電子相関の強い系に対する第一原理運動量依存局所変分埋論：鉄の電子状態への応用

Doctoral Thesis of Philosophy

First-Principles Theory of Momentum Dependent Local Ansatz to Correlated Electron Systems — Application to Iron —

September 2016

By

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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.

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Abstract

We have developed the first-principles momentum-dependent local ansatz (MLA) wavefunction method on the basis of the tight-binding LDA+U Hamiltonian in order to describe quantitatively electron correlations in the real system. The MLA wavefunction expands the Hilbert space for correlated electrons by applying the intra-orbital correlators, the inter-orbital charge-charge correlators, and the inter-orbital spin-spin correlators with momentum-dependent variational parameters to the Hartree-Fock uncorrelated state, so that it reduces to the correct Rayleigh-Schrödinger perturbation theory in the weak correlation limit and can describe quantitatively the ground state as well as related low-energy excitations in solids.

We first performed the lowest-order numerical calculations for paramagnetic bcc Fe in order to clarify the basic behavior of the theory. We found that the MLA yields a reasonable correlation energy gain, and the inter-orbital correlations as well as the intra-orbital correlations plays an important role in the energy gain. The charge fluctuation is suppressed rapidly with increasing the Coulomb interaction strength. Calculated charge fluctuation for Fe is found to be comparable to the result of the local ansatz (LA) in the d-band model. The amplitude of local moment is smaller than the d-band LA value. We also found the strong momentum dependence of the momentum distribution function (MDF), and obtained the mass enhancements m^*/m = 1.4 for Fe from the jump of the MDF at the Fermi level.

We next performed the self-consistent calculations using the new ansatz for the variational parameters which interpolates between the weak and the atomic limit. We obtained the correlation energy -0.076 Ry for bcc Fe, the charge fluctuations for d electrons $\langle(\delta n_d)^2\rangle$= 1.51, and the amplitude of local moment $\langle \boldsymbol{S}^2 \rangle$ = 2.61. The latter is in good agreement with the experimental value 2.58. We find that the inter-orbital charge-charge correlations between d electrons make a significant contribution to the correlation energy and charge fluctuations, while the intra-orbital and inter-orbital spin-spin correlations make a dominant contribution to the amplitude of local moment.

We also obtained the MDF along high-symmetry lines for Fe. We found that the MDF for d electrons with e_g symmetry show a large deviation from the Fermi-Dirac function. The analyses of projected MDF indicate that the s and p electrons behave as independent electrons, while d electrons behave as correlated electrons. The average mass enhancement factor m^*/m is found to be governed by the intra-orbital and inter-orbital spin-spin correlations. Calculated m^*/m = 1.65 is shown to be consistent with the experimental data and agrees well with the recent results of theoretical calculations.

DEDICATED
TO
MY PARENTS AND MY WIFE

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Contents

Chapter 1

Introduction

The density functional theory (DFT) has been well developed in the past half century towards quantitative description of the properties of solids, and acts nowadays as a powerful tool for explaining the ground-state properties of materials and their electronic structure. The DFT is based on the Hohenberg-Kohn theorem which states that the ground-state is given by the functional of electron density [1] and the Kohn-Sham method in which the charge and spin densities are obtained from an independent electron system [2]. All the many-body effects are included in the exchange-correlation potential as a functional of charge and spin densities in the DFT. The local density approximation (LDA) or generalized gradient approximation (GGA) to the DFT potential allows us to implement the first-principles band calculations for various systems.

The LDA and GGA explain many aspects in solids such as the cohesive properties, the Fermi surface in metals, and optical properties of metallic systems [3, 4]. The DFT also explains quantitatively the ground-state magnetism of 3d transition metals and alloys. The first-principles band calculations with use of the LDA, for example, yield the magnetization per atom 2.15 $\mu_{\rm B}$ for Fe and 0.59 $\mu_{\rm B}$ for Ni [5], which are in good agreement with the experimental values 2.22 $\mu_{\rm B}$ and 0.62 $\mu_{\rm B}$ [6, 7], respectively.

On the other hand, the DFT theory is not sufficient to describe properly the properties of more correlated electron systems. The theory cannot describe the magnetic moment and the metal-insulator phase transition above the Néel temperature in cuprates [8], and much overestimates the ground-states magnetic moment in Fe-pnictides [9, 10], while it underestimates the moment in cuprates [8]. Furthermore it is not applicable to the finite-temperature magnetism such as the Curie temperature and the Curie-Weiss law in susceptibility of transition metals. The Stoner theory based on the DFT band calculations yields the Curie temperatures ($T_{\rm C}$), 6000 K for Fe and 3000 K for Ni [11, 12], which are 6 or 5 times as large as the observed values, 1040 K for Fe and 630 K for Ni [13, 14].

The DFT also fails in explaining the ϵ-Fe [15], cuprates [16], heavy-fermion system [16], the reduction of the cohesive energy in 3d transition metals [17], the formation of a satellite peak in the X-ray photoemission spectroscopy (XPS) data of Ni [18,19], and the angle resolved photoemission spectroscopy (ARPES) data in Fe-pnictides [20].

The second point is that the DFT is based on the Hohenberg-Kohn theorem. Thus the physical quantities expressed by the two-particle operators as well as excitation spectra cannot be calculated. The DFT is based on the Kohn-Sham scheme. Thus the momentum distribution function as well as related mass enhancement factor cannot be described by the DFT when the electron correlations become significant. Moreover, the LDA and GGA potentials in the DFT band theory do not correctly describe the orbital correlations as well as the Hund-rule correlations in the paramagnetic

state and thus the ground-state energy is overestimated in general in the paramagnetic state. These properties cannot be understood without taking into account directly the many-body effects, $i.e.$, electron correlation effects.

In order to describe the many-body phenomena which cannot be explained by the band theory, various theories have been developed so far. These theories are based on the variational method [16, 21, 22], the Green function techniques [23], as well as the numerical techniques such as the exact diagonalization method and the quantum Monte-Carlo (QMC) technique [24]. The dynamical mean field theory (DMFT) combined with the LDA+U Hamiltonian [25–27], is such an approach based on the Green function technique and the effective medium method. The DMFT is equivalent to the first-principles dynamical coherent potential approximation (DCPA) developed by Kakehashi [30, 31]. In these approaches, we can replace the surrounding interactions with an effective medium and solve the impurity problem using various methods. The theories have been applied to many systems with strong electron correlations [31].

The variational approach is the simplest and oldest methods to treat electron correlations at the ground state. The trial wavefunction is chosen to include the minimum basis set with variational parameters. One can determine the variational parameters on the basis of variational principles.

The Gutzwiller wavefunction (GW) [32–34] is one of the popular ansatz, and has been applied to a number of correlated electron systems. The method has been extended to the first-principles version on the basis of the LDA+U Hamiltonian [35, 36]. The first-principles GW theory has been applied to many systems such as Ni [37] and Fe pnictides [38, 39], and clarified the physics of electron correlations in the magnetism, the heavyfermion behavior, and the metal-insulator transition.

The local ansatz (LA) wavefunction [16, 21, 22] is an approach from the weakly correlated limit. It makes use of the Hilbert space expanded by the two-particle operators which appear in the residual Coulomb interactions. The Baeriswyl wavefunction expands the Hilbert space applying the hopping operators onto the atomic wavefunctions, aiming at an accurate description of electron correlations in the strong interaction regime. There are various trial wavefunctions which describe the nonlocal electron correlations [40–43]. These wavefunctions are usually treated by means of numerical techniques such as the variational Monte Carlo method [44, 45].

The wavefunctions mentioned above, however, do not reduce to the second-order perturbation theory in the weak Coulomb interaction limit. Therefore it does not describe quantitatively the properties of correlated electron system. This is serious for quantitative description of effective mass enhancement factor associated with the low energy excitations in the vicinity of the Fermi surface, because it is obtained by a renormalization of the counterpart in the weak Coulomb interaction limit according to the Fermi liquid theory.

In order to overcome the difficulty, we recently proposed the momentum-dependent local ansatz (MLA) wavefunction which goes beyond the GW [46–50]. The MLA is an extension of the LA in which the residual Coulomb interaction operators are used to expand the Hilbert space for describing electron correlations [51–53]. In the MLA, we expand the Hilbert space by means of the two-particle excited states with momentum-dependent variational parameters in the momentum space, and project these states onto the local orbitals again. In this way, we can obtain more flexible correlated electron states. The theory overcomes the Gutzwiller wavefunction method and describes quantitatively the physical quantities.

In this thesis, we extend the MLA to the first-principles version on the basis of the tight-binding (TB) LDA+U Hamiltonian towards the quantitative description of correlated electron system. It should be noted that we have three kinds of Coulomb interactions in the TB LDA+U Hamiltonian: the intra-orbital interactions, the inter-orbital charge-charge interaction, and the inter-orbital

spin-spin interactions. Accordingly, we introduce three kinds of correlators with the momentum-dependent variational parameters: the intra-orbital correlators, the inter-orbital charge-charge correlators, and the inter-orbital spin-spin correlators, respectively, and construct the first-principles MLA wavefunction applying them to the Hartree-Fock wavefunction in order to expand the Hilbert space for describing correlated electrons. We can derive the correlation energy within the single-site approximation (SSA), and obtain the self-consistent equations for the momentum-dependent variational parameters. After determination of the variational parameters, charge fluctuations, amplitude of magnetic moment, momentum distribution function (MDF), as well as the mass enhancement factor (MEF) are obtained immediately from the wavefunctions.

We emphasize that the first-principles MLA reduces to the Rayleigh-Schrödinger perturbation theory exactly as it should be, and the theory quantitatively describes the ground-state properties of correlated electron system, as will be demonstrated in the numerical calculations for the paramagnetic Fe. In particular, the present theory accurately describes the momentum-dependent correlated states associated with two-particle excitations. We will clarify that the first-principles MLA quantitatively describes the momentum-dependence of the MDF as well as the momentum-dependent MEF.

Another new feature of the first-principles MLA is that there are three kinds of correlations in the wavefunctions: the intra-orbital correlations, the inter-orbital charge-charge correlations, and the inter-orbital spin-spin correlations (, $i.e.$, the Hund-rule correlations). We will clarify in this thesis the role of these correlations in various physical properties and the interplay of s, p, and d electrons in the MDF and the MEF.

As we have mentioned, alternative approach to describe electron correlations quantitatively is the first-principles LDA+DMFT (DCPA) theory [26–31]. The LDA+DMFT is a powerful method to strongly correlated electrons. The accuracy of the DMFT however strongly depends on the solver of the impurity problem for correlated electrons [54–56]. The Quantum Monte-Carlo method (QMC) can describe accurately the finite-temperature properties of the system. But its efficiency is strongly reduced at low temperatures, and the QMC even causes the negative sign problem which prevents us from systematic investigations over wide range of interaction parameters. The exact diagonalization method (ED) is useful to study exactly the physical properties at zero temperature. But it cannot describe the low energy properties associated with the Fermi surface. The numerical renormalization group theory (NRG) describes accurately the low energy excitations, but it does not accurately describe the excitations in high-energy region as well as the energy integrated quantities. Furthermore it is not applicable to the realistic systems because of the numerical difficulty.

The MLA on the other hand describes quantitatively the quasi-particle weight associated with the low energy excitations as well as the energy-integrated quantities such as the total energy and momentum distribution function without numerical difficulty. In particular, we will show that the first-principles MLA quantitatively explains the mass enhancement factor of bcc Fe obtained by the ARPES experiment [57] while the LDA+DMFT combined with the three-body theory at zero temperature does not [57]. Furthermore the MLA allows us to calculate any static physical quantity because the wavefunction is known. These facts indicate that the first-principles MLA is competitive to the LDA+DMFT at zero temperature and thus it is a suitable approach to correlated electrons.

In the following chapter we review the recent development of correlated wavefunction methods such as the Gutzwiller wavefunction (GW), the local ansatz wavefunction (LA), the MLA, and the hybrid MLA in the single-band Hubbard model. In particular, we present the formulation

of the MLA, and discuss quantitative aspects of the MLA for the correlation energy, the double occupation number and the MDF with their numerical results.

In Chapter 3 we present the first-principles MLA. We start from the TB LDA+U Hamiltonian, and introduce the first-principles MLA wavefunction for correlated electron system. We obtain the correlation energy in the SSA, and derive the self-consistent equations for the momentum-dependent variational parameters using the variational principle. We derive the expressions of the electron number, the charge fluctuations, the amplitude of local moment, and the MDF using the Feynman-Hellmann theorem.

In Chapter 4 we obtain the variational parameters in the weak Coulomb interaction regime solving the self-consistent equations. We express the physical quantities in the lowest-order interaction limit. We will apply the theory to bcc Fe as a numerical example. The bcc Fe is one of the most extensively investigated materials in both theory and experiment. Nevertheless, quantitative aspects of various physical quantities in bcc Fe and role of electron correlations in those quantities have not yet been clarified. We first calculate the Hartree-Fock energy bands of bcc Fe for the TB LDA+U Hamiltonian to perform the correlation calculations. Next we calculate various quantities for correlated electrons using the Laplace transform of the Hartree-Fock local density of states. We present the numerical results for the correlation energy, the charge fluctuations, the amplitude of local moment, and the MDF. In the calculation of the MDF we assume the constant amplitudes of eigen vectors for d electrons at each $\boldsymbol{k}$ point, and discuss the momentum-dependence of the MDF. We also calculate the MEF from the jump of the MDF at the Fermi level. We find that the calculated MEF is comparable to the experimental value.

In Chapter 5 we propose the new ansatz of variational parameters for more correlated electrons, which interpolates between the weak and the atomic limit, and solve the self-consistent equations for the variational parameters numerically. We present the numerical results for Fe, and clarify the role of intra-orbital and inter-orbital correlations on the correlation energy gain, the charge fluctuation, and the formation of magnetic moment. We also calculate the MDF for Fe along high-symmetry lines of the first Brillouin zone, and demonstrate a large deviation of the MDF from the Fermi-Dirac function due to d electrons with e_g symmetry. We will show that calculated MEF are consistent with the experimental data as well as recent result of theoretical calculations. Finally in Chapter 6 we summarize our results, and discuss the future problems.

Chapter 2

Wavefunction Methods

The DFT does not describe quantitatively the ground-state properties in the correlated electron system. In this chapter, we review the wavefunction methods in order to clarify the new features of the momentum-dependent local ansatz (MLA) wavefunctions. We discuss the Gutzwiller wavefunction (GW), the local ansatz wavefunction (LA), the MLA, and the MLA with hybrid wavefunction (MLA-HB) [48, 50]. In particular, we elucidate the quantitative aspects of the MLA on the basis of the numerical results of calculations in infinite dimensions.

2.1 Wavefunction methods

The wavefunction method is based on the variational principles for the wavefunction. It states that the expectation value E of the Hamiltonian H for any trial wavefunction $|\Psi\rangle$ is equal to or larger than the ground states energy E_0.

$$E = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} \geq E_0 \, . \tag{2.1}$$

The variational principle allows us to find an approximate but best wavefunction for a given ansatz, and its energy expectation value gives us the upper limit of the exact ground state energy. In the actual application of Eq. (2.1), it is important that we adopt a size-consistent wavefunction close to the exact one and calculate the energy expectation value as accurate as we can in order to avoid uncertainty.

We consider in this chapter the tight-binding model Hamiltonian with intra-atomic Coulomb interaction called the Hubbard model [60, 61], for simplicity.

$$H = \sum_{i\sigma} \epsilon_0 n_{i\sigma} + \sum_{ij\sigma} t_{ij} a^{\dagger}_{i\sigma} a_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} \, . \tag{2.2}$$

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

The Hamiltonian can be separated into the Hartree-Fock mean field Hamiltonian H_0 and the residual interaction part as follows:

$$H = H_0 + U \sum_{i} O_i \, , \tag{2.3}$$

$$H_0 = \sum_{i\sigma}(\epsilon_0 + U\langle n_{i-\sigma}\rangle_0)\hat{n}_{i\sigma} + \sum_{ij\sigma} t_{ij}a^\dagger_{i\sigma}a_{j\sigma} - U\sum_i \langle n_{i\uparrow}\rangle_0\langle n_{i\downarrow}\rangle_0 \ . \tag{2.4}$$

Here $\langle\sim\rangle_0$ denotes the Hartree-Fock average at the ground state. The operator O_i in the residual interaction is defined by $O_i = \delta n_{i\uparrow}\delta n_{i\downarrow}$ and $\delta n_{i\sigma} = n_{i\sigma} - \langle n_{i\sigma}\rangle_0$.

The Hartree-Fock ground state wavefunction $|\Phi\rangle$ is given by

$$|\Phi\rangle = \Big[\prod_{k\sigma}^{\rm occ} a^\dagger_{k\sigma}\Big]\,|0\rangle \ . \tag{2.5}$$

Here $\prod_{k\sigma}^{\rm occ}$ means taking the products over the momentum k and spin σ of electrons below the Fermi level. $|0\rangle$ denotes the vacuum state. $a^\dagger_{k\sigma}$ is the creation operator for an electron with momentum k and spin σ; $a^\dagger_{k\sigma} = \sum_i a^\dagger_{i\sigma}\langle i|k\rangle$. $\langle i|k\rangle$ (= $\exp\,(-{\rm i}\,\boldsymbol{k}\cdot\boldsymbol{R}_i)/\sqrt{N}$) is an overlap integral between the localized orbital on site i and Bloch state $\boldsymbol{k}$. $\boldsymbol{R}_i$ denotes atomics position of site i, and N is the number of sites.

The energy difference between the ground state for the correlated electrons and the Hartree-Fock one is given by

$$E_c = \langle H\rangle - \langle H\rangle_0 = \frac{\langle\Psi|\tilde{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \ . \tag{2.6}$$

Here $\tilde{H} = H - \langle H\rangle_0$. It is the energy gain due to correlated motion of electrons, and is called the correlation energy.

2.2 Gutzwiller wavefunction

The wave function proposed by Gutzwiller [32–34] reduces the amplitudes of doubly occupied states in the Hartree-Fock ground state. It is given by

$$|\Psi_{\rm G}\rangle = \Big[\prod_i (1-(1-g)n_{i\uparrow}n_{i\downarrow})\Big]\,|\phi\rangle \ . \tag{2.7}$$

The wavefunction describes on-site electron correlations by making use of a projection operator $n_{i\uparrow}n_{i\downarrow}$ on to the Hartree-Fock state. The parameter $1-g$ denotes the amplitudes of doubly occupied states. The variational parameter $g = 1$ corresponds to the Hartree-Fock state, while $g = 0$ corresponds to the atomic state with no doubly occupied state. Varying the variational parameters g from 1 to 0, one can choose the best amplitude of doubly occupied states for correlated electrons on the basis of the variational principle (2.1).

Gutzwiller obtained approximately the ground state energy by making use of a quasichemical method [34]. In the nonmagnetic state at half-filling, we obtain a simple result for the ground state energy per atom in infinite dimensions as [34]

$$\epsilon_{\rm G} = -\frac{1}{8}U_{\rm C}\Big(1-\frac{U}{U_{\rm C}}\Big) \ . \tag{2.8}$$

The ground state energy increases with increasing U and becomes zero at $U = U_{\rm C}$. For $U > U_{\rm C}$, we have a solution $\epsilon_{\rm G}$ with $g = 0$. Therefore the metal-insulator transition occurs at $U = U_{\rm C}$.

Similarly, the double occupation number per atom linearly decreases with increasing U at half-filling as

$$d_{\rm G} = \frac{1}{4}\Big(1-\frac{U}{U_{\rm C}}\Big) \ , \tag{2.9}$$

and $d_{\rm G} = 0$ beyond $U_{\rm C}$. We call the state $d_{\rm G} = 0$ the Brinkman-Rice atomic state. It is therefore realized for $U > U_{\rm C}$, *i.e.*, in the insulating state.

The momentum distribution for the Gutzwiller wavefunction is known to be flat below and above the Fermi level [34], and shows a jump at the Fermi level. We obtain the quasiparticle weight according to the Fermi liquid theory as

$$Z_{\rm G} = \left(1 - \frac{U^2}{U_{\rm C}^2}\right) . \tag{2.10}$$

Beyond $U_{\rm C}$, the jumps disappears and the distribution becomes completely flat.

2.3 Local ansatz wavefunction

The Hartree-Fock Hamiltonian neglects the charge (or spin) fluctuation $\{O_i\} = \{\delta n_{i\uparrow}\delta n_{i\downarrow}\}$ which appear in the residual interactions. An alternative way to take into account electron correlations is therefore to include the Hilbert space expanded by the fluctuation $\{O_i\}$. The wavefunction can describe the weak Coulomb interaction regime. Such a wavefunction is called the local ansatz (LA) [51–53]. It is given by

$$|\Psi_{\rm LA}\rangle = \Big[\prod_i (1 - \eta_{\rm LA} O_i)\Big] \, |\phi\rangle \, . \tag{2.11}$$

Here $\eta_{\rm LA}$ is a variational parameter.

In the single-site approximation, the correlation energy per atom is given as follows [58, 59]:

$$\epsilon_c({\rm LA}) = \frac{-2\eta_{\rm LA}\langle O_i \tilde{H}\rangle_0 + \eta_{\rm LA}^2 \langle O_i \tilde{H} O_i\rangle_0}{1 + \eta_{\rm LA}^2 \langle O_i^2\rangle_0} \, . \tag{2.12}$$

Each element of $\langle O_i \tilde{H}\rangle_0$, $\langle O_i \tilde{H} O_i\rangle_0$, and $\langle O_i^2\rangle_0$ are expressed by the electron number $\langle n_{i\sigma}\rangle_0$ and the Hartree-Fock local density of states $\rho_{i\sigma}(\epsilon)$. Minimizing the energy $\epsilon_c({\rm LA})$ with respect to the variational parameters $\eta_{\rm LA}$, we obtain

$$\eta_{\rm LA} = \frac{-\langle O_i \tilde{H} O_i\rangle_0 + \sqrt{\langle O_i \tilde{H} O_i\rangle_0^2 + 4\langle O_i \tilde{H}\rangle_0^2 \langle O_i^2\rangle_0}}{2\langle O_i \tilde{H}\rangle_0 \langle O_i^2\rangle_0} \, . \tag{2.13}$$

In the nonmagnetic state at half-filling, the double occupation number in the LA has a simple form,

$$\langle n_{i\uparrow} n_{i\downarrow}\rangle_{\rm LA} = \frac{1}{4}\left(1 - \frac{\eta_{\rm LA}/2}{1 + \eta_{\rm LA}^2/16}\right) . \tag{2.14}$$

The momentum distribution function in the LA is expressed as

$$\langle n_{k\sigma}\rangle_{\rm LA} = \frac{1}{2}(1+Z) f(\epsilon_{k\sigma}) + \frac{1}{2}(1-Z)(1 - f(\epsilon_{k\sigma})). \tag{2.15}$$

Here $f(\epsilon_{k\sigma})$ is the Fermi distribution function and Z is the quasipartical weight. Here ϵ_k is the Fourier transform of t_{ij}. The quasipartical weight as the jumps in the momentum distribution on the Fermi surface is obtained analytically for half-filling as follows:

$$Z_{\rm LA} = 1 - \frac{\eta_{\rm LA}^2/4}{1 + \eta_{\rm LA}^2/16} \, . \tag{2.16}$$

The LA is suitable for the description of correlated-electron systems with a weak or intermediate Coulomb interaction strength, while the Gutzwiller wavefunction is more suitable in the strongly correlated region.

2.4 Other wavefunctions methods

There are many other wavefunctions which have been proposed. Both the Gutzwiller and the LA wavefunctions do not explicitly include the inter-site correlation operators. The wavefunction proposed by Jastrow [40] describes the inter-site density density correlations and has the form

$$|\Psi_{\rm J}\rangle = \exp(-\sum_{(i,j)} f_{ij} n_i n_j)|\phi\rangle \ . \tag{2.17}$$

Here $n_i = n_{i\uparrow} + n_{i\downarrow}$ is the density operator on site i. $|\phi\rangle$ represents the ground-state of non-interacting fermions. $f_{ij} = \int d^3x d^3x' |\psi_i(\boldsymbol{r})|^2 |\psi_j(\boldsymbol{r'})|^2 f(\boldsymbol{r}-\boldsymbol{r'})$ is variational parameters depending on sites i and j. $\psi_i(\boldsymbol{r})$ denotes the atomic wavefunction on site i and the function $f(\boldsymbol{r}-\boldsymbol{r'})$ is the varitional function of the displacement $\boldsymbol{r}-\boldsymbol{r'}$. The wavefunction $|\Psi_{\rm J}\rangle$ describes the inter-site long-range density-density correlations. However, the applications are limited to the weakly correlated systems and the low-dimensional systems. Note that the Gutzwiller wavefunction is expressed as

$$|\Psi_{\rm G}\rangle = e^{\eta_{\rm G} \sum_i n_{i\uparrow} n_{i\downarrow}} |\phi\rangle \propto e^{\frac{1}{2}\eta_{\rm G} \sum_i n_i n_i} |\phi\rangle \ . \tag{2.18}$$

where the variational parameters $\eta_{\rm G}$ and g are related through $\eta_{\rm G}$= ln g. Therefore the on-site Jastrow wavefunction is equivalent to the Gutzwiller wavefunction.

A wavefunction being suitable in the strong correlation regime is the Baeriswyl wavefunction [62, 63]. It is constructed by applying a hopping operator $\hat{T} = -\sum_{ij\sigma} t_{ij} a^\dagger_{i\sigma} a_{j\sigma}$ onto the atomic wavefunction $|\Psi_\infty\rangle$ as

$$|\Psi_{\rm B}\rangle = e^{-\eta_{\rm B}\hat{T}} |\Psi_\infty\rangle \ . \tag{2.19}$$

The operator $\exp(-\eta_{\rm B}\hat{T})$ creates the electron hopping states from the atomic one and the variational parameter $\eta_{\rm B}$ controls the hopping rate to minimize the energy. The Baeriswyl wavefunction describes well the insulator state in the strong correlated regime. However, it is not easy to describe the metallic state.

In order to describe the doublon (doubly occupied state-holon (empty state) bound state, which appears in the super-exchange process in the strong Coulomb interaction regime, one can consider the wavefunction [42] as

$$|\Psi_{\rm dh}\rangle = e^{-\alpha\hat{Q}} |\Psi_{\rm G}\rangle \ . \tag{2.20}$$

Here $\hat{Q} = \sum_i [\hat{d}_i \prod_\tau (1-\hat{h}_{i+\tau}) + \hat{h}_i \prod_\tau (1-\hat{d}_{i+\tau})]$. $\hat{d}_i = n_{i\uparrow} n_{i\downarrow}$ ($\hat{h}_i = (1-n_{i\uparrow})(1-n_{i\downarrow})$) is the doublon (holon) operator, and is taken over the nearest-neighbor sites. The variational parameter controls the amplitudes of the nearest-neighbor doublon holon bound states. The ground state of the nonlocal wavefunctions are usually calculated by means of the numerical technique called the variational Monte Carlo method (VMC) [44, 45].

2.5 Momentum dependent local ansatz wavefunction

Most of the wavefunctions mentioned in the last section aim to describe correlated electrons in the intermediate and strong Coulomb interaction regimes. The behavior of these wavefunctions

in the weak Coulomb interaction regime was not discussed seriously. Kakehashi *et al.* [46] have recently pointed out that the wavefunctions mentioned above do not yield the exact results in the weak Coulomb interaction limit according to the Rayleigh-Schrödinger perturbation theory of the wavefunction. They proposed a new wavefunction called the momentum-dependent local ansatz (MLA) which is consistent with the perturbation theory. The MLA is a new wavefunction which reproduces well-known results in infinite dimensions [26]. In the following subsection, we introduce the MLA that describes exactly the correlated electrons in the weak Coulomb interaction limit, and elucidate the results obtained by the MLA wavefunction in infinite dimensions.

2.5.1 Momentum dependent local ansatz wavefunction method

The momentum dependent local ansatz (MLA) wavefunction is constructed from the local-ansatz (LA) wavefunction (2.11) so as to reproduce the result of the Rayleigh-Schrödinger perturbation theory. Let us expand the LA wavefunction (2.11) in the weak Coulomb interaction limit as

$$|\Psi_{\rm LA}\rangle = |\phi\rangle + |\phi_1\rangle_{\rm LA} + \cdots . \tag{2.21}$$

Here

$$|\phi_1\rangle_{\rm LA} = -\sum_i \sum_{k_1 k_1' k_2 k_2'} \langle k_1'|i\rangle\langle i|k_1\rangle\langle k_2'|i\rangle\langle i|k_2\rangle \eta_{\rm LA} \delta(a^\dagger_{k_2'\downarrow} a_{k_2\downarrow})\delta(a^\dagger_{k_1'\uparrow} a_{k_1\uparrow})\ |\phi\rangle\ . \tag{2.22}$$

$\langle i|k\rangle = \exp(-i\boldsymbol{k}\cdot\boldsymbol{R}_i)/\sqrt{N}$ is an overlap integral between the localized orbital on site i and Bloch state $\boldsymbol{k}$, and $\delta(a^\dagger_{k'\sigma'}a_{k\sigma}) = a^\dagger_{k'\sigma'}a_{k\sigma} - \langle a^\dagger_{k'\sigma'}a_{k\sigma}\rangle_0$.

The Rayleigh-Schrödinger perturbation theory for the exact ground-state wavefunction, on the other hand, yields the following form

$$|\Psi\rangle = |\phi\rangle + |\phi_1\rangle + \cdots , \tag{2.23}$$

$$|\phi_1\rangle = -\sum_i \sum_{k_1 k_1' k_2 k_2'} \langle k_1'|i\rangle\langle i|k_1\rangle\langle k_2'|i\rangle\langle i|k_2\rangle \eta^{(0)}_{k_2' k_2 k_1' k_1} \delta(a^\dagger_{k_2'\downarrow} a_{k_2\downarrow})\delta(a^\dagger_{k_1'\uparrow} a_{k_1\uparrow})\ |\phi\rangle\ . \tag{2.24}$$

The amplitude is given by

$$\eta^{(0)}_{k_2' k_2 k_1' k_1} = -U \lim_{z\to 0} \frac{f(\tilde{\epsilon}_{k_1\uparrow})(1-f(\tilde{\epsilon}_{k_1'\uparrow}))f(\tilde{\epsilon}_{k_2\downarrow})(1-f(\tilde{\epsilon}_{k_2'\downarrow}))}{z - \epsilon_{k_1'\uparrow} + \epsilon_{k_1\uparrow} - \epsilon_{k_2'\downarrow} + \epsilon_{k_2\uparrow}} . \tag{2.25}$$

Here $f(\epsilon)$ 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 Hartree-Fock one-electron energy eigenvalue given by $\epsilon_{k\sigma} = \epsilon_0 + U\langle n_{i-\sigma}\rangle_0 + \epsilon_k$, ϵ_k being the Fourier transform of t_{ij}.

Comparing Eq. (2.24) with Eq. (2.22), we find that one has to take into account the momentum dependence of the variational parameters in order to reproduce the perturbation theory in the weak Coulomb interaction limit. In the MLA, we introduce a new local ansatz operator $\tilde{O}_i$ such that

$$\tilde{O}_i = \sum_{k_1 k_1' k_2 k_2'} \langle k_1'|i\rangle\langle i|k_1\rangle\langle k_2'|i\rangle\langle i|k_2\rangle \eta_{k_2' k_2 k_1' k_1} \delta(a^\dagger_{k_2'\downarrow} a_{k_2\downarrow})\delta(a^\dagger_{k_1'\uparrow} a_{k_1\uparrow}) , \tag{2.26}$$

and construct a new wavefunction with momentum-dependent variational parameters $\{\eta_{k_2' k_2 k_1' k_1}\}$ as follows [46]:

$$|\Psi\rangle = \Big[\prod_i (1-\tilde{O}_i)\Big]\ |\phi\rangle\ . \tag{2.27}$$

The total energy is given as

$$\langle H\rangle = \langle H\rangle_0 + N\epsilon_c. \tag{2.28}$$

Here $\langle H\rangle_0$ denotes the Hartree-Fock energy, ϵ_c is the correlation energy per atom. In the single-site approximation (SSA), the correlation energy ϵ_c is given as follows (see Sec 3.4 in details):

$$\epsilon_c = \frac{-\langle \tilde{O}_i^\dagger \tilde{H}\rangle_0 - \langle \tilde{H}\tilde{O}_i\rangle_0 + \langle \tilde{O}_i^\dagger \tilde{H}\tilde{O}_i\rangle_0}{1+\langle \tilde{O}_i^\dagger \tilde{O}_i\rangle_0}\ . \tag{2.29}$$

Here $\tilde{H} = H - \langle H\rangle_0$

By making use of Wick's theorem, $\langle \tilde{H}\tilde{O}_i\rangle_0 (= \langle \tilde{O}_i^\dagger \tilde{H}\rangle_0^*)$, $\langle \tilde{O}_i^\dagger \tilde{H}\tilde{O}_i\rangle_0$, and $\langle \tilde{O}_i^\dagger \tilde{O}_i\rangle_0$ are given by

$$\langle \tilde{H}\tilde{O}_i\rangle_0 = \frac{U}{N^4}\sum_{k_1k_1'k_2k_2'} \eta_{k_2'k_2k_1'k_1}\tilde{f}_{k_2'k_2k_1'k_1}, \tag{2.30}$$

$$\begin{aligned}\langle \tilde{O}_i^\dagger \tilde{H}\tilde{O}_i\rangle_0 = \frac{1}{N^4}\sum_{k_1k_1'k_2k_2'} \eta^*_{k_2'k_2k_1'k_1}\tilde{f}_{k_2'k_2k_1'k_1}\Big[&\Delta E_{k_2'k_2k_1'k_1}\eta_{k_2'k_2k_1'k_1}\\ &+\frac{U}{N^2}\Big\{\sum_{k_3k_4} f(\tilde{\epsilon}_{k_3\uparrow})f(\tilde{\epsilon}_{k_4\downarrow})\eta_{k_2'k_4k_1'k_3} - \sum_{k_3'k_4}(1-f(\tilde{\epsilon}_{k_3'\uparrow}))f(\tilde{\epsilon}_{k_4\downarrow})\eta_{k_2'k_4k_3'k_1}\\ &-\sum_{k_3k_4'} f(\tilde{\epsilon}_{k_3\uparrow})(1-f(\tilde{\epsilon}_{k_4'\downarrow}))\eta_{k_4'\kappa_2k_1'k_3} + \sum_{k_3'k_4'}(1-f(\tilde{\epsilon}_{k_3'\uparrow}))(1-f(\tilde{\epsilon}_{k_4'\downarrow}))\eta_{k_4'k_2k_3'k_1}\Big\}\Big],\end{aligned} \tag{2.31}$$

$$\langle \tilde{O}_i^\dagger \tilde{O}_i\rangle_0 = \frac{1}{N^4}\sum_{k_1k_1'k_2k_2'} |\eta_{k_2'k_2k_1'k_1}|^2\tilde{f}_{k_2'k_2k_1'k_1}. \tag{2.32}$$

Here $\tilde{f}_{k_2'k_2k_1'k_1}$ is the Fermi factor; $\tilde{f}_{k_2'k_2k_1'k_1} = f(\tilde{\epsilon}_{k_1\uparrow})(1-f(\tilde{\epsilon}_{k_1'\uparrow}))f(\tilde{\epsilon}_{k_2\downarrow})(1-f(\tilde{\epsilon}_{k_2'\downarrow})$. $\tilde{\epsilon}_{k\sigma} = \epsilon_{k\sigma}-\mu$, $\epsilon_{k\sigma}$ being the one-electron energy eigenvalue for H_0. $\Delta E_{k_2'k_2k_1'k_1} = \epsilon_{k_2'\downarrow} - \epsilon_{k_2\downarrow} + \epsilon_{k_1'\uparrow} - \epsilon_{k_1\uparrow}$ denotes the two-particle excitation energy from the ground state $|\phi\rangle$.

Minimizing the correlation energy (2.29), we obtain the self-consistent equations for $\{\eta_{k_2'k_2k_1'k_1}\}$ in the SSA as follows:

$$\begin{aligned}&(\Delta E_{k_2'k_2k_1'k_1} - \epsilon_c)\eta_{k_2'k_2k_1'k_1}\\ &+\frac{U}{N^2}\Big[\sum_{k_3k_4} f(\tilde{\epsilon}_{k_3\uparrow})f(\tilde{\epsilon}_{k_4\downarrow})\eta_{k_2'k_4k_1'k_3} - \sum_{k_3k_4'} f(\tilde{\epsilon}_{k_3\uparrow})(1-f(\tilde{\epsilon}_{k_4'\downarrow}))\eta_{k_4'k_2k_1'k_3}\\ &\sum_{k_3'k_4}(1-f(\tilde{\epsilon}_{k_3'\uparrow}))f(\tilde{\epsilon}_{k_4\downarrow})\eta_{k_2'k_4k_3'k_1} + \sum_{k_3'k_4'}(1-f(\tilde{\epsilon}_{k_3'\uparrow}))(1-f(\tilde{\epsilon}_{k_4'\downarrow}))\eta_{k_4'k_2k_3'k_1}\Big] = U.\end{aligned} \tag{2.33}$$

It is possible to solve approximately the above equation for $\eta_{k_2'k_2k_1'k_1}$ for a given ϵ_c. We first note that $\eta_{k_2'k_2k_1'k_1}$ should vanish in the weak U limit. Thus, we can omit the second term at the lhs (left-hand side) of Eq. (2.33) in the weak interaction limit. Then we obtain the solution as $\eta_{k_2'k_2k_1'k_1} = U/(\Delta E_{k_2'k_2k_1'k_1} - \epsilon_c)$. In the atomic limit, on the other hand, we have $\Delta E_{k_2'k_2k_1'k_1} = 0$,

and find a k-independent solution η. Therefore we approximate $\{\eta_{k'_2k_2k'_1k_1}\}$ in the second term with a k-independent solution η, so that we obtain an approximate solution which interpolates between the weak and strong Coulomb interaction regimes.

$$\eta_{k'_2k_2k'_1k_1}(\tilde{\eta},\epsilon_c)=\frac{U\tilde{\eta}}{\Delta E_{k'_2k_2k'_1k_1}-\epsilon_c}. \tag{2.34}$$

Here $\tilde{\eta}$ is a renormalization factor to be variable.

When we adopt the approximate form (2.34), we have the following inequality.

$$E_0\le E(\{\eta^*_{k'_2k_2k'_1k_1}\})\le E(\{\eta_{k'_2k_2k'_1k_1}(\eta,\epsilon_c)\}), \tag{2.35}$$

where $\eta^*_{k'_2k_2k'_1k_1}$ is the exact stationary value. Therefore $\tilde{\eta}$ is again determined from the stationary condition of the correlation energy ϵ_c.

$$\tilde{\eta}=\frac{1}{1+\frac{UC}{D}}. \tag{2.36}$$

Here

$$\begin{aligned}C=&\frac{1}{N^6}\sum_{k_1k'_1k_2k'_2}\frac{\tilde{f}_{k_2k'_2k_1k'_1}}{(\Delta E_{k'_2k_2k'_1k_1}-\epsilon_c)}\\&\times\Big[\sum_{k_3k_4}\frac{f(\tilde{\epsilon}_{k_3\uparrow})f(\tilde{\epsilon}_{k_4\downarrow})}{(\Delta E_{k'_2k_4k'_1k_3}-\epsilon_c)}-\sum_{k'_3k_4}\frac{(1-f(\tilde{\epsilon}_{k'_3\uparrow}))f(\tilde{\epsilon}_{k_4\downarrow})}{(\Delta E_{k'_2k_4k'_3k_1}-\epsilon_c)}\\&-\sum_{k_3k'_4}\frac{f(\tilde{\epsilon}_{k_3\uparrow})(1-f(\tilde{\epsilon}_{k'_4\downarrow}))}{(\Delta E_{k'_4k_2k'_1k_3}-\epsilon_c)}+\sum_{k'_3k'_4}\frac{(1-f(\tilde{\epsilon}_{k'_3\uparrow}))(1-f(\tilde{\epsilon}_{k'_4\downarrow}))}{(\Delta E_{k'_4k_2k'_3k_1}-\epsilon_c)}\Big],\end{aligned} \tag{2.37}$$

$$D=\frac{1}{N^4}\sum_{k_1k'_1k_2k'_2}\frac{\tilde{f}_{k_2k'_2k_1k'_1}}{(\Delta E_{k'_2k_2k'_1k_1}-\epsilon_c)}. \tag{2.38}$$

Note that $\tilde{\eta}$ in Eq. (2.36) is given as a function of ϵ_c, and ϵ_c in Eq. (2.29) depends on $\tilde{\eta}$ and ϵ_c. Thus both equations are solved self-consistently. This is the self-consistent MLA which starts from the Hartree-Fock wavefunction. The self-consistency is significant when the average electron number deviates from half-filling.

In the numerical calculations of C, D, $\langle\tilde{H}\tilde{O}_i\rangle_0$, $\langle\tilde{O}_i^\dagger\tilde{H}\tilde{O}_i\rangle_0$, and $\langle\tilde{O}_i^\dagger\tilde{O}_i\rangle_0$, the six-fold $\boldsymbol{k}$ sums appear. This means that one has to perform the six-fold integrals in the energy representation. One can reduce the six-fold integrals into two-fold ones by using the Laplace transformation.

$$\frac{1}{z-\epsilon_4+\epsilon_3-\epsilon_2+\epsilon_1+\epsilon_c}=-i\int_0^\infty dt\; e^{i(z-\epsilon_4+\epsilon_3-\epsilon_2+\epsilon_1+\epsilon_c)t}. \tag{2.39}$$

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

For example, $\langle\tilde{H}\tilde{O}_i\rangle_0$ is expressed by Eq. (2.30). Substituting Eq. (2.34) into Eq. (2.30), we have the following expression with four-fold energy integrals as follows.

$$\begin{aligned}\langle\tilde{H}\tilde{O}_i\rangle_0&=\langle\tilde{O}_i^\dagger\tilde{H}\rangle_0^*\\&=U^2\tilde{\eta}\int\frac{\Big[\prod_{n=1}^4 d\epsilon_n\Big]\Big[\prod_{n=1}^4\rho(\epsilon_n)\Big]f(\tilde{\epsilon}_{1\uparrow})(1-f(\tilde{\epsilon}_{2\uparrow}))f(\tilde{\epsilon}_{3\downarrow})(1-f(\tilde{\epsilon}_{4\downarrow})}{\epsilon_4-\epsilon_3+\epsilon_2-\epsilon_1-\epsilon_c}.\end{aligned} \tag{2.40}$$

Here $\tilde{\epsilon}_{n\sigma} = \epsilon_n + \tilde{\epsilon}_\sigma$ and $\tilde{\epsilon}_\sigma = \epsilon_0 + U\langle n_{i-\sigma}\rangle - \mu$ is the atomic level measured from the chemical potential μ, and $\rho(\epsilon)$ is the density of states for the one-electron energy eigen values of the non-interacting system t_{ij}. Making use of the Laplace transformation (2.39), we find the following expression given by a single time integral:

$$\langle \tilde{H}\tilde{O}_i\rangle_0 = \langle \tilde{O}_i^\dagger \tilde{H}\rangle_0^* = iU^2\tilde{\eta}\int_0^\infty dt \mathrm{e}^{i\epsilon_c t} a_\uparrow(-t)a_\downarrow(-t)b_\uparrow(t)b_\downarrow(t). \tag{2.41}$$

Here $a_\sigma(t)$ and $b_\sigma(t)$ are defined by

$$a_\sigma(t) = \int d\epsilon \mathrm{e}^{-i\epsilon t}\rho(\epsilon)f(\epsilon+\tilde{\epsilon}_\sigma), \tag{2.42}$$

$$b_\sigma(t) = \int d\epsilon \mathrm{e}^{-i\epsilon t}\rho(\epsilon)[1-f(\epsilon+\tilde{\epsilon}_\sigma)]. \tag{2.43}$$

We obtain the expressions of the other matrix elements $\langle \tilde{O}_i^\dagger \tilde{H}\tilde{O}_i\rangle_0$ and $\langle \tilde{O}_i^\dagger \tilde{O}_i\rangle_0$ as follows.

$$\langle \tilde{O}_i^\dagger \tilde{H}\tilde{O}_i\rangle_0 = \langle \tilde{O}_i^\dagger \tilde{H}_0\tilde{O}_i\rangle_0 + U\langle \tilde{O}_i^\dagger O_i\tilde{O}_i\rangle_0, \tag{2.44}$$

$$\begin{aligned}\langle \tilde{O}_i^\dagger \tilde{H}_0\tilde{O}_i\rangle_0 = -U^2\tilde{\eta}^2\int_0^\infty dtdt' \mathrm{e}^{i\epsilon_c(t+t')}\Big[&a_\uparrow(-t-t')b_\uparrow(t+t')a_\downarrow(-t-t')b_{1\downarrow}(t+t')\\ &- a_\uparrow(-t-t')b_\uparrow(t+t')a_{1\downarrow}(-t-t')b_\downarrow(t+t')\\ &+ a_\uparrow(-t-t')b_{1\uparrow}(t+t')a_\downarrow(-t-t')b_\downarrow(t+t')\\ &- a_{1\uparrow}(-t-t')b_\uparrow(t+t')a_\downarrow(-t-t')b_\downarrow(t+t')\Big],\end{aligned} \tag{2.45}$$

$$\begin{aligned}\langle \tilde{O}_i^\dagger O_i\tilde{O}_i\rangle_0 = -U^2\tilde{\eta}^2\int_0^\infty dtdt' \mathrm{e}^{i\epsilon_c(t+t')}\Big[&a_\uparrow(-t)b_\uparrow(t+t')a_\downarrow(-t)b_\downarrow(t+t')a_\uparrow(-t')a_\downarrow(-t')\\ &- a_\uparrow(-t)b_\uparrow(t+t')a_\downarrow(-t-t')b_\downarrow(t)a_\uparrow(-t')b_\downarrow(t')\\ &- a_\uparrow(-t-t')b_\uparrow(t)a_\downarrow(-t)b_\downarrow(t+t')b_\uparrow(t')a_\downarrow(-t')\\ &+ a_\uparrow(-t-t')b_\uparrow(t)a_\downarrow(-t-t')b_\downarrow(t)b_\uparrow(t')b_\downarrow(t')\Big],\end{aligned} \tag{2.46}$$

$$\langle \tilde{O}_i^\dagger \tilde{O}_i\rangle_0 = -U^2\tilde{\eta}^2\int_0^\infty dtdt' \mathrm{e}^{i\epsilon_c(t+t')}a_\uparrow(-t-t')b_\uparrow(t+t')a_\downarrow(-t-t')b_\downarrow(t+t'). \tag{2.47}$$

Here $a_\sigma(t)$ and $b_\sigma(t)$ are given Eqs. (2.42) and (2.43). $a_{1\sigma}(t)$ and $b_{1\sigma}(t)$ are defined by

$$a_{1\sigma}(t) = \int d\epsilon \mathrm{e}^{-i\epsilon t}\epsilon\rho(\epsilon)f(\epsilon+\tilde{\epsilon}_\sigma), \tag{2.48}$$

$$b_{1\sigma}(t) = \int d\epsilon \mathrm{e}^{-i\epsilon t}\epsilon\rho(\epsilon)[1-f(\epsilon+\tilde{\epsilon}_\sigma)]. \tag{2.49}$$

Electron number, momentum distribution, double occupation numbers are obtained as follows:

$$\langle n_i \rangle = \langle n_i \rangle_0 + \frac{\sum_\sigma \langle \tilde{O}_i^\dagger \tilde{n}_{i\sigma} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0} \,, \tag{2.50}$$

$$\langle n_{k\sigma} \rangle = \langle n_{k\sigma} \rangle_0 + \frac{N \langle \tilde{O}_i^\dagger \tilde{n}_{k\sigma} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0} \,, \tag{2.51}$$

$$\langle n_{i\uparrow} n_{i\downarrow} \rangle = \langle n_{i\uparrow} \rangle_0 \langle n_{i\downarrow} \rangle_0 + \langle n_{i\uparrow} n_{i\downarrow} \rangle_c \,. \tag{2.52}$$

$$\langle n_{i\uparrow} n_{i\downarrow} \rangle_c = \frac{-\langle \tilde{O}_i^\dagger O_i \rangle_0 - \langle O_i \tilde{O}_i \rangle_0 + \langle \tilde{O}_i^\dagger O_i \tilde{O}_i \rangle_0 + \sum_\sigma \langle n_{i-\sigma} \rangle \langle \tilde{O}_i^\dagger \tilde{n}_{i\sigma} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0} \,. \tag{2.53}$$

Here the second terms at the rhs (right-hand side) of the above expressions (2.50) $\sim$ (2.52) are correlation corrections. They are calculated by using Wick's theorem and the Laplace transformation.

2.5.2 Numerical results of MLA and LA

The MLA improves the LA irrespective of the Coulomb interaction strength and the electron number. In order to demonstrate the fact, we present in this section the numerical results for the hypercubic lattice in infinite dimensions [64]. In this case, the density of states (DOS) for the noninteracting system is given by $\rho(\epsilon) = (1/\sqrt{\pi}) \exp(-\epsilon^2)$.

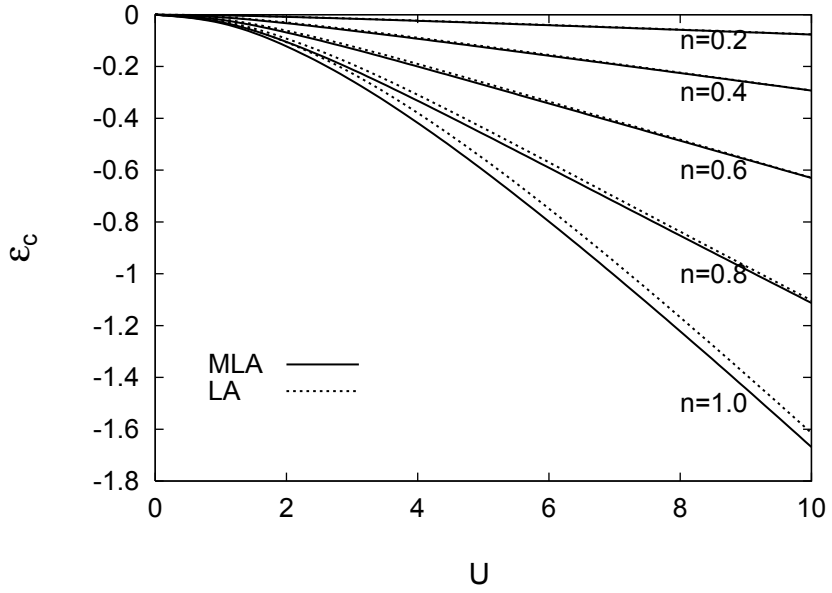

Figure 2.1: The correlation energies ϵ_c per atom versus Coulomb interaction energy parameter U in the MLA (solid curve) and the LA (dashed curve) for various electron number n (Ref. [47]).

Figure 2.1 shows the correlation energy per atom as a function of U for various electron numbers. We verify that the ground state energy in the MLA is lower than that of the LA over all Coulomb interactions U and electron numbers n. In particular, the small U behavior of ϵ_c in the MLA is exact. For a given U, the difference between the LA and the MLA increases with increasing n and becomes maximum at half-filling because the number of doubly occupied sites in the Hartree-Fock ground state increases with increasing electron number.

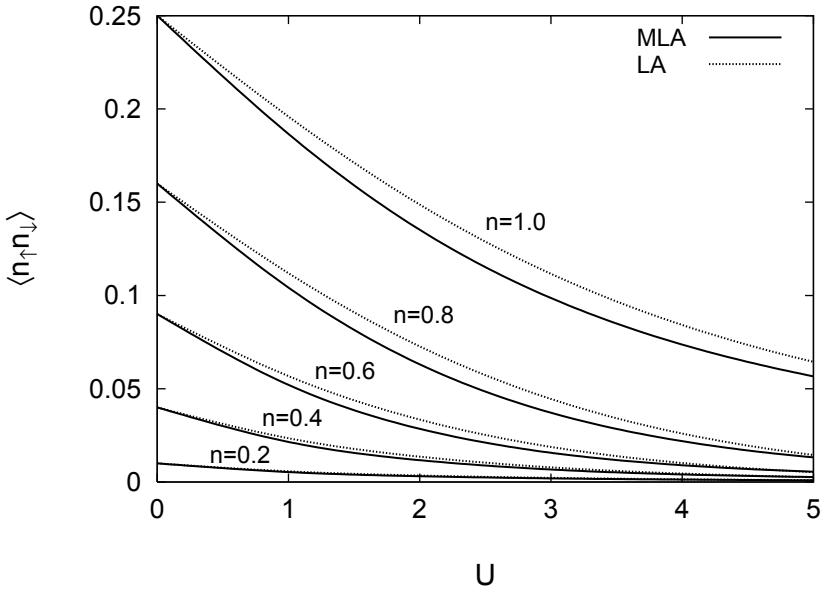

Figure 2.2: The double occupation number $\langle n_\uparrow n_\downarrow \rangle$ versus Coulomb interaction energy U curves in the MLA (solid curve) and the LA (dotted curve) (Ref. [47]).

The double occupation number decreases with increasing interaction U irrespective of electron number n so as to suppress the loss of Coulomb interaction energy as seen in Fig. 2.2. We find that the MLA wavefunction gives greater reduction in the double occupancy as compared with that of the LA.

The momentum dependence of the variational parameters causes qualitative change in the momentum distribution as shown in Fig. 2.3. The momentum distribution in the LA and the GW are constant below and above the Fermi level as mentioned in the last section, while the distribution in the MLA monotonically decreases with increasing energy $\epsilon_{k\sigma}$ below and above the Fermi level, as it should [65].

The quasiparticle weight obtained from the jump in the momentum distribution at the Fermi level is also much improved by taking into account the momentum dependence of variational parameters. Figure 2.4 shows the quasiparticle weight Z as a function of the Coulomb interaction strength U in various methods at half-filling. The quasiparticle weight in the LA changes as $Z_{\rm LA} = (1-3\eta_{\rm LA}^2/16)/(1+\eta_{\rm LA}^2/16)$ (see Eq. (2.16)) and vanishes at $U_{c2}({\rm LA}) = 24/\sqrt{3\pi}$ (= 7.82). In the GW [66], the quasiparticle weight decreases as $Z_{\rm G} = 1 - (U/U_{c2})^2$ (see Eq. (2.10)), and vanishes at $U_{c2}({\rm GW}) = 8/\sqrt{\pi}$ (= 4.51). These curves deviate strongly from the curve obtained by the numerical renormalization group (NRG) method [65] which is considered to be the best. The curve in the MLA on the other hand is close to the that of the NRG, and significantly improves upon the LA, though calculated U_{c2} (MLA) = 3.40 is somewhat smaller than the value U_{c2} (NRG) = 4.10.

The numerical results mentioned above indicate that the momentum dependence of the variational parameters much improves upon the LA as well as the GW in the metallic region. In particular, this is significant in order to describe the properties associated with the low-energy excitations.

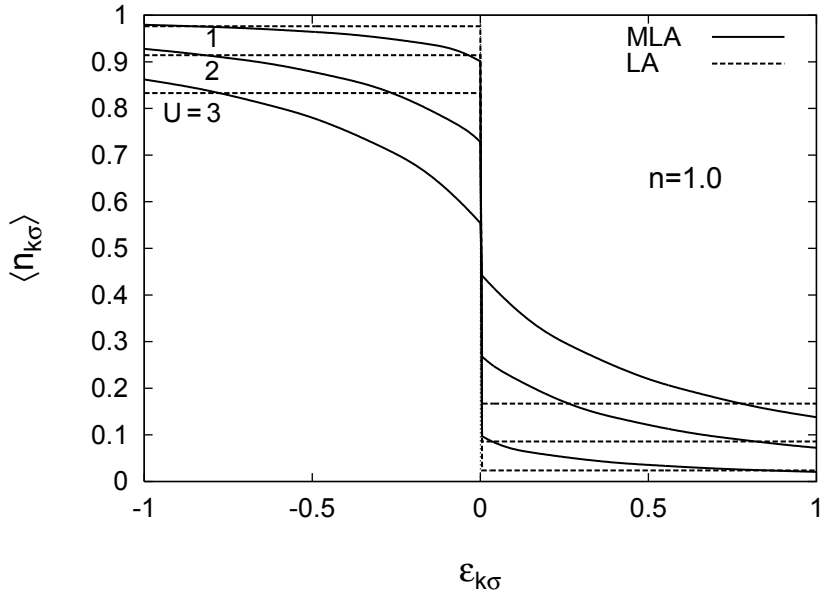

Figure 2.3: The momentum distribution as a function of energy $\epsilon_{k\sigma}$ for various Coulomb interaction energy parameters U at half-filling (n = 1.0) (Ref. [47]). The MLA: solid curves, the LA: dashed curves.

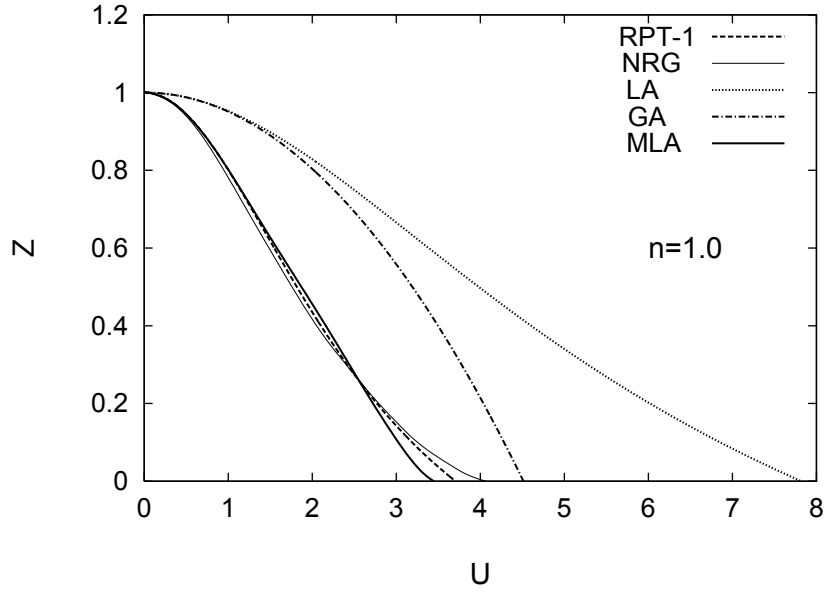

Figure 2.4: Quasiparticle-weight versus Coulomb interaction curves in various theories (Ref. [47]). The RPT-1 (Renormalized Perturbation Theory): dashed curve (Ref. [65]), the NRG: thin solid curve (Ref. [67]), the LA: dotted curve, the MLA: solid curve, and the GW: dot-dashed curve.

2.5.3 Alloy analogy wavefunction

The MLA describes the electron correlations in the weak Coulomb interaction limit exactly, and much improves the LA wavefunction, as we have seen in the last section. It cannot, however, suppress sufficiently the loss of Coulomb interaction energy in the strongly correlated region. Usual way to take into account more correlations is to expand the Hilbert space applying additional correlators with variational parameters onto the Hartree-Fock wavefunction. In particular, the correlator which suppresses the double occupancy is required in the strongly correlated regime. Such an extension, however, would make it more difficult to treat the wavefunction analytically. An alternative way to overcome the difficulty is to start from a wavefunction which is more suitable for the strongly correlated electrons. In this section we consider the alloy analogy wavefunction towards an improvement of the MLA from the latter point of view.

The Hartree-Fock approximation is exact in energy up to the first order with respect to the Coulomb interaction energy, therefore the wavefunction is suitable as a starting state for describing correlations in the weak and intermediate Coulomb interaction regime. However, the wavefunction is not suitable in the strongly correlated region because it allows for the double occupation of electrons at each site.

Hubbard proposed an alternative one-electron picture in the strong Coulomb interaction regime [61]. Let us consider the atomic limit. There each electron number $\hat{n}_{i\sigma}$ is a good quantum number taking a value $n_{i\sigma} = 0$ or 1. We distinguish in this section the number operator $\hat{n}_{i\sigma}$ with the c-number $n_{i\sigma}(= 0 \text{ or } 1)$. When the electron hopping is switched on in the strongly correlated region, an electron with spin σ should move slowly from site to site, and feel a different potential $Un_{i-\sigma} = U$ or 0, instead of the Hartree-Fock average potential $U\langle\hat{n}_{i-\sigma}\rangle_0$, depending on whether the opposite-spin electron is occupied or unoccupied on the same site. Hubbard regarded the 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. This is the alloy-analogy (AA) picture for strongly correlated electrons.

The AA Hamiltonian is given by

$$H_{\rm AA} = \sum_{i\sigma}(\epsilon_0 + Un_{i-\sigma})\hat{n}_{i\sigma} + \sum_{ij\sigma} t_{ij}a^\dagger_{i\sigma}a_{j\sigma} - U\sum_i (n_{i\uparrow}\langle\hat{n}_{i\downarrow}\rangle_{\rm AA} + n_{i\downarrow}\langle\hat{n}_{i\uparrow}\rangle_{\rm AA}) + U\sum_i \langle\hat{n}_{i\uparrow}\rangle_{\rm AA}\langle\hat{n}_{i\downarrow}\rangle_{\rm AA}. \tag{2.54}$$

Here $\langle\sim\rangle_{\rm AA}$ denotes the AA average $\langle\phi_{\rm AA}|(\sim)|\phi_{\rm AA}\rangle$ with respect to the ground state wavefunction $|\phi_{\rm AA}\rangle$ of the AA Hamiltonian $H_{\rm AA}$. $n_{i\sigma}$ is a c-number taking a value 0 or 1. Each configuration $\{n_{i\sigma}\}$ is considered as a snapshort in time development.

The ground state energy E_0 satisfies the following inequality for any configuration of $\{n_{i\sigma}\}$.

$$E_0 \le \langle H\rangle_{\rm AA} = \langle H_{\rm AA}\rangle_{\rm AA}. \tag{2.55}$$

Thus, when we take the configurational average on $\{n_{i\sigma}\}$, we have

$$E_0 \le \overline{\langle H\rangle}_{\rm AA}. \tag{2.56}$$

Here the upper bar denotes the configurational average.

The configurational averages of various quantities can be obtained with use of the single-site approximation (SSA) called the coherent potential approximation (CPA) [68–70]. Note that the

averaged electron number is obtained from the local density of state (LDOS) for an electron with spin σ, $i.e.$, $\rho_{i\sigma}(\epsilon)$, as follows:

$$\langle \hat{n}_{i\sigma} \rangle_{\rm AA} = \int f(\epsilon) \rho_{i\sigma}(\epsilon) d\epsilon, \tag{2.57}$$

and the LDOS is obtained from the one-electron Green function as

$$\rho_{i\sigma}(\epsilon) = -\frac{1}{\pi} {\rm Im} G_{ii\sigma}(z). \tag{2.58}$$

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

$$G_{ii\sigma}(z) = [(z - \boldsymbol{H}_\sigma)^{-1}]_{ii}. \tag{2.59}$$

Here $(\boldsymbol{H}_\sigma)_{ij}$ is the one-electron Hamiltonian matrix for the AA Hamiltonian minus chemical potential μ.

In the CPA, we replace the random potential at the surrounding sites with an energy-dependent coherent potential $\Sigma_\sigma(z)$. The on-site impurity Green function $G_{ii\sigma}(z)$ is then obtained as follows:

$$G_{ii\sigma}(z) = \frac{1}{F_\sigma(z)^{-1} - \epsilon_{i\sigma} + \Sigma_\sigma(z)}. \tag{2.60}$$

Here $\epsilon_{i\sigma} = \epsilon_0 - \mu + U n_{i-\sigma}$. $F_\sigma(z)$ is the on-site Green function for the coherent system in which all the random potentials have been replaced by the coherent potentials.

$$F_\sigma(z) = \int \frac{\rho(\epsilon) d\epsilon}{z - \Sigma_\sigma(z) - \epsilon}. \tag{2.61}$$

Note that $\rho(\epsilon)$ is the DOS per site per spin for the non-interacting system. The coherent potential $\Sigma_\sigma(z)$ is determined from the self-consistent condition:

$$\overline{G_{00\sigma}(z)} = F_\sigma(z). \tag{2.62}$$

The configurational average of the impurity Green function is given as

$$\overline{G_{00\sigma}(z)} = \frac{\langle \hat{n}_{i-\sigma} \rangle_{\rm AA}}{F_\sigma(z)^{-1} - \epsilon_0 + \mu - U + \Sigma_\sigma(z)} + \frac{1 - \langle \hat{n}_{i-\sigma} \rangle_{\rm AA}}{F_\sigma(z)^{-1} - \epsilon_0 + \mu + \Sigma_\sigma(z)}. \tag{2.63}$$

The ground state wavefunction $\phi_{\rm AA}$for the alloy-analogy Hamiltonian (2.54) provides us with a good starting wave function for the strongly correlated electrons, though such a wavefunction depends on electron configuration $\{n_{i\sigma}\}$ via atomic potentials.

2.5.4 MLA with hybrid wavefunction

We can improve the MLA correlated wavefunction using the best starting wavefunction. The Hartree-Fock (HF) wavefunction $|\phi_{\rm HF}\rangle$ (=$|\phi\rangle$) works best in the weakly correlated region. In the strongly correlated region the alloy-analogy (AA) wavefunction $|\phi_{\rm AA}\rangle$ works better. Therefore we introduce a hybrid (HB) wavefunction $|\phi_{\rm HB}\rangle$ which is the ground state of a hybrid Hamiltonian $H_{\rm HB}$. The Hamiltonian is defined by a linear combination of the HF and AA Hamiltonians [49]:

$$\begin{aligned} H_{\rm HB} = & \sum_{i\sigma} (\bar{U} \langle n_{i-\sigma} \rangle_{\rm HB} + \tilde{U} n_{i-\sigma}) \hat{n}_{i\sigma} + \sum_{ij\sigma} t_{ij} a^\dagger_{i\sigma} a_{j\sigma} \\ & - (\bar{U} - \tilde{U}) \sum_i \langle \hat{n}_{i\uparrow} \rangle_{\rm HB} \langle \hat{n}_{i\downarrow} \rangle_{\rm HB} - \tilde{U} \sum_i (n_{i\uparrow} \langle \hat{n}_{i\downarrow} \rangle_{\rm HB} + n_{i\downarrow} \langle \hat{n}_{i\uparrow} \rangle_{\rm HB}). \end{aligned} \tag{2.64}$$

Here $\langle\sim\rangle_{\rm HB}$ denotes the HB average $\langle\phi_{\rm HB}|(\sim)|\phi_{\rm HB}\rangle$, $\bar{U}=(1-w)U$, and $\tilde{U}=wU$. w is the weight in the linear combination; $H_{\rm HB}=(1-w)H_{\rm HF}+wH_{\rm AA}$, where $H_{\rm HF}$ denotes the Hartree-Fock Hamiltonian. $H_{\rm HB}$ reduces to the HF (AA) Hamiltonian when $w=0$ ($w=1$).

