1 \kappa'_1 \kappa_2 \kappa'_2} |\langle \kappa'_1 | i \rangle|^2 |\langle \kappa_1 | i \rangle|^2 |\langle \kappa'_2 | i \rangle|^2 |\langle \kappa_2 | i \rangle|^2 \frac{\tilde{f}_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}}{(\Delta E_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} - \epsilon_c)} \\ & \times \left\{ \sum_{\kappa_3 \kappa_4} |\langle \kappa_3 | i \rangle|^2 |\langle \kappa_4 | i \rangle|^2 \frac{f(\tilde{\epsilon}_{\kappa_3 \uparrow}) f(\tilde{\epsilon}_{\kappa_4 \downarrow})}{(\Delta E_{\kappa'_2 \kappa_4 \kappa'_1 \kappa_3} - \epsilon_c)} \right. \\ & - \sum_{\kappa'_3 \kappa_4} |\langle \kappa'_3 | i \rangle|^2 |\langle \kappa_4 | i \rangle|^2 \frac{[1 - f(\tilde{\epsilon}_{\kappa'_3 \uparrow})] f(\tilde{\epsilon}_{\kappa_4 \downarrow})}{(\Delta E_{\kappa'_2 \kappa_4 \kappa'_3 \kappa_1} - \epsilon_c)} \\ & - \sum_{\kappa_3 \kappa'_4} |\langle \kappa_3 | i \rangle|^2 |\langle \kappa'_4 | i \rangle|^2 \frac{f(\tilde{\epsilon}_{\kappa_3 \uparrow}) [1 - f(\tilde{\epsilon}_{\kappa'_4 \downarrow})]}{(\Delta E_{\kappa'_4 \kappa_2 \kappa'_1 \kappa_3} - \epsilon_c)} \\ & \left. + \sum_{\kappa'_3 \kappa'_4} |\langle \kappa'_3 | i \rangle|^2 |\langle \kappa'_4 | i \rangle|^2 \frac{[1 - f(\tilde{\epsilon}_{\kappa'_3 \uparrow})] [1 - f(\tilde{\epsilon}_{\kappa'_4 \downarrow})]}{(\Delta E_{\kappa'_4 \kappa_2 \kappa'_3 \kappa_1} - \epsilon_c)} \right\}, \quad (4.51) \end{aligned}$$

and

$$D = \sum_{\kappa_1 \kappa'_1 \kappa_2 \kappa'_2} |\langle \kappa'_1 | i \rangle|^2 |\langle \kappa_1 | i \rangle|^2 |\langle \kappa'_2 | i \rangle|^2 |\langle \kappa_2 | i \rangle|^2 \frac{\tilde{f}_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}}{(\Delta E_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} - \epsilon_c)}. \quad (4.52)$$

In the energy representation, the coefficients C and D are expressed as follows:

$$\begin{aligned}
C = & \int \left[\prod_{n=1}^6 d\epsilon_n \right] \rho_{\uparrow}(\epsilon_1) \rho_{\uparrow}(\epsilon_2) \rho_{\downarrow}(\epsilon_3) \rho_{\downarrow}(\epsilon_4) \rho_{\uparrow}(\epsilon_5) \rho_{\downarrow}(\epsilon_6) f(\epsilon_1) (1 - f(\epsilon_2)) f(\epsilon_3) (1 - f(\epsilon_4)) \\
& \times f(\epsilon_5) f(\epsilon_6) (\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c)^{-1} (\epsilon_4 - \epsilon_6 + \epsilon_2 - \epsilon_5 - \epsilon_c)^{-1} \\
& - \int \left[\prod_{n=1}^6 d\epsilon_n \right] \rho_{\uparrow}(\epsilon_1) \rho_{\uparrow}(\epsilon_2) \rho_{\downarrow}(\epsilon_3) \rho_{\downarrow}(\epsilon_4) \rho_{\uparrow}(\epsilon_5) \rho_{\downarrow}(\epsilon_6) f(\epsilon_1) (1 - f(\epsilon_2)) f(\epsilon_3) (1 - f(\epsilon_4)) \\
& \times (1 - f(\epsilon_5)) f(\epsilon_6) (\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c)^{-1} (\epsilon_4 - \epsilon_6 + \epsilon_5 - \epsilon_1 - \epsilon_c)^{-1} \\
& - \int \left[\prod_{n=1}^6 d\epsilon_n \right] \rho_{\uparrow}(\epsilon_1) \rho_{\uparrow}(\epsilon_2) \rho_{\downarrow}(\epsilon_3) \rho_{\downarrow}(\epsilon_4) \rho_{\uparrow}(\epsilon_5) \rho_{\downarrow}(\epsilon_6) f(\epsilon_1) (1 - f(\epsilon_2)) f(\epsilon_3) (1 - f(\epsilon_4)) \\
& \times f(\epsilon_5) (1 - f(\epsilon_6)) (\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c)^{-1} (\epsilon_6 - \epsilon_3 + \epsilon_2 - \epsilon_5 - \epsilon_c)^{-1} \\
& + \int \left[\prod_{n=1}^6 d\epsilon_n \right] \rho_{\uparrow}(\epsilon_1) \rho_{\uparrow}(\epsilon_2) \rho_{\downarrow}(\epsilon_3) \rho_{\downarrow}(\epsilon_4) \rho_{\uparrow}(\epsilon_5) \rho_{\downarrow}(\epsilon_6) f(\epsilon_1) (1 - f(\epsilon_2)) f(\epsilon_3) (1 - f(\epsilon_4)) \\
& \times (1 - f(\epsilon_5)) (1 - f(\epsilon_6)) (\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c)^{-1} (\epsilon_6 - \epsilon_3 + \epsilon_5 - \epsilon_1 - \epsilon_c)^{-1}, \quad (4.53)
\end{aligned}$$

and

$$D = \int \frac{\left[\prod_{n=1}^4 d\epsilon_n \right] \rho_{\uparrow}(\epsilon_1) \rho_{\uparrow}(\epsilon_2) \rho_{\downarrow}(\epsilon_3) \rho_{\downarrow}(\epsilon_4) f(\epsilon_1) (1 - f(\epsilon_2)) f(\epsilon_3) (1 - f(\epsilon_4))}{\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c}. \quad (4.54)$$

The expression of C , *i.e.*, Eq. (4.53) consists of 6-fold multiple integrals. Therefore we reduce these integrals to the 2-folds using the Laplace transform (3.52). The Laplace transformation of C and D are given as follows.

$$\begin{aligned}
C = & - \int_0^{\infty} dt dt' e^{i\epsilon_c(t+t')} \left[a_{\uparrow}(-t) b_{\uparrow}(t+t') a_{\downarrow}(-t) b_{\downarrow}(t+t') a_{\uparrow}(-t') a_{\downarrow}(-t') \right. \\
& - a_{\uparrow}(-t-t') b_{\uparrow}(t) a_{\downarrow}(-t) b_{\downarrow}(t+t') b_{\uparrow}(t') a_{\downarrow}(-t') \\
& - a_{\uparrow}(-t) b_{\uparrow}(t+t') a_{\downarrow}(-t-t') b_{\downarrow}(t) a_{\uparrow}(-t') b_{\downarrow}(t') \\
& \left. + a_{\uparrow}(-t-t') b_{\uparrow}(t) a_{\downarrow}(-t-t') b_{\downarrow}(t) b_{\uparrow}(t') b_{\downarrow}(t') \right]. \quad (4.55)
\end{aligned}$$

$$D = -i \int_0^{\infty} dt e^{i\epsilon_c t} a_{\uparrow}(-t) b_{\uparrow}(t) a_{\downarrow}(-t) b_{\downarrow}(t). \quad (4.56)$$

Here

$$a_{\sigma}(t) = \int d\epsilon \rho_{\sigma}(\epsilon) f(\epsilon) e^{-i\epsilon t}, \quad (4.57)$$

$$b_{\sigma}(t) = \int d\epsilon \rho_{\sigma}(\epsilon) (1 - f(\epsilon)) e^{-i\epsilon t}. \quad (4.58)$$

The total energy per atom is obtained by taking the configurational average as follows (see Eq. (4.32)).

$$\langle H \rangle = \overline{\langle H \rangle}_{\text{AA}} + \bar{\epsilon}_c. \quad (4.59)$$

The AA energy $\overline{\langle H \rangle}_{AA}$ has been given by Eq. (4.4). The correlation energy can be obtained as follows in the SSA.

$$\bar{\epsilon}_c = \sum_{\alpha} P_{\alpha} \epsilon_{c\alpha}. \quad (4.60)$$

Here P_{α} ($\alpha = 0, 1 \uparrow, 1 \downarrow, 2$) are the probability for the on-site configuration α . $\epsilon_{c\alpha}$ denotes the correlation energy for a given configuration α .

$$\epsilon_{c\alpha} = \left[\frac{-\langle \tilde{O}_i^{\dagger} \tilde{H} \rangle_{AA} - \langle \tilde{H} \tilde{O}_i \rangle_{AA} + \langle \tilde{O}_i^{\dagger} \tilde{H} \tilde{O}_i \rangle_{AA}}{1 + \langle \tilde{O}_i^{\dagger} \tilde{O}_i \rangle_{AA}} \right]_{\alpha}. \quad (4.61)$$

The quantities $\langle \tilde{H} \tilde{O}_i \rangle_{AA}$, $\langle \tilde{O}_i^{\dagger} \tilde{H} \tilde{O}_i \rangle_{AA}$, and $\langle \tilde{O}_i^{\dagger} \tilde{O}_i \rangle_{AA}$ are given by Eqs. (4.44), (4.45), and (4.48) in which the local densities of states have been given by the single-site ones, *i.e.*, Eq. (4.14). The Laplace transform of these expression are as follows:

$$\langle \tilde{O}_i^{\dagger} \tilde{O}_i \rangle_{AA\alpha} = -U^2 \tilde{\eta}_{\alpha}^2 \int_0^{\infty} dt dt' e^{i\epsilon_{c\alpha}(t+t')} [a_{\uparrow}(-t-t') b_{\uparrow}(t+t') a_{\downarrow}(-t-t') b_{\downarrow}(t+t')]_{\alpha}, \quad (4.62)$$

$$\langle \tilde{H} \tilde{O}_i \rangle_{AA\alpha} = \langle \tilde{O}_i^{\dagger} \tilde{H} \rangle_{AA\alpha}^* = iU^2 \tilde{\eta}_{\alpha} \int_0^{\infty} dt e^{i\epsilon_{c\alpha} t} [a_{\uparrow}(-t) a_{\downarrow}(-t) b_{\uparrow}(t) b_{\downarrow}(t)]_{\alpha}, \quad (4.63)$$

$$\begin{aligned} \langle \tilde{O}_i^{\dagger} \tilde{H} \tilde{O}_i \rangle_{AA\alpha} = & -U^2 \tilde{\eta}_{\alpha}^2 \int_0^{\infty} dt dt' e^{i\epsilon_{c\alpha}(t+t')} [a_{\uparrow}(-t-t') b_{\uparrow}(t+t') a_{\downarrow}(-t-t') b_{\downarrow}(t+t') \\ & - a_{\uparrow}(-t-t') b_{\uparrow}(t+t') a_{\downarrow}(-t-t') b_{\downarrow}(t+t') \\ & + a_{\uparrow}(-t-t') b_{\uparrow}(t+t') a_{\downarrow}(-t-t') b_{\downarrow}(t+t') \\ & - a_{\uparrow}(-t-t') b_{\uparrow}(t+t') a_{\downarrow}(-t-t') b_{\downarrow}(t+t')]_{\alpha}, \end{aligned} \quad (4.64)$$

$$\begin{aligned} \langle \tilde{O}_i^{\dagger} \tilde{O}_i \tilde{O}_i \rangle_{AA\alpha} = & -U^2 \tilde{\eta}_{\alpha}^2 \int_0^{\infty} dt dt' e^{i\epsilon_{c\alpha}(t+t')} [a_{\uparrow}(-t) b_{\uparrow}(t+t') a_{\downarrow}(-t) b_{\downarrow}(t+t') a_{\uparrow}(-t') a_{\downarrow}(-t') \\ & - a_{\uparrow}(-t) b_{\uparrow}(t+t') a_{\downarrow}(-t-t') b_{\downarrow}(t) a_{\uparrow}(-t') b_{\downarrow}(t') \\ & - a_{\uparrow}(-t-t') b_{\uparrow}(t) a_{\downarrow}(-t) b_{\downarrow}(t+t') b_{\uparrow}(t') a_{\downarrow}(-t') \\ & + a_{\uparrow}(-t-t') b_{\uparrow}(t) a_{\downarrow}(-t-t') b_{\downarrow}(t) b_{\uparrow}(t') b_{\downarrow}(t')]_{\alpha}. \end{aligned} \quad (4.65)$$

Here,

$$\tilde{\eta}_{\alpha} = \frac{1}{1 + \frac{UC_{\alpha}}{D_{\alpha}}}. \quad (4.66)$$

$$\begin{aligned} C_{\alpha} = & - \int_0^{\infty} dt dt' e^{i\epsilon_{c\alpha}(t+t')} [a_{\uparrow}(-t) b_{\uparrow}(t+t') a_{\downarrow}(-t) b_{\downarrow}(t+t') a_{\uparrow}(-t') a_{\downarrow}(-t') \\ & - a_{\uparrow}(-t-t') b_{\uparrow}(t) a_{\downarrow}(-t) b_{\downarrow}(t+t') b_{\uparrow}(t') a_{\downarrow}(-t') \\ & - a_{\uparrow}(-t) b_{\uparrow}(t+t') a_{\downarrow}(-t-t') b_{\downarrow}(t) a_{\uparrow}(-t') b_{\downarrow}(t') \\ & + a_{\uparrow}(-t-t') b_{\uparrow}(t) a_{\downarrow}(-t-t') b_{\downarrow}(t) b_{\uparrow}(t') b_{\downarrow}(t')]_{\alpha}. \end{aligned} \quad (4.67)$$

Table 4.1: The atomic level $\epsilon_{i\sigma}$ for the up-spin (\uparrow) and the down-spin (\downarrow) state in various on-site configurations.

| Configuration | $\epsilon_{i\uparrow}$ | $\epsilon_{i\downarrow}$ |
|---------------|------------------------|--------------------------|
| 00 | ϵ_0 | ϵ_0 |
| 10 | ϵ_0 | $\epsilon_0 + U$ |
| 01 | $\epsilon_0 + U$ | ϵ_0 |
| 11 | $\epsilon_0 + U$ | $\epsilon_0 + U$ |

$$D_\alpha = -i \int_0^\infty dt e^{i\epsilon_\alpha t} [a_\uparrow(-t)b_\uparrow(t)a_\downarrow(-t)b_\downarrow(t)]_\alpha. \quad (4.68)$$

As we have mentioned before, for the empty site *i.e.*, $\alpha = 00$, the atomic level $\epsilon_{i\sigma}$ in Eq. (4.8) for the up-spin (\uparrow) and down-spin (\downarrow) state becomes ϵ_0 . We summarize the results for all other configurations in Table 4.1. Therefore we can express a_\uparrow and a_\downarrow by a_{ϵ_0} and a_{ϵ_0+U} . Therefore,

$$a_{\beta\sigma}(t) = \int d\epsilon \rho_{\beta\sigma}(\epsilon) f(\epsilon) e^{-i\epsilon t}, \quad (4.69)$$

$$b_{\beta\sigma}(t) = \int d\epsilon \rho_{\beta\sigma}(\epsilon) (1 - f(\epsilon)) e^{-i\epsilon t}, \quad (4.70)$$

$$a_{1\beta\sigma}(t) = \int d\epsilon \rho_{\beta\sigma}(\epsilon) f(\epsilon) \epsilon e^{-i\epsilon t}, \quad (4.71)$$

$$b_{1\beta\sigma}(t) = \int d\epsilon \rho_{\beta\sigma}(\epsilon) (1 - f(\epsilon)) \epsilon e^{-i\epsilon t}. \quad (4.72)$$

Here $\beta = \epsilon_0$ or $\epsilon_0 + U$. The densities of states $\rho_{\epsilon_0\sigma}(\epsilon)$ and $\rho_{\epsilon_0+U\sigma}(\epsilon)$ have been given by Eqs. (4.17) and (4.20), respectively.

The double occupation number $\langle \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \rangle$ is obtained from $\partial \langle H \rangle / \partial U_i$. Making use of the single-site energy (3.24) and the Feynman-Hellmann theorem [32], and taking the configurational average, we obtain the following expression.

$$\langle \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \rangle = \overline{\langle \hat{n}_{i\uparrow} \rangle_{AA} \langle \hat{n}_{i\downarrow} \rangle_{AA}} + \overline{\langle \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \rangle_c}. \quad (4.73)$$

Here the AA contribution of the double occupancy $\overline{\langle \hat{n}_{i\uparrow} \rangle_{AA} \langle \hat{n}_{i\downarrow} \rangle_{AA}}$ has been given by Eq. (4.15). The second term is the correlation contribution given as follows.

$$\overline{\langle \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \rangle_c} = \sum_\alpha P_\alpha \langle \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \rangle_{c\alpha}, \quad (4.74)$$

$$\langle \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \rangle_{c\alpha} = \left[\frac{-\langle \tilde{O}_i^\dagger O_i \rangle_{AA} - \langle O_i \tilde{O}_i \rangle_{AA} + \langle \tilde{O}_i^\dagger O_i \tilde{O}_i \rangle_{AA} + \sum_\sigma \langle \hat{n}_{i-\sigma} \rangle_{AA} \langle \tilde{O}_i^\dagger \tilde{n}_{i\sigma} \tilde{O}_i \rangle_{AA}}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_{AA}} \right]_\alpha, \quad (4.75)$$

$$\begin{aligned} \langle \tilde{O}_i^\dagger O_i \rangle_{AA} + \langle O_i \tilde{O}_i \rangle_{AA} &= 2U\tilde{\eta} \int \left[\prod_{n=1}^4 d\epsilon_n \right] \rho_\uparrow(\epsilon_1) \rho_\uparrow(\epsilon_2) \rho_\downarrow(\epsilon_3) \rho_\downarrow(\epsilon_4) \\ &\quad \times \frac{f(\epsilon_1)(1-f(\epsilon_2))f(\epsilon_3)(1-f(\epsilon_4))}{\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c}, \end{aligned} \quad (4.76)$$

$$\begin{aligned} \langle \tilde{O}_i^\dagger \tilde{n}_{i\sigma} \tilde{O}_i \rangle_{AA} &= U^2 \tilde{\eta}^2 \int \left[\prod_{n=1}^5 d\epsilon_n \right] \rho_{-\sigma}(\epsilon_1) \rho_{-\sigma}(\epsilon_2) \rho_\sigma(\epsilon_3) \rho_\sigma(\epsilon_4) \rho_\sigma(\epsilon_5) \\ &\quad \times \frac{f(\epsilon_1)(1-f(\epsilon_2))f(\epsilon_3)(1-f(\epsilon_4))}{\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c} \\ &\quad \times \left[\frac{1-f(\epsilon_5)}{\epsilon_5 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c} - \frac{f(\epsilon_5)}{\epsilon_4 - \epsilon_5 + \epsilon_2 - \epsilon_1 - \epsilon_c} \right]. \end{aligned} \quad (4.77)$$

The quantities $\langle \tilde{O}_i^\dagger O_i \tilde{O}_i \rangle_{AA}$ and $\langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_{AA}$ have been given by Eqs. (4.47) and (4.48), respectively. The Laplace transform of the expressions $\langle \tilde{O}_i^\dagger O_i \rangle_{AA\alpha} + \langle O_i \tilde{O}_i \rangle_{AA\alpha}$ and $\langle \tilde{O}_i^\dagger \tilde{n}_{i\sigma} \tilde{O}_i \rangle_{AA\alpha}$ are written, respectively, as follows.

$$\langle \tilde{O}_i^\dagger O_i \rangle_{AA\alpha} + \langle O_i \tilde{O}_i \rangle_{AA\alpha} = 2iU\tilde{\eta}_\alpha \int_0^\infty dt e^{i\epsilon_c t} [a_\uparrow(-t)b_\uparrow(t)a_\downarrow(-t)b_\downarrow(t)]_\alpha, \quad (4.78)$$

$$\begin{aligned} \langle \tilde{O}_i^\dagger \tilde{n}_{i\sigma} \tilde{O}_i \rangle_{AA\alpha} &= -U^2 \tilde{\eta}_\alpha^2 \int_0^\infty dt dt' e^{i\epsilon_c \alpha (t+t')} [a_{-\sigma}(-t-t')b_{-\sigma}(t+t')a_\sigma(-t-t')b_\sigma(t)b_\sigma(t') \\ &\quad - a_{-\sigma}(-t-t')b_{-\sigma}(t+t')a_\sigma(-t)b_\sigma(t+t')a_\sigma(t')]_\alpha. \end{aligned} \quad (4.79)$$

The quantities $\langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_{AA\alpha}$ and $\langle \tilde{O}_i^\dagger O_i \tilde{O}_i \rangle_{AA\alpha}$ have been given by Eqs. (4.62) and (4.65), respectively.

