METHODOLOGICAL STUDY OF COMPUTATIONAL APPROACHES TO ADDRESS THE PROBLEM OF STRONG CORRELATIONS.

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ABSTRACT OF THE DISSERTATION

Methodological study of computational approaches to address the problem of strong correlations.

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The main focus of this thesis is the detailed investigation of computational methods to tackle strongly correlated materials in which a rich variety of exotic phenomena are found.

A many-body problem with sizable electronic correlations can no longer be explained by independent-particle approximations such as density functional theory (DFT) or tightbinding approaches. The influence of an electron to the others is too strong for each electron to be treated as an independent quasiparticle and consequently those standard band-structure methods fail even at a qualitative level.

One of the most powerful approaches for strong correlations is the dynamical meanfield theory (DMFT), which has enlightened the understanding of the Mott transition based on the Hubbard model. For realistic applications, the dynamical mean-field theory is combined with various independent-particles approaches. The most widely used one is the DMFT combined with the DFT in the local density approximation (LDA), so-called LDA+DMFT. In this approach, the electrons in the weakly correlated orbitals are calculated by LDA while others in the strongly correlated orbitals are treated by DMFT. Recently, the method combining DMFT with Hedin's GW approximation was also developed, in which the momentum-dependent self-energy is also added. In this thesis, we discuss the application of those methodologies based on DMFT. First, we apply the dynamical mean-field theory to solve the 3-dimensional Hubbard model in Chap. 3. In this application, we model the interface between the thermodynamically coexisting metal and Mott insulator. We show how to model the required slab geometry and extract the electronic spectra. We construct an effective Landau free energy and compute the variation of its parameters across the phase diagram. Finally, using a linear mixture of the density and double-occupancy, we identify a natural Ising order parameter which unifies the treatment of the bandwidth and filling controlled Mott transitions.

Secondly, we study the double-counting problem, a subtle issue that arises in LDA+DMFT. We propose a highly precise double-counting functional, in which the intersection of LDA and DMFT is calculated exactly, and implement a parameter-free version of the LDA+DMFT that is tested on one of the simplest strongly correlated systems, the H2 molecule. We show that the exact double-counting treatment along with a good DMFT projector leads to very accurate and total energy and excitation spectrum of H_2 molecule.

Finally, we implement various versions of GW+DMFT, in its fully self-consistent way, one shot GW approximation, and quasiparticle self-consistent scheme, and studied how well these combined methods perform on H₂ molecule as compared to more established methods such as LDA+DMFT. We found that most flavors of GW+DMFT break down in strongly correlated regime due to causality violation. Among GW+DMFT methods, only the selfconsistent quasiparticle GW+DMFT with static double-counting, and a new method with causal double-counting, correctly recover the atomic limit at large H-atom separation. While some flavors of GW+DMFT improve the single-electron spectra of LDA+DMFT, the total energy is best predicted by LDA+DMFT, for which the exact double-counting is known, and is static.

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Dedication

To my parents,

who always encouraged me to go on every adventure and keeped me on the right path.

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Chapter 1

Introduction

The discovery of quantum mechanics in the early 20th century opened a completely different viewpoint toward small scales and low energy of atom atom and subatomic particles. From this fundamental microscopic theory, condensed matter physics has long sought to understand the macroscopic properties of systems such as heat capacity, magnetism and electric conductivity of materials. Nowadays, the field encompasses a wide range of phenomena in solids including high Tc superconductivity, topological insulator and metal-insulator transition.

The development of condensed matter physics is tied to the interplay between experimental and theoretical approaches. Experiment continues to raise questions based on new observations owing to the development of fine technologies. For example, technologies such as molecular beam epitaxy (MBE) now allow experimentalists to synthesize two-dimensional materials, which is a whole zoo of exotic phenomena of low energy physics. These experimental observations then stimulate the development of theories which provide new frameworks explaining such behaviors.

From the theoretical perspective, condensed matter physics is all about reasonable approximations to the exact solution, which is impossible to solve in most cases. For example, in the Hartree-Fock (HF) approximation, the correlation effect is completely neglected (by definition that the correlation energy is the exact energy minus the HF energy) where the band gaps are severely overestimated. In the local density approximation (LDA), one of the density functional theorem (DFT) schemes, the local electron density at each point in the space is mapped onto the degenerate electronic gas and the exchange-correlation is taken by that of the local electronic gas at the point. Therefore the spatial fluctuation is totally frozen.



Figure 1.1: Half-filled (one electron per site) 1-dimensional Hubbard model. When t >> U, the kinetic energy is so substantial that electrons behaves like independent particles and therefore occupy N/2 states of the s-band (wave-like). On the other hand, in the regime U >> t, the Coulomb interaction energy of a doubly-occupied site is too costly that electrons do not jump into other site (particle-like)

Among theoretical approaches, the independent quasiparticle assumption is the most frequently used framework, which is a good approximation for weakly correlated materials. Those are materials where electrons are highly itinerant, i.e., electrons are quite delocalized over the solid. In such cases, electrons can be depicted as wave-like independent quasiparticles. In such systems, the kinetic energy of electrons dominates the interaction energy. The most frequently used and notable method, density functional theory (DFT), where the electron-electron interaction is incorporated as a static mean-field, has successfully predicted physical properties of these class of materials. In molecular systems, Hartree-Fock (HF) is considered a good approximation for orbital energy calculation.

The independent-particle approximation is very intuitive and has been used as a primitive basis to determine whether given materials are metals, insulators or semi-conductors. However, in materials containing partially filled d- or f- orbitals, the Coulomb interaction between electrons is so strong that the independent-particle picture simply breaks down. These materials are often called *strongly correlated systems*.

Let us imagine a one-dimensional chain model with one electron per site (Fig. 1.1). We allow electrons to move from one site to another with the transfer matrix t and require the



Figure 1.2: Schematic representation of the energy level for a Mott-Hubbard insulator. [1]

onsite Coulomb energy U

$$U = \int d\mathbf{r}_1 \int d\mathbf{r}_2 |\phi(\mathbf{r}_1)|^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} |\phi(\mathbf{r}_2)|^2.$$
(1.1)

if two electrons occupy the same site. According to the band theory (independent-particle approximation), the underlying band is always half-filled no matter what the ratio U/t is. In the limit $t \ll U$, this is a correct picture and we can calculate the effect of on-site interaction U using perturbation theory with the ground state as the Bloch solution (wave-like). In the limit $U/t \gg 1$, however, two electrons occupying the same site cost so much energy (U) that the charge transfer process is suppressed. Therefore, in this limit, we should conclude that the system becomes an insulator that contradicts the prediction of the band theory.

This phenomena is known as "Mott transition" that was first recognized in 1937 [2]. It can be found in a variety of transition metal oxides. For example, Peierls used the above argument to explain the reason for NiO to be an insulator. In NiO, each Ni²⁺ ion keeps 8 *d*-electrons out of 10 vacancies in *d*-orbital but charge transfer does not occur because of large Coulomb interaction which splits the 3*d*-band with the energy gap U - 2tz where z is the number of nearest neighbors. (Fig. 1.2 [1]) The most interesting case arises when the kinetic energy and Coulomb interaction energy of a system are comparable to each other. In this middle regime, electrons exhibit both itinerant and localized behaviors, giving rise to numerous fascinating phenomena such as heavy fermions, Mott-Hubbard metal insulator transitions and High Tc superconductivity. At the same time, this is the most difficult regime to solve because one should approach the problem with a mixed representation of local basis and Bloch wavefunction to properly describe the wave-particle duality.

Among many theoretical developments to deal with strongly correlated systems, the dynamical mean-field theory (DMFT) [3, 4] has been very successful. Due to its non-perturbative nature it was able to describe the phenomena of the first order metal insulator transition even in its most simplistic form of the single band Hubbard model [4]. With realistic extension, DMFT has been combined with DFT within the LDA framework (LDA+DMFT). This combination of LDA and DMFT has been very successful in describing materials with open d and f shells both for their spectral properties, as well as computing total energy [5] and free energy [6] of crystal phases. Recently, DMFT has also been successfully applied to molecules [7, 8].

Instead of LDA, Hedin's GW approximation has been also suggested to combine with DMFT to give a momentum-dependent self-energy to the system. Furthermore, since GW is a diagrammatic method based on Green's function formalism, it can easily interface with DMFT without the double-counting issue, which indicates it can be a possibly better alternative to LDA+DMFT.

In this thesis, we will mainly discuss the methodologies based on dynamical mean-field theory and its applications. In Chapter 2, the main idea of dynamical mean-field theory (DMFT) is discussed in the limit of large dimension and we will derive the self-consistent DMFT equations based on the Hubbard model. We will also introduce the idea of mapping the local site onto an auxiliary impurity system and briefly discuss one of the most powerful impurity solvers, continuous time quantum Monte-Carlo (CTQMC). In Chapter 3, we will present our recent work on 3-dimensional Hubbard model, where we model the interface between the thermodynamically coexisting metal and Mott insulator and solve the problem based on the DMFT framework. In Chapter 4, the general derivation of LDA+DMFT will be

discussed as well as the double-counting issue. We will finally discuss the general formalism of GW+DMFT and give a detailed comparison between various types of GW+DMFT in Chapter 5.

Chapter 2

Dynamical Mean-Field Theory

This chapter is devoted to dynamical mean-field theory (DMFT), the central theme of this article. DMFT is a method to determine the physics of correlated electrons in solids. In the materials where electrons are strongly correlated, independent-quasiparticle approximation, which is the basis of conventional band theory techniques such as density functional theory, breaks down. DMFT provides a non-perturbative treatment for correlated electrons, which can apply not only to the fermi gas limit (band theory) and the atomic limit (t-J model and etc), but also to the middle regime where kinetic and interaction energy compete within a single framework.

Historically, there were two major steps for its formulation. First of all, Vollhardt and Metzner [9] introduced the infinite lattice coordination limit to the many-body lattice problem. In such a limit, they found that the diagrammatic analysis becomes substantially simpler while the competition between the local interaction and kinetic term is still retrained to give a qualitative picture of the 3-dimensional Hubbard model.

A second significant step was achieved by Kotliar and Georges [3] who mapped the a lattice Hubbard model onto the Anderson impurity model that consists of interacting local degrees of freedom in a non-interacting bath. This self-consistent mapping of local site onto an auxiliary impurity is the essential basis of the dynamical mean-field theory. It allowed theorists to develop and solve a wide range of models on the lattice based on both analytic and numerical approaches such as continuous-time quantum Monte-Carlo (CTQMC) that was developed to solve the Anderson impurity model (AIM).

In this chapter, we will explore the basic construction of the dynamical mean-field theory and how it can be solved by mapping the lattice problem onto an auxiliary impurity system. In the technical sense, the DMFT approach approximates the self-energy to be a local quantity. Using scaling analysis, we will show how the large lattice coordination number (or a hypercubic lattice in the high dimension) leads to the local self-energy approximation.

2.1 Archetype: Mean-field theory for Ising model

Mean-field theory is one of the feasible techniques for many-body problems, which gives a qualitative description for classical and quantum systems. A many-body problem is in general very hard to solve because too many degrees of freedom are interacting with each other. Mean-field theory typically approximates the effect of all other particles on a given individual as an averaged field, thus reduces the many-body problem to an effective onebody problem.

Although it is used widely, the term is rather vague because of no unique way of constructing a mean-field approximation. One of the well-established ways for lattice system is to take an advantage the limit of large coordination number z (number of nearest neighbors). This way of mean-field approximation turns the lattice problem into an effective single-site problem. The key idea is to approximate the local dynamics by the single-site interacting with the effective bath caused by the rest of the crystal.

To give a good intuition, we shall analyze a mean-fielt theory for the Ising model, which is treated as a classical counterpart of dynamical mean-field theory for quantum many-boday lattice problems.

The mean-field approach The Ising model with nearest-neighbor interaction is illustrated by the following Hamiltonian:

$$H = -J\sum_{\langle ij\rangle} s_i s_j - h\sum_i s_i, \qquad (2.1)$$

where the system is ferromagnetic (J > 0) and the *h* is an external magnetic field uniformly applied to this system. Let us focus on the local dynamics of a particular single-site *o*. A mean-field approach suggests regarding the local magnetic field as the thermally-averaged magnetic field generated by nearest neighbors. Therefore, h_{eff} is described as:

$$h_{\text{eff}} = J \sum_{i} \langle s_i \rangle + h = z J m + h, \qquad (2.2)$$

where z is the coordination number of the site and we used translational invariance $\langle s_i \rangle = m$). This approximation is completely justified when $z \to \infty$ by the general statistical rule that the fluctuation of random variables falls off as 1/z. Then, the local dynamics of a single-site is governed by the effective local Hamiltonian H_{loc} and its partition function Z_{loc} :

$$H_{loc} = -s_0 h_{\text{eff}} \tag{2.3}$$

$$Z_{loc} = \cosh\left(\beta h_{\text{eff}}\right) \tag{2.4}$$

From the statistical mechanics point of view, the local magnetization $\langle s_o \rangle = m$ is regained by

$$m = -\frac{\partial}{\partial h_{\text{eff}}} f \Big|_{h_{\text{eff}}=0} = \frac{1}{\beta} \frac{\partial}{\partial h_{\text{eff}}} \ln Z_{loc} \Big|_{h_{\text{eff}}=0} = \tanh(\beta h_{\text{eff}})$$

= $\tanh\beta(zJm+h).$ (2.5)

Therefore, local magnetization can be determined by this self-consistent equation. It is easily noted that in the limit of $z \to \infty$, J has to be properly scaled by $J = J^*/z$, fixing J^* to a finite value in order to prevent the blow-up of the free-energy per site. The Hubbard - Stratonovich transformation [10] actually uses this scaled $J = J^*/z$ to show that the solution of Ising model exactly coincides with that of mean-field theory in the $z \to \infty$ limit, in which mean-field theory is justified.

2.2 Dynamical mean-field approach for correlated electrons in lattice

2.2.1 Hubbard model

One of the simplest model for correlated electrons in solids is the single-band Hubbard model which has been widely used to describe exotic phenomena such as Mott transition and high temperature superconductivity of strongly correlated correlated systems. Electrons in this model are described by only two terms, the transfer matrix t (hopping) and the onsite Coulomb interaction U when two electrons occupy the same site, which can be written as

$$H = -t \sum_{\langle ij \rangle, \sigma} (c_{i\sigma}^{\dagger} c_{j\sigma} + h.c) + \sum_{i} U \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} - \mu \sum_{i} c_{i\sigma}^{\dagger} c_{i\sigma}.$$
(2.6)

where $c_{i\sigma}^{\dagger}(c_{i\sigma})$ is a creation (annihilation) operator of electrons with spin σ at the site *i*.

The competition between the kinetic energy and Coulomb interaction in the Hubbard model captures the key feature of strongly correlated materials. When the second term (U) is very small, the tight-binding solution dominates the physics and the second term U only comes as perturbation, leading to quasi-particle with small shifted energy. On the other hand, in the limit where U/t >> 1, t acts as perturbation on the isolated magnetic moment leading to t-J model, giving rise to many interesting magnetic structure, such as ferromagnetic, antiferromagnetic depending on the exact solutions of the model.

Despite its simple structure, it is very difficult to solve the Hubbard model in the regime where $U/t \sim 1$. As mean-field solution of the Ising model becomes exact in the large coordination number limit, our goal is to develop a similar argument for many-body lattice problems such as a Hubbard model.

Quantum theories for many-body problems generally relies on the Green function. A Green function can be written in real and imaginary time axis but in this article, since most of the implementation is based on the imaginary time and Matsubara frequency a finite temperature, we will focus on the imaginary time formalism.

The (imaginary) time-ordered single-particle Green's function $G_{\alpha\beta}(\tau - \tau')$ is defined as

$$G_{\alpha\beta}(\tau) = -\langle Tc_{\alpha}(\tau)c_{\beta}^{\dagger}(0)\rangle \tag{2.7}$$

where T denotes a *time ordering* operator. The Green's function can be then interpreted as the probability amplitude of between particles (for $\tau > 0$) or holes (for $\tau > 0$) in an equilibrium state.

Not only does the single particle Green's function serve as the smallest building block of



Figure 2.1: The Cayley tree for connectivity z = 3. One can imagine $z \rightarrow \infty$ for the Bethe lattice.

perturbation expansion, we can also directly calculate numerous important physical observables from it. For example, the electronic density ρ , total electronic energy E and spectral function $A_k(\omega)$ of the system are given by (See Ref. [11]),

$$\rho(\mathbf{r},\mathbf{r}') = \langle \psi^{\dagger}(\mathbf{r})\psi(\mathbf{r}')\rangle = -G(\mathbf{r},\mathbf{r}';\tau=0^{-}) = -T\sum_{i\omega}e^{i\omega_{n}0^{+}}G(\mathbf{r},\mathbf{r}';i\omega_{n}), \qquad (2.8)$$

$$E = \operatorname{Tr}(H_0\rho) + \frac{1}{2}\operatorname{Tr}(\Sigma G)$$
(2.9)

$$A(\mathbf{r}, \mathbf{r}'; \omega) = -\frac{1}{\pi} \operatorname{Im} G(\mathbf{r}, \mathbf{r}'; \omega + i0^{+}).$$
(2.10)

where the self-energy Σ can be also obtained by the Dyson equation $G^{-1} = G_0^{-1} - \Sigma$.

2.2.2 Proper scaling of coupling constant in infinite coordination lattice

We saw in the semi-classical Ising model that the coupling constant should be scaled as $J = J_*/z$ and the mean-field solution becomes exact as $z \rightarrow \infty$. Now it is natural to ask what is the proper scaling for the coupling constant in the fully quantum-mechanical lattice models.

To give an insight, let us consider the Hubbard model in the Bethe lattice with U = 0to see what the Green's function of the simple tight-binding Hamiltonian in the $z \rightarrow \infty$ limit looks like. The Bethe lattice is a Cayley tree with the infinite connectivity as depicted in the Fig. 2.1. As it will turn out shortly, we claim that the appropriate scaling for the nearest hopping parameter is $t = -t_*/\sqrt{z}$. The on-site Green's function of a given site is then written

$$G_{00}^{-1}(\xi) = \xi - \frac{t_*^2}{z} \sum_{j=1}^{z} \tilde{G}_{jj}^{(0)}(\xi)$$
(2.11)

where the summation is over the nearest neighbors of the site 0 and $\tilde{G}_{jj}^{(0)}$ is the local green's function at site j with the site 0 removed. When the coordination number z goes to infinity, we have $\tilde{G}_{jj}^{(0)} \sim G_{jj} = G_{00}$ and the equation becomes self-consistent:

$$G_{00}^{-1}(\xi) = \xi - t_*^2 G_{00}(\xi), \qquad (2.12)$$

whose analytic solution is

$$G_{00}(\xi) = \frac{1}{2t_*^2} (\xi - \sqrt{\xi^2 - 4t_*^2}).$$
(2.13)

In the solution, the sign is chosen in the way that $G_{00}(\xi) \rightarrow 0$ as $|\xi| \rightarrow \infty$. One can see that the self-consistent equation and its solution above can be justified due to the scaling of $t \rightarrow t_*/z$.

Another illustration for this scaling can be discussed in the d-dimensional hyperlattice with nearest neighbor hopping at $d \to \infty$ where the dispersion is given by $\varepsilon_k = -2t \sum_{n=1}^d \cos(k_n)$. First, we can think of a random variable $X_n = \sqrt{2} \cos k_n$ with uniform distribution $k_i \in$ $[-\pi, \pi]$. Note that the mean is $\int_{-\pi} \pi \frac{dk_i}{2\pi} X_i = 0$ and the variance $\int_{-\pi} \pi \frac{dk_i}{2\pi} X_i^2 = 1$. Since each X_n can be thought of as an independent and identical distribution (i.i.d.), from central limit theorem $\bar{X} = \frac{1}{\sqrt{d}} \sum_{n=1}^d X_n$ should follow a normal distribution N(0, 1) in the limit of $d \to \infty$. Since the density of state can be thought of as the distribution function of $\varepsilon_k = -t\sqrt{2d}\bar{X}$, with the scaling $t = t_*/\sqrt{2d}$, we can write down a finite density of state

$$\rho(\varepsilon) = \frac{1}{\sqrt{2\pi}t_*} \exp\left[-\frac{\varepsilon^2}{2t_*^2}\right].$$
(2.14)

Since the Green's function is the probability amplitude between two electronic states, the leading order of Green's function between two nearest sites i, j is proportional to the hopping parameter t: $G_{ij} \sim t \sim 1/\sqrt{d}$. In general, it can be proven for any i, j that (see Ref. [4])

$$G_{ij} \sim O(1/d^{\frac{|i-j|}{2}})$$
 (2.15)



Figure 2.2: An example of the 2nd-order self-energy component.

where |i - j| is Manhattan metric which counts the number of hops between i and j site. It is important to note that although the propagator between two sites vanishes as $1/\sqrt{d}$, the electron is not localized at a site due to the infinite number of nearest sites. Indeed, the probability to jump from a site 0 to the nearest neighbor j is $\sum_{j=1}^{z} |G_{0j}|^2 \sim O(1)$.

2.2.3 Simplification of diagrams in the $d \rightarrow \infty$ limit

Now, using the scaling property we derived above, let us consider irreducible single-particle self-energy that connects i and j site, $\Sigma_{ij}(i\omega)$. In the Fig 2.2, we present a second order diagram for example. Dots denote the corresponding on-site vertices while the lines represent the propagator between two sites. The site i and j is connected by three propagators in the second-order diagram, which means this diagram scales as $O(1/d^{3/2})$ or even smaller. Therefore, it is at least a factor $\frac{1}{d}$ smaller than the direct propagator that connects i and j site. Thus, non-local amputated diagrams should vanish as the factor $\frac{1}{z}$. Since it becomes even smaller in the higher order terms, we conclude that any non-local components of the self-energy in the large d limit is excluded and only local skeleton terms survive, namely, the self-energy becomes momentum independent:

$$\Sigma_{ij} = \delta_{ij} \Sigma_{ii} \text{ or } \Sigma_k = \Sigma_{ii}. \tag{2.16}$$

In the limit of infinite dimension, therefore, the self-energy becomes local quantity which can be solely determined by other local quantities such as the local Green's function (equivalently, a dynamical Weiss-field as we shall see later in the section) and local interaction.

