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KNIGHT SHIFT ANOMALIES IN HEAVY ELECTRON MATERIALS

DISSERTATION

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

By

Eunsik Kim, B.S., M.S.

* * * * *

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To My Parents

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CHAPTER I

Introduction and Review

1.1 Introduction

This dissertation is concerned with Knight shift anomalies, which are a deviation from a linear relation of the Knight shift $K(T)$ to the magnetic susceptibility $\chi(T)$ below the Kondo temperature T_0 , in heavy electron materials. In the NMR experiment, the measured resonance frequency in the metallic compound is shifted from that for another nonmetallic compound which contains the same NMR nuclei in as close as possible to the same environment. The Knight shift, the shift in the resonance frequency of nuclear magnetic resonance study, is due to the hyperfine interaction between the nuclear spin and conduction electrons polarized by the applied magnetic field. The origin of the Knight shift anomalies in metals with localized magnetic moments which undergo the Kondo effect has been a subject of great interest in the condensed matter community over a period of nearly twenty five years [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11]. If the impurities in metals have local magnetic moments, they display interesting properties comparing to metals with nonmagnetic impurities, such as resistivity minimum and anomalies in specific heat and susceptibility. This Kondo

effect is a consequence of the magnetic ion and conduction electron interaction. The central physical concept is that the many body screening cloud surrounding a Kondo impurity site should give rise to an anomalous temperature dependent Knight shift at nuclear sites due to the coupling of the local moment to the nuclear spin through the screening cloud [1, 3, 4, 5, 9, 10]. Such a “non-linear Knight shift anomaly” is to be distinguished from the non-linear susceptibility related to the field dependence of χ . Another way to describe this effect is to say that in the absence of an anomaly, the contribution $K(\vec{r}, T)$ from a local moment at distance $\vec{r}$ from the nucleus can be written as $f(\vec{r})\chi(T)$. This factorization does not hold if there is an anomaly (instead $K(\vec{r}, T) = f(\vec{r}, T)\chi(T)$ due to the temperature dependent polarization cloud). After Heeger [1] suggested that the anomalous spin cloud was detected at low temperatures, the existence of a conduction electron spin cloud with huge coherence length $\xi_K = \hbar v_F / k_B T_0$, where v_F is the Fermi velocity and T_0 is the Kondo temperature has been the main issue of this area.

To help clear up this conflict is the main motivation of this dissertation. The Knight shift calculations presented here are the first performed using a realistic impurity model.

This dissertation is organized as follows. The rest of this chapter is a review of the Kondo effect and the Knight shift anomaly in heavy electron materials. First, general characteristics of the Kondo effect are discussed. In the next section, the Knight shift will be briefly introduced, and I will review from the early to recent works about Knight shift anomalies of heavy electron systems, for both theoretical

and experimental studies. This review will motivate this dissertation work.

In chapter II, the model Hamiltonian is introduced for both Ce and U compound. Also methods which are used to evaluate the Knight shift, such as the Non Crossing Approximation(NCA) and average-T matrix approximation(ATA) are briefly explained. Results from the RKKY interaction will be mentioned as a comparison. Our formalisms for the numerical calculation are explained, and a detailed derivation of the Knight shift Feynman diagram will be given in the appendices.

In the next chapter, the numerical results for Ce and Yb ions which are single channel Kondo materials and for U ions in a proposed quadrupolar Kondo alloy will be examined and compared with the experimental results. The calculated NMR Knight shift of Ce and Yb compounds show low temperature anomalies and agree well with the experimental results. But, there is no calculated Knight shift anomaly for the proposed quadrupolar Kondo U compound, in contrast to experiment.

The last chapter includes conclusions and directions for future work.

1.2 Kondo Effect

1.2.1 Resistivity Minimum

The existence of localized moments in dilute alloys that couple to conduction electrons has important consequences for the electrical conductivity. The magnetic impurities act as scattering centers, and if they are the predominant type of impurity or lattice imperfection, then at low enough temperatures the scattering they cause will

be the primary source of electrical resistance. The nonmagnetic scatterers lead to a temperature independent term toward which the resistivity monotonically drops with decreasing temperature (the so-called residual resistivity). In magnetic alloys, however, it has been known since 1930[12] that instead of dropping monotonically the resistivity has a rather shallow minimum occurring at a low temperature that depends weakly on the concentration of magnetic impurities (see Fig 1.1). This has been observed in alloys of Cu, Ag, Au, Mg, Zn, with Cr, Mn, and Fe as impurities, among others.

In 1963, Kondo [14] explained that this minimum arises from some unexpected features of the scattering of conduction electrons off a local magnetic moment. The Hamiltonian of this simplified model is

$$\mathcal{H} = \sum_{\mathbf{k}\alpha} c_{\mathbf{k}} c_{\mathbf{k}\alpha}^{\dagger} c_{\mathbf{k}\alpha} - \frac{J}{2N} \sum_{\mathbf{k}\mathbf{k}'} c_{\mathbf{k}\alpha}^{\dagger} \vec{\sigma}_{\alpha\beta} c_{\mathbf{k}'\alpha} \cdot \vec{S}_I \quad (1.1)$$

where $c_{\mathbf{k}\alpha}$ is the annihilation operator of the conduction electron, α is the spin index, $\vec{\sigma}$ are Pauli matrices, $\vec{S}_I$ is the spin operator of the impurity, and $J < 0$ is the exchange coupling. The coupling between conduction electrons and local moments leads to scattering events in which the electron spin is flipped (with a compensating change of spin on the local moment). The anomalously high scattering probability of magnetic ions at low temperatures is a consequence of the dynamic nature of the scattering induced by the exchange coupling and the sharpness of the Fermi surface at low temperatures. Prior to Kondo's analysis, this scattering was treated only to leading order in perturbation theory and was found not to differ qualitatively from nonmagnetic scattering. Kondo discovered, however, that in all higher orders of

Figure 1.1: The resistivity minimum for various dilute alloys of iron in copper. (R_0 is the resistivity at 0°C .) The position of the minimum depends on the concentration of iron. ([13])

perturbation theory the magnetic scattering cross section is divergent, yielding an infinite resistivity.

The divergence depends critically on there being a sharp cutoff in the conduction electron wave vector distribution, as there is at $T = 0$. Subsequent analysis by Kondo and others has shown that the thermal rounding of the electron distribution removes the divergence, yielding instead a term in the impurity contribution to the resistivity that increases with decreasing temperature. The central result is that the spin-dependent contribution to the resistivity is

$$\rho_{\text{spin}} = c\rho_M \left[1 + \frac{3zJ}{E_F} \ln T \right] = c\rho_0 - c\rho_1 \ln T \quad (1.2)$$

where J is the exchange energy, z the number of nearest neighbors, c the concentration, and ρ_M is a measure of the strength of the exchange scattering. The spin resistivity increases toward low temperatures if J is negative. Adding this term to the phonon contribution, which decreases as the temperature falls as T^5 gives the total resistivity. The total resistivity is

$$\rho = aT^5 + c\rho_0 - c\rho_1 \ln T \quad (1.3)$$

with a minimum at

$$\frac{d\rho}{dT} = 5aT^4 - c\rho_1/T = 0 \quad (1.4)$$

whence

$$T_{\text{min}} = (c\rho_1/5a)^{1/5} \quad (1.5)$$

The temperature at which the resistivity is a minimum varies as the one-fifth power of the concentration of the magnetic impurity, in agreement with experiment at least for Fe in Cu.

In spite of the simple model Hamiltonian, a magnetic $S_I = 1/2$ local moment interacting with the conduction electron gas, this result is an indication that the problem is explicitly a many body problem, meaning that the electron in state $\vec{k}$ which is being scattered is sensitive to the occupation of all other electron states $\vec{q}$.

1.2.2 Other Physical Properties

This Kondo model can explain the anomalies in the transport coefficients, specific heat and magnetic susceptibility for some alloys with magnetic impurities. All the anomalies connect with the crossover from magnetic behavior to non-magnetic behavior characterized by Kondo temperature T_0 . At high temperatures $T > T_0$, the impurity resistivity increases logarithmically as the temperature decreases, and saturates to a finite value at low temperatures below $T < T_0$. The magnetic susceptibility has a Curie-Weiss form at high temperatures and shows Pauli paramagnetism at low temperatures. It is explained by the fact that the magnetic moments which exist at high temperatures are screened out by the conduction electron spin clouds at low temperatures with the formation of a singlet ground state. This conduction spin cloud and the Knight shift anomaly will be discussed more in the next section.

For this single channel Kondo model, there is only one characteristic energy scale, the Kondo temperature T_0 , provided that the temperature T is much smaller than the conduction electron bandwidth D , and corrections of order T/D are neglected. The Kondo temperature is given by

$$k_B T_0 = D[N(0)J]^{1/2} \exp(-1/N(0)J), \quad (1.6)$$

where $N(0)$ is the conduction electron density of states at the Fermi level. Any physical quantities are universal functions of T/T_0 , and only T_0 is material dependent.

The Kondo effect is characterized by the development of the Kondo resonance peak near the Fermi level in the local atomic spectral functions. The narrow but highly peaked structure with width of order of the Kondo energy scale leads to anomalies in various measurable physical properties which we mentioned earlier.

1.3 Review of the Knight Shift Anomalies of Heavy Electron Materials

In this section, first we will introduce the Knight shift for the general case. Then theoretical and experimental works about the Knight shift anomaly for the heavy electron materials will be reviewed. Whether there is an observable conduction electron spin cloud with huge coherence length has been an issue in condensed matter physics more than 25 years and this is our main motivation to carry out this dissertation.

1.3.1 Introduction to the Knight Shift

We consider a nucleus that possesses a magnetic moment $\vec{\mu}_N$ and an angular momentum $\hbar\vec{I}$. The two quantities are parallel, and we may write

$$\vec{\mu}_N = g_N \hbar \vec{I} \quad (1.7)$$

where g_N is the nuclear g factor. By convention $\vec{I}$ denotes the nuclear angular momentum measured in units of $\hbar$.

The energy of interaction with the applied magnetic field is

$$U = -\vec{\mu}_N \cdot \vec{B}_a \quad (1.8)$$

if $\vec{B}_a = B_0 \hat{z}$, then

$$U = -\mu_z B_0 = -g_N \hbar B_0 I_z. \quad (1.9)$$

An equal splitting of the $(2I + 1)$ sub-levels is produced and the allowed values of I_z are $m_I = I, I - 1, \dots, -I$, and $U = -m_I g_N \hbar B_0$.

There can be resonance absorption of electromagnetic radiation of angular frequency ω_0 , if $\hbar\omega_0$ denotes the energy difference between the adjacent levels. Thus, $\hbar\omega_0 = g_N \hbar B_0$, or

$$\omega_0 = g_N B_0. \quad (1.10)$$

This nuclear magnetic resonant absorption may be observed in a number of ways. One method is to place a sample of the material being investigated in a microwave cavity tuned to a particular frequency, and to apply a slowly varying magnetic field. Resonance may be detected from the characteristics of the electronic circuit in which the cavity is placed. Then applied field at resonance is measured. Other methods involve fixing the applied static field and varying the radio-frequency (rf) perturbing field and looking for a resonant frequency. The measured resonance frequency depends on not only the externally applied magnetic field but also the hyperfine field.

The hyperfine interaction is the magnetic interaction between the magnetic moment of a nucleus and the magnetic moment of an electron. To an observer stationed on the nucleus, the interaction is caused by the magnetic field produced by the magnetic moment of the electron and by the motion of the electron about the nucleus.

The contact hyperfine interaction which arises from the electron spin current about the nucleus has an important role in solids. The contact hyperfine interaction has the form

$$U = a\vec{\mu}_I \cdot \vec{\mu}_B \sim \vec{I} \cdot \vec{S} \quad (1.11)$$

where $\vec{I}$ is the nuclear spin in units of $\hbar$ and $\vec{S}$ is the electron spin density at the nucleus. At a fixed frequency the resonance of the nuclear spin is observed at a slightly different magnetic field in a metal than in a diamagnetic solid containing the same NMR nuclei in as nearly as possible the same environment except for the absence of the metallic state. The effect is known as the Knight shift or the metallic shift. It is due to the hyperfine interaction between the nucleus and the conduction electrons polarized by the magnetic field. This Knight shift measurement is a valuable tool for the study of conduction electrons near the Fermi level in the metal.

1.3.2 Conduction Electron Cloud

In the simplest approximation, the added electron is bound into a singlet with the impurity [15]. Because of the falloff the amplitude of wave function with the energy ϵ_k , only states within roughly $\delta k \sim (k_B T_0 / E_F) k_F$ of the Fermi surface are involved in the singlet. As a result, in coordinate space, the singlet wave function extends to a very large distance of order $(\delta k)^{-1}$. Heeger *et al.* [16] calculated the susceptibility at $T = 0K$ using the Appelbaum-Kondo theory [17, 18] and found

$$\chi = \chi_{\text{Pauli}} + \chi_L + \chi_Q \quad (1.12)$$

where

$$\chi_L = \chi_Q = |J|\rho[\mu^2/(9/8)k_B T_0] \quad (1.13)$$

Equations (1.12) and (1.13) give the very interesting result that one half the excess susceptibility is localized on the impurity site (χ_L) and one-half is associated with the partially polarized quasi particle(χ_Q). The associated spin polarization around the partially magnetized impurity is given by

$$\sigma(r) = \sigma_0 + \sigma_{RKKY}(r) + \sigma_Q(r) \quad (1.14)$$

where σ_0 is the uniform polarization due to the external field, $\sigma_{RKKY}(r)$ is the usual RKKY term as written in Eq. 2.43, and $\sigma_Q(0)$ is the quasiparticle term

$$\langle \sigma_Q(r) \rangle = \langle S_z \rangle \frac{3}{2} N \frac{k_B T_0}{E_F} \left(\frac{\sin k_F r}{k_F r} \right)^2 \ln^2(r/\xi). \quad (1.15)$$

where $\xi_K = (2E_F/k_B T_0)k_F^{-1}$. This expression is valid for $r < \xi_K$, and at greater distances $\sigma_Q(r)$ rapidly approaches zero. In both the RKKY term and $\sigma_Q(r)$ term the value $\langle S_z \rangle$ is not the free spin value but is determined by the local susceptibility χ_L . The existence of the RKKY term for $T < T_0$ was shown by Suhl [19].

The technique of nuclear magnetic resonance has been of primary importance in the development of our current understanding of the localized moment problem. The reasons are twofold. First, the nuclei in the host metal in the vicinity of the impurity are sensitive to local perturbations in the spin density(via the hyperfine interaction) and the charge density(via the nuclear quadrupolar interaction). Moreover, the nuclei themselves are only weakly coupled to the electronic system and therefore act as passive "spies" into the phenomena of interest. Secondly, the nuclear relaxation is

sensitive to the low-lying excitations of the electronic system and consequently can provide information on the dynamical aspects of the impurity problem. For the most part NMR experiments in heavy electron compounds are carried out on the nuclei on the non- f ions, so that coupling to the f moments occurs via indirect interactions such as transferred hyperfine and dipolar fields.

The NMR experiment of Boyce and Slichter [2] on Fe impurities in Cu metals showed no evidence for the Knight shift anomaly at low temperature and were interpreted to indicate the absence of this screening cloud or the screening cloud of size of order a lattice spacing. This mixed results have led to theoretical discussions about the sizes of the screening conduction electron spin cloud or even the existence.

In contrast, pronounced Knight shift anomalies have been observed in the concentrated heavy electron materials CeSn_3 [6, 8] and YbCuAl [7, 8], which have been described as Kondo lattice systems with $T_0 \simeq 400\text{K}$. In view of the Boyce-Slichter result, the question is raised whether these anomalies represent a coherent effect of the periodic lattice rather than a single ion effect. However, recent experiments on the proposed quadrupolar Kondo alloy[20, 21] $\text{Y}_{1-x}\text{U}_x\text{Pd}_3$ demonstrate that for concentrations of 0.1-0.2 there are pronounced non-linearities in the Y Knight shift for sufficiently large distances away from the U ion[11].

Ishii [4, 5] calculated the field induced spin polarization for the degenerated Anderson model and confirmed that anomalous spin cloud is formed outside of the Kondo screening length ξ_K at $T \rightarrow 0$. The spin polarization $\sigma(r)$ for electron-hole symmetry

case ($c_d = -U/2$) is given by

$$\sigma(r) = \frac{\chi H}{g\mu_B} \frac{\cos 2k_F r}{4\pi r^3} \left[1 - \frac{2E_F}{k_F r \Delta} \bar{\gamma} \right]. \quad (1.16)$$

where $\bar{\gamma} = \chi_{\uparrow\uparrow}$ for $U \rightarrow 0$ and $3/2(2l+3)\chi_{\uparrow\uparrow}$ for $U \rightarrow \infty$. $\chi_{\uparrow\uparrow}$ changes from $(g\mu_B)^2/2\pi\Gamma$ for $U = 0$ to $(g\mu_B)^2 S(S+1)/3k_B T_0$ for $s-d$ Exchange model ($U = \infty$). Therefore coherence length $\xi_K = 2E_F/k_F \Delta \bar{\gamma}$ varies from $2\hbar v_F/\Gamma$ at $U = 0$ to $2\pi\hbar v_F/3k_B T_0$ in the $s-d$ limit. Also, for strong $U/\pi\Gamma$ limit, spin polarization is calculated for $r < \xi_K$. It is given by

$$\sigma(r) = \frac{4\Gamma}{\pi U} \frac{\chi H}{g\mu_B} \frac{\cos 2k_F r}{4\pi r^3}. \quad (1.17)$$

By the relation $4V^2/U = -J/2N$ [22], Above spin polarization is just the RKKY spin polarization. Compare the equations (1.16) and (1.17), conduction electron spin cloud which is formed outside the Kondo coherence length has RKKY form but with $2N/N(0)J$ times bigger amplitude than the spin cloud inside the Kondo coherence length.

K. Chen C. Jayaprakash and H.R. Krishna-Muthy [9] calculated zero frequency response function $C(\vec{r}, T)$ around magnetic impurity, using perturbative thermodynamic scaling procedure and nonperturbative renormalization group method for $S = 1/2$ Kondo model. Host nuclei near a magnetic impurity produce satellites in the tail of main resonance peak of NMR experiment, with a Knight shift given by $K + \Delta K$, where K is the Knight shift of the pure host Host nuclei near a magnetic impurity produce satellites in the tail of main resonance peak of NMR experiment, with a Knight shift given by $K + \Delta K$, where $K = \rho_0 g_e/2$ is the Knight shift of the

pure host. Then ΔK is

$$\Delta K = C(\vec{r}, T) - K \quad (1.18)$$

They showed that this Knight shift is factorized to the temperature and spatial dependence forms, such as

$$\Delta K = F(\vec{r})\chi(T) \quad (1.19)$$

where $\chi(T)$ is the magnetic susceptibility. The computed $F(r)$ shows the RKKY interaction form.

The conduction electron spin polarization in the Anderson model has been studied with the NCA previously by W. Pollwein *et al.* [34]. But this study was carried out only for the spin 1/2 model with infinite Coulomb repulsion, and for a limited parameter regime (only results for very low T_0 values and short distances ($r \ll \xi_K$) have been numerically calculated). In consequence, no strong evidence was found for a Knight shift anisotropy in this previous work.

Recently, E. Sørensen and I. Affleck [23, 24, 25] showed that the Kondo coherence length $\xi_K = \hbar v_F / k_B T_0$, varies when temperature changes by combining a finite size scaling ansatz with density matrix renormalization group calculations. They write the scaling hypothesis for three dimensional susceptibility is

$$\chi_{\text{imp}} = \chi - \rho/2 = \frac{1}{8\pi^2 v_F r^2} \cos(2k_F r) f(rT/v_F, T/T_0) \quad (r \gg 1/k_F; T, T_0 \ll E_F), \quad (1.20)$$

where f is a real universal scaling function. $\rho/2$ is the standard Pauli bulk susceptibility with ρ the density of states per spin. At higher temperatures $T > T_0$, the local susceptibility shows RKKY behavior and at lower temperatures $T < T_0$ it has

a local Fermi liquid form. So the Knight shift has longer range at low temperatures where the conduction electron screening cloud has formed than at high temperatures where it has not. They tried to explain the experiment by Boyce and Slichter [2] by possible factorization of the scaling functions deep inside the screening cloud where the experiments was done.

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CHAPTER II

Model

In this chapter, the model Hamiltonian and formalisms which are used to evaluate the magnetic susceptibility and the Knight shift are developed.

We use the $U = \infty$ single impurity Anderson model as our model Hamiltonian. Schematics of this model are shown in Fig 2.1 This $U = \infty$ can be a good approximation in the limit when the ratio of the virtual $4f$ level width Γ to the on site Coulomb interaction U is small. For the real materials this energy is of the order of $U = 5\text{eV}$ [1, 2], and the hybridization width in our calculation is of the order of $\Gamma = 0.1\text{eV}$.

This model Hamiltonian is introduced in the first section for both Ce(Yb) compounds which are concentrated heavy electron materials and U compounds which are proposed quadrupolar Kondo alloys. Spin-orbit coupling is included for all materials, but the crystal electric field is included only for the U ions. In the next section, the non-crossing approximation (NCA), which is the method we used to derive the Knight shift, will be reviewed. The RKKY interaction will be briefly discussed in section 2.3

In section 2.4, we derive the magnetic susceptibility in NCA, and the next section

Figure 2.1: Schematics of the $U = \infty$ single impurity Anderson model for Ce ions. D is the conduction band width and V is the single particle hybridization strength. On site Coulomb interaction U is infinity in our model.

gives the Knight shift evaluation. The leading order Feynman diagram which is used for evaluation is introduced. The last section is devoted to inclusion of the lattice coherence effects on the Knight shift. Also, the average-T matrix approximation which is used to include the effects of coherence is explained in the last section. Exact formalisms are derived in the appendices.

2.1 Model Hamiltonian

We used the on-site Coulomb interaction $U = \infty$ single impurity Anderson model [3]. For Ce(Yb) ions, we keep f^0 and f^1 (f^{14} and f^{13}) configurations, and for U ions, we keep f^2 and f^3 configurations. For Ce and Yb ions, spin orbit coupling is included and for U ions, spin orbit coupling and also crystal field splittings are included. The crystal electric field(CEF) will split the spin-orbit multiplet. The CEF can mix two different angular momentum multiplets(j, j'), but the correction, of order $| \langle j || H_{CEF} || j' \rangle |^2 / \Delta_{so}$ by the second order perturbation theory, but the shift is small, is of the order of $0.1 \times \Delta_{CEF}$. So the mixing term between two different j 's in the presence of CEF is neglected. These effects in the Anderson model were first considered by Hirst [5] based on group theory.