Similarly, the momentum distribution $\langle \hat{n}_{k\sigma} \rangle$ is obtained from $\partial \langle H \rangle / \partial \epsilon_k$ as follows.

$$\langle \hat{n}_{k\sigma} \rangle = \overline{\langle \hat{n}_{k\sigma} \rangle}_{AA} + \overline{\langle \hat{n}_{k\sigma} \rangle}_c. \quad (4.80)$$

The AA contribution of the momentum distribution $\overline{\langle \hat{n}_{k\sigma} \rangle}_{AA}$ has been given by Eq. (4.26). The correlation contribution $\overline{\langle \hat{n}_{k\sigma} \rangle}_c$ is expressed as follows.

$$\overline{\langle \hat{n}_{k\sigma} \rangle}_c = \sum_\alpha P_\alpha \langle \hat{n}_{k\sigma} \rangle_{c\alpha}, \quad (4.81)$$

$$\langle \hat{n}_{k\sigma} \rangle_{c\alpha} = \left[\frac{N \langle \tilde{O}_i \tilde{n}_{k\sigma} \tilde{O}_i \rangle_{AA}}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_{AA}} \right]_\alpha. \quad (4.82)$$

Here $\tilde{n}_{k\sigma} = \hat{n}_{k\sigma} - \langle \hat{n}_{k\sigma} \rangle_{AA}$, the numerator on the r.h.s. is given by

$$\begin{aligned} N \langle \tilde{O}_i \tilde{n}_{k\sigma} \tilde{O}_i \rangle_{AA} &= U^2 \tilde{\eta}^2 \int \left[\prod_{n=1}^4 d\epsilon_n \right] \rho_\sigma(\epsilon_1) \rho_{-\sigma}(\epsilon_2) \rho_{-\sigma}(\epsilon_3) \rho_{k\sigma}(\epsilon_4) f(\epsilon_2)(1-f(\epsilon_3)) \\ &\quad \times \left\{ \frac{f(\epsilon_1)(1-f(\epsilon_4))}{(\epsilon_3 - \epsilon_2 + \epsilon_4 - \epsilon_1 - \epsilon_c)^2} - \frac{(1-f(\epsilon_1))f(\epsilon_4)}{(\epsilon_3 - \epsilon_2 + \epsilon_1 - \epsilon_4 - \epsilon_c)^2} \right\}. \end{aligned} \quad (4.83)$$

The DOS in the momentum representation $\rho_{k\sigma}(\epsilon)$ has been given by Eq. (4.27) in the SSA. The correlation contribution quantity $\langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_{AA}$ is given by Eq. (4.48). The Laplace transform of the quantity $N \langle \tilde{O}_i^\dagger \tilde{n}_{k\sigma} \tilde{O}_i \rangle_{0\alpha} \equiv [N \langle \tilde{O}_i^\dagger \tilde{n}_{k\sigma} \tilde{O}_i \rangle_{AA}]_\alpha$ is given as follows.

$$N \langle \tilde{O}_i^\dagger \tilde{n}_{k\sigma} \tilde{O}_i \rangle_{AA\alpha} = U^2 \tilde{\eta}_\alpha^2 \int_0^\infty dt dt' e^{i\epsilon_{c\alpha}(t+t')} a_{-\sigma}(-t-t') b_{-\sigma}(t+t') \\ \times [b_\sigma(t+t') a_{k\sigma}(-t-t') - a_\sigma(-t-t') b_{k\sigma}(t+t')]_\alpha. \quad (4.84)$$

Here

$$a_{k\sigma}(t) = \int d\epsilon \rho_{k\sigma}(\epsilon) f(\epsilon) e^{-i\epsilon t}, \quad (4.85)$$

$$b_{k\sigma}(t) = \int d\epsilon \rho_{k\sigma}(\epsilon) [1 - f(\epsilon)] e^{-i\epsilon t}. \quad (4.86)$$

Therefore, we calculate the correlation energy $\epsilon_{c\alpha}$ (Eq. (4.61)) self-consistently with use of Eqs. (4.44), (4.45), (4.48), and (4.50), and calculate the average correlation energy $\bar{\epsilon}_c$ (Eq. (4.60)) as well as the average AA energy $\langle H \rangle_{AA}$ (Eq. (4.4)). Then we obtain the ground-state energy $\langle H \rangle$ (Eq. (4.59)) in the MLA-AA.

4.3 Numerical results: half-filled band Hubbard model

To examine the validity of the MLA-AA, we have performed the numerical calculations for the half-filled band Hubbard model with nearest neighbor transfer integral on the hypercubic lattice in infinite dimensions, where the SSA works best [39, 42]. We assumed here the non-magnetic case. In this case, the density of states for non-interacting system is given by $\rho(\epsilon) = (1/\sqrt{\pi}) \exp(-\epsilon^2)$ [42]. The energy unit is chosen to be $\int d\epsilon \rho(\epsilon) \epsilon^2 = 1/2$. The characteristic band width W is given by $W = 2$ in this unit.

Figure 4.2 shows the calculated results of the ground-state energy vs Coulomb interaction energy curves. In the weak Coulomb interaction regime ($U/W \lesssim 1$), the total energy of the MLA-HF is lower than the GW. On the other hand, we observe that the MLA-AA gives lower energy in comparison with the GW in the strong Coulomb interaction regime ($U/W > 1$). We obtain the critical Coulomb interaction $U_{c2} = 3.40$ at which the effective mass diverges. But before U approaches U_{c2} we find that the AA state showing the insulating state is stabilized, and the metal-insulator transition occurs at the critical Coulomb interaction $U_c = 3.26$. The transition is of the first order in the present approach, and is consistent with the result of NRG method, although the calculated U_{c2} is somewhat smaller than that obtained by NRG (*i.e.*, $U_{c2} = 4.1$) [34]. The MLA-HF leads to the total energy lower than that of the GW up to the critical Coulomb interaction U_c and the MLA-AA gives the same behavior in the range $U > U_c$. More important is that the MLA scheme gives lower energy than the GW for overall Coulomb interaction regime and therefore can overcome the limitation of the GW.

We present in Fig. 4.3 the double occupation number $\langle \hat{n}_\uparrow \hat{n}_\downarrow \rangle$ as a function of Coulomb interaction energy U at half-filling. It decreases from $1/4$ with increasing Coulomb interaction, so as to reduce the loss of Coulomb energy U . The MLA-HF state reduces the double occupancy more than the GW in the weakly correlated region, and jumps to the MLA-AA state at U_c . In the strongly correlated regime, the MLA-AA gives finite value of double occupancy, while the GW gives the

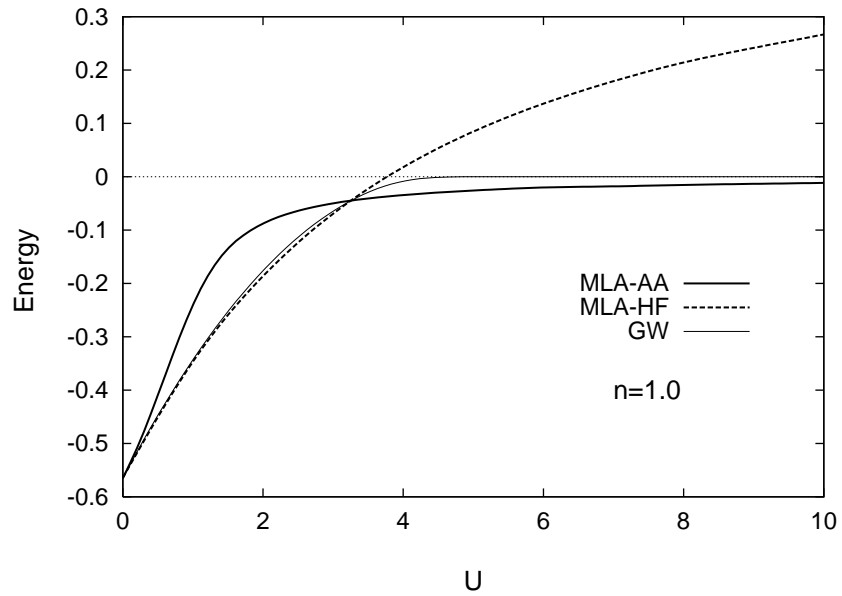


Figure 4.2: The energy vs Coulomb interaction energy U curves in the MLA-AA (solid curve), MLA-HF (dashed curve), and the GW (thin solid curve) for the electron number $n = 1.0$.

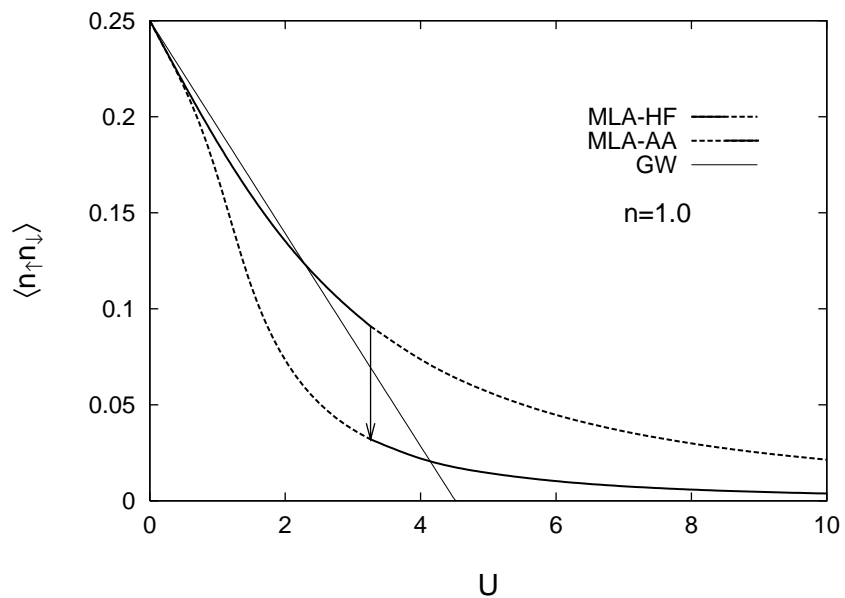


Figure 4.3: The double occupation number $\langle n_{\uparrow}n_{\downarrow} \rangle$ vs Coulomb interaction energy U curve for the electron number $n = 1.0$ in the MLA-HF (solid-dashed curve), the MLA-AA (dashed-solid curve), and the GW (thin solid curve). The arrow shows a jump from the metallic state to the insulator at $U_c = 3.26$.

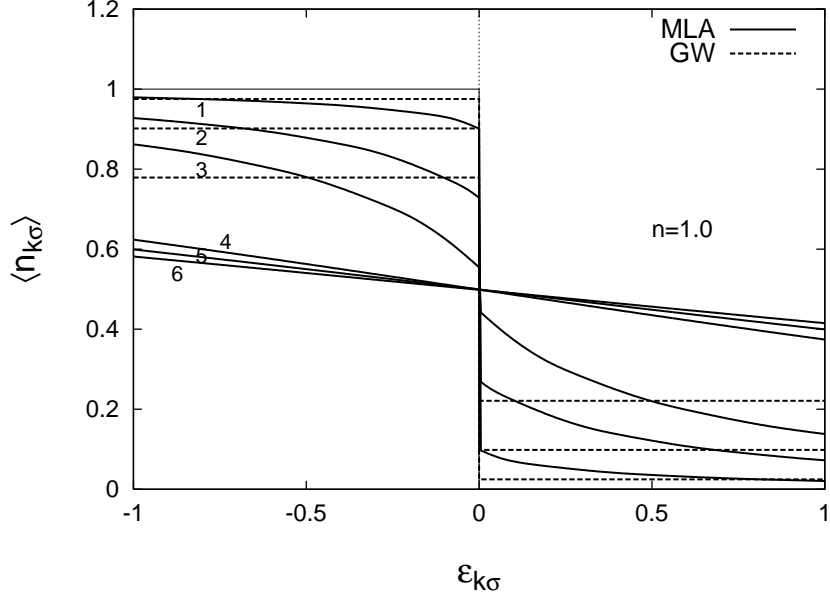


Figure 4.4: The momentum distribution as a function of energy $\epsilon_{k\sigma}$ for various Coulomb interaction energy parameters $U = 1.0, 2.0, 3.0, 4.0, 5.0, 6.0$ at half-filling. The MLA: solid curve, the GW: dashed curve, and the HF: thin solid curve.

Brinkman-Rice atom state. This verifies an improvement over the GW in the strongly correlated regime. The double occupancy for the MLA scheme at U_c is 0.032, and is consistent with the result of the Quantum Monte Carlo (≈ 0.024) [43], though the latter uses the semi-elliptical density of states.

The momentum distribution for the MLA shows a clear momentum-dependence as a function of the HF one electron energy $\epsilon_{k\sigma}$ as shown in Fig. 4.4. It decreases monotonically with increasing $\epsilon_{k\sigma}$ and shows a jump at the Fermi energy in the metallic state. The distribution for the GW on the other hand, is constant below and above the Fermi level [7, 8, 9]. The jump decreases with increasing U , and disappears beyond U_c , indicating the insulating state. The curve becomes flatter with further increase of U . Note that it leads to a Fermi liquid state for the weak Coulomb interaction regime and non Fermi liquid state in the strong Coulomb interaction regime.

In summary, we have shown that the MLA can describe the strong Coulomb interaction regimes by changing the starting wavefunction from the HartreeFock (HF) type to an alloy-analogy (AA) type wavefunction. Numerical results based on the half-filled band Hubbard model on the hypercubic lattice in infinite dimensions show that the new wavefunction yields the ground-state energy lower than the Gutzwiller wavefunction (GW) in the strong Coulomb interaction regime. Calculated double occupation number is smaller than the result of the GW in the metallic regime, and is finite in the insulator regime. Furthermore, the momentum distribution shows a distinct momentum-dependence in both the metallic and insulator regions, which are qualitatively different from those of the GW.

Chapter 5

Momentum Dependent Local-Ansatz Approach with Hybrid Wavefunction

In this chapter, we introduce a hybrid (HB) wavefunction whose potential can flexibly change from the Hartree-Fock type to the alloy-analogy type by varying a weighting factor from zero to one. On the basis of the HB function we propose a new variational theory of momentum-dependent local-ansatz (MLA). The theory [28] describes reasonably electron correlations from the weak to the strong Coulomb interaction regime.

5.1 Hybrid wavefunction

We reconsider in this section the single-band Hubbard model [10, 11, 12].

$$H = \sum_{i\sigma} (\epsilon_0 - \mu) \hat{n}_{i\sigma} + \sum_{ij\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}. \quad (5.1)$$

Here ϵ_0 (μ) is the atomic level (chemical potential), t_{ij} is the transfer integral between sites i and j . U is the intra-atomic Coulomb energy parameter. $a_{i\sigma}^\dagger$ ($a_{i\sigma}$) denotes the creation (annihilation) operator for an electron on site i with spin σ , and $\hat{n}_{i\sigma} = a_{i\sigma}^\dagger a_{i\sigma}$ is the electron density operator on site i for spin σ .

In the HF approximation (see Eq. (2.22)), we neglected the fluctuations $\delta \hat{n}_{i\uparrow} \delta \hat{n}_{i\downarrow}$ and replace the many-body Hamiltonian (5.1) with an effective Hamiltonian H_{HF} showing independent-particle motion.

$$H_{\text{HF}} = \sum_{i\sigma} (\epsilon_0 - \mu + U \langle n_{i-\sigma} \rangle_0) \hat{n}_{i\sigma} + \sum_{ij\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} - U \sum_i \langle n_{i\uparrow} \rangle_0 \langle n_{i\downarrow} \rangle_0. \quad (5.2)$$

Here $\langle \sim \rangle_0$ denotes the HF average $\langle \phi_0 | (\sim) | \phi_0 \rangle$, and $\langle n_{i\sigma} \rangle_0$ is the average electron number on site i with spin σ . $|\phi_0\rangle$ denotes the ground-state HF wavefunction for the Hamiltonian H_{HF} .

In the AA approximation (see Eq. (4.1)) on the other hand, we considered the strong Coulomb interaction regime, where electrons with spin σ move slowly from site to site due to electron correlations. Instead of the HF average potential $U \langle \hat{n}_{i-\sigma} \rangle_0$, electrons should feel there a potential U or 0 , depending on the occupation of an electron with opposite spin on the same site. Hubbard regarded this system as an alloy with different random potentials $\epsilon_0 + U$ and ϵ_0 . The AA Hamiltonian was

defined as follows (see Eq. (4.1)).

$$H_{AA} = \sum_{i\sigma} (\epsilon_0 - \mu + U n_{i-\sigma}) \hat{n}_{i\sigma} + \sum_{ij\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} - U \sum_i (n_{i\uparrow} \langle n_{i\downarrow} \rangle_{AA} + n_{i\downarrow} \langle n_{i\uparrow} \rangle_{AA}) + U \sum_i \langle n_{i\uparrow} \rangle_{AA} \langle n_{i\downarrow} \rangle_{AA}. \quad (5.3)$$

Here $\langle \sim \rangle_{AA}$ denotes the AA average $\langle \phi_{AA} | (\sim) | \phi_{AA} \rangle$ with respect to the ground-state wavefunction $|\phi_{AA}\rangle$ of the AA Hamiltonian H_{AA} . Since the electrons with opposite spin are treated to be static in the AA approximation, related operators $\{\hat{n}_{i-\sigma}\}$ are regarded as a random static C number $n_{i-\sigma}$ (0 or 1). Each configuration $\{n_{i\sigma}\}$ is considered as a snapshot in time development.

The HF Hamiltonian works best in the weakly correlated regime, while the AA Hamiltonian works better in the strongly correlated regime. In order to obtain better wavefunction for any interaction strength U , we introduce the following HB Hamiltonian which is a linear combination of the HF and the AA Hamiltonians.

$$H_{HB} = \sum_{i\sigma} (\epsilon_0 - \mu + \bar{U} \langle n_{i-\sigma} \rangle_{HB} + \tilde{U} n_{i-\sigma}) \hat{n}_{i\sigma} + \sum_{ij\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} - (\bar{U} - \tilde{U}) \sum_i \langle n_{i\uparrow} \rangle_{HB} \langle n_{i\downarrow} \rangle_{HB} - \tilde{U} \sum_i (n_{i\uparrow} \langle n_{i\downarrow} \rangle_{HB} + n_{i\downarrow} \langle n_{i\uparrow} \rangle_{HB}). \quad (5.4)$$

Here $\langle \sim \rangle_{HB}$ denotes the HB average $\langle \phi_{HB} | (\sim) | \phi_{HB} \rangle$ with respect to the ground-state $|\phi_{HB}\rangle$ of the HB Hamiltonian, $\bar{U} = (1-w)U$ and $\tilde{U} = wU$. We introduced a variational parameter w . Note that $H_{HB} (= (1-w)H_{HF} + wH_{AA})$ reduces to the HF Hamiltonian when $w = 0$, while H_{HB} reduces to the AA when $w = 1.0$.

The ground-state energy E satisfies the following inequality for a normalized wavefunction $|\phi_{HB}\rangle$.

$$E \leq \langle \phi_{HB} | H | \phi_{HB} \rangle = \langle H_{HB} \rangle_{HB}. \quad (5.5)$$

The HB ground-state energy per atom is obtained by taking the configurational average.

$$\overline{\langle H \rangle}_{HB} = n\mu + 2 \int_{-\infty}^0 \epsilon \overline{\rho_{i\sigma}(\epsilon)} d\epsilon - (\bar{U} - \tilde{U}) \overline{\langle n_{i\uparrow} \rangle_{HB} \langle n_{i\downarrow} \rangle_{HB}} - \tilde{U} (\overline{\langle n_{i\uparrow} \rangle_{HB} \langle n_{i\downarrow} \rangle_{HB}} + \overline{\langle n_{i\downarrow} \rangle_{HB} \langle n_{i\uparrow} \rangle_{HB}}). \quad (5.6)$$

Here we assumed the system with one atom per unit cell. $\langle H \rangle_{HB}$ denotes the HB average $\langle \phi_{HB} | H | \phi_{HB} \rangle$. The upper bar denotes the configurational average and n is the electron number per atom. $\rho_{i\sigma}(\epsilon)$ is the local density of states (DOS) and is obtained from the one-electron Green function.

$$\rho_{i\sigma}(\epsilon) = -\frac{1}{\pi} \text{Im} G_{ii\sigma}(z). \quad (5.7)$$

The Green function $G_{ii\sigma}(z)$ is defined here by

$$G_{ii\sigma}(z) = [(z - \mathbf{H}_\sigma)^{-1}]_{ij}. \quad (5.8)$$

Note that $z = \epsilon + i\delta$, δ being the infinitesimal positive number. $(\mathbf{H}_\sigma)_{ij}$ is the one-electron Hamiltonian matrix for the HB Hamiltonian (5.4), which is defined by

$$(\mathbf{H}_\sigma)_{ij} = (\epsilon_0 - \mu + \bar{U} \langle n_{i-\sigma} \rangle_{HB} + \tilde{U} n_{i-\sigma}) \delta_{ij} + t_{ij} (1 - \delta_{ij}). \quad (5.9)$$

The average electron number $\langle n_{i\sigma} \rangle_{\text{HB}}$ with respect to the HB Hamiltonian (5.4) is given as

$$\langle n_{i\sigma} \rangle_{\text{HB}} = \int f(\epsilon) \rho_{i\sigma}(\epsilon) d\epsilon, \quad (5.10)$$

$f(\epsilon)$ being the Fermi distribution function.