Based on one-band Hubbard model with the local self-energy, we can simply obtain the self-consistent equation for local Green's function. Since the Green's function is given by $G_k(i\omega)^{-1} = (i\omega) + \mu - \varepsilon_k - \Sigma$, the local Green's function is given by the Hilbert transformation

$$G(i\omega) = \tilde{D}(\xi) \equiv \int_{-\infty}^{\infty} d\varepsilon D(\varepsilon) \frac{1}{\xi - \varepsilon}$$
(2.17)

where $\xi = i\omega + \mu - \Sigma(i\omega)$. We define the inverse transformation R such that

$$R[\tilde{D}(\xi)] = R[G] = \xi.$$
(2.18)

For the Bethe lattice, from (2.13) and $D(\varepsilon) = -\frac{1}{\pi} \text{Im}G(\varepsilon + i0^+) = \sqrt{4t_*^2 - \varepsilon^2}/2\pi t_*^2$, one can easily show that

$$\tilde{D}(\xi) = \frac{1}{2t_*^2} (\xi - \sqrt{\xi^2 - 4t_*^2}).$$
(2.19)

Then by simply solving with respect to ξ , we can obtain the inverse transformation

$$R[G] = t_*^2 G + \frac{1}{G} = \xi = i\omega + \mu - \Sigma(i\omega)$$
(2.20)

and clearly the self-energy is obtained only from the local (interacting) Green's function G.

2.2.4 Derivation of DMFT effective action: Reduction to a single-site problem

In order to formulate the mean-field theory for correlated lattice system similar to what we did for Ising model, we need to derive an effective action of a local site by integrating out the degrees of freedom of all other sites. We will develop this procedure for the case of a single-band Hubbard model using the scaling analysis in the previous section. The partition function of the system in the language of functional integral is written as

$$Z = \int \prod_{i\sigma} D\bar{c}_{i\sigma} Dc_{i\sigma} \exp(-S[\bar{c}_{i\sigma}, c_{i\sigma}])$$
(2.21)

where the index i denotes the site number. The imaginary-time action S within the functional integral formalism is

$$S = \int_0^\beta d\tau \left[\sum_{i,\sigma} \bar{c}_{i\sigma}(\tau) \left(\frac{d}{d\tau} - \mu \right) c_{i\sigma}(\tau) + H[\bar{c}(\tau), c(\tau)] \right]$$
(2.22)



Figure 2.3: The lattice model divided into the three parts: the local site (S_0) , the hybridization (S_{hyb}) and the cavity (S_{cavity}) .

where the $\bar{c}(\tau), c(\tau)$ follow Grassmann algebra. *H* is the Hamiltonian of the one band Hubbard model

$$H[\bar{c}_{i\sigma}, c_{i\sigma}] = -t \sum_{\langle ij \rangle, \sigma} (\bar{c}_{i\sigma}c_{j\sigma} + h.c) + \sum_{i} U n_{i\uparrow} n_{i\downarrow}.$$
(2.23)

Since we eventually want to derive the effective action for a local site (denote it as 0th site), we divide the system into the local site, the cavity, which is the lattice with the 0th site removed, and the hybridization between them. Therefore we write down the action as $S = S_0 + S_{\text{cavity}} + S_{\text{hyb}}.$ Each of the components is written as

$$S_0 = \int_0^\beta d\tau \left[\bar{c}_{0\sigma} (\frac{d}{d\tau} - \mu) c_{0\sigma} + U n_{0\uparrow} n_{0\downarrow} \right]$$
(2.24)

$$S_{\text{cavity}} = \int_{0}^{\beta} d\tau \left[\sum_{i \neq 0, \sigma} \bar{c}_{i\sigma} (\frac{d}{d\tau} - \mu) c_{i\sigma} - t \sum_{\langle i, j \neq 0 \rangle, \sigma} (\bar{c}_{i\sigma} c_{j\sigma} + h.c) + \sum_{i \neq 0, \sigma} U n_{i\uparrow} n_{i\downarrow} \right]$$
(2.25)

$$S_{\text{hyb}} = \int_0^\beta d\tau \bigg[-t \sum_{\langle i \neq 0 \rangle, \sigma} (\bar{c}_{i\sigma} c_{0\sigma} + h.c) \bigg].$$
(2.26)

To integrate out degrees of freedom of the cavity, we rewrite the partition function as

$$Z = \int D\bar{c}_{0\sigma} Dc_{0\sigma} \exp(-S_0) \int \prod_{i \neq 0,\sigma} D\bar{c}_{i\sigma} Dc_{i\sigma} \exp(-S_{\text{cavity}} - S_{\text{hyb}}).$$
(2.27)

In the functional integral for cavity degrees of freedom, $\bar{c}_{0\sigma}$, $c_{0\sigma}$ in S_{hyb} serve as source terms. Using the perturbation theory (the linked-cluster theorem) with S_{cavity} as the unperturbed action, we can evaluate the second integral as

$$\int \prod_{i \neq 0,\sigma} D\bar{c}_{i\sigma} Dc_{i\sigma} \exp(-S_{\text{cavity}} - S_{\text{hyb}}) = Z_{\text{cavity}} \exp(-\Delta S[\bar{c}_{0\sigma}, c_{0\sigma}])$$
(2.28)

where the Z_{cavity} is the partition function of the cavity. ΔS is by definition

$$\Delta S[\bar{c}_{0\sigma}, c_{0\sigma}] = \sum_{n=1}^{\infty} \Delta S^{(n)} = \sum_{n=1}^{\infty} t^{2n} \sum_{i_1, \cdots, i_n, i'_1, \cdots, i'_n} \int_0^\beta \prod_{j=1}^n d\tau_j d\tau'_j$$
$$\bar{c}_{0\sigma}(\tau_1) \cdots \bar{c}_{0\sigma}(\tau_n) c_{0\sigma}(\tau'_1) \cdots c_{0\sigma}(\tau'_n) G^{(0)}_{i_1, \cdots, i_n, i'_1, \cdots, i'_n}(\tau_1, \dots, \tau_n; \tau'_1, \dots, \tau'_n). \quad (2.29)$$

where $G_{i_1,\dots,i_n,i'_1,\dots,i'_n}^{(0)}(\tau_1,\dots,\tau_n;\tau'_1,\dots,\tau'_n)$ is *n*-point connected Green's function of the fully interacting cavity with the indices $\{i_1,\dots,i_n,i'_1,\dots,i'_n\}$ being nearest neighbors of 0th site. The superscript (0) means that it is the cavity Green's function with 0th site removed.

Considering the scaling $t = t_*/\sqrt{z}$, only the one-particle cavity Green's functions (n = 1)survive in the limit of infinite coordination number, that is, $\Delta S = \Delta S^{(1)}$. Therefore, the effective action for the local quantity $\bar{c}_{0\sigma}$, $c_{0\sigma}$ is obtained by

$$S_{\text{eff}} = S_0 + \Delta S^{(1)}$$

= $-\int_0^\beta d\tau \int_0^\beta d\tau' \bar{c}_{0\sigma}(\tau) \mathcal{G}_0(\tau - \tau') c_{0\sigma}(\tau') + \int_0^\beta d\tau U n_{0\uparrow}(\tau) n_{0\downarrow}(\tau)$ (2.30)

where the Weiss-field \mathcal{G}_0 is defined as

$$\mathcal{G}_0^{-1}(\tau - \tau') = -\left(\frac{d}{d\tau} - \mu\right)\delta_{\tau\tau'} - \sum_{ij} t_{0i}^* G_{ij}^{(0)}(\tau - \tau')t_{j0}^*.$$
(2.31)

The second term of the last expression originates from the first order term (n=1) of Eq. (2.29). This construction of effective local action allows us to calculate any local observables solely with S_{eff} because

$$\langle A[\bar{c}_{0\sigma}, c_{0\sigma}] \rangle = \frac{\operatorname{Tr}\left[A[\bar{c}_{0\sigma}, c_{0\sigma}] \exp(-S)\right]}{\operatorname{Tr}\exp(-S)} = \frac{Z_{\operatorname{cavity}}\operatorname{Tr}\left[A[\bar{c}_{0\sigma}, c_{0\sigma}] \exp(-S_{\operatorname{eff}})\right]}{Z_{\operatorname{cavity}}\operatorname{Tr}\exp(-S_{\operatorname{eff}})}$$
$$= \frac{\operatorname{Tr}\left[A[\bar{c}_{0\sigma}, c_{0\sigma}] \exp(-S_{\operatorname{eff}})\right]}{\operatorname{Tr}\exp(-S_{\operatorname{eff}})} = \langle A[\bar{c}_{0\sigma}, c_{0\sigma}] \rangle_{\operatorname{eff}}.$$
(2.32)

Since we obtain the Weiss field for the case of Hubbard model, the next step is to obtain the self-consistent equation, a closed set of equations for local variables.

We consider the Bethe lattice, the Cayley tree of $z = \infty$. Since there is only one path between any *i*, *j* that are nearest neighbors of 0th site in a Cayley tree, $G_{ij}^{(0)}$ is always zero unless i = j. Furthermore, in the limit of $z \rightarrow \infty$, the local Green's function of the cavity should not differ from that of the original site. Therefore in the Bathe lattice case, we have $G_{ii}^{(0)} = G_{ii} = G_{00}$. So the local Weiss-field of Bethe lattice is given by

$$\mathcal{G}_0^{-1}(i\omega) = i\omega + \mu - t_*^2 G_{00}(i\omega)$$
(2.33)

We put this equation to construct S_{eff} in (2.30) and then from Eq. (2.32), the local Green's function is obtained by

$$G_{00}(\tau - \tau') = -\left\langle Tc_{0\sigma}(\tau)\bar{c}_{0\sigma}(\tau')\right\rangle_{\text{eff}} = -\frac{\text{Tr}\left[Tc_{0\sigma}(\tau)\bar{c}_{0\sigma}(\tau')\exp(-S_{\text{eff}})\right]}{\text{Tr}\exp(-S_{\text{eff}})}.$$
(2.34)

Hence, if we assume that we have a method to evaluate the Grassmann integral (2.34), then (2.30), (2.33) and (2.34) form a closed set of equations and we can evaluate G_{00} self-consistently.

In the Bethe lattice, the Hilbert transform reads $R[G_{00}] = t_*^2 G_{00} + 1/G_{00} = i\omega + \mu - \Sigma$. Putting this relation into (2.33), we obtain the following Dyson equation

$$\mathcal{G}(i\omega)^{-1} = G_{00}^{-1}(i\omega) = \mathcal{G}_0(i\omega)^{-1} - \Sigma(i\omega).$$
 (2.35)

Therefore the self-energy component obtained from the effective action (2.30) indeed coincides with the actual local self-energy of the system.

This property also applies to a general lattice in the infinite dimension. First of all, Hubbard showed in his early work [12] that the cavity Green's function is related to the full lattice Green's function by

$$G_{ij}^{(0)} = G_{ij} - \frac{G_{i0}G_{0j}}{G_{00}}$$
(2.36)

In the above expression, the second term is subtracted because it is the term contributing

to G_{ij} but not to $G_{ij}^{(0)}$ through 0th site. For an interacting Hamiltonian, this relation is only true for $d = \infty$. Then Eq. (2.31) becomes

$$\mathcal{G}_0(i\omega) = i\omega + \mu - \sum_{ij} t_{0i} G_{ij} t_{j0} + \frac{\left(\sum_i t_{0i} G_{i0}\right)^2}{G_{00}}.$$
(2.37)

The Green's function of the lattice in the infinite dimension is $G_k = \frac{1}{i\omega + \mu - \varepsilon_k - \Sigma}$ with a k-independent self-energy Σ . Fourier analysis then gives us

$$\sum_{i} t_{0i} G_{i0} = \sum_{k} \varepsilon_k G_k = \sum_{k} (\varepsilon_k - \xi G_k + \xi G_k) = -1 + \xi G_{00}$$
(2.38)

$$\sum_{ij} t_{0i} G_{ij} t_{j0} = \sum_k \varepsilon_k^2 G_k = \sum_k \left(\varepsilon_k (\varepsilon_k - \xi) G_k + \xi \varepsilon_k G_k \right) = -\xi + \xi^2 G_{00}$$
(2.39)

where $\xi = i\omega + \mu - \Sigma = R[G_{00}]$. Inserting into (2.37), we obtain the Dyson equation (2.35) for a general lattice in $d = \infty$ case.

In practice, we solve the closed set of self-consistent equations (2.31), (2.34) and (2.35) in the following iterative loop:

(1) Starting with an initial guess self-energy Σ , we calculate the local self-energy:

$$G = \int d\varepsilon D(\varepsilon) \frac{1}{i\omega + \mu - \varepsilon - \Sigma(i\omega)}$$
(2.40)

(2) From the Dyson equation, compute the Weiss-field:

$$\mathcal{G}_0^{-1} = G^{-1} + \Sigma \tag{2.41}$$

(3) Obtain the new local Green's function G from the effective action

$$G^{(new)} = -\frac{\operatorname{Tr}\left[Tc_{0\sigma}(\tau)\bar{c}_{0\sigma}(\tau')\exp(-S_{\text{eff}})\right]}{\operatorname{Tr}\exp(-S_{\text{eff}})}$$
(2.42)

(4) Go back to step (1) with the new self-energy $\Sigma^{(new)} = G^{new -1} - \mathcal{G}_0^{-1}$.

Each of the steps is quite straightforward except the step (3). It is the heart of DMFT loop, solving the new Green's function given a effective single-site action. In the next

chapter, we will focus on the formulation of Anderson impurity model and a state-of-theart technique continuous-time Monte Carlo as an impurity solver.

Finally, we mention in passing that the local interaction U is not affected when we integrate out the cavity degrees of freedom because the local interaction is not coupled with the other sites. In general interaction, however, the effective local interaction in the auxiliary impurity must be calculated carefully similar to that of \mathcal{G}_0 . The renormalization of the impurity interaction makes the problem even more complicated especially when DMFT is applied to real material calculation combined with band structure methods such as DFT.

2.2.5 Impurity representation

In the previous section, we have shown that one can solve the infinite coordination lattices problem by solving an auxiliary single-site problem with action (2.34). We also have argued that the lattice self-energy of this problem is purely local and the self-energy of the the auxiliary single-site system is identical to the local self-energy of the lattice. To give some physical insights, let us introduce the impurity representation, which provides a Hamiltonian formulation for the effective action formalism that we derived above.

The Anderson impurity model (AIM) is given by

$$H = \varepsilon_{d} d_{\sigma}^{\dagger} d_{\sigma} + U \hat{n}_{d\uparrow} \hat{n}_{d\downarrow} + \underbrace{\sum_{k,\sigma} \widetilde{\varepsilon}_{k\sigma} c_{k\sigma}}_{H_{\text{bath}}} + \underbrace{\sum_{k,\sigma} V_{k} (c_{k\sigma}^{\dagger} d_{\sigma} + h.c)}_{H_{\text{hyb}}}.$$
(2.43)

Physically, AIM describes a fully interacting localized impurity surrounded by a noninteracting conduction band (bath), where electrons can channel between them through the transfer matrix V_k . This simple model is one of the canonical topics in solid-state physics, which has stimulated many of physical ideas as well as the numerical techniques.

It is importance to notice that the corresponding effective impurity action of AIM, S_{eff} , with the bath degrees of freedom integrated out,

$$S_{\text{eff}}[\bar{d}_{\sigma}, d_{\sigma}] = -\int_{0}^{\beta} d\tau \int_{0}^{\beta} d\tau' \bar{d}_{\sigma}(\tau) \mathcal{G}_{0}(\tau - \tau') d_{\sigma}(\tau') + \int_{0}^{\beta} d\tau U n_{d\uparrow}(\tau) n_{d\downarrow}(\tau), \qquad (2.44)$$

has the same form as the local effective action of an infinite coordination lattice (2.30). In AIM case, the Weiss-field \mathcal{G}_0 is given by

$$\mathcal{G}_0(i\omega) = i\omega - \varepsilon_d - \Delta(i\omega) \tag{2.45}$$

where the hybridization function Δ , which is the consequence of renormalization of the bath degree's of freedom, reads

$$\Delta(i\omega) = \sum_{k} \frac{|V_k|^2}{i\omega - \varepsilon_k}.$$
(2.46)

The original infinite dimensional lattice problem is then equivalent to solving the corresponding impurity problem which causes the same hybridization function given by the cavity. That is why the impurity solver for AIM lies at the heart of DMFT.

2.3 Continuous-time Quantum Monte-Carlo

In this section, we introduce continuous-time quantum Monte-Carlo (CTQMC), one of the start-of-the-art methods for AIM solution. CTQMC plays one of the most important roles in the DMFT implementations since the quality of the computation directly relies on the impurity solver.

In the strong coupling version of CTQMC [47, 48, 49], where the diagram expansion is computed in powers of hybridization $\Delta(i\omega)$ with the local atomic limit as the unperturbed solution. Then the Monte Carlo importance sampling is used to sample the Feynman diagrams. For each perturbation order k, we regroup the diagrams into a determinant of a matrix of size $k \times k$

$$Z_{\rm imp} = \int \mathcal{D}\bar{d}_{\sigma}\mathcal{D}d_{\sigma}\exp(-S_{\rm eff}[\bar{d}_{\sigma}, d_{\sigma}])$$
(2.47)

where the effective impurity action (2.44) can be rewritten as

$$S_{\text{eff}}[\bar{d}_{\sigma}, d_{\sigma}] = S_{\text{atom}}[\bar{d}_{\sigma}, d_{\sigma}] + \sum_{\alpha, \alpha'} \int_{0}^{\beta} d\tau \int_{0}^{\beta} d\tau' \bar{d}_{\alpha}(\tau) \Delta_{\alpha, \alpha'}(\tau - \tau') d_{\alpha}'(\tau').$$
(2.48)

We can expand Eq. (2.47) in powers of hybridization function $\Delta(i\omega)$

$$Z_{\rm imp} = \int \mathcal{D}\bar{d}_{\sigma}\mathcal{D}d_{\sigma} \exp(-S_{\rm atom} - \Delta S)$$

$$= Z_{\rm atom} \sum_{k} \frac{1}{k!} \int_{0}^{\beta} d\tau_{1} \int_{0}^{\beta} d\tau_{1}' \cdots \int_{0}^{\beta} d\tau_{k} \int_{0}^{\beta} d\tau_{k}'$$

$$\times \sum_{\alpha_{1},\alpha_{1}',\cdots,\alpha_{k},\alpha_{k}'} \left\langle Td_{\alpha_{1}}(\tau_{1})\bar{d}_{\alpha_{1}'}(\tau_{1}')\cdots d_{\alpha_{k}}(\tau_{k})\bar{d}_{\alpha_{k}'}(\tau_{k}') \right\rangle_{\rm atom} \times \frac{1}{k!} \mathcal{D}_{k} \quad (2.49)$$

where \mathcal{D}_k is by definition a determinant of the $k \times k$ matrix whose component is $\Delta_{\alpha_i \alpha_j}(\tau_i, \tau'_j)$

$$\mathcal{D}_{k} = \text{Det} \begin{pmatrix} \Delta_{\alpha_{1}\alpha_{1}}(\tau_{1},\tau_{1}') & \cdots & \cdots & \Delta_{\alpha_{1}\alpha_{k}}(\tau_{1},\tau_{k}') \\ \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \\ \Delta_{\alpha_{k}\alpha_{1}}(\tau_{k},\tau_{1}') & \cdots & \cdots & \Delta_{\alpha_{k}\alpha_{k}}(\tau_{k},\tau_{k}') \end{pmatrix}$$
(2.50)

Here, S_{atom} is the impurity part of the action including the local interaction matrix, $[d, d^{\dagger}]$ is the fermion operator, and α_k represents the bath degrees of freedom including spin and orbital indices. The matrix in the determinant is the hybridization matrix regrouped from the Δ elements at each perturbation order k.

We need two Monte Carlo steps to be implemented: (i) the insertion of two kinks at random times τ_{new} and τ'_{new} (chosen uniformly $[0, \beta)$), corresponding to a random baths α and α' , and (ii) removal of two kinks by removing one creation operator and one annihilation operator. The detailed balance condition requires that the probability inserting two kinks at random times τ_{new} and τ'_{new} , which is chosen uniformly in the interval $[0, \beta)$, is

$$P_{add} = min\left[\left(\frac{\beta N_b}{k+1}\right)^2 \frac{Z_{new}}{Z_{old}} \frac{\mathcal{D}_{new}}{\mathcal{D}_{old}}, 1\right]$$
(2.51)

where N_b is the number of baths, k is the current perturbation order (number of kinks/2), Z_{new} is the cluster matrix element

$$Z_{new} = \left\langle T d_{\alpha_{new}}(\tau_{new}) \bar{d}_{\alpha'_{new}}(\tau'_{new}) d_{\alpha_1}(\tau_1) \bar{d}_{\alpha'_1}(\tau'_1) \cdots d_{\alpha_k}(\tau_k) \bar{d}_{\alpha'_k}(\tau'_k) \right\rangle_{\text{atom}}$$
(2.52)

and $\mathcal{D}_{new}/\mathcal{D}_{old}$ is the ratio between the new and the old determinant of baths Δ . The factors of (βN_b) enter because of the increase of the phase space when adding a kink (increase of entropy) while the factor 1/(k+1) comes from factorials in Eq. (2.49). Similarly, the probability to remove two kinks, chosen randomly between $[1, \dots, k]$ is

$$P_{rem} = min \left[\left(\frac{k}{\beta N_b} \right)^2 \frac{Z_{new}}{Z_{old}} \frac{\mathcal{D}_{new}}{\mathcal{D}_{old}}, 1 \right]$$
(2.53)

The expectation value of an observable (hatO), expressible in terms of local fermionic operators d, d^{\dagger} , can be calculated by sampling over the atomic states by the Monte Carlo method:

$$\langle \hat{O} \rangle = \frac{1}{Z_{\rm imp}} Z_{\rm atom} \sum_{k=0}^{\infty} \frac{1}{k!} \int_{0}^{\beta} d\tau_{1} \int_{0}^{\beta} d\tau_{1}' \cdots \int_{0}^{\beta} d\tau_{k} \int_{0}^{\beta} d\tau_{k} \\ \times \sum_{\alpha_{1},\alpha_{1}',\cdots,\alpha_{k},\alpha_{k}'} \left\langle T \hat{O} d_{\alpha_{1}}(\tau_{1}) \bar{d}_{\alpha_{1}'}(\tau_{1}') \cdots d_{\alpha_{k}}(\tau_{k}) \bar{d}_{\alpha_{k}'}(\tau_{k}') \right\rangle_{\rm atom} \times \frac{1}{k!} \mathcal{D}_{k} \quad (2.54)$$

Then the imaginary time local Greens function can be written as:

$$G_{\alpha\alpha'}(\tau - \tau') = -\langle Td_{\alpha}(\tau)\bar{d}_{\alpha'}(\tau')\rangle$$

$$= \frac{1}{Z_{\rm imp}} Z_{\rm atom} \sum_{k=0}^{\infty} \frac{1}{k!} \int_{0}^{\beta} d\tau_{1} \int_{0}^{\beta} d\tau_{1}' \cdots \int_{0}^{\beta} d\tau_{k} \int_{0}^{\beta} d\tau_{k}'$$

$$\times \sum_{\alpha_{1},\alpha_{1}',\cdots,\alpha_{k},\alpha_{k}'} \left\langle Td_{\alpha}(\tau)\bar{d}_{\alpha'}(\tau')d_{\alpha_{1}}(\tau)\bar{d}_{\alpha_{1}'}(\tau_{1}')\cdots d_{\alpha_{k}}(\tau_{k})\bar{d}_{\alpha_{k}'}(\tau_{k}')\right\rangle_{\rm atom} \times \frac{1}{k!} \mathcal{D}_{k} \quad (2.55)$$

One can compute the Greens function of conduction bath electrons. As the conduction electron operators are added in the partition function, the size of the hybridization matrix is increased from $k \times k$ to $(k+1) \times (k+1)$ by adding one row and one column. The impurity Greens function is obtained from the relation between the impurity Greens function and the conduction electron Greens function. The local Greens function can be obtained by sampling the determinant of hybridization matrix from which one row and one column are removed. This procedure is explained in Ref. [81] in details.