The new MLA with the HB wavefunction is given by

$$|\Psi\rangle=\Big[\prod_i(1-\tilde{O}_i)\Big]|\phi_{\rm HB}\rangle. \tag{2.65}$$

The local operators $\{\tilde{O}_i\}$ have been modified as follows:

$$\tilde{O}_i=\sum_{\kappa_1\kappa_1'\kappa_2\kappa_2'}\langle\kappa_1'|i\rangle\langle i|\kappa_1\rangle\langle\kappa_2'|i\rangle\langle i|\kappa_2\rangle\eta_{\kappa_2'\kappa_2\kappa_1'\kappa_1}\delta(a^\dagger_{\kappa_{2\downarrow}'}a_{\kappa_{2\downarrow}})\delta(a^\dagger_{\kappa_{1\uparrow}'}a_{\kappa_{1\uparrow}})\ . \tag{2.66}$$

Here $\eta_{\kappa_2'\kappa_2\kappa_1'\kappa_1}$is a variational parameter, $a^\dagger_{\kappa\sigma}$ and $a_{\kappa\sigma}$ are the creation and annihilation operators which diagonalize the Hamiltonian $H_{\rm HB}$ (2.64), and $\langle\kappa|i\rangle$ are overlap integrals defined by $a_{\kappa\sigma}=\sum_i a_{i\sigma}\langle\kappa|i\rangle$. Furthermore $\delta(a^\dagger_{\kappa'\sigma}a_{\kappa\sigma})=a^\dagger_{\kappa'\sigma}a_{\kappa\sigma}-\langle a^\dagger_{\kappa'\sigma}a_{\kappa\sigma}\rangle_{\rm HB}$.

The ground state energy E_0 again satisfies the following inequality for any wavefunction $|\Psi\rangle$.

$$E_0\le\langle H\rangle_{\rm HB}+N\epsilon_c. \tag{2.67}$$

The correlation energy per atom ϵ_c in the single-site approximation (SSA) is obtained as follows.

$$\epsilon_c=\frac{-\langle\tilde{O}_i^\dagger\tilde{H}\rangle_{\rm HB}-\langle\tilde{H}\tilde{O}_i\rangle_{\rm HB}+\langle\tilde{O}_i^\dagger\tilde{H}\tilde{O}_i\rangle_{\rm HB}}{1+\langle\tilde{O}_i^\dagger\tilde{O}_i\rangle_{\rm HB}}\ . \tag{2.68}$$

Here $\tilde{H}=H-\langle H\rangle_{\rm HB}$

The energy elements $\langle\tilde{H}\tilde{O}_i\rangle_{\rm HB}$,$\langle\tilde{O}_i^\dagger\tilde{H}\tilde{O}_i\rangle_{\rm HB}$, and $\langle\tilde{O}_i^\dagger\tilde{O}_i\rangle_{\rm HB}$ are given by

$$\langle\tilde{H}\tilde{O}_i\rangle_{\rm HB}=U\sum_{\kappa_1\kappa_1'\kappa_2\kappa_2'}|\langle\kappa_1'|i\rangle|^2|\langle\kappa_1|i\rangle|^2|\langle\kappa_2'|i\rangle|^2|\langle\kappa_2|i\rangle|^2\eta_{\kappa_2'\kappa_2\kappa_1'\kappa_1}\tilde{f}_{\kappa_2'\kappa_2\kappa_1'\kappa_1}, \tag{2.69}$$

$$\begin{aligned}\langle\tilde{O}_i^\dagger\tilde{H}\tilde{O}_i\rangle_{\rm HB}=&\sum_{\kappa_1\kappa_1'\kappa_2\kappa_2'}|\langle\kappa_1'|i\rangle|^2|\langle\kappa_1|i\rangle|^2|\langle\kappa_2'|i\rangle|^2|\langle\kappa_2|i\rangle|^2\\&\times\eta^*_{\kappa_2'\kappa_2\kappa_1'\kappa_1}\tilde{f}_{\kappa_2'\kappa_2\kappa_1'\kappa_1}\Big[\Delta E_{\kappa_2'\kappa_2\kappa_1'\kappa_1}\eta_{\kappa_2'\kappa_2\kappa_1'\kappa_1}\\&+U\Big\{\sum_{\kappa_3\kappa_4}|\langle\kappa_3|i\rangle|^2|\langle\kappa_4|i\rangle|^2f(\tilde{\epsilon}_{\kappa_3\uparrow})f(\tilde{\epsilon}_{\kappa_4\downarrow})\eta_{\kappa_2'\kappa_4\kappa_1'\kappa_3}\\&-\sum_{\kappa_3'\kappa_4}|\langle\kappa_3'|i\rangle|^2|\langle\kappa_4|i\rangle|^2(1-f(\tilde{\epsilon}_{\kappa_3'\uparrow}))f(\tilde{\epsilon}_{\kappa_4\downarrow})\eta_{\kappa_2'\kappa_4\kappa_3'\kappa_1}\\&-\sum_{\kappa_3\kappa_4'}|\langle\kappa_3|i\rangle|^2|\langle\kappa_4'|i\rangle|^2f(\tilde{\epsilon}_{\kappa_3\uparrow})(1-f(\tilde{\epsilon}_{\kappa_4'\downarrow}))\eta_{\kappa_4'\kappa_2\kappa_1'\kappa_3}\\&+\sum_{\kappa_3'\kappa_4'}|\langle\kappa_3'|i\rangle|^2|\langle\kappa_4'|i\rangle|^2(1-f(\tilde{\epsilon}_{\kappa_3'\uparrow}))(1-f(\tilde{\epsilon}_{\kappa_4'\downarrow}))\eta_{\kappa_4'\kappa_2\kappa_3'\kappa_1}\Big\}\Big],\end{aligned} \tag{2.70}$$

$$\langle\tilde{O}_i^\dagger\tilde{O}_i\rangle_{\rm HB}=\sum_{\kappa_1\kappa_1'\kappa_2\kappa_2'}|\langle\kappa_1'|i\rangle|^2|\langle\kappa_1|i\rangle|^2|\langle\kappa_2'|i\rangle|^2|\langle\kappa_2|i\rangle|^2|\eta_{\kappa_2'\kappa_2\kappa_1'\kappa_1}|^2\tilde{f}_{\kappa_2'\kappa_2\kappa_1'\kappa_1}. \tag{2.71}$$

Here $\tilde{f}_{\kappa_2'\kappa_2\kappa_1'\kappa_1}$ is the Fermi factor; $\tilde{f}_{\kappa_2'\kappa_2\kappa_1'\kappa_1} = f(\tilde{\epsilon}_{\kappa_1\uparrow})(1-f(\tilde{\epsilon}_{\kappa_1'\uparrow}))f(\tilde{\epsilon}_{\kappa_2\downarrow})(1-f(\tilde{\epsilon}_{\kappa_2'\downarrow})$. $\tilde{\epsilon}_{\kappa\sigma} = \epsilon_{\kappa\sigma}-\mu$, $\epsilon_{\kappa\sigma}$ being the one-electron energy eigenvalue for $H_{\rm HB}$. $\Delta E_{\kappa_2'\kappa_2\kappa_1'\kappa_1} = \epsilon_{\kappa_2'\downarrow}-\epsilon_{\kappa_2\downarrow}+\epsilon_{\kappa_1'\uparrow}-\epsilon_{\kappa_1\uparrow}$ denotes the two-particle excitation energy from the ground state $|\phi_{\rm HB}\rangle$.

From the stationary condition $\delta\epsilon_c = 0$, we obtain the self-consistent equations for $\{\eta_{\kappa_2'\kappa_2\kappa_1'\kappa_1}\}$, and again obtain an approximate form variational parameters

$$\eta_{\kappa_2'\kappa_2\kappa_1'\kappa_1}(\tilde{\eta},\epsilon_c) = \frac{U\tilde{\eta}}{\Delta E_{\kappa_2'\kappa_2\kappa_1'\kappa_1}-\epsilon_c}. \tag{2.72}$$

Substituting the above expression into $\langle\tilde{H}\tilde{O}_i\rangle_{\rm HB}$,$\langle\tilde{O}_i^\dagger\tilde{H}\tilde{O}_i\rangle_{\rm HB}$, and $\langle\tilde{O}_i^\dagger\tilde{O}_i\rangle_{\rm HB}$, we have the forms such as $\langle\tilde{H}\tilde{O}_i\rangle_{\rm HB} = \langle\tilde{O}_i^*\tilde{H}\rangle_{\rm HB} = \tilde{A}U^2\tilde{\eta}$, $\langle\tilde{O}_i^\dagger\tilde{H}\tilde{O}_i\rangle_{\rm HB} = \tilde{B}U^2\tilde{\eta}^2$, and $\langle\tilde{O}_i^\dagger\tilde{O}_i\rangle_{\rm HB} = \tilde{C}U^2\tilde{\eta}^2$. Minimizing the energy ϵ_c with respect to $\tilde{\eta}$, we obtain

$$\tilde{\eta} = \frac{-\tilde{B}+\sqrt{\tilde{B}^2+4\tilde{A}^2\tilde{C}U^2}}{2\tilde{A}\tilde{C}U^2}. \tag{2.73}$$

The total energy should be obtained by taking the configurational average as

$$\langle H\rangle = \overline{\langle H\rangle}_{\rm HB} + N\overline{\epsilon_c}. \tag{2.74}$$

The HB ground state energy is given by

$$\begin{aligned}\overline{\langle H\rangle}_{\rm HB} = n\mu + \sum_\sigma \int_{-\infty}^0 \epsilon\overline{\rho_{i\sigma}(\epsilon)}d\epsilon \\ - (\bar{U}-\tilde{U})\overline{\langle\hat{n}_{i\uparrow}\rangle_{\rm HB}\langle\hat{n}_{i\downarrow}\rangle_{\rm HB}} - \tilde{U}(\overline{n_{i\uparrow}\hat{n}_{i\downarrow}\rangle_{\rm HB}} + \overline{n_{i\downarrow}\hat{n}_{i\uparrow}\rangle}_{\rm HB}).\end{aligned} \tag{2.75}$$

Here $\rho_{i\sigma}(\epsilon)$ is the local density of states (LDOS). It is obtained from the one-electron Green function

$$\rho_{i\sigma}(\epsilon) = -\frac{1}{\pi}{\rm Im}G_{ii\sigma}(z), \tag{2.76}$$

and the Green function $G_{ii\sigma}(z)$ is defined by Eq. (2.59), in which $\boldsymbol{H}_\sigma$ has been replaced by the one-electron Hamiltonian matrix for the HB Hamiltonian (2.64); $(\boldsymbol{H}_\sigma)_{ij} = (\epsilon_0-\mu+\bar{U}\langle\hat{n}_{i-\sigma}\rangle_{\rm HB}+\tilde{U}n_{i-\sigma})\delta_{ij}+t_{ij}(1-\delta_{ij})$. The average electron number $\langle\hat{n}_{i\sigma}\rangle_{\rm HB}$ is given by the LDOS as

$$\langle\hat{n}_{i\sigma}\rangle_{\rm HB} = \int f(\epsilon)\rho_{i\sigma}(\epsilon)d\epsilon. \tag{2.77}$$

Since the HB Hamiltonian contains a random potential and the energy $\overline{\langle H\rangle}_{\rm HB}$ is given by the LDOS, we can calculate the ground state energy by means of the alloy-analogy approximation, ($i.e.$, the CPA) as explained in the last subsection. In the CPA, we replace the random potentials at the surrounding sites with a coherent potential $\Sigma_\sigma(z)$. The on-site impurity Green function is obtained as follows:

$$G_{ii\sigma}(z) = \frac{1}{F_\sigma(z)^{-1}-\epsilon_0+\mu-\bar{U}\langle\hat{n}_{i-\sigma}\rangle_{\rm HB}-\tilde{U}n_{i-\sigma}+\Sigma_\sigma(z)}. \tag{2.78}$$

Here $F_\sigma(z)$ is the coherent Green function given by Eq. (2.61).

The self-consistent condition to determine the coherent potential $\Sigma_\sigma(z)$ is given by Eq. (2.62). However, $G_{ii\sigma}(z)$ for the HB potential fully depends on the 4 local configurations $\alpha = (n_{i\uparrow}, n_{i\downarrow})$ via the Hartree-Fock type potential $\bar{U}\langle\hat{n}_{i-\sigma}\rangle_{\rm HB}$ in the denominator. Thus the configurational average of $G_{00\sigma}$ is given by

$$\overline{G_{00\sigma}} = \sum_\alpha P_\alpha G^\alpha_{00\sigma}(z). \tag{2.79}$$

Here P_α is the probability when taking a configuration α. Note that instead of the configurations α = 00, 10, 01, 11, one can make use of an alternative notation ν = 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). In this notation, we can express P_α as P_0, $P_{1\uparrow}$, $P_{1\downarrow}$, and P_2. The impurity Green functions $G^\alpha_{00\sigma}(z)$ are given as follows:

$$G^{00}_{00\sigma}(z) = \frac{1}{F_\sigma(z)^{-1} - \epsilon_0 + \mu - \bar{U}\langle\hat{n}_{-\sigma}\rangle_{00} + \Sigma_\sigma(z)}, \tag{2.80}$$

$$G^{10}_{00\uparrow}(z) = \frac{1}{F_\sigma(z)^{-1} - \epsilon_0 + \mu - \bar{U}\langle\hat{n}_{\downarrow}\rangle_{10} + \Sigma_\sigma(z)}, \tag{2.81}$$

$$G^{10}_{00\downarrow}(z) = \frac{1}{F_\sigma(z)^{-1} - \epsilon_0 + \mu - \bar{U}\langle\hat{n}_{\uparrow}\rangle_{10} - \tilde{U} + \Sigma_\sigma(z)}, \tag{2.82}$$

$$G^{01}_{00\uparrow}(z) = \frac{1}{F_\sigma(z)^{-1} - \epsilon_0 + \mu - \bar{U}\langle\hat{n}_{\downarrow}\rangle_{01} - \tilde{U} + \Sigma_\sigma(z)}, \tag{2.83}$$

$$G^{01}_{00\downarrow}(z) = \frac{1}{F_\sigma(z)^{-1} - \epsilon_0 + \mu - \bar{U}\langle\hat{n}_{\uparrow}\rangle_{01} + \Sigma_\sigma(z)}, \tag{2.84}$$

$$G^{11}_{00\uparrow}(z) = \frac{1}{F_\sigma(z)^{-1} - \epsilon_0 + \mu - \bar{U}\langle\hat{n}_{-\sigma}\rangle_{11} - \tilde{U} + \Sigma_\sigma(z)}. \tag{2.85}$$

and the electron number for a given configuration in the denominators is given by

$$\langle\hat{n}_\sigma\rangle_\alpha = \int f(\epsilon)\rho^\alpha_\sigma(\epsilon)d\epsilon, \tag{2.86}$$

$$\rho^\alpha_\sigma(\epsilon) = -\frac{1}{\pi}{\rm Im}G^\alpha_{00\sigma}(z). \tag{2.87}$$

The above expressions mean that the electron numbers $\langle\hat{n}_\sigma\rangle_\alpha$ have to be solved self-consistently for a given configuration with probabilities $\{P_\alpha\}$ and for an effective medium $\Sigma_\sigma(z)$. The latter is obtained from the CPA Eq. (2.62).

The third and last terms at the rhs of Eq. (2.75) are calculated in the SSA as follows:

$$\overline{\langle\hat{n}_{i\uparrow}\rangle_{\rm HB}\hat{n}_{i\downarrow}\rangle_{\rm HB}} = \sum_\alpha P_\alpha\langle\hat{n}_{i\uparrow}\rangle_\alpha\langle\hat{n}_{i\downarrow}\rangle_\alpha, \tag{2.88}$$

$$\sum_{\sigma} \overline{n_{i\sigma}\langle \hat{n}_{i-\sigma}\rangle_{\rm HB}} = \sum_{\sigma}\sum_{\alpha} P_{\alpha} n_{\sigma}^{\alpha} \langle \hat{n}_{-\sigma}\rangle_{\alpha}. \tag{2.89}$$

Here $n_{\uparrow}^{\alpha}$ = 0, 1, 0,1 and $n_{\downarrow}^{\alpha}$= 0, 0, 1,1 for α= 00, 10, 01, 11, respectively.

The on-site probability satisfies the sum rule $P_0 + P_{1\uparrow} + P_{1\downarrow} + P_2$= 1, and the probability of finding an electron with spin $\uparrow$ ($\downarrow$) on a site is given by $P_{\uparrow(\downarrow)} = P_{1\uparrow(1\downarrow)} + P_2$. Therefore, $P_0, P_{1\uparrow}$, and $P_{1\downarrow}$are given by the probability P_2 in the paramagnetic state.

An approximate form of P_2 for the hybrid wavefunction is derived as follows. We have two kinds of approximate expressions for the operator $\hat{n}_{\uparrow}\hat{n}_{\downarrow}$ according to the alloy-analogy (AA) and Hartree-Fock (HF) approximation.

$$\hat{n}_{\uparrow}\hat{n}_{\downarrow} \approx n_{\uparrow}\hat{n}_{\downarrow} + n_{\downarrow}\hat{n}_{\uparrow} - n_{\uparrow}n_{\downarrow} \quad ({\rm AA}), \tag{2.90}$$

$$\hat{n}_{\uparrow}\hat{n}_{\downarrow} \approx \hat{n}_{\uparrow}\langle \hat{n}_{\downarrow}\rangle_{\rm HB} + \hat{n}_{\downarrow}\langle \hat{n}_{\uparrow}\rangle_{\rm HB} - \langle \hat{n}_{\uparrow}\rangle_{\rm HB}\langle \hat{n}_{\downarrow}\rangle_{\rm HB} \quad ({\rm HF}). \tag{2.91}$$

In the HB scheme, we superpose the above expressions with the weights w and $1-w$, respectively. Taking the quantum mechanical and configurational average, we obtain an approximate form of $P_2 (= \overline{\langle \hat{n}_{\uparrow}\hat{n}_{\downarrow}\rangle})$. Then, we have the term $w\overline{\langle n_{\uparrow}n_{\downarrow}\rangle} + (1-w)\overline{\langle \hat{n}_{\uparrow}\rangle_{\rm HB}\langle \hat{n}_{\downarrow}\rangle_{\rm HB}}$ at the rhs, which may be again regarded as the probability P_2 in the HB scheme. Thus we obtain an approximate form of P_2 as follows:

$$P_2 = \frac{1}{2} w(\overline{n_{\uparrow}\langle \hat{n}_{\downarrow}\rangle_{\rm HB}} + \overline{n_{\downarrow}\langle \hat{n}_{\uparrow}\rangle_{\rm HB}}) + (1-w)\overline{\langle \hat{n}_{\uparrow}\rangle_{\rm HB}\langle \hat{n}_{\downarrow}\rangle_{\rm HB}}. \tag{2.92}$$

Since the rhs of Eq. (2.92) is given by Eqs. (2.88) and (2.89), we can self-consistently obtain the probabilities $\{P_{\alpha}\}$.

Finally, the correlation energy $\bar{\epsilon}_c$ is obtain as

$$\bar{\epsilon}_c = \sum_{\alpha} P_{\alpha}\epsilon_{c\alpha}. \tag{2.93}$$

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

$$\epsilon_{c\alpha} = \Big[\frac{-\langle \tilde{O}_i^{\dagger}\tilde{H}\rangle_{\rm HB} - \langle \tilde{H}\tilde{O}_i\rangle_{\rm HB} + \langle \tilde{O}_i^{\dagger}\tilde{H}\tilde{O}_i\rangle_{\rm HB}}{1 + \langle \tilde{O}_i^{\dagger}\tilde{O}_i\rangle_{\rm HB}}\Big]_{\alpha}. \tag{2.94}$$

The quantities $\langle \tilde{H}\tilde{O}_i\rangle_{\rm HB}$, $\langle \tilde{O}_i^{\dagger}\tilde{H}\tilde{O}_i\rangle_{\rm HB}$, and $\langle \tilde{O}_i^{\dagger}\tilde{O}_i\rangle_{\rm HB}$ are expressed by the LDOS for the HB Hamiltonian, therefore the correlation energy $\epsilon_{c\alpha}$ is obtained from the LDOS $\rho_{\sigma}^{\alpha}(\epsilon)$ in the single-site CPA.

The double occupation number is obtained from $\partial\langle H\rangle/\partial U$. Making use of the SSA, we obtain

$$\overline{\langle \hat{n}_{\uparrow}\hat{n}_{\downarrow}\rangle} = \overline{\langle \hat{n}_{\uparrow}\rangle_{\rm HB}\langle \hat{n}_{\downarrow}\rangle_{\rm HB}} + \overline{\langle \hat{n}_{\uparrow}\hat{n}_{\downarrow}\rangle}_c. \tag{2.95}$$

Here $\overline{\langle \hat{n}_{\uparrow}\rangle_{\rm HB}\langle \hat{n}_{\downarrow}\rangle_{\rm HB}}$ has been obtained in Eq. (2.88), and the correlation correction $\overline{\langle \hat{n}_{\uparrow}\hat{n}_{\downarrow}\rangle}_c$ is given by

$$\overline{\langle \hat{n}_{\uparrow}\hat{n}_{\downarrow}\rangle}_c = \sum_{\alpha} P_{\alpha}\langle \hat{n}_{\uparrow}\hat{n}_{\downarrow}\rangle_{c\alpha}. \tag{2.96}$$

Here $\langle \hat{n}_\uparrow \hat{n}_\downarrow \rangle_{c\alpha}$ is the correlation correction for a given configuration α, and is given by Eq. (2.53) in which the operator $\tilde{O}_i$ has been replaced by Eq. (2.66) and the average $\langle \sim \rangle$ has been replaced by $\langle \sim \rangle_{\rm HB}$.

The momentum distribution $\langle n_{k\sigma} \rangle$ is obtained from $\partial \langle H \rangle / \partial (\epsilon_k - \sigma h)$ as follows:

$$\langle n_{k\sigma} \rangle = \overline{\langle n_{k\sigma} \rangle}_{\rm HB} + \overline{\langle n_{k\sigma} \rangle}_c. \tag{2.97}$$

Here $\overline{\langle n_{k\sigma} \rangle}_{\rm HB}$ is the momentum distribution in the hybrid state.

$$\overline{\langle n_{k\sigma} \rangle}_{\rm HB} = \int f(\epsilon) \rho_{k\sigma}(\epsilon) d\epsilon, \tag{2.98}$$

$$\rho_{k\sigma}(\epsilon) = -\frac{1}{\pi} {\rm Im} F_{k\sigma}. \tag{2.99}$$

The Green function in the momentum representation is given in the CPA as follows:

$$F_{k\sigma} = \frac{1}{z - \Sigma_\sigma(z) - \epsilon_k}. \tag{2.100}$$

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

The correlation correction $\overline{\langle n_{k\sigma} \rangle}_c$ is given as follows:

$$\overline{\langle n_{k\sigma} \rangle}_c = \sum_\alpha P_\alpha \langle n_{k\sigma} \rangle_{c\alpha}. \tag{2.101}$$

Here $\langle n_{k\sigma} \rangle_{c\alpha}$ is the correlation correction for the configuration α, and is given by the second term at the rhs of Eq. (2.50) in which $\tilde{O}_i$ has been replaced by Eq. (2.66) and the average $\langle \sim \rangle$ has been replaced by $\langle \sim \rangle_{\rm HB}$.

2.5.5 Numerical results of MLA with hybrid wavefunction

The MLA with HB wavefunction improves further for the description of electron correlations in the strongly correlated region. One can verify the fact by means of some numerical calculations in infinite dimensions. The ground state energy in the MLA-HB was obtained by varying w from 0 to 1 for each value of U. Figure 2.5 shows the ground state energy obtained by various methods on the hypercubic lattice in infinite dimensions at half-filling. The energy in the LA monotonically increases with increasing Coulomb interaction energy and becomes positive beyond U = 3.4 because it does not suppress sufficiently the double occupancy in the strongly correlated region.

The ground state energy in the GW is lower than that of the LA, and approaches zero at U_c (GW) = 4.51 with increasing Coulomb interaction. The Brinkman-Rice atomic state is realized beyond U_c (GW). The ground state energy of the MLA-HB is the lowest among three wavefunctions over all Coulomb interactions U. Note that there is a cusp in the energy versus U curve at U_c (MLA) = 2.81. The Fermi-liquid ground state with w = 0 is obtained below U_c (MLA), while the disordered local moment solution with infinitesimal w is stabilized beyond U_c (MLA) [49].

As shown in Fig. 2.6, the double occupation number $\langle n_\uparrow n_\downarrow \rangle$ in the GW linearly decreases with increasing U according to Eq. (2.9). In the case of the LA, it monotonically decreases according to Eq. (2.14). The double occupation number in the MLA-HB is lower than that in the LA and GW in the weak Coulomb interaction regime and jumps from 0.106 to 0.045 at U_c (MLA) = 2.81,

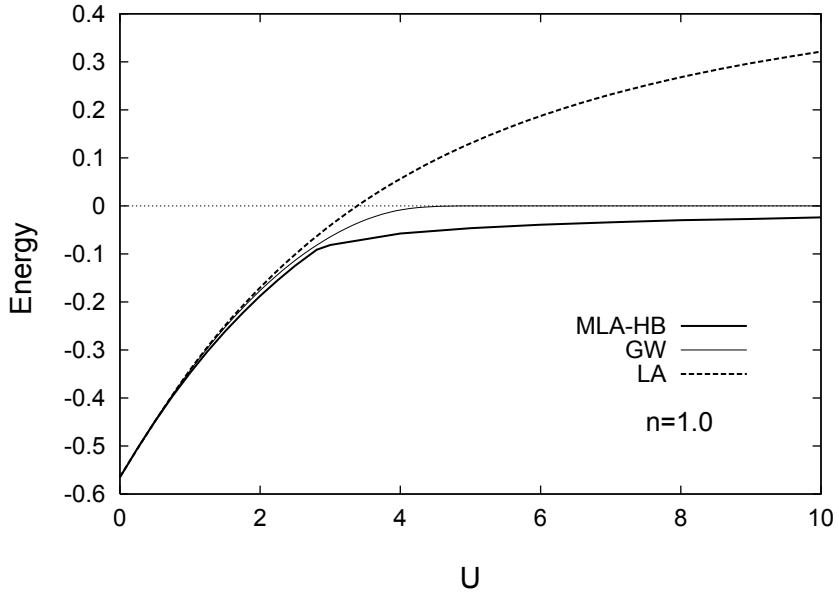

Figure 2.5: The energy versus Coulomb interaction energy U curves in the MLA-HB (solid curve), the GW (thin solid curve), and the LA (dotted curve) at half-filling (n = 1.0) (Ref. [49]).

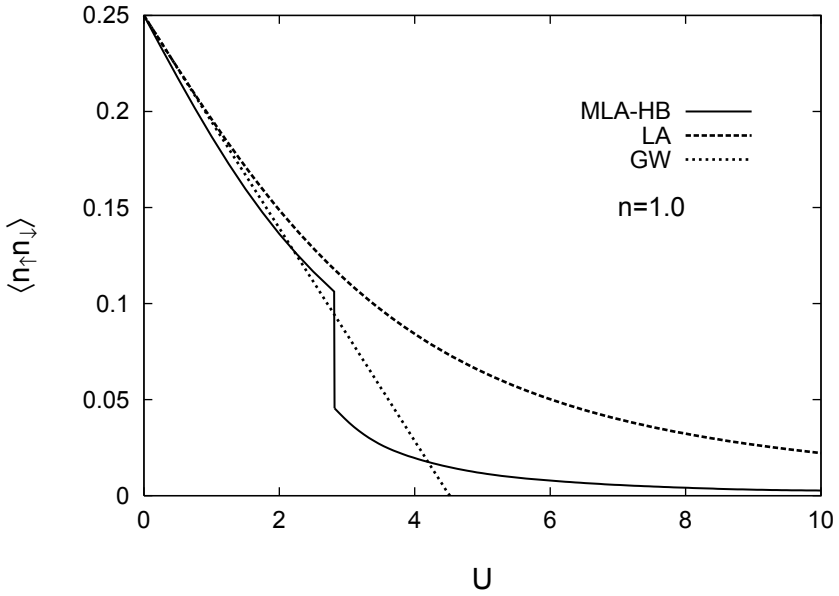

Figure 2.6: The double occupation $\langle n_\uparrow n_\downarrow \rangle$ number versus Coulomb interaction energy U curves in the MLA-HB (solid curve), the GW (dotted curve), and the LA (dot-dashed curve) at half-filling (n = 1.0) (Ref. [49]).

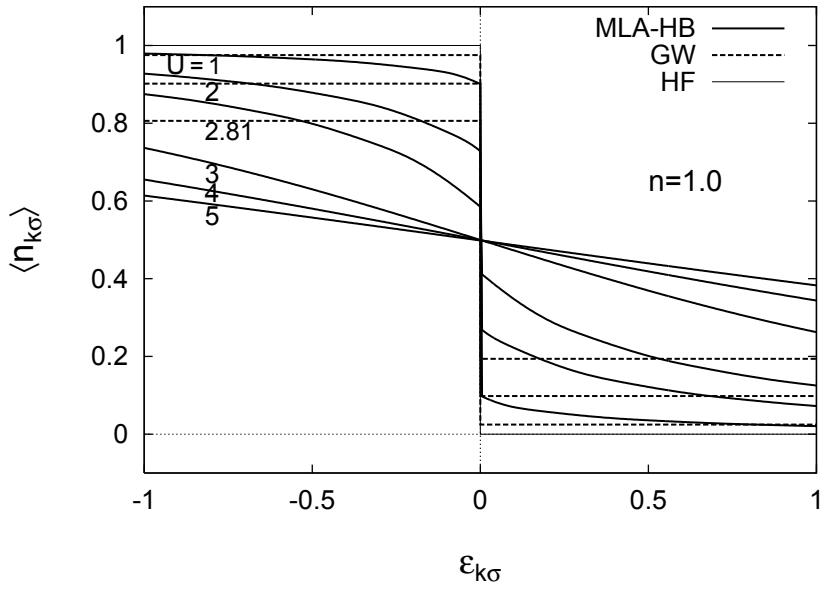

Figure 2.7: The momentum distribution as a function of energy $\epsilon_{k\sigma}$ for various Coulomb interaction energy parameters U=1.0, 2.0, 2.81,4.0, and 5.0 at half-filling (n = 1.0) (Ref. [49]). The MLA: solid curves, the LA: dashed curves.

indicating the metal-insulator transition. Beyond U_c (MLA), it again monotonically decreases 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, because the MLA takes into account the electron hopping from the atomic state.

The momentum distribution in the MLA-HB has the same behavior as the MLA-HF in the metallic region; it decreases monotonically with increasing energy $\epsilon_{k\sigma}$ and shows a jump at the Fermi level, while it disappears beyond U_c (MLA) as shown in Fig. 2.7. With further increase of U, the curve becomes flatter. These results indicate that the MLA-HB improves upon the GW. Note that the distributions in the GW are constant below and above the Fermi level irrespective of U. The quasiparticle weight in the MLA-HB is the same as in the MLA-HF in the metallic region (see Fig. 2.4). With the metal-insulator transition at U_c (MLA) = 2.81, it disappears. The existence of the first-order transition at $U = U_c$ is in agreement with the result of the NRG [67], though U_c in the NRG has not yet been published.

Chapter 3

First-Principles Momentum Dependent Local Ansatz Wavefunction

In the last chapter we discussed recent development of wavefunction method. Most of the wavefunction methods do not reduce to the exact Rayleigh-Schrödinger perturbation theory in the weak interaction limit. In this chapter we introduce the tight-binding LDA+U Hamiltonian, and construct the first-principles momentum dependent local ansatz wavefunction (MLA). Within the single-site approximation (SSA), we derive the correlation energy, the self-consistent equations for variational parameters, and other physical quantities.

3.1 Tight-binding LDA+U Hamiltonian

We consider the transition-metal system with an atom in the unit cell for simplicity, and adopt the first-principles LDA+U Hamiltonian, which is based on the tight-binding linear muffin-tin orbital method. [27, 31]

$$H = H_1 + H_2 \,. \tag{3.1}$$

H_1 and H_2 denote the non-interacting and interacting parts of the Hamiltonian H. The former is given by

$$H_1 = \sum_{iL\sigma} \epsilon_L^0 \, \hat{n}_{iL\sigma} + \sum_{iLjL'\sigma} t_{iLjL'} \, a_{iL\sigma}^\dagger \, a_{jL'\sigma} \,. \tag{3.2}$$

Here ϵ_L^0 is the atomic level of orbital L on site i. $t_{iLjL'}$ is the transfer integral between iL and jL'. $L = (l, m)$ denotes the $s\,(l = 0)$, $p\,(l = 1)$, and $d\,(l = 2)$ orbitals. $a_{iL\sigma}^\dagger (a_{iL\sigma})$ is the creation (annihilation) operator for an electron on site i with orbital L and spin σ, and $\hat{n}_{iL\sigma} = a_{iL\sigma}^\dagger a_{iL\sigma}$ is the number operator. The atomic level ϵ_L^0 in H_1 is calculated from the LDA atomic level ϵ_L by subtracting the double counting potential as $\epsilon_L^0 = \epsilon_L - \partial E_{\rm LDA}^{\rm U} / \partial n_{iL\sigma}$. Here $n_{iL\sigma}$ is the charge density at the ground-state, $E_{\rm LDA}^{\rm U}$ is a LDA functional for the intra-atomic Coulomb interactions.

In the LDA+U Hamiltonian we assume that the sp electrons are well described by the LDA in the band theory, and take into account only on-site Coulomb interactions between $d\,(l = 2)$ electrons, so that the interaction part H_2 in Eq. (3.1) is expressed as follows.

$$H_2 = \sum_i \Big[\sum_m U_{mm} \, \hat{n}_{ilm\uparrow} \, \hat{n}_{ilm\downarrow} + \sum_{(m,m')} \Big(U_{mm'} - \frac{1}{2} J_{mm'} \Big) \, \hat{n}_{ilm} \, \hat{n}_{ilm'} - 2 \sum_{(m,m')} J_{mm'} \, \hat{\boldsymbol{s}}_{ilm} \cdot \hat{\boldsymbol{s}}_{ilm'} \Big] \,. \tag{3.3}$$

Here $U_{mm}\,(U_{mm'})$ and $J_{mm'}$ denote the intra-orbital (inter-orbital) Coulomb and exchange interactions between d electrons, respectively. $\hat{n}_{ilm}\,(\hat{\boldsymbol{s}}_{ilm})$ with $l = 2$ is the charge (spin) density operator for d electrons on site i and orbital m. The operator $\hat{\boldsymbol{s}}_{iL}$ is defined as $\hat{\boldsymbol{s}}_{iL} = \sum_{\gamma\gamma'} a^{\dagger}_{iL\gamma}(\boldsymbol{\sigma})_{\gamma\gamma'}\, a_{iL\gamma'}/2$. $\boldsymbol{\sigma}$ denotes the Pauli spin matrices.

We note that the charge and spin fluctuations are defined as follows.

$$\delta\hat{n}_{ilm\uparrow}\delta\hat{n}_{ilm\downarrow} = \hat{n}_{ilm\uparrow}\hat{n}_{ilm\downarrow} - \langle n_{ilm\uparrow}\rangle_0\hat{n}_{ilm\downarrow} - \langle n_{ilm\downarrow}\rangle_0\hat{n}_{ilm\uparrow} + \langle n_{ilm\uparrow}\rangle_0\langle n_{ilm\downarrow}\rangle_0, \tag{3.4}$$

$$\delta\hat{n}_{ilm}\delta\hat{n}_{ilm'} = \hat{n}_{ilm}\hat{n}_{ilm'} - \langle n_{ilm}\rangle_0\hat{n}_{ilm'} - \langle n_{ilm'}\rangle_0\hat{n}_{ilm} + \langle n_{ilm}\rangle_0\langle n_{ilm'}\rangle_0, \tag{3.5}$$

$$\delta\hat{\boldsymbol{s}}_{ilm}\cdot\delta\hat{\boldsymbol{s}}_{ilm'} = \hat{\boldsymbol{s}}_{ilm}\cdot\hat{\boldsymbol{s}}_{ilm'} - \langle \boldsymbol{s}_{ilm}\rangle_0\cdot\hat{\boldsymbol{s}}_{ilm'} - \langle \boldsymbol{s}_{ilm'}\rangle_0\cdot\hat{\boldsymbol{s}}_{ilm} + \langle \boldsymbol{s}_{ilm}\rangle_0\cdot\langle \boldsymbol{s}_{ilm'}\rangle_0. \tag{3.6}$$

Here δA for an operator A is defined by $\delta A = A - \langle A\rangle_0$, $\langle\sim\rangle_0$ being the average in the Hartree-Fock approximation. Using the above relations, we can rewrite the Hamiltonian H as the sum of the Hartree-Fock Hamiltonian H_0 and the residual interactions $H_{\rm I}$.

$$H = H_0 + H_{\rm I}. \tag{3.7}$$

The Hartree-Fock Hamiltonian H_0 is obtained as

$$\begin{aligned} H_0 = &\sum_{iL\sigma}\Big(\epsilon^0_{iL} + \Big[U_{mm}\langle n_{ilm-\sigma}\rangle_0 + \sum_{m'\neq m}(U_{mm'} - \frac{1}{2}J_{mm'})\langle n_{ilm}\rangle_0 \\ &- \frac{1}{2}\sum_{m'\neq m} J_{mm'}\langle m_{ilm'}\rangle_0\sigma\Big]\delta_{ld}\Big)\hat{n}_{iL\sigma} + \sum_{iLjL'\sigma} t_{iLjL'}a^{\dagger}_{iL\sigma}\,a_{jL'\sigma} \\ &- \sum_{im} U_{mm}\langle n_{idm\uparrow}\rangle_0\langle n_{idm\downarrow}\rangle_0 - \sum_i\sum_{(m,m')}(U_{mm'} - \frac{1}{2}J_{mm'})\langle n_{idm}\rangle_0\langle n_{idm}\rangle_0 \\ &+ 2\sum_i\sum_{(m,m')} J_{mm'}\langle \boldsymbol{s}_{ilm}\rangle_0\cdot\langle \boldsymbol{s}_{ilm'}\rangle_0\,. \end{aligned} \tag{3.8}$$

The last three parts are known as the double counting (d.c.) terms.

The residual interaction $H_{\rm I}$ is given by

$$H_{\rm I} = \sum_i\Big[\sum_L U^{(0)}_{LL}\,O^{(0)}_{iLL} + \sum_{(L,L')} U^{(1)}_{LL'}\,O^{(1)}_{iLL'} + \sum_{(L,L')} U^{(2)}_{LL'}\,O^{(2)}_{iLL'}\Big]. \tag{3.9}$$

The first term denotes the intra-orbital interactions, the second term is the inter-orbital charge-charge interactions, and the third term expresses the inter-orbital spin-spin interactions, respectively. The Coulomb interaction energy parameters $U^{(\alpha)}_{LL'}$ are defined by $U_{LL}\delta_{LL'}$ $(\alpha = 0)$, $U_{LL'} - J_{LL'}/2$ $(\alpha = 1)$, and $-2J_{LL'}$ $(\alpha = 2)$, respectively. The two-particle operators $O^{(0)}_{iLL}$, $O^{(1)}_{iLL'}$, and $O^{(2)}_{iLL'}$ are defined by

$$O^{(0)}_{iLL} = \delta\hat{n}_{ilm\uparrow}\,\delta\hat{n}_{ilm\downarrow}\,, \tag{3.10}$$

$$O^{(1)}_{iLL'} = \delta\hat{n}_{ilm}\,\delta\hat{n}_{ilm'}\,, \tag{3.11}$$

$$O^{(2)}_{iLL'} = \delta\hat{\boldsymbol{s}}_{ilm}\cdot\delta\hat{\boldsymbol{s}}_{ilm'}\,. \tag{3.12}$$

3.2 Wavefunction in the weak Coulomb interaction limit

We clarify here the exact form of the wavefunction in the weak Coulomb interaction limit on the basis of the Rayleigh-Schrödinger perturbation theory.

The eigen-value equation for the ground-state is given by

$$H|\Psi\rangle = E|\Psi\rangle. \tag{3.13}$$

The Hamiltonian H is expressed as the sum of the Hartree-Fock Hamiltonian H_0 and the residual interaction $H_{\rm I}$.

$$H = H_0 + H_{\rm I}. \tag{3.14}$$

The zeroth-order Hartree-Fock eigenvalues and the eigenfunctions are obtained from the eigen-value equation as follows.

$$H_0|\phi_n\rangle = E_n^{(0)}|\phi_n\rangle. \tag{3.15}$$

The energy eigen-value $E_n^{(0)}$ is given by

$$E_n^{(0)} = \sum_{\nu k\sigma} \epsilon_{k\nu\sigma}\hat{n}_{k\nu\sigma} - {\rm d.c.} \tag{3.16}$$

Here $\epsilon_{k\nu\sigma}$ is the Hartree-Fock one electron energy eigenvalue with momentum k, band index ν, and spin σ. The second term $'{\rm d.c.}'$ at the rhs of Eq. (3.16) denotes the Hartree-Fock double counting term as found in Eq. (3.8). The wavefunction $|\phi_n\rangle$ is given by

$$|\phi_n\rangle = \Big[\prod_{k\nu}(a^\dagger_{k\nu\uparrow})^{n_{k\nu\uparrow}}\Big]\Big[\prod_{k\nu}(a^\dagger_{k\nu\downarrow})^{n_{k\nu\downarrow}}\Big]|0\rangle. \tag{3.17}$$

Here we assume that $|\phi_0\rangle$ is the ground state of H_0, and $E_0^{(0)}$ is the Hartree-Fock ground-state energy.

According to the Rayleigh-Schrödinger perturbation theory for the nondegenerate ground-state, the wavefunction is given as follows.

$$\begin{aligned}|\Psi\rangle &= |\psi_0\rangle + |\psi_1\rangle + \cdots \\ &= |\phi_0\rangle - \sum_{n\neq 0}|\phi_n\rangle\frac{\langle\phi_n|H_I|\phi_0\rangle}{E_n^{(0)} - E_0^{(0)}} + \cdots .\end{aligned} \tag{3.18}$$

The ground-state energy is obtained as

$$\begin{aligned}E =& E^{(0)} + E^{(1)} + \cdots \\ &= E_0^{(0)} + \langle\phi_0|H_I|\phi_0\rangle + \cdots .\end{aligned} \tag{3.19}$$

The zeroth-order energy is given by

$$\begin{aligned}E_0^{(0)} =& \sum_{k\nu\sigma}^{occ}\epsilon_{\nu k\sigma} - \sum_{im} U_{mm}\langle n_{idm\uparrow}\rangle_0\langle n_{idm\downarrow}\rangle_0 \\ &- \sum_i\sum_{(m,m)}(U_{mm'} - \frac{1}{2}J_{mm'})\langle n_{idm}\rangle_0\langle n_{idm'}\rangle_0 + 2\sum_i\sum_{(m,m)} J_{mm'}\langle \boldsymbol{s}_{ilm}\rangle_0\cdot\langle \boldsymbol{s}_{ilm'}\rangle_0.\end{aligned} \tag{3.20}$$

The first-order correction vanishes as follows.

$$\begin{aligned} E^{(1)} &= \langle\phi_0|H_I|\phi_0\rangle \\ &= \sum_i \Big[\sum_L U^{(0)}_{LL}\ \langle O^{(0)}_{iLL}\rangle_0 + \sum_{(L,L')} U^{(1)}_{LL'}\ \langle O^{(1)}_{iLL'}\rangle_0 + 2 \sum_{(L,L')} U^{(2)}_{LL'}\ \langle O^{(2)}_{iLL'}\rangle_0 \Big] = 0\ , \end{aligned} \tag{3.21}$$

since $\langle O^{(0)}_{iLL}\rangle_0 = \langle O^{(1)}_{iLL'}\rangle_0 = \langle O^{(2)}_{iLL'}\rangle_0 = 0$.

The first-order correction to the wavefunction is expressed as

$$|\psi_1\rangle = \lim_{z\to 0} \sum_{n\neq 0} \frac{1}{z - E^{(0)}_n + E^{(0)}_0} |\phi_n\rangle\langle\phi_n|H_I|\phi_0\rangle. \tag{3.22}$$

Because $\langle\phi_0|H_I|\phi_0\rangle = 0$, Eq. (3.22) is expressed as follows.

$$|\psi_1\rangle = \lim_{z\to 0} \frac{1}{z - \tilde{H}_0} H_I|\phi_0\rangle. \tag{3.23}$$

Here $\tilde{H}_0 = H_0 - \langle H\rangle_0$.

Now assume that $\{\chi_{iL}(\boldsymbol{r})\}$ is an orthogonal basis set consisting of the local orbitals with L on site i and $\{\psi_{kn\sigma}(\boldsymbol{r})\}$ are the Hartree-Fock one-electron energy eigenfunction with momentum k, band index n, and spin σ. The field operator $\varphi_\sigma(\boldsymbol{r})$ is then expressed as follows

$$\varphi_\sigma(\boldsymbol{r}) = \sum_{iL} a_{iL\sigma}\chi_{iL}(\boldsymbol{r}) = \sum_{kn} a_{kn\sigma}\psi_{kn\sigma}(\boldsymbol{r}). \tag{3.24}$$

Here $a_{kn\sigma}$ is the annihilation operator for the electron with momentum k, band index n, and spin σ. They are defined as

$$a_{kn\sigma} = \sum_{iL} a_{iL\sigma}\langle kn|iL\rangle_\sigma, \tag{3.25}$$

$$\psi_{kn\sigma}(\boldsymbol{r}) = \sum_{iL} \chi_{iL}(\boldsymbol{r})\langle iL|kn\rangle_\sigma, \tag{3.26}$$

and

$$\langle iL|kn\rangle_\sigma = u_{Ln\sigma}(\boldsymbol{k})\frac{1}{\sqrt{N}} e^{-i\boldsymbol{k}\cdot\boldsymbol{R}_i}. \tag{3.27}$$

Here $u_{Ln\sigma}(\boldsymbol{k})$ is the eigen vector at a given $\boldsymbol{k}$ point. We also assumed one atom per unit cell for simplicity.

Using the relations (3.25), the intra-orbital, inter-orbital charge-charge and inter-orbital spin-spin operator are expressed in the momentum representation as follows.

$$\begin{aligned} O^{(0)}_{iLL} &= \delta\hat{n}_{idm\uparrow}\delta\hat{n}_{idm\downarrow} \\ &= \sum_{\{kn\}} \langle k'_1 n'_1|iL\rangle_\uparrow\langle iL|k_1 n_1\rangle_\uparrow\langle k'_2 n'_2|iL\rangle_\downarrow\langle iL|k_2 n_2\rangle_\downarrow \\ &\times \delta(a^\dagger_{k'_2 n'_2\downarrow} a_{k_2 n_2\downarrow})\delta(a^\dagger_{k'_1 n'_1\uparrow} a_{k_1 n_1\uparrow}), \end{aligned} \tag{3.28}$$

$$
\begin{aligned}
O^{(1)}_{iLL'} &= \delta\hat{n}_{idm}\delta\hat{n}_{idm'} \\
&= \sum_{\{kn\sigma\}} \langle k'_1 n'_1|iL'\rangle_\sigma \langle iL'|k_1 n_1\rangle_\sigma \langle k'_2 n'_2|iL\rangle_{\sigma'} \langle iL|k_2 n_2\rangle_{\sigma'} \\
&\times \delta(a^\dagger_{k'_2 n'_2 \sigma'} a_{k_2 n_2 \sigma'})\delta(a^\dagger_{k'_1 n'_1 \sigma} a_{k_1 n_1 \sigma}),
\end{aligned} \tag{3.29}
$$

$$
\begin{aligned}
O^{(2)}_{iLL'} &= \delta\hat{\boldsymbol{s}}_{idm} \cdot \delta\hat{\boldsymbol{s}}_{idm'} \\
&= \sum_{\{kn\sigma\}} \langle k'_1 n'_1|iL'\rangle_{\sigma'} \langle iL'|k_1 n_1\rangle_\sigma \langle k'_2 n'_2|iL\rangle_{\sigma'''} \langle iL|k_2 n_2\rangle_{\sigma''} \\
&\times \frac{1}{4}(\boldsymbol{\sigma})_{\sigma\sigma'}(\boldsymbol{\sigma})_{\sigma'''\sigma''}\delta(a^\dagger_{k'_2 n'_2 \sigma'''} a_{k_2 n_2 \sigma''})\delta(a^\dagger_{k'_1 n'_1 \sigma'} a_{k_1 n_1 \sigma}).
\end{aligned} \tag{3.30}
$$

Note that the last part of the rhs of the above equation is written as

$$
\begin{aligned}
&\frac{1}{4}(\boldsymbol{\sigma})_{\sigma\sigma'} \cdot (\boldsymbol{\sigma})_{\sigma'''\sigma''}\delta(a^\dagger_{k'_2 n'_2 \sigma'''} a_{k_2 n_2 \sigma''})\delta(a^\dagger_{k'_1 n'_1 \sigma'} a_{k_1 n_1 \sigma}) \\
&= \frac{1}{2}\delta_{\sigma'\uparrow}\delta_{\sigma\downarrow}\delta_{\sigma'''\downarrow}\delta_{\sigma''\uparrow}\delta(a^\dagger_{k'_2 n'_2 \downarrow} a_{k_2 n_2 \uparrow})\delta(a^\dagger_{k'_1 n'_1 \downarrow} a_{k_1 n_1 \uparrow}) \\
&+ \frac{1}{2}\delta_{\sigma'\downarrow}\delta_{\sigma\uparrow}\delta_{\sigma'''\uparrow}\delta_{\sigma''\downarrow}\delta(a^\dagger_{k'_2 n'_2 \uparrow} a_{k_2 n_2 \downarrow})\delta(a^\dagger_{k'_1 n'_1 \uparrow} a_{k_1 n_1 \downarrow}) \\
&+ \frac{1}{4}\sigma\sigma''\delta(a^\dagger_{k'_2 n'_2 \sigma''} a_{k_2 n_2 \sigma''})\delta(a^\dagger_{k'_1 n'_1 \sigma} a_{k_1 n_1 \sigma}).
\end{aligned} \tag{3.31}
$$

Substituting Eq. (3.31) into Eq. (3.30), we obtain

$$
\begin{aligned}
O^{(2)}_{iLL'} &= \sum_{\{kn\sigma\}} \langle k'_1 n'_1|iL'\rangle_{\sigma'} \langle iL'|k_1 n_1\rangle_\sigma \langle k'_2 n'_2|iL\rangle_{\sigma'''} \langle iL|k_2 n_2\rangle_{\sigma''} \\
&\times \frac{1}{2}\Big[\delta_{\sigma'\uparrow}\delta_{\sigma\downarrow}\delta_{\sigma'''\downarrow}\delta_{\sigma''\uparrow}\delta(a^\dagger_{k'_2 n'_2 \downarrow} a_{k_2 n_2 \uparrow})\delta(a^\dagger_{k'_1 n'_1 \downarrow} a_{k_1 n_1 \uparrow}) \\
&+ \delta_{\sigma'\downarrow}\delta_{\sigma\uparrow}\delta_{\sigma'''\uparrow}\delta_{\sigma''\downarrow}\delta(a^\dagger_{k'_2 n'_2 \uparrow} a_{k_2 n_2 \downarrow})\delta(a^\dagger_{k'_1 n'_1 \uparrow} a_{k_1 n_1 \downarrow}) \\
&+ \frac{1}{2}\sigma\sigma''\delta(a^\dagger_{k'_2 n'_2 \sigma''} a_{k_2 n_2 \sigma''})\delta(a^\dagger_{k'_1 n'_1 \sigma} a_{k_1 n_1 \sigma})\Big].
\end{aligned} \tag{3.32}
$$

Substituting Eq. (3.9) with Eqs. (3.28), (3.29), and (3.32) into Eq. (3.23), and using Eqs. (3.16)

and (3.20), we obtain the first-order correction of the wavefunction as follows.

$$
\begin{aligned}
|\psi_1\rangle = \sum_i \Big[& \sum_L \sum_{\{kn\}} \langle k_1' n_1' | iL\rangle_\uparrow \langle iL | k_1 n_1\rangle_\uparrow \langle k_2' n_2' | iL\rangle_\downarrow \langle iL | k_2 n_2\rangle_\downarrow \\
& \times \eta_{Lk_2'n_2'k_2n_2k_1'n_1'k_1n_1} \delta(a^\dagger_{k_2'n_2'\downarrow} a_{k_2n_2\downarrow}) \delta(a^\dagger_{k_1'n_1'\uparrow} a_{k_1n_1\uparrow}) |\phi_0\rangle \\
& + \sum_{(L,L')} \sum_{\{kn\}} \sum_{\sigma\sigma'} \langle k_1' n_1' | iL'\rangle_\sigma \langle iL' | k_1 n_1\rangle_\sigma \langle k_2' n_2' | iL\rangle_{\sigma'} \langle iL | k_2 n_2\rangle_{\sigma'} \\
& \times \zeta^{(\sigma'\sigma)}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1} \delta(a^\dagger_{k_2'n_2'\sigma'} a_{k_2n_2\sigma'}) \delta(a^\dagger_{k_1'n_1'\sigma} a_{k_1n_1\sigma}) |\phi_0\rangle \\
& - \sum_{(L,L')} \sum_{\{kn\}} \Big[\langle k_1' n_1' | iL'\rangle_\uparrow \langle iL' | k_1 n_1\rangle_\downarrow \langle k_2' n_2' | iL\rangle_\downarrow \langle iL | k_2 n_2\rangle_\uparrow \\
& \times \xi^{(+)}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1} \delta(a^\dagger_{k_2'n_2'\downarrow} a_{k_2n_2\uparrow}) \delta(a^\dagger_{k_1'n_1'\uparrow} a_{k_1n_1\downarrow}) |\phi_0\rangle \\
& + \langle k_1' n_1' | iL'\rangle_\downarrow \langle iL' | k_1 n_1\rangle_\uparrow \langle k_2' n_2' | iL\rangle_\uparrow \langle iL | k_2 n_2\rangle_\downarrow \\
& \times \xi^{(-)}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1} \delta(a^\dagger_{k_2'n_2'\uparrow} a_{k_2n_2\downarrow}) \delta(a^\dagger_{k_1'n_1'\downarrow} a_{k_1n_1\uparrow}) |\phi_0\rangle \\
& + \frac{1}{2} \sum_{\sigma\sigma''} \sigma\sigma'' \langle k_1' n_1' | iL'\rangle_\sigma \langle iL' | k_1 n_1\rangle_\sigma \langle k_2' n_2' | iL\rangle_{\sigma''} \langle iL | k_2 n_2\rangle_{\sigma''} \\
& \times \xi^{(\sigma''\sigma)}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1} \delta(a^\dagger_{k_2'n_2'\sigma''} a_{k_2n_2\sigma''}) \delta(a^\dagger_{k_1'n_1'\sigma} a_{k_1n_1\sigma}) |\phi_0\rangle \Big] \Big].
\end{aligned} \tag{3.33}
$$

Here the momentum-dependent parameters $\eta_{Lk_2'n_2'k_2n_2k_1'n_1'k_1n_1}$, $\zeta^{(\sigma'\sigma)}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1}$, $\xi^{(+)}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1}$, $\xi^{(-)}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1}$, and $\xi^{(\sigma'\sigma)}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1}$ are defined as follows

$$
\eta_{Lk_2'n_2'k_2n_2k_1'n_1'k_1n_1} = \frac{U_{LL}}{z - \epsilon_{k_2'n_2'\downarrow} + \epsilon_{k_2n_2\downarrow} - \epsilon_{k_1'n_1'\uparrow} + \epsilon_{k_1n_1\uparrow}}, \tag{3.34}
$$

$$
\zeta^{(\sigma'\sigma)}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1} = \frac{(U_{LL'} - J_{LL'}/2)}{z - \epsilon_{k_2'n_2'\sigma} + \epsilon_{k_2n_2\sigma} - \epsilon_{k_1'n_1'\sigma'} + \epsilon_{k_1n_1\sigma'}}, \tag{3.35}
$$

$$
\xi^{(+)}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1} = \frac{-J_{LL'}}{z - \epsilon_{k_2'n_2'\downarrow} + \epsilon_{k_2n_2\uparrow} - \epsilon_{k_1'n_1'\uparrow} + \epsilon_{k_1n_1\downarrow}}, \tag{3.36}
$$

$$
\xi^{(-)}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1} = \frac{-J_{LL'}}{z - \epsilon_{k_2'n_2'\uparrow} + \epsilon_{k_2n_2\downarrow} - \epsilon_{k_1'n_1'\downarrow} + \epsilon_{k_1n_1\uparrow}}, \tag{3.37}
$$

$$
\xi^{(\sigma'\sigma)}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1} = \frac{-J_{LL'}}{z - \epsilon_{k_2'n_2'\sigma'} + \epsilon_{k_2n_2\sigma'} - \epsilon_{k_1'n_1'\sigma} + \epsilon_{k_1n_1\sigma}}. \tag{3.38}
$$

We have dropped the Fermi factor $f(\tilde{\epsilon}_{k_1n_1\sigma_1})(1-f(\tilde{\epsilon}_{k_1'n_1'\sigma_1'}))f(\tilde{\epsilon}_{k_2n_2\sigma_2})(1-f(\tilde{\epsilon}_{k_2'n_2'\sigma_2'}))$ in the above expressions because it is included in the states $\{\delta(a^\dagger_{k_2'n_2'\sigma_2'} a_{k_2n_2\sigma_2})\delta(a^\dagger_{k_1'n_1'\sigma_1'} a_{k_1n_1\sigma_1})|\phi_0\rangle\}$.

We can simplify the first-order correction of the wavefunction (3.33) as follows

$$
|\psi_1\rangle = -\sum_i \Big(\sum_L \tilde{O}^{(0)}_{iLL} + \sum_{(L,L')} \tilde{O}^{(1)}_{iLL'} + \sum_{(L,L')} \tilde{O}^{(2)}_{iLL'} \Big) |\phi_0\rangle. \tag{3.39}
$$

Here the local operators $\tilde{O}^{(0)}_{iLL}$, $\tilde{O}^{(1)}_{iLL'}$, and $\tilde{O}^{(2)}_{iLL'}$ are defined as follows.

$$\tilde{O}^{(0)}_{iLL} = \sum_{\{kn\}} \langle k'_1 n'_1 | iL \rangle_\uparrow \langle iL | k_1 n_1 \rangle_\uparrow \langle k'_2 n'_2 | iL \rangle_\downarrow \langle iL | k_2 n_2 \rangle_\downarrow \\ \times \eta_{Lk'_2 n'_2 k_2 n_2 k'_1 n'_1 k_1 n_1} \delta(a^\dagger_{k'_2 n'_2 \downarrow} a_{k_2 n_2 \downarrow}) \delta(a^\dagger_{k'_1 n'_1 \uparrow} a_{k_1 n_1 \uparrow}), \tag{3.40}$$

$$\tilde{O}^{(1)}_{iLL'} = \sum_{\{kn\}} \sum_{\sigma\sigma'} \langle k'_1 n'_1 | iL' \rangle_\sigma \langle iL' | k_1 n_1 \rangle_\sigma \langle k'_2 n'_2 | iL \rangle_{\sigma'} \langle iL | k_2 n_2 \rangle_{\sigma'} \\ \times \zeta^{(\sigma'\sigma)}_{LL' k'_2 n'_2 k_2 n_2 k'_1 n'_1 k_1 n_1} \delta(a^\dagger_{k'_2 n'_2 \sigma'} a_{k_2 n_2 \sigma'}) \delta(a^\dagger_{k'_1 n'_1 \sigma} a_{k_1 n_1 \sigma}), \tag{3.41}$$

and

$$\begin{aligned} \tilde{O}^{(2)}_{iLL'} = \Big[& \sum_{\{kn\}} \langle k'_1 n'_1 | iL' \rangle_\uparrow \langle iL' | k_1 n_1 \rangle_\downarrow \langle k'_2 n'_2 | iL \rangle_\downarrow \langle iL | k_2 n_2 \rangle_\uparrow \\ & \times \xi^{(+)}_{LL' k'_2 n'_2 k_2 n_2 k'_1 n'_1 k_1 n_1} \delta(a^\dagger_{k'_2 n'_2 \downarrow} a_{k_2 n_2 \uparrow}) \delta(a^\dagger_{k'_1 n'_1 \uparrow} a_{k_1 n_1 \downarrow}) \\ & + \langle k'_1 n'_1 | iL' \rangle_\downarrow \langle iL' | k_1 n_1 \rangle_\uparrow \langle k'_2 n'_2 | iL \rangle_\uparrow \langle iL | k_2 n_2 \rangle_\downarrow \\ & \times \xi^{(-)}_{LL' k'_2 n'_2 k_2 n_2 k'_1 n'_1 k_1 n_1} \delta(a^\dagger_{k'_2 n'_2 \uparrow} a_{k_2 n_2 \downarrow}) \delta(a^\dagger_{k'_1 n'_1 \downarrow} a_{k_1 n_1 \uparrow}) \\ & + \frac{1}{2} \sum_{\sigma\sigma'} \sigma\sigma' \langle k'_1 n'_1 | iL' \rangle_\sigma \langle iL' | k_1 n_1 \rangle_\sigma \langle k'_2 n'_2 | iL \rangle_{\sigma'} \langle iL | k_2 n_2 \rangle_{\sigma'} \\ & \times \xi^{(\sigma'\sigma)}_{LL' k'_2 n'_2 k_2 n_2 k'_1 n'_1 k_1 n_1} \delta(a^\dagger_{k'_2 n'_2 \sigma'} a_{k_2 n_2 \sigma'}) \delta(a^\dagger_{k'_1 n'_1 \sigma} a_{k_1 n_1 \sigma}) \Big]. \end{aligned} \tag{3.42}$$

3.3 First-principles momentum dependent local ansatz wavefunction

The local operators $\tilde{O}^{(0)}_{iLL}$, $\tilde{O}^{(1)}_{iLL'}$, and $\tilde{O}^{(2)}_{iLL'}$ produce the Hilbert space in the weak Coulomb interaction limit. We generalize these correlators as

$$\tilde{O}^{(\alpha)}_{iLL'} = \sum_{\{kn\sigma\}} \langle k'_2 n'_2 | iL \rangle_{\sigma'_2} \langle iL | k_2 n_2 \rangle_{\sigma_2} \langle k'_1 n'_1 | iL' \rangle_{\sigma'_1} \langle iL' | k_1 n_1 \rangle_{\sigma_1} \\ \times \lambda^{(\alpha)}_{LL' \{2'21'1\}} \, \delta(a^\dagger_{k'_2 n'_2 \sigma'_2} a_{k_2 n_2 \sigma_2}) \, \delta(a^\dagger_{k'_1 n'_1 \sigma'_1} a_{k_1 n_1 \sigma_1}) \, . \tag{3.43}$$

Here α denotes the three types of operators $\alpha = 0$, 1, and 2. $a^\dagger_{kn\sigma}(a_{kn\sigma})$ is the creation (annihilation) operator for an electron with momentum $\boldsymbol{k}$, band index n, and spin σ.

The momentum dependent amplitudes $\lambda^{(\alpha)}_{LL'\{2'21'1\}}$ in Eq. (3.43) are given by

$$\lambda^{(0)}_{LL'\{2'21'1\}} = \eta_{Lk'_2 n'_2 k_2 n_2 k'_1 n'_1 k_1 n_1} \, \delta_{LL'} \, \delta_{\sigma'_2 \downarrow} \, \delta_{\sigma_2 \downarrow} \, \delta_{\sigma'_1 \uparrow} \, \delta_{\sigma_1 \uparrow} \, , \tag{3.44}$$

$$\lambda^{(1)}_{LL'\{2'21'1\}} = \zeta^{(\sigma_2\sigma_1)}_{LL' k'_2 n'_2 k_2 n_2 k'_1 n'_1 k_1 n_1} \, \delta_{\sigma'_2 \sigma_2} \, \delta_{\sigma'_1 \sigma_1} \, , \tag{3.45}$$

$$\lambda^{(2)}_{LL'\{2'21'1\}} = \sum_\sigma \xi^{(\sigma)}_{LL' k'_2 n'_2 k_2 n_2 k'_1 n'_1 k_1 n_1} \, \delta_{\sigma'_2 - \sigma} \, \delta_{\sigma_2 \sigma} \, \delta_{\sigma'_1 \sigma} \, \delta_{\sigma_1 - \sigma} \\ + \frac{1}{2} \sigma_1 \sigma_2 \, \xi^{(\sigma_2\sigma_1)}_{LL' k'_2 n'_2 k_2 n_2 k'_1 n'_1 k_1 n_1} \, \delta_{\sigma'_2 \sigma_2} \, \delta_{\sigma'_1 \sigma_1} \, . \tag{3.46}$$

Here $\{2'21'1\}$ is defined by $\{2'21'1\}$=$k_2'n_2'\sigma_2'k_2n_2\sigma_2k_1'n_1'\sigma_1'k_1n_1\sigma_1$. Now, the amplitudes $\eta_{Lk_2'n_2'k_2n_2k_1'n_1'k_1n_1}$, $\zeta^{(\sigma_2\sigma_1)}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1}$, $\xi^{(\sigma)}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1}$, and $\xi^{(\sigma_2\sigma_1)}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1}$ are regarded as the momentum dependent variational parameters to be determined.

