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Strong Correlation Effects in Metallic Systems

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the
Graduate School of The Ohio State University

By

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ABSTRACT

The strong correlation effects due to on-site Coulomb interaction are studied in cerium compounds, Ce$_M^3$ ($M$=Pb, In, Sn, Pd), and in a Hubbard model with orbital degeneracy. In the first half of the dissertation, we have computed the material-specific properties of the cerium compounds by combining the local density approximation and the non-crossing approximation. The electron hopping matrix elements between Ce-4f orbitals and the conduction bands are obtained by the linearized muffin-tin orbital method and are fed in as the model parameters in the Anderson impurity model. For the many-body technique we have used a self-consistent diagrammatic method, known as the non-crossing approximation. The calculations correctly bear out the heavy fermion behavior for CePb$_3$ and CeIn$_3$ systems giving much smaller Kondo temperatures than the crystalline electric field splittings with the doublet cubic irreducible representation as the ground multiplet configuration. For the strongly hybridizing systems, CeSn$_3$ and CePd$_3$, the Kondo temperatures are predicted to be larger than the crystalline electric field splittings, leading to screened magnetic moments at temperatures below the Kondo temperature. These realistic calculations are expected to resolve some of the long-standing controversies in interpreting experiments. In the second part, we study the metal-insulator transition in the multi-orbital Hubbard model as a model for the alkali-doped fullerides, A$_3$C$_{60}$, with the quantum Monte Carlo method. The dynamical aspects of the transition are
studied by analytic continuation of imaginary time Monte Carlo data by means of the maximum entropy method. The multiplicity of the orbitals enhances the hopping of electrons leading to a metallic solution for experimental parameters relevant to $A_3C_{60}$ systems. The Hund's rule exchange coupling effectively increases the Coulomb repulsion between electrons on the same site and, therefore, the competition between the effects of enhanced hopping and the Hund's rule exchange coupling is expected.
To My Parents
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>ii</td>
</tr>
<tr>
<td>Dedication</td>
<td>iv</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>v</td>
</tr>
<tr>
<td>Vita</td>
<td>vii</td>
</tr>
<tr>
<td>List of Tables</td>
<td>x</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xi</td>
</tr>
<tr>
<td>Chapters:</td>
<td></td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Material Oriented Computation for Cerium Compounds: Electronic</td>
<td>9</td>
</tr>
<tr>
<td>Structures and Many-body Effects</td>
<td></td>
</tr>
<tr>
<td>1.2 Metal Insulator Transitions in Hubbard Model with Orbital Degeneracy: Quantum Monte Carlo Calculation</td>
<td>14</td>
</tr>
<tr>
<td>2. Calculation of Hybridization for CeM₃ systems</td>
<td>19</td>
</tr>
<tr>
<td>2.1 Hybridizations in Dilute and Concentrated Limits</td>
<td>21</td>
</tr>
<tr>
<td>2.1.1 Concentrated Limit (CeM₃)</td>
<td>21</td>
</tr>
<tr>
<td>2.1.2 Dilute Limit (CeₓLa₁₋ₓM₃ with x (\rightarrow) 0)</td>
<td>23</td>
</tr>
<tr>
<td>2.2 Calculated Hybridization for CeM₃ ((M)=Pb, In, Sn, Pd)</td>
<td>26</td>
</tr>
<tr>
<td>2.2.1 Density of States of CeM₃</td>
<td>27</td>
</tr>
<tr>
<td>2.2.2 Results for Concentrated and Dilute Limit Hybridization</td>
<td>33</td>
</tr>
<tr>
<td>2.2.3 Hybridizations for CeM₃ ((M)=Pb, In, Sn, Pd)</td>
<td>37</td>
</tr>
</tbody>
</table>

3.1 Energy Scales of the Problem ................................................. 42
3.2 Formalisms ................................................................. 44
3.3 Results ........................................................................ 51
  3.3.1 Spectral Functions ................................................ 51
  3.3.2 Crystalline Electric Field Splittings and Kondo Temperatures 59
  3.3.3 Magnetic Susceptibility ........................................... 61

4. Multi-band Hubbard Model in Infinite Dimensions: Quantum Monte Carlo Calculation .............................................. 70

4.1 Model: Alkali-doped Fullerides ........................................... 73
  4.1.1 On-site Interaction for Multi-orbitals ....................... 74
  4.1.2 Dynamical Mean Field Theory .............................. 76
4.2 Quantum Monte Carlo Method ........................................... 79
  4.2.1 Discrete Hubbard-Stratonovich Transformation .......... 81
  4.2.2 Hirsch-Fye Algorithm ........................................... 83
4.3 Mott-Hubbard Metal Insulator Transition ......................... 87
  4.3.1 Enhanced Hopping with Degenerate Model; \( J = 0 \) Case .... 90
  4.3.2 Hund's Coupling; \( J > 0 \) Case ................................ 96
4.4 Dynamical Properties: Maximum Entropy Method .......... 98
  4.4.1 Formalism ....................................................... 100
  4.4.2 Spectral Function and Optical Conductivity ............. 105

5. Conclusions and Further Directions ........................................ 112

Appendices:
A. Linearized Muffin-Tin Orbital Method .............................. 117
B. Qualitative Discussion on Large Kondo Temperature Estimate for CePd₃ 123

Bibliography ................................................................. 128
<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Lattice constants of compounds</td>
<td>27</td>
</tr>
<tr>
<td>2.2 Electronic configurations of elements</td>
<td>31</td>
</tr>
<tr>
<td>3.1 Electronic configuration of ligand atom M (EC), ground multiplet $\Gamma_{\text{grd}}$, CEF splittings $\Delta_{78}$ and Kondo temperatures $T_K$ for $\text{Ce}<em>x\text{La}</em>{1-x}M_3$ systems. Positive $\Delta_{78}$ indicates a stable $\Gamma_7$ ground doublet on the Ce sites. Units in Kelvin. (*: $\Delta_{78}$ not experimentally deducible for $\Delta_{78} \ll T_K$)</td>
<td>61</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Crystal structure of Ce$M_3$ materials</td>
<td>10</td>
</tr>
<tr>
<td>1.2 Experimental comparison of Ce$M_3(M=\text{Pb, In, Sn, Pd}):$ Bremsstrahlung isochromat spectroscopy and static magnetic susceptibility</td>
<td>11</td>
</tr>
<tr>
<td>1.3 Schematic picture of energy levels of C$<em>{60}$ molecule and the density of states of $A_3C</em>{60}$ system</td>
<td>15</td>
</tr>
<tr>
<td>2.1 Schematic picture of concentrated limit</td>
<td>21</td>
</tr>
<tr>
<td>2.2 Schematic picture of dilute limit</td>
<td>24</td>
</tr>
<tr>
<td>2.3 Density of states of CePb$_3$</td>
<td>29</td>
</tr>
<tr>
<td>2.4 Total density of states of Ce$M_3$</td>
<td>30</td>
</tr>
<tr>
<td>2.5 Projected density of states of Ce-$f$ orbital</td>
<td>32</td>
</tr>
<tr>
<td>2.6 Hybridization of Ce$<em>x$La$</em>{1-x}$Pb$_3$ in concentrated ($x = 1$) and dilute ($x \to 0$) limits</td>
<td>35</td>
</tr>
<tr>
<td>2.7 Hybridization of Ce$<em>x$La$</em>{1-x}$Pb$_3$ ($x \to 0$) and LaPb$_3$ systems</td>
<td>36</td>
</tr>
<tr>
<td>2.8 Hybridization of Ce$M_3 (M=\text{Pb, In, Sn, Pd})$</td>
<td>38</td>
</tr>
<tr>
<td>3.1 Schematic picture of the splitting of the atomic energy levels of Ce$^{4+}$</td>
<td>43</td>
</tr>
<tr>
<td>3.2 $f$-spectral function for CePb$_3$</td>
<td>53</td>
</tr>
<tr>
<td>3.3 $f$-spectral functions for Ce$M_3 (M=\text{In, Sn, Pd})$</td>
<td>57</td>
</tr>
</tbody>
</table>
3.4 NCA magnetic susceptibilities, $\chi(T)$, for CePb$_3$ and CeIn$_3$ fitted to the $\chi(T)$ with Lorentzian hybridizations ............................................................. 62

3.5 f magnetic moment spectrum for CePb$_3$ .................................................. 64

3.6 Theoretical and experimental magnetic susceptibilities for CeM$_3$ ($M=$Pb, In, Sn, Pd) ......................................................................................................... 65

3.7 Theoretical magnetic susceptibilities for CeSn$_3$ at several $\epsilon_f$ with comparison to the experiments .............................................................................. 66

4.1 Schematic plot of one-electron spectral functions in insulating and metallic regime .................................................................................................. 89

4.2 Hopping of an extra electron in the half-filled lattice for $N_{\text{deg}} = 3$ . . 92

4.3 The occupancy $n_d$ versus the $d$-level energy $\epsilon_d$ .............................. 93

4.4 The occupancy $n_d$ versus the Coulomb repulsion $U$ at fixed $\epsilon_d = \epsilon_d - (N_{\text{deg}} - \frac{1}{2})U + 0.2$ ................................................................. 95

4.5 $n_d$ vs. $\epsilon_d - \epsilon_{\text{ph}}$ at $J = 0.0, 0.2, 0.5$ ........................................... 97

4.6 Spectral functions for $N_{\text{deg}} = 1$ ...................................................... 105

4.7 Spectral functions for $N_{\text{deg}} = 1, 2, 3$ at $U = 4$ .............................. 106

4.8 Optical conductivity and resistivity for $N_{\text{deg}} = 2$ at $U = 4$, $\epsilon_d = -1$ . 110

B.1 Plot for the solution of the ground state energy with a model Lorentzian hybridization function ................................................................. 124

B.2 Static magnetic susceptibility with decreasing Lorentzian band-width 125
CHAPTER 1

INTRODUCTION

For the last several decades, a large branch of condensed matter theory has been very successful in describing many-electron systems in nature. Traditionally, the study of electronic materials is approached from two different perspectives: band theory and the many-body theory. The different philosophy lies in how to treat the interaction between electrons. Ironically enough, the two methods owe their successes to approximating or stressing the Coulomb interactions, depending upon the system of interest.

Loosely speaking, the band theory includes the Coulomb interaction through a mean field addition to the atomic potential, which can provide, in principle, an approach for the ground state properties within the density functional theory [1]. The greatest strength of the band theory is its capability of predicting the properties of many solids, much aided by efficient algorithms [2] and the rapid growth of computing power. This theory has served as a method for first-principles calculations of material-dependent properties and the crystalline symmetries. On the other hand, the many-body theory puts much stress on the qualitative understanding of properties of many-particle systems caused by the strong Coulomb interaction, especially dynamical properties. Due to our inability to solve a model with complicated full
interactions, much simplification is made by truncating irrelevant interactions, which is justified only \textit{posteriori} by comparing the qualitative trend with experiments.

In this dissertation, we attempt to include physics usually neglected in the simplified Hamiltonians such as the impurity Anderson model with structureless conduction density of states and the non-degenerate Hubbard model. The first project (in chapter 2 and 3) focuses on the material-specific information concerning the very diverse physical phenomena in the cerium heavy fermion compounds. Even in mature fields such as the study of heavy fermion materials, there are still unsettled controversies [3, 4]. In some cases, we cannot say where the discrepancy between the theory and the experiment lies – does the disagreement come from the fundamental failure of modeling or insufficient information on the detailed electronic structure? To clear up the question, it is essential to carry out materials-oriented many-body calculations on systems of interest.

Recently stimulated by the high-\(T_C\) superconductivities, theorists have tried to understand the many-body aspects of the materials by computing the electronic structures [5, 6]. However, their approach did not properly include the many-body effects which are still anything but clear to this date. Although it has been understood that the present technique of the electronic structure calculations are good enough to predict the high energy scales such as the Coulomb interaction parameters and the crystalline electric field (CEF) splittings for those high-\(T_C\) superconducting materials, the low temperature physics driven by the many-body interactions have not been consistently predicted with the information from the electronic structure calculations, due to the extreme sensitivity of the energy scale to the model parameters.
Heavy fermion systems such as lanthanides and actinides show interesting many-body effects, often called "Kondo effect". The $f$-orbitals in lanthanides or actinides, due to their very localized wave-functions, experience strong on-site Coulomb repulsion, $U$, between $f$-electrons occupying the same site. At high temperatures the systems exhibit magnetic behavior in the form of localized moments from Ce$^{4+}$-$4f^1$ orbitals, leading to a Curie-Weiss magnetic susceptibilities $\chi_{ff}(T) \sim \mu_{ff}^2 / T$. As the temperature lowers, through the hopping of electrons back and forth between the $f$-orbital and the conduction states, the spins of the conduction electrons screen out the magnetic moment of the $f$-orbital in the many-body ground state. The ground state, a singlet, has the lower energy eigenvalue than that of the lowest magnetic state by the many-body energy scale $T_K$, "Kondo temperature". The Kondo temperatures in real materials range from a few to a few hundred Kelvins. At temperatures below $T_K$, the system may recover to the Fermi liquid metal with the Fermi energy replaced by the Kondo temperature. The small "effective Fermi energies", or Kondo temperatures, result in the large effective mass of the many-body state with $100 \sim 1000m_e$, hence the name "heavy fermion" materials.

We model the cerium compounds, Ce$M_3$ systems, in terms of the impurity Anderson model as

$$H = \sum_{\kappa\sigma} \varepsilon_{\kappa\sigma} c_{\kappa\sigma}^\dagger c_{\kappa\sigma} + \frac{1}{\sqrt{N_s}} \sum_{\kappa,\sigma,m} (V_{\kappa m} c_{\kappa\sigma} f_m^\dagger + h.c.) + \sum_m \varepsilon_{f_m} f_m^\dagger f_m + \sum_{m < m'} U_{mm'} n_{f_m} n_{f_{m'}},$$

(1.1)

where $m$ is the label of cubic CEF states for Ce-$4f^1$ configurations, $V_{\kappa m}$ the hopping (or hybridization) matrix element between conduction electron ($c_{\kappa\sigma}$) and $f$-orbital ($f_m$), $N_s$ the number of sites, $\varepsilon_{f_m}$ the $f$-level energy measured from the Fermi level, $U_{mm'}$ the on-site Coulomb repulsion for $f$-electrons in states $m, m'$. We calculate its
model parameters within the local density approximation with the linear muffin-tin orbital method. The electronic structure in the calculation is then fed into the model via the hybridization strength function between CEF $m, m'$ defined as

$$\Gamma_{mm'}(\epsilon) = \pi \sum_{n, k, \sigma} V_{n^*k, m} V_{n, k, m'} \delta(\epsilon - \epsilon_{n, k, \sigma}). \quad (1.2)$$

Due to the atomic nature of the localized $f$-orbitals, the parameters $\epsilon_f, U$ are rather constant among Ce-systems and the hybridization is the most crucial parameter in the model with the electronic structure information. The Anderson model is approximately solved by using a diagrammatic method, known as the non-crossing approximation (NCA) in infinite-$U$ limit.

In the second part of the dissertation (chapter 4), we discuss the on-site Coulomb interaction in a lattice of ion with degeneracy of the electronic orbitals. In recent years, the role of orbital degeneracy in the strongly-interacting electron systems has attracted attention [7, 8, 9]. Although many of the materials of interest are multiband systems, the role of the orbital degeneracy has often been ignored for the sake of simplicity. With the advent of the colossal magnetoresistance materials [10] and the proposed triplet pairing superconductivity in Sr$_2$RuO$_4$ [11], the interaction between orbitals is now thought to be crucial in explaining those phenomena.

A newly discovered superconducting material, Sr$_2$RuO$_4$, has been suggested as a candidate for the electronic analogue of the triplet-pairing $^3$He [11]. Despite its layered perovskite structure as the cuprate high-$T_C$ superconducting material, La$_{2-x}$Sr$_x$CuO$_4$, Sr$_2$RuO$_4$ compound exhibits the Fermi-liquid behavior with resistivity of $T^2$ law, in contrast to the non-Fermi liquid behavior in the doped cuprates in the normal state. Moreover, SrRuO$_3$ material, the 3-dimensional analogue of Sr$_2$RuO$_4$, orders ferromagnetically. These observations have led to a suggestion that the superconductivity
in the Sr$_2$RuO$_4$ compound might be from the triplet pairing state driven by strong Hund's rule coupling. To model the triplet spin states from 4d$^4$ orbital of Ru$^{++}$ ion, it becomes essential to consider the nondegenerate orbital in the basis.

The role of multi-orbital in the alkali-doped fullerides is less dramatic. Although it has been generally accepted that the insulating C$_{60}$ solid becomes conducting in A$_3$C$_{60}$ ($A=K, Rb, Cs$ etc.) material when doped with alkali atoms $A$, there have been questions concerning the strong Coulomb interaction between electrons on the same C$_{60}$ site [12]. First of all, $A_3C_{60}$ system has puzzled many-body theorists because the system is metallic despite the strong on-site repulsion $U(= 1 \sim 1.5$ eV) with a narrow band-width $W(= \approx 0.5$ eV) [13]. If naively interpreted in terms of non-degenerate Hubbard model, the system should belong in the insulating regime at $U/W \geq 1.5$ [14].

The possibility of metallic $A_3C_{60}$ has first been pointed out by Lu [15] where he used the Gutzwiller approximation in the multi-orbital Hubbard model. Recently, Gunnarsson et al. [7] have employed the exact diagonalization method and the diffusion Monte Carlo method to calculate the insulating gap in a finite $A_3C_{60}$ lattice. They found that $U_c$ behaves as proportional to $\sqrt{N_{\text{deg}}}$ with orbital degeneracy $N_{\text{deg}}$. It has been argued that the orbital degree of freedom increases the effective hopping of conducting electron by factor of $\sqrt{N_{\text{deg}}}$.

We study the multi-orbital Hubbard model with finite Coulomb interaction using the quantum Monte Carlo (QMC) method in the infinite dimensional approximations [14]. Mostly we deal with how the metal insulator transition (MIT) is affected by the orbital degeneracy. Here we are interested in the qualitative change in the critical value of the Coulomb repulsion for the MIT. As a model for $A_3C_{60}$, this approach
serves as the crudest picture given that the realistic electronic structure information is ignored, not to mention the strong phonon-electron interactions. We use the infinite dimensional approximation primarily due to its simplicity as a method for the lattice model. The approximation is justified by the large coordination number of Ce at face-centered-cubic (f.c.c.) sites and the short range of the (screened) Coulomb interaction.

The Hubbard model consists of two terms: kinetic and Coulomb potential energies.

\[ H = H_{\text{cond}} + H_{\text{Coulomb}}, \]

where

\[ H_{\text{cond}} = -\sum_{ij,m,\sigma} (t_{ij}c_{i,m,\sigma}^\dagger c_{j,m,\sigma} + \text{h.c.}) + \epsilon_d \sum_{i m, \sigma} n_{i m, \sigma} \] (1.3)

\[ H_{\text{Coulomb}} = \frac{1}{2} \sum_{i m, m', n' n', \sigma, \sigma'} \langle mn'|U|nn'\rangle c_{i,m,\sigma}^\dagger c_{m',\sigma'} c_{i,n',\sigma'}^\dagger c_{n,\sigma}. \]

The transfer integral \( t_{ij} \), the hopping matrix element between site \( i \) and \( j \), is assumed to be independent of the orbital, \( m \), and spin, \( \sigma \), since we are interested in the qualitative behavior at MIT, not in the details of electronic structures. The potential energy has only on-site Coulomb repulsions summed over all possible combinations of orbitals with \( \langle mn'|U|nn'\rangle \sim U \). As will be discussed in more detail in later chapter, the different combination of orbitals experiences different repulsion. The Pauli exclusion principle results in the Hund’s rule coupling which favors the atomic state as the maximal spin state.

These two terms in the model contain the most basic physics in the MIT. When the Coulomb repulsion is much larger than the kinetic energy \( U \gg W \) the electrons cannot conduct due to the large inter-configuration energy. For \( W \gg U \), the system is in the limit of free electron gas and conducting. When \( W \) and \( U \) becomes comparable, the system develops a many-body state (often called “quasi-particle” state) near
the chemical potential. This peak comes from the scattering of the spin degrees of
freedom of electrons from the so-called "super-exchange" and the dispersion of this
peak governs the low temperature behavior.

The QMC method is an ideal technique for the MIT since it assumes no uncon-
trollable approximation and is an exact method within controllable systematic and
statistical error bounds. In particular, since the MIT involves the energy scale of
the Coulomb repulsion, the QMC method does not suffer from the long running time
at low temperature. For the purpose of identifying the MIT, I have examined the
occupation number as a function of the chemical potential. When the system has the
chemical potential inside the insulating gap, the occupation number does not change
with infinitesimal change of the chemical potential.

The critical value of the Coulomb repulsion $U_c$ increased as a function of $N_{\text{deg}}$
although it is not decisive whether the dependence is $N_{\text{deg}}$. On the other hand,
the Hund’s rule coupling effectively increases the repulsion between electrons on-
site, thus compensating the effect of the enhanced hopping. In the case of $A_3C_{60}$,
the Hund’s rule coupling is known to be one order of magnitude smaller than the
Coulomb repulsion $U$ and the enhanced hopping becomes the dominant factor.

The dynamical information of the model is extracted from the numerical analytic
continuation. The QMC method is formulated with the imaginary-time variable and
therefore is more reliable for predicting the thermodynamic properties. Although, in
principle, it should be possible to obtain the dynamical information of the model from
the QMC, the numerical analytic continuation problem has been a notoriously difficult
problem given noisy data. The dynamical information is very important since the
transport properties such as optical conductivity, d.c. resistivity and spin-relaxation
time have direct relevance to the experiments. In particular, the one-particle spectral functions can provide visual information regarding the MIT. For instance we can observe the manifestation of the enhanced hopping argument in the broadening of the upper and lower Hubbard band in the spectral function.

In recent years, the problem of the numerical analytic continuation has become somewhat promising with the development of the maximum entropy method for the QMC [16]. The method utilizes the statistical inference to find the most probable spectral function given the data of the imaginary-time Green's function. It finds the solution \{A(\omega)\} avoiding over-fitting and under-fitting to the noisy data by balancing the deviation from the data and the "entropy" of the proposed solution. We shall define this entropy precisely later. Although in some cases, especially for large degeneracy case at low temperature, we find that the present computation is not long enough to produce the reliable spectral functions, we could obtain the systematic trends in the spectral function as a function of the orbital degeneracy.

The organization of the thesis is as follows. In the rest of this chapter we discuss in more detail the CeM$_3$ and A$_3$C$_{60}$ systems. In chapter 2, the electronic structure calculation is discussed along with the hybridization functions for CeM$_3$. The detailed formalism for the Muffin-Tin orbital method as an implementation of the local density approximation is found in the appendix A. Computed physical observables from the NCA are presented in chapter 3. A qualitative discussion of crystalline electric field splitting and Kondo temperature is given at the lowest order of expansion. For comparison with experiments we discuss the spectral function and the magnetic susceptibilities. The multi-orbital Hubbard model for the A$_3$C$_{60}$ materials is discussed with the QMC method. We discuss two aspects of orbital degeneracy, competition
between the kinetic energy and the Hund's coupling. Also results for analytic continuation of the one-particle spectral function by the MEM is given with an application to the optical conductivity. In chapter 5 we summarize the work and present some directions for improvement of the present projects. Appendix B gives qualitative discussion how CePd₃ can have large Kondo temperature despite the small conduction density of states near the Fermi energy.

1.1 Material Oriented Computation for Cerium Compounds: Electronic Structures and Many-body Effects

For decades, the Kondo effect has been intensively studied among condensed matter physicists [17, 18, 19, 20, 21]. The qualitative understanding of the cerium-based systems (single-channel Kondo systems) is rather satisfactory. However there are still hot controversies, even whether the Kondo model is ever applicable to some of the cerium-systems [3, 4]. It seems there have not enough theoretical effects to prove or disprove the applicability of the Kondo model to the heavy fermion systems in terms of first-principles calculation. It is one of the goals of this dissertation to test the validity of the impurity model by identifying the energy scales of CeM₃ systems.

We have chosen CeM₃ series with M=Pb, In, Sn, Pd as our system for this research. They are very intriguing since their Kondo temperatures are drastically different ranging from few to several hundred Kelvin, while all compounds form in the same cubic Cu₃Au crystalline structure, as figure 1.1. Figures 1.2 illustrates the drastic changes in physical properties among CeM₃ systems. In the left plot [22], the Bremsstrahlung isochromat spectroscopies (BIS) for series of CeM₃ compounds. This spectroscopy measures the energy needed to excite the system by adding one f electron. The most interesting part is the excitation of 4f⁰ → 4f¹ process, marked
Figure 1.1: Crystal structure of Ce$M_3$ materials. The Ce atoms are at the cubic corners and the ligand atoms $M$ are on the face centers.

The weight of the peak, the amount of admixture of $4f^0$ in the ground state, is, in the Kondo picture, proportional to the low energy scale, $T_K$. Note that even with the same crystal structure, the weight changes drastically with decreasing order CeRh$_3$ > CePd$_3$ > CeSn$_3$ > CePb$_3$, CeIn$_3$. The weight of $4f^1$ peaks for CePb$_3$ and CeIn$_3$ are so small that they cannot be seen within the resolution of the BIS at $\sim 0.5$ eV. We also note that the runs were done at $T = 300K$, at least two orders of magnitude above the expected $T_K$ values for CeIn$_3$ and CePb$_3$, and as such we would not expect any significant weight to be left in the central Kondo resonance peak.

The change in $T_K$ can be more clearly pointed out by the static magnetic susceptibility $\chi(T)$ in the right plot of figure 1.2. While $\chi(T)$ of CeSn$_3$ [25] and CePd$_3$ [26] converged to a finite value at low temperature, $\chi(T)$ of CePb$_3$ [23] and CeIn$_3$ [24] did not roll over down to the lowest temperature in the measurement. Since the magnetic moment is screened by the conduction electrons at temperature lower than $T_K$, this
Figure 1.2: Experimental comparison of Ce$M_3$($M$=Pb, In, Sn, Pd): Bremsstrahlung isochromat spectroscopy (BIS) and static magnetic susceptibility. The $f^0 \leftrightarrow f^1$ admixture, measured by the weight in the BIS spectrum [22] (marked as $4f^1$ in the left plot) changes drastically among the series of Ce$M_3$. The same trend can be seen from the magnetic susceptibilities [23, 24, 25, 26], where the magnetic moment is screened at higher temperature for materials of larger $f^0 \leftrightarrow f^1$ admixture.
plot clearly demonstrates the strong coupling of 4f-orbital of CeSn₃ and CePd₃ to the conduction electrons.

There have been numerous efforts to understand heavy fermion systems from the band theoretic point of view [27, 28, 29, 30, 31, 32], which treats the strong on-site Coulomb interaction within the local density approximation (LDA). Although some of these approaches attempted to compute the CEF splittings [28, 32], they underestimate the correlation effects of the localized orbitals. In particular, the LDA becomes less reliable for rare-earth and actinide compounds since the band-width of f-orbitals (usually estimated to be few tenths of eV in LDA) is much smaller than the Coulomb repulsion (of order a few eV) and thus the free electron-gas formula for the exchange-correlation energy is highly questionable.