Chapter 3

DMFT calculation on 3D Hubbard model: metal-insulator interface

The metal-insulator transition is one of the fundamental phenomena for understanding phases of matter in interacting solid state systems. In these materials, a transition between a metal and a Mott insulator is driven by temperature, pressure or chemical doping drives. In large classes of materials [13], the Mott transition has dominantly been found to be first-order and its understanding is key to eventual device applications [14]. First-order transitions exhibit phase separation, and the thickness of the interface between the two thermodynamic phases contains information about the free energy functional [15]. Specifically, the thickness of the interface allows direct access to the ratio of the potential to kinetic energy terms in the free energy, which is related to the barrier height between the two minima of the double-well. While phase separation at the Mott transition is theoretically well-studied [16, 17, 18, 19, 20, 21], the interface between the thermodynamically coexisting metal and Mott insulator is not. The recent development of experimental probes with nanometer-scale spatial resolution [22, 23, 24] has allowed the direct observation of the real-space structure of these interfaces.

As a first step towards characterizing the metal-Mott interface [25], we compute the real-space structure of the interfaces for the canonical example of a correlated system, the single-band Hubbard model. We use techniques in the spirit of work on correlated surfaces [26, 27] and heterostructures [28, 29, 30, 31, 32]. We extract the evolution of the density, double-occupancy and spectral features across the interface, allowing us to determine the parameters of the underlying free energy across the phase diagram.


Figure 3.1: Evolution of the local spectra (top panel), density (middle) and double occupancy (bottom) across the interface between a correlated metal (left edge) and a Mott insulator (right edge). Clearly visible is the transfer of spectral weight from the low-energy quasiparticles to the Hubbard bands as we spatially traverse the interface. We have chosen parameters of the Hubbard model where the transition from the insulator is to a hole-doped metal: $\mu = 0.95(U/2)$, U = 1.97D and T = 0.01D, where D = 6t is the half-bandwidth.

3.1 Landau free energy

The Mott transition can be tuned by two parameters besides temperature: the chemical potential μ and correlation strength U. At half-filling, extensive work has shown the first-order transition is analogous to the liquid-gas transition, placing the Mott transition within the Ising universality class [33, 34, 35, 36, 37, 38, 39, 40]. In this work, we extend the construction away from half-filling into the μ -U plane [41]. Since we are interested in the metal-Mott interface, we work at temperatures below the critical point to construct our Landau theory.

We choose our fields to be the quantities conjugate to the external parameters (μ, U) , namely the density $n = \langle n \rangle$ and double occupancy $d = \langle n_{\uparrow}n_{\downarrow} \rangle$, a construction hinted at in [42]. The transition between the metal and paramagnetic Mott insulator does not break any symmetries [13, 43], so the terms in the free energy functional $\mathcal{F}[n, d]$ are unconstrained. The free energy generically will have one global minimum, and should a transition exist, it will occur via the switching between two discrete minima as no symmetry forces a locus of states to simultaneously lower in energy. We will explicitly construct the scalar order parameter in the following

Along the Mott transition line in the μ -U plane, the two minima will have the same energy. To facilitate analytic calculation, we take the two minima to be symmetric, an assumption certainly not justified by symmetry, but which will prove to be a good approximation. Writing the fields as $\vec{\phi} = (n, d)$, the free energy functional takes a double-well form,

$$\mathcal{F}[\vec{\phi}] = \frac{1}{2} D(\nabla \vec{\phi})^2 + \lambda (\vec{\phi} - \vec{\phi}_{\rm i})^2 (\vec{\phi} - \vec{\phi}_{\rm m})^2, \qquad (3.1)$$

where $\vec{\phi}_i = (n_i, d_i)$ and $\vec{\phi}_m = (n_m, d_m)$ are the insulating and metallic minima. A note on units: we work on a discrete lattice to easily connect with computation and set the lattice spacing a = 1. Thus the gradient is understood to be discrete $\nabla \vec{\phi}_j \sim \vec{\phi}_{j+1} - \vec{\phi}_j$, where jis the lattice site, the free energy $F = \sum_j \mathcal{F}[\vec{\phi}_j]$, and both λ and D have units of energy. We choose D to be the half-bandwidth and omit an overall (dimensionless) normalization to the free energy.



Figure 3.2: Generic Mott phase diagram, as realized by the single-band Hubbard model on a cubic lattice at T = 0.005D, where D = 6t is the half-bandwidth. Dots label values of (μ, U) lying on first-order Mott transition line used for interface calculations. Lines mark the spinodals U_{c1} and U_{c2} where the insulating and metallic solutions respectively vanish. The diagram is symmetric about $\mu/(U/2) = 1$.

A domain wall is given by the standard solution used, e.g. in the theory of instantons [44],

$$\vec{\phi}(x_j) = \frac{\vec{\phi}_{\rm m} + \vec{\phi}_{\rm i}}{2} + \frac{\vec{\phi}_{\rm m} - \vec{\phi}_{\rm i}}{2} \tanh\left(\frac{x_j - x_0}{2l}\right) \tag{3.2}$$

where x_j is the coordinate of the *j*th site and the wall thickness is $l^{-2} = 2(\lambda/D)(\vec{\phi}_{\rm m} - \vec{\phi}_{\rm i})^2$. Note the fields $\vec{\phi}$ do not transform as a vector and the notation is for convenience. Determining the dependence of $\vec{\phi}_{\rm i}$, $\vec{\phi}_{\rm m}$ and λ/D on (U,T) requires microscopic modeling.

3.2 Modeling the Interface

The Hubbard hamiltonian is the "standard model" of correlated electrons. Its two terms describe the competition between kinetic energy, which delocalizes electrons to promote metallic behavior, and mutual electron repulsion, which tends to localize electrons onto sites and drive the transition to a Mott insulator. We work with the simplest one-band case



Figure 3.3: Geometry used to model the metal-Mott interface. The transition region, described by site-dependent self-energies Σ_i , is sandwiched between a semi-infinite bulk Fermi liquid and Mott insulator by fixing the bulk self-energies to Σ_{metal} and Σ_{ins} on the left and right. We assume translational invariance in the y and z directions.

on a cubic lattice,

$$H = \sum_{\mathbf{k}\sigma} (\epsilon_k - \mu) n_{\mathbf{k}\sigma} + U \sum_j n_{j\uparrow} n_{j\downarrow}, \qquad (3.3)$$

where we take $\epsilon_{\mathbf{k}} = -2t(\cos k_x + \cos k_y + \cos k_z)$ and use the half bandwidth D = 6tas the unit of energy in all the following. We will index the sites by $j = (n_1, n_2, n_3)$ in the following. Ignoring ordered phases, which is a reasonable assumption at intermediate temperatures or in the presence of frustration, the phase diagram generically consists of a Mott insulating region for large U and a range of μ corresponding to half-filling, and a Fermi liquid everywhere else. To find the first-order transition line, we use standard single-site dynamical mean-field theory (DMFT) [9, 45, 46] with a continuous-time quantum monte carlo (CTQMC) hybridization expansion impurity solver [47, 48, 49]. The phase diagram at T = 0.005D is plotted in Fig. 3.2, along with the two spinodals U_{c1} and U_{c2} between which both solutions exist.

To model the interface in the coexistence regime, we fix our parameters to a point on the first-order line (dots in Fig. 3.2), then partition the lattice into three regions along the x-axis (see Fig. 3.3): metal $(n_1 \leq 0)$, insulator $(n_1 \geq N + 1)$, and a *transition* region $(1 \leq n_1 \leq N)$. Here n_1 is the site index along the x-axis and we take N = 20 large enough to capture the interface. We perform an inhomogenous DMFT calculation by setting the self-energy of the lattice $\Sigma_{n_1n_1'} = \delta_{n_1n_1'}\Sigma_{n_1}$ to

$$\Sigma_{n_1} = \begin{cases} \Sigma_{\text{metal}} & n_1 \le 0\\ \Sigma_{n_1} & 1 \le n_1 \le N \\ \Sigma_{\text{ins}} & n_1 \ge N + 1 \end{cases}$$
(3.4)

Only the self-energies Σ_{n_1} in the transition region are updated, while Σ_{metal} and Σ_{ins} are fixed boundary conditions taken from the single-site DMFT solution. Our setup assumes the interface is perpendicular to one of the crystal directions (x) and the system is translationally invariant in the other two (y and z) so self-energies are independent of n_2 and n_3 .

To render the equations soluble in the transition region, we compute the lattice Green's function and use its local component $G_{n_1n_1}$ to map the system to a chain of N auxiliary impurity problems [32],

$$G_{n_1n_1}(i\omega_n) = \frac{1}{i\omega_n - E_{\rm imp} - \Delta_{n_1}(i\omega_n) - \Sigma_{n_1}(i\omega_n)}.$$
(3.5)

Using the extracted impurity levels E_{imp} and hybridization functions Δ_{n_1} , we obtain the new local self-energies Σ_{n_1} and iterate to convergence. The procedure for computing the local Green's function is provided in the Supplementary Material.

3.3 Calculation details

The Green's function of the lattice is given by

$$G_{\mathbf{R}\mathbf{R}'} = [(i\omega + \mu)\delta_{\mathbf{R}\mathbf{R}'} - t_{\mathbf{R}\mathbf{R}'} - \Sigma_{\mathbf{R}\mathbf{R}'}]^{-1}$$
(3.6)

where **R** is a lattice vector $\mathbf{R} = (n_1, n_2, n_3)$ with the cubic primitive lattice vector and $t_{\mathbf{RR'}}$ denotes the nearest neighbor hopping. To see the spatial variation across the two different phases, we divide the lattice into three regions: metallic ($\mathcal{M} : -\infty < n_1 \leq 0$), insulating $(\mathcal{I} : N + 1 \leq n_1 < \infty)$ and transition ($\mathcal{T} : 1 \leq n_1 \leq N$) region. So \mathcal{T} is sandwiched by \mathcal{M}



Figure 3.4: Variation of the density (top) and double occupancy (bottom) across the interface at several points along the Mott transition line at T = 0.01D. Thin lines are fits to the standard solution for a double-well potential $a + b \tanh((x_i - x_0)/2l)$, allowing extraction of the parameters for the underlying free energy. Curves are shifted horizontally by varying amounts for clarity. The chemical potential is in units of U/2, as detailed in the right-hand table of Table 3.1

and \mathcal{I} . Then we assign to each site the localized self-energy $\Sigma_{n_1n'_1} = \delta_{n_1n'_1}\Sigma_{n_1}$ with

$$\Sigma_{n_1} = \begin{cases} \Sigma_{\text{metal}} & (n_1 \in \mathcal{M}) \\ \Sigma_{n_1} & (n_1 \in \mathcal{T}) \\ \Sigma_{\text{ins}} & (n_1 \in \mathcal{I}) \end{cases}$$
(3.7)

Note that in the metallic and insulating regimes, the self-energy is fixed to Σ_{metal} and Σ_{ins} respectively, while we allow the local self-energy in the transition regime to vary across the sites.

The Fourier transformation of Eq. (3.6) along y and z directions gives the following matrix form of Green's function in the mixed representation $(n_1; k_y, k_z)$ $(n_1$ is the site index of x):

$$\left[G(k_y, k_z; i\omega)\right]_{n_1 n'_1} = \left[\left[(i\omega + \mu - \varepsilon(k_y, k_z) - \Sigma_{n_1}(i\omega))\hat{I} - \hat{t}\right]^{-1}\right]_{n_1 n'_1}$$
(3.8)

where $\hat{t} = -t(\delta_{n_1,n'_1+1} + \delta_{n_1,n'_1-1})$ and $\varepsilon(k_y,k_z) = -2t(\cos(k_ya) + \cos(k_za))$. To apply DMFT to the transition regime, we must calculate the local component of the Green's function at each site and map each onto an auxiliary impurity.

We can rewrite Eq. (3.8) in a block matrix divided into the three regimes \mathcal{M}, \mathcal{T} and \mathcal{I} , that is,

$$[G(k_y, k_z; i\omega)]_{n_1n_1'} = \begin{bmatrix} F_{\mathcal{M}} & & & & \\ & t & & & \\ & t & & & \\ & & t & & \\ & & F_{\mathcal{T}} & & \\ & & & t & \\ & & & & F_{\mathcal{I}} \end{bmatrix}^{-1}$$
(3.9)

where we define the three block matrices by

$$[F_{\mathcal{M}}]_{n_{1}n'_{1}} = \underbrace{(i\omega + \mu - \varepsilon(k_{y}, k_{z}) - \Sigma_{\mathcal{M}}(i\omega))}_{\equiv z_{\mathcal{M}}} \delta_{n_{1}n'_{1}} - t_{n_{1}n'_{1}}$$
$$[F_{\mathcal{T}}]_{n_{1}n'_{1}} = \underbrace{(i\omega + \mu - \varepsilon(k_{y}, k_{z}) - \Sigma_{n_{1}}(i\omega))}_{\equiv z_{n_{1}}} \delta_{n_{1}n'_{1}} - t_{n_{1}n'_{1}}$$
$$[F_{\mathcal{I}}]_{n_{1}n'_{1}} = \underbrace{(i\omega + \mu - \varepsilon(k_{y}, k_{z}) - \Sigma_{ins}(i\omega))}_{\equiv z_{\mathcal{I}}} \delta_{n_{1}n'_{1}} - t_{n_{1}n'_{1}}$$

Note that $z_{\mathcal{M}}$ and $z_{\mathcal{I}}$ are fixed while z_{n_1} varies across the sites.

Using block matrix inversion

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \hline \mathbf{C} & \mathbf{D} \end{bmatrix}^{-1} \bigg|_{\mathbf{c}\mathbf{A}} = [\mathbf{A} - \mathbf{B}\mathbf{D}^{-1}\mathbf{C}]^{-1}$$
(3.10)

we obtain the complete form of Green's function in the transition regime \mathcal{T} (a $N \times N$ matrix) into which all the degrees of freedom of metallic and insulating regions are incorporated:

$$[G(k_{y}, k_{z})]|_{n_{1}, n_{1}' \in \mathcal{T}} = \left[\underbrace{[F_{\mathcal{T}}]}_{\mathbf{A}} - \underbrace{(\hat{t}_{\mathcal{T}\mathcal{M}}[F_{\mathcal{M}}]^{-1}\hat{t}_{\mathcal{M}\mathcal{T}} + \hat{t}_{\mathcal{T}\mathcal{I}}[F_{\mathcal{I}}]^{-1}\hat{t}_{\mathcal{I}\mathcal{T}}}_{\mathbf{BD}^{-1}\mathbf{C}}\right]^{-1}$$

$$= \begin{bmatrix} z_{11} - t^{2}R_{\mathcal{M}} & t & 0 \\ t & z_{22} & t & \\ & t & \ddots & \ddots & \\ & & t & \ddots & \ddots & \\ & & & \ddots & \ddots & t & \\ & & & t & z_{N-1,N-1} & t \\ & & & t & z_{NN} - t^{2}R_{\mathcal{I}} \end{bmatrix}^{-1}$$

$$(3.11)$$

where $R_{\mathcal{M}} \equiv [F_{\mathcal{M}}^{-1}]_{00}$, $R_{\mathcal{I}} \equiv [F_{\mathcal{I}}^{-1}]_{N+1,N+1}$ and $\hat{t}_{\mathcal{T}\mathcal{M}(\mathcal{I})}$ is the overlap between \mathcal{T} and $\mathcal{M}(\mathcal{I})$. The effect of integrating out the degrees of freedom in \mathcal{M} and \mathcal{I} is captured by $t^2 R_{\mathcal{M}}$ and $t^2 R_{\mathcal{I}}$ at the (1,1) and (N,N) components respectively.

To compute $R_{\mathcal{M}}$ and $R_{\mathcal{I}}$, we again rely on Eq. (3.10). Since $[F_{\mathcal{M}}]$ takes a symmetric

tridiagonal matrix form equal to

$$F_{\mathcal{M}} = \begin{bmatrix} z_{\mathcal{M}} & t & & \\ t & z_{\mathcal{M}} & t & \\ & t & z_{\mathcal{M}} & \ddots \\ & & \ddots & \ddots \end{bmatrix} = \begin{bmatrix} z_{\mathcal{M}} & t & & \\ \hline t & & \\ & F_{\mathcal{M}} & \\ & & \end{bmatrix}$$
(3.12)

we see the matrix repeats itself inside. As a direct consequence of (3.10), we obtain the following recursive equation:

$$[F_{\mathcal{M}}^{-1}]_{00} = R_{\mathcal{M}} = \frac{1}{z_{\mathcal{M}} - t^2 R_{\mathcal{M}}}$$
(3.13)

where the solution is

$$R_{\mathcal{M}} = \frac{z_{\mathcal{M}} - \sqrt{(z_{\mathcal{M}})^2 - 1}}{t}.$$
 (3.14)

 $R_{\mathcal{I}}$ is obtained by the same procedure.

Finally, we need to convert the mixed representation form (3.9) into the pure real-space representation. Performing the inverse Fourier transformation with respect to k_y and k_z , we can obtain the local Green's function at the site n_1

$$[G]_{n_1n_1} = \int \frac{d^2k}{(2\pi)^2} [G(k_y, k_z)]_{n_1n_1}$$

=
$$\int d\varepsilon [G(\varepsilon)]_{n_1n_1} D^{2D}(\varepsilon)$$
(3.15)

where the ε dependence of G comes from $\varepsilon = \varepsilon(k_y, k_z)$. Here, $D^{2D}(\varepsilon)$ is the density of states of non-interacting 2D square lattice whose analytic expression is known and the integration (3.15) is performed numerically.

3.4 Results

The evolution of the density n double occupancy d for along the Mott transition line is displayed in Fig. 3.4 at a temperature of T = 0.005D. At the particle-hole symmetric point, there is no jump in density between the metal and Mott insulator, while the change

$\mu/(U/2)$	U/D	$n_{ m i}$	d_{i}	$n_{ m m}$	d_{m}	λ/D	α
1.00	2.04	1.0000	0.0241	1.0000	0.0357	2410	0°
0.95	2.05	1.0000	0.0238	0.9978	0.0330	3170	13°
0.90	2.08	0.9999	0.0229	0.9960	0.0297	2510	30°
0.85	2.13	0.9998	0.0216	0.9947	0.0262	1780	48°
$\mu/(U/2)$	U/D	$n_{\rm i}$	d_{i}	$n_{ m m}$	$d_{ m m}$	λ/D	α
1.000	1.962	1.0000	0.0261	1.0000	0.0353	1420	0°
0.975	1.965	1.0000	0.0259	0.9997	0.0341	1590	2°
0.950	1.970	1.0000	0.0258	0.9994	0.0330	1890	5°
0.925	1.985	0.9999	0.0253	0.9992	0.0306	2480	8°
0.900	2.005	0.9998	0.0248	0.9991	0.0283	3190	12°

Table 3.1: Extracted parameters of Landau free energy for T = 0.005D (left) and T = 0.01D (right), where D = 6t is the half-bandwidth. The position along the Mott transition line is parameterized by the chemical potential μ , or equivalently, the electron repulsion. The shifts in the density and double-occupancy for the Mott insulator (n_i, d_i) and metal (n_m, d_m) are quite small for the one-band model, which when combined with fact that the interface widths $l \sim O(1)$, produces large values of λ/D . The angle α specifies how much of n is admixed into the d to form the Ising order parameter (see Eq. 3.16).

in double-occupancy is maximal. As we progress along the transition line (which we parameterize with the chemical potential μ) towards the hole-doped side, the density difference between the metal and insulator increases. Additionally, the density of the insulator drops below unity because we are at finite temperature. In contrast, the jump in double occupancy decreases.

The variation of both quantities fit well to Eq. 3.2 for the double well potential, albeit with slightly different length scales, and we use the average of the two wall widths to compute λ . The small difference in length scales implies the potential is not perfectly symmetric (as expected), and that the path in (n, d) space between the two minima is close to, but not exactly, a straight line (see Fig. 3.5). The extracted parameters for the Landau free energy are presented in Table 3.1.

We also analytically continue the Matsubara self-energies produced by the impurity solver to the real axis to compute the variation of the spectral density across the interface. We plot in Fig. 3.1 the spectra for parameters $\mu = 0.95(U/2)$, U = 1.97D and T = 0.01D, which is slightly on the hole-doped side. Starting from the metallic solution, we find that the quasiparticle peak shift slightly downwards and disappears into the lower Hubbard band as we progress to the Mott insulator. The gap between the Hubbard bands slightly narrow.



Figure 3.5: Trajectory in (n, d) space as the system evolves across the interface from the insulating to the metallic minima at $\mu = 0.95(U/2)$, U = 2.05D, T = 0.005D. The extracted Landau parameters are used to plot the contours of the double-well potential. The dotted lines trace the shift of the minima along the Mott transition line at T = 0.005D.

The extracted parameters combined with our ansatz (Eq. 3.1) allow us to reconstruct the free energy. Shown in Fig. 3.5 is a representative case for $\mu = 0.95$, U = 2.05, T = 0.005D. We have plotted the trajectory in (n, d) space as the system evolves from the metallic to insulating minima, superimposed with contour lines of the potential constructed using the extracted parameters. The movement of the two minima as we step along the Mott transition line is shown in the dotted lines.

As promised, we explicitly construct the order parameter field Δ as a linear combination of n and d, owing to the fact that the trajectory is almost straight. The construction is essentially geometric: we take the line segment joining the two minima and parameterize it with an angle α :

$$\Delta = (n - \bar{n})\sin\alpha + (d - \bar{d})\cos\alpha \tag{3.16}$$

where $\bar{n} = (n_i + n_m)/2$ and $\bar{d} = (d_i + d_m)/2$. The angles are tabulated in Table 3.1. At particle-hole symmetry, the angle is zero and the variation of the order parameter is entirely driven by the double occupancy. Increasing angles imply the density becomes a larger component of the order parameter, which occurs as we progress to larger correlation strengths.