By making use of the local operators $\tilde{O}^{(0)}_{iLL}$, $\tilde{O}^{(1)}_{iLL'}$ and $\tilde{O}^{(2)}_{iLL'}$, we can construct a local ansatz wavefunction with momentum dependent variational parameters.

$$|\Psi_{\rm MLA}\rangle = \Big[\prod_i \Big(1 - \sum_L \tilde{O}^{(0)}_{iLL} - \sum_{(L,L')} \tilde{O}^{(1)}_{iLL'} - \sum_{(L,L')} \tilde{O}^{(2)}_{iLL'}\Big)\Big]\ |\phi_0\rangle\,. \tag{3.47}$$

The two-particle correlators $\tilde{O}^{(0)}_{iLL}$, $\tilde{O}^{(1)}_{iLL'}$, and $\tilde{O}^{(2)}_{iLL'}$ describe the intra-orbital correlations, the inter-orbital charge-charge correlations, and the inter-orbital spin-spin correlations (, $i.e.$, the Hund-rule correlations), respectively. Note that the momentum-dependent local ansatz (MLA) wavefunction $|\Psi_{\rm MLA}\rangle$ reduces to the LA $|\Psi_{\rm LA}\rangle$ when the variational parameters $\{\lambda^{(\alpha)}_{LL'\{2'21'1\}}\}$ are taken to be momentum-independent.

3.4 Ground state energy in the single-site approximation

The energy expectation values for the MLA wavefunction can be obtained analytically within the single-site approximation (SSA). The correlation energy for the MLA wavefunction is given by.

$$\langle\tilde{H}\rangle = \frac{\langle\Psi_{\rm MLA}|\tilde{H}|\Psi_{\rm MLA}\rangle}{\langle\Psi_{\rm MLA}|\Psi_{\rm MLA}\rangle} = \frac{A_N}{B_N}\,. \tag{3.48}$$

Here $\tilde{H} = H - \langle H\rangle_0$. A_N and B_N are defined as follows:

$$A_N = \left\langle \left[\prod_i \left(1-\tilde{O}_i^\dagger\right)\right] \tilde{H} \left[\prod_i \left(1-\tilde{O}_i\right)\right]\right\rangle_0, \tag{3.49}$$

$$B_N = \left\langle \left[\prod_i \left(1-\tilde{O}_i^\dagger\right)\right] \left[\prod_i \left(1-\tilde{O}_i\right)\right]\right\rangle_0. \tag{3.50}$$

The operator $\tilde{O}_i$ is defined by

$$\tilde{O}_i = \sum_L \tilde{O}^{(0)}_{iLL} + \sum_{(L,L')} \tilde{O}^{(1)}_{iLL'} + \sum_{(L,L')} \tilde{O}^{(2)}_{iLL'}. \tag{3.51}$$

Expanding B_N with respect to site 1, we obtain

$$\begin{aligned} B_N = B^{(1)}_{N-1} &- \left\langle \tilde{O}_1^\dagger \left[\prod_i{}^{(1)} \left(1-\tilde{O}_i^\dagger\right)\right] \left[\prod_i{}^{(1)} \left(1-\tilde{O}_i\right)\right]\right\rangle_0 \\ &- \left\langle \left[\prod_i{}^{(1)} \left(1-\tilde{O}_i^\dagger\right)\right] \tilde{O}_1 \left[\prod_i{}^{(1)} \left(1-\tilde{O}_i\right)\right]\right\rangle_0 \\ &+ \left\langle \tilde{O}_1^\dagger \left[\prod_i{}^{(1)} \left(1-\tilde{O}_i^\dagger\right)\right] \tilde{O}_1 \left[\prod_i{}^{(1)} \left(1-\tilde{O}_i\right)\right]\right\rangle_0, \end{aligned} \tag{3.52}$$

and

$$B_{N-1}^{(1)} = \left\langle \left[\prod_i^{(1)} \left(1 - \tilde{O}_i^\dagger\right) \right] \left[\prod_i^{(1)} \left(1 - \tilde{O}_i\right) \right] \right\rangle_0 . \tag{3.53}$$

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

When we apply Wick's theorem (see Appendix A) for the calculations of B_N, we neglect the contractions between different sites. This is the single-site approximation, and then Eq. (3.52) is expressed as

$$B_N = \left\langle \left(1 - \tilde{O}_1^\dagger\right) \left(1 - \tilde{O}_1\right) \right\rangle_0 B_{N-1}^{(1)} . \tag{3.54}$$

We adopt 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 $\tilde{H}$ and the other terms in which $\tilde{H}$ is contracted to the other operators $\tilde{O}_i (i \neq 1)$. We have then in the single-site approximation

$$A_N = \left\langle \left(1 - \tilde{O}_1^\dagger\right) \tilde{H} \left(1 - \tilde{O}_1\right) \right\rangle_0 B_{N-1}^{(1)} + \left\langle \left(1 - \tilde{O}_1^\dagger\right) \left(1 - \tilde{O}_1\right) \right\rangle_0 A_{N-1}^{(1)} , \tag{3.55}$$

and

$$A_{N-1}^{(1)} = \left\langle \left[\prod_i^{(1)} \left(1 - \tilde{O}_i^\dagger\right) \right] \tilde{H} \left[\prod_i^{(1)} \left(1 - \tilde{O}_i\right) \right] \right\rangle_0 . \tag{3.56}$$

Successive application of the recursive relation Eq. (3.54) and Eq. (3.55) leads to the following expressions.

$$A_N = \sum_i \left\langle \left(1 - \tilde{O}_i^\dagger\right) \tilde{H} \left(1 - \tilde{O}_i\right) \right\rangle_0 B_{N-1}^{(i)} . \tag{3.57}$$

$$B_N = \prod_i \left\langle \left(1 - \tilde{O}_i^\dagger\right) \left(1 - \tilde{O}_i\right) \right\rangle_0 = \left\langle \left(1 - \tilde{O}_i^\dagger\right) \left(1 - \tilde{O}_i\right) \right\rangle_0 B_{N-1}^{(i)} . \tag{3.58}$$

Taking the ratio A_N / B_N, we obtain the correlation energy in the SSA as follows.

$$N\epsilon_c = \langle \tilde{H} \rangle = \sum_i \frac{\langle (1 - \tilde{O}_i^\dagger) \tilde{H} (1 - \tilde{O}_i) \rangle_0}{\langle (1 - \tilde{O}_i^\dagger)(1 - \tilde{O}_i) \rangle_0} . \tag{3.59}$$

Assuming a site per unit cell and using the relation $\langle \tilde{O}_i^\dagger \rangle_0 = \langle \tilde{O}_i \rangle_0 = 0$, we obtain the correlation energy per site as follows.

$$\epsilon_c = \frac{-\langle \tilde{O}_i{}^\dagger \tilde{H} \rangle_0 - \langle \tilde{H} \tilde{O}_i \rangle_0 + \langle \tilde{O}_i{}^\dagger \tilde{H} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i{}^\dagger \tilde{O}_i \rangle_0} . \tag{3.60}$$

The Hamiltonian $\tilde{H}$ is expressed by $\tilde{H} = \tilde{H}_0 + H_I$. Since $\langle \tilde{O}_i{}^\dagger \tilde{H}_0 \rangle = 0$, we obtain the correlation energy ϵ_c as follows.

$$\epsilon_c = \frac{-\langle \tilde{O}_i{}^\dagger H_I \rangle_0 - \langle H_I \tilde{O}_i \rangle_0 + \langle \tilde{O}_i{}^\dagger \tilde{H} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i{}^\dagger \tilde{O}_i \rangle_0} . \tag{3.61}$$

This is the correlation energy per site in the SSA.

The elements in the correlation energy (3.61) are calculated with use of Wick's theorem. They are summarized as follows.

$$\langle H_I \tilde{O}_i \rangle_0 = \sum_{\alpha\alpha'} \sum_{\langle LL' \rangle} \sum_{\langle L''L''' \rangle} \sum_{\{kn\sigma\}}^{2'21'1} U^{(\alpha)}_{LL'} \, \lambda^{(\alpha')}_{L''L'''\{2'21'1\}} \, P^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}) \,, \tag{3.62}$$

$$\langle \tilde{O}_i{}^\dagger \tilde{H} \tilde{O}_i \rangle_0 = \langle \tilde{O}_i{}^\dagger \tilde{H}_0 \tilde{O}_i \rangle_0 + \langle \tilde{O}_i{}^\dagger H_I \tilde{O}_i \rangle_0 \,, \tag{3.63}$$

$$\langle \tilde{O}_i{}^\dagger \tilde{H}_0 \tilde{O}_i \rangle_0 = \sum_{\alpha\alpha'} \sum_{\langle LL' \rangle} \sum_{\langle L''L''' \rangle} \sum_{\{kn\sigma\}}^{2'21'1} \sum_{\{k'n'\sigma'\}}^{4'43'3} \lambda^{(\alpha)*}_{LL'\{2'21'1\}} \, \lambda^{(\alpha')}_{L''L'''\{4'43'3\}} \, Q^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}\{4'43'3\}) \,, \tag{3.64}$$

$$\langle \tilde{O}_i{}^\dagger H_I \tilde{O}_i \rangle_0 = \sum_{\alpha\alpha'} \sum_{\langle LL' \rangle} \sum_{\langle L''L''' \rangle} \sum_{\{kn\sigma\}}^{2'21'1} \sum_{\{k'n'\sigma'\}}^{4'43'3} \lambda^{(\alpha)*}_{LL'\{2'21'1\}} \, \lambda^{(\alpha')}_{L''L'''\{4'43'3\}} \, R^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}\{4'43'3\}) \,, \tag{3.65}$$

$$\langle \tilde{O}_i{}^\dagger \tilde{O}_i \rangle_0 = \sum_{\alpha\alpha'} \sum_{\langle LL' \rangle} \sum_{\langle L''L''' \rangle} \sum_{\{kn\sigma\}}^{2'21'1} \sum_{\{k'n'\sigma'\}}^{4'43'3} \lambda^{(\alpha)*}_{LL'\{2'21'1\}} \lambda^{(\alpha')}_{L''L'''\{4'43'3\}} S^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}\{4'43'3\}) \,. \tag{3.66}$$

Here the sum $\sum_{\langle LL' \rangle}$ is defined by $\sum_L$ when L'=L, and by $\sum_{(L,L')}$ when $L' \neq L$. $Q^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}\{4'43'3\})$, $S^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}\{4'43'3\})$, and $P^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\})$ are obtained with use of Wick's theorem as follows.

$$\begin{aligned}
&Q^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}\{4'43'3\}) \\
&= \langle iL|k'_2 n'_2\rangle_{\sigma'_2} \langle k_2 n_2|iL\rangle_{\sigma_2} \langle iL'|k'_1 n'_1\rangle_{\sigma'_1} \langle k_1 n_1|iL'\rangle_{\sigma_1} \\
&\times \langle k'_4 n'_4|iL''\rangle_{\sigma'_4} \langle iL''|k_4 n_4\rangle_{\sigma_4} \langle k'_3 n'_3|iL'''\rangle_{\sigma'_3} \langle iL'''|k_3 n_3\rangle_{\sigma_3} \\
&\times \Delta E(\{k'_2 n'_2 \sigma'_2 k_2 n_2 \sigma_2 k'_1 n'_1 \sigma'_1 k_1 n_1 \sigma_1\}) \\
&\times (\delta_{14}\delta_{23}\delta_{1'4'}\delta_{2'3'} - \delta_{14}\delta_{23}\delta_{1'3'}\delta_{2'4'} + \delta_{13}\delta_{24}\delta_{1'3'}\delta_{2'4'} - \delta_{13}\delta_{24}\delta_{1'4'}\delta_{2'3'}) \\
&\times \langle n_{k_1 n_1 \sigma_1}\rangle_0 (1 - \langle n_{k'_1 n'_1 \sigma'_1}\rangle_0) \langle n_{k_2 n_2 \sigma_2}\rangle_0 (1 - \langle n_{k'_2 n'_2 \sigma'_2}\rangle_0) \,,
\end{aligned} \tag{3.67}$$

$$\begin{aligned}
&S^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}\{4'43'3\}) \\
&= \Big(\langle k'_1 n'_1|iL''\rangle_{\sigma'_1} \langle iL''|k_1 n_1\rangle_{\sigma_1} \langle k'_2 n'_2|iL'''\rangle_{\sigma'_2} \langle iL'''|k_2 n_2\rangle_{\sigma_2} \delta_{14}\delta_{1'4'}\delta_{23}\delta_{2'3'} \\
&- \langle k'_2 n'_2|iL''\rangle_{\sigma'_2} \langle iL''|k_1 n_1\rangle_{\sigma_1} \langle k'_1 n'_1|iL'''\rangle_{\sigma'_1} \langle iL'''|k_2 n_2\rangle_{\sigma_2} \delta_{14}\delta_{1'3'}\delta_{23}\delta_{2'4'} \\
&- \langle k'_1 n'_1|iL''\rangle_{\sigma'_1} \langle iL''|k_2 n_2\rangle_{\sigma_2} \langle k'_2 n'_2|iL'''\rangle_{\sigma'_2} \langle iL'''|k_1 n_1\rangle_{\sigma_1} \delta_{13}\delta_{1'4'}\delta_{24}\delta_{2'3'} \\
&+ \langle k'_2 n'_2|iL''\rangle_{\sigma'_2} \langle iL''|k_2 n_2\rangle_{\sigma_2} \langle k'_1 n'_1|iL'''\rangle_{\sigma'_1} \langle iL'''|k_1 n_1\rangle_{\sigma_1} \delta_{13}\delta_{1'3'}\delta_{24}\delta_{2'4'} \Big) \\
&\times \langle iL|k'_2 n'_2\rangle_{\sigma'_2} \langle k_2 n_2|iL\rangle_{\sigma_2} \langle iL'|k'_1 n'_1\rangle_{\sigma'_1} \langle k_1 n_1|iL'\rangle_{\sigma_1} \\
&\times \langle n_{k_1 n_1 \sigma_1}\rangle_0 (1 - \langle n_{k'_1 n'_1 \sigma'_1}\rangle_0) \langle n_{k_2 n_2 \sigma_2}\rangle_0 (1 - \langle n_{k'_2 n'_2 \sigma'_2}\rangle_0) \,,
\end{aligned} \tag{3.68}$$

$$
\begin{aligned}
&P^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}) \\
&= \sum_{\{kn\sigma\}}^{44'33'} C^{(\alpha)}_{\sigma'_4\sigma_4\sigma'_3\sigma_3} \langle k'_4 n'_4|iL\rangle_{\sigma'_4}\langle iL|k_4n_4\rangle_{\sigma_4}\langle k'_3n'_3|iL'\rangle_{\sigma'_3}\langle iL'|k_3n_3\rangle_{\sigma_3} \\
&\times \Big(\delta_{2'4}\delta_{24'}\delta_{1'3}\delta_{13'} - \delta_{2'3}\delta_{24'}\delta_{1'4}\delta_{13'} - \delta_{24'}\delta_{23'}\delta_{1'3}\delta_{14'} + \delta_{2'3}\delta_{23'}\delta_{1'4}\delta_{14'}\Big) \\
&\times \langle k'_2n'_2|iL''\rangle_{\sigma'_2}\langle iL''|k_2n_2\rangle_{\sigma_2}\langle k'_1n'_1|iL'''\rangle_{\sigma'_1}\langle iL'''|k_1n_1\rangle_{\sigma_1} \\
&\times \langle n_{k_1n_1\sigma_1}\rangle_0(1-\langle n_{k'_1n'_1\sigma'_1}\rangle_0)\langle n_{k_2n_2\sigma_2}\rangle_0(1-\langle n_{k'_2n'_2\sigma'_2}\rangle_0)\,.
\end{aligned}
\tag{3.69}
$$

The elements $R^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}\{4'43'3\})$ in Eq. (3.65) are more complicated. They are expressed by

$$
R^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}\{4'43'3\}) = \sum_{\alpha''}\sum_{\langle L^{\rm iv}L^{\rm v}\rangle} U^{(\alpha'')}_{L^{\rm iv}L^{\rm v}} R^{(\alpha\alpha''\alpha')}_{LL'L^{\rm iv}L^{\rm v}L''L'''}(\{2'21'1\}\{4'43'3\}). \tag{3.70}
$$

Here

$$
\begin{aligned}
&R^{(\alpha\alpha''\alpha')}_{LL'L^{\rm iv}L^{\rm v}L''L'''}(\{2'21'1\}\{4'43'3\}) \\
&= \sum_{\{kn\sigma\}}^{66'55'} \langle k'_2n'_2|iL\rangle_{\sigma'_2}\langle iL|k_2n_2\rangle_{\sigma_2}\langle k'_1n'_1|iL'\rangle_{\sigma'_1}\langle iL'|k_1n_1\rangle_{\sigma_1} \\
&\times \langle k'_4n'_4|iL''\rangle_{\sigma'_4}\langle iL''|k_4n_4\rangle_{\sigma_4}\langle k'_3n'_3|iL'''\rangle_{\sigma'_3}\langle iL'''|k_3n_3\rangle_{\sigma_3} \\
&\times \Big\langle \delta(a^\dagger_{k'_2n'_2\sigma'_2}a_{k_2n_2\sigma_2})\delta(a^\dagger_{k'_1n'_1\sigma'_1}a_{k_1n_1\sigma_1})\; O^{(\alpha'')}_{L^{\rm iv}L^{\rm v}}\; \delta(a^\dagger_{k'_4n'_4\sigma'_4}a_{k_4n_4\sigma_4})\delta(a^\dagger_{k'_3n'_3\sigma'_3}a_{k_3n_3\sigma_3})\Big\rangle_0 .
\end{aligned}
\tag{3.71}
$$

The average at the rhs of Eq. (3.71) is again calculated by means of Wick's theorem.

3.5 Self-consistent equation of variational parameters

The variational parameters η's, ζ's, and ξ's in the correlators $\{\tilde{O}^{(\alpha)}_{iLL'}\}$ are obtained from the variational principle for the ground-state energy E.

$$
\langle H\rangle = \langle H\rangle_0 + N\epsilon_c \geq E\,. \tag{3.72}
$$

Here $\langle H\rangle_0$ is the ground-state energy in the Hartree-Fock approximation $\langle H\rangle_0 = \langle H_0\rangle_0 = E^{(0)}_0$, and is given in Eq. (3.20). The correlation energy per atom ϵ_c is defined by $N\epsilon_c \equiv \langle\tilde{H}\rangle = \langle H\rangle - \langle H\rangle_0$. N is the number of atoms, and $\langle\sim\rangle$ denotes the full average with respect to $|\Psi_{\rm MLA}\rangle$.

We obtain from Eq. (3.61) as

$$
\begin{aligned}
\left(1+\sum_{\alpha\alpha'}\langle\tilde{O}_i{}^\dagger\tilde{O}_i\rangle_0\right)^2 \delta\epsilon_c = \Big[&-\sum_\alpha\langle(\delta\tilde{O}_i{}^\dagger)\tilde{H}\rangle_0 - \sum_\alpha\langle\tilde{H}\delta\tilde{O}_i\rangle_0 \\
&+\sum_{\alpha\alpha'}\langle(\delta\tilde{O}_i{}^\dagger)\tilde{H}\tilde{O}_i\rangle_0 + \sum_{\alpha\alpha'}\langle\tilde{O}_i{}^\dagger\tilde{H}\delta\tilde{O}_i\rangle_0\Big]\times\left(1+\sum_{\alpha\alpha'}\langle\tilde{O}_i{}^\dagger\tilde{O}_i\rangle_0\right) \\
&-\left(-\langle\tilde{O}_i{}^\dagger\tilde{H}\rangle_0 - \langle\tilde{H}\tilde{O}_i\rangle_0 + \langle\tilde{O}_i{}^\dagger\tilde{H}\tilde{O}_i\rangle_0\right)\times\sum_{\alpha\alpha'}\left(\langle(\delta\tilde{O}_i{}^\dagger)\tilde{O}_i\rangle_0 + \langle\tilde{O}_i{}^\dagger\delta\tilde{O}_i\rangle_0\right).
\end{aligned}
\tag{3.73}
$$

Thus, the stationary condition $\delta\epsilon_c = 0$ yields the following equation.

$$-\langle(\delta\tilde{O}_i^\dagger)H_I\rangle_0 + \langle(\delta\tilde{O}_i^\dagger)\tilde{H}\tilde{O}_i\rangle_0 - \epsilon_c\langle(\delta\tilde{O}_i^\dagger)\tilde{O}_i\rangle_0 + c.c. = 0\,. \tag{3.74}$$

Here $c.c.$ denotes conjugate of complex of the first three terms. Using Eqs. (3.62) - (3.66), the above equation is expressed as follows.

$$\begin{aligned}
&\sum_{\alpha'}\sum_{\langle L''L'''\rangle}\sum_{\{kn\sigma\}}^{4'43'3}\Big[Q^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}\{4'43'3\}) \\
&-\epsilon_c\, S^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}\{4'43'3\}) + \sum_{\alpha''}\sum_{\langle\bar{L}\bar{L}'\rangle} U^{(\alpha'')}_{\bar{L}\bar{L}'} R^{(\alpha\alpha''\alpha')}_{LL'\bar{L}\bar{L}'L''L'''}(\{2'21'1\}\{4'43'3\})\Big]\,\lambda^{(\alpha')}_{L''L'''\{4'43'3\}} \\
&= \sum_{\alpha'}\sum_{\langle L''L'''\rangle} U^{(\alpha')}_{L''L'''}\, P^{(\alpha'\alpha)*}_{L''L'''LL'}(\{2'21'1\})\,.
\end{aligned} \tag{3.75}$$

The explicit expressions of $P^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}), Q^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}\{4'43'3\})$, and $S^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}\{4'43'3\})$ have been given in Eqs. (3.67) $\sim$ (3.69).

3.6 Various quantities in the first-principles MLA

In this section, we obtain the physical quantities such as electron number, charge fluctuation, amplitude of local moment, and momentum distribution functions in the first-principles MLA.

3.6.1 Electron number

The Fermi level $\epsilon_{\rm F}$ is determined from the conduction electron number n_e via the relation,

$$n_e = \sum_L \langle n_{iL}\rangle\,. \tag{3.76}$$

The electron number of orbital L on site i, $\langle n_{iL}\rangle$ is expressed as follows.

$$\langle n_{iL}\rangle = \langle n_{iL}\rangle_0 + \langle\tilde{n}_{iL}\rangle\,. \tag{3.77}$$

Here the first term $\langle n_{iL}\rangle_0$ denotes the Hartree-Fock electron number. The second term $\langle\tilde{n}_{iL}\rangle$ at the rhs is the correlation correction.

We can derive the formula for the average of an operator $\tilde{A}$ in the SSA taking the same steps as in the correlation energy (3.61) as follows.

$$\langle\tilde{A}\rangle = \sum_i \frac{-\langle\tilde{O_i}^\dagger\tilde{A}\rangle_0 - \langle\tilde{A}\tilde{O}_i\rangle_0 + \langle\tilde{O_i}^\dagger\tilde{A}\tilde{O}_i\rangle_0}{1+\langle\tilde{O_i}^\dagger\tilde{O}_i\rangle_0}\,. \tag{3.78}$$

Using the formula, the correlation corrections is obtained in the SSA as follows

$$\langle\tilde{n}_{iL}\rangle = \frac{-\langle\tilde{O}_i^\dagger\tilde{n}_{iL}\rangle_0 - \langle\tilde{n}_{iL}\tilde{O}_i\rangle_0 + \langle\tilde{O}_i^\dagger\tilde{n}_{iL}\tilde{O}_i\rangle_0}{1+\langle\tilde{O}_i^\dagger\tilde{O}_i\rangle_0}. \tag{3.79}$$

Note that $\langle\tilde{n}_{iL}\tilde{O}_i\rangle_0 = \langle\tilde{O}_i^\dagger\tilde{n}_{iL}\rangle_0^* = 0$. Thus

$$\langle\tilde{n}_{iL}\rangle = \frac{\langle\tilde{O}_i^\dagger\tilde{n}_{iL}\tilde{O}_i\rangle_0}{1+\langle\tilde{O_i}^\dagger\tilde{O}_i\rangle_0}\,. \tag{3.80}$$

We can also derive the same expression using the Feynman-Hellmann theorem (See Appendix B).

3.6.2 Charge fluctuations

The charge fluctuations is defined as

$$\langle(\delta n_{id})^2\rangle = \langle n_{id}^2\rangle - \langle n_{id}\rangle^2. \tag{3.81}$$

Here $n_{id} = \sum_L^d n_{iL}$. $\langle n_{id}^2\rangle$ at the rhs of Eq. (3.81) is given as

$$\langle n_{id}^2\rangle = \langle n_{id}\rangle + 2\sum_L^d \langle n_{iL\uparrow}\cdot n_{iL\downarrow}\rangle + 2\sum_{(L,L')}^d \langle n_{iL}\cdot n_{iL'}\rangle. \tag{3.82}$$

The terms $\langle n_{iL\uparrow}\cdot n_{iL\downarrow}\rangle$ and $\langle n_{iL}\cdot n_{iL'}\rangle$ are known as double occupation number and inter-orbital charge-charge correlations, respectively.

Note that the operators $O^{(0)}_{iLL}$ and $O^{(1)}_{iLL'}$ are given by Eqs. (3.10) and (3.11):

$$O^{(0)}_{iLL} = \delta n_{iL\uparrow}\delta n_{iL\downarrow}, \tag{3.83}$$

$$O^{(1)}_{iLL'} = \delta n_{iL}\delta n_{iL'}. \tag{3.84}$$

Here and hereafter we omit the hat of the operators for simplicity. Using the above expressions we obtain the double occupation number as

$$\langle n_{iL\uparrow}n_{iL\downarrow}\rangle = \langle O^{(0)}_{iLL}\rangle + \langle\tilde{n}_{iL\uparrow}\rangle\langle n_{iL\downarrow}\rangle_0 + \langle n_{iL\uparrow}\rangle_0\langle\tilde{n}_{iL\downarrow}\rangle + \langle n_{iL\uparrow}\rangle_0\langle n_{iL\downarrow}\rangle_0. \tag{3.85}$$

Similarly, we obtain the inter-orbital charge-charge correlations as follows.

$$\langle n_{iL}n_{iL'}\rangle = \langle O^{(1)}_{iLL'}\rangle + \langle\tilde{n}_{iL}\rangle\langle n_{iL'}\rangle_0 + \langle n_{iL}\rangle_0\langle\tilde{n}_{iL'}\rangle + \langle n_{iL}\rangle_0\langle n_{iL'}\rangle_0. \tag{3.86}$$

Substituting Eqs. (3.85) and (3.86) into Eq. (3.82), we obtain the expression of $\langle n_{id}^2\rangle$ as

$$\begin{aligned}\langle n_{id}^2\rangle =& \langle n_{id}\rangle + 2\sum_L^d\langle O^{(0)}_{iLL}\rangle + 2\sum_{L\sigma}^d\langle\tilde{n}_{iL\sigma}\rangle\langle\tilde{n}_{iL-\sigma}\rangle_0 \\ &+ \sum_{L\sigma}^d\langle\delta n_{iL\sigma}\rangle_0\langle\delta n_{iL-\sigma}\rangle_0 + 2\sum_{(L,L)}^d\langle O^{(1)}_{iLL'}\rangle \\ &+ 2\sum_{(L,L)}^d\{\langle\tilde{n}_{iL}\rangle\langle\tilde{n}_{iL'}\rangle_0 + \langle n_{iL}\rangle_0\langle\tilde{n}_{iL'}\rangle\} + 2\sum_{(L,L)}^d\langle n_{iL}\rangle_0\langle n_{iL'}\rangle_0.\end{aligned} \tag{3.87}$$

On the other hand, we obtain the term $\langle n_{id}\rangle^2$ as follows

$$\begin{aligned}\langle n_{id}\rangle^2 =& \langle\tilde{n}_{id}\rangle^2 + \sum_L^d\langle n_{iL}\rangle_0^2 \\ &+ 2\sum_{(L,L')}^d\langle n_{iL}\rangle_0\langle n_{iL'}\rangle_0 + 2\sum_L^d\langle\tilde{n}_{iL}\rangle\langle n_{iL}\rangle_0 \\ &+ 2\sum_{(L,L')}^d\langle\tilde{n}_{iL}\rangle\langle n_{iL'}\rangle_0 + 2\sum_{(L,L')}^d\langle\tilde{n}_{iL'}\rangle\langle n_{iL}\rangle_0.\end{aligned} \tag{3.88}$$

Substituting Eqs. (3.87) and (3.88) into Eq. (3.81), we obtain the charge fluctuations $\langle(\delta n_{id})^2\rangle$ as follows.

$$\langle(\delta n_{id})^2\rangle = \sum_{L\sigma}^{d}\langle n_{iL\sigma}\rangle_0(1-\langle n_{iL\sigma}\rangle_0) + \sum_{L\sigma}^{d}\langle\tilde{n}_{iL\sigma}\rangle(1-2\langle n_{iL\sigma}\rangle_0) - \langle\tilde{n}_{id}\rangle^2 + 2\sum_{L}^{d}\langle O_{iLL}^{(0)}\rangle + 2\sum_{(L,L')}^{d}\langle O_{iLL'}^{(1)}\rangle\,, \tag{3.89}$$

We can also obtain the same expression using Feynman-Hellmann theorem. The derivation is given in Appendix B.

According to the formula (3.78), we obtain the expression for $\langle O_{iLL'}^{(\alpha)}\rangle$ for (α = 0, 1) at the rhs of Eq. (3.89) as follows

$$\langle O_{iLL'}^{(\alpha)}\rangle = \frac{-\langle\tilde{O}_i{}^{\dagger}O_{iLL'}^{(\alpha)}\rangle_0 - \langle O_{iLL'}^{(\alpha)}\tilde{O}_i\rangle_0 + \langle\tilde{O}_i{}^{\dagger}O_{iLL'}^{(\alpha)}\tilde{O}_i\rangle_0}{1+\langle\tilde{O}_i{}^{\dagger}\tilde{O}_i\rangle_0}\,. \tag{3.90}$$

3.6.3 Amplitude of local moment

The amplitude of local magnetic moment for d electrons is given by

$$\langle\boldsymbol{m}_{id}^2\rangle = 3\sum_{L}^{d} {m_{iL}^z}^2 + 2\sum_{(L,L')}^{d}\langle\boldsymbol{m}_{iL}\cdot\boldsymbol{m}_{iL'}\rangle. \tag{3.91}$$

Here the local magnetic moments for d electrons are defined by $\boldsymbol{m}_{id} = \sum_L^d \boldsymbol{m}_{iL} = 2\sum_L^d \boldsymbol{S}_{iL}$. m_{iL}^z is given by

$$m_{iL}^z = n_{iL\uparrow} - n_{iL\downarrow}. \tag{3.92}$$

Thus we obtain

$$\langle {m_{iL}^z}^2\rangle = \langle n_{iL}\rangle - 2\langle n_{iL\uparrow}n_{iL\downarrow}\rangle. \tag{3.93}$$

Substituting Eq. (3.93) into Eq. (3.91), we obtain

$$\langle\boldsymbol{m}_{id}^2\rangle = 3\sum_{L}^{d}\langle n_{iL}\rangle - 6\sum_{L}^{d}\langle n_{iL\uparrow}n_{iL\downarrow}\rangle + 2\sum_{(L,L')}^{d}\langle\boldsymbol{m}_{iL}\cdot\boldsymbol{m}_{iL'}\rangle. \tag{3.94}$$

Since $\boldsymbol{m}_{iL} = 2\boldsymbol{s}_{iL}$, we can write Eq. (3.94) as

$$\langle\boldsymbol{m}_{id}^2\rangle = 3\sum_{L}^{d}\langle n_{iL}\rangle - 6\sum_{L}^{d}\langle n_{iL\uparrow}n_{iL\downarrow}\rangle + 8\sum_{(L,L')}^{d}\langle\boldsymbol{s}_{iL}\cdot\boldsymbol{s}_{iL'}\rangle. \tag{3.95}$$

Using the operator $O_{iLL'}^{(2)}$ is given by Eq. (3.12):

$$O_{iLL'}^{(2)} = \delta\boldsymbol{s}_{iL}\cdot\delta\boldsymbol{s}_{iL'}, \tag{3.96}$$

we obtain the inter-orbital spin-spin interaction as follows.

$$\langle \boldsymbol{s}_{iL} \cdot \boldsymbol{s}_{iL'} \rangle = \langle O^{(2)}_{iLL'} \rangle + \frac{1}{4}(\langle \delta m_{iL} \rangle \langle m_{iL'} \rangle_0 + \langle \delta m_{iL'} \rangle \langle m_{iL} \rangle_0 + \langle m_{iL} \rangle_0 \langle m_{iL'} \rangle_0). \tag{3.97}$$

Substituting Eqs. (3.85) and (3.97) into Eq. (3.95), we obtain the expression of $\langle \boldsymbol{m}^2_{id} \rangle$ as

$$\begin{aligned}\langle \boldsymbol{m}^2_{id} \rangle =& 3 \sum_{L}^{d} (\langle \delta n_{iL} \rangle + \langle n_{iL} \rangle_0) \\ & - 6 \sum_{L}^{d} \{ \langle O^{(0)}_{iLL} \rangle + \sum_{\sigma} \langle \delta n_{iL\sigma} \rangle \langle n_{iL-\sigma} \rangle_0 + \frac{1}{2} \sum_{\sigma} \langle n_{iL\sigma} \rangle_0 \langle n_{iL-\sigma} \rangle_0 \} \\ & + 8 \sum_{(L,L')}^{d} \{ \langle O^{(2)}_{iLL'} \rangle + \frac{1}{4}(\langle \delta m_{iL} \rangle \langle m_{iL'} \rangle_0 + \langle \delta m_{iL'} \rangle \langle m_{iL} \rangle_0 + \langle m_{iL} \rangle_0 \langle m_{iL'} \rangle_0) \}. \end{aligned} \tag{3.98}$$

Using the relations $\langle m_{iL} \rangle = \sum_\sigma \sigma \langle n_{iL\sigma} \rangle$ and $\langle \boldsymbol{S}^2 \rangle = \langle \boldsymbol{m}^2_{id} \rangle / 4$, we obtain the expression of $\langle \boldsymbol{S}^2 \rangle$ from Eq. (3.98) as follows.

$$\begin{aligned}\langle \boldsymbol{S}^2 \rangle =& \frac{3}{4} \sum_{L\sigma}^{d} \langle n_{iL\sigma} \rangle_0 (1 - \langle n_{iL\sigma} \rangle_0) + \frac{3}{4} \sum_{L\sigma}^{d} \langle \tilde{n}_{iL\sigma} \rangle (1 - 2\langle n_{iL-\sigma} \rangle_0) \\ & - \frac{3}{2} \sum_{L}^{d} \langle O^{(0)}_{iLL} \rangle + 2 \sum_{(L,L')}^{d} \langle O^{(2)}_{iLL'} \rangle . \end{aligned} \tag{3.99}$$

We can calculate the average $\langle O^{(\alpha)}_{iLL'} \rangle$ (α = 0, 2) at the rhs of Eq. (3.99) using the formula (3.90). We can obtain the same expression of the amplitude $\langle \boldsymbol{S}^2 \rangle$ using the Feynman-Hellmann theorem. The derivation is given in Appendix B.

3.6.4 Momentum distribution function

The momentum distribution function (MDF) is expressed as follows.

$$\langle n_{kn\sigma} \rangle = \langle n_{kn\sigma} \rangle_0 + \langle \tilde{n}_{kn\sigma} \rangle. \tag{3.100}$$

Here the first term $\langle n_{kn\sigma} \rangle_0$ denotes the Hartree-Fock electron number. The second term $\langle \tilde{n}_{kn\sigma} \rangle$ at the rhs is the correlation correction of the MDF.

We can obtain the expression of $\langle \tilde{n}_{kn\sigma} \rangle$ according to the formula (3.78) in the SSA.

$$\langle \tilde{n}_{kn\sigma} \rangle = \frac{-N \langle \tilde{O}^\dagger_i \tilde{n}_{kn\sigma} \rangle_0 - N \langle \tilde{n}_{kn\sigma} \tilde{O}_i \rangle_0 + N \langle \tilde{O}^\dagger_i \tilde{n}_{kn\sigma} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}^\dagger_i \tilde{O}_i \rangle_0}. \tag{3.101}$$

Since $\langle \tilde{n}_{kn\sigma} \tilde{O}_i \rangle = 0$, the above expression reduces as follows.

$$\langle \tilde{n}_{kn\sigma} \rangle = \frac{N \langle \tilde{O}^\dagger_i \tilde{n}_{kn\sigma} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}^\dagger_i \tilde{O}_i \rangle_0}. \tag{3.102}$$

Finally we obtain the expression of the MDF from Eqs. (3.100) and (3.102) as follows.

$$\langle n_{kn\sigma} \rangle = \langle n_{kn\sigma} \rangle_0 + \frac{N \langle \tilde{O}^\dagger_i \tilde{n}_{kn\sigma} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}^\dagger_i \tilde{O}_i \rangle_0}. \tag{3.103}$$

We can also derive the same expression of the MDF using the Feynman-Hellmann theorem. The derivation is given in Appendix B.

Chapter 4

First-Principles MLA in the Weak Coulomb Interaction Regime

In last chapter we constructed the MLA wavefunction on the basis of TB-LDA+U Hamiltonian, and derived the self-consistent equations for momentum-dependent variational parameters. In this chapter, we introduce the lowest-order variational treatments of the MLA solving the self-consistent equations in the weak Coulomb interaction regime, and present the numerical results of correlation energy, charge fluctuations, formation of atomic magnetic moment as well as the momentum distribution function as a function of Coulomb interaction strength [71].

4.1 Variational parameters in the weak Coulomb interaction regime

We obtained the self-consistent equation (3.75) from the stationary condition $\delta\epsilon_c = 0$ in Sec 3.5:

$$\sum_{\alpha'} \sum_{\langle L''L'''\rangle} \sum_{\{kn\sigma\}}^{4'43'3} \Big[Q^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}\{4'43'3\}) - \epsilon_c\, S^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}\{4'43'3\}) + \sum_{\alpha''} \sum_{\langle \bar{L}\bar{L}'\rangle} U^{(\alpha'')}_{\bar{L}\bar{L}'} R^{(\alpha\alpha''\alpha')}_{LL'\bar{L}\bar{L}'L''L'''}(\{2'21'1\}\{4'43'3\}) \Big] \lambda^{(\alpha')}_{L''L'''\{4'43'3\}} = \sum_{\alpha'} \sum_{\langle L''L'''\rangle} U^{(\alpha')}_{L''L'''}\, P^{(\alpha'\alpha)*}_{L''L'''LL'}(\{2'21'1\})\,. \tag{4.1}$$

In the weak Coulomb interaction limit, the third term at the lhs of the self-consistent equation (4.1) can be neglected because it is higher order in $\{U^{(\alpha)}_{LL'}\}$. Equation (4.1) is then expressed as follows.

$$\sum_{\alpha'} \sum_{\langle L''L'''\rangle} \sum_{\{kn\sigma\}}^{4'43'3} \Big[Q^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}\{4'43'3\}) - \epsilon_c\, S^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}\{4'43'3\}) \Big] \lambda^{(\alpha')}_{L''L'''\{4'43'3\}} = \sum_{\alpha'} \sum_{\langle L''L'''\rangle} U^{(\alpha')}_{L''L'''} P^{(\alpha'\alpha)*}_{L''L'''LL'}(\{2'21'1\})\,. \tag{4.2}$$

Substituting Eqs. (3.67) $\sim$ (3.69) into Eq. (4.2), we obtain

$$
\begin{aligned}
&\sum_{\alpha'}\sum_{\langle L''L'''\rangle}\Big(\Delta E(\{k_2'n_2'\sigma_2'k_2n_2\sigma_2k_1'n_1'\sigma_1'k_1n_1\sigma_1\})-\epsilon_c\Big)\\
&\times\Big[\langle k_1'n_1'|iL''\rangle_{\sigma_1'}\langle iL''|k_1n_1\rangle_{\sigma_1}\langle k_2'n_2'|iL'''\rangle_{\sigma_2'}\langle iL'''|k_2n_2\rangle_{\sigma_2}\lambda^{(\alpha')}_{L''L'''\{1'12'2\}}\\
&-\langle k_2'n_2'|iL''\rangle_{\sigma_2'}\langle iL''|k_1n_1\rangle_{\sigma_1}\langle k_1'n_1'|iL'''\rangle_{\sigma_1'}\langle iL'''|k_2n_2\rangle_{\sigma_2}\lambda^{(\alpha')}_{L''L'''\{2'11'2\}}\\
&-\langle k_1'n_1'|iL''\rangle_{\sigma_1'}\langle iL''|k_2n_2\rangle_{\sigma_2}\langle k_2'n_2'|iL'''\rangle_{\sigma_2'}\langle iL'''|k_1n_1\rangle_{\sigma_1}\lambda^{(\alpha')}_{L''L'''\{1'22'1\}}\\
&+\langle k_2'n_2'|iL''\rangle_{\sigma_2'}\langle iL''|k_2n_2\rangle_{\sigma_2}\langle k_1'n_1'|iL'''\rangle_{\sigma_1'}\langle iL'''|k_1n_1\rangle_{\sigma_1}\lambda^{(\alpha')}_{L''L'''\{2'21'1\}}\Big]\\
&=\sum_{\alpha'}\sum_{\langle L''L'''\rangle}U^{(\alpha')}_{L''L'''}\Big[C^{(\alpha')}_{\sigma_2\sigma_2'\sigma_1\sigma_1'}\langle iL''|k_2n_2\rangle_{\sigma_2}\langle k_2'n_2'|iL''\rangle_{\sigma_2'}\langle iL'''|k_1n_1\rangle_{\sigma_1}\langle k_1'n_1'|iL'''\rangle_{\sigma_1'}\\
&\qquad-C^{(\alpha')}_{\sigma_2\sigma_1'\sigma_1\sigma_2'}\langle iL''|k_2n_2\rangle_{\sigma_2}\langle k_1'n_1'|iL''\rangle_{\sigma_1'}\langle iL'''|k_1n_1\rangle_{\sigma_1}\langle k_2'n_2'|iL'''\rangle_{\sigma_2'}\\
&\qquad-C^{(\alpha')}_{\sigma_1\sigma_2'\sigma_2\sigma_1'}\langle iL''|k_1n_1\rangle_{\sigma_1}\langle k_2'n_2'|iL''\rangle_{\sigma_2'}\langle iL'''|k_2n_2\rangle_{\sigma_2}\langle k_1'n_1'|iL'''\rangle_{\sigma_1'}\\
&\qquad+C^{(\alpha')}_{\sigma_1\sigma_1'\sigma_2\sigma_2'}\langle iL''|k_1n_1\rangle_{\sigma_1}\langle k_1'n_1'|iL''\rangle_{\sigma_1'}\langle iL'''|k_2n_2\rangle_{\sigma_2}\langle k_2'n_2'|iL'''\rangle_{\sigma_2'}\Big]. \qquad (4.3)
\end{aligned}
$$

Here $\Delta E_{k_2'n_2'\sigma_2'k_2n_2\sigma_2k_1'n_1'\sigma_1'k_1n_1\sigma_1}$ is the two-particle excitation energy defined by $\Delta E_{k_2'n_2'\sigma_2'k_2n_2\sigma_2k_1'n_1'\sigma_1'k_1n_1\sigma_1}=\epsilon_{k_2'n_2'\sigma_2'}-\epsilon_{k_2n_2\sigma_2}+\epsilon_{k_1'n_1'\sigma_1'}-\epsilon_{k_1n_1\sigma_1}$. $C^{(\alpha)}_{\sigma_2\sigma_2'\sigma_1\sigma_1'}$ is defined by

$$
C^{(\alpha)}_{\sigma_2\sigma_2'\sigma_1\sigma_1'}=\begin{cases}\delta_{\sigma_2'\downarrow}\,\delta_{\sigma_2\downarrow}\,\delta_{\sigma_1'\uparrow}\,\delta_{\sigma_1\uparrow} & (\alpha=0)\\ \delta_{\sigma_2'\sigma_2}\,\delta_{\sigma_1'\sigma_1} & (\alpha=1)\\ \frac{1}{4}(\boldsymbol{\sigma})_{\sigma_1\sigma_1'}\cdot(\boldsymbol{\sigma})_{\sigma_2\sigma_2'} & (\alpha=2)\,.\end{cases} \qquad (4.4)
$$

Using the expression of the overlap integral $\langle iL|kn\rangle_\sigma = u_{Ln\sigma}(\boldsymbol{k})e^{-i\boldsymbol{k}\cdot\boldsymbol{R}_i}/\sqrt{N}$ and defining $a_{LL'\{2'21'1\}}$ by

$$
a_{LL'\{2'21'1\}}=u^*_{Ln_2'\sigma_2'}(\boldsymbol{k_2'})\,u_{Ln_2\sigma_2}(\boldsymbol{k}_2)\,u^*_{L'n_1'\sigma_1'}(\boldsymbol{k_1'})\,u_{L'n_1\sigma_1}(\boldsymbol{k}_1)\,, \qquad (4.5)
$$

we can simplify the self-consistent equation (4.3) as follows.

$$
\begin{aligned}
&\sum_{\alpha}\sum_{\langle LL'\rangle}\Big(a_{LL'\{2'21'1\}}\lambda^{(\alpha)}_{LL'\{2'21'1\}}-a_{LL'\{1'22'1\}}\lambda^{(\alpha)}_{LL'\{1'22'1\}}\\
&\qquad-a_{LL'\{2'11'2\}}\lambda^{(\alpha)}_{LL'\{2'11'2\}}+a_{LL'\{1'12'2\}}\lambda^{(\alpha)}_{LL'\{1'12'2\}}\Big)\\
&=\sum_{\alpha}\sum_{\langle LL'\rangle}\Big(\Delta E(\{k_2'n_2'\sigma_2'k_2n_2\sigma_2k_1'n_1'\sigma_1'k_1n_1\sigma_1\})-\epsilon_c\Big)^{-1}\\
&\qquad\times U^{(\alpha)}_{LL'}\Big(C^{(\alpha)}_{\sigma_2\sigma_2'\sigma_1\sigma_1'}a_{LL'\{2'21'1\}}-C^{(\alpha)}_{\sigma_2\sigma_1'\sigma_1\sigma_2'}a_{LL'\{1'22'1\}}\\
&\qquad\qquad-C^{(\alpha)}_{\sigma_1\sigma_2'\sigma_2\sigma_1'}a_{LL'\{2'11'2\}}+C^{(\alpha)}_{\sigma_1\sigma_1'\sigma_2\sigma_2'}a_{LL'\{1'12'2\}}\Big)\,. \qquad (4.6)
\end{aligned}
$$

Then, we find the following solution by inspection.

$$
\lambda^{(\alpha)}_{LL'\{2'21'1\}}=\frac{C^{(\alpha)}_{\sigma_2\sigma_2'\sigma_1\sigma_1'}U^{(\alpha)}_{LL'}}{\Delta E_{k_2'n_2'\sigma_2'k_2n_2\sigma_2k_1'n_1'\sigma_1'k_1n_1\sigma_1}-\epsilon_c}\,. \qquad (4.7)
$$

Using Eqs. (3.44), (3.45), (3.46), (4.4), and (4.7), we obtain the variational parameters η's, ζ's, and ξ's in the weak Coulomb interaction limit as follows.

$$\eta_{Lk_2'n_2'k_2n_2k_1'n_1'k_1n_1} = \frac{U_{LL}}{\epsilon_{k_2'n_2'\downarrow} - \epsilon_{k_2n_2\downarrow} + \epsilon_{k_1'n_1'\uparrow} - \epsilon_{k_1n_1\uparrow} - \epsilon_c}, \tag{4.8}$$

$$\zeta^{(\sigma\sigma')}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1} = \frac{(U_{LL'} - J_{LL'}/2)}{\epsilon_{k_2'n_2'\sigma'} - \epsilon_{k_2n_2\sigma} + \epsilon_{k_1'n_1'\sigma'} - \epsilon_{k_1n_1\sigma} - \epsilon_c}, \tag{4.9}$$

$$\xi^{(\sigma)}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1} = \frac{J_{LL'}}{\epsilon_{k_2'n_2'-\sigma} - \epsilon_{k_2n_2\sigma} + \epsilon_{k_1'n_1'\sigma} - \epsilon_{k_1n_1-\sigma} - \epsilon_c}, \tag{4.10}$$

$$\xi^{(\sigma\sigma')}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1} = \frac{J_{LL'}}{\epsilon_{k_2'n_2'\sigma'} - \epsilon_{k_2n_2\sigma} + \epsilon_{k_1'n_1'\sigma'} - \epsilon_{k_1n_1\sigma} - \epsilon_c}. \tag{4.11}$$

We make use of these variational parameters for the calculations of the physical quantities in the weak Coulomb interaction regime.

4.2 Various quantities in the weak Coulomb interaction regime

In the lowest-order approximation, we can neglect the higher order terms in physical quantities. Then we obtain the correlation energy from Eq. (3.61) as follows.

$$\epsilon_c = -\langle \tilde{O}_i^{\dagger} H_I \rangle_0 - \langle H_I \tilde{O}_i \rangle_0 + \langle \tilde{O}_i^{\dagger} \tilde{H}_0 \tilde{O}_i \rangle_0 \,. \tag{4.12}$$

We can obtain the matrix elements $\langle H_I \tilde{O}_i \rangle_0$ and $\langle \tilde{O}_i^{\dagger} \tilde{H}_0 \tilde{O}_i \rangle_0$ from the Hartree-Fock local density of states using the Laplace transformations. The explicit expression of these matrix elements are summarized in Appendix C.

The electron number is obtained from Eq. (3.77) as follows.

$$\langle n_{iL} \rangle = \langle n_{iL} \rangle_0 + \langle \tilde{n}_{iL} \rangle \,. \tag{4.13}$$

Here the first term denotes the Hartree-Fock electron number. The second terms is known as correlation correction. We obtain the correlation corrections in the lowest-order approximation as follows.

$$\langle \tilde{n}_{iL} \rangle = \langle \tilde{O}_i^{\dagger} \tilde{n}_{iL} \tilde{O}_i \rangle_0 \,. \tag{4.14}$$

The expression with use of the Laplace transformation is given in Appendix C.

We obtain the charge fluctuations and the amplitude of local moment from Eqs. (3.89) and (3.99) as follows:

$$\begin{aligned} \langle (\delta n_{id})^2 \rangle = & \sum_{L\sigma}^{d} \langle n_{iL\sigma} \rangle_0 (1 - \langle n_{iL\sigma} \rangle_0) + \sum_{L\sigma}^{d} \langle \tilde{n}_{iL\sigma} \rangle (1 - 2\langle n_{iL\sigma} \rangle_0) \\ & - \langle \tilde{n}_{id} \rangle^2 + 2 \sum_{L}^{d} \langle O^{(0)}_{iLL} \rangle + 2 \sum_{(L,L')}^{d} \langle O^{(1)}_{iLL'} \rangle \,, \end{aligned} \tag{4.15}$$

$$\langle \boldsymbol{S}^2 \rangle = \frac{3}{4}\sum_{L\sigma}^{d}\langle n_{iL\sigma}\rangle_0(1-\langle n_{iL\sigma}\rangle_0) + \frac{3}{4}\sum_{L\sigma}^{d}\langle \tilde{n}_{iL\sigma}\rangle(1-2\langle n_{iL-\sigma}\rangle_0) - \frac{3}{2}\sum_{L}^{d}\langle O^{(0)}_{iLL}\rangle + 2\sum_{(L,L')}^{d}\langle O^{(2)}_{iLL'}\rangle\,. \tag{4.16}$$

The averages $\sum_{\langle LL'\rangle}\langle O^{(\alpha)}_{iLL'}\rangle$ in the lowest-order approximation are obtained from Eq. (3.90) as follows.

$$\sum_{\langle LL'\rangle}\langle O^{(\alpha)}_{iLL'}\rangle = -\sum_{\langle LL'\rangle}\langle \tilde{O}_i{}^{\dagger} O^{(\alpha)}_{iLL'}\rangle_0 - \sum_{\langle LL'\rangle}\langle O^{(\alpha)}_{iLL'}\tilde{O}_i\rangle_0 + \sum_{\langle LL'\rangle}\langle \tilde{O}_i{}^{\dagger} O^{(\alpha)}_{iLL'}\tilde{O}_i\rangle_0\,. \tag{4.17}$$

All the matrix elements at the rhs of the above equation are expressed with use of Laplace transformation (2.39), and are summarized in Appendix C.

4.3 Numerical results of BCC Iron in the lowest order

Bcc iron shows a simple ferromagnetism. The band theory can explain the ground state magnetization. But the other physical properties such as the magnetic energy, the cohesive energy, and low-temperature specific heat have not yet been quantitatively or even qualitatively explained by the band theory. The band theory also cannot describe charge fluctuations, amplitude of local moments, and the momentum distribution function.

In this section we examine the accuracy of the first-principles MLA in the lowest-order approximation, comparing the numerical results for bcc Fe with those of the LA+d band theory as well as the experimental data.

4.3.1 Hartree-Fock band structure and density of states Fe

We performed the Hartree-Fock band calculations for bcc Fe in the paramagnetic state as the first step to investigate the correlation effects using the first-principles MLA. We adopted the orbital-independent Coulomb and exchange integrals with U_{LL} = U_0 = 0.2749 Ry, $U_{LL'}$ = U_1 = 0.1426 Ry, and $J_{LL'}$ = J= 0.0662 Ry obtained by Anisimov $et\ al.$ [25, 27].

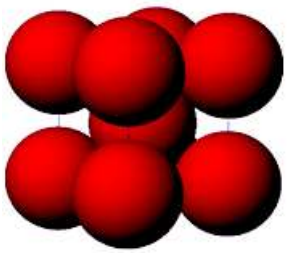

Figure 4.1: Crystal structure of bcc Fe.

The crystal structure of bcc Fe is shown in Fig. 4.1. The space group of bcc Fe is given by $Im\bar{3}m$ (229). We used the experimental value of the lattice parameter a=5.406476 a.u. The

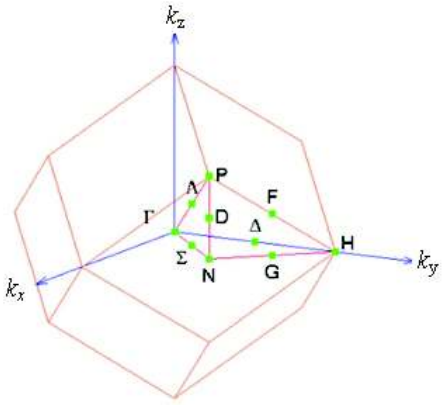

Figure 4.2: First Brillouin zone of bcc crystal structure.

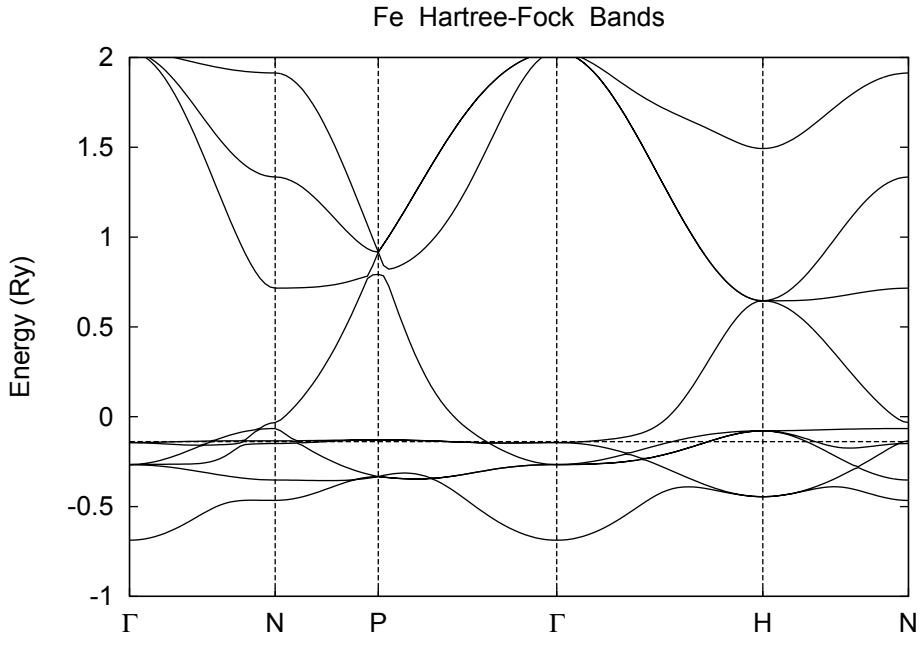

Figure 4.3: Hartree-Fock one-electron energy bands of bcc Fe along the high-symmetry lines of the first Brillouin zone.

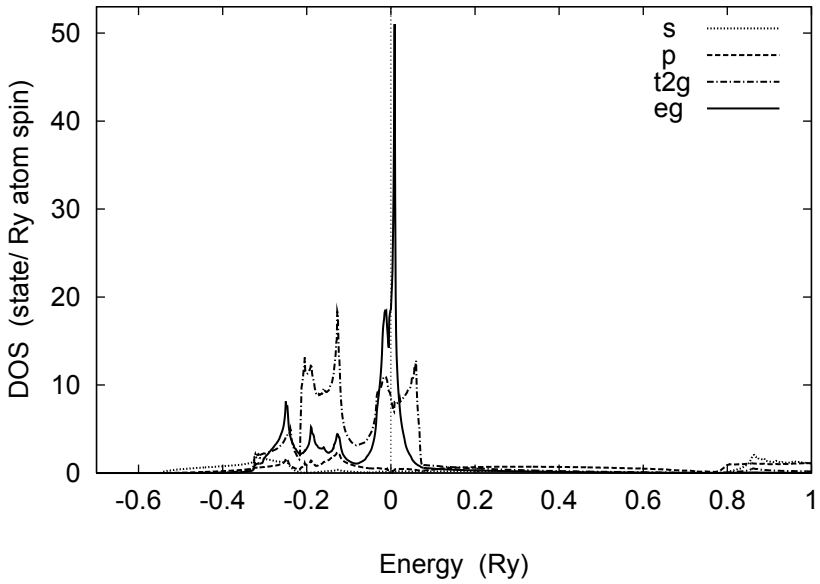

Figure 4.4: Hartree-Fock densities of states of bcc Fe. The s electrons: dotted curve, the p electrons: dashed curve, the t_{2g} electrons: dot-dashed curve, and the e_g electrons: solid curve. The energy is measured from the Fermi level $\epsilon_{\rm F}$.

first Brillouin zone (BZ) of bcc crystal structure is shown in Fig. 4.2. We adopted the BZ mesh $24 \times 24 \times 24$ for numerical $\boldsymbol{k}$-point integrations. Furthermore l = $3d, 4s$, and $4p$ orbitals were taken into account in the calculations. Solving the Hartree-Fock equations for the tight-binding LDA+U Hamiltonian, we obtained the one-electron energy eigenvalues $\epsilon_{kn\sigma}$ for paramagnetic Fe. Figure 4.3 shows the energy band curves along high-symmetry lines (Γ-N-P-Γ-H-N) in the first Brillouin zone. The band structure for d electrons in the Hartree-Fock approximation is similar to that obtained by the usual LDA band theory, though the former bands sink by 0.064 Ry as compared with the latter. Note that the e_g bands near the Fermi level along the (Γ-N-P-Γ) line are much narrower than the t_{2g} ones. The other sp bands are mostly far from the Fermi level $\epsilon_{\rm F}$, thus the Fermi surface of Fe is mainly determined by the d-bands.

Calculated local densities of states (LDOS) are shown in Fig. 4.4. The sharp peak on the Fermi level is created by the e_g electrons, while the shoulder above the Fermi level and the second peak around -0.2 Ry are created by the t_{2g} electrons.

4.3.2 Lowest-order results for bcc Fe

We obtained the variational parameters (4.8) $\sim$ (4.11) in the lowest order (see Sec. 4.1). In order to see a systematic change of the physical quantities of bcc Fe with increasing interaction strength, we scaled U_0, U_1, and J as αU_0, αU_1, and αJ using a scaling factor α from 0 to 1, and performed the lowest-order calculations. Figure 4.5 shows the calculated correlation energy as a function of αU_0. With increasing αU_0 (as well as αU_1 and αJ), we find that the correlation energy ϵ_c monotonically decrease. We obtain $\epsilon_c = -0.0516$ Ry for $\alpha = 1$ (case of Fe) and $U_1 = J = 0$, $i.e.$, the correlation energy due to intra-orbital correlations. When we take into account the inter-orbitals correlations ($U_0, U_1, J \neq 0$), the correlation energy ϵ_c decreases further and we obtain

$\epsilon_c = -0.1101$ Ry when $\alpha = 1$. The inter-orbitals correlation energy gain is comparable to the intra-orbital correlations energy.

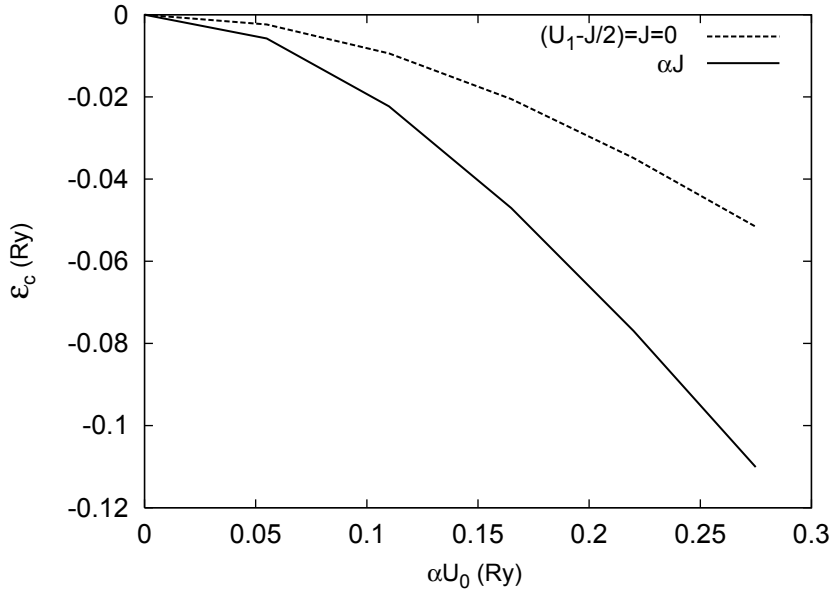

Figure 4.5: The correlation energy ϵ_c as a function of Coulomb interaction strength αU_0 for the paramagnetic Fe. Dashed curve: the result without inter-orbital correlations ($i.e., U_1 - J/2 = J = 0$), solid curve: the result with both the intra- and inter-orbital correlations.

The correlation energy gain is accompanied by the suppression of charge fluctuations. We calculated the charge fluctuations for d electrons $\langle(\delta n_{id})^2\rangle = \langle n_{id}^2\rangle - \langle n_{id}\rangle^2$ as a function of αU_0. As shown in Fig. 4.6, the charge fluctuation in the Hartree-Fock approximation is 2.2. The intra-orbital correlations suppress the charge fluctuations and yields $\langle(\delta n_{id})^2\rangle$=1.6 for $\alpha U_0 = 0.27$ Ry for Fe. The inter-orbital correlations more rapidly decrease the charge fluctuation with increasing αU_0 as seen in Fig. 4.6. Calculated charge fluctuation is $\langle(\delta n_{id})^2\rangle \approx 1.21$ for $\alpha U_0 = 0.27$ Ry. The result is comparable to the value of the LA with the d-band model, $\langle(\delta n_{id})^2\rangle \approx 1.0$ [21], but is somewhat larger than that of the LA because the present theory takes into account the hybridization between the d and sp electrons.

We calculated the amplitude of local moment $\langle \boldsymbol{S}^2\rangle$ as a function of αU_0 as shown in Fig. 4.7. We have $\langle \boldsymbol{S}^2\rangle = 1.65$ for the Hartree-Fock uncorrelated electrons. The amplitudes of local moment monotonically increase with increasing the Coulomb interaction strength αU_0, and we find $\langle \boldsymbol{S}^2\rangle \approx 2.41$ for $\alpha U_0 = 0.27$ Ry (Fe) in the lowest-order calculations. The result is comparable to the value of the LA with the d-band model [21], $\langle \boldsymbol{S}^2\rangle \approx 2.91$, but is somewhat smaller than that of the LA because the present theory takes into account the hybridization between the d and sp electrons.

The momentum distribution function (MDF) is obtained from the formula (3.103):

$$\langle n_{kn\sigma}\rangle = f(\tilde{\epsilon}_{kn\sigma}) + \frac{N\langle \tilde{O}_i^\dagger \tilde{n}_{kn\sigma}\tilde{O}_i\rangle_0}{1 + \langle \tilde{O}_i{}^\dagger \tilde{O}_i\rangle_0}\,. \tag{4.18}$$

Note that the first term at the rhs (right-hand-side) is the momentum distribution in the Hartree-Fock approximation $\langle n_{kn\sigma}\rangle_0$, which is given by the Fermi distribution function at zero temperature $f(\tilde{\epsilon}_{kn\sigma}) = \theta(-\tilde{\epsilon}_{kn\sigma})$. Here θ denotes the step function, and $\tilde{\epsilon}_{kn\sigma}$ is the Hartree-Fock one-electron

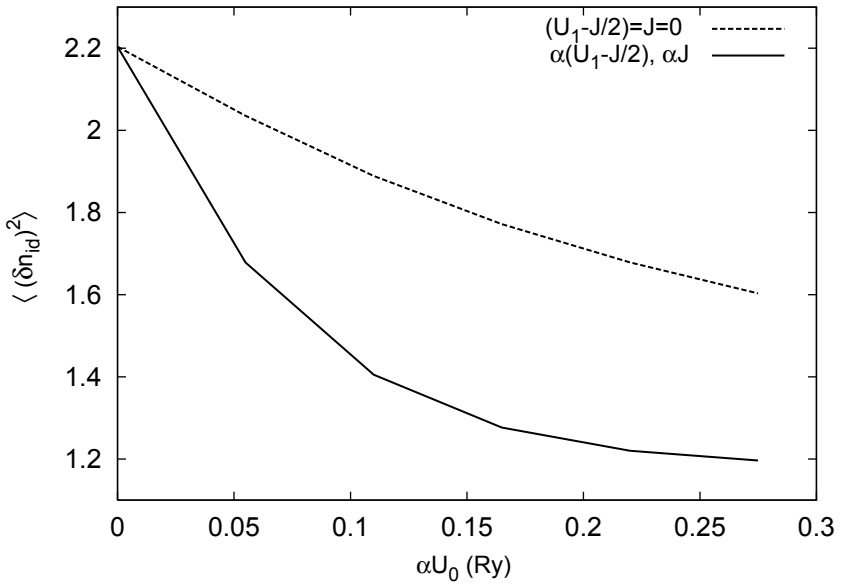

Figure 4.6: The charge fluctuation $\langle(\delta n_{id})^2\rangle$ vs Coulomb interaction strength αU_0 curve for the paramagnetic Fe. Dashed curve: the result without inter-orbital correlations, solid curve: the result with both the intra- and inter-orbital correlations.