To extend the LDA to include many-body contribution Steiner et al. [33] considered the second order perturbation in $U$ in uranium systems. The mass-enhancement in the specific heats in UIr₃, UPt₃ and UAu₃ computed through the second order in the Coulomb repulsion accounted very well for the experimental values. However, the inclusion of the higher order terms is yet to be done for better estimate of the mass-enhancement and, more importantly, for the estimate of the Kondo temperature which is usually overestimated by finite order perturbation theories.

Levy and Zhang [34] proposed a new scheme to understand the CEF splitting and the Kondo effect in a more consistent way. They argued that the dominant contribution for the CEF splitting is induced by the hybridization strength and the Kondo temperature is obtained by the same hybridization. The hybridization-induced CEF splitting is accounted for by the second order perturbational shift of the energy level of irreducible cubic representation of the Ce-4$f^{1}$ states. When a Ce-4$f^{1}$ CEF
state decays to an higher energy state of (particle excitation + $4f^0$), the $4f^1$ CEF level receives a leading second order perturbational shift which is proportional to the hybridization strength. Therefore, the two different CEF levels have different hybridization strengths and they split in energy. Although, in addition to the CEF splitting induced by hybridization, $4f$-levels also experience different electrostatic potential from the charge distribution of the ligand ions, we ignore this point charge contribution [30, 32] in cerium systems due to their relatively large hybridization compared to higher lanthanides such as Pr, Sm etc.

We have applied the linearized Muffin-Tin orbital (LMTO) method [2] to Ce$M_3$ systems to obtain the hybridization. The hybridizations for Ce$_x$La$_{1-x}$M$_3$, in the context of the Anderson impurity model, are calculated in the concentrated ($x \to 1$) [29] and dilute ($x \to 0$) limits. The computed hybridization function is then fed into the Anderson impurity model and we solve the model using the non-crossing approximation in the infinite-$U$ limit. The NCA is a self-consistent diagrammatic method in expansion in $1/N_g$, $N_g$ the orbital degeneracy of the ground multiplet configuration of Ce-$4f^1$ orbital. The infinite-$U$ approximation is equivalent to truncating the Hilbert space to $f^0$ and $f^1$ configurations [18]. Even though the approximations look rather strong at first glance, it has been noted [19] that they can provide a reasonable numerical description for many Ce-compounds.

As summarized later (in table 3.1), we have correctly predicted the trend in "heaviness" among Ce$M_3$ series [35]. CePb$_3$ and CeIn$_3$ systems have large CEF splittings with doublet ground state configuration leading to very small Kondo temperatures. It is discussed that at temperatures down to few Kelvin the physical properties are dominated by the CEF splitting. On the other hand, CeSn$_3$ and CePd$_3$ display the
mixed valence phenomena with much larger $T_K$ than CEF splittings. Their magnetic moments are screened out at $T$ near $T_K$ through anti-ferromagnetic coupling to conduction electrons.

1.2 Metal Insulator Transitions in Hubbard Model with Orbital Degeneracy: Quantum Monte Carlo Calculation

In the many-body theory community, the Hubbard model has been extremely popular, much as the Ising model has been the "standard model" in the statistical mechanics. In particular, the mystery of the high-$T_C$ superconductivity has provided unending enthusiasm toward this deceivingly simple model. Despite the simple structure of the Hamiltonian, the model has amazingly rich physics from the Mott-Hubbard metal insulator transition to the helical magnetic ordering. The model is made up of two terms, the kinetic energy and the potential energy from the on-site Coulomb interaction. Depending upon the ratio of the two terms the system ranges from the Heisenberg anti-ferromagnet in the strong interaction limit to a simple metal in the small interaction limit.

In chapter 4, we study the metal insulator transition driven by the Coulomb interaction. We are motivated by the example of the alkali-doped fullerides, $A_3C_{60}$ systems. Although it has been commonly thought that these systems can be well described by the band theory, it has been continuously a mystery that the strong on-site repulsion (1-1.5 eV) between two electrons on the same $C_{60}$ site did not bring the system to an insulator despite the small bandwidth ($\sim 0.5$ eV) of the valence band [13]. Considering the strong intra-molecular interaction, the $A_3C_{60}$ is expected to be an insulator if interpreted in terms of non-degenerate Hubbard model. Even though we accept that $A_3C_{60}$ is a metal, it is still an important question whether
It il it H it

Figure 1.3: Schematic picture of energy levels of C\textsubscript{60} molecule and the density of states of A\textsubscript{3}C\textsubscript{60} system. The molecular orbital of C\textsubscript{60} is filled up with 60 valence electrons up to the $h_u$-HOMO (highest occupied molecular orbital) states. The $t_{1u}$-LUMO (lowest unoccupied molecular orbital) states have the orbital degeneracy 3. Upon doping of the alkali-atom, K, the LUMO states form a band with width of $\sim$0.5 eV. The $t_{1u}$-band is half-filled and predicted as a metal by the LDA.

due to the small inter-molecular hoppings, the LUMO and HOMO bands do not merge and solid C\textsubscript{60}, crystallizing in an FCC structure, is a band insulator [13]. When the solid C\textsubscript{60} is alkali-doped, the alkali-atoms act as passive donors of electrons and the 3 extra electrons go to the $t_{1u}$-LUMO band of the solid-C\textsubscript{60}. Now the number of valence electrons per unit cell is an odd number and the LDA predicts A\textsubscript{3}C\textsubscript{60} as a metal.
The effort to understand the metallic solution for $A_3C_{60}$ systems despite the strong Coulomb repulsion was first given by Lu [15]. The Gutzwiller approximation was used to calculate the critical Coulomb repulsion $U_c$ and Lu showed that $U_c(N_{\text{deg}}) = (N_{\text{deg}} + 1)U_c$ at half-filling, which corresponds to $4U_c(1)$ for $A_3C_{60}$ systems. More rigorous numerical studies [7, 8, 9] have recently been carried out for the determination of the critical Coulomb repulsion as a function of $N_{\text{deg}}$. Gunnarsson et al [7] argued that the effective hopping probability for the charge excitation, due to (at least short ranged) the anti-ferromagnetic ordering of spins, is enhanced by the orbital degeneracy. Although their calculations are performed on a finite lattice only up to degeneracy 3, they clearly show that the $U_c$ increases with the degeneracy and allow for the possibility that the $A_3C_{60}$ system can be understood as a metal near the MIT.

In this thesis, the lattice problem is simplified in the limit of infinite spatial dimensions, i.e., $d = \infty$. The simplification comes from the rigorous mapping of the lattice Hamiltonian to an effective impurity Hamiltonian. Note that to have a physically meaningful limit in the Hamiltonian, Eq. (1.3), the hopping integral should be scaled such that the total hopping probability from a given site $zt^2$ is finite, with $z$ the coordination number $\sim d$, i.e., $t \sim 1/\sqrt{d}$. The statistical fluctuations from neighbors with respect to a chosen site becomes negligible from the central limit theorem with the scaling of the hopping integral as proportional to $1/\sqrt{d}$ [14]. Therefore, the lattice model is rigorously mapped to an effective impurity model which, in the case of Hubbard model, becomes the Anderson impurity model. The $d = \infty$ approximation, also known as the dynamic mean field theory or the local approximation, is appropriate for the MIT in $A_3C_{60}$ systems since the MIT is a transition driven locally in nature.
and moreover, the C₆₀ lattice in A₃C₆₀ forms a f.c.c. structure with coordination number 12.

The effective impurity model is solved by the QMC. The QMC for the Anderson impurity model is well studied [37]. The MIT is identified by studying the occupation number versus the chemical potential. As expected the critical value of the Coulomb interaction, $U_c$, increased with $N_{\text{deg}}$ due to the enhanced hopping integral approximately as $\sqrt{N_{\text{deg}}}$, with $N_{\text{deg}}$ the orbital degeneracy, in agreement with Ref. [7]. With the orbital degeneracy, we introduce an exchange interaction which is responsible for aligning the spin states, deriving for the Hund's coupling which accounts for the tendency of atomic electrons in partially filled shell to spin-align. With this term, the effective on-site repulsion is increased linearly in $N_{\text{deg}}$, favoring the insulating solution. Therefore, with the orbital degeneracy we expect competition between the kinetic energy and the Hund's coupling.

Finally, the QMC data in the imaginary-time formalism is analytically continued using the statistical inference, more specifically, the maximum Entropy method (MEM) [16]. Analytic continuation of the inherently noisy one-particle Green's function at imaginary time $\tau$, $\{G(\tau)\}$, has been a notoriously ill-posed problem which critically hampered the use of the QMC as a tool for dynamical properties. The most difficult problem in the numerical analytic continuation is as follows: if fitted too "honestly" to the data, the images (spectral functions) tend to have unphysical and unpredictable features from the noise in the data. On the other hand, if the data is forced to be smooth, the real physical features are simply lost. The MEM finds the most probable spectral functions, e.g., $A(\omega)$ in the case for $\{G(\tau)\}$, by balancing the likelihood function, $L$, to the data and the entropy, $S$, of the proposed solution.
The likelihood function accounts for the "honest" fitting to the data and therefore, without the entropy term, it over-fits to the noise. The entropy term, a functional of $A(\omega)$ independent of the data, produces the most unbiased (and smooth) solution in the absence of that data and incorporates the prior knowledge through the so-called default model. By maximizing $L - \alpha S$ with a carefully chosen Lagrange multiplier $\alpha$, the MEM circumvents the danger of over-fitting which plagues the direct transformation methods like Padé approximants and incorporates the prior information of $A(\omega)$.

Once the MEM is under control with reliable statistical errors we can compute the spectral function and transport properties such as the optical conductivity. We have studied the one-particle spectral function with the orbital degeneracy $N_{\text{deg}}$, where we see the broadened charge excitation peaks as an evidence of the effectively enhanced hopping in agreement with Ref [7]. The computed optical conductivity, for $N_{\text{deg}} = 2$ at half-filling, preserves the Fermi-liquid behavior (in the paramagnetic phase). At this point the calculations for the transport properties are still under progress.
CHAPTER 2

CALCULATION OF HYBRIDIZATION FOR CeM₃ SYSTEMS

In describing a metal alloy with magnetic impurities such as transition metal, rare-earth or actinide ions, it becomes crucial to understand how the localized d- or f-electron couples to the conduction states. Due to the short spatial extent of the wave-function, the d or f-orbitals of the heavy ions have significantly small hopping (or hybridization) matrix elements with the conduction states. Among the heavy ion systems, Ce-systems have been especially popular. Some compounds with rare-earths heavier than Ce have extremely small overlap with other orbitals that their crystalline electric field levels have been well described by the point charge method [30]. On the other hand, for some actinides such as uranium systems which have rather large overlap strength compared to Ce-systems, the availability of the Anderson impurity model, Eq. (1.1), is not clearly established [27]. Ce-compounds have been ideal materials for strongly correlated electron system due to their hybridization strength on the borderline of the itinerant and the localized moment electron system.

The most sensitive parameter to govern the low temperature physics of Ce-systems is the hybridization strength between the f-orbital and the other ligand bands. Other parameters such as the f-level energy, $\epsilon_f$ and the on-site Coulomb repulsion $U_{ff}$ are
rather material independent, although the other orbitals provide screening of the Coulomb potential felt by $f$-electrons [38]. Although it is possible to compute the parameters like $\epsilon_f, U_{ff}$ [5, 39], they are not the objects of study in this work.

The hybridization of Ce-$4f^1$ cubic crystalline field states to other states, $s, p, d$ of Ce and ligand orbitals, are calculated in the context of Anderson impurity model. The hybridization, $\langle \alpha | V | m \rangle$, is conveniently parameterized in terms of the hybridization broadening function as

$$\Gamma_{mm'}(\epsilon) = \pi \sum_\alpha \langle m | V | \alpha \rangle \rho_\alpha(\epsilon) \langle \alpha | V | m \rangle,$$

where $\alpha$ is the index of orbital states which $m, m'$-th cubic CEF of $f$-orbital couple to, $V$ the electronic potential felt by the $f$-orbital, and $\rho_\alpha(\epsilon)$ is the spectral function of the $\alpha$-orbital of the medium to which the $f$-orbital couples. The $\alpha$-orbital corresponds to the conduction orbitals in the Anderson impurity model. This hybridization broadening quantifies the strength of (Fourier transformed) probability per unit time for the $f$-electron emitted from a site to come back to the same site after traveling around the lattice.

We will study how to interpret the the hybridization strengths in both lattice and dilute limits as an input to the impurity Anderson model. In the following sections we will (i) sketch how to compute the hybridization in the two limits, and (ii) present and discuss the calculated hybridizations. The formalism of the LMTO method is described in appendix A.
2.1 Hybridizations in Dilute and Concentrated Limits

2.1.1 Concentrated Limit (CeM₃)

When we are dealing with systems with Ce atoms on every lattice site, what do we mean by a description in terms of an impurity Anderson model? We single out a Ce-\( f \) orbital, say at the origin and treat the the rest of the lattice as an effective medium acting as the conduction band sea. This idea parallels that of the dynamical mean field theory [14], where the lattice problem can be rigorously mapped into an impurity problem by singling out a site which interacts with the dynamic medium. In our approach we interpret the lattice as a static effective medium in the sense of the local density approximation (LDA). Here, the lattice effects, such as magnetic ordering of Ce-\( f \) moments or superconductivity, do not appear. In our scheme the effect of the lattice can only be reflected in the energy eigenvalues of the band calculations in the LDA.
The hybridization broadening function can be expressed as

\[ \Gamma_{mm'}^{\text{med}}(\varepsilon) = -\text{Im} \sum_{R,R'} V_{\alpha R m} V_{\alpha' R' m'}^* G'_{\alpha \alpha'}(R, R', \varepsilon + i\eta), \quad (2.2) \]

where \( V_{\alpha R m} \) is the hybridization matrix element between \( \alpha \)-th orbital at \( R \) with the \( f \)-orbital at the origin, \( G'_{\alpha \alpha'}(R, R', \varepsilon + i\eta) \) the retarded Green's function of an electron emitted with state \( \alpha \) at site \( R \) and destroyed with state \( \alpha' \) at site \( R' \) with \( f \)-orbital at origin excluded. We shall approximate the site-excluded Green's function \( G'_{\alpha \alpha'}(R, R', \varepsilon + i\eta) \) as the one from the LDA calculation.

The site-excluded Green's function can be related to the Green's function in the full lattice through the Dyson's equation. For the moment, we imagine we solve the lattice cerium systems in the LDA by treating the central \( f \)-orbital in a mean field approximation, as well as all other orbitals. Then we can compute the Greens function \( G_{mm'}^{\text{LDA}}(\varepsilon) \) from projected densities of states (PDOS) to various cubic CEFs by Hilbert transformations;

\[
G_{mm'}^{\text{LDA}}(\varepsilon \pm i\eta) = \int dz \frac{\rho_{mm'}^{\text{LDA}}(z)}{\varepsilon \pm i\eta - z} = P \int dz \frac{\rho_{mm'}^{\text{LDA}}(z)}{\varepsilon - z} \mp i\pi \rho_{mm'}^{\text{LDA}}(\varepsilon) \quad (2.3)
\]

where \( \rho_{mm'}^{\text{LDA}}(\varepsilon) \) is the density of states projected to \( m, m' \)-th cubic CEF, \( \eta \) an infinitesimal number. We have kept all the possible 14 \( f \)-states for Ce-4\( f^1 \) leading to a 14 \( \times \) 14 matrix \( G_{mm'}^{\text{LDA}}(\varepsilon \pm i\eta) \). The PDOS is computed as

\[
\rho_{mm'}^{\text{LDA}}(\varepsilon) = \sum_{nk\sigma} \langle m|nk\sigma\rangle \langle nk\sigma|m\rangle \delta(\varepsilon - \epsilon_{nk\sigma}), \quad (2.5)
\]

where \( n \) is the band index, \( k \) the wave vector in the first Brillouin zone, \( \sigma \) is the spin index, \( \epsilon_{nk\sigma} \) the energy eigenvalue of the full lattice. \( \langle m|nk\sigma|nk\sigma|m\rangle \) is computed in
the LMTO formalism as in Eq. (A.23). Now, the site-excluded Green's function is related to the lattice Green's function as

\[
\left[ G^{LDA}(\omega) \right]_{m'm'}^{-1} = \left[ G^0(\omega) \right]_{m'm'}^{-1} - [V_R G'(R,R',\omega)V_R]_{m'm'}, \tag{2.6}
\]

where \( G^0(\omega) \) is the on-site unperturbed \( f \)-Green's function

\[
\left[ G^0(\omega) \right]_{m'm'} = (\omega - \epsilon_m^{LDA})^{-1} \delta_{m'm'}, \tag{2.7}
\]

with \( \epsilon_m^{LDA} \) the LDA-calculated \( f \)-level energy of \( m \)-th cubic CEF state. Taking the difference of Eq. (2.6) for \( \omega = \epsilon + i\eta \) and \( \epsilon - i\eta \), we have the concentrated limit hybridization of Eq. (2.2) using Eq. (2.4) as

\[
\Gamma_{m'm'}^{med}(\epsilon) = -\frac{i}{2} \left[ G^{LDA}(\omega + i\eta)^{-1} - G^{LDA}(\omega - i\eta)^{-1} \right]_{m'm'}. \tag{2.8}
\]

### 2.1.2 Dilute Limit (Ce\(_x\)La\(_{1-x}\)\(_M_3\) with \( x \to 0 \))

Consider the dilute limit \( \text{Ce}_x\text{La}_{1-x}\text{M}_3 \). The system can be understood as an impurity Anderson model. An underlying assumption is that the \( f \)-orbital of Lanthanum atoms lies far above the Fermi surface, at about 5 - 6 eV \([22, 40]\), so that it does not contribute to the many-body physics and that the conduction band spectra are rigid enough that those of \( \text{CeM}_3 \) and \( \text{LaM}_3 \) are almost identical. This point will be discussed in greater detail later.

The most straightforward way of calculating the hybridization is by evaluating the overlap of wave-functions with the atomic potential. However this would require the usage of orthonormalized wave-functions, which are not easy to get since the LMTOs are originally non-orthogonal. (See Appendix A or Refs. \([2, 41]\) for details.) Note that the Muffin-Tin orbitals(MTO) are set up in such a way that each valence orbital is augmented to be orthogonal to the core states but still not orthogonal
Figure 2.2: Schematic picture of dilute limit. The $f$-orbital at origin couples to the ligand orbitals on neighboring sites which do not include $f$-orbitals.

to other orbitals at different sites. Due to this non-orthogonality, two orbitals of different angular momenta mix significantly in the Bloch state. Therefore, the MTOs do not serve as the basis wave-function corresponding to the Wannier orbitals in the model Hamiltonian. Moreover, to calculate the conduction band spectrum with non-$f$ ligands we have to run again the LDA without the band-$f$ hopping with the self-consistent potential of the full LDA.

As an alternative, one can also compute the impurity limit by the super-cell method. In the method, we approach the impurity limit by setting a new unit cell (super cell) made up of $N - 1$ old unit cells of La$_3$ and 1 unit cell of Ce$_3$. By increasing the size of the super cell, $N$, we can rigorously compute the impurity limit. However, those direct ways of calculating the hopping matrix elements are complicated and numerically expensive.

Instead of directly calculating the overlap matrix elements, we compute the hopping matrix elements by reconstructing the Hamiltonian matrix from the energy eigenvalues and eigenvectors of the Ce$_3$ system. The hopping matrix elements obtained
this way are summed over the wave-vectors in the Brillouin zone by the irreducible tetrahedra method [42]. Our procedure is as follows:

(I) Perform the LDA calculation for the concentrated systems, i.e., CeM₃ with the lattice constants of LaM₃. Then the all the orbital overlaps and the potential overlaps are implicitly included in the LMTO eigenvalue equations. However, once we solve the equation with eigenvalues and eigenvectors we can easily reconstruct the Hamiltonian in the orthonormal basis by a unitary transformation. More specifically, we can re-sum the on-site MTO and the tails of the off-site MTOs in the Bloch wave-function. Since the tails of MTOs at other sites are constructed to be expanded in terms of on-site MTOs, we can re-organize the terms with respect to the on-site angular momentum basis, i.e., in the one-center expression. (See Eq. (A.10))

(II) We interpret the eigenvalues and the unitary-transformed eigenvectors as the solution of a lattice resonant level model. This is a reasonable first approximation since the LDA eventually solves the one-electron problem with the self-consistent LDA potentials which already include Coulomb interactions, at least, in the mean-field sense. We obtain the conduction band spectrum, εₙₑₜₜₑₑ, by block-diagonalizing only the non-f orbitals. Now, by doing the unitary transformation for f-ligand elements according to the basis of the diagonalized conduction bands, we can read off the f-ligand matrix elements of the final Hamiltonian and identify them as Vₙₑₜₜₑₑₖₜₜₑₑ, the hopping matrix element between m-th cubic CEF state of Ce-4f and the conduction Bloch state with band index nₑ.

(III) Sum Vₙₑₜₜₑₑₖₜₜₑₑₖₜₜₑₑ over the wave vectors and the band indices for equal-energy states to get the impurity limit hybridization Γₙₑₜₜₑₑₜₜₑₑ(ε),

\[
\Gamma^{\text{imp}}_{mₘ'ₘ}(ε) = \pi \sum_{nₑₜₜₑₑ} V^*ₙₑₜₜₑₑₖₜₜₑₑₖₜₜₑₑ Vₙₑₜₜₑₑₖₜₜₑₑₖₜₜₑₑ δ(ε - εₙₑₜₜₑₑ). \tag{2.9}
\]
The k-summation over the 1st Brillouin zone is performed by the irreducible tetrahedra method [42].

(IV) Finally we adjust the chemical potential for impurity limit. Since we need the Fermi energy to hold the number of electrons for Ce$_x$La$_{1-x}$M$_3$|$_{x\to 0}$, not CeM$_3$ for which the actual calculation is performed, we have to move the Fermi level as

$$\int_{E_{low}}^{E_F} N(\epsilon) d\epsilon = N(LaM_3),$$

where $N(\epsilon)$ is the density of states computed for CeM$_3$, $N(LaM_3)$ the number of valence electrons in unit cell, $E_{low}$ the low edge of energy of the calculation. Note that $N(LaM_3) = N(CeM_3) - 1$, since La has one less valence electron in the 4f orbital.

2.2 Calculated Hybridization for CeM$_3$ ($M$=Pb, In, Sn, Pd)

We have employed an ab initio calculation in the sense that we only used as the free parameters the lattice constants of each compound. We used the linearized muffin-tin orbital (LMTO) methods with potential based on the local density approximation. We choose the LMTO method because the MTOs are expanded in terms of angular momentum basis and it is easy to unitary-transform the eigen-functions to the basis of cubic crystal electric field states. Also the LMTO method gives a good starting description for systems with heavy ions such as transition metals.

We used 165 wave vectors $k$ in the irreducible Brillouin zone to obtain the self-consistent solution of the density of states. The self-consistent solution has been reached after about 10 iterations. In the atomic sphere approximation (ASA) the Wigner-Seitz (WS) radii of Ce and ligand ion are set to be the same as

$$\frac{4\pi}{3} \left( S_{Ce}^3 + 3S_M^3 \right) = a^3 \quad \text{with} \quad S_{Ce} = S_M, \quad (2.11)$$

26
Table 2.1: Lattice constants of compounds

<table>
<thead>
<tr>
<th></th>
<th>$a$ (in $\AA$)</th>
<th>$a$ (in $\AA$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CePb$_3$</td>
<td>4.874</td>
<td>LaPb$_3$</td>
</tr>
<tr>
<td>CeIn$_3$</td>
<td>4.689</td>
<td>LaIn$_3$</td>
</tr>
<tr>
<td>CeSn$_3$</td>
<td>4.721</td>
<td>LaSn$_3$</td>
</tr>
<tr>
<td>CePd$_3$</td>
<td>4.129</td>
<td>LaPd$_3$</td>
</tr>
</tbody>
</table>

where $S_{Ce}(S_M)$ is the WS radius of Ce ($M$) and $a$ the lattice constant of the system. The lattice constants of the systems are listed in table 2.1.

### 2.2.1 Density of States of CeM$_3$

The density of states of CePb$_3$ system is shown in figure 2.3, where most of the spectral weight is provided by Pb-$s,p$ and Ce-$d$ orbitals. CeM$_3$ ($M=$Pb, In, Sn) systems have major contributions from Ce-$d$, $f$ and $M$-$s,p$ orbitals. The occupation number of the $f$-orbital is calculated by integrating the projected density of states (PDOS) of $f$-orbital up to the Fermi energy and is usually estimated to be 1.2-1.3. These LDA-estimated occupation numbers are usually larger than the experimental values which are slightly less than 1. The Ce-$4f$ DOS is localized near the Fermi energy (dashed line) with estimated band width about 0.1 eV, or about $10^3$ K. This overestimation of $f$-band-width by the LDA results from the failure of proper consideration of strong Coulomb interaction between $f$-electrons. Although the LDA calculation pushes the $f$-level above the Fermi energy giving the total occupation number near 1, it fails qualitatively in estimating the band width. Based on experiments we know the low-$T$ characteristic energy, known as the Kondo temperature $T_K$, range from a few Kelvin to a few hundred Kelvin, far from the $\sim 0.1$ eV estimated
from the LDA. As found in the photoemission [4, 43, 44, 45] and inverse photoemission experiments [40], the spectral weight of the $f$-orbital splits into an ionization peak below the Fermi energy at about $-2$ eV and an electron-affinity peak above the Fermi energy at about $4$ eV. There is also another peak sitting near the Fermi energy coming from the many-body effect, known as Kondo effect, coming from scattering from spin degrees of freedom off the Ce-$f$ localized moments. This many-body peak has a width of the order of $k_B T_K$.

Unlike the $f$-states, the conduction band is spread over the range of 1 Rydberg. As depicted in the Figure 2.4, one can analyze the major orbital character at certain energy range. Since Ce atoms are positively ionized (Ce$^{+3}$) giving off 3 electrons, one extra electron is given to each ligand atom, whose approximate electronic configurations are listed in table 2.2, which can also be checked by the integrated projected-DOS up to the Fermi energy as in figure 2.3. For ligands $M=\text{Pb, In, Sn}$, the s-orbital lies lowest. While the s-orbitals of Pb and Sn are completely filled and form a band separated from other bands, the s-orbital of In lies closer to the Fermi energy and merges with the p-orbital band, since the In has a core with one unit less positively charged. The p-DOS's are rather flat below and above the Fermi energy. The spectrum above the Fermi surface has considerable weight from the d-orbital of Ce. Since the Ce atoms are not nearest neighbors and both $f$ and d-orbitals are localized in space, we speculate that the coupling between Ce-d and $f$ are not direct but mediated though ligand p-orbitals.