3.5 Summary

In this work, we have taken a first step towards characterizing the metal-Mott interface by modeling its spatial properties, constructing a Landau free energy and identifying an Ising order parameter. The key parameter of the free energy which could not be obtained by previous solutions in homogenous geometries is the interface width l, which is directly related to the double-well barrier height via λ/D . We also comment that while in general for first-order transitions which do not possess an organizing symmetry, any number of fields can be chosen to construct the free energy [34, 35, 40], the choice of the quantities conjugate to the physical tuning parameters μ and U allow for an especially transparent construction of the order parameter which can uniformly treat both the bandwidth and filling controlled transitions.

We want to point out the simplifying assumptions used: (1) we took the interface to be perpendicular to a crystallographic axis, (2) we only included nearest-neighbor hopping to simplify the formulae, (3) we made the slow-varying approximation, assuming each site was an independent impurity affecting the others only via the hybridization, and (4) we have ignored the long-range Coulomb interaction. Relaxing these assumptions to capture more realistic scenarios warrant further investigation.

We expect that future calculations on realistic systems will provide quantitative results for comparison with near-field optics and STM observations, and more speculatively, could provide a new constraint on the value of U in these compounds. Finally, while we have guessed the form of the Landau free energy and numerically determined its parameters, especially satisfying for future work would be a microscopic derivation from the appropriate mean-field theory.

Chapter 4

Combined DFT and DMFT: Exact double-counting formulation

Over the past few decades, many theoretical frameworks have been developed to describe real materials with strong correlation, in which quasi-particle approaches such as density functional theory (DFT) [50, 51] essentially fail due to the large Coulomb interaction between electrons. As we discussed, dynamical mean field theory (DMFT) [3, 4] has brought about a revolution in the theory of strong correlations after its exact treatment of local dynamic correlations successfully described the Mott transition in lattice models such as the Hubbard model [52]. Since the method is very flexible and versatile, and scales linearly with the system size, it has been quickly adapted for many solid state problem, including electronic structure calculations.

The most commonly used DMFT approximation in solid state is combination of LDA and DMFT (LDA+DMFT) [53], where some selected correlated orbitals are treated by DMFT while the rest of the electronic states are treated by LDA. The LDA+DMFT method has been very successful in various problems involving strong electronic correlations in solids and very recently it was also applied to molecules [7, 54] and nano-systems [55, 56].

However, the application of this methodology to solids has a few ambiguities, which limit the precision of the method: i) the DMFT method needs the partially screened Coulomb interaction, which is hard to predict from first principles, ii) the part of the correlations treated by both LDA and DMFT – called double-counting – is not known exactly, and a phenomenological form [57] has been most often used (for discussion see [58] and [59]).

In this chapter we introduce the general formalism of LDA+DMFT and also propose a double-counting functional for LDA+DMFT, which is an exact intersection of the two methods and results in highly precise electronic structure method with no ambiguity in subtracting doubly counted correlation effect [60]. We implemented and test this idea of exact double-counting in one of the simplest strongly correlated systems, H_2 molecule, where we can neglect the screening effect. We also suggest the extension of this double-counting functional to the solid state calculations, where additional complexity of screening will need to be addressed.

4.1 Density functional theory

Density Functional Theory (DFT) is a quantum mechanical theory of many-body system. It is a powerful and popular used in condensed matter physics as well as quantum chemistry for calculating electronic structure of an electronic system.

The main idea of DFT is that any property of a system of many interactiong particles can be viewed as a functional of the ground state density. This idea was initiated early by Thomas [61] and Fermi [62], and the modern formulation of DFT is wrriten by P. Hohenberg and W. Kohn in their famous paper[50, 63].

In this section, we introduce DFT briefly by first considering the cornerstones of modern DFT, the Hohenberg-Kohn theorems. We then move to the Kohn-Sham ansatz to DFT. Next we consider the practical approximations of exchange correlation and ionic core potentials.

4.1.1 Hohenberg-Kohn theorem

The idea of Thomas and Fermi was intuitive, but a proof of this had to waited for a long time. In 1964, Hohenberg and Kohn [50, 63] formulated and proved a theorem that gave solid mathematical background for that idea. The formulation applies to any system of interacting particles in an external potential $V(\vec{r})_{ext}$, including any problem of electrons and fixed nuclei, where hamiltonian can be written

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \vec{\nabla}_i^2 + \sum_i V_{ext}(\vec{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|^2}.$$
(4.1)

Hohenberg-Kohn theorem are summarized as following two theorem.

Theorem 1. The external potential $V(\vec{r})_{ext}$ is univocally determined by the electronic density $n(\vec{r})$, apart from a trivial addictive constant

Proof. We prove this theorem by using reductio ad absurdum. Suppose that there are two different potentials $V_{ext}^{(1)}$ and $V_{ext}^{(2)}$ which differ by more than only a additive constant and which lead to same ground state density $n(\vec{r})$. These two potential lead to two different Hamiltonian, $H^{(1)}$ and $H^{(2)}$, which have different ground state wavefunctions, $\Psi^{(1)}$ and $\Psi^{(2)}$, and corresponding ground state energies $E_0^{(1)}$ and $E_0^{(2)}$. According to Rayleigh-Ritz's variational principle we have:

$$E_0^{(1)} < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle = \langle \Psi^{(2)} | \hat{H}^{(2)} | \Psi^{(2)} \rangle + \langle \Psi^{(2)} | \hat{H}^{(1)} - \hat{H}^{(2)} | \Psi^{(2)} \rangle$$

$$= E_0^{(2)} + \int d^3 \vec{r} [V_{ext}^{(1)}(\vec{r}) - V_{ext}^{(2)}(\vec{r})] n(\vec{r}).$$
(4.2)

By interchanging superscript (1) and (2), we have:

$$E_0^{(2)} < E_0^{(1)} + \int d^3 \vec{r} [V_{ext}^{(2)}(\vec{r}) - V_{ext}^{(1)}(\vec{r})] n(\vec{r}).$$
(4.3)

Adding these two inequalities we arrive an at the contradictory inequality $E_0^{(1)} + E_0^{(2)} < E_0^{(1)} + E_0^{(2)}$. Therefore, there can not be two potential $V_{ext}^{(1)}$ and $V_{ext}^{(2)}$, which differing by more than a addictive constant and correspond to the same ground state electronic density. This proves the first theorem of Hohenberg and Kohn.

Corollary. Since $n(\vec{r})$ univocally determines the Hamiltonian $(V_{ext}(\vec{r}))$ except for a constant shift of energy, it also determise the many-body wavefunctions for all states (ground and excited), which should be obtained by solving Schödinder equation. Therefore, all properties of the system are completely determined given only the ground state density $n(\vec{r})$.

Theorem 2. An universal functional for the energy E[n] in terms of the density $n(\vec{r})$ can be defined, valid for any external potential $V_{ext}(\vec{r})$. For any particular $V_{ext}(\vec{r})$ the ground state is the global minimum value of this functional and the density that minimizes this

functional is the ground state density.

Proof. Since all properties such as kinetic energy, interaction energy, etc., are uniquely determined if the density $n(\vec{r})$ is specified. So that such properties can be viewed as functionals of density $n(\vec{r})$ and we can write total energy as a functional of density as

$$E_{HK}[n] = T[n] + E_{int}[n] + \int d^3 r V_{ext}(\vec{r}) n(\vec{r})$$

$$\equiv F_{HK}[n] + \int d^3 r V_{ext}(\vec{r}) n(\vec{r}).$$
(4.4)

The functional $F_{HK}[n]$ defined above includes all internal energies, kinetic and potential, of the interacting electron system,

$$F_{HK}[n] = T[n] + E_{int}[n], (4.5)$$

which must be universal by construction since the kinetic energy and interaction energy of the electron are functionals only of the density.

If the electron system has ground state density $n^{(1)}(\vec{r})$ corresponding to external potential $V_{ext}(\vec{r})$. The Hohenberg-Kohn functional defined above is equal to the expectation value of the Hamiltonian in the unique ground state, which has wavefunction $\Psi^{(1)}$

$$E^{(1)} = E_{HK}[n^{(1)}] = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle.$$
(4.6)

If $n^{(2)}(\vec{r})$ is a different density, which corresponding to a different wavefunction $\Psi^{(2)}$, it follow immediately that the energy $E^{(2)}$ of this state is greater than $E^{(1)}$, since

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle = E^{(2)}.$$
(4.7)

Thus, the energy given by Eq. 4.4 in terms of the Hohenberg-Kohn functionals evaluated for the correct ground state density $n_0(\vec{r})$ is indeed lower than the value of this expression of any other density $n(\vec{r})$.

It follows if the Hohenberg-Kohn functional $F_{HK}[n]$ was known, by minimizing the total energy of the system, Eq. 4.4, with respect to variations of density function $n(\vec{r})$, one would find the exact ground state density and energy.

Here, we want to note that DFT can describe both ground and excited states. In fact, since the density determines the potential univocally, by solving the full many-body Schrödinger equation we can determine univocally the many-body wave functions, ground and excited states. The only problem is practical rather than conceptual, because of the inherent difficulty in solving the full many-body problem.

4.1.2 Kohn-Sham ansatz

The density functional theory does not provide us a way to understand the properties of considering interacting system merely by looking at the form of density. In addition, there is no known way to directly connect kinetic energy and density. The only way to calculate the kinetic energy exactly is to revert kinetic energy functionals to the usual expression in term of a set of N wavefunctions of system of N non-interacting particles. This is the idea of Kohn-Sham approach [51, 63] to density functional theory. The ansatz of Kohn and Sham is assuming that the ground state density of considering interacting system is equal to that of some chosen non-interacting systems. The independent-particle equations for the non-interacting system can be solved exactly (by analysis or numerical) with all difficulties of many-body problem incorporate into an exchange-correlation functional of the original interacting system with the limitation of accuracy of that of approximation in exchange-correlation functional.

The Hamiltonian of the non-interacting reference system can be written

$$\hat{\mathcal{H}}_R = \sum_{\sigma} \sum_{i=1}^{N^{\sigma}} \left[-\frac{\hbar^2}{2m} \vec{\nabla}_i^2 + v_R^{\sigma}(\vec{r_i}) \right], \qquad (4.8)$$

where, σ is spin index and number of electron is $N = N^{\uparrow} + N^{\downarrow}$. The potential $v_R(\vec{r})$, or reference potential, is such a potential that the ground state density of this non-interacting system coincides with that of original interacting system, $n(\vec{r})$. The ground state has one electron in each of N^{σ} orbitals $\varphi_i^{\sigma}(\vec{r})$ with lowest eigenvalues ε_i^{σ} of independent-particle

Hamiltonian

$$\hat{H}_{R} = -\frac{\hbar^{2}}{2m}\vec{\nabla}^{2} + v_{R}^{\sigma}(\vec{r}).$$
(4.9)

The electron density of reference system is

$$n(\vec{r}) = \sum_{\sigma} n(\vec{r}, \sigma) = \sum_{\sigma} \sum_{i=1}^{N^{\sigma}} |\varphi_i^{\sigma}(\vec{r})|^2, \qquad (4.10)$$

the independent-particle kinetic energy T_R is given by

$$T_R = -\frac{\hbar^2}{2m} \sum_{\sigma} \sum_{i=1}^{N^{\sigma}} \langle \varphi_i^{\sigma} | \vec{\nabla}^2 | \varphi_i^{\sigma} \rangle = -\frac{\hbar^2}{2m} \sum_{\sigma} \sum_{i=1}^{N^{\sigma}} | \vec{\nabla} \varphi_i^{\sigma} |^2, \qquad (4.11)$$

the Hartree energy

$$E_H[n] = \frac{1}{2} \int d^3 \vec{r} d^3 \vec{r'} \frac{n(\vec{r}) n(\vec{r'})}{|\vec{r} - \vec{r'}|}.$$
(4.12)

The Kohn-sham approach to the full interacting many-body problem is to rewrite the Hohenberg-Kohn expression for the ground state energy 4.4 in the form

$$E_{KS} = T_R[n] + \int d^3 \vec{r} V_{ext}(\vec{r}) n(\vec{r}) + E_H[n] + E_{xc}[n].$$
(4.13)

Comparing Hohenberg-Kohn expression for the total energy 4.4 and that of Kohn-Sham 4.13 shows that E_{xc} can be written in terms of the Hohenberg-Kohn functional 4.4 as

$$E_{xc}[n] = F_{HK}[n] - (T_R[n] + E_H[n]), \qquad (4.14)$$

or in a more other form

$$E_{xc}[n] = \left(\langle \hat{T} \rangle - T_R[n]\right) + \left(\langle \hat{V}_{int} \rangle - E_H[n]\right).$$
(4.15)

This exchange-correlation functional accounts also for the kinetic correlation ignored in $T_R[n]$.

Varying the wavefunction of independent-particle on Kohn-Sham expression for the total

energy 4.13 we can drive the variational equation

$$\frac{\delta E_{KS}}{\delta \varphi_i^{\sigma*}(\vec{r})} = \frac{\delta T_R}{\delta \varphi_i^{\sigma*}(\vec{r})} + \left[\frac{\delta E_{ext}}{\delta n(\vec{r},\sigma)} + \frac{\delta E_H}{\delta n(\vec{r},\sigma)} + \frac{\delta E_{xc}}{\delta n(\vec{r},\sigma)}\right] \frac{\delta n(\vec{r},\sigma)}{\delta \varphi_i^{\sigma*}(\vec{r})} = 0, \tag{4.16}$$

subject to the orthonormalization conditions

$$\langle \varphi_i^{\sigma}(\vec{r}) | \varphi_j^{\sigma'}(\vec{r}) \rangle = \delta_{i,j} \delta_{\sigma,\sigma'}.$$
(4.17)

Using expressions for density $n(\vec{r})$ 4.10 and kinetic energy T_R 4.11,

$$\frac{\delta T_R}{\delta \varphi_i^{\sigma*}(\vec{r})} = -\frac{\hbar^2}{2m} \vec{\nabla}^2 \varphi_i^{\sigma}(\vec{r}); \\ \frac{\delta n(\vec{r},\sigma)}{\delta \varphi_i^{\sigma*}(\vec{r})} = \varphi_i^{\sigma}(\vec{r}),$$
(4.18)

the variation equation leads to the Kohn-Sham equation:

$$(H_{KS}^{\sigma} - \varepsilon_i^{\sigma})\varphi_i^{\sigma}(\vec{r}) = 0, \qquad (4.19)$$

where the ε_i are the eigenvalues, and H_{KS} is the effective Hamiltonian

$$H_{KS}^{\sigma}(\vec{r}) = -\frac{\hbar^2}{2m} \vec{\nabla}^2 + V_{KS}^{\sigma}(\vec{r}), \qquad (4.20)$$

with

$$V_{KS}^{\sigma}(\vec{r}) = V_{ext}(\vec{r}) + \frac{\delta E_H}{\delta n(\vec{r},\sigma)} + \frac{\delta E_{xc}}{\delta n(\vec{r},\sigma)}$$
$$= V_{ext}(\vec{r}) + V_H(\vec{r}) + V_{xc}^{\sigma}(\vec{r}).$$
(4.21)

Equations 4.19, 4.20 and 4.21 are the Kohn-Sham equations. The equations are in the same form of independent-particle equations with a potential that must be found selfconsistently with the resulting density.

4.1.3 Approximation of exchange-correlation energy: LDA

In order to perform a calculation based on DFT with Kohn-Sham approach we need to know the last unknown term, exchange-correlation term, in the Kohn-Sham expression for total energy 4.13. In the Kohn-Sham's seminal paper [51], they suggested an approximation for this term, in which the exchange-correlation energy is simply an integral over space of exchange-correlation energy of homogeneous electron gas with density value assumed to be that of the considering system at that point. In other word, they considered a general inhomogeneous electron gas system as a locally homogeneous electron gas system. This approximation is called Local Density Approximation (LDA). We can write the exchangecorrelation energy as

$$E_{xc}^{LDA}[n] = \int d^3 \vec{r} n(\vec{r}) \varepsilon_{xc}^{LDA}(n(\vec{r})), \qquad (4.22)$$

where $\varepsilon_{xc}^{LDA}(n(\vec{r}))$ is the density of exchange-correlation energy of homogeneous electron gas of density $n(\vec{r})$ and can be further split into exchange and correlation contributions

$$\varepsilon_{xc}^{LDA}(n(\vec{r})) = \varepsilon_x^{LDA}(n(\vec{r})) + \varepsilon_c^{LDA}(n(\vec{r})).$$
(4.23)

The exchange term is exactly given by Slater's expression

$$\varepsilon_x^D(n(\vec{r})) = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} n(\vec{r})^{1/3} = -\frac{3}{4} \left(\frac{9}{4\pi^2}\right)^{1/3} \frac{1}{r_s},\tag{4.24}$$

where $r_s = (3/4\pi n)^{1/3} = (9\pi/4)^{1/3} k_F$ is the average distance between electrons. The correlation term parameterized by Perdew and Zunger [64] based on Ceperley and Alder's quantum Monte Carlo simulation result [65]

$$\varepsilon_{C}^{PZ}(n(\vec{r})) = \begin{cases} Alnr_{s} + B + Cr_{s}lnr_{s} + Dr_{s}, & r_{s} \leq 1, \\ \gamma/(1 + \beta_{1}\sqrt{r_{s}} + \beta_{2}r_{s}), & r_{s} > 1. \end{cases}$$
(4.25)

where, $A = 0.0311, B = -0.048, C = 0.002, D = -0.0116, \gamma = -0.1423, \beta_1 = 1.0529$ and $\beta_2 = 0.334.$

4.2 Functional Formalism of LDA+DMFT

To construct the DMFT framework, we resort to the Baym-Kadanoff formalism [66, 67], which defines a functional of the full Green's function by (see also [53])

$$\Gamma[G] = \operatorname{Tr}\log(G) - \operatorname{Tr}((G_0^{-1} - G^{-1})G) + \Phi[G].$$
(4.26)

where the G_0 is the non-interacting Green's function in the absence of the Coulomb interaction

$$G_0(\mathbf{r}, \mathbf{r}'; i\omega) = [(i\omega + \mu + \nabla^2 - V_{ext}(\mathbf{r}))\delta(\mathbf{r} - \mathbf{r}')]^{-1}, \qquad (4.27)$$

and V_{ext} is the potential created by the ions. $\Phi[G]$ is the so-called Luttinger-Ward functional and is equal to the sum of all skeleton Feynman diagrams consisting of G and Coulomb interaction $v(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|}$. $\Gamma[G]$ is extremized by the exact Green's function and gives the free energy of the system in the extremum.

In the LDA+DMFT formalism, we approximate the Luttinger-Ward functional with

$$\Phi^{\text{LDA}+\text{DMFT}}[G] = E_H[\rho] + E_{xc}^{\text{LDA}}[\rho] + \Phi^{\text{DMFT}}[\mathcal{G}_{loc}] - \Phi_{DC}[G]$$
(4.28)

where $E_{xc}^{\text{LDA}}[\rho]$ is the LDA exchange-correlation functional (4.22) introduced in the previous section, $\Phi^{\text{DMFT}}[\mathcal{G}_{loc}]$ is the DMFT functional that only depends on the local Green's function \mathcal{G}_{loc} and the local interaction, and lastly Φ_{DC} is the *double-counting* functional which subtracts the correlation part that is counted twice by DMFT and LDA. In the next section, we will introduce so-called exact double-counting functional.

In terms of the LW functional language, the DMFT functional $\Phi^{\text{DMFT}}[\mathcal{G}_{loc}]$ approximates the exact Luttinger functional $\Phi[G]$ by its local counterpart [53],

$$\Phi^{\text{DMFT}}[\mathcal{G}_{loc}] = \sum_{\mathbf{R}} \Phi_{\mathcal{U}}[\mathcal{G}_{loc}^{\mathbf{R}}]$$
(4.29)

which contains all skeleton Feynman diagrams constructed from the local Green's function $\mathcal{G}_{loc}^{\mathbf{R}}$ centered on the local site \mathbf{R} , and the corresponding local Coulomb repulsion $\mathcal{U}^{\mathbf{R}}$. Notice that the exact functional Φ and the DMFT functional Φ^{DMFT} have exactly the same topological structure in terms of Feynman diagrams. The only difference is that Φ is a functional of full Green's function G and bare Coulomb interaction v while Φ^{DMFT} is a functional of $\mathcal{G}_{loc}^{\mathbf{R}}$ and $\mathcal{U}^{\mathbf{R}}$.

The essential DMFT variable $\mathcal{G}_{loc}^{\mathbf{R}}$ can be computed by projecting the Green's function of the whole system onto the defined DMFT local orbitals. We define here the projection operator \hat{P} as

$$\mathcal{G}_{loc}^{\mathbf{R}} = \hat{P}^{\mathbf{R}} G \equiv |\chi_{\mathbf{R}}^{L}\rangle \langle \chi_{\mathbf{R}}^{L} | G | \chi_{\mathbf{R}}^{L'} \rangle \langle \chi_{\mathbf{R}}^{L'} |$$
(4.30)

where $\{|\chi_{\mathbf{R}}^{L}\rangle\}$ is a local orbital set centered on a given nucleus at \mathbf{R} , and \mathbf{L} is an orbital index. To compute $\Phi_{\mathcal{U}}[\mathcal{G}_{loc}^{\mathbf{R}}]$ the system is mapped to a quantum impurity model, for which $\mathcal{G}_{imp} = \mathcal{G}_{loc}^{\mathbf{R}}$ so that the exact solution of the impurity problem $\Phi_{\mathcal{U}}[\mathcal{G}_{imp}]$ delivers desired LW functional. The DMFT self-energy is then obtained from the auxiliary impurity self-energy, as required by the Baym-Kadanoff formalism:

$$\Sigma^{\text{DMFT}} = \frac{\delta \Phi^{\text{DMFT}}}{\delta G} = \sum_{\mathbf{R}} \frac{\delta \mathcal{G}_{loc}^{\mathbf{R}}}{\delta G} \frac{\delta \Phi_{v}[\mathcal{G}_{loc}^{\mathbf{R}}]}{\delta \mathcal{G}_{loc}^{\mathbf{R}}}$$
$$= \sum_{\mathbf{R},LL'} |\chi_{\mathbf{R}}^{L}\rangle \Sigma_{imp}^{\mathbf{R},LL'} \langle \chi_{\mathbf{R}}^{L'}| \equiv \hat{E} \Sigma_{imp}$$
(4.31)

where we define the embedding \hat{E} . This embedding process is the inverse operation of the projector \hat{P} , mapping the self-energy of the auxiliary impurity back into the Hilbert space of the original system.