Since the HB Hamiltonian contains a random potential, we obtain the local DOS making use of the coherent potential approximation (CPA) [40, 41]. In the CPA, we replace the random potentials at the surrounding sites with a coherent potentials $\Sigma_\sigma(z)$. The on-site impurity Green function $G_{ii\sigma}(z)$ is then obtained as follows.

$$G_{ii\sigma}(z) = \frac{1}{F_\sigma(z)^{-1} - \epsilon_0 + \mu - \bar{U} \langle n_{i-\sigma} \rangle_{\text{HB}} - \tilde{U} n_{i-\sigma} + \Sigma_\sigma(z)}. \quad (5.11)$$

Here $F_\sigma(z)$ is the on-site Green function for the coherent system in which all the random potentials have been replaced by the coherent ones, and has been given by Eq. (4.11):

$$F_\sigma(z) = \int \frac{\rho(\epsilon) d\epsilon}{z - \Sigma_\sigma(z) - \epsilon}. \quad (5.12)$$

Here $\rho(\epsilon)$ is the DOS per site for the noninteracting system.

The coherent potential $\Sigma_\sigma(z)$ is determined from a self-consistent condition.

$$\overline{G_{00\sigma}(z)} = F_\sigma(z). \quad (5.13)$$

The configurational average of the impurity Green function is now given as

$$\overline{G_{00\sigma}(z)} = \sum_{\alpha} P_{\alpha} G_{00\sigma}^{\alpha}(z). \quad (5.14)$$

Here $\alpha = 00, 10, 01, 11$ denotes the on-site electron configuration $(n_{0\uparrow}, n_{0\downarrow})$. Alternative notation $\nu = 0$ (empty on a site), $1 \uparrow$ (occupied by an electron with spin \uparrow), $1 \downarrow$ (occupied by an electron with spin \downarrow) and 2 (occupied by 2 electrons) is also useful. In this case, the probability P_{α} for the configuration α is expressed as $P_0, P_{1\uparrow}, P_{1\downarrow}$, and P_2 .

The impurity Green functions in Eq. (5.14) for each configuration are given as follows.

$$G_{00\sigma}^{00}(z) = \frac{1}{F_\sigma(z)^{-1} - \epsilon_0 + \mu - \bar{U} \langle n_{-\sigma} \rangle_{00} + \Sigma_\sigma(z)}, \quad (5.15)$$

$$G_{00\uparrow}^{10}(z) = \frac{1}{F_\sigma(z)^{-1} - \epsilon_0 + \mu - \bar{U} \langle n_{\downarrow} \rangle_{10} + \Sigma_\sigma(z)}, \quad (5.16)$$

$$G_{00\downarrow}^{10}(z) = \frac{1}{F_\sigma(z)^{-1} - \epsilon_0 + \mu - \bar{U} \langle n_{\uparrow} \rangle_{10} - \tilde{U} + \Sigma_\sigma(z)}, \quad (5.17)$$

$$G_{00\uparrow}^{01}(z) = \frac{1}{F_\sigma(z)^{-1} - \epsilon_0 + \mu - \bar{U} \langle n_{\downarrow} \rangle_{01} - \tilde{U} + \Sigma_\sigma(z)}, \quad (5.18)$$

$$G_{00\downarrow}^{01}(z) = \frac{1}{F_\sigma(z)^{-1} - \epsilon_0 + \mu - \overline{U}\langle n_\uparrow \rangle_{01} + \Sigma_\sigma(z)}, \quad (5.19)$$

$$G_{00\sigma}^{11}(z) = \frac{1}{F_\sigma(z)^{-1} - \epsilon_0 + \mu - \overline{U}\langle n_{-\sigma} \rangle_{11} - \tilde{U} + \Sigma_\sigma(z)}. \quad (5.20)$$

Here the electron number in the denominator is given by

$$\langle n_\sigma \rangle_\alpha = \int f(\epsilon) \rho_\sigma^\alpha(\epsilon) d\epsilon, \quad (5.21)$$

$$\rho_\sigma^\alpha(\epsilon) = -\frac{1}{\pi} \text{Im} G_{00\sigma}^\alpha(z). \quad (5.22)$$

Furthermore, the average DOS in the second term at the right hand side (r.h.s.) of Eq. (5.6) is given by

$$\overline{\rho_{i\sigma}(\epsilon)} = -\frac{1}{\pi} \text{Im} \overline{G_{00\sigma}(z)} = \sum_\alpha P_\alpha \rho_\sigma^\alpha(\epsilon). \quad (5.23)$$

It should be noted that $P_0 + P_{1\uparrow} + P_{1\downarrow} + P_2 = 1$, and the probability of finding an electron with spin \uparrow (\downarrow) on a site is given by $P_{\uparrow(\downarrow)} = P_{1\uparrow(1\downarrow)} + P_2$. Three statistical probabilities P_0 , $P_{1\uparrow}$, and $P_{1\downarrow}$ are therefore given by the probability P_2 .

The expression of P_2 is derived as follows. We first make the following approximations for the AA and the HF Hamiltonians, respectively.

$$\hat{n}_\uparrow \hat{n}_\downarrow \approx n_\uparrow \hat{n}_\downarrow + n_\downarrow \hat{n}_\uparrow - n_\uparrow n_\downarrow \quad (\text{AA}), \quad (5.24)$$

$$\hat{n}_\uparrow \hat{n}_\downarrow \approx \hat{n}_\uparrow \langle \hat{n}_\downarrow \rangle + \hat{n}_\downarrow \langle \hat{n}_\uparrow \rangle - \langle \hat{n}_\uparrow \rangle \langle \hat{n}_\downarrow \rangle \quad (\text{HF}). \quad (5.25)$$

In the HB scheme, we approximate the averages $\langle \sim \rangle$ at the r.h.s. of the above expressions with those of the HB Hamiltonian (5.4), and superpose Eqs. (5.24) and (5.25) with the weight w and $(1-w)$, respectively. Taking the the quantum mechanical average of the superposed double occupation number as well as the configurational average, we obtain the probability of the double occupation $P_2 (= \overline{\langle n_\uparrow n_\downarrow \rangle})$ in the HB approximation as follows.

$$\begin{aligned} P_2 &= w (\overline{\langle n_\uparrow \rangle \langle n_\downarrow \rangle} + \overline{\langle n_\downarrow \rangle \langle n_\uparrow \rangle} - \overline{\langle n_\uparrow n_\downarrow \rangle}) + (1-w) \overline{\langle n_\downarrow \rangle \langle n_\uparrow \rangle} \\ &= w \overline{\langle n_\uparrow \rangle \langle n_\downarrow \rangle} + (1-w) \overline{\langle n_\uparrow \rangle \langle n_\downarrow \rangle} + w \overline{\langle n_\downarrow \rangle \langle n_\uparrow \rangle} + (1-w) \overline{\langle n_\uparrow \rangle \langle n_\downarrow \rangle} \\ &\quad - [w \overline{\langle n_\uparrow n_\downarrow \rangle} + (1-w) \overline{\langle n_\uparrow \rangle \langle n_\downarrow \rangle}]. \end{aligned} \quad (5.26)$$

The last term at the r.h.s. of Eq. (5.26) may be regarded as the probability P_2 . Therefore, we obtain

$$P_2 \approx \frac{1}{2} [(\overline{\langle w n_\uparrow + (1-w) \langle n_\uparrow \rangle \rangle \langle n_\downarrow \rangle} + \overline{\langle w n_\downarrow + (1-w) \langle n_\downarrow \rangle \rangle \langle n_\uparrow \rangle})], \quad (5.27)$$

i.e.,

$$P_2 = \frac{1}{2} w (\overline{\langle n_\uparrow \rangle \langle n_\downarrow \rangle} + \overline{\langle n_\downarrow \rangle \langle n_\uparrow \rangle}) + (1-w) \overline{\langle n_\uparrow \rangle \langle n_\downarrow \rangle}. \quad (5.28)$$

In the single-site approximation, the last term at the r.h.s. of Eq. (5.28) is expressed as follows.

$$\begin{aligned}\overline{\langle n_\uparrow \rangle \langle n_\downarrow \rangle} &= \sum_{\alpha} P_{\alpha} \langle n_\uparrow \rangle_{\alpha} \langle n_\downarrow \rangle_{\alpha} \\ &= P_0 \langle n_\uparrow \rangle_{00} \langle n_\downarrow \rangle_{00} + P_{1\uparrow} \langle n_\uparrow \rangle_{10} \langle n_\downarrow \rangle_{10} + P_{1\downarrow} \langle n_\uparrow \rangle_{01} \langle n_\downarrow \rangle_{01} + P_2 \langle n_\uparrow \rangle_{11} \langle n_\downarrow \rangle_{11} .\end{aligned}\quad (5.29)$$

In the non-magnetic case, we have

$$\begin{aligned}\overline{\langle n_\uparrow \rangle \langle n_\downarrow \rangle} &= \langle n_\uparrow \rangle_{00}^2 + (P_\uparrow + P_\downarrow) (\langle n_\uparrow \rangle_{10} \langle n_\uparrow \rangle_{01} - \langle n_\uparrow \rangle_{00}^2) \\ &\quad + P_2 (\langle n_\uparrow \rangle_{00}^2 - 2 \langle n_\uparrow \rangle_{10} \langle n_\uparrow \rangle_{01} + \langle n_\uparrow \rangle_{11}^2) .\end{aligned}\quad (5.30)$$

Similarly,

$$\overline{n_\uparrow \langle n_\downarrow \rangle} + \overline{n_\downarrow \langle n_\uparrow \rangle} = (P_\uparrow + P_\downarrow) \langle n_\uparrow \rangle_{01} + 2P_2 (\langle n_\uparrow \rangle_{11} - \langle n_\uparrow \rangle_{01}) .\quad (5.31)$$

Substituting Eqs. (5.30) and (5.31) into Eq. (5.28), we obtain the final expression of P_2 .

$$P_2 = \frac{(1-w) \langle n_\uparrow \rangle_{00}^2 + (P_\uparrow + P_\downarrow) \{1/2 w \langle n_\uparrow \rangle_{01} + (1-w) \langle n_\uparrow \rangle_{10} \langle n_\uparrow \rangle_{01} - \langle n_\uparrow \rangle_{00}^2\}}{1 - w (\langle n_\uparrow \rangle_{11} - \langle n_\uparrow \rangle_{01}) - (1-w) (\langle n_\uparrow \rangle_{00}^2 - 2 \langle n_\uparrow \rangle_{10} \langle n_\uparrow \rangle_{01} + \langle n_\uparrow \rangle_{11}^2)} .\quad (5.32)$$

The double occupation numbers at the r.h.s. of Eq. (5.6) are obtained in the SSA as follows.

$$\overline{\langle n_{i\uparrow} n_{i\downarrow} \rangle}_{\text{HB}} = \overline{\langle n_{i\uparrow} \rangle}_{\text{HB}} \overline{\langle n_{i\downarrow} \rangle}_{\text{HB}} = \sum_{\alpha} P_{\alpha} \langle n_\uparrow \rangle_{\alpha} \langle n_\downarrow \rangle_{\alpha} ,\quad (5.33)$$

$$\overline{n_{i\uparrow} \langle n_{i\downarrow} \rangle}_{\text{HB}} + \overline{n_{i\downarrow} \langle n_{i\uparrow} \rangle}_{\text{HB}} = (P_\uparrow + P_\downarrow) \langle n_\uparrow \rangle_{01} + 2P_2 (\langle n_\uparrow \rangle_{11} - \langle n_\uparrow \rangle_{01}) .\quad (5.34)$$

The momentum distribution in the HB scheme is given by

$$\overline{\langle n_{k\sigma} \rangle}_{\text{HB}} = \int f(\epsilon) \rho_{k\sigma}(\epsilon) d\epsilon ,\quad (5.35)$$

$$\rho_{k\sigma}(\epsilon) = -\frac{1}{\pi} \text{Im} F_{k\sigma} ,\quad (5.36)$$

$$F_{k\sigma} = \frac{1}{z - \Sigma_{\sigma}(z) - \epsilon_k} .\quad (5.37)$$

Here ϵ_k is the eigenvalue of t_{ij} with momentum k .

In summary, to determine the ground-state energy of the HB wavefunction $\overline{\langle H \rangle}_{\text{HB}}$ in Eq. (5.6), we first determine the coherent potential $\Sigma_{\sigma}(z)$ self-consistently by making use of Eqs. (5.12), (5.13), and (5.14). In the self-consistent loop the impurity Green function for each configuration and corresponding electron number are determined by Eqs. (5.15)-(5.20) and (5.22), respectively. The probability P_2 in the self-consistent loop is also determined by Eq. (5.32).

5.2 Local-ansatz + hybrid wavefunction approach with momentum dependent variational parameters

The momentum dependent local-ansatz (MLA) wavefunction is based on the local-ansatz (LA) proposed by Stollhoff and Fulde: $|\Psi_{\text{LA}}\rangle = [\prod_i (1 - \eta_{\text{LA}} O_i)] |\phi_0\rangle$ [13, 14, 15]. Here $O_i = \delta n_{i\uparrow} \delta n_{i\downarrow}$ are the residual interaction, the amplitude η_{LA} is determined variationally. The operators $\{O_i\}$ expand the Hilbert space to describe the weak Coulomb interaction regime. The LA however does not yield the exact result in the weak interaction limit. The MLA wavefunction (Eq. 3.9) which describes exactly the weak Coulomb interaction limit was constructed in Chap. 3 as follows [24, 25].

$$|\Psi_{\text{MLA}}\rangle = \prod_i (1 - \tilde{O}_i) |\phi_0\rangle, \quad (5.38)$$

$$\tilde{O}_i = \sum_{k_1 k'_1 k_2 k'_2} \langle k'_1 | i \rangle \langle i | k_1 \rangle \langle k'_2 | i \rangle \langle i | k_2 \rangle \eta_{k'_2 k_2 k'_1 k_1} \delta(a_{k'_2 \downarrow}^\dagger a_{k_2 \downarrow}) \delta(a_{k'_1 \uparrow}^\dagger a_{k_1 \uparrow}). \quad (5.39)$$

Here $\langle i | k \rangle = \exp(-i\mathbf{k} \cdot \mathbf{R}_i) / \sqrt{N}$ is an overlap integral between the localized orbital and the Bloch state with momentum \mathbf{k} , \mathbf{R}_i denotes atomic position, and N is the number of sites. $\eta_{k'_2 k_2 k'_1 k_1}$ is a momentum dependent variational parameter. $a_{k\sigma}^\dagger$ ($a_{k\sigma}$) denotes a creation (annihilation) operator for an electron with momentum \mathbf{k} and spin σ , and $\delta(a_{k'\sigma}^\dagger a_{k\sigma}) = a_{k'\sigma}^\dagger a_{k\sigma} - \langle a_{k'\sigma}^\dagger a_{k\sigma} \rangle_0$.

In this chapter, we generalize the wavefunction (5.38) to be suitable in both the strong and the weak Coulomb interaction regimes. The idea is to adopt the HB ground-state wavefunction $|\phi_{\text{HB}}\rangle$ for the Hamiltonian H_{HB} (5.4) as a starting wavefunction, and to apply a new correlator $\prod_i (1 - \tilde{O}_i)$ as follows.

$$|\Psi_{\text{MLA-HB}}\rangle = \prod_i (1 - \tilde{O}_i) |\phi_{\text{HB}}\rangle. \quad (5.40)$$

Note that the local operators $\{\tilde{O}_i\}$ have been modified as follows.

$$\tilde{O}_i = \sum_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} \langle \kappa'_1 | i \rangle \langle i | \kappa_1 \rangle \langle \kappa'_2 | i \rangle \langle i | \kappa_2 \rangle \eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} \delta(a_{\kappa'_2 \downarrow}^\dagger a_{\kappa_2 \downarrow}) \delta(a_{\kappa'_1 \uparrow}^\dagger a_{\kappa_1 \uparrow}). \quad (5.41)$$

Here $\eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}$ is a variational parameter, $a_{\kappa\sigma}^\dagger$ and $a_{\kappa\sigma}$ are the creation and annihilation operators which diagonalize the Hamiltonian H_{HB} (5.4), and $\delta(a_{\kappa'\sigma}^\dagger a_{\kappa\sigma}) = a_{\kappa'\sigma}^\dagger a_{\kappa\sigma} - \langle a_{\kappa'\sigma}^\dagger a_{\kappa\sigma} \rangle_{\text{HB}}$. It should be noted that the MLA-HB wavefunction (5.40) reduces to the MLA-HF with the uniform potential $U \langle n_{i-\sigma} \rangle_0$ when the variational parameter $w = 0$, and reduces to the MLA-AA with the random potential $U n_{i-\sigma}$ when $w = 1$. The MLA-HB wavefunction interpolates between the two wavefunctions.

The ground-state energy E satisfies the following inequality for any wavefunction $|\Psi\rangle$.

$$E \leq \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \langle H \rangle_{\text{HB}} + N\epsilon_c. \quad (5.42)$$

Here $\langle H \rangle_{\text{HB}}$ denotes the energy for the HB wavefunction. ϵ_c is the correlation energy defined by

$$N\epsilon_c = \frac{\langle \Psi | \tilde{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad (5.43)$$

with $\tilde{H} = H - \langle H \rangle_{\text{HB}}$. Since it depends on the electron configuration $\{n_{i\sigma}\}$ via the AA potential, we have to take into account the configurational average at the end. To determine the variational parameters, we minimize the ground-state energy.

It is not easy to calculate exactly the correlation energy with use of the HB wavefunction (5.40). Therefore, we adopt again the single-site approximation (SSA). The average of $\langle \tilde{A} \rangle$ of an operator $\tilde{A} = A - \langle A \rangle_{\text{HB}}$ with respect to the wavefunction (5.40) is then given as follows.

$$\langle \tilde{A} \rangle = \sum_i \frac{\langle (1 - \tilde{O}_i^\dagger) \tilde{A} (1 - \tilde{O}_i) \rangle_{\text{HB}}}{\langle (1 - \tilde{O}_i^\dagger) (1 - \tilde{O}_i) \rangle_{\text{HB}}} . \quad (5.44)$$

The detailed derivation of the above formula has been given in Sec. 3.2.1. Making use of the above formula, the correlation energy per atom is obtained as follows.

$$\epsilon_c = \frac{-\langle \tilde{O}_i^\dagger \tilde{H} \rangle_{\text{HB}} - \langle \tilde{H} \tilde{O}_i \rangle_{\text{HB}} + \langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_{\text{HB}}}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_{\text{HB}}} . \quad (5.45)$$

Each term in the correlation energy (5.45) can be calculated by making use of Wick's theorem as follows.

$$\langle \tilde{H} \tilde{O}_i \rangle_{\text{HB}} = U \sum_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} \langle \kappa'_1 | i \rangle \langle i | \kappa_1 \rangle \langle \kappa'_2 | i \rangle \langle i | \kappa_2 \rangle \sum_j \langle \kappa_1 | j \rangle \langle j | \kappa'_1 \rangle \langle \kappa_2 | j \rangle \langle j | \kappa'_2 \rangle \eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} \tilde{f}_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} , \quad (5.46)$$

$$\langle \tilde{O}_i^\dagger \tilde{H} \rangle_{\text{HB}} = \langle \tilde{H} \tilde{O}_i \rangle_{\text{HB}}^* , \quad (5.47)$$

$$\begin{aligned} & \langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_{\text{HB}} \\ &= \sum_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} \langle i | \kappa'_1 \rangle \langle \kappa_1 | i \rangle \langle i | \kappa'_2 \rangle \langle \kappa_2 | i \rangle \eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}^* \tilde{f}_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} \sum_{\kappa'_4 \kappa_4 \kappa'_3 \kappa_3} \langle \kappa'_3 | i \rangle \langle i | \kappa_3 \rangle \langle \kappa'_4 | i \rangle \langle i | \kappa_4 \rangle \\ & \times (\Delta E_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} \delta_{\kappa_1 \kappa_3} \delta_{\kappa'_1 \kappa'_3} \delta_{\kappa_2 \kappa_4} \delta_{\kappa'_2 \kappa'_4} + U_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1 \kappa'_4 \kappa_4 \kappa'_3 \kappa_3}) \eta_{\kappa'_4 \kappa_4 \kappa'_3 \kappa_3} , \end{aligned} \quad (5.48)$$

$$\begin{aligned} U_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1 \kappa'_4 \kappa_4 \kappa'_3 \kappa_3} &= U \sum_j [\langle j | \kappa_1 \rangle \langle \kappa_3 | j \rangle f(\tilde{\epsilon}_{\kappa_3 \uparrow}) \delta_{\kappa'_1 \kappa'_3} - \langle \kappa'_1 | j \rangle \langle j | \kappa'_3 \rangle (1 - f(\tilde{\epsilon}_{\kappa'_3 \uparrow})) \delta_{\kappa_1 \kappa_3}] \\ & \times [\langle j | \kappa_2 \rangle \langle \kappa_4 | j \rangle f(\tilde{\epsilon}_{\kappa_4 \downarrow}) \delta_{\kappa'_2 \kappa'_4} - \langle \kappa'_2 | j \rangle \langle j | \kappa'_4 \rangle (1 - f(\tilde{\epsilon}_{\kappa'_4 \downarrow})) \delta_{\kappa_2 \kappa_4}] , \end{aligned} \quad (5.49)$$

$$\langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_{\text{HB}} = \sum_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} |\langle \kappa'_1 | i \rangle|^2 |\langle \kappa_1 | i \rangle|^2 |\langle \kappa'_2 | i \rangle|^2 |\langle \kappa_2 | i \rangle|^2 |\eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}|^2 \tilde{f}_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} . \quad (5.50)$$

Here $\tilde{f}_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}$ is a Fermi factor of two-particle excitations which is defined by $\tilde{f}_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} = f(\tilde{\epsilon}_{\kappa_1 \uparrow}) (1 - f(\tilde{\epsilon}_{\kappa'_1 \uparrow})) f(\tilde{\epsilon}_{\kappa_2 \downarrow}) (1 - f(\tilde{\epsilon}_{\kappa'_2 \downarrow}))$, $f(\epsilon)$ is the Fermi distribution function at zero temperature, $\tilde{\epsilon}_{\kappa\sigma} = \epsilon_{\kappa\sigma} - \mu$, and $\epsilon_{\kappa\sigma}$ is the one-electron energy eigenvalue for the HB Hamiltonian. Moreover, $\Delta E_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} = \epsilon_{\kappa'_2 \downarrow} - \epsilon_{\kappa_2 \downarrow} + \epsilon_{\kappa'_1 \uparrow} - \epsilon_{\kappa_1 \uparrow}$ is a two-particle excitation energy.