Unlike the other three compounds, CePd$_3$ has very peculiar electronic structure; the dominating conduction orbital character is Pd-d. The position of Pd-d peaks match well with the photoemission experiment [46]. Although the d-orbitals are
Figure 2.3: Density of states of CePb$_3$. The most dominant contributions arise from Ce-\textit{d,f} and Pb-\textit{s,p} orbitals. The Ce-4\textit{f} orbitals lie above the Fermi energy (dotted line) at about 0.2-0.6 eV.
Figure 2.4: Total density of states of Ce$M_3$. Except for CePd$_3$, Ce$_x$La$_{1-x}$M$_3$ ($M$=Pb, In, Sn) systems have dominant contributions for the DOS from Ce-$d$, $f$ and M-$s$, $p$ orbitals. The CePd$_3$ system has a large DOS arising from the Pd-$d$ orbital below the Fermi energy and has remarkably small spectral weight near the Fermi energy.
elemental ionic (in CeMg)

<table>
<thead>
<tr>
<th>Element</th>
<th>Elemental Configuration</th>
<th>Ionic (in CeMg) Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>[Xe]4f15d16s2</td>
<td>[Xe]4f1</td>
</tr>
<tr>
<td>La</td>
<td>[Xe]5d16s2</td>
<td>[Xe]</td>
</tr>
<tr>
<td>Pb</td>
<td>[Xe]6s26p2</td>
<td>[Xe]6s26p2</td>
</tr>
<tr>
<td>In</td>
<td>[Kr]5s25p1</td>
<td>[Kr]5s25p2</td>
</tr>
<tr>
<td>Sn</td>
<td>[Kr]5s25p2</td>
<td>[Kr]5s25p3</td>
</tr>
<tr>
<td>Pd</td>
<td>[Kr]4d10</td>
<td>[Kr]4d10</td>
</tr>
</tbody>
</table>

Table 2.2: **Electronic configurations of elements.** In the CeMg system, the ligand atom is negatively ionized by receiving one extra electron and the rare-earth atoms are positively ionized by giving off 3 electrons.

Completely filled with 10 electrons, the center of the orbitals is not far from the Fermi energy and their coupling to the Ce-f orbitals is very strong. The strong coupling can be anticipated from the significantly small lattice spacing compared to others. (See Table 2.1.) The small DOS near Fermi energy may be responsible for the large resistivity and its sensitivity to pressure [47].

The LMTO program in the calculation deals with the spin-orbit coupling as the perturbation of the Pauli Hamiltonian [2]. Among the leading order perturbation terms, the spin-orbit interaction term

\[
\xi_s \cdot l = c^2 \frac{2}{r} \frac{du}{dr} s \cdot l,
\]

(2.12)

where \(c\) is the speed of light, \(v\) the potential function. Other terms from the perturbation (mass-velocity and the Darwin terms) are absorbed in the potential parameters in the LMTO formalism. Since the spin-orbit coupling term connects the different spin states, we have to double the basis set including the spin degree of freedom. The spin-orbit coupling effects are not negligible for heavy-ion systems with atomic number larger than about 20. Since the strength of the spin-orbit coupling for the
Figure 2.5: Projected density of states of Ce-\( f \) orbital. The PDOS's are plotted for cubic irreducible representations. The angular momentum states \( J = 5/2 \) and \( 7/2 \) are energetically resolvable by the splitting of about 0.35 eV. Note that the \( |\frac{5}{2}; \Gamma_7\rangle - |\frac{7}{2}; \Gamma_8\rangle \) splitting is not resolvable from the PDOS.
The PDOS of Ce-f orbitals for CePb₃ are shown at higher resolution in figure 2.5. Two major peaks in the total f-PDOS plot are from angular momentum states \( J = \frac{5}{2} \) and \( J = \frac{7}{2} \). As shown in the figure, we measured the spin-orbit splitting as the peak separation between \( J = \frac{5}{2} \) and \( J = \frac{7}{2} \)-PDOS. Even though the \( J = \frac{5}{2} \) and \( J = \frac{7}{2} \) states are well separated, the broadening of PDOS makes the peak separation not well-defined. Thus, after the self-consistent potential is obtained, we turn off the band-f overlap for an extra LDA run and read off the well-defined peak separation between \( J = \frac{5}{2} \) and \( J = \frac{7}{2} \)-PDOS. The spin-orbit splittings in all compounds are estimated to be about 0.34 eV which agree reasonably well with experimental values [4].

Note that the PDOS for \( |J = \frac{5}{2}, \Gamma_7\rangle \) and \( |J = \frac{5}{2}, \Gamma_8\rangle \) overlap significantly. If the two PDOSs indeed overlap so strongly, the CEF splitting is not only unresolvable theoretically but also meaningless, although they are measurable in neutron scattering experiments [48, 49]. This failure to resolve CEF levels in the LDA may be traced back to the negligence of strong correlations in Ce and indicates that we need a many-body treatment to properly handle the CEF problem.

2.2.2 Results for Concentrated and Dilute Limit Hybridization

Hybridizations in concentrated and dilute limits are shown in figure 2.6 for CePb₃. The overall shape is similar to the conduction electron DOS. As expected, the concentrated and dilute limit hybridizations are almost identical except near the Fermi surface. Although in principle it is possible to sort out the detailed structure, we do
not attempt to do it since it is very tedious and difficult to label which peak corresponds to which orbital, except for special cases. For example, one can explain why the lower half part of ligand-\( s \)-contribution (near \(-8 \text{ eV}\)) to hybridization is considerably suppressed. The Bloch states about this energy are bonding states of \( s \)-orbitals, thus rather flat in space with the same sign. Since the \( f \)-orbitals have odd angular momenta, its overlap to the bonding states cancels due to different parities.

The concentrated limit hybridization has sharp peaks above the Fermi energy at \( 0 \sim 1 \text{ eV} \). These come from \( f \)-orbitals present in the effective medium. On the other hand, the dilute limit hybridization broadening does not have such \( f \)-peaks since it represents the hopping to the conduction band without Ce-\( f \) orbitals. In addition to the \( f \)-peaks, a close inspection tells that the spectral weight near the Fermi energy is redistributed. For example, the peak marked as \( a' \) in figure 2.6 (b) is pushed away from the Fermi energy to the peak \( a \) in (a) due to the presence of \( f \)-orbitals in the medium. Moreover, one can see that the weight of peak \( a' \) decreased and was transferred to the region of \( f \)-spikes. The same argument can apply to the peak above the Fermi energy sitting at near 1-3 eV. The peaks in the concentrated limit have smaller weight and are pushed away from the Fermi energy.

In figure 2.7 (b), we present the hybridization of LaPb\(_3\) in the concentrated limit and compare with that of Ce\(_x\)La\(_{1-x}\)Pb\(_3\)\((x \rightarrow 0)\). The point to note is the rigidity of the conduction band with respect to the energy level of \( f \)-orbital and, therefore, the affirmation of the validity of an impurity calculation. Although the position of La-\( f \) orbitals are pushed well above the Fermi energy, one can easily see the overall shape and relative positions of peaks in DOS are almost identical to the dilute limit.
Figure 2.6: Hybridization of Ce₃La₁₋ₓPb₃ in concentrated (x = 1) and dilute (x → 0) limits. The hybridization broadening functions for the doublet (Γ₇; thick line) and the quartet (Γ₈; thin line) multiplets are plotted. Note that the larger hybridization for the doublet states above the Fermi energy results in the larger level repulsion for Γ₇-CEF states, hence the ground state multiplet. The concentrated (Γ_{med}(ε)) and impurity (Γ_{imp}(ε)) limits are nearly identical for high energy regime, while the concentrated limit has the lattice-\(f\) character right above the Fermi surface (dashed line). The peak \(a'\) in the impurity limit is pushed down to the peak \(a\) due to the presence of the lattice-\(f\) states.
Figure 2.7: Hybridization of $\text{Ce}_x\text{La}_{1-x}\text{Pb}_3(x \to 0)$ and $\text{LaPb}_3$ systems. The shape of the two cases are very similar, except for the overall magnitude. This rigidity of the conduction band justifies the assumption that La plays the same role as Ce with 4f-orbital located far above the Fermi energy.
of \( \text{Ce}_x\text{La}_{1-x}\text{Pb}_3 \) as in figure 2.7 (a). Also, there is a very good resemblance of hybridizations between concentrated \( \text{LaPb}_3 \) and dilute \( (\text{Ce,La})\text{Pb}_3 \), especially near the Fermi energy. These also consolidate our assumption that the hybridization is rather insensitive to how we treat the Ce-\( f \) orbitals such as via a mean field inclusion of local Coulomb interactions. Since the La atoms are one unit less positively charged, the \( f \)-level is located well above that of Ce-\( f \) and the overall magnitude of hybridization is large due to the less localized nature of La-\( f \) orbital. Note that since \( \epsilon_f(\text{La}) > 0 \), \( \text{LaPb}_3 \) does not show many-body effects from the \( f \)-orbitals.

### 2.2.3 Hybridizations for Ce\( M_3 \) (\( M=\text{Pb, In, Sn, Pd} \))

In addition to Ce\( \text{Pb}_3 \), the results for Ce\( M_3 \) (\( M=\text{In, Sn, Pd} \)) are presented in figure 2.8. The first two compounds show similar structures in the hybridization function as in the case of DOS in figure 2.4. The overall magnitude for CeSn\(_3\) is larger than CePb\(_3\) and CeIn\(_3\), especially near the Fermi energy. Thus CeSn\(_3\) can be expected to have larger Kondo energy than CePb\(_3\) and CeIn\(_3\). More detailed discussion will be given in connection with the non-crossing approximation after the many-body calculation is carried out with these hybridizations.
Figure 2.8: Hybridization of CeM$_3$ ($M=$Pb, In, Sn, Pd). The dip, marked as a arrow, in the hybridization of CeIn$_3$ system leads to a small Kondo temperature. (See chapter 3.) The Pd-$d$ orbitals in CePd$_3$ compounds dominate the hybridization with huge (scaled down by 1/10) values of about 2 eV at maximum. As in figure 2.6, the thick line denotes the hybridization function for $|\frac{5}{2}; \Gamma_7\rangle$ and the thin line for $|\frac{5}{2}; \Gamma_8\rangle$. 
CHAPTER 3

STRONG CORRELATION EFFECTS IN CE-\textit{F} ORBITALS: NON-CROSSING APPROXIMATION

In the previous chapter we noted that the local density approximation does not produce a reliable description for the strong correlation effects of the Ce-\textit{f} orbitals. In this chapter we discuss a treatment of the many-body effects using an approximate diagrammatic method, known as the non-crossing approximation (NCA). The negligence of the correlation effect results in the gross overestimation of the \textit{f}-band width, which not only misses by orders of magnitudes the low temperature energy scale \textit{i.e.}, Kondo temperature but also fails to give a reliable estimate of the crystalline electric field splitting due to large overlap of projected DOSs for different cubic irreducible representations (irreps).

In order to incorporate the many-body effects with the detailed electronic structure, we study a model Hamiltonian with Coulomb repulsion between \textit{f}-electrons. The model of interest is the \textit{impurity} Anderson model. Although one needs to solve a \textit{lattice} Anderson model for systems with cerium atoms on regular lattice in the concentrated limit, the rigorous treatment of the lattice effects are out of the scope of this project. With the impurity Hamiltonian, we do not concentrate on the lattice effects which result from the collective effects of Ce-\textit{f} orbitals in the lattice, such as magnetic
ordering and superconductivity [24, 50]. Since for many materials, such lattice effects occur only after the Kondo screening is in effect [50], we can describe the systems with the impurity model up to $T$ higher than $T_{coh}$, the coherence temperature. In this regime the $f$-orbital at each Ce site has independent phase relation to neighboring sites and they are treated as incoherent impurities with a finite concentration.

The Anderson impurity model describes a localized orbital embedded in metallic host. The Ce-$4f$ orbitals are highly localized in space with strong Coulomb interaction $U$ considerably larger than the hopping strength of $f$-electrons. Specifically, as seen in the previous chapters, the overall magnitude of the hybridizations is usually $\leq 0.2$ eV whereas the Coulomb interaction is about $6 \sim 7$ eV [44, 45]. Given this strong correlation physics, we set up a model Hamiltonian with elements such as conduction bands, localized orbitals, Coulomb interaction within the localized orbitals and the hopping elements:

$$ H = \sum_{k\sigma} \epsilon_{k\sigma} c_{k\sigma}^\dagger c_{k\sigma} + \frac{1}{\sqrt{N_s}} \sum_{k\sigma,m} (V_{k\sigma m} c_{k\sigma} f_m^\dagger + h.c.) + \sum_{m} \epsilon_{f_m} f_m^\dagger f_m + \sum_{m} U_{mm'} n_{f_m} n_{f_m'}, $$

(3.1)

where $m$ is the label of cubic irrep states, $V_{k\sigma m}$ the hopping matrix element between conduction electron ($c_{k\sigma}$) and $f$-orbital ($f_m$), $N_s$ the number of sites, $\epsilon_{f_m}$ the $f$-level energy measured from the Fermi level, $U_{mm'}$ the on-site Coulomb repulsion for $f$-electrons in states $m, m'$.

Before jumping into the solution of the Anderson model, we shall discuss what has been left out of the model. We can write the first-principles Hamiltonian in terms of total field operators $\psi(\mathbf{r}) \equiv \psi_c(\mathbf{r}) + \psi_f(\mathbf{r})$ with $c(f)$ denoting conduction ($f$) orbitals.
Then we have the full Coulomb interaction term given by

\[
\int dr dr' \psi^\dagger(r) \psi(r) U(r - r') \psi^\dagger(r') \psi(r'), \quad \text{with} \quad U(r - r') = \frac{e^2}{|r - r'|}
\]  

(3.2)

leading to terms like

\[
\int dr \psi^\dagger(r) \psi_f(r) \left[ \int dr' U(r - r') \psi^\dagger(r') \psi(r') \right] + h.c., \quad U\text{-induced hopping} 
\]

(3.3)

\[
\int dr \psi^\dagger_f(r) \psi_f(r) \left[ \int dr' U(r - r') \psi^\dagger(r') \psi(r') \right], \quad \text{screening the} \ \epsilon_f \text{level.} 
\]

(3.4)

The first term, in the square bracket in Eq. (3.4), taken as a mean value, can be absorbed in the hopping term in the model Hamiltonian, Eq. (3.1), in addition to hopping terms from one-body Hamiltonian. The Eq. (3.4) can be similarly understood as a shift in the \( \epsilon_f \) level position. This mean field approximations for these terms should be carefully examined for each quantity you are looking at. For instance, in the core electron photoemission experiment of Ce [51], the d-electron density operators in the square bracket in Eq. (3.4) couple to the f-electrons and the observed spectra bear out the many-body effects of the system. However in the following analysis of this work, the dynamic effects of those terms are ignored and we assume that the mean field contributions are already taken into account in the hybridization obtained from the LDA calculations.

The conduction band spectra \( \epsilon_{k\sigma} \) are understood as whatever electronic continuum the Ce-f electron couples to. Thus, in the dilute limit they are the conduction band for Ce-s, p, d and M-s, p, d without Ce-f array. In the concentrated limit the energy levels are those of the effective medium, i.e., the whole lattice of CeM3 minus one f-site at origin. Therefore, strictly speaking, we mean the label k as the quantum number of the medium. When we confine ourselves to non-transport properties we do not need the information of the energy eigenvalues with respect to the direction of
wave vectors. As we shall see, what we need is the hybridization broadening function, the total of hopping rate summed over equi-energy wave-vectors,

$$\Gamma_{mm'}(\epsilon) = \pi \sum_{n,\sigma} V_{n\sigma}^* V_{n\sigma} \delta(\epsilon - \epsilon_{n\sigma}).$$  \tag{3.5}

The last two terms in the Hamiltonian, Eq. (3.1), describe the atomic limit of the $f$-electron. Although they are usually called atomic, we should remember that the bare atomic interactions are heavily screened by conduction electrons, as previously pointed out. Still, the realistic values for $\epsilon_f$ and $U_{mm'}$ are rather constant throughout the compounds with $\epsilon_f \approx -2$ eV and $U \approx 6$ eV [43, 45]. We set $\epsilon_f$ to be -2 eV for most of the calculation. For the Coulomb interaction we take $U$ to infinity, truncating the multiply occupied $f$-configurations from the Hilbert space.

### 3.1 Energy Scales of the Problem

The most important goal in this chapter is to predict how the different energy scales come into play in real materials and find the correct trend among them. Let us first organize the hierarchy of characteristic energies of the model. In real materials, the band width of the valence band, $D$, is larger than the Coulomb interaction strength, $U$. Note that the band width of the valence electrons, order of 1 Rydberg, are usually larger than the Coulomb interaction strengths. However, since we are employing the infinite-$U$ approximation in this chapter, $D$ is the largest energy parameter in the model in the infinite-$U$ approximation.

Next comes the $\epsilon_f$ level energy near $-2.0$ eV. A schematic diagram of the atomic energy levels of Ce$^{4+}$ in metal is sketched in figure 3.1. There have been theoretical efforts to calculate this quantity by including the screening of ionic Ce by conduction electrons [38, 39]. Also from the photoemission spectroscopy (PES) experiments one
Figure 3.1: Schematic picture of the splitting of the atomic energy levels of Ce$^{4+}$. The $f$-level energy, $\epsilon_f$, is at $-2.0$ eV which is the energy required to move the 4$f$-electron to the Fermi level. The $f$-level is first split by the spin-orbit coupling into $J = \frac{5}{2} \oplus \frac{7}{2}$ total angular momentum states. The ground Hund's rule multiplet then splits into the cubic irreducible representations $\Gamma_7 \oplus \Gamma_8$ in the cubic lattice. Note that $|\epsilon_f| \gg \Delta_{\text{SO}} \gg \Delta_{\text{CEF}}$. The numbers in parenthesis are the degeneracies of the level.

can see broad ionization peaks near $-2.0$ eV in the spectrum [43]. Although it is not always possible to determine the $\epsilon_f$ value due to the limited resolution of PES and the shift of $\epsilon_f$ by the band-$f$ hybridization, for most of Ce materials $\epsilon_f$ values are observed to be near $-2.0$ eV.

The Ce-4$f^1$ configuration has 14 possible states and the atomic states split to total angular momentum states with $J = \frac{5}{2}$ and $J = \frac{7}{2}$ by spin-orbit (SO) interaction. The LMTO code has the SO interaction included perturbatively and it produced the SO splitting $\Delta_{\text{SO}}$ with $\Delta_{\text{SO}} \approx 0.35$ eV. (See figure 2.5.) Hund’s rules predict that Ce-4$f^1$ has $J = \frac{5}{2}$ as the ground state angular momentum quantum number from the spin-orbit coupling. We will put the effect of Hund coupling in the $\epsilon_{f\text{m}}$ in the parameter of the Hamiltonian, i.e., $\epsilon_f(J = \frac{7}{2}) - \epsilon_f(J = \frac{5}{2}) = \Delta_{\text{SO}}$. 

43
Now come the central questions of this project. Namely,

**Which of the cubic CEF levels of Ce-4f^1 is lowest in energy in cubic environment?**

When a Ce-f orbital is embedded in a lattice, the angular momentum eigenstates can no longer be energy eigenstates and they split into cubic irreps. In a cubic environment, the half-integer angular momentum states split into doublets \((\Gamma_6, \Gamma_7)\) and quartets \((\Gamma_8)\). In particular, the ground multiplet \(|J = \frac{5}{2}\rangle\) splits into \(\Gamma_7 \oplus \Gamma_8\). Hence, we want to compute the sign and magnitude of \(\Delta_{78} \equiv E_{\Gamma_8} - E_{\Gamma_7}\). Experimentally, for CePb_3 and CeIn_3, the doublet \((\Gamma_7)\) is known to be lower in energy and the CEF splitting \(\Delta_{78}\) is positive and is of order of 10 meV [48, 50].

**How do the two energy scale, \(T_K\) and \(\Delta_{78}\), compare?**

The most remarkable physics emerging from localized orbitals in metal is the Kondo phenomena, responsible for the low temperature behaviors. The scattering of conduction electrons off the localized orbital causes the flip of spin degrees of freedom with anti-ferromagnetic exchange interaction of strength \(J_{\text{ex}} \sim V^2/\epsilon_f\) [52]. This magnetic scattering induces a resonance near the Fermi surface with energy width given by the Kondo temperature, \(T_K\). \(T_K\) ranges from few Kelvin to several hundred Kelvin. For instance CeSn_3 and CePd_3 exhibit \(T_K\) of several hundred Kelvin with \(T_K > \Delta_{78}\), whereas for CePb_3 and CeIn_3 \(T_K \ll \Delta_{78}\).

### 3.2 Formalisms

Instead of expanding the theory in the Coulomb repulsion \(U\) or the hybridization \(V_{\text{km}}\), we choose as the expansion parameter the inverse of the orbital degeneracy of the ground multiplet of Ce-4f^1 orbital, \(N_g\). In order to have a meaningful limit, we
scale the hopping matrix element $V_{k\alpha m}$ as proportional to $1/\sqrt{N_g}$. With this scaling form with the $N_g \to \infty$ limit, we can formulate a well-defined theory as an expansion of inverse of orbital degeneracy, $1/N_g$ [18, 19, 53, 54]. Although in realistic situations the degeneracy can be as small as 2, it has been shown that this expansion gives us reasonable numerical results [19]. In the case of $T_K \ll \Delta_{78}$, the higher multiplet $\Gamma_8$ does not participate in the scattering of conduction electrons, leading to $N_g=2$. It only renormalizes the scattering strength via virtual fluctuations. In the case of $T_K \gg \Delta_{78}$, conduction electrons see the $J = \frac{3}{2}$ multiplet as a whole and both $\Gamma_7$ and $\Gamma_8$ participate in the scattering process and effectively $N_g \approx 6$.

The infinite-$U$ limit is equivalent to discarding the multiply occupied $f$-orbital configurations. Therefore we will restrict our Hilbert space for the $f$-configurations to $f^0$ and $f^1$, that is,

$$\sum_m f_m^† f_m \leq 1. \quad (3.6)$$

Now given that the fermion operators $f_m(f_m^†)$ appearing in the Hamiltonian in Eq. (3.1) no longer represent the physical process of annihilation (creation), since, for example, $f_m^† |f^1;m\rangle$ will bring us to an $f^2$ configuration which is forbidden. To overcome this problem, we choose to use the slave-boson technique [18]. We enlarge the Hilbert space by introducing a pseudo-vacuum $|0\rangle$ and then define the empty and singly occupied states as created by pseudo-fermion $f_m^\dagger$ and pseudo(or slave)-boson $b^\dagger$;

$$|f^0\rangle \rightarrow b^\dagger |0\rangle \quad \text{and} \quad |f^1;m\rangle \rightarrow f_m^\dagger |0\rangle. \quad (3.7)$$

An annihilation (creation) of one physical $f$-electron is expressed as

$$f_m \rightarrow b^\dagger f_m \quad \text{and} \quad f_m^† \rightarrow f_m^\dagger b. \quad (3.8)$$

45
Since all the terms in the Hamiltonian conserve the number of pseudo fermions and bosons, once we start from a physical state we will not evolve into any non-physical states. Therefore we replace the inequality Eq. (3.6) by a more mathematically manageable equality
\[ Q \equiv b^\dagger b + \sum_m \tilde{f}_m^\dagger \tilde{f}_m = 1. \]  
(3.9)

With this constraint, the Hamiltonian now reads
\[ H = \sum_{k\sigma} \epsilon_{k\sigma} c_{k\sigma}^\dagger c_{k\sigma} + \frac{1}{\sqrt{N}} \sum_{k\sigma,m} (V_{k\sigma m} c_{k\sigma} \tilde{f}_m^\dagger b + h.c.) + \sum_m \epsilon_m \tilde{f}_m^\dagger \tilde{f}_m. \]  
(3.10)

For mathematical convenience, we work with the grand-canonical ensemble with a chemical potential term, i.e.,
\[ H_\lambda = H - \lambda \left( b^\dagger b + \sum_m \tilde{f}_m^\dagger \tilde{f}_m \right). \]  
(3.11)

To constrain the pseudo-particle Fock space to physically meaningful states with \( Q = 1 \), we project out the physical states in the limit \( \lambda \to -\infty \), as shown in Ref. [18].

In the limit of \( N_g \to \infty \), the solution for the slave-boson technique is achieved by satisfying the self-consistency condition for the lowest order skeleton diagrams for pseudo-boson and pseudo-fermion Green’s functions, \( G_0(\omega) \) and \( G_{mm'}(\omega) \) where
\[ G_0(\omega) = \ll b; b^\dagger \gg_{\omega+i0^+} \]  
(3.12)
\[ G_{mm'}(\omega) = \ll \tilde{f}_m; \tilde{f}_m^\dagger \gg_{\omega+i0^+}, \]  
(3.13)

where \( \ll a; b \gg_z \equiv \int_0^\beta d\tau e^{-z\tau} \langle T a(\tau)b(0) \rangle \). Since \( G_{mm'}(\omega) \)'s are not diagonal, we define the pseudo-fermion self-energy \( \Sigma_{mm''}(\omega) \) by a \( 14 \times 14 \) matrix Dyson’s equation as
\[ G_{mm'}(\omega) = G_0^0(\omega) \delta_{mm'} + \sum_{m''} G_{m''}^0(\omega) \Sigma_{mm''}(\omega) G_{m''m'}(\omega), \]  
(3.14)
where $G_{m}^{0}(\omega) = (\omega - \epsilon_{m})^{-1}$. Similarly, the Dyson’s equation for the pseudo-boson reads

$$G_{0}(\omega) = [\omega - \Sigma(\omega)]^{-1}. \quad (3.15)$$

Now the self-consistent integral equations of NCA become

$$\Sigma_{0}(\omega) = \frac{1}{\pi} \sum_{m,m'} \int d\epsilon \Gamma_{mm'}(\epsilon) f(\epsilon) G_{m'm}(\omega + \epsilon), \quad (3.16)$$

$$\Sigma_{mm'}(\omega) = \frac{1}{\pi} \int d\epsilon \Gamma_{mm'}(\epsilon) (1 - f(\epsilon)) G_{0}(\omega - \epsilon), \quad (3.17)$$

where $f(\epsilon)$ is the Fermi-Dirac function. The solid line in the diagram denotes the conduction electron Green’s function, the (double) dashed line the dressed $f^{1}$ (pseudo-fermion)-Green’s function from index $m$ to $m'$, the (double) wiggly line the dressed $f^{0}$ (pseudo-boson)-Green’s function. Although these integral equations contain all orders of $1/N_{g}$, the NCA is correct only up to $O(1/N_{g})$. The hybridization functions $\Gamma_{mm'}(\epsilon)$ are input from the LDA calculations.