4.3 Exact Double-Counting of LDA+DMFT

To derive the double-counting functional, we need to identify the exchange-correlation overlap between LDA and DMFT. However, there is a discrepancy between the DMFT functional $\Phi^{\text{DMFT}}[\mathcal{G}_{loc}]$ and the LDA functional $E_{xc}^{\text{LDA}}[\rho]$ because DMFT consists of all skeleton diagrams computed in the corresponding auxiliary impurity system while LDA takes the highly nonlinear exchange-correlation of uniform electronic gas that cannot separate orbitalwise. The double-counting issue arises because it is not clear how to identify the exact overlap between the two methods, that is, what physical process in one is also accounted in the other and vice-versa. In practice, it is usually approximated by the the atomic limit formula in the context of LDA+U [57, 68]. In this section, we give a rigorous derivation for the double-counting formula of LDA+DMFT which has not been proposed before and will be tested on H_2 molecule, one of the simplest strongly correlated systems.

We first note that the DMFT approximation can be obtained by replacing the full Green's function G and bare Coulomb interaction $v(|\mathbf{r} - \mathbf{r}'|)$ with the local counterpart \mathcal{G}_{loc} and \mathcal{U} in the exact LW functional, that is, $\Phi[G] \rightarrow \Phi_{\mathcal{U}}^{\text{DMFT}}[\mathcal{G}_{loc}]$. For diagrammatic approximations such as Hartree-Fock or GW, $v \rightarrow \mathcal{U}$ and $G \rightarrow \mathcal{G}_{loc}$ directly give the DMFT truncation of these methods. For Hartree functional, the local DMFT counterpart is

$$E^{H}[\rho] = \frac{1}{2} \int_{\mathbf{rr}'} \rho(\mathbf{r}) \rho(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') \longrightarrow E^{H}_{\mathcal{U}}[\hat{P}\rho] = \frac{1}{2} \int_{\mathbf{rr}'} [\rho_{loc}(\mathbf{r})][\rho_{loc}(\mathbf{r})]\mathcal{U}(\mathbf{r} - \mathbf{r}')$$
(4.32)

where the $\hat{P}\rho(\mathbf{r}) = \rho_{loc}(\mathbf{r}) = -\hat{P}G(\mathbf{r}, \mathbf{r}; \tau = 0^{-})$. On the other hand, for the *GW* functional, we have

$$\Phi^{GW}[G] = \frac{1}{2} \operatorname{Tr} \log(1 - GGv) \longrightarrow \Phi^{GW}_{\mathcal{U}}[\hat{P}G] = \frac{1}{2} \operatorname{Tr} \log(1 - \mathcal{G}_{loc}\mathcal{G}_{loc}\mathcal{U}).$$
(4.33)

For both methods, we can analytically evaluate the double-counting terms as long as we are given the form of the screened interaction \mathcal{U} .

Finally, let us derive the exact double-counting, for the LDA exchange-correlation functional, i.e., taking the DMFT truncation on it. However, this case is not so simple as we did for Hartree and GW because it is not explicit how the LDA correlation functional depends on the given interaction \mathcal{U} . As discussed in 4.1.3, the correlation part $E_c^{\text{LDA}}[\rho]$ is obtained by quantum Monte-Carlo simulation based on the bare Coulomb interaction $v(\mathbf{r}, \mathbf{r}')$.

In the following work, we investigate this double-counting in the H₂ molecule, where there is virtually no screening effect. Therefore, we can take for this problem the bare Coulomb interaction as the effective interaction in the DMFT local space, i.e., $\mathcal{U} \sim v$. Since there is no need to change the form of the LDA functional, the truncation $G \rightarrow \hat{P}G = \mathcal{G}_{loc}$ simply gives the double-counting functional

$$\Phi_{DC}[\hat{P}\rho] = \sum_{\mathbf{R}} \left(E^{H}[\rho_{loc}^{\mathbf{R}}] + E_{xc}^{LDA}[\rho_{loc}^{\mathbf{R}}] \right)$$
(4.34)

and we will discuss the quality of this double-counting functional in the result section.

Although LDA+DMFT is very often used in solid-state electronic structure calculations, such a rigorous approach has never been suggested before. This is because in the solids, there is additional complexity of screening, whereby the core, semicore and other states excluded by the DMFT model screen the Coulomb interaction in the DMFT correlated space. Therefore the derivation of the DMFT Luttinger-Ward functional in solids requires not only the substitution of the total Green's function G by \mathcal{G}_{local} but also unscreened Coulomb repulsion $v = \frac{1}{|\mathbf{r}-\mathbf{r}'|}$ by screened one

$$\mathcal{U} = \frac{e^{-\lambda |\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|}.$$
(4.35)

For solid state calculations, therefore, in order order to use a similar functional as (4.34), we need to recompute the LDA exchange-correlation functional for the electron gas model based on the Yukawa screened potential (4.35) using the quantum Monte-Carlo calculation. Now the parameter space is two-dimensional: one is r_s , a function of density, and the other is the inverse screening length λ . The same screened form of the Coulomb repulsion has to be then used in the DMFT impurity calculation, i.e.,

$$\mathcal{U}_{m_1m_2m_3m_4} = \langle m_1m_2 | \frac{e^{-\lambda |\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} | m_3m_4 \rangle.$$
(4.36)

Notice that the screening length λ is uniquely determined by the screened Coulomb parameter \mathcal{U} , which can be estimated by constrained LDA [69] or constrained RPA [70]. In other words, we first calculate the $\mathcal{U}_{m_1m_2m_3m_4}$ using cRPA or whatever reasonable method, and the corresponding λ is determined by (4.36). Our double-counting term is then written as

$$\Phi_{DC}[\hat{P}\rho] = \sum_{\mathbf{R}} \left(E^{H}[\rho_{loc}^{\mathbf{R}};\lambda] + E_{xc}^{LDA}[\rho_{loc}^{\mathbf{R}};\lambda] \right).$$
(4.37)

This idea has been recently realized in [71] by K. Haule, the academic advisor of the author of this article. The quality using this functional tested in $SrVO_3$ and $LaVO_3$ was improved showing better agreement to experiment. The work also showed that among the conventionally used double-counting schemes, the nominal double-counting was in the best agreement to this exact double-counting scheme.

4.4 Implementation in H₂ molecule

The study of correlations in small molecules can be a testbed for the quality of electronic structure methods because numerically exact results exist. From the DMFT view point, this has a particularly strong appeal because the screening of the Coulomb repulsion can be negligible and therefore the ambiguities due to screening, present in solid state, can be decoupled from the issues concerning construction of the functional and its precision. In addition, the short-range nature of dynamical correlation in molecules [72, 73] further justifies the applicability of DMFT to molecules. While H_n clusters [7] and H- cubic solid [54] have been investigated within the DMFT framework, the simplest case of H_2 molecule, which shows very strong correlations at large nuclear separation, has not been studied yet by DMFT.

We apply the LDA+DMFT formalism with the exact double-counting that we proposed in the previous section to H_2 molecule. Since we can neglect the screening effect in H_2 , this simple toy model allows us to focus on the quality of the newly proposed double-counting functional free from the issue of determining the effective interaction in the DMFT local space.

Our basis set is the eigenfunctions of H_2^+ exactly solved by the methodology of Ref. [74]. We denote the ground state and the first excited state by $|1\sigma_g\rangle$ and $|1\sigma_u\rangle$, respectively. Typically between other 20-30 excited states are used as a basis for H_2 calculation for good convergence.

Since DMFT is a basis set dependent approximation, its quality depends essentially on the choice of the projector [75, 76, 77, 78, 79, 80], which maps the continuous problem to a discrete set of sites (lattice), each consisting of only a few important degrees of freedom (orbitals). In this work, we restrict our discussion to the simplest possible DMFT approximation, taking only one correlated orbital per site. Since the two sites are equivalent by the symmetry, the problem reduces to a single site one orbital impurity problem, which can be solved to very high precision by the continuous time quantum Monte Carlo method [47], as implemented in Ref. [81].

A good choice of the DMFT projector should have large overlap with the most active states around the Fermi level, should be well localized on an atom, recover atomic solution in the large separation limit, and finally should not depend on the self-consistent charge density. Without the last condition, it is impossible to obtain a stationary solution by extremizing Luttinger-Ward functional.

A natural choice of the DMFT projector of this H_2 problem is the linear combination of the lowest bonding $|1\sigma_g\rangle$ and anti-bonding state $|1\sigma_u\rangle$ of H_2^+ system, which we define as the "left" (L) and the "right" (R) localized orbital,

$$|\chi_L\rangle = \frac{1}{\sqrt{2}}(|1\sigma_g\rangle - |1\sigma_u\rangle),$$

$$|\chi_R\rangle = \frac{1}{\sqrt{2}}(|1\sigma_g\rangle + |1\sigma_u\rangle).$$
 (4.38)

that naturally recover 1s state of each site at large atomic separation. Over 96% of the electronic charge of the DMFT solution is contained in these two states and since they do not explicitly depend on the DMFT Green's function, these are a good choice for DMFT orbital.

We define the DMFT local Green's function for the left atom by the projection

$$\mathcal{G}_{loc}^{L}(\omega) \equiv \hat{P}^{L}G = |\chi_{L}\rangle \langle \chi_{L} | G(\mathbf{r}, \mathbf{r}', \omega) | \chi_{L} \rangle \langle \chi_{L} |$$
(4.39)

where no orbital index appears since each impurity has only one orbital. The impurity self-energy is embedded into real space by the inverse of the projection, i.e., $\Sigma(\mathbf{r}, \mathbf{r}', \omega) =$ $|\chi_L\rangle\Sigma^L(\omega)\langle\chi_L| + |\chi_R\rangle\Sigma^R(\omega)\langle\chi_R|$. Due to the symmetry of the problem, $\Sigma^L = \Sigma^R$ and $G^L = G^R$.

We mention in passing that the alternative choice of projector, which selects as the correlated orbital 1s state of each atom, leads to a result of worse quality than presented here, because such choice does not capture the majority of the active degrees of freedom at equilibrium internuclear separation. Consequently, more time consuming cluster-DMFT method needs to be used to obtain similar quality results, as recently found in Ref. [7]. We

discuss the quality of other choices of the local orbital in detail in Appendix.

In this work, we want to compare the LDA+DMFT result with a variety of other methods. First, we discuss the Hartree-Fock approximation. In this case,

$$\Phi^{\rm HF}[G] = E^{H}[\rho] + E^{X}[\rho], \qquad (4.40)$$

where the each component is

$$E^{H}[\rho] = \frac{1}{2} \int_{\mathbf{rr}'} \rho(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}')$$
(4.41)

$$E^{X}[\rho] = -\frac{1}{2} \sum_{\sigma} \int_{\mathbf{r}\mathbf{r}'} \rho^{\sigma}(\mathbf{r}, \mathbf{r}') v(\mathbf{r} - \mathbf{r}') \rho^{\sigma}(\mathbf{r}', \mathbf{r}).$$
(4.42)

The potential is then computed by

$$v^{H} + v^{X} = \frac{\delta \Phi^{\text{HF}}}{\delta G^{\sigma}(\mathbf{r}, \mathbf{r}'; i\omega)} = \frac{\delta(\mathbf{r} - \mathbf{r}')\rho(\mathbf{r}) - \rho^{\sigma}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
(4.43)

The flexibility of the DMFT approximation allows one to treat some parts of the functional exactly, such as the Hartree-Fock terms. This approximation is denoted by HF+DMFT, i.e.,

$$\Phi^{\rm HF+DMFT}[G] = E^{H}[\rho] + E^{X}[\rho] + \Phi^{\rm DMFT}[\mathcal{G}_{loc}] - \Phi^{\rm HF}_{DC}[\rho_{loc}]$$
(4.44)

Since local part of the Hartree and exchange term is present also in DMFT, we have to subtract terms counted twice

$$\Phi_{DC}^{\rm HF}[\rho_{loc}] = \sum_{\mathbf{R}} E^{H}[\rho_{loc}^{\mathbf{R}}] + E^{X}[\rho_{loc}^{\mathbf{R}}]$$

$$= \frac{1}{2} \int_{\mathbf{rr}'} \rho_{loc}^{\mathbf{R}}(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') \rho_{loc}^{\mathbf{R}}(\mathbf{r}') - \frac{1}{2} \sum_{\sigma} \int_{\mathbf{rr}'} \rho_{loc}^{\mathbf{R},\sigma}(\mathbf{r},\mathbf{r}') v(\mathbf{r} - \mathbf{r}') \rho_{loc}^{\mathbf{R},\sigma}(\mathbf{r}',\mathbf{r})$$
(4.45)
(4.45)

where $\rho_{loc}^{\mathbf{R}} = |\chi_{\mathbf{R}}\rangle \langle \chi_{\mathbf{R}} | \rho | \chi_{\mathbf{R}} \rangle \langle \chi_{\mathbf{R}} |$. In the application of H₂, the site index R takes {L, R}.

Finally, we implement the LDA+DMFT functional for the application of H_2 , in which the DMFT correlations (truncated to small subset of important degrees of freedom) and LDA static correlations complement each other. The functional is

$$\Phi^{LDA+DMFT}[G] = \Phi^{H}[\rho] + \Phi^{X}[\rho] + \Phi^{LDA}_{c}[\rho] + \sum_{\mathbf{R}} \Phi^{DMFT}[\mathcal{G}_{loc}^{\mathbf{R}}] - \sum_{\mathbf{R}} \Phi_{DC}[\rho_{loc}^{\mathbf{R}}] \quad (4.47)$$

where the LDA correlation functional is characterized by the parametrization used in (4.25). Note that in this implementation the exact-exchange functional $\Phi^X[\rho]$ is used because the non-local exchange is large in molecular systems. We also discuss the implementation based on the Slater exchange functional (4.24) and present its result in the Appendix.

The doubly counted correlation term is contained in

$$\Phi_{DC}[\rho_{loc}] = \sum_{\mathbf{R}} \Phi^{H}[\rho_{loc}^{\mathbf{R}}] + \Phi^{X}[\rho_{loc}^{\mathbf{R}}] + \Phi_{c}^{LDA}[\rho_{loc}^{\mathbf{R}}], \qquad (4.48)$$

where the double-counted LDA correlation is

$$\Phi_c^{LDA}[\rho_{loc}^{\mathbf{R}}] = \int_{\mathbf{r}} \varepsilon_c(\rho_{loc}^{\mathbf{R}}(\mathbf{r}))\rho_{loc}^{\mathbf{R}}(\mathbf{r}).$$
(4.49)

This is the exact intersection between LDA and DMFT approximation since it parallels the derivation of the DMFT approximation starting from the exact functional (For details, see Appendix). The double-counting term is hence a "DMFT"-like approximation to the LDA correlation functional. Namely, just as the replacement of the total G by its local counterpart $\mathcal{G}_{loc}^{\mathbf{R}}$ in the exact functional leads to the DMFT approximation, replacing total ρ by $\rho_{loc}^{\mathbf{R}}$ in LDA functional gives the intersection of the two methods.

4.5 Results

In Fig. C.1 we compare the total energy curves of the H₂ molecule versus nuclear separation obtained by different electronic structure methods to the exact result from Ref. [82]. The Hartree-Fock method describes the equilibrium distance quite well ($R \approx 1.39$ compared to exact 1.402), but the energy is severely overestimated, in particularly upon dissociation. This well-known problem is attributed to static correlation that arises in situations with degeneracy or near-degeneracy, as in many transition metal solids and strongly correlated systems.



Figure 4.1: (Color online) Total energy curves of the H_2 molecule versus interatomic distance R calculated by different methods: LDA+DMFT, HF+DMFT, LDA, and HF. The GW and exact result are also presented for comparison.

Due to missing correlations, at large distance the Hartree-Fock method predicts that the two electrons is both found at one nucleus with the same probability as finding them away from each at its own nucleus. By including static local correlations, the LDA method improves on the energy at large distance, although it is still way higher than the energy of two hydrogen atoms. The equilibrium distance is overestimated by LDA ($R \approx 1.46$) and the total energy at equilibrium is similar to its Hartree-Fock value. We also include in the plot the result of the self-consistent GW calculation from Ref. [83], which gives a quite lower total energy at equilibrium and severely overestimated dissociation energy which is comparable to that of LDA.

At large interatomic separation, the static correlations are not adequate because of the near-degeneracy of many body states, which can not be well described by electron density alone. The DMFT uses the dynamical concept of the Green's function and captures correctly the atomic limit. This is because at large interatomic distance the impurity hybridization function, which describes the hoping between the two ions, vanishes, and consequently the impurity solver recovers the exact atomic limit. The inclusion of dynamic correlations by DMFT (HF+DMFT) also substantially improves the total energy for all distances, including at equilibrium, and the error of the total energy is below 1% for almost all distance, except around $R \approx 3.6$, where error increases to 2%. This transition region close to dissociation is notoriously difficult, because correlations beyond single site have significant contribution, and therefore the cluster DMFT is needed to avoid this error [7]. The predicted equilibrium distance is slightly overestimated ($R \approx 1.44$).

Finally, the combination of LDA and DMFT gives surprisingly precise total energy curve. Except around the transition to dissociation ($R \approx 3.6$), it predicts total energy within 0.2% of the exact result, and correct equilibrium distance $R \approx 1.4$. Such success of LDA+DMFT implies that LDA and DMFT capture complementary parts of correlations. While DMFT includes all local dynamical correlations at a single H-ion, it neglects Coulomb repulsion between electrons that are located at different ions, and poorly describes the correlations in the regions close to the midpoint, where $\rho_{local}^{R}(\mathbf{r})$ and $\rho_{local}^{L}(\mathbf{r})$ are comparable in size. In this case, DMFT correlations are approximated by a linear sum of two independent terms, the left and right correlations, which misses the essential non-linearity of the electronic correlations. This situation is very common in solid state calculation, where charges solely from the most localized orbitals (such as d or f) are treated by DMFT, while majority of the electronic charge is described by the LDA correlations. On the other hand, LDA adds correlations due to all electronic charge, which is a static and purely local approximation. The two methods are clearly complementary, and lead to extremely precise total energy when correctly combined.

To gain deeper insight into correlation energy, we plot in Fig. B.1 the correlated energy of the LDA and LDA+DMFT versus ion separation. The LDA correlation energy slightly decreases with increasing distance [84] in contrast to physical expectations. On the other hand, the LDA+DMFT correlation is small when the two ions are close, and it increases sharply with increasing distance, signaling a Mott-like transition, where we find the DMFT self-energy develops a non-analytic pole between highest occupied molecular orbital



Figure 4.2: (Color online) (a) Correlation energy of LDA and LDA+DMFT versus interatomic separation in H₂ molecule. The DMFT correlation is evaluated by $\Phi^{\text{LDA}+\text{DMFT},C} = \Phi^{\text{LDA},C} + \sum_i E^{\text{DMFT},i} - \sum_i \Phi^{DC}[\rho^i_{local}]$, where potential energy $E^{\text{DMFT},i} = \frac{1}{2}\text{Tr}(\Sigma^i_{loc}\mathcal{G}^i_{loc})$. (b) LDA+DMFT double-counting potential V_{DC} versus R, which is defined as the functional derivative of $\Phi^{DC}[\rho^i_{local}]$ given in Eq. 4.49.

(HOMO) and lowest unoccupied molecular orbital (LUMO).

In the lower panel of Fig. B.1, the exact double-counting potential within LDA+DMFT defined as $V_{DC} = \langle \chi_i | \delta \Phi^{DC} / \delta \rho_{local}^i | \chi_i \rangle$ versus R is displayed. The often used phenomenological form U(n - 1/2), first introduced in the context of LDA+U [57], is also shown for comparison. The exact double-counting is kept somewhat smaller than the phenomenological form, and its variation is almost entirely due to variation of local Coulomb repulsion $U = \langle \chi_i \chi_i | v(\mathbf{r} - \mathbf{r}') | \chi_i \chi_i \rangle$, with proportionality constant $V_{DC} \approx 0.412U$. In the solid state calculations, the self-consistent form of the double-counting U(n - 1/2) is also often found too large and is many times reduced (see discussion in Ref. [58].)

In Fig. 4.3, we plot the LDA+DMFT spectral function at equilibrium distance R = 1.4, which has been analytically continued to the real axis by Padé method. The highest



Figure 4.3: (Color online) LDA+DMFT spectral function (red) presented with the HOMO and LUMO energy of LDA (blue), and the exact –IE and EA (black).

occupied quasi-particle peak (HOMO, below 0) has the physical meaning of minus the ionization energy $(-IE = E_{H_2} - E_{H_2^+})$ while the lowest unoccupied peak (LUMO, above 0) corresponds to electron affinity (EA = $E_{H_2^-} - E_{H_2}$). These quantities are called vertical IE and vertical EA, respectively, because these energies of removal/addition of an electron are calculated with fixed interatomic separation R. The exact -IE (-1.207 Ry) and EA (0.224 Ry) are presented as black vertical lines, calculated from the total energy difference using the exact methods [74, 82, 85]. We also mark the position of LDA HOMO (-0.754 Ry) and LDA LUMO (0.084 Ry) with blue lines.

The LDA HOMO is almost 40% off the -IE and the LDA LUMO is around 60% off the EA. This failure of Kohn-Sham (KS) eigenvalues is due to delocalization error of LDA functional, connected with the well known underestimation of band-gaps by LDA [86, 87]. On the other hand, the spectral function of LDA+DMFT, in which the KS eigenvalues are renormalized by DMFT self-energy, shows a sharp resonance around -1.110 Ry (7% of error bar), a substantial improvement from 40% error bar of LDA HOMO. The LUMO peak is also refined from 0.084 Ry (LDA) to 0.192 Ry which is only 0.032 Ry off the exact value.

Although LDA+DMFT spectral function considerably improves the LDA excitations, it still deviates from the exact result (for -IE, it is about 7% off). In order to obtain an insight into this mismatch of the LDA+DMFT spectral function and the exact result, we investigated H_2 in two different ways using GW-RPA approach: (a) one considering GW correlation in the entire Hilbert space and (b) the other where GW is solely confined to the DMFT projected space (Eq (5.43)). Firstly, we found no significant total energy difference (~ 0.005*Ry*) between two schemes. On the other hand, for spectral function, the scheme (a) yields its –IE peak very close to the exact value within 0.1% error while that of the scheme (b), in which GW correlation is restricted to the minimal DMFT orbitals, is also 7% off the exact –IE peak. This indicates that the correlation of the rest of the Hilbert space needs to be included to predict an accurate spectra of H₂ although the correlation within the minimal orbital set (Eq. (5.43)) is enough to capture the total energy precisely. We believe that multi-orbital LDA+DMFT framework, where the DMFT correlations are also extended to higher excited states of the system, would lead to progressively better results.