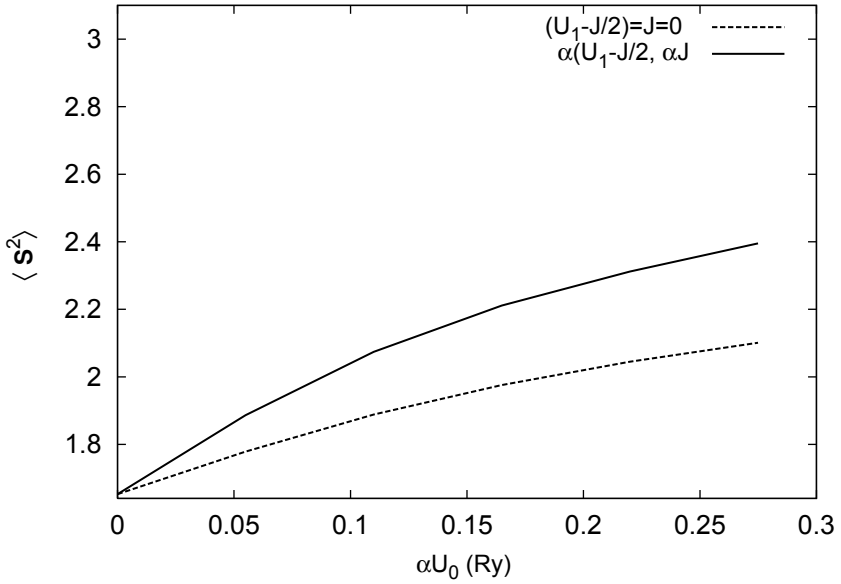

Figure 4.7: The amplitude of local moment $\langle \boldsymbol{S}^2\rangle$ vs Coulomb interaction strength αU_0 curve for the paramagnetic Fe. Dashed curve: the result without inter-orbital correlations, solid curve: the result with both the intra- and inter-orbital correlations.

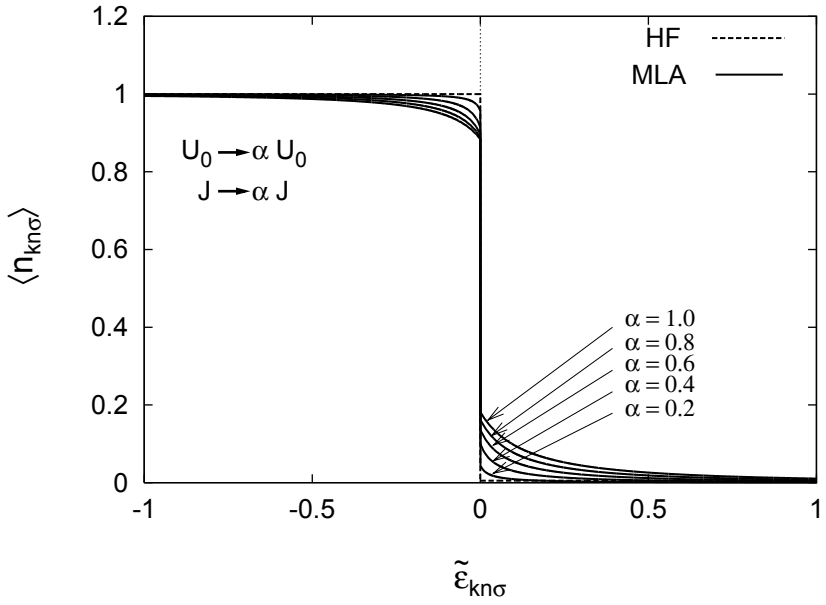

Figure 4.8: The momentum distribution $\langle n_{kn\sigma}\rangle$ as a function of the energy $\tilde{\epsilon}_{kn\sigma}$ for various scaling factors α of the Coulomb and exchange energies. Dash line denotes the distribution in the Hartree-Fock approximation.

energy measured from the Fermi level. The second term at the rhs of Eq. (4.18) describes the correlation correction. The numerator is expressed by

$$N\langle \tilde{O}_i^\dagger \tilde{n}_{kn\sigma}\tilde{O}_i\rangle_0 = U_{LL'}^{(\alpha)2} q_\tau^{(\alpha)}\Big[\sum_{\langle LL'\rangle}^{d}\left(B_{LL'}(\epsilon_{kn\sigma})|u_{Ln\sigma}(\boldsymbol{k})|^2 + B_{L'L}(\epsilon_{kn\sigma})|u_{L'n\sigma}(\boldsymbol{k})|^2\right) f(-\tilde{\epsilon}_{kn\sigma}) - \sum_{\langle LL'\rangle}^{d}\left(C_{LL'}(\epsilon_{kn\sigma})|u_{Ln\sigma}(\boldsymbol{k})|^2 + C_{L'L}(\epsilon_{kn\sigma})|u_{L'n\sigma}(\boldsymbol{k})|^2\right) f(\tilde{\epsilon}_{kn\sigma})\Big]. \quad (4.19)$$

Here $q_\tau^{(\alpha)}$ is a constant factor taking the value 1 for α=0, 2 for α=1, 1/8 for α=2, τ=l, and 1/4 for α=2, τ=t, respectively. $\{B_{LL'}(\epsilon_{kn\sigma})\}$ and $\{C_{LL'}(\epsilon_{kn\sigma})\}$ are expressed by the Laplace transformations of the Hartree-Fock local density of states (see Appendix C). The correlation correction consists of the terms being proportional to $|u_{Ln\sigma}(\boldsymbol{k})|^2\ f(\tilde{\epsilon}_{kn\sigma})$ and those being proportional to $|u_{Ln\sigma}(\boldsymbol{k})|^2\ f(-\tilde{\epsilon}_{kn\sigma})$. Here $\{u_{Ln\sigma}(\boldsymbol{k})\}$ are the eigenvectors for a given $\boldsymbol{k}$ point. Note that L in the amplitude $|u_{Ln\sigma}(\boldsymbol{k})|^2$ is d orbitals. For the sp bands the overlap of the eigenvetor $(, i.e., u_{Ln\sigma}(\boldsymbol{k}))$ is negligible, thus the second term at the rhs of Eq. (4.18) is small. Therefore the MDF of sp bands are expected to be the Fermi-Dirac distribution function $f(\tilde{\epsilon}_{kn\sigma})$, and the quasipartical weight as well as the effective mass are close to 1 for sp bands. On the other hand, the overlap of the eigenvetor is expected to be close to 1 for the d-bands. When we replace $|u_{Ln\sigma}(\boldsymbol{k})|^2$ with 1/5 in Eq.

(4.19) as a rough approximation for the d-like branch n near the Fermi level, we obtain

$$N\langle\tilde{O}_i^\dagger\tilde{n}_{kn\sigma}\tilde{O}_i\rangle_0 = \frac{1}{5}U_{LL'}^{(\alpha)2}q_\tau^{(\alpha)}\Big[\sum_{\langle LL'\rangle}^{d}\left(B_{LL'}(\epsilon_{kn\sigma})+B_{L'L}(\epsilon_{kn\sigma})\right)f(-\tilde{\epsilon}_{kn\sigma}) - \sum_{\langle LL'\rangle}^{d}\left(C_{LL'}(\epsilon_{kn\sigma})+C_{L'L}(\epsilon_{kn\sigma})\right)f(\tilde{\epsilon}_{kn\sigma})\Big]. \tag{4.20}$$

Then, $N\langle\tilde{O}_i^\dagger\tilde{n}_{kn\sigma}\tilde{O}_i\rangle_0$ depends on the momentum only via the energy $\tilde{\epsilon}_{kn\sigma}$ as in the single-band model. The quasipartical weight is less than 1 for the d-bands. Figure 4.8 shows the calculated result of momentum distributions for d electrons in this approximation. We find clear momentum dependence of $\langle n_{kn\sigma}\rangle$ via $\tilde{\epsilon}_{kn\sigma}$. We also find that the momentum dependence is developed with increasing the Coulomb and exchange interactions.

We calculated the mass enhancement from the jump of the MDF at the Fermi level. We obtain the mass enhancement $m^*/m = 1.4$ for $\alpha = 1.0$ (, $i.e.$, for bcc Fe). This value should be compared with the experimental renormalization values $1.38 \sim 2.12$ which are obtained from the comparison of the LDA density of states at $\epsilon_{\rm F}$ with those obtained from the T-linear specific heat coefficient at low temperatures [72–74]. We have to calculate $\langle n_{kn\sigma}\rangle$ taking into account the $\boldsymbol{k}$-dependence of $|u_{Ln\sigma}(\boldsymbol{k})|^2$ in more detailed calculations. This will be done in Sec 5.2.

Chapter 5

First-Principles MLA with Self-Consistent Variational Parameters

In the last chapter, we presented the ground state of paramagnetic bcc Fe in the lowest order approximation. In order to describe more correlated electrons, we derive in this chapter the self-consistent equations for new variational parameter ansatz, and obtain the expressions for various physical quantities. We then solve the self-consistent equations numerically, and clarify the ground state properties of bcc Fe [75, 76].

5.1 Self-consistent equations for new variational parameter ansatz

We derived the solution for variational parameters (4.8) - (4.11) in the weak Coulomb interaction limit. In order to describe more correlated electrons, we have to solve the full self-consistent equations (3.74). To obtain approximate solution for Eq. (3.74) in correlated electrons, we propose the following variational parameter ansatz which interpolate between the weak Coulomb interaction limit and the atomic limit as follows.

$$\eta_{Lk_2'n_2'k_2n_2k_1'n_1'k_1n_1} = \frac{U_{LL}\tilde{\eta}_{LL}}{\epsilon_{k_2'n_2'\downarrow} - \epsilon_{k_2n_2\downarrow} + \epsilon_{k_1'n_1'\uparrow} - \epsilon_{k_1n_1\uparrow} - \epsilon_c}, \tag{5.1}$$

$$\zeta^{(\sigma\sigma')}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1} = \frac{(U_{LL'} - J_{LL'}/2)\tilde{\zeta}^{(\sigma\sigma')}_{LL'}}{\epsilon_{k_2'n_2'\sigma'} - \epsilon_{k_2n_2\sigma} + \epsilon_{k_1'n_1'\sigma'} - \epsilon_{k_1n_1\sigma} - \epsilon_c}, \tag{5.2}$$

$$\xi^{(\sigma)}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1} = \frac{J_{LL'}\tilde{\xi}^{(\sigma)}_{LL'}}{\epsilon_{k_2'n_2'-\sigma} - \epsilon_{k_2n_2\sigma} + \epsilon_{k_1'n_1'\sigma} - \epsilon_{k_1n_1-\sigma} - \epsilon_c}, \tag{5.3}$$

$$\xi^{(\sigma\sigma')}_{LL'k_2'n_2'k_2n_2k_1'n_1'k_1n_1} = \frac{J_{LL'}\tilde{\xi}^{(\sigma\sigma')}_{LL'}}{\epsilon_{k_2'n_2'\sigma'} - \epsilon_{k_2n_2\sigma} + \epsilon_{k_1'n_1'\sigma'} - \epsilon_{k_1n_1\sigma} - \epsilon_c}. \tag{5.4}$$

Here the renormalization factors $\tilde{\eta}_{LL}$, $\tilde{\zeta}^{(\sigma\sigma')}_{LL'}$, $\tilde{\xi}^{(\sigma)}_{tLL'}$, and $\tilde{\xi}^{(\sigma\sigma')}_{lLL'}$ are new variational parameters to be determined.

Substituting the above expressions into Eqs. (3.44)-(3.46), we obtain the following form of the variational parameters $\lambda^{(\alpha)}_{LL'\{2'21'1\}}$:

$$\lambda^{(\alpha)}_{LL'\{2'21'1\}} = \frac{U^{(\alpha)}_{LL'}\sum_\tau C^{(\alpha)}_{\tau\sigma_2'\sigma_2\sigma_1'\sigma_1}\tilde{\lambda}^{(\sigma\sigma')}_{\alpha\tau LL'}}{\Delta E_{k_2'n_2'\sigma_2'k_2n_2\sigma_2k_1'n_1'\sigma_1'k_1n_1\sigma_1} - \epsilon_c}. \tag{5.5}$$

Here the spin-dependent coefficients $C^{(\alpha)}_{\tau\sigma_2'\sigma_2\sigma_1'\sigma_1}$ are defined by

$$C^{(\alpha)}_{\tau\sigma_2'\sigma_2\sigma_1'\sigma_1} = \begin{cases} \delta_{\sigma_2'\downarrow}\delta_{\sigma_2\downarrow}\delta_{\sigma_1'\uparrow}\delta_{\sigma_1\uparrow} & (\alpha=0) \\ \delta_{\sigma_2'\sigma_2}\delta_{\sigma_1'\sigma_1} & (\alpha=1) \\ -\frac{1}{4}\sigma_1\sigma_2\delta_{\sigma_2'\sigma_2}\delta_{\sigma_1'\sigma_1} & (\alpha=2,\tau=l) \\ -\frac{1}{2}\sum_\sigma \delta_{\sigma_2'-\sigma}\delta_{\sigma_2\sigma}\delta_{\sigma_1'\sigma}\delta_{\sigma_1-\sigma} & (\alpha=2,\tau=t)\,. \end{cases} \tag{5.6}$$

Note that $l\,(t)$ implies the longitudinal (transverse) component. The renormalization factors $\tilde{\lambda}^{(\sigma\sigma')}_{\alpha\tau LL'}$ are defined as follows.

$$\tilde{\lambda}^{(\sigma\sigma')}_{\alpha\tau LL'} = \begin{cases} \tilde{\eta}_{LL'}\delta_{LL'}\delta_{\sigma'-\sigma} & (\alpha=0) \\ \tilde{\zeta}^{(\sigma\sigma')}_{LL'} & (\alpha=1) \\ \tilde{\xi}^{(\sigma'\sigma)}_{lLL'} & (\alpha=2,\tau=l) \\ \tilde{\xi}^{(\sigma)}_{tLL'}\delta_{\sigma'\sigma} & (\alpha=2,\tau=t)\,. \end{cases} \tag{5.7}$$

Note that the correlation energy ϵ_c is given by Eq. (3.61) in the SSA.

$$\epsilon_c = \frac{-\langle\tilde{O}_i{}^\dagger H_I\rangle_0 - \langle H_I\tilde{O}_i\rangle_0 + \langle\tilde{O}_i{}^\dagger\tilde{H}\tilde{O}_i\rangle_0}{1+\langle\tilde{O}_i{}^\dagger\tilde{O}_i\rangle_0}\,. \tag{5.8}$$

Substituting Eq. (5.5) into the matrix elements in Eq. (5.8) (, *i.e.*, (3.62) - (3.66)), we find the following expressions of the elements.

$$\langle\tilde{H}_I\tilde{O}_i\rangle_0 = \sum_{\alpha\alpha'}\sum_{\langle LL'\rangle}\sum_{\langle L''L'''\rangle} U^{(\alpha)}_{LL'}\,U^{(\alpha')}_{L''L'''}\sum_{\tau\sigma\sigma'}\tilde{\lambda}^{(\sigma\sigma')}_{\alpha'\tau L''L'''}\,P^{(\alpha\alpha')}_{\tau LL'L''L'''\sigma\sigma'}\,, \tag{5.9}$$

$$\langle\tilde{O}_i{}^\dagger\tilde{H}\tilde{O}_i\rangle_0 = \langle\tilde{O}_i{}^\dagger\tilde{H}_0\tilde{O}_i\rangle_0 + \langle\tilde{O}_i{}^\dagger\tilde{H}_I\tilde{O}_i\rangle_0\,. \tag{5.10}$$

Here

$$\langle\tilde{O}_i{}^\dagger\tilde{H}_0\tilde{O}_i\rangle_0 = \sum_{\alpha\alpha'}\sum_{\langle LL'\rangle}\sum_{\langle L''L'''\rangle} U^{(\alpha)}_{LL'}\,U^{(\alpha')}_{L''L'''}\sum_{\tau\sigma\sigma'}\sum_{\tau'\sigma''\sigma'''}\tilde{\lambda}^{(\sigma\sigma')*}_{\alpha\tau LL'}\,\tilde{\lambda}^{(\sigma''\sigma''')}_{\alpha'\tau'L''L'''}\,Q^{(\alpha\alpha')}_{\tau\tau'LL'L''L'''\sigma\sigma'\sigma''\sigma'''}\,, \tag{5.11}$$

$$\langle\tilde{O}_i{}^\dagger\tilde{H}_I\tilde{O}_i\rangle_0 = \sum_{\alpha}\sum_{\langle LL'\rangle} U^{(\alpha)}_{LL'}\sum_{\tau\sigma\sigma'}\tilde{\lambda}^{(\sigma\sigma')*}_{\alpha\tau LL'}\,K^{(\alpha)}_{\tau LL'\sigma\sigma'}\,. \tag{5.12}$$

$K^{(\alpha)}_{\tau LL'\sigma\sigma'}$ at the rhs of Eq. (5.12) is defined by

$$K^{(\alpha)}_{\tau LL'\sigma\sigma'} = \sum_{\alpha'}\sum_{\langle L''L'''\rangle}\sum_{\tau'\sigma''\sigma'''} U^{(\alpha')}_{L''L'''}\,R^{(\alpha\alpha')}_{\tau\tau'LL'L''L'''\sigma\sigma'\sigma''\sigma'''}\,\tilde{\lambda}^{(\sigma''\sigma''')}_{\alpha'\tau'L''L'''}\,, \tag{5.13}$$

and

$$R^{(\alpha\alpha')}_{\tau\tau'LL'L''L'''\sigma\sigma'\sigma''\sigma'''} = \sum_{\{kn\sigma\}}^{2'211'}\sum_{\{kn\sigma\}}^{4'433'}\frac{C^{(\alpha)}_{\tau\sigma_2'\sigma_2\sigma_1'\sigma_1}C^{(\alpha')}_{\tau'\sigma_4'\sigma_4\sigma_3'\sigma_3}R^{(\alpha\alpha')}_{LL'L''L'''}(\{2'21'1\}\{4'43'3\})}{(\Delta E_{k_2'n_2'\sigma_2'k_2n_2\sigma_2k_1'n_1'\sigma_1'k_1n_1\sigma_1}-\epsilon_c)(\Delta E_{k_4'n_4'\sigma_4'k_4n_4\sigma_4k_3'n_3'\sigma_3'k_3n_3\sigma_3}-\epsilon_c)}\,. \tag{5.14}$$

Furthermore,

$$\langle \tilde{O}_i{}^\dagger \tilde{O}_i \rangle_0 = \sum_{\alpha\alpha'} \sum_{\langle LL' \rangle} \sum_{\langle L''L''' \rangle} U^{(\alpha)}_{LL'}\, U^{(\alpha')}_{L''L'''} \sum_{\tau\sigma\sigma'} \sum_{\tau'\sigma''\sigma'''} \tilde{\lambda}^{(\sigma\sigma')*}_{\alpha\tau LL'}\, \tilde{\lambda}^{(\sigma''\sigma''')}_{\alpha'\tau' L''L'''}\, S^{(\alpha\alpha')}_{\tau\tau' LL'L''L'''\sigma\sigma'\sigma''\sigma'''} \,. \quad (5.15)$$

The coefficients $P^{(\alpha\alpha')}_{\tau LL'L''L'''\sigma\sigma'}$, $Q^{(\alpha\alpha')}_{\tau\tau' LL'L''L'''\sigma\sigma'\sigma''\sigma'''}$, $S^{(\alpha\alpha')}_{\tau\tau' LL'L''L'''\sigma\sigma'\sigma''\sigma'''}$, and $K^{(\alpha)}_{\tau LL'\sigma\sigma'}$ are obtained by making use of the Laplace transformations. Their explicit expressions are given in Appendix D.

The self-consistent equations for new variational parameters are obtained from the stationary condition $\delta\epsilon_c = 0$ for Eq. (5.8):

$$-\langle (\delta\tilde{O}_i^\dagger) H_I \rangle_0 + \langle (\delta\tilde{O}_i^\dagger) \tilde{H} \tilde{O}_i \rangle_0 - \epsilon_c \langle (\delta\tilde{O}_i^\dagger) \tilde{O}_i \rangle_0 + c.c. = 0 \,. \quad (5.16)$$

Substituting the expressions (5.9) $\sim$ (5.15) into the above equation, we find the self-consistent equations for the variational parameters $\tilde{\lambda}^{(\sigma\sigma')}_{\alpha\tau' LL'}$ as follows.

$$\sum_{\alpha'} \sum_{\langle L''L''' \rangle} \sum_{\tau'\sigma''\sigma'''} U^{(\alpha')}_{L''L'''} \left(Q^{(\alpha\alpha')}_{\tau\tau' LL'L''L'''\sigma\sigma'\sigma''\sigma'''} - \epsilon_c\, S^{(\alpha\alpha')}_{\tau\tau' LL'L''L'''\sigma\sigma'\sigma''\sigma'''} \right) \tilde{\lambda}^{(\sigma''\sigma''')}_{\alpha'\tau' L''L'''}$$
$$= \sum_{\alpha'} \sum_{\langle L''L''' \rangle} U^{(\alpha')}_{L''L'''}\, P^{(\alpha'\alpha)}_{\tau L''L'''LL'\sigma\sigma'} - K^{(\alpha)}_{\tau LL'\sigma\sigma'} \,. \quad (5.17)$$

We can verify $Q^{(\alpha\alpha')}_{\tau\tau' LL'L''L'''\sigma\sigma'\sigma''\sigma'''} \propto \delta_{\tau\tau'}\delta_{\langle LL' \rangle\langle L''L''' \rangle}$, $S^{(\alpha\alpha')}_{\tau\tau' LL'L''L'''\sigma\sigma'\sigma''\sigma'''} \propto \delta_{\tau\tau'}\delta_{\langle LL' \rangle\langle L''L''' \rangle}$, and $P^{(\alpha\alpha')}_{\tau LL'L''L'''\sigma\sigma'} \propto \delta_{\langle LL' \rangle\langle L''L''' \rangle}$. Thus the self-consistent equation (5.17) is simplified as follows.

$$\sum_{\alpha'} \sum_{\sigma''\sigma'''} U^{(\alpha')}_{LL'} \left(Q^{(\alpha\alpha')}_{\tau\tau LL'LL'\sigma\sigma'\sigma''\sigma'''} - \epsilon_c S^{(\alpha\alpha')}_{\tau\tau LL'LL'\sigma\sigma'\sigma''\sigma'''} \right) \tilde{\lambda}^{(\sigma''\sigma''')}_{\alpha'\tau LL'}$$
$$= \sum_{\alpha'} U^{(\alpha')}_{L''L'''} P^{(\alpha'\alpha)}_{\tau LL'LL'\sigma\sigma'} - K^{(\alpha)}_{\tau LL'\sigma\sigma'}. \quad (5.18)$$

Defining $\tilde{Q}^{(\alpha\alpha')}_{\tau\tau LL'LL'\sigma\sigma'\sigma''\sigma'''}$ by

$$\tilde{Q}^{(\alpha\alpha')}_{\tau\tau' LL'LL'\sigma\sigma'\sigma''\sigma'''} = Q^{(\alpha\alpha')}_{\tau\tau' LL'LL'\sigma\sigma'\sigma''\sigma'''} - \epsilon_c S^{(\alpha\alpha')}_{\tau\tau' LL'LL'\sigma\sigma'\sigma''\sigma'''}, \quad (5.19)$$

we can express the self-consistent equation (5.18) as follows.

$$\sum_{\alpha'} \sum_{\sigma''\sigma'''} U^{(\alpha')}_{LL'} \tilde{Q}^{(\alpha\alpha')}_{\tau\tau LL'LL'\sigma\sigma'\sigma''\sigma'''} \tilde{\lambda}^{(\sigma''\sigma''')}_{\alpha'\tau LL'} = \sum_{\alpha'} U^{(\alpha')}_{L''L'''} P^{(\alpha'\alpha)}_{\tau LL'LL'\sigma\sigma'} - K^{(\alpha)}_{\tau LL'\sigma\sigma'}. \quad (5.20)$$

Furthermore, we can verify that $\tilde{Q}^{(\alpha\alpha')}_{\tau\tau' LL'LL'\sigma\sigma'\sigma''\sigma'''} \propto \delta_{\sigma''\sigma}\delta_{\sigma'''\sigma'}$. Thus we reach the following self-consistent equations for the variational parameters $\{\tilde{\lambda}^{(\sigma\sigma')}_{\alpha'\tau LL'}\}$:

$$\sum_{\alpha'} U^{(\alpha')}_{LL'} \tilde{Q}^{(\alpha\alpha')}_{\tau LL'\sigma\sigma'} \tilde{\lambda}^{(\sigma\sigma')}_{\alpha'\tau LL'} = \sum_{\alpha'} U^{(\alpha')}_{LL'} P^{(\alpha'\alpha)}_{\tau LL'\sigma\sigma'} - K^{(\alpha)}_{\tau LL'\sigma\sigma'}. \quad (5.21)$$

Here we defined $\tilde{Q}^{(\alpha\alpha')}_{\tau LL'\sigma\sigma'}$ and $P^{(\alpha'\alpha)}_{\tau LL'\sigma\sigma'}$ as follows.

$$\tilde{Q}^{(\alpha\alpha')}_{\tau LL'\sigma\sigma'} = \tilde{Q}^{(\alpha\alpha')}_{\tau\tau LL'LL'\sigma\sigma'\sigma\sigma'}, \quad (5.22)$$

$$P^{(\alpha'\alpha)}_{\tau LL'\sigma\sigma'} = P^{(\alpha'\alpha)}_{\tau LL'LL'\sigma\sigma'}. \tag{5.23}$$

For $\alpha = 0$, we have $\tilde{Q}^{(0\alpha')}_{\tau LL'\sigma\sigma'} \propto \delta_{\alpha'0}$ and $P^{(0\alpha')}_{\tau LL'\sigma\sigma'} \propto \delta_{\alpha'0}$. Thus we obtain from Eq. (5.21)

$$U^{(0)}_{LL'}\tilde{Q}^{(00)}_{\tau LL'\sigma\sigma'}\tilde{\lambda}^{(\sigma\sigma')}_{0\tau LL'} = U^{(0)}_{LL'}P^{(00)}_{\tau LL'\sigma\sigma'} - K^{(0)}_{\tau LL'\sigma\sigma'}. \tag{5.24}$$

Furthermore note that $U^{(0)}_{LL'} \propto \delta_{LL'}, \tilde{Q}^{(00)}_{\tau LL'\sigma\sigma'} \propto \delta_{\sigma\downarrow}\delta_{\sigma'\uparrow}$, and $P^{(00)}_{\tau LL'\sigma\sigma'} \propto \delta_{\sigma\downarrow}\delta_{\sigma'\uparrow}$. Thus we obtain the self-consistent equation for the variational parameters $\tilde{\lambda}^{(\downarrow\uparrow)}_{0LL}$ as follows.

$$\tilde{\lambda}^{(\downarrow\uparrow)}_{0LL} = \tilde{Q}^{(00)-1}_{LL\downarrow\uparrow}(P^{(00)}_{LL\downarrow\uparrow} - {U^{(0)}_{LL}}^{-1}K^{(00)}_{LL\downarrow\uparrow}). \tag{5.25}$$

Next, we obtain the self-consistent equations for $\tilde{\lambda}^{(\sigma\sigma')}_{1LL'}$ and $\tilde{\lambda}^{(\sigma\sigma')}_{2lLL'}$ from Eq. (5.21) for $\alpha = 1$ and $\alpha = 2$ ($\tau = l$) as follows.

$$U^{(1)}_{LL'}\tilde{Q}^{(11)}_{LL'\sigma\sigma'}\tilde{\lambda}^{(\sigma\sigma')}_{1LL'} + U^{(2)}_{LL'}\tilde{Q}^{(12)}_{lLL'\sigma\sigma'}\tilde{\lambda}^{(\sigma\sigma')}_{2lLL'} = U^{(1)}_{LL'}P^{(11)}_{LL'\sigma\sigma'} + U^{(2)}_{LL'}P^{(21)}_{LL'\sigma\sigma'} - K^{(1)}_{LL'\sigma\sigma'}, \tag{5.26}$$

$$U^{(1)}_{LL'}\tilde{Q}^{(21)}_{lLL'\sigma\sigma'}\tilde{\lambda}^{(\sigma\sigma')}_{1LL'} + U^{(2)}_{LL'}\tilde{Q}^{(22)}_{lLL'\sigma\sigma'}\tilde{\lambda}^{(\sigma\sigma')}_{2lLL'} = U^{(1)}_{LL'}P^{(21)}_{LL'\sigma\sigma'} + U^{(2)}_{LL'}P^{(22)}_{LL'\sigma\sigma'} - K^{(2)}_{lLL'\sigma\sigma'}. \tag{5.27}$$

Since $\tilde{\lambda}^{(\sigma\sigma')}_{1LL'}$ and $\tilde{\lambda}^{(\sigma\sigma')}_{2lLL'}$ should contain 4 independent variables, we express here the spin- dependent $\tilde{\lambda}^{(\sigma\sigma')}_{1LL'}$ and $\tilde{\lambda}^{(\sigma\sigma')}_{2lLL'}$ as follows (see Appendix E).

$$\tilde{\lambda}^{(\sigma\sigma')}_{1LL'} = \tilde{\lambda}_{1LL'} + \lambda^{(s)}_{1LL'}\sigma\delta_{\sigma'-\sigma}, \tag{5.28}$$

$$\tilde{\lambda}^{(\sigma\sigma')}_{2lLL'} = \tilde{\lambda}_{2lLL'} + \lambda^{(s)}_{2lLL'}\sigma\delta_{\sigma'\sigma}. \tag{5.29}$$

Substituting Eqs. (5.28) and (5.29) into Eqs. (5.26) and (5.27), and taking sum with respect to σ and σ', we find the following self-consistent equations.

$$\begin{aligned} U^{(1)}_{LL'}\bar{Q}^{(11)}_{LL'}\tilde{\lambda}_{1LL'} + U^{(1)}_{LL'}\bar{Q}^{(11)}_{4LL'}\lambda^{(s)}_{1LL'} + U^{(2)}_{LL'}\bar{Q}^{(12)}_{lLL'}\lambda_{2lLL'} + U^{(2)}_{LL'}\bar{Q}^{(12)}_{2lLL'}\lambda^{(s)}_{2lLL'} \\ = U^{(1)}_{LL'}\bar{P}^{(11)}_{LL'} + U^{(2)}_{LL'}\bar{P}^{(21)}_{LL'} - \bar{K}^{(1)}_{LL'}, \end{aligned} \tag{5.30}$$

$$\begin{aligned} U^{(1)}_{LL'}\bar{Q}^{(21)}_{LL'}\tilde{\lambda}_{1LL'} + U^{(1)}_{LL'}\bar{Q}^{(21)}_{4LL'}\lambda^{(s)}_{1LL'} + U^{(2)}_{LL'}\bar{Q}^{(22)}_{lLL'}\lambda_{2lLL'} + U^{(2)}_{LL'}\bar{Q}^{(22)}_{2lLL'}\lambda^{(s)}_{2lLL'} \\ = U^{(1)}_{LL'}\bar{P}^{(12)}_{LL'} + U^{(2)}_{LL'}\bar{P}^{(22)}_{LL'} - \bar{K}^{(2)}_{LL'}. \end{aligned} \tag{5.31}$$

Here we defined $\bar{Q}^{(\alpha\alpha')}_{\tau\tau'LL'}$, $\bar{Q}^{(\alpha\alpha')}_{n\tau\tau'LL'}$ (n = 2, 4), $\bar{P}^{(\alpha\alpha')}_{\tau'LL'}$, and $\bar{K}^{(\alpha)}_{\tau LL'}$ as follows.

$$\bar{Q}^{(\alpha\alpha')}_{\tau\tau'LL'} = \sum_{\sigma\sigma'}\tilde{Q}^{(\alpha\alpha')}_{\tau\tau'LL'\sigma\sigma'}, \tag{5.32}$$

$$\bar{Q}^{(\alpha\alpha')}_{2\tau\tau'LL'} = \sum_{\sigma}\sigma\tilde{Q}^{(\alpha\alpha')}_{\tau\tau'LL'\sigma\sigma'}, \tag{5.33}$$

$$\bar{Q}^{(\alpha\alpha')}_{4\tau\tau'LL'} = \sum_{\sigma}\sigma\tilde{Q}^{(\alpha\alpha')}_{\tau\tau'LL'\sigma-\sigma}, \tag{5.34}$$

$$\bar{P}^{(\alpha\alpha')}_{\tau' LL'} = \sum_{\sigma\sigma'} P^{(\alpha\alpha')}_{\tau' LL'\sigma\sigma'}, \tag{5.35}$$

and

$$\bar{K}^{(\alpha)}_{\tau LL'} = \sum_{\sigma\sigma'} K^{(\alpha)}_{\tau LL'\sigma\sigma'}. \tag{5.36}$$

Next from Eq. (5.26) with condition $\sigma = \sigma'$, we obtain

$$\begin{aligned} U^{(1)}_{LL'}\tilde{Q}^{(11)}_{LL'\sigma\sigma}\tilde{\lambda}^{(\sigma\sigma)}_{1LL'} + U^{(2)}_{LL'}\tilde{Q}^{(12)}_{lLL'\sigma\sigma}\tilde{\lambda}^{(\sigma\sigma)}_{2lLL'} + U^{(2)}_{LL'}\tilde{Q}^{(12)}_{lLL'\sigma\sigma}\tilde{\lambda}^{(s)}_{2lLL'}\sigma \\ = U^{(1)}_{LL'}P^{(11)}_{LL'\sigma\sigma} + U^{(2)}_{LL'}P^{(21)}_{LL'\sigma\sigma} - K^{(1)}_{LL'\sigma\sigma}. \end{aligned} \tag{5.37}$$

Multiplying both sides of Eq. (5.37) by σ and taking sum over σ, we obtain

$$U^{(1)}_{LL'}\bar{Q}^{(11)}_{2LL'}\tilde{\lambda}_{1LL'} + U^{(2)}_{LL'}\bar{Q}^{(12)}_{lLL'}\tilde{\lambda}_{2lLL'} + U^{(2)}_{LL'}\bar{Q}^{(12)}_{1lLL'}\lambda^{(s)}_{2lLL'} = U^{(1)}_{LL'}P^{(11)}_{2LL'} + U^{(2)}_{LL'}P^{(21)}_{2LL'} - K^{(1)}_{2LL'}. \tag{5.38}$$

Here

$$\bar{Q}^{(\alpha\alpha')}_{1\tau\tau' LL'} = \sum_{\sigma} \tilde{Q}^{(\alpha\alpha')}_{\tau\tau' LL'\sigma\sigma}, \tag{5.39}$$

$$\bar{Q}^{(\alpha\alpha')}_{2\tau LL'} = \sum_{\sigma} \sigma\tilde{Q}^{(\alpha\alpha')}_{\tau\tau' LL'\sigma\sigma}, \tag{5.40}$$

$$P^{(\alpha\alpha')}_{2\tau' LL'} = \sum_{\sigma} \sigma P^{(\alpha\alpha')}_{\tau' LL'\sigma\sigma}, \tag{5.41}$$

$$K^{(\alpha)}_{\tau LL'} = \sum_{\sigma} \sigma K^{(\alpha)}_{\tau LL'\sigma\sigma}. \tag{5.42}$$

Solving Eq. (5.38) with respect to $\lambda^{(s)}_{2lLL'}$, we find

$$\lambda^{(s)}_{2lLL'} = \frac{-1}{U^{(2)}_{LL'}\tilde{Q}^{(12)}_{1lLL'}}\left[U^{(1)}_{LL'}\left(\tilde{Q}^{(11)}_{2LL'}\tilde{\lambda}_{1LL'} - P^{(11)}_{2LL'}\right) + U^{(2)}_{LL'}\left(\tilde{Q}^{(12)}_{2lLL'}\tilde{\lambda}_{2lLL'} - P^{(21)}_{2LL'}\right) - K^{(1)}_{2LL'}\right]. \tag{5.43}$$

In the same way, we find an alternative expression for $\lambda^{(s)}_{2lLL'}$ from Eq. (5.27) as follows.

$$\lambda^{(s)}_{2lLL'} = \frac{-1}{U^{(2)}_{LL'}\tilde{Q}^{(22)}_{1lLL'}}\left[U^{(1)}_{LL'}\left(\tilde{Q}^{(21)}_{2LL'}\tilde{\lambda}_{1LL'} - P^{(12)}_{2lLL'}\right) + U^{(2)}_{LL'}\left(\tilde{Q}^{(22)}_{2llLL'}\tilde{\lambda}_{2lLL'} - P^{(22)}_{2lLL'}\right) - K^{(2)}_{2lLL'}\right]. \tag{5.44}$$

Next, we obtain from Eq. (5.26) with condition $\sigma' = -\sigma$

$$\begin{aligned} U^{(1)}_{LL'}\tilde{Q}^{(11)}_{LL'\sigma-\sigma}\tilde{\lambda}_{1LL'} + U^{(2)}_{LL'}\tilde{Q}^{(12)}_{lLL'\sigma-\sigma}\tilde{\lambda}_{2lLL'} + U^{(1)}_{LL'}\tilde{Q}^{(11)}_{lLL'\sigma-\sigma}\lambda^{(s)}_{1LL'}\sigma \\ = U^{(1)}_{LL'}P^{(11)}_{LL'\sigma\sigma} + U^{(2)}_{LL'}P^{(21)}_{LL'\sigma\sigma} - K^{(1)}_{LL'\sigma\sigma}. \end{aligned} \tag{5.45}$$

Multiplying both sides of Eq. (5.45) by σ and taking sum over σ, we obtain

$$U^{(1)}_{LL'}\bar{Q}^{(11)}_{4LL'}\tilde{\lambda}_{1LL'} + U^{(1)}_{LL'}\bar{Q}^{(11)}_{3LL'}\lambda^{(s)}_{1LL'} + U^{(2)}_{LL'}\bar{Q}^{(12)}_{4lLL'}\lambda_{2lLL'} = U^{(1)}_{LL'}\bar{P}^{(11)}_{4LL'} + U^{(2)}_{LL'}\bar{P}^{(21)}_{4LL'} - K^{(1)}_{4LL'}. \tag{5.46}$$

Here

$$\bar{Q}^{(\alpha\alpha')}_{3\tau\tau'LL'} = \sum_{\sigma}\tilde{Q}^{(\alpha\alpha')}_{\tau\tau'LL'\sigma-\sigma}, \tag{5.47}$$

$$\bar{Q}^{(\alpha\alpha')}_{4\tau\tau'LL'} = \sum_{\sigma}\sigma\tilde{Q}^{(\alpha\alpha')}_{\tau\tau'LL'\sigma-\sigma}, \tag{5.48}$$

$$\bar{P}^{(\alpha\alpha')}_{4\tau'LL'} = \sum_{\sigma}\sigma P^{(\alpha\alpha')}_{\tau'LL'\sigma-\sigma}, \tag{5.49}$$

$$\bar{K}^{(\alpha)}_{4\tau LL'} = \sum_{\sigma}\sigma K^{(\alpha)}_{\tau LL'\sigma-\sigma}. \tag{5.50}$$

Solving Eq. (5.46) with respect to $\lambda^{(s)}_{1LL'}$, we find

$$\lambda^{(s)}_{1LL'} = \frac{-1}{U^{(1)}_{LL'}\bar{Q}^{(11)}_{3LL'}}\left[U^{(1)}_{LL'}\left(\bar{Q}^{(11)}_{4LL'}\tilde{\lambda}_{1LL'} - \bar{P}^{(11)}_{4LL'}\right) + U^{(2)}_{LL'}\left(\bar{Q}^{(12)}_{4lLL'}\tilde{\lambda}_{2lLL'} - \bar{P}^{(21)}_{4LL'}\right) - \bar{K}^{(1)}_{4LL'}\right]. \tag{5.51}$$

In the same way, we find an alternative expression for $\lambda^{(s)}_{2lLL'}$ from Eq. (5.27) as follows.

$$\lambda^{(s)}_{1LL'} = \frac{-1}{U^{(1)}_{LL'}\bar{Q}^{(21)}_{3lLL'}}\left[U^{(1)}_{LL'}\left(\bar{Q}^{(21)}_{4lLL'}\tilde{\lambda}_{1LL'} - \bar{P}^{(12)}_{4LL'}\right) + U^{(2)}_{LL'}\left(\bar{Q}^{(12)}_{4lLL'}\tilde{\lambda}_{2lLL'} - \bar{P}^{(21)}_{4lLL'}\right) - \bar{K}^{(2)}_{4lLL'}\right]. \tag{5.52}$$

Substituting Eqs. (5.43) and (5.51) ((5.44) and (5.52)) into Eq. (5.30) ((5.31)), we obtain the following equations for $\lambda^{(s)}_{1LL'}$ and $\lambda^{(s)}_{2lLL'}$.

$$U^{(1)}_{LL'}\hat{Q}^{(11)}_{LL'}\tilde{\lambda}_{1LL'} + U^{(2)}_{LL'}\hat{Q}^{(12)}_{lLL'}\tilde{\lambda}_{2lLL'} = U^{(1)}_{LL'}\hat{P}^{(11)}_{LL'} + U^{(2)}_{LL'}\hat{P}^{(21)}_{LL'} - \hat{K}^{(1)}_{LL'}, \tag{5.53}$$

$$U^{(1)}_{LL'}\hat{Q}^{(21)}_{LL'}\tilde{\lambda}_{1LL'} + U^{(2)}_{LL'}\hat{Q}^{(22)}_{llLL'}\tilde{\lambda}_{2lLL'} = U^{(1)}_{LL'}\hat{P}^{(12)}_{lLL'} + U^{(2)}_{LL'}\hat{P}^{(22)}_{lLL'} - \hat{K}^{(2)}_{LL'}. \tag{5.54}$$

Here

$$\hat{Q}^{(1\alpha)}_{\tau LL'} = \bar{Q}^{(1\alpha)}_{\tau LL'} - \frac{\bar{Q}^{(12)}_{2lLL'}}{\bar{Q}^{(12)}_{1lLL'}}\bar{Q}^{(1\alpha)}_{2\tau LL'} - \frac{\bar{Q}^{(11)}_{4LL'}}{\bar{Q}^{(11)}_{3LL'}}\bar{Q}^{(1\alpha)}_{4\tau LL'}, \tag{5.55}$$

$$\hat{Q}^{(2\alpha)}_{\tau LL'} = \bar{Q}^{(2\alpha)}_{\tau LL'} - \frac{\bar{Q}^{(22)}_{2lLL'}}{\bar{Q}^{(22)}_{1lLL'}}\bar{Q}^{(1\alpha)}_{2\tau LL'} - \frac{\bar{Q}^{(21)}_{4lLL'}}{\bar{Q}^{(21)}_{3lLL'}}\bar{Q}^{(2\alpha)}_{4\tau LL'}, \tag{5.56}$$

$$\hat{P}^{(\alpha 1)}_{LL'} = \bar{P}^{(\alpha 1)}_{LL'} - \frac{\bar{Q}^{(12)}_{2lLL'}}{\bar{Q}^{(12)}_{1lLL'}} \bar{P}^{(\alpha 1)}_{2LL'} - \frac{\bar{Q}^{(11)}_{4LL'}}{\bar{Q}^{(11)}_{3LL'}} \bar{P}^{(\alpha 1)}_{4LL'}, \tag{5.57}$$

$$\hat{P}^{(\alpha 2)}_{lLL'} = \bar{P}^{(\alpha 2)}_{lLL'} - \frac{\bar{Q}^{(22)}_{2llLL'}}{\bar{Q}^{(22)}_{1llLL'}} \bar{P}^{(\alpha 2)}_{2lLL'} - \frac{\bar{Q}^{(21)}_{4lLL'}}{\bar{Q}^{(21)}_{3lLL'}} \bar{P}^{(\alpha 2)}_{4lLL'}, \tag{5.58}$$

$$\hat{K}^{(\alpha)}_{\tau LL'} = \bar{K}^{(\alpha)}_{\tau LL'} - \frac{\bar{Q}^{(\alpha 2)}_{2\tau lLL'}}{\bar{Q}^{(12)}_{1\tau lLL'}} \bar{K}^{(\alpha)}_{2\tau LL'} - \frac{\bar{Q}^{(\alpha 1)}_{4\tau LL'}}{\bar{Q}^{(\alpha 1)}_{3\tau LL'}} \bar{K}^{(\alpha)}_{4\tau LL'}. \tag{5.59}$$

Solving Eqs. (5.53) and (5.54), we obtain the variational parameters $\lambda_{1LL'}$ and $\lambda_{2lLL'}$ as follows.

$$\begin{aligned}\tilde{\lambda}_{1LL'} = U^{(1)-1}_{LL'} \left(\det \hat{Q}_{LL'}\right)^{-1} \Big[& U^{(1)}_{LL'} \left(\hat{Q}^{(22)}_{llLL'} \hat{P}^{(11)}_{LL'} - \hat{Q}^{(12)}_{lLL'} \hat{P}^{(12)}_{LL'} \right) \\ & + U^{(2)}_{LL'} \left(\hat{Q}^{(22)}_{llLL'} \hat{P}^{(21)}_{LL'} - \hat{Q}^{(12)}_{lLL'} \hat{P}^{(22)}_{LL'} \right) - \left(\hat{Q}^{(22)}_{llLL'} \hat{K}^{(1)}_{LL'} - \hat{Q}^{(12)}_{lLL'} \hat{K}^{(2)}_{lLL'} \right) \Big],\end{aligned} \tag{5.60}$$

$$\begin{aligned}\tilde{\lambda}_{2lLL'} = U^{(2)-1}_{LL'} \left(\det \hat{Q}_{LL'}\right)^{-1} \Big[& U^{(1)}_{LL'} \left(\hat{Q}^{(22)}_{LL'} \hat{P}^{(12)}_{LL'} - \hat{Q}^{(21)}_{lLL'} \hat{P}^{(11)}_{LL'} \right) \\ & + U^{(2)}_{LL'} \left(\hat{Q}^{(11)}_{LL'} \hat{P}^{(21)}_{lLL'} - \hat{Q}^{(11)}_{LL'} \hat{P}^{(22)}_{LL'} \right) - \left(\hat{Q}^{(22)}_{llLL'} \hat{K}^{(2)}_{lLL'} - \hat{Q}^{(21)}_{lLL'} \hat{K}^{(1)}_{LL'} \right) \Big].\end{aligned} \tag{5.61}$$

Next, we consider the case $\alpha = 2$ and $\tau = t$ in Eq. (5.21). Note that the elements $\tilde{Q}^{(20)}_{tLL'}$, $\tilde{Q}^{(21)}_{tLL'}$, $P^{(02)}_{tLL'\sigma\sigma'}$, $P^{(12)}_{tLL'\sigma\sigma'}$ vanish. Furthermore, $\tilde{Q}^{(22)}_{tLL'\sigma\sigma'}$, $P^{(22)}_{tLL'\sigma\sigma'} \propto \delta_{\sigma\sigma'}$. Thus we obtain form Eq. (5.21)

$$U^{(2)}_{LL'} \tilde{Q}^{(22)}_{ttLL'\sigma-\sigma} \tilde{\lambda}^{(\sigma-\sigma)}_{2tLL'} = U^{(2)}_{LL'} P^{(22)}_{tLL'\sigma-\sigma} - K^{(2)}_{tLL'\sigma-\sigma}, \tag{5.62}$$

or

$$\tilde{\lambda}^{(\sigma-\sigma)}_{2tLL'} = \tilde{Q}^{(22)-1}_{ttLL'\sigma-\sigma} (P^{(22)}_{tLL'\sigma-\sigma} - U^{(2)-1}_{LL'} K^{(2)}_{tLL'\sigma-\sigma}). \tag{5.63}$$

Equations (5.25), (5.60), (5.61), and (5.63) are self-consistent equations for variational parameters $\{\tilde{\lambda}^{(\sigma\sigma')}_{\alpha\tau LL'}\}$:

$$\tilde{\lambda}^{(\downarrow\uparrow)}_{0LL} = \tilde{Q}^{(00)-1}_{LL\downarrow\uparrow} (P^{(00)}_{LL\downarrow\uparrow} - U^{(0)-1}_{LL} K^{(00)}_{LL\downarrow\uparrow}), \tag{5.64}$$

$$\begin{aligned}\tilde{\lambda}_{1LL'} = U^{(1)-1}_{LL'} \left(\det \hat{Q}_{LL'}\right)^{-1} \Big[& U^{(1)}_{LL'} \left(\hat{Q}^{(22)}_{llLL'} \hat{P}^{(11)}_{LL'} - \hat{Q}^{(12)}_{lLL'} \hat{P}^{(12)}_{LL'} \right) \\ & + U^{(2)}_{LL'} \left(\hat{Q}^{(22)}_{llLL'} \hat{P}^{(21)}_{LL'} - \hat{Q}^{(12)}_{lLL'} \hat{P}^{(22)}_{LL'} \right) - \left(\hat{Q}^{(22)}_{llLL'} \hat{K}^{(1)}_{LL'} - \hat{Q}^{(12)}_{lLL'} \hat{K}^{(2)}_{lLL'} \right) \Big],\end{aligned} \tag{5.65}$$

$$\begin{aligned}\tilde{\lambda}_{2lLL'} = U^{(2)-1}_{LL'} \left(\det \hat{Q}_{LL'}\right)^{-1} \Big[& U^{(1)}_{LL'} \left(\hat{Q}^{(22)}_{LL'} \hat{P}^{(12)}_{LL'} - \hat{Q}^{(21)}_{lLL'} \hat{P}^{(11)}_{LL'} \right) \\ & + U^{(2)}_{LL'} \left(\hat{Q}^{(11)}_{LL'} \hat{P}^{(21)}_{lLL'} - \hat{Q}^{(11)}_{LL'} \hat{P}^{(22)}_{LL'} \right) - \left(\hat{Q}^{(22)}_{llLL'} \hat{K}^{(2)}_{lLL'} - \hat{Q}^{(21)}_{lLL'} \hat{K}^{(1)}_{LL'} \right) \Big],\end{aligned} \tag{5.66}$$

$$\tilde{\lambda}^{(\sigma-\sigma)}_{2tLL'} = \tilde{Q}^{(22)-1}_{ttLL'\sigma-\sigma}(P^{(22)}_{tLL'\sigma-\sigma} - U^{(2)-1}_{LL'} K^{(2)}_{tLL'\sigma-\sigma}). \tag{5.67}$$

We can determine the variational parameters $\tilde{\lambda}^{(\downarrow\uparrow)}_{0LL}$, $\tilde{\lambda}_{1LL'}$, $\lambda^{(s)}_{1LL'}$, $\tilde{\lambda}_{2lLL'}$, $\lambda^{(s)}_{2lLL'}$, $\tilde{\lambda}^{(\sigma-\sigma)}_{2tLL'}$ solving these equations self-consistently.

In the non-magnetic state, we have

$$P^{(00)}_{LL\downarrow\uparrow} = P_{LL}, \qquad P^{(11)}_{LL'\sigma\sigma'} = P_{LL'}, \tag{5.68}$$

$$P^{(12)}_{LL'\sigma\sigma'} = \sigma\sigma' P_{LL'}, \qquad P^{(12)}_{lLL'\sigma\sigma'} = -\frac{1}{4}\sigma\sigma' P_{LL'}, \tag{5.69}$$

$$P^{(22)}_{lLL'\sigma\sigma'} = -\frac{1}{16} P_{LL'}, \qquad P^{(22)}_{tLL'\sigma-\sigma} = \frac{1}{4} P_{LL'}, \tag{5.70}$$

$$Q^{(00)}_{LL\downarrow\uparrow} = Q_{LL}, \qquad Q^{(11)}_{LL'\sigma\sigma'} = Q_{LL'}, \tag{5.71}$$

$$Q^{(12)}_{LL'\sigma\sigma'} = Q^{(21)}_{LL'\sigma\sigma'} = -\frac{1}{4}\sigma\sigma' Q_{LL'}, \tag{5.72}$$

$$Q^{(22)}_{lLL'\sigma\sigma'} = \frac{1}{16} Q_{LL'}, \qquad Q^{(22)}_{tLL'\sigma\sigma'} = \frac{1}{4} Q_{LL'}, \tag{5.73}$$

$$S^{(00)}_{LL\downarrow\uparrow} = S_{LL}, \qquad S^{(11)}_{LL'\sigma\sigma'} = S_{LL'}, \tag{5.74}$$

$$S^{(12)}_{LL'\sigma\sigma'} = S^{(21)}_{LL'\sigma\sigma'} = -\frac{1}{4}\sigma\sigma' S_{LL'}, \tag{5.75}$$

$$S^{(22)}_{lLL'\sigma\sigma'} = \frac{1}{16} S_{LL'}, \qquad S^{(22)}_{tLL'\sigma\sigma'} = \frac{1}{4} S_{LL'}. \tag{5.76}$$

Here $P_{LL'}$, $Q_{LL'}$, and $S_{LL'}$ are given by

$$P_{LL'} = i\int_0^\infty dt e^{i\epsilon_c t} a_L(-t) a_{L'}(-t) b_L(t) b_{L'}(t), \tag{5.77}$$

$$\begin{aligned} Q_{LL'} = -\int_0^\infty dt dt' e^{i\epsilon_c(t+t')} \Big[& a_{L'}(-t-t') b_{L'}(t+t') a_L(-t-t') b_{L1}(t+t') \\ & - a_{L'}(-t-t') b_{L'}(t+t') a_{L1}(-t-t') b_L(t+t') \\ & + a_{L'}(-t-t') b_{L'1}(t+t') a_L(-t-t') b_L(t+t') \\ & - a_{L'1}(-t-t') b_{L'}(t+t') a_L(-t-t') b_L(t+t') \Big], \end{aligned} \tag{5.78}$$

and

$$S_{LL'} = -\int_0^\infty dtdt' e^{i\epsilon_c(t+t')} a_{L'}(-t-t') b_{L'}(t+t') a_L(-t-t') b_L(t+t'). \tag{5.79}$$

The functions of $a_L(t)$, $b_L(t)$, $a_{L1}(t)$, and $b_{L1}(t)$ are given as follows.

$$a_L(t) = \int_0^\infty dt e^{-i\epsilon t} \rho_L(\epsilon) f(\tilde{\epsilon}), \tag{5.80}$$

$$b_L(t) = \int_0^\infty dt e^{-i\epsilon t} \rho_L(\epsilon) [1 - f(\tilde{\epsilon})], \tag{5.81}$$

$$a_{L1}(t) = \int_0^\infty dt e^{-i\epsilon t} \epsilon \rho_L(\epsilon) f(\tilde{\epsilon}), \tag{5.82}$$

$$b_{L1}(t) = \int_0^\infty dt e^{-i\epsilon t} \epsilon \rho_L(\epsilon) [1 - f(\tilde{\epsilon})]. \tag{5.83}$$

Here $\rho_L(\epsilon)$ is the Hartree-Fock local density of states. It is defined as follows.

$$\rho_L(\epsilon) = \sum_{kn} |\langle iL|kn\rangle|^2 \, \delta(\epsilon - \epsilon_{kn}) \, . \tag{5.84}$$

Thus, $\tilde{Q}^{(\alpha\alpha')}_{\tau LL'\sigma\sigma}$ defined by Eq. (5.22) are expressed as follows.

$$\tilde{Q}^{(00)}_{LL\downarrow\uparrow} = \tilde{Q}_{LL}, \qquad \tilde{Q}^{(11)}_{LL'\sigma\sigma'} = \tilde{Q}_{LL'}, \tag{5.85}$$

$$\tilde{Q}^{(12)}_{LL'\sigma\sigma'} = \tilde{Q}^{(21)}_{LL'\sigma\sigma'} = -\frac{1}{4}\sigma\sigma'\tilde{Q}_{LL'}, \tag{5.86}$$

$$\tilde{Q}^{(22)}_{lLL'\sigma\sigma'} = \frac{1}{16}\tilde{Q}_{LL'}, \qquad \tilde{Q}^{(22)}_{tLL'\sigma\sigma'} = \frac{1}{4}\tilde{Q}_{LL'}. \tag{5.87}$$

Here $\tilde{Q}_{LL'}$ are defined by

$$\tilde{Q}_{LL'} = Q_{LL'} - \epsilon_c S_{LL'}. \tag{5.88}$$

According to Eqs. (5.32), (5.39), (5.40), (5.47), and (5.48), we obtain the matrix elements $\bar{Q}$ in the paramagnetic state as follows.

$$\bar{Q}^{(11)}_{LL'} = 4\tilde{Q}_{LL'}, \tag{5.89}$$

$$\bar{Q}^{(21)}_{lLL'} = \bar{Q}^{(12)}_{lLL'} = 0, \tag{5.90}$$

$$\bar{Q}^{(11)}_{1LL'} = \bar{Q}^{(11)}_{3LL'} = 2\tilde{Q}_{LL'}, \tag{5.91}$$

$$\bar{Q}^{(21)}_{1lLL'} = \bar{Q}^{(12)}_{1lLL'} = -\frac{1}{2}\tilde{Q}_{LL'}, \tag{5.92}$$

$$\bar{Q}^{(22)}_{llLL'} = \frac{1}{4}\tilde{Q}_{LL'}, \tag{5.93}$$

$$\bar{Q}^{(22)}_{1llLL'} = \bar{Q}^{(22)}_{3llLL'} = \frac{1}{8}\tilde{Q}_{LL'}, \tag{5.94}$$

and

$$\bar{Q}^{(\alpha\alpha')}_{2\tau\tau'LL'} = \bar{Q}^{(\alpha\alpha')}_{4\tau\tau'LL'} = 0. \tag{5.95}$$

We also obtain the matrix elements of $\bar{P}$ in the paramagnetic state using Eqs. (5.35), (5.41) and (5.49) as follows.

$$\bar{P}^{(11)}_{LL'} = 4P_{LL'}, \tag{5.96}$$

$$\bar{P}^{(21)}_{LL'} = \bar{P}^{(12)}_{lLL'} = 0, \tag{5.97}$$

$$\bar{P}^{(22)}_{LL'} = -\frac{1}{4}P_{LL'}, \tag{5.98}$$

$$\bar{P}^{(\alpha\alpha')}_{2\tau'LL'} = \bar{P}^{(\alpha\alpha')}_{4\tau'LL'} = 0. \tag{5.99}$$

Thus we obtain from Eqs. (5.55) $\sim$ (5.57)

$$\hat{Q}^{(\alpha\alpha')}_{\tau'LL'} = \bar{Q}^{(\alpha\alpha')}_{\tau'LL'}, \tag{5.100}$$

$$\hat{P}^{(\alpha\alpha')}_{\tau'LL'} = \bar{P}^{(\alpha\alpha')}_{\tau'LL'}, \tag{5.101}$$

and

$$\hat{K}^{(\alpha)}_{\tau LL'} = \bar{K}^{(\alpha)}_{\tau LL'}. \tag{5.102}$$

Finally in the paramagnetic state the self-consistent equations (5.64), (5.65), (5.66), and (5.67) reduce to the following equations.

$$\tilde{\lambda}_{0LL} = \tilde{Q}^{-1}_{LL}\left(P_{LL} - U^{(0)-1}_{LL}\, K^{(0)}_{LL}\right), \tag{5.103}$$

$$\tilde{\lambda}_{1LL'} = \tilde{Q}^{-1}_{LL'}\left(P_{LL'} - \frac{1}{4}\, U^{(1)-1}_{LL'}\, \bar{K}^{(1)}_{LL'}\right), \tag{5.104}$$

$$\tilde{\lambda}_{2lLL'} = -\tilde{Q}^{-1}_{LL'}\left(P_{LL'} + 4\, U^{(2)-1}_{LL'}\, \bar{K}^{(2)}_{lLL'}\right), \tag{5.105}$$

$$\tilde{\lambda}^{(\sigma-\sigma)}_{2tLL'} = -\tilde{Q}^{-1}_{LL'}\left(P_{LL'} + 4\, U^{(2)-1}_{LL'}\, K^{(2)}_{tLL'\sigma-\sigma}\right). \tag{5.106}$$

Here $\tilde{Q}_{LL'} = Q_{LL'} - \epsilon_c S_{LL'}$, $K^{(0)}_{LL'} = K^{(0)}_{LL'\downarrow\uparrow}$, $\bar{K}^{(1)}_{LL'} = \sum_{\sigma\sigma'} K^{(1)}_{LL'\sigma\sigma'}$, $\bar{K}^{(2)}_{lLL'} = \sum_{\sigma\sigma'} K^{(2)}_{lLL'\sigma\sigma'}$.

Furthermore, we can verify that $K^{(2)}_{tLL'} = K^{(2)}_{tLL'\sigma-\sigma}$ are independent of σ in the non-magnetic state. This means that $\tilde{\lambda}^{(+-)}_{2tLL'} = \tilde{\lambda}^{(-+)}_{2tLL'} = \tilde{\lambda}_{2tLL'}$. Thus Eq. (5.106) reduces as follows

$$\tilde{\lambda}_{2tLL'} = -\tilde{Q}^{-1}_{LL'} \left(P_{LL'} + 4\, U^{(2)-1}_{LL'}\, K^{(2)}_{tLL'} \right) . \tag{5.107}$$

Note that in the weak Coulomb interaction limit, we can neglect the higher order terms, $i.e.$, $U^{(0)-1}_{LL}\, K^{(0)}_{LL} \to 0$, and $\tilde{Q}^{-1}_{LL} \to P_{LL'}$ in Eq. (5.103), so that we obtain from Eq. (5.103)

$$\tilde{\lambda}_{0LL} = \tilde{\eta}_{LL} \to 1. \tag{5.108}$$

In the same way, one can verify from Eqs. (5.104), (5.105), and (5.107) in the weak Coulomb interaction limit.

$$\tilde{\lambda}_{1LL'} = \tilde{\zeta}_{LL'} \to 1, \tag{5.109}$$

$$\tilde{\lambda}_{2lLL'} = \tilde{\xi}_{lLL'} \to -1, \tag{5.110}$$

$$\tilde{\lambda}_{2tLL'} = \tilde{\xi}_{tLL'} \to -1. \tag{5.111}$$

These variational parameters (5.108)$\sim$ (5.111) have been used in the lowest-order calculations in Chapter 4.

The self-consistent equations (5.103) $\sim$ (5.105) and (5.107) contain the higher-order terms $\{K, \bar{K}\}$. We can obtain these terms from Eq. (5.13). Note that $\{\bar{K}\}$ are defined by sum with respect to σ of $\{K\}$. The higher-order correlation terms $\{K\}$ are summarized as follows:

$$K^{(0)}_{LL} = U^{(0)2}_{LL}\Omega_{LL}\tilde{\lambda}_{0LL} + 4\sum_{L'\neq L} U^{(1)2}_{LL'} M_{LL'}\tilde{\lambda}_{1LL} + \frac{1}{4}\sum_{L'\neq L} U^{(2)2}_{LL'} M_{LL'} \left(\tilde{\lambda}_{2lLL'} + 2\tilde{\lambda}_{2tLL'} \right) . \tag{5.112}$$

$$\begin{aligned} \bar{K}^{(1)}_{LL'} &= 4U^{(1)}_{LL'} \left(U^{(0)}_{LL'} M_{LL'}\tilde{\lambda}_{0LL} + U^{(0)}_{L'L'} M_{L'L}\tilde{\lambda}_{0L'L'} \right) \\ &+ 4U^{(1)}_{LL'} \left(U^{(0)}_{LL}\Xi_{L'LL} + U^{(0)}_{L'L'}\Xi_{LL'L} + U^{(1)}_{LL'}\Omega_{LL'} \right) \tilde{\lambda}_{1LL'} \\ &+ 8 \sum_{L''(\neq L,L')} U^{(1)}_{LL''} U^{(1)}_{L'L''} \left(\Xi_{LL'L''}\tilde{\lambda}_{1LL''} + \Xi_{L'LL''}\tilde{\lambda}_{1L'L''} \right) \\ &- \frac{1}{4} U^{(2)2}_{LL'}\Omega_{LL'}\tilde{\lambda}_{2lLL'} - \frac{1}{2} U^{(2)2}_{LL'}\Omega_{LL'}\tilde{\lambda}_{2tLL'}. \end{aligned} \tag{5.113}$$

$$\begin{aligned} \bar{K}^{(2)}_{lLL'} &= \frac{1}{4} U^{(2)}_{LL'} \left(U^{(0)}_{LL} M_{LL'}\tilde{\lambda}_{0LL'} + U^{(0)}_{L'L'} M_{L'L}\tilde{\lambda}_{0L'L'} \right) - \frac{1}{4} U^{(1)}_{LL'} U^{(2)}_{LL'}\Omega_{LL'}\tilde{\lambda}_{1LL'} \\ &- \frac{1}{4} U^{(2)}_{LL'} \left(U^{(0)}_{LL}\Xi_{L'LL} + U^{(0)}_{L'L'}\Xi_{LL'L'} - U^{(1)}_{LL'}\Omega_{LL'} \right) \tilde{\lambda}_{2lL'L'} \\ &- \frac{1}{8} \sum_{L''(\neq L,L')} U^{(2)}_{LL''} U^{(2)}_{L'L''} \left(\Xi_{LL'L''}\tilde{\lambda}_{2lLL''} + \Xi_{L'LL''}\tilde{\lambda}_{2lL'L''} \right) \\ &- \frac{1}{8} U^{(2)2}_{LL'} W_{LL'}\tilde{\lambda}_{2tLL'}. \end{aligned} \tag{5.114}$$

$$K^{(2)}_{tLL'} = \frac{1}{4}U^{(2)}_{LL'}\left(U^{(0)}_{LL}M_{LL'}\tilde{\lambda}_{0LL} + U^{(0)}_{L'L'}M_{L'L}\tilde{\lambda}_{0L'L'} - U^{(1)}_{LL'}\Omega_{LL'}\tilde{\lambda}_{1LL'}\right)$$
$$- \frac{1}{16}U^{(2)2}_{LL'}\tilde{\lambda}_{2lLL'} + \frac{1}{4}U^{(2)}_{LL'}\left(U^{(1)}_{LL'} + \frac{1}{4}U^{(2)}_{LL'}\right)\Omega_{LL'}\tilde{\lambda}_{2tLL'}$$
$$+ \frac{1}{8}\sum_{L(\neq L,L')} U^{(2)}_{LL''}U^{(2)}_{L'L''}\Xi_{LL'L''}\tilde{\lambda}_{2tLL''} + \frac{1}{8}\sum_{L(\neq L,L')} U^{(2)}_{LL''}U^{(2)}_{L'L''}\Xi_{L'LL''}\tilde{\lambda}_{2tLL'}. \quad (5.115)$$

The final expressions of all the matrix elements of correlation energy ϵ_c and the self-consistent equations for variational parameters are given in Appendix F (see Eqs. (F.22) $\sim$ (F.25), and Eqs. (F.33) $\sim$ (F.39)). The explicit expressions of $M_{LL'}$, $W_{LL'}$, $\Omega_{LL'}$, and $\Xi_{LL'L''}$ are also given in Appendix C (see Eqs. (C.19) $\sim$ (C.23)).