The actual computation is done by keeping the spectral functions $\rho_{0}(\zeta), \rho_{mm'}(\zeta)$, rather than dealing with Green’s functions, via the spectral representation

$$G_{0}(\omega) = \int d\zeta \frac{\rho_{0}(\zeta)}{\omega - \zeta + i\eta}, \quad (3.18)$$

$$G_{mm'}(\omega) = \int d\zeta \frac{\rho_{mm'}(\zeta)}{\omega - \zeta + i\eta}, \quad (3.19)$$

where $\rho_{0}(\zeta)$ and $\rho_{mm'}(\zeta)$ are spectral functions for pseudo-boson and pseudo-fermions, respectively. We also define negative frequency spectral functions $\rho_{0}^{(-)}(\zeta)$ and $\rho_{mm'}^{(-)}(\zeta)$ as

$$\rho_{0}^{(-)}(\zeta) = e^{-\beta(\omega-E_{0})}\rho_{0}(\zeta), \quad \rho_{mm'}^{(-)}(\zeta) = e^{-\beta(\omega-E_{0})}\rho_{mm'}(\zeta), \quad (3.20)$$
where $E_0$ is so-called the threshold energy, which is close to the value of the ground state energy. The self-consistent integral equations for the negative frequency spectral function can be similarly derived as Eqs. (3.17-3.17) by introducing the negative frequency self-energy functions $\Sigma_0^{(-)}(\zeta) = e^{-\beta(\omega-E_0)}\Sigma_0(\zeta)$ and $\Sigma_{mm'}^{(-)}(\zeta) = e^{-\beta(\omega-E_0)}\Sigma_{mm'}(\zeta)$.

Since physical observables are usually expressed as combination of spectral function and the Boltzmann factor which is fastly diverging or decaying, we need to keep the negative spectral function separately from the usual spectral functions. For instance, the $f$-orbital partition function $Z_f(T)$ is expressed as

$$Z_f(T) \equiv Z_{\text{tot}}/Z_{\text{cond}} = \int d\omega e^{-\beta\omega} \left( \rho_0(\omega) + \sum_m \rho_{mm}(\omega) \right) = e^{\beta E_0} \int d\omega \left( \rho_0^{(-)}(\omega) + \sum_m \rho_{mm}^{(-)}(\omega) \right). \quad (3.21)$$

Now we can analyze the elementary features of the system by examining the self-consistent equations (3.17) to the order of $O((1/N_g)^0)$. To the lowest order, the pseudo-fermions are non-interacting i.e., $\rho_{mm}(\epsilon) = \delta(\epsilon - \epsilon_{fm})$, since $\Gamma_{mm}(\epsilon) \propto 1/N_g$. $\Sigma_{mm'}(\epsilon)$ is of order $O(1/N_g)$ and to the lowest order, we do not have mixing between different total angular momenta, hence no off-diagonal Greens functions. The the equation (3.17) becomes, at $T = 0$,

$$\Sigma_0^{(-)}(\omega) = \frac{1}{\pi} \sum_m \int_{-D}^{0} d\epsilon \frac{\Gamma_{mm}(\epsilon)}{\epsilon + \omega - \epsilon_{fm} + i\eta}, \quad (3.22)$$

with $-D$ the lower band edge. Now, for simplicity, assuming a flat hybridization function $\Gamma_{mm}(\epsilon) = \Gamma_m$, we reach an equation

$$\Sigma_0^{(-)}(\omega) = \sum_m \frac{\Gamma_m}{\pi} \left\{ \ln \left| \frac{\epsilon_{fm} - \omega}{D} \right| - i\pi \theta(\omega - \epsilon_{fm}) \right\}. \quad (3.23)$$

$\epsilon_{f}, \Gamma_g, \epsilon_{ex}, N_{ex}, \Gamma_{ex}$ denote the $f$-level energy, hybridization strength for the ground multiplet, energy for the excited multiplet, degeneracy and hybridization strength for
the excited multiplet, respectively. We introduce the CEF splitting $\Delta_{\text{CEF}}(\equiv \epsilon_{\text{ex}} - \epsilon_{f})$, whatever drives the splitting. Then we find the 1-particle energies $E_0$ at the poles of the pseudo-boson Green’s function from $E_0 - \text{Re}\Sigma^0_0(E_0) = 0$. This equation can have several solutions.

First, the solution $E_0\approx 0$ is simply the perturbed boson energy from the unperturbed empty state with $\epsilon(0^0) = 0$ and carries the most of the spectral weight. This peak is responsible for the charge excitation peak at $\epsilon_f$ in the PES experiment. Since the imaginary part of the self-energy is $N_g \Gamma_g + N_{\text{ex}} \Gamma_{\text{ex}}$, the peak is heavily damped.

The second solution $E_0$, corresponding to the ground state energy, exists below $\epsilon_{fg}$. Let us define a new energy scale $T_0$, the zero-th order estimate of $T_K$, as $E_0 = \epsilon_{fg} - T_0$. In the weak hybridization limit where $\Gamma_g, \Gamma_{\text{ex}}, \Delta_{\text{CEF}}, T_0 \ll |\epsilon_{fg}|$, we have an equation for $T_0$,

$$\epsilon_{fg} = \frac{N_g \Gamma_g}{\pi} \ln \left( \frac{T_0}{D} \right) + \frac{N_{\text{ex}} \Gamma_{\text{ex}}}{\pi} \ln \left( \frac{\Delta_{\text{CEF}}}{D} \right).$$

Consequently,

$$T_0 = D \left( \frac{D}{\Delta_{\text{CEF}}} \right) \frac{N_{\text{ex}} \Gamma_{\text{ex}}}{N_g \Gamma_g} \exp \left( \frac{\pi \epsilon_{fg}}{N_g \Gamma_g} \right).$$

Moreover, the spectral weight of this pole is given as the renormalization factor $Z$ where

$$Z = \left[ 1 - \frac{\partial \text{Re}\Sigma^0_0(\omega)}{\partial \omega} \right]_{\omega = \epsilon_{fg} - T_0}^{-1} \approx \frac{\pi T_0}{N_g \Gamma_g}.$$

The lowest energy pole $\epsilon_{fg} - T_0$ has no damping and serves as the ground state energy of the system. This ground state has zero spin, same as the empty state, and is made up of a local moment anti-ferromagnetically screened by conduction holes admixed with the empty state.

Finally, when the hybridization is so small that $T_0 \ll \Delta_{\text{CEF}}$, relevant for CePb$_3$ and CeIn$_3$, there exists another physically meaningful solution, which comes from the
logarithmic term from the $\Gamma_{ex}$-term in Eq. (3.23). The solution at $\epsilon_{ex} - T_{ex} (T_{ex} \ll \Delta_{CEF})$ is given by

$$T_{ex} = D \left( \frac{D}{\Delta_{CEF}} \right)^{N_g \Gamma_g} e^{\frac{\pi \epsilon_{ex}}{N_g \Gamma_g}},$$

with the damping factor $N_g \Gamma_g$ in the self-energy. Due to the damping, this only becomes significant with the weakly hybridizing systems such as CePb$_3$, ind. This solution is responsible for the side-band peaks for CEF or SO excitations.

Note that $T_0$ is expressed as a non-analytic function of the hybridization. Therefore any finite order perturbation theory in terms of hybridizations would not capture the essential many-body physics. The presence of the excited multiplets contribute to $T_0$ constructively, but through algebraic rather than exponential factors (See Eq. (3.27)).

On the other hand, we also need to look at the first order correction to the $f^1$ states, since the hybridization-induced CEF splitting comes from the shift in the pseudo-fermion self-energies. To the lowest order, the self-energy becomes

$$\Sigma_{mm'}(\omega) = \frac{\Gamma_{mm'}}{\pi} \int_0^D d\omega G_0^0(\omega - \epsilon),$$

with the boson Greens function of order $O(1)$, $G_0^0(\omega)$. Although any simple expression for the integral is not handy, we can at least make a crude estimate of it. Since the boson spectral function carries the most of its weight near $\omega = 0$, we approximate the shift as

$$\Delta \epsilon_{fm} = \text{Re} \Sigma_{mm}(\epsilon_{fm}) \approx \frac{\Gamma_m}{\pi} \int_0^D d\epsilon \frac{1}{\epsilon_{fm} - \epsilon} \approx \frac{\Gamma_m}{\pi} \ln \left| \frac{\epsilon_{fm}}{D} \right| < 0,$$

which is nothing but the second order perturbation theory [32, 34]. Although the $b$-peak at $\omega = 0$ is significantly broadened approximately by $\sum_m \Gamma_m$ and the NCA contains terms of infinite orders of $O(1/N_g)$, the perturbative shift gives us a rough
estimate of the shift. The shift is always negative and directly proportional to the hybridization strength. The CEF level with the strongest hybridization among the ground Hund's multiplet will receive the maximum shift and becomes the ground CEF level.

The CEFs also receive an additional contribution from $f^1 \leftrightarrow f^2$ virtual fluctuations which is ignored in the infinite-$U$ NCA and, therefore, we put this shift by hand into the model parameter $\epsilon_f$ levels. The second order perturbative shift for CEF level $\Gamma_m$ is computed using

$$
\Delta E_m^{\text{pert}} = \int_D d\epsilon \frac{\Gamma_{mm}(\epsilon)}{-\epsilon + 2\epsilon_f + U - \epsilon_f},
$$

where $-\epsilon$ is the energy of the hole, $\epsilon_f$ is the same for CEFs belonging to the same angular momentum state and the Coulomb interaction $U$ is set to 6 eV. We have included the relative shift to the CEF, more specifically, the calculated shift $\Delta_{78}^{\text{pert}} = E_{8}^{\text{pert}} - E_{7}^{\text{pert}}$ is added to the energy level of $|J = \frac{5}{2}, \Gamma_8\rangle$. Therefore, the input parameter of $\epsilon_{f_m}$ for the NCA is $\epsilon_{\frac{5}{2} \Gamma_8} = \epsilon_{\frac{5}{2}} + \Delta_{78}^{\text{pert}}$ and $\epsilon_{\frac{3}{2} \Gamma_7} = \epsilon_{\frac{3}{2}} = -2.0$ eV.

3.3 Results

3.3.1 Spectral Functions

The spectral function can be measured by photo-emission spectroscopy (PES) [4, 43, 44, 45] and isochromat Bremsstrahlung spectroscopy (BIS) [40] experiments. PES is performed by counting the emitted electrons from the sample due to the absorption of photons and measure the difference of the final and initial many-body states. BIS measures emitted photons which carry the extra energy after an injected electron loses the energy while settling in the sample. Despite the limited resolutions of PES and BIS, about 0.1 eV and 0.5 eV, respectively, they serve as very important
tools for probing the one electron spectra. The measured spectra of PES and BIS are proportional to the imaginary part of the single-particle Green’s function. We assume here that the photo-emitted electron has very high energies (50—1000 eV) that we can neglect, in the “sudden approximation”, the interaction of the electron with the many-body state left behind [17]. Also the energy dependence of the dipole operator matrix elements and the interference between the f-level and conduction band emissions are assumed to be negligible. Then the spectral function obtained from the spectroscopy experiments can be written in the following Lehman representation as

\[
\rho_{\text{PES}}(\epsilon) = \sum_\alpha |(N-1, \alpha| f_m | N; gs) |^2 \delta(\epsilon + E_{gs}^N - E_{\alpha}^{N+1}), \quad \epsilon > 0 \tag{3.31}
\]

\[
\rho_{\text{BIS}}(\epsilon) = \sum_\alpha |(N+1, \alpha| f_m^\dagger | N; gs) |^2 \delta(\epsilon + E_{gs}^N - E_{\alpha}^{N+1}), \quad \epsilon < 0 \tag{3.32}
\]

where \(E_{\alpha}^N(E_{gs}^N)\) denotes the \(\alpha\)-th (ground state) eigenvalue among \(N\)-particle states.

In the slave-boson formulation, the physical process of removing(adding) one \(f\)-electron amounts to removing the pseudo-fermion(boson) and then creating a pseudo-boson(fermion). Therefore the \(f\)-electron spectral function \(\rho_f(\omega)\) is expressed in terms of a convolution of pseudo-fermion and pseudo-boson operator as

\[
\rho_f(\omega) = \frac{1 + e^{-\beta \omega}}{Z_f} \sum_m \int_{-\infty}^{\infty} d\epsilon e^{-\beta \epsilon} \rho_0(\epsilon) \rho_m(\epsilon + \omega). \tag{3.33}
\]

The computed \(f\)-spectral function for the dilute limit of CePb$_3$ is shown in figure 3.2.

The calculated spectral function has the characteristics of both electronic structure and many-body effects. Although the LDA-DOS has the most of \(f\)-weight near the Fermi energy \(E_F\) with negligibly small admixture with the conduction electrons below \(E_F\), the weight of the many-body spectral function is spread all over the region of conduction band. As shown in the figure 3.2, there emerge several new features absent in the LDA, namely, the Kondo resonance (KR), CEF, side-band CEF, SO peaks and
Figure 3.2: $f$-spectral function for CePb$_3$. The spin-orbit and CEF peaks appear at $\Delta_{78}$ and $\Delta_{SO}$, respectively, accompanied by the side-band peaks at the negative frequency side. The Kondo resonance peak from the ground CEF (doublet, $\Gamma_\gamma$) emerges at the Fermi energy. The charge excitation peak from $f^1 \rightarrow f^0$ is at $\sim \epsilon_f$ as a broad envelop function with the electronic structures. The different lines are for temperatures from 1164 K to 0.54 K.
the broad envelop of the ionization peak at near \( \epsilon_f \). The different curves in the figure are from temperatures from 1164 K down to 0.544 K.

Now, let us discuss the many-body features of the spectral function. First, near the Fermi energy emerges a very sharp structure, which is blown up in the inset. The structure is actually composed of three peaks. The central peak lying very close to the Fermi energy is the Kondo resonance (KR) due to the screening of the ground CEF level, \( |\frac{3}{2}; \Gamma_7\rangle \). The width of the KR peak is \( \sim \pi T_K/2 \).

Second, above and below the Fermi energy, two peaks appear near the energy scale of CEF splitting. The positive energy peak (marked as CEF peak in the figure) originates from electron-adding transition. The negative energy peak, so called side-band CEF peak, results from exciting \( f^1 \Gamma_7 \) to the \( \Gamma_8 \)-admixture in the bosonic excitation. The physical processes involved will be detailed below. Similarly for the SO multiplets, two peaks, corresponding to absorption and emission of \( f \)-electrons, show up at energy scale of \( \sim \pm \Delta_{SO} \).

Third, unlike the LDA-DOS, there is a broad excitation (marked as dashed line in the figure) near \( \epsilon_f \), which corresponds to the energy \( |\epsilon_f| \) necessary to pull out one \( f \)-electron at \( \epsilon_f \) to the Fermi energy \( (f^1 \rightarrow f^0) \). The detailed structure reflects the conduction band DOS, or more precisely proportional to \( \Gamma_m(\epsilon) \). The width of the \( (f^1 \rightarrow f^0) \) bump is of order \( \sum_m \Gamma_{mm} \). Since our approximation neglects dynamical transfer of \( f^1 \rightarrow f^2 \), we do not have another excitation peak at \( \omega = \epsilon_f + U \), which is experimentally observed. (See figure 1.2.)

To understand the origin of the low energy peaks, KR and CEF peaks, first we look at the energy eigenstates. These are most easily understood in the variational trial wave-function as in Ref. [17]. Let us denote \( |\Omega; f^n \Gamma_m\rangle \) as the direct product
of non-interacting Fermi sea with \( f \)-electronic configuration \( f^n \Gamma_m \). As seen in the zero-th order analysis of NCA, the ground state is a spin-singlet state. It turns out that the ground state can be written approximately as

\[
|G_S\rangle = \sqrt{\frac{\pi T_K}{N_g \Gamma_g}} |\Omega; f^0\rangle + \sum_{k\sigma m} \alpha_{k\sigma m} |\Omega; f^1 \Gamma_m\rangle + \sum_{k\sigma m} \beta_{k\sigma m} |\Omega; f^1 \Gamma_{8m}\rangle, \tag{3.34}
\]

where the hole-\( f^1 \) pairs form linear combination of singlets and the coefficients \( \alpha_{k\sigma m}, \beta_{k\sigma m} \) satisfy \( \sum_{k\sigma m} (|\alpha_{k\sigma m}|^2 + |\beta_{k\sigma m}|^2) = 1 - \frac{\pi T_K}{N_g \Gamma_g} \approx 1 \). The energy of the state is \( E_0 = \epsilon_{f_\sigma} - T_K \). Note that \( \sum_{k\sigma m} |\alpha_{k\sigma m}|^2 \gg \sum_{k\sigma m} |\beta_{k\sigma m}|^2 \).

The Kondo resonance peak, seen primarily in the additive spectrum, comes by making a transition from the term \( G_0 \) in Eq. (3.34) to \( |\Omega; f^1 \Gamma_7\rangle \), a state of \((N + 1)\)-particles.

\[
\sqrt{\frac{\pi T_K}{N_g \Gamma_g}} |\Omega; f^0\rangle \rightarrow |\Omega; f^1 \Gamma_7\rangle \tag{3.35}
\]

Since \( |\Omega; f^1 \Gamma_7\rangle \) has energy \( \epsilon_{f_\sigma} \) measured from the energy of the Fermi sea, the energy involved in the transition is \( T_K \) and the weight of the peak is \( \pi T_K / N_g \Gamma_g \). The CEF peak is from the transition, term \( G_0 \) to \( |\Omega; f^1 \Gamma_8\rangle \), with energy transfer of \( \epsilon_{f_\sigma} - E_0 \approx \epsilon_{f_\sigma} - \epsilon_{f_\sigma} = \Delta_{\gamma_8} \).

\[
\sqrt{\frac{\pi T_K}{N_g \Gamma_g}} |\Omega; f^0\rangle \rightarrow |\Omega; f^1 \Gamma_8\rangle \tag{3.36}
\]

As can be seen in the previous two equations, the weights of the KR and CEF peaks should be the same, \( \pi T_K / N_g \Gamma_g \). However, the lowest temperature of the calculation in figure 3.2 was not sufficiently smaller than the Kondo temperature due to numerical instabilities and the KR peak has not reached the same weight as the CEF peak[19]. For CeSn_3 and CePd_3 KR and SO peaks have the same weight, as seen in figure 3.3.

The side-band peak, below the Fermi energy at \( \omega \approx -\Delta_{\gamma_8} \), emerges through a less apparent process. Just as the ground multiplet \( \Gamma_7 \) has been screened to form
a ground state, the CEF $\Gamma_8$ can also couple anti-ferromagnetically with surrounding conduction electrons to form another singlet state $|S = 0, \Gamma_8\rangle$ at energy $\epsilon_{f8} - T_{ex}$ as explained in the previous section with Eq. (3.27),

$$
|S = 0, \Gamma_8\rangle = \sqrt{\frac{\pi T_{ex}}{N_{ex} \Gamma_8}} |\Omega; f^0\rangle + \sum_{k\sigma m} \alpha'_{k\sigma m} |\Omega; f^1 \Gamma_{7m}\rangle + \sum_{k\sigma m} \beta'_{k\sigma m} |\Omega; f^1 \Gamma_{8m}\rangle.
$$

(3.37)

where, most of the weight comes from the excited CEF-\$\Gamma_8$, i.e., $\sum_{k\sigma m} |\alpha'_{k\sigma m}|^2 \ll \sum_{k\sigma m} |\beta'_{k\sigma m}|^2$. The side-band peak results from the process

$$
\sum_{k\sigma m} \alpha'_{k\sigma m} |\Omega; f^1 \Gamma_{7m}\rangle \xrightarrow{\text{remove} \text{ hole}} |\Omega; f^0\rangle \xrightarrow{\text{evolve} \text{ hole}} |S = 0, \Gamma_8\rangle,
$$

(3.38)

at $\omega = -\Delta_{78} + T_{ex}$. The physics of the SO and SO side-band peaks arise similarly.

The spectral function of CeIn$_3$ in figure 3.3 is similar to that of CePb$_3$. The Kondo temperatures in each plot are estimated from a fit to the NCA curves with known $T_K$. Details will be mentioned in the next section. As in the case of CePb$_3$ the KR peak begins to emerge but less fully developed than CePb$_3$. One point worth mentioning is that although the estimated Kondo temperature for CeIn$_3$ is smaller than CePb$_3$, the CEF splitting of CeIn$_3$ is about twice as large. This is, naively speaking, contradictory to the common belief since, assuming structureless flat hybridization, larger CEF splitting implies the larger hybridization which would consequently give larger $T_K$ due to its exponential sensitivity to the hybridization as in Eq. (3.25). However the rapid variation of hybridization as a function of energy can explain this fact; the sudden dip in the hybridization (marked as an arrow in figure 2.8) right below the Fermi energy gives small contribution to $T_K$, although the overall larger hybridization of CeIn$_3$ induces the twice as large $\Delta_{78}$ compared to that of CePb$_3$.
Figure 3.3: $f$-spectral functions for Ce$M_3$ ($M=$In, Sn, Pd). The spectral function for CeIn$_3$ compound is similar to that of CePb$_3$. CeSn$_3$ and CePd$_3$ compounds have large $T_K (>\Delta_{78})$ and the CEF peaks merge into one Kondo resonance peak. The spin-orbit peak is separated from the Kondo resonance peak by $\sim \Delta_{SO}$ with nearly the same weight.
The spectral function of CeSn₃ shows much different shape from CePb₃ and CeIn₃. First, there are no separation of KR and CEF peaks. Since the estimated CEF splitting, 150 K, is significantly smaller than the Kondo temperature, 400 K, both the doublet (Γ₇) and the quartet (Γ₈) participate to the singlet formation. Once the conduction electrons compensate the magnetic moments of Γ₇ and Γ₈ altogether at higher energy scale $T_K$, there are no more magnetic moment degrees of freedom to scatter off the electrons and the CEFs do not split at lower energy scale $\Delta_{78}$. Thanks to the high value of $T_K$ we have reached a fully converged curve with strong Kondo resonance. The peak position of the KR peak is around $T_K$, 400 K. Note that, as mentioned earlier, the weights of KR and SO peaks are the same. The weak shoulder at about $-0.4$ eV is the side-band peak for the SO splitting.

As the theoretical curves for CePd₃ show, most of its spectral weight is in the KR and SO peaks. This provides an extreme example of a valence fluctuating material. The occupation number for $f$-orbital is 0.742 at 940 K, showing significant admixture of $f^1$ and $f^0$. The computed KR peak appeared at 0.3 eV, which is grossly overestimated compared to the $T_K \approx 650$ K from the neutron scattering experiment [26]. We suspect that the overestimate of the Kondo temperature results from the overestimation of the hybridization from the Pd-$d$ orbitals due to the negligence of the correlations in Pd-$d$ orbitals. Although it has been thought that the Kondo temperature is the function of the hybridization at the Fermi energy, CePd₃ provides a counter-example in that $T_K$ depends on the integral of the whole hole spectrum. A qualitative discussion of the large $T_K$ in CePd₃ is given in appendix B.

Note that the computed spectral functions show the same trend as in the BIS experiment in figure 1.2, where the CePd₃ has the second largest $4f^4$-peak next to
CeRh$_3$ followed by CeSn$_3$. The 4f$^1$-spectral weights of CePb$_3$ and CeIn$_3$ were too small to be observed with the resolution of BIS, $\sim 0.5$ eV (and the measurement temperature was at least two orders of magnitude above the Kondo scale for these materials, which is consistent with the picture that the Kondo resonance melts above $T_K$).

### 3.3.2 Crystalline Electric Field Splittings and Kondo Temperatures

For the heavy fermion systems, CePb$_3$ and CeIn$_3$, the theoretical Kondo temperatures are so small that we could not reach low enough temperatures below $T_K$ because of the numerical instability of the discrete mesh system for the frequency variable in Eqs. (3.17-3.17). Therefore, for systems with small $T_K$, we decided to estimate the Kondo temperatures based on the fit to $\chi(T)$ curves with known $T_K$.

First, we have checked the reliability of the NCA by comparing the magnetic susceptibility, $\chi(T)$, with the numerical renormalization group calculation [55]. The two methods, even at $N_g = 2$, produced the overlapping $T \chi(T)$ curves at low temperatures below $T_K$ by fitting the energy scale in the NRG scaling function. Although the $\chi_{NCA}(T)$ curve at high temperatures does not agree well with $\chi_{NRG}(T)$ due to higher energy configurations such as CEF levels and $f^2$ states, the $\chi_{NCA}(T)$ at low $T$ shows good scaling behavior with the single energy scale given as $T_K$. Note that whatever the high energy levels are in the NCA, the curves produced the same low $T$ behavior as long as they have the same $T_K$. Moreover, the values of $T_K$ from the NCA, Eq. (3.39) without the excited CEF levels, and NRG-estimate for $T_K$ [55] agreed well to within a numerical factor of order unity. The $T_K$ expression of the NCA with CEF
splitting $\Delta_{78}$ becomes (with $\Gamma_7(0) = \Gamma_8(0), \Gamma_g \equiv \Gamma_7$)

$$T_{K,NCA} = D \left( \frac{\Gamma_g(0)}{\pi |\epsilon_f|} \right)^{1/N_g} \left( \frac{D}{\Delta_{78}} \right)^{N_{\epsilon f}/N_g} \exp \left( \frac{\pi \epsilon_f}{N_g \Gamma_g(0)} \right).$$ (3.39)

where $D$ is the band width with Lorentzian hybridization with strength $\Gamma$ at $\epsilon = 0$, i.e., $\Gamma(\epsilon) = \Gamma/(1 + (\epsilon/D)^2)$.

Since we now have a reliable analytical form of $T_K$ for the Lorentzian DOS, we can fit the susceptibilities of realistic calculations to the curves of the Lorentzian DOS result with known $T_K$ as shown in figure 3.4. At $T \ll T_K$, all physical quantities are functions of only $T/T_K$. We carefully adjust the parameters for the Lorentzian-DOS calculations (filled symbols) and match the low energy part of the curve to the $\Gamma_7$-contribution of the CeM$_3$ susceptibility (open symbols). Once the Lorentzian DOS calculation matches the that of CeM$_3$, we compute $T_K$ by an analytic expression, Eq. (3.39).

The systems with strong hybridization, CeSn$_3$ and CePd$_3$, have well-developed KR peaks and we measure the $T_K$ as the peak separation between the spectral functions of the pseudo-boson and the $\Gamma_7$ pseudo-fermion. For all compounds, we measured the CEF splitting, $\Delta_{78}$, as the peak separation between the spectral functions of $\Gamma_7$ and $\Gamma_8$ pseudo-fermions.