4.6 summary

In summary, a good implementation of LDA+DMFT with a high-quality projector and exact double-counting that have been introduced here, can rival many quantum chemistry methods in its precision. In the DMFT case, since the most time consuming part of the method – the inclusion of correlations on a given ion – scales linearly with the system size, it holds great promise in future quantum chemistry and solid state applications, although it still needs to be tested in other molecular systems to establish its ultimate usefulness in quantum chemistry applications. We have showed that the H_2 molecule is a very good testing ground for electronic structure methods addressing correlation problem, especially because the screening effects are not obscuring problems connected with the choice of the functional to be minimized. The present methodology will be useful in further developing other electronic structure methods such as GW+DMFT, where the precise form of the functional, the level of self-consistency, screening, and double-counting still need to be adequately addressed.

Chapter 5 Combined GW and DMFT

The dynamical mean-field theory (DMFT) [3, 4] has been very successful to describe correlated electrons, and due to its non-perturbative nature it was able to describe the phenomena of the first order metal insulator transition even in its most simplistic form of the single band Hubbard model [4]. Due to the flexibility of the DMFT, it has been extended in many directions, adding bosonic bath to treat long range spin [88, 89] or coulomb interactions [90], extending the range of correlations from a site to clusters [91] to address the issue of momentum space differentiation, and finally it has been combined with DFT to become more realistic [53]. This combination of DFT and DMFT (DFT+DMFT) has been very successful in describing materials with open d and f shells both for their spectral properties, as well as computing total energy [5] and free energy [6] of crystal phases. Recently, DMFT has also been successfully applied to molecules [7, 8].

Hedin's GW approximation [92, 93] is a many-body perturbative technique, which approximates the self-energy by the lowest order diagram in the screened Coulomb interaction: $\Sigma = -GW$. As opposed to the ground state nature of DFT, where the gaps of the Kohn-Sham spectrum have no physical meaning, in GW approximation the target is the single particle Green's function and therefore the single particle excitation spectrum of GW is expected to be a better prediction than the Kohn-Sham spectrum. Since GW is a diagrammatic method, and DMFT can also be expressed in the diagrammatic form, the combination of the GW and DMFT (GW+DMFT) was proposed [94, 95] as a possibly better alternative to DFT+DMFT. Furthermore, the momentum dependence of GW self-energy is expected to complement the local nature of the DMFT, in particular when the DMFT locality is enforced in less localized basis, such as in the basis of Wannier orbitals. [96, 97, 98].

Most of GW calculations for solid-state systems in practice rely on one-shot GW scheme

(generally denoted as G_0W_0). In this scheme, the GW self-energy is computed only once and the non-interacting Green's function G_0 is obtained from the Kohn-Sham DFT spectrum [99]. The one-shot GW method has been successful for many materials with weak to moderate electronic correlation, giving very good approximation for bandgaps in semiconductors [100]. To remove the dependence on the DFT spectrum through G_0 , the scheme called quasiparticle self-consistent QS-GW was developed [101, 102, 103] where the noninteracting G_0 is determined in a self-consistent way from the GW spectrum.

While the success of the DFT+DMFT is now supported by the numerous applications to solid state systems, which are too numerous to review here, the GW+DMFT method is still in its infancy. Nevertheless, several calculations implementing some flavor of GW+DMFT have been reported recently, both for real materials [104, 105, 106, 107, 108] and for models [109, 110, 111]. However a comprehensive test of numerous GW+DMFT schemes, and their appropriateness for calculating spectra or energy, is still lacking.

Small molecules have served as very good test beds to investigate electronic structure methods. For example, Lin *et al.* [7] applied DMFT to hydrogen chain (H_n) where they found the cluster DMFT produces comparable accuracy to density matrix renormalization group (DMRG). Our previous study of LDA+DMFT on H_2 molecule [60] demonstrated that single-site DMFT with a good choice of local orbitals and exact double-counting method gives extremely precise total energy, and also considerably improves the spectra, as compared to LDA.

In this chapter we perform a comprehensive test of various flavors of GW+DMFT, from fully self-consistent GW+DMFT to G_0W_0 +DMFT and QSGW+DMFT [112]. We compute the total energy and the spectra of H₂ molecule for all these methods, and compare them to DFT+DMFT and the exact solution.

We find that the strongly correlated regime is very challenging for most of GW+DMFT methods, and most of them fail due to causality violation, which has not been properly addressed before. The only exception is the quasiparticle self-consistent method, i.e., QSGW+DMFT. The latter recovers the correct atomic limit only when combined with the static double-counting, in which case it gives comparable spectra and energy to the results of LDA+DMFT.

Close to the equilibrium volume, which can be characterized as the weakly to moderately correlated regime, most of GW+DMFT schemes considerably improve the spectra, as compared to LDA+DMFT, however, the total energy rivals LDA+DMFT total energy only in the fully self-consistent version, which however breaks down in the correlated regime. The quasiparticle method with static double-counting, which performs well in the correlated regime, does not give very accurate total energy in the moderately correlated regime, as it is not derivable from a functional.

Our study demonstrates that the QSGW+DMFT, in combination with static doublecounting, is a promising direction for computing spectra of correlated systems both in moderate to strongly correlated regime. On the other hand, the GW+DMFT methods tested in this work, do not rival LDA+DMFT in predicting the total energy of the system.

5.1 Functional approach for DMFT, GW and GW+DMFT

Let us start by refreshing the Baym-Kadanoff (BK) formalism [66, 67], which provides the functional of the Green's function G

$$\Gamma[G] = \operatorname{Tr}\log G - \operatorname{Tr}((G_0^{-1} - G^{-1})G) + \Phi_v[G], \qquad (5.1)$$

that is stationary for the exact Green's function G, and gives the grand potential, when evaluated on the exact Green's function G (for details see also [53]). Here G_0 is the noninteracting Green's function $G_0^{-1} = [i\omega + \mu - \nabla^2 + V_{ext}(\mathbf{r})]\delta(\mathbf{r}, \mathbf{r}')$ and V_{ext} is the potential due to nuclei. The last term $\Phi_v[G]$ is the so-called Luttinger-Ward (LW) functional, which is the sum of all skeleton diagrams constructed by the Green's function G and the Coulomb repulsion $v(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|}$. The derivative of the LW functional with respect to G gives the exact self-energy of the system

$$\frac{\delta \Phi_v[G]}{\delta G} = \Sigma. \tag{5.2}$$

The stationarity of the functional $\Gamma[G]$ at the exact G ($\delta\Gamma/\delta G = 0$) is ensured by the Dyson equation

$$G^{-1} - [i\omega + \mu - \nabla^2 + V_{ext}(\mathbf{r})]\delta(\mathbf{r}, \mathbf{r}') + \Sigma = 0.$$
(5.3)
The functional $\Phi_v[G]$ is diagrammatically known, but its evaluation is extremely difficult due to fermionic minus sign problem [113]. Nevertheless, this formalism is extremely useful because many good approximations can be devised by approximating Φ rather than Γ , and such approximations were shown to be conserving [66, 67].

One can classify these approximations into two classes: those that truncate correlations in the real space, and those that truncate in the space of Feynman diagrams. In LDA the functional Φ is truncated in real space so that exchange and correlations are local to a point in 3D space, i.e., each point in 3D space is mapped to an independent auxiliary problem of electron gas. In the DMFT the functional Φ is also truncated in real space, but the locality is constraint to a site on the lattice, which is mapped to an auxiliary problem of quantum impurity.

On the other hand, in Hartree-Fock and GW theories, the truncation is done in the space of Feynman diagrams but the complete space dependence of the self-energy is kept. The GW+DMFT can then be seen as the hybrid between these two classes of approaches, as it truncates Feynman diagrams only for the long range part of the correlations, while the short-range correlations can be exactly accounted for by the DMFT.

5.1.1 DMFT

In DMFT method, the locality of correlations is explored and the LW-functional is truncated so that it is a functional of the local Green's function (G_{loc}) only, i.e., it contains all skeleton Feynman diagrams that are constructed from G_{loc} and interaction v, and all diagrams that are outside this range, are removed. In realistic systems, the DMFT method is defined only, once the projector to the local Green's function is specified. In this work, we will use the real space projectors, defined by

$$G_{loc}^{\mathbf{R}} = \hat{P}G \equiv \sum_{LL'} |\chi_{\mathbf{R}}^L\rangle \langle \chi_{\mathbf{R}}^L | G | \chi_{\mathbf{R}}^{L'}\rangle \langle \chi_{\mathbf{R}}^{L'} |.$$
(5.4)

where $\{|\chi_{\mathbf{R}}^L\rangle\}$ is a local orbital set centered on a given nucleus at \mathbf{R} , and L is an orbital index. In the single-orbital DMFT case, which we will test in this work, no sum over L is needed.

The DMFT LW-functional is then

$$\Phi^{\text{DMFT}}[G] = \sum_{\mathbf{R}} \Phi_v[G_{loc}^{\mathbf{R}}].$$
(5.5)

and the functional $\Phi_v[G_{loc}]$ has the same dependence on G_{loc} as the exact functional $\Phi_v[G]$ on G, except that it has finite range. This is because any Feynman diagram of arbitrary topology that is contained in exact $\Phi_v[G]$ is also contained in approximate $\Phi_v[G_{loc}]$. In solid state applications of DMFT, the interaction v has to be replaced by the screened interaction \mathcal{U} due to the fact that many degrees of freedom are being removed from consideration. Screening in molecules is negligible, hence we can safely take $\mathcal{U} = v$ for the molecular systems.

5.1.2 *GW*

Hedin found a closed set of equations based on a Greens function formalism whose solution is the answer to the many-body problem [92]. The variables of those equations that are coupled with each other are the one-particle Greens function G, the screened interaction W, the polarization P, the vertex Γ and the self-energy Σ :

$$G(1,2) = G_0(1,2) + \int d(34)G_0(1,3)\Sigma(3,4)G(4,2)$$
(5.6)

$$\Sigma(1,2) = i \int d(3,4)G(1,3^+)W(1,4)\Gamma(3,2,4)$$
(5.7)

$$P(1,2) = -i \int d(3,4)G(1,3)\Gamma(3,4,2)G(4,1^{+})$$
(5.8)

$$W(1,2) = v(1,2) + \int d(3,4)v(1,3)P(3,4)W(4,2)$$
(5.9)

$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \int d(4,5,6,7) \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6)G(7,5)\Gamma(6,7,3)$$
(5.10)

Those coupled equations above are called Hedin's equations, which provides the exact solution to given many-body system. Although one might attempt to solve Hedin's equations self-consistently, in the technical sense, the problem is quite impossible to solve exactly.

In order to make the problem more feasible to solve, Hedin suggested so-called GW approximation, where we only take the first order of $\Gamma(1,2,3) = \delta(1,2)\delta(1,3)$. Then the

equation becomes

$$G(1,2) = G_0(1,2) + \int d(34)G_0(1,3)\Sigma(3,4)G(4,2)$$
(5.11)

$$\Sigma(1,2) = iG(1,2)W(2,1^{+})$$
(5.12)

$$P(1,2) = -iG(1,2)G(2,1^{+})$$
(5.13)

$$W(1,2) = v(1,2) + \int d(3,4)v(1,3)P(3,4)W(4,2).$$
(5.14)

The name GW is named after the form $\Sigma = iGW$ and the polarization calculated by P = -iGG is also called random-phase approximation (RPA).

A further approximation $\Sigma = iG_0W_0$ is the most widely used scheme, often called oneshot GW or simply G_0W_0 , in which the Green's function is fixed with some non-interacting Green's function. In many cases, we calculate G_0 based on the eigenvalues of the DFT solution [99].

On the other hand, If we solve the equations above equations in a fully self-consistent manner, the scheme is called self-consistent GW. It is only the self-consistent GW scheme where we can define the Luttinger-Ward functional for GW diagrams. Now we follow here the sign convention of the imaginary time formalism so the equations become $\Sigma^{GW} = -GW$ and P = 2GG. The factor 2 is for spin degrees of freedom. From (5.2), its functional form can be written as

$$\Phi_v^{GW}[G] = -\sum_{n=1}^{\infty} \frac{1}{2n} [\operatorname{Tr}(2GvG)]^n = \frac{1}{2} \operatorname{Tr} \log(1 - 2GvG)$$
(5.15)

where the first term (n=1) corresponds to the exchange functional $E_v^X[\rho]$.

5.1.3 *GW*+DMFT

Just like in LDA+DMFT, LW functional of GW+DMFT is a combination of GW functional augmented with the DMFT functional for the local degrees of freedom, i.e.,

$$\Phi^{GW+\text{DMFT}}[G] = E_v^H[\rho] + \Phi_v^{GW}[G] + \sum_{\mathbf{R}} (\Phi_v[G_{loc}^{\mathbf{R}}] - \Phi^{DC}[G_{loc}^{\mathbf{R}}]).$$
(5.16)

The double-counting of GW+DMFT is obtained by applying the DMFT approximation on the GW functional, leading to

$$\Phi^{DC}[G_{loc}^{\mathbf{R}}] = E_v^H[\rho_{loc}^{\mathbf{R}}] + \Phi_v^{GW}[G_{loc}^{\mathbf{R}}]$$
$$= E_v^H[\rho_{loc}^{\mathbf{R}}] + \frac{1}{2} \operatorname{Tr} \log(1 - 2G_{loc}^{\mathbf{R}} v G_{loc}^{\mathbf{R}}).$$
(5.17)

To converge the GW+DMFT equations, we implemented the following steps:

(1) Starting with an initial non-interacting Green's function $G = G_0$, we construct

$$P(\tau) = 2G(\tau)G(-\tau) \tag{5.18}$$

$$W(i\nu) = v/(1 - P(i\nu)v)$$
(5.19)

where all variables above are general matrices.

(2) The GW self-energy is given by:

$$\Sigma^{GW}(\mathbf{rr}';\tau) = -G(\mathbf{rr}';\tau)W(\mathbf{rr}';\tau)$$
(5.20)

(3) From (5.17), we see that the double-counted GW contribution to the self-energy is :

$$\Sigma_{DC}^{GW}(\tau) = \frac{\delta \Phi_v^{GW}[G_{loc}^{\mathbf{R}}]}{\delta G_{loc}^{\mathbf{R}}} = -G_{loc}^{\mathbf{R}}(\tau) W_{loc}(\tau)$$
(5.21)

where the local components are computed by

$$G_{loc}^{\mathbf{R}} = \hat{P}^{\mathbf{R}}G \tag{5.22}$$

$$P_{loc}(\tau) = 2G_{loc}^{\mathbf{R}}(\tau)G_{loc}^{\mathbf{R}}(-\tau)$$
(5.23)

$$W_{loc}(i\nu) = v/(1 - P_{loc}(i\nu)v).$$
(5.24)

- (4) Electron density is given by $\rho = G(\tau = 0^{-})$.
- (5) Next we calculate the Hartree potential

$$V^{H}(\mathbf{r}) = \frac{\delta \Phi^{H}[\rho]}{\delta \rho(\mathbf{r})} = \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}').$$
(5.25)

(6) $(DMFT \ loop)$ Using local Green's function at each site $G_{loc}^{\mathbf{R}} = \hat{P}_{\mathbf{R}}G$ and the interaction v, we construct the auxiliary impurity model, which delivers the impurity self-energy

$$\Sigma_{imp} = \frac{\delta \Phi_v[G_{loc}^{\mathbf{R}}]}{\delta G_{loc}^{\mathbf{R}}}$$
(5.26)

(7) Putting together GW, DMFT and DC, the total self-energy is obtained by

$$\Sigma = \Sigma^{GW} + \sum_{\mathbf{R},LL'} |\chi_{\mathbf{R}}^L \rangle (\Sigma_{imp}^{\mathbf{R},LL'} - \Sigma_{DC}^{\mathbf{R},LL'}) \langle \chi_{\mathbf{R}}^{L'}|$$
(5.27)

The double-counting is $\Sigma_{DC}(i\omega) = V_{loc}^H + \Sigma_{DC}^{GW}(i\omega)$, with Σ_{DC}^{GW} evaluated in (3), and the local Hartree V_{loc}^H is

$$V_{loc}^{H} = \frac{\delta \Phi^{H}[\rho_{loc}]}{\delta \rho_{loc}}$$
$$= \sum_{LL'} |\chi_{\mathbf{R}}^{L}\rangle \langle \chi_{\mathbf{R}}^{L}|V^{H}[\rho_{loc}]|\chi_{\mathbf{R}}^{L'}\rangle \langle \chi_{\mathbf{R}}^{L'}|.$$
(5.28)

(8) From Dyson equation (5.3), the total Green's function is given by

$$G^{-1} = [i\omega + \mu + \nabla^2 - V_{ext} - V^H]\delta(\mathbf{r} - \mathbf{r}') - \Sigma(\mathbf{rr}'; i\omega), \qquad (5.29)$$

where the chemical potential is determined by enforcing charge neutrality, i.e.,

$$\int d\mathbf{r}\rho(\mathbf{r}) = \int d\mathbf{r}G(\mathbf{r},\mathbf{r};\tau=0^{-}) = Z_{nuclei}$$
(5.30)

(9) For Fully self-consistent GW+DMFT, go back to (1). All variables are updated until self-consistency is reached. For $G_0 W_0 + DMFT$, go to (4). Therefore the GW selfenergy (5.20) and its local counterpart (5.21) do not change over the iterative process while the impurity self-energy, total density and the Green's function are updated.

5.1.4 Quasiparticle self-consistent *GW*+DMFT and its double-counting

First, let us discuss the quasiparticle self-consistent GW [101, 102, 103]. It is similar to G_0W_0 in that the polarization $P = 2G^{\rm QP}G^{\rm QP}$ and the self-energy $\Sigma = -G^{\rm QP}W^{\rm QP}$ are computed from a free-particle Green's function $G^{\rm QP} = 1/(\omega + \mu - H^{\rm QP})$, in which $H^{\rm QP}$ is a Hermitian non-interacting Hamiltonian, which is however determined in a self-consistent way from the GW spectra.

Refs. [101, 102, 103] proposed to solve the following quasiparticle equation

$$\left[-\nabla^2 + V_{ext} + V^H + \operatorname{Re}\Sigma^{GW}(E_n) - E_n\right] |\psi_n\rangle = 0.$$
(5.31)

to determined the Hermitian quasiparticle Hamiltonian with the form $[H^{\rm QP} - E_n] |\psi_n\rangle = 0$. Since the GW self-energy has a weak frequency dependence, we may use $\operatorname{Re}\Sigma^{GW}(\omega) \approx$

 $\operatorname{Re}\Sigma^{GW}(0) + \frac{\partial \operatorname{Re}\Sigma^{GW}(0)}{\partial \omega} \omega = \operatorname{Re}\Sigma^{GW}(0) + (1 - Z^{-1})\omega$ where the quasiparticle renormalization amplitude matrix is

$$Z^{-1} = 1 - \frac{\partial \operatorname{Re}\Sigma^{GW}(0)}{\partial \omega}, \qquad (5.32)$$

which gives the following form for the quasiparticle Hamiltonian

$$H^{\rm QP} = Z^{1/2} \big[-\nabla^2 + V_{ext} + V^H + \text{Re}\Sigma^{GW}(0) \big] Z^{1/2}.$$
(5.33)

Since the QSGW procedure provides a static effective Hamiltonian in which the GW spectral information is encoded, one might think that QSGW Hamiltonian can simply

replace the KS Hamiltonian of DFT+DMFT and yield better accuracy. However, to implement QSGW+DMFT, there is a subtle issue concerning the double-counting between the H^{QP} and DMFT correlation.

Since H^{QP} is constructed based on the real part of GW self-energy, one may attempt to approximate $H^{\text{QP}} + \Sigma(i\omega) = H^{\text{QP}} + \hat{E}(\Sigma_{imp}(i\omega) - \text{Re}\Sigma_{DC}^{GW}(i\omega))$. But this self-energy obviously violates the causality condition as it does not respect the Kramers-Kronig relation. In the following, we will introduce two double-counting schemes, which obey the Kramers-Kronig relation.

Static double-counting (SDC)

In the simplest approach, we can take the double-counting as the zero-frequency value of the local-GW self-energy, i.e.,

$$\Sigma^{SDC} = V_{loc}^{H} + \operatorname{Re}\Sigma_{DC}^{GW}(\omega = 0)$$
(5.34)

where Σ_{DC}^{GW} is the exact DC given by Eq. (5.21). Recently, the combined method QSGW+DMFT, has been implemented for real materials in Ref. [108], in which the static double-counting was employed.

We implement QSGW+DMFT as follows:

- (1) We start with initial values for G^{QP} , $\rho(\mathbf{r})$ and $\Sigma_{imp}(i\omega)$. We take their LDA counterparts H^{KS} , $(G^{\text{QP}})^{-1} = i\omega + \mu H^{KS}$ and ρ^{LDA} . For the impurity self-energy, we start with the local Hartree-Fock.
- (2) Self-energies are constructed $\Sigma^{GW} = -G^{QP}W^{QP}$ and $\Sigma^{GW}_{DC} = -G^{QP}_{loc}W^{QP}_{loc}$ and then we obtain the double counting $\Sigma^{SDC} = V^H_{loc} + \Sigma^{GW}_{DC}(w=0)$.
- (3) Next, the Hartree potential is computed from the density

$$V^{H}(\mathbf{r}) = \frac{\delta \Phi^{H}[\rho]}{\delta \rho(\mathbf{r})} = \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}')\rho(\mathbf{r}').$$
(5.35)

(4) The quasiparticle Hamiltonian H^{QP} is computed using Eq. (5.33), so that new $(G^{\text{QP}})^{-1} =$

 $i\omega + \mu - H^{\text{QP}}.$

(5) The total Green's function is then given by

$$G = \frac{1}{i\omega + \mu - H^{\text{QP}} - \hat{E}(\Sigma_{imp} - \Sigma^{SDC})}.$$
(5.36)

- (6) The density and the chemical potential are computed from $\rho(\mathbf{r}) = G(\mathbf{r}, \mathbf{r}, \tau = 0^{-1})$.
- (7) (DMFT loop) from the local Green's function $G_{loc}^{\mathbf{R}} = \hat{P}^{\mathbf{R}}G$ and the interaction v, the impurity solver calculates a new impurity self-energy:

$$(G_{loc}^{\mathbf{R}}, v) \to \Sigma_{imp}(i\omega).$$
 (5.37)

(8) With updated variables G^{QP} , ρ and Σ^{imp} , go to the step (2).

The main difference between our QSGW+DMFT and that of Ref. [108] is that the quasiparticle H^{QP} in Ref. [108] was calculated from QSGW only, and the feedback of the DMFT self-energy on H^{QP} was ignored. In our case, we recompute H^{QP} from the physical selfconsistent Green's function in every iteration.