It should be noted that the rhs of Eqs. (5.103) $\sim$ (5.105) and (5.107) contain the correlation energy ϵ_c, the Fermi level ϵ_F, as well as the variational parameters $\{\tilde{\lambda}_{\tau\alpha LL'}\}$. Thus Eqs. (5.8), (5.103) $\sim$ (5.105), (5.107), and (3.77) have to be solved self-consistently. Then we can calculate the physical quantities such as charge fluctuations and amplitude of local moments.

5.2 Various physical quantities for new variational parameters

The correlation energy has been given in Eq. (5.8):

$$\epsilon_c = \frac{-\langle \tilde{O_i}^\dagger H_I\rangle_0 - \langle H_I\tilde{O}_i\rangle_0 + \langle \tilde{O_i}^\dagger \tilde{H}\tilde{O}_i\rangle_0}{1 + \langle \tilde{O_i}^\dagger \tilde{O}_i\rangle_0}\,. \quad (5.116)$$

The expressions of the matrix elements of ϵ_c with use of the variational ansatz (5.5) have been obtained in Eqs. (5.9) $\sim$ (5.15). The explicit expressions in the paramagnetic state are given in Appendix F.

The Fermi level ϵ_F is determined from the conduction electron number n_e via the relation,

$$n_e = \sum_L \langle n_{iL}\rangle\,. \quad (5.117)$$

Here the electron number for orbital L on site i has been obtained in Eq. (3.80):

$$\langle n_{iL}\rangle = \langle n_{iL}\rangle_0 + \frac{\langle \tilde{O}_i^\dagger \tilde{n}_{iL}\tilde{O}_i\rangle_0}{1 + \langle \tilde{O_i}^\dagger \tilde{O}_i\rangle_0}\,. \quad (5.118)$$

The explicit expression of the correlation correction $\langle \tilde{n}_{iL}\rangle$ is obtained with use of the ansatz (5.5). The expression is given in Appendix G.

The charge fluctuations and amplitude of local moment are obtained in Eqs. (3.89) and (3.99):

$$\langle (\delta n_{id})^2\rangle = \sum_{L\sigma}^{d}\langle n_{iL\sigma}\rangle_0(1 - \langle n_{iL\sigma}\rangle_0) + \sum_{L\sigma}^{d}\langle \tilde{n}_{iL\sigma}\rangle(1 - 2\langle n_{iL\sigma}\rangle_0)$$
$$- \langle \tilde{n}_{id}\rangle^2 + 2\sum_{L}^{d}\langle O^{(0)}_{iLL}\rangle + 2\sum_{(L,L')}^{d}\langle O^{(1)}_{iLL'}\rangle\,, \quad (5.119)$$

$$\langle \boldsymbol{S}^2 \rangle = \frac{3}{4}\sum_{L\sigma}^{d}\langle n_{iL\sigma}\rangle_0(1-\langle n_{iL\sigma}\rangle_0) + \frac{3}{4}\sum_{L\sigma}^{d}\langle \tilde{n}_{iL\sigma}\rangle(1-2\langle n_{iL-\sigma}\rangle_0) - \frac{3}{2}\sum_{L}^{d}\langle O^{(0)}_{iLL}\rangle + 2\sum_{(L,L')}^{d}\langle O^{(2)}_{iLL'}\rangle\,. \tag{5.120}$$

Here

$$\sum_{\langle LL'\rangle}\langle O^{(\alpha)}_{iLL'}\rangle = \frac{-\sum_{\langle LL'\rangle}\langle \tilde{O_i}^{\dagger} O^{(\alpha)}_{iLL'}\rangle_0 - \sum_{\langle LL'\rangle}\langle O^{(\alpha)}_{iLL'}\tilde{O}_i\rangle_0 + \sum_{\langle LL'\rangle}\langle \tilde{O_i}^{\dagger} O^{(\alpha)}_{iLL'}\tilde{O}_i\rangle_0}{1+\langle \tilde{O_i}^{\dagger}\tilde{O}_i\rangle_0}\,. \tag{5.121}$$

Explicit expressions of $\langle \tilde{n}_{iL}\rangle$ and $\{\langle O^{(\alpha)}_{iLL'}\rangle\}$ with use of the varitional parameters $\{\tilde{\lambda}^{(\sigma\sigma')}_{\alpha\tau LL'}\}$ are given in Appendices G and H, respectively.

The momentum distribution function (MDF) has been given in Eq. (3.103).

$$\langle n_{kn\sigma}\rangle = f(\tilde{\epsilon}_{kn\sigma}) + \frac{N\langle \tilde{O}^{\dagger}_i \tilde{n}_{kn\sigma}\tilde{O}_i\rangle_0}{1+\langle \tilde{O_i}^{\dagger}\tilde{O}_i\rangle_0}\,. \tag{5.122}$$

The first term at the rhs is the MDF for the Hartree-Fock independent electrons, which is given by the Fermi distribution function at zero temperature $f(\tilde{\epsilon}_{kn\sigma})$. $\tilde{\epsilon}_{kn\sigma}$ is the Hartree-Fock one-electron energy measured from the Fermi level $\epsilon_{\rm F}$. The second term at the rhs of Eq. (5.122) is the correlation corrections, where $\tilde{n}_{kn\sigma}$ is defined by $\tilde{n}_{kn\sigma} = n_{kn\sigma} - \langle n_{kn\sigma}\rangle_0$. The numerator is expressed as follows (see Appendix I).

$$N\langle \tilde{O}^{\dagger}_i \tilde{n}_{kn\sigma}\tilde{O}_i\rangle_0 = \sum_{\alpha\tau\ \langle LL'\rangle} q^{(\alpha)}_{\tau}\, U^{(\alpha)2}_{LL'}\, \tilde{\lambda}^2_{\alpha\tau LL'}\left(\hat{B}_{LL'n\sigma}(\boldsymbol{k})\, f(-\tilde{\epsilon}_{kn\sigma}) - \hat{C}_{LL'n\sigma}(\boldsymbol{k})\, f(\tilde{\epsilon}_{kn\sigma})\right). \tag{5.123}$$

Here $q^{(\alpha)}_{\tau}$ is a constant factor taking the value 1 for α=0, 2 for α=1, 1/8 for α=2, τ=l, and 1/4 for α=2, τ=t, respectively. $\hat{B}_{LL'n\sigma}(\boldsymbol{k})$ is a momentum-dependent particle contribution above ϵ_F and is expressed as follows.

$$\hat{B}_{LL'n\sigma}(\boldsymbol{k}) = |u_{Ln\sigma}(\boldsymbol{k})|^2 B_{L'L\sigma}(\epsilon_{kn\sigma}) + |u_{L'n\sigma}(\boldsymbol{k})|^2 B_{LL'\sigma}(\epsilon_{kn\sigma})\,, \tag{5.124}$$

where $\{u_{Ln\sigma}(\boldsymbol{k})\}$ are the eigenvectors for a given $\boldsymbol{k}$ point. The hole contribution $\hat{C}_{LL'n\sigma}(\boldsymbol{k})$ is defined by Eq. (5.124) in which the energy dependent terms $B_{LL'\sigma}(\epsilon_{kn\sigma})$ have been replaced by $C_{LL'\sigma}(\epsilon_{kn\sigma})$. These are given by the Laplace transformation of the local density of states in the Hartree-Fock approximation. Their explicit expressions in the paramagnetic state are given in Appendix I (see Eqs. (I.4), and (I.5)).

The quasiparticle weight $Z_{k_{\rm F}n}$ characterizes the low energy excitations in metals. It is obtained by taking the difference between $\langle n_{kn\sigma}\rangle$ below and above the Fermi level $\epsilon_{\rm F}$. Taking average over the Fermi surface, we obtain the average quasiparticle weight Z.

$$Z = 1 + \frac{\overline{\delta(N\langle \tilde{O}^{\dagger}_i \tilde{n}_{kn\sigma}\tilde{O}_i\rangle_0)_{k_{\rm F}}}}{1+\langle \tilde{O_i}^{\dagger}\tilde{O}_i\rangle_0}\,. \tag{5.125}$$

Here the first term at the rhs denotes the Hartree-Fock contribution part. The second term at the rhs is the correlation corrections. The upper bar in the numerator denotes the average over the Fermi

surface, and $\delta(N\langle\tilde{O}_i^\dagger\tilde{n}_{kn\sigma}\tilde{O}_i\rangle_0)_{k_\mathrm{F}}$ means the amount of jump at the wavevector $\boldsymbol{k}_\mathrm{F}$ on the Fermi surface. The explicit expression of $\overline{\delta(N\langle\tilde{O}_i^\dagger\tilde{n}_{kn\sigma}\tilde{O}_i\rangle_0)_{k_\mathrm{F}}}$ is given in Appendix I (see Eq. (I.9)).

In order to clarify the role of s, p, and d electrons, we consider here the projected MDF for orbital L defined by $\langle n_{kL\sigma}\rangle = \sum_n \langle n_{kn\sigma}\rangle |u_{Ln\sigma}(\boldsymbol{k})|^2$. Furthermore, we replace the energy $\epsilon_{kn\sigma}$ in the expression with $\epsilon_{kL\sigma} = \sum_n \epsilon_{kn\sigma}|u_{Ln\sigma}(\boldsymbol{k})|^2$, *i.e.*, a common energy band projected onto the orbital L. We have then

$$\langle n_{kL\sigma}\rangle = f(\tilde{\epsilon}_{kL\sigma}) + \frac{N\langle\tilde{O}_i^\dagger\tilde{n}_{kL\sigma}\tilde{O}_i\rangle_0}{1+\langle\tilde{O}_i{}^\dagger\tilde{O}_i\rangle_0}\,. \tag{5.126}$$

We can also define the partial MDF $\langle n_{kl\sigma}\rangle$ for $l(=s,p,d)$ electrons by

$$\langle n_{kl\sigma}\rangle = \frac{1}{2l+1}\sum_m \langle n_{kL\sigma}\rangle. \tag{5.127}$$

We can define the quasiparticle weight Z_L for the electrons with orbital symmetry L by the jump of $\langle n_{kL\sigma}\rangle$ on the Fermi surface ϵ_F.

$$Z_L = 1 + \frac{\overline{\delta(N\langle\tilde{O}_i^\dagger\tilde{n}_{kL\sigma}\tilde{O}_i\rangle_0)_{k_F}}}{1+\langle\tilde{O}_i{}^\dagger\tilde{O}_i\rangle_0}\,. \tag{5.128}$$

It should be noted that the projected MDF depend on the momentum $\boldsymbol{k}$ only via $\tilde{\epsilon}_{kL\sigma}$. The explicit expressions of the correlation corrections at the rhs of Eqs. (5.126) and (5.128) are given in Appendix I (see Eqs. (I.15), and (I.17)). Moreover we can verify the sum rule,

$$Z = \frac{1}{D}\sum_L Z_L = \frac{1}{D}\sum_l (2l+1)Z_l\,. \tag{5.129}$$

Here $Z_l(=\sum_m Z_L/(2l+1))$ is the quasipartical weight for $l(=s,p,d)$ electrons, and D is the number of orbitals ($D=9$ in the present case). The relation allows us to interpret Z_L as a partial quasiparticle weight for electrons with orbital L.

5.3 Self-consistent numerical results of BCC iron

The bcc Fe has extensively been investigated theoretically with use of the realistic Hamiltonians with s, p, and d orbitals at the ground states and at finite temperatures [77–81]. But quantitative aspects on the physical properties of Fe have not yet been fully clarified even at the ground state. We performed self-consistent numerical calculations for the paramagnetic bcc Fe in order to clarify the quantitative aspects of the first-principles MLA and the effects of electron correlations in the properties of Fe. In this section, we present the self-consistent results for paramagnetic Fe.

The transfer integrals and the atomic level have been calculated with use of the Stuttgart tight-binding LMTO (linear muffin-tin orbital) package and the LDA+U scheme. We adopted the Coulomb and exchange integrals $U_{LL} = U_0 = 0.2749$ Ry, $U_{LL'} = U_1 = 0.1426$ Ry, and $J_{LL'} = J = 0.0662$ Ry. These values are obtained from the relations $U_0 = U + 8J/5, U_1 = U - 2J/5$ using the average values $U = 0.1691$ Ry and $J = 0.0662$ Ry by Anisimov *et al.* [25]. Note that we adopted here the relation $U_0 = U_1 + 2J$ for the cubic system.

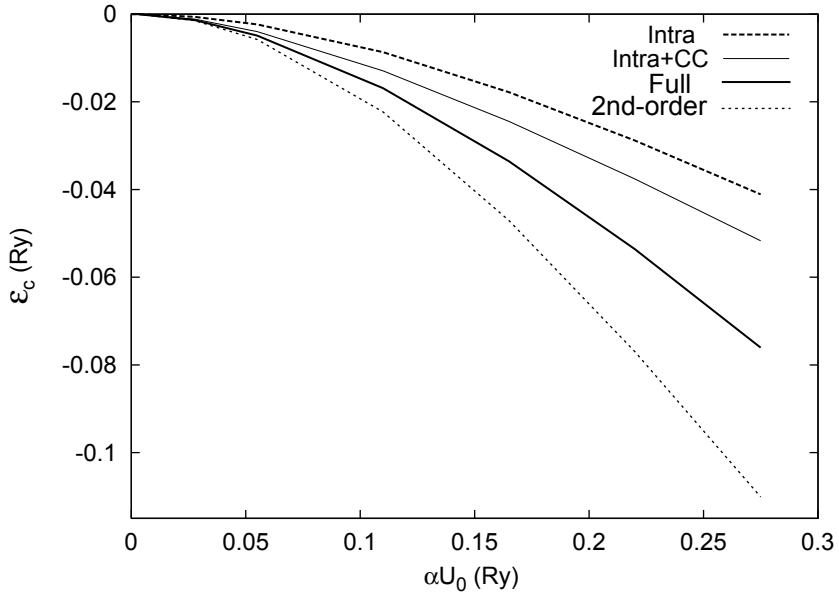

Figure 5.1: The correlation energy ϵ_c as a function of Coulomb interaction strength αU_0. Dashed curve: the result with only the intra-orbital correlations, thin solid curve: the result with both the intra-orbital and inter-orbital charge-charge correlations, solid curve: the result with full correlations. The thin dashed curve indicates the result of the second-order calculations with $\tilde{\eta}_{LL} = \tilde{\zeta}_{LL'} = 1$, and $\tilde{\xi}_{tLL'} = \tilde{\xi}_{lLL'} = -1$. The paramagnetic bcc Fe corresponds to αU_0=0.27 Ry.

We solved the self-consistent equations for variational parameters, Eqs. (5.8), (5.103) $\sim$ (5.106), and (5.117), and obtained various quantities according to their expressions presented in the last section. In order to understand the systematic change due to the Coulomb interaction strength, we scaled U_0, U_1, and J as αU_0, αU_1, and αJ using a scaling factor α from 0 to 1. We present the correlation energy ϵ_c in Fig. 5.1 as a function of αU_0. With increasing αU_0 (as well as αU_1 and αJ), the self-consistent correlation energy ϵ_c monotonically decreases. The second-order result of ϵ_c with $\tilde{\eta}_{LL} = \tilde{\zeta}_{LL'} = 1$, and $\tilde{\xi}_{tLL'} = \tilde{\xi}_{lLL'} = -1$ starts to deviate from the self-consistent ϵ_c at $\alpha U_0 \lesssim 0.05$ Ry, and overestimates the energy gain beyond the value.

In the first-principles MLA, we can describe the intra-orbital, the inter-orbital charge-charge, and the inter-orbital spin-spin correlations by means of the correlators, $\tilde{O}^{(0)}_{iLL}$, $\tilde{O}^{(1)}_{iLL'}$, and $\tilde{O}^{(2)}_{iLL'}$. When we take into account only the intra-orbital correlations ($, i.e., \tilde{\zeta}_{LL'} = \tilde{\xi}_{tLL'} = \tilde{\xi}_{lLL'} = 0$), we find the correlation energy $\epsilon_c = -0.041$ Ry for $\alpha U_0 = 0.27$ Ry ($, i.e.,$ for Fe). When we take into account both the intra-orbital and inter-orbital charge-charge correlations ($, i.e., \tilde{\xi}_{tLL'} = \tilde{\xi}_{lLL'} = 0$), the correlation energy decreases and $\epsilon_c = -0.050$ Ry for Fe. When we add further the inter-orbital spin-spin correlations, the correlation energy decreases further and we obtain $\epsilon_c = -0.076$ Ry for Fe. We find that the inter-orbital correlations make a significant contribution to the correlation energy. The lowest-order correlation energy gain overestimate compared to the self-consistent correlation energy.

The correlation energy gain is accompanied by the suppression of charge fluctuations. We calculated the charge fluctuations for d electrons $\langle(\delta n_d)^2\rangle = \langle n_d^2\rangle - \langle n_d\rangle^2$ as a function of αU_0 as shown in Fig. 5.2. The charge fluctuation in the Hartree-Fock approximation is 2.20. It is suppressed rapidly with increasing the Coulomb interaction strength αU_0. We obtain the charge fluc-

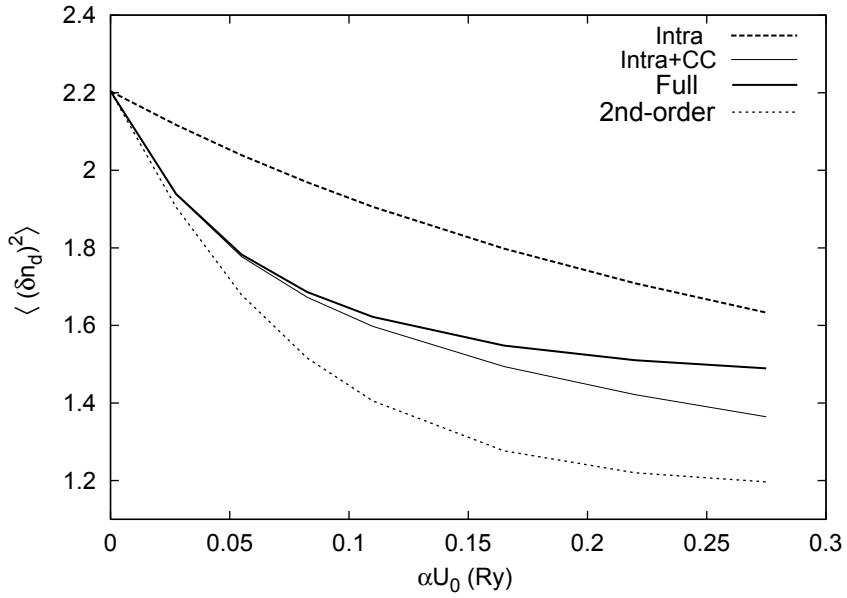

Figure 5.2: The charge fluctuation $\langle(\delta n_d)^2\rangle$ vs Coulomb interaction strength αU_0 curves. Dashed curve: the result with only the intra-orbital correlations, thin solid curve: the result with both the intra-orbital and inter-orbital charge-charge correlations, solid curve: the result with full correlations. The thin dashed curve indicates the second-order result. The paramagnetic bcc Fe corresponds to αU_0 = 0.27 Ry.

tuations $\langle(\delta n_d)^2\rangle$=1.51 for $\alpha U_0 = 0.27$ Ry (Fe). The lowest-order result of calculations deviates downward from the self-consistent result even for a small αU_0 with increasing αU_0; it overestimates the suppression of charge fluctuations. We examined the contributions of the three kinds of correlations to $\langle(\delta n_d)^2\rangle$. The intra-orbital correlations suppress the charge fluctuations, and lead to $\langle(\delta n_d)^2\rangle = 1.73$ for $\alpha U_0 = 0.27$ Ry (Fe). When we add the inter-orbital charge-charge correlations, the charge fluctuation decreases further, and we have $\langle(\delta n_d)^2\rangle$=1.36 for Fe. The result is comparable to the value of the LA with the d-band model [21], *i.e.*, $\langle(\delta n_d)^2\rangle \approx 1.0$, though it is somewhat larger than that of the LA because the present theory takes into account the hybridization between the d and sp electrons and the latter delocalizes the d electrons. We also notice that the inter-orbital spin-spin correlations also delocalize the d electrons, so that we finally obtain $\langle(\delta n_d)^2\rangle$=1.51, which is considerably larger than that was obtained by the LA and the d band model.

Formation of atomic magnetic moments also originates in the d electron correlations, and determines the magnetic properties of Fe at finite temperatures. We calculated the amplitude of local moment $\langle \boldsymbol{S}^2 \rangle$ as a function of αU_0 as shown in Fig. 5.3. We have $\langle \boldsymbol{S}^2 \rangle = 1.65$ for the Hartree-Fock uncorrelated electrons. The amplitudes of local moment monotonically increase with increasing the Coulomb interaction strength αU_0, and we find $\langle \boldsymbol{S}^2 \rangle \approx 2.61$ for Fe in the full self-consistent calculations. The lowest-order calculations underestimate the amplitude, and result in $\langle \boldsymbol{S}^2 \rangle \approx 2.41$ for $\alpha U_0 = 0.27$ Ry (Fe) as mentioned in Sec. 4.3.2. The self-consistent result is comparable to the value of the LA with the d-band model [21], $\langle \boldsymbol{S}^2 \rangle \approx 2.91$, but is somewhat smaller than that of the LA because the present theory takes into account the hybridization between the d and sp electrons. It should be noted that the enhancement of the amplitude is caused by both the intra-orbital and inter-orbital spin-spin correlations, and the effects of the inter-orbital charge-charge correlations

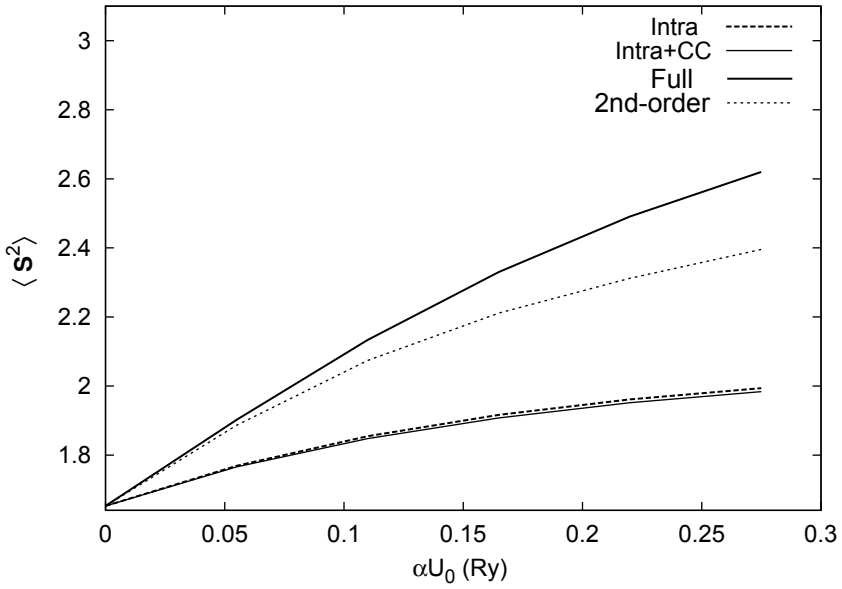

Figure 5.3: The amplitude of local moment as a function of the Coulomb interaction strength αU_0. Dashed curve: the result with only the intra-orbital correlations, thin solid curve: the result with both the intra-orbital and inter-orbital charge-charge correlations, solid curve: the result with full correlations, thin dashed curve: the second-order result. The paramagnetic bcc Fe corresponds to αU_0 = 0.27 Ry.

are negligible as seen in Fig. 4.8. Although there are no direct measurements of the amplitude of local moment $\langle \boldsymbol{S}^2 \rangle$ for the bcc Fe, one can estimate the experimental value from the observed effective Bohr magneton number $p_{\rm eff}$ $(= 3.20)$ [82], because the Rhodes-Wolhfarth ratio of the bcc Fe is equal to 1.0 within 5% error. In this case, we have the experimental value $\langle \boldsymbol{S}^2 \rangle = p_{\rm eff}^2/4 = 2.56$, which is in good agreement with the present result $\langle \boldsymbol{S}^2 \rangle = 2.61$.

We have calculated the MDF in paramagnetic Fe using Eq. (5.122). Figure 5.4 shows the result along high-symmetry lines. (Note that the wavevector $\boldsymbol{k}$ is measured in the unit of $2\pi/a$, a being the lattice constant.) We find strong momentum dependence of along $\langle n_{kn\sigma} \rangle$ the lines, which is not described by the Hartree-Fock wavefunction.

At point Γ, we have a free-electron-like MDF $\langle n_{kn\sigma} \rangle = 1.00$ for s electrons with the Hartree-Fock one-electron energy $\epsilon_{kn\sigma} = -0.69$ Ry $(< \epsilon_{\rm F})$ (see in Fig. 4.3), while we have the MDF $\langle n_{kn\sigma} \rangle = 0.97$ for d electrons with t_{2g} symmetry, which are associated with the Hartree-Fock one-electron energy $\epsilon_{kn\sigma} = -0.27$ Ry $(< \epsilon_{\rm F})$, and the MDF $\langle n_{kn\sigma} \rangle = 0.82$ for d electrons with e_g symmetry with the energy $\epsilon_{kn\sigma} = -0.14$ Ry $(> \epsilon_{\rm F})$ in Fig. 4.3. For the p electrons associated with the energy $\epsilon_{kn\sigma}$ = 2.03 Ry $(> \epsilon_{\rm F})$, we again have a free-electron-like $\langle n_{kn\sigma} \rangle = 0.00$.

When the momentum $\boldsymbol{k}$ moves toward point N along the Γ-N line, the MDF for t_{2g} electrons splits into three branches. The first branch is almost constant and has a value $\langle n_{kn\sigma} \rangle = 0.98$ at point N. The second branch jumps down at $\boldsymbol{k}_F$ = (0.39, 0.39, 0.00) on the Fermi surface and approaches $\langle n_{kn\sigma} \rangle = 0.00$ at point N. The third branch decreases with the change in $\boldsymbol{k}$ toward point N, jumps down at $\boldsymbol{k}_F$ = (0.28, 0.28, 0.00), and approaches $\langle n_{kn\sigma} \rangle = 0.088$ at point N. The MDF for e_g electrons splits into two branches. The branch with $3z^2 - r^2$ symmetry increases and approaches to $\langle n_{kn\sigma} \rangle = 0.86$ at point N. The second branch with $x^2 - y^2$ symmetry decreases along the Γ-N lines, jumps down at $\boldsymbol{k}_F = (0.23, 0.23, 0.00)$, and approaches $\langle n_{kn\sigma} \rangle = 0.25$ at point N.

The s electron branch of the MDF hardly changes and approaches to the value $\langle n_{kn\sigma} \rangle = 0.99$ at point N. The p electron branch also shows flat behavior with $\langle n_{kn\sigma} \rangle = 0.00$ because there is no hybridization with d electrons and their one-electron energies are far above the Fermi level (see Fig. 4.3)

Table 5.1: Mass enhancement factors for e_g electrons at various wavevectors $\boldsymbol{k}$ on the Fermi surface.

$\boldsymbol{k}$	(0.23, 0.23, 0.00)	(0.50, 0.50, 0.28)	(0.32, 0.32, 0.32)	(0.00, 0.17, 0.00)
m^*_{kn}/m	1.84	1.71	1.78	1.82

Table 5.2: Mass enhancement factors for t_{2g} electrons at various wavevectors $\boldsymbol{k}$ on the Fermi surface.

$\boldsymbol{k}$	(0.28, 0.28, 0.00)	(0.39, 0.39, 0.00)	(0.50, 0.50, 0.09)	(0.20, 0.20, 0.20)
m^*_{kn}/m	1.28	1.14	1.16	1.25

$\boldsymbol{k}$	(0.00, 0.58, 0.00)	(0.00, 0.73, 0.00)	(0.15, 0.85, 0.00)	(0.18, 0.82, 0.00)
m^*_{kn}/m	1.29	1.27	1.27	1.29

The basic behavior of the MDF for s, p, and d electrons mentioned above is also seen on the other high-symmetry N-P, P-Γ, Γ-H, and H-N lines. We find that the MDF branches associated with e_g electrons show large deviations from 0 and 1, indicating strong electron correlations. The MDF associated with t_{2g} electrons also shows significant deviations from 0 and 1. On the other hand, the s- and p-like MDFs have values close to 1 or 0, indicating that the independent electron band picture is applicable to their electrons.

The jump of the MDF on the Fermi surface gives the quasi-particle weight Z_{kn} or the inverse mass enhancement factor (m^*_{kn}/m = 1) according to the Fermi liquid theory. Since the hybridization between the sp and d electrons excludes the sp-like bands near the Fermi level, most of the Fermi surface of the bcc Fe is formed by the d bands. The mass enhancement factors for e_g and t_{2g} electrons calculated along high-symmetry lines are presented in Tables I and II, respectively. We find that the mass enhancements for e_g electrons are momentum-dependent and show considerably large values of m_{kn}/m =1.71 $\sim$ 1.84, because these electrons form narrow bands near the Fermi level. The t_{2g} electrons yield smaller enhancements of m_{kn}/m = 1.14 $\sim$ 1.29.

We have calculated the averaged mass enhancement factor over the Fermi surface and obtained $m^*/m = 1.648$. In order to examine the dependence of m^*/m on the Coulomb integrals, we performed the same calculations using the alternative set $U_{LL} = 0.3233$ Ry, $U_{LL'} = 0.1932$ Ry, and $J_{LL'} = 0.0650$ Ry, which was adopted in our LDA+DCPA calculations. We obtained $m^*_{nk}/m = 1.551$, a deviation of only 6% from the value of 1.648. We also suggest that the ferromagnetic spin polarization may reduce the mass enhancement by about 5% because of the change in the weight between e_g and t_{2g} electrons on the Fermi surface.

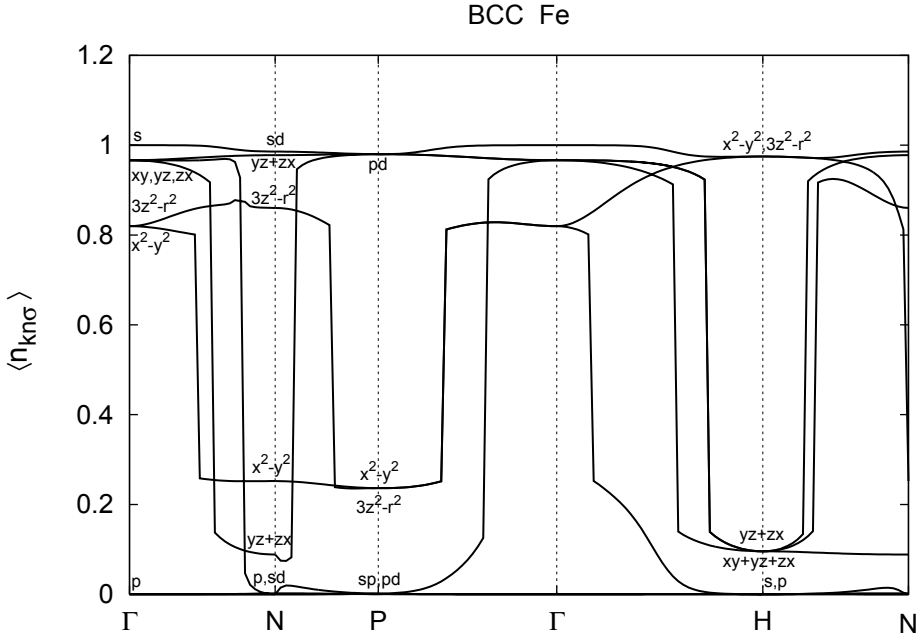

Figure 5.4: Momentum distribution functions ($\langle \epsilon_{kn\sigma} \rangle$) along high-symmetry lines for bcc Fe. Orbital symmetry functions and their hybridized states for the branches at high-symmetry points are written in the figure.

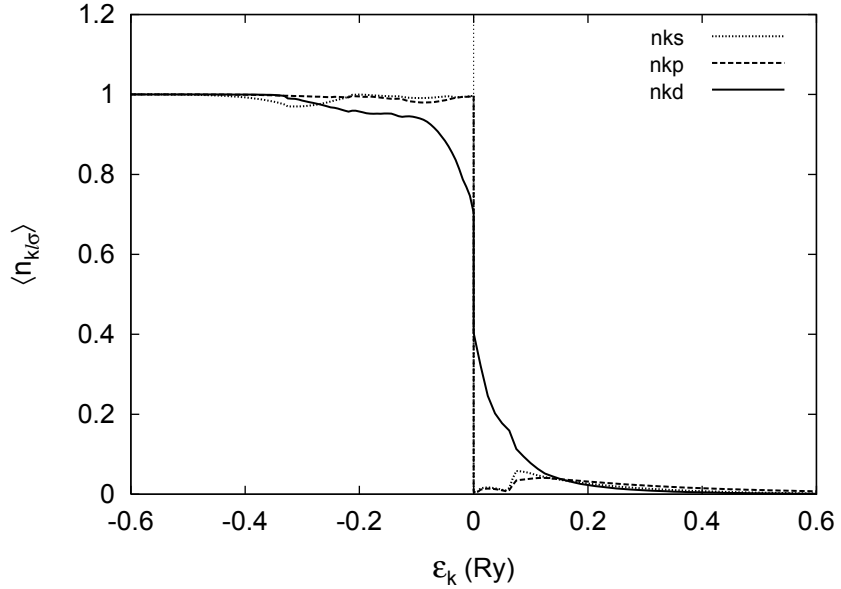

Figure 5.5: The partial momentum distribution functions $\langle n_{kl\sigma} \rangle$ as a function of the energy ϵ_k(= $\epsilon_{kL\sigma}$- $\epsilon_{\rm F}$). Dotted curve: the momentum distribution function for s electrons, dashed curve: the momentum distribution function for p electrons, solid curve: the momentum distribution function for d electrons.

As we have mentioned in the introduction, the MLA can describe the momentum dependence of the momentum distribution function (MDF). We calculated the partial MDF projected onto each orbital l in order to examine the role of s, p, and d electrons. They are defined by Eq. (5.127). Figure 5.5 shows the calculated MDF. In the case of s and p bands the partial MDF are approximately flat below and above the Fermi level $\epsilon_{\rm F}$, and jump at $\epsilon_{\rm F}$. Therefore the s and p electrons behave as an independent electron. The deviation from 1 or 0 are caused by the hybridization with d electrons. On the other hand, the partial MDF for d electrons shows a strong momentum dependence due to electron correlations.

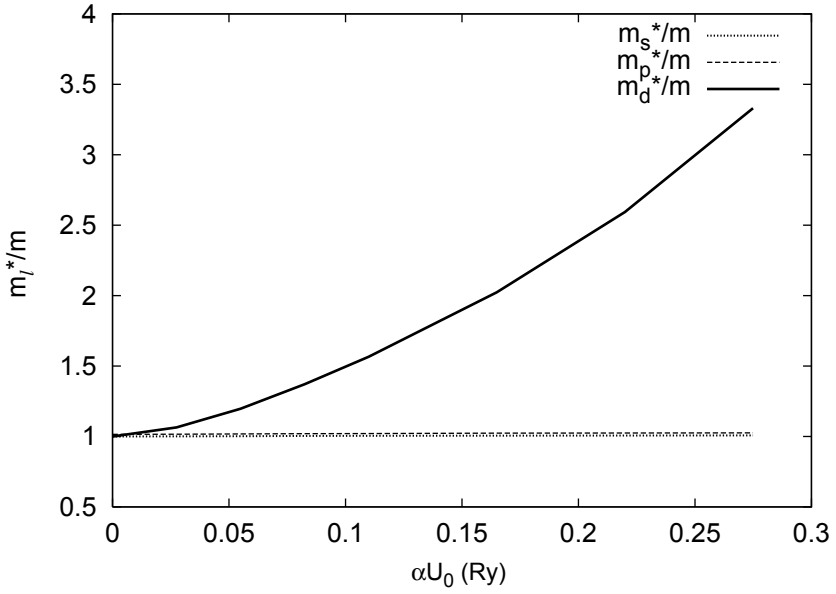

Figure 5.6: The orbital-dependent mass enhancement m_l^*/m as a function of the Coulomb interaction strength αU_0. Dotted curve: m_s^*/m (l=0), dashed curve: m_p^*/m (l=1), solid curve: m_d^*/m (l=2).

According to the Fermi liquid theory, the mass enhancement factor ($i.e.$, the inverse quasiparticle weight) is obtained from the jump at the Fermi level in the MDF. We calculated the orbital-dependent mass enhancement m_l^*/m_0 for s, p and d electrons as a function of αU_0 as shown in Fig. 5.6. The d electron mass enhancement rapidly increases with increasing the Coulomb interaction strength αU_0, while the mass enhancements for the sp electrons almost remain constant and behave as independent electrons irrespective of αU_0. Calculated mass enhancements are m_s^*/m=m_p^*/m = 1.01, and m_d^*/m = 3.33 for Fe, respectively. Note that the mass enhancement of the d electrons is significantly larger than the Hartree-Fock value 1.0.

We calculated the average mass enhancement m^*/m $(= 1/Z)$ as a function of αU_0. Calculated m^*/m vs Coulomb interaction curve is presented in Fig. 5.7. The curves with the intra-orbital correlations as well as the curve with both the intra-orbital and inter-orbital charge-charge correlations are also presented there. By comparing these three curves, we find that the mass enhancement m^*/m for Fe (αU_0 = 0.27 Ry) is dominated by both the intra-orbital and inter-orbital spin-spin correlations, though the inter-orbital charge-charge correlations also make a significant contribution in the weak interaction regime ($\alpha U_0 \lesssim$ 0.05 Ry).

The mass enhancement for the bcc Fe has recently been investigated on the basis of the first-principles theories. Katanin $et\ al.$ [83] obtained $m_{t_{2g}}^*/m$ = 1.163 for t_{2g} electrons at 1000K with

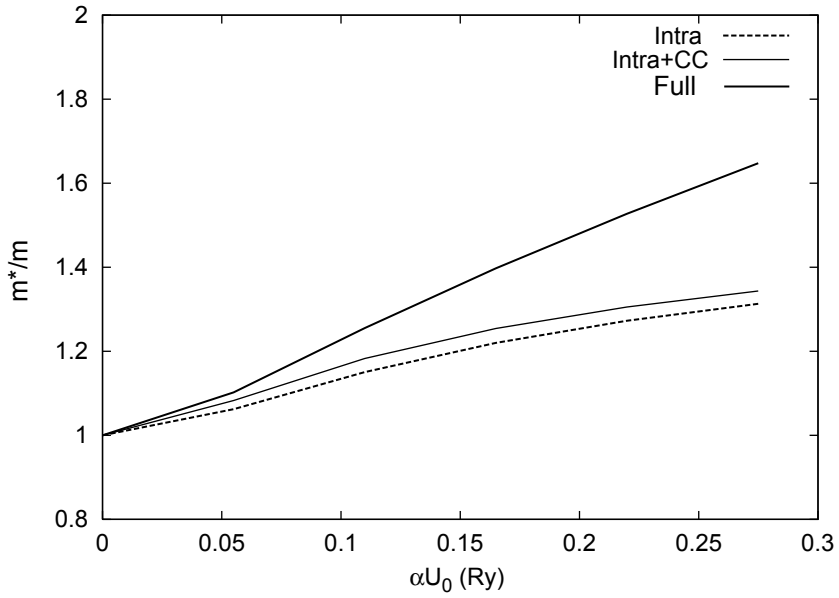

Figure 5.7: The mass enhancement factor m^*/m as a function of the Coulomb interaction strength αU_0. Dashed curve: mass enhancement due to the intra-orbital correlations, thin solid curve: mass enhancement due to both the intra-orbital and inter-orbital charge-charge correlations, solid curve: the result with the full correlations.

use of the LDA+DMFT combined with the QMC technique, but they could not obtain the mass enhancement for e_g electrons because of the non-Fermi liquid behavior due to strong fluctuations in the narrow e_g band at finite temperatures. More recently, Pourovski $et\ al.$ [15] performed the LDA+DMFT calculations for bcc Fe with use of the continuous-time QMC technique. They obtained m^*/m=1.577 for bcc Fe being in agreement with our present result m^*/m = 1.65. The first-principles Gutzwiller calculations by Deng $et\ al.$ [77] led to a reasonable value m^*/m = 1.56. But they used too large a Coulomb interaction parameter U = 7.0 eV. Recent results based on the LDA+Gutzwiller theory with use of a reasonable value U = 2.5 eV and J=1.2 eV show that $m^*_{e_g}/m$ = 1.08 for e_g electrons and $m^*_{t_{2g}}/m$ = 1.05 for t_{2g} electrons, [84] which are too small as compared with the other results of calculations mentioned above. The present result m^*/m = 1.65 is comparable to the experimental value $m^*/m = 1.38 \sim 2.12$ obtained from the low temperature specific heat data [72–74], and the recent result $m^*/m = 1.7$ obtained by the angle resolved photoemission spectroscopy (ARPES) [57].

Chapter 6

Summary and Discussion

We have developed the first-principles momentum dependent local ansatz (MLA) wavefunction method using the tight-binding (TB) LDA+U Hamiltonian towards the quantitative description of correlated electrons in the real system. The wavefunction is constructed by applying the momentum-dependent intra-orbital correlators, the inter-orbital charge-charge correlators, and the spin-spin correlators to the Hartree-Fock uncorrelated wavefunction. The MLA reduces to the Rayleigh-Schrödinger perturbation theory in the weak correlation limit as it should be, and describes quantitatively the ground state and related low-energy excitations in solids.

We have verified in the single-band model that the MLA improves the local ansatz approach (LA) irrespective of the electron number and the Coulomb interaction energy, and more strongly suppresses the double occupation number as compared with the LA. In particular, the momentum distribution functions (MDF) show a clear momentum dependence, while those in the LA and the Gutzwiller wavefunction (GW) show a flat behavior below and above the Fermi level. One can improve the MLA by changing the starting wavefunction from the Hartree-Fock (HF) wavefunction to the hybrid (HB) one. The HB-MLA is applicable to both the weak and the strong Coulomb interaction systems.

We first investigated the first-principles MLA in the weakly correlated regime. We solved the self-consistent equations for the momentum-dependent variational parameters in the weak interaction limit, and obtained the correlation energy in the single-site approximation (SSA) as well as the other physical quantities such as the electron number, the charge fluctuations, the amplitude of local moment, and the MDF.

We performed numerical calculations for the paramagnetic bcc Fe in order to clarify the basic behavior of the first-principles MLA in the weak Coulomb interaction regime. We obtained the correlation energy ϵ_c=-0.0516 Ry due to intra-orbital correlations of Fe. When we take into account the inter-orbital correlations, the correlation energy ϵ_c decreases further and we obtain ϵ_c = -0.1101 Ry for Fe. The inter-orbital correlation energy is comparable to the intra-orbital correlations energy in the lowest order. Calculated charge fluctuation is suppressed by correlations and we obtained $\langle(\delta n_d)^2\rangle \approx 1.2$ for Fe. The result is comparable to the value of the LA with the d-band model, $\langle(\delta n_d)^2\rangle \approx 1.0$, but is somewhat larger than that of the LA because the present theory takes into account the hybridization between the d and sp electrons. We find that the amplitude of local moment $\langle \boldsymbol{S}^2\rangle \approx 2.41$ for Fe in the lowest-order calculations. The result is larger than the Hartree-Fock value $\langle \boldsymbol{S}^2\rangle = 1.65$ because of the Hund-rule correlations, but is somewhat smaller than that of the d-band model+LA value $\langle \boldsymbol{S}^2\rangle = 2.91$ because the present theory takes into account the hybridization between the sp and d electrons. We also calculated the MDF as well

as the effective mass enhancement factor assuming the constant eigen vectors for d electrons. We found a clear momentum dependence of the MDF via energy eigen value $\tilde{\epsilon}_{kn\sigma}$. We obtained the mass enhancement m^*/m= 1.4 for Fe from a jump at the Fermi level, which is comparable to the experimental values $1.38 \sim 2.12$ obtained from the T-linear specific heat at low temperatures.

In order to clarify the first-principles MLA and related correlation effects in more correlated regime, we derived the self-consistent equations for the variational parameters on the basis of the variational parameters ansatz which interpolates between the weak and atomic limits, and obtained the expressions of the other physical quantities. We investigated the correlated electron state of the paramagnetic bcc Fe solving the self-consistent equations for momentum-dependent variational parameters. We obtained the correlation energy $\epsilon_c = -0.076$ Ry for the paramagnetic Fe, and found that the inter-orbital correlation contribution is comparable to the intra-orbital one in the case of Fe. The charge fluctuations $\langle(\delta n_d)^2\rangle$ are suppressed with increasing the Coulomb interaction strength. We obtained $\langle(\delta n_d)^2\rangle$ = 1.51 for Fe, which is larger than the value $\langle(\delta n_d)^2\rangle \approx 1.0$ calculated by the LA+d band model. The discrepancy is partly caused by the hybridization between sp and d electrons and partly caused by the Hund-rule correlations. The amplitude of local moment $\langle \boldsymbol{S}^2\rangle$ increases with increasing the Coulomb interaction strength. We obtained $\langle \boldsymbol{S}^2\rangle = 2.61$ for Fe. The result shows a good agreement with the experimental value 2.56 estimated from the effective Bohr magneton number of the Curie-Weiss susceptibility. The lowest-order calculations underestimate the amplitude of local moment.

We investigated the MDF for bcc Fe. The MDF depends on the momentum $\boldsymbol{k}$ via both the energy $\epsilon_{kn\sigma}$ and the eigenvector $u_{Ln\sigma}(\boldsymbol{k})$. We obtained the first-principles MDF bands for Fe along high-symmetry lines, and clarified the band structure of the MDF for s, p, and d electrons for the first time. We found a large deviation from the Fermi-Dirac distribution function for the branches associated with e_g and t_{2g} electrons, while the sp electron branches follow the usual band theory. We obtained the momentum-dependent mass enhancement factors m^*_{kn}/m along the high-symmetry line. We found the mass enhancements $m_{e_g}/m = 1.8$ for e_g electrons and $m_{t_{2g}}/m = 1.2$ for t_{2g} electrons.

We examined the MDF projected onto each orbital. We found that the d electrons cause a significant momentum dependence, though the sp electrons behave as independent electrons. We obtained the mass enhancement factors $m^*_s/m = m^*_p/m = 1.01$, and $m^*_d/m = 3.33$ for s, p, and d electrons, respectively, indicating that the d electrons behave as correlated electrons. The average mass enhancement m^*/m increases with increasing interaction strength. We found that the intra-orbital and inter-orbital spin-spin correlations , $i.e.$, spin fluctuations cause the mass enhancement of Fe. We obtained the average mass enhancement $m^*/m = 1.65$ for Fe. The value 1.65 is consistent with the experimental values obtained from the low-temperature specific heat data $m^*/m = 1.38 \sim 2.12$, and the ARPES data 1.7, as well as the recent theoretical result 1.577 based on the finite-temperature LDA+DMFT calculations. The first-principles Gutzwiller theory underestimates the mass enhancement factor of bcc Fe, indicating the significance of the momentum dependence of the variational parameters in the MLA.

Although we established in this thesis the quantitative aspects of the first-principles MLA, there are many works left for future. First, present calculations for Fe are limited to the paramagnetic state. We have to perform the ferromagnetic calculations to clarify the ground state of Fe, Co, and Ni on the basis of the first-principles MLA. Furthermore we have to examine the quantitative aspects of the theory for more correlated electron systems such as Fe pnictides and the heavyfermion compounds. These problems are left for future work.

Second, in order to describe the strongly correlated electron systems showing the metal-insulator

transition, we have to apply the MLA with HB wavefunction. We have to extend the HB-MLA to the first-principles version for the quantitative description of the metal-insulator transitions.

We also point out that the MLA wavefunction method is limited to the single-site approximation. Inclusion of nonlocal correlations is desired to describe the magnetism, the metal-insulator transition, and the frustrated electrons in low-dimensional systems. There one needs to introduce explicitly the nonlocal correlators with momentum dependent variational parameters. Extension of the first-principles MLA to the nonlocal case will open a new door to a wide range of applications of the theory to correlated electron systems.

Appendix A

Appendix: Wick's Theorem

We used Wick's theorem in Chapters 3, 4, and 5 to calculate the average of operator products in many-body problems. In this Appendix, we derive Wick's theorem and its extension.

We can prove the Wick's theorem as follows.

$$\langle A_1 A_2 A_3 A_4 ... A_{2n-1} A_{2n} \rangle_0 = \sum_{\{\text{contractions}\}} (-)^{\delta(P)} \langle A_{i_1} A_{i_2} \rangle_0 \langle A_{i_3} A_{i_4} \rangle_0 ..... \langle A_{i_{2n-1}} A_{i_{2n}} \rangle_0. \quad \text{(A.1)}$$

Let us consider the average of the operator products with respect to the non-interacting Hamiltonian H_0 as follows.

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

Here $\{A_i\}$ are creation or annihilation operators that satisfy the relations

$$A_i A_j + A_j A_i = (ij). \quad \text{(A.3)}$$

For example, a_k and $a_k^\dagger$ satisfy the above relations:

$$a_k a_{k'} + a_{k'} a_k = a_k^\dagger a_{k'}^\dagger + a_{k'}^\dagger a_k^\dagger = 0, \quad \text{(A.4)}$$

$$a_k^\dagger a_{k'} + a_{k'} a_k^\dagger = \delta_{kk'}. \quad \text{(A.5)}$$

The non-interacting Hamiltonian is assumed as

$$H_0 = \sum_k \epsilon_k n_k. \quad \text{(A.6)}$$

Then, we obtain

$$\langle a_k^\dagger a_{k'}^\dagger \rangle_0 = \langle a_k a_{k'} \rangle_0 = 0, \quad \text{(A.7)}$$

$$\langle a_k^\dagger a_{k'} \rangle_0 = \langle a_k a_{k'}^\dagger \rangle_0 = 0 \ \ (k \neq k'). \quad \text{(A.8)}$$

and

$$\langle a_k^\dagger a_k \rangle_0 = \langle n_k \rangle_0 = \frac{1}{1 + e^{\beta \epsilon_k}}, \quad \text{(A.9)}$$

$$\langle a_k a_k^\dagger \rangle_0 = 1 - \langle n_k \rangle_0 = \frac{1}{1 + e^{-\beta \epsilon_k}}. \quad \text{(A.10)}$$

Thus

$$A_i A_j = \frac{(ij)}{1 + e^{\pm \beta \epsilon_k}}. \quad \text{(A.11)}$$

Here $+$ for $A_i = a_k^\dagger$ and $-$ for $A_i = a_k$ in the denominator. $\langle A_i A_j \rangle$ is called the contraction of a pair (ij).

Using the anti-commutation relation (A.3), one can exchange A_1 with A_2 in the average

$$\langle A_1 A_2 ..... A_{2n} \rangle_0 = (12) \langle A_3 ...., A_{2n} \rangle_0 - \langle A_3 A_2 A_1 ..... A_{2n} \rangle_0. \tag{A.12}$$

Repeating the same procedures, one can move A_1 to the end of the products as follows.

$$\begin{aligned} \langle A_1 A_2 ..... A_{2n} \rangle_0 = & (12) \langle A_3 ... A_{2n} \rangle_0 - (13) \langle A_2 A_4 .... A_{2n} \rangle_0 \\ & + ... \\ & + (1, 2n) \langle A_2 A_4 .... A_{2n-1} \rangle_0 - \langle A_2 A_3 .... A_{2n} A_1 \rangle_0. \end{aligned} \tag{A.13}$$

Note that we have the relation

$$a_k(\beta) = e^{\beta H_0} a_k e^{-\beta H_0}. \tag{A.14}$$

Differentiating the above equation with respect to β, we obtain

$$\frac{\partial a_k(\beta)}{\partial \beta} = e^{\beta H_0} (H_0 a_k - a_k H_0) e^{-\beta H_0}. \tag{A.15}$$

By making use of $H_0 = \sum_{k'} \epsilon_{k'} a_{k'}^\dagger a_{k'}$, $n_{k'} = a_{k'}^\dagger a_{k'}$ and the anti-commutation relation $a_k a_k^\dagger = \delta_{kk'} - a_k^\dagger a_k$ into $H_0 a_k - a_k H_0$, we obtain

$$\begin{aligned} H_0 a_k - a_k H_0 &= \sum_{k'} \epsilon_{k'} (a_{k'}^\dagger a_{k'} a_k - a_k a_{k'}^\dagger a_{k'}) \\ &= \sum_{k'} \epsilon_{k'} (a_{k'}^\dagger a_{k'} a_k + a_{k'}^\dagger a_k a_{k'} - a_{k'} \delta_{kk'}) \\ &= -\epsilon_k a_k. \end{aligned} \tag{A.16}$$

Thus Eq. (A.15) is expressed by

$$\frac{\partial a_k(\beta)}{\partial \beta} = -\epsilon_k a_k. \tag{A.17}$$

If we consider the relation $a_k(0) = a_k$. We obtain from Eq. (A.17).

$$a_k(\beta) = a_k e^{-\beta \epsilon_k}. \tag{A.18}$$

Similarly,

$$a_k^\dagger(\beta) = a_k^\dagger e^{-\beta \epsilon_k}. \tag{A.19}$$

From these relations, we have

$$a_k e^{-\beta H_0} = e^{-\beta H_0} a_k e^{-\beta \epsilon_k}, \tag{A.20}$$

$$a_k^\dagger e^{-\beta H_0} = e^{-\beta H_0} a_k^\dagger e^{\beta \epsilon_k}. \tag{A.21}$$

Let us consider the thermal average in Eq. (A.13).

$$\langle A_2 ..... A_{2n} A_1 \rangle_0 = \frac{\mathrm{tr}(A_2 ..... A_{2n} A_1 e^{-\beta H_0})}{\mathrm{tr}(e^{-\beta H_0})}. \tag{A.22}$$

Using Eqs. (A.20) and (A.21), we have the following relation.

$$A_i e^{-\beta H_0} = e^{\pm\beta\epsilon_k} e^{-\beta H_0} A_i. \tag{A.23}$$

Here $+$ for $A_i = a_k^\dagger$ and $-$ for $A_i = a_k$. Substituting Eq. (A.23) into (A.22), we obtain

$$\langle A_2.....A_{2n}A_1\rangle_0 = \frac{e^{\pm\epsilon_1}\mathrm{tr}(A_2.....A_{2n}A_1 e^{-\beta H_0})}{\mathrm{tr}(e^{-\beta H_0})}. \tag{A.24}$$

Hence

$$\langle A_2.....A_{2n}A_1\rangle_0 = e^{\pm\epsilon_1}\langle A_1A_2.....A_{2n}\rangle_0. \tag{A.25}$$

Here we used the relation $\mathrm{tr}(AB) = \mathrm{tr}(BA)$.

Substituting Eq. (A.25) into Eq. (A.13), we obtain

$$\begin{aligned}(1 + e^{\pm\beta\epsilon_1})\langle A_1A_2.....A_{2n}\rangle_0 = (12)\langle A_3...A_{2n}\rangle_0 - (13)\langle A_2A_4....A_{2n}\rangle_0 \\ + ... + (1,2n)\langle A_2A_3....A_{2n-1}\rangle_0.\end{aligned} \tag{A.26}$$

Thus we obtain

$$\begin{aligned}\langle A_1A_2.....A_{2n}\rangle_0 = \langle A_1A_2\rangle_0\langle A_3.....A_{2n}\rangle_0 - \langle A_1A_3\rangle_0\langle A_2A_4.....A_{2n}\rangle_0 \\ + ... + \langle A_1A_{2n}\rangle_0\langle A_2A_3.....A_{2n-1}\rangle_0.\end{aligned} \tag{A.27}$$

Repeating the same procedure for the remaining multiple products, we reach Wick's theorem.

$$\langle A_1A_2A_3A_4...A_{2n-1}A_{2n}\rangle_0 = \sum_{\{\text{contractions}\}} (-)^{\delta(P)}\langle A_{i_1}A_{i_2}\rangle_0\langle A_{i_3}A_{i_4}\rangle_0.....\langle A_{i_{2n-1}}A_{i_{2n}}\rangle_0. \tag{A.28}$$

Here the sum at rhs is taken over all possible pairs of contractions. $(-1)^{\delta(P)}$ takes $+$ or $-$ depending on whether $(i_1, i_2, i_3, ...i_{2n})$ is even or odd in permutation and

$$\sum_{\{\text{contractions}\}} = \sum_{\substack{i_1<i_2, i_3<i_4, ..., i_{2n-1}<i_{2n} \\ i_1 < i_3 < i_5 < ..... < i_{2n-1}}}$$

For the calculations of operator products $\langle\delta(A_1A_2)\delta(A_3A_4).....\delta(A_{2n-1}A_{2n})\rangle_0$, we can prove the extended Wick's theorem as follows:

$$\langle\delta(A_1A_2)\delta(A_3A_4).....\delta(A_{2n-1}A_{2n})\rangle_0 = \sum_{\{\text{contractions}\}}{}' (-)^{\delta(P)}\langle A_{i_1}A_{i_2}\rangle_0\langle A_{i_3}A_{i_4}\rangle_0.....\langle A_{i_{2n-1}}A_{i_{2n}}\rangle_0. \tag{A.29}$$

Here

$$\delta(A_iA_j) = A_iA_j - \langle A_iA_j\rangle_0. \tag{A.30}$$

The sum is taken over all possible pairs of contractions without self-pairs such as $\langle A_{i_{2n-1}}A_{i_{2n}}\rangle$. $(-)^{\delta(p)}$ takes $+(-)$ when $(i_1, i_2, ...i_{2n})$ is even (odd) in the permutations.

One can check that the theorem holds true for $n = 1, 2$. In fact

$$\langle\delta(A_1A_2)\rangle_0 = \langle A_1A_2\rangle_0 = \langle A_1A_2\rangle_0 = 0. \tag{A.31}$$

and

$$\begin{aligned}\langle\delta(A_1A_2)\delta(A_3A_4)\rangle_0 &= \langle A_1A_2A_3A_4\rangle_0 - \langle A_1A_2\rangle_0\langle A_3A_4\rangle_0 \\ &- \langle A_3A_4\rangle_0\langle A_1A_2\rangle_0 + (-)^2\langle A_1A_2\rangle_0\langle A_3A_4\rangle_0 \\ &= \langle A_1A_2A_3A_4\rangle_0 - \langle A_1A_2\rangle_0\langle\delta(A_3A_4)\rangle_0 \\ &- \langle A_3A_4\rangle_0\langle\delta(A_1A_2)\rangle_0 - \langle A_1A_2\rangle_0\langle A_3A_4\rangle_0. \end{aligned} \tag{A.32}$$

In the same way, one can prove that

$$\begin{aligned}&\langle\delta(A_1A_2)\delta(A_3A_4).....\delta(A_{2n-1}A_{2n})\rangle_0 \\ &= \langle A_1A_2A_3A_4.....A_{2n-1}A_{2n}\rangle_0 \\ &- \sum_i \langle A_{2i-1}A_{2i}\rangle_0\langle\delta(A_1A_2)..2i....\delta(A_{2n-1}A_{2n})\rangle_0 \\ &- \sum_i \sum_{j(>i)} \langle A_{2i-1}A_{2i}\rangle_0\langle A_{2j-1}A_{2j}\rangle_0\langle\delta(A_1A_2)..2i....2j....\delta(A_{2n-1}A_{2n})\rangle_0 \\ &- \sum_i \sum_{j(>i)} \sum_{k(>j)} \langle A_{2i-1}A_{2i}\rangle_0\langle A_{2j-1}A_{2j}\rangle_0\langle A_{2k-1}A_{2k}\rangle_0\langle\delta(A_1A_2)..2i....2j....2k....\delta(A_{2n-1}A_{2n})\rangle_0 \\ &- ..... \\ &- \langle A_1A_2\rangle_0\langle A_3A_4\rangle_0.....\langle A_{2n-1}A_{2n}\rangle_0. \end{aligned} \tag{A.33}$$

Therefore, we obtain the term $\langle\delta(A_1A_2)\delta(A_3A_4).....\delta(A_{2n-1}A_{2n})\rangle_0$ as follows.

$=$ (sum over all possible combinations of products of contractions)
$-$ (single self-pair terms)
$-$ (double self-pair terms)
$-$ (triple self-pair terms)
$-$ .....
$-$ (n self-pair terms)
$=$ sum over all possible combinations of products of contractions without any self-pairs.

Thus the extended Wick's theorem (A.29) holds true.

Appendix B

Appendix: Calculation of Physical Quantities using Feynman-Hellmann Theorem

In this Appendix we prove the Feynman-Hellmann theorem and derive physical quantities using the theorem.

1. Feynman-Hellmann theorem

Consider a system with Hamiltonian $H(\lambda)$ that depends on some parameter λ. Let $\Psi(\lambda)$ be a eigen function of $H(\lambda)$ with eigen value $E(\lambda)$

$$H(\lambda)|\Psi(\lambda)\rangle = E(\lambda)|\Psi(\lambda)\rangle. \tag{B.1}$$

We assume that $\Psi(\lambda)$ is normalized so that

$$\langle\Psi(\lambda)|\Psi(\lambda)\rangle = 1. \tag{B.2}$$

The Feynman-Hellmann theorem states that the derivative of the total energy with respect to a parameter is equal to the expectation value of the derivative of the Hamiltonian with respect to the same parameter.

$$\frac{\partial E(\lambda)}{\partial\lambda} = \left\langle \Psi(\lambda) \left| \frac{\partial H(\lambda)}{\partial\lambda} \right| \Psi(\lambda) \right\rangle. \tag{B.3}$$

In order to prove the above relation, we start from the ground-state energy obtain from Eq. (B.1).

$$E(\lambda) = \langle\Psi(\lambda)|H(\lambda)|\Psi(\lambda)\rangle. \tag{B.4}$$

Differentiating both sides, we have

$$\frac{\partial E(\lambda)}{\partial\lambda} = \left\langle \frac{\partial\Psi(\lambda)}{\partial\lambda} |H(\lambda)| \Psi(\lambda) \right\rangle + \left\langle \Psi(\lambda) \left| \frac{\partial H(\lambda)}{\partial\lambda} \right| \Psi(\lambda) \right\rangle + \left\langle H(\lambda) |\Psi(\lambda)| \frac{\partial\Psi(\lambda)}{\partial\lambda} \right\rangle. \tag{B.5}$$

Using the relation (B.1), Eq. (B.5) is expressed as follows.

$$\frac{\partial E(\lambda)}{\partial\lambda} = \left\langle \frac{\partial\Psi(\lambda)}{\partial\lambda} |H(\lambda)|\Psi(\lambda) \right\rangle + E(\lambda) \left[\left\langle \Psi(\lambda)| \frac{\partial\Psi(\lambda)}{\partial\lambda} \right\rangle + \left\langle \frac{\Psi(\lambda)}{\partial\lambda} |\Psi(\lambda) \right\rangle \right]. \tag{B.6}$$

Since $|\Psi(\lambda)\rangle$ is normalized, we have from Eq. (B.2)

$$\left\langle \frac{\Psi(\lambda)}{\partial\lambda}\middle|\Psi(\lambda)\right\rangle + \left\langle \Psi(\lambda)\middle|\frac{\partial\Psi(\lambda)}{\partial\lambda}\right\rangle = 0. \tag{B.7}$$

From Eqs. (B.6) and (B.7), we obtain

$$\frac{\partial E(\lambda)}{\partial\lambda} = \left\langle \Psi(\lambda)\left|\frac{\partial H(\lambda)}{\partial\lambda}\right|\Psi(\lambda)\right\rangle. \tag{B.8}$$

which is the Feynman-Hellmann theorem.

Let us consider the Feynman-Hellmann theorem with use of the correlation energy. The correlation energy is defined by

$$E_c = \langle H\rangle - \langle H\rangle_0. \tag{B.9}$$

Here the $\langle H\rangle_0$ is the ground-state energy in the Hartree-Fock approximation $\langle H\rangle_0 = \langle H_0\rangle_0$, H_0 being the Hartree-Fock Hamiltonian defined in Chapter 3. Thus,

$$\langle H\rangle = \langle H\rangle_0 + E_c. \tag{B.10}$$

Therefore,

$$\frac{\partial\langle H\rangle}{\partial\lambda} = \frac{\partial\langle H\rangle_0}{\partial\lambda} + \frac{\partial E_c}{\partial\lambda}. \tag{B.11}$$

Since $|\phi_0\rangle$ is the ground state of H_0, we obtain

$$\frac{\partial\langle H\rangle_0}{\partial\lambda} = \left\langle \frac{\partial H_0}{\partial\lambda}\right\rangle_0, \tag{B.12}$$

according to the Feynman-Hellmann theorem. Thus we obtain

$$\frac{\partial\langle H\rangle}{\partial\lambda} = \left\langle \frac{\partial H_0}{\partial\lambda}\right\rangle_0 + \frac{\partial E_c}{\partial\lambda}. \tag{B.13}$$

Let us consider the first term at the rhs of Eq. (B.13). We consider the change of the Hartree-Fock Hamiltonian H_0 via λ as

$$\delta H_0 = (\delta H)_{nm} + (\delta H_0)_\lambda. \tag{B.14}$$

Here $(\sim)_{nm}$ means the change when the electron number n and the magnetic moment m in the Hartree-Fock potential are fixed.

$$\langle\delta H_0\rangle_0 = \langle(\delta H)_{nm}\rangle_0 + \langle(\delta H_0)_\lambda\rangle_0. \tag{B.15}$$

We can prove that the change of Hartree-Fock Hamiltonian via the λ is $\langle(\delta H_0)_\lambda\rangle_0 = 0$ because of the stationary properties in the Hartree-Fock approximation. Therefore we obtain from Eq. (B.15) as

$$\langle\delta H_0\rangle_0 = \langle(\delta H_0)_{nm}\rangle_0. \tag{B.16}$$

Thus,

$$\left\langle \frac{\partial H_0}{\partial \lambda} \right\rangle_0 = \left\langle \phi_0 \left| \left(\frac{\partial H_0}{\partial \lambda} \right)_{nm} \right| \phi_0 \right\rangle . \tag{B.17}$$

In the same way, we can write the correlation energy as

$$\frac{\partial E_c}{\partial \lambda} = \left\langle \frac{\partial \tilde{H}}{\partial \lambda} \right\rangle = \left\langle \frac{\partial H}{\partial \lambda} - \left\langle \left(\frac{\partial H_0}{\partial \lambda} \right)_{nm} \right\rangle_0 \right\rangle = \left(\frac{\partial E_c}{\partial \lambda} \right)_{dir} . \tag{B.18}$$

Here $\left\langle \partial H/\partial\lambda - \langle (\partial H_0/\partial\lambda)_{nm} \rangle_0 \right\rangle$ means that one takes the derivative of $\tilde{H}$ with respect to λ which appear explicitly in $\tilde{H} = H - \langle H \rangle_0$.