Table 3.1 lists the experimental values (in the concentrated limit) of $T_K$ and $\Delta_{78}$ and the NCA values for both concentrated and dilute limits. One of the most important points of this work rests on the fact that, for heavy fermion systems, CePb$_3$ and CeIn$_3$, the calculation produces self-consistently smaller $T_K$ than CEF splitting with the doublet ground multiplet. Also for the high $T_K$ systems, CeSn$_3$ and CePd$_3$, the computed CEF splittings are smaller than the Kondo temperature.
Table 3.1: Electronic configuration of ligand atom M (EC), ground multiplet $\Gamma_{grd}$, CEF splittings $\Delta_{78}$ and Kondo temperatures $T_K$ for Ce$_x$La$_{1-x}$M$_3$ systems. Positive $\Delta_{78}$ indicates a stable $\Gamma_7$ ground doublet on the Ce sites. Units in Kelvin. (*: $\Delta_{78}$ not experimentally deducible for $\Delta_{78} \ll T_K$)

<table>
<thead>
<tr>
<th>M</th>
<th>EC</th>
<th>$\Gamma_{grd}$</th>
<th>$\Delta_{78}^{\text{exp}}/T_K^{\text{exp}}$</th>
<th>$\Delta_{78}^{\text{1x1}}/T_K^{\text{1x1}}$</th>
<th>$\Delta_{78}^{\text{10x10}}/T_K^{\text{10x10}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>6s$^2$6p$^2$</td>
<td>$\Gamma_7$</td>
<td>67/3 [50]</td>
<td>60/0.053</td>
<td>45/8.8</td>
</tr>
<tr>
<td>In</td>
<td>4d$^{10}$5s$^2$5p$^1$</td>
<td>$\Gamma_7$</td>
<td>183/(&lt; 11) [48]</td>
<td>125/0.016</td>
<td>80/3.1</td>
</tr>
<tr>
<td>Sn</td>
<td>4d$^{10}$5s$^2$5p$^2$</td>
<td>$\Gamma^*_7$</td>
<td>-/450 [25]</td>
<td>159/400</td>
<td>176/238</td>
</tr>
<tr>
<td>Pd</td>
<td>4d$^{10}$</td>
<td>$\Gamma^*_8$</td>
<td>-/700 [26]</td>
<td>215/3210</td>
<td>314/2600</td>
</tr>
</tbody>
</table>

The large discrepancy between the two limits in the case of CePb$_3$ needs to be mentioned. The experiment [23] on Ce$_x$La$_{1-x}$Pb$_3$ shows that the system has concentration-independent Kondo temperatures, in disagreement with our calculation. We suspect the relative position and strength of the peaks $a, a'$ in figure 2.6 are responsible for the discrepancy. The estimated value of $T_K$ is extremely sensitive upon the parameters, $\epsilon_f, \Gamma_{m'm'}(\epsilon)$. For instance in the case of CePb$_3$, the argument in the exponential of Eq. (3.39) is approximately $-30$ so that a small fractional error can easily result in a huge difference in the estimated $T_K$. The more precise and rigorous calculation for the peaks $a, a'$ can be done by the super-cell calculation. But, at this point, we do not have a clear solution of this problem.

### 3.3.3 Magnetic Susceptibility

The Kondo phenomenon manifests itself in screening of the localized $f$-magnetic moment anti-ferromagnetically by the conduction electrons. At high temperatures $T \gg T_K$, the $f$-orbital is singly occupied with well-defined magnetic moment. Thus, the magnetic susceptibility displays the Curie-Weiss form with $\chi_{ff}(T) \approx \mu_{eff}^2/3(T -$
Figure 3.4: NCA magnetic susceptibilities, $\chi(T)$, for CePb$_3$ and CeIn$_3$ fit to the $\chi(T)$ with Lorentzian hybridizations. The NCA-LDA computed $\chi(T)$'s (open symbols) are fitted by the $\chi(T)$'s (filled symbols) from the NCA with Lorentzian hybridizations. The Kondo temperatures $T_K$ for the Lorentzian hybridizations are calculated from the analytic expression Eq. (3.39). Note that whatever the fitting parameters are, the $\chi(T)$'s at low temperatures show the scaling behavior as long as they have the same $T_K$. 
\( \theta \), where \( \mu_{\text{eff}} \) is the effective magnetic moment, \( \theta \) the Néel temperature. When the temperature drops below \( T_K \), the quantum fluctuation of \( f \)-hopping takes over and the ground multiplet of the \( f \)-moment is completely screened with energy scale \( T_K \).

Once the moment is screened, it only acts as an effective non-magnetic scatterer and the magnetic susceptibility becomes the temperature-independent Pauli-type paramagnetic susceptibility, \( \chi_{ff}(T) \approx \mu_{\text{eff}}^2 / 3T_K \).

In the presence of the CEFs, there is a contribution to the total magnetic susceptibility due to mixing between different irreps, known as the Van Vleck susceptibility. When there is a strong overlap between ground and first excited CEFs such as in \( \text{CeS}n_3 \) and \( \text{CeP}d_3 \), the van Vleck susceptibility \( \chi_{vv}(T) \) are no longer negligible. Since the energy scale involved in the mixing is nothing but the CEF splitting \( \Delta_{78} \), the \( \chi_{vv}(T) \) contribution goes as \( \sim |(\Gamma_7 | \tilde{\mu} | \Gamma_8)|^2 / 3\Delta_{78} \).

The magnetic susceptibility can be written as a convolution of pseudo-fermion spectral functions. From linear response theory, the dynamic magnetic susceptibility, \( \chi_{ff}(\omega) \), can be expressed as \([19, 56]\)

\[
\chi_{ff}(\omega) = \ll \dot{M}_z; \dot{M}_z \gg_{\omega \rightarrow 0} \, , \tag{3.40}
\]

where \( \dot{M} = \sum_{mm'} |f_{m}\rangle \langle \mu| \langle m'| \rangle \dot{f}_{m'} \), \( \dot{M} = \mu_B(\hat{L} + 2\hat{S}) \) and \( \mu_B \) the Bohr magneton. The imaginary part of the dynamic susceptibility is the \( f \) moment spectrum, \( \chi''(\omega) \), which can be expanded with respect to the CEF states via

\[
\chi''(\omega) = \sum_{mm'} \mu_{mm'}^2 \int d\epsilon \frac{e^{-\beta \epsilon}}{Z_f} \left[ \rho_{mm}(\epsilon) \rho_{m'm'}(\epsilon + \omega) - \rho_{m'm'}(\epsilon) \rho_{mm}(\epsilon - \omega) \right] \, , \tag{3.42}
\]

where \( \mu_{mm'} = \langle m | \mu | m' \rangle \). The contribution from off-diagonal spectral functions \( \rho_{mm'}(\epsilon) \) are neglected since they are usually small. The magnetic spectrum can be
Figure 3.5: \textit{f magnetic moment spectrum for CePb}. The \textit{f}-magnetic spectrum, \(\chi''(\omega)\) shows the Kondo resonance (KR) and CEF peaks at near zero frequency and \(\Delta g\), respectively. The peak positions approach the Kondo temperature, marked as an arrow. The temperature set is the same as in figure 3.2.

Directly measured by neutron scattering experiments which can provide information for the CEF splittings [26, 48, 50]. Computed \(\chi''(\omega)\) curves are plotted in figure 3.5. The broad excitations at near 70 meV is from the CEF splitting and the sharp structure near \(\omega \approx 0\) represents the magnetic excitation of the Kondo singlet state.
Figure 3.6: Theoretical (open symbols) and experimental (filled symbols) magnetic susceptibilities for CeM₃ (M=Pb, In, Sn, Pd). The heavy fermion compounds, CePb₃ [23] and CeIn₃ [24], show cross-over behavior from |5/2; Γ₇ + Γ₈⟩ to |5/2; Γ₇⟩ magnetic states at the energy scale of CEF splitting. The deviation of experimental χ(T) from the theory below Δ₇₈ is thought to be from the onset of magnetic ordering of the systems. The high Tₖ systems, CeSn₃ [25] and CePd₃ [26], show saturated χ(T) at T < Tₖ as the Pauli paramagnetic susceptibility.
Figure 3.7: Theoretical magnetic susceptibilities for CeSn₃ at several $\epsilon_f$ with comparison to the experiments [25]. With the LDA-computed hybridization, an $\epsilon_f$ value between −2.1 and −2.2 eV gives $\chi(T)$ closer to the experimental data. The underestimated bump size at near 150 K is thought to come from the overestimated CEF splitting, $\Delta_{78}$. 
The static magnetic susceptibility, which is zero frequency limit of dynamic susceptibility, can be obtained from \[19\]

\[\chi_ff(T) = -\sum_{mm'} \mu_{mm'}^2 \int d\epsilon \frac{e^{-\beta\epsilon}}{Z_f} [\text{Re}G_m(\epsilon)\rho_{mm'}(\epsilon) + \text{Re}G_{m'}(\epsilon)\rho_m(\epsilon)]. \tag{3.43}\]

\(\chi_ff(T)\) for various materials are shown in figure 3.6. Based on the form of Curie-magnetic susceptibility we define the effective \(f\)-moment as

\[\mu_{eff}^2(T) = 3T\chi_ff(T). \tag{3.44}\]

As mentioned earlier, \(\chi_ff(T)\) saturates to a constant value at temperature below \(T_K\), which translates to the fact that \(\mu_{eff}^2(T) \to 0\). Thus the ground state magnetic moment is singlet.

The theoretical and experimental static magnetic susceptibilities for heavy fermion compounds (CePb3 [23], CeIn3 [24]) and high \(T_K\) compounds (CeSn3 [25], CePd3 [26]) show remarkably different behavior, as plotted in figure 3.6. The estimated theoretical \(T_K\) was so small that CePb3 and CeIn3 did not show any sign of saturation down to the lowest accessible temperature. However, they clearly show the cross-over behavior due to CEF splitting. At high temperatures, \(\chi_ff(T)\) follows the Curie-Weiss law with the effective magnetic moment from \(J = \frac{5}{2}\) multiplet. As \(T\) gets lower, the quartet CEF (\(\Gamma_8\)) is depleted and the magnetic moment of the doublet CEF (\(\Gamma_7\)) takes over with smaller magnitude. Below \(\Delta_{T8}\) \(\chi_ff(T)\) regains the Curie-Weiss behavior. Since CeIn3 has a larger CEF splitting, the deviation from the Curie-Weiss law occurs earlier. However inside the Curie-Weiss regime, the two curves for CePb3 and CeIn3 agree very well. The experimental \(\chi(T)\) curves deviate from the theoretical curves below \(\Delta_{T8}\), probably due to the on-set of the anti-ferromagnetic ordering of \(4f\)-moments at 1.2 K [57] and 11 K [48] for CePb3 and CeIn3, respectively.
In the past there have been experimental estimates of $T_K$ of CeIn$_3$ based upon the $f$ moment screening from the magnetic susceptibility [24, 48]. In the papers, authors have observed significant decrease of the effective magnetic moment of CeIn$_3$ near 50 K and they reported it as the Kondo temperature. However we argue that the deviation from the Curie-Weiss behavior is due to the CEF splitting effect not the Kondo effect. The experimental $\chi(T)$ clearly did not reach the moment compensation until the on-set of the anti-ferromagnetism at 11 K. We predict the Kondo temperature of CeIn$_3$ to be much smaller than the CEF splitting, which is supported by the BIS experiment [22] where the $f^0 \leftrightarrow f^1$ peak in CeIn$_3$ has not been resolved while CeSn$_3$ has significant spectral weight for the process. Realistically, CeIn$_3$ undergoes the anti-ferromagnetic phase transition at 11 K and the experimental $T_K$ estimate is not available. Our model completely ignores the inter-site coherence effect which is responsible for the magnetic ordering. Therefore, we speculate that the $f$-moments in CeIn$_3$ order before they are screened out due to Kondo effect.

Unlike the heavy fermion systems, the high $T_K$ compounds show fully screened magnetic moments. In particular, the data for CeSn$_3$ displays key features of the orbitally degenerate Anderson model: a Curie-Weiss law at high $T$, maximum at a fraction of $T_K$, flat Pauli-like region below $T_K$. The maximum of $\chi_{ff}(T)$ occurs near 150 K ($\approx 0.38T_K$), which signifies the finite energy excitation at $T_K$ from the particle-hole asymmetry [58] present in the multi-orbital Anderson model. Note that at particle-hole symmetry in the non-degenerate Anderson model, $\chi_{ff}(T)$ saturates without going through a maximum. Also, the theoretical curve for CePd$_3$ displays the maximum at about 1200 K, $0.33T_K$. Although the experimental $\chi(T)$ for CeSn$_3$
system agrees well except for the overall multiplicative factor, the theory and experiment disagree significantly for CePd$_3$. Other than the theoretical overestimate of $T_K$, our calculation does not explain the up-turn of $\chi(T)$ below $T_K$, about which these are still debate whether it is due to the lattice effects or defects.

The computed magnetic susceptibilities for CeSn$_3$ at several $\epsilon_f$ are plotted with experimental data in figure 3.7. For all the previous calculations we have used the $f$-level energy as $-2.0$ eV. Since the theoretical values at $\epsilon_f = -2.0$ eV are consistently smaller than the experimental values, we have played with several different $\epsilon_f$ values and apparently, choosing $\epsilon_f$ between $-2.1$ and $-2.2$ eV gives the best result, given the hybridization derived from the LDA calculation. Other than the $\epsilon_f$ values, we do not have any free parameters. Despite the crudeness of the approximation evolved in the LMTO method, the assumption of infinite $U$, expansions in $1/N_g$, and the exponential sensitivity of $T_K$ upon model parameters, we have obtained reasonable agreement with experiments.

However, still, we do not match the bump height of $\chi_{ff}(T)$. As mentioned in the previous paragraph, since the bump is proportional to particle-hole asymmetry due to orbital degeneracy, we speculate we have overestimated the CEF splitting which partially lifts the degeneracy of $J = \frac{5}{2}$ multiplet, hence making the effective orbital degeneracy smaller than 6. Indeed, if the CEF splitting is forced to be zero, the bump size can be pushed much closer to the experimental curves [59].

69
CHAPTER 4

MULTI-BAND HUBBARD MODEL IN INFINITE DIMENSIONS: QUANTUM MONTE CARLO CALCULATION

In this chapter we study the strongly correlated systems in infinite spatial dimensions using the Quantum Monte Carlo (QMC) technique. The interest here is to investigate the role of orbital degeneracy in the metal-insulator transition (MIT) of the Hubbard model as opposed to the MIT of non-degenerate model. In particular, I have focused on the manifestation of this transition in dynamical properties. The Hubbard model, the minimal lattice model in condensed matter theory, consists of conduction electrons interacting through on-site Coulomb interaction. The model, despite its simplicity, displays enormously rich physics depending on its parameters. One of the most well-known properties of the model is the MIT driven by the strong correlation from the on-site Coulomb interaction, $U$ [14, 60, 61].

Although there have been countless number of papers on the MIT for the non-degenerate Hubbard model, the role of multiple bands have in the past been overlooked or ignored. Recently, however, attention has turned to the multi-orbital systems stimulated by the colossal magnetoresistance materials, alkali-doped $C_{60}$, and the new superconductor $\text{Sr}_2\text{RuO}_4$. As a first approach to the multi-orbital physics, we
will concentrate on the MIT of the Hubbard model with orbital degeneracy \([7, 8, 9]\). Even though it has been believed that the alkali-doped fullerides system \(A_3C_{60}\) can be well-described by a conventional band theory, the strong Coulomb repulsion on the \(C_{60}\) site may result in a strongly correlated metal. Since the band-width of \(A_3C_{60}\) (0.4 eV) is more than two times smaller than the on-site Coulomb repulsion (1-1.5 eV), one can naively predict the system belongs to a Mott-insulator, if interpreted in terms of the non-degenerate Hubbard model. However, the alkali-doped fullerides are metals despite the large resistivity at zero temperature [62].

A possibility has been pointed out that the problem can be understood by introducing orbital degeneracy in the Hubbard model [7, 15]. The multi-band model introduces two new physical aspects: first, an increased degree of freedom for the movement of electrons and second, new kinds of interactions between orbitals on-site. Most importantly for \(A_3C_{60}\) systems, the effective hopping of electrons is enhanced by the degeneracy and the \(A_3C_{60}\) system can lie in the metallic regime. Specifically the critical Coulomb interaction strength \(U_c\) at half filling increases by a factor of \(\sqrt{N_{\text{deg}}}\) with the orbital degeneracy \(N_{\text{deg}}\) due to enhanced effective hopping [7]. Thus the \(U_c\) for \(A_3C_{60}\) is roughly \(\sqrt{3}U_c(N_{\text{deg}} = 1) \approx 2.6W \approx 1.0\) eV, putting the experimental value on the verge of MIT, with \(W\) the band-width and \(U_c(1) \approx 1.5\) [7].

With the orbital degeneracy, one has to consider the interactions between different on-site states. Due to the exchange asymmetry of fermion states, we have different interaction strengths between the parallel-spin states and the anti-parallel spin states, which leads to the Hund's rule exchange coupling. When the Hund's coupling is taken into account, the effective local repulsion increases linearly with orbital degeneracy, \(i.e., \Delta U \approx N_{\text{deg}}J\). Therefore a finite \(J\) plays the role of favoring the insulating phase.
Combining this with the enhancement of hopping in the previous paragraph, we can roughly express the critical Coulomb repulsion as

$$U_c(N_{\text{deg}}, J) \approx \sqrt{N_{\text{deg}}} U_c(1, 0) - N_{\text{deg}} J.$$  \hfill (4.1)

In infinite spatial dimension, large coordination number reduces the lattice problem into an impurity problem in a self-consistent dynamic mean field [14, 63]. Since the interaction is still local and strong, we cannot ignore the quantum mechanical fluctuations and we still have to solve a many-body Hamiltonian with an Anderson impurity embedded in an effective medium. It has been shown that the infinite dimensional approach is a very powerful technique for studying the metal-insulator transition [14].

To solve the Anderson impurity Hamiltonian, we have applied the quantum Monte Carlo (QMC) technique. It calculates the imaginary-time Green's function by sampling through the Hilbert space with importance sampling [64]. Since many of the physical properties can be derived from the Green's functions, one can measure the observables through stochastic averages of functionals of the Green's function. The advantage of the method is that it assumes no uncontrollable model approximations, (e.g., assumptions on infinite-$U$ or large $N_{\text{deg}}$) and is non-perturbative in nature. Therefore, once we can obtain a statistically converging values for an observable, it can be taken as an exact value within error bounds. The QMC algorithm for the Anderson impurity model has been extensively studied [37] and can be coded relatively easily.

Finally, we study the dynamic properties of the model by analytically continuing the imaginary-time Green's function to real-time quantities. The analytic continuation is carried out by the Maximum Entropy Method (MEM) [16]. This method
incorporates the prior knowledge, e.g., sum rules, in finding the most probable, if not exact, spectral function from the probability theory. It finds the solution which balances the error estimate and the entropy of the measured distribution of imaginary-time Green's function, in close analogy to the minimization of free energy in the statistical mechanical systems. The method has been successful in inferring meaningful information from noisy data and is thought to be the best so far available. With the analytically continued Green's function we calculate the optical conductivity and d.c. resistivity as examples for transport properties.

4.1 Model: Alkali-doped Fullerides

Our main interest here will be on the MIT in the alkali-doped fullerides. When alkali-doped, the lattice of C\textsubscript{60} becomes conducting from insulating C\textsubscript{60}-solid. The C\textsubscript{60}-solid has been well-understood as a band insulator where the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) are separated by about 1 eV [13]. When the alkali-atoms are added, they sit on high symmetry points in the face-centered-cubic (fcc) C\textsubscript{60}-solid and the alkali-atoms only act as passive donors of electrons. The three electrons given up by 3 alkali atoms half-fill the triply degenerate \( t_{1u} \) orbital [65].

As noted earlier, the width of \( t_{1u} \)-derived band is about 0.4 eV and the on-site Coulomb repulsion \( U \) is about 1 - 1.5 eV [13]. Since \( U/W > 2 \) it is natural to consider a Hubbard model with orbital degeneracy as a simplest model. There are many complications in the \( A_3C_{60} \) systems, such as the rotational disorder of the C\textsubscript{60} molecules and the coupling of the rotational mode to the conduction electrons, which have been believed to induce superconductivity in \( A_3C_{60} \) [36, 66]. However, all
those details are ignored in this Thesis and the system is modeled by a Hubbard Hamiltonian given by
\[ H = - \sum_{ij,m_\sigma} (t_{ij} c_{im_\sigma}^\dagger c_{jm_\sigma} + h.c.) + \epsilon_d \sum_{im_\sigma} n_{im_\sigma} + H_{\text{Coulomb}}, \]  
where \( t_{ij} \) is the hopping matrix between site \( i \) and \( j \), \( \epsilon_d \) the \( d \)-level energy as the center of the non-interacting band, \( H_{\text{Coulomb}} \) is the Coulomb interaction term which will be explained in the next subsection. Note that we suppressed the hopping between different orbitals, \textit{i.e.}, \( t_{ij}^{mm'} = t_{ij} \delta_{mm'} \). Although from a realistic point of view there is no reason for that to be true, we take such simplification since the MIT is essentially driven by local interaction and we will not be interested in the splitting of atomic orbitals due to the lattice symmetry [67].

### 4.1.1 On-site Interaction for Multi-orbitals

The on-site interaction is derived from the Coulomb interaction
\[ H_{\text{Coulomb}} = \frac{1}{2} \int \! drdr' \rho(r)U(r-r')\rho(r'), \]  
where \( \rho(r) = \sum_{\sigma} \psi^\dagger_\sigma(r)\psi_\sigma(r) \).

The field operator can be expanded in terms of molecular orbitals [12]. For the case of \( A_3C_{60} \), since the Fermi energy cuts \textit{only} the \( t_{1u} \)-derived band and the upper and lower bands are separated by gaps of order 1 eV, it becomes a good approximation to include \textit{only} the \( t_{1u} \)-derived band in the model. Now \( A_3C_{60} \) is modeled with a band with degeneracy 3 at half-filling. The interacting part of the Hamiltonian in the basis of molecular states reads
\[ H_{\text{Coulomb}} = \frac{1}{2} \sum_{\text{imm'}nn'\sigma\sigma'} \langle mm'|U|nn'\rangle c_{im\sigma}^\dagger c_{im'\sigma'}^\dagger c_{in\sigma'} c_{in'\sigma}, \]
where \( \langle mm'|U|nn'\rangle = \int \! drdr' \phi^*_{m'}(r)\phi_{m'}(r)U(r-r')\phi^*_n(r')\phi_n(r') \).
with the $m$-th molecular orbital function $\phi_m(r)$ and $i$ the site index.

The study of the parameters $\langle mm'|U|nn'\rangle$ itself is a serious project [60, 68] and we will make simplifications on them. We introduce two independent parameters $U$ and $J$ defined as [69]

$$U = \langle mm|U|m'm'\rangle, \text{ where } m \neq m'$$
$$J = \langle mm'|U|m'm\rangle, \text{ where } m \neq m'. \quad (4.7)$$

The interactions considered are depicted in the following diagrams.

To preserve the rotational symmetry both in orbital and spin space, we sum all four diagrams over $m, m', \sigma, \sigma'$ without the constraint, $m = m'$. Then the interaction Hamiltonian reads

$$H_{\text{Coulomb}} = \sum_i h_i^\text{Coulomb} \quad (4.9)$$

$$= \frac{U}{2} \sum_{imm'm'} c_{im\sigma}^\dagger c_{im'\sigma'} c_{im'\sigma'}^\dagger c_{im\sigma} + \frac{J}{2} \sum_{imm'm'} c_{im\sigma}^\dagger c_{im'\sigma'} c_{im'\sigma'}^\dagger c_{im\sigma} \quad (4.10)$$

$$= (U + J) \sum_m n_{im\uparrow} n_{im\downarrow} + (U - J) \sum_{im'\sigma} n_{im\sigma} n_{im'\sigma'}$$

$$+ U \sum_{im \neq m'} n_{im\uparrow} n_{im'\downarrow} + J \sum_{m \leq m'} c_{im\uparrow}^\dagger c_{im\downarrow} c_{im'\downarrow}^\dagger c_{im\uparrow} \quad (4.11)$$

$$+(\text{one-body terms}).$$

In most cases, the $U \gg J$ [60] and we have ignored all other combinations not included in Eq. (4.7).
When $J > 0$, the Hund’s coupling physics is anticipated by inspecting the terms A and B in Eq. (4.11). Since the repulsion between the electrons occupying the same spin states have smaller values, spins favor parallel alignment. The energy cost of flipping one aligned spin is of order $J$ and therefore $J$ becomes the coupling constant for the Hund’s coupling. Although, in order to maintain the full rotational symmetry, the term-D in Eq. (4.11) is required, the term poses a great deal of computational difficulty, since with the term we have to keep the off-diagonal Green’s functions. The term-D not only introduces more interaction terms but consumes much more time in updating the Green’s function in the Monte Carlo process. Thus we discarded the term-D in our QMC calculation. By doing that, we are not guaranteed to have the full rotational symmetry, but we still partially capture the Hund’s rule physics.

### 4.1.2 Dynamical Mean Field Theory

Since it has been shown that the lattice model in infinite dimension can be mapped to an impurity model [63], usage of the dynamical mean field theory (DMFT), also known as the local approximation, has become very fashionable among many-body theorists. The biggest strength of the method is its simplicity. Just like the mean-field theory in the statistical mechanics, a site sees the environment as a mean field since the statistical fluctuations of the local field can be shown negligible because of the central limit theorem. However, the mean field in the Quantum system has its own dynamics – even the non-interacting fermion sea has the dynamics such as one-particle spectrum, particle-hole excitation etc.

To have a meaningful limit in the infinite dimension, we scale the hopping integral $t_{ij}$ as proportional to $1/\sqrt{d}$. In the hypercubic lattice, we choose $t_{ij}$ to be non-zero
only between nearest neighbors and use the unit $t^* = 1$ with $t_{ij} = t^*/2\sqrt{d}$. The energy spectrum has the form of tight-binding method \( i.e., \epsilon_k = \epsilon_d - \sqrt{d-1} \sum_{n=1}^d \cos(k_n) \) with \( k \) measured in the unit of lattice constant. In the \( d \to \infty \) limit, the density of states for the free electrons can be written in a simple Gaussian with a band-width \( \sqrt{2} \) from the central limit theorem:

\[
D(\epsilon) = \frac{1}{\sqrt{\pi}} e^{-(\epsilon - \epsilon_d)^2}
\]

On the Bethe lattice, the non-interacting DOS becomes a semi-circular density of states with a band-width \( D \) as

\[
D(\epsilon) = \frac{2}{\pi D^2} \sqrt{D^2 - (\epsilon - \epsilon_d)^2}.
\]

We will use both of the above DOS forms in the discussion.

The most important claim of the DMFT is that the self-energy becomes purely local in the limit of infinite dimension. This fact can be seen most easily by taking an example. The self-energy in the position space can be expanded as

\[
\Sigma_{ij} = \delta_{ij} + G_{ii} U + G_{ij} U + \cdots
\]

The solid line represents the non-interacting Green’s function \( G_{ij}^0(\tau) \) and the dotted line denotes the on-site Coulomb interaction. The first term, the Hubbard term, is diagonal in space and zero for \( i \neq j \) since the Coulomb interaction is on-site. We show that the second term becomes negligible for \( i \neq j \) in \( d \to \infty \) limit. The second term is proportional to \( U^2 G_{ij}^0(\tau)^2 G_{ji}^0(\tau) \). The Green’s function \( G_{ij}^0(\tau) \) is proportional to \( \epsilon^{i-j} \), where \( |i - j| \) denotes the distance between site \( i \) and \( j \). Since \( t \propto 1/\sqrt{d} \),
the second term in the self-energy is proportional to $d^{-3|i-j|/2}$ and goes to zero when $i$ and $j$ are distinct. Higher order terms also vanish for distinct $i, j$ sites in infinite spatial dimensions.