Dynamical double-counting (DDC)

Although the static local GW term is subtracted, one can expect that the spectral function is possibly over-renormalized because H^{QSGW} , which is renormalized by GW, is again renormalized by the DMFT self-energy.

This is a very subtle issue for QSGW+DMFT because the dynamical effects of GW self-energy are incorporated in the static QSGW Hamiltonian H^{QP} , therefore we would like to subtract the local part of this renormalization.

To overcome this problem, we first construct a *non-local* quasiparticle Hamiltonian H_{nonloc}^{QP} where not only GW but also the subtraction of the local GW is incorporated. The bandwidth of correlated orbitals of H_{nonloc}^{QP} must be wider than H^{QP} because we *unrenormalize* the local GW effect in H_{nonloc}^{QP} . This widened band is then corrected by the impurity self-energy, which is expected to be more accurate than the local GW self-energy.

In order to define the non-local quasiparticle Hamiltonian H_{nonloc}^{QP} , using the non-local GW self-energy we write

$$\Sigma_{nonloc}^{GW}(\omega) = \Sigma^{GW}(\omega) - \Sigma_{DC}^{GW}(\omega), \qquad (5.38)$$

and we compute

$$\bar{Z}^{-1} = 1 - \frac{\partial \Sigma_{nonloc}^{GW}(0)}{\partial \omega}$$
(5.39)

and then we define

$$H_{nonloc}^{\rm QP} = \bar{Z}^{1/2} \big[-\nabla + V_{ext} + V^H + \Sigma_{nonloc}^{GW}(0) \big] \bar{Z}^{1/2}.$$
(5.40)

The above algorithm then has to be modified so that the step (5) in computing the total Green's function uses

$$G = \frac{1}{i\omega + \mu - H_{nonloc}^{\text{QP}} - \hat{E}(\Sigma_{imp} - V_{loc}^{H})}.$$
(5.41)

rather then (5.36).

This DDC approach shares the basic idea of the scheme introduced by Tomczak in Ref. [114], where he calculated the H_{nonloc}^{QP} along the real frequency. On the other hand, we implement the scheme based on the Matsubara formalism using linearization of the GW self-energy.

5.1.5 Causal double-counting scheme for GW+DMFT

We propose here another type of double-counting for GW+DMFT, which we denote as causal double-counting (CDC). As will be clear in the III. A. 1, GW+DMFT with the exact double-counting (Eq. (5.21)) suffers a causality violation that does not allow GW+DMFT to work in the strongly correlated regime. To avoid the causality breakdown, we introduce causal double-counting (CDC) functional

$$\Sigma^{DC} = \hat{P} \Sigma^{GW}. \tag{5.42}$$

and we will discuss why this double-counting scheme allows us to avoid the causality issue in the III. A. 2.

One can notice that the CDC is not exact because this double-counting contains the diagrams in which the degrees of freedom of the DMFT local orbitals and the rest of the space interact through the screened interaction W, which is not contained in the DMFT self-energy. Nevertheless, it allows GW+DMFT to work in the strongly correlated regime without violating the causality.

5.1.6 Computational details

In this work we use only the single site DMFT combined with LDA and various flavors of GW. We use the same choice of the DMFT projector as in our previous study of LDA+DMFT [60], the linear combination of the lowest two orbitals of H_2^+ cation, $|1s\sigma_g\rangle$ (bonding) and $|1p\sigma_u\rangle$ (anti-bonding) state. We denote them as the "left" (L) and the "right" (R) localized orbital:

$$|\chi_L\rangle = \frac{1}{\sqrt{2}} (|1s\sigma_g\rangle - |1p\sigma_u\rangle),$$

$$|\chi_R\rangle = \frac{1}{\sqrt{2}} (|1s\sigma_g\rangle + |1p\sigma_u\rangle).$$
(5.43)

This orbital set is a good choice for the DMFT projector because i) they are well-localized at each atomic site, ii) they naturally recover 1s orbital (the ground state of H) on each site at large atomic separation, iii) over 96% of the electronic charge of the DMFT solution is contained in these two states, which implies most of correlation can be captured within the single site approach, and iv) they do not explicitly depend on the self-consistent charge density. The last condition is especially important for a stationarity of the DMFT solution, given that we are extremizing the Luttinger-Ward functional.

Since H_2^+ is a one-electron problem, the solution is achieved by solving the single-particle Schrödinger's equation. We follow a recursive approach (see Ref. [74]) to solve H_2^+ cation and several lowest orbital energies are presented in Fig. 5.1.

The entire Hilbert space of H_2 is spanned by approximately 30 Gaussian orbitals (correlationconsistent basis set, cc-pVTZ [115]). We want to emphasize that the GW calculation in



Figure 5.1: (Color online) The lowest two orbital energies of H_2^+ cation as a function of R, which are taken to define the DMFT projector (Eq. (5.43)).

this study is converged with respect to the size of the basis set, which is very challenging in solid state applications, and this is another reason why such tests of GW+DMFT are important and useful.

We evaluate the ground state energy of GW+DMFT schemes using the Galitskii-Migdal formula

$$E = \operatorname{Tr}(H_0\rho) + \frac{1}{2}\operatorname{Tr}(\Sigma G)$$
(5.44)

where H_0 is the non-interacting part of Hamiltonian $H_0 = -\nabla^2 + v_{ext}$, ρ is the total electron density, and G is the total Green's function of the system.

The inverse temperature is set to be $\beta = 1/k_BT = 100Ry^{-1}$. Since the orbital energy gap of H₂ is order of several Ry, this temperature is sufficiently low and therefore describes the ground state.

5.2 Results and discussion

The H_2 molecule is a archetypical correlated system, often taken as an example to demonstrate the failure of methods that use the single slater determinant ansatz, such as Hartree-Fock and LDA. In the dissociation limit, such methods predict delocalized ground state, which never recovers correct atomic limit. *GW* approximation, a many-body perturbative method, only slightly improves on LDA in this strongly correlated limit as well. The electronic correlations are only moderate around equilibrium distance (R = 1.4 a.u.), nevertheless none of these methods (LDA, HF or GW) give an accurate total energy compared to the exact solution, achieved by the configuration interaction (CI) method.

In addition the prediction of the ionization energy (IE) from single particle spectral function is a very good indicator of the quality of the predicted single particle spectra within a given approximation. As is known from the exact solution, the ionization energy is the energy required to remove a single electron, i.e.,

$$H_2 + IE \rightarrow H_2^+ + e^-$$

$$\Rightarrow IE = E(H_2^+) - E(H_2)$$
(5.45)

where $E(\text{H}_2^+)$ is the ground state energy of H_2^+ . We computed the single particle Green's function in all tested approaches, and checked how well they predict the position of the peak in the spectral function corresponding to the IE energy.

5.2.1 **GW+DMFT**

Total energy

Fig. C.1 show the total energy of several GW+DMFT methods and compares it to the results of LDA+DMFT, HF, GW and the exact solution. The LDA+DMFT results were already presented in our previous work [60], where we checked the accuracy of this approximation, and we showed the importance of using the exact double-counting within LDA+DMFT. The accuracy of the predicted total energy within LDA+DMFT is excellent, giving correct limit at large distance R of -2.0 Ry, and overall error below 1%, with only exception around the breking of the molecule (R = 3.5 - 4), where non-local corrections become important. At equilibrium distance, the error is less than 0.2%.

As shown in Fig. C.1 all methods tested here give better total energy than Hartree Fock (3.5% error) around the equilibrium distance (R = 1.4). The self-consistent GW gives error of approximately 1.3%. Inclusion of the correlations captured by the DMFT improves the total energy substantially, for example the fully self-consistent GW+DMFT has an error of 0.3% (very similar to 0.2% in LDA+DMFT), In G_0W_0 +DMFT calculation, with G_0



Figure 5.2: (Color online) The ground state energy of GW+DMFT versus R presented with the HF, GW, LDA+DMFT and exact result for comparison. (*inset*) We also added the total energy results of G_0W_0 +DMFT without charge self-consistency (dashed lines).

being based on the Hartree-Fock Hamiltonian ($[G_0W_0]^{\text{HF}}$ +DMFT), the accuracy is almost as good as in GW+DMFT, while in $[G_0W_0]^{\text{LDA}}$ +DMFT, the total energy is slightly less precise.

To show the effects of self-consistency of GW+DMFT in detail, we display in the inset of Fig. C.1 the G_0W_0 +DMFT result at different self-consistent level. The dashed line shows G_0W_0 +DMFT calculation where the total electronic charge is not updated, which is the common practice in solid state applications. In this approach, we first perform selfconsistent LDA (or HF) calculation, and then we fix the Hartree potential V^H and GW selfenergy $\Sigma^{GW} = G_0^{\text{LDA}(\text{HF})}W_0^{\text{LDA}(\text{HF})}$ at the LDA (HF) level, and we perform self-consistent DMFT calculation. Alternatively, when the electronic charge is updated self-consistently on the GW+DMFT charge, the accuracy of the total energy clearly improves.

It is interesting to note that the charge self-consistency has much stronger effect on the total energy than the choice of the non-interacting G^0 in G^0W^0 . Both G^0W^0 +DMFT methods are quite close to the GW+DMFT results when the charge is updated, and much worse when charge is fixed at the LDA/HF level. Perhaps this is not very surprising, as the Hartree term contributes most to the total energy. For total energy calculation, the charge self-consistency is then much more important than the choice of G_0 , despite the fact that the G_0 based on LDA is substantially worse (37% error for IE) than the HF spectra (2% error for IE).

In Fig. C.1 we could not continue GW+DMFT methods towards the the atomic limit, most interesting correlated regime. The fully self-consistent GW+DMFT and $G_0^{\text{HF}}W_0^{\text{HF}}$ +DMFT break down around R = 3 a.u, while $G_0^{\text{LDA}}W_0^{\text{LDA}}$ +DMFT breaks down already at R =2.5 a.u.. The reason for such dramatic failure of GW+DMFT is the causality violation, which we will address in the next section. This is one of the most significant findings of our work, which shows that the self-consistent GW+DMFT or G_0W_0 +DMFT, when using exact double-counting, have no future in addressing the problem of strong correlations.

Causality breakdown

To solve the DMFT problem, and sum all local skeleton diagrams $\Phi_v[G_{loc}^{\mathbf{R}}]$ we construct an auxiliary impurity problem, which has the same interaction v as the original problem, and $G_{loc}^{\mathbf{R}} = \mathcal{G}_{imp}$. Note that in solid-state systems we need to renormalize interaction v due to screening effects, which is not needed here. Note also that this mapping of the local skeleton diagrams to an impurity model is exact, and no further approximation is made in this step. Furthermore, it is convenient to represent the impurity Green's function in terms of proper and improper self-energy (Σ_{imp} and Δ), i.e.,

$$\mathcal{G}_{imp} = \frac{1}{\omega - \varepsilon_{imp} - \Delta - \Sigma_{imp}} \tag{5.46}$$

where Σ is the self-energy due to the Coulomb interaction, while improper part Δ is due to the hybridization of this site with the medium, and is therefore commonly referred to as the Weiss mean field. The causality is violated if any of the three quantities \mathcal{G}_{imp} , Σ_{imp} , or Δ acquire positive imaginary part at any frequency point on the real or imaginary axis.

We want to write the DMFT self-consistency condition $\mathcal{G}_{imp} = \hat{P}G$ in such a way that the Weiss mean field Δ from Eq. 5.46 is expressed explicitly. To derive Δ , we will first eliminate the degrees of freedom which are not corrected by the DMFT (the 30 Gaussian orbitals Hilbert space, which has no overlap with the DMFT projectors). We will call this part of the Hilbert space r. The part of the Hilbert space, which is corrected by the DMFT will be denoted by d. In the second step, we will extract the Green's function of a single site, which is needed by the single site DMFT, and appears in the equation for hybridization Δ .

We start with the Green's function of GW+DMFT from Eq.5.29:

$$G = \left(\omega + \mu - H^H - \Sigma^{GW} - \hat{E}(\Sigma_{imp} - \Sigma^{GW}_{DC})\right)^{-1}$$
(5.47)

where we denoted $H^H = -\nabla^2 + v_{ext} + v^H$. We next write it in the block form, where dd part of the matrix is corrected by the DMFT, and the rest is not:

$$G = \begin{pmatrix} \left[\omega + \mu - H^H - \Sigma^{GW}\right]_{dd} - \Sigma_{imp} + \Sigma^{GW}_{DC} & - \left[H^H + \Sigma^{GW}\right]_{dr} \\ - \left[H^H + \Sigma^{GW}\right]_{rd} & \left[\omega + \mu - H^H - \Sigma^{GW}\right]_{rr} \end{pmatrix}^{-1}$$
(5.48)

We then eliminate the r part of the matrix, so that the G_{dd} becomes

$$G_{dd} = \left[\mathbb{1}(\omega + \mu - \Sigma_{imp} + \Sigma_{DC}^{GW}) - (H^H + \Sigma^{GW})_{dd} - M_{dr}M_{rr}^{-1}M_{rd}\right]^{-1}$$
(5.49)

where we denoted

$$M_{dr(rd)} = [H^H + \Sigma^{GW}]_{dr(rd)}$$

$$M_{rr} = [\omega + \mu - H^H - \Sigma^{GW}]_{rr}.$$
 (5.50)

We emphasized here that the dd part of G is still a matrix, in our case 2×2 for the two H atoms. In solid state, the dd part would be an infinite matrix, containing the correlated degrees of freedom, but written in real space. In the second step we express the Green's function of a single site, as needed by the DMFT. We first define a matrix S:

$$S \equiv (H^{H} + \Sigma^{GW})_{dd} + M_{dr} M_{rr}^{-1} M_{rd}$$
(5.51)

so that

$$G_{dd} = \left[\mathbb{1}(\omega + \mu - \Sigma_{imp} + \Sigma_{DC}^{GW}) - S\right]^{-1}$$
(5.52)

and then the local Green's function becomes

$$G_{loc} = \frac{1}{\omega + \mu - \Sigma_{imp} + \Sigma_{DC}^{GW} - S_{11} - S_{12} \frac{1}{\omega + \mu - \Sigma_{imp} + \Sigma_{DC}^{GW} - S_{22}} S_{21}}$$
(5.53)

The crucial point is that in the correlated regime Σ_{imp} becomes large (diverges) and therefore we can neglect the last term in the denominator. Physically, this comes from the fact that in the correlated regime the correlated sites (H-atoms) decouple, and the effective hopping between them is thus cut-off by the appearance of large local Σ_{imp} , and therefore DMFT is able to recover the correct atomic limit. We thus have

$$G_{loc} = \frac{1}{\omega + \mu - \Sigma_{imp} + \Sigma_{DC}^{GW} - S_{11} - O(\frac{1}{\Sigma_{imp}})}$$
(5.54)

and comparing Eq. 5.54 with Eq. 5.46 revelas

$$\Delta = \underbrace{\left(M_{dr} \frac{1}{(\omega+\mu)\mathbb{1}_{R} - H_{rr}^{H} - \Sigma_{rr}^{GW}} M_{rd}\right)_{11}}_{\equiv \Delta_{R}} + (\tilde{\Sigma}_{11}^{GW} - \tilde{\Sigma}_{DC}^{GW}) + O(\frac{1}{\Sigma_{imp}})$$
(5.55)

where the tilde notation on the self-energy means $\tilde{\Sigma}(\omega) = \Sigma(\omega) - \Sigma(\infty)$, and $\varepsilon_{imp} = -\mu + H_{dd}^H + \Sigma_{dd}^{GW}(\infty) - \Sigma_{DC \ dd}^{GW}(\infty)$. Note that $\Sigma_{11}^{GW} = \hat{P}\Sigma^{GW}$.

Although we used in Eq. 5.53 the fact that S is a 2×2 matrix, it is very easy to check that the resulting Eq. 5.55 is valid in general, even in the solid state with infinite number of correlated sites, a long as Σ_{imp} is large, and sites decouple.

While the first term in Eq. 5.55 (Δ_R) is always causal, the second term is generally not, and its imaginary part can have any sign. It has usually the non-causal sign, because the Σ_{DC}^{GW} tends to be larger than Σ_{dd}^{GW} . As we will show in the section below, in the correlated regime Δ_R becomes small, and then the hybridization becomes non-causal. Naively one would expect that Σ_{11}^{GW} and Σ_{DC}^{GW} would cancel, but they do not, because the projected local self-energy $\Sigma_{11}^{GW} = \hat{P} \Sigma^{GW}$ is

$$\Sigma_{11}^{GW} = [-GW]_{11} = -G_{loc}W_{1111} - \sum_{r \neq 1} G_{rr}W_{1r1r}$$
(5.56)

with the screened Coulomb interaction $W = v[1 - Pv]^{-1}$. Here $G_{11} = G_{loc}$. On the other hand, the double-counted term Σ_{DC}^{GW} is

$$\Sigma_{DC}^{GW} = -G_{loc}W_{loc}.$$
(5.57)

with the screened local interaction defined by $W_{loc} = v[1 - G_{loc}vG_{loc}]^{-1}$. The two terms are then always different.

Note also that within LDA+DMFT, this problem does not occur, because DC is static, and projected Kohn-Sham hamiltonian is also static, hence causality can not be violated.

In the dissociation regime $(R > 3.5 \sim 4.0)$ the hopping between the two H-atoms should vanish, and this can be achieved by diverging impurity self-energy, so that the last term in the denominator of Eq. 5.53, vanishes. In this way we recover the exact atomic limit. And indeed this is how LDA+DMFT achieves the exact atomic limit. On the other hand GW+DMFT breaks down in this regime, and we will show below that this is because $Im\Sigma_{11}^{GW} < Im\Sigma_{DC}^{GW}$.

In Fig. 5.3(a) we show the imaginary part of Δ on the imaginary frequency axis. It is clear that for $R \gtrsim 3.5$ the imaginary part of Δ becomes positive in some frequency regime, violating the causality. In Figs. 5.3(b) and (c), we also present the terms appearing in Eq. 5.55, i.e., Δ_R and $(\hat{P}\tilde{\Sigma}^{GW} - \tilde{\Sigma}^{GW}_{DC})$. Clearly Δ_R is always causal, while $(\hat{P}\tilde{\Sigma}^{GW} - \tilde{\Sigma}^{GW}_{DC})$ has the wrong sign. In the weakly to moderately correlated regime, the last term in the denominator of (5.53) is large since the hopping between the two DMFT orbital, S_{12} , is substantial as the two site are close to each other. Therefore, this term outweighs the noncausal term $(\hat{P}\tilde{\Sigma}^{GW} - \tilde{\Sigma}^{GW}_{DC})$ and the causality is not yet violated in the weakly correlated regime.

One might ask then how is such causality violation avoided in the exact solution, .i.e.,



Figure 5.3: (Color online) The imaginary part of (a) the hybridization function $\Delta(i\omega)$, and its component (b) $\Delta_R(i\omega)$ and (c) $\Delta \Sigma_{DC}^{GW}(i\omega)$ of Eq. (5.55). For the two cases (R=4.0 and 5.0) in which the causality break down, we took the result of the first iteration.

when we replace Σ^{GW} with sum of all non-local Feynman diagrams. We know that in this case we should recover the exact solution. In this particular case, Σ_{DC} would vanish, as all terms are non-local and thus nothing is double-counted. We would then need to see that the projection of the non-local diagrams to the correlated site is positive. But there is a second possibility, which is more likely in low dimensional systems and molecules, namely that the non-local part of the self-energy diverges simultaneously with the local part, and therefore the separation into diverging local and well-behaved non-local part is not possible. In another words, we would not be able to neglect the last term in the denominator Eq. 5.53, because S_{12} is as large as Σ_{imp} . In GW+DMFT, the GW self-energy is always Fermi-liquid



Figure 5.4: The total energy result of GW+DMFT with causal double-counting (CDC) scheme

like and it never diverges.

As clear from the above argument, the causality is not violated if we take the CDC (Eq. (5.42)) because $P\hat{\Sigma}^{GW} - \Sigma^{DC} = 0$. We present the total energy of this scheme in the Fig. 5.4.

In the moderate correlated regime (around R = 1.4), the CDC scheme is worse than exact double-counting scheme both in total energy and spectral function. The error of the total energy of GW+DMFT with CDC, 0.8%, is worse than that of LDA+DMFT (0.2%) or GW+DMFT with exact DC (0.3%). However, it is very important that the CDC doublecounting works correctly at the large distance regime, where all the exact double-counting schemes fail due to the causality violation. As clearly seen, the CDC total energy converges to -2.0.

Although CDC is an ad-hoc scheme, it allows GW+DMFT to work in the strongly correlated regime without violating the causality. Since GW+DMFT is meant for strongly correlated solids where Z is typically small, we argue that the GW+DMFT for solid-state calculation is better when the CDC scheme is used and the effect of using the CDC instead of the exact double-counting should be investigated systematically.

Spectral function

In this section, we present the spectral function, the imaginary part of the Green's function summed over all diagonal component. We choose the zero of energy corresponding to dissociation of the molecule, so that the negative peak in spectra corresponds to the ionization energy. The Padé method is used for analytic continuation from imaginary frequency to real frequency. We mention in passing that Padé approximation is very accurate here, and we found only very minor sensitivity of the pole position (around 0.1%) depending on the choice of the input parameter for Padé method.

In Fig. 5.5 we display the spectral function for R = 1.4 (the equilibrium distance), which corresponds to the moderately correlated regime. The peak position, measured from the vacuum (not from the chemical potential) corresponds to the IE. The LDA prediction for IE is 40% off the exact value. This failure is related to the band gap underestimation in solid-state calculation. On the contrary, the HF prediction is very good in this regime, and is only 1.5% off the exact value. The GW approximation slightly improves on HF, and its IE in the moderately correlated regime is only 1.2% of the exact value.

In Fig. 5.5a we also show the LDA+DMFT prediction, which substantially improves the LDA value from 40% error down to 7.6% error. Nevertheless, the LDA+DMFT spectra is not very accurate, as it builds on too inaccurate starting spectra.

We expect that GW in combination with DMFT improves the GW result. Indeed when combining GW and DMFT in a fully self-consistent way, the error is only 0.9% and when using G_0W_0 from HF (which itself is quite precise), the error is only 0.7%. Somewhat worse is the result of G_0W_0 +DMFT when G_0 is taken from LDA. The error in this case is quite comparable to LDA+DMFT error, but it seems the combination of DMFT and G_0W_0 overcorrects the LDA.

Notice also that the charge self-consistency has almost no effect on the spectra, while we showed before that charge self-consistency is crucial for the accuracy of the total energy. On the other hand, the choice of G_0 is crucial for spectra, but not for the total energy.