Finally, we obtain the following formula from Eqs. (B.13), (B.17), and (B.18).

$$\frac{\partial \langle H \rangle}{\partial \lambda} = \left\langle \left(\frac{\partial H_0}{\partial \lambda} \right)_{nm} \right\rangle_0 + \left(\frac{\partial E_c}{\partial \lambda} \right)_{dir} \tag{B.19}$$

and

$$\left(\frac{\partial E_c}{\partial \lambda} \right)_{dir} = \left\langle \left(\frac{\partial \tilde{H}}{\partial \lambda} \right)_{nm} \right\rangle . \tag{B.20}$$

Here $(\partial E_c/\partial\lambda)_{dir}$ means taking the derivative of E_c with respect to λ which appear explicitly in $\tilde{H}$.

2. Electron number $\langle n_{iL} \rangle$

The TB-LDA+U Hamiltonian is written in Eq. (3.1):

$$\begin{aligned} H = & \sum_{iL\sigma} \epsilon^0_{iL\sigma} n_{iL\sigma} + \sum_{iLjL'\sigma} t_{iLjL'} a^\dagger_{iL\sigma} a_{jL\sigma} \\ & + \sum_i \Big[\sum_m U_{mm}\, n_{ilm\uparrow}\, n_{ilm\downarrow} + \sum_{(m,m')} \Big(U_{mm'} - \frac{1}{2} J_{mm'} \Big) n_{ilm}\, n_{ilm'} - 2 \sum_{(m,m')} J_{mm'}\, \boldsymbol{s}_{ilm} \cdot \boldsymbol{s}_{ilm'} \Big] . \end{aligned} \tag{B.21}$$

Using the formula (B.19) for $\partial\langle H\rangle/\partial\lambda$, we have

$$\frac{\partial \langle H \rangle}{\partial \epsilon^0_{iL}} = \left\langle \left(\frac{\partial H_0}{\partial \epsilon^0_{iL}} \right)_{nm} \right\rangle_0 + \frac{\partial E_c}{\partial \epsilon^0_{iL}} . \tag{B.22}$$

Here $(\sim)_{nm}$ denotes the derivatives with respect to any parameters with constant charge and moment, and E_c is the total correlation energy. Making use of the Feynman-Hellmann theorem,

$$\frac{\partial \langle H \rangle}{\partial \epsilon^0_{iL}} = \langle n_{iL} \rangle . \tag{B.23}$$

Since $(\partial H_0/\partial\epsilon^0_{iL})_{nm} = \langle n_{iL}\rangle$, we obtain

$$\langle n_{iL}\rangle = \langle n_{iL}\rangle_0 + \frac{\partial E_c}{\partial \epsilon^0_{iL}}. \tag{B.24}$$

Here

$$\begin{aligned}\frac{\partial E_c}{\partial \epsilon^0_{iL}} = &\left\langle \left(\frac{\partial \tilde{H}}{\partial \epsilon^0_{iL}}\right)_{nm}\right\rangle_0 \\ &+ \sum_j \frac{-\left\langle \tilde{O}^\dagger_j \frac{\partial \tilde{H}}{\partial \epsilon^0_{iL}}\right\rangle_0 - \left\langle \frac{\partial \tilde{H}}{\partial \epsilon^0_{iL}}\tilde{O}_j\right\rangle_0 + \left\langle \tilde{O}^\dagger_j \frac{\partial \tilde{H}}{\partial \epsilon^0_{iL}}\tilde{O}_j\right\rangle_0}{1+\langle \tilde{O}^\dagger_j \tilde{O}_j\rangle_0}.\end{aligned} \tag{B.25}$$

The Hamiltonian is expressed by $\tilde{H} = \tilde{H}_0 + H_I$. Thus

$$\left(\frac{\partial \tilde{H}}{\partial \epsilon^0_{iL}}\right) = \tilde{n}_{iL}. \tag{B.26}$$

Therefore,

$$\frac{\partial E_c}{\partial \epsilon^0_{iL}} = \sum_j \frac{-\langle \tilde{O}^\dagger_j \tilde{n}_{iL}\rangle_0 - \langle \tilde{n}_{iL}\tilde{O}_j\rangle_0 + \langle \tilde{O}^\dagger_j \tilde{n}_{iL}\tilde{O}_j\rangle_0}{1+\langle \tilde{O}^\dagger_j \tilde{O}_j\rangle_0}. \tag{B.27}$$

In the SSA, we can omit the off-diagonal elements ($j \neq i$). Thus, we obtain the following formula

$$\langle n_{iL}\rangle = \langle n_{iL}\rangle_0 + \frac{-\langle \tilde{O}^\dagger_i \tilde{n}_{iL}\rangle_0 - \langle \tilde{n}_{iL}\tilde{O}_i\rangle_0 + \langle \tilde{O}^\dagger_i \tilde{n}_{iL}\tilde{O}_i\rangle_0}{1+\langle \tilde{O}^\dagger_i \tilde{O}_i\rangle_0}. \tag{B.28}$$

Note that $\langle \tilde{n}_{iL}\tilde{O}_i\rangle_0 = \langle \tilde{O}^\dagger_i \tilde{n}_{iL}\rangle^*_0 = 0$. Thus

$$\langle n_{iL}\rangle = \langle n_{iL}\rangle_0 + \frac{\langle \tilde{O}^\dagger_i \tilde{n}_{iL}\tilde{O}_i\rangle_0}{1+\langle \tilde{O}^\dagger_i \tilde{O}_i\rangle_0}. \tag{B.29}$$

Here $\langle n_{iL}\rangle_0$ denotes the Hartree-Fock electron number. The second term at the rhs (right-hand-side) is the correlation correction of electron number.

$$\langle \tilde{n}_{iL\sigma}\rangle = \frac{\langle \tilde{O}^\dagger_i \tilde{n}_{iL\sigma}\tilde{O}_i\rangle_0}{1+\langle \tilde{O_i}^\dagger \tilde{O}_i\rangle_0}. \tag{B.30}$$

Equation (B.29) is identical with Eq. (3.80) in Sec 3.6.1.

3. Local charge fluctuations $\langle(\delta n_{id})^2\rangle$

The local charge fluctuations of d electrons on site i is defined as

$$\langle(\delta n_{id})^2\rangle = \langle n^2_{id}\rangle - \langle n_{id}\rangle^2. \tag{B.31}$$

Here $\langle n_{id}^2 \rangle$ is given by

$$\langle n_{id}^2 \rangle = \langle n_{id} \rangle + 2 \sum_{L}^{d} \langle n_{iL\uparrow} \cdot n_{iL\downarrow} \rangle + 2 \sum_{(L,L')}^{d} \langle n_{iL} \cdot n_{iL'} \rangle. \tag{B.32}$$

The double occupation number $\langle n_{iL\uparrow} \cdot n_{iL\downarrow} \rangle$ and inter-orbital charge-charge correlations $\langle n_{iL} \cdot n_{iL'} \rangle$ are obtain from the Hamiltonian Eq. (B.21) using the Feynman-Hellmann theorem (B.19) as follows.

$$\langle n_{iL\uparrow} n_{iL\downarrow} \rangle = \frac{\partial \langle H \rangle}{\partial U_{imm}}, \tag{B.33}$$

$$\langle n_{iL} n_{iL'} \rangle = \frac{\partial \langle H \rangle}{\partial U_{imm'}}. \tag{B.34}$$

Now, the total correlation energy is defined as

$$\langle H \rangle = \langle H \rangle_0 + E_c. \tag{B.35}$$

Taking the derivative of $\langle H \rangle$ with respect to U_{imm} and using the relation $\langle H \rangle_0 = \langle H_0 \rangle$ we obtain

$$\frac{\partial \langle H \rangle}{\partial U_{imm}} = \frac{\partial \langle H_0 \rangle_0}{\partial U_{imm}} + \frac{\partial E_c}{\partial U_{imm}}. \tag{B.36}$$

According to the formula of the derivatives $\partial \langle H \rangle / \partial \lambda$,

$$\frac{\partial \langle H \rangle}{\partial \lambda} = \left\langle \left(\frac{\partial H_0}{\partial \lambda} \right)_{nm} \right\rangle_0 + \left(\frac{\partial E_c}{\partial \lambda} \right)_{dir}, \tag{B.37}$$

and

$$\left(\frac{\partial E_c}{\partial \lambda} \right)_{dir} = \left\langle \left(\frac{\partial H}{\partial \lambda} \right)_{nm} \right\rangle. \tag{B.38}$$

We obtain

$$\begin{aligned} \frac{\partial \langle H \rangle}{\partial U_{imm}} = & \left\langle \left(\frac{\partial H_0}{\partial U_{imm}} \right)_{nm} \right\rangle_0 \\ & + \sum_j \frac{- \left\langle \tilde{O}_j^\dagger \dfrac{\partial \tilde{H}}{\partial U_{imm}} \right\rangle_0 - \left\langle \dfrac{\partial \tilde{H}}{\partial U_{imm}} \tilde{O}_j \right\rangle_0 + \left\langle \tilde{O}_j^\dagger \dfrac{\partial \tilde{H}}{\partial U_{imm}} \tilde{O}_j \right\rangle_0}{1 + \langle \tilde{O}_j^\dagger \tilde{O}_j \rangle_0}. \end{aligned} \tag{B.39}$$

Note that

$$\left\langle \left(\frac{\partial H_0}{\partial U_{imm}} \right) \right\rangle_0 = \langle n_{iL\uparrow} \rangle_0 \langle n_{iL\downarrow} \rangle_0, \tag{B.40}$$

$$\left(\frac{\partial \tilde{H}}{\partial U_{imm}} \right)_{nm} = \sum_\sigma \langle n_{idm-\sigma} \rangle_0 \tilde{n}_{idm\sigma} + O_{imm}^{(0)}. \tag{B.41}$$

Substituting Eqs. (B.40) and (B.41) into Eq. (B.39) and making the SSA, we find

$$\begin{aligned}\langle n_{iL\uparrow}n_{iL\downarrow}\rangle &= \langle n_{iL\uparrow}\rangle_0\langle n_{iL\downarrow}\rangle_0 \\ &+ \frac{-\sum_\sigma\langle n_{iL-\sigma}\rangle_0\langle\tilde{O}_i^\dagger\tilde{n}_{iL\sigma}\rangle_0 - \sum_\sigma\langle n_{iL-\sigma}\rangle_0\langle\tilde{n}_{iL\sigma}\tilde{O}_i\rangle_0 + \sum_\sigma\langle n_{iL-\sigma}\rangle_0\langle\tilde{O}_i^\dagger\tilde{n}_{iL\sigma}\tilde{O}_i\rangle_0}{1+\langle\tilde{O}_i^\dagger\tilde{O}_i\rangle_0} \\ &+ \frac{-\langle\tilde{O}_i^\dagger O_{iL}^{(0)}\rangle_0 - \langle O_{iL}^{(0)}\tilde{O}_i\rangle_0 + \langle\tilde{O}_i^\dagger O_{iL}^{(0)}\tilde{O}_i\rangle_0}{1+\langle\tilde{O}_i^\dagger\tilde{O}_i\rangle_0}. \end{aligned} \tag{B.42}$$

Note that $\langle\tilde{O}_i^\dagger\tilde{n}_{iL\sigma}\rangle_0 = \langle\tilde{n}_{iL\sigma}\tilde{O}_i\rangle_0 = 0$. Moreover using (B.30) we find

$$\begin{aligned}\langle n_{iL\uparrow}n_{iL\downarrow}\rangle &= \langle n_{iL\uparrow}\rangle_0\langle n_{iL\downarrow}\rangle_0 + \sum_\sigma\langle n_{iL-\sigma}\rangle_0\langle\tilde{n}_{iL\sigma}\rangle \\ &+ \frac{-\langle\tilde{O}_i^\dagger O_{iL}^{(0)}\rangle_0 - \langle O_{iL}^{(0)}\tilde{O}_i\rangle_0 + \langle\tilde{O}_i^\dagger O_{iL}^{(0)}\tilde{O}_i\rangle_0}{1+\langle\tilde{O}_i^\dagger\tilde{O}_i\rangle_0}. \end{aligned} \tag{B.43}$$

Next we calculate the inter-orbital charge- charge correlations via the relation as (B.34):

$$\langle n_{ilm}n_{ilm'}\rangle = \frac{\partial\langle H\rangle}{\partial U_{imm'}}. \tag{B.44}$$

Here using the relation $\langle H\rangle = \langle H\rangle_0 + E_c$, we obtain the inter-orbital charge- charge correlations as follows.

$$\langle n_{ilm}n_{ilm'}\rangle = \frac{\partial\langle H_0\rangle_0}{\partial U_{imm'}} + \frac{\partial E_c}{\partial U_{imm'}}. \tag{B.45}$$

Using the formula of $\partial\langle H\rangle/\partial\lambda$, *i.e.*, (B.37) we have

$$\frac{\partial\langle H\rangle}{\partial U_{imm'}} = \left\langle\left(\frac{\partial H_0}{\partial U_{imm'}}\right)_{nm}\right\rangle + \frac{\partial E_c}{\partial U_{imm'}}. \tag{B.46}$$

Here

$$\frac{\partial E_c}{\partial U_{imm'}} = \sum_j \frac{-\left\langle\tilde{O}_j^\dagger\frac{\partial\tilde{H}}{\partial U_{imm'}}\right\rangle_0 - \left\langle\frac{\partial\tilde{H}}{\partial U_{imm'}}\tilde{O}_j\right\rangle_0 + \left\langle\tilde{O}_j^\dagger\frac{\partial\tilde{H}}{\partial U_{imm'}}\tilde{O}_j\right\rangle_0}{1+\langle\tilde{O}_j^\dagger\tilde{O}_j\rangle_0}, \tag{B.47}$$

$$\left\langle\left(\frac{\partial H_0}{\partial U_{imm'}}\right)_{nm}\right\rangle_0 = \langle n_{idm}\rangle_0\langle n_{idm'}\rangle_0, \tag{B.48}$$

$$\left\langle\tilde{O}_j^\dagger\frac{\partial\tilde{H}}{\partial U_{imm'}}\right\rangle_0 = \langle n_{idm'}\rangle_0\langle\tilde{O}_j^\dagger\tilde{n}_{idm}\rangle_0 + \langle n_{idm}\rangle_0\langle\tilde{n}_{idm'}\tilde{O}_j\rangle_0 + \langle\tilde{O}_j^\dagger O_{iLL'}^{(1)}\rangle_0, \tag{B.49}$$

$$\left\langle\frac{\partial\tilde{H}}{\partial U_{imm'}}\tilde{O}_j\right\rangle_0 = \langle n_{idm'}\rangle_0\langle\tilde{n}_{idm}\tilde{O}_j\rangle_0 + \langle n_{idm}\rangle_0\langle\tilde{n}_{idm'}\tilde{O}_j\rangle_0 + \langle O_{iLL'}^{(1)}\tilde{O}_j\rangle_0, \tag{B.50}$$

$$\left\langle \tilde{O}_j^\dagger \frac{\partial \tilde{H}}{\partial U_{imm'}} \tilde{O}_j \right\rangle_0 = \langle n_{idm'} \tilde{O}_j \rangle_0 \langle \tilde{O}_j^\dagger \tilde{n}_{idm} \tilde{O}_j \rangle_0 + \langle n_{idm} \rangle_0 \langle \tilde{O}_j^\dagger \tilde{n}_{idm'} \tilde{O}_j \rangle_0 + \langle \tilde{O}_j^\dagger O^{(1)}_{iLL'} \tilde{O}_j \rangle_0. \quad \text{(B.51)}$$

Finally we obtain the correlation energy in the SSA as follows.

$$\begin{aligned} \frac{\partial E_c}{\partial U_{iLL'}} &= \langle n_{iL'} \rangle_0 \langle \tilde{n}_{iL} \rangle + \langle n_{iL} \rangle_0 \langle \tilde{n}_{iL'} \rangle \\ &+ \frac{-\langle \tilde{O}_i^\dagger O^{(1)}_{iLL'} \rangle_0 - \langle O^{(1)}_{iLL'} \tilde{O}_i \rangle_0 + \langle \tilde{O}_i^\dagger O^{(1)}_{iLL'} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0}. \end{aligned} \quad \text{(B.52)}$$

Here we used the relation $\langle \tilde{O}_j^\dagger \tilde{n}_{idm} \rangle_0 = \langle \tilde{n}_{idm'} \tilde{O}_j \rangle_0 = 0$, and Eq. (B.30).

Substituting Eqs. (B.48) and (B.52) into Eq. (B.46), we obtain the charge-charge correlations in the SSA as follows.

$$\begin{aligned} \langle n_{iL} n_{iL'} \rangle &= \langle n_{iL} \rangle_0 \langle n_{iL'} \rangle_0 + \langle n_{iL'} \rangle_0 \langle \tilde{n}_{iL} \rangle + \langle n_{iL} \rangle_0 \langle \tilde{n}_{iL'} \rangle \\ &+ \frac{-\langle \tilde{O}_i^\dagger O^{(1)}_{iLL'} \rangle_0 - \langle O^{(1)}_{iLL'} \tilde{O}_i \rangle_0 + \langle \tilde{O}_i^\dagger O^{(1)}_{iLL'} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0}. \end{aligned} \quad \text{(B.53)}$$

The operators of $O^{(0)}_{iLL}$ and $O^{(1)}_{iLL'}$ are defined by Eqs. (3.28) and (3.29):

$$O^{(0)}_{iLL} = \delta n_{iL\uparrow} \delta n_{iL\downarrow}, \quad \text{(B.54)}$$

$$O^{(1)}_{iLL'} = \delta n_{iL} \delta n_{iL'}. \quad \text{(B.55)}$$

According to the formula (3.78), we obtain the average of $O^{(\alpha)}_{iLL,}$ for $\alpha = 0, 1$ as follows

$$\langle O^{(\alpha)}_{iLL'} \rangle = \frac{-\langle \tilde{O_i}^\dagger O^{(\alpha)}_{iLL'} \rangle_0 - \langle O^{(\alpha)}_{iLL'} \tilde{O}_i \rangle_0 + \langle \tilde{O_i}^\dagger O^{(\alpha)}_{iLL'} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O_i}^\dagger \tilde{O}_i \rangle_0}. \quad \text{(B.56)}$$

Using the above relation we obtain the alternative expression of the double occupation number as

$$\langle n_{iL\uparrow} n_{iL\downarrow} \rangle = \langle O^{(0)}_{iLL} \rangle + \langle \tilde{n}_{iL\uparrow} \rangle \langle n_{iL\downarrow} \rangle_0 + \langle n_{iL\uparrow} \rangle_0 \langle \tilde{n}_{iL\downarrow} \rangle + \langle n_{iL\uparrow} \rangle_0 \langle n_{iL\downarrow} \rangle_0. \quad \text{(B.57)}$$

Similarly, we obtain the inter-orbital charge-charge correlations term as follows.

$$\langle n_{iL} n_{iL'} \rangle = \langle O^{(1)}_{iLL'} \rangle + \langle \tilde{n}_{iL} \rangle \langle n_{iL'} \rangle_0 + \langle n_{iL} \rangle_0 \langle \tilde{n}_{iL'} \rangle + \langle n_{iL} \rangle_0 \langle n_{iL'} \rangle_0. \quad \text{(B.58)}$$

Substituting Eqs. (B.57) and (B.58) into Eq. (B.32), we obtain the expression of $\langle n_{id}^2 \rangle$ as

$$\begin{aligned} \langle n_{id}^2 \rangle =& \langle n_{id} \rangle + 2 \sum_L^d \langle O^{(0)}_{iLL} \rangle + 2 \sum_{L\sigma}^d \langle \tilde{n}_{iL\sigma} \rangle \langle \tilde{n}_{iL-\sigma} \rangle_0 \\ &+ \sum_{L\sigma}^d \langle \tilde{n}_{iL\sigma} \rangle_0 \langle \tilde{n}_{iL-\sigma} \rangle_0 + 2 \sum_{(L,L)}^d \langle O^{(1)}_{iLL'} \rangle \\ &+ 2 \sum_{(L,L)}^d \{ \langle \tilde{n}_{iL} \rangle \langle \tilde{n}_{iL'} \rangle_0 + \langle n_{iL} \rangle_0 \langle \tilde{n}_{iL'} \rangle \} + 2 \sum_{(L,L)}^d \langle n_{iL} \rangle_0 \langle n_{iL'} \rangle_0. \end{aligned} \quad \text{(B.59)}$$

On the other hand, we obtain the term $\langle n_{id}\rangle^2$ as follows

$$\begin{aligned}\langle n_{id}\rangle^2 =&\langle \tilde{n}_{id}\rangle^2 + \sum_L^d \langle n_{iL}\rangle_0^2 \\ &+ 2\sum_{(L,L')}^d \langle n_{iL}\rangle_0\langle n_{iL'}\rangle_0 + 2\sum_L^d \langle \tilde{n}_{iL}\rangle\langle n_{iL}\rangle_0 \\ &+ 2\sum_{(L,L')}^d \langle \tilde{n}_{iL}\rangle\langle n_{iL'}\rangle_0 + 2\sum_{(L,L)}^d \langle \tilde{n}_{iL'}\rangle\langle n_{iL}\rangle_0. \end{aligned} \tag{B.60}$$

Substituting Eqs. (B.59) and (B.60) into Eq. (B.31), we obtain the expression of $\langle(\delta n_{id})^2\rangle$ as

$$\begin{aligned}\langle(\delta n_{id})^2\rangle =& \sum_{L\sigma}^d \langle n_{iL\sigma}\rangle_0(1-\langle n_{iL\sigma}\rangle_0) + \sum_{L\sigma}^d \langle \tilde{n}_{iL\sigma}\rangle(1-2\langle n_{iL\sigma}\rangle_0) \\ &- \langle \tilde{n}_{id}\rangle^2 + 2\sum_L^d \langle O_{iLL}^{(0)}\rangle + 2\sum_{(L,L')}^d \langle O_{iLL'}^{(1)}\rangle\,. \end{aligned} \tag{B.61}$$

Here the first term at the rhs of Eq. (B.61) denotes the Hartree-Fock contributions. $\langle \tilde{n}_{iL\sigma}\rangle$ in the second term is given by Eq. (B.30) in which $\tilde{n}_{iL}$ has been replaced by $\tilde{n}_{iL\sigma}$, and is equal to $\langle \tilde{n}_{iL}\rangle/2$ in the paramagnetic state. $\langle \tilde{n}_{id}\rangle$ in the third term is defined by $\sum_L^d \langle \tilde{n}_{iL}\rangle$. The remaining correlation corrections at the rhs of Eqs. (B.61) is obtained from the residual interaction elements $\langle O_{iLL'}^{(\alpha)}\rangle$ using the formula (3.78) as follows.

$$\sum_{\langle LL'\rangle}\langle O_{iLL'}^{(\alpha)}\rangle = \frac{-\sum_{\langle LL'\rangle}\langle \tilde{O_i}^\dagger O_{iLL'}^{(\alpha)}\rangle_0 - \sum_{\langle LL'\rangle}\langle O_{iLL'}^{(\alpha)}\tilde{O}_i\rangle_0 + \sum_{\langle LL'\rangle}\langle \tilde{O_i}^\dagger O_{iLL'}^{(\alpha)}\tilde{O}_i\rangle_0}{1+\langle \tilde{O_i}^\dagger \tilde{O}_i\rangle_0}\,. \tag{B.62}$$

Equation (B.61) is identical with Eq. (3.89) in Sec. 3.6.2.

4. Amplitude of local magnetic moment $\langle \boldsymbol{S}^2\rangle$

The magnetic moment of d-orbital is defined as

$$\langle \boldsymbol{m}_{id}^2\rangle = 3\sum_L^d {m_{iL}^z}^2 + 2\sum_{(L,L')}^d \langle \boldsymbol{m}_{iL}\cdot\boldsymbol{m}_{iL'}\rangle. \tag{B.63}$$

Here m_{iL}^z is defined by

$$m_{iL}^z = n_{iL\uparrow} - n_{iL\downarrow}. \tag{B.64}$$

Thus we obtain

$$\langle {m_{iL}^z}^2\rangle = \langle n_{iL}\rangle - 2\langle n_{iL\uparrow}n_{iL\downarrow}\rangle. \tag{B.65}$$

Substituting Eq. (B.65) into Eq. (B.63), we obtain

$$\langle \boldsymbol{m}_{id}^2 \rangle = 3\sum_{L}^{d}\langle n_{iL}\rangle - 6\sum_{L}^{d}\langle n_{iL\uparrow}n_{iL\downarrow}\rangle + 2\sum_{(L,L')}^{d}\langle \boldsymbol{m}_{iL}\cdot\boldsymbol{m}_{iL'}\rangle. \tag{B.66}$$

Since, $\boldsymbol{m}_{iL} = 2\boldsymbol{s}_{iL}$, we can write Eq. (B.66) as

$$\langle \boldsymbol{m}_{id}^2 \rangle = 3\sum_{L}^{d}\langle n_{iL}\rangle - 6\sum_{L}^{d}\langle n_{iL\uparrow}n_{iL\downarrow}\rangle + 8\sum_{(L,L')}^{d}\langle \boldsymbol{s}_{iL}\cdot\boldsymbol{s}_{iL'}\rangle. \tag{B.67}$$

The inter-orbital spin-spin correlators $\langle \boldsymbol{s}_{ilm}\cdot\boldsymbol{s}_{ilm'}\rangle$ is obtained from the relation (B.21).

$$\langle \boldsymbol{s}_{iL}\cdot\boldsymbol{s}_{iL'}\rangle = -\frac{1}{2}\frac{\partial\langle H\rangle}{\partial J_{imm'}}. \tag{B.68}$$

Using the relation $\langle H\rangle = \langle H\rangle_0 + E_c$ and the formula (B.19) of $\partial\langle H\rangle/\partial\lambda$, we have

$$\frac{\partial\langle H\rangle}{\partial J_{imm'}} = \left\langle \left(\frac{\partial H_0}{\partial J_{imm'}}\right)_{nm}\right\rangle + \frac{\partial E_c}{\partial J_{imm'}}. \tag{B.69}$$

Here

$$\frac{\partial E_c}{\partial J_{imm'}} = \sum_j \frac{-\left\langle \tilde{O}_j^\dagger \dfrac{\partial\tilde{H}}{\partial J_{imm'}}\right\rangle_0 - \left\langle \dfrac{\partial\tilde{H}}{\partial U_{imm'}}\tilde{O}_j\right\rangle_0 + \left\langle \tilde{O}_j^\dagger \dfrac{\partial\tilde{H}}{\partial J_{imm'}}\tilde{O}_j\right\rangle_0}{1+\langle\tilde{O}_j^\dagger\tilde{O}_j\rangle_0}, \tag{B.70}$$

$$\left\langle \left(\frac{\partial H_0}{\partial J_{imm'}}\right)_{nm}\right\rangle_0 = -\frac{1}{2}\langle m_{idm}\rangle_0\langle m_{idm'}\rangle_0, \tag{B.71}$$

$$\left\langle \tilde{O}_j^\dagger\frac{\partial\tilde{H}}{\partial J_{imm'}}\right\rangle_0 = -\frac{1}{2}\langle m_{idm'}\rangle_0\langle\tilde{O}_j^\dagger\tilde{m}_{idm}\rangle_0 - \frac{1}{2}\langle m_{idm}\rangle_0\langle\tilde{m}_{idm'}\tilde{O}_j\rangle_0 - 2\langle\tilde{O}_j^\dagger O_{iLL'}^{(2)}\rangle_0, \tag{B.72}$$

$$\left\langle \frac{\partial\tilde{H}}{\partial J_{imm'}}\tilde{O}_j\right\rangle_0 = -\frac{1}{2}\langle m_{idm'}\rangle_0\langle\tilde{O}_j^\dagger\tilde{m}_{idm}\rangle_0 - \frac{1}{2}\langle m_{idm}\rangle_0\langle\tilde{m}_{idm'}\tilde{O}_j\rangle_0 - 2\langle O_{iLL'}^{(2)}\tilde{O}_j\rangle_0, \tag{B.73}$$

$$\left\langle \tilde{O}_j^\dagger\frac{\partial\tilde{H}}{\partial J_{imm'}}\tilde{O}_j\right\rangle_0 = -\frac{1}{2}\langle m_{idm'}\tilde{O}_j\rangle_0\langle\tilde{O}_j^\dagger\tilde{m}_{idm}\tilde{O}_j\rangle_0 - \frac{1}{2}\langle m_{idm}\rangle_0\langle\tilde{O}_j^\dagger\tilde{m}_{idm'}\tilde{O}_j\rangle_0 - 2\langle\tilde{O}_j^\dagger O_{iLL'}^{(2)}\tilde{O}_j\rangle_0. \tag{B.74}$$

Since $\langle\tilde{O}_j^\dagger\tilde{m}_{idm}\rangle_0 = \langle\tilde{m}_{idm'}\tilde{O}_j\rangle_0 = 0$, we obtain the correlation energy in the SSA as follows

$$\begin{aligned}-\frac{1}{2}\frac{\partial E_c}{\partial J_{iLL'}} &= \frac{1}{4}\left(\langle m_{iL'}\rangle_0\langle\tilde{m}_{iL}\rangle + \langle m_{iL}\rangle_0\langle\tilde{m}_{iL'}\rangle\right)\\ &\quad + \frac{-\langle\tilde{O}_i^\dagger O_{iLL'}^{(2)}\rangle_0 - \langle O_{iLL'}^{(2)}\tilde{O}_i\rangle_0 + \langle\tilde{O}_i^\dagger O_{iLL'}^{(2)}\tilde{O}_i\rangle_0}{1+\langle\tilde{O}_i^\dagger\tilde{O}_i\rangle_0}.\end{aligned} \tag{B.75}$$

From Eqs. (B.67), (B.69), and (B.75), we obtained the spin-spin correlations as

$$\langle \boldsymbol{s}_{iL} \cdot \boldsymbol{s}_{iL'} \rangle = \frac{1}{4}\langle m_{iL}\rangle_0\langle m_{iL'}\rangle_0 + \frac{1}{4}(\langle m_{iL'}\rangle_0\langle \tilde{m}_{iL}\rangle + \langle m_{iL}\rangle_0\langle \tilde{m}_{iL'}\rangle) + \frac{-\langle \tilde{O}_i^\dagger O_{iLL'}^{(2)}\rangle_0 - \langle O_{iLL'}^{(2)}\tilde{O}_i\rangle_0 + \langle \tilde{O}_i^\dagger O_{iLL'}^{(2)}\tilde{O}_i\rangle_0}{1+\langle \tilde{O}_i^\dagger \tilde{O}_i\rangle_0}. \tag{B.76}$$

Since

$$\langle O_{iLL'}^{(2)}\rangle = \frac{-\langle \tilde{O}_i^\dagger O_{iLL'}^{(2)}\rangle_0 - \langle O_{iLL'}^{(2)}\tilde{O}_i\rangle_0 + \langle \tilde{O}_i^\dagger O_{iLL'}^{(2)}\tilde{O}_i\rangle_0}{1+\langle \tilde{O}_i^\dagger \tilde{O}_i\rangle_0}. \tag{B.77}$$

We obtain the alternative expression of inter-orbital spin-spin interaction as follows.

$$\langle \boldsymbol{s}_{iL} \cdot \boldsymbol{s}_{iL'} \rangle = \langle O_{iLL'}^{(2)}\rangle + \frac{1}{4}(\langle \delta m_{iL}\rangle\langle m_{iL'}\rangle_0 + \langle \delta m_{iL'}\rangle\langle m_{iL}\rangle_0 + \langle m_{iL}\rangle_0\langle m_{iL'}\rangle_0). \tag{B.78}$$

Substituting Eqs. (B.57) and (B.78) into Eq. (B.67), we obtain the expression of $\langle \boldsymbol{m}_{id}^2\rangle$ as

$$\begin{aligned}\langle \boldsymbol{m}_{id}^2\rangle =& 3\sum_L^d(\langle \tilde{n}_{iL}\rangle + \langle n_{iL}\rangle_0) \\ &- 6\sum_L^d\{\langle O_{iLL}^{(0)}\rangle + \sum_\sigma \langle \tilde{n}_{iL\sigma}\rangle\langle n_{iL-\sigma}\rangle_0 + \frac{1}{2}\sum_\sigma \langle n_{iL\sigma}\rangle_0\langle n_{iL-\sigma}\rangle_0\} \\ &+ 8\sum_{(L,L)}^d\{\langle O_{iLL'}^{(2)}\rangle + \frac{1}{4}(\langle \tilde{m}_{iL}\rangle\langle m_{iL'}\rangle_0 + \langle \tilde{m}_{iL'}\rangle\langle m_{iL}\rangle_0 + \langle m_{iL}\rangle_0\langle m_{iL'}\rangle_0)\}.\end{aligned} \tag{B.79}$$

Since $\langle m_{iL}\rangle = \sum_\sigma \sigma\langle n_{iL\sigma}\rangle$, we obtain the alternative form of $\langle \boldsymbol{m}_{id}^2\rangle$ as

$$\begin{aligned}\langle \boldsymbol{S}^2\rangle =& \frac{3}{4}\sum_{L\sigma}^d\langle n_{iL\sigma}\rangle_0(1-\langle n_{iL\sigma}\rangle_0) + \frac{3}{4}\sum_{L\sigma}^d\langle \tilde{n}_{iL\sigma}\rangle(1-2\langle n_{iL-\sigma}\rangle_0) \\ &- \frac{3}{2}\sum_L^d\langle O_{iLL}^{(0)}\rangle + 2\sum_{(L,L')}^d\langle O_{iLL'}^{(2)}\rangle.\end{aligned} \tag{B.80}$$

Here the first term at the rhs of Eq. (B.80) denotes the Hartree-Fock contributions. $\langle \tilde{n}_{iL\sigma}\rangle$ in the second term is given by Eq. (B.30) in which $\tilde{n}_{iL}$ has been replaced by $\tilde{n}_{iL\sigma}$, and is equal to $\langle \tilde{n}_{iL}\rangle/2$ in the paramagnetic state. The remaining correlation corrections at the rhs of Eq. (B.80) are obtained from the residual interaction elements $\langle O_{iLL'}^{(\alpha)}\rangle$ using the formula (B.62). Equation (B.80) is identical with Eq. (3.99) in Sec. 3.6.3.

5. Momentum distribution function $\langle n_{kn\sigma}\rangle$

In the momentum representation the Hamiltonian is expressed as

$$H = H_0 + H_I. \tag{B.81}$$

The Hartree-Fock Hamiltonian is given in Eq. (3.9):

$$H_0 = \sum_{kn\sigma} \epsilon_{kn\sigma} n_{kn\sigma} - \sum_{im} U_{imm} \langle n_{idm\uparrow} \rangle_0 \langle n_{idm\downarrow} \rangle_0 - \sum_i \sum_{(m,m')} (U_{imm'} - \frac{1}{2} J_{imm'}) \langle n_{idm} \rangle_0 \langle n_{idm'} \rangle_0 + 2 \sum_i \sum_{(m,m')} J_{imm'} \langle \boldsymbol{s}_{idm} \rangle_0 \cdot \langle \boldsymbol{s}_{idm'} \rangle_0. \quad \text{(B.82)}$$

Thus

$$\tilde{H} = \tilde{H}_0 + H_I, \quad \text{(B.83)}$$

$$\tilde{H}_0 = \sum_{kn\sigma} \epsilon_{kn\sigma} \tilde{n}_{kn\sigma}. \quad \text{(B.84)}$$

$\langle n_{kn\sigma} \rangle$ is obtained with use of the Feynman-Hellmann theorem as follows.

$$\langle n_{kn\sigma} \rangle = \left\langle \frac{\partial H}{\partial \epsilon_{kn\sigma}} \right\rangle = \frac{\partial \langle H \rangle}{\partial \epsilon_{kn\sigma}}. \quad \text{(B.85)}$$

The rhs is obtained by means of the formula (B.19).

$$\frac{\partial \langle H \rangle}{\partial \epsilon_{kn\sigma}} = \left\langle \left(\frac{\partial H_0}{\partial \epsilon_{kn\sigma}} \right)_{nm} \right\rangle_0 + \frac{\partial E_c}{\partial \epsilon_{kn\sigma}}. \quad \text{(B.86)}$$

Here

$$\frac{\partial E_c}{\partial \epsilon_{kn\sigma}} = \sum_j \frac{-\left\langle \tilde{O}_j^\dagger \frac{\partial \tilde{H}}{\partial \epsilon_{kn\sigma}} \right\rangle_0 - \left\langle \frac{\partial \tilde{H}}{\partial \epsilon_{kn\sigma}} \tilde{O}_j \right\rangle_0 + \left\langle \tilde{O}_j^\dagger \frac{\partial \tilde{H}}{\partial \epsilon_{kn\sigma}} \tilde{O}_j \right\rangle_0}{1 + \langle \tilde{O}_j^\dagger \tilde{O}_j \rangle_0}. \quad \text{(B.87)}$$

and

$$\left(\frac{\partial \tilde{H}}{\epsilon_{kn\sigma}} \right)_{nm} = \tilde{n}_{kn\sigma}. \quad \text{(B.88)}$$

Assuming an atom per unit cell, we have from Eqs. (B.85), (B.86), and (B.88)

$$\langle n_{kn\sigma} \rangle = \langle n_{kn\sigma} \rangle_0 + \frac{-N \langle \tilde{O}_i^\dagger \tilde{n}_{kn\sigma} \rangle_0 - N \langle \tilde{n}_{kn\sigma} \tilde{O}_i \rangle_0 + N \langle \tilde{O}_i^\dagger \tilde{n}_{kn\sigma} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0}. \quad \text{(B.89)}$$

Since $\langle \tilde{n}_{kn\sigma} \tilde{O}_i \rangle = 0$, we reach

$$\langle n_{kn\sigma} \rangle = \langle n_{kn\sigma} \rangle_0 + \frac{N \langle \tilde{O}_i^\dagger \tilde{n}_{kn\sigma} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0}. \quad \text{(B.90)}$$

Equation (B.90) is identical with Eq. (3.103) in Sec. 3.6.4. We present these relations Eqs. (B.29), (B.61), (B.80), and (B.90) in Chapter 3. We also used these relations for the calculations of physical quantities in Chapters 4 and 5.

Appendix C

Appendix: Matrix Elements in the Lowest-Order Approximation

We present in this Appendix the matrix elements and related quantities in the lowest-order approximations in Sec. 4.2. These expressions are needed in the numerical calculations in Sec. 4.3.

Assume that orbital L belongs to an irreducible representation Γ. We also assume that the Coulomb interaction $U^{(\alpha)}_{LL'}$ only depend on the types of the irreducible representation Γ and Γ' to which orbitals L and L' belong; $U^{(\alpha)}_{LL'} = U^{(\alpha)}_{\Gamma\Gamma'}$. We obtain the expressions of the matrix elements and related quantities as follows by using the Laplace transformation (2.39). The matrix elements of the correlation energy ϵ_c in Eq. (4.12) are given as follows.

$$\begin{aligned}\langle H_I \tilde{O}_i\rangle_0 = &\sum_{\Gamma} d_\Gamma U^{(0)2}_{\Gamma\Gamma} P_{\Gamma\Gamma} \\ &+ 2\sum_{\Gamma} d_\Gamma(d_\Gamma-1) U^{(1)2}_{\Gamma\Gamma} P_{\Gamma\Gamma} + 4\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(1)2}_{\Gamma\Gamma'} P_{\Gamma\Gamma'} \\ &+ \frac{1}{8}\sum_{\Gamma} d_\Gamma(d_\Gamma-1) U^{(2)2}_{\Gamma\Gamma} P_{\Gamma\Gamma} + \frac{1}{4}\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(2)2}_{\Gamma\Gamma'} P_{\Gamma\Gamma'} \\ &+ \frac{1}{4}\sum_{\Gamma} d_\Gamma(d_\Gamma-1) U^{(2)2}_{\Gamma\Gamma} P_{\Gamma\Gamma} + \frac{1}{4}\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(2)2}_{\Gamma\Gamma'} P_{\Gamma\Gamma'} \ , \end{aligned} \tag{C.1}$$

$$\begin{aligned}\langle \tilde{O}_i{}^\dagger \tilde{H}_0 \tilde{O}_i\rangle_0 = &\sum_{\Gamma} d_\Gamma U^{(0)2}_{\Gamma\Gamma} Q_{\Gamma\Gamma} \\ &+ 2\sum_{\Gamma} d_\Gamma(d_\Gamma-1) U^{(1)2}_{\Gamma\Gamma} Q_{\Gamma\Gamma} + 4\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(1)2}_{\Gamma\Gamma'} P_{\Gamma\Gamma'} \\ &+ \frac{1}{8}\sum_{\Gamma} d_\Gamma(d_\Gamma-1) U^{(2)2}_{\Gamma\Gamma} Q_{\Gamma\Gamma} + \frac{1}{4}\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(2)2}_{\Gamma\Gamma'} Q_{\Gamma\Gamma'} \\ &+ \frac{1}{4}\sum_{\Gamma} d_\Gamma(d_\Gamma-1) U^{(2)2}_{\Gamma\Gamma} Q_{\Gamma\Gamma} + \frac{1}{2}\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(2)2}_{\Gamma\Gamma'} Q_{\Gamma\Gamma'} \ . \end{aligned} \tag{C.2}$$

Here d_Γ is the dimensions for the representation Γ, and

$$P_{\Gamma\Gamma'} = i \int_0^\infty dt e^{i\epsilon_c t}\, a_\Gamma(-t)\, a_{\Gamma'}(-t)\, b_\Gamma(t)\, b_{\Gamma'}(t)\,, \tag{C.3}$$

$$\begin{aligned} Q_{\Gamma\Gamma'} = -\int_0^\infty dt\, dt' e^{i\epsilon_c(t+t')} \Big[& a_{\Gamma'}(-t-t')\, b_{\Gamma'}(t+t')\, a_\Gamma(-t-t')\, b_{\Gamma 1}(t+t') \\ & - a_{\Gamma'}(-t-t')\, b_{\Gamma'}(t+t')\, a_{\Gamma 1}(-t-t')\, b_\Gamma(t+t') \\ & + a_{\Gamma'}(-t-t')\, b_{\Gamma' 1}(t+t')\, a_\Gamma(-t-t')\, b_\Gamma(t+t') \\ & - a_{\Gamma' 1}(-t-t')\, b_{\Gamma'}(t+t')\, a_\Gamma(-t-t')\, b_\Gamma(t+t') \Big]. \end{aligned} \tag{C.4}$$

The correlation part of electron number in Eq. (4.14) is obtained as follows.

$$\begin{aligned} \langle \tilde{O}_i^\dagger \tilde{n}_{iL} \tilde{O}_i \rangle_0 = & \; 2\, A_{\Gamma\Gamma} \Big[U_{\Gamma\Gamma}^{(0)^2} + (d_\Gamma - 1)\, A_{\Gamma\Gamma} \left(2\, U_{\Gamma\Gamma}^{(1)^2} + \frac{3}{8}\, U_{\Gamma\Gamma}^{(2)^2} \right) \Big] \\ & + 2 \sum_{\Gamma' \neq \Gamma}^{d} d_{\Gamma'}\, A_{\Gamma'\Gamma} \left[2\, U_{\Gamma\Gamma'}^{(1)^2} + \frac{3}{8}\, U_{\Gamma\Gamma'}^{(2)^2} \right]. \end{aligned} \tag{C.5}$$

Here

$$\begin{aligned} A_{\Gamma\Gamma'} = -\int_0^\infty dt\, dt' e^{i\epsilon_c(t+t')} \Big[& a_{\Gamma'}(-t-t')\, b_{\Gamma'}(t+t')\, a_\Gamma(-t-t')\, b_\Gamma(t)\, b_\Gamma(t') \\ & - a_{\Gamma'}(-t-t')\, b_{\Gamma'}(t+t')\, b_\Gamma(t+t')\, a_\Gamma(-t)\, a_\Gamma(-t') \Big]. \end{aligned} \tag{C.6}$$

The residual interaction elements $\sum_{\langle LL' \rangle} \langle O_{iLL'}^{(\alpha)} \rangle$ (α= 0, 1, and 2) in charge fluctuations (4.15) and amplitude of local moment (4.16) are obtained as follows.

$$\sum_{\langle LL' \rangle} \langle O_{iLL'}^{(\alpha)} \rangle = -\sum_{\langle LL' \rangle} \langle \tilde{O}_i{}^\dagger O_{iLL'}^{(\alpha)} \rangle_0 - \sum_{\langle LL' \rangle} \langle O_{iLL'}^{(\alpha)} \tilde{O}_i \rangle_0 + \sum_{\langle LL' \rangle} \langle \tilde{O}_i{}^\dagger O_{iLL'}^{(\alpha)} \tilde{O}_i \rangle_0 \,. \tag{C.7}$$

Here

$$\sum_L \langle O_{iLL}^{(0)} \tilde{O}_i \rangle_0 = \sum_\Gamma d_\Gamma\, U_{\Gamma\Gamma}^{(0)}\, P_{\Gamma\Gamma}\,, \tag{C.8}$$

$$\sum_{(L,L')} \langle O_{iLL'}^{(1)} \tilde{O}_i \rangle_0 = 2 \sum_\Gamma d_\Gamma\, (d_\Gamma - 1)\, U_{\Gamma\Gamma}^{(1)}\, P_{\Gamma\Gamma} + 4 \sum_{(\Gamma,\Gamma')} d_\Gamma\, d_{\Gamma'} U_{\Gamma\Gamma'}^{(1)}\, P_{\Gamma\Gamma'}\,, \tag{C.9}$$

$$\begin{aligned} \sum_{(L,L')} \langle O_{iLL'}^{(2)} \tilde{O}_i \rangle_0 = & \; \frac{3}{8} \sum_\Gamma d_\Gamma\, (d_\Gamma - 1)\, U_{\Gamma\Gamma}^{(2)}\, P_{\Gamma\Gamma} \\ & + \frac{3}{4} \sum_{(\Gamma,\Gamma')} d_\Gamma\, d_{\Gamma'} U_{\Gamma\Gamma'}^{(2)}\, P_{\Gamma\Gamma'}\,. \end{aligned} \tag{C.10}$$

The matrix element $\sum_{\langle LL' \rangle} \langle \tilde{O}_i{}^\dagger O_{iLL'}^{(\alpha)} \tilde{O}_i \rangle_0$ are obtained as follows.

$$\begin{aligned} \sum_L \langle \tilde{O}_i^\dagger O_{iLL}^{(0)} \tilde{O}_i \rangle_0 = & \sum_\Gamma d_\Gamma\, U_{\Gamma\Gamma}^{(0)^2}\, \Omega_{\Gamma\Gamma} \\ & + \sum_\Gamma d_\Gamma (d_\Gamma - 1) \left(4\, U_{\Gamma\Gamma}^{(1)^2} - \frac{1}{4}\, U_{\Gamma\Gamma}^{(2)^2} \right) \Xi_{\Gamma\Gamma\Gamma} \\ & + \sum_{(\Gamma,\Gamma')} d_\Gamma\, d_{\Gamma'} \left(4\, U_{\Gamma\Gamma'}^{(1)^2} - \frac{1}{4}\, U_{\Gamma\Gamma'}^{(2)^2} \right) \left(\Xi_{\Gamma'\Gamma\Gamma} + \Xi_{\Gamma\Gamma'\Gamma'} \right), \end{aligned} \tag{C.11}$$

$$\sum_{(L,L')} \langle \tilde{O}_i^\dagger O_{iLL'}^{(1)} \tilde{O}_i \rangle_0 = 8 \sum_{\Gamma} d_\Gamma (d_\Gamma - 1) U_{\Gamma\Gamma}^{(1)} U_{\Gamma\Gamma}^{(0)} M_{\Gamma\Gamma}$$
$$+ 8 \sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U_{\Gamma\Gamma'}^{(1)} \Big(U_{\Gamma\Gamma}^{(0)} M_{\Gamma\Gamma'} + U_{\Gamma'\Gamma'}^{(0)} M_{\Gamma'\Gamma} \Big)$$
$$+ 2 \sum_{\Gamma} d_\Gamma \, (d_\Gamma - 1) \, U_{\Gamma\Gamma}^{(1)} \Big(U_{\Gamma\Gamma}^{(1)} \Omega_{\Gamma\Gamma} + T_{\Gamma\Gamma}^{(11)} \Big)$$
$$+ 4 \sum_{(\Gamma,\Gamma')} d_\Gamma \, d_{\Gamma'} \, U_{\Gamma\Gamma'}^{(1)} \Big(U_{\Gamma\Gamma'}^{(1)} \Omega_{\Gamma\Gamma'} + T_{\Gamma\Gamma'}^{(11)} \Big)$$
$$+ \frac{3}{8} \sum_{\Gamma} d_\Gamma \, (d_\Gamma - 1) \Omega_{\Gamma\Gamma}$$
$$+ \frac{3}{4} \sum_{(\Gamma,\Gamma')} d_\Gamma \, d_{\Gamma'} \, U_{\Gamma\Gamma'}^{(2)^2} \Omega_{\Gamma\Gamma'} \, , \tag{C.12}$$

Here

$$T_{\Gamma\Gamma'}^{(11)} = -2 \Big(U_{\Gamma\Gamma}^{(1)} \, \Xi_{\Gamma\Gamma'\Gamma} + U_{\Gamma'\Gamma}^{(1)} \, \Xi_{\Gamma'\Gamma\Gamma} \Big)$$
$$- 2 \Big(U_{\Gamma\Gamma'}^{(1)} \, \Xi_{\Gamma\Gamma'\Gamma'} + U_{\Gamma'\Gamma'}^{(1)} \, \Xi_{\Gamma'\Gamma\Gamma'} \Big)$$
$$+ 2 \sum_{\Gamma''} d_{\Gamma''} \, \Big(U_{\Gamma\Gamma''}^{(1)} \, \Xi_{\Gamma\Gamma'\Gamma''} + U_{\Gamma'\Gamma''}^{(1)} \, \Xi_{\Gamma'\Gamma\Gamma''} \Big) \, . \tag{C.13}$$

Finally we have

$$\sum_{(L,L')} \langle \tilde{O}_i^\dagger O_{iLL'}^{(2)} \tilde{O}_i \rangle_0 = \sum_{\Gamma} d_\Gamma \, U_{\Gamma\Gamma}^{(0)} \hat{K}_{\Gamma\Gamma}^{(0)}$$
$$+ \frac{1}{2} \sum_{\Gamma} d_\Gamma \, (d_\Gamma - 1) \, \Big[4 \, U_{\Gamma\Gamma}^{(1)} \hat{K}_{\Gamma\Gamma 1}^{(1)} + \frac{1}{4} \, U_{\Gamma\Gamma}^{(2)} \hat{K}_{\Gamma\Gamma 2}^{(1)} \Big]$$
$$+ \sum_{(\Gamma,\Gamma')} d_\Gamma \, d_{\Gamma'} \, \Big[4 \, U_{\Gamma\Gamma'}^{(1)} \hat{K}_{\Gamma\Gamma' 1}^{(1)} + \frac{1}{4} \, U_{\Gamma\Gamma'}^{(2)} \hat{K}_{\Gamma\Gamma' 2}^{(1)} \Big]$$
$$- \sum_{\Gamma} d_\Gamma \, (d_\Gamma - 1) \, U_{\Gamma\Gamma}^{(2)} \hat{K}_{t\Gamma\Gamma}^{(2)} - \sum_{(\Gamma,\Gamma')} d_\Gamma \, d_{\Gamma'} \, U_{\Gamma\Gamma'}^{(2)} \hat{K}_{t\Gamma\Gamma'}^{(2)} \, . \tag{C.14}$$

Here

$$\hat{K}_{\Gamma\Gamma}^{(0)} = -\frac{3}{4} \, (d_\Gamma - 1) \, U_{\Gamma\Gamma}^{(2)} M_{\Gamma\Gamma} - \frac{3}{4} \sum_{\Gamma'(\neq\Gamma)} d_{\Gamma'} \, U_{\Gamma\Gamma'}^{(2)} M_{\Gamma\Gamma'} \, , \tag{C.15}$$

$$\hat{K}_{\Gamma\Gamma' 1}^{(1)} = \frac{3}{16} \, U_{\Gamma\Gamma'}^{(2)} \Omega_{\Gamma\Gamma'} \, , \tag{C.16}$$

$$\begin{aligned}\hat{K}^{(1)}_{\Gamma\Gamma' 2} = &-U^{(0)}_{\Gamma\Gamma}\, M_{\Gamma\Gamma'} - U^{(0)}_{\Gamma'\Gamma'}\, M_{\Gamma'\Gamma} + U^{(1)}_{\Gamma\Gamma'}\, \Omega_{\Gamma\Gamma'} - \frac{1}{2}\, U^{(2)}_{\Gamma\Gamma'}\, W_{\Gamma\Gamma'} \\ &- \frac{1}{2}\Big(U^{(2)}_{\Gamma\Gamma}\, \Xi_{\Gamma\Gamma'\Gamma} + U^{(2)}_{\Gamma'\Gamma}\, \Xi_{\Gamma'\Gamma\Gamma}\Big) \\ &- \frac{1}{2}\left(U^{(2)}_{\Gamma\Gamma'}\, \Xi_{\Gamma\Gamma'\Gamma'} + U^{(2)}_{\Gamma'\Gamma'}\, \Xi_{\Gamma'\Gamma\Gamma'}\right) \\ &+ \frac{1}{2}\sum_{\Gamma''} d_{\Gamma''}\left(U^{(2)}_{\Gamma\Gamma''}\, \Xi_{\Gamma\Gamma'\Gamma''} + U^{(2)}_{\Gamma'\Gamma''}\, \Xi_{\Gamma'\Gamma\Gamma''}\right), \end{aligned} \tag{C.17}$$

$$\begin{aligned}\hat{K}^{(2)}_{t\Gamma\Gamma'} = &\frac{1}{4}\left(U^{(0)}_{\Gamma\Gamma} M_{\Gamma\Gamma'} + U^{(0)}_{\Gamma'\Gamma'}\, M_{\Gamma'\Gamma}\right) \\ &- \frac{1}{4}\left(4U^{(1)}_{\Gamma\Gamma'}\Omega_{\Gamma\Gamma'} - U^{(2)}_{\Gamma\Gamma'} W_{\Gamma\Gamma'} + \frac{1}{4} U^{(2)}_{\Gamma\Gamma'}\Omega_{\Gamma\Gamma'}\right) \\ &+ \frac{1}{8}\left(U^{(2)}_{\Gamma\Gamma}\Xi_{\Gamma\Gamma'\Gamma} + U^{(2)}_{\Gamma'\Gamma}\Xi_{\Gamma'\Gamma\Gamma}\right) \\ &+ \frac{1}{8}\left(U^{(2)}_{\Gamma\Gamma'}\Xi_{\Gamma\Gamma'\Gamma'} + U^{(2)}_{\Gamma'\Gamma'}\Xi_{\Gamma'\Gamma\Gamma'}\right) \\ &- \frac{1}{8}\sum_{\Gamma''} d_{\Gamma''}\left(U^{(2)}_{\Gamma\Gamma''}\, \Xi_{\Gamma\Gamma'\Gamma''} + U^{(2)}_{\Gamma'\Gamma''}\, \Xi_{\Gamma'\Gamma\Gamma''}\right). \end{aligned} \tag{C.18}$$

The quantities $M_{\Gamma\Gamma'}$, $\Xi_{\Gamma\Gamma'\Gamma''}$, $\Omega_{\Gamma\Gamma'}$, $W_{\Gamma\Gamma'}$, $Z_{1\Gamma\Gamma'}$, $Z_{2\Gamma\Gamma'}$, $Z_{3\Gamma\Gamma'}$, and $Z_{1\Gamma\Gamma'}$ in the above expressions are given as follows.

$$M_{\Gamma\Gamma'} = \Xi_{\Gamma\Gamma\Gamma'} = -\int_0^\infty dt\, dt' e^{i\epsilon_c(t+t')}\, a_\Gamma(-t)\, b_\Gamma(t)\, a_\Gamma(-t-t')\, b_\Gamma(t+t')\, a_{\Gamma'}(-t')\, b_{\Gamma'}(t')\,, \tag{C.19}$$

$$\Xi_{\Gamma'\Gamma\Gamma} = -\int_0^\infty dt\, dt' e^{i\epsilon_c(t+t')}\, a_\Gamma(-t)\, b_\Gamma(t)\, a_{\Gamma'}(-t-t')\, b_{\Gamma'}(t+t')\, a_\Gamma(-t')\, b_\Gamma(t')\,, \tag{C.20}$$

$$\Xi_{\Gamma\Gamma'\Gamma''} = -\int_0^\infty dt\, dt' e^{i\epsilon_c(t+t')}\, a_{\Gamma'}(-t)\, b_{\Gamma'}(t)\, a_\Gamma(-t-t')\, b_\Gamma(t+t')\, a_{\Gamma''}(-t')\, b_{\Gamma''}(t')\,, \tag{C.21}$$

$$\Omega_{\Gamma\Gamma'} = -\left(Z_{1\Gamma\Gamma'} + Z_{2\Gamma\Gamma'} - Z_{3\Gamma\Gamma'} - Z_{4\Gamma\Gamma'}\right), \tag{C.22}$$

$$W_{\Gamma\Gamma'} = \left(Z_{1\Gamma\Gamma'} + Z_{2\Gamma\Gamma'} + Z_{3\Gamma\Gamma'} + Z_{4\Gamma\Gamma'}\right), \tag{C.23}$$

$$Z_{1\Gamma\Gamma'} = -\int_0^\infty dt\, dt' e^{i\epsilon_c(t+t')}\, a_{\Gamma'}(-t)\, b_{\Gamma'}(t+t')\, a_\Gamma(-t-t')\, b_\Gamma(t)\, a_{\Gamma'}(-t')\, b_\Gamma(t')\,, \tag{C.24}$$

$$Z_{2\Gamma\Gamma'} = -\int_0^\infty dt\, dt' e^{i\epsilon_c(t+t')}\, a_{\Gamma'}(-t-t')\, b_{\Gamma'}(t)\, a_\Gamma(-t)\, b_\Gamma(t+t')\, b_{\Gamma'}(t')\, a_\Gamma(-t')\,, \tag{C.25}$$

$$Z_{3\Gamma\Gamma'} = -\int_0^\infty dt\, dt' e^{i\epsilon_c(t+t')}\, a_{\Gamma'}(-t)\, b_{\Gamma'}(t+t')\, a_\Gamma(-t)\, b_\Gamma(t+t')\, a_{\Gamma'}(-t')\, a_\Gamma(-t')\,, \quad \text{(C.26)}$$

$$Z_{4\Gamma\Gamma'} = -\int_0^\infty dt\, dt' e^{i\epsilon_c(t+t')}\, a_{\Gamma'}(-t-t')\, b_{\Gamma'}(t)\, a_\Gamma(-t-t')\, b_\Gamma(t)\, b_{\Gamma'}(t')\, b_\Gamma(t')\,. \quad \text{(C.27)}$$

Here $a_\Gamma(t)$, $b_\Gamma(t)$, $a_{1\Gamma}(t)$, and $b_{1\Gamma}(t)$ are the Laplace transforms with respect to the local density of states $\rho_\Gamma(\epsilon)$.

$$a_\Gamma(t) = \int_{-\infty}^\infty d\epsilon\, e^{-i\epsilon t} f(\tilde{\epsilon})\, \rho_\Gamma(\epsilon)\,, \quad \text{(C.28)}$$

$$b_\Gamma(t) = \int_{-\infty}^\infty d\epsilon\, e^{-i\epsilon t} f(-\tilde{\epsilon})\, \rho_\Gamma(\epsilon)\,, \quad \text{(C.29)}$$

$$a_{\Gamma 1}(t) = \int_{-\infty}^\infty d\epsilon\, e^{-i\epsilon t} \epsilon\, f(\tilde{\epsilon})\, \rho_\Gamma(\epsilon)\,, \quad \text{(C.30)}$$

$$b_{\Gamma 1}(t) = \int_{-\infty}^\infty d\epsilon\, e^{-i\epsilon t} \epsilon\, f(-\tilde{\epsilon})\, \rho_\Gamma(\epsilon)\,. \quad \text{(C.31)}$$

$\rho_\Gamma(\epsilon)$ at the rhs is the Hartree-Fock local density of states for orbital L belonging to the representation Γ.

$$\rho_\Gamma(\epsilon) = \frac{1}{d_\Gamma} \sum_L^{d_\Gamma} \rho_L(\epsilon)\,, \quad \text{(C.32)}$$

$$\rho_L(\epsilon) = \sum_{kn} |\langle iL|kn\rangle|^2\, \delta(\epsilon - \epsilon_{kn})\,. \quad \text{(C.33)}$$

Next we obtain the expressions of the numerator in the second part of the momentum distribution function Eq. (4.18) in Sec. 4.3.2 are given as follows.

$$\begin{aligned} N\langle \tilde{O}_i^\dagger \tilde{n}_{kn\sigma} \tilde{O}_i\rangle_0 = U_{LL'}^{(\alpha)2} q_\tau^{(\alpha)} \Big[&\sum_{\langle LL'\rangle}^{d} \left(B_{LL'}(\epsilon_{kn\sigma}) |u_{Ln\sigma}(\boldsymbol{k})|^2 + B_{L'L}(\epsilon_{kn\sigma}) |u_{L'n\sigma}(\boldsymbol{k})|^2 \right) f(-\tilde{\epsilon}_{kn\sigma}) \\ &- \sum_{\langle LL'\rangle}^{d} \left(C_{LL'}(\epsilon_{kn\sigma}) |u_{Ln\sigma}(\boldsymbol{k})|^2 + C_{L'L}(\epsilon_{kn\sigma}) |u_{L'n\sigma}(\boldsymbol{k})|^2 \right) f(\tilde{\epsilon}_{kn\sigma}) \Big]. \end{aligned} \quad \text{(C.34)}$$

Assuming that orbital L belongs to an irreducible representation Γ, $B_{LL'}(\epsilon_{kn})$ and $C_{LL'}(\epsilon_{kn})$ are expressed as follows.

$$B_{\Gamma\Gamma'}(\epsilon_{kn}) = -\int_0^\infty dt\, dt' e^{i(\epsilon_c - \epsilon_{kn})(t+t')}\, a_\Gamma(-t-t')\, b_\Gamma(t+t')\, a_{\Gamma'}(-t-t')\,, \quad \text{(C.35)}$$

$$C_{\Gamma\Gamma'}(\epsilon_{kn}) = -\int_0^\infty dt\, dt' e^{i(\epsilon_c+\epsilon_{kn})(t+t')}\, a_\Gamma(-t-t')\, b_\Gamma(t+t')\, b_{\Gamma'}(t+t')\,. \tag{C.36}$$

The denominator of the momentum distribution function (4.18) is expressed by

$$\begin{aligned}\langle \tilde{O}_i{}^\dagger \tilde{O}_i\rangle_0 = &\sum_\Gamma d_\Gamma U^{(0)2}_{\Gamma\Gamma} S_{\Gamma\Gamma} \\ &+ 2\sum_\Gamma d_\Gamma(d_\Gamma-1) U^{(1)2}_{\Gamma\Gamma} S_{\Gamma\Gamma} + 4\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(1)2}_{\Gamma\Gamma'} S_{\Gamma\Gamma'} \\ &+ \frac{1}{8}\sum_\Gamma d_\Gamma(d_\Gamma-1) U^{(2)2}_{\Gamma\Gamma} S_{\Gamma\Gamma} + \frac{1}{4}\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(2)2}_{\Gamma\Gamma'} S_{\Gamma\Gamma'} \\ &+ \frac{1}{4}\sum_\Gamma d_\Gamma(d_\Gamma-1) U^{(2)2}_{\Gamma\Gamma} S_{\Gamma\Gamma} + \frac{1}{2}\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(2)2}_{\Gamma\Gamma'} S_{\Gamma\Gamma'}\,.\end{aligned} \tag{C.37}$$

Here

$$S_{\Gamma\Gamma'} = -\int_0^\infty dt\, dt' e^{i\epsilon_c(t+t')}\, a_\Gamma(-t-t')\, a_{\Gamma'}(-t-t')\, b_\Gamma(t+t')\, b_{\Gamma'}(t+t')\,. \tag{C.38}$$

Appendix D

Appendix: Matrix Elements of Correlation Energy: (5.9) $\sim$ (5.12) and (5.15)

In this Appendix, we present the explicit expressions of the matrix elements of the correlation energy ϵ_c in Eq. (5.8); Eqs. (5.9) $\sim$ (5.12), and (5.15) by using Wick's theorem and the Laplace transformation (2.39).