The fact that the self-energy is local implies that the model can be rewritten as a

an effective impurity Hamiltonian. The Hubbard model can be mapped to an Anderson impurity Hamiltonian $H_{\text{DMFT}}$ such that the corresponding conduction electron Hamiltonian $H_{\text{cond}}$ reproduces the energy spectrum of the site-excluded Hamiltonian $H - V_{\text{Coulomb}}$:

$$ H_{\text{DMFT}} = H_{\text{cond}} + V_{\text{Coulomb}}, $$

(4.15)

where

$$ H_{\text{cond}} = -\sum_{i \neq 0, j \neq 0, m} (\xi_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \text{h.c.}) - \sum_{i \neq 0, m} (\epsilon_0 c_{0\sigma}^\dagger c_{i\sigma} + \text{h.c.}) + \epsilon_d \sum_{i \neq 0, m} n_{i\sigma}, $$

(4.16)

and the new hopping parameter $\xi_{ij}$ should be chosen as to make the impurity Green's function at the origin from $H_{\text{DMFT}}$ the same as the local Green's function from the lattice Hamiltonian. Now with the Anderson impurity model, we treat the orbital at origin and other on different footing and we will denote the orbital at origin with $d$ and others with $c$.

The impurity Green's function $G_{\text{DMFT}}(i\omega_n)$ is calculated by QMC and can be expressed by the Dyson's equation as

$$ G_{\text{DMFT}}(i\omega_n)^{-1} = G(i\omega_n)^{-1} - \Sigma(i\omega_n), $$

(4.17)

where $G(i\omega_n)$ is the "effective medium" Green's function of orbital at origin from $H_{\text{cond}}$ and $\Sigma(i\omega_n)$ is its self-energy. The local Green's function can be obtained by a
summation of \( k \)-Green's function over the wave-vectors, with the self-energy calculated from the impurity Hamiltonian as

\[
G_{00}(i\omega_n) = \sum_k G_k(i\omega_n) = \int d\epsilon \frac{D(\epsilon)}{i\omega_n - \epsilon - \Sigma(i\omega_n)}.
\] (4.18)

Noting \( G_{\text{DMFT}}(i\omega_n) = G_{00}(i\omega_n) \), we now have a self-consistent loop by Eqs. (4.17-4.18), as follows.

i) choose a trial \( \mathcal{G}(i\omega_n) \)

ii) solve \( H_{\text{DMFT}} \) by a many-body technique, such as QMC

iii) compute the self-energy \( \Sigma(i\omega_n) \) by Eq. (4.17)

iv) compute the local Green's function \( G_{00}(i\omega_n) \) by Eq. (4.18)

v) update the site-excluded Green's function \( \mathcal{G}(i\omega_n) \)

\[
\mathcal{G}(i\omega_n)^{-1} = G_{00}(i\omega_n)^{-1} + \Sigma(i\omega_n)
\]

vi) go to ii) and repeat until it converges.

4.2 Quantum Monte Carlo Method

Technically, the most difficult part of the DMFT is to solve the Anderson impurity model in the effective medium. Here we are going to use a quantum Monte Carlo technique. The quantum Monte Carlo technique computes the physical quantities through sampling over the Hilbert space with sampling weight proportional to the Boltzmann factor in the partition function. The greatest strength of the method is that, in principle, it does not involve any uncontrolled approximations. As long as the data is de-correlated, the numerical value of observables in QMC can be an exact
within controllable statistical and discretization errors. One advantage of learning the method is that the Monte Carlo technique is a very general method and can be applied to various fields in science.

The most difficult problem of the QMC in the fermion problem is that we cannot represent the fermion operator in terms of (real or complex) numbers, since the field operators are \textit{anti-commuting}. To overcome this problem, we choose to use the Hubbard-Stratonovich transformation in the Lagrange formulation [70]. This transformation introduces the bosonic (or Ising) degrees of freedom coupled to the fermion operator at the imaginary-time point and makes the the fermion degrees of freedom integrable. Thus we reduce the original interacting Hamiltonian into an integrable Lagrangian where the fermion is coupled to a \textit{temporally} fluctuating boson (or Ising) field. Once we integrate out the fermion fields, we are left with an effective bosonic Lagrangian and we perform the Monte Carlo sampling by discretizing the imaginary-time variable.

A long-standing problem, known as the \textit{fermion sign-problem}, in the fermion MC has hampered the quantum simulation since, for specific boson (or Ising) configurations, the effective "Boltzmann factor" in the partition function is not positive. Although the total sum over the whole boson (or Ising) configurations should be positive by almost cancelling the terms of opposite sign and only leaving a small finite number, the individual terms are not guaranteed to be positive. Realistically, this usually becomes a very difficult obstacle since the computing time is limited and we can only sample small portion of the Hilbert space, even with the importance sampling. In those cases, we have a large noise-to-signal ratio and cannot predict quantities with certainty.
4.2.1 Discrete Hubbard-Stratonovich Transformation

Now we describe the procedure of QMC. We split a quantum mechanical Hamiltonian $H$ into $H = H_0 + H'$ where $H'$ contains the interacting term. The partition function $Z(\beta)$ at temperature $T(= 1/\beta)$ can be written as

$$Z(\beta) = \text{Tr} e^{-\beta H} = \lim_{L \to \infty} \text{Tr} \left( e^{-\Delta \tau H} \right)^L,$$

where $\Delta \tau = \beta/L$. In real calculations, we set $\Delta \tau$ smaller than the inverse of the largest energy scale in the model, i.e., $1/U$. Extrapolation of observables to the $\Delta \tau \to 0$ should be performed for publishable data. However in this dissertation we only report the data obtained at $\Delta \tau = 1/3, 1/4$ without performing the extrapolation.

An important step is so-called the Trotter break-up [71], where the exponential of total Hamiltonian $H$ at each time slice is factorized into a product of exponentials with $H_0$ and $H'$:

$$e^{-\Delta \tau H} = e^{-\Delta \tau H_0} e^{-\Delta \tau H'} + O(\Delta \tau^2).$$

Since $H_0$ and $H'$ do not commute in general, the factorization is only approximate up to order $\Delta \tau^2$. Most of the physical observables have errors of order $\Delta \tau^2$ from the Trotter break-up [72] and the averaged QMC data is plotted versus $\Delta \tau^2$ to be extrapolated to $\Delta \tau = 0$ values.

The factor $e^{-\Delta \tau H'}$ can be made into a quadratic form in fermion operators by introducing new discrete real numbers (Ising fields) [73] – discrete Hubbard-Stratonovich (HS) transformation – since the number of fermion states are finite due to the Pauli exclusion principle. For example, a Coulomb interaction interaction between a pair of states can be written as

$$\exp(-\Delta \tau Un_1 n_2) = \frac{1}{2} \sum_{\mu=\pm 1} \exp \left[ \lambda \mu (n_1 - n_2) + \frac{1}{2} (n_1 + n_2) \right] \text{ for } U > 0$$
\[
\frac{1}{2} \sum_{\mu = \pm 1} \exp \left[ \lambda' \mu (n_1 + n_2) + \frac{1}{2} (n_1 - n_2) \right] \quad \text{for } U < 0, (4.22)
\]

where \( \cosh \lambda = \exp(\Delta \tau U/2) \) and \( \cosh \lambda' = \exp(-\Delta \tau U/2) \). The new (Ising) variable \( \mu \) on the right hand side mimics the correlation effect. Let us take an example with a positive \( U \). When \( \mu = +1 \), the second state tends to be occupied while the first state tends to be empty due to their opposite signs. In other words, the Ising field on the site at time \( \tau \) inhibits double electron occupancy much as the Coulomb repulsion. Thus, when \( \mu \) is sampled evenly over \( \pm 1 \), the HS-transformed Hamiltonian produces the same effect as the Coulomb interaction.

We transform the first three multi-band Coulomb interaction terms in Eq. (4.22). At each time slice \( l \), we introduce three sets of Ising fields \( \mu^A, \mu^B, \mu^C \) corresponding terms-A, B, C in Eq. (4.11).

\[
-\Delta \tau h_{\text{Coulomb}}^0 \rightarrow \lambda^A \sum_m \mu^A_m(l)(n_{m\uparrow} - n_{m\downarrow}) + \lambda^B \sum_{m < m'} \mu^B_{mm'}(l)(n_{m\sigma} - n_{m'\sigma}) + \lambda^C \sum_{m \neq m'} \mu^C_{mm'}(l)(n_{m\uparrow} - n_{m'\downarrow}) + \left[ (N_{\text{deg}} - \frac{1}{2})U + \left( 1 - \frac{N_{\text{deg}}}{2} \right)J \right] \sum_{m\sigma} n_{m\sigma},
\]

where

\[
\cosh \lambda^A = e^{\Delta \tau (U+J)/2}, \quad \cosh \lambda^B = e^{\Delta \tau (U-J)/2}, \quad \cosh \lambda^C = e^{\Delta \tau U/2}. \quad (4.24)
\]

The last term can be absorbed to the non-interacting term and redefines the \( d \)-level energy as

\[
\epsilon'_d = \epsilon_d + (N_{\text{deg}} - \frac{1}{2})U + \left( 1 - \frac{N_{\text{deg}}}{2} \right)J. \quad (4.25)
\]
Note that the Ising fields are random variables defined at each time slice. For the sake of notation, we define the first three terms in Eq. (4.23) as $\hat{V}(\{\mu(l)\})$. The total number of Ising fields is $N_{\text{deg}}(2N_{\text{deg}} - 1)$.

When the configuration of Ising fields is frozen, $\hat{V}(\{\mu(l)\})$ is separable to spin-up and spin-down parts, i.e., $\hat{V}(\{\mu(l)\}) = \hat{V}_{\uparrow}(\{\mu(l)\}) + \hat{V}_{\downarrow}(\{\mu(l)\})$. Therefore at a frozen $\{\mu(l)\}$, both spin and time translational symmetry are broken. The symmetry of the model is recovered when the Ising fields are allowed to fluctuate and sampled over large enough Hilbert space.

### 4.2.2 Hirsch-Fye Algorithm

With the Trotter break-up and HS-transformation, we compute the partition function by taking the trace over the fermion fields and then summing over the Ising fields by the Monte Carlo technique. Since the transformed Hamiltonian is quadratic in fermion operators, we can formally integrate them out using the Grassmann Algebra [56]. Then the partition function can be written as

$$Z(\beta) = 2^{-N} \sum_{\{\mu\}} Z_{\tau}[\mu] Z_{\nu}[\mu],$$

(4.26)

where $N = LN_{\text{deg}}(2N_{\text{deg}} - 1)$ and for a fixed Ising field configuration $\{\mu\}$,

$$Z_{\sigma}[\mu] = \det O_{\sigma}[\mu],$$

(4.27)

with

$$O_{\sigma}[\mu] = \begin{bmatrix}
I & 0 & 0 & \ldots & e^{-\Delta \tau H_0} e V_\sigma[\mu_1] \\
-e^{-\Delta \tau H_0} e V_\sigma[\mu_1] & I & 0 & \ldots & 0 \\
0 & -e^{-\Delta \tau H_0} e V_\sigma[\mu_2] & I & \ldots & 0 \\
& & & \ddots & \ddots & \ddots \\
& & & & I
\end{bmatrix}. \quad (4.28)$$

The block matrices in $O_{\sigma}[\mu]$ are $M \times M$ where $M$ is the total number of orbital states in the model, conduction electron states plus $d$-states.

83
However, since the Anderson impurity model involves the interaction only with the impurity or $d$-states, we do not need such big matrices [37]. Multiplying $c^{-V}$ to $\mathcal{O}$ from the right, we have

$$\mathcal{O}_\sigma[\mu]c^{-V[\mu]} = \begin{bmatrix} e^{-V_\sigma[\mu_1]} & 0 & \cdots \\ -e^{-\Delta \tau \mathcal{H}_0} & e^{-V_\sigma[\mu_2]} & \cdots \\ \cdots & \cdots & \cdots \end{bmatrix}.$$ 

Since the off-diagonal block $e^{-\Delta \tau \mathcal{H}_0}$ does not depend upon the Ising configuration, we can cancel the block taking the difference between different Ising configurations, as

$$\mathcal{O}_\sigma e^{-V} - \mathcal{O}_\sigma' e^{-V'} = e^{-V} - e^{-V'}, \quad (4.29)$$

where we used short-hand notation. Now defining the 'Monte Carlo' Green's function $g_\sigma[\mu]$ as

$$g_\sigma = \mathcal{O}_\sigma^{-1}, \quad (4.30)$$

we have an important relation between Green's functions for different Ising configurations;

$$g'_\sigma = [I - (g_\sigma - I)(e^{V' - V} - I)]^{-1} g_\sigma. \quad (4.31)$$

Since $V$ has non-zero elements only between $d$-orbitals, the $d-d$ sector of $g$, $g_{dd}[\mu']$ depends only upon $g_{dd}[\mu]$ and all other elements of $g$ are irrelevant. Thus we only need to keep track of $g_{dd}$.

The MC-Green's function defined as Eq. (4.30) has the same physical meaning of $G(\tau)$ in text books [56], except for the sign convention and that $g_\sigma(l,l')$ does not have the time-translational symmetry. Denoting $B_l = \exp(-\Delta \tau \mathcal{H}_0)\exp(V(\mu_l))$, the MC-Green's function becomes [70]

$$g(l,l') = \begin{cases} B_{l-1} B_{l-2} \cdots B_l (I + B_{l-1} \cdots B_1 B_L \cdots B_l)^{-1} & l > l' \\ (I + B_{l-1} \cdots B_1 B_L \cdots B_l)^{-1} & l = l' \\ -B_{l-1} \cdots B_1 B_L \cdots B_l (I + B_{l-1} \cdots B_1 B_L \cdots B_l)^{-1} & l < l' \end{cases}. \quad (4.32)$$
For a non-interacting system, the MC-Green's function takes a familiar form,

\[
g(l, l') = \begin{cases} 
\exp(-\tau H_0)(I + \exp(-\beta H_0))^{-1}, & l \geq l' \\
-\exp((\beta + \tau) H_0)(I + \exp(-\beta H_0))^{-1}, & l < l'
\end{cases},
\]

where \( \tau = (l - l')\Delta \tau \). Note that for \( l = l' \), the MC-Green's function is defined as \( G(\tau = 0^+) \).

Furthermore, when updating the Ising fields from \( \{\mu\} \) to \( \{\mu'\} \), the acceptance ratio of the move can be expressed only with the d-Green's function at the initial configuration \( \{\mu\} \). The acceptance ratio \( R \) \( (\equiv R_t R_4) \) can be written using

\[
R_\sigma = \frac{Z_\sigma[\mu']}{Z_\sigma[\mu]} = \frac{\det \mathcal{O}'_\sigma}{\det \mathcal{O}_\sigma} = \det \left[ I - (g_\sigma - I)(e^{\nu'} - I) \right].
\]

The procedure is as follows: for a proposed move for a given Ising configuration, compute \( R \) and compare with a random number in interval \([0,1]\). Within the Metropolis algorithm \([64]\), we accept the move if the random number is smaller than \( R \) or reject otherwise.

For a fixed Ising field, one can calculate the physical observables rather easily. Many of the thermodynamic quantities can be directly expressed in terms of MC-Green's function. For example, the local transverse spin magnetic susceptibility \( \chi_{+-}(T) \) can be computed as follows:

\[
\chi_{+-}(T) = \frac{1}{2} \int_{0}^{\beta} \langle S_+ (\tau) S_- (0) + S_- (\tau) S_+ (0) \rangle
= \frac{1}{2} \int_{0}^{\beta} \langle d_+^\dagger (\tau) d_+ (0) d_- (0) + d_-^\dagger (\tau) d_- (0) d_+ (0) \rangle.
\]

Given an Ising configuration, the Hamiltonian is quadratic in fermion operators and we can safely use Wick's theorem to contract the same spin operators. Thus,

\[
\chi_{+-}(T) = -\frac{\beta}{2L^2} \sum_{\langle ll' \rangle} g_\tau (l', l + l') g_\tau (l + l', l) + g_\tau (l', l + l') g_\tau (l + l', l')
\]
\[- \sum_{l'} g_{\ell}(l', l') + g_{\tau}(l', l') \gg, \] (4.36)

where \(\ll \gg\) means average over accepted sequence of \(\{\mu\}\). When \(l + l'\) exceeds \(L\), we replace \(g_\sigma(l + l' - L, l')\) based on the relation \(G(\beta - \tau) = -G(-\tau)\).

The last term in Eq. (4.36) is necessary to correct the first term near \(\tau = 0^+\) and we replaced the term \(g_\sigma(l', l + l')_{l \to 0^+}\) by \(g_\sigma(l', l'') - 1\).

The sequence of configurations generated by the MC sampling is a Markov chain, i.e., a process such that a successive event is not stochastically independent from the previous event. To reduce the correlation between adjacent data, the measurement should be done after skipping an auto-correlation time. The auto-correlation time strongly depends on the model and its parameters. Especially, at low temperature, the correlation time tends to be very long and it makes it difficult to obtain statistically independent data. To deal with the effect, we monitor the error bars as a function of increasing skip interval, and use the minimum skip interval for which the error bars cease to depend on the magnitude of the interval. In our calculation we take measurements after \(n\text{skips}\) and average \(n\text{meas}\) measurements, the process being called binning. The binned average represents one event. Then we repeat each events \(n\text{run}\) times and we analyze the \(n\text{run}\) values, computing the average, standard deviation, and report error bars. Therefore in our scheme of measurement, \(n\text{skip} \cdot n\text{meas}\) becomes the interval for de-correlation.

To obtain good data, we sometimes make MC-sweeps millions of times. In the process of updating, the numerical error from the precision of machine accumulates. Therefore, in order to prevent such errors, we refresh the Green's function after some number of updates. By by Eq. (4.31), the Green's function \(g_\sigma[\mu]\) is refreshed from the initial Green's function \(g_\sigma[\mu = 0]\), which is stored at the start of the MC calculation.
In summary, the Monte Carlo procedure goes as follows:

- Set up a starting Green’s function $g_0$ with all the Ising fields set to zero. $g_0$ can be obtained either from a perturbation theory or read from the data of previous temperature calculation.

- Compute a first MC-Green’s function with an arbitrary Ising configuration, say, all $\mu = +1$.

- Update the MC-Green’s function $g_\sigma$ with probability ratio $R$. We split the global update into local moves, that is, we propose a change in $\{\mu\}$ only at a time-slice $l$ and sweep through the entire $l = 1, \ldots, L$. If the proposal is accepted, update the MC-Green’s function with Eq. (4.31).

- After some updates, reconstruct the MC-Green’s function to prevent the accumulation of numerical errors.

- Measure the observables after each nskip MC sweeps. Average nmeas values of observables and save them as a data point. With collected nrun data points we analyze the data with average and error bars.

### 4.3 Mott-Hubbard Metal Insulator Transition

Since 1937, when the transition-metal oxides were reported [74] to have very drastic change in the conductivity ranging by factor of $10^9$ with slightly different chemical composition, the phenomena, known as the Mott-Hubbard metal-insulator transition, became one of the most commonly discussed topics in condensed matter physics. The metal-insulator transition driven by a strong Coulomb interaction is an important subject in the study of correlation effects in solids. It has been shown that, in some
of transition metals \cite{75} with partially filled \(d\)-orbitals, the solid can have both insulating and conducting states depending on the ratio of the Coulomb energy and the kinetic energy.

Let us take an example where the Coulomb interaction \(U\) is considerably larger than the hopping matrix element \(t\) with \(d\)-occupation number \(n\). When one electron is forced to move, we have to pick up one electron from one site \(d^n \rightarrow d^{n-1}\) and put it into a \(d\)-orbital at different site \(d^n \rightarrow d^{n+1}\). Therefore the potential energy cost in moving the electron is the sum of ionization energy, \(E^+ (\equiv E(d^n) - E(d^{d-1}))\), plus the electron affinity energy, \(E^- (\equiv E(d^n) - E(d^{n+1}))\). These energies can be measured by photoemission \((E^+)\) and inverse-photoemission \((E^-)\) experiments \cite{13}. Once the particle (or hole) excitation is created, it can move without costing more Coulomb energy. So the energy level of ionized state broadens due to the hopping of the extra electron (hole). The width of the band, \(W\), is proportional to the hopping matrix element \(t\). The spectral function for \(U \gg t\) is sketched in figure 4.1. The negative energy excitation (the so-called the lower Hubbard band, LHB) comes from the removal of one \(d\)-electron and the positive energy excitation (the upper Hubbard band, UHB) from the addition of \(d\)-electron (See Eq. (3.32)). Both lower and upper bands are broadened by hopping with band-width \(W\). The least amount of energy to excite the system, therefore, is the energy difference from the lower edge of UHB to the upper edge of the LHB, \(U - W\).

As \(U\) gets smaller and becomes comparable to the band width \(W\), the UHB and the LHB merge and the system becomes conducting. In addition to this naive picture of merging UHB and LHB, there emerges a very interesting many-body effect. Near the Fermi energy a sharp peak appears as in figure 4.1. The physical origin of this peak can
be understood with an analogy to the impurity Anderson model, which is a legitimate comparison in view of the DMFT. Since the electron is a fermion with spin half, it has both charge and spin degrees of freedom. The UHB and LHB are due to the charge excitations driven by the Coulomb interaction. At low temperature, the charge degree of freedom can be treated as a virtual excitation in the low energy Hamiltonian written in terms of spin degree of freedom, which is nothing but the Kondo Hamiltonian [52] at an effective impurity site. The Kondo Hamiltonian describes the magnetic scattering, which results in a resonant scattering with energy scale $T_K$. Therefore the peak near the Fermi energy, so-called the quasi-particle (q.p.) peak, is the new many-body resonant state from the magnetic scattering between conduction electrons, and is related to the Kondo resonance discussed in earlier chapters. Note that in the lattice model within the DMFT, the "conduction spectrum" of the effective medium is self-consistently connected to the q.p. peak and, therefore, the $T_K$ in analogy should be understood as a parameter changing with temperature, unlike the $T_K$ in ordinary Anderson impurity models.

Figure 4.1: Schematic plot of one-electron spectral functions in insulating and metallic regime. In insulating regime ($U \gg t$), the upper and lower Hubbard bands are separated by $U$ and develops a gap proportional to $\sim U - W$ with bandwidth $W(\sim t)$. In the metallic regime the upper and lower Hubbard bands merge and the new many-body quasi-particle state emerges near the chemical potential.
4.3.1 Enhanced Hopping with Degenerate Model; $J = 0$ Case

The degeneracy of the orbitals can increase the mobility of the electron (hole), hence favoring the metallicity. The argument goes in a similar way [7] as in the previous section. For the moment, let us ignore the exchange interaction $J$ in Eq. (4.11). For the simplicity of argument, look at the case at half-filling where the Coulomb interaction $U$ is larger than the hopping element $t$.

The ground configuration of the system at half-filling is the anti-ferromagnetically ordered spin configuration as sketched in figure 4.2. Although the spins in the same site do not have to be aligned at $J = 0$ and without inter-orbital hopping, the neighboring spins with the same orbital index should anti-align for its lower energy. With $U \gg t$, the electrons cannot hop due to the large energy cost.

Now, when we add one extra electron with orbital index $m$, its spin should anti-align with previously occupying electron at the $m$-th orbital and can move around without paying the Coulomb energy. Then what is the probability for the extra-charge to hop to neighbors? Since the neighbors should anti-ferromagnetically align per orbital, the possibility is to hop any of $N_{\text{deg}}$ electrons. In other words, the probability of hopping is proportional to $N_{\text{deg}}t^2$ instead of just $t^2$ in the single-band model. Since the extra-charge degree of freedom moves around with effective hopping matrix element $\sqrt{N_{\text{deg}}t}$, the band-width increases to $\sqrt{N_{\text{deg}}W}$. Therefore the gap in the insulating phase narrows with $N_{\text{deg}}$ as $U - \sqrt{N_{\text{deg}}W}$.

Although the above argument looks quite simple and elementary, it is far from trivial. For instance, we may ask "How can we understand the fact, within the density functional theory, that the non-interacting band-width $W$ increases to $\sqrt{N_{\text{deg}}W}$ as $U$ becomes large?" If we go back to the previous argument, we realize that the successive
hoppings involve alternating spins, as indicated in figure 4.2. Note that the enhanced hopping involves the propagation of charge excitation as opposed to the electron hopping with fixed spin in the simple tight-binding picture. To implement the $\sqrt{N_{\text{deg}}}$ behavior in the local density approximation, the anti-ferromagnetically aligned spin configuration should be properly taken into account in the formulation with better exchange-correlation function.

It should also be noted that the DMFT in this work does not consider the long-range spin or orbital ordering. Even without the long range anti-ferromagnetic order, we can still apply the previous argument for the enhanced hopping as long as the DMFT has the short range anti-ferromagnetic correlations. Along that line of logic, it would be interesting to examine how the MIT is affected in the presence of long range order or frustration.

We have identified the metal-insulator transition by plotting the occupation number versus the chemical potential. When the chemical potential sits within the gap for large $U$ cases, the occupation number does not change with the chemical potential. Figure 4.3 shows the occupation number plotted versus the chemical potential. The calculations have been done near half-filling ($n_d = N_{\text{deg}}$). The systems have particle-hole symmetry at $\epsilon_d = \epsilon_{ph}$ ($\epsilon_{ph} = (N_{\text{deg}} - \frac{1}{2})U + (1 - \frac{N_{\text{deg}}}{2})J$, see Eq. (4.25)). To compare the cases for $N_{\text{deg}} = 1, 2, 3$ the occupation number is plotted $n_d - N_{\text{deg}}$ versus $\epsilon_d - \epsilon_{ph}$. The parameters are $U = 4$ and $\beta = 16$ with $\Delta \tau = 1/4$. In order to see the MIT clearly, a semi-circular DOS with $D = 1$ (bandwidth $W = 2$, see Eq. (4.13)) is used for a sharp-edged free DOS. The ratio $U/W$ is chosen to be 2, where the lattice is predicted to be in the insulating regime for the non-degenerate orbital in the infinite dimension [14].
Figure 4.2: Hopping of an extra electron in the half-filled lattice for $N_{\text{deg}} = 3$. Since spins of each orbital index should anti-align between nearest sites, the hopping electron should be anti-parallel to the electron spin in the neighbor for the same orbital index. This leaves the three ways to hop an electron and therefore the effective hopping matrix becomes $\sqrt{3}t$ instead of $t$. 
Figure 4.3: The occupancy $n_d$ versus the $d$-level energy $\varepsilon_d$. The axes are drawn with respect to the particle-hole symmetric values; $n_d = N_{\text{deg}}$ and $\varepsilon_{\text{ph}} = \varepsilon_d - (N_{\text{deg}} - \frac{1}{2})U$. The constant $n_d$ vs. $\varepsilon_d$ represents the insulating states, as $\partial n_d / \partial \varepsilon_d \propto N(0) = 0$. At $U/W = 2$, the Hubbard models with $N_{\text{deg}} = 1, 2$ show an insulating phase, while the $N_{\text{deg}} = 3$ case has only a metallic state for these parameter values.
In the $N_{\text{deg}} = 1$ case, the occupation number stayed at 1 until the chemical potential is shifted nearly 1.0 energy unit from the particle-hole symmetric point (marked as a down-arrow). The point where the occupation deviates from 1 is when the chemical potential hits the upper edge of the LHB. Once the system is in the metallic regime the DOS is finite at the Fermi energy and has a finite slope, or finite compressibility defined as $-\partial n / \partial \epsilon_d$. We define the MIT at finite temperature based on the compressibility and conclude the non-degenerate Hubbard model undergoes the MIT at $U/W = 2$ and $T = 1/16$.