2.1.1 Ce^{3+} and Yb^{3+} Ions

We shall first discuss the situation for Ce^{3+} and Yb^{3+} ions, and write down the model only for the Ce case(the Yb^{3+} ion has a lone $4f$ hole and our procedure describes this

Table 1: Relation between Ce and Yb compounds and their parameter values. j_g is the ground state spin-orbit multiplet angular momentum and j_{ex} is the excited state multiplet angular momentum. $N_g(N_{ex})$ is the degeneracy of the ground (first excited) state multiplet. ϵ_f is the energy of the ground state. and Δ_{so} is the energy difference between the j_g and j_{ex} multiplets

	Ce	Yb
Configuration	$4f^1$ $4f^0$	$4f^{13}$ $4f^{14}$
j_g	5/2	7/2
j_{ex}	7/2	5/2
N_g	6	8
N_{ex}	8	6
ϵ_f	-2eV	-1eV
Δ_{so}	0.29eV	1.3eV

with a simple particle hole transformation).

For a single Ce site at the origin, the model is

$$\mathcal{H} = \mathcal{H}_c + \mathcal{H}_f + \mathcal{H}_{cf} + \mathcal{H}_\tau \quad (2.1)$$

with

$$\mathcal{H}_c = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} c_{\vec{k}\sigma}^\dagger c_{\vec{k}\sigma} \quad (2.2)$$

the conduction band term for electrons with a broad featureless density of states of width D , taken to be Lorentzian here for convenience, with

$$\mathcal{H}_f = \sum_{jm_j} \epsilon_{fj} |f^1 jm_j\rangle \langle f^1 jm_j| \quad (2.3)$$

where $j = 5/2, 7/2$ indexes the angular momentum multiplets of the Ce ion having azimuthal quantum numbers m , with $\epsilon_{f5/2} = -2\text{eV}$, $\epsilon_{f7/2} = \epsilon_{f5/2} + \Delta_{so} = -1.71\text{eV}$

(we take the f^0 configuration at zero energy), with

$$\mathcal{H}_{cf} = \sum_{\vec{k}jm\sigma} [V_{\vec{k}j\sigma m} c_{\vec{k}\sigma}^\dagger |f^0 0\rangle \langle f^1 jm| + h.c.] \quad (2.4)$$

where $V_{\vec{k}j\sigma m} = V Y_{3m, -\sigma}(\hat{k}) \langle 3m_j - \sigma, 1/2\sigma | jm_j \rangle / \sqrt{N_s}$, V being the one particle hybridization strength and N_s the number of sites. We can rewrite the hybridization Hamiltonian as

$$\mathcal{H}_{cf} = \sum_{kjm_j} [V_k c_{kjm_j}^\dagger |f^0 0\rangle \langle f^1 jm_j| + h.c.] \quad (2.5)$$

where

$$c_{kjm_j}^\dagger = \sum_{m\sigma} \langle 3m \frac{1}{2}\sigma | jm_j \rangle c_{km\sigma}^\dagger \quad (2.6)$$

with $c_{km\sigma} = k \int d\hat{k} Y_{3m}^*(\hat{k}) c_{\vec{k}\sigma}$. For the Yb case, the hybridization Hamiltonian is given by

$$\mathcal{H}_{cf} = \sum_{kjm_j} [V_k c_{kjm_j}^\dagger |f^{13} j - m_j\rangle \langle f^{14} 0| + h.c.]. \quad (2.7)$$

$\mathcal{H}_z$, the Zeeman energy of the electronic system for a magnetic field H_z applied along the z -axis is given by

$$\mathcal{H}_z = -\mu_B H_z [2 \sum_{\vec{k}\sigma} \sigma n_{\vec{k},\sigma} - \sum_{jm} g_j m |f^1 jm\rangle \langle f^1 jm|]. \quad (2.8)$$

In addition to this, we must add a term coupling the nuclear spin system to the conduction electrons, which we take to be of a simple contact form $\sim \vec{I}(\vec{r}) \cdot \vec{S}(\vec{r})$ for each nuclear spin $\vec{I}(\vec{r})$ at position $\vec{r}$ with $\vec{S}(\vec{r})$ the conduction spin density at the nuclear site, and a nuclear Zeeman term. In terms of the parameters, the Kondo scale characterizing the low energy physics is given by

$$k_B T_0 = D \left(\frac{\Gamma}{\pi |\epsilon_f|} \right)^{1/N_g} \left(\frac{D}{\Delta_{so}} \right)^{N_{ez}/N_g} \exp\left(\frac{\pi \epsilon_f}{N_g \Gamma} \right) \quad (2.9)$$

where the single particle hybridization width $\Gamma = \pi N(0)V^2$ with $N(0)$ which is the density of the states at the Fermi energy. Other parameters are defined in Table 1.

2.1.2 U^{4+} Ions

For the U compound which has the cubic $AuCu_3$ structure, the crystal field effect (CEF), which arises from the inhomogeneous electrostatic field produced by the neighboring charges of crystal lattice, must be included. This crystal electric field effects lift the angular momentum degeneracy of U ions and their spin-orbit multiplet decomposes into irreducible representation of the cubic field. The $f^2, j = 4$ Hund's rule ground state of U compound is split to a Γ_3 nonmagnetic doublet, Γ_5 and Γ_4 magnetic triplet and Γ_1 singlet states[6]. And $f^3, j = 9/2$ spin-orbit multiplet is split to Γ_7 doublet and two Γ_8 quartets. For simple example, the electrostatic potential in CEF Hamiltonian can be derived by the point charge model which takes only the nearest neighbor point ions of charge Z . Generally the CEF potential only depends on the crystal symmetry and operator equivalent method [4] is used for the calculation. For explicit derivation, see Appendix A and the articles by K.R. Lea, M.J. Leask and W.P. Wolf [7] and by M.T. Hutchings [8]. The eigenstates of Γ_i CEF states for $j = 4$ and $j = 9/2$ multiplets are in Table 3 and Table 4 [7, 8]. In cubic symmetry, the coefficients of CEF states depend upon the parameter x which is fixed by the ratio of the fourth and sixth degree terms in a short distance expansion of the cubic field in the Hamiltonian of the crystal electric field, and upon the parameter W which is an overall scale factor fixed by the crystal field strength. In this calculation, we use

Table 2: Parameter values for $\text{Y}_{0.8}\text{U}_{0.2}\text{Pd}_3$ in unit of conduction electron band width $D = 3\text{eV}$. For the definition of x and W , see Appendix A. x_2 and W_2 are for f^2 configuration and x_3 and W_3 are for f^3 configuration.

c_f	-0.333
Δ_{35}	0.003
Δ_{34}	0.008175
Δ_{31}	0.019621
Δ_{681}	0.000136
Δ_{682}	0.013190
Γ	0.15
x_2	-0.648
W_2	-3.95×10^{-4}
x_3	0.3693
W_3	2.746×10^{-4}

$x_3 = 0.3693$ and $W_3 = 2.746 \times 10^{-4}$ to have $j = 9/2$ Γ_6 for the ground state of the f^3 configuration and $x_2 = -0.648$ and $W_2 = -3.95 \times 10^{-4}$ to have $j = 4$ Γ_3 for the ground state for f^2 configuration. For further details, see Appendix A. The choice of the overall phase is arbitrary in defining the CEF eigenstates.

Before proceeding further, we provide a brief description of the different irrep labels of the cubic group:

- (1) Γ_1 and Γ_2 are orbital singlets.
- (2) Γ_3 is an orbital (non-magnetic, or non-Kramers') doublet and usually labeled by $\pm$.

Table 3: Crystal electric field energy eigenstate for $j = 4$ multiplet in the cubic symmetry. The coefficient is independent of x

$j = 4$ multiplet	states
$ \Gamma_1\rangle$	$\sqrt{\frac{5}{24}} 4\rangle + \sqrt{\frac{7}{12}} 0\rangle + \sqrt{\frac{5}{24}} -4\rangle$
$ \Gamma_3; +\rangle$	$\frac{1}{\sqrt{2}}(2\rangle + -2\rangle)$
$ \Gamma_3; -\rangle$	$-\sqrt{\frac{5}{24}} 4\rangle + \sqrt{\frac{7}{12}} 0\rangle - \sqrt{\frac{5}{24}} -4\rangle$
$ \Gamma_4; 0\rangle$	$\frac{1}{\sqrt{2}}(4\rangle - -4\rangle)$
$ \Gamma_4; \pm 1\rangle$	$\frac{1}{\sqrt{8}} \mp 3\rangle + \sqrt{\frac{7}{8}} \pm 1\rangle$
$ \Gamma_6; 0\rangle$	$\frac{1}{\sqrt{2}}(2\rangle - -2\rangle)$
$ \Gamma_6; \pm 1\rangle$	$\frac{1}{\sqrt{8}} \mp 3\rangle - \sqrt{\frac{7}{8}} \pm 1\rangle$

Table 4: Crystal electric field energy eigenstate for $j = 9/2$ multiplet in the cubic symmetry, the coefficient a_i 's and b_j 's depend on the x which is the parameter which depends on the ratio of the fourth and sixth degree cubic field in the Hamiltonian of the crystal electric field. In this calculation, we use $x_3 = 0.3693$ and $W_3 = 2.746 \times 10^{-4}$ to have $j = 9/2$ Γ_6 for the ground state of the f^3 configuration and $x_2 = -0.648$ and $W_2 = -3.95 \times 10^{-4}$ to have $j = 4$ Γ_3 for the ground state for f^2 configuration.

$j = 9/2$ multiplet	states
$ \Gamma_6; \pm\rangle$	$\sqrt{\frac{9}{24}} \pm \frac{9}{2}\rangle + \sqrt{\frac{1}{24}} \mp \frac{7}{2}\rangle + \sqrt{\frac{7}{12}} \pm \frac{1}{2}\rangle$
$ \Gamma_{8a}; 1, \pm\rangle$	$a_1 \pm \frac{9}{2}\rangle + a_2 \mp \frac{7}{2}\rangle + a_3 \pm \frac{1}{2}\rangle$
$ \Gamma_{8a}; 2, \pm\rangle$	$b_1 \pm \frac{5}{2}\rangle + b_2 \mp \frac{3}{2}\rangle$
$ \Gamma_{8b}; 1, \pm\rangle$	$a_6 \pm \frac{9}{2}\rangle + a_7 \mp \frac{7}{2}\rangle + a_8 \pm \frac{1}{2}\rangle$
$ \Gamma_{8b}; 2, \pm\rangle$	$b_3 \pm \frac{5}{2}\rangle + b_4 \mp \frac{3}{2}\rangle$

For $x = 0.3693$, $a_1 = -0.1290$, $a_2 = -0.1582$, $a_3 = 0.9789$, $b_1 = 0.7361$, $b_2 = -0.6769$, $a_6 = 0.7800$, $a_7 = -0.6358$, $a_8 = 0.0016$, $b_3 = 0.6769$, and $b_4 = 0.7361$.

Table 5: Crystal electric field energy eigenstates for $j = 5/2$ multiplet in the cubic symmetry.

$j = 5/2$ Multiplet	States
$ \Gamma_7^{(5/2)}; \uparrow / \downarrow\rangle$	$-\sqrt{\frac{1}{6}} \pm 5/2\rangle + \sqrt{\frac{5}{6}} \mp 3/2\rangle$
$ \Gamma_6^{(5/2)}; +, \uparrow / \downarrow\rangle$	$ \pm 1/2\rangle$
$ \Gamma_8^{(5/2)}; -, \uparrow / \downarrow\rangle$	$\sqrt{\frac{5}{6}} \pm 5/2\rangle + \sqrt{\frac{1}{6}} \mp 3/2\rangle$

(3) Γ_4 and Γ_8 are magnetic triplets and labeled by $0, \pm 1$.

(4) Γ_6 and Γ_7 are magnetic Kramers' doublets and labeled with pseudo-spin $\uparrow$ or $\downarrow$.

That is, the Γ_6 and Γ_7 CEF states are similar to the $j = 1/2$ angular momentum manifold.

(5) Γ_8 is a magnetic quartet ($\Gamma_8 = \Gamma_3 \otimes \Gamma_7$), and labeled by $\pm \uparrow / \downarrow$.

Now, let's consider the conduction electrons. According to the Anderson model picture, the conduction electrons can hop on and off the atomic orbitals at the impurity site. For the f electrons in U, we expect the $l = 3$ conduction electron partial waves are most strongly coupled to the f electrons. For the isotropic hybridization, only the $l = 3$ components can hybridize with the f orbitals. In the presence of the spin-orbit coupling, we have $j = 5/2, 7/2$ conduction electron states. These j multiplets further split into the CEF irreducible representations, Γ_6, Γ_7 doublets and Γ_8 quartet in crystal environment. The CEF eigenstates for $j = 5/2$, and $j = 7/2$ multiplets are listed in Table 5 and Table 6.

Table 6: Crystal electric field energy eigenstates for $j = 7/2$ multiplet in the cubic symmetry.

$j = 7/2$ Multiplet	States
$ \Gamma_6^{(7/2)}; \uparrow / \downarrow\rangle$	$\pm\sqrt{\frac{5}{12}} \mp 7/2\rangle \pm \sqrt{\frac{7}{12}} \pm 1/2\rangle$
$ \Gamma_7^{(7/2)}; \uparrow / \downarrow\rangle$	$\pm\frac{\sqrt{3}}{2} \pm 5/2\rangle \mp \frac{1}{2} \mp 3/2\rangle$
$ \Gamma_8^{(7/2)}; +, \uparrow / \downarrow\rangle$	$\pm\sqrt{\frac{7}{12}} \mp 7/2\rangle \mp \sqrt{\frac{5}{12}} \pm 1/2\rangle$
$ \Gamma_8^{(7/2)}; -, \uparrow / \downarrow\rangle$	$\pm\frac{1}{2} \pm 5/2\rangle \pm \frac{\sqrt{3}}{2} \mp 3/2\rangle$

The hybridization Hamiltonian of our model U compound in the absence of the CEF is given by

$$\mathcal{H}_{cf} = \sum_{kj_c m_c} \sum_{m_2 m_3} [V_k c_{kj_c m_c}^\dagger \Lambda(j_c m_c; f^2 j_2 = 4m_2 | f^3 j_3 = \frac{9}{2} m_3) | f^2 j_2 = 4m_2 \rangle \langle f^3 j_3 = \frac{9}{2} m_3 | + h.c.], \quad (2.10)$$

Here the reduced matrix elements are

$$\begin{aligned} \Lambda(j_c m_c; f^2 j_2 = 4m_2 | f^3 j_3 = \frac{9}{2} m_3) &\equiv \langle f^2 j_2 = 4m_2 | f_{j_c m_c} | f^3 j_3 = \frac{9}{2} m_3 \rangle \\ &= K(j_c j_2 | j_3) \langle j_c m_c; j_2 m_2 | j_3 m_3 \rangle \end{aligned} \quad (2.11)$$

where $j_c = 5/2, 7/2$. The Wigner-Eckart theorem is used for the last line and the prefactor $K(j_c j_2 | j_3)$ is the fractional parentage coefficient. In our calculation where $j_2 = 4$ and $j_3 = 9/2$, $K(j_c j_2 | j_3) = \sqrt{7/9}$ for both $j_c = 5/2$ and $j_c = 7/2$. The Clebsch-Gordan coefficients $\langle j_c m_c; j_2 m_2 | j_3 m_3 \rangle$ are listed in Appendix B. If there is a crystal electric field, the Anderson hybridization between the CEF states Γ 's needs to

Table 7: Selection rules for the Anderson hybridization between $f^2 \Gamma$ and $f^3 \Gamma$ CEF states. The meaning, for example, is that a Γ_6 conduction electron doublet can combine with the $f_2 \Gamma_3$ doublet to make an $f^3 \Gamma_8$ quartet.

$\Gamma_c \otimes f^2 \Gamma$	$f^3 \Gamma$ CEF states
$\Gamma_c \otimes \Gamma_1$	Γ_c
$\Gamma_6 \otimes \Gamma_3$	Γ_8
$\Gamma_7 \otimes \Gamma_3$	Γ_8
$\Gamma_8 \otimes \Gamma_3$	$\Gamma_6 \oplus \Gamma_7 \oplus \Gamma_8$
$\Gamma_6 \otimes \Gamma_4$	$\Gamma_6 \oplus \Gamma_8$
$\Gamma_7 \otimes \Gamma_4$	$\Gamma_7 \oplus \Gamma_8$
$\Gamma_8 \otimes \Gamma_4$	$\Gamma_6 \oplus \Gamma_7 \oplus 2\Gamma_8$
$\Gamma_6 \otimes \Gamma_5$	$\Gamma_7 \oplus \Gamma_8$
$\Gamma_7 \otimes \Gamma_5$	$\Gamma_6 \oplus \Gamma_8$
$\Gamma_8 \otimes \Gamma_5$	$\Gamma_6 \oplus \Gamma_7 \oplus 2\Gamma_8$

be evaluated. We have

$$\begin{aligned}
 \mathcal{H}_{cf} &= \sum_{kjc\Gamma_c\alpha_c} \sum_{\Gamma\alpha\Gamma\beta} [V_k c_{kjc\Gamma_c\alpha_c}^\dagger \Lambda(jc\Gamma_c\alpha_c; 4\Gamma\alpha | \frac{9}{2}\Gamma\beta) |f^2 4\Gamma\alpha\rangle \langle f^3 \frac{9}{2}\Gamma\beta| + h.c.] \\
 &= \sum_{kjc\Gamma_c\alpha_c} \sum_{\Gamma\alpha\Gamma\beta} [V_k K(jc; 4 | \frac{9}{2}) \langle jc\Gamma_c\alpha_c; 4\Gamma\alpha | \frac{9}{2}\Gamma\beta \rangle c_{kjc\Gamma_c\alpha_c}^\dagger |f^2 4\Gamma\alpha\rangle \langle f^3 \frac{9}{2}\Gamma\beta| + h.c.],
 \end{aligned} \tag{2.12}$$

The reduced matrix $\Lambda(jc\Gamma_c\alpha_c; 4\Gamma\alpha | \frac{9}{2}\Gamma\beta)$ is implicitly defined in above equation. All the possible selection rules for the hybridization are listed in Table 7.

2.2 Non Crossing Approximation

We treat the Anderson Hamiltonian with the non-crossing approximation (NCA), a self-consistent diagrammatic perturbation theory discussed at length in the paper of Bickers *et al.*[10]. As we discussed above, the Anderson model which can be canonically transformed by the Schrieffer and Wolff transformation to the Kondo model at $U = \infty$ limit, is a good model Hamiltonian to describe heavy electron materials with f electrons. There have been techniques already developed, such as the Fermi liquid, Bethe ansatz approaches and numerical renormalization method which provide exact results for the ground state and thermodynamics for more general models. $1/N$ expansions and large N methods which have been successfully applied in other areas of physics such as critical phenomena and field theory are applied to this system with the new variable N , the large orbital degeneracy of the ground state of f electrons. This is useful because it provides ways of calculating the dynamic response functions, such as the one electron Green's functions and dynamic susceptibility. It was noted that, in a perturbative $1/N$ expansion, the f -electron spectral density exhibits a singularity at $\omega = T_A$, with $T_A \simeq D \exp(\pi \epsilon_f / N \Gamma)$. This singularity remains order by order, preventing a complete description of f photoemission and electronic transport. In order to remove this singularity, it is necessary to perform an infinite-order resummation in $1/N$. Resummations have been investigated within a variety of contexts, including the variational approach and the saddle-point approach. There are also techniques using partial resummations of diagrammatic perturbation theory [10, 12, 13, 14, 15, 16, 18, 19, 20, 21, 22, 23, 24]. Partial resummations incorporate

many desirable features of low-order perturbative expansions, provide a more satisfactory treatment of dynamic properties, and are simple to apply in finite-temperature calculations. In contrast, partial resummations are not appropriate in the Fermi-liquid regime, where a systematic treatment of low-energy electron-hole processes is essential. In this sense, the non-crossing approximation(NCA), a self-consistent diagrammatic perturbation theory discussed below serves a functional complementary to the other resummation approaches.

This method makes possible a more extensive comparison between the theoretical predictions and experimental results. The large N approaches give new insights from the simplifications that are found in the large N limit. These simple approximation schemes work very well for values of N that are of interest in applications to rare earth impurities. For example, the lowest spin-orbit split multiplet for Ce $4f^1$ has $j = 5/2$, corresponding to $N = 6$, and for Yb $4f^{13}$, $j = 7/2$, corresponding to $N = 8$. Even for $N = 2$ one can get good semi-quantitative results, which can be accurate to within a few percent for some quantities. It does show pathological behavior (due to the truncation of the diagrammatic expansion) for a temperature scale $T_p \ll T_0$ in this conventional Anderson model, provided the f^1 occupancy $n_f \geq 0.7$. In practice, this is not a problem for $N \geq 4$ as shown in Ref. [10], in that comparison of NCA results with exact thermodynamics from the Bethe-Ansatz shows agreement at the few percent level above T_p . Hence, this is a reliable method for our purposes.

In the NCA , our starting basis is the conduction band plus the atomic Hamiltonian projected to the atomic electron Fock space and treat the hybridization between

the conduction band and the atomic orbital as a perturbation. The strength of this approach is that the strong on-site Coulomb interaction for atomic electrons are treated accurately. The conventional Feynman diagram technique which uses Wick's theorem can not be applied for strongly correlated problems. Pseudo particle Green's functions are introduced for each atomic electron occupation state which is neither fermionic nor bosonic. Thus, a special Green's function technique was developed by many investigators [10, 12, 13, 14, 15, 16]. This approach may be justified by expansion in $1/N$ which reorders the diagrams by treating NV^2 as $O(1)$. Here N is the nominal atomic ground state degeneracy and V is the hybridization strength between the conduction band and the atomic orbitals.

The approach in the NCA is to write a propagator for each ionic state of the Ce site (i.e., f^1 $j = 5/2, 7/2$ and f^0 in the present model for Ce ions), insert a self-energy into the propagators of pseudo particles. This gives coupled integral equations for the ionic propagator self energies, $\Sigma_0(z)$, $\Sigma_{jm}(z)$. From the leading order diagrams of Fig. 2.2, the coupled equations for the self energies are

$$\begin{aligned}\Sigma_0(z) &= V^2 \sum_j N_j \sum_k \frac{f_k}{z + \epsilon_k - \epsilon_{fjm} - \Sigma_{jm}(z + \epsilon_k)} \\ &= V^2 \sum_j N_j \sum_k f_k G_{jm}(z + \epsilon_k)\end{aligned}\tag{2.13}$$

$$\begin{aligned}\Sigma_{jm}(z) &= V^2 \sum_k \frac{1 - f_k}{z - \epsilon_k - \Sigma_0(z - \epsilon_k)} \\ &= V^2 \sum_k (1 - f_k) D(z - \epsilon_k),\end{aligned}\tag{2.14}$$

where V is the hybridization strength between the conduction band and the atomic orbitals and N_j is the degeneracy of the spin-orbit multiplet j . The pseudo fermion

Figure 2.2: Leading order Feynman diagrams for self energies

(a) pseudoboson self energy, $\Sigma_0(z)$

(b) pseudo fermion(f^1, j multiplet) self energy $\Sigma_{jm}(z)$.