The above expressions (5.46) and (5.49) contain nonlocal terms via summation over j (*i.e.*, \sum_j). We thus make additional SSA that we only take into account the local term ($j = i$), so that $\langle \tilde{H} \tilde{O}_i \rangle_{\text{HB}} (= \langle \tilde{O}_i^\dagger \tilde{H} \rangle_{\text{HB}}^*)$ and $\langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_{\text{HB}}$ reduce as follows.

$$\langle \tilde{H} \tilde{O}_i \rangle_{\text{HB}} = U \sum_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} |\langle \kappa'_1 | i \rangle|^2 |\langle \kappa_1 | i \rangle|^2 |\langle \kappa'_2 | i \rangle|^2 |\langle \kappa_2 | i \rangle|^2 \eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} \tilde{f}_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} , \quad (5.51)$$

$$\begin{aligned}
\langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_{\text{HB}} = & \sum_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} |\langle \kappa'_1 | i \rangle|^2 |\langle \kappa_1 | i \rangle|^2 |\langle \kappa'_2 | i \rangle|^2 |\langle \kappa_2 | i \rangle|^2 \\
& \times \eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}^* \tilde{f}_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} \left[\Delta E_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} \eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} \right. \\
& + U \left\{ \sum_{\kappa_3 \kappa_4} |\langle \kappa_3 | i \rangle|^2 |\langle \kappa_4 | i \rangle|^2 f(\tilde{\epsilon}_{\kappa_3 \uparrow}) f(\tilde{\epsilon}_{\kappa_4 \downarrow}) \eta_{\kappa'_2 \kappa_4 \kappa'_1 \kappa_3} \right. \\
& - \sum_{\kappa'_3 \kappa_4} |\langle \kappa'_3 | i \rangle|^2 |\langle \kappa_4 | i \rangle|^2 (1 - f(\tilde{\epsilon}_{\kappa'_3 \uparrow})) f(\tilde{\epsilon}_{\kappa_4 \downarrow}) \eta_{\kappa'_2 \kappa_4 \kappa'_3 \kappa_1} \\
& - \sum_{\kappa_3 \kappa'_4} |\langle \kappa_3 | i \rangle|^2 |\langle \kappa'_4 | i \rangle|^2 f(\tilde{\epsilon}_{\kappa_3 \uparrow}) (1 - f(\tilde{\epsilon}_{\kappa'_4 \downarrow})) \eta_{\kappa'_4 \kappa_2 \kappa'_1 \kappa_3} \\
& \left. \left. + \sum_{\kappa'_3 \kappa'_4} |\langle \kappa'_3 | i \rangle|^2 |\langle \kappa'_4 | i \rangle|^2 (1 - f(\tilde{\epsilon}_{\kappa'_3 \uparrow})) (1 - f(\tilde{\epsilon}_{\kappa'_4 \downarrow})) \eta_{\kappa'_4 \kappa_2 \kappa'_3 \kappa_1} \right\} \right]. \quad (5.52)
\end{aligned}$$

In order to obtain the variational parameters $\{\eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}\}$, we minimize the correlation energy ϵ_c , *i.e.*, Eq. (5.45) with Eqs. (5.50), (5.51), and (5.52). The self-consistent equations for $\{\eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}\}$ in the SSA are obtained as follows.

$$\begin{aligned}
(\Delta E_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} - \epsilon_c) \eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} + U \left[\sum_{\kappa_3 \kappa_4} |\langle \kappa_3 | i \rangle|^2 |\langle \kappa_4 | i \rangle|^2 f(\tilde{\epsilon}_{\kappa_3 \uparrow}) f(\tilde{\epsilon}_{\kappa_4 \downarrow}) \eta_{\kappa'_2 \kappa_4 \kappa'_1 \kappa_3} \right. \\
- \sum_{\kappa'_3 \kappa_4} |\langle \kappa'_3 | i \rangle|^2 |\langle \kappa_4 | i \rangle|^2 (1 - f(\tilde{\epsilon}_{\kappa'_3 \uparrow})) f(\tilde{\epsilon}_{\kappa_4 \downarrow}) \eta_{\kappa'_2 \kappa_4 \kappa'_3 \kappa_1} \\
- \sum_{\kappa_3 \kappa'_4} |\langle \kappa_3 | i \rangle|^2 |\langle \kappa'_4 | i \rangle|^2 f(\tilde{\epsilon}_{\kappa_3 \uparrow}) (1 - f(\tilde{\epsilon}_{\kappa'_4 \downarrow})) \eta_{\kappa'_4 \kappa_2 \kappa'_1 \kappa_3} \\
\left. + \sum_{\kappa'_3 \kappa'_4} |\langle \kappa'_3 | i \rangle|^2 |\langle \kappa'_4 | i \rangle|^2 (1 - f(\tilde{\epsilon}_{\kappa'_3 \uparrow})) (1 - f(\tilde{\epsilon}_{\kappa'_4 \downarrow})) \eta_{\kappa'_4 \kappa_2 \kappa'_3 \kappa_1} \right] = U. \quad (5.53)
\end{aligned}$$

It is not easy to find the solution of Eq. (5.53) for the intermediate strength of Coulomb interaction U . To solve the equation approximately, we consider an interpolate solution which is valid in both the weak Coulomb interaction limit and the atomic limit. Note that the first term at the left hand side (l.h.s.) of Eq. (5.53) is dominant and the second term is negligible in the weak Coulomb interaction limit. In the atomic limit, the momentum dependence of $\eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}$ is negligible. Thus, we approximate $\{\eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}\}$ in the second term at the l.h.s. of Eq. (5.53) with a momentum independent parameter η which is suitable for the atomic region. Solving the equation, we obtain

$$\eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}(\tilde{\eta}, \epsilon_c) = \frac{U \tilde{\eta}}{\Delta E_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1} - \epsilon_c}. \quad (5.54)$$

Here $\tilde{\eta} = [1 - \eta(1 - 2\langle n_{i\uparrow} \rangle_{\text{HB}})(1 - 2\langle n_{i\downarrow} \rangle_{\text{HB}})]$.

The ground-state correlation energy is obtained by substituting the variational parameters (5.54) into Eq. (5.45). Each element in the energy is given as follows.

$$\langle \tilde{H} \tilde{O}_i \rangle_{\text{HB}} = \langle \tilde{O}_i^\dagger \tilde{H} \rangle_{\text{HB}}^* = A U^2 \tilde{\eta}, \quad (5.55)$$

$$\langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_{\text{HB}} = B U^2 \tilde{\eta}^2 = \langle \tilde{O}_i^\dagger \tilde{H}_0 \tilde{O}_i \rangle_{\text{HB}} + U \langle \tilde{O}_i^\dagger O_i \tilde{O}_i \rangle_{\text{HB}}, \quad (5.56)$$

$$\langle \tilde{O}_i^\dagger \tilde{H}_0 \tilde{O}_i \rangle_{\text{HB}} = B_1 U^2 \tilde{\eta}^2, \quad (5.57)$$

$$\langle \tilde{O}_i^\dagger O_i \tilde{O}_i \rangle_{\text{HB}} = B_2 U^2 \tilde{\eta}^2, \quad (5.58)$$

$$\langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_{\text{HB}} = C U^2 \tilde{\eta}^2. \quad (5.59)$$

Here

$$A = \int \frac{\left[\prod_{n=1}^4 d\epsilon_n \right] \rho_\uparrow(\epsilon_1) \rho_\uparrow(\epsilon_2) \rho_\downarrow(\epsilon_3) \rho_\downarrow(\epsilon_4) f(\epsilon_1) (1-f(\epsilon_2)) f(\epsilon_3) (1-f(\epsilon_4))}{\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c}, \quad (5.60)$$

$$B = B_1 + U B_2, \quad (5.61)$$

$$B_1 = \int \frac{\left[\prod_{n=1}^4 d\epsilon_n \right] \rho_\uparrow(\epsilon_1) \rho_\uparrow(\epsilon_2) \rho_\downarrow(\epsilon_3) \rho_\downarrow(\epsilon_4) f(\epsilon_1) (1-f(\epsilon_2)) f(\epsilon_3) (1-f(\epsilon_4))}{(\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1)^{-1} (\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c)^2}, \quad (5.62)$$

$$B_2 = \int \frac{\left[\prod_{n=1}^4 d\epsilon_n \right] \rho_\uparrow(\epsilon_1) \rho_\uparrow(\epsilon_2) \rho_\downarrow(\epsilon_3) \rho_\downarrow(\epsilon_4) f(\epsilon_1) (1-f(\epsilon_2)) f(\epsilon_3) (1-f(\epsilon_4))}{\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c} \\ \times \left[\int \frac{d\epsilon_5 d\epsilon_6 \rho_\uparrow(\epsilon_5) \rho_\downarrow(\epsilon_6) f(\epsilon_5) f(\epsilon_6)}{\epsilon_4 - \epsilon_6 + \epsilon_2 - \epsilon_5 - \epsilon_c} - \int \frac{d\epsilon_5 d\epsilon_6 \rho_\uparrow(\epsilon_5) \rho_\downarrow(\epsilon_6) f(\epsilon_5) (1-f(\epsilon_6))}{\epsilon_6 - \epsilon_3 + \epsilon_2 - \epsilon_5 - \epsilon_c} \right. \\ \left. - \int \frac{d\epsilon_5 d\epsilon_6 \rho_\uparrow(\epsilon_5) \rho_\downarrow(\epsilon_6) (1-f(\epsilon_5)) f(\epsilon_6)}{\epsilon_4 - \epsilon_6 + \epsilon_5 - \epsilon_1 - \epsilon_c} + \int \frac{d\epsilon_5 d\epsilon_6 \rho_\uparrow(\epsilon_5) \rho_\downarrow(\epsilon_6) (1-f(\epsilon_5)) (1-f(\epsilon_6))}{\epsilon_6 - \epsilon_3 + \epsilon_5 - \epsilon_1 - \epsilon_c} \right], \quad (5.63)$$

$$C = \int \frac{\left[\prod_{n=1}^4 d\epsilon_n \right] \rho_\uparrow(\epsilon_1) \rho_\uparrow(\epsilon_2) \rho_\downarrow(\epsilon_3) \rho_\downarrow(\epsilon_4) f(\epsilon_1) (1-f(\epsilon_2)) f(\epsilon_3) (1-f(\epsilon_4))}{(\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c)^2}. \quad (5.64)$$

Here $\rho_\sigma(\epsilon)$ is the local DOS for the one-electron energy eigenvalues of the HB Hamiltonian matrix (5.9).

The best value of $\tilde{\eta}$ should be determined variationally. In fact, when we adopt the approximate form (5.54) as a trial set of amplitudes, we have a following inequality

$$E \leq \langle H \rangle(w, \{\eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}^*\}) \leq \langle H \rangle(w, \{\eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}(\tilde{\eta}, \epsilon_c)\}). \quad (5.65)$$

Here $\{\eta_{\kappa'_2 \kappa_2 \kappa'_1 \kappa_1}^*\}$ are the exact solution for the Eq. (5.53). The above relation implies that the best value of $\tilde{\eta}$ can be again determined from the stationary condition (*i.e.*, $\delta\epsilon_c = 0$), so that we obtain

$$\tilde{\eta} = \frac{-B + \sqrt{B^2 + 4A^2CU^2}}{2ACU^2}. \quad (5.66)$$

The total energy per atom should be obtained by taking the configurational average.

$$\langle H \rangle = \overline{\langle H \rangle}_{\text{HB}} + \bar{\epsilon}_c. \quad (5.67)$$

The HB contribution $\overline{\langle H \rangle}_{\text{HB}}$ has been given by Eq. (5.6). The correlation energy can be obtained as follows.

$$\bar{\epsilon}_c = \sum_{\alpha} P_{\alpha} \epsilon_{c\alpha}. \quad (5.68)$$

Here $\epsilon_{c\alpha}$ denotes the correlation energy for a given on-site configuration α .

$$\epsilon_{c\alpha} = \left[\frac{-\langle \tilde{O}_i^{\dagger} \tilde{H} \rangle_{\text{HB}} - \langle \tilde{H} \tilde{O}_i \rangle_{\text{HB}} + \langle \tilde{O}_i^{\dagger} \tilde{H} \tilde{O}_i \rangle_{\text{HB}}}{1 + \langle \tilde{O}_i^{\dagger} \tilde{O}_i \rangle_{\text{HB}}} \right]_{\alpha}. \quad (5.69)$$

The quantities $\langle \tilde{H} \tilde{O}_i \rangle_{\text{HB}}$, $\langle \tilde{O}_i^{\dagger} \tilde{H} \tilde{O}_i \rangle_{\text{HB}}$, and $\langle \tilde{O}_i^{\dagger} \tilde{O}_i \rangle_{\text{HB}}$ are given by Eqs. (5.55), (5.56), and (5.59), respectively, in which the local DOS have been replaced by those of the single-site CPA, *i.e.*, Eq. (5.22).

Laplace transforms of the physical quantities (3.59)-(3.63) are given as follows.

$$A_{\alpha} = i \int_0^{\infty} dt e^{i\epsilon_{c\alpha} t} a_{\alpha\uparrow}(-t) a_{\alpha\downarrow}(-t) b_{\alpha\uparrow}(t) b_{\alpha\downarrow}(t), \quad (5.70)$$

$$\begin{aligned} B_{1\alpha} = & - \int_0^{\infty} dt dt' e^{i\epsilon_{c\alpha}(t+t')} \\ & \times [a_{\alpha\uparrow}(-t-t') b_{\alpha\uparrow}(t+t') a_{\alpha\downarrow}(-t-t') b_{1\alpha\downarrow}(t+t') \\ & - a_{\alpha\uparrow}(-t-t') b_{\alpha\uparrow}(t+t') a_{1\alpha\downarrow}(-t-t') b_{\alpha\downarrow}(t+t') \\ & + a_{\alpha\uparrow}(-t-t') b_{1\alpha\uparrow}(t+t') a_{\alpha\downarrow}(-t-t') b_{\alpha\downarrow}(t+t') \\ & - a_{1\alpha\uparrow}(-t-t') b_{\alpha\uparrow}(t+t') a_{\alpha\downarrow}(-t-t') b_{\alpha\downarrow}(t+t')], \end{aligned} \quad (5.71)$$

$$\begin{aligned} B_{2\alpha} = & - \int_0^{\infty} dt dt' e^{i\epsilon_{c\alpha}(t+t')} \\ & \times [a_{\alpha\uparrow}(-t) b_{\alpha\uparrow}(t+t') a_{\alpha\downarrow}(-t) b_{\alpha\downarrow}(t+t') a_{\alpha\uparrow}(-t') a_{\alpha\downarrow}(-t') \\ & - a_{\alpha\uparrow}(-t) b_{\alpha\uparrow}(t+t') a_{\alpha\downarrow}(-t-t') b_{\alpha\downarrow}(t) a_{\alpha\uparrow}(-t') b_{\alpha\downarrow}(t') \\ & - a_{\alpha\uparrow}(-t-t') b_{\alpha\uparrow}(t) a_{\alpha\downarrow}(-t) b_{\alpha\downarrow}(t+t') b_{\alpha\uparrow}(t') a_{\alpha\downarrow}(-t') \\ & + a_{\alpha\uparrow}(-t-t') b_{\alpha\uparrow}(t) a_{\alpha\downarrow}(-t-t') b_{\alpha\downarrow}(t) b_{\alpha\uparrow}(t') b_{\alpha\downarrow}(t')], \end{aligned} \quad (5.72)$$

$$C_{\alpha} = - \int_0^{\infty} dt dt' e^{i\epsilon_{c\alpha}(t+t')} a_{\alpha\uparrow}(-t-t') b_{\alpha\uparrow}(t+t') a_{\alpha\downarrow}(-t-t') b_{\alpha\downarrow}(t+t'). \quad (5.73)$$

Here α denotes the local electron configuration ($\alpha = 0, 1 \uparrow, 1 \downarrow, 2$), and

$$a_{\alpha\sigma}(t) = \int d\epsilon \rho_{\sigma}^{\alpha}(\epsilon) f(\epsilon) e^{-i\epsilon t}, \quad (5.74)$$

$$b_{\alpha\sigma}(t) = \int d\epsilon \rho_{\sigma}^{\alpha}(\epsilon) [1 - f(\epsilon)] e^{-i\epsilon t}, \quad (5.75)$$

$$a_{1\alpha\sigma}(t) = \int d\epsilon \rho_\sigma^\alpha(\epsilon) f(\epsilon) \epsilon e^{-i\epsilon t}, \quad (5.76)$$

$$b_{1\alpha\sigma}(t) = \int d\epsilon \rho_\sigma^\alpha(\epsilon) [1 - f(\epsilon)] \epsilon e^{-i\epsilon t}. \quad (5.77)$$

The double occupation number $\langle n_{i\uparrow} n_{i\downarrow} \rangle$ is obtained from $\partial \langle H \rangle / \partial U_i$. Making use of the single-site energy (5.45), the Feynman-Hellmann theorem [32] and taking the configurational average, we obtain the following expression.

$$\langle n_{i\uparrow} n_{i\downarrow} \rangle = \overline{\langle n_{i\uparrow} \rangle_{\text{HB}} \langle n_{i\downarrow} \rangle_{\text{HB}}} + \overline{\langle n_{i\uparrow} n_{i\downarrow} \rangle_c}, \quad (5.78)$$

Here the HB contribution of the double occupancy $\overline{\langle n_{i\uparrow} \rangle_{\text{HB}} \langle n_{i\downarrow} \rangle_{\text{HB}}}$ has been given by Eq. (5.33). The second term is the correlation contribution given as follows.

$$\overline{\langle n_{i\uparrow} n_{i\downarrow} \rangle_c} = \sum_\alpha P_\alpha \langle n_{i\uparrow} n_{i\downarrow} \rangle_{c\alpha}, \quad (5.79)$$

$$\langle n_{i\uparrow} n_{i\downarrow} \rangle_{c\alpha} = \left[\frac{-\langle \tilde{O}_i^\dagger O_i \rangle_{\text{HB}} - \langle O_i \tilde{O}_i \rangle_{\text{HB}} + \langle \tilde{O}_i^\dagger O_i \tilde{O}_i \rangle_{\text{HB}} + \sum_\sigma \langle n_{i-\sigma} \rangle_{\text{HB}} \langle \tilde{O}_i^\dagger \tilde{n}_{i\sigma} \tilde{O}_i \rangle_{\text{HB}}}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_{\text{HB}}} \right]_\alpha, \quad (5.80)$$

$$\begin{aligned} \langle \tilde{O}_i^\dagger O_i \rangle_{\text{HB}} + \langle O_i \tilde{O}_i \rangle_{\text{HB}} &= 2U\tilde{\eta} \int \left[\prod_{n=1}^4 d\epsilon_n \right] \rho_\uparrow(\epsilon_1) \rho_\uparrow(\epsilon_2) \rho_\downarrow(\epsilon_3) \rho_\downarrow(\epsilon_4) \\ &\quad \times \frac{f(\epsilon_1)(1-f(\epsilon_2))f(\epsilon_3)(1-f(\epsilon_4))}{\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c}, \end{aligned} \quad (5.81)$$

$$\begin{aligned} \langle \tilde{O}_i^\dagger \tilde{n}_{i\sigma} \tilde{O}_i \rangle_{\text{HB}} &= U^2 \tilde{\eta}^2 \int \left[\prod_{n=1}^5 d\epsilon_n \right] \rho_{-\sigma}(\epsilon_1) \rho_{-\sigma}(\epsilon_2) \rho_\sigma(\epsilon_3) \rho_\sigma(\epsilon_4) \rho_\sigma(\epsilon_5) \\ &\quad \times \frac{f(\epsilon_1)(1-f(\epsilon_2))f(\epsilon_3)(1-f(\epsilon_4))}{\epsilon_4 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c} \\ &\quad \times \left[\frac{1-f(\epsilon_5)}{\epsilon_5 - \epsilon_3 + \epsilon_2 - \epsilon_1 - \epsilon_c} - \frac{f(\epsilon_5)}{\epsilon_4 - \epsilon_5 + \epsilon_2 - \epsilon_1 - \epsilon_c} \right]. \end{aligned} \quad (5.82)$$

The quantities $\langle \tilde{O}_i^\dagger O_i \tilde{O}_i \rangle_{\text{HB}}$ and $\langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_{\text{HB}}$ are defined by Eqs. (5.58) and (5.59), respectively.