When the orbital degeneracy is introduced, the system tends to favor the metallic regime. For the doubly degenerate orbital system, the occupancy deviated from $N_{\text{deg}}$ for lower chemical potential magnitude (at $0.3W$, marked as up-arrow) than in the non-degenerate case. We can interpret the result as the effective band-width becoming wider, in accordance with the argument of the enhanced hopping. As the degeneracy is further increased to 3, the insulating regime disappeared. With the chemical potential slightly away from the particle-hole symmetry, the occupancy dropped from 3, unlike $N_{\text{deg}} = 1, 2$, implying $N(0) \propto \partial n_d / \partial \epsilon_d > 0$.

To identify the critical value of the Coulomb repulsion, $U_c$, we fixed the $d$-level energy at $(N_{\text{deg}} - \frac{1}{2})U + 0.2$ and computed $n_d$ scanning through $U$. The computations were carried out at temperatures $T = 1/12, 1/16$. Being slightly away from half-filling, the occupation number equal to $N_{\text{deg}}$ indicates that the system has insulating solution. The strengths of Coulomb repulsions where the occupation numbers deviate from $N_{\text{deg}}$ at $T = 1/16$ are marked as arrows. Although $U_c$ did not change much with temperature for $N_{\text{deg}} = 1, 2$, the $N_{\text{deg}} = 3$ case shows that $T = 1/16$ is not low enough
Figure 4.4: The occupancy $n_d$ versus the Coulomb repulsion $U$ at fixed $\epsilon_d = \epsilon_d - (N_{\text{deg}} - \frac{1}{2})U + 0.2$. The critical value of $U$ at the cross-over between insulating and metallic solutions increased with $N_{\text{deg}}$. The temperature, $T = 1/16$, is not low enough for $N_{\text{deg}} = 3$ case to equate $U_c = 2.3W$ as the zero-temperature quantum critical point. Due to the weak functional dependency of $\sqrt{N_{\text{deg}}}$ and small $N_{\text{deg}}$, we cannot conclude from these data that $U_c(N_{\text{deg}}) = \sqrt{N_{\text{deg}}}U_c(1)$. (See inset.)
to assume that the value \( U_c/W = 2.3 \) is the zero-temperature quantum critical point for the MIT.

The critical values, \( U_c(N_{\text{deg}})/U_c(1) \), where the solution crosses over from insulator to metal are plotted in the inset of figure 4.4, where the corresponding temperature is 1/16. Due to the weak functional dependency of \( \sqrt{N_{\text{deg}}} \), it is not clear, if at all, that the our calculation bears out the predicted functional form, \( U_c(N_{\text{deg}}) = \sqrt{N_{\text{deg}}} U_c(1) \). Furthermore, it is not at all obvious that for smaller values of \( N_{\text{deg}} \) and \( U \), the argument with figure 4.1 should still hold with the square-root dependency. However, at least, our results clearly shows that the metallic solution is favored for large orbital degeneracy.

We find that, for \( N_{\text{deg}} = 3 \), \( U_c/W \leq 2.3 \) in reasonable agreement with Ref. [7], considering the finite temperature in our calculation. For \( A_3C_{60} \), this value of \( U_c \) puts the experimental ratio near the edge of MIT transition. Therefore, it is theoretically possible, if not decisively proven, that \( A_3C_{60} \) can be described as a strongly correlated metal.

### 4.3.2 Hund’s Coupling; \( J > 0 \) Case

When the exchange interaction \( J \) in Eq. (4.11) is included, the Coulomb repulsion is effectively increased, favoring the insulating phase. Numerical calculation confirms that the insulating phase is expanded with finite positive \( J \). Figure 4.5 shows the plot of \( n_d \) vs. \( \epsilon_d - \epsilon_{ph} \) with \( J = 0.0, 0.2, 0.5, 1.0 \) at \( N_{\text{deg}} = 2 \) and \( \beta = 16. \) \( \epsilon_d \)'s where the metallic phases begin are pushed to higher values with \( \Delta \epsilon_d \) approximately linear in \( J \).
Figure 4.5: \( n_d \) vs. \( \epsilon_d - \epsilon_{ph} \) at \( J = 0.0, 0.2, 0.5 \). For positive \( J \) the on-set of metallic solution is shifted to larger value of \( \epsilon_d \) from the particle-hole symmetric parameter, \( \epsilon_{ph} \). The shift is roughly linear in \( J \), leading to a suggestion that the on-site Coulomb interaction is responsible with \( \Delta U(J) = N_{deg}J \).
The phenomena can be easily understood by considering the change in the on-site energy. As in the QMC calculations, we confine ourselves to near half-filling. The effective on-site Coulomb repulsion can be computed as $E(N_{\text{deg}} + 1) + E(N_{\text{deg}} - 1) - 2E(N_{\text{deg}})$ from the on-site Hamiltonian Eq. (4.11). For $J > 0$ the ground state configuration at half-filling is the spin-maximum state, where all spins are aligned. Thus $E(N_{\text{deg}}) = (U - J)N_{\text{deg}}(N_{\text{deg}} - 1)/2$. Similarly, $E(N_{\text{deg}} + 1) = (U - J)N_{\text{deg}}(N_{\text{deg}} - 1)/2 + (U + J) + U(N_{\text{deg}} - 1)$ and $E(N_{\text{deg}} - 1) = (U - J)(N_{\text{deg}} - 1)(N_{\text{deg}} - 2)/2$. Therefore

$$U_{\text{eff}} = U + N_{\text{deg}}J,$$  \hspace{1cm} (4.37)

Also, we have to remember that the hopping of electrons leaves behind a trail of broken Hund’s multiplets. Therefore, there would be additional effective repulsion to Eq. (4.37).

Combined with the enhanced hopping in the previous paragraph, the critical $U$ at MIT can be expressed as

$$U_c(N_{\text{deg}}, J) \approx \sqrt{N_{\text{deg}}}U_c(1, 0) - N_{\text{deg}}J.$$  \hspace{1cm} (4.38)

In case of $C_{60}$ solid, a photoemission experiment [13] reported $U = 1.6 \pm 0.2$ eV and $J = 0.2 \pm 0.1$ eV. Therefore $J$ corresponds to $0.5 \pm 0.25$ in our energy unit assuming that $U, J$ do not change for $A_3C_{60}$ systems.

### 4.4 Dynamical Properties: Maximum Entropy Method

Obtaining the dynamical information has been a great limitation in the quantum Monte Carlo method. The transport properties, such as resistivity and spin-relaxation, cannot be obtained from the thermodynamic potential. Since those transport quantities have direct relevance to experiments, it has been a long time goal to
have a reliable method to evaluate them. We have formulated the QMC method in terms of finite temperature Green's functions defined along imaginary-time, and, in principle, we should be able to extract all the necessary information by analytically continuing the Green's function in Matsubara frequency into real frequency.

However, realistically, the problem becomes a somewhat hopeless task due to the statistical noise and correlated data obtained with the QMC. This problem can be seen clearly from the following equation relating the measured Green's function $G(t)$ and the spectral function $A(\omega)$ defined on real frequency.

$$G(t) = \int_{-\infty}^{\infty} d\omega \frac{e^{-\gamma \omega}}{1 + e^{-\beta \omega}} A(\omega), \quad (4.39)$$

where $A(\omega)$ is defined as the imaginary part of a retarded Green's function, $A(\omega) = -\pi^{-1} \text{Im} G(\omega + i\eta)$. Note that, due to the exponential decay of the thermal factor in the integrand, the information in the high frequency part of $A(\omega)$ gets lost and is not reflected in the data $G(t)$. To put it another way, when the data $G(t)$ has statistical errors, inherent in the simulation, the error gets amplified immensely and there can exist many set of $A(\omega)$ which can satisfy Eq. (4.39) within error bounds.

The greatest danger of fitting the noisy data to a ill-posed problem such the analytic continuation is that the noise is blindly over-fitted and the image becomes highly sensitive to data and completely unpredictable. The straightforward fitting of the data, using e.g., the Padé approximant technique quickly becomes disastrous with noise. The maximum Entropy method (MEM) is designed to anneal out the meaningless noise by balancing the information in the data and the prior knowledge such as sum rules and the known high frequency form of the spectrum. Since the spectral functions satisfy the sum rule $\int_{-\infty}^{\infty} d\omega A(\omega) = 1$ and $A(\omega) > 0$, one can view them as a probability distribution. Then we formulate the problem of the analytic
continuation as equivalent to finding a most probable spectral function given the MC-data and sum rules.

### 4.4.1 Formalism

The question of the most probable spectral function given the data and prior information is studied in the framework of the statistical inference—we ask "what \( \{A(\omega_i)\mid i = 1, \cdots, N_\omega\} \) maximizes the probability \( P(A|\tilde{G}, I) \) given the data of Green’s function \( \tilde{G} \) and the prior information \( I \)?" \( \tilde{G} \) denotes the MC-data of \( G(\tau_l) \) \( (l = 1, \cdots, L) \), and \( I \) the prior information of the spectral function such as sum rules. We name the probability \( P(A|\tilde{G}, I) \) the posterior probability for quantity \( A \). As noted before, the process of finding \( A \) from \( \tilde{G} \) is an ill-posed transformation, we rewrite the posterior probability using the Bayesian statistics [76] as

\[
P(A|\tilde{G}, I) = \frac{P(\tilde{G}|A, I)P(A|I)}{P(\tilde{G}|I)}. \tag{4.40}
\]

\( P(\tilde{G}|A, I) \) is called the likelihood function, the probability for getting the data \( \tilde{G} \) given an assumed spectral function \( A \) and the prior information. The likelihood function quantifies the deviation of measured data \( \tilde{G} \) from a fixed \( G(A) \) derived by Eq. (4.39). \( P(A|I) \) is called the prior probability, the probability for \( A \) without any data. \( P(\tilde{G}|I) \) is the evidence, which is a normalization constant independent of \( A \), i.e., \( P(\tilde{G}|I) = \int dA \ P(\tilde{G}|A, I)P(A|I) \). In the following paragraphs we discuss the likelihood function and the prior probability.

Practically it is impossible to know the form of the likelihood function since it depends upon the Hamiltonian and its parameters, the Trotter break-up and the detailed procedure of MC-sampling. However, with very large amounts of data, the likelihood function is expected to assume a Gaussian form, from the central limit
theorem, like

\[ P(\bar{G}|A, I) = \prod_{i=1}^{L} \frac{\sigma_i}{\sqrt{2\pi}} \exp \left[ -\frac{(\bar{G}_i - G_i(A))^2}{2\sigma_i^2} \right], \]

(4.41)

where \( \bar{G}_i \) is the average of measured \( G(\tau_i) \), \( G_i(A) \) computed \( G(\tau_i) \) from a given \( A(\omega) \), \( \sigma_i \) the error estimate of measured \( G(\tau_i) \), \( \sigma_i = \sqrt{\langle G(\tau_i) - \bar{G}_i \rangle^2/(M - 1)} \) with \( M \) the number of data points.

However, in real circumstances, there are a few major problems. First, the incompleteness of data the distribution of \( G_i \) can only be modeled with a Gaussian for very large and high-quality data. For instance, when the system has gap-like structure, the Green’s function decays exponentially with \( \tau \) and, therefore \( G(\tau) \) at \( \tau \sim \beta/2 \) becomes so small that its mean value is comparable to the standard deviation of the data. In that case, with the positivity of \( G(\tau) \), the distribution naturally becomes highly skewed, deviating from the Gaussian form.

Secondly, the Monte Carlo measurements are not completely independent at different sweeps. Since the MC-process is a Markov chain, there is a relaxation time for the statistical correlations to dissipate. This becomes a serious problem at low temperature, where the relaxation time goes to infinity. There have been efforts to improve on this critical slowing-down phenomena in statistical mechanics [77], by proposing global (or domain) spin flips as opposed to the conventional local spin flip. However, in the quantum systems, the effective Hamiltonian in HS-fields becomes a long-range interacting model in imaginary time and computationally there is no gain in calculating the acceptance rate \( R \) in Eq. (4.34).

Obviously, the way to overcome the problem of the skewed data is to make the bin size big enough that the central limit theorem guarantees the distribution closer to a
Gaussian. However this requires longer running time and it quickly becomes unrealistically large. In most of the MC-runs for the analytic continuation, we have used nskip=4-10, nmeas=400-600 and nrun=400-600, with the total number of sweeps being order of $10^8-7$. For some sets of parameters, that size of runs is still insufficient.

Finally, the data $G_l$ and $G_r$ are correlated in incomplete data, since the $G(\tau)$ tends to be continuous. Therefore, $\langle (G(\tau_l) - \bar{G}_l)(G(\tau_r) - \bar{G}_r) \rangle \neq 0$ in general and we can no longer use the form of Eq. (4.41). As an improvement of the Eq. (4.41), we calculate the covariance matrix \[C_{ij}\] as

$$C_{ij} = \frac{\langle (G(\tau_i) - \bar{G}_i)(G(\tau_j) - \bar{G}_j) \rangle}{M - 1} = \frac{1}{M(M - 1)} \sum_{m=1}^{M} (G_{im}^n - \bar{G}_i)(G_{jm}^n - \bar{G}_j), \quad (4.42)$$

where $M$ is the size of data, \(\{G_{im}^n | m = 1, \cdots, M\}\) the measured sequence of $G(\tau_i)$, $\bar{G}_l$ the average of $G(\tau_l)$, i.e., $\bar{G}_l = \sum_{m=1}^{M} G_{im}^n / M$. With the covariance matrix, the likelihood function becomes, assuming the validity of the central limit theorem,

$$P(\bar{G} | A, I) \propto e^{\frac{1}{2} \chi^2}, \quad (4.43)$$

where

$$\chi^2 = \sum_{i,j}^{L} (\bar{G}_i - G_i(A))[C^{-1}]_{ij} (\bar{G}_j - G_j(A)). \quad (4.44)$$

In the following calculations, we have used this form of likelihood function.

The second important quantity to discuss is the prior probability $P(A|I)$, the probability for $A$ in the absence of any data. The functional form of the prior is chosen such that its maximization would lead to the least biased solution. From the probability theory, we apply the principle of maximum entropy for that purpose;

$$P(A|I) \propto e^{\alpha S}, \quad (4.45)$$
where

\[ S = - \int d\omega \left[ A(\omega) - m(\omega) - A(\omega) \ln \left( \frac{A(\omega)}{m(\omega)} \right) \right]. \]  

(4.46)

\( \alpha \) is a numerical constant as yet unknown and \( m(\omega) \) the \textit{default model}.

The default model provides the high frequency guidance for \( A(\omega) \), as well as a first guess. The entropy term \( S \) becomes maximum when \( A(\omega) = m(\omega) \) and, therefore with weak noisy data, the MEM finds a solution close to the default model. In many of the cases, a particular choice of the default model is \textit{overruled} by the data. From experience, unless the high-frequency part of \( m(\omega) \) has critically different behavior, the images produced by the MEM method have been more sensitive to the quality of the data rather than to the default model. In practice we choose the default model as a simple Gaussian at high temperature, where we can obtain high-quality data. The default model for the next lower temperature is simply the spectral function of the previous (higher \( T \)) run. By making the temperature step small enough we can \textit{anneal} out the arbitrariness of the initial default model. We have found that the spectral functions (images) for the low temperature depends more upon the annealing procedure, such as size of temperature step, rather than the initial default model.

Now, with the likelihood function and the prior probability we can write the posterior probability \( P(A|G, I) \), up to the overall normalization constant, as

\[ P(A|G, I) = e^Q, \]  

(4.47)

where

\[ Q = \alpha S - \frac{1}{2} \chi^2. \]  

(4.48)

So the problem has come to finding the solution, at certain \( \alpha \), \( \delta Q/\delta A|_\alpha = 0 \). However what value of \( \alpha \) do we choose? \( \alpha \) controls the balance between the tight-fit to the
data from the likelihood function and the no-fit or structurelessness from the entropic term. When \( \alpha \) is chosen too large, the entropic term wins and the new image simply resembles the default model and the new physical information is washed out. On the other hand, if \( \alpha \) is chosen too small, \( G(A) \) fits to the noisy data too tightly, leading to spurious peaks over-fitted to statistical errors.

Among several versions for choosing \( \alpha \), here we will discuss two methods, the historic maximum entropy and the classical maximum entropy. First, the historic maximum entropy method finds \( \alpha \) which makes

\[
\chi^2 = L, \tag{4.49}
\]

with \( L \) the number of time-slices \([79]\). The equality is justifiable only when the data is an extremely good Gaussian. It has been known that Eq. (4.49) forces \( \chi \) to be too large allowing the solution, \( G(A, \alpha) \), to deviate too much from the data. Consequently the historic maximum entropy tends to under-fit the data and the resulting image may become overly smooth. Although the smoothness prevents the spurious ringing due to over-fitting, it also has danger of smearing out the physical peaks present in the data.

On the other hand, the classical maximum entropy method, developed later than the historic maximum entropy method, deals with \( \alpha \) more logically in terms of the probability theory. It treats \( \alpha \) as a random variable on the same footing as we do \( A(\omega) \) \([79, 80]\). \( \alpha \) is chosen when it maximizes \( P(\alpha|\bar{G}) = \int DA \ P(A, \alpha|\bar{G}) \). Once \( \alpha \) is fixed, we find the solution \( A, \alpha \) maximizing \( P(A|\alpha, \bar{G}) \). Eq. (4.49), with incomplete data, becomes

\[
\chi^2 + N_y = L, \tag{4.50}
\]

104
Figure 4.6: Spectral functions for $N_{\text{deg}} = 1$. (a) For $U = 4$ and $\epsilon_d = -U/2$ at half-filling, the weight of spectral function at $\omega = 0$ is depleted as $\beta(=1/T)$ increases. At $\beta = 16$, inside the gap it develops a tiny and sharp peak at $\omega = 0$, which is an artifact of Gaussian DOS in $d = \infty$. (b) Away from half-filling, $\epsilon_d = -1$, the system becomes metallic as the upper edge of LHP overlaps with the chemical potential. There emerges a sharp quasi-particle (q.p.) spectrum slightly above $\omega = 0$ with width $\epsilon_F$ which serves as the low $T$ energy scale. (c) As $U$ decreases, the model systems makes transition to a metal solution with larger q.p. spectral weight.

with $N_g$ the number of good data. $N_g$, roughly speaking, represents the number of meaningful $\bar{G}$s, which are counted by the number of small enough $\sigma_i$ in the covariance matrix. Comparing with Eq. (4.49), the classical maximum entropy method performs a tighter fit to the data. Although most of our calculation is done using the classical maximum entropy method, the image sometimes depends sensitively upon the $\alpha$ values [16] and much care should be taken in each case.

4.4.2 Spectral Function and Optical Conductivity

For all the MEM calculations, we have used a Gaussian DOS, Eq. (4.12), for the free electron DOS since a DOS with sharp edge such as the semi-circular DOS, Eq. (4.13), can cause artifacts like ringing in MEM. The bandwidth $W$ of the Gaussian
Figure 4.7: Spectral functions for $N_{\text{deg}} = 1, 2, 3$ at $U = 4$. (a) The quasi-particle peak becomes dominant for large $N_{\text{deg}}$. The effective band-width of the charge excitation peaks are broadened with increasing $N_{\text{deg}}$ due to the enhanced hopping for one-particle (hole) doped states, as discussed in figure 4.1. The more of weight of the charge excitation peaks are transferred to q.p. peak for larger $N_{\text{deg}}$. (b) At a fixed $\epsilon_d = -1$, all three cases have the total occupations 0.9-1.0 and the integrated weight up to the chemical potential is roughly $1/N_{\text{deg}}$. 
DOS is $\sqrt{2}$. First, the cases for $N_{\text{deg}} = 1$ are shown in figure 4.6. The temperature set shown has $\beta = 4, 8, 16$, although the annealing was performed with smaller temperature intervals. In the first plot (a) at $U = 4$, where it is predicted to belong in the insulating phase [14], the spectral weight near $\omega = 0$ is depleted as $T$ goes lower. However, due to the Gaussian DOS which has non-vanishing tail at large $\omega$, there appears a tiny and sharp peak inside the *apparent* gap. With a realistic DOS input in the local approximation, one can expect a true gap for $U/W > 2$ as in figure 4.3. In the DMFT, the critical value of $U$ at MIT is known to be $U_c/W \approx 1.5$ [14] at half-filling.

As we move the center of band, $\epsilon_d$, toward the Fermi energy the system undergoes the phase transition from an insulator to a metal. The plot (b) illustrates the case at $U = 4$ and $\epsilon_d = -1$. Although the half band-width of our Gaussian is $1/\sqrt{2}$, the non-interacting band still has enough states lying near the Fermi-energy and a rather sharp q.p. peak develops near $\omega = 0$. Precisely, the q.p. energy is slightly above zero, for the same reason as the Anderson impurity model in the previous chapter. Since the $d^0$-configuration has smaller excitation to $d^1$ than those for $d^1 \leftrightarrow d^2$, the singlet ground state has larger admixture of $d^0$ than $d^2$. Therefore the q.p. peak is observed by *adding* electrons by the BIS experiments, corresponding to $\omega > 0$ in the spectral function.

We have lowered the Coulomb repulsion to $U = 2$, maintaining the particle-hole symmetry. Here we control the MIT by varying the strength of $U$. As expected, when $U$ becomes comparable to the band-width the system becomes metallic. Note that the distance between the UHB and LHB is approximately $U$. Since the charge excitation costs less energy in (c) than in (b), the q.p. peak in (c) has much larger weight. The
width of the q.p. peak defines the new energy scale, \( \epsilon_F \), in the low temperatures and acts as the effective Fermi energy. As an analogy to the free electron theory, the effective mass \( m^* \) is inversely proportional to \( \epsilon_F \). Therefore the case (b) is more strongly correlated than case (c). With smaller \( U \), the LHB, UHB and the q.p. peak merge and the one-electron theory would suffice.

Figure 4.7 illustrates how the spectral function changes with \( N_{\text{deg}} \). At half-filling in plot (a), the spectral weight at the chemical potential increased with \( N_{\text{deg}} \), confirming the effectively enhanced hopping. Note that, with larger \( N_{\text{deg}} \), the charge excitation peaks have larger half-width-at-half-maximum (HWHM) and more of their spectral weight is transferred to the q.p. peak. The increasing HWHM with \( N_{\text{deg}} \) agrees with the argument in figure 4.1, where the effective band-width of ionization (affinity) peak becomes broadened by factor of \( \sqrt{N_{\text{deg}}} \). This dynamical calculation once again proves that the effective hopping is actually enhanced with \( N_{\text{deg}} \). The stronger q.p. peaks for large \( N_{\text{deg}} \) result from the larger spectral weight at the chemical potential from the broader bands. In plot (b), the d-level energy is fixed at \(-1\). The total occupation numbers of d-orbital for \( N_{\text{deg}} = 1, 2, 3 \) are rather insensitive to \( N_{\text{deg}} \) with 0.930, 0.915 and 0.912, respectively. That is because \( |\epsilon_d| \ll U \) and the doubly occupied configuration exists in small quantum weight and therefore barely affects the total \( n_d \). In the paramagnetic phase, the total occupation number is evenly distributed to each orbital and the spectral weight of the LHB roughly goes as \( 1/N_{\text{deg}} \).

In figure 4.7 (b), the \( N_{\text{deg}} = 3 \) spectral function has unexpected shoulder near \( \omega = 0 \). We do not have any physical argument to support the existence of this shoulder and furthermore this structure tends to damp out as we increase the running time. We have consistently found such a trend of apparently spurious shoulders appearing in
the low temperature and in high degeneracy calculations. At the moment we suspect the spurious peak(s), or ringing, result from the highly correlated measurement in the Monte Carlo process. In other words, the correlated data have underestimated error bars which overemphasize the likelihood function with incorrect average values, Eq. (4.44), and the MEM is over-fitting the image to the noise.

Once the spectral functions are under control, we can compute transport properties from analytically continued $A(\omega), \Sigma(\omega)$, etc. Here we will discuss the $q = 0$ optical conductivity which can be expressed as the current-current correlation function through Kubo's formula [56];

$$\sigma(\omega) = \text{Re} \frac{1}{\omega} \ll j_2; j_2 \gg_{\omega + i\eta},$$  \hspace{1cm} (4.51)

where

$$j = \sum_{k\sigma} v_k n_{k\sigma}, \text{ with } v_k = 2t \sum_{i=1}^{d} \tilde{e}_i \sin k_i.$$  \hspace{1cm} (4.52)

In $d = \infty$, the vertex correction in the $j - j$ correlation function vanishes and, after some manipulation [81], the optical conductivity can be written as

$$\sigma(\omega) = \pi \sigma_0 \int d\omega' \int d\epsilon D(\epsilon) A(\epsilon, \omega') A(\epsilon, \omega + \omega') \frac{f(\omega') - f(\omega' + \omega)}{\omega}, \text{ with } \sigma_0 = \frac{\pi e^2 t^2}{2\hbar}.$$  \hspace{1cm} (4.53)

The unit $\sigma_0$, for systems with band-width 1 eV, corresponds to $10^{-3} \cdots 10^{-2} (\mu\text{Omega cm})^{-1}$. In the derivation, the summation of $v_{k\sigma}^2$ at vertices simply results in the free DOS and the optical conductivity is basically a convolution of two spectral functions. Note that $A(\epsilon, \omega)$ is the spectral function of electron at $k$ with $\epsilon_k = \epsilon$, taken as the imaginary part of $G_k(\omega) = (\omega - \epsilon_k - \Sigma(\omega))^{-1}$. The self-energy $\Sigma(\omega)$ is calculated from Eq. (4.18) with analytically continued $G(\omega + i\eta)$, using the IMSL root-finding subroutines.
Figure 4.8: Optical conductivity and resistivity for $N_{\text{deg}} = 2$ at $U = 4$, $\epsilon_d = -1$. The optical conductivity is made up of three excitations from transition between three structures in the spectral functions plotted in the inset (a). The spectral functions at $\beta = 2, 4, 6, 8, 10, 12, 16$ have q.p peak, LHB, UHB marked as $a$, $b$, $c$, respectively. The Drude peak, arising from the scattering within the q.p. peak, gets strong for low $T$. The d.c. resistivity $\rho(T)$ is computed as the inverse of the static limit of $\sigma(\omega)$, which illustrates the Fermi liquid picture hold for multi-band Hubbard model at half-filling below the critical $U$ value. The unit of $\rho(T)$ corresponds to $10^3 \cdots 10^2 \mu\Omega\text{cm}$ for band-width 1 eV.
The optical conductivity for \( N_{\text{deg}} = 2 \) and \( U = 4, \epsilon_d = -2 \) is plotted in figure 4.8. The inset (a) shows the spectral functions at \( \beta = 2, 4, 6, 8, 10, 12, 16 \) with three peaks labeled as \( a, b, c \). The main plot shows the optical conductivity from the same set of temperatures. As marked in the figure, \( \sigma(\omega) \) has peaks corresponding to transitions between major peaks in the spectral function. For example the Drude peak (marked as \( a - a \)) is coming from the scattering within the q.p. peak \( a \). The resistivity \( \rho(T) \) is calculated by the \( \omega \to 0 \) limit of the conductivity, \( \rho(T)^{-1} = \lim_{\omega \to 0} \sigma(\omega) \). The resistivity, plotted with \( T^2 \) in inset (b), is linear in \( T^2 \), preserving the Fermi liquid picture for the multi-orbital Hubbard model at half-filling, below the critical \( U \) value and neglecting the possibility of anti-ferromagnetic order.
CHAPTER 5

CONCLUSIONS AND FURTHER DIRECTIONS

In cerium compounds, $\text{Ce}_x\text{La}_{1-x}M_3 (M=\text{Pb, In, Sn, Pd})$, we have applied the Anderson impurity model with parameters obtained from the local density approximation in the impurity ($x \to 0$) and concentrated ($x \to 1$) limits. Depending upon the relative magnitudes of the CEF splittings and Kondo temperatures, the materials are categorized as heavy fermion ($\text{CePb}_3$, $\text{CeIn}_3$) and high $T_K$ ($\text{CeSn}_3$, $\text{CePd}_3$) systems. The combination of band theory with the many-body technique produced the correct trend of crystalline electric field (CEF) splittings and Kondo temperatures in the $\text{CeM}_3$ compounds. For the heavy fermion systems, $\text{CePb}_3$ and $\text{CeIn}_3$, the doublet CEF, $\Gamma_7$, has been found to be the ground multiplet with CEF splittings much larger than the Kondo temperatures. The Kondo temperatures are predicted to be some fraction of a Kelvin in disagreement with experiment, which is not surprising considering the accuracy of our approximations involved in the LDA and the NCA with infinite-$U$. It should be noted that, in the intermediate temperature range the physics is dominated by the cross-over behavior due to the CEF splittings.