Green's functions for f^1 $j = 5/2, 7/2$ angular momentum multiplets are

$$G_{jm}(z) = \frac{1}{z - \epsilon_{fj} - \Sigma_{jm}(z)} \quad (2.15)$$

and the pseudo boson Green's function for the f^0 is

$$D(z) = \frac{1}{z - \Sigma_0(z)}. \quad (2.16)$$

It is convenient to introduce the spectral functions $A_{jm}(\omega)$, and $B(\omega)$ for pseudo-particle Green's functions.

$$\begin{aligned} G_{jm}(i\omega) &= \int \frac{d\rho}{\pi} \frac{A_{jm}(\rho)}{i\omega - \rho} \\ A_{jm}(\omega) &= -\text{Im } G_{jm}(\omega) \end{aligned} \quad (2.17)$$

$$\begin{aligned} D(i\nu) &= \int \frac{d\zeta}{\pi} \frac{B(\zeta)}{i\nu - \zeta} \\ B(\nu) &= -\text{Im } D(\nu) \end{aligned} \quad (2.18)$$

In addition to spectral functions $A_{jm}(\rho)$ and $B(\zeta)$, it is necessary to introduce negative frequency spectral functions $A_{jm}^{(-)}(\rho)$ and $B^{(-)}(\zeta)$. These spectra are given by

$$A_{jm}^{(-)}(\rho, T) = A_{jm}(\rho, T) e^{-\beta(\rho - E_0)} \quad (2.19)$$

$$B^{(-)}(\zeta, T) = B(\zeta, T) e^{-\beta(\zeta - E_0)}. \quad (2.20)$$

The impurity partition function Z_{4f} is given by

$$\begin{aligned} Z_{4f}(T) &= \int \frac{d\zeta}{\pi} [\sum_{jm} A_{jm}(\zeta, T) + B(\zeta, T)] e^{-\beta\zeta} \\ &= e^{-\beta E_0} \int \frac{d\zeta}{\pi} [\sum_{jm} A_{jm}^{(-)}(\zeta, T) + B^{(-)}(\zeta, T)]. \end{aligned} \quad (2.21)$$

Thus at $T \rightarrow 0$, $Z_{4f}(T)$ becomes

$$Z_{4f}(0) = e^{-\beta E_0}. \quad (2.22)$$

The iteration of these coupled equations for the self energies generates a set of diagrams which includes all non-crossing diagrams (but does not correspond to any specific order in the $1/N$ expansion by treating NV^2 as $O(1)$). The set of diagrams summed by these equations includes all the terms of order $O(1)$ and $O(1/N)$ and a subset of contributions from the higher order terms. The lowest order diagrams which are not included are of order $O(1/N^2)$. All the diagrams that enter at $O(1)$ and $O(1/N)$ have non-crossing conduction lines. Though the vertex correction, which is $O(1/N^2)$, is not included, this approach is a conserving approximation [14].

These self-consistent integral equations are solved to second order in the hybridization for the ionic propagator self energies. Then physical properties, such as resistivity and magnetic susceptibility χ , are calculated as convolutions of these propagators. Fig. 2.3 shows a leading order Feynman diagram for the static magnetic susceptibility and its convolution integral is given by Eq. (2.47). This is discussed more in section 2.4.

Our numerical procedure, briefly, consists of solving the NCA integral equations for the Anderson Hamiltonian specified above on a logarithmic mesh with order 600 points chosen to be centered about the singular structures near the ground state energy $E_0 \sim \epsilon_{f5/2}$. We then feed the self-consistent propagators for the empty and singly occupied orbitals into the convolution integrals obtained from the diagram of Fig. 2.4, which allows for evaluation of the Knight shift at arbitrary angle and dis-

tance from the nuclear site. This will be explained more in section 2.5. It is convenient to take the nuclear site as the origin in this case leading to phase factors $e^{-i\vec{k}\cdot\vec{R}}$ in the hybridization Hamiltonian $\mathcal{H}_{cf}$, where $\vec{R}$ is the nuclear-Ce site separation. These factors give the oscillations and position space angular dependence in the Knight shift K .

2.3 RKKY Interaction

An important mechanism of magnetic coupling between localized magnetic moments in metals depends on the ability of conduction electrons to interact magnetically with the local moments and to propagate between different magnetic sites. How the conduction electrons can polarize and propagate was first shown by Ruderman and Kittel[29]. They dealt with nuclear magnetic moments immersed in a distribution of conduction electrons. Kasuya and then Yosida developed and extended the theory to $s - f$ and $s - d$ interactions. The mechanism has become known as the RKKY(Ruderman-Kittel-Kasuya-Yosida) interaction[30, 31, 32, 33]. The RKKY interaction is given by the coupling between the magnetic moments of two nuclei via their hyperfine interaction with the conduction electrons. When the localized magnetic moments(nuclear or electronic) coexist with the Fermi sea of the conduction electrons, the interaction between local moments is mediated by conduction electrons. Their direct magnetic dipolar interaction is very weak and effectively screened by the orbital electrons. While the distance between localized moments is fixed in a crystal, the spin polarization of the conduction electron is not localized in the vicinity

of the local moment but is oscillatory and long-ranged. The mechanism can be simply visualized as follows. Consider a single localized magnetic moment surrounded by a gas of conduction electrons. The local moment is on a lattice site in the metal. The effect of the local moment is to make the site on which it is placed a region favorable for a conduction electron of parallel magnetic moment but unfavorable for an electron of antiparallel moment. In order to take advantage of the magnetic interaction, a parallel electron will distort its wavefunction so as to be larger in the vicinity of the local moment. This is brought about by mixing in other electron states of the same spin orientation. The result is as if only states above the Fermi level are added. The wavefunctions of the added states are such that they are all in phase with each other at the position of the local moment, so that they may interfere constructively at that point. Since they must correspond to a range of wavevectors and therefore a range of wavelengths, they must get out of step as the distance from the local moment increases, and begin to interfere destructively. The original uniform distribution of electrons with parallel spin is changed to have an oscillatory behavior which dies out as the distance from the local moment increases.

Likewise, conduction electrons with antiparallel spin change their wavefunctions so as to be smaller in the vicinity of the local moment. In just the same way this produces a corresponding oscillatory absence of antiparallel spin. The overall effect is to give an oscillatory distribution of spin density in the region of the local moment. Since the attraction of electrons with parallel spin is exactly matched by the repulsion of those with antiparallel spin at all points, and all have the same charge, the

distribution of charge density remains uniform throughout. The periodicity of the spin density oscillation is set by the wavelengths of the conduction electrons at the Fermi level. That is, it is dominated by the Fermi momentum. The exact form of the spin density distribution and its variation with distance must depend on how the electron wavelength varies with energy at the Fermi level, which is given by the (E, k) relationship. The RKKY theory was worked out for free electrons having a spherical Fermi surface. The correlation effects are neglected and one electron energy is assumed to be $\hbar^2 k^2 / 2m$. More complicated situations have not yet been investigated widely.

When a second atom bearing a local magnetic moment is situated at an arbitrary distance from the first it interacts ferromagnetically or antiferromagnetically depending on whether it is in a positive or a negative part of the polarization wave from the first atom. According to the RKKY theory the strength of the magnetic coupling between atoms a relatively large distance r apart varies according to

$$(1/r^3) \cos(2k_F r) \quad (2.23)$$

where k_F represents the Fermi momentum(see below for the derivations).

The most important properties of this mechanism of magnetic coupling are the following. First, the magnetic interaction has a long range character, certainly of much longer range than any direct exchange involving charge overlap between adjacent atoms. Second, quite large variations in the strength of the interaction and even reversal of its sign are possible with small changes in the relationship between the interatomic distance and the periodicity of the spin density.

Conduction electrons play two roles at the same time when local magnetic moments stem from the atomic open shell. The Kondo effect results in the screening of the magnetic moments, while RKKY interaction contributes to the magnetic ordering. In heavy fermion materials, the competition between two seems to play an important role in determining their ground state configurations.

Now, let's derive the RKKY interaction term using perturbation theory. The nuclear spin induces the dipolar magnetic field.

$$\begin{aligned}\vec{A}(\vec{x}) &= -\vec{\mu}_n \times \nabla \frac{1}{r} \\ B_{ni}(\vec{x}) &= \mu_{nj} [\partial_i \partial_j - \frac{1}{3} \delta_{ij} \nabla^2] \frac{1}{r} + \frac{8\pi}{3} \mu_{ni} \delta(\vec{x})\end{aligned}\quad (2.24)$$

where $\vec{\mu}_n = g_n \mu_N \vec{I}$ is the nuclear magnetic moment. Then the conduction electron interacts with the nuclear spin through the hyperfine interaction, which is usually given as the Fermi contact interaction, i.e. delta function form.

$$H_{hf} = -\vec{\mu}_e \cdot \vec{B}_n. \quad (2.25)$$

Here $\vec{\mu}_e = -g_e \mu_B \vec{S}$ is the nuclear and the electronic magnetic moments. The first term in $\vec{B}_n$, when coupled to the conduction electrons, selects the transition $\Delta l = 2$. In the s-wave scattering channel, only the delta function term survives. The interaction Hamiltonian is given by

$$H_1 = - \int d^3x \vec{M}_e(\vec{x}) \cdot \vec{B}_n(\vec{x}) \quad (2.26)$$

where

$$\vec{M}_e(\vec{x}) = -\frac{g_e \mu_B}{2} \psi^\dagger(\vec{x}) \vec{\sigma} \psi(\vec{x}). \quad (2.27)$$

Keeping only the Fermi contact term, we can model the hyperfine interaction between the nuclear moments and the conduction electrons is

$$H_1 = J \int d^3x \psi^\dagger(\vec{x}) \vec{S} \psi(\vec{x}) \cdot \vec{I}(\vec{x}) \quad (2.28)$$

where

$$\vec{I}(\vec{x}) = \sum_i \vec{I}_i \delta(\vec{x} - \vec{X}_i) \quad (2.29)$$

and $J = \frac{8\pi}{3} g_e g_n \mu_B \mu_N$.

In case that the localized moments are electronic, for example, in rare earth and transition metal compounds, the coupling to the conduction electrons is dominated by the Coulomb exchange interaction rather than by the dipolar interaction. This case can also be modeled by the Fermi contact interaction.

Assuming the Fermi contact interaction between the local moments and the conduction electrons, we are going to study the free electronic system with magnetic impurities.

To begin with, we calculate the spin density for conduction electrons modified by single magnetic impurity $\vec{I}$ at the origin.

Then the Hamiltonian is

$$H_0 = \sum_{\vec{k}\alpha} c_{\vec{k}} c_{\vec{k}\alpha}^\dagger c_{\vec{k}\alpha} \quad (2.30)$$

$$H_1 = \frac{J}{2V} \sum_{\vec{k}\vec{k}'} c_{\vec{k}\alpha}^\dagger \vec{\sigma}_{\alpha\beta} c_{\vec{k}'\alpha} \cdot \vec{I} \quad (2.31)$$

Applying first order perturbation theory, we find the modified plane wave state

$$|\psi_{\vec{k}\alpha}\rangle = |\vec{k}\alpha\rangle + \sum_{\vec{k}'\beta} |\vec{k}'\beta\rangle \frac{\langle \vec{k}'\beta | H_1 | \vec{k}\alpha \rangle}{\epsilon_{\vec{k}} - \epsilon_{\vec{k}'}} \quad (2.32)$$

with

$$\langle \vec{k}|\beta|H_1|\vec{k}\alpha\rangle = \frac{J}{2V}\vec{\sigma}_{\beta\alpha} \cdot \vec{l}. \quad (2.33)$$

Here $|\vec{k}\alpha\rangle$ is the plane wave state characterized by momentum $\vec{k}$ and the spin χ_α .

Now the calculation is straightforward when projected to the position space($\hbar \equiv 1$).

The perturbed wave function is

$$\begin{aligned} \psi_{\vec{k}\alpha}(\vec{x}) = \langle \vec{x}|\psi_{\vec{k}\alpha}\rangle &= \langle \vec{x}|\vec{k}\alpha\rangle + \frac{J}{2V} \sum_{\beta} \chi_{\beta} \vec{\sigma}_{\beta\alpha} \cdot \vec{l} \frac{1}{\sqrt{V}} \sum_{\vec{k}'} \frac{e^{i\vec{k}' \cdot \vec{x}}}{\epsilon_{\vec{k}} - \epsilon_{\vec{k}'}} \\ &= \langle \vec{x}|\vec{k}\alpha\rangle + \frac{mJ}{8\pi^3 \sqrt{V}} \sum_{\beta} \chi_{\beta} \vec{\sigma}_{\beta\alpha} \cdot \vec{l} \int d^3 k' \frac{e^{i\vec{k}' \cdot \vec{x}}}{k^2 - k'^2} \\ &= \langle \vec{x}|\vec{k}\alpha\rangle + \frac{mJ}{4\pi} \frac{1}{\sqrt{V}} \sum_{\beta} \chi_{\beta} \vec{\sigma}_{\beta\alpha} \cdot \vec{l} \frac{\cos kr}{r} \end{aligned} \quad (2.34)$$

where $\int d^3 k' \frac{e^{i\vec{k}' \cdot \vec{x}}}{k^2 - k'^2} = -\frac{2\pi^2}{r} \cos kr$ is used to evaluate the last line.

Then the density for the spin state α up to $O(J)$ is

$$\begin{aligned} \rho_{\vec{k}\alpha}(\vec{x}) &\equiv |\psi_{\vec{k}\alpha}(\vec{x})|^2 \\ &\approx \frac{1}{V} \left[1 - \frac{mJ}{2\pi} \vec{\sigma}_{\alpha\alpha} \cdot \vec{l} \frac{\cos kr}{r} \cos(\vec{k} \cdot \vec{x}) \right]. \end{aligned} \quad (2.35)$$

Hence the density in the real space is given by summing over all occupied states. We find

$$\begin{aligned} \rho_{\alpha}(\vec{x}) &\equiv \sum_{\vec{k}} \rho_{\vec{k}\alpha}(\vec{x}) f_{\vec{k}} \\ &= \frac{k_F^3}{6\pi^2} - \frac{mJ}{2\pi r} \vec{\sigma}_{\alpha\alpha} \cdot \vec{l} \frac{1}{V} \sum_{\vec{k} < \vec{k}_F} \cos kr \cos(\vec{k} \cdot \vec{x}); \text{ at } T = 0 \\ &= \frac{k_F^3}{6\pi^2} \left[1 + \frac{3mJk_F}{\pi} \vec{\sigma}_{\alpha\alpha} \cdot \vec{l} F(2k_F r) \right] \end{aligned} \quad (2.36)$$

where

$$F(x) = \frac{1}{x^2} \frac{d}{dx} \left(\frac{\sin x}{x} \right)$$

$$= \frac{1}{x^3} \left[\cos x - \frac{\sin x}{x} \right] = -\frac{1}{x^2} j_1(x) \quad (2.37)$$

and

$$\frac{1}{V} \sum_{k < k_F} \cos kr \cos(\vec{k} \cdot \vec{x}) = -\frac{k_F^4 r}{\pi^2} F(2k_F r). \quad (2.38)$$

Thus the conduction electron spin density shows spatially alternating structure as a function of distance from the local magnetic impurity. The physical interpretation for the spin density is clear. Suppose antiferromagnetic coupling, *i.e.* $J > 0$. Then the antiparallel conduction spins will be more populated near the local moment, which is true of the above result since $F(x) \sim -1/3x$ for $x \ll 1$ and $\sigma_{\uparrow\downarrow} = -\hat{z}$.

The indirect exchange interaction between a system of localized magnetic moments mediated by the conduction electrons will be discussed. This will be done by calculating the change in the total energy of electronic system in the presence of the local magnetic moments. Put Eq. (2.29) to Eq. (2.31), then the perturbing Hamiltonian is

$$H_1 = \frac{J}{2V} \sum_i \sum_{\vec{k}\beta} c_{\vec{k}\alpha}^\dagger \vec{\sigma}_{\alpha\beta} c_{\vec{k}\beta} \cdot \vec{I}_i e^{i(\vec{k}' - \vec{k}) \cdot \vec{R}_i} \quad (2.39)$$

The first order energy correction is

$$\begin{aligned} \Delta^{(1)} &= \sum_{\vec{k}\alpha} \langle \vec{k}\alpha | H_1 | \vec{k}\alpha \rangle \\ &\cong \frac{J}{2V} \sum_{\vec{k}\alpha} \sum_i \vec{\sigma}_{\alpha\alpha} \cdot \vec{I}_i \\ &= 0 \end{aligned} \quad (2.40)$$

where

$$\langle \vec{k}'\beta | H_1 | \vec{k}\alpha \rangle = \frac{J}{2V} \sum_i \vec{\sigma}_{\beta\alpha} \cdot \vec{I}_i e^{i(\vec{k}' - \vec{k}) \cdot \vec{R}_i}, \quad (2.41)$$

In the above derivation, the fact that $Tr[\vec{\sigma}] = 0$ has been used. The non-vanishing leading term comes from the second order correction:

$$\begin{aligned}
\Delta^{(2)} &= \sum_{\vec{k}\vec{k}'} \sum_{\alpha\beta} \frac{|\langle \vec{k}'\beta | H_1 | \vec{k}\alpha \rangle|^2}{\epsilon_{\vec{k}} - \epsilon_{\vec{k}'}} f_{\vec{k}} [1 - f_{\vec{k}'}] \\
&= \frac{mJ^2}{2V^2} \sum_{\alpha\beta} \sum_{ij} \vec{\sigma}_{\beta\alpha} \cdot \vec{I}_i \vec{\sigma}_{\alpha\beta} \cdot \vec{I}_j \sum_{\vec{k}\vec{k}'} \frac{e^{i(\vec{k}'-\vec{k})\cdot\vec{X}_{ij}}}{k^2 - k'^2} f_{\vec{k}} [1 - f_{\vec{k}'}] \\
&= \frac{mJ^2}{V^2} \sum_{ij} \vec{I}_i \cdot \vec{I}_j \sum_{\vec{k}\vec{k}'} \frac{e^{i(\vec{k}'-\vec{k})\cdot\vec{X}_{ij}}}{k^2 - k'^2} f_{\vec{k}} [1 - f_{\vec{k}'}].
\end{aligned} \tag{2.42}$$

Here $\sum_{\alpha\beta} \vec{\sigma}_{\beta\alpha} \cdot \vec{I}_i \vec{\sigma}_{\alpha\beta} \cdot \vec{I}_j = Tr[\vec{\sigma} \cdot \vec{I}_i \vec{\sigma} \cdot \vec{I}_j] = 2\vec{I}_i \cdot \vec{I}_j$ has been used. $\vec{X}_{ij}$ is the short hand notation for $\vec{X}_i - \vec{X}_j$. At $T = 0K$

$$\begin{aligned}
\Delta^{(2)} &= \frac{mJ^2}{V^2} \sum_{ij} \vec{I}_i \cdot \vec{I}_j \sum_{\vec{k} < k_F} \sum_{\vec{k}' > k_F} \frac{e^{i(\vec{k}'-\vec{k})\cdot\vec{X}_{ij}}}{k^2 - k'^2} \\
&= \frac{mJ^2 k_F^4}{4\pi^3} \sum_{ij} \vec{I}_i \cdot \vec{I}_j F(2k_F |\vec{X}_{ij}|).
\end{aligned} \tag{2.43}$$

The physical meaning of this expression is clear. We arrived at this result assuming that the perturbation due to magnetic impurities is very small to the conduction electronic system. The energy correction to the ground state of the electronic system can be effectively interpreted as coming from the mutual interaction between the local magnetic moments. One notable point is that the exchange integral changes its sign over the distance, thus leading to the alternating ferromagnetic and antiferromagnetic couplings between local moments. For small x , $F(x) \rightarrow -1/3x$, so that the oscillatory interaction for x less than the first zero of $F(x)$ is ferromagnetic independent of the sign of J . The first zero occurs at $x = 4.49$.

The Knight shift of Heavy electron materials is induced by the indirect interactions of the magnetic impurity and host nuclear spin mediated by the conduction electrons.

Without the charge fluctuations introduced by the hybridization interaction between conduction electron and f electron, this indirect interaction has the RKKY interaction form. So at high temperatures, the Knight shift follows the RKKY interaction and at low temperatures where the Kondo effect appears, the Knight shift can show deviation from the RKKY form.

2.4 Magnetic Susceptibility

The static magnetic susceptibility is a direct indicator of the nature of the ground state for the magnetic Kondo model. Near room temperature, the susceptibility $\chi(T)$ displays a Curie-Weiss temperature dependence for most heavy-electron materials. And it shows linear relation with the Knight shift $K(T)$. This can be say that

$$K(\vec{r}, T) = f(\vec{r})\chi(T). \quad (2.44)$$

At low temperature, $\chi(T)$ does not follow the Curie-Weiss law and for some systems, a linear relation of the Knight shift $K(T)$ and to the magnetic susceptibility doesn't hold. If there is a Knight shift anomaly, the factorization of the above equation does not hold($K(\vec{r}, T) = f(\vec{r}, T)\chi(T)$). This section describes the magnetic susceptibility calculation in the zero field limit. The magnetization operator conjugate to the field has the form

$$\begin{aligned} M_z &= \sum_m g_j \mu_B m (f_{jm}^\dagger f_{jm} + \sum_c c_{cjm}^\dagger c_{cjm}) \\ &= \sum_m g_j \mu_B m O_m \end{aligned} \quad (2.45)$$

Figure 2.3: **Leading order Feynman diagram for static magnetic susceptibility.** In this diagram, only f electrons are coupled to the field

where g_j is the Landé g factor for the j multiplet. The Kubo formula, for the static susceptibility of single j multiplet with degeneracy N_j is given

$$\begin{aligned}\chi_j(T) &= \frac{(g_j\mu_B)^2 j(j+1)}{3} \frac{N_j}{Z_{4f}(T)} \int_0^\beta d\tau \langle T_\tau O_m(\tau) O_m \rangle \\ &= \mu_j^2 \frac{N_j}{Z_{4f}(T)} \int_0^\beta d\tau \langle T_\tau O_m(\tau) O_m \rangle\end{aligned}\quad (2.46)$$

where μ_j is the effective magnetic moment which is defined as $\mu_j^2 = (g_j\mu_B)^2 j(j+1)/3$ and $Z_{4f}(T)$ is the impurity partition function. In general the magnetic susceptibility comes from self-correlation of the conduction band magnetization(χ_{cc}), the self-correlation of the f magnetization(χ_{ff}), and the mutual correlation of f and band components(χ_{cf}). The leading diagram comes from the second term where the only f electrons are couple to the field and this gives a good approximation. This diagram for magnetic susceptibility is in Fig. 2.3. Then, in the NCA, above equation can be written

$$\chi(T) = \sum_j \frac{\mu_j^2 N_j}{Z_{4f}(T)} 2 \int \frac{d\zeta}{\pi} A_{jm}^{(-)}(\zeta, T) \text{Re} G_{jm}(\zeta, T) \quad (2.47)$$

The dynamic magnetic susceptibility measures the magnetic excitation structure.