The element (5.81) for the calculation of the double occupancy is expressed using the Laplace transform as follows

$$\langle \tilde{O}_i^\dagger O_i \rangle_{\text{HB}\alpha} + \langle O_i \tilde{O}_i \rangle_{\text{HB}\alpha} = 2iU\tilde{\eta}_\alpha \int_0^\infty dt e^{i\epsilon_\alpha t} a_{\alpha\uparrow}(-t) b_{\alpha\uparrow}(t) a_{\alpha\downarrow}(-t) b_{\alpha\downarrow}(t). \quad (5.83)$$

The correlation contribution to the electron number (5.82) which appears in the calculation of the double occupation number is expressed as

$$\begin{aligned} \langle \tilde{O}_i^\dagger \tilde{n}_{i\sigma} \tilde{O}_i \rangle_{\text{HB}\alpha} &= -U^2 \tilde{\eta}_\alpha^2 \int_0^\infty dt dt' e^{i\epsilon_\alpha(t+t')} \\ &\quad \times [a_{\alpha(-\sigma)}(-t-t') b_{\alpha(-\sigma)}(t+t') a_{\alpha\sigma}(-t-t') b_{\alpha\sigma}(t) b_{\alpha\sigma}(t') \\ &\quad - a_{\alpha(-\sigma)}(-t-t') b_{\alpha(-\sigma)}(t+t') a_{\alpha\sigma}(-t) b_{\alpha\sigma}(t+t') a_{\alpha\sigma}(t')]. \end{aligned} \quad (5.84)$$

Similarly, the momentum distribution $\langle n_{k\sigma} \rangle$ is obtained from $\partial \langle H \rangle / \partial \epsilon_k$ as follows.

$$\langle n_{k\sigma} \rangle = \overline{\langle n_{k\sigma} \rangle}_{\text{HB}} + \overline{\langle n_{k\sigma} \rangle}_c. \quad (5.85)$$

The HB contribution of the momentum distribution $\overline{\langle n_{k\sigma} \rangle}_{\text{HB}}$ has been given by Eq. (5.35). The correlation contribution $\overline{\langle n_{k\sigma} \rangle}_c$ is expressed as follows.

$$\overline{\langle n_{k\sigma} \rangle}_c = \sum_{\alpha} P_{\alpha} \langle n_{k\sigma} \rangle_{c\alpha}, \quad (5.86)$$

$$\langle n_{k\sigma} \rangle_{c\alpha} = \left[\frac{N \langle \tilde{O}_i^{\dagger} \tilde{n}_{k\sigma} \tilde{O}_i \rangle_{\text{HB}}}{1 + \langle \tilde{O}_i^{\dagger} \tilde{O}_i \rangle_{\text{HB}}} \right]_{\alpha}, \quad (5.87)$$

$$\begin{aligned} N \langle \tilde{O}_i^{\dagger} \tilde{n}_{k\sigma} \tilde{O}_i \rangle_{\text{HB}} &= U^2 \tilde{\eta}^2 \int \left[\prod_{n=1}^4 d\epsilon_n \right] \rho_{\sigma}(\epsilon_1) \rho_{-\sigma}(\epsilon_2) \rho_{-\sigma}(\epsilon_3) \rho_{k\sigma}(\epsilon_4) f(\epsilon_2) (1 - f(\epsilon_3)) \\ &\times \left\{ \frac{f(\epsilon_1) (1 - f(\epsilon_4))}{(\epsilon_3 - \epsilon_2 + \epsilon_4 - \epsilon_1 - \epsilon_c)^2} - \frac{(1 - f(\epsilon_1)) f(\epsilon_4)}{(\epsilon_3 - \epsilon_2 + \epsilon_1 - \epsilon_4 - \epsilon_c)^2} \right\}. \end{aligned} \quad (5.88)$$

Here $\tilde{n}_{k\sigma} = n_{k\sigma} - \langle n_{k\sigma} \rangle_{\text{HB}}$. The DOS in the momentum representation $\rho_{k\sigma}(\epsilon)$ has been given by Eq. (5.36) in the SSA. The correlation contribution quantity $\langle \tilde{O}_i^{\dagger} \tilde{O}_i \rangle_{\text{HB}}$ is given by Eq. (5.59).

The correlation contribution to the momentum distribution function (5.88) is given by

$$\begin{aligned} N \langle \tilde{O}_i^{\dagger} \tilde{n}_{k\sigma} \tilde{O}_i \rangle_{0\alpha} &= U^2 \tilde{\eta}_{\alpha}^2 \int_0^{\infty} dt dt' e^{i\epsilon_{c\alpha}(t+t')} a_{\alpha(-\sigma)}(-t-t') b_{\alpha(-\sigma)}(t+t') \\ &\times [b_{\alpha\sigma}(t+t') a_{k\sigma}(-t-t') - a_{\alpha\sigma}(-t-t') b_{k\sigma}(t+t')]. \end{aligned} \quad (5.89)$$

Here

$$a_{k\sigma}(t) = \int d\epsilon \rho_{k\sigma}(\epsilon) f(\epsilon) e^{-i\epsilon t}, \quad (5.90)$$

$$b_{k\sigma}(t) = \int d\epsilon \rho_{k\sigma}(\epsilon) [1 - f(\epsilon)] e^{-i\epsilon t}. \quad (5.91)$$

In summary, we calculate the correlation energy $\epsilon_{c\alpha}$ (Eq. (5.69)) self-consistently with use of Eqs. (5.55), (5.56), (5.59), and (5.66) for a given weight w , and calculate the average correlation energy $\bar{\epsilon}_c$ (Eq. (5.68)) as well as the average HB energy $\overline{\langle H \rangle}_{\text{HB}}$ (Eq. (5.6)). Then we obtain the total energy $\langle H \rangle(w)$ (Eq. (5.67)) for a given w . Varying w from 0 to 1 numerically, we obtain the ground-state energy $\langle H \rangle$ in the MLA-HB.

5.3 Numerical results: half-filled band Hubbard model

We have performed the numerical calculations to investigate the validity of momentum dependent local-ansatz approach (MLA) with hybrid (HB) variational wavefunction (*i.e.*, MLA-HB). We adopted here the half-filled band Hubbard model on the hypercubic lattice in infinite dimensions,

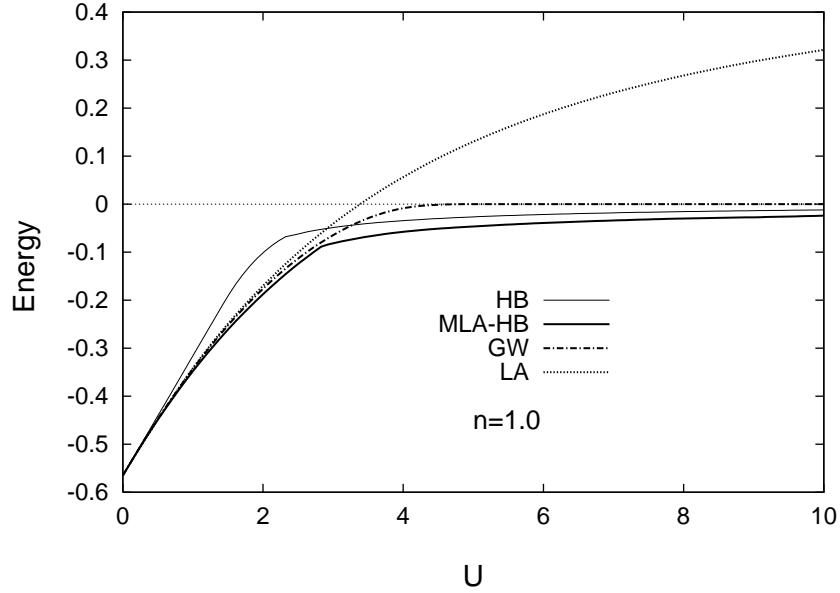


Figure 5.1: The energy vs Coulomb interaction energy U curves in the HB (thin solid curve), the MLA-HB (solid curve), the GW (dot-dashed curve) and the LA (dotted curve) for the electron number $n = 1.0$.

where the SSA works best [39, 42], and considered the non-magnetic case. In this case, the density of states (DOS) for non-interacting system is given by $\rho(\epsilon) = (1/\sqrt{\pi}) \exp(-\epsilon^2)$ [42]. The energy unit is chosen to be $\int d\epsilon \rho(\epsilon) \epsilon^2 = 1/2$. The characteristic band width W is given by $W = 2$ in this unit.

The results of the ground-state energy vs Coulomb interaction energy curves are shown in Fig. 5.1. The energy of the HB wavefunction (without correlation) linearly increases with increasing Coulomb interaction strength U in the weak U regime. At $U_{c0} = 1.43$, the system shows a transition from the Fermi liquid (FL) state ($w = 0$) to a non-Fermi liquid (NFL) state ($w \neq 0$), and shows a kink at the critical Coulomb interaction $U_c = 2.31$, indicating the metal-insulator transition. The transition is of the first order in the present approach. The HB wavefunction gives lower energy in comparison with the GW and the LA in the strong Coulomb interaction regime ($U/W \gtrsim 1.5$). The MLA-HB wavefunction further lowers the energy. In the weak Coulomb interaction regime, the ground-state energy of the MLA-HB is the lowest among the HB, LA, GW, and the MLA-HB. The MLA-HB shows the first-order transition at $U_c = 2.81$ from the FL to the NFL, indicating the metal-insulator transition. The MLA-HB scheme gives lower energy for overall Coulomb interaction and therefore overcomes the GW.

Figure 5.2 shows the double occupation number $\langle n_{\uparrow} n_{\downarrow} \rangle$ as a function of Coulomb interaction energy U at half-filling. In the case of the HB, the double occupancy is constant ($1/4$) up to $U_{c0} = 1.43$, and decreases rapidly up to the critical point $U_c = 2.31$, at which it jumps from 0.110 to 0.060. In the strong Coulomb interaction regime the double occupancy decreases with increasing U and vanishes in the atomic limit. In the case of the MLA-HB, the double occupation number decreases smoothly from $1/4$ with increasing Coulomb interaction so as to reduce the loss of Coulomb energy U . Note that the MLA-HB reduces more the double occupancy as compared with that of the HB, GW and LA in the weak U region. The double occupancy in the MLA-HB jumps from 0.106 to 0.045 at the transition point $U_c = 2.81$, and again monotonically decreases

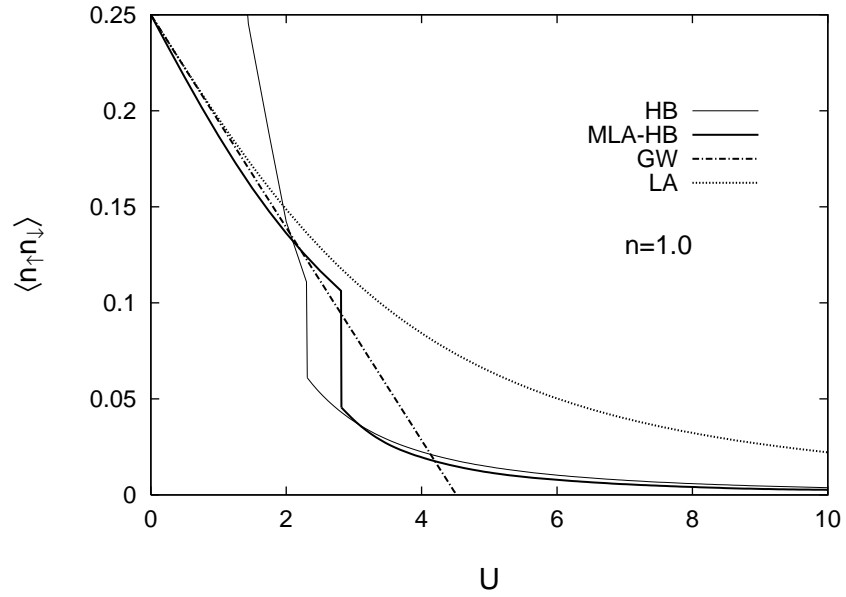


Figure 5.2: The double occupation number $\langle n_{\uparrow}n_{\downarrow} \rangle$ vs Coulomb interaction energy U curves at half-filling ($n = 1.0$) in the HB (thin solid curve), the MLA-HB (solid curve), the GW (dot-dashed curve), and the LA (dotted curve).

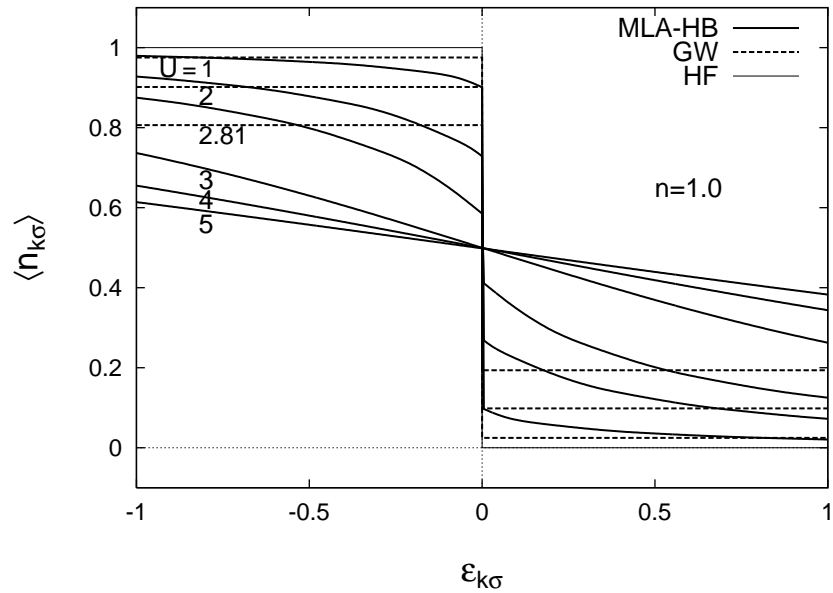


Figure 5.3: The momentum distribution as a function of energy $\epsilon_{k\sigma}$ for various Coulomb interaction energy parameters $U = 1.0, 2.0, 2.81, 3.0, 4.0$ and 5.0 at half-filling. The MLA-HB: solid curves, the GW: dashed curves, and the HF: thin solid curve.

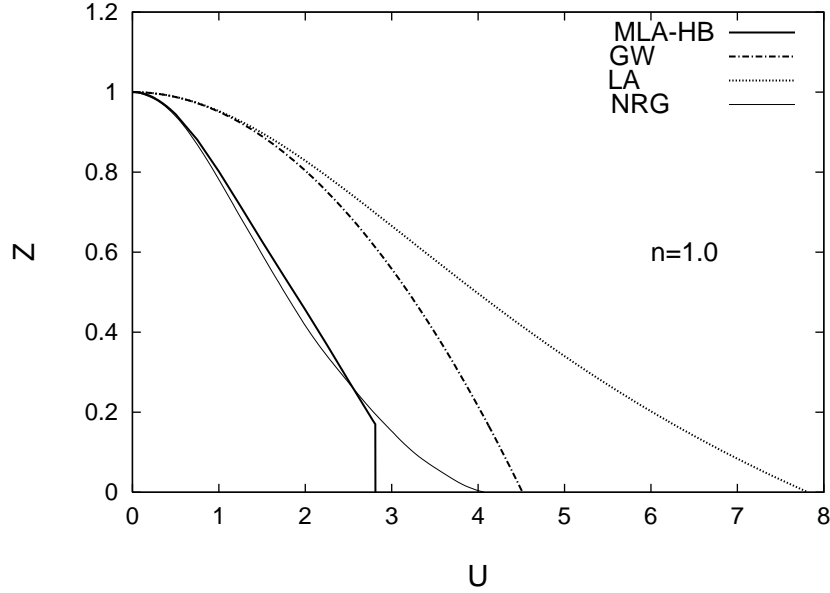


Figure 5.4: Quasiparticle-weight vs. Coulomb interaction curves in various theories. The MLA-HB: solid curve, the GW: dot-dashed, the LA: dotted curve, and the NRG: thin solid curve [34].

with increasing U . Note that the double occupancy in the MLA-HB remains finite in the strong U regime as it should be, while the GW gives the Brinkman-Rice atom.

The momentum distribution for the MLA-HB is shown in Fig. 5.3. It decreases monotonically with increasing $\epsilon_{k\sigma}$ and shows a jump at the Fermi energy in the metallic regime. The jump decreases with increasing U , and disappears beyond U_c . When we further increase the Coulomb interaction U the curve becomes flatter. Note that the momentum distributions for the GW are constant below and above the Fermi level [7, 8, 9]. These results indicate that the MLA-HB improves the GW.

The quasiparticle weight Z (*i.e.*, inverse effective mass) is obtained from the jump at the Fermi level in the momentum distribution according to the Fermi liquid theory [35, 36, 37, 38]. Calculated quasiparticle weight vs Coulomb interaction curves are shown in Fig. 5.4. The GW and the LA curves strongly deviate from the curve of the NRG [34] which is considered to be the best. The MLA-HB is close to the NRG in the metallic regime, and vanishes beyond $U_c = 2.81$. It should be noted that the NRG also shows the first order transition at a critical Coulomb interaction U_c before Z vanishes at $U_{c2} = 4.1$. [34] The values of U_c in the NRG, however, has not yet been published.

Chapter 6

Summary and Discussions

We have proposed a new local-ansatz wavefunction with momentum-dependent variational parameters (*i.e.*, MLA-HF). It is constructed by using the ‘flexible’ local operators which produce the two-particle excited states in the momentum space from the Hartree-Fock state and project those states onto the local excited states in the real space. The best wavefunction is chosen by controlling the momentum dependent variational parameters of the excited states in the momentum space on the basis of the variational principle. We obtained the ground-state energy of the MLA within a single-site approximation. Minimizing the energy, we derived a self-consistent equation for the variational parameters, and obtained an approximate solution which interpolates between the weak Coulomb interaction limit and the atomic limit. The MLA self-consistently determines both the variational amplitude $\tilde{\eta}$ and the correlation energy ϵ_c making use of variational principles. The correlation energy in the MLA agrees with the result of the second-order perturbation theory in infinite dimensions in the weak Coulomb interaction limit and yields the correct atomic limit as it should be.

To examine the improvement and validity of the MLA-HF theory, we performed in Chap. 3 the numerical calculations for the half-filled band as well as the non-half-filled band on the basis of the Hubbard model on the hypercubic lattice in infinite dimensions. We have investigated the effects of the best choice of the variational parameter $\tilde{\eta}$ on various physical quantities especially in the non-half-filled case. In the correlation energy calculations, the non-self-consistent $\tilde{\eta}$ (*i.e.*, Eq. (3.42)) yields the same results as the self-consistent case in the weak Coulomb interaction regime. But in the intermediate- and strong- Coulomb interaction regimes we found that the self-consistency of the variational parameter becomes significant; the self-consistent $\tilde{\eta}$ yields the result being better than the non-self-consistent case. We observed that the self-consistent MLA yields reasonable momentum distribution functions while the non-self-consistent one leads to a unphysical bump in the vicinity of the Fermi level. From these facts we conclude that the self-consistency of $\tilde{\eta}$ is indispensable for understanding electron correlations.

Within the self-consistent MLA-HF [25], we have clarified the role of the momentum dependence of variational parameters in comparison with the original Local-Ansatz (LA). We demonstrated that the self-consistent MLA improves the LA irrespective of the Coulomb interaction energy parameter U and electron number n . The correlation energy in the MLA is lower than those of the LA and the GW in the weak and intermediate Coulomb interaction regimes. Thus we verified that the MLA wavefunction is better than both the LA and the GW in these regimes. The double occupation number is suppressed as compared with the LA both in the same interaction regimes. We found that the calculated momentum distribution functions show a distinct momentum dependence. This is qualitatively different from the LA and the GW because both of them lead to the

momentum-independence of the distributions below and above the Fermi level. We also found that the quasiparticle weight in the MLA-HF is close to those of the NRG in the range $0 < U \lesssim 2.5$, while the LA and the GW much overestimate them. The results suggest that the MLA-HF is applicable to the systems with $U/W \lesssim 1.5$, for example, to the systems like transition metals and alloys. Here W denotes the band width of the noninteracting system. In the MLA-HF calculation [25] the critical Coulomb interaction U_{c2} at half-filling was obtained from the vanishment of the quasiparticle weights. It is $U_{c2} = 3.21$ for the non self-consistent $\tilde{\eta}$ and $U_{c2} = 3.40$ for the self-consistent $\tilde{\eta}$, respectively. The latter is comparable to $U_{c2} = 4.10$, the best value in the NRG, while the LA and the GW give larger values $U_{c2} = 7.82$ and 4.51 , respectively.

We have proposed an improved momentum dependent local-ansatz wavefunction in Chap. 4 *i.e.*, the MLA-AA. It allows us to describe electron correlations starting from the alloy-analogy (AA) limits instead of the Hartree-Fock (HF) state. The MLA-HF describes the Fermi-liquid state, while the MLA-AA describes the insulator state. We have performed the numerical calculations for the half-filled band Hubbard model on the hypercubic lattice in infinite dimensions, and demonstrated that the ground state energy for the MLA-AA is lower than the GW in the strong Coulomb interaction regime [27]. It yields the metal-insulator transition at $U_c = 3.26$. The double occupation number is suppressed in the weak and intermediate Coulomb interaction regimes as compared with the GW, jumps at U_c , and remains finite in the strongly correlated regime as it should be. Finally, we found the momentum distribution functions showing a distinct momentum dependence in both the metallic and insulator regimes. These results indicate that the MLA-AA approach [27] can overcome the limitations of the original MLA-HF [24, 25], and goes beyond the GW in the strong U regime.