The high $T_K$ systems, $\text{CeSn}_3$ and $\text{CePd}_3$, had larger hybridization strength and, accordingly, had a larger Kondo temperature than the CEF splittings. The computed spectral functions showed the strong Kondo resonance without the CEF splitting and
the static magnetic susceptibilities converged to a finite value for $T$ going to zero. A comparison of the computed magnetic susceptibilities for CeSn$_3$ systems with the experiments shows that the calculations are good considering the sensitive dependence of $T_K$ upon the model parameters. However, it seems that we overestimated the hybridization strength for the CePd$_3$ system, especially the contribution from the filled Pd-$d^{10}$ orbitals. Note that, contrary to the common belief that $T_K$ is a function of the hybridization at the Fermi energy, CePd$_3$ provides an example in which the large hybridization deep inside the Fermi sea can lead to a large Kondo temperature even with the small hybridization at the Fermi energy.

I have so far presented the material-oriented many-body calculations and demonstrated the need for the realistic calculations. Without first-principles calculations, it would be over-simplifying and confusing to interpret the experimental results based on the simplified model Hamiltonian, as pointed out in the cases of CeIn$_3$ and CePd$_3$. Although we have consistently produced correct trends of low temperature behaviors in Ce$M_3$ compounds, there still remain many unanswered questions, such as discrepancy of the concentrated and impurity limit calculations for CePb$_3$, CeIn$_3$ systems, and the grossly overestimated $T_K$ for the CePd$_3$ compound. Also, some of the experimental up-turn of the magnetic susceptibility of CePd$_3$ at low $T$ should be clarified as to whether it can be explained within the impurity model.

The improvement of the project can come in several ways. First, we can compute the model parameters $\epsilon_f$, $U$ from the local density approximation [39]. With those additional ab initio parameters, the calculation will be more self-consistent. Second, the inclusion of the finite-$U$ is implemented in the NCA by allowing the $f^2$ configurations in the Hilbert space. The renormalization of $T_K$ by the inclusion of the finite-$U$
is expected to improve the theoretical prediction of $T_K$. Finally, the lattice physics can be studied by the dynamical mean field approximation [14]. This might help to settle down the on-going controversies regarding the validity of impurity models in some cerium compounds [3, 4].

In the second half of the dissertation we have discussed the role of orbital degeneracy in the Hubbard model, especially at the metal-insulator transition (MIT). Motivated by recent developments of the multi-band physics in colossal magnetoresistance materials, superconductivity in $\text{Sr}_2\text{RuO}_4$, and alkali-doped fullerides, the multi-band Hubbard model has received much attention. In this dissertation, the role of the orbital degeneracy in the Hubbard model has been studied by the quantum Monte Carlo (QMC) within the dynamical mean field theory. We also applied the maximum entropy method for the analytic continuation of the QMC-Green's function to the real frequency spectral functions and studied the dynamical manifestation of the MIT.

The orbital degeneracy increases the degree of freedom for the charge excitation to move around the lattice. The strong Coulomb interaction, in the insulating phase, anti-aligns the spins on the adjacent sites and, due to the orbital degeneracy, the hopping probability is enhanced by factor of $N_{\text{deg}}$, the orbital degeneracy. The larger effective band-width narrows the excitation gap in the insulating regime and the critical value of $U$ for the MIT becomes proportional to $\sqrt{N_{\text{deg}}}$. We have studied the MIT by computing the occupation number versus the chemical potential or $d$-level energy, $\epsilon_d$. The existence of the insulating phase is found when the occupation number is independent of the chemical potential, or $-\partial n_d/\partial \epsilon_d \propto A(0) = 0$ with the spectral function at the chemical potential $A(0)$. The insulator phase diminished at a fixed $U$ with increasing orbital degeneracy. Especially, at $U/W = 2$ and $N_{\text{deg}} = 3$,
the Hubbard model remained metallic for all values of the chemical potential. In contrast, the one-band Hubbard model goes insulating for this \( U/W \) value.

The critical value of Coulomb repulsion, \( U_c \), is approximately estimated by computing the occupation numbers at \( \epsilon_d \) slightly off from half-filling. Even though \( U_c(N_{\text{deg}}) \) increased with \( N_{\text{deg}} \), the data is not sufficient to conclude that the specific functional dependency is \( \sqrt{N_{\text{deg}}} \). At this point, it is not even clear whether the system with moderate values of \( N_{\text{deg}} \) and \( U \) should follow the predicted relation, \( U_c(N_{\text{deg}}) = \sqrt{N_{\text{deg}}} U_c(1) \).

The Hund’s rule exchange coupling \( J \) pushes \( U_c \) to larger values, where the increment is proportional to \( J \). We argue that the linear dependency is from the effectively increased on-site Coulomb energy for particle (hole) excitations, which is estimated to be \( N_{\text{deg}} J \). In contrast to the enhanced hopping strength, the inclusion of the Hund’s rule exchange energy favors the insulating solution. Therefore, we expect there is competition between the two different effects in the multi-band models. For \( A_2C_{60} \) systems, the exchange interaction is about one order of magnitude smaller than the Hubbard \( U \) and the enhanced hopping has a larger effect on the MIT.

The dynamical properties are calculated from the analytic continuation by means of the maximum entropy method (MEM). Although the method requires very high-quality data, especially for the large degeneracy systems, we can analyze important dynamical information of the model. The upper and lower Hubbard bands in the spectral function are broadened with increasing \( N_{\text{deg}} \), which accordingly results in the stronger quasi-particle excitations near the Fermi energy. As an application of the analytic continuation, we have computed the optical conductivity which showed the strong Drude peak with \( T^2 \) d.c. resistivity in the metallic regime.
Generally speaking, the QMC calculation is still an on-going project. Most of the effort has been put into obtaining the reliable one-electron spectral function free of any suspicious ringing induced by the MEM. With regard to the dynamical properties, the question of how the quasi-particle peak behaves with the orbital degeneracy should be studied. Although the argument of Gunnarsson et al. [7] proved to be positive for the role of degeneracy at MIT, it would be very interesting to study the properties of the strongly correlated metal near the MIT. The weight of the quasi-particle excitation can be studied by transport properties, as exemplified in the Drude peak of the optical conductivity.

With growing interest in the multi-band systems, the present work can provide the starting point of the future research. The instabilities of the multi-band model can be studied within the dynamical mean field theory, for instance, we can look for the on-site $p$-wave pairing instability in Sr$_2$RuO$_4$. In similar context, the ferromagnetic ordering, as in SrRuO$_3$, driven by the Hund’s rule coupling and its competition with anti-ferromagnetic ordering, as in Heisenberg magnets.
APPENDIX A

LINEARIZED MUFFIN-TIN ORBITAL METHOD

The linearized muffin-tin orbital (LMTO) method [2, 41] is in an efficient and fast way of implementing electronic structure calculations within the local density approximation (LDA). The efficiency of the method lies in approximating the Muffin-Tin (MT) orbitals being divided into inside and tail parts, with minimal set of basis functions. By separating the inside and tail part of the orbital, we can independently treat the two aspects, the potential defined inside the MT and the kinematics of tails only determined by the crystal structure of the material. The basic idea is that the wave function inside the MT is determined by the MT potential and the energy-independent tails are smoothly joined by boundary conditions at the MT radius, $S$. The information of crystal structure is reflected in matching the boundary condition at $S$ of the Bloch sum of MTOs.

More speed can be gained by defining the muffin-tin orbital (MTO) as energy independent, like the atomic orbitals in the linear combination of atomic orbitals (LCAO). However unlike LCAO, the MTO is augmented such that the tail of an MTO is orthogonal to the core states of the neighboring sites and therefore we need much fewer basis states. The core electrons, for example [Xe] in the Ce atom with the electronic configuration [Xe]5s²5p¹, are treated as inert and the next $s, p, d, f$ orbitals

117
are counted as valence electrons, and orthogonal to the [Xe] orbitals. The s-orbital in
the calculation represents the 5s if the lower s states are dumped as the core electrons.
Hence, usually the LMTO calculation involves the minimal set of orbitals where there
are only one s, p, d, f set per atom.

The solution $\phi_l(r, E)$ inside the MT radius $S$ at energy $E$ is obtained by directly
integrating the Schrödinger equation up to $S$. Now we linearize the wave function
$\phi_l(r, E)$ of angular momentum $l$ as a Taylor series around a reference energy, $E_{ul}$:

$$\phi_l(r, E) = \phi_l(r, E_{ul}) + (E - E_{ul})\dot{\phi}_l(r, E_{ul}), \quad (A.1)$$

where

$$\dot{\phi}_l(r, E_{ul}) = \frac{\partial \phi_l(r, E)}{\partial E}|_{E=E_{ul}}. \quad (A.2)$$

This linearization is a good approximation if $E$ lies within $\sim \langle \phi^2_{ul} \rangle^{-1/2}$ with $\langle \phi^2_{ul} \rangle = \int_0^S dr \dot{\phi}^2_{ul}(r)$. Hence inside the validity range, we only need to calculate the wave
function only at $E_{ul}$. Moreover, when it comes to evaluating matrix elements of
Hamiltonian and overlaps, all relevant elements can be parameterized in terms of
several (4 per angular momentum) parameters.

On the other hand, the tail part of the MTO is more dramatically approximated
by so-called the atomic sphere approximation (ASA) [2]. This approximation involves
two approximations. First, in the interstitial region the tail is set to be $\sim r^{-l-1}$. In
the original MT method the tail should be a linear combination of Bessel functions,
$J_l(kr), N_l(kr)$, with $\hbar^2 k^2 / 2m = E - V_{MT}$. The aim of the ASA is that by doing
this we do not involve the energy $E$ in the tail. This set-up can enormously increase
the speed of computation by *tabulating* once and for all the structure factor which
contains the information of tail-mixing effects between sites without worrying about
what is happening inside the MT sphere. A second approximation is that we set the MT radius $S$ equal to the Wigner-Seitz radius. In other words, we are replacing the unit polygons by spheres with the same volume. By making the spherical unit cell we can simplify integrals inside the sphere. Also by setting the MT radius be equal to the the Wigner-Seitz radius, we can minimize the errors involved with the interstitial region and optimize the overall results.

Instead of expressing the wave functions about the energy $E$, we parameterize the wave function around $E_{\nu l}$ with respect to the logarithmic derivatives $D$ of $\phi_l(r, E)$ at the MT radius. If the wave function is parameterized in terms of $E$, the equation for boundary conditions ends up being a eigenvalue equation non-linear in $E$ (KKR-ASA equation, p.18 of Ref. [41]). On the other hand, by expressing the trial wave function as explicitly energy-independent, we can use variational method which gives usual eigenvalue problem in the form of $(H - \lambda_0)\alpha = 0$ (LMTO-ASA equation, Eq. (A.18)), as in the LCAO method.

The $L$-th ($L$ denoting $(l, m)$) wavefunction inside the muffin-tin radius $S$, $\Phi_L(r, D)$, with the logarithmic derivative $D$ at the radius is linearized about a fixed reference energy $E_{\nu l}$ as follows:

$$
\Phi_L(D, r) = i^l Y_l(\mathbf{r}) \left( \phi_l(r, E_{\nu l}) + \omega_l(D) \dot{\phi}_l(r, E_{\nu l}) \right),
$$  

(A.3)

where $\phi_l(r, E_{\nu})$ is the solution of the Schrödinger equation inside the muffin-tin sphere and $\dot{\phi}_l(r, E_{\nu})$ is the energy derivative. The solution $\phi_{\nu l}(r)$ is normalized as $\int_0^S r^2 \phi_{\nu l}(r)^2 dr = 1$. From now on, when the radial argument of radial functions is omitted, and they denote the functional values at $r = S$. The parameter $\omega_l(D)$ is
chosen to make the logarithmic derivative at the MT radius be \( D \);

\[
\omega_l(D) = -\frac{\phi_{\mu} D - D_{\nu}}{\phi_{\mu} D - D_{\nu}},
\]

(4.4)

where \( D_{\nu} = \partial \log \phi_{\mu}(r)/\partial \log r \big|_{r=S} \) and \( D_{\mu} = \partial \log \phi_{\mu}(r)/\partial \log r \big|_{r=S} \). When \( E \approx E_{\nu} \) (now \( E \) viewed as a function of the boundary condition parameter \( D \)), \( E(D) - E_{\nu} = \omega_l(D) \) in the lowest order approximation.

By the ASA, there are only two relevant \( D \)'s: \( l, -l - 1 \) (frequently denoted as + and −). Note that when we express inside other MT sphere at origin the tail of a MTO centered at \( \mathbf{R} \), \( (S/|r - \mathbf{R}|)^{l+1} i^l Y_{lm}(\hat{r}) \), it is expanded by the radial function with positive powers as \( (r/S)^{l''} \) from the expansion theorem [82];

\[
\left( \frac{S}{|r - \mathbf{R}|} \right)^{l+1} i^l Y_{lm}(\hat{r}) = -\sqrt{4\pi} \sum_{l'} \frac{g_{l''} Y_{l''}}{2(2l' + 1)} \left( \frac{r}{S} \right)^{l''} i^{l''} Y_{l''}(\hat{r}) \left( \frac{S}{R} \right)^{l''+1} Y_{l''}(\hat{R}),
\]

(A.5)

where \( l'' = l + l' \), \( m'' = m' - m \) and \( g_{l''} \)'s are Gaunt coefficients which can be expressed in terms of the Condon and Shortley coefficients. With this expansion theorem in mind, we proceed the augmentation of the MTO \( \chi_{l'}(r) \) as follows:

\[
\Phi_{l'}(-l - 1, r)/\Phi_{l'}(-l - 1, S), r < S \quad (A.6)
\]

\[
(S/r)^{l+1} i^l Y_{lm}(\hat{r}), \text{ interstitial region} \quad (A.7)
\]

\[-\sqrt{4\pi} \sum_{l'} \frac{g_{l''} \Phi_{l'}(l', r - \mathbf{R})}{2(2l' + 1) \Phi_{l'}(l', S)} \left( \frac{S}{R} \right)^{l''+1} Y_{l''}(\hat{R}), \text{ inside other MT sphere at } \mathbf{R} \quad (A.8)
\]

Note that the in the last expression \( \Phi_{l'}(l', r - \mathbf{R})/\Phi_{l'}(l', S) \) is substituted in place of \( (r/S)^{l''} i^{l''} Y_{l''}(\hat{r}) \) in the expansion theorem. By doing this we can ensure that the tail part is orthogonal to the core states of the neighboring atoms.

We construct a Bloch sum with above MTO's

\[
\chi^k_{l}(k) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \chi_{l}(r - \mathbf{R}),
\]

(A.9)
which can be re-expressed in the one-center expansion inside the muffin-tin at the origin, thanks to the augmentation Eqs. (A.7-A.8):

\[
\chi^k_L(r) = \frac{\Phi_L(-l-1,-r)}{\Phi_l(-l-1)} - \sum_{L'} \frac{\Phi_{L'}(l',r)}{2(2l'+1)\Phi_{l'}(l')} S^k_{L',L}. \tag{A.10}
\]

Here, the second part of the one-center expansion is the sum of tails coming from neighboring sites and the \textit{canonical structure constants} \( S^k_{L',L} \) are defined by

\[
S^k_{L',L} = g_{L',L} \sum_{R \neq 0} e^{i\mathbf{k} \cdot \mathbf{R}} \left( \frac{S}{R} \right)^{l''+1} \sqrt{4\pi i^{-l''}} Y_{l''}^{*} m_{m'}(\hat{R}). \tag{A.11}
\]

This structure constants only depend upon the crystal structure, not the potentials inside the muffin-tins. Thus this matrix is calculated and tabulated once and for all compounds with the same crystal structure.

The LMTO Hamiltonian and overlap matrices are written in the bases of these Bloch sum of MTO's:

\[
\Psi^{ik}(r) = \sum_L a^{ik}_L \chi^k_L(r). \tag{A.12}
\]

The Hamiltonian \( H^k \) and the overlap \( O^k \) matrices (per \( k \)) are \([2, 41]\)

\[
H^k = \Pi^\dagger \Omega + E_v \Pi^\dagger \Pi + E_v \Omega^\dagger \langle \dot{\phi}^2 \rangle \Omega \tag{A.13}
\]

\[
O^k = \Pi^\dagger \Pi + \Omega^\dagger \langle \dot{\phi}^2 \rangle \Omega, \tag{A.14}
\]

where

\[
\Pi = \left[ \frac{1}{\sqrt{S/2 \Phi(-)}} \right]_l \delta_{L',L} - \left[ \frac{\sqrt{S/2 \Phi(-)}}{\omega(-) - \omega(+)} \right]_{l'} S^k_{L',L}, \tag{A.15}
\]

\[
\Omega = \left[ \frac{\omega(-)}{\sqrt{S/2 \Phi(-)}} \right]_l \delta_{L',L} - \left[ \frac{\sqrt{S/2 \Phi(-) \omega(+)}}{\omega(-) - \omega(+)} \right]_{l'} S^k_{L',L}, \tag{A.16}
\]

\[
\langle \dot{\phi}^2 \rangle = \langle \dot{\phi}_v^2 \rangle \delta_{L',L} \text{ and } E_v = E_v \delta_{L',L}. \tag{A.17}
\]

Since the tails of MTO's are constructed from the power law function \( r^{-l-1} \), the overlap matrix is long-ranged and has different decaying rates for \( l \). Thus in this
construction the overlap matrix is far from unitary and the eigenvalues of the matrix range over several orders of magnitude. With these $H^k$ and $O^k$ matrices constructed, one solves the LMTO-ASA eigenvalue problem

$$\sum_{L'} (H^k - E^k O^k)_{L,L'} a_{L'}^k = 0. \quad (A.18)$$

After solving the eigenvalue problem (using the Cholesky decomposition method [83]), the wave function can be written in a one-center expression inside the MT:

$$\Psi^{ijk}(r) = \sum_L \Psi^{ijk}_L(r)$$

$$= \sum_L \left\{ A_{L}^{ijk} \phi_{\nu L}(r) + B_{L}^{ijk} \phi_{\nu L'}(r) \right\}, \quad (A.20)$$

where

$$A_{L}^{ijk} = \sum_{L'} \Omega_{L_{L'},a_{L'}^{jk}}, \quad B_{L}^{ijk} = \sum_{L'} \Omega_{L_{L'},a_{L'}^{jk}}. \quad (A.21)$$

Now we calculate the $L$ character of the band eigenstate $C_L^{jk}$ by

$$C_L^{jk} = \langle \Psi_L^{jk} | \Psi_L^{jk} \rangle = |A_{L}^{jk}|^2 + |B_{L}^{jk}|^2, \quad (A.22)$$

where we have used the orthogonality, $\langle \phi_{\nu L} | \phi_{\nu L'} \rangle = 0$. Obviously, from the orthogonality of eigenstates in the linear algebra,

$$\sum_{L} (\Psi_L^{jk} | \Psi_L^{jk}) = (A^{jk})^\dagger \cdot A^{jk} + (B^{jk})^\dagger \cdot B^{jk} = (a^{jk})^\dagger O^k a^{jk} = \delta_{jj'},$$

and the eigenvectors of different band solution can be orthonormalized.

For the density of states projected to the cubic irreducible representation (irrep) the solution Eq. (A.21) is transformed to the cubic irrep basis. Now introducing the spin index, in the presence of spin-orbit interaction, the weight of cubic irreps of $m, m', C_{mm'}^{jk}$, are calculated by

$$C_{mm'}^{jk} = \sum_{LL', \sigma \sigma'} U_{m,L \sigma}(A_{L \sigma}^{jk} A_{L' \sigma'}^{jk*} + (\phi_{\nu L}^2) B_{L \sigma}^{jk} B_{L' \sigma'}^{jk*}) U_{L', \sigma', m'}^\dagger. \quad (A.23)$$

where $U_{m,L \sigma}$ is the unitary transformation matrix from $LS$-basis to cubic irreps.

122
APPENDIX B

QUALITATIVE DISCUSSION ON LARGE KONDO TEMPERATURE ESTIMATE FOR CePd₃

CePd₃ has a large Kondo temperature (~700 K [26]) despite a small Fermi surface [46, 47]. From the common understanding of the Anderson impurity model, these two experimental indications are hard to be compatible since the Kondo temperature is known to depend upon the hybridization strength at the Fermi energy as in Eq. (3.39). However, in qualitative agreement with experiment, the NCA calculation produces a very large Kondo temperature estimate.

To understand the origin of the large $T_K$, we first analyze the solution of the ground state energy from the pole of the pseudo-boson Green’s function (See Eq. (3.18).) To emulate the Pd-DOS, we model the hybridization broadening as a Lorentzian with width $D$ centered at $\epsilon_0$ with strength $g$ as

$$\Gamma(\epsilon) = gD(\epsilon) = g\frac{D}{(\epsilon - \epsilon_0)^2 + D^2}. \quad (B.1)$$

Ignoring the spin-orbit and CEF splitting for simplicity and denoting the orbital degeneracy as $N_f$, the equality $\omega = \text{Re}\Sigma_0^R(\omega)$ becomes with Eq. (3.18)

$$\frac{\pi\omega}{N_fg} = D(\epsilon_f - \omega) \left\{ \ln \frac{\omega - \epsilon_f}{\sqrt{\epsilon_0^2 + D^2}} + \frac{\omega - \epsilon_f + \epsilon_0}{D} \left( \frac{\pi}{2} + \tan^{-1}\left( \frac{\epsilon_0}{D} \right) \right) \right\}. \quad (B.2)$$
Figure B.1: Plot for the solution of the ground state energy with a model Lorentzian hybridization function. The crossing point (A,B) of the thick curve $(\pi \Sigma_0^0(\omega)/N_{fg})$ and the line line $(\pi \omega/N_{fg})$ represents the ground state energy, from Eq. (B.2). The Lorentzian hybridization is chosen to be centered at $\epsilon_0 = -2.5$ below $\epsilon_f(= -2.0)$ with a narrow band-width ($D = 0.5$) to mimic the Pd-DOS. The solution crosses over from a many-body state (A for $g = 2$) to a one-body state (B for $g = 3$) as the hybridization decreases.
Figure B.2: Static magnetic susceptibility with decreasing Lorentzian bandwidth. The magnetic susceptibility evolved from a usual Kondo shape to a "Schottky-like" shape. The small $\chi(T)$ for $D = 0.5$ results from the small conduction-DOS near the Fermi energy. Experiments [26] do not agree qualitatively with this trend in $\chi(T)$ where we speculate that CePd$_3$ corresponds to solution with small $D$. 
The Eq. (B.2) is plotted in figure B.1.

In the small $D$ limit ($D \ll |\epsilon_0 - \epsilon_f|$), the previous equation simplifies to

$$\frac{\pi \omega}{N_f g} \approx D(\epsilon_f - \omega) \ln \left| \frac{\omega - \epsilon_f}{\epsilon_0} \right| + \frac{1}{\omega - \epsilon_f + \epsilon_0}. \tag{B.3}$$

When the hybridization strength $g$ is small ($g = 2$), the solution from the logarithmic term $A$ (denoted as $A$ in the plot) gives the usual Kondo temperature estimate $T_K \sim \exp(\pi \epsilon_f/N_f \Gamma(0))$, which is a very small number due to the small spectral DOS at the Fermi energy. The major contribution for the Kondo screening of the $f$-moment is from the conduction continuum states near the Fermi energy. However, when the hybridization strength is increased to $g = 3$ the ground state solution is from the algebraic term $B$, which results from the singlet formation of $f$-level and the localized $d$-state. The binding energy of this state is, therefore, algebraic and much larger than the Kondo temperatures of solution $A$. Roughly speaking, this screening is done by the local $d$-electrons within atomic scale from the impurity, as opposed to the (fragile) Kondo screening in which the conduction electrons within the Kondo screening length $\sim \hbar v_F/k_B T_K$ participate, where $v_F$ is the Fermi velocity and $k_B$ the Boltzmann factor.

Although we speculate the solution type-$B$ is responsible for the large Kondo temperature in CePd$_3$ despite its small DOS at the Fermi energy, there are still remaining mysteries. One of them is the static magnetic susceptibility. As discussed in the previous paragraph, as the band-width $D$ decreased from 2.25 to 0.5 (figure B.2), the $\chi(T)$ curve evolved from the usual Kondo shape [19] to a "Schottky-like" shape with the peak located at the binding energy. For the narrow band, there is little spectral weight near the Fermi surface and the spin-polarization in the Pauli-paramagnetic
susceptibility does not happen, hence \( \chi(0) \to 0 \) as \( D \to 0 \). This observation disagrees with experiments where \( \chi(0) \) is large and of order \( N_0 \mu^2_{e_{\text{eff}}} / 3k_B T_K \) provided we neglect the controversial up-turn of \( \chi(T) \) at low temperatures [26].
BIBLIOGRAPHY

129