The dynamic magnetic susceptibility is defined as the spin-spin correlation function and can be measured directly from the neutron scattering experiments. The absorptive part of the dynamic susceptibility for the single multiplet is given by

$$\begin{aligned}\chi_j''(\omega, T) &= \mu_j^2 \frac{N_j}{Z_{4f}(T)} \int \frac{d\zeta}{\pi} (A_{jm}(\zeta + \omega) A_{jm}^{(-)}(\zeta) - A_{jm}(\zeta - \omega) A_{jm}^{(-)}(\zeta)) \\ &= \frac{\mu_j^2 N_j}{Z_{4f}(T)} (1 - e^{-\beta\omega}) \int \frac{d\zeta}{\pi} A_{jm}(\zeta + \omega) A_{jm}^{(-)}(\zeta).\end{aligned}\quad (2.48)$$

Note that the $\chi_j''(\omega, T)$ is odd in ω . The susceptibility sum rule is derived from the zero frequency limit of the Hilbert transform of $\chi_j''(\omega, T)$,

$$\chi(T) = \chi'(0, T) = \int \frac{d\omega}{\pi} \frac{\chi_j''(\omega, T)}{\omega} \quad (2.49)$$

where $\chi(T)$ is defined in Eq. (2.47). From above Eq. (2.48), the total magnetic intensity sum rule follows:

$$\int \frac{d\omega}{\pi} \frac{\chi_j''(\omega, T)}{1 - e^{-\beta\omega}} = \mu_j^2 n_j(T) \quad (2.50)$$

where $n_j(T) = N_j \int \frac{d\zeta}{\pi} A_{jm}^{(-)}(\zeta, T) / Z_{4f}(T)$ is the occupancy of the individual multiplet.

Also we can get the van Vleck magnetic susceptibility between j and j' angular momentum multiplet.

$$\begin{aligned}\chi_{m_j m_{j'}}'' &= \mu_B^2 \frac{|\langle jm_j | J_z + S_z | j' m_{j'} \rangle|^2}{Z_{4f}(T)} \int \frac{d\zeta}{\pi} (A_{jm_j}(\zeta + \omega) A_{j'm_{j'}}^{(-)}(\zeta) \\ &\quad - A_{j'm_{j'}}(\zeta - \omega) A_{jm_j}^{(-)}(\zeta)) \\ &= \mu_B^2 \frac{|\langle jm_j | J_z + S_z | j' m_{j'} \rangle|^2}{Z_{4f}(T)} (1 - e^{-\beta\omega}) \int \frac{d\zeta}{\pi} A_{jm_j}(\zeta + \omega) A_{j'm_{j'}}^{(-)}(\zeta)\end{aligned}\quad (2.51)$$

where

$$\chi_{ij}''(-\omega) = -\chi_{ji}''(\omega). \quad (2.52)$$

With $\langle \frac{5}{2}, m | J_z + S_z | \frac{7}{2}, m' \rangle = -(\sqrt{49 - 4m^2}/14)\delta_{mm'}$, the total van Vleck susceptibility for $j = 5/2$ and $j' = 7/2$ is

$$\begin{aligned}
 \chi''_{vv}(\omega) &= \sum_{m, m'} \chi''_{m, m'}(\omega) \\
 &= \sum_{m=-\frac{5}{2}}^{\frac{5}{2}} \frac{49 - 4m^2}{196} \mu_B^2 \frac{(1 - e^{-\beta\omega})}{Z_{4f}(T)} \int \frac{d\zeta}{\pi} A_{jm}(\zeta + \omega) A_{j'm}^{(-)}(\zeta) \\
 &= \frac{8}{7} \mu_B^2 \frac{(1 - e^{-\beta\omega})}{Z_{4f}(T)} \int \frac{d\zeta}{\pi} A_{jm}(\zeta + \omega) A_{j'm}^{(-)}(\zeta). \tag{2.53}
 \end{aligned}$$

For Ce ions, both the $j = 5/2, 7/2$ contribution to the static magnetic susceptibility and the van Vleck susceptibility are considered. For Yb ions, only the static susceptibility of $j = 7/2$ ground spin-orbit multiplet is calculated because that the energy gap between two spin orbit multiplets ($j = 7/2$ and $j = 5/2$) is large (see Table 1 for the exact value). For U compound, only the van Vleck susceptibility between different Γ states is calculated because the Γ_3 ground state is a non-magnetic doublet.

2.5 Knight Shift

In NMR experiments for Kondo or heavy electron materials, the measurements are typically done on the nuclei of the non- f ions (though for Yb, NMR can be done directly at the f site), so that coupling to the f moments occurs via indirect interactions. Knight shift measurements on these nuclear spins can probe the local induced magnetic fields. The additional fields come from all the possible polarization sources. For f electrons, the radius of their shells is small and they are well screened, so there is little possibility of direct overlap interactions between the nucleus spin and local moments. In particular, the polarization of conduction electrons by the polarized

local Kondo impurities, *i.e.* the transferred *f*-electron polarization, might have the most significant temperature dependent contribution.

To calculate the Knight shift we need to evaluate the Feynman diagram in Fig 2.4 which is the lowest order diagram coupling the nuclear spin to, say, Ce magnetic moments, ignoring direct Coulomb coupling. All the propagators are self explained in the figure. For the incoherent calculation, the conduction electrons are assumed to belong to a broad, featureless, and symmetric band of half width *D*. The conduction electron propagator is a bare electron propagator. And when the the lattice coherence effects of conduction electrons are included, the self energy arising from the scattering of conduction electron at every *f* site is included in the conduction electron propagator.

The Knight shift for a nuclear spin or muon at $\vec{r}$ is approximated as

$$K(r, \theta) = -\frac{8\pi V^2}{3N_s} \frac{g_e \mu_B^2}{\Omega} \sum f_{jj'}(\alpha, \theta) \int k^2 dk \int k'^2 dk' I_{jj'}(\epsilon_k, \epsilon_{k'}), \quad (2.54)$$

where g_e is the electron *g*-factor and μ_B is the Bohr magneton. Here θ is the angle between *z* axis and the bond direction $\vec{r}$ which connects the nucleus or muon to a given *f* ion in the crystal and α is the angle between the field axis and bond axis. $I_{jj'}(\epsilon_k, \epsilon_{k'})$ is given by

$$\begin{aligned} I_{jj'}(\epsilon_k, \epsilon_{k'}) &= j_3(kr)j_3(k'r) \frac{1}{Z_{4f}} \sum_{\omega, \nu} G_0(k\sigma, i\omega) G_0(k'\sigma', i\omega) \\ &\quad \times G_{jm}(i(\omega + \nu)) G_{j'm'}(i(\omega + \nu)) D(i\nu) \\ &= 2 \frac{j_3(kr)j_3(k'r)}{\epsilon_k - \epsilon_{k'}} (f(\epsilon_k) I_{1jj'}(\epsilon_k) + (1 - f(\epsilon_k)) I_{2jj'}(\epsilon_k)), \end{aligned} \quad (2.55)$$

Figure 2.4: Feynman Diagram for the Knight shift calculation for Ce ions. This is the lowest order diagram of coupling between Ce local moment and nuclear spin in the infinite U Anderson model. All the propagators are self explained in the figure. For the incoherent calculation the conduction electron propagator is a bare electron propagator and when the coherence effect of conduction electron is included, it becomes a dressed propagator.

where

$$\begin{aligned} I_{1jj'}(\epsilon_k) &= \frac{2}{Z_{A_f}} \int \frac{d\zeta}{\pi} \int \frac{d\rho}{\pi} \frac{B^{(-)}(\zeta) A_{jm}(\rho) \text{Re} G_{j'm'}(\rho)}{\epsilon_k + \zeta - \rho} \\ &= \frac{1}{Z_{A_f}} \int \frac{d\zeta}{\pi} B^{(-)}(\zeta) \text{Re} G_{jm}(\zeta + \epsilon_k) \text{Re} G_{j'm'}(\zeta + \epsilon_k) \end{aligned} \quad (2.56)$$

$$\begin{aligned} I_{2jj'}(\epsilon_k) &= \frac{-2}{Z_{A_f}} \int \frac{d\rho}{\pi} \int \frac{d\zeta}{\pi} \frac{B(\zeta) A_{jm}^{(-)}(\rho) \text{Re} G_{j'm'}(\rho)}{\epsilon_k + \zeta - \rho} \\ &= \frac{2}{Z_{A_f}} \int \frac{d\rho}{\pi} A_{jm}^{(-)}(\rho) \text{Re} G_{j'm'}(\rho) \text{Re} D(\rho - \epsilon_k). \end{aligned} \quad (2.57)$$

The derivation is explained in detail in Appendix C.

We can analytically evaluate the inner k' integral,

$$\int_0^\infty k'^2 dk' \frac{j_3(k'r)}{k'^2 - k'^2}; \quad (2.58)$$

the results are presented in Appendix D.

The angular dependence term of the Knight shift, $f_{jj'}(\alpha, \theta)$ is given by when field is in the z direction, *i.e.* $\theta = \alpha$ and nuclear spin $I = 1/2$,

$$f_{jj'}(\theta) = \cos^2 \theta f_{jj'}^z + \frac{\sin^2 \theta}{4} (f_{jj'}^{1-} + f_{jj'}^{2-} + f_{jj'}^{1+} + f_{jj'}^{2+}). \quad (2.59)$$

Here $f_{jj'}^z(\theta)$ is

$$\begin{aligned} f_{jj'}^z(\theta) &= \sum_{m_j, m_{j'}} \langle jm_j | J_z + S_z | j' m_{j'} \rangle \sigma_{\alpha\alpha}^z \langle j' m_{j'} | \hat{r} \rangle \langle \hat{r} | jm_j \rangle \\ &= \sum_{m_j, \alpha, m_3} \alpha \langle jm_j | J_z + S_z | j' m_{j'} \rangle \langle j' m_{j'} | 3m_3; \frac{1}{2} \alpha \rangle \\ &\quad \times \langle 3m_3; \frac{1}{2} \alpha | jm_j \rangle |Y_{3m_3}(\hat{r})|^2. \end{aligned} \quad (2.60)$$

And $f_{jj'}^{1\pm}(\theta)$ and $f_{jj'}^{2\pm}(\theta)$ are

$$f_{jj'}^{1\pm}(\theta) = \sum_{m_j, m_{j'}, \alpha, \beta} \langle j, m_j | J_\pm | j', m_{j'} \rangle \langle j' m_{j'} | \hat{r} \rangle \sigma_{\alpha\beta}^\mp \langle \hat{r} | j, m_j \rangle$$

$$\begin{aligned}
&= \sum_{m_j, m_{j'}, m_3, m'_3, \alpha, \beta} \langle j, m_j | J_{\pm} | j', m_{j'} \rangle \langle j' m_{j'} | 3m'_3; \frac{1}{2} \alpha \rangle \\
&\quad \times \langle 3m'_3; \frac{1}{2} \alpha | \sigma_{\alpha, \beta}^{\mp} | 3m_3; \frac{1}{2} \beta \rangle \langle 3m_3; \frac{1}{2} \beta | j m_j \rangle Y_{3m_3}^*(\hat{r}) Y_{3m'_3}(\hat{r}) \quad (2.61)
\end{aligned}$$

$$\begin{aligned}
f^{2\pm jj'}(\theta) &= \sum_{m_j, m_{j'}, \alpha, \beta} \langle j m_j | S_{\pm} | j', m_{j'} \rangle \langle j' m_{j'} | \hat{r} \rangle \sigma_{\alpha, \beta}^{\mp}(\hat{r} | j, m_j) \\
&= \sum_{m_j, m_{j'}, m_3, m'_3, \alpha, \beta} \langle j, m_j | S_{\pm} | j', m_{j'} \rangle \langle j' m_{j'} | 3m'_3; \frac{1}{2} \alpha \rangle \\
&\quad \times \langle 3m'_3; \frac{1}{2} \alpha | \sigma_{\alpha, \beta}^{\mp} | 3m_3; \frac{1}{2} \beta \rangle \langle 3m_3; \frac{1}{2} \beta | j m_j \rangle Y_{3m_3}^*(\hat{r}) Y_{3m'_3}(\hat{r}) \quad (2.62)
\end{aligned}$$

The explicit value for $f_{jj'}(\theta)$ is

$$1) j = j' = 5/2$$

$$f_{\frac{5}{2}\frac{5}{2}}(\theta) = \frac{9}{28\pi} (1 - 8 \sin^2 \theta + 6 \sin^4 \theta) \quad (2.63)$$

$$2) j = j' = 7/2$$

$$f_{\frac{7}{2}\frac{7}{2}}(\theta) = \frac{2}{7\pi} [2 + 12 \sin^2 \theta - 9 \sin^4 \theta] \quad (2.64)$$

and $f(\theta)$ for van Vleck Knight shift is

$$f_{\frac{7}{2}\frac{7}{2}}(\theta) = \frac{3}{28\pi} [4 - 4 \sin^2 \theta + 3 \sin^4 \theta]. \quad (2.65)$$

To assess the relevance of this single site physics to the periodic compound CeSn_3 , we also carried out incoherent lattice sums over a few hundreds shells of Ce atoms around the Sn. For each shell the distance r and angle θ of Ce ion is calculated and the Knight shift of each ion is evaluated for given position. Then, the contribution from each ion is added to get the total Knight shift assuming that this single site physics can describe the Knight shift contribution of each ion. For the U compound, impurity configuration averaging is also carried out. This single site physics is known

to be a good approximation at high temperatures where the ions are incoherent with one other, and known to provide a very accurate description of the thermodynamics in many cases. For the cubic crystal, such as CeSn_3 , $\text{Y}_{1-x}\text{U}_x\text{Pd}_3$, we fixed field in the z direction and do the reference frame averaging whether Sn atom is in the xz plane or the xy plane. Note that yz plane is equivalent to xz .

For YbCuAl case which has the hexagonal symmetry, we have to consider three possible field directions, along the x , y and z axis. Al has an $I = 5/2$ nuclear spin and the NMR shift was obtained from derivative spectra of the central ($1/2 \leftrightarrow -1/2$) NMR transition. Then

$$f_{jj'}(\alpha, \theta) = A \cos \alpha f_{jj'}^z(\theta) + \frac{B}{4} \sin \alpha [f_{jj'}^+(\theta) + f_{jj'}^-(\theta)]. \quad (2.66)$$

where $f_{jj'}^\pm = f_{jj'}^{1\pm} + f_{jj'}^{2\pm}$. Also A and B are given by

$$\begin{aligned} A &= \frac{1}{4}(25 \cos^5 \theta - 26 \cos^3 \theta + 5 \cos \theta) \\ B &= \frac{1}{4} \sin \theta (25 \cos^4 \theta - 14 \cos^2 \theta + 1). \end{aligned} \quad (2.67)$$

Then, for $j = 7/2$

$$\begin{aligned} f_{\frac{7}{2}\frac{7}{2}}(\alpha, \theta) &= [A \cos \alpha \frac{4}{7\pi} (1 + 3 \sin^2 \theta) + \frac{B}{4} 2 \sin \alpha \frac{4}{7\pi} (5 + 3 \cos^2 \theta)] \\ &= \frac{2}{7\pi} [2A \cos \alpha (1 + 3 \sin^2 \theta) + B \sin \alpha (5 + 3 \cos^2 \theta)], \end{aligned} \quad (2.68)$$

and for $j = 5/2$

$$\begin{aligned} f_{\frac{5}{2}\frac{5}{2}}(\alpha, \theta) &= [A \cos \alpha \frac{9}{28\pi} (1 - 4 \sin^2 \theta) + \frac{B}{4} 2 \sin \alpha (-\frac{9}{14\pi}) (3 - 2 \sin^2 \theta)] \\ &= \frac{9}{28\pi} [A \cos \alpha (1 - 4 \sin^2 \theta) - B \sin \alpha (3 - 2 \sin^2 \theta)], \end{aligned} \quad (2.69)$$

For YbCuAl compound we don't consider van Vleck contribution because of the large energy gap between the $j = 7/2$ ground state and $j = 5/2$ state.

For the detailed derivation see Appendix E.

To the extent that the dynamics of the empty orbital can be neglected, this expression factorizes into a nearly temperature independent RKKY interaction (modified due to the spin-orbit coupling and anisotropic hybridization from the original form) times the f -electron susceptibility. Thus, no anomaly results from the diagram in this limit. In this limit, the susceptibility in the diagram corresponds to the the leading order estimate used in Ref. [10] to compare with exact Bethe-Ansatz results.

However, for $T = 0$, the empty orbital propagator may be written in an approximate two-pole form, one with amplitude $1 - Z$, $Z = \pi k_B T_0 / N\Gamma$, centered near zero energy, and one with amplitude Z centered at $\epsilon_g \sim \epsilon_f - k_B T_0$ which reflects the anomalous ground state mixing due to the Kondo effect. And the single occupied propagator has a simple pole structure.

$$\begin{aligned}
 B(\omega) &= (1 - Z)\delta(\omega) + Z\delta(\omega - \epsilon_g) \\
 A_m(\omega) &= \delta(\omega - \epsilon_f) \\
 B^{(-)}(\omega) &= Z\delta(\omega - \epsilon_g) \\
 A_m^{(-)}(\omega) &= \frac{1 - Z}{2}\delta(\omega - \epsilon_g).
 \end{aligned} \tag{2.70}$$

Then

$$\begin{aligned}
 I_1(\epsilon_k) &= Z/(k_B T_0 - \epsilon_k)^2 \\
 I_2(\epsilon_k) &= \frac{1 - Z}{k_B T_0} \left(\frac{1 - Z}{\epsilon_k - \epsilon_f} + \frac{Z}{\epsilon_k} \right)
 \end{aligned} \tag{2.71}$$

Now, we can perform the k integral putting above equations in Eq. (2.55). At low temperatures only conduction electrons which momentum close the k_F participate in the interaction. we can rewrite k as

$$k = k_F + (k - k_F) = k_F + \frac{c_k}{\hbar v_F} \quad (2.72)$$

Then we can write

$$e^{ikr} = e^{ik_F r} e^{ic_k r / \hbar v_F} \quad (2.73)$$

Small c_k gives large contribution to the Knight shift. The contribution from the I_1 depends on whether $r \gg \hbar v_F / k_B T_0$. For $r \gg \hbar v_F / k_B T_0$ only very small $c_k < k_B T_0$ contribute the k integral and we can think that $1/(k_B T_0 - c_k) \approx 1/k_B T_0$ and this contribution has the amplitude $Z/k_B T_0 = \pi/N\Gamma$. For $r \ll \hbar v_F / k_B T_0$, the Knight shift has contributions from $c_k > k_B T_0$ and this term has the amplitude Z/D . The amplitude of the Knight shift at outside of the coherence length $\xi_k = \hbar v_F / k_B T_0$ is $D/k_B T_0$ times bigger than that at inside the the Kondo screening cloud. This term can give the Knight shift anomaly. Because c_f is much bigger than the c_k , the first term of I_2 gives conventional RKKY oscillations modulo the anisotropy and altered range dependence induced by the $m, \hat{k}$ dependence of the hybridization. The amplitude of the second term goes to zero above the Kondo temperature. This term also may give the anticipated anomalous Knight shift, and within such a two-pole approximation may be seen to be finite within ξ_K , have a stronger distance dependence in that regime, but possess an amplitude of order Z only within this distance regime. Beyond ξ_K , the amplitude is of order $1/N$ and the shape of the spin oscillations is the same as that found from the high frequency pole of the empty orbital propagator.

The diagram of Fig. 2.4 has been studied with the NCA previously [34], but only for the spin 1/2 model with infinite Coulomb repulsion, and for a limited parameter regime (very low T_0 values) and short distances ($r \ll \xi_K$). In consequence, no strong evidence was found for a Knight shift anomaly in this previous work.

2.6 Coherent Lattice Effects

We include the coherent lattice effect within the local approximation ($d = \infty$ expansion) to the lattice model. In this approximation a conduction electron self energy is included using the average -T matrix approximation which is assuming that conduction electron scatters off every f -electron site. In contrast, in the incoherent limit, we ignore these multiple scattering processes. This coherent lattice effect may reduce the Kondo screening length [35]. The Anderson lattice model for spin 1/2 has a conduction electron Green's function given by [36]

$$\begin{aligned} G_c(\vec{k}, \omega, T) &= (\omega - \epsilon_k - \Sigma_c(\omega, T))^{-1} \\ &= (\omega - \epsilon_k - \frac{V^2}{\omega - \epsilon_f - \Sigma_f^{int}(\vec{k}, \omega, T)})^{-1}. \end{aligned} \quad (2.74)$$

Where $\Sigma_f^{int}(\vec{k}, \omega, T)$ is the f -electron self energy arising from $f - f$ interactions. The wave-vector dependence of the self energy comes from the possibility of intersite interactions. The same results follow for the N-fold degenerate model. The f electron self energy comes from the $f - f$ interaction (Σ_f^{int}) and hybridization with the conduction

electrons. This hybridization energy is given by

$$V^2 D(\omega) = \frac{V^2}{N_s} \sum_{\vec{k}} \frac{1}{\omega - \epsilon_{\vec{k}}}. \quad (2.75)$$

For featureless symmetric band $D(\omega)V^2$ becomes $i\Gamma$. Where $\Gamma = \pi N(0)V^2$ is the single particle hybridization width ($N(0)$ the density of state at the Fermi energy).

For perfect metal the conductivity of conduction electrons becomes infinity when temperature goes to zero. The electron conductivity decreased by the scattering at the localized f site. In heavy electron systems, electrical and thermal currents are mostly carried by the delocalized band electrons. The localized f -electrons also can contribute to the conductivity through a momentum dependent hybridization. Since the vertex correction is neglected in the NCA, the conduction electron Green's function is determined completely through Σ_f , any resistance solely arises from the damping of band states due to the imaginary part of Σ_f . (This damping involves transfer of momentum to the f -states which are treated as immobile. In reality, the dissipation of momentum may involve couplings of these f -states to other bands or to lattice degrees of freedom, the discussion of which is beyond the scope of this dissertation.) So, the realistic estimate of Σ_f is important to study the lattice coherent effects. By the standard Fermi-liquid phase space argument [25], the imaginary part of the f -electron self energy is given, for low frequencies and temperatures

$$-\text{Im}\Sigma_{Af}(\omega, T) \sim \omega^2 + (\pi k_B T)^2 + \Gamma \quad (2.76)$$

In the NCA calculation, due to the approximation involved, the minimum value in $-\text{Im}\Sigma_{Af}(\omega, T)$ does not occur precisely at the Fermi energy (though it differs only by

a small fraction of T_0) and is not equal to Γ [26]. So in our numerical calculations, low temperature minimum Γ_{NCA} is calculated by extrapolation of the $\text{Im}\Sigma_{4f}(\omega, T)$ and it is replaced by Γ .

Perturbation theory in the hybridization for the Anderson model may be formally divided into intra- and inter-site terms. Intra-site terms are already treated to all orders through the NCA approximation. In this calculation we treat intersite coupling in terms of perturbation theory. From among the intersite terms, we distinguish those involving simple hopping of conduction electrons from one site to another from those involving transfer of particle hole pairs(through the interaction terms) between sites which thus describe intersite interactions. We only consider these simple hopping processes. Using the average- T approximation, these simple hopping terms is easily summed. This summation is described in Appendix G.1. Here the conduction electron can not be scattered at the same f electron site twice and this site restriction gives the cancellation of the hybridization self energy term $(-i\Gamma)$ in full $4f$ Green's function.