We have proposed in Chap. 5 a new hybrid (HB) wavefunction and combined it with the momentum dependent local-ansatz approach MLA (*i.e.*, the MLA-HB) to describe the correlated electron system from the weak to the strong Coulomb interaction regime [28]. The HB wavefunction is the ground-state for the HB Hamiltonian and was used as a starting wavefunction of the MLA-HB. The HB Hamiltonian was constructed by a superposition of the HF Hamiltonian and the AA one. The weight w of superposition is regarded as a variational parameter. When we adopt $w = 0$ (1), the HB wavefunction reduces to the HF (AA) state. In the MLA-HB, the best wavefunction is chosen by controlling the momentum dependent variational parameters for the two-particle excited states as well as the HB parameter w . We obtained the ground-state energy of the MLA-HB within a single-site approximation, and derived an approximate solution for the self-consistent equations of the variational parameters, which interpolates between the weak Coulomb interaction limit and the atomic limit.

To examine the improvement and validity of the theory, we have performed the numerical calculations for the half-filled band Hubbard model on the hypercubic lattice in infinite dimensions. In the case of the HB wavefunction we clarified that the ground-state energy increases linearly in the weak U regime and it shows a lower energy as compared with the GW and the LA in the strong U regime. The double occupation number is constant up to the $U = 1.43$ (*i.e.*, $\langle n_{\uparrow}n_{\downarrow} \rangle_{\text{HB}} = 0.25$) and then decreases rapidly to the critical value $U_c = 2.31$ at which the first-order metal-insulator transition occurs. In the strong U regime the $\langle n_{\uparrow}n_{\downarrow} \rangle_{\text{HB}}$ remains finite.

We have demonstrated that the ground-state energy of the MLA-HB [28] is lower than those of the HB, GW and the LA in the whole Coulomb interaction regime. In the weak and intermediate Coulomb interaction regimes, the double occupation number is suppressed as compared with the others. It jumps at $U_c = 2.81$ and remains finite in the strongly correlated regime as it should be. The momentum distribution functions show a distinct momentum dependence in both the weak and

the strong U regimes. Moreover, we found that the behavior of the quasiparticle weight is close to the NRG one. The above mentioned results indicate that the MLA-HB approach overcomes the limitations of the original MLA [24, 25], and describes reasonably correlated electrons from the weak to the strong Coulomb interaction regime, so that it goes beyond the GW in the whole Coulomb interaction U regime.

In the MLA approach we have adopted the single-site approximation which neglects the non-local correlations. In order to take into account the correlations properly, one has to consider the contractions between the intersite operators in the calculation of the energy with use of Wick's theorem. Furthermore, one has to extend the correlator to the nonlocal case. For example, one can modify the correlator $\prod_i(1 - \tilde{O}_i)$ as $\exp(-\sum_{(i,j)} \tilde{O}_{ij}) \prod_i(1 - \tilde{O}_i)$. Here we introduced a nonlocal operator $\tilde{O}_{ij} = \sum_{k_1 k'_1 k_2 k'_2} \langle k'_1 | i \rangle \langle i | k_1 \rangle \langle k'_2 | j \rangle \langle j | k_2 \rangle \eta_{k'_2 k_2 k'_1 k_1} \delta(a_{k'_2 \downarrow}^\dagger a_{k_2 \downarrow}) \delta(a_{k'_1 \uparrow}^\dagger a_{k_1 \uparrow})$ for the description of the intersite correlations. It is worth for us to extend our single-site theory to the cluster taking into account the nonlocal effects mentioned above.

It should also be noted that the present form of the MLA ansatz is not necessarily enough to describe the strongly correlated electrons. For example, it cannot suppress the double occupancy for infinitely large U when the electron number per atom becomes less than one. In order to solve the problem one has to modify the correlators $(1 - \tilde{O}_i)$ as $(1 - \tilde{O}_i - \zeta \delta n_i)$. Here ζ is a new variational parameter and $\delta n_i = n_i - \langle n_i \rangle$. The term δn_i is needed to cover the Hilbert space related to the double occupancy. The additional variational parameter ζ therefore should suppress the double occupancy.

Although more quantitative theories based on the quantum monte carlo (QMC) method and the numerical renormalization group (NRG) method have been developed, the MLA approach presented in this work is sufficiently simple, analytic, and therefore applicable to more complex systems. It also allows us to calculate any static averages with use of the wavefunction. Thus it is possible to apply the MLA approach to the multiband Hubbard model and to combine it with the first-principles tight-binding Hamiltonian. Such a theory should provide us with a useful tool for understanding the properties of correlated electrons and their physics in the realistic systems. These improvements and extensions of the theory are left for future work.

Appendix A

Appendix: Gutzwiller wavefunction

In this Appendix we derive the expression of the total energy of the Gutzwiller wavefunction, which is used in Sect. 2.4.1. The Hartree-Fock (HF) ground-state is expressed by an independent-particle state as follows.

$$|\phi_0\rangle = \left(\prod_k^{N_\uparrow} a_{k\uparrow}^\dagger \right) \left(\prod_k^{N_\downarrow} a_{k\downarrow}^\dagger \right) |0\rangle. \quad (\text{A.1})$$

Here N_σ denotes the total electron number for the spin σ . Making use of a unitary transform such as $a_{k\sigma}^\dagger = \sum_i a_{i\sigma}^\dagger e^{ikR_i} / \sqrt{L}$, we obtain the wavefunction in the real space representation as follows.

$$|\phi_0\rangle = \sum_{C(N_\uparrow, N_\downarrow)} \det \left(\frac{1}{\sqrt{L}} e^{i\mathbf{k}_i \cdot \mathbf{R}_{l(j)}} \right) \det \left(\frac{1}{\sqrt{L}} e^{i\mathbf{k}_i \cdot \mathbf{R}_{m(j)}} \right) \left(\prod_i^{N_\uparrow} a_{l(i)\uparrow}^\dagger \right) \left(\prod_i^{N_\downarrow} a_{m(i)\downarrow}^\dagger \right) |0\rangle. \quad (\text{A.2})$$

Here L denotes the number of lattice. \mathbf{k}_i is the momentum of the i -th electron below the Fermi level. A set of sites $(l(1), l(2), \dots, l(N_\uparrow))$ ($(m(1), m(2), \dots, m(N_\downarrow))$) denote a configuration of electrons with up (down) spin on the lattice, and $(\mathbf{R}_{l(1)}, \mathbf{R}_{l(2)}, \dots, \mathbf{R}_{l(N_\uparrow)})$ denote the positions of the sites. The determinants are defined for the matrices whose (i, j) element is given by $(1/\sqrt{L})\exp(i\mathbf{k}_i \cdot \mathbf{R}_{l(j)})$ and $(1/\sqrt{L})\exp(i\mathbf{k}_i \cdot \mathbf{R}_{m(j)})$, respectively. Furthermore, $\sum_{C(N_\uparrow, N_\downarrow)}$ means the sum over all the configurations of electrons on a lattice when electron numbers of up and down spins are given. It should be noted that the $\{l(i)\}$ ($\{m(i)\}$) are ordered as $l(1) < l(2) < \dots < l(N_\uparrow)$ ($m(1) < m(2) < \dots < m(N_\downarrow)$) in the Fock-space.

In the HF wavefunction, doubly occupied sites appear irrespective of the Coulomb interaction strength U in various electron configurations on a lattice. Such a state with doubly occupied sites causes a loss of Coulomb interaction energy. In the correlated electron system, the probability amplitudes of the doubly occupied states must be reduced to decrease the total energy. In order to describe the on-site electron correlations, Gutzwiller introduced a correlated wavefunction as follows.

$$|\Psi_{\text{GW}}\rangle = \left[\prod_i^L (1 - (1 - g)n_{i\uparrow}n_{i\downarrow}) \right] |\phi_0\rangle. \quad (\text{A.3})$$

Here $n_{i\uparrow}n_{i\downarrow}$ is a projection operator that chooses the doubly occupied state on site i , and g is a variational parameter controlling the amplitude of doubly occupied states in the HF wavefunction. Note that the $g = 1$ state corresponds to an uncorrelated state; and the $g = 0$ state corresponds to the atomic state in which all the doubly occupied states have been removed.

Substituting (A.2) in to the GW (A.3), we obtain the real space representation as follows.

$$|\Psi\rangle = \sum_D g^D \sum_{C(D, N_\uparrow, N_\downarrow)} \det\left(\frac{1}{\sqrt{L}} e^{i\mathbf{k}_i \cdot \mathbf{R}_{l(j)}}\right) \det\left(\frac{1}{\sqrt{L}} e^{i\mathbf{k}_i \cdot \mathbf{R}_{m(j)}}\right) \left(\prod_i^{N_\uparrow} a_{l(i)\uparrow}^\dagger\right) \left(\prod_i^{N_\downarrow} a_{m(i)\downarrow}^\dagger\right) |0\rangle. \quad (\text{A.4})$$

Here D is the number of doubly occupied sites, and $C(D, N_\uparrow, N_\downarrow)$ denotes the electron configurations on a lattice when D, N_\uparrow , and N_\downarrow are given.

The energy of the Hubbard Hamiltonian (2.11) with $\epsilon_0 = 0$ is then given as follows.

$$E(g) = \frac{\sum_{ij\sigma} t_{ij} \langle \Psi | a_{i\sigma}^\dagger a_{j\sigma} | \Psi \rangle + U \langle \Psi | \sum_i n_{i\uparrow} n_{i\downarrow} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (\text{A.5})$$

Each term at the r.h.s. is given as follows.

$$\begin{aligned} \langle \Psi | \Psi \rangle &= \sum_D g^{2D} \sum_{C(D, N_\uparrow, N_\downarrow)} \left(w_\uparrow(\mathbf{R} - \mathbf{R}') \left| \begin{array}{cccc} \mathbf{R}_{l(1)} & \mathbf{R}_{l(2)} & \cdots & \mathbf{R}_{l(N_\uparrow)} \\ \mathbf{R}_{l(1)} & \mathbf{R}_{l(2)} & \cdots & \mathbf{R}_{l(N_\uparrow)} \end{array} \right. \right) \\ &\times \left(w_\downarrow(\mathbf{R} - \mathbf{R}') \left| \begin{array}{cccc} \mathbf{R}_{m(1)} & \mathbf{R}_{m(2)} & \cdots & \mathbf{R}_{m(N_\downarrow)} \\ \mathbf{R}_{m(1)} & \mathbf{R}_{m(2)} & \cdots & \mathbf{R}_{m(N_\downarrow)} \end{array} \right. \right), \end{aligned} \quad (\text{A.6})$$

$$\begin{aligned} \langle \Psi | \sum_i n_{i\uparrow} n_{i\downarrow} | \Psi \rangle &= \sum_D D g^{2D} \sum_{C(D, N_\uparrow, N_\downarrow)} \left(w_\uparrow(\mathbf{R} - \mathbf{R}') \left| \begin{array}{cccc} \mathbf{R}_{l(1)} & \mathbf{R}_{l(2)} & \cdots & \mathbf{R}_{l(N_\uparrow)} \\ \mathbf{R}_{l(1)} & \mathbf{R}_{l(2)} & \cdots & \mathbf{R}_{l(N_\uparrow)} \end{array} \right. \right) \\ &\times \left(w_\downarrow(\mathbf{R} - \mathbf{R}') \left| \begin{array}{cccc} \mathbf{R}_{m(1)} & \mathbf{R}_{m(2)} & \cdots & \mathbf{R}_{m(N_\downarrow)} \\ \mathbf{R}_{m(1)} & \mathbf{R}_{m(2)} & \cdots & \mathbf{R}_{m(N_\downarrow)} \end{array} \right. \right). \end{aligned} \quad (\text{A.7})$$

Here the function $w_\sigma(\mathbf{R} - \mathbf{R}')$ is defined by

$$w_\sigma(\mathbf{R} - \mathbf{R}') = \frac{1}{L} \sum_{\mathbf{k}_n}^{N_\sigma} e^{i\mathbf{k}_n \cdot (\mathbf{R} - \mathbf{R}')}. \quad (\text{A.8})$$

The Gutzwiller overlap function with function $w_\sigma(\mathbf{R} - \mathbf{R}')$ in (A.6) and (A.7) is defined by

$$\left(f(x, y) \left| \begin{array}{cccc} x_1 & x_2 & \cdots & x_n \\ y_1 & y_2 & \cdots & y_n \end{array} \right. \right) = \left| \begin{array}{cccc} f(x_1, y_1) & f(x_1, y_2) & \cdots & f(x_1, y_n) \\ f(x_2, y_1) & f(x_2, y_2) & \cdots & f(x_2, y_n) \\ \cdots & \cdots & \cdots & \cdots \\ f(x_n, y_1) & f(x_n, y_2) & \cdots & f(x_n, y_n) \end{array} \right|. \quad (\text{A.9})$$

In order to calculate the electron hopping term in the numerator of (A.5), we classify the configuration $C(D, N_\uparrow, N_\downarrow)$ into 4 parts according to the 4 electron configurations on sites i and j ; $C(D, N_\uparrow, N_\downarrow, i\uparrow = j\uparrow = 0)$, $C(D, N_\uparrow, N_\downarrow, i\uparrow = 0, j\uparrow = 1)$, $C(D, N_\uparrow, N_\downarrow, i\uparrow = 1, j\uparrow = 0)$, and $C(D, N_\uparrow, N_\downarrow, i\uparrow = j\uparrow = 1)$. When the electron hopping operator $a_{i\uparrow}^\dagger a_{j\uparrow}$ is applied to Ψ , the configuration $C(D, N_\uparrow, N_\downarrow, i\uparrow = 0, j\uparrow = 1)$ remains among 4 types of configurations. The number of doubly occupied states in each configuration of $a_{i\uparrow}^\dagger a_{j\uparrow} | \Psi \rangle$ can changes from D according to

the configuration of the down spin electron on sites i and j . When we express the configuration as $(i, j) = \begin{pmatrix} i\uparrow & j\uparrow \\ i\downarrow & j\downarrow \end{pmatrix}$, the number of the doubly occupied states of $a_{i\uparrow}^\dagger a_{j\uparrow} |\Psi\rangle$ is given by D for $(i, j) = \begin{pmatrix} 01 \\ 00 \end{pmatrix}$, $D - 1$ for $(i, j) = \begin{pmatrix} 01 \\ 01 \end{pmatrix}$, $D + 1$ for $(i, j) = \begin{pmatrix} 01 \\ 10 \end{pmatrix}$, and D for $(i, j) = \begin{pmatrix} 01 \\ 11 \end{pmatrix}$. We therefore obtain

$$\begin{aligned}
& \langle \Psi | a_{i\uparrow}^\dagger a_{j\downarrow} | \Psi \rangle \\
&= \left[\sum_D g^{2D} \sum_{C(D, N_\uparrow, N_\downarrow, (i, j) = \begin{pmatrix} 01 \\ 00 \end{pmatrix})} + \sum_D g^{2D-1} \sum_{C(D, N_\uparrow, N_\downarrow, (i, j) = \begin{pmatrix} 01 \\ 01 \end{pmatrix})} \right. \\
& \quad \left. + \sum_D g^{2D+1} \sum_{C(D, N_\uparrow, N_\downarrow, (i, j) = \begin{pmatrix} 01 \\ 10 \end{pmatrix})} + \sum_D g^{2D} \sum_{C(D, N_\uparrow, N_\downarrow, (i, j) = \begin{pmatrix} 01 \\ 11 \end{pmatrix})} \right] \\
& \quad \times \left(w_\uparrow(\mathbf{R} - \mathbf{R}') \begin{vmatrix} \mathbf{R}_{l(1)} & \mathbf{R}_{l(2)} & \cdots & \mathbf{R}_{l(N_\uparrow)} \\ \mathbf{R}_{l(1)} & \mathbf{R}_{l(2)} & \cdots & \mathbf{R}_{l(N_\uparrow)} \end{vmatrix} \right) \\
& \quad \times \left(w_\downarrow(\mathbf{R} - \mathbf{R}') \begin{vmatrix} \mathbf{R}_{m(1)} & \mathbf{R}_{m(2)} & \cdots & \mathbf{R}_{m(N_\downarrow)} \\ \mathbf{R}_{m(1)} & \mathbf{R}_{m(2)} & \cdots & \mathbf{R}_{m(N_\downarrow)} \end{vmatrix} \right). \tag{A.10}
\end{aligned}$$

The configuration in the above expression (A.10), for example $C(D, N_\uparrow, N_\downarrow, (i, j) = \begin{pmatrix} 01 \\ 00 \end{pmatrix})$ means the electron configuration when D , N_\uparrow , and N_\downarrow are given, and there is no electron on site i , but site j is occupied by an up-spin electron.

The difficulty in the Gutzwiller variational method is how to take the sums with respect to the electron configurations in each term of the energy containing the overlap function of $w_\sigma(\mathbf{R} - \mathbf{R}')$. Gutzwiller replaced these overlap functions with their average values. This is called the Gutzwiller approximation. For example in the calculation of the norm $\langle \Psi | \Psi \rangle$, we make the following approximation.

$$\begin{aligned}
\langle \Psi | \Psi \rangle &\approx \sum_D g^{2D} \sum_{C(D, N_\uparrow, N_\downarrow)} \left[\frac{1}{(\sum_D \sum_{C(D, N_\uparrow, N_\downarrow)})} \sum_D \sum_{C(D, N_\uparrow, N_\downarrow)} \right] \\
& \quad \times \left(w_\uparrow(\mathbf{R} - \mathbf{R}') \begin{vmatrix} \mathbf{R}_{l(1)} & \mathbf{R}_{l(2)} & \cdots & \mathbf{R}_{l(N_\uparrow)} \\ \mathbf{R}_{l(1)} & \mathbf{R}_{l(2)} & \cdots & \mathbf{R}_{l(N_\uparrow)} \end{vmatrix} \right) \\
& \quad \times \left(w_\downarrow(\mathbf{R} - \mathbf{R}') \begin{vmatrix} \mathbf{R}_{m(1)} & \mathbf{R}_{m(2)} & \cdots & \mathbf{R}_{m(N_\downarrow)} \\ \mathbf{R}_{m(1)} & \mathbf{R}_{m(2)} & \cdots & \mathbf{R}_{m(N_\downarrow)} \end{vmatrix} \right). \tag{A.11}
\end{aligned}$$

We then obtain

$$\langle \Psi | \Psi \rangle \approx \frac{W_0(g)}{W_0(1)} \langle \phi_0 | \phi_0 \rangle. \tag{A.12}$$

Here $\langle \phi_0 | \phi_0 \rangle = 1$. $W_0(g)$ is a sum over all configurations of correlation weight g^{2D} for double occupation number. It is defined by

$$W_0(g) = \sum_D \sum_{C(D, N_\uparrow, N_\downarrow)} g^{2D}. \tag{A.13}$$

In the same way, we obtain

$$\langle \Psi | a_{i\uparrow}^\dagger a_{j\uparrow} | \Psi \rangle \approx \frac{W_{1\uparrow}(g)}{W_{1\uparrow}(1)} \langle \phi_0 | a_{i\uparrow}^\dagger a_{j\uparrow} | \phi_0 \rangle, \tag{A.14}$$

$$\langle \Psi | n_{i\uparrow} n_{i\downarrow} | \Psi \rangle \approx \frac{W_2(g)}{W_2(1)} \langle \phi_0 | n_{i\uparrow} n_{i\downarrow} | \phi_0 \rangle . \quad (\text{A.15})$$

Here

$$\begin{aligned} W_{1\uparrow}(g) = & \sum_D g^{2D} \sum_{C(D, N_\uparrow, N_\downarrow, (i,j)=\begin{pmatrix} 01 \\ 00 \end{pmatrix})} + \sum_D g^{2D-1} \sum_{C(D, N_\uparrow, N_\downarrow, (i,j)=\begin{pmatrix} 01 \\ 01 \end{pmatrix})} \\ & + \sum_D g^{2D+1} \sum_{C(D, N_\uparrow, N_\downarrow, (i,j)=\begin{pmatrix} 01 \\ 10 \end{pmatrix})} + \sum_D g^{2D} \sum_{C(D, N_\uparrow, N_\downarrow, (i,j)=\begin{pmatrix} 01 \\ 11 \end{pmatrix})} , \end{aligned} \quad (\text{A.16})$$

$$W_2(g) = \sum_D \sum_{C(D, N_\uparrow, N_\downarrow)} D g^{2D} . \quad (\text{A.17})$$

The weighting functions $W_0(g)$, $W_1(g)$, and $W_2(g)$ are expressed by the following type of the hypergeometric functions.

$$\begin{aligned} & F(\alpha - N_\uparrow, \beta - N_\downarrow, L - N + \gamma; g^2) \\ & = \sum_{D=0}^{\infty} \frac{(L - N + \gamma - 1)! (\alpha - N_\uparrow + D - 1)! (\beta - N_\downarrow + D - 1)! g^{2D}}{D! (L - N + \gamma + D - 1)! (\alpha - N_\uparrow - 1)! (\beta - N_\downarrow - 1)!} . \end{aligned} \quad (\text{A.18})$$

Here N is the total number of electrons. α , β , and γ are integers of order of 1. In the evaluation of the sums over D in these functions, we can adopt the maximum term approximation because D is a macroscopic variable. The weights for each D term proportional to

$$\frac{(\alpha - N_\uparrow + D - 1)! (\beta - N_\downarrow + D - 1)! g^{2D}}{D! (L - N + \gamma + D - 1)!} . \quad (\text{A.19})$$

The representative value of D that minimizes the above factor is given by

$$g^2 = \frac{D(L - N_\uparrow + D)}{(N_\uparrow - D)(N_\downarrow - D)} . \quad (\text{A.20})$$

By making use of the representative value D , we can express the total energy as follows.

$$E(g) = \sum_{\sigma} q_{\sigma} \left(\sum_k^{N_{\sigma}} \epsilon_k \right) + UD . \quad (\text{A.21})$$

Here the band narrowing factor q_{σ} is given as

$$q_{\sigma} = \frac{\left(\sqrt{(N_{\sigma} - D)(L - N + D)} + \sqrt{D(N_{-\sigma} - D)} \right)^2}{N_{\sigma}(L - N_{\sigma})} . \quad (\text{A.22})$$

Equations (A.21) and (A.22) are identical with (2.32) and (2.33) in Sect. 2.4.1.