The elements for $\langle \tilde{H}_I \tilde{O}_i \rangle_0$ in Eq. (5.9), *i.e.*, $P^{(\alpha\alpha')}_{\tau LL'L''L'''\sigma\sigma'}$ are obtained as follows.

$$P^{(00)}_{LL'L''L'''\downarrow\uparrow} = i\int_0^\infty dt e^{i\epsilon_c t} a_{L\downarrow}(-t)a_{L\uparrow}(-t)b_{L\downarrow}(t)b_{L\uparrow}(t)\delta_{LL'}\delta_{LL''}\delta_{L''L'''}, \tag{D.1}$$

$$\begin{aligned} P^{(11)}_{LL'L''L'''\sigma\sigma'} = i\int_0^\infty dt e^{i\epsilon_c t}\Big[& a_{L\sigma}(-t)a_{L'\sigma'}(-t)b_{L\sigma}(t)b_{L'\sigma'}(t)\delta_{LL''}\delta_{L'L'''} \\ & + a_{L\sigma'}(-t)a_{L'\sigma}(-t)b_{L\sigma'}(t)b_{L'\sigma}(t)\delta_{L'L''}\delta_{LL'''}\Big], \end{aligned} \tag{D.2}$$

$$\begin{aligned} P^{(21)}_{LL'L''L'''\sigma\sigma'} = i\int_0^\infty dt e^{i\epsilon_c t}\sigma\sigma'[& a_{L\sigma}(-t)a_{L'\sigma'}(-t)b_{L\sigma}(t)b_{L'\sigma'}(t)\delta_{LL''}\delta_{L'L'''} \\ & + a_{L\sigma'}(-t)a_{L'\sigma}(-t)b_{L\sigma'}(t)b_{L'\sigma}(t)\delta_{L'L''}\delta_{LL'''}], \end{aligned} \tag{D.3}$$

$$\begin{aligned} P^{(12)}_{lLL'L''L'''\sigma\sigma'} = -\frac{1}{4}i\sigma\sigma'\int_0^\infty dt e^{i\epsilon_c t}\Big[& a_{L\sigma'}(-t)a_{L'\sigma}(-t)b_{L\sigma'}(t)b_{L'\sigma}(t)\delta_{LL''}\delta_{L'L'''} \\ & + a_{L\sigma}(-t)a_{L'\sigma'}(-t)b_{L\sigma}(t)b_{L'\sigma'}(t)\delta_{L'L''}\delta_{LL'''}\Big], \end{aligned} \tag{D.4}$$

$$\begin{aligned} P^{(22)}_{tLL'L''L'''\sigma} = \frac{1}{8}i\int_0^\infty dt e^{i\epsilon_c t}\Big[& a_{L\sigma}(-t)a_{L'-\sigma}(-t)b_{L\sigma}(t)b_{L'-\sigma}(t)\delta_{LL''}\delta_{L'L'''} \\ & + a_{L-\sigma}(-t)a_{L'\sigma}(-t)b_{L\sigma}(t)b_{L'-\sigma}(t)\delta_{L'L''}\delta_{LL'''}\Big], \end{aligned} \tag{D.5}$$

$$\begin{aligned} P^{(12)}_{lLL'L''L'''\sigma\sigma'} = -\frac{1}{16}i\int_0^\infty dt e^{i\epsilon_c t}\Big[& a_{L\sigma}(-t)a_{L'\sigma'}(-t)b_{L\sigma}(t)b_{L'\sigma'}(t)\delta_{LL''}\delta_{L'L'''} \\ & + a_{L\sigma'}(-t)a_{L'\sigma}(-t)b_{L\sigma'}(t)b_{L'\sigma}(t)\delta_{L'L''}\delta_{LL'''}\Big]. \end{aligned} \tag{D.6}$$

Here $a_{L\sigma}(t)$ and $b_{L\sigma}(t)$ are given by

$$a_{L\sigma}(t) = \int_0^\infty dt e^{-i\epsilon t} \rho_{iL\sigma}(\epsilon) f(\tilde{\epsilon}), \tag{D.7}$$

$$b_{L\sigma}(t) = \int_0^\infty dt e^{-i\epsilon t} \rho_{iL\sigma}(\epsilon) [1 - f(\tilde{\epsilon})], \tag{D.8}$$

Similarly, the elements of $\langle \tilde{O_i}^\dagger \tilde{H}_0 \tilde{O_i} \rangle_0$ in Eq. (5.11), *i.e.*, $Q^{(\alpha\alpha')}_{\tau LL'L''L'''\sigma\sigma'}$ are obtained as follows.

$$\begin{aligned} Q^{(00)}_{LL'L''L'''\sigma\sigma'\sigma''\sigma'''} &= -\Big(\delta_{LL'}\delta_{LL''}\delta_{L''L'''}\delta_{\sigma\downarrow}\delta_{\sigma'\uparrow}\delta_{\sigma''\downarrow}\delta_{\sigma'''\uparrow}\Big) \\ &\times \int_0^\infty dt dt' e^{i\epsilon_c(t+t')} \Big[a_{L\uparrow}(-t-t') b_{L\uparrow}(t+t') a_{L\downarrow}(-t-t') b_{L1\downarrow}(t+t') \\ &\quad - a_{L\uparrow}(-t-t') b_{L\uparrow}(t+t') a_{L1\downarrow}(-t-t') b_{L\downarrow}(t+t') \\ &\quad + a_{L\uparrow}(-t-t') b_{L1\uparrow}(t+t') a_{L\downarrow}(-t-t') b_{L\downarrow}(t+t') \\ &\quad - a_{L1\uparrow}(-t-t') b_{L\uparrow}(t+t') a_{L\downarrow}(-t-t') b_{L\downarrow}(t+t') \Big], \end{aligned} \tag{D.9}$$

$$Q^{(01)}_{LL'L''L'''\sigma\sigma'\sigma''\sigma'''} = Q^{(10)}_{LL'L''L'''\sigma\sigma'\sigma''\sigma'''} = 0, \tag{D.10}$$

$$Q^{(02)}_{LL'L''L'''\sigma\sigma'\sigma''\sigma'''} = Q^{(20)}_{LL'L''L'''\sigma\sigma'\sigma''\sigma'''} = 0, \tag{D.11}$$

$$\begin{aligned} Q^{(11)}_{LL'L''L'''\sigma\sigma'\sigma''\sigma'''} &= -\Big(\delta_{L'L''}\delta_{LL'''}\delta_{\sigma\sigma'''}\delta_{\sigma'\sigma''} + \delta_{LL''}\delta_{L'L'''}\delta_{\sigma''\sigma}\delta_{\sigma'''\sigma'}\Big) \\ &\times \int_0^\infty dt dt' e^{i\epsilon_c(t+t')} \Big[a_{L'\sigma'}(-t-t') b_{L'\sigma'}(t+t') a_{L\sigma}(-t-t') b_{L1\sigma}(t+t') \\ &\quad - a_{L'\sigma'}(-t-t') b_{L'\sigma'}(t+t') a_{L1\sigma}(-t-t') b_{L\sigma}(t+t') \\ &\quad + a_{L'\sigma'}(-t-t') b_{L'1\sigma'}(t+t') a_{L\sigma}(-t-t') b_{L\sigma}(t+t') \\ &\quad - a_{L'1\sigma'}(-t-t') b_{L'\sigma'}(t+t') a_{L\sigma}(-t-t') b_{L\sigma}(t+t') \Big], \end{aligned} \tag{D.12}$$

$$Q^{(12)}_{tLL'L''L'''\sigma\sigma'\sigma''\sigma'''} = Q^{(21)}_{tLL'L''L'''\sigma\sigma'\sigma''\sigma'''} = 0, \tag{D.13}$$

$$\begin{aligned} Q^{(12)}_{lLL'L''L'''\sigma\sigma'\sigma''\sigma'''} &= Q^{(21)}_{lLL'L''L'''\sigma\sigma'\sigma''\sigma'''} \\ &= -\frac{1}{4}\sigma\sigma'\Big(\delta_{L'L''}\delta_{LL'''}\delta_{\sigma\sigma'''}\delta_{\sigma'\sigma''} + \delta_{LL''}\delta_{L'L'''}\delta_{\sigma''\sigma}\delta_{\sigma'''\sigma'}\Big) \\ &\times \int_0^\infty dt dt' e^{i\epsilon_c(t+t')} \Big[a_{L'\sigma'}(-t-t') b_{L'\sigma'}(t+t') a_{L\sigma}(-t-t') b_{L1\sigma}(t+t') \\ &\quad - a_{L'\sigma'}(-t-t') b_{L'\sigma'}(t+t') a_{L1\sigma}(-t-t') b_{L\sigma}(t+t') \\ &\quad + a_{L'\sigma'}(-t-t') b_{L'1\sigma'}(t+t') a_{L\sigma}(-t-t') b_{L\sigma}(t+t') \\ &\quad - a_{L'1\sigma'}(-t-t') b_{L'\sigma'}(t+t') a_{L\sigma}(-t-t') b_{L\sigma}(t+t') \Big], \end{aligned} \tag{D.14}$$

$$Q^{(22)}_{ttLL'L''L'''\sigma\sigma'\sigma''\sigma'''} = -\frac{1}{4}\Big(\delta_{L'L''}\delta_{LL'''}\delta_{\sigma''-\sigma} + \delta_{LL''}\delta_{L'L'''}\delta_{\sigma''\sigma}\Big)\delta_{\sigma'-\sigma}\delta_{\sigma'''-\sigma''}$$
$$\times \int_0^\infty dtdt' e^{i\epsilon_c(t+t')}\Big[a_{L'\sigma'}(-t-t')b_{L'\sigma'}(t+t')a_{L\sigma}(-t-t')b_{L1\sigma}(t+t')$$
$$- a_{L'\sigma'}(-t-t')b_{L'\sigma'}(t+t')a_{L1\sigma}(-t-t')b_{L\sigma}(t+t')$$
$$+ a_{L'\sigma'}(-t-t')b_{L'1\sigma'}(t+t')a_{L\sigma}(-t-t')b_{L\sigma}(t+t')$$
$$- a_{L'1\sigma'}(-t-t')b_{L'\sigma'}(t+t')a_{L\sigma}(-t-t')b_{L\sigma}(t+t')\Big], \tag{D.15}$$

$$Q^{(22)}_{llLL'L''L'''\sigma\sigma'\sigma''\sigma'''} = -\frac{1}{16}\Big(\delta_{L'L''}\delta_{LL'''}\delta_{\sigma\sigma'''}\delta_{\sigma'\sigma''} + \delta_{LL''}\delta_{L'L'''}\delta_{\sigma\sigma''}\delta_{\sigma'\sigma'''}\Big)$$
$$\times \int_0^\infty dtdt' e^{i\epsilon_c(t+t')}\Big[a_{L'\sigma'}(-t-t')b_{L'\sigma'}(t+t')a_{L\sigma}(-t-t')b_{L1\sigma}(t+t')$$
$$- a_{L'\sigma'}(-t-t')b_{L'\sigma'}(t+t')a_{L1\sigma}(-t-t')b_{L\sigma}(t+t')$$
$$+ a_{L'\sigma'}(-t-t')b_{L'1\sigma'}(t+t')a_{L\sigma}(-t-t')b_{L\sigma}(t+t')$$
$$- a_{L'1\sigma'}(-t-t')b_{L'\sigma'}(t+t')a_{L\sigma}(-t-t')b_{L\sigma}(t+t')\Big]. \tag{D.16}$$

Here $a_{L1\sigma}(t)$ and $b_{L1\sigma}(t)$ are given by

$$a_{L1\sigma}(t) = \int_0^\infty dt e^{-i\epsilon t}\epsilon\rho_{iL\sigma}(\epsilon)f(\tilde{\epsilon}), \tag{D.17}$$

$$b_{L1\sigma}(t) = \int_0^\infty dt e^{-i\epsilon t}\epsilon\rho_{iL\sigma}(\epsilon)[1-f(\tilde{\epsilon})]. \tag{D.18}$$

The elements of $\langle\tilde{O}_i{}^\dagger\tilde{O}_i\rangle_0$ in Eq. (5.15), $i.e.$, $S^{(\alpha\alpha')}_{\tau LL'L''L'''\sigma\sigma'}$ are obtained as follows.

$$S^{(00)}_{LL'L''L'''\sigma\sigma'\sigma''\sigma'''} = -\Big(\delta_{LL'}\delta_{LL''}\delta_{L''L'''}\delta_{\sigma\downarrow}\delta_{\sigma'\uparrow}\delta_{\sigma''\downarrow}\delta_{\sigma'''\uparrow}\Big)$$
$$\times \int_0^\infty dtdt' e^{i\epsilon_c(t+t')}a_{L\uparrow}(-t-t')b_{L\uparrow}(t+t')a_{L\downarrow}(-t-t')b_{L\downarrow}(t+t'), \tag{D.19}$$

$$S^{(01)}_{LL'L''L'''\sigma\sigma'\sigma''\sigma'''} = S^{(10)}_{LL'L''L'''\sigma\sigma'\sigma''\sigma'''} = 0, \tag{D.20}$$

$$S^{(02)}_{LL'L''L'''\sigma\sigma'\sigma''\sigma'''} = S^{(20)}_{LL'L''L'''\sigma\sigma'\sigma''\sigma'''} = 0, \tag{D.21}$$

$$S^{(12)}_{LL'L''L'''\sigma\sigma'\sigma''\sigma'''} = -\frac{1}{4}\sigma\sigma'\Big(\delta_{L'L''}\delta_{LL'''}\delta_{\sigma\sigma'''}\delta_{\sigma'\sigma''} + \delta_{LL''}\delta_{L'L'''}\delta_{\sigma''\sigma}\delta_{\sigma'''\sigma'}\Big)$$
$$\times \int_0^\infty dtdt' e^{i\epsilon_c(t+t')}a_{L'\sigma'}(-t-t')b_{L'\sigma'}(t+t')a_{L\sigma}(-t-t')b_{L\sigma}(t+t'), \tag{D.22}$$

$$S^{(22)}_{tlLL'L''L'''\sigma\sigma'\sigma''\sigma'''} = S^{(22)}_{ltLL'L''L'''\sigma\sigma'\sigma''\sigma'''} = 0, \tag{D.23}$$

$$\begin{aligned} S^{(22)}_{ttLL'L''L'''\sigma\sigma'\sigma''\sigma'''} &= -\frac{1}{4}\Big(\delta_{L'L''}\delta_{LL'''}\delta_{\sigma''-\sigma} + \delta_{LL''}\delta_{L'L'''}\delta_{\sigma''\sigma}\Big)\delta_{\sigma'-\sigma}\delta_{\sigma'''-\sigma''} \\ &\times \int_0^\infty dtdt' e^{i\epsilon_c(t+t')} a_{L'-\sigma}(-t-t')b_{L'\sigma}(t+t')a_{L\sigma}(-t-t')b_{L-\sigma}(t+t'), \end{aligned} \tag{D.24}$$

and

$$\begin{aligned} S^{(22)}_{llLL'L''L'''\sigma\sigma'\sigma''\sigma'''} &= -\frac{1}{16}\Big(\delta_{L'L''}\delta_{LL'''}\delta_{\sigma''\sigma'}\delta_{\sigma'''\sigma} + \delta_{LL''}\delta_{L'L'''}\delta_{\sigma''\sigma}\delta_{\sigma'''\sigma'}\Big) \\ &\times \int_0^\infty dtdt' e^{i\epsilon_c(t+t')} a_{L'\sigma'}(-t-t')b_{L'\sigma'}(t+t')a_{L\sigma}(-t-t')b_{L\sigma}(t+t'). \end{aligned} \tag{D.25}$$

The elements of $\langle \tilde{O}_i{}^\dagger \tilde{H}_I \tilde{O}_i\rangle_0$ in Eq. (5.12), *i.e.*, $K^{(\alpha)}_{\tau LL'\sigma\sigma'}$ are obtained as follows.

$$K^{(0)}_{LL\uparrow\downarrow} = K^{(00)}_{LL\uparrow\downarrow} + K^{(01)}_{LL\uparrow\downarrow} + K^{(02l)}_{LL\uparrow\downarrow} + K^{(02t)}_{LL\uparrow\downarrow}. \tag{D.26}$$

Here

$$\begin{aligned} K^{(00)}_{LL\uparrow\downarrow} &= -U^{(0)2}_{LL}\int_0^\infty dtdt' e^{i\epsilon_c(t+t')} \\ &\times \Big[a_{L\uparrow}(-t)b_{L\uparrow}(t+t')a_{L\downarrow}(-t)b_{L\downarrow}(t+t')a_{L\uparrow}(-t')a_{L\downarrow}(-t') \\ &- a_{L\uparrow}(-t)b_{L\uparrow}(t+t')a_{L\downarrow}(-t-t')b_{L\downarrow}(t)a_{L\uparrow}(-t')b_{L\downarrow}(t') \\ &- a_{L\uparrow}(-t-t')b_{L\uparrow}(t)a_{L\downarrow}(-t)b_{L\downarrow}(t+t')b_{L\uparrow}(t')a_{L\downarrow}(-t') \\ &+ a_{L\uparrow}(-t-t')b_{L\uparrow}(t)a_{L\downarrow}(-t-t')b_{L\downarrow}(t)b_{L\uparrow}(t')b_{L\downarrow}(t')\Big]\tilde{\lambda}^{(\uparrow\downarrow)}_{0LL}, \end{aligned} \tag{D.27}$$

$$\begin{aligned} K^{(01)}_{LL\uparrow\downarrow} &= -\sum_{L'\neq L}\sum_{\sigma\sigma'} U^{(1)2}_{LL'}\int_0^\infty dtdt' e^{i\epsilon_c(t+t')} \\ &\times a_{L-\sigma}(-t)b_{L-\sigma}(t)a_{L\sigma}(-t-t')b_{L\sigma}(t+t')a_{L'\sigma'}(-t')b_{L'\sigma'}(t')\tilde{\lambda}^{(\sigma\sigma')}_{1LL'}, \end{aligned} \tag{D.28}$$

$$\begin{aligned} K^{(02l)}_{LL\uparrow\downarrow} &= \frac{1}{4}\sum_{L'\neq L}\sum_{\sigma\sigma'}\sigma\sigma' U^{(1)}_{LL'}U^{(2)}_{LL'}\int_0^\infty dtdt' e^{i\epsilon_c(t+t')} \\ &\times a_{L-\sigma}(-t)b_{L-\sigma}(t)a_{L\sigma}(-t-t')b_{L\sigma}(t+t')a_{L'\sigma'}(-t')b_{L'\sigma'}(t')\tilde{\lambda}^{(\sigma\sigma')}_{2lLL'}, \end{aligned} \tag{D.29}$$

$$\begin{aligned} K^{(02t)}_{LL\uparrow\downarrow} &= -\frac{1}{4}\sum_{L'\neq L}\sum_{\sigma} U^{(2)2}_{LL'}\int_0^\infty dtdt' e^{i\epsilon_c(t+t')} \\ &\times a_{L-\sigma}(-t)b_{L-\sigma}(t+t')a_{L\sigma}(-t-t')b_{L\sigma}(t)a_{L'-\sigma}(-t')b_{L'\sigma}(t')\tilde{\lambda}^{(\sigma-\sigma)}_{2tLL'}, \end{aligned} \tag{D.30}$$

$$K^{(1)}_{LL'\sigma\sigma'} = K^{(10)}_{LL'\sigma\sigma'} + K^{(11)}_{LL'\sigma\sigma'} + K^{(12l)}_{LL'\sigma\sigma'} + K^{(12t)}_{LL'\sigma\sigma'}. \tag{D.31}$$

Here

$$
\begin{aligned}
K^{(10)}_{LL'\sigma\sigma'} = & -U^{(0)}_{L'L'}U^{(1)}_{LL'}\int_0^\infty dtdt' e^{i\epsilon_c(t+t')} \\
& \times a_{L-\sigma}(-t)b_{L-\sigma}(t)a_{L\sigma}(-t-t')b_{L\sigma}(t+t')a_{L'\sigma'}(-t')b_{L'\sigma'}(t')\tilde{\lambda}^{(\uparrow\downarrow)}_{0LL} \\
& + \frac{1}{4}\sigma\sigma' U^{(0)}_{LL}U^{(2)}_{LL'}\int_0^\infty dtdt' e^{i\epsilon_c(t+t')}a_{L\uparrow}(-t)b_{L\uparrow}(t)a_{L\downarrow}(-t-t')b_{L\downarrow}(t+t') \\
& \times \Big(a_{L'\sigma'}(-t')b_{L'\sigma'}(t') + a_{L\sigma}(-t')b_{L\sigma}(t')\Big)\tilde{\lambda}^{(\uparrow\downarrow)}_{0L'L'}, \qquad \text{(D.32)}
\end{aligned}
$$

$$
\begin{aligned}
K^{(11)}_{LL'\sigma\sigma'} = & -2\sum_{L''(\neq L)}\sum_{\sigma''}U^{(1)}_{LL''}(U^{(1)}_{L'L''} + \frac{1}{4}\sigma'\sigma'' U^{(2)}_{L'L''})\int_0^\infty dtdt' e^{i\epsilon_c(t+t')} \\
& \times a_{L'\sigma'}(-t)b_{L'\sigma'}(t)a_{L\sigma}(-t-t')b_{L\sigma}(t+t')a_{L''\sigma''}(-t')b_{L''\sigma''}(t')\tilde{\lambda}^{(\sigma\sigma'')}_{1LL''} \\
& - 2\sum_{L''(\neq L')}\sum_{\sigma''}U^{(1)}_{L'L''}(U^{(1)}_{LL''} + \frac{1}{4}\sigma\sigma'' U^{(2)}_{LL''})\int_0^\infty dtdt' e^{i\epsilon_c(t+t')} \\
& \times a_{L'\sigma'}(-t-t')b_{L'\sigma'}(t+t')a_{L\sigma}(-t)b_{L\sigma}(t')a_{L''\sigma''}(-t')b_{L''\sigma''}(t)\tilde{\lambda}^{(\sigma'\sigma'')}_{1L'L''} \\
& + U^{(1)}_{LL'}(U^{(1)}_{LL'} + \frac{1}{4}\sigma\sigma' U^{(2)}_{LL'})\int_0^\infty dtdt' e^{i\epsilon_c(t+t')} \\
& \times \Big[a_{L'\sigma'}(-t)b_{L'\sigma'}(t+t')a_{L\sigma}(-t-t')b_{L\sigma}(t)a_{L'\sigma'}(-t')b_{L\sigma}(t') \\
& + a_{L'\sigma'}(-t-t')b_{L'\sigma'}(t)a_{L\sigma}(-t)b_{L\sigma}(t+t')b_{L'\sigma'}(t')a_{L\sigma}(-t') \\
& - a_{L'\sigma'}(-t)b_{L'\sigma'}(t+t')a_{L\sigma}(-t)b_{L\sigma}(t+t')a_{L'\sigma'}(-t')a_{L\sigma}(-t') \\
& - a_{L'\sigma'}(-t-t')b_{L'\sigma'}(t)a_{L\sigma}(-t-t')b_{L\sigma}(t)b_{L'\sigma'}(t')b_{L\sigma}(t')\Big]\tilde{\lambda}^{(\sigma\sigma')}_{1LL'}, \qquad \text{(D.33)}
\end{aligned}
$$

$$
\begin{aligned}
K^{(12l)}_{LL'\sigma\sigma'} = & -\frac{1}{4}\sigma\sigma' U^{(2)}_{LL'} U^{(0)}_{LL} \int_0^\infty dt dt' e^{i\epsilon_c(t+t')} \\
& \times a_{L\sigma'}(-t-t') b_{L\sigma'}(t+t') a_{L\sigma}(-t) b_{L\sigma}(t) a_{L-\sigma}(-t') b_{L-\sigma}(t') \tilde{\lambda}^{(\sigma\sigma')}_{2lLL'} \\
& - \frac{1}{4}\sigma\sigma' U^{(2)}_{LL'} U^{(0)}_{L'L'} \int_0^\infty dt dt' e^{i\epsilon_c(t+t')} \\
& \times a_{L\sigma'}(-t) b_{L\sigma'}(t) a_{L\sigma}(-t-t') b_{L\sigma}(t+t') a_{L-\sigma'}(-t') b_{L-\sigma}(t') \tilde{\lambda}^{(\sigma-\sigma')}_{2lLL'} \\
& + \frac{1}{2}\sigma \sum_{L''(\neq L)} \sum_{\sigma''} U^{(2)}_{LL''} (\sigma'' U^{(1)}_{L'L''} + \frac{1}{4}\sigma' U^{(2)}_{L'L''}) \int_0^\infty dt dt' e^{i\epsilon_c(t+t')} \\
& \times a_{L'\sigma'}(-t) b_{L'\sigma'}(t) a_{L\sigma}(-t-t') b_{L\sigma}(t+t') a_{L''\sigma''}(-t') b_{L''\sigma''}(t') \tilde{\lambda}^{(\sigma\sigma'')}_{2lLL''} \\
& + \frac{1}{2}\sigma \sum_{L''(\neq L)} \sum_{\sigma''} U^{(2)}_{L'L''} (\sigma'' U^{(1)}_{LL''} + \frac{1}{4}\sigma U^{(2)}_{LL''}) \int_0^\infty dt dt' e^{i\epsilon_c(t+t')} \\
& \times a_{L'\sigma'}(-t-t') b_{L'\sigma'}(t+t') a_{L\sigma}(-t) b_{L\sigma}(t) a_{L''\sigma''}(-t') b_{L''\sigma''}(t') \tilde{\lambda}^{(\sigma'\sigma'')}_{2lLL''} \\
& - \frac{1}{4} U^{(2)}_{LL'} (\sigma\sigma' U^{(1)}_{LL'} + \frac{1}{4} U^{(2)}_{LL'}) \int_0^\infty dt dt' e^{i\epsilon_c(t+t')} \\
& \times \Big[a_{L'\sigma'}(-t) b_{L'\sigma'}(t+t') a_{L\sigma}(-t-t') b_{L\sigma}(t) a_{L'\sigma'}(-t') b_{L\sigma}(t') \\
& + a_{L'\sigma'}(-t-t') b_{L'\sigma'}(t) a_{L\sigma}(-t) b_{L\sigma}(t+t') b_{L'\sigma'}(t') a_{L\sigma}(-t') \\
& - a_{L'\sigma'}(-t) b_{L'\sigma'}(t+t') a_{L\sigma}(-t) b_{L\sigma}(t+t') a_{L'\sigma'}(-t') a_{L\sigma}(-t') \\
& - a_{L'\sigma'}(-t-t') b_{L'\sigma'}(t) a_{L\sigma}(-t-t') b_{L\sigma}(t) b_{L'\sigma'}(t') b_{L\sigma}(t') \Big] \tilde{\lambda}^{(\sigma\sigma')}_{2lLL'},
\end{aligned} \tag{D.34}
$$

$$
\begin{aligned}
K^{(12t)}_{LL'\sigma\sigma'} = & \frac{1}{4} U^{(2)}_{LL'} U^{(2)}_{LL'} \int_0^\infty dt dt' e^{i\epsilon_c(t+t')} \\
& \times \Big[- a_{L'\sigma}(-t) b_{L'\sigma}(t+t') a_{L\sigma}(-t-t') b_{L\sigma}(t) a_{L'-\sigma}(-t') b_{L-\sigma}(t') \delta_{\sigma\sigma'} \tilde{\lambda}^{(\sigma-\sigma)}_{2tLL'} \\
& - a_{L'\sigma}(-t-t') b_{L'\sigma}(t) a_{L\sigma}(-t) b_{L\sigma}(t+t') b_{L'-\sigma}(t') a_{L-\sigma}(-t') \delta_{\sigma\sigma'} \tilde{\lambda}^{(-\sigma\sigma)}_{2tLL'} \\
& + a_{L'-\sigma}(-t) b_{L-\sigma'}(t+t') a_{L\sigma}(-t) b_{L\sigma}(t+t') a_{L'\sigma}(-t') a_{L-\sigma}(-t') \delta_{\sigma-\sigma'} \tilde{\lambda}^{(-\sigma\sigma)}_{2tLL'} \\
& + a_{L'-\sigma}(-t-t') b_{L'-\sigma}(t) a_{L\sigma}(-t-t') b_{L\sigma}(t) b_{L'\sigma}(t') b_{L-\sigma}(t') \delta_{\sigma-\sigma'} \tilde{\lambda}^{(\sigma-\sigma)}_{2tLL'} \Big],
\end{aligned} \tag{D.35}
$$

$$
K^{(2)}_{lLL'\sigma\sigma'} = -\frac{1}{4}\sigma\sigma' K^{(1)}_{LL'\sigma\sigma'}. \tag{D.36}
$$

$$
K^{(2)}_{tLL'\sigma\sigma'} = K^{(20)}_{tLL'\sigma\sigma'} + K^{(21)}_{tLL'\sigma\sigma'} + K^{(22l)}_{tLL'\sigma\sigma'} + K^{(22t)}_{tLL'\sigma\sigma'}. \tag{D.37}
$$

$$
\begin{aligned}
K^{(20)}_{LL'\sigma\sigma'} = & -\frac{1}{4}\delta_{\sigma-\sigma'} U^{(0)}_{LL} U^{(2)}_{LL'} \int_0^\infty dt dt' e^{i\epsilon_c(t+t')} \\
& \times a_{L-\sigma}(-t) b_{L-\sigma}(t+t') a_{L\sigma}(-t-t') b_{L\sigma}(t) a_{L'-\sigma}(-t') b_{L'\sigma}(t') \tilde{\lambda}^{(\downarrow\uparrow)}_{0LL} \\
& - \frac{1}{4}\delta_{\sigma-\sigma'} U^{(0)}_{L'L'} U^{(2)}_{LL'} \int_0^\infty dt dt' e^{i\epsilon_c(t+t')} \\
& \times a_{L\sigma}(-t) b_{L\sigma}(t+t') a_{L-\sigma}(-t-t') b_{L-\sigma}(t) a_{L'\sigma}(-t') b_{L'-\sigma}(t') \tilde{\lambda}^{(\downarrow\uparrow)}_{0L'L'},
\end{aligned} \tag{D.38}
$$

$$
\begin{aligned}
K^{(21)}_{tLL'\sigma\sigma'} &= \frac{1}{4}\delta_{\sigma-\sigma'}U^{(1)}_{LL'}U^{(2)}_{LL'}\int_0^\infty dtdt' e^{i\epsilon_c(t+t')} \\
&\times \Big[- a_{L'\sigma}(-t)b_{L'\sigma}(t+t')a_{L\sigma}(-t-t')b_{L\sigma}(t)a_{L'-\sigma}(-t')b_{L-\sigma}(t')\tilde{\lambda}^{(\sigma\sigma)}_{1LL'} \\
&- a_{L'-\sigma}(-t-t')b_{L'-\sigma}(t)a_{L-\sigma}(-t)b_{L-\sigma}(t+t')b_{L'\sigma}(t')a_{L\sigma}(-t')\tilde{\lambda}^{(-\sigma-\sigma)}_{1LL'} \\
&+ a_{L'\sigma}(-t)b_{L'\sigma}(t+t')a_{L-\sigma}(-t)b_{L-\sigma}(t+t')a_{L'-\sigma}(-t')a_{L\sigma}(-t')\tilde{\lambda}^{(-\sigma\sigma)}_{1LL'} \\
&+ a_{L'-\sigma}(-t-t')b_{L'-\sigma}(t)a_{L\sigma}(-t-t')b_{L\sigma}(t)b_{L'\sigma}(t')b_{L-\sigma}(t')\tilde{\lambda}^{(\sigma-\sigma)}_{1LL'}\Big], \qquad \text{(D.39)}
\end{aligned}
$$

$$
\begin{aligned}
K^{(22l)}_{tLL'\sigma\sigma'} &= \frac{1}{16}\delta_{\sigma-\sigma'}U^{(2)}_{LL'}U^{(2)}_{LL'}\int_0^\infty dtdt' e^{i\epsilon_c(t+t')} \\
&\times \Big[a_{L'\sigma}(-t)b_{L'\sigma}(t+t')a_{L\sigma}(-t-t')b_{L\sigma}(t)a_{L'-\sigma}(-t')b_{L-\sigma}(t')\tilde{\lambda}^{(\sigma\sigma)}_{2lLL'} \\
&+ a_{L'-\sigma}(-t-t')b_{L'-\sigma}(t)a_{L-\sigma}(-t)b_{L-\sigma}(t+t')b_{L'\sigma}(t')a_{L\sigma}(-t')\tilde{\lambda}^{(-\sigma-\sigma)}_{2lLL'} \\
&+ a_{L'\sigma}(-t)b_{L'\sigma}(t+t')a_{L-\sigma}(-t)b_{L-\sigma}(t+t')a_{L'-\sigma}(-t')a_{L\sigma}(-t')\tilde{\lambda}^{(-\sigma\sigma)}_{2lLL'} \\
&+ a_{L'-\sigma}(-t-t')b_{L'-\sigma}(t)a_{L\sigma}(-t-t')b_{L\sigma}(t)b_{L'\sigma}(t')b_{L-\sigma}(t')\tilde{\lambda}^{(\sigma-\sigma)}_{2lLL'}\Big], \qquad \text{(D.40)}
\end{aligned}
$$

$$
\begin{aligned}
K^{(22t)}_{tLL'\sigma\sigma'} &= \frac{1}{4}\delta_{\sigma-\sigma'}U^{(2)}_{LL'}U^{(1)}_{LL'}\int_0^\infty dtdt' e^{i\epsilon_c(t+t')} \\
&\times \Big[a_{L'\sigma}(-t)b_{L'\sigma}(t+t')a_{L\sigma}(-t-t')b_{L-\sigma}(t)a_{L'-\sigma}(-t')b_{L-\sigma}(t') \\
&+ a_{L'-\sigma}(-t-t')b_{L'\sigma}(t)a_{L\sigma}(-t)b_{L-\sigma}(t+t')b_{L'\sigma}(t')a_{L\sigma}(-t') \\
&- a_{L'-\sigma}(-t)b_{L'\sigma}(t+t')a_{L\sigma}(-t)b_{L-\sigma}(t+t')a_{L'-\sigma}(-t')a_{L\sigma}(-t') \\
&- a_{L'-\sigma}(-t-t')b_{L'\sigma}(t)a_{L\sigma}(-t-t')b_{L-\sigma}(t)b_{L-\sigma}(t')b_{L'\sigma}(t')\Big]\tilde{\lambda}^{(\sigma-\sigma)}_{2tLL'} \\
&- \frac{1}{2}\sum_{L''(\neq L)} U^{(2)}_{LL''}U^{(2)}_{L'L''}\delta_{\sigma-\sigma'}\int_0^\infty dtdt' e^{i\epsilon_c(t+t')} \\
&\times a_{L'-\sigma}(-t)b_{L'\sigma}(t)a_{L\sigma}(-t-t')b_{L-\sigma}(t+t')a_{L''-\sigma}(-t')b_{L''\sigma}(t')\tilde{\lambda}^{(\sigma-\sigma)}_{2tLL''} \\
&- \frac{1}{2}\sum_{L''(\neq L)} U^{(2)}_{LL''}U^{(2)}_{L'L''}\delta_{\sigma-\sigma'}\int_0^\infty dtdt' e^{i\epsilon_c(t+t')} \\
&\times a_{L'-\sigma}(-t-t')b_{L'\sigma}(t+t')a_{L\sigma}(-t)b_{L-\sigma}(t)a_{L''\sigma}(-t')b_{L''-\sigma}(t')\tilde{\lambda}^{(-\sigma\sigma)}_{2tL'L''} \\
&+ \frac{1}{16}\delta_{\sigma-\sigma'}U^{(2)}_{LL'}U^{(2)}_{LL'}\int_0^\infty dtdt' e^{i\epsilon_c(t+t')} \\
&\times \Big[a_{L'\sigma}(-t)b_{L'\sigma}(t+t')a_{L\sigma}(-t-t')b_{L-\sigma}(t)a_{L'-\sigma}(-t')b_{L-\sigma}(t')\tilde{\lambda}^{(\sigma-\sigma)}_{2tLL'} \\
&+ a_{L'-\sigma}(-t-t')b_{L'\sigma}(t)a_{L\sigma}(-t)b_{L-\sigma}(t+t')a_{L\sigma}(-t')b_{L'\sigma}(t')\tilde{\lambda}^{(\sigma-\sigma)}_{2tLL'} \\
&- 2a_{L'-\sigma}(-t)b_{L'\sigma}(t+t')a_{L-\sigma}(-t)b_{L-\sigma}(t+t') \\
&\times \Big(a_{L'\sigma}(-t')a_{L-\sigma}(-t')\tilde{\lambda}^{(-\sigma\sigma)}_{2tLL'} - \frac{1}{2}a_{L'-\sigma}(-t')a_{L\sigma}(-t')\tilde{\lambda}^{(\sigma-\sigma)}_{2tLL'}\Big) \\
&- 2a_{L'-\sigma}(-t-t')b_{L'\sigma}(t)a_{L\sigma}(-t-t')b_{L-\sigma}(t) \\
&\times \Big(b_{L'-\sigma}(t')b_{L\sigma}(t')\tilde{\lambda}^{(-\sigma\sigma)}_{2lLL'} - \frac{1}{2}b_{L'\sigma}(t')b_{L-\sigma}(t')\tilde{\lambda}^{(\sigma-\sigma)}_{2tLL'}\Big)\Big]. \qquad \text{(D.41)}
\end{aligned}
$$

Appendix E

Appendix: Overcompleteness of the Variational Parameters

In this Appendix, we discuss the overcompleteness of the vatiational parameters $\tilde{\lambda}^{(\sigma\sigma')}_{1LL'}$ and $\tilde{\lambda}^{(\sigma\sigma')}_{2lLL'}$ and derive their expressions (5.28) and (5.29) in Sec. 5.1. The self-consistent equations for the parameters are given in Eq. (5.21) as follows.

$$\sum_{\alpha'} U^{(\alpha')}_{LL'} \tilde{Q}^{(\alpha\alpha')}_{\tau LL'\sigma\sigma'} \tilde{\lambda}^{(\sigma\sigma')}_{\alpha'\tau LL'} = \sum_{\alpha'} U^{(\alpha')}_{LL'} P^{(\alpha'\alpha)}_{\tau LL'\sigma\sigma'} - K^{(\alpha)}_{\tau LL'\sigma\sigma'}. \tag{E.1}$$

The self-consistent equations for $\tilde{\lambda}^{(\sigma\sigma')}_{1LL'}$ and $\tilde{\lambda}^{(\sigma\sigma')}_{2lLL'}$ in the weak Coulomb interaction limit have been obtained as follows.

$$U^{(1)}_{LL'} P^{(11)}_{LL'\sigma\sigma'} \tilde{\lambda}^{(\sigma\sigma')}_{1LL'} + U^{(2)}_{LL'} P^{(12)}_{lLL'\sigma\sigma'} \tilde{\lambda}^{(\sigma\sigma')}_{2lLL'} = U^{(1)}_{LL'} P^{(11)}_{LL'\sigma\sigma'} + U^{(2)}_{LL'} P^{(21)}_{LL'\sigma\sigma'}. \tag{E.2}$$

$$-U^{(1)}_{LL'} P^{(21)}_{LL'\sigma\sigma'} \tilde{\lambda}^{(\sigma\sigma')}_{1LL'} - U^{(2)}_{LL'} P^{(12)}_{lLL'\sigma\sigma'} \tilde{\lambda}^{(\sigma\sigma')}_{2lLL'} = U^{(1)}_{LL'} P^{(12)}_{lLL'\sigma\sigma'} + U^{(2)}_{LL'} P^{(22)}_{lLL'\sigma\sigma'}. \tag{E.3}$$

On the other hand, we have

$$P^{(11)}_{LL'\sigma\sigma'} = P_{LL'\sigma\sigma'}, \tag{E.4}$$

$$P^{(21)}_{LL'\sigma\sigma'} = -P^{(12)}_{LL'\sigma\sigma'}, \tag{E.5}$$

$$P^{(12)}_{lLL'\sigma\sigma'} = -\frac{1}{4}\sigma\sigma' P_{LL'\sigma\sigma'}, \tag{E.6}$$

$$P^{(22)}_{lLL'\sigma\sigma'} = -\frac{1}{16} P_{LL'\sigma\sigma'}, \tag{E.7}$$

Using the relations (E.4) $\sim$ (E.7), the self-consistent equations (E.2) and (E.3) are expressed as follows.

$$U^{(1)}_{LL'} \tilde{\lambda}^{(\sigma\sigma')}_{1LL'} - \frac{1}{4}\sigma\sigma' U^{(2)}_{LL'} \tilde{\lambda}^{(\sigma\sigma')}_{2lLL'} = U^{(1)}_{LL'} + \frac{1}{4}\sigma\sigma' U^{(2)}_{LL'}, \tag{E.8}$$

$$U^{(1)}_{LL'}\tilde{\lambda}^{(\sigma\sigma')}_{1LL'} - \frac{1}{4}\sigma\sigma' U^{(2)}_{LL'}\tilde{\lambda}^{(\sigma\sigma')}_{2lLL'} = U^{(1)}_{LL'} + \frac{1}{4}\sigma\sigma' U^{(2)}_{LL'}. \tag{E.9}$$

Equations (E.8) and (E.9) are the same equation, so that one can not obtain $\tilde{\lambda}^{(\sigma\sigma')}_{1LL'}$ and $\tilde{\lambda}^{(\sigma\sigma')}_{2lLL'}$ uniquely.

Note that we made use of the Hilbert space for $\tilde{\lambda}^{(\sigma\sigma')}_{1LL'}$ and $\tilde{\lambda}^{(\sigma\sigma')}_{2lLL'}$ as follows.

$$\frac{U^{(1)}_{LL'}\tilde{\lambda}^{(\sigma\sigma')}_{1LL'} - \frac{1}{4}\sigma\sigma' U^{(2)}_{LL'}\tilde{\lambda}^{(\sigma\sigma')}_{2lLL'}}{\Delta E_{k'_2 n'_2 \sigma k_2 n_2 \sigma k'_1 n'_1 \sigma' k_1 n_1 \sigma'} - \epsilon_c} \times \delta(a^\dagger_{k'_2 n'_2 \sigma} a_{k_2 n_2 \sigma})\delta(a^\dagger_{k'_1 n'_1 \sigma'} a_{k_1 n_1 \sigma'})|\phi\rangle$$

There are 8 independent variables $\{\tilde{\lambda}^{(\sigma\sigma')}_{1LL'}, \tilde{\lambda}^{(\sigma\sigma')}_{2lLL'}\}$ with respect to spins σ', $\sigma = \pm$, while there are only 4 independent states with respect to spins in the Hilbert space. Thus, $\{\tilde{\lambda}^{(\sigma\sigma')}_{1LL'}, \tilde{\lambda}^{(\sigma\sigma')}_{2lLL'}\}$ are overcomplete.

We have to reduce the number of independent variational parameters less than or equal to 4 to find a unique state using variational parameters. Let us find 2×2 independent variables:

$$\nu_{\sigma\sigma'} = U^{(1)}_{LL'}\tilde{\lambda}^{(\sigma\sigma')}_{1LL'} - \frac{1}{4}\sigma\sigma' U^{(2)}_{LL'}\tilde{\lambda}^{(\sigma\sigma')}_{2lLL'}. \tag{E.10}$$

Now we can write

$$(1)_{\sigma\sigma'} = \delta_{\sigma\sigma'}, \tag{E.11}$$

$$(\sigma_x)_{\sigma\sigma'} = \delta_{\sigma'-\sigma}, \tag{E.12}$$

$$(\sigma_y)_{\sigma\sigma'} = -i\sigma\delta_{\sigma'-\sigma}, \tag{E.13}$$

$$(\sigma_z)_{\sigma\sigma'} = \sigma\delta_{\sigma\sigma'}. \tag{E.14}$$

Thus, 2×2 matrix $\nu_{\sigma\sigma'}$ is expressed as follows.

$$\begin{aligned}\nu_{\sigma\sigma'} &= (a1 + b\sigma_x + c\sigma_y + d\sigma_z)_{\sigma\sigma'} \\ &= (a + d\sigma)\delta_{\sigma\sigma'} + (b - ic\sigma)\delta_{\sigma'-\sigma}.\end{aligned} \tag{E.15}$$

For example, we can assume the following form with 4 independent parameters $\tilde{\lambda}_{1LL'}$, $\lambda^{(s)}_{1LL'}$, $\tilde{\lambda}_{2lLL'}$, and $\lambda^{(s)}_{2lLL'}$ such that

$$\tilde{\lambda}^{(\sigma\sigma')}_{1LL'} = \tilde{\lambda}_{1LL'} + \lambda^{(s)}_{1LL'}\sigma\delta_{\sigma'-\sigma}, \tag{E.16}$$

$$\tilde{\lambda}^{(\sigma\sigma')}_{2lLL'} = \tilde{\lambda}_{2lLL'} + \lambda^{(s)}_{2lLL'}\sigma\delta_{\sigma'\sigma}. \tag{E.17}$$

Then we obtain

$$\begin{aligned}\nu_{\sigma\sigma'} = &\left[U^{(1)}_{LL'}\tilde{\lambda}_{1LL'} - \frac{1}{4}U^{(2)}_{LL'}\left(\tilde{\lambda}_{2lLL'} + \lambda^{(s)}_{2lLL'}\right)\right]\delta_{\sigma\sigma'} \\ &+ \left[U^{(1)}_{LL'}\left(\tilde{\lambda}_{1LL'} + \lambda^{(s)}_{1LL'}\sigma\right) + \frac{1}{4}U^{(2)}_{LL'}\tilde{\lambda}_{2lLL'}\right]\delta_{\sigma'-\sigma}.\end{aligned} \tag{E.18}$$

When $\lambda^{(s)}_{1LL'} = \lambda^{(s)}_{2lLL'} = 0$, we put the weights for diagonal and off-diagonal elements, $U^{(1)}_{LL'}\tilde{\lambda}_{1LL'} - U^{(2)}_{LL'}\tilde{\lambda}_{2lLL'}/4$ and $U^{(1)}_{LL'}\tilde{\lambda}_{1LL'} + U^{(2)}_{LL'}\tilde{\lambda}_{2lLL'}/4$, respectively. When $\lambda^{(s)}_{1LL'} \neq \lambda^{(s)}_{2lLL'} \neq 0$, we put asymmetric weights for diagonal and off-diagonal elements, $U^{(1)}_{LL'}\tilde{\lambda}_{1LL'} - U^{(2)}_{LL'}\tilde{\lambda}_{2lLL'}/4 - U^{(1)}_{LL'}\lambda^{(s)}_{2lLL'}\sigma$ and $U^{(1)}_{LL'}\tilde{\lambda}_{1LL'} + U^{(1)}_{LL'}\lambda^{(s)}_{1LL'}\sigma + U^{(2)}_{LL'}\tilde{\lambda}_{2lLL'}/4$.

The equations (E.16) and (E.17) are identical with Eqs. (5.28) and (5.29). We used these equations in Chapter 5 to overcome the problem of overcompleteness of the variational parameters $\tilde{\lambda}^{(\sigma\sigma')}_{1LL'}$ and $\tilde{\lambda}^{(\sigma\sigma')}_{2lLL'}$.

Appendix F

Appendix: Matrix Elements of Correlation Energy and Self-Consistent Equations

In this Appendix we present the expressions of all the matrix elements in the correlation energy Eq. (5.8) and the self-consistent Eqs. (5.103) $\sim$ (5.106). We obtained the matrix elements $\langle H_I \tilde{O}_i \rangle_0$, $\langle \tilde{O_i}^\dagger \tilde{H} \tilde{O}_i \rangle_0$, and $\langle \tilde{O_i}^\dagger \tilde{O}_i \rangle_0$ for the variational parameter ansatz (5.5) (,*i.e.*, Eqs. (5.9), (5.10), and (5.16)) with use of the Laplace transformation (2.39) as follows.

$$\begin{aligned}\langle H_I \tilde{O}_i \rangle_0 = & \sum_L U_{LL}^{(0)2} P_{LL\downarrow\uparrow}^{(00)} \tilde{\lambda}_{0LL}^{(\downarrow\uparrow)} \\ & + \sum_{\langle LL' \rangle} \sum_{\sigma\sigma'} U_{LL'}^{(1)} (U_{LL'}^{(1)} P_{LL'\sigma\sigma'}^{(11)} + U_{LL'}^{(2)} P_{LL'\sigma\sigma'}^{(21)}) \tilde{\lambda}_{1LL'}^{(\sigma\sigma')} \\ & + \sum_{\langle LL' \rangle} \sum_{\sigma\sigma'} U_{LL'}^{(2)} (U_{LL'}^{(1)} P_{lLL'\sigma\sigma'}^{(12)} + U_{LL'}^{(2)} P_{lLL'\sigma\sigma'}^{(22)}) \tilde{\lambda}_{2lLL'}^{(\sigma\sigma')} \\ & + \sum_{\langle LL' \rangle} \sum_{\sigma} U_{LL'}^{(2)2} P_{tLL'\sigma-\sigma}^{(22)} \tilde{\lambda}_{2tLL'}^{(\sigma-\sigma)}, \end{aligned} \tag{F.1}$$

$$\langle \tilde{O_i}^\dagger \tilde{H} \tilde{O}_i \rangle_0 = \langle \tilde{O_i}^\dagger \tilde{H}_0 \tilde{O}_i \rangle_0 + \langle \tilde{O_i}^\dagger H_I \tilde{O}_i \rangle_0 \,, \tag{F.2}$$

$$\begin{aligned}\langle \tilde{O_i}^\dagger \tilde{H}_0 \tilde{O}_i \rangle_0 = & \sum_L U_{LL}^{(0)2} Q_{LL\downarrow\uparrow}^{(00)} \tilde{\lambda}_{0LL}^{(\downarrow\uparrow)} + \sum_{\langle LL' \rangle} \sum_{\sigma\sigma'} U_{LL'}^{(1)2} Q_{LL'\sigma\sigma'}^{(11)} \tilde{\lambda}_{1LL'}^{(\sigma\sigma')2} \\ & + 2 \sum_{\langle LL' \rangle} \sum_{\sigma\sigma'} U_{LL'}^{(1)} U_{LL'}^{(2)} Q_{lLL'\sigma\sigma'}^{(12)} \tilde{\lambda}_{1LL'}^{(\sigma\sigma')} \tilde{\lambda}_{2lLL'}^{(\sigma\sigma')} + \sum_{\langle LL' \rangle} \sum_{\sigma\sigma'} U_{LL'}^{(2)2} Q_{lLL'\sigma\sigma'}^{(22)} \tilde{\lambda}_{2lLL'}^{(\sigma\sigma')} \\ & + \sum_{\langle LL' \rangle} \sum_{\sigma} U_{LL'}^{(2)2} \tilde{\lambda}_{2tLL'}^{(\sigma-\sigma)} Q_{tLL'\sigma-\sigma}^{(22)} \tilde{\lambda}_{2tLL'}^{(\sigma-\sigma)}, \end{aligned} \tag{F.3}$$

$$\begin{aligned}\langle \tilde{O_i}^\dagger H_I \tilde{O}_i \rangle_0 = & \sum_L U_{LL}^{(0)} \tilde{\lambda}_{0LL}^{(\downarrow\uparrow)} K_{LL\downarrow\uparrow}^{(0)} \\ & + \sum_{\langle LL' \rangle} \sum_{\sigma\sigma'} \left(U_{LL'}^{(1)} \tilde{\lambda}_{1LL'}^{(\sigma\sigma')*} - \frac{1}{4} \sigma\sigma' U_{LL'}^{(2)} \tilde{\lambda}_{2lLL'}^{(\sigma\sigma')*} \right) K_{LL'\sigma\sigma'}^{(1)} \\ & + \sum_{\langle LL' \rangle} U_{LL'}^{(2)} \tilde{\lambda}_{2tLL'}^{(\sigma,-\sigma)*} K_{tLL'\sigma-\sigma}^{(2)} \,, \end{aligned} \tag{F.4}$$

and

$$\langle \tilde{O_i}^{\dagger} \tilde{O_i} \rangle_0 = \sum_L U^{(0)2}_{LL} S^{(00)}_{LL\downarrow\uparrow} \tilde{\lambda}^{(\downarrow\uparrow)}_{0LL} + \sum_{\langle LL' \rangle} \sum_{\sigma\sigma'} U^{(1)2}_{LL'} S^{(11)}_{LL'\sigma\sigma'} \tilde{\lambda}^{(\sigma\sigma')2}_{1LL'}$$
$$+ 2 \sum_{\langle LL' \rangle} \sum_{\sigma\sigma'} U^{(1)}_{LL'} U^{(2)}_{LL'} S^{(12)}_{lLL'\sigma\sigma'} \tilde{\lambda}^{(\sigma\sigma')}_{1LL'} \tilde{\lambda}^{(\sigma\sigma')}_{2lLL'} + \sum_{\langle LL' \rangle} \sum_{\sigma\sigma'} U^{(2)2}_{LL'} S^{(22)}_{lLL'\sigma\sigma'} \tilde{\lambda}^{(\sigma\sigma')}_{2lLL'}$$
$$+ \sum_{\langle LL' \rangle} \sum_{\sigma} U^{(2)2}_{LL'} \tilde{\lambda}^{(\sigma-\sigma)}_{2tLL'} S^{(22)}_{tLL'\sigma-\sigma} \tilde{\lambda}^{(\sigma-\sigma)}_{2tLL'}. \tag{F.5}$$

Here $\{P\}$, $\{Q\}$, and $\{S\}$ are obtained by using the Laplace transformation (2.39). We obtain the relations between the components of $\{P\}$, $\{Q\}$, and $\{S\}$ as follows.

$$P^{(00)}_{LL\downarrow\uparrow} = P_{LL\downarrow\uparrow}, \tag{F.6}$$

$$P^{(11)}_{LL'\sigma\sigma'} = P_{LL'\sigma\sigma'}, \tag{F.7}$$

$$P^{(12)}_{LL'\sigma\sigma'} = \sigma\sigma' P_{LL'\sigma\sigma'}, \tag{F.8}$$

$$P^{(21)}_{LL'\sigma\sigma'} = -\frac{1}{4}\sigma\sigma' P_{LL'\sigma\sigma'}, \tag{F.9}$$

$$P^{(22)}_{lLL'\sigma\sigma'} = -\frac{1}{16} P_{LL'\sigma\sigma'}, \tag{F.10}$$

and

$$P^{(22)}_{tLL'\sigma-\sigma} = \frac{1}{4} P_{LL'\sigma-\sigma}. \tag{F.11}$$

For the $\{Q\}$ components,

$$Q^{(00)}_{LL\downarrow\uparrow} = Q_{LL\downarrow\uparrow}, \tag{F.12}$$

$$Q^{(11)}_{LL'\sigma\sigma'} = Q_{LL'\sigma\sigma'}, \tag{F.13}$$

$$Q^{(12)}_{LL'\sigma\sigma'} = -\frac{1}{4}\sigma\sigma' Q_{LL'\sigma\sigma'}, \tag{F.14}$$

$$Q^{(22)}_{lLL'\sigma\sigma'} = -\frac{1}{16} Q_{LL'\sigma\sigma'}, \tag{F.15}$$

and

$$Q^{(22)}_{tLL'\sigma-\sigma} = \frac{1}{4} Q_{LL'\sigma-\sigma}. \tag{F.16}$$

The $\{S\}$ components in Eq. (F.5) are expressed by $\{Q\}$ in which Q has been replaced by S. The elements $\{K\}$ are the higher order corrections. We summarize these terms as follows.

$$K^{(0)}_{LL} = K^{(0)}_{LL\downarrow\uparrow}, \tag{F.17}$$

$$\bar{K}^{(1)}_{LL'} = \sum_{\sigma\sigma'} K^{(1)}_{LL'\sigma\sigma'}, \tag{F.18}$$

$$\bar{K}^{(2)}_{lLL'} = \sum_{\sigma\sigma'} K^{(2)}_{lLL'\sigma\sigma'}, \tag{F.19}$$

$$K^{(2)}_{lLL'\sigma\sigma'} = -\frac{1}{4}\sigma\sigma' K^{(1)}_{LL'\sigma\sigma'}, \tag{F.20}$$

and

$$K^{(2)}_{tLL'} = K^{(2)}_{tLL'\sigma-\sigma}\,. \tag{F.21}$$

We assume that the orbital L belongs to an irreducible representation Γ of the point symmetry with dimensions d_Γ. Moreover we assume for simplicity that the Coulomb interactions $U^{(\alpha)}_{LL'}$ only depend on the types of the irreducible representations Γ and Γ' to which the orbitals L and L' belong; $U^{(\alpha)}_{LL'} = U^{(\alpha)}_{\Gamma\Gamma'}$. Then the final expressions of the elements for the correlation energy (5.8) in the paramagnetic state are given as follows.

$$\begin{aligned}
\langle H_I \tilde{O}_i\rangle_0 = &\sum_\Gamma d_\Gamma U^{(0)2}_{\Gamma\Gamma} P_{\Gamma\Gamma}\tilde{\lambda}_{0\Gamma\Gamma} \\
&+ 2\sum_\Gamma d_\Gamma(d_\Gamma-1)U^{(1)2}_{\Gamma\Gamma}P_{\Gamma\Gamma}\tilde{\lambda}_{1\Gamma\Gamma} + 4\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(1)2}_{\Gamma\Gamma'}P_{\Gamma\Gamma'}\tilde{\lambda}_{1\Gamma\Gamma'} \\
&- \frac{1}{8}\sum_\Gamma d_\Gamma(d_\Gamma-1)U^{(2)2}_{\Gamma\Gamma}P_{\Gamma\Gamma}\tilde{\lambda}_{2l\Gamma\Gamma} - \frac{1}{4}\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(2)2}_{\Gamma\Gamma'}P_{\Gamma\Gamma'}\tilde{\lambda}_{2l\Gamma\Gamma'} \\
&- \frac{1}{4}\sum_\Gamma d_\Gamma(d_\Gamma-1)U^{(2)2}_{\Gamma\Gamma}P_{\Gamma\Gamma}\tilde{\lambda}_{2t\Gamma\Gamma} - \frac{1}{2}\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(2)2}_{\Gamma\Gamma'}P_{\Gamma\Gamma'}\tilde{\lambda}_{2t\Gamma\Gamma'}\,,
\end{aligned} \tag{F.22}$$

$$\begin{aligned}
\langle \tilde{O}_i{}^\dagger \tilde{H}_0 \tilde{O}_i\rangle_0 = &\sum_\Gamma d_\Gamma U^{(0)2}_{\Gamma\Gamma} Q_{\Gamma\Gamma}\tilde{\lambda}^2_{0\Gamma\Gamma} \\
&+ 2\sum_\Gamma d_\Gamma(d_\Gamma-1)U^{(1)2}_{\Gamma\Gamma}Q_{\Gamma\Gamma}\tilde{\lambda}^2_{1\Gamma\Gamma} + 4\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(1)2}_{\Gamma\Gamma'}P_{\Gamma\Gamma'}\tilde{\lambda}^2_{1\Gamma\Gamma'} \\
&+ \frac{1}{8}\sum_\Gamma d_\Gamma(d_\Gamma-1)U^{(2)2}_{\Gamma\Gamma}Q_{\Gamma\Gamma}\tilde{\lambda}^2_{2l\Gamma\Gamma} + \frac{1}{4}\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(2)2}_{\Gamma\Gamma'}Q_{\Gamma\Gamma'}\tilde{\lambda}^2_{2l\Gamma\Gamma'} \\
&+ \frac{1}{4}\sum_\Gamma d_\Gamma(d_\Gamma-1)U^{(2)2}_{\Gamma\Gamma}Q_{\Gamma\Gamma}\tilde{\lambda}^2_{2t\Gamma\Gamma} + \frac{1}{2}\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(2)2}_{\Gamma\Gamma'}Q_{\Gamma\Gamma'}\tilde{\lambda}^2_{2t\Gamma\Gamma'}\,,
\end{aligned} \tag{F.23}$$

$$\begin{aligned}\langle \tilde{O_i}^\dagger H_I \tilde{O_i}\rangle_0 = &\sum_\Gamma d_\Gamma U^{(0)}_{\Gamma\Gamma} K^{(0)}_{\Gamma\Gamma} \tilde{\lambda}_{0\Gamma\Gamma} \\ &+ 2\sum_\Gamma d_\Gamma(d_\Gamma-1) U^{(1)}_{\Gamma\Gamma} K^{(1)}_{\Gamma\Gamma 1} \tilde{\lambda}_{1\Gamma\Gamma} + 4\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(1)}_{\Gamma\Gamma'} K^{(1)}_{\Gamma\Gamma' 1} \tilde{\lambda}_{1\Gamma\Gamma'} \\ &- \frac{1}{8}\sum_\Gamma d_\Gamma(d_\Gamma-1) U^{(2)}_{\Gamma\Gamma} K^{(1)}_{\Gamma\Gamma 2} \tilde{\lambda}_{2l\Gamma\Gamma} - \frac{1}{4}\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(2)}_{\Gamma\Gamma'} K^{(1)}_{\Gamma\Gamma' 2} \tilde{\lambda}_{2l\Gamma\Gamma'} \\ &+ \sum_\Gamma d_\Gamma(d_\Gamma-1) U^{(2)}_{\Gamma\Gamma} K^{(2)}_{t\Gamma\Gamma} \tilde{\lambda}_{2t\Gamma\Gamma} + 2\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(2)}_{\Gamma\Gamma'} K^{(2)}_{t\Gamma\Gamma'} \tilde{\lambda}_{2t\Gamma\Gamma'} \,, \end{aligned} \tag{F.24}$$

$$\begin{aligned}\langle \tilde{O_i}^\dagger \tilde{O_i}\rangle_0 = &\sum_\Gamma d_\Gamma U^{(0)2}_{\Gamma\Gamma} S_{\Gamma\Gamma} \tilde{\lambda}^2_{0\Gamma\Gamma} \\ &+ 2\sum_\Gamma d_\Gamma(d_\Gamma-1) U^{(1)2}_{\Gamma\Gamma} S_{\Gamma\Gamma} \tilde{\lambda}^2_{1\Gamma\Gamma} + 4\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(1)2}_{\Gamma\Gamma'} S_{\Gamma\Gamma'} \tilde{\lambda}^2_{1\Gamma\Gamma'} \\ &+ \frac{1}{8}\sum_\Gamma d_\Gamma(d_\Gamma-1) U^{(2)2}_{\Gamma\Gamma} S_{\Gamma\Gamma} \tilde{\lambda}^2_{2l\Gamma\Gamma} + \frac{1}{4}\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(2)2}_{\Gamma\Gamma'} S_{\Gamma\Gamma'} \tilde{\lambda}^2_{2l\Gamma\Gamma'} \\ &+ \frac{1}{4}\sum_\Gamma d_\Gamma(d_\Gamma-1) U^{(2)2}_{\Gamma\Gamma} S_{\Gamma\Gamma} \tilde{\lambda}^2_{2t\Gamma\Gamma} + \frac{1}{2}\sum_{(\Gamma,\Gamma')} d_\Gamma d_{\Gamma'} U^{(2)2}_{\Gamma\Gamma'} S_{\Gamma\Gamma'} \tilde{\lambda}^2_{2t\Gamma\Gamma'} \,. \end{aligned} \tag{F.25}$$

The elements $P_{\Gamma\Gamma'}$, $Q_{\Gamma\Gamma'}$, and $S_{\Gamma\Gamma'}$ have been given in Appendix C by means of the Laplace transform of the local density of states $\rho_\Gamma(\epsilon)$ in the Hartree-Fock approximation. $K^{(\alpha)}_{\tau\Gamma\Gamma'}$ are given by.