Specifically, the band electron self energy is written within this approximation as [27, 28]

$$\begin{aligned}\Sigma_c(\omega, T) &= V^2[(G_{4f}(\omega, T))^{(-1)} + V^2 D(\omega)]^{(-1)} \\ &= V^2 G_{4f}^{(int)}(\omega, T),\end{aligned}\tag{2.77}$$

where G_{4f} is the the full $4f$ Green's function and defined in the Appendix F. And

The neglect of the intersite interaction terms leads to a purely frequency dependent self-energy for the conduction electrons. At low frequency and temperatures the damping in Eq. (2.77) vanishes, so that of Eq. (2.74) describes quasiparticles in an

effective hybridized band structure. In our calculation, the f -electrons have $j = 5/2$ and $j = 7/2$ states by spin-orbit coupling. Thus the conduction electron self energy has two terms from each j state.

$$\begin{aligned}\Sigma_c(\omega, \alpha, T) &= \sum_{j, m_j} |\langle j, m_j | V(\vec{k}) | \vec{k}, \alpha \rangle|^2 G_{4fj}^{(int)}(\omega) \\ &= 4\pi \sum_{j, m_j} |\langle j, m_j | 3m_3; \frac{1}{2}\alpha \rangle|^2 |Y_{3m_3}(\hat{k})|^2 V^2 G_{4fj}^{(int)}(\omega)\end{aligned}\quad (2.78)$$

where $V(\vec{k}) = V$ is the one particle hybridization strength, chosen independent of $|\vec{k}|$ in this calculation. Then

$$\begin{aligned}\sum_m |\langle \frac{5}{2}m | 3m_3; \frac{1}{2}\alpha \rangle|^2 |Y_{3m_3}(\hat{k})|^2 &= \frac{3}{4\pi} \\ \sum_m |\langle \frac{7}{2}, m | 3m_3; \frac{1}{2}\alpha \rangle|^2 |Y_{3m_3}(\hat{k})|^2 &= \frac{1}{\pi}.\end{aligned}\quad (2.79)$$

Thus the conduction electron self energy has simple form

$$\Sigma_c(\omega, \alpha, T) = V^2(3G_{4f5/2}^{(int)} + 4G_{4f7/2}^{(int)}). \quad (2.80)$$

With the inclusion of lattice coherent effects, the $I_{jj'}(c_k, c_{k'})$ term in the Knight shift calculation is changed from the incoherent form, Eq. (2.55).

$$\int k^2 dk \int k'^2 dk' I_{jj'}(c_k, c_{k'}) = - \int \frac{d\xi}{\pi} \text{Im} J(\xi) \text{Re} J(\xi) [f(\xi) I_{1jj'}(\xi) + (1 - f(\xi)) I_{2jj'}(\xi)] \quad (2.81)$$

where

$$\begin{aligned}J(\xi) &= \int dk \frac{k^2 j_3(kr)}{\xi - c_k - \Sigma_c(\xi)} \\ I_{1jj'}(\xi) &= \frac{2}{Z_{4f}} \int \frac{d\zeta}{\pi} \int \frac{d\rho}{\pi} \frac{(B^{(-)}(\zeta) A_{jm}(\rho) \text{Re} G_{j'm'}(\rho)}{\xi + \zeta - \rho}\end{aligned}\quad (2.82)$$

$$= \frac{1}{Z_{4f}} \int \frac{d\zeta}{\pi} B^{(-)}(\zeta) \text{Re} G_{jm}(\zeta + \xi) \text{Re} G_{j'm'}(\zeta + \xi) \quad (2.83)$$

$$\begin{aligned} I_{2jj'}(\xi) &= \frac{-2}{Z_{4f}} \int \frac{d\zeta}{\pi} \int \frac{d\rho}{\pi} \frac{B(\zeta) A_{jm}^{(-)}(\rho) \text{Re} G_{j'm'}(\rho)}{\xi + \zeta - \rho} \\ &= \frac{2}{Z_{4f}} \int \frac{d\rho}{\pi} A_{jm}^{(-)}(\rho) \text{Re} G_{j'm'}(\rho) \text{Re} D(\rho - \xi). \end{aligned} \quad (2.84)$$

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CHAPTER III

Results

In this chapter, the numerically calculated results of the Knight shift $K(T)$ and magnetic susceptibility $\chi(T)$ of heavy electron materials such as CeSn_3 , YbCuAl , and $\text{U}_{0.2}\text{Y}_{0.8}\text{Pd}_3$ will be presented. CeSn_3 and YbCuAl are concentrated heavy electron materials and $\text{U}_{0.2}\text{Y}_{0.8}\text{Pd}_3$ is a proposed two channel quadrupolar Kondo heavy electron compound.

First, the Knight shifts $K(\vec{r}, T)$ are systematically calculated for different Kondo temperature T_0 which is controlled by hybridization width $\Gamma = \pi N(0)V^2$, where $N(0)$ is the conduction electron density of states at the Fermi energy and V is the one particle hybridization strength, for Ce and Yb compounds. These results show that the magnitude of the Knight shift anomaly depends on the distance $\vec{r}$ between local magnetic moment and nucleus and Kondo temperature T_0 . There is an anomaly even for the small distance $\vec{r}$. The magnitude of deviation between a linear K vs χ relation is systematically increased when the distances are increased and the Kondo temperatures are increased. These results are shown in Fig. 3.5 and Fig. 3.6. These calculations support Ishii's idea of an anomalous conduction electron spin density cloud [1, 2] which sets in beyond the Kondo screening length $\xi_K = \hbar v_F / k_B T_0$, where

v_F is the Fermi velocity.

The lattice sum is carried out over a few hundred shells to be compared with the experimental results. In section 3.2 the results for CeSn_3 are compared with experiments. Both the ^{119}Sn NMR Knight shift and μsr Knight shift are studied. Also the influence of lattice coherence of the conduction electrons on both the NMR and positive muon Knight shift is investigated using the average T-matrix approximation and the numerically calculated results for CeSn_3 are compared with the experiments and also the calculated incoherent Knight shift. The calculated ^{119}Sn NMR Knight shift agrees well with the experiment, but the μsr Knight shift doesn't agree with experimental result even though it shows an anomaly.

For YbCuAl , because of its complicated crystal structure, only the incoherent lattice sum is carried over several thousand atoms. The calculated ^{27}Al NMR Knight shift results are mentioned in section 3.3. These results show excellent agreement with the experiments.

In the last section the Knight shift and magnetic susceptibility of $\text{U}_{0.2}\text{Y}_{0.8}\text{Pd}_3$ is discussed. We do a full incoherent lattice sum and impurity configuration averaging for $\text{U}_{0.2}\text{Y}_{0.8}\text{Pd}_3$. Our study doesn't show the low temperature Knight shift anomaly like experiment.

3.1 Systematic Calculations

To see the systematic behavior of magnetic susceptibility and the Knight shift, $\chi(T)$ and $K(\vec{r}, T)$ are calculated for different Kondo temperature T_0 . For spin-orbit cou-

pling and zero crystal field splitting, T_0 is given by

$$k_B T_0 = D \left(\frac{\Gamma}{\pi |\epsilon_f|} \right)^{1/N_g} \left(\frac{D}{\Delta_{so}} \right)^{N_{ex}/N_g} \exp\left(\frac{\pi \epsilon_f}{N_g \Gamma} \right), \quad (3.1)$$

where N_g is the degeneracy of the ground spin orbit multiplet, N_{ex} is the degeneracy of the excited multiplet, ϵ_f is the energy level position of the ground multiplet, Δ_{so} is the energy gap between two spin orbit multiplets, and $\Gamma = \pi N(0)V^2$ is the hybridization width (D is the physical Lorentzian bandwidth of the conduction electron). The values of the each parameters for Ce and Yb ions are listed in Table 1.

For several different hybridization widths Γ , the Knight shift was studied as a function of temperatures and distance $\vec{r}$ between the local impurity spin and nucleus at fixed angle θ between $\vec{r}$ and quantization axis $\vec{k} - \vec{k}'$. In these calculations all other variables such as ϵ_f , and Δ_{so} were fixed to the values which give best magnetic susceptibility $\chi(T)$ fit to experimental results of CeSn₃ for Ce ions and YbCuAl for Yb ions (see section 3.2 and section 3.3 for the parameter values.). The Knight shift is scaled to the susceptibility by matching at high temperatures. For all the calculations the conduction electron band width D was assumed to be 3eV. Because of the small gap between $j = 5/2$ and $j = 7/2$ states of Ce compound ($\Delta_{so} = 0.29\text{eV}$ for Ce ions and $\Delta_{so} = 1.30\text{eV}$ for Yb ions), the van Vleck term is included for only Ce compound studies.

Fig. 3.2 shows calculated Knight shift $K(\vec{r}, T)$ as a function of separation r and temperatures T at fixed angle $\theta = 0$ and hybridization width $\Gamma = 0.050667D$ ($T_0 = 430\text{K}$) for Ce ions on a large scale. We use dimensionless variable $k_F r$ with the Fermi wave vector $k_F = 0.65\text{\AA}^{-1}$ instead of r . The Knight shift on a fine scale

Figure 3.1: Knight shift $K(r, T)$ at fixed angle $\theta = 0$ and Kondo temperature $T_0 = 430$ K for Ce ions on a fine scale. We use dimensionless variable $k_F r$ with the Fermi wave vector $k_F = 0.65 \text{ \AA}^{-1}$ instead of r . Around $k_F r = 3.2$ the lines of $T = 104$ K and $T = 52$ K are crossed. This can be explained that the Knight shift summation converges faster at higher temperatures and it has longer range at lower temperatures as mentioned by E.S. Sørensen and I. Affleck [3, 4, 5].

Figure 3.2: Knight shift $K(r, T)$ at fixed angle $\theta = 0$ and Kondo temperature $T_0 = 430K$ for Ce ions. We use dimensionless variable $k_F r$ with the Fermi wave vector $k_F = 0.65\text{\AA}^{-1}$ instead of r . This shows an oscillatory behavior like the RKKY interaction form and the amplitude is decreased as the temperature is increased and the distance r is increased. The calculations are done at the same temperatures in Fig 3.1.

Figure 3.3: Knight shift $K(r, T)$ at fixed angle $\theta = \pi/2$ and Kondo temperature $T_0 = 430$ K for Ce ions on a fine scale. We use dimensionless variable $k_F r$ (with the Fermi wave vector $k_F = 0.65 \text{ \AA}^{-1}$). Knight shift has maximum amplitude around $T = 104$ K. Around $k_F r = 2.8$ the lines of $T = 174$ K and $T = 52$ K are crossed. This can be explained that the Knight shift summation converges faster at higher temperatures and it has longer range at lower temperatures as mentioned by E.S. Sørensen and I. Affleck [3, 4, 5].

Figure 3.4: **Knight shift $K(r, T)$ at fixed angle $\theta = \pi/2$ and Kondo temperature $T_0 = 430K$ for Ce ions.** We use dimensionless variable $k_F r$ (with the Fermi wave vector $k_F = 0.65\text{\AA}^{-1}$). This shows an oscillatory behavior like the RKKY interaction form and the amplitude is decreased as the temperature is increased and the distance r is increased. The calculations are done at the temperatures in Fig 3.1.

is shown in Fig. 3.1. The Knight shift shows an oscillatory behavior like RKKY interaction form and the total magnitudes are decreased when distance is increased. $|K(T)|$ at fixed distance r is first increased and then decreased (it becomes almost constant). when temperature is lowered. In the Fig. 3.1, we can see that the lines of $T = 104K$ and $T = 52K$ are crossed around $k_F r = 3.2$. The temperature where $K(T)$ has the maximum value is a function of separation r and has lower value with larger separation r . This can be explained that the Knight shift converges faster at higher temperatures and it has longer range at lower temperatures as mention by E.S. Sørensen and I. Affleck [3, 4, 5]. The Knight shifts of Yb ions show similar behaviors.

For a fixed Kondo temperature T_0 and distance r , the knight shift $K(T)$ shows a linear relation with the magnetic susceptibility $\chi(T)$ at high temperature and it starts to deviate from the linear relation and shows an anomaly when temperature is lower than T_{max} which has the maximum value of $\chi(T)$. Fig. 3.5 shows the Knight shift at $\theta = 0$, $T_0 = 380K$ as a function of magnetic susceptibility for different separation, with temperature as an implicit variable for Ce ions. These show a linear K vs. χ relation at high temperatures (in this figure, high temperatures correspond to the lower left corner) and show non-linear K - vs. - χ relations at low temperatures. The anomaly, *i.e.* the magnitude of the non-linearity, diminishes as the separation r is decreased. In Fig. 3.6, the Knight shift is investigated at $k_F r = 3.3$, and $\theta = 0$ for different Kondo temperatures. Like Fig. 3.5, temperature is an implicit variable and high temperatures correspond to the lower left corner. The magnitude of deviation from the linear relation is decreased when the Kondo temperature is reduced. For Ce

compound $k_F \xi_K \approx 25$ where $\xi_K = \hbar v_F / k_B T_0$ is the Kondo screening length with the Fermi velocity v_F . So our calculation is done comparable to the coherence length but inside the conduction electron screening spin cloud. Very similar results are obtained for Yb compounds.

This results confirms the Ishii's argument [1, 2] that when the radius r is bigger than Kondo screening length $\xi_K = \hbar v_F / k_B T_0$, where v_F is the Fermi velocity, the anomalous conduction spin density cloud sets. Inside this radius, conventional temperature independent RKKY oscillations dominate of the kind observed by Boyce and Slichter. Outside the screening length, at $T = 0$, the anomalous term will dominate also with an RKKY form but an amplitude of order D , the conduction bandwidth, compared with $D(N(0)J)^2$ for the Ruderman-Kittel term, where $N(0)$ is the conduction electron density of states at the Fermi energy and J the conduction electron-local moment exchange coupling. Ishii did not calculate the explicit temperature dependence of this structure, but did anticipate that it would vanish above the Kondo scale. Scaling analysis confirmed the asymptotic factorization of the Knight shift for short distance and low temperature [6]. A possible understanding of the Boyce and Slichter results, then, is the Cu nuclei they sampled were at distances $r \ll \xi_K$ from the Fe ions. But, in our calculation, the anomaly is still present and the magnitude is surprisingly large for short distance. A heuristic basis for understanding this is the two-pole approximation, as discussed in section 2.5.

Figure 3.5: Calculated Knight shift $K(T)$ for a single Ce site vs. susceptibility $\chi(T)$ for varying separation with the Kondo scale used to fit the CeSn_3 $\chi(T)$ (see Fig. 3.7). For each plot the angle is held at $\theta = 0$ with respect to the nuclear moment-Ce axis. The diagram of Fig. 2.4 is used to calculate $K(T)$. The magnitude of the non-linearity diminishes as k_{Fr} is reduced. The theoretical Knight shifts have been shifted by offset and scale factors to match the susceptibility; this does not affect the relative size of the anomaly.

Figure 3.6: Calculated Knight shift $K(T)$ vs. susceptibility $\chi(T)$ for a single Ce site at $k_{Fr} = 3.33$ from a nuclear moment and angle $\Theta = 0$. Fixing the f -level energy $\epsilon_{5/2} = -2\text{eV}$, and the spin orbit splitting $\Delta_{so} = 0.29\text{eV}$, the hybridization is varied to illustrate the dependence of the nonlinearity on the magnitude of T_0 (which ranges from 750 K to 130 K in these calculations as Γ varies from 0.165eV to 0.130eV). The diagram of Fig. 2.4 is used to calculate $K(T)$. The magnitude of the non-linearity diminishes as T_0 is reduced. The theoretical Knight shift has been shifted by a common offset and scale factor to match the susceptibility.

3.2 CeSn₃

The compound CeSn₃ has the f.c.c. AuCu₃ type of crystal structure. The local symmetry at every cerium site is cubic. At high temperatures, the magnetic susceptibility $\chi(T)$ of CeSn₃ shows typical Curie-Weiss-like behavior, followed by a maximum at $T_{max} \approx 40K$ and tending to a constant value at $T = 0$ [7, 8]. CeSn₃ has positive amplitude of Knight shift for the ¹¹⁹Sn nuclei. However, the calculated amplitude of the Knight shift before the scaling is actually negative, which implies that the fit is sensible only if the assumed contact coupling between conduction and nuclear spins is negative, which actually makes sense because the Sn nucleus should dominantly couple through core polarization, which produces a negative effective constant coupling. The NMR Knight shift $K(T)$ and $\chi(T)$ are related linearly above T_{max} . But the Knight shift doesn't follow the magnetic susceptibility below T_{max} and has weaker temperature dependence. The ¹¹⁹Sn NMR Knight shift has a positive anomaly, *i.e.* it has larger magnitude than that of magnetic susceptibility below the T_{max} . The positive muon spin rotation(μ sr) measurement shows that the positive muon Knight shift also exhibits an anomaly below T_{max} , but it has a different sign with respect to the susceptibility as compared to the NMR Knight shift [8].

3.2.1 NMR Knight Shift

To study the Knight shift for CeSn₃, first the hybridization width Γ for CeSn₃ is decided by comparing the calculated magnetic susceptibility and experimental magnetic

susceptibility, assuming a conduction electron density of states half width $D = 3eV$. As in the systematic calculation, a fixed value for parameter $c_{j5/2} = -2eV = -0.6667D$ is assumed, and $\Delta_{so} = 0.29eV = 0.096667D$ is used. Then D is varied a little to fine tune the results. Temperature is increased and the total magnitude of magnetic susceptibility is decreased when D is increased. The Knight shift is calculated with this fixed Kondo temperature (specified by $\Gamma = 0.050666D$) and conduction band width $D = 2.655eV$. The Kondo temperature which is given by the Eq. 3.1 is $T_0 = 0.0123$ in units of D *i.e.* $T_0 = 380K$.

For the Knight shift, an incoherent lattice sum is carried over several hundred shells of surrounding Ce ions about a given ^{119}Sn nucleus. We assume the Knight shift contribution of each ion to be described by this single impurity model, known to be a good approximation at high temperatures where the ions are incoherent with one another, and known to provide a very accurate description of the thermodynamics in many cases

Because Sn is on the face of each unit cell, we also average the Knight shift over the reference frame determined by whether ^{119}Sn is on the xy plane, or the xz plane (for $\vec{H} \parallel \hat{z}$). Note that yz is equivalent to xz . Like the systematic calculation, a Van-Vleck term is included for both magnetic susceptibility $\chi(T)$ and the Knight shift $K(T)$ calculation. The Knight shift is scaled by an intermediate range temperature match to the susceptibility, because the experimental data is measured only up to room temperatures.

As shown in Fig. 3.7 the results agree well with the experiments in spite of the

Figure 3.7: Temperature dependence of ^{110}Sn Knight Shift $K(T)$ and $\text{Ce } \chi(T)$ (both calculated and experimental results [7, 8]) for CeSn_3 . The theoretical $K(T)$ is calculated using the diagram of Fig.2.4 and with T_0 chosen to fit the experimental $\chi(T)$ data. A full (incoherent) lattice sum is carried out over several hundred shells of atoms.

oversimplified conduction electron band structure. Experimentally the ^{119}Sn NMR Knight shift has a positive sign and is linearly related to Ce magnetic susceptibility $\chi(T)$ at high temperatures. $K(T)$ shows an anomalous deviation from Ce $\chi(T)$ at low temperatures and the magnitude is bigger than χ . The calculated amplitude of the Knight shift before the scaling is actually negative, which implies that the fit is sensible only if the assumed contact coupling between conduction and nuclear spins is negative, which actually makes sense because the Sn nucleus should dominantly couple through core polarization. At high temperatures above 400K , $K(T)$ is reduced slowly with increasing temperature and shows deviation from χ . Experiment measures the Knight shift only up to 300K , so we are not sure whether this behavior is a numerical effect or real implicit effect. The magnitude of the anomalous contribution goes down with distance from the Sn nucleus and the theoretical data at a fixed distance which most closely match those of experiment are taken $k_{Fr} = 2.1$ and $\theta = 0$. Note that this distance is very short to compare with the Kondo screening length $\xi_K = \hbar v_F / k_B T_0 \approx 25 / k_F$.

3.2.2 Lattice Coherence Effects

In the lattice, the repeated scattering of conduction electrons off the Ce ions (in every unit cell) may have the effect of reducing the screening length [9]. These lattice coherence effects are studied within a local approximation ($d = \infty$ expansion) to the lattice model. The conduction electron propagator in Fig. 2.4 becomes dressed and the conduction electron self energy is calculated using the average T-matrix

approximation, which is exact for a Lorentzian density of states within the local approximation [10, 11], and otherwise corresponds to the first iteration. The same parameters for the incoherent Knight shift calculation are used for coherent lattice sum. In the NCA calculation, due to the approximation involved, the minimum value in $-\text{Im}\Sigma_f(\omega, T)$ does not occur precisely at the Fermi energy (though it differs only by a small fraction of T_0) and is not equal to Γ . So the extrapolated low temperature minimum Γ_{NCA} is replaced by Γ .

The average magnitude and amplitude of the oscillation of the Knight shift is decreased from the that of the incoherent lattice sum because of the damping effects brought in by the imaginary part of conduction electron self energy. To test this idea, we added a phenomenological constant damping to the incoherent lattice sum. Fig. 3.8 shows the result for small damping, $-\text{Im}\Sigma_f = 0.01$ and Fig. 3.9 shows the results for large damping, $-\text{Im}\Sigma_f = 1$. In these figures $K(T) = \sum_{k_{\text{F}} < k_{\text{F}0}} K(r, T)$. This study shows that the amplitude of oscillation is reduced when the damping is increased. And the Knight shift converges the faster when the damping is the bigger. An impurity at large distance doesn't contribute to the total Knight shift because of the large damping, *i.e.* short life time of the conduction electrons. Also Fig. 3.10 shows the Knight shift calculated with the coherent lattice sum. It shows a behavior intermediate between small and large damping calculations.

The calculated results fit experimental data well in the region of temperatures between $100K$ and $250K$ where the experimental data exist. At low temperature, the Knight shift with coherent lattice effects also shows an anomaly, with a little

Figure 3.8: **Temperature dependence of Knight Shift $K(T)$ with small constant damping $-\text{Im}\Sigma_f = 0.01$ in incoherent lattice sum.** In this figure $K(T) = \sum_{k_{Fr} < k_{Fr_0}} K(r, T)$. The calculations are done at the same temperatures in Fig. 3.1. The small absolute magnitude corresponds to the high temperature and it increases as the temperatures goes down. The convergence is slower than the coherence lattice sum.