Appendix B

Appendix: Wick's theorem

In order to calculate the operator products of many-body problems in Chapter 3, 4, and 5, we use the Wick's theorem. In this appendix we describe the detailed derivation of the Wick theorem. When we treat many-body problems, we encounter the average of the operator products with respect to the non-interacting Hamiltonian H_0 as follows:

$$\langle A_1 A_2 \dots A_{2n} \rangle_0. \quad (\text{B.1})$$

The subscript zero denotes the thermal average of the independent-particle Hamiltonian. Here $\{A_i\}$ are creation or annihilation operators that satisfy the following relations

$$A_i A_j + A_j A_i = (i, j). \quad (\text{B.2})$$

i.e.,

$$a_k^\dagger a_{k'}^\dagger + a_{k'}^\dagger a_k^\dagger = a_k a_{k'} + a_{k'} a_k = 0, \quad (\text{B.3})$$

$$a_k^\dagger a_{k'} + a_{k'} a_k^\dagger = \delta_{kk'}. \quad (\text{B.4})$$

Note that, $H_0 = \sum_k \epsilon_k n_k$. Thus,

$$\langle a_k^\dagger a_{k'}^\dagger \rangle_0 = \langle a_k a_{k'} \rangle_0 = 0, \quad (\text{B.5})$$

$$\langle a_k^\dagger a_{k'} \rangle_0 = \langle a_k a_{k'}^\dagger \rangle_0 = 0 \quad (k \neq k'), \quad (\text{B.6})$$

and

$$\langle a_k^\dagger a_k \rangle_0 = \langle n_k \rangle_0 = \frac{1}{1 + e^{\beta \epsilon_k}}, \quad (\text{B.7})$$

$$\langle a_k a_k^\dagger \rangle_0 = 1 - \langle a_k^\dagger a_k \rangle_0 = \frac{1}{1 + e^{-\beta \epsilon_k}}. \quad (\text{B.8})$$

Thus

$$\langle A_i A_j \rangle_0 = \frac{(ij)}{1 + e^{\pm \beta \epsilon_i}}. \quad (\text{B.9})$$

Here + for $A_i = a_k^\dagger$ and - for $A_i = a_k$ in the denominator. $\langle A_i A_j \rangle_0$ is called the contraction of a pair (ij) .

Using this anti-commutation relation, one can exchange A_1 with A_2 in the average

$$\langle A_1 A_2 \dots, A_{2n} \rangle_0 = (12) \langle A_3 \dots, A_{2n} \rangle_0 - \langle A_2 A_1 A_3 \dots, A_{2n} \rangle_0. \quad (\text{B.10})$$

Hence

$$\langle A_2 \dots A_{2n} A_1 \rangle_0 = e^{\pm\beta\epsilon_1} \langle A_1 A_2 \dots A_{2n} \rangle_0. \quad (\text{B.23})$$

Here we made use of the identity $\text{tr}(AB) = \text{tr}(BA)$.

Substituting Eq. (B.23) into Eq. (B.11), we obtain,

$$(1 + e^{\pm\beta\epsilon_1}) \langle A_1 A_2 \dots A_{2n} \rangle_0 = (12) \langle A_3 \dots A_{2n} \rangle_0 - (13) \langle A_2 A_4 \dots A_{2n} \rangle_0 \\ + \dots + (1, 2n) \langle A_2 A_3 \dots A_{2n-1} \rangle_0. \quad (\text{B.24})$$

Thus now using the Eq. (B.24), we obtain,

$$\langle A_1 A_2 \dots A_{2n} \rangle_0 = \langle A_1 A_2 \rangle \langle A_3 \dots A_{2n} \rangle_0 - \langle A_1 A_3 \rangle \langle A_2 A_4 \dots A_{2n} \rangle_0 \\ + \dots + \langle A_1 A_{2n} \rangle \langle A_2 A_3 \dots A_{2n-1} \rangle_0. \quad (\text{B.25})$$

This way, one can reduce the number of products in the average. Repeating the same procedure for the remaining multiple products, we reach the Wick theorem

$$\langle A_1 A_2 \dots A_{2n} \rangle_0 = \sum_{\{\text{contractions}\}} (-1)^{\delta(P)} \langle A_{i_1} A_{i_2} \rangle_0 \langle A_{i_3} A_{i_4} \rangle_0 \dots \langle A_{i_{2n-1}} A_{i_{2n}} \rangle_0. \quad (\text{B.26})$$

Here the sum on the r.h.s. is taken over all possible pairs of contractions. $(-1)^{\delta(P)}$ takes + or - depending on whether $(i_1, i_2, i_3, \dots, i_{2n})$ is even or odd in permutation and

$$\sum_{\{\text{contractions}\}} = \sum \begin{matrix} i_1 < i_2, i_3 < i_4, \dots, i_{2n-1} < i_{2n} \\ i_1 < i_3 < i_5 < \dots < i_{2n-1} \end{matrix} .$$

Appendix C

Appendix: Density of states in infinite dimensions

To perform the numerical calculation in Chapter 3, 4, and 5, we adopt the hypercubic lattice in infinite dimensions. In this Appendix we describe the Gaussian density of states in infinite dimensions.

The tight-binding Hamiltonian with one atom per primitive unit cell is expressed as

$$H_{ij} = \epsilon_0 \delta_{ij} + t_{ij}(1 - \delta_{ij}). \quad (\text{C.1})$$

Here ϵ_0 is the atomic level and t_{ij} is the transfer integral between sites i and j . The eigen value equation is given by

$$\sum_j H_{ij} \langle j|k \rangle = \epsilon_k \langle i|k \rangle. \quad (\text{C.2})$$

The energy eigen value ϵ_k is obtained by the Fourier transformation as

$$\epsilon_k = \sum_j H_{j0} e^{ikR_j}, \quad (\text{C.3})$$

i.e.

$$\epsilon_k = \epsilon_0 + \sum_{j \neq 0} t_{j0} e^{ikR_j}. \quad (\text{C.4})$$

let us consider the Hamiltonian in the d -dimensional hyper-cubic lattice. We have then the d -dimensional \mathbf{k} vector $\mathbf{k} = (\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_d)$ in the first Brillouin zone defined by

$$-\frac{\pi}{a} < k_n < \frac{\pi}{a} \quad (n = 1, 2, \dots, d). \quad (\text{C.5})$$

Here a represents a lattice constant. In addition, there are $2d$ NN sites. We therefore obtain for the NN hopping model in Eq. (C.4)

$$\epsilon_k = \epsilon_0 + t \sum_{j \neq 0}^{2d} e^{ikR_j}. \quad (\text{C.6})$$

i.e.

$$\epsilon_k = \epsilon_0 + 2t \sum_{n=1}^d \cos k_n a. \quad (\text{C.7})$$

This is the energy eigen values for the d -dimensional simple-cubic lattice.

Since the band width $W = 4d|t|$ diverges when $d \rightarrow \infty$, we adopt the renormalized transfer t in the following, which is defined by

$$t_{ij} = -\frac{t}{\sqrt{2d}}. \quad (\text{C.8})$$

Then the Eq. (C.7) becomes

$$\epsilon_k = \epsilon_0 - \frac{2t}{\sqrt{2d}} \sum_{n=1}^d \cos k_n. \quad (\text{C.9})$$

Here we adopted the unit $a = 1$.

The density of states (DOS) is calculated as follows.

$$\rho(\epsilon) = \frac{1}{N} \sum_k \delta(\epsilon - \epsilon_k). \quad (\text{C.10})$$

Since there are $dk_n/(2\pi/L)$ states in the region $[k_n, k_n + dk_n]$ one can use the replacement

$$\sum_{k_n} \rightarrow \int \frac{dk_n}{2\pi/L}. \quad (\text{C.11})$$

Here L is the size of the crystal along the x_n axis.

Since there are L lattice points along x_n axis, we have a relation $N = L^d$. Therefore,

$$\rho(\epsilon) = \int \left[\prod_{n=1}^d \frac{dk_n}{2\pi} \right] \delta(\epsilon - \epsilon_k). \quad (\text{C.12})$$

In order to obtain the DOS in infinite dimensions, we introduce the characteristic function $\Phi_d(s)$ of the (DOS) as follows.

$$\Phi_d(s) \equiv \int d\epsilon e^{is\epsilon} \rho(\epsilon) = \int \left[\prod_{n=1}^d \frac{dk_n}{2\pi} \right] e^{is\epsilon_k}. \quad (\text{C.13})$$

i.e.,

$$\Phi_d(s) = e^{is\epsilon_0} \left[\int_{-\pi}^{\pi} \frac{dk_n}{2\pi} e^{-i\alpha \cos kn} \right]^d \quad (\text{C.14})$$

where

$$\alpha = \frac{2ts}{\sqrt{2d}}. \quad (\text{C.15})$$

Let us consider the following integral.

$$\int_{-\pi}^{\pi} dx e^{-i\alpha \cos x} = \sum_{n=0}^{\infty} \frac{(-i\alpha)^n}{n!} \int_{-\pi}^{\pi} \cos^n x dx. \quad (\text{C.16})$$

Here

$$\int_{-\pi}^{\pi} dx = 2\pi, \quad (\text{C.17})$$

$$\int_{-\pi}^{\pi} \cos x dx = [\sin x]_{-\pi}^{\pi} = 0, \quad (\text{C.18})$$

$$\int_{-\pi}^{\pi} \cos^2 x \, dx = \int_{-\pi}^{\pi} \frac{1 + \cos 2x}{2} dx = \frac{1}{2} [x + \frac{1}{2} \sin 2x]_{-\pi}^{\pi} = \pi, \quad (\text{C.19})$$

$$\int_{-\pi}^{\pi} \cos^{2n+1} x \, dx = 0, \quad (\text{C.20})$$

$$\begin{aligned} \int_{-\pi}^{\pi} \cos^{2n} x \, dx &= \int_{-\pi}^{\pi} \left[\left(\frac{1}{2}\right)^{2n-1} + [\cos 2nx + \binom{2n}{1} \cos 2(2n-1)x \right. \\ &\quad \left. + \binom{2n}{2} \cos 2(n-2)x \cdots + \binom{2n}{n-1} \cos 2x] + \left(\frac{1}{2}\right)^{2n} \right] dx, \\ &= \binom{2n}{n} \left(\frac{1}{2}\right)^{2n} 2\pi, \\ &= \frac{(2n)!}{(n!)^2} \frac{2\pi}{2^{2n}}. \end{aligned} \quad (\text{C.21})$$

Therefore,

$$\int_{-\pi}^{\pi} dx e^{-i\alpha \cos x} = \sum_{n=0}^{\infty} \frac{(-i\alpha)^{2n}}{(2n)!} \frac{(2n)!}{(n!)^2} \frac{2\pi}{2^{2n}}, \quad (\text{C.22})$$

i.e.,

$$\int_{-\pi}^{\pi} dx e^{-i\alpha \cos x} = 2\pi \sum_{n=0}^{\infty} \frac{(-)^n}{(n!)^2} \left(\frac{\alpha}{2}\right)^{2n}. \quad (\text{C.23})$$

Where the Bessel function $J_0(z)$ is

$$J_0(z) = \sum_{n=0}^{\infty} \frac{(-)^n (z/2)^{2n}}{(n!)^2}. \quad (\text{C.24})$$

We obtain

$$\int_{-\pi}^{\pi} \frac{dk_n}{2\pi} e^{-i\alpha \cos k_n} = J_0(\alpha). \quad (\text{C.25})$$

Therefore,

$$\Phi_d(s) = e^{is\epsilon_0} [J_0(\alpha)]^d. \quad (\text{C.26})$$

Let us expand the Bessel function $J_0(\alpha)$ with respect to s .

$$J_0(\alpha) = \sum_{n=0}^{\infty} \frac{(-)^n}{(n!)^2} \left(\frac{\alpha}{2}\right)^{2n} = 1 - \left(\frac{\alpha}{2}\right)^2 + \frac{1}{4} \left(\frac{\alpha}{2}\right)^4 + \cdots \quad (\text{C.27})$$

$$\begin{aligned} [J_0(\alpha)]^d &= \left[1 - \left(\frac{\alpha}{2}\right)^2 + \frac{1}{4} \left(\frac{\alpha}{2}\right)^4 + \cdots \right]^d, \\ &= 1 - \binom{d}{1} \left(\frac{\alpha}{2}\right)^2 + \binom{d}{2} \left[-\left(\frac{\alpha}{2}\right)^2 \right]^2 + \binom{d}{1} \frac{1}{4} \left(\frac{\alpha}{2}\right)^4 + \cdots, \\ &= 1 - d \left(\frac{\alpha}{2}\right)^2 + \left[\frac{1}{2} d(d-1) + \frac{1}{4} d \right] \left(\frac{\alpha}{2}\right)^4 + \cdots, \\ &= 1 - d \left(\frac{\alpha}{2}\right)^2 + \frac{1}{4} d(2d-1) \left(\frac{\alpha}{2}\right)^4 + \cdots, \end{aligned} \quad (\text{C.28})$$

Now assume the cumulant expansion of $[J_0(\alpha)]^d$ as

$$\begin{aligned}
[J_0(\alpha)]^d &= \exp \left[c_1 \left(\frac{\alpha}{2} \right)^2 + c_2 \left(\frac{\alpha}{2} \right)^4 + \dots \right], \\
&= \sum_{n=0}^{\infty} \frac{1}{n!} \left[c_1 \left(\frac{\alpha}{2} \right)^2 + c_2 \left(\frac{\alpha}{2} \right)^4 + \dots \right]^n, \\
&= 1 + \left[c_1 \left(\frac{\alpha}{2} \right)^2 + c_2 \left(\frac{\alpha}{2} \right)^4 + \dots \right] + \frac{1}{2} \left[c_1 \left(\frac{\alpha}{2} \right)^2 + c_2 \left(\frac{\alpha}{2} \right)^4 + \dots \right]^2, \\
&= 1 + c_1 \left(\frac{\alpha}{2} \right)^2 + \frac{1}{2} (2c_2 + c_1^2) \left(\frac{\alpha}{2} \right)^4 + \dots.
\end{aligned} \tag{C.29}$$

Compare the above equation with Eq. (C.28), we obtain

$$\begin{cases} c_1 = -d. \\ \frac{1}{2}(2c_2 + c_1^2) = \frac{1}{4}d(2d - 1). \\ \dots \end{cases}$$

i.e.,

$$\begin{aligned}
c_1 &= -d. \\
c_2 &= \frac{1}{4}d(2d - 1) - \frac{1}{2}c_1^2 = -\frac{1}{4}d.
\end{aligned}$$

Therefore,

$$\begin{aligned}
[J_0(\alpha)]^d &= \exp \left[-d \left(\frac{\alpha}{2} \right)^2 - \frac{1}{4} \left(\frac{\alpha}{2} \right)^4 + \dots \right], \\
&= \exp \left[-d \left(\frac{t^2 s^2}{2d} \right) - \frac{1}{4} \left(\frac{t^4 s^4}{4d^2} \right) + \dots \right].
\end{aligned} \tag{C.30}$$

i.e.,

$$\begin{aligned}
[J_0(\alpha)]^d &= \exp \left[-d \left(\frac{t^2 s^2}{2d} \right) - \frac{1}{4} \left(\frac{t^4 s^4}{4d^2} \right) + \dots \right], \\
&\rightarrow e^{-\frac{t^2}{2} s^2} \quad (d \rightarrow \infty).
\end{aligned} \tag{C.31}$$

Thus, Eq. (C.26) becomes,

$$\Phi_d(s) = e^{is\epsilon_0 - \frac{t^2}{2} s^2}. \tag{C.32}$$

This is the characteristic function for the Gaussian DOS.

$$\rho(\epsilon) = \frac{1}{\sqrt{2\pi}|t|} e^{-\frac{(\epsilon - \epsilon_0)^2}{2t^2}}. \tag{C.33}$$

Thus we obtain the DOS on the hyper-cubic lattice in infinite dimensions. We used this type of lattice to perform the numerical calculation in Chapter 3, 4, and 5.

Appendix D

Appendix: Fermi liquid theory

In this appendix we derived the formula of the quasiparticle weight Z on the basis of the Fermi liquid theory, which is used in Sect. 3.5.2 and 5.3. The concept of the Fermi liquid was developed by *Landau* and has been extended by *Abrikosov*, *Khalatnikov*, *Nozieres*, *Pines*, *Silin* and others [35, 36, 37, 38]. It explains why the low temperature properties of metals resemble so much those of a free electron system, i.e., with neglect electron-electron repulsions. It describes the electronic parameters like the effective mass or density of states. A crucial part of that concept is the notion of quasiparticles and quasiholes. In this Appendix we will explain the discontinuity of the momentum distribution at the Fermi surface in connection to the quasiparticle weight.

Let us suppose that we start from a system of non-interacting electrons and that the interaction is slowly turned on. The basic assumption of the Fermi liquid theory is that the classification of the energy levels remains unchanged. This implies that the energy levels must not cross as the interaction sets in. The distribution function $n_{\mathbf{k}\sigma}$ helps to classify the excitation energies of non-interacting electron system. If we know the $n_{\mathbf{k}\sigma}$, we can easily calculate the energy of the system. In order to leave the classification of the energy levels unchanged when the interaction is turned on, the energy of the interaction system must again be a function of the distribution function $n_{\mathbf{k}\sigma}$. Whereas before $n_{\mathbf{k}\sigma}$ described the distribution of non-interacting electrons, it now describes the distribution of the excitations which, following *Landau*, are called quasiparticle.

The energy variation δE due to the change of the configuration is assumed to be expressed as

$$\delta E = \sum_{\mathbf{k}\sigma} E_{\mathbf{k}\sigma} \delta n_{\mathbf{k}\sigma} + \frac{1}{2} \sum_{\mathbf{k}\sigma \mathbf{k}'\sigma'} f(\mathbf{k}\sigma, \mathbf{k}'\sigma') \delta n_{\mathbf{k}\sigma} \delta n_{\mathbf{k}'\sigma'} + \dots \quad (\text{D.1})$$

Here $E_{\mathbf{k}\sigma}$ serves as a definition of the quasiparticle energy and $\delta n_{\mathbf{k}\sigma}$ is the infinitesimal amount of $n_{\mathbf{k}\sigma}$. The function $f(\mathbf{k}\sigma, \mathbf{k}'\sigma')$, introduced by Landau, characterizes the electron-electron interactions.

Since the number of microscopic states do not change one may assume the following form of the entropy S for the interacting system under given configuration $\{n_{\mathbf{k}\sigma}\}$.

$$S = - \sum_{\mathbf{k}\sigma} [n_{\mathbf{k}\sigma} \ln n_{\mathbf{k}\sigma} + (1 - n_{\mathbf{k}\sigma}) \ln(1 - n_{\mathbf{k}\sigma})] . \quad (\text{D.2})$$

In the equilibrium state, the distribution $\{n_{\mathbf{k}\sigma}\}$ which minimizes the number of microscopic states W under given energy E and electron number N will be realized.

$$S = \ln W_{\max} \quad \text{when } E \text{ and } N = \text{constant},$$

i.e.,

$$\delta [S - \beta E - \alpha N] = 0 . \quad (\text{D.3})$$

Here

$$\delta S = - \sum_{\mathbf{k}\sigma} [\ln n_{\mathbf{k}\sigma} - \ln(1 - n_{\mathbf{k}\sigma})] \delta n_{\mathbf{k}\sigma} , \quad (\text{D.4})$$

$$\delta E = \sum_{\mathbf{k}\sigma} E_{\mathbf{k}\sigma} \delta n_{\mathbf{k}\sigma} , \quad (\text{D.5})$$

$$\delta N = \sum_{\mathbf{k}\sigma} \delta n_{\mathbf{k}\sigma} . \quad (\text{D.6})$$

Thus

$$- \sum_{\mathbf{k}\sigma} \left[\ln \frac{n_{\mathbf{k}\sigma}}{1 - n_{\mathbf{k}\sigma}} + \beta E_{\mathbf{k}\sigma} + \alpha \right] \delta n_{\mathbf{k}\sigma} = 0 \quad (\text{D.7})$$

Note that the noninteracting particles obey Fermi-Dirac statistics, the quasiparticles do so too, and consequently, the occupation probability $n_{\mathbf{k}\sigma}$ of a quasiparticle state is given by

$$n_{\mathbf{k}\sigma} = \frac{1}{e^{\beta(E_{\mathbf{k}\sigma} - \mu)} + 1} . \quad (\text{D.8})$$

Here $\mu = -\beta^{-1}\alpha$ denotes the chemical potential. The meaning of β is given as follows

$$\begin{aligned} \delta S &= - \sum_{\mathbf{k}\sigma} [\ln n_{\mathbf{k}\sigma} - \ln(1 - n_{\mathbf{k}\sigma})] \delta n_{\mathbf{k}\sigma} \\ &= \sum_{\mathbf{k}\sigma} \beta(E_{\mathbf{k}\sigma} - \mu) \delta n_{\mathbf{k}\sigma} \\ &= \beta \delta E . \end{aligned} \quad (\text{D.9})$$

Therefore

$$\frac{\delta S}{\delta E} = \beta = \frac{1}{T} . \quad (\text{D.10})$$

This means that β is the inverse temperature.