$$\begin{aligned} K^{(0)}_{\Gamma\Gamma} = &\, U^{(0)^2}_{\Gamma\Gamma} \Omega_{\Gamma\Gamma}\, \tilde{\lambda}_{0\Gamma\Gamma} + 4\,(d_\Gamma - 1)\, U^{(1)^2}_{\Gamma\Gamma}\, M_{\Gamma\Gamma}\, \tilde{\lambda}_{1\Gamma\Gamma} \\ &+ 4\sum_{\Gamma'(\neq\Gamma)} d_{\Gamma'}\, U^{(1)^2}_{\Gamma\Gamma'}\, M_{\Gamma\Gamma'}\, \tilde{\lambda}_{1\Gamma\Gamma'} + \frac{1}{4}\,(d_\Gamma - 1)\, U^{(2)^2}_{\Gamma\Gamma} M_{\Gamma\Gamma} \left(\tilde{\lambda}_{2l\Gamma\Gamma} + 2\,\tilde{\lambda}_{2t\Gamma\Gamma}\right) \\ &+ \frac{1}{4}\sum_{\Gamma'(\neq\Gamma)} d_{\Gamma'}\, U^{(2)^2}_{\Gamma\Gamma'} M_{\Gamma\Gamma'} \left(\tilde{\lambda}_{2l\Gamma\Gamma'} + 2\,\tilde{\lambda}_{2t\Gamma\Gamma'}\right). \end{aligned} \tag{F.26}$$

$$\begin{aligned} K^{(1)}_{\Gamma\Gamma 1} = &\, 2U^{(1)}_{\Gamma\Gamma} U^{(0)}_{\Gamma\Gamma} M_{\Gamma\Gamma} \tilde{\lambda}_{0\Gamma\Gamma} \\ &U^{(1)}_{\Gamma\Gamma}\Big[2U^{(0)}_{\Gamma\Gamma} M_{\Gamma\Gamma} + U^{(1)}_{\Gamma\Gamma}\Omega_{\Gamma\Gamma} 4(d_\Gamma - 2) U^{(1)}_{\Gamma\Gamma} M_{\Gamma\Gamma}\Big] \tilde{\lambda}_{1\Gamma\Gamma} \\ &+ \sum_{\Gamma''(\neq\Gamma)} d_{\Gamma''} U^{(1)}_{\Gamma\Gamma''} M_{\Gamma\Gamma''} \tilde{\lambda}_{1\Gamma\Gamma''} - \frac{1}{16} U^{(2)2}_{\Gamma\Gamma} \Omega_{\Gamma\Gamma} \Big(\tilde{\lambda}_{2l\Gamma\Gamma} + \tilde{\lambda}_{2t\Gamma\Gamma'}\Big). \end{aligned} \tag{F.27}$$

$$
\begin{aligned}
K^{(1)}_{\Gamma\Gamma'1} &= U^{(1)}_{\Gamma\Gamma'}\Big(U^{(0)}_{\Gamma\Gamma}M_{\Gamma\Gamma'}\tilde{\lambda}_{0\Gamma\Gamma} + U^{(0)}_{\Gamma'\Gamma'}M_{\Gamma'\Gamma}\tilde{\lambda}_{0\Gamma'\Gamma'}\Big)\\
&+ U^{(1)}_{\Gamma\Gamma'}\Big(U^{(0)}_{\Gamma\Gamma}\Xi_{\Gamma'\Gamma\Gamma} + U^{(0)}_{\Gamma'\Gamma'}\Xi_{\Gamma\Gamma'\Gamma} + U^{(1)}_{\Gamma'\Gamma'}\Omega_{\Gamma\Gamma'}\Big)\tilde{\lambda}_{1\Gamma\Gamma'}\\
&+ 2(d_\Gamma-1)U^{(1)}_{\Gamma\Gamma}U^{(1)}_{\Gamma\Gamma'}\Big(\Xi_{\Gamma\Gamma'\Gamma}\tilde{\lambda}_{1\Gamma\Gamma} + \Xi_{\Gamma'\Gamma\Gamma}\tilde{\lambda}_{1\Gamma'\Gamma}\Big)\\
&+ 2(d_{\Gamma'}-1)U^{(1)}_{\Gamma\Gamma'}U^{(1)}_{\Gamma'\Gamma'}\Big(\Xi_{\Gamma\Gamma'\Gamma'}\tilde{\lambda}_{1\Gamma\Gamma'} + \Xi_{\Gamma'\Gamma\Gamma'}\tilde{\lambda}_{1\Gamma'\Gamma'}\Big)\\
&+ 2\sum_{\Gamma''(\neq\Gamma,\Gamma')} d_{\Gamma''}U^{(1)}_{\Gamma\Gamma''}U^{(1)}_{\Gamma'\Gamma''}\Big(\Xi_{\Gamma\Gamma'\Gamma''}\tilde{\lambda}_{1\Gamma\Gamma''} + \Xi_{\Gamma'\Gamma\Gamma''}\tilde{\lambda}_{1\Gamma'\Gamma''}\Big)\\
&- \frac{1}{16}U^{(2)2}_{\Gamma\Gamma'}\Omega_{\Gamma\Gamma'}\Big(\tilde{\lambda}_{2l\Gamma\Gamma} + \tilde{\lambda}_{2t\Gamma\Gamma'}\Big).
\end{aligned}
\tag{F.28}
$$

$$
\begin{aligned}
K^{(1)}_{\Gamma\Gamma2} &= -2U^{(2)}_{\Gamma\Gamma}U^{(0)}_{\Gamma\Gamma}M_{\Gamma\Gamma}\tilde{\lambda}_{0\Gamma\Gamma} + U^{(1)}_{\Gamma\Gamma}U^{(2)}_{\Gamma\Gamma}\Omega_{\Gamma\Gamma}\tilde{\lambda}_{1\Gamma\Gamma}\\
&+ U^{(2)}_{\Gamma\Gamma}\Big[2U^{(0)}_{\Gamma\Gamma}M_{\Gamma\Gamma} - U^{(1)}_{\Gamma\Gamma}\Omega_{\Gamma\Gamma} - (d_\Gamma-2)U^{(2)}_{\Gamma\Gamma}M_{\Gamma\Gamma}\Big]\tilde{\lambda}_{2l\Gamma\Gamma}\\
&- \sum_{\Gamma''\neq\Gamma} d_{\Gamma''}U^{(2)2}_{\Gamma\Gamma''}M_{\Gamma\Gamma''}\tilde{\lambda}_{2l\Gamma\Gamma''} + \frac{1}{2}U^{(2)2}_{\Gamma\Gamma}W_{\Gamma\Gamma}\tilde{\lambda}_{2t\Gamma\Gamma}.
\end{aligned}
\tag{F.29}
$$

$$
\begin{aligned}
K^{(1)}_{\Gamma\Gamma'2} &= U^{(2)}_{\Gamma\Gamma'}\Big(U^{(0)}_{\Gamma\Gamma}M_{\Gamma\Gamma'}\tilde{\lambda}_{0\Gamma\Gamma} + U^{(0)}_{\Gamma'\Gamma'}M_{\Gamma'\Gamma}\tilde{\lambda}_{0\Gamma'\Gamma'}\Big)\\
&+ U^{(1)}_{\Gamma\Gamma'}U^{(2)}_{\Gamma\Gamma'}\Omega_{\Gamma\Gamma'}\tilde{\lambda}_{1\Gamma\Gamma'} + \frac{1}{2}U^{(2)2}_{\Gamma\Gamma'}W_{\Gamma\Gamma'}\tilde{\lambda}_{2t\Gamma\Gamma'}\\
&+ U^{(2)}_{\Gamma\Gamma'}\Big(U^{(0)}_{\Gamma\Gamma}\Xi_{\Gamma'\Gamma\Gamma} + U^{(0)}_{\Gamma'\Gamma'}\Xi_{\Gamma\Gamma'\Gamma} - U^{(1)}_{\Gamma'\Gamma'}\Omega_{\Gamma\Gamma'}\Big)\tilde{\lambda}_{2l\Gamma\Gamma'}\\
&- \frac{1}{2}(d_\Gamma-1)U^{(2)}_{\Gamma\Gamma}U^{(2)}_{\Gamma\Gamma'}\Big(\Xi_{\Gamma\Gamma'\Gamma}\tilde{\lambda}_{2l\Gamma\Gamma} + \Xi_{\Gamma'\Gamma\Gamma}\tilde{\lambda}_{2l\Gamma'\Gamma}\Big)\\
&- \frac{1}{2}(d_{\Gamma'}-1)U^{(2)}_{\Gamma\Gamma'}U^{(2)}_{\Gamma'\Gamma'}\Big(\Xi_{\Gamma\Gamma'\Gamma'}\tilde{\lambda}_{2l\Gamma\Gamma'} + \Xi_{\Gamma'\Gamma\Gamma'}\tilde{\lambda}_{2l\Gamma'\Gamma'}\Big)\\
&- \frac{1}{2}\sum_{\Gamma''(\neq\Gamma,\Gamma')} d_{\Gamma''}U^{(2)}_{\Gamma\Gamma''}U^{(2)}_{\Gamma'\Gamma''}\Big(\Xi_{\Gamma\Gamma'\Gamma''}\tilde{\lambda}_{2l\Gamma\Gamma''} + \Xi_{\Gamma'\Gamma\Gamma''}\tilde{\lambda}_{2l\Gamma'\Gamma''}\Big).
\end{aligned}
\tag{F.30}
$$

$$
\begin{aligned}
K^{(2)}_{t\Gamma\Gamma} &= \frac{1}{2}U^{(2)}_{\Gamma\Gamma}U^{(0)}_{\Gamma\Gamma}M_{\Gamma\Gamma}\tilde{\lambda}_{0\Gamma\Gamma} - \frac{1}{4}U^{(1)}_{\Gamma\Gamma}U^{(2)}_{\Gamma\Gamma}\Omega_{\Gamma\Gamma}\tilde{\lambda}_{1\Gamma\Gamma} - \frac{1}{16}U^{(2)2}_{\Gamma\Gamma}W_{\Gamma\Gamma}\tilde{\lambda}_{2l\Gamma\Gamma}\\
&+ \frac{1}{4}U^{(2)}_{\Gamma\Gamma}\Big(U^{(1)}_{\Gamma\Gamma} + \frac{1}{4}U^{(2)}_{\Gamma\Gamma}\Big)\Omega_{\Gamma\Gamma}\tilde{\lambda}_{2t\Gamma\Gamma} + \frac{1}{4}(d_\Gamma-2)U^{(2)2}_{\Gamma\Gamma}M_{\Gamma\Gamma}\tilde{\lambda}_{2t\Gamma\Gamma}\\
&+ \frac{1}{4}\sum_{\Gamma''(\neq\Gamma)} d_{\Gamma''}U^{(2)2}_{\Gamma\Gamma''}M_{\Gamma\Gamma''}\tilde{\lambda}_{2t\Gamma\Gamma''}.
\end{aligned}
\tag{F.31}
$$

$$
\begin{aligned}
K^{(2)}_{t\Gamma\Gamma'} &= \frac{1}{4}U^{(2)}_{\Gamma\Gamma'}\Big(U^{(0)}_{\Gamma\Gamma}M_{\Gamma\Gamma'}\tilde{\lambda}_{0\Gamma\Gamma} + U^{(0)}_{\Gamma'\Gamma'}M_{\Gamma'\Gamma}\tilde{\lambda}_{0\Gamma'\Gamma'}\Big) \\
&- \frac{1}{4}U^{(1)}_{\Gamma\Gamma'}U^{(2)}_{\Gamma\Gamma'}\Omega_{\Gamma\Gamma'}\tilde{\lambda}_{1\Gamma\Gamma'} - \frac{1}{16}U^{(2)2}_{\Gamma\Gamma'}W_{\Gamma\Gamma'}\tilde{\lambda}_{2l\Gamma\Gamma'} \\
&+ \frac{1}{4}U^{(2)}_{\Gamma\Gamma'}\Big(U^{(1)}_{\Gamma\Gamma'} + \frac{1}{4}U^{(2)}_{\Gamma\Gamma'}\Big)\Omega_{\Gamma\Gamma'}\tilde{\lambda}_{2t\Gamma\Gamma'} \\
&+ \frac{1}{8}(d_\Gamma - 1)U^{(2)}_{\Gamma\Gamma}U^{(2)}_{\Gamma'\Gamma}\Big(\Xi_{\Gamma\Gamma'\Gamma}\tilde{\lambda}_{2t\Gamma\Gamma} + \Xi_{\Gamma'\Gamma\Gamma}\tilde{\lambda}_{2t\Gamma'\Gamma}\Big) \\
&+ \frac{1}{8}(d_{\Gamma'} - 1)U^{(2)}_{\Gamma'\Gamma'}U^{(2)}_{\Gamma\Gamma'}\Big(\Xi_{\Gamma\Gamma'\Gamma'}\tilde{\lambda}_{2t\Gamma\Gamma'} + \Xi_{\Gamma'\Gamma\Gamma}\tilde{\lambda}_{2t\Gamma'\Gamma'}\Big) \\
&+ \frac{1}{8}\sum_{\Gamma''(\neq\Gamma,\Gamma')} d_{\Gamma''}U^{(2)}_{\Gamma\Gamma''}U^{(2)}_{\Gamma'\Gamma''}\Big(\Xi_{\Gamma\Gamma'\Gamma''}\tilde{\lambda}_{2t\Gamma\Gamma''} + \Xi_{\Gamma'\Gamma\Gamma''}\tilde{\lambda}_{2t\Gamma'\Gamma''}\Big). \qquad \text{(F.32)}
\end{aligned}
$$

Here $M_{\Gamma\Gamma'}$, $\Xi_{\Gamma\Gamma'\Gamma''}$, $\Omega_{\Gamma\Gamma'}$, and $W_{\Gamma\Gamma'}$ are given in Appendix C by means of the Laplace transform of the local density of states $\rho_\Gamma(\epsilon)$ in the Hartree-Fock approximation.

The final expressions of the elements for the self-consistent equations (5.103) $\sim$ (5.106) in the paramagnetic state are expressed with use of the irreducible representation Γ and Γ' to which the orbitals L and L' belong.

$$\tilde{\lambda}_{0\Gamma\Gamma} = \tilde{Q}^{-1}_{\Gamma\Gamma}\left(P_{\Gamma\Gamma} - U^{(0)-1}_{\Gamma\Gamma}\,K^{(0)}_{\Gamma\Gamma}\right), \qquad \text{(F.33)}$$

$$\tilde{\lambda}_{1\Gamma\Gamma} = \tilde{Q}^{-1}_{LL'}\left(P_{\Gamma\Gamma} - \frac{1}{4}\,U^{(1)-1}_{\Gamma\Gamma}\,\bar{K}^{(1)}_{\Gamma\Gamma}\right), \qquad \text{(F.34)}$$

$$\tilde{\lambda}_{1\Gamma\Gamma'} = \tilde{Q}^{-1}_{LL'}\left(P_{\Gamma\Gamma'} - \frac{1}{4}\,U^{(1)-1}_{\Gamma\Gamma'}\,\bar{K}^{(1)}_{\Gamma\Gamma'}\right), \qquad \text{(F.35)}$$

$$\tilde{\lambda}_{2l\Gamma\Gamma} = -\tilde{Q}^{-1}_{\Gamma\Gamma}\left(P_{\Gamma\Gamma} + 4\,U^{(2)-1}_{\Gamma\Gamma}\,\bar{K}^{(2)}_{l\Gamma\Gamma}\right), \qquad \text{(F.36)}$$

$$\tilde{\lambda}_{2l\Gamma\Gamma'} = -\tilde{Q}^{-1}_{\Gamma\Gamma'}\left(P_{\Gamma\Gamma'} + 4\,U^{(2)-1}_{\Gamma\Gamma'}\,\bar{K}^{(2)}_{l\Gamma\Gamma'}\right), \qquad \text{(F.37)}$$

$$\tilde{\lambda}_{2t\Gamma\Gamma} = -\tilde{Q}^{-1}_{\Gamma\Gamma}\left(P_{\Gamma\Gamma} + 4\,U^{(2)-1}_{\Gamma\Gamma}\,K^{(2)}_{t\Gamma\Gamma}\right), \qquad \text{(F.38)}$$

$$\tilde{\lambda}_{2t\Gamma\Gamma'} = -\tilde{Q}^{-1}_{\Gamma\Gamma'}\left(P_{\Gamma\Gamma'} + 4\,U^{(2)-1}_{\Gamma\Gamma'}\,K^{(2)}_{t\Gamma\Gamma'}\right). \qquad \text{(F.39)}$$

Each element at the rhs of the above expressions (F.33) $\sim$ (F.39) is expressed as follows.

$$
\begin{aligned}
K^{(0)}_{\Gamma\Gamma} &= {U^{(0)}_{\Gamma\Gamma}}^2\Omega_{\Gamma\Gamma}\,\tilde{\lambda}_{0\Gamma\Gamma} + 4\,(d_\Gamma - 1)\,{U^{(1)}_{\Gamma\Gamma}}^2\,M_{\Gamma\Gamma}\,\tilde{\lambda}_{1\Gamma\Gamma} \\
&+ 4\sum_{\Gamma'(\neq\Gamma)} d_{\Gamma'}\,{U^{(1)}_{\Gamma\Gamma'}}^2\,M_{\Gamma\Gamma'}\,\tilde{\lambda}_{1\Gamma\Gamma'} + \frac{1}{4}\,(d_\Gamma - 1)\,{U^{(2)}_{\Gamma\Gamma}}^2 M_{\Gamma\Gamma}\left(\tilde{\lambda}_{2l\Gamma\Gamma} + 2\,\tilde{\lambda}_{2t\Gamma\Gamma}\right) \\
&+ \frac{1}{4}\sum_{\Gamma'(\neq\Gamma)} d_{\Gamma'}\,{U^{(2)}_{\Gamma\Gamma'}}^2 M_{\Gamma\Gamma'}\left(\tilde{\lambda}_{2l\Gamma\Gamma'} + 2\,\tilde{\lambda}_{2t\Gamma\Gamma'}\right), \qquad \text{(F.40)}
\end{aligned}
$$

$$
\begin{aligned}
\bar{K}^{(1)}_{\Gamma\Gamma} &= 8\,U^{(1)}_{\Gamma\Gamma}\,U^{(0)}_{\Gamma\Gamma}\,M_{\Gamma\Gamma}\,\tilde{\lambda}_{0\Gamma\Gamma} \\
&+ 4\,U^{(1)}_{\Gamma\Gamma}\left[2\,U^{(0)}_{\Gamma\Gamma}\,\Xi_{\Gamma\Gamma\Gamma} + U^{(1)}_{\Gamma\Gamma}\,\Omega_{\Gamma\Gamma} + 4\,(d_\Gamma - 2)\,U^{(1)}_{\Gamma\Gamma}\,\Xi_{\Gamma\Gamma\Gamma}\right]\tilde{\lambda}_{1\Gamma\Gamma} \\
&+ 16\,U^{(1)}_{\Gamma\Gamma}\sum_{\Gamma''(\neq\Gamma)} d_{\Gamma''}\,U^{(1)}_{\Gamma\Gamma''}\,\Xi_{\Gamma\Gamma\Gamma''}\,\tilde{\lambda}_{1\Gamma\Gamma''} - \frac{1}{4}\,U^{(2)^2}_{\Gamma\Gamma}\,\Omega_{\Gamma\Gamma}\left(\tilde{\lambda}_{2l\Gamma\Gamma} + 2\,\tilde{\lambda}_{2t\Gamma\Gamma}\right), \qquad \text{(F.41)}
\end{aligned}
$$

$$
\begin{aligned}
\bar{K}^{(1)}_{\Gamma\Gamma'} &= 4\, U^{(1)}_{\Gamma\Gamma'}\, \Big(U^{(0)}_{\Gamma\Gamma}\, M_{\Gamma\Gamma'}\, \tilde{\lambda}_{0\Gamma\Gamma} + U^{(0)}_{\Gamma'\Gamma'}\, M_{\Gamma'\Gamma}\, \tilde{\lambda}_{0\Gamma'\Gamma'} \Big) \\
&\quad + 4\, U^{(1)}_{\Gamma\Gamma'}\, \Big(U^{(0)}_{\Gamma\Gamma}\, \Xi_{\Gamma'\Gamma\Gamma} + U^{(0)}_{\Gamma'\Gamma'}\, \Xi_{\Gamma\Gamma'\Gamma'} + U^{(1)}_{\Gamma\Gamma'}\, \Omega_{\Gamma\Gamma'} \Big)\, \tilde{\lambda}_{1\Gamma\Gamma'} \\
&\quad + 8\, (d_\Gamma - 1)\, U^{(1)}_{\Gamma\Gamma}\, U^{(1)}_{\Gamma\Gamma'}\, \Big(\Xi_{\Gamma\Gamma'\Gamma}\, \tilde{\lambda}_{1\Gamma\Gamma} + \Xi_{\Gamma'\Gamma\Gamma}\, \tilde{\lambda}_{1\Gamma'\Gamma} \Big) \\
&\quad + 8\, (d_{\Gamma'} - 1)\, U^{(1)}_{\Gamma\Gamma'}\, U^{(1)}_{\Gamma'\Gamma'}\, \Big(\Xi_{\Gamma\Gamma'\Gamma'}\, \tilde{\lambda}_{1\Gamma\Gamma'} + \Xi_{\Gamma'\Gamma\Gamma'}\, \tilde{\lambda}_{1\Gamma'\Gamma'} \Big) \\
&\quad + 8 \sum_{\Gamma''(\neq\Gamma,\Gamma')} d_{\Gamma''}\, U^{(1)}_{\Gamma\Gamma''}\, U^{(1)}_{\Gamma'\Gamma''}\, \Big(\Xi_{\Gamma\Gamma'\Gamma''}\, \tilde{\lambda}_{1\Gamma\Gamma''} + \Xi_{\Gamma'\Gamma\Gamma''}\, \tilde{\lambda}_{1\Gamma'\Gamma''} \Big) \\
&\quad - \frac{1}{4}\, U^{(2)^2}_{\Gamma\Gamma'}\, \Omega_{\Gamma\Gamma'}\, \Big(\tilde{\lambda}_{2l\Gamma\Gamma'} + 2\, \tilde{\lambda}_{2t\Gamma\Gamma'} \Big)\,,
\end{aligned}
\tag{F.42}
$$

$$
\begin{aligned}
\bar{K}^{(2)}_{l\Gamma\Gamma} &= \frac{1}{2}\, U^{(2)}_{\Gamma\Gamma}\, U^{(0)}_{\Gamma\Gamma}\, M_{\Gamma\Gamma}\, \tilde{\lambda}_{0\Gamma\Gamma} - \frac{1}{4}\, U^{(1)}_{\Gamma\Gamma}\, U^{(2)}_{\Gamma\Gamma}\, \Omega_{\Gamma\Gamma}\, \tilde{\lambda}_{1\Gamma\Gamma} \\
&\quad - \frac{1}{4}\, U^{(2)}_{\Gamma\Gamma}\, \Big[2\, U^{(0)}_{\Gamma\Gamma}\, \Xi_{\Gamma\Gamma\Gamma} - U^{(1)}_{\Gamma\Gamma}\, \Omega_{\Gamma\Gamma} - (d_\Gamma - 2)\, U^{(2)}_{\Gamma\Gamma}\, \Xi_{\Gamma\Gamma\Gamma} \Big]\, \tilde{\lambda}_{2l\Gamma\Gamma} \\
&\quad + \frac{1}{4} \sum_{\Gamma''(\neq\Gamma)} d_{\Gamma''}\, U^{(2)^2}_{\Gamma\Gamma}\, \Xi_{\Gamma\Gamma\Gamma''}\, \tilde{\lambda}_{2l\Gamma\Gamma''} - \frac{1}{8}\, U^{(2)^2}_{\Gamma\Gamma}\, W_{\Gamma\Gamma}\, \tilde{\lambda}_{2t\Gamma\Gamma''}\,,
\end{aligned}
\tag{F.43}
$$

$$
\begin{aligned}
\bar{K}^{(2)}_{l\Gamma\Gamma'} &= \frac{1}{4}\, U^{(2)}_{\Gamma\Gamma'}\, \Big(U^{(0)}_{\Gamma\Gamma}\, M_{\Gamma\Gamma'}\, \tilde{\lambda}_{0\Gamma\Gamma} + U^{(0)}_{\Gamma'\Gamma'}\, M_{\Gamma'\Gamma}\, \tilde{\lambda}_{0\Gamma'\Gamma'} \Big) \\
&\quad + \frac{1}{4}\, U^{(2)}_{\Gamma\Gamma'}\, \Big(U^{(0)}_{\Gamma\Gamma}\, \Xi_{\Gamma'\Gamma\Gamma} + U^{(0)}_{\Gamma'\Gamma'}\, \Xi_{\Gamma\Gamma'\Gamma'} - U^{(1)}_{\Gamma\Gamma'}\, \Omega_{\Gamma\Gamma'} \Big)\, \tilde{\lambda}_{2l\Gamma\Gamma'} \\
&\quad + \frac{1}{8}\, (d_\Gamma - 1)\, U^{(2)}_{\Gamma\Gamma}\, U^{(2)}_{\Gamma\Gamma'}\, \Big(\Xi_{\Gamma\Gamma'\Gamma}\, \tilde{\lambda}_{2l\Gamma\Gamma} + \Xi_{\Gamma'\Gamma\Gamma}\, \tilde{\lambda}_{2l\Gamma'\Gamma} \Big) \\
&\quad + \frac{1}{8}\, (d_{\Gamma'} - 1)\, U^{(2)}_{\Gamma\Gamma'}\, U^{(2)}_{\Gamma'\Gamma'}\, \Big(\Xi_{\Gamma\Gamma'\Gamma'}\, \tilde{\lambda}_{2l\Gamma\Gamma'} + \Xi_{\Gamma'\Gamma\Gamma'}\, \tilde{\lambda}_{2l\Gamma'\Gamma'} \Big) \\
&\quad - \frac{1}{8} \sum_{\Gamma''(\neq\Gamma,\Gamma')} d_{\Gamma''}\, U^{(2)}_{\Gamma'\Gamma''}\, U^{(2)}_{\Gamma\Gamma''}\, \Big(\Xi_{\Gamma\Gamma'\Gamma''}\, \tilde{\lambda}_{2l\Gamma\Gamma''} + \Xi_{\Gamma'\Gamma\Gamma''}\, \tilde{\lambda}_{2l\Gamma'\Gamma''} \Big) \\
&\quad - \frac{1}{4}\, U^{(1)}_{\Gamma\Gamma'}\, U^{(2)}_{\Gamma\Gamma'}\, \Omega_{\Gamma\Gamma'}\, \tilde{\lambda}_{1\Gamma\Gamma'} - \frac{1}{8}\, U^{(2)^2}_{\Gamma\Gamma'}\, W_{\Gamma\Gamma'}\, \tilde{\lambda}_{2t\Gamma\Gamma'}\,,
\end{aligned}
\tag{F.44}
$$

$$
\begin{aligned}
K^{(2)}_{t\Gamma\Gamma} &= \frac{1}{2}\, U^{(2)}_{\Gamma\Gamma}\, U^{(0)}_{\Gamma\Gamma}\, M_{\Gamma\Gamma}\, \tilde{\lambda}_{0\Gamma\Gamma} - \frac{1}{4}\, U^{(2)}_{\Gamma\Gamma}\, U^{(1)}_{\Gamma\Gamma}\, \Omega_{\Gamma\Gamma}\, \tilde{\lambda}_{1\Gamma\Gamma} \\
&\quad - \frac{1}{16}\, U^{(2)^2}_{\Gamma\Gamma}\, W_{\Gamma\Gamma}\, \tilde{\lambda}_{2l\Gamma\Gamma} + \frac{1}{4}\, U^{(2)}_{\Gamma\Gamma}\, \Big(U^{(1)}_{\Gamma\Gamma} + \frac{1}{4}\, U^{(2)}_{\Gamma\Gamma} \Big)\, \Omega_{\Gamma\Gamma}\, \tilde{\lambda}_{2t\Gamma\Gamma} \\
&\quad + \frac{1}{4}\, (d_\Gamma - 2)\, U^{(2)^2}_{\Gamma\Gamma}\, \Xi_{\Gamma\Gamma\Gamma}\, \tilde{\lambda}_{2t\Gamma\Gamma} + \frac{1}{4} \sum_{\Gamma''(\neq\Gamma)} d_{\Gamma''}\, U^{(2)^2}_{\Gamma\Gamma''}\, \Xi_{\Gamma\Gamma\Gamma''}\, \tilde{\lambda}_{2t\Gamma\Gamma''}\,,
\end{aligned}
\tag{F.45}
$$

$$
\begin{aligned}
K^{(2)}_{t\Gamma\Gamma'} = & \frac{1}{4}\, U^{(2)}_{\Gamma\Gamma'} \left(U^{(0)}_{\Gamma\Gamma}\; M_{\Gamma\Gamma'}\; \tilde{\lambda}_{0\Gamma\Gamma} + U^{(0)}_{\Gamma'\Gamma'}\; M_{\Gamma'\Gamma}\; \tilde{\lambda}_{0\Gamma'\Gamma'} \right) \\
& - \frac{1}{4}\, U^{(1)}_{\Gamma\Gamma'}\, U^{(2)}_{\Gamma\Gamma'}\, \Omega_{\Gamma\Gamma'}\, \tilde{\lambda}_{1\Gamma\Gamma'} - \frac{1}{16}\, {U^{(2)}_{\Gamma\Gamma'}}^2\, W_{\Gamma\Gamma'}\, \tilde{\lambda}_{2l\Gamma\Gamma'} \\
& + \frac{1}{4}\, U^{(2)}_{\Gamma\Gamma'} \left(U^{(1)}_{\Gamma\Gamma'} + \frac{1}{4}\, U^{(2)}_{\Gamma\Gamma'} \right) \Omega_{\Gamma\Gamma'}\, \tilde{\lambda}_{2t\Gamma\Gamma'} \\
& + \frac{1}{8}\, (d_\Gamma - 1)\, U^{(2)}_{\Gamma\Gamma}\, U^{(2)}_{\Gamma'\Gamma} \left(\Xi_{\Gamma\Gamma'\Gamma}\, \tilde{\lambda}_{2t\Gamma\Gamma} + \Xi_{\Gamma'\Gamma\Gamma}\, \tilde{\lambda}_{2t\Gamma'\Gamma} \right) \\
& + \frac{1}{8}\, (d_{\Gamma'} - 1)\, U^{(2)}_{\Gamma\Gamma'}\, U^{(2)}_{\Gamma'\Gamma'} \left(\Xi_{\Gamma\Gamma'\Gamma'}\, \tilde{\lambda}_{2t\Gamma\Gamma'} + \Xi_{\Gamma'\Gamma\Gamma'}\, \tilde{\lambda}_{2t\Gamma'\Gamma'} \right) \\
& + \frac{1}{8} \sum_{\Gamma''(\neq\Gamma,\Gamma')} d_{\Gamma''}\, U^{(2)}_{\Gamma\Gamma''}\, U^{(2)}_{\Gamma'\Gamma''} \left(\Xi_{\Gamma\Gamma'\Gamma''}\, \tilde{\lambda}_{2t\Gamma\Gamma''} + \Xi_{\Gamma'\Gamma\Gamma''}\, \tilde{\lambda}_{2t\Gamma'\Gamma''} \right) . \qquad \text{(F.46)}
\end{aligned}
$$

Appendix G

Appendix: Correlation Correction to Electron Number

In this Appendix, we present the explicit expression of the correlation correction to the electron number of orbital L in Eq. (5.118) in Sec. 5.2.

$$\langle \tilde{n}_{iL} \rangle = \frac{\langle \tilde{O}_i^\dagger \tilde{n}_{iL} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i{}^\dagger \tilde{O}_i \rangle_0} \,. \tag{G.1}$$

The denominator is the renormalization factor of the wavefunction. Expression of $\langle \tilde{O}_i{}^\dagger \tilde{O}_i \rangle_0$ has been given by Eqs. (F.5) and (F.25). The numerator is expressed as follows.

$$\begin{aligned}
\langle \tilde{O}_i{}^\dagger \tilde{n}_{iL} \tilde{O}_i \rangle_0 = & \sum_L U^{(0)2}_{LL} A^{(00)}_{LLL^\nu \downarrow\uparrow} \tilde{\lambda}^{(\downarrow\uparrow)}_{0LL} + \sum_{\langle LL' \rangle} \sum_{\sigma\sigma'} U^{(1)2}_{LL'} A^{(11)}_{LL'L^\nu \sigma\sigma'\sigma^\nu} \tilde{\lambda}^{(\sigma\sigma')2}_{1LL'} \\
& + 2 \sum_{\langle LL' \rangle} \sum_{\sigma\sigma'} U^{(1)}_{LL'} U^{(2)}_{LL'} A^{(12)}_{lLL'L^\nu \sigma\sigma'\sigma^\nu} \tilde{\lambda}^{(\sigma\sigma')}_{1LL'} \tilde{\lambda}^{(\sigma\sigma')}_{2lLL'} \\
& + \sum_{\langle LL' \rangle} \sum_{\sigma\sigma'} U^{(2)2}_{LL'} A^{(22)}_{lLL'L^\nu \sigma\sigma'\sigma^\nu} \tilde{\lambda}^{(\sigma\sigma')}_{2lLL'} \\
& + \sum_{\langle LL' \rangle} \sum_{\sigma} U^{(2)2}_{LL'} \tilde{\lambda}^{(\sigma-\sigma)}_{2tLL'} A^{(22)}_{tLL'L^\nu \sigma-\sigma\sigma^\nu} \tilde{\lambda}^{(\sigma-\sigma)}_{2tLL'} .
\end{aligned} \tag{G.2}$$

Here the elements $\{A\}$ are expressed by the Laplace transformation. We obtain the relation between the $\{A\}$ components as follows

$$A^{(00)}_{LL\downarrow\uparrow} = A_{LL\downarrow\uparrow}, \tag{G.3}$$

$$A^{(11)}_{LL'\sigma\sigma'} = A_{LL'\sigma\sigma'}, \tag{G.4}$$

$$A^{(12)}_{LL'\sigma\sigma'} = -\frac{1}{4} \sigma\sigma' A_{LL'\sigma\sigma'}, \tag{G.5}$$

$$A^{(22)}_{lLL'\sigma\sigma'} = \frac{1}{16} A_{LL'\sigma\sigma'}, \tag{G.6}$$

and

$$A^{(22)}_{tLL'\sigma-\sigma} = \frac{1}{4} A_{LL'\sigma}. \tag{G.7}$$

In the paramagnetic state, the correlation correction (G.2) is expressed as follows with use of the irreducible representation Γ with dimensions d_Γ to which the orbital L belongs.

$$\begin{aligned}\langle \tilde{O}_i^\dagger \tilde{n}_{iL} \tilde{O}_i \rangle_0 = 2\, A_{\Gamma\Gamma} \Big[& U^{(0)^2}_{\Gamma\Gamma}\ \tilde{\lambda}^2_{0\Gamma\Gamma} \\ & + (d_\Gamma - 1)\, A_{\Gamma\Gamma} \left(2\, U^{(1)^2}_{\Gamma\Gamma}\ \tilde{\lambda}^2_{1\Gamma\Gamma} + \frac{1}{8}\, U^{(2)^2}_{\Gamma\Gamma}\ (\tilde{\lambda}^2_{2l\Gamma\Gamma} + 2\, \tilde{\lambda}^2_{2t\Gamma\Gamma}) \right) \Big] \\ & + 2 \sum_{\Gamma' \neq \Gamma}^{d} d_{\Gamma'}\, A_{\Gamma'\Gamma} \left[2\, U^{(1)^2}_{\Gamma\Gamma'}\ \tilde{\lambda}^2_{1\Gamma\Gamma'} + \frac{1}{8}\, U^{(2)^2}_{\Gamma\Gamma'} \left(\tilde{\lambda}^2_{2l\Gamma\Gamma'} + 2\, \tilde{\lambda}^2_{2t\Gamma\Gamma'} \right) \right]. \end{aligned} \tag{G.8}$$

Here

$$\begin{aligned} A_{\Gamma\Gamma'} = -\int_0^\infty dt\, dt' e^{i\epsilon_c(t+t')} \Big[& a_{\Gamma'}(-t-t')\, b_{\Gamma'}(t+t')\, a_\Gamma(-t-t')\, b_\Gamma(t)\, b_\Gamma(t') \\ & - a_{\Gamma'}(-t-t')\, b_{\Gamma'}(t+t')\, b_\Gamma(t+t')\, a_\Gamma(-t)\, a_\Gamma(-t') \Big]. \end{aligned} \tag{G.9}$$

The functions $a_\Gamma(t)$ and $b_\Gamma(t)$ have been given in Eqs. (C.28) and (C.29) in Appendix C.

Appendix H

Appendix: Expressions of the Average Residual Interaction Elements

In this Appendix, we present the explicit expressions of the residual interactions. The expressions are given in Sec. 5.2, which were obtained by using Wick's theorem.

The residual interaction elements $\sum_{\langle LL'\rangle}\langle O^{(\alpha)}_{iLL'}\rangle$ for α = 0, 1, and 2 are given by Eq. (5.121):

$$\sum_{\langle LL'\rangle}\langle O^{(\alpha)}_{iLL'}\rangle = \frac{-\sum_{\langle LL'\rangle}\langle \tilde{O}_i{}^{\dagger} O^{(\alpha)}_{iLL'}\rangle_0 - \sum_{\langle LL'\rangle}\langle O^{(\alpha)}_{iLL'}\tilde{O}_i\rangle_0 + \sum_{\langle LL'\rangle}\langle \tilde{O}_i{}^{\dagger} O^{(\alpha)}_{iLL'}\tilde{O}_i\rangle_0}{1+\langle \tilde{O}_i{}^{\dagger}\tilde{O}_i\rangle_0}\,. \tag{H.1}$$

Here

$$\sum_{L}\langle O^{(0)}_{iLL}\tilde{O}_i\rangle_0 = \sum_{\Gamma} d_\Gamma\, U^{(0)}_{\Gamma\Gamma}\, P_{\Gamma\Gamma}\, \tilde{\lambda}_{0\Gamma\Gamma}\,, \tag{H.2}$$

$$\sum_{(L,L')}\langle O^{(1)}_{iLL'}\tilde{O}_i\rangle_0 = 2\sum_{\Gamma} d_\Gamma\,(d_\Gamma-1)\, U^{(1)}_{\Gamma\Gamma}\, P_{\Gamma\Gamma}\, \tilde{\lambda}_{1\Gamma\Gamma} + 4\sum_{(\Gamma,\Gamma')} d_\Gamma\, d_{\Gamma'} U^{(1)}_{\Gamma\Gamma'}\, P_{\Gamma\Gamma'}\, \tilde{\lambda}_{1\Gamma\Gamma'}\,, \tag{H.3}$$

$$\begin{aligned}\sum_{(L,L')}\langle O^{(2)}_{iLL'}\tilde{O}_i\rangle_0 = &-\frac{1}{8}\sum_{\Gamma} d_\Gamma\,(d_\Gamma-1)\, U^{(2)}_{\Gamma\Gamma}\, P_{\Gamma\Gamma}\left(\tilde{\lambda}_{2l\Gamma\Gamma} + 2\,\tilde{\lambda}_{2t\Gamma\Gamma}\right)\\ &-\frac{1}{4}\sum_{(\Gamma,\Gamma')} d_\Gamma\, d_{\Gamma'} U^{(2)}_{\Gamma\Gamma'}\, P_{\Gamma\Gamma'}\left(\tilde{\lambda}_{2l\Gamma\Gamma'} + 2\,\tilde{\lambda}_{2t\Gamma\Gamma'}\right),\end{aligned} \tag{H.4}$$

$$\begin{aligned}\sum_{L}\langle \tilde{O}_i^{\dagger} O^{(0)}_{iLL}\tilde{O}_i\rangle_0 = &\sum_{\Gamma} d_\Gamma\, U^{(0)^2}_{\Gamma\Gamma}\,\tilde{\lambda}^2_{0\Gamma\Gamma}\,\Omega_{\Gamma\Gamma}\\ &+\sum_{\Gamma} d_\Gamma\,(d_\Gamma-1)\left(4\,U^{(1)^2}_{\Gamma\Gamma}\,\tilde{\lambda}^2_{1\Gamma\Gamma} - \frac{1}{4}\,U^{(2)^2}_{\Gamma\Gamma}\,\tilde{\lambda}^2_{2l\Gamma\Gamma}\right)\Xi_{\Gamma\Gamma\Gamma}\\ &+\sum_{(\Gamma,\Gamma')} d_\Gamma\, d_{\Gamma'}\left(4\,U^{(1)^2}_{\Gamma\Gamma'}\,\tilde{\lambda}^2_{1\Gamma\Gamma'} - \frac{1}{4}\,U^{(2)^2}_{\Gamma\Gamma'}\,\tilde{\lambda}^2_{2l\Gamma\Gamma'}\right)\left(\Xi_{\Gamma'\Gamma\Gamma} + \Xi_{\Gamma\Gamma'\Gamma'}\right),\end{aligned} \tag{H.5}$$

$$\sum_{(L,L')} \langle \tilde{O}_i^\dagger O_{iLL'}^{(1)} \tilde{O}_i \rangle_0 = 8 \sum_\Gamma d_\Gamma \, (d_\Gamma - 1) \, U_{\Gamma\Gamma}^{(1)} \, \tilde{\lambda}_{1\Gamma\Gamma} \, U_{\Gamma\Gamma}^{(0)} \, \tilde{\lambda}_{0\Gamma\Gamma} \, M_{\Gamma\Gamma}$$
$$+ 8 \sum_{(\Gamma,\Gamma')} d_\Gamma \, d_{\Gamma'} \, U_{\Gamma\Gamma'}^{(1)} \, \tilde{\lambda}_{1\Gamma\Gamma'} \left(U_{\Gamma\Gamma}^{(0)} \, \tilde{\lambda}_{0\Gamma\Gamma} \, M_{\Gamma\Gamma'} + U_{\Gamma'\Gamma'}^{(0)} \, \tilde{\lambda}_{0\Gamma'\Gamma'} \, M_{\Gamma'\Gamma} \right)$$
$$+ 2 \sum_\Gamma d_\Gamma \, (d_\Gamma - 1) \, U_{\Gamma\Gamma}^{(1)} \, \tilde{\lambda}_{1\Gamma\Gamma} \left(U_{\Gamma\Gamma}^{(1)} \, \tilde{\lambda}_{1\Gamma\Gamma} \, \Omega_{\Gamma\Gamma} + T_{\Gamma\Gamma}^{(11)} \right)$$
$$+ 4 \sum_{(\Gamma,\Gamma')} d_\Gamma \, d_{\Gamma'} \, U_{\Gamma\Gamma'}^{(1)} \, \tilde{\lambda}_{1\Gamma\Gamma'} \left(U_{\Gamma\Gamma'}^{(1)} \, \tilde{\lambda}_{1\Gamma\Gamma'} \, \Omega_{\Gamma\Gamma'} + T_{\Gamma\Gamma'}^{(11)} \right)$$
$$+ \frac{1}{8} \sum_\Gamma d_\Gamma \, (d_\Gamma - 1) \, {U_{\Gamma\Gamma}^{(2)}}^2 \left(\tilde{\lambda}_{2l\Gamma\Gamma}^2 + 2 \, \tilde{\lambda}_{2t\Gamma\Gamma}^2 \right) \Omega_{\Gamma\Gamma}$$
$$+ \frac{1}{4} \sum_{(\Gamma,\Gamma')} d_\Gamma \, d_{\Gamma'} \, {U_{\Gamma\Gamma'}^{(2)}}^2 \left(\tilde{\lambda}_{2l\Gamma\Gamma'}^2 + 2 \, \tilde{\lambda}_{2t\Gamma\Gamma'}^2 \right) \Omega_{\Gamma\Gamma'} \, . \tag{H.6}$$

Here

$$T_{\Gamma\Gamma'}^{(11)} = -2 \left(U_{\Gamma\Gamma}^{(1)} \, \Xi_{\Gamma\Gamma'\Gamma} \, \tilde{\lambda}_{1\Gamma\Gamma} + U_{\Gamma'\Gamma}^{(1)} \, \Xi_{\Gamma'\Gamma\Gamma} \, \tilde{\lambda}_{1\Gamma'\Gamma} \right)$$
$$- 2 \left(U_{\Gamma\Gamma'}^{(1)} \, \Xi_{\Gamma\Gamma'\Gamma'} \, \tilde{\lambda}_{1\Gamma\Gamma'} + U_{\Gamma'\Gamma'}^{(1)} \, \Xi_{\Gamma'\Gamma\Gamma'} \, \tilde{\lambda}_{1\Gamma'\Gamma'} \right)$$
$$+ 2 \sum_{\Gamma''} d_{\Gamma''} \left(U_{\Gamma\Gamma''}^{(1)} \, \Xi_{\Gamma\Gamma'\Gamma''} \, \tilde{\lambda}_{1\Gamma\Gamma''} + U_{\Gamma'\Gamma''}^{(1)} \, \Xi_{\Gamma'\Gamma\Gamma''} \, \tilde{\lambda}_{1\Gamma'\Gamma''} \right) . \tag{H.7}$$

Finally we have

$$\sum_{(L,L')} \langle \tilde{O}_i^\dagger O_{iLL'}^{(2)} \tilde{O}_i \rangle_0 = \sum_\Gamma d_\Gamma \, U_{\Gamma\Gamma}^{(0)} \, \tilde{\lambda}_{0\Gamma\Gamma} \, \hat{K}_{\Gamma\Gamma}^{(0)}$$
$$+ \frac{1}{2} \sum_\Gamma d_\Gamma \, (d_\Gamma - 1) \left[4 \, U_{\Gamma\Gamma}^{(1)} \, \tilde{\lambda}_{1\Gamma\Gamma} \, \hat{K}_{\Gamma\Gamma 1}^{(1)} - \frac{1}{4} \, U_{\Gamma\Gamma}^{(2)} \, \tilde{\lambda}_{2l\Gamma\Gamma} \, \hat{K}_{\Gamma\Gamma 2}^{(1)} \right]$$
$$+ \sum_{(\Gamma,\Gamma')} d_\Gamma \, d_{\Gamma'} \left[4 \, U_{\Gamma\Gamma'}^{(1)} \, \tilde{\lambda}_{1\Gamma\Gamma'} \, \hat{K}_{\Gamma\Gamma' 1}^{(1)} - \frac{1}{4} \, U_{\Gamma\Gamma'}^{(2)} \, \tilde{\lambda}_{2l\Gamma\Gamma'} \, \hat{K}_{\Gamma\Gamma' 2}^{(1)} \right]$$
$$+ \sum_\Gamma d_\Gamma \, (d_\Gamma - 1) \, U_{\Gamma\Gamma}^{(2)} \, \tilde{\lambda}_{2t\Gamma\Gamma} \, \hat{K}_{t\Gamma\Gamma}^{(2)} + \sum_{(\Gamma,\Gamma')} d_\Gamma \, d_{\Gamma'} \, U_{\Gamma\Gamma'}^{(2)} \, \tilde{\lambda}_{2t\Gamma\Gamma'} \, \hat{K}_{t\Gamma\Gamma'}^{(2)} \, . \tag{H.8}$$

Here

$$\hat{K}_{\Gamma\Gamma}^{(0)} = \frac{1}{4} \, (d_\Gamma - 1) \, U_{\Gamma\Gamma}^{(2)} \left(\tilde{\lambda}_{2l\Gamma\Gamma} + 2 \, \tilde{\lambda}_{2t\Gamma\Gamma} \right) M_{\Gamma\Gamma}$$
$$+ \frac{1}{4} \sum_{\Gamma'(\neq\Gamma)} d_{\Gamma'} \, U_{\Gamma\Gamma'}^{(2)} \left(\tilde{\lambda}_{2l\Gamma\Gamma'} + 2 \, \tilde{\lambda}_{2t\Gamma\Gamma'} \right) M_{\Gamma\Gamma'} \, , \tag{H.9}$$

$$\hat{K}_{\Gamma\Gamma' 1}^{(1)} = -\frac{1}{16} \, U_{\Gamma\Gamma'}^{(2)} \left(\tilde{\lambda}_{2l\Gamma\Gamma'} + 2 \, \tilde{\lambda}_{2t\Gamma\Gamma'} \right) \Omega_{\Gamma\Gamma'} \, . \tag{H.10}$$

$$
\begin{aligned}
\hat{K}^{(1)}_{\Gamma\Gamma'2} = & -U^{(0)}_{\Gamma\Gamma}\, M_{\Gamma\Gamma'}\, \tilde{\lambda}_{0\Gamma\Gamma} - U^{(0)}_{\Gamma'\Gamma'}\, M_{\Gamma'\Gamma}\, \tilde{\lambda}_{0\Gamma'\Gamma'} \\
& + U^{(1)}_{\Gamma\Gamma'}\, \Omega_{\Gamma\Gamma'}\, \tilde{\lambda}_{1\Gamma\Gamma'} + \frac{1}{2}\, U^{(2)}_{\Gamma\Gamma'}\, W_{\Gamma\Gamma'}\, \tilde{\lambda}_{2t\Gamma\Gamma'} \\
& + \frac{1}{2}\left(U^{(2)}_{\Gamma\Gamma}\, \Xi_{\Gamma\Gamma'\Gamma}\, \tilde{\lambda}_{2l\Gamma\Gamma} + U^{(2)}_{\Gamma'\Gamma}\, \Xi_{\Gamma'\Gamma\Gamma}\, \tilde{\lambda}_{2l\Gamma'\Gamma} \right) \\
& + \frac{1}{2}\left(U^{(2)}_{\Gamma\Gamma'}\, \Xi_{\Gamma\Gamma'\Gamma'}\, \tilde{\lambda}_{2l\Gamma\Gamma'} + U^{(2)}_{\Gamma'\Gamma'}\, \Xi_{\Gamma'\Gamma\Gamma'}\, \tilde{\lambda}_{2l\Gamma'\Gamma'} \right) \\
& - \frac{1}{2} \sum_{\Gamma''} d_{\Gamma''} \left(U^{(2)}_{\Gamma\Gamma''}\, \Xi_{\Gamma\Gamma'\Gamma''}\, \tilde{\lambda}_{2l\Gamma\Gamma''} + U^{(2)}_{\Gamma'\Gamma''}\, \Xi_{\Gamma'\Gamma\Gamma''}\, \tilde{\lambda}_{2l\Gamma'\Gamma''} \right) .
\end{aligned}
\tag{H.11}
$$

$$
\begin{aligned}
\hat{K}^{(2)}_{t\Gamma\Gamma'} = & \frac{1}{4}\left(U^{(0)}_{\Gamma\Gamma}\, M_{\Gamma\Gamma'}\, \tilde{\lambda}_{0\Gamma\Gamma} + U^{(0)}_{\Gamma'\Gamma'}\, M_{\Gamma'\Gamma}\, \tilde{\lambda}_{0\Gamma'\Gamma'} \right) \\
& - \frac{1}{4}\left(4\, U^{(1)}_{\Gamma\Gamma'}\, \Omega_{\Gamma\Gamma'}\, \tilde{\lambda}_{1\Gamma\Gamma'} + U^{(2)}_{\Gamma\Gamma'}\, W_{\Gamma\Gamma'}\, \tilde{\lambda}_{2l\Gamma\Gamma'} - \frac{1}{4}\, U^{(2)}_{\Gamma\Gamma'}\, \Omega_{\Gamma\Gamma'}\, \tilde{\lambda}_{2t\Gamma\Gamma'} \right) \\
& - \frac{1}{8}\left(U^{(2)}_{\Gamma\Gamma}\, \Xi_{\Gamma\Gamma'\Gamma}\, \tilde{\lambda}_{2t\Gamma\Gamma} + U^{(2)}_{\Gamma'\Gamma}\, \Xi_{\Gamma'\Gamma\Gamma}\, \tilde{\lambda}_{2t\Gamma'\Gamma} \right) \\
& - \frac{1}{8}\left(U^{(2)}_{\Gamma\Gamma'}\, \Xi_{\Gamma\Gamma'\Gamma'}\, \tilde{\lambda}_{2t\Gamma\Gamma'} + U^{(2)}_{\Gamma'\Gamma'}\, \Xi_{\Gamma'\Gamma\Gamma'}\, \tilde{\lambda}_{2t\Gamma'\Gamma'} \right) \\
& + \frac{1}{8} \sum_{\Gamma''} d_{\Gamma''} \left(U^{(2)}_{\Gamma\Gamma''}\, \Xi_{\Gamma\Gamma'\Gamma''}\, \tilde{\lambda}_{2t\Gamma\Gamma''} + U^{(2)}_{\Gamma'\Gamma''}\, \Xi_{\Gamma'\Gamma\Gamma''}\, \tilde{\lambda}_{2t\Gamma'\Gamma''} \right) .
\end{aligned}
\tag{H.12}
$$

The expressions of $P_{\Gamma\Gamma'}$, $M_{\Gamma\Gamma'}$, $\Xi_{\Gamma\Gamma'\Gamma''}$, $\Omega_{\Gamma\Gamma'}$, and $W_{\Gamma\Gamma'}$ at the rhs of the above expressions have been given in Appendix C (see Eqs. (C.19) $\sim$ (C.23)).

Appendix I

Appendix: Momentum Distribution Function

In this Appendix, we present the explicit expressions of the momentum distribution function (5.122) in the paramagnetic state, and derive the average quasiparticle weights (5.125) and (5.128).

The numerator of the correlation correction to the momentum distribution $\langle n_{kn\sigma} \rangle$ is given in Eq. (5.123):

$$N\langle \tilde{O}_i^\dagger \tilde{n}_{kn\sigma} \tilde{O}_i \rangle_0 = \sum_{\alpha\tau} \sum_{\langle LL' \rangle} q_\tau^{(\alpha)} \, U_{LL'}^{(\alpha)2} \, \tilde{\lambda}_{\alpha\tau LL'}^2 \left(\hat{B}_{LL'n}(\boldsymbol{k}) \, f(-\tilde{\epsilon}_{kn}) - \hat{C}_{LL'n}(\boldsymbol{k}) \, f(\tilde{\epsilon}_{kn}) \right). \tag{I.1}$$

The particle and hole contributions, $\hat{B}_{LL'n}(\boldsymbol{k})$ and $\hat{C}_{LL'n}(\boldsymbol{k})$ are expressed by Eq. (5.124):

$$\hat{B}_{LL'n}(\boldsymbol{k}) = |u_{Ln}(\boldsymbol{k})|^2 B_{L'L}(\epsilon_{kn}) + |u_{L'n}(\boldsymbol{k})|^2 B_{LL'}(\epsilon_{kn}) \,, \tag{I.2}$$

$$\hat{C}_{LL'n}(\boldsymbol{k}) = |u_{Ln}(\boldsymbol{k})|^2 C_{L'L}(\epsilon_{kn}) + |u_{L'n}(\boldsymbol{k})|^2 C_{LL'}(\epsilon_{kn}) \,. \tag{I.3}$$

Assuming that orbital L belongs to an irreducible representation Γ, we obtain the expressions of the $B_{LL'}(\epsilon_{kn})$ and $C_{LL'}(\epsilon_{kn})$ as follows.

$$B_{\Gamma\Gamma'}(\epsilon_{kn}) = -\int_0^\infty dt \, dt' e^{i(\epsilon_c - \epsilon_{kn})(t+t')} \, a_\Gamma(-t-t') \, b_\Gamma(t+t') \, a_{\Gamma'}(-t-t') \,, \tag{I.4}$$

$$C_{\Gamma\Gamma'}(\epsilon_{kn}) = -\int_0^\infty dt \, dt' e^{i(\epsilon_c + \epsilon_{kn})(t+t')} \, a_\Gamma(-t-t') \, b_\Gamma(t+t') \, b_{\Gamma'}(t+t') \,. \tag{I.5}$$

The quasiparticle weight is obtained from the jump at the Fermi level: $Z_{k_{\rm F}n} = \langle n_{kn\sigma} \rangle_{k_{\rm F-}} - \langle n_{kn\sigma} \rangle_{k_{\rm F+}}$. Here $k_{\rm F-}$ ($k_{\rm F+}$) means the wavevector just below (above) the Fermi surface. According to Eq. (5.123), it is given by

$$Z_{k_{\rm F}n} = 1 + \frac{\delta(N\langle \tilde{O}_i^\dagger \tilde{n}_{kn\sigma} \tilde{O}_i \rangle_0)_{k_{\rm F}}}{1 + \langle \tilde{O}_i{}^\dagger \tilde{O}_i \rangle_0} \,. \tag{I.6}$$

Here the numerator of the correlation corrections is given by

$$\delta(N\langle\tilde{O}_i^\dagger\tilde{n}_{kn\sigma}\tilde{O}_i\rangle_0)_{k_{\rm F}} = -\sum_{\Gamma}\Big[d_\Gamma\, U_{\Gamma\Gamma}^{(0)^2}\,\tilde{\lambda}_{0\Gamma\Gamma}^2 + 2\,d_\Gamma\,(d_\Gamma-1)\,U_{\Gamma\Gamma}^{(1)^2}\,\tilde{\lambda}_{1\Gamma\Gamma}^2 + \frac{1}{8}\,d_\Gamma\,(d_\Gamma-1)\,U_{\Gamma\Gamma}^{(2)^2}\,\Big(\tilde{\lambda}_{2l\Gamma\Gamma}^2+2\,\tilde{\lambda}_{2t\Gamma\Gamma}^2\Big)\Big]\times\Big(\hat{B}_{\Gamma\Gamma n}(\boldsymbol{k}_{\rm F})+\hat{C}_{\Gamma\Gamma n}(\boldsymbol{k}_{\rm F})\Big) - \sum_{(\Gamma,\Gamma')} d_\Gamma\,d_{\Gamma'}\Big[2\,U_{\Gamma\Gamma'}^{(1)^2}\,\tilde{\lambda}_{1\Gamma\Gamma'}^2+\frac{1}{8}\,U_{\Gamma\Gamma'}^{(2)^2}\,\Big(\tilde{\lambda}_{2l\Gamma\Gamma'}^2+2\,\tilde{\lambda}_{2t\Gamma\Gamma'}^2\Big)\Big]\times\Big(\hat{B}_{\Gamma\Gamma' n}(\boldsymbol{k}_{\rm F})+\hat{C}_{\Gamma\Gamma' n}(\boldsymbol{k}_{\rm F})\Big)\,. \tag{I.7}$$

$\hat{B}_{\Gamma\Gamma' n}(\boldsymbol{k}_{\rm F})$ and $\hat{C}_{\Gamma\Gamma' n}(\boldsymbol{k}_{\rm F})$ are defined by Eqs. (I.2) and (I.3) in which L and L' have been replaced by their irreducible representations Γ and Γ'.

Taking average over the Fermi surface, we obtain the average quasiparticle weight Z, Eq. (5.125) as follows.

$$Z = 1 + \frac{\overline{\delta(N\langle\tilde{O}_i^\dagger\tilde{n}_{kn\sigma}\tilde{O}_i\rangle_0)_{k_{\rm F}}}}{1+\langle\tilde{O}_i{}^\dagger\tilde{O}_i\rangle_0}\,, \tag{I.8}$$

$$\overline{\delta(N\langle\tilde{O}_i^\dagger\tilde{n}_{kn\sigma}\tilde{O}_i\rangle_0)_{k_{\rm F}}} = -\sum_{\Gamma}\Big[\,d_\Gamma U_{\Gamma\Gamma}^{(0)^2}\,\tilde{\lambda}_{0\Gamma\Gamma}^2 + 2\,d_\Gamma\,(d_\Gamma-1)\,U_{\Gamma\Gamma}^{(1)^2}\,\tilde{\lambda}_{1\Gamma\Gamma}^2 + \frac{1}{8}\,d_\Gamma\,(d_\Gamma-1)\,U_{\Gamma\Gamma}^{(2)^2}\,\Big(\tilde{\lambda}_{2l\Gamma\Gamma}^2+2\,\tilde{\lambda}_{2t\Gamma\Gamma}^2\Big)\Big]\times\Big(\bar{B}_{\Gamma\Gamma n}(\boldsymbol{k}_{\rm F})+\bar{C}_{\Gamma\Gamma n}(\boldsymbol{k}_{\rm F})\Big) - \sum_{(\Gamma,\Gamma')} d_\Gamma\,d_{\Gamma'}\Big[2\,U_{\Gamma\Gamma'}^{(1)^2}\,\tilde{\lambda}_{1\Gamma\Gamma'}^2+\frac{1}{8}\,U_{\Gamma\Gamma'}^{(2)^2}\,\Big(\tilde{\lambda}_{2l\Gamma\Gamma'}^2+2\,\tilde{\lambda}_{2t\Gamma\Gamma'}^2\Big)\Big]\times\Big(\bar{B}_{\Gamma\Gamma' n}(\boldsymbol{k}_{\rm F})+\bar{C}_{\Gamma\Gamma' n}(\boldsymbol{k}_{\rm F})\Big)\,. \tag{I.9}$$

Here $\bar{B}_{\Gamma\Gamma' n}(\boldsymbol{k}_{\rm F})$ and $\bar{C}_{\Gamma\Gamma' n}(\boldsymbol{k}_{\rm F})$ are defined by

$$\bar{B}_{\Gamma'\Gamma n}(\boldsymbol{k}_{\rm F}) = \overline{|u_{\Gamma n}(\boldsymbol{k}_{\rm F})|^2}\,B_{\Gamma'\Gamma}(\epsilon_{\rm F}) + \overline{|u_{\Gamma' n}(\boldsymbol{k}_{\rm F})|^2}\,B_{\Gamma\Gamma'}(\epsilon_{\rm F})\,, \tag{I.10}$$

$$\bar{C}_{\Gamma\Gamma' n}(\boldsymbol{k}_{\rm F}) = \overline{|u_{\Gamma n}(\boldsymbol{k}_{\rm F})|^2}\,C_{\Gamma'\Gamma}(\epsilon_{\rm F}) + \overline{|u_{\Gamma' n}(\boldsymbol{k}_{\rm F})|^2}\,C_{\Gamma\Gamma'}(\epsilon_{\rm F})\,. \tag{I.11}$$

The average amplitude of eigenvector $\overline{|u_{\Gamma n}(\boldsymbol{k}_{\rm F})|^2}$ is obtained as follows.

$$\overline{|u_{\Gamma n}(\boldsymbol{k}_{\rm F})|^2} = \frac{\sum_{kn}^{\epsilon_{\rm F}\langle\epsilon_{kn}\langle\epsilon_{\rm F}+\Delta}|u_{\Gamma n}(\boldsymbol{k})|^2}{\sum_{kn}^{\epsilon_{\rm F}\langle\epsilon_{kn}\langle\epsilon_{\rm F}+\Delta}} = \frac{\rho_\Gamma(\epsilon_{\rm F})}{\rho(\epsilon_{\rm F})}\,. \tag{I.12}$$

Here $\rho_\Gamma(\epsilon_{\rm F})$ ($\rho(\epsilon_{\rm F})$) is the partial (total) density of states at the Fermi level $\epsilon_{\rm F}$.

The projected momentum distribution function (MDF) is defined by

$$\langle n_{kL\sigma}\rangle = \sum_n \langle n_{kn\sigma}\rangle |u_{Ln\sigma}(\boldsymbol{k})|^2\,. \tag{I.13}$$

Using the formula (B.29), we obtain the expression of the projected MDF, Eq.(5.126):

$$\langle n_{kL\sigma}\rangle = f(\tilde{\epsilon}_{kL\sigma}) + \frac{N\langle\tilde{O}_i^\dagger\tilde{n}_{kL\sigma}\tilde{O}_i\rangle_0}{1+\langle\tilde{O}_i{}^\dagger\tilde{O}_i\rangle_0}\,. \tag{I.14}$$

The correlation correction of the projected MDF at the rhs is expressed as follows after taking the average over $\boldsymbol{k}$ with constant energy ϵ_{kL} as in Eq. (I.12).

$$
\begin{aligned}
N\langle\tilde{O}_i^\dagger\tilde{n}_{kL\sigma}\tilde{O}_i\rangle_0 = \frac{D\,\rho_\Gamma(\epsilon_{kL})}{\rho(\epsilon_{kL})}\sum_{\Gamma'}\Big[&d_{\Gamma'}\,U^{(0)^2}_{\Gamma'\Gamma'}\,\tilde{\lambda}^2_{0\Gamma'\Gamma'} + 2\,d_{\Gamma'}\,(d_{\Gamma'}-1)\,U^{(1)^2}_{\Gamma'\Gamma'}\,\tilde{\lambda}^2_{1\Gamma'\Gamma'} \\
&+\frac{1}{8}\,d_{\Gamma'}\,(d_{\Gamma'}-1)\,U^{(2)^2}_{\Gamma'\Gamma'}\Big(\tilde{\lambda}^2_{2l\Gamma'\Gamma'}+2\,\tilde{\lambda}^2_{2t\Gamma'\Gamma'}\Big)\Big] \\
&\times\frac{\rho_{\Gamma'}(\epsilon_{kL})}{\rho(\epsilon_{kL})}\Big(B_{\Gamma'\Gamma'}(\epsilon_{kL})\,f(-\tilde{\epsilon}_{kL}) - C_{\Gamma'\Gamma'}(\epsilon_{kL})\,f(\tilde{\epsilon}_{kL})\Big) \\
+\frac{D\,\rho_\Gamma(\epsilon_{kL})}{\rho(\epsilon_{kL})}\sum_{(\Gamma',\Gamma'')}&d_{\Gamma'}\,d_{\Gamma''}\Big[2\,U^{(1)^2}_{\Gamma'\Gamma''}\,\tilde{\lambda}^2_{1\Gamma'\Gamma''}+\frac{1}{8}\,U^{(2)^2}_{\Gamma'\Gamma''}\,\Big(\tilde{\lambda}^2_{2l\Gamma'\Gamma''}+2\,\tilde{\lambda}^2_{2t\Gamma'\Gamma''}\Big)\Big] \\
&\times\Big[\frac{\rho_{\Gamma'}\,(\epsilon_{kL})}{\rho(\epsilon_{kL})}\Big(B_{\Gamma''\Gamma'}(\epsilon_{kL})\,f(-\tilde{\epsilon}_{kL}) - C_{\Gamma''\Gamma'}(\epsilon_{kL})\,f(\tilde{\epsilon}_{kL})\Big) \\
&+\frac{\rho_{\Gamma''}(\epsilon_{kL})}{\rho(\epsilon_{kL})}\Big(B_{\Gamma'\Gamma''}(\epsilon_{kL})\,f(-\tilde{\epsilon}_{kL}) - C_{\Gamma'\Gamma''}(\epsilon_{kL})\,f(\tilde{\epsilon}_{kL})\Big)\Big]\,. \qquad \text{(I.15)}
\end{aligned}
$$

This is the explicit expression of the numerator of the second term of Eq. (5.126).

With use of Eqs. (I.14) and (I.15), the partial quasiparticle weight Z_L is given by Eq. (5.128):

$$
Z_L = 1 + \frac{\overline{\delta(N\langle\tilde{O}_i^\dagger\tilde{n}_{kL\sigma}\tilde{O}_i\rangle_0)}_{k_{\rm F}}}{1+\langle\tilde{O}_i{}^\dagger\tilde{O}_i\rangle_0}\,, \qquad \text{(I.16)}
$$

and the explicit expression of the numerator of the correlation correction is given as follows.

$$
\begin{aligned}
\overline{\delta(N\langle\tilde{O}_i^\dagger\tilde{n}_{kL\sigma}\tilde{O}_i\rangle_0)}_{k_{\rm F}} = -\sum_{\Gamma}\Big[&d_\Gamma\,U^{(0)^2}_{\Gamma\Gamma}\,\tilde{\lambda}^2_{0\Gamma\Gamma} + 2\,d_\Gamma\,(d_\Gamma-1)\,U^{(1)^2}_{\Gamma\Gamma}\,\tilde{\lambda}^2_{1\Gamma\Gamma} \\
&+\frac{1}{8}\,d_\Gamma\,(d_\Gamma-1)\,U^{(2)^2}_{\Gamma\Gamma}\,\Big(\tilde{\lambda}^2_{2l\Gamma\Gamma}+2\,\tilde{\lambda}^2_{2t\Gamma\Gamma}\Big)\Big]\times\frac{\rho_\Gamma(\epsilon_{\rm F})}{\rho(\epsilon_{\rm F})}\,\Big(B_{\Gamma\Gamma}(\epsilon_{\rm F})+C_{\Gamma\Gamma}(\epsilon_{\rm F})\Big) \\
-\sum_{(\Gamma,\Gamma')}&d_\Gamma\,d_{\Gamma'}\Big[2\,U^{(1)^2}_{\Gamma\Gamma'}\,\tilde{\lambda}^2_{1\Gamma\Gamma'}+\frac{1}{8}\,U^{(2)^2}_{\Gamma\Gamma'}\,\Big(\tilde{\lambda}^2_{2l\Gamma\Gamma'}+2\,\tilde{\lambda}^2_{2t\Gamma\Gamma'}\Big)\Big] \\
&\times\Big[\frac{\rho_\Gamma(\epsilon_{\rm F})}{\rho(\epsilon_{\rm F})}\,\Big(B_{\Gamma'\Gamma}(\epsilon_{\rm F})+C_{\Gamma'\Gamma}(\epsilon_{\rm F})\Big)+\frac{\rho_{\Gamma'}(\epsilon_{\rm F})}{\rho(\epsilon_{\rm F})}\,\Big(B_{\Gamma\Gamma'}(\epsilon_{\rm F})+C_{\Gamma\Gamma'}(\epsilon_{\rm F})\Big)\Big]\,. \qquad \text{(I.17)}
\end{aligned}
$$

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