Figure 3.9: **Temperature dependence of Knight Shift $K(T)$ with large constant damping $-\text{Im}\Sigma_f = 1$ in incoherent lattice sum.** In this figure $K(T) = \sum_{k_{Fr} < k_{Fr_0}} K(r, T)$. The calculations are done at the same temperatures in Fig. 3.1. The small absolute magnitude corresponds to the high temperature and it increases as the temperatures goes down. They converge very fast, an impurity at large distance doesn't contribute to the total Knight shift because of the large damping, *i.e.* short life time of the conduction electrons.

Figure 3.10: **Temperature dependence of Knight Shift $K(T)$ with coherent lattice sum.** In this figure $K(T) = \sum_{k_{Fr} < k_{Fr_0}} K(r, T)$. The calculations are done at the same temperatures in Fig. 3.1. The small absolute magnitude corresponds to the high temperature and it increases as the temperatures goes down. The convergence is faster than the small damping case but slower than larger damping case.

Figure 3.11: Temperature dependence of ^{110}Sn Knight Shift $K(T)$ with coherence effect and $\text{Ce } \chi(T)$ (both calculated and experimental results [7, 8]) for CeSn_3 . The theoretical $K(T)$ is calculated using the diagram of Fig. 2.4 and with T_0 chosen to fit the experimental $\chi(T)$ data. A full coherent lattice sum is carried out over several hundred shells of atoms using the average T-matrix approximation to approximate the coherent conduction self energy.

Table 8: Explicit values of both incoherent and coherent Knight shift at high temperatures. They have similar values because coherent lattice effects are small at high temperatures. These are unadjusted data.

Temperature	Knight Shift	
	Incoherent	Coherent
925K	-0.3579	-0.44855
615K	-2.4078	-2.42525
555K	-3.0157	-2.84562
490K	-3.7184	-3.34231
430	-4.5380	-3.95714

discrepancy with the experiment. At higher temperatures it shows tails which has bigger values than the experimental susceptibility(see Fig. 3.11). If we fit the results to this high temperature magnetic susceptibility, then the Knight shift has bigger values at the maximum temperature and shows sharp changes with temperature changes. We are not sure which is the best way to fit the result with the experiment. The calculated magnitudes(before the scaling to fit the experimental results) of both incoherent and coherent Knight shift have similar values at high temperatures where coherent lattice effects are small. Explicit values are shown in Table 8.

3.2.3 μ sr Knight Shift

Positive muons, stopped in a solid, come to rest at interstitial sites, where the muon spin performs a Larmor precession in the local magnetic field. The muon Knight shift

is then a measure of the local magnetic susceptibility. From volume considerations it is most likely that the muon preferentially occupies the octahedral interstices of the AuCu_3 structure (as it does in metals with the closely related fcc structure), rather than the tetrahedral sites. There are, however, two inequivalent octahedral sites, one at the center of the cubic unit cell and the other at the middle of the Ce atoms which has a non-cubic symmetry. So in principle two resonances are expected. In the experiment by Wehr and *et.al* [12], only one resonance was observed because either the muon performs a site average by fast diffusion or the frequency difference is small with respect to the apparent width of the signal which is given by the muon lifetime and the intrinsic width γ .

In the Curie-Weiss regime of CeSn_3 above 200K, the temperature dependence of the positive muon Knight shift is linearly related to the bulk magnetic susceptibility. In the intermediate valence regime of CeSn_3 the local magnetization as experienced by the muon decreases more strongly below 200K than the magnetization of the $4f$ state as deduced from the bulk susceptibility. This behavior reflects either a modification of the transferred hyperfine fields between the $4f$ moments and the muon or the signals the influence of an additional negative Knight shift contribution which was absent or small in the high temperature ranges. Comparing with the NMR Knight shift, the μsr Knight shift has a maximum at higher temperature and the sign of anomaly is opposite. This anomalous reduction of positive muon Knight shift might be regarded as an indication for an additional negative d-electron Knight shift contribution[12]. In terms of a band picture, the increase of d character at the Fermi level can be

understood as a $4f - 5d$ hybridization effect. It is supported by de Haas-van Alphen measurements [14]. Positive muons sitting between Ce atoms should be particularly sensitive to variations in the $5d$ states from the symmetry of these orbitals.

The μ^+ Knight shift was calculated for the both possible muon sites. Both incoherent and coherent lattice sums are carried over several hundred shells of Ce atoms. All other parameters for the calculations are same as for the ^{119}Sn NMR Knight shift calculations. Fig. 3.12 shows the results assuming that muon sits at the center of the cubic unit cell. At high temperatures, the calculated μ_{sr} Knight shift agrees well with the experimental data and shows a linear relation with the bulk magnetic susceptibility. Both incoherent and coherent lattice sum studies give the correct magnitude for the low temperature Knight shift anomaly but the wrong sign. Also the maxima occur at lower temperature and the magnitude is bigger than the experiment.

The results assuming that muon occupies the middle of the Ce-Ce band axis are shown in Fig. 3.13. In this case, results with the incoherent lattice sum show similar behavior of the results of previous calculations (assuming the muon sits at the center of the unit cell), *i.e.* the maximum occurs at lower temperature and the sign of anomaly is opposite with respect to the magnetic susceptibility, but the magnitude of anomaly is bigger. But the result of the coherent lattice sum shows very interesting behavior even though it does not agree with experiment. The Knight shift starts to deviate from the linear relation at higher temperature and the magnitude of anomaly is larger than experimental result. Note that the sign of the anomaly is agrees with experiment. There is a possibility to fit the experimental data by averaging the μ_{sr}

Figure 3.12: Temperature dependence of positive muon Knight Shift $K'(T)$ and Ce $\chi(T)$ (both calculated and experimental results[8, 12] for CeSn_3 . The theoretical $K'(T)$ is calculated assuming that muon sits at the center of cubic unit cell. Other parameters are same as for the ^{119}Sn NMR Knight shift calculation.

Figure 3.13: Temperature dependence of positive muon Knight Shift $K(T)$ and Ce $\chi(T)$ (both calculated and experimental results [8, 12]) for CeSn_3 . The theoretical $K(T)$ is calculated assuming that muon sits at the middle of the axis between the Ce atoms. Other parameters are same as for the ^{119}Sn NMR Knight shift calculation.

Knight shift from both positions. But, there is no experimental data which gives information about the fractional site occupancy.

Also, if the muon is not situated at a site of cubic symmetry, dipolar fields from the induced local moments may give the dominant contribution to the positive muon Knight shift. The magnetic dipole which is inversely related to the mass, can give comparable contribution to the positive muon Knight shift contrast to the ^{119}Sn NMR Knight shift [13]. The direct dipolar interaction energy of two magnetic dipoles $\vec{m}_1$ and $\vec{m}_2$, separated by $\vec{r}$ is given

$$U = \frac{1}{r^3}[\vec{m}_1 \cdot \vec{m}_2 - 3(\vec{m}_1 \cdot \hat{r})(\vec{m}_2 \cdot \hat{r})] \quad (3.2)$$

The dipolar part of the Knight shift tracks directly the atomic susceptibility of the nearest neighbor f-electron ions while the contact hyperfine contribution is what we are interested in.

Perhaps part of the discrepancy between experimental results and calculations are arising from the presence of dipolar fields. This idea will be investigated in the near future.

3.3 YbCuAl

The ternary inter-metallic compound YbCuAl has the hexagonal Fe_2P type crystal structure [15, 16], in which each Yb atom has the same local environment. The structure of YbCuAl is shown in Fig. 3.14.

At low temperatures, the magnetic susceptibility $\chi(T)$ has a large constant value ($\chi(0) =$

Figure 3.14: Crystal structure of YbCuAl (hexagonal Fe₂P type) [15, 16].

$25.5 \times 10^{-3} \text{ e.m.u./mole Yb atoms}$) and a maximum value at $T_{max} \approx 27 \text{ K}$. There is a Curie-Weiss like behavior above T_{max} [8, 17, 18]. ^{27}Al NMR shift data were obtained from derivative spectra of the central ($1/2 \leftrightarrow -1/2$) NMR transition. Above T_{max} , χ and K track each other, as expected if only one mechanism is appreciably temperature dependent. Here the Yb magnetization is the obvious candidate for the temperature-dependent contributions to both $\chi(T)$ and $K(T)$. This linear $K(\chi)$ relation has been used to determine the relative scales of the $\chi(T)$ and shift coordinate axes in Fig. 3.15. The linear relation breaks down below T_{max} .

The ^{27}Al NMR Knight shift has negative sign and the absolute magnitude of the low temperature Knight shift is smaller than magnetic susceptibility, opposite to the case of CeSn_3 . For YbCuAl , the ground state energy for f state is taken as $\epsilon_{f7/2} = -1 \text{ eV} = -0.333D$ and $\Delta_{so} = 1.3 \text{ eV} = 0.4333D$. Because of the large value of Δ_{so} , we can neglect the interaction between $j = 7/2$ ground state and $j = 5/2$ excited state. Without this Van-Vleck term, we can estimate the conduction electron band half width D using the zero temperature magnetic susceptibility $\chi(0)$ value.

$$\chi(0) = \frac{g_j^2 j(j+1) u_B^2 N_0}{3k_B T_0} \quad (3.3)$$

With $\chi(0) = 25.5 \times 10^{-3}$, we get $k_B T_0 = 8.7974 \times 10^{-3} \text{ eV}$. Also with the relation

$$\left(\frac{T_0}{D}\right)_{exp} = \left(\frac{T_0}{D}\right)_{the} \quad (3.4)$$

where $D_{the} = 3 \text{ eV}$, and $(T_0/D)_{the} = 0.00184$, we get $D_{exp} = 4.7812 \text{ eV}$. But, we get the best magnetic susceptibility fit with $D = 3.5 \text{ eV}$ and $\Gamma = 0.02033D$. The incoherent lattice sum is carried out for over 8000 shells of atoms because of the complicated crystal structure. Each shell only includes a few atoms.

Figure 3.15: Temperature dependence of ^{27}Al Knight Shift $K(T)$ and Yb $\chi(T)$ (both calculated and experimental results [8, 17, 18]) for YbCuAl. The theoretical $K(T)$ is calculated using the diagram of Fig. 2.4 and with T_0 chosen to fit the experimental $\chi(T)$ data. A full (incoherent) lattice sum is carried out over twenty four thousand atoms.

Calculated results are shown in Fig. 3.15. Both the magnetic susceptibility and the Knight shift agree well with experimental results and can explain both the magnitude and sign of Knight shift anomaly in spite of the oversimplified conduction electron band structure.

3.4 $Y_{0.8}U_{0.2}Pd_3$

The $Y_{1-x}U_xPd_3$ system has aroused great interest, following the discovery of non-Fermi liquid behaviour for uranium concentrations around $x = 0.2$ [19, 20, 21]. This discrepancy has been interpreted as possibly arising from a two channel quadrupolar Kondo effect [19, 22] or from critical effects of a new kind of second-order phase transition at zero temperature [23]. We will mainly discuss the composition $x = 0.2$.

$Y_{0.8}U_{0.2}Pd_3$ has a cubic $AuCu_3$ crystal structure. The $j = 4$ ground state of U^{4+} is split to Γ_1 singlet, Γ_3 nonmagnetic doublet, and Γ_4 and Γ_5 magnetic triplet. Knowledge of the crystal field ground state is a crucial test for the validity of the quadrupolar Kondo model and there are several neutron scattering experiments to decide the ground state of $Y_{0.8}U_{0.2}Pd_3$ [24, 25, 26]. Mook *et. al.* [24] interpreted their results in terms of a crystal field level scheme with a Γ_3 doublet ground state and Γ_5 and Γ_4 excited triplet states at 5 and 16 meV, respectively and thus support the two channel quadrupolar Kondo effect interpretation. In this case, $\chi(T)$ originates in the Van-Vleck susceptibility associated with transition from a Γ_3 nonmagnetic ground doublet into excited-state Γ_5 and Γ_4 triplets. The Γ_3 is described by a quadrupolar pseudospin. This couples to pseudospin variables of a conduction Γ_8 quartet in time-

reversed channels, the antiferromagnetic pseudospin coupling is mediated by virtual charge fluctuations to magnetic doublets in excited-state configurations.

McEwen *et al.* [25] saw a magnetic origin peak at 36meV and another peak around 4meV and explained this with the transition between Γ_3 ground state with excited states Γ_4 , Γ_1 and Γ_5 . They couldn't find a peak at 16meV .

But Dai *et.al* [26] reported a Γ_5 magnetic ground state with polarized inelastic neutron scattering experiment and Γ_3 and Γ_4 excited states at 5, 39 meV . But there is no quasielastic scattering around $\hbar\omega = 3.6\text{meV}$ ($\sim 42\text{K} = k_b T_0$), expected for a conventional magnetic Kondo effect.

For $x = 0.1$ and 0.2 , a breakdown of the expected linearity between the NMR Knight shift and the bulk susceptibility χ is found below $\sim 50\text{K}$ [27]. The magnetic susceptibility exhibited an upturn at low temperatures (Curie tail), indicating the presence of magnetic impurities (see Fig.3.16). The impurity magnetic susceptibility was subtracted [28]. The temperature dependence of $\chi(T)$ [24] suggests that the mechanism for the two channel behavior is the quadrupolar Kondo effect [22].

$$\frac{\chi(T)}{\chi(0)} \approx 1 - A\left(\frac{T}{T_0}\right)^{(1/2)} \quad (3.5)$$

In our study, we consider f^2 and f^3 configurations for U ions. By the Hund's rule, only the lowest f^2 , $j = 4$ and f^3 , $j = 9/2$ spin-orbit state is kept for the calculation. $j = 4$ states is split to Γ_3 ground doublet, Γ_5 , Γ_4 and Γ_1 excited state and $j = 9/2$ multiplet is split to Γ_6 doublet and two Γ_8 quartets. The conduction electron band width D is assumed to be 3eV . All parameter values are listed in Table 2 in the unit of D . where ϵ_f is the energy of $j = 4$ multiplet and Δ_{ij} is the energy difference between

Figure 3.16: Temperature dependence of ^{89}Y Knight Shift $K(T)$ and $\text{U } \chi(T)$ (both calculated and experimental results [27, 28]) for $\text{Y}_{0.8}\text{U}_{0.2}\text{Pd}_3$. The theoretical $K(T)$ is calculated using the diagram of Fig. 2.4 and with T_0 chosen to fit the experimental $\chi(T)$ data. A full (incoherent) lattice sum and impurity configuration averaging is carried out over a several shells.

crystal field split Γ_i and Γ_j states. Γ is the single impurity hybridization width. The incoherent lattice sum is carried out over three hundred shells with impurity configuration averaging.

Fig. 3.16 shows both the experimental and calculated magnetic susceptibility and ^{89}Y NMR Knight shift. In our calculation, both the bulk magnetic susceptibility and the Knight shift become constant when the temperature goes to zero and thus a Knight shift anomaly doesn't arise. Our calculated magnetic susceptibility saturates when the temperature goes to zero and doesn't show the low temperature singularity like experiment. This may arise from the numerical calculation or from intrinsic properties such that real ground state may be magnetic as discussed earlier. But, the calculated Knight shift agrees well with the experimental data in magnitude and temperature dependence.

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CHAPTER IV

Summary and Future Work

4.1 Summary

In this dissertation, we have calculated the magnetic susceptibility and the Knight shift for the heavy electron materials within the infinite- U single impurity Anderson model using NCA method. Ours is the first study to display low temperature Knight shift anomaly in a realistic impurity model calculation though it has an oversimplified conduction electron band structure.

First, we systematically studied the magnetic susceptibility $\chi(T)$ and the Knight shift $K(\vec{r}, T)$ for Ce and Yb ions, where $\vec{r}$ is the distance between the local impurity spin and the nucleus spin. They are calculated for different Kondo temperature T_0 which is controlled by the hybridization width Γ . The Knight shift shows an oscillatory behavior like the RKKY interaction and the magnitude is decreased with increasing r and first increased and almost saturated when temperatures are decreased. The Knight shift and magnetic susceptibility have linear relations at high temperatures and start to deviate from each other at low temperatures. We can systematically show that the Knight shift anomaly is increased when the Kondo temperature T_0 is

increased and the separation r is increased.

For CeSn_3 , which is a concentrated heavy electron materials, both the ^{119}Sn NMR Knight shift and positive muon Knight shift are numerically calculated and compared with the experimental results. First, the lattice effect is included by carrying out the incoherent lattice sum. The Knight shifts of a few hundreds shells of Ce ions around the Sn nucleus are added. Also lattice coherent effects by conduction electrons scattering at every f site are included using the average-T matrix approximation.

The calculated magnetic susceptibility and ^{119}Sn NMR Knight shift show excellent agreement with experimental results for both incoherent and coherent calculations. The positive muon Knight shifts are calculated for both possible sitting positions of muon (center of the cubic unit cell and middle of Ce-Ce bond axis). Comparing with the experimental ^{119}Sn Knight shift, the measured μsr Knight shift has a maximum at higher temperatures and sign of anomaly is opposite. Our numerical results have lower maximum temperatures and the sign of anomaly is opposite to the experimental results except the result of the lattice coherent calculation assuming that muon sits middle of Ce ions which has higher maximum temperature and very large negative anomaly. There is a possibility that we can have results which agree with the experiments by averaging out the Knight shifts from both positions, but there is no experimental informations concerning the fractional site occupancy. Also, there may be effects due to direct dipole-dipole interactions, and this contribution can be comparable to the effects of indirect interaction because of light mass of positive muon [1].

For YbCuAl, the ^{27}Al NMR Knight shift shows anomaly with opposite sign to CeSn₃ compound, only incoherent lattice sum is carried out over 8 thousands shells of Yb ions around Al nucleus because of its complicated crystal structure. Our calculations agree very well with the experiments. Our study can explain both signs of the Knight shift anomaly.

For proposed quadrupolar Kondo alloy $\text{Y}_{0.8}\text{U}_{0.2}\text{Pd}_3$, ^{89}Y NMR Knight shift is calculated. We included the crystal electric field effects and considered the nonmagnetic $j = 4 \Gamma_3$ doublet and $j = 9/2 \Gamma_6$ doublet as the lowest energy states for the f^2 and f^3 configurations. The incoherent lattice sum by carrying out over three hundred shells with impurity configuration averaging. In our calculation, both the bulk magnetic susceptibility and the Knight shift become constant when the temperature goes to zero and thus a Knight shift anomaly doesn't arise. Our calculated magnetic susceptibility saturates when temperature goes to zero and doesn't show the low temperature singularity like experiment. This may be due to the numerical calculation or intrinsic properties of the real ground state. may be magnetic as discussed earlier. But, the calculated Knight shift agrees well with the experimental data in magnitude and temperature dependence.

In our calculations we can explain that the Knight shift anomaly in heavy electron materials with the simplified single impurity Kondo effect. There exists the Knight shift anomaly at short distance $r < \xi_K$, with amplitude proportional to T_0/Γ .

4.2 Direction for Future Work

Our calculations show generally good agreement with experimental results in spite of the oversimplified band structure. Especially, the short distance Knight shift depends on the detailed structure on conduction electron band and our calculation shows large contributions from the short distance Knight shift. For future work, we can include more realistic conduction electron band structure which can be calculated with LMTO (linearized Muffin-Tin Orbital) method.

Also for positive muon Knight shift of CeSn_3 compound, we can not neglect the direct dipole-dipole interaction for noncubic symmetry site (between the middle of Ce-Ce ions). because of the light mass of muon this effects can give comparable contribution to the Knight shift.

For the U ions, we need more information about the CEF ground state. In our study, $f^2 \Gamma_3$ nonmagnetic doublet is assumed as a ground state. But, there is a controversy about which CEF state is the ground state. If the ground state is magnetic we can not use two channel quadrupolar Kondo model. After we get more information, we can tell whether the discrepancy of magnetic susceptibility between experiment and our model study comes from an intrinsic property of compound or the wrong the choice of the ground state. Also, we can think of the case that different CEF states have different hyperfine interaction. Each hyperfine field induces the different Knight shift and this can be the reason of a anomaly.

We can perform the Knight shift calculations for other heavy fermion materials, such as URu_2Si_2 and PrNi_5 , which show the μsr Knight shift anomaly.

For the Knight shift evaluation, the vertex correction which arises from the inclusion of the higher order hybridization can be considered.

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Appendix A

Crystal Electric Field Effect

In the crystal lattice, magnetic ions feel an electrostatic field produced by the neighboring ions. This crystal field lifts the degeneracy of the angular momentum of the magnetic ions. The most common method to calculate the effect of the crystal electric field is the operator equivalent techniques [1] which exploits the Wigner-Eckart theorem to replace the electrostatic potential terms in the Hamiltonian by operators in the angular momentum space of the ground multiplet. It depends on the symmetry of the crystal and the orbital angular momentum j of the magnetic electrons. The most general Hamiltonian with cubic symmetry [2, 3] can be written as

$$\mathcal{H}_{cef} = B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4) \quad (\text{A.1})$$

where

$$\begin{aligned} O_4^0 &= 35J_z^4 - [30J(J+1) - 25]J_z^2 - 6J(J+1) + 3J^2(J+1)^2 \\ O_4^4 &= \frac{1}{2}(J_+^4 + J_-^4) \\ O_6^0 &= 231J_z^6 - 105[3J(J+1) - 7]J_z^4 + [105J^2(J+1)^2 - 525J(J+1) + 294]J_z^2 \\ &\quad - 5J^3(J+1)^3 + 40J^2(J+1)^2 - 60J(J+1) \end{aligned}$$

$$O_6^4 = \frac{1}{4}[11J_z^2 - J(J+1) - 38](J_+^4 + J_-^4) + \frac{1}{4}(J_+^4 + J_-^4)[11J_z^2 - J(J+1) - 38]. \quad (\text{A.2})$$

The coefficients B_4 and B_6 are the factors which determine the scale of the crystal field splittings. In a simple point charge model, they are linear functions of $\langle r^4 \rangle$ and $\langle r^6 \rangle$, the mean fourth and sixth powers of the radii of the magnetic electrons, and thus depend on the detailed nature of the magnetic ion wave functions. We treat these as phenomenological parameters because these are very difficult to calculate quantitatively.

Following Ref [3], we rewrite the Hamiltonian as

$$\mathcal{H}_{ceJ} = B_4 F(4) \frac{O_4}{F(4)} + B_6 F(6) \frac{O_6}{F(6)}, \quad (\text{A.3})$$

where

$O_4 = [(O_4^0 + 5O_4^4)]$, and $O_6 = [O_6^0 - 21O_6^4]$ and $F(4)$ and $F(6)$ is the common factors to all the matrix elements of fourth and sixth degree terms. In order to cover all the possible values of the ratio between the fourth and sixth degree terms, we put

$$B_4 F(4) = Wx \quad (\text{A.4})$$

$$B_6 F(6) = W(1 - |x|) \quad (\text{A.5})$$

where $-1 < x < +1$.

It follows that

$$\frac{B_4}{B_6} = \frac{x}{1 - |x|} \frac{F(6)}{F(4)}, \quad (\text{A.6})$$

so that $B_4/B_6 = 0$ for $x = 0$ and $B_4/B_6 = \pm\infty$ for $x = \pm 1$.

Rewriting Eq. (A.3) we have

$$\mathcal{H}_{cef} = W \left[x \left(\frac{O_4}{F(4)} \right) + (1 - |x|) \left(\frac{O_6}{F(6)} \right) \right]. \quad (\text{A.7})$$

Here, the eigenvalue is related the crystal electric energy by the scale factor W .

In our calculations, we need the relations between parameters x_2 and W_2 for f^2 configuration and x_3 and W_3 for f^3 configuration of U ions. To get $j = 4 \Gamma_3$ and $j = 9/2 \Gamma_6$ the ground states of f^2 and f^3 configuration, we choose $x_2 < 0$ and $x_3 > 0$ and $W_2 < 0$. W_2 is decided by the energy splitting between Γ_3 and Γ_5 states, Δ_{35} .

$$W_2 = -\Delta_{35}/(84 + 114x_2) \quad (\text{A.8})$$

From the Eq. (A.4), Eq. (A.5) and Eq. (A.6), and factors which is given in Table I of reference [3], we get the relations of parameters between f^2 and f^3 configurations.

$$-3.143x_3(1 - |x_2|) = x_2(1 - |x_3|) \quad (\text{A.9})$$

$$W_3 = 0.3963W_2 \frac{x_2}{x_3} \quad (\text{A.10})$$

From the above equations we get $x_3 = 0.3693$ and $W_3 = 2.746 \times 10^{-4}$ for $x_2 = -0.648$ and $W_2 = -3.95 \times 10^{-4}$.

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Appendix B

Clebsch-Gordan Coefficients

These are the Clebsch-Gordan coefficients for hybridization interaction between $f^2 j = 4$ and $f^3 j = 9/2$ of U compound.

Table 9: Clebsch-Gordan coefficients for $j_c = 5/2$, $j_2 = 4$, and $j_3 = 9/2$, where $m_3 = m_c + m_2$.

$\frac{m_c}{m_2}$	$-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$
-4	0	0	$\sqrt{\frac{14}{33}}$	$\sqrt{\frac{14}{33}}$	$\sqrt{\frac{7}{33}}$	$\sqrt{\frac{5}{99}}$
-3	0	$-\sqrt{\frac{14}{33}}$	0	$\sqrt{\frac{7}{33}}$	$\sqrt{\frac{32}{99}}$	$\sqrt{\frac{5}{33}}$
-2	$\sqrt{\frac{5}{33}}$	$-\sqrt{\frac{3}{11}}$	$-\sqrt{\frac{3}{22}}$	$\sqrt{\frac{25}{1386}}$	$\sqrt{\frac{11}{42}}$	$\sqrt{\frac{125}{402}}$
-1	$\sqrt{\frac{10}{33}}$	$-\sqrt{\frac{2}{33}}$	$-\sqrt{\frac{169}{693}}$	$-\sqrt{\frac{8}{231}}$	$\sqrt{\frac{25}{231}}$	$\sqrt{\frac{250}{693}}$
0	$\sqrt{\frac{25}{66}}$	$\sqrt{\frac{5}{1386}}$	$-\sqrt{\frac{40}{231}}$	$-\sqrt{\frac{40}{231}}$	$\sqrt{\frac{5}{1386}}$	$\sqrt{\frac{25}{66}}$
1	$\sqrt{\frac{250}{693}}$	$\sqrt{\frac{25}{231}}$	$-\sqrt{\frac{8}{231}}$	$-\sqrt{\frac{169}{693}}$	$-\sqrt{\frac{2}{33}}$	$\sqrt{\frac{10}{33}}$
2	$\sqrt{\frac{125}{462}}$	$\sqrt{\frac{11}{42}}$	$\sqrt{\frac{25}{1386}}$	$-\sqrt{\frac{3}{22}}$	$-\sqrt{\frac{3}{11}}$	$\sqrt{\frac{5}{33}}$
3	$\sqrt{\frac{5}{33}}$	$\sqrt{\frac{32}{99}}$	$\sqrt{\frac{7}{33}}$	0	$-\sqrt{\frac{14}{33}}$	0
4	$\sqrt{\frac{5}{99}}$	$\sqrt{\frac{7}{33}}$	$\sqrt{\frac{14}{33}}$	$\sqrt{\frac{14}{33}}$	0	0

Table 10: Clebsch-Gordan coefficients for $j_c = 7/2$, $j_2 = 4$, and $j_3 = 9/2$, where $m_3 = m_c + m_2$.

$\frac{m_c}{m_2}$	$-\frac{7}{2}$	$-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$
-4	0	0	0	$-2\sqrt{\frac{7}{143}}$	$-\frac{8}{3}\sqrt{\frac{7}{143}}$	$-2\sqrt{\frac{35}{429}}$	$-4\sqrt{\frac{5}{429}}$
-3	0	0	$\sqrt{\frac{105}{286}}$	$\frac{7}{3}\sqrt{\frac{7}{286}}$	$-\frac{1}{3}\sqrt{\frac{7}{286}}$	$-\sqrt{\frac{45}{286}}$	$\sqrt{0.2806915}$
-2	0	$-\sqrt{\frac{45}{143}}$	$\sqrt{\frac{5}{429}}$	$\frac{16}{3}\sqrt{\frac{1}{143}}$	$\sqrt{0.1202132}$	$-\frac{1}{200}\sqrt{\frac{333}{10}}$	$-\frac{1}{8}\sqrt{\frac{111}{10}}$
-1	$\sqrt{\frac{35}{286}}$	$-\frac{1}{3}\sqrt{\frac{55}{26}}$	$-2\sqrt{\frac{10}{429}}$	$2\sqrt{\frac{6}{1001}}$	$\frac{27}{2}\sqrt{\frac{1}{1001}}$	$\frac{5}{2}\sqrt{\frac{15}{1001}}$	$-\frac{1}{40}\sqrt{\frac{333}{10}}$
0	$\frac{1}{3}\sqrt{\frac{350}{143}}$	$-\frac{5}{3}\sqrt{\frac{2}{143}}$	$-10\sqrt{\frac{2}{1001}}$	$-\sqrt{\frac{45}{1001}}$	$\sqrt{\frac{45}{1001}}$	$10\sqrt{\frac{2}{1001}}$	$\frac{5}{3}\sqrt{\frac{2}{143}}$
1	$\frac{5}{3}\sqrt{\frac{35}{286}}$	$\frac{1}{40}\sqrt{\frac{333}{10}}$	$-\frac{5}{2}\sqrt{\frac{15}{1001}}$	$-\frac{27}{2}\sqrt{\frac{1}{1001}}$	$-\sqrt{\frac{24}{1001}}$	$2\sqrt{\frac{10}{429}}$	$\frac{1}{3}\sqrt{\frac{55}{26}}$
2	$5\sqrt{\frac{5}{429}}$	$\frac{1}{8}\sqrt{\frac{111}{10}}$	$\frac{1}{200}\sqrt{\frac{333}{10}}$	$\sqrt{0.1202132}$	$-\frac{16}{3}\sqrt{\frac{1}{143}}$	$-\sqrt{\frac{5}{429}}$	$3\sqrt{\frac{5}{143}}$
3	$\frac{5}{6}\sqrt{\frac{35}{143}}$	$\sqrt{0.2806915}$	$3\sqrt{\frac{5}{286}}$	$\frac{1}{3}\sqrt{\frac{7}{286}}$	$-\frac{7}{3}\sqrt{\frac{7}{286}}$	$-\sqrt{\frac{105}{286}}$	0
4	$\frac{1}{3}\sqrt{\frac{70}{143}}$	$4\sqrt{\frac{5}{429}}$	$2\sqrt{\frac{35}{429}}$	$\frac{8}{3}\sqrt{\frac{7}{143}}$	$2\sqrt{\frac{7}{143}}$	0	0

Appendix C

Evaluation of Knight shift k Sum

In this appendix, the form of $I(c_k, c_{k'})$ expressed in Eq. (2.54) is derived. We define

$$I_{jj'}(c_k, c_{k'}) = j_3(kr)j_3(k'r)\frac{1}{\beta^2}\sum_{\omega,\nu}G_0(k\sigma, i\omega)G_0(k'\sigma', i\omega) \\ \times G_{jm}(i(\omega + \nu))G_{j'm'}(i(\omega + \nu))D(i\nu) \quad (C.1)$$

where $\omega[\nu] = (2n + 1)\pi i/\beta[2n\pi i/\beta]$ and the usual fermion(boson) Matsubara frequencies. G_0 is the bare conduction electron propagator, G_{jm} is a pseudofermion propagator for spin-orbit multiplet j , and D is a pseudoboson propagator. For the coherent calculation the bare conduction propagator is replaced by the dressed electron propagator. This coherence effects will be considered in Appendix G.

It is convenient to introduce the spectral function $A_m(\omega)$, and $B(\omega)$ for pseudo-particle Green's functions.

$$G_{jm}(i\omega) = \int \frac{d\rho}{\pi} \frac{A_{jm}(\rho)}{i\omega - \rho} \\ A_{jm}(\omega) = -\text{Im } G_{jm}(\omega) \quad (C.2)$$

$$D(i\nu) = \int \frac{d\zeta}{\pi} \frac{B(\zeta)}{i\nu - \zeta} \\ B(\nu) = -\text{Im } D(\nu) \quad (C.3)$$

In addition to spectral functions $A_m(\rho)$ and $B(\zeta)$, it is necessary to introduce negative frequency spectral functions $A_{jm}^{(-)}(\rho)$ and $B^{(-)}(\zeta)$. These spectra are given by

$$A_{jm}^{(-)}(\rho, T) = A_{jm}(\rho, T)e^{-\beta(\rho-E_0)} \quad (C.4)$$

$$B^{(-)}(\zeta, T) = B(\zeta, T)e^{-\beta(\zeta-E_0)}, \quad (C.5)$$

where E_0 is the ground state energy in the $Q = 1$ subspace relative to that of the Fermi sea. The impurity partition function Z_{Af} is given by

$$\begin{aligned} Z_{Af}(T) &= \int \frac{d\zeta}{\pi} [\sum_{jm} A_{jm}(\zeta, T) + B(\zeta, T)] e^{-\beta\zeta} \\ &= e^{-\beta E_0} \int \frac{d\zeta}{\pi} [\sum_{jm} A_{jm}^{(-)}(\zeta, T) + B^{(-)}(\zeta, T)]. \end{aligned} \quad (C.6)$$

Thus at $T \rightarrow 0$, $Z_{Af}(T)$ becomes

$$Z_{Af}(0) = e^{-\beta E_0}. \quad (C.7)$$

Then Eq. (C.1) can be rewritten as

$$\begin{aligned} I_{jj'}(\epsilon_k, \epsilon_{k'}) &= \frac{1}{Z_{Af}} j_3(kr) j_3(k'r) \frac{1}{\beta^2} \sum_{\omega, \nu} \frac{1}{i\omega - \epsilon_k} \frac{1}{i\omega - \epsilon_{k'}} \int \frac{d\zeta}{\pi} \frac{B(\zeta)}{i\nu - \zeta} \\ &\times \int \frac{d\rho}{\pi} \frac{A_{jm}(\rho)}{i(\omega + \nu) - \rho} \int \frac{d\rho'}{\pi} \frac{A_{jm'}(\rho')}{i(\omega + \nu) - \rho'}. \end{aligned} \quad (C.8)$$

Let's first do the ν summation.

$$\begin{aligned} (A) &= \frac{1}{\beta} \sum_{\nu} \frac{1}{i\nu - \zeta} \frac{1}{i(\omega + \nu) - \rho} \frac{1}{i(\omega + \nu) - \rho'} \\ &= \frac{f(\rho)}{(\rho - \rho')(\rho - i\omega - \zeta)} + \frac{f(\rho')}{(\rho' - \rho)(\rho' - i\omega - \zeta)} - \frac{N(\zeta)}{(i\omega + \zeta - \rho)(i\omega + \zeta - \rho')} \\ &= \frac{2f(\rho)}{(\rho - \rho')(\rho - i\omega - \zeta)} - \frac{N(\zeta)}{(\rho - \rho')} \left(\frac{1}{i\omega + \zeta - \rho} - \frac{1}{i\omega + \zeta - \rho'} \right) \\ &= \frac{2f(\rho) - 2N(\zeta)}{(\rho - \rho')(\rho - i\omega - \zeta)} \end{aligned} \quad (C.9)$$

where $f(\rho)[N(\zeta)] = (e^{\beta\rho} + 1)^{-1}[(e^{\beta\zeta} - 1)^{-1}]$. In this Eq. (C.9), only $(\rho - \zeta - i\omega)$ term is depend on ω . Including Eq. (C.9) to Eq. (C.8) we get

$$\begin{aligned} I_{jj'}(c_k, c_{k'}) &= j_3(kr)j_3(k'r)\frac{1}{\beta}\sum_{\omega}\frac{1}{i\omega - c_k}\frac{1}{i\omega - c_{k'}}\int\frac{d\zeta}{\pi}B(\zeta)\int\frac{d\rho}{\pi}A_{jm}(\rho) \\ &\times\int\frac{d\rho'}{\pi}A_{j'm'}(\rho')\frac{2f(\rho) - 2N(\zeta)}{(\rho - \rho')(\rho - i\omega - \zeta)}. \end{aligned} \quad (C.10)$$

Let's do the ω sum. We get

$$\begin{aligned} (B) &= \frac{1}{\beta}\sum_{\omega}\frac{1}{i\omega - c_k}\frac{1}{i\omega - c_{k'}}\frac{1}{(\rho - i\omega - \zeta)} \\ &= \frac{f(c_k)}{(c_k - c_{k'})(\rho - c_k - \zeta)} + \frac{f(c_{k'})}{(c_{k'} - c_k)(\rho - c_{k'} - \zeta)} + \frac{f(\rho - \zeta)}{(\rho - \zeta - c_k)(\rho - \zeta - c_{k'})} \\ &= \frac{f(c_k)}{(c_k - c_{k'})(\rho - c_k - \zeta)} + \frac{f(c_{k'})}{(c_{k'} - c_k)(\rho - c_{k'} - \zeta)} \\ &\quad - \frac{f(\rho - \zeta)}{(c_k - c_{k'})}\left(\frac{1}{c_k + \zeta - \rho} - \frac{1}{c_{k'} + \zeta - \rho}\right) \\ &= \frac{2f(c_k) - 2f(\rho - \zeta)}{(c_k - c_{k'})(c_k + \zeta - \rho)}. \end{aligned} \quad (C.11)$$

With Eq. (C.11), then $I_{jj'}(c_k, c_{k'})$ is written

$$\begin{aligned} I_{jj'}(c_k, c_{k'}) &= \frac{1}{Z_{Af}}j_3(kr)j_3(k'r)\int\frac{d\zeta}{\pi}B(\zeta)\int\frac{d\rho}{\pi}A_{jm}(\rho)\int\frac{d\rho'}{\pi}A_{j'm'}(\rho') \\ &\times\frac{(2f(\rho) - 2N(\zeta))(2f(c_k) - 2f(\rho - \zeta))}{(c_k - c_{k'})(\rho - \rho')(c_k + \zeta - \rho)}. \end{aligned} \quad (C.12)$$

Now taking the $\lambda \rightarrow -\infty$ projection

$$\begin{aligned} e^{-\beta\lambda}(N(\zeta) - f(\rho)) &= e^{-\beta\lambda}\left(\frac{1}{e^{\beta(\zeta-\lambda)} - 1} + \frac{1}{e^{\beta(\rho-\lambda)} + 1}\right) \\ &= e^{-\beta\zeta} + e^{-\beta\rho}. \end{aligned} \quad (C.13)$$

Also with the relation

$$\int\frac{d\rho'}{\pi}\frac{A_{j'm'}(\rho')}{\rho - \rho'} = \text{Re}G_{j'm'}(\rho), \quad (C.14)$$

then

$$I_{jj'}(c_k, c_{k'}) = \frac{4}{Z_{4f}} j_3(kr) j_3(k'r) \int \frac{d\zeta}{\pi} B(\zeta) \int \frac{d\rho}{\pi} A_{jm}(\rho) \text{Re} G_{j'm'}(\rho) \times \frac{(e^{-\beta\zeta} + e^{-\beta\rho})(f(c_k) - f(\rho - \zeta))}{(c_k - c_{k'})(c_k + \zeta - \rho)}. \quad (\text{C.15})$$

Also with $f(\rho - \zeta)(e^{-\beta\zeta} + e^{-\beta\rho}) = e^{-\beta\rho}$

$$I_{jj'}(c_k, c_{k'}) = \frac{4}{Z_{4f}} \frac{j_3(kr) j_3(k'r)}{c_k - c_{k'}} \int \frac{d\zeta}{\pi} \int \frac{d\rho}{\pi} \left[\frac{(B^{(-)}(\zeta) A_{jm}(\rho) \text{Re} G_{j'm'}(\rho) f(c_k))}{c_k + \zeta - \rho} + \frac{B(\zeta) A_{jm}^{(-)}(\rho) \text{Re} G_{j'm'}(\rho) (f(c_k) - 1)}{c_k + \zeta - \rho} \right]. \quad (\text{C.16})$$

The above equation, can be rewritten

$$I_{jj'}(c_k, c_{k'}) = 2 \frac{j_3(kr) j_3(k'r)}{c_k - c_{k'}} (f(c_k) I_{1jj'}(c_k) + (1 - f(c_k)) I_{2jj'}(c_k)) \quad (\text{C.17})$$

where

$$\begin{aligned} I_1(c_k) &= \frac{2}{Z_{4f}} \int \frac{d\zeta}{\pi} \int \frac{d\rho}{\pi} \frac{(B^{(-)}(\zeta) A_{jm}(\rho) \text{Re} G_{j'm'}(\rho))}{c_k + \zeta - \rho} \\ &= \frac{1}{Z_{4f}} \int \frac{d\zeta}{\pi} B^{(-)}(\zeta) \text{Re} G_{jm}(\zeta + c_k) \text{Re} G_{j'm'}(\zeta + c_k) \end{aligned} \quad (\text{C.18})$$

$$\begin{aligned} I_{2jj'}(c_k) &= \frac{-2}{Z_{4f}} \int \frac{d\zeta}{\pi} \int \frac{d\rho}{\pi} \frac{B(\zeta) A_{jm}^{(-)}(\rho) \text{Re} G_{j'm'}(\rho))}{c_k + \zeta - \rho} \\ &= \frac{2}{Z_{4f}} \int \frac{d\rho}{\pi} A_{jm}^{(-)}(\rho) \text{Re} G_{j'm'}(\rho) \text{Re} D(\rho - c_k). \end{aligned} \quad (\text{C.19})$$

Appendix D

Analytic Calculations of Inner k' Integral in the Knight shift

We can calculate the inner k' integral analytically. This is given by

$$\int_0^\infty k'^2 dk' \frac{j_3(k'r)}{k^2 - k'^2} \quad (\text{D.1})$$

where j_n is the spherical Bessel function, with recurrence relation given by

$$f_{n-1}(x) + f_{n+1}(x) = \frac{2n+1}{x} f_n(x). \quad (\text{D.2})$$

The relevant spherical Bessel functions are

$$j_0(x) = \frac{\sin x}{x} \quad (\text{D.3})$$

$$j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x} \quad (\text{D.4})$$

$$j_2(x) = \left(\frac{3}{x^3} - \frac{1}{x}\right) \sin x - \frac{3}{x^2} \cos x \quad (\text{D.5})$$

$$\begin{aligned} j_3(x) &= \frac{5}{x} j_2(x) - j_1(x) \\ &= \left(\frac{15}{x^4} - \frac{6}{x^2}\right) \sin x - \left(\frac{15}{x^3} + \frac{1}{x}\right) \cos x \end{aligned} \quad (\text{D.6})$$

and so the above integration is broken into 4 terms which may be expressed in terms of Sine and Cosine integrals.

The first term is

$$\begin{aligned}
 (1) &= \int_0^\infty dk' \frac{k'^2}{k^2 - k'^2} \frac{\cos k'r}{k'r} \\
 &= \frac{1}{r} \int_0^\infty dk' k' \frac{\cos k'r}{k^2 - k'^2} \\
 &= \frac{1}{r} \int_0^\infty dk' k' \cos k'r \frac{1}{2k'} \left(\frac{1}{k - k'} - \frac{1}{k + k'} \right) \\
 &= \frac{1}{2r} \int_0^\infty dk' \cos k'r \left(\frac{1}{k - k'} - \frac{1}{k + k'} \right) \\
 &= -\frac{1}{2r} [g(-kr) + g(kr)] \\
 &= \frac{1}{2r} [Ci(-kr) \cos(-kr) + si(-kr) \sin(-kr) + Ci(kr) \cos kr + si(kr) \sin kr] \\
 &= \frac{1}{r} [Ci(kr) \cos kr + si(kr) \sin kr + \frac{\pi}{2} \sin kr] \tag{D.7}
 \end{aligned}$$

where the Sine and Cosine integrals are

$$Si(z) = \int_0^z \frac{\sin t}{t} dt \tag{D.8}$$

$$si(z) = Si(z) - \frac{\pi}{2} \tag{D.9}$$

$$Ci(z) = \gamma + \ln z + \int_0^z \frac{\cos t - 1}{t} dt. \tag{D.10}$$

We can also define the auxiliary functions $f(z)$, $g(z)$ by

$$f(z) = Ci(z) \sin z - si(z) \cos z \tag{D.11}$$

$$g(z) = -Ci(z) \cos z - si(z) \sin z \tag{D.12}$$

where

$$f(z) = \int_0^\infty \frac{\sin t}{t + z} dt = \int_0^\infty \frac{e^{-zt}}{t^2 + 1} dt \tag{D.13}$$

$$g(z) = \int_0^\infty \frac{\cos t}{t + z} dt = \int_0^\infty \frac{te^{-zt}}{t^2 + 1} dt. \tag{D.14}$$

Then the Sine and Cosine integrals are given in terms of the auxiliary functions by

$$si(z) = -f(z) \cos z - g(z) \sin z \quad (D.15)$$

$$Ci(z) = f(z) \sin z - g(z) \cos z. \quad (D.16)$$

The Sine and Cosine integral have the symmetry relations

$$\begin{aligned} Si(-z) &= -Si(z) \\ Si(\bar{z}) &= \overline{Si(z)} \end{aligned} \quad (D.17)$$

$$\begin{aligned} Ci(-z) &= Ci(z) - i\pi \quad (0 < \arg z < \pi) \\ Ci(\bar{z}) &= \overline{Ci(z)}. \end{aligned} \quad (D.18)$$

The second term in our integration is

$$\begin{aligned} (2) &= \int_0^\infty dk' \frac{k'^2}{k^2 - k'^2} \frac{-6 \sin k'r}{(k'r)^2} \\ &= \frac{-6}{r^2} \int_0^\infty dk' \frac{\sin k'r}{k^2 - k'^2} \\ &= \frac{-6}{r^2} \int_0^\infty dk' \frac{1}{2k} \left(\frac{\sin k'r}{k - k'} + \frac{\sin k'r}{k + k'} \right) \\ &= \frac{-3}{kr^2} [f(-kr) + f(kr)] \\ &= \frac{-3}{kr^2} [-Ci(-kr) \sin(-kr) + si(-kr) \cos(-kr) + Ci(kr) \sin kr - si(kr) \cos kr] \\ &= \frac{-6}{kr^2} [Ci(kr) \sin kr - si(kr) \cos kr + \frac{\pi}{2} \cos kr]. \end{aligned} \quad (D.19)$$

The third term is

$$\begin{aligned} (3) &= \int_0^\infty dk' \frac{k'^2}{k^2 - k'^2} \frac{-15 \cos k'r}{(k'r)^3} \\ &= \frac{-15}{r^3} \int_0^\infty dk' \frac{\cos k'r}{k'(k^2 - k'^2)} \end{aligned}$$

$$\begin{aligned}
&= \frac{-15}{r^3} \int_0^\infty dk' \frac{\cos k'r}{2k^2} \left(\frac{2}{k'} + \frac{1}{k-k'} + \frac{1}{k+k'} \right) \\
&= \frac{-15}{2k^2 r^3} [2g(0) - g(-kr) + g(kr)] \\
&= \frac{-15}{k^2 r^3} [-Ci(0) + Ci(kr) \cos kr + si(kr) \sin kr + \frac{\pi}{2} \sin kr]. \quad (D.20)
\end{aligned}$$

$Ci(0)$ is divergent logarithmically, but is exactly canceled by a term from next integral.

Our fourth term in the integral is given by

$$\begin{aligned}
(4) &= \int_0^\infty dk' \frac{k'^2}{k^2 - k'^2} \frac{15 \sin k'r}{(k'r)^4} \\
&= \frac{15}{r^4} \int_0^\infty dk' \frac{\sin k'r}{k'^2(k^2 - k'^2)} \\
&= \frac{15}{k^2 r^4} \int_0^\infty dk' \sin k'r \left(\frac{1}{k^2 - k'^2} + \frac{1}{k'^2} \right) \\
&= \frac{15}{k^2 r^4} \left[\frac{-r^2}{6} (2) + \int_0^\infty dk' \frac{\sin k'r}{k'^2} \right] \\
&= \frac{15}{k^3 r^4} [Ci(kr) \sin kr - si(kr) \cos kr + \frac{\pi}{2} \cos kr - k \frac{\sin k'r}{k'} \Big|_0^\infty + kr \int_0^\infty dk' \frac{\cos k'r}{k'}] \\
&= \frac{15}{k^3 r^4} [Ci(kr) \sin kr - si(kr) \cos kr + \frac{\pi}{2} \cos kr] + \frac{15}{k^2 r^3} [1 - Ci(0)]. \quad (D.21)
\end{aligned}$$

Note the explicit cancellation of $Ci(0)$ between Eq. (D.20) and Eq. (D.21). Putting (1)-(4) together, we have our inner momentum integral in our Knight shift expression define in Eq. (D.1) given by

$$\begin{aligned}
\int_0^\infty k'^2 dk' \frac{j_3(k'r)}{k^2 - k'^2} &= \frac{1}{r} [Ci(kr) \cos kr + si(kr) \sin kr + \frac{\pi}{2} \sin kr] \\
&\quad - \frac{6}{kr^2} [Ci(kr) \sin kr - si(kr) \cos kr + \frac{\pi}{2} \cos kr] \\
&\quad - \frac{15}{k^2 r^3} [Ci(kr) \cos kr + si(kr) \sin kr + \frac{\pi}{2} \sin kr - 1] \\
&\quad + \frac{15}{k^3 r^4} [Ci(kr) \sin kr - si(kr) \cos kr + \frac{\pi}{2} \cos kr]. \quad (D.22)
\end{aligned}$$

LIST OF REFERENCES

- [1] See pp. 231-233 in *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables* eds. by M. Abramowitz and I.A. Stegun (1970)

Appendix E

Angular Dependence of the Knight Shift

In this appendix the derivation of $f_{jj'}(\alpha, \theta)$, the angular dependence of the Knight shift, will be discussed. To calculate the angular terms in Knight shift we need some prefactors. First the Landé g -factor is given by

$$g(jls) = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}. \quad (\text{E.1})$$

For $l = 3$ and $s = 1/2$ which is the case for $4f^1$ and $4f^{13}$ configuration, $j = 5/2$ and $7/2$ are possible by spin-orbit interaction. So, we will only evaluate values for $j = 5/2$ and $7/2$. So Landé g -factor value is $g(5/2, 3, 1/2) = 6/7$ and $g(7/2, 3, 1/2) = 8/7$.

Also the effective magnetic moment μ_j is given by

$$\mu_j^2 = \mu_B^2 g_j^2 j(j+1)/3, \quad (\text{E.2})$$

where $\mu_B = eh/2mc$ is Bohr magneton. $\mu_j^2 = (15/7)\mu_B^2$ for $j = 5/2$ and $\mu_j^2 = (48/7)\mu_B^2$ for $j = 7/2$.

Also we need to calculate the expectation value of spin operator in the z direction

$$\langle jm_j | J_z + S_z | j'm_{j'} \rangle = m_j \delta_{jj'} + \langle jm_j | S_z | j'm_{j'} \rangle. \quad (\text{E.3})$$

Then for $j = j'$, by Wigner-Eckart theorem

$$\langle jm_j | J_z + S_z | jm_j \rangle = \delta_{m_j, m_j} g_j m_j. \quad (\text{E.4})$$

And for $j \neq j'$

$$\begin{aligned} \langle jm_j | J_z + S_z | j' m_j \rangle &= \langle jm_j | S_z | j' m_j \rangle \\ &= \delta_{m_j, m_j} \sum_{m_l \alpha m'_l \beta} \langle jm_j | l m_l; s \alpha \rangle \langle l m_l; s \alpha | S_z | l m'_l; s \beta \rangle \langle l m'_l; s \beta | j' m_j \rangle \\ &= \delta_{m_j, m_j} \sum_{m_l m'_l \alpha \beta} \alpha \delta_{\alpha \beta} \delta_{m_l m'_l} \langle jm_j | l m_l; s \alpha \rangle \langle l m'_l; s \beta | j' m_j \rangle \\ &= \delta_{m_j, m_j} \sum_{m_l \alpha} \alpha \langle jm_j | l m_l; s \alpha \rangle \langle l m_l; s \alpha | j' m_j \rangle \end{aligned} \quad (\text{E.5})$$

where $\alpha = \pm 1/2$. For $l = 3$, $s = 1/2$, $j = 5/2$ and $j' = 7/2$

$$\begin{aligned} \langle \frac{5}{2} m_j | S_z | \frac{7}{2} m_j \rangle &= \delta_{m_j, m_j} \sum_{m_3 \alpha} \alpha \langle \frac{5}{2} m_j | 3 m_3; s \alpha \rangle \langle 3 m_3; s \alpha | \frac{7}{2} m_j \rangle \\ &= \delta_{m_j, m_j} \sum_{\alpha} \alpha \left(\frac{7 \pm 2m_j}{14} \right)^{1/2} (\mp) \left(\frac{7 \mp 2m_j}{14} \right)^{1/2} \\ &= -\frac{\sqrt{49 - 4m_j^2}}{14} \delta_{m_j, m_j}. \end{aligned} \quad (\text{E.6})$$

Then

$$\begin{aligned} \langle \frac{5}{2} m_j | S_z | \frac{7}{2} m_j \rangle &= -\frac{\sqrt{12}}{7} \text{ for } m_j = \pm 1/2 \\ &= -\frac{\sqrt{10}}{7} \text{ for } m_j = \pm 3/2 \\ &= -\frac{\sqrt{6}}{7} \text{ for } m_j = \pm 5/2 \end{aligned} \quad (\text{E.7})$$

given .

$$\langle j_1 m - \alpha; \frac{1}{2} \alpha | j, m \rangle = \left(\frac{j_1 \pm m/2}{2j_1 + 1} \right)^{1/2} \text{ for } j = j_1 + 1/2 \quad (\text{E.8})$$

$$= \mp \left(\frac{j_1 \mp m/2}{2j_1 + 1} \right)^{1/2} \text{ for } j = j_1 - 1/2 \quad (\text{E.9})$$

where for $\alpha = \pm 1/2$ and $j_1 = 3$

$$\langle 3m_3; \frac{1}{2} \pm \frac{1}{2} | \frac{7}{2} m \rangle = (\frac{7 \pm 2m}{14})^{1/2} \text{ for } j = 7/2 \quad (\text{E.10})$$

$$\langle 3m_3; \frac{1}{2} \pm \frac{1}{2} | \frac{5}{2} m \rangle = \mp (\frac{7 \mp 2m}{14})^{1/2} \text{ for } j = 5/2. \quad (\text{E.11})$$

In the Knight shift calculation the angular dependence comes from the Zeeman term in the Hamiltonian.

$$\mathcal{H}_z = -\mu_B H_z (L_z + 2S_z) = -\mu_B H_z (J_z + S_z), \quad (\text{E.12})$$

where external magnetic field $\vec{H} = H_z \hat{z}$.

Now let's calculate the angular part of the Knight shift. To do the lattice sum, we have to consider the difference of the field axis and the bond direction $\vec{r}$ which connects the nucleus or muon to a given f ion. Let the angle between the field axis and $\vec{r}$ is α , and the angle between the z axis and bond axis is θ . First when the field is along the z direction, i.e. $\theta = \alpha$ and nuclear spin $I = 1/2$, the angular momentum operator J_z , which is quantized in the bond direction becomes $\cos \theta J_z - \sin \theta J_x = \cos \theta J_z - \sin \theta (J_+ + J_-)/2$ in the new reference frame when the material has the cubic symmetry. Also, the nuclear spin operator σ_z becomes $\cos \theta \sigma_z - \sin \theta \sigma_x = \cos \theta \sigma_z - \sin \theta (\sigma_+ + \sigma_-)/2$. Then the surviving terms in the Knight shift calculation are

$$\cos^2 \theta \sigma_z (J_z + S_z) + \sin^2 \theta \sigma_x (J_x + S_x) = \cos^2 \theta \sigma_z (J_z + S_z) + \frac{\sin^2 \theta}{4} (\sigma_+ (J_- + S_-) + \sigma_- (J_+ + S_+)). \quad (\text{E.13})$$

Then the total angular part is

$$f_{jj'}(\theta) = \cos^2 \theta f_{jj'}^z + \frac{\sin^2 \theta}{4} (f_{jj'}^{1-} + f_{jj'}^{2-} + f_{jj'}^{1+} + f_{jj'}^{2+}). \quad (\text{E.14})$$

Where $f_{jj'}^z$ is

$$\begin{aligned}
 f_{jj'}^z(\theta) &= \sum_{m_j, m_{j'}, \alpha} \langle jm_j | J_z + s_z | j' m_{j'} \rangle \sigma_{\alpha\alpha}^z \langle j' m_{j'} | \hat{r} \rangle \langle \hat{r} | jm_j \rangle \\
 &= \sum_{m_j, \alpha m_3} \alpha \langle jm_j | J_z + S_z | j' m_{j'} \rangle \langle j' m_{j'} | 3m_3; \frac{1}{2}\alpha \rangle \\
 &\quad \times \langle 3m_3; \frac{1}{2}\alpha | jm_j \rangle |Y_{3m_3}(\hat{r})|^2
 \end{aligned} \tag{E.15}$$

where $\alpha = \pm 1/2$.

Then for $1) j = j'$

$$\begin{aligned}
 f_{jj}^z(\theta) &= \sum_{m_j, m'_j, \alpha m_3} \alpha \langle jm_j | J_z + S_z | jm'_j \rangle \langle jm'_j | 3m_3; \frac{1}{2}\alpha \rangle \langle 3m_3; \frac{1}{2}\alpha | jm_j \rangle |Y_{3m_3}(\hat{r})|^2 \\
 &= \sum_{m_j, \alpha} g_j m_j \alpha |\langle jm_j | 3m_j - \alpha; \frac{1}{2}\alpha \rangle|^2 |Y_{3m_j - \alpha}(\hat{r})|^2
 \end{aligned} \tag{E.16}$$

The explicit form of the spherical harmonics $Y_{3m}(\theta, \phi)$ is given by

$$\begin{aligned}
 Y_{33} &= -\frac{1}{4} \sqrt{\frac{35}{4\pi}} \sin^3 \theta e^{3i\phi} \\
 Y_{32} &= \frac{1}{4} \sqrt{\frac{105}{2\pi}} \sin^2 \theta \cos \theta e^{2i\phi} \\
 Y_{31} &= -\frac{1}{4} \sqrt{\frac{21}{4\pi}} \sin \theta (5 \cos^2 \theta - 1) e^{i\phi} \\
 Y_{30} &= \sqrt{\frac{7}{4\pi}} \left(\frac{5}{2} \cos^3 \theta - \frac{3}{2} \cos \theta \right) \\
 Y_{l-m}(\theta, \phi) &= (-1)^m Y_{lm}^*(\theta, \phi).
 \end{aligned} \tag{E.17}$$

With the above equation and Eq. (E.10) and Eq. (E.11)

$$\begin{aligned}
 f_{\frac{5}{2}\frac{5}{2}}^z(\theta) &= \frac{6}{7} \sum_{m\alpha} m \alpha \frac{7 \mp 2m}{14} |Y_{3m-\alpha}|^2 \\
 &= \frac{9}{28\pi} (1 - 4 \sin^2 \theta)
 \end{aligned} \tag{E.18}$$

$$\begin{aligned}
f_{\frac{7}{2}\frac{1}{2}}^{\pm}(\theta) &= \frac{8}{7} \sum_{m\alpha} m\alpha \frac{7 \pm 2m}{14} |Y_{3m-\alpha}|^2 \\
&= \frac{4}{7\pi} (1 + 3 \sin^2 \theta).
\end{aligned} \tag{E.19}$$

2) $j \neq j'$, i.e. $j = 5/2$ and $j' = 7/2$

This term gives the van Vleck Knight shift

$$\begin{aligned}
f_{\frac{5}{2}\frac{1}{2}}^{\pm}(\theta) &= \sum_{m_j \alpha m_3} \alpha \langle j m_j | J_z + S_z | j' m_{j'} \rangle \langle j' m_{j'} | 3m_3; \frac{1}{2} \alpha \rangle \langle 3m_3; \frac{1}{2} \alpha | j m_j \rangle |Y_{3m_3}(\hat{r})|^2 \\
&= \sum_{m \alpha m_3} \alpha \langle \frac{5}{2} m | S_z | \frac{7}{2} m \rangle \langle \frac{7}{2} m | 3m_3; \frac{1}{2} \alpha \rangle \langle 3m_3; \frac{1}{2} \alpha | \frac{5}{2} m \rangle |Y_{3m_3}(\hat{r})|^2 \\
&= \sum_{m \alpha} \alpha \frac{-\sqrt{49-4m^2}}{14} \sqrt{\frac{7 \pm 2m}{14}} \mp \sqrt{\frac{7 \mp 2m}{14}} |Y_{3m-\alpha}|^2 \\
&= \sum_m \frac{1}{2} \frac{49-4m^2}{196} (|Y_{3m-\frac{1}{2}}|^2 + |Y_{3m+\frac{1}{2}}|^2) \\
&= \frac{3}{14\pi} (2 - \sin^2 \theta).
\end{aligned} \tag{E.20}$$

Now let's derive $f_{jj'}^{\pm}$, the angular part of Knight shift from the second term of Eq. (E.13), where $j = j'$

$$\begin{aligned}
f_{jj'}^{\pm}(\theta) &= \sum_{m_j m_{j'} \alpha \beta} \langle j, m_j | J_{\pm} | j', m_{j'} \rangle \langle j' m_{j'} | \hat{r} \rangle \sigma_{\alpha\beta}^{\mp}(\hat{r}) \langle j, m_j | \\
&= \sum_{m_j, m_{j'}, m_3, m'_3, \alpha, \beta} \langle j, m_j | J_{\pm} | j', m_{j'} \rangle \langle j' m_{j'} | 3m'_3; \frac{1}{2} \alpha \rangle \\
&\quad \times \langle 3m'_3; \frac{1}{2} \alpha | \sigma_{\alpha\beta}^{\mp} | 3m_3; \frac{1}{2} \beta \rangle \langle 3m_3; \frac{1}{2} \beta | j m_j \rangle Y_{3m_3}^*(\hat{r}) Y_{3m'_3}(\hat{r})
\end{aligned} \tag{E.21}$$

with $\langle j, m_j | J_{\pm} | j', m_{j'} \rangle = \sqrt{(j \pm m_j)(j \mp m_j + 1)} \delta_{jj'} \delta_{m_j, m_{j'} \mp 1}$

and $\langle 3m'_3; \frac{1}{2} \alpha | \sigma_{\alpha\beta}^{\mp} | 3m_3; \frac{1}{2} \beta \rangle = \sqrt{\frac{3}{4} - \beta(\beta \mp 1)} \delta_{\alpha\beta \mp 1} \delta_{m_3 m'_3} = \delta_{\beta, \pm \frac{1}{2}}$.

The above equation gives

$$f_{jj}^{\pm}(\theta) = \sum_{m_j} \sqrt{(j \pm m_j)(j \mp m_j \mp 1)} \langle j m_j \mp 1 | 3m'_3; \frac{1}{2} \mp \frac{1}{2} \rangle \langle 3m_3; \frac{1}{2} \pm \frac{1}{2} | j m_j \rangle |Y_{3m_j \mp \frac{1}{2}}(\hat{r})|^2. \tag{E.22}$$

Hence

$$\begin{aligned}
 f_{jj'}^{2\pm}(\theta) &= \sum_{m_j, m_{j'}, \alpha, \beta} \langle jm_j | S_{\pm} | j', m_{j'} \rangle \langle j' m_{j'} | \hat{r} \rangle \sigma_{\alpha\beta}^{\mp} \langle \hat{r} | j, m_j \rangle \\
 &= \sum_{m_j, m_{j'}, m_3, m'_3, \alpha, \beta} \langle j, m_j | S_{\pm} | j', m_{j'} \rangle \langle j' m_{j'} | 3m'_3; \frac{1}{2}\alpha \rangle \\
 &\quad \times \langle 3m'_3; \frac{1}{2}\alpha | \sigma_{\alpha\beta}^{\mp} | 3m_3; \frac{1}{2}\beta \rangle \langle 3m_3; \frac{1}{2}\beta | jm_j \rangle Y_{3m_3}^*(\hat{r}) Y_{3m'_3}(\hat{r}) \quad (\text{E.23})
 \end{aligned}$$

where

$$\begin{aligned}
 \langle jm_j | S_{\pm} | jm'_j \rangle &= \sum_{m_3, m'_3, \alpha, \beta} \langle jm_j | 3m_3; \frac{1}{2}\alpha \rangle \langle 3m_3; \frac{1}{2}\alpha | S_{\pm} | 3m'_3; \frac{1}{2}\beta \rangle \langle 3m'_3; \frac{1}{2}\beta | jm'_j \rangle \\
 &= \sum_{m_3} \langle jm_j | 3m_3; \frac{1}{2} \pm \frac{1}{2} \rangle \langle 3m_3; \frac{1}{2} \mp \frac{1}{2} | jm'_j \rangle \\
 &= -\frac{\sqrt{(7 \mp 2m)(5 \pm 2m)}}{14} \delta_{m'_j, m_j \mp 1} \text{ for } j = 5/2 \\
 &= \frac{\sqrt{(7 \pm 2m)(9 \mp 2m)}}{14} \delta_{m'_j, m_j \mp 1} \text{ for } j = 7/2. \quad (\text{E.24})
 \end{aligned}$$

Then

$$\begin{aligned}
 f_{jj'}^{2\pm}(\theta) &= \sum_{m_j} \langle jm_j | S_{\pm} | jm_j \mp 1 \rangle \langle jm_j \mp 1 | 3m'_3; \frac{1}{2} \mp \frac{1}{2} \rangle \langle 3m_3; \frac{1}{2} \pm \frac{1}{2} | jm_j \rangle |Y_{3m_j \mp \frac{1}{2}}(\hat{r})|^2 \\
 &= |\langle jm_j \mp 1 | 3m'_3; \frac{1}{2} \mp \frac{1}{2} \rangle|^2 |\langle 3m_3; \frac{1}{2} \pm \frac{1}{2} | jm_j \rangle|^2 |Y_{3m_j \mp \frac{1}{2}}(\hat{r})|^2. \quad (\text{E.25})
 \end{aligned}$$

1) contribution from $j = 5/2$. Defines

$$\begin{aligned}
 f_{\frac{5}{2}\frac{5}{2}}^{\pm}(\theta) &= f_{\frac{5}{2}\frac{5}{2}}^{1\pm} + f_{\frac{5}{2}\frac{5}{2}}^{2\pm} \\
 &= \sum_{m_j} \sqrt{\left(\frac{5}{2} \pm m_j\right) \left(\frac{5}{2} \mp m_j + 1\right)} (\pm) \sqrt{\frac{7 \pm 2(m_j \mp 1)}{14}} (\mp) \sqrt{\frac{7 \mp 2m_j}{14}} |Y_{3m_j \mp \frac{1}{2}}(\hat{r})|^2 \\
 &\quad + \sum_{m_j} \frac{7 \pm 2(m_j \mp 1)}{14} \frac{7 \mp 2m_j}{14} |Y_{3m_j \mp \frac{1}{2}}(\hat{r})|^2
 \end{aligned}$$

$$\begin{aligned}
&= \sum_{m_j} -\frac{(5 \pm 2m_j)(7 \mp 2m_j)}{28} \left(1 - \frac{1}{7}\right) |Y_{3m_j, \mp \frac{1}{2}}(\hat{r})|^2 \\
&= -\frac{6}{7} \sum_{m_j} \frac{(5 \pm 2m_j)(7 \mp 2m_j)}{28} |Y_{3m_j, \mp \frac{1}{2}}(\hat{r})|^2 \\
&= -\frac{6}{49} (10|Y_{32}|^2 + 16|Y_{31}|^2 + 9|Y_{30}|^2) \\
&= -\frac{9}{14\pi} [3 - 2\sin^2 \theta] = -\frac{9}{14\pi} [1 + 2\cos^2 \theta] \\
&= g_{j=\frac{5}{2}} f_{\frac{5}{2}\frac{1}{2}}^{\pm}
\end{aligned} \tag{E.26}$$

Then

$$\begin{aligned}
f_{\frac{5}{2}\frac{1}{2}}^{\pm}(\theta) &= [\cos^2 \theta \frac{9}{28\pi} (1 - 4\sin^2 \theta) + \frac{\sin^2 \theta}{4} 2(-\frac{9}{14\pi})(1 + 2\cos^2 \theta)] \\
&= \frac{9}{28\pi} [\cos^2 \theta - 4\sin^2 \theta \cos^2 \theta - \sin^2 \theta - 2\sin^2 \theta \cos^2 \theta] \\
&= \frac{9}{28\pi} [\cos^2 \theta - 6\sin^2 \theta \cos^2 \theta - \sin^2 \theta] \\
&= \frac{9}{28\pi} [(1 - \sin^2 \theta) - 6\sin^2 \theta (1 - \sin^2 \theta) - \sin^2 \theta] \