The quasiparticle energy $E_{\mathbf{k}\sigma}$ can be regarded as a renormalization of the non-interacting energy $\epsilon_{\mathbf{k}\sigma}$.

$$E_{\mathbf{k}\sigma} = \frac{\epsilon_{\mathbf{k}\sigma}}{\alpha_{\mathbf{k}\sigma}} . \quad (\text{D.11})$$

Here $\alpha_{\mathbf{k}\sigma}$ is a renormalization factor. When we adopt the free electron model, the energy $\epsilon_{\mathbf{k}\sigma}$ is written as

$$\epsilon_{\mathbf{k}\sigma} = \frac{\hbar^2 \mathbf{k}^2}{2m} . \quad (\text{D.12})$$

Using the same formula for the quasiparticle energy $E_{\mathbf{k}\sigma}$, we may write it as

$$E_{\mathbf{k}\sigma} = \frac{\hbar^2 \mathbf{k}^2}{2m_{\mathbf{k}}^*} . \quad (\text{D.13})$$

Here we introduced an effective mass $m_{\mathbf{k}}^*$. From Eqs. (D.11), (D.12), and (D.13), we obtain

$$\alpha_{\mathbf{k}\sigma} = \frac{m_{\mathbf{k}}^*}{m} . \quad (\text{D.14})$$

Thus the renormalization factor $\alpha_{k\sigma}$ defined by (D.11) is called the mass enhancement factor.

We can recognize that the mass enhancement factor enhances the low-temperature specific heat by a factor of α . According to the statistical mechanics, the low-temperature specific heat of Fermi liquid is written as

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{V,N} = \frac{\partial}{\partial T} \left(\sum_{k\sigma} E_{k\sigma} n_{k\sigma} \right) - \sum_{k\sigma} \frac{\partial E_{k\sigma}}{\partial T} n_{k\sigma} . \quad (\text{D.15})$$

Neglecting the temperature dependence of $E_{k\sigma}$ at low temperatures, we have an expression

$$\begin{aligned} \sum_{k\sigma} E_{k\sigma} n_{k\sigma} &= \sum_{k\sigma} \int d\omega \delta(\omega - E_{k\sigma}) E_{k\sigma} f(E_{k\sigma}) \\ &= \sum_{k\sigma} \int d\omega \delta(\omega - E_{k\sigma}) \omega f(\omega) \\ &= \int d\omega \rho(\omega) \omega f(\omega) . \end{aligned} \quad (\text{D.16})$$

Here $\rho(\omega)$ is called the quasiparticle energy density of states.

$$\rho(\omega) \equiv \sum_{k\sigma} \delta(\omega - E_{k\sigma}) . \quad (\text{D.17})$$

Therefore

$$C_V = \frac{\partial}{\partial T} \int d\omega \rho(\omega) \omega f(\omega) . \quad (\text{D.18})$$

Making use of the low-temperature expansion formula

$$\int g(\omega) f(\omega) d\omega = \int^\mu g(\omega) d\omega + \frac{\pi^2}{6} T^2 g'(\mu) + \dots . \quad (\text{D.19})$$

The one electron energy is expressed as follows.

$$\int \omega \rho(\omega) f(\omega) d\omega = \int^\mu \omega \rho(\omega) d\omega + (\mu - \epsilon_F) \epsilon_F \rho(\epsilon_F) + \frac{\pi^2}{6} T^2 [\rho(\mu) + \mu \rho'(\mu)] + \dots . \quad (\text{D.20})$$

The temperature change $\mu - \epsilon_F$ is obtained as follows:

$$\begin{aligned} N &= \sum_{k\sigma} n_{k\sigma} = \int \rho(\omega) f(\omega) d\omega \\ &= \int^{\epsilon_F} \rho(\omega) d\omega + (\mu - \epsilon_F) \rho(\epsilon_F) + \frac{\pi^2}{6} T^2 \rho'(\mu) + \dots , \end{aligned} \quad (\text{D.21})$$

i.e.,

$$(\mu - \epsilon_F) \rho(\epsilon_F) = -\frac{\pi^2}{6} T^2 \rho'(\mu) + \dots . \quad (\text{D.22})$$

Thus

$$\int \omega \rho(\omega) f(\omega) d\omega = \int^{\epsilon_F} \rho(\omega) d\omega + \frac{\pi^2}{6} T^2 [\rho(\mu) + (\mu - \epsilon_F) \rho'(\mu)] \dots . \quad (\text{D.23})$$

Therefore the expression of the specific heat of the Fermi liquid (D.18) in the lowest order at constant volume, is written as

$$C_V = \frac{1}{3}\pi^2\rho(\epsilon_F)T, \quad (\text{D.24})$$

$$\rho(\epsilon_F) = \sum_{\mathbf{k}\sigma} \delta(\epsilon_F - E_{\mathbf{k}\sigma}). \quad (\text{D.25})$$

When

$$E_{\mathbf{k}\sigma} \approx \frac{\epsilon_{\mathbf{k}\sigma}}{\alpha}, \quad (\text{D.26})$$

we have

$$\epsilon_F = \frac{\epsilon_F^0}{\alpha}, \quad (\text{D.27})$$

and

$$\begin{aligned} \rho(\epsilon_F) &= \sum_{\mathbf{k}\sigma} \delta\left(\frac{\epsilon_F^0 - \epsilon_{\mathbf{k}\sigma}}{\alpha}\right) \\ &= \sum_{\mathbf{k}\sigma} \alpha \delta(\epsilon_F^0 - \epsilon_{\mathbf{k}\sigma}) \\ &= \alpha \rho^{(0)}(\epsilon_F^0). \end{aligned} \quad (\text{D.28})$$

Here

$$\rho^{(0)}(\epsilon_F^0) = \sum_{\mathbf{k}\sigma} \delta(\epsilon_F^0 - \epsilon_{\mathbf{k}\sigma}). \quad (\text{D.29})$$

Thus

$$C_V = \alpha C_V^{(0)}, \quad (\text{D.30})$$

$$C_V^{(0)} = \frac{1}{3}\pi^2 \rho^{(0)}(\epsilon_F^0) T. \quad (\text{D.31})$$

Therefore the mass enhancement factor α enhances the low temperatures specific heat of the Fermi liquid by $\alpha = m^*/m$.

We now look at the microscopic theory of the Landau Fermi liquid. The Green function on the complex plane is obtained by the analytic continuation of the temperature Green function.

$$G_{\mathbf{k}\sigma}(z) = \int \frac{\rho_{\mathbf{k}\sigma}(\epsilon)}{z - \epsilon} d\epsilon = \frac{1}{z - \epsilon_{\mathbf{k}\sigma} - \Sigma_{\mathbf{k}\sigma}(z)}. \quad (\text{D.32})$$

Here $z = \omega + i\delta$, δ is the infinitesimal positive number. The function $\Sigma_{\mathbf{k}\sigma}(z)$ is called the self-energy. The self-energy $\Sigma_{\mathbf{k}\sigma}(z)$ of a Fermi liquid has the general form

$$\Sigma_{\mathbf{k}\sigma}(z) = \Sigma_{\mathbf{k}\sigma}(0) + \left(\frac{\partial \Sigma_{\mathbf{k}\sigma}}{\partial z}\right)_{\omega=0} \omega + \dots. \quad (\text{D.33})$$

Let us linearize the self-energy around the Fermi level

$$\begin{aligned}
G_{\mathbf{k}\sigma}(z) &= \frac{1}{z - \epsilon_{\mathbf{k}\sigma} - \Sigma_{\mathbf{k}\sigma}(0) - (\partial\Sigma_{\mathbf{k}\sigma}(0)/\partial z)z + \dots} \\
&= \frac{1}{\alpha'_{\mathbf{k}\sigma}z - \epsilon_{\mathbf{k}\sigma} - \Sigma_{\mathbf{k}\sigma}(0)} + \dots \\
&= \frac{1}{(\text{Re}\alpha'_{\mathbf{k}\sigma})z - \epsilon_{\mathbf{k}\sigma} - \text{Re}\Sigma_{\mathbf{k}\sigma}(0) + i(z\text{Im}\alpha'_{\mathbf{k}\sigma} - \text{Im}\Sigma_{\mathbf{k}\sigma}(0))} \\
&= \frac{1/\text{Re}\alpha'_{\mathbf{k}\sigma}}{z - \frac{\epsilon_{\mathbf{k}\sigma} + \text{Re}\Sigma_{\mathbf{k}\sigma}(0)}{\text{Re}\alpha'_{\mathbf{k}\sigma}} + i\frac{z\text{Im}\alpha'_{\mathbf{k}\sigma} - \text{Im}\Sigma_{\mathbf{k}\sigma}(0)}{\text{Re}\alpha'_{\mathbf{k}\sigma}}}.
\end{aligned} \tag{D.34}$$

Here $\alpha'_{\mathbf{k}\sigma} = 1 - \partial\Sigma_{\mathbf{k}\sigma}(0)/\partial\omega$. Thus

$$G_{\mathbf{k}\sigma}(z) = \frac{\alpha_{\mathbf{k}\sigma}^{-1}}{z - E_{\mathbf{k}\sigma} + i\Gamma_{\mathbf{k}\sigma}}. \tag{D.35}$$

Here we defined the mass enhancement factor $\alpha_{\mathbf{k}\sigma}$ by $\text{Re}\alpha'_{\mathbf{k}\sigma}$:

$$\alpha_{\mathbf{k}\sigma} = 1 - \frac{\partial\text{Re}\Sigma_{\mathbf{k}\sigma}(0)}{\partial\omega} = \frac{m_{\mathbf{k}}^*}{m}. \tag{D.36}$$

In case of the phenomenological Fermi liquid theory, it is defined by Eq. D.14.

The quasiparticle energy $E_{\mathbf{k}\sigma}$ is defined by

$$E_{\mathbf{k}\sigma} = \frac{\tilde{\epsilon}_{\mathbf{k}\sigma}}{\alpha_{\mathbf{k}\sigma}} = \frac{\tilde{\epsilon}_{\mathbf{k}\sigma}}{1 - \frac{\partial\text{Re}\Sigma_{\mathbf{k}\sigma}(0)}{\partial\omega}}. \tag{D.37}$$

Here we defined the energy $\tilde{\epsilon}_{\mathbf{k}\sigma}$ by $\tilde{\epsilon}_{\mathbf{k}\sigma} = \epsilon_{\mathbf{k}\sigma} + \text{Re}\Sigma_{\mathbf{k}\sigma}(0)$. The quasiparticle energy of the Fermi liquid from the microscopic point of view (Eq. D.37) is connected to the phenomenological one by Eq. (D.11). The life time $\Gamma_{\mathbf{k}\sigma}$ is defined as

$$\Gamma_{\mathbf{k}\sigma} = \frac{z\text{Im}\alpha'_{\mathbf{k}\sigma} - \text{Im}\Sigma_{\mathbf{k}\sigma}(0)}{\alpha_{\mathbf{k}\sigma}}. \tag{D.38}$$

For the Fermi liquid state

$$\Gamma_{\mathbf{k}\sigma}(0) = -\frac{\text{Im}\Sigma_{\mathbf{k}\sigma}(0)}{\alpha_{\mathbf{k}\sigma}} = 0. \tag{D.39}$$

The quasiparticle weight $Z_{\mathbf{k}\sigma}$ is defined by

$$Z_{\mathbf{k}\sigma} = \alpha_{\mathbf{k}\sigma}^{-1} = \left(1 - \frac{\partial\text{Re}\Sigma_{\mathbf{k}\sigma}(0)}{\partial\omega}\right)^{-1} = \frac{m}{m_{\mathbf{k}}^*}. \tag{D.40}$$

The retarded Green function near the Fermi level ($w \approx 0$) is therefore written in terms of the quasiparticle weight $Z_{\mathbf{k}\sigma}$, the quasiparticle energy $E_{\mathbf{k}\sigma}$, and the life time $\Gamma_{\mathbf{k}\sigma}$ as follows.

$$G_{\mathbf{k}\sigma}(z) = \frac{Z_{\mathbf{k}\sigma}}{z - E_{\mathbf{k}\sigma} + i\Gamma_{\mathbf{k}\sigma}} + \text{incoh.} \tag{D.41}$$

The second term on the right hand side denotes the other incoherent contribution.

The imaginary part of the self-energy may be small near the Fermi level in the Fermi liquid state. Note that the single particle DOS $\rho_{k\sigma}(\omega)$ is connected to the quasi-particle DOS $\rho_{k\sigma}^{QP}(\omega) = \delta(\omega - E_{k\sigma})$ as

$$\begin{aligned}\rho_{k\sigma}(\omega) &= -\frac{1}{\pi} \text{Im} G_{k\sigma}(z) \\ &\approx -\frac{1}{\pi} \text{Im} \frac{Z_{k\sigma}}{z - E_{k\sigma}} = Z_{k\sigma} \delta(\omega - E_{k\sigma})\end{aligned}\quad (\text{D.42})$$

The momentum distribution $\langle n_{k\sigma} \rangle$ is expressed as

$$\begin{aligned}\langle n_{k\sigma} \rangle &= \int d\omega f(\omega) \rho_{k\sigma}(\omega) \\ &= \int d\omega f(\omega) [Z_{k\sigma} \delta(\omega - E_{k\sigma}) + incoh.] \\ &= Z_{k\sigma} \theta(-E_{k\sigma}) + incoh.\end{aligned}\quad (\text{D.43})$$

Thus, the quasiparticle weight $Z_{k\sigma}$ describes the discontinuity in the momentum distribution function of electrons on the Fermi surface $k = k_F$.

$$\delta \langle n_{k\sigma} \rangle |_{k=k_F} = Z_{k\sigma} = \frac{m}{m_k^*} \quad (\text{D.44})$$

We show this schematically in Fig. D.1. We have used this formula of the jump of the momentum distribution at the Fermi level to measure the quasiparticle weight in subsection 3.5.2.

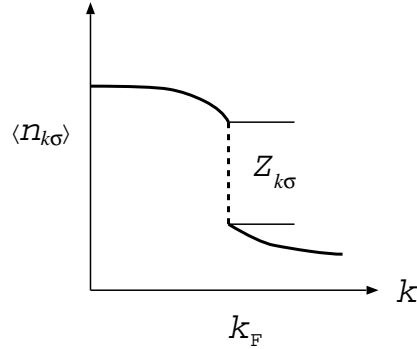


Figure D.1: Discontinuity $Z_{k\sigma}$ in the momentum distribution $\langle n_{k\sigma} \rangle$

Appendix E

Appendix: Coherent potential approximation

In order to understand the properties of the alloys one must know their electronic structure from a microscopic point of view. Electronic structure calculations in disorder alloys, however, is not easy. The difficulty is that there is no translational symmetry in the system so that we cannot apply the Bloch theory. We present in this appendix the coherent potential approximation (CPA) [41] to calculate the electronic structure of alloys in the single site approximation, which is used in chapter 4.

Let us consider a substitutional binary alloy with A and B atom which are randomly distributed. The one electron Hamiltonian is given by

$$(H_\sigma)_{ij} = \epsilon_{\alpha\sigma}\delta_{ij} + t_{ij}(1 - \delta_{ij}) . \quad (\text{E.1})$$

Here t_{ij} is the transfer integral between sites i and j . c_α denotes the concentration of atom α .

$$c_\alpha = \begin{cases} c_A = \langle n_{-\sigma} \rangle & (\alpha = A) \\ c_B = 1 - \langle n_{-\sigma} \rangle & (\alpha = B) . \end{cases} \quad (\text{E.2})$$

$n_{-\sigma}$ denotes the average electron number per site. The atomic level $\epsilon_{\alpha\sigma}$ is defined by

$$\epsilon_{\alpha\sigma} = \begin{cases} \epsilon_A = \epsilon_0 + U - \mu & (\alpha = A) \\ \epsilon_B = \epsilon_0 - \mu & (\alpha = B) . \end{cases} \quad (\text{E.3})$$

ϵ_0 is the atomic energy, U is the on-site Coulomb interaction energy parameter, and μ is the chemical potential. The Green function $G_{ij}(z)$ for the Hamiltonian is defined by

$$G_{ij}(z) = [(z - H_\sigma)^{-1}]_{ij} . \quad (\text{E.4})$$

In the binary alloys we neglect the disorder of transfer integrals called the off-diagonal disorder. Because the atomic levels $\epsilon_{\alpha\sigma}$ are random variables, the Bloch theory is not applicable for the calculation of the Green function. We make use of the coherent potential approximation (CPA) to obtain the Green function with use of the locator expansion [40]. Introducing the locator matrix L by means of

$$(L)_{ij} = L_i\delta_{ij} = (z - \epsilon_{\alpha\sigma})^{-1}\delta_{ij} , \quad (\text{E.5})$$

we express the Green function matrix as

$$G = (L^{-1} - t)^{-1} = (1 - Lt)^{-1}L \quad (\text{E.6})$$

where t denotes the transfer integral matrix t_{ij} . Thus,

$$G = L + LtG \quad (\text{E.7})$$

Expanding the Green function with respect to t , we obtain

$$G_{ii}(Z) = L_i + \sum_{j \neq i} L_i t_{ij} L_j t_{ji} L_i + \sum_{j \neq i} \sum_{k \neq j, i} L_i t_{ij} L_j t_{jk} L_k t_{ki} L_i + \dots \quad (\text{E.8})$$

Here we have omitted the spin suffix for simplicity. The r.h.s. of (E.8) consists of the contribution from all the paths which start from site i and end at the same site i . They are expressed as follows by using the sum of all paths S_i which start from site i and end at site i without returning to site i on the way.

$$G_{ii}(Z) = L_i + L_i S_i L_i + L_i S_i L_i S_i L_i + \dots = (L_i^{-1} - S_i)^{-1}. \quad (\text{E.9})$$

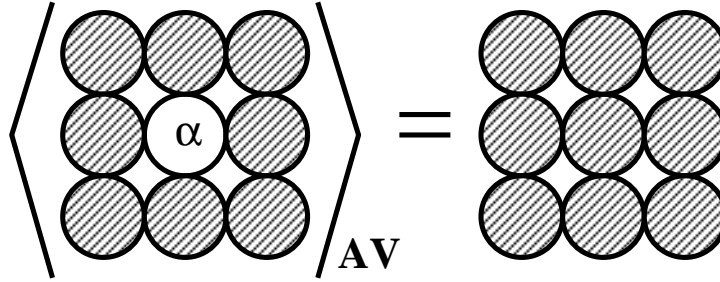


Figure E.1: Schematic representation of the coherent potential approximation. The central site is occupied by an atom α ($=$ A or B). The hatched sites are occupied by a coherent potential $\Sigma_\sigma(z)$. $\langle \rangle_{AV}$ at the l.h.s. means a configurational average on the central site.

In the above expression, all the information outside the central atom i is in the self-energy S_i . To obtain the Green function $G_{ii}(z)$ in a single-site approximation, we approximate the random potentials on the surrounding sites with an energy-dependent coherent potential $\Sigma_\sigma(z)$ (see the l. h. s. of Fig. E.1). We have then an impurity Green function for atom α on site i from (E.9) as follows.

$$G_{\alpha\sigma}(z) = (L_{\alpha\sigma}^{-1} - \mathcal{S}_\sigma)^{-1} \quad (\text{E.10})$$

Here $L_{\alpha\sigma}^{-1} = z - \epsilon_{\alpha\sigma}$ is the inverse locator on the central site with a type of atom α . \mathcal{S}_σ is the self energy in which all the atomic levels have been replaced by the coherent potential $\Sigma_\sigma(z)$. Note that we have omitted the site indices for simplicity and have recovered the spin suffix.

The self-energy \mathcal{S}_σ is obtained from the coherent Green function $F_\sigma(z)$ in which all the sites are occupied by the coherent potential (see the r. h. s. of Fig. E.1)

$$F_\sigma(z) = (\mathcal{L}_\sigma^{-1} - \mathcal{S}_\sigma)^{-1}. \quad (\text{E.11})$$

Here $\mathcal{L}_\sigma^{-1}(z) = z - \Sigma_\sigma(z)$. Substituting \mathcal{S}_σ obtained from (E.11) into (E.10), we obtain the impurity Green function as follows.

$$G_{\alpha\sigma}(z) = (L_{\alpha\sigma}^{-1} - \mathcal{L}_\sigma^{-1}(z) + F_\sigma^{-1}(z))^{-1}. \quad (\text{E.12})$$

Since the coherent Green function $F_\sigma(z)$ is defined by $F_\sigma(z) = [(z - \Sigma_\sigma(z) - t)^{-1}]_{ii}$, it is obtained from the following formula.

$$F_\sigma(z) = \int \frac{\rho(\epsilon)d\epsilon}{z - \Sigma_\sigma(z) - \epsilon} . \quad (\text{E.13})$$

Here $\rho(\epsilon)$ is the density of states (DOS) for the energy eigen values of transfer matrix t_{ij} . We use the above expression in Sect. 4.1 (Eq. 4.11).

The coherent potential $\Sigma_\sigma(z)$ is obtained from the condition that the configurational average of the impurity Green function (E.12) should be identical with the coherent Green function (see Fig. E.1).

$$\overline{G_{00\sigma}(z)} = F_\sigma(z) . \quad (\text{E.14})$$

Here

$$\overline{G_{00\sigma}(z)} = \sum_{\alpha} c_{\alpha} G_{\alpha\sigma}(z) . \quad (\text{E.15})$$

The equation (E.14) is known as the CPA equation which is essentially the same as Eq. (4.12) in Sect. 4.1.

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