Figure 5.5: (Color online) Spectral function for R = 1.4 where the exact IE is $-1.206 \ a.u.$ Each errorbar is presented in the legend. (*upper panel*) GW, LDA, HF and LDA+DMFT for comparison. (*lower panel*) GW+DMFT schemes with different self-consistent conditions. The dashed lines indicates the result without charge self-consistency

We note that the GW+DMFT with CDC is worse than . We attribute this inaccuracy to the fact that the CDC scheme includes the interactions between the DMFT space and the rest of Hilbert space, which is not supposed to be involved in the local impurity self-energy. Therefore, CDC scheme in this scheme is less precise than the GW+DMFT with the exact DC.

On the other hand, at the large separation limit (Fig. 5.6) where the correlation effects are strong, the CDC scheme is the only GW+DMFT method that works without causality violation. It successfully reproduces the spectral function close to the exact value and



Figure 5.6: The spectral function (*upper panel* R=1.4, *upper panel* R=5.0) calculated by GW+DMFT with causal double-counting (CDC) scheme

its quality is comparable to that of LDA+DMFT. All other methods without the DMFT treatment, LDA, HF and GW, are far from the exact ones due to the failure of perturbation theory.

We notice that DMFT considerably improves the total energy of GW in this regime, while the spectra seems barely affected. This is because the renormalization amplitude from local GW self-energy and the DMFT self-energy are almost the same in this weakly correlated regime, and their values are 0.935 and 0.928, respectively.

5.2.2 **QS***GW*+**DMFT**

As shown above, the self-consistent GW+DMFT fails in the correlated regime due to causality violation, which comes from the fact that double-counted self-energy is dynamic and too large. In QSGW the GW spectra is represented by an approximate static Hermitian Hamiltonian, and in this case we expect that approximating the double-counting by a static value might be a reasonable choice. We denoted this choice by SDC. As discussed above, the



Figure 5.7: (Color online) The ground state energy of the QSGW+DMFT results with two different schemes of double-counting. The inset shows the magnification around the equilibrium distance.

static DC term tends to over-count the renormalization effects, and this can be somewhat remediet by choosing dynamic double counting, which we denote by DDC.

In Figs. 5.7 we display the total energy of QSGW+DMFT together with GW, LDA+DMFTand exact total energy. Because the quasiparticle approximation is not derivable from a functional, the energies are unfortunately not very good. At equilibrium, the QSGW+DMFTenergy is very similar to GW energy, while in the correlated regime the addition of DMFT slightly improves the GW energy. Nevertheless, the dynamic double-counting does not recover correct atomic limit, even though DMFT is expected to be exact in the atomic limit. This failure is again due to the double-counting issue, namely, when impurity self-energy is diverging, the hybridization should vanish, but when a dynamic double-counting is used, hybridization does not vanish, and the atomic limit is not reached. In solid state applications, this would correspond to a missed Mott transition in the strongly correlated limit. We



Figure 5.8: (Color online) The QSGW+DMFT spectral results with two different doublecounting schemes at R = 1.4, compared with GW, LDA, HF and LDA+DMFT

see in Fig. 5.7 that only a static DC correctly reproduces atomic limit. But unfortunately the total energy is substantially worse than corresponding LDA+DMFT result. This is not unexpected, as only methods derivable from a functional are expected to give precise total energies. [83]

Next we show the spectral functions of QSGW+DMFT at equilibrium position. Fig. 5.8 compares the GW, LDA+DMFT and two version of QSGW+DMFT schemes with the exact solution. For the static double-counting (SDC) scheme, the spectra is not good, and very comparable to LDA+DMFT result. The origin of the error is however quite different, in QSGW it is due to the double renormalization by both the GW and DMFT, while in LDA+DMFT it is due to missing non-local correlations.

The dynamic double-counting scheme (DDC) substantially improves the spectra in this weakly correlated regime, and the error of IE is only 1%, comparable to the fully self consistent GW+DMFT. However, the DDC scheme is much worse in the strongly correlated regime, both for energy and for spectra.



Figure 5.9: (Color online) Spectral function for R = 5.0. (*upper panel*) Perturbative schemes: HF, LDA and GW. (*lower panel*) LDA+DMFT and QSGW+DMFT with two different double-counting functional.

In Figs. 5.9 we present results at R = 5.0, deep in the correlated regime, where excitations of two almost independent H atoms are expected, with the value close to -1.0 Ry. In this regime QSGW+DMFT with static double-counting (SDC) and LDA+DMFT perform reasonably well, while dynamic double-counting (DDC) fails very similarly to GW approximation. This failure of DDC was also reported in Ref. [105], where a similar scheme to our DDC was tested on SrVO₃.

5.3 Summary

We have implemented GW+DMFT and QSGW+DMFT scheme for H₂ molecule, and we compared the total energy and spectral function with the exact result, and LDA+DMFT. For GW+DMFT, five different calculations have been performed: (i) fully self-consistent GW+DMFT, (ii) $[G_0W_0]^{\text{HF}}$ +DMFT where G_0 is taken from Hartree-Fock, (iii) $[G_0W_0]^{\text{LDA}}$ +DMFT with G_0 from LDA, (iv) $[G_0W_0]^{\text{HF}}$ +DMFT but without charge self-consistency, (v) $[G_0W_0]^{\text{LDA}}$ +DMFT without charge self-consistency. 1) In the strongly correlated regime only LDA+DMFT and QSGW+DMFT with static double-counting give good spectra, and only LDA+DMFT gives good total energy.

2) Most of GW+DMFT schemes fail in the correlated regime due to causality violation. While QSGW+DMFT does not suffer causality violation, it performs reasonably well in the correlated regime only when using the static double-counting.

3) In the Fermi liquid regime of weak to moderate correlations, fully self-consistent GW+DMFT is excellent, both for total energy and spectra.

4) The spectra in the weakly correlated regime is also very accurately obtained by $[G_0W_0]^{\text{HF}}$ +DMFT, but less precise with $[G_0W_0]^{\text{LDA}}$ +DMFT. The QSGW+DMFT with static double-counting, which performs well in correlated regime, is less precise here, as it renormalizes spectra twice. The dynamic double-counting remedies this shortcoming in the weakly correlated regime, but fails in the strongly correlated regime.

5) Total energy in the weakly correlated regime is good in all GW+DMFT schemes (but not in QSGW+DMFT), provided the charge is computed self-consistently.

Chapter 6

Conclusion

In this thesis, we have investigated various applications of the dynamical mean-field theory focused on the methodological aspects: 3D tight-binding model with DMFT, LDA+DMFT and GW+DMFT.

In the 3D Hubbard model, we have given rise to the metal-Mott interface by solving its spatial properties based on DMFT, constructing a Landau free energy and identifying an Ising order parameter. From the solution of the inhomogeneous geometries of metal and Mott insulator, we could relate the interface width l directly to the double-well barrier height via λ/D . We also show that the choice of the quantities conjugate to the physical tuning parameters μ and U allow for an especially transparent construction of the order parameter which can uniformly treat both the bandwidth and filling controlled transitions.

In the study of LDA+DMFT, we proposed the exact double-counting scheme, from which we could reach a very accurate total energy and spectral result in H_2 molecule. In this small molecule, the LDA+DMFT approach becomes a parameter-free scheme since the effective interaction in the DMFT space is simply calculated by the bare Coulomb matrix due to the lack of the screening effect. Our careful construction of the exact doublecounting functional and a good projector has led to a highly precise results in total energy and excitation spectrum. This exact double-counting scheme has been recently extended to solid-state application.

Finally, we have implemented GW+DMFT and QSGW+DMFT scheme and compare the total energy and spectral results for H₂ molecule. For GW+DMFT, we tested the fully self-consistent GW+DMFT, and G_0W_0 +DMFT where G_0 is taken from Hartree-Fock and LDA. We also investigated the effect of charge self-consistency in G_0W_0 +DMFT schemes.

It is shown in our work that due to the mismatch of the projected GW self-energy and

the exact double-counting, causality violation prevents most of GW+DMFT schemes from working in the correlated regime. In the strongly correlated regime only LDA+DMFT and QSGW+DMFT with static double-counting give good spectra, and only LDA+DMFT gives good total energy. While QSGW+DMFT does not suffer causality violation, it performs reasonably well in the correlated regime only when using the static double-counting.

In the Fermi liquid regime of weak to moderate correlations, however, fully self-consistent GW+DMFT is excellent, both for total energy and spectra. For G_0W_0 +DMFT in this regime, we found that the spectra does not sensitively depend on the charge self-consistency but largely depend on the method which the G_0 is based on. On the other hand, the total energy is largely affected by the charge self-consistency while both $G_0^{\rm HF}$ and $G_0^{\rm LDA}$ give a good accuracy. The QSGW+DMFT with static double-counting, which performs well in correlated regime, is less precise in the weakly correlated regime, as it renormalizes spectra twice while the dynamic double-counting scheme improves this shortcoming in this regime.

In summary, the strongly correlated regime is more challenging to describe by GW+DMFT as previously thought, and the causality violation seriously impacts the prospects of using GW+DMFT in this regime. On the other hand, using QSGW+DMFT in this regime leads to somewhat better spectra than employing less demanding LDA+DMFT, but it does not lead to better total energies.

Appendix A

The double-counting functional in detail

We firstly define the projected local Green's function for the *i*-th atom using the DMFT projector $|\chi_i\rangle$ (Eq. (5.43)):

$$G^{i}(\omega) = \langle \chi_{i} | G(\omega) | \chi_{i} \rangle \tag{A.1}$$

where the index i specifies the atomic site L or R and in position space it takes the form of

$$\mathcal{G}^{i}(\omega; \mathbf{r}, \mathbf{r}') = \chi_{i}(\mathbf{r})G^{i}(i\omega)\chi_{i}^{*}(\mathbf{r}').$$
(A.2)

For more complete model, we define projectors containing orbital index α as well as the site index i, $|\chi^i_{\alpha}\rangle$, which is relevant for molecules with heavier atoms. The local Green's function in DMFT basis is then written as $G^i_{\alpha\alpha'} = \langle \chi^i_{\alpha} | G(\omega) | \chi^i_{\alpha'} \rangle$ and its position space version is $\mathcal{G}^i(\mathbf{r}, \mathbf{r}') = \sum_{\alpha, \alpha'} \chi^i_{\alpha}(\mathbf{r}) G^i_{\alpha\alpha'} \chi^{i*}_{\alpha'}(\mathbf{r}')$.

The Luttinger-Ward functional for LDA+DMFT approximation is

$$\Phi^{LDA+DMFT} =$$

$$\sum_{i} \Phi^{DMFT}[G^{i}_{local}] + \Phi^{LDA}[\rho] - \sum_{i} \Phi^{DC}[\rho^{i}_{local}].$$
(A.3)

Here the local density ρ_{local}^{i} is defined in the same way as $\mathcal{G}^{i}(\mathbf{r}, \mathbf{r}')$ from $G(\mathbf{r}, \mathbf{r}')$, namely,

$$\rho_{local}^{i}(\mathbf{r}) = \chi_{i}(\mathbf{r})n_{local}^{i}\chi_{i}^{*}(\mathbf{r})$$
(A.4)

where n_{local}^{i} is local occupation.

The double-counting energy can be split into Hartree-Fock part Φ_{HF}^{DC} and the correlation part Φ_c^{DC} . The Hartree-Fock part is straightforward to evaluate in DMFT basis as

$$\Phi_{HF}^{DC}[\rho_{local}^{i}] = \frac{1}{2} \sum_{\sigma\sigma'} \langle \chi_{i}\chi_{i}|U_{C}|\chi_{i}\chi_{i}\rangle \times$$

$$(n_{local,\sigma}^{i}n_{local,\sigma'}^{i} - \delta_{\sigma\sigma'}n_{local,\sigma}^{i}n_{local,\sigma}^{i}).$$
(A.5)

When a single orbital per site is considered with the above defined projector, the Hartree-Fock energy and potential simplify to

$$\Phi_{HF}^{DC}[\rho_{local}^{i}] = \frac{1}{4} U_{local} (n_{local}^{i})^{2}$$
(A.6)

$$V_{HF}^{DC}[\rho_{local}^{i}] \equiv \frac{\delta \Phi_{HF}^{DC}[n_{local}^{i}]}{\delta n_{local}^{i}} = \frac{1}{2} U_{local} n_{local}^{i}$$
(A.7)

where $U_{local} = \langle \chi_i \chi_i | U_C | \chi_i \chi_i \rangle$ is the local Coulomb matrix element. When multiple orbitals are considered by DMFT, the Hartree-Fock double counting term generalizes to $\Phi_{HF}^{DC} = \frac{1}{2} \sum_{\alpha\beta\gamma\delta,\sigma\sigma'} \langle \chi_{i\alpha}\chi_{i\beta} | U_C | \chi_{i\gamma}\chi_{i\delta} \rangle (n_{\alpha\delta}^{\sigma} n_{\beta\gamma}^{\sigma'} - \delta_{\sigma\sigma'} n_{\alpha\gamma}^{\sigma} n_{\beta\delta}^{\sigma})$. where $\alpha\beta\gamma\delta$ run over active orbitals on a given atom.

The double-counting for correlation energy within LDA+DMFT we propose here is

$$\Phi_c^{DC}[\rho_{local}^i] = \int_{\mathbf{r}} \varepsilon_c^{LDA}(\rho_{local}^i(\mathbf{r}), U_C)\rho_{local}^i(\mathbf{r})$$
(A.8)

This is exactly DMFT approximation of LDA correlation functional, truncating $G(\mathbf{r}, \mathbf{r}') \rightarrow \mathcal{G}^{i}(\mathbf{r}, \mathbf{r}')$ that yields $\rho(\mathbf{r}) \rightarrow \rho^{i}_{local}(\mathbf{r})$. The expression $\varepsilon_{c}^{LDA}(\rho^{i}_{local}(\mathbf{r}), U_{C})$ in Eq. (A.8) implies that it is a functional of both density and Coulomb interaction $U_{C}(\mathbf{r}, \mathbf{r}') = \frac{2}{|\mathbf{r}-\mathbf{r}'|}$. In solid state, we should replace $U_{C}(\mathbf{r}, \mathbf{r}')$ with a screened one $\mathcal{U}^{\lambda}_{C}(\mathbf{r}, \mathbf{r}') = \frac{2e^{-\lambda|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}$ and therefore we need to obtain the LDA correlation functional with respect to two parameters ρ and λ for exact double counting. In small molecular systems such as H₂ screening effect is negligible $(\mathcal{U}^{\lambda}_{C}(\mathbf{r}, \mathbf{r}') \approx U_{C}(\mathbf{r}, \mathbf{r}'))$ and therefore the functional form of the LDA correlation ε_{c}^{LDA} in double-counting (A.8) is intact. The double counting potential V_{DC}^i in the DMFT basis can be easily computed:

$$V_{DC}^{i} \equiv \frac{\delta \Phi_{c}^{DC}[\rho_{local}^{i}]}{\delta n_{local}^{i}} = \int_{\mathbf{r}} |\chi_{i}(\mathbf{r})|^{2} V_{c}^{LDA}[\rho_{local}^{i}(\mathbf{r})]$$
(A.9)

where V_c^{LDA} is the LDA correlation potential that takes the form of $V_c^{LDA} \equiv \varepsilon_c^{LDA} + \delta \varepsilon_c^{LDA} / \delta \rho$. In derivation, we used the relation (A.4) and the chain rule. In more general case with multiple local degrees of freedom, the form of local density (A.4) should be replaced with $\rho_{local}(\mathbf{r}) = \sum_{\alpha,\alpha'} \chi_{\alpha}^i(\mathbf{r}) \rho_{\alpha\alpha'}^i \chi_{\alpha'}^{i*}(\mathbf{r})$ where $\rho_{\alpha\alpha'}^i = \langle \chi_{\alpha}^i | \hat{\rho} | \chi_{\alpha'}^i \rangle$ is projected density matrix onto site *i*.

Appendix B

DMFT on H₂ Problem: Orbital Dependence

A good choice of DMFT orbital should be orbitals that consist of most active levels near the Fermi level, well localized, and moreover, should not depend on the self-consistent charge density. Also the result becomes better if more orbitals are treated dynamically. But of course the basis set convergence is at present not possible to achieve in solid-state applications, so it is important to study such simple systems.

In solid state applications, it is also important that the occupation of the correlated orbital is not too far from nominal valence. And typically well localized orbitals in transition metal oxides give the best nominal occupancy, because oxygen has very long tails which penetrated into transition metal muffin-thin sphere. Nevertheless, it is important to constrain the orbital to have the symmetry of the most active narrow state, i.e., t_{2g} symmetry for early transition metal oxides (TMO), or e_g symmetry for late TMO's.

The most popular choice of correlated orbitals in the context of DMFT are either i) quasi-atomic orbitals, or ii) Wannier functions.

The quasi-atomic orbitals are typically constructed in real space from the solution of the Schroedinger equation of a subsystem (in solid state usually the solution of the Schroedinger equation centered at the correlated ion having certain relevant spherical symmetry, i.e., d or f), and hence their projection into the LDA Kohn-Sham orbitals can span very large energy range. The physical choice of orbitals is such that they have the largest overlap to Kohn-Sham states near the Fermi level, however, due to their strong localization there is nonzero overlap even at very high energy. Typically such orbitals are a very good starting point for DMFT calculation because they avoid mixing excessive amounts of electron-negative ion charge (such as oxygen) into correlated orbital.

The alternative is to more aggressively constrain the energy range of the projection to

the Kohn-Sham space, which is achieved by construction of the Wannier orbitals. These orbitals typically faithfully represent all states of Kohn-Sham Hamiltonian in some chosen energy window, but are as local as possible, given the constraint. When the energy range in constructing Wannier orbitals is large, there is very little difference between the quasiatomic orbitals and Wannier orbitals. However, when the energy range is small, it can lead to severe overestimation of valence, i.e., can give valence very far from nominal valence (for concrete example see PRB 90, 075136 (2014)).

There is another important consideration, which is usually overlooked. The DMFT approximation is stationary only if the projector does not depend on the Green's function. Let's define local Green's function by the projector \hat{P}_i ,

$$\mathcal{G}_{local}^{i} = \hat{P}_{i}G \tag{B.1}$$

The DMFT approximation is the stationary solution of the LDA+DMFT (or HF+DMFT) Luttinger-Ward function only if

$$\frac{\delta P_i}{\delta G} = 0,\tag{B.2}$$

hence, the projector should not dependent on the electron density or the Kohn-Sham orbitals. Only such stationary formulation of DMFT leads to robust solution of the DMFT equations (independent of small details of the implementation) and allows precise evaluation of the total energy. It is clear that the popular choice of Wannier orbitals, which in the simplest case takes the form

$$|W_{\alpha}\rangle = \sum_{k,i} |\psi_{ik}\rangle \langle \psi_{ik}| |\phi_{\beta}\rangle (\frac{1}{\sqrt{O_k}})_{\beta\alpha}$$
(B.3)

 $(O_{k\alpha\beta} = \sum_{i} \langle \phi_{\alpha} | \psi_{ik} \rangle \langle \psi_{ik} | \phi_{\beta} \rangle)$, lead to neither stationary DMFT solution nor stationary total energy since Kohn-Sham states ψ_{ik} depend on the electron density and hence on G.

It is hence important to have a projector that does not depend on the solution itself (on the self-consistent G) and at the same time has correct limits. For example, at large R, we want to project to 1s state of a single H atom. Similarly, in more general case of a solid,



Figure B.1: (Color online) The total energy curve of LDA+DMFT scheme with the local orbital from the lowest even and odd orbital of non-interacting H_2^+ Hamiltonian (the original orbitals used in the main article, red), of LDA effective Hamiltonian (blue), and with 1s orbital itself as the local orbital (green).

we want to recover atomic orbitals in the limit of large separation.

Hence, the lowest bonding and anti-bonding orbital of H_{2+} , the combinations of which are local orbitals centered on the right/left atom, are an obvious choice, but of course not the only choice.

To show how results depend on the choice of the orbital, we show in Fig. B.1 LDA+DMFT results obtained by three different choices of the local orbital. i) Projected localized orbitals (PLO): We constructed Wannier-like orbital using Eq. B.3, where ψ_{ik} are self-consistent Kohn-Sham orbitals from LDA step, and $|\phi\rangle_{\alpha}$ is Hydrogen 1s orbital. ii) "1s": We used Hydrogen 1s orbital, but orthogonalized function centered on the right/left site to obtain normalized projector. iii) The original choice used in the manuscript, which uses the exact solution of H_2^+ problem.

The (PLO) Wannier orbital seems to be quite accurate very near the equilibrium volume, but strongly deviates at larger volumes from the exact result. Since the DMFT solution is not stationary for such orbital, the results are numerically less stable and, in our opinion, less reliable.

The Hydrogen 1s orbital, when properly normalized, performs equally well at large distance. This is not surprising since H_2^+ solution does not deviate much from 1s orbital at large R. But this choice is inaccurate near equilibrium distance, because some of the active degrees of freedom are not properly captured by such fixed orbital. Namely, the local charge ρ_{local} , obtained by projection to local orbital, deviates substantially from the total charge of the system at small R, hence larger error is found in this method.

Appendix C

Exact Double-Counting Based on Slater Exchange Functional

In the implementation of LDA+DMFT on H_2 in Chapter 4 and 5, we used the *exact* exchange functional instead of the Slater exchange scheme, which is a local theory mainly used in LDA calculation. This is because the local approximation for the exchange is very poor in molecular systems, even worse than in solids. While correlations are very local, the exchange is not. We rephrased the sentence in the manuscript to be more clear on this point.

We also tested a simplified version of the semilocal exchange to show how one can cheaply improve semilocal exchange in molecular systems. The most important non-local part of the exchange is the following term

$$\Phi^{leading-nonlocal}[\rho] = -\frac{1}{2} \sum_{\sigma\sigma'} \langle \phi_R(\mathbf{r})\phi_L(\mathbf{r}')|V_C|\phi_L(\mathbf{r}')\phi_R(\mathbf{r})\rangle \langle \phi_R|\rho|\phi_L\rangle \langle \phi_L|\rho|\phi_R\rangle \quad (C.1)$$

If one adds to LDA semilocal exchange $\Phi^{X,LDA}[\rho]$ the leading non-local correction $\Phi^{leading-nonlocal}[\rho]$, the result is already better than HF+DMFT at equilibrium R, and much better than HF or LDA alone. Figure C.1 compares this approximations (named "LDA(semi-local)+DMFT") with the other two approximations presented in the manuscript HF+DMFT, and LDA+DMFT to show that the quality of such approximation is reasonable considering its simplicity.


Figure C.1: (Color online) The total energy curve of the semi local version of LDA+DMFT scheme (blue) proposed here, compared to LDA+DMFT (exact exchange, red), HF+DMFT (cyan) and the exact (black) energy curve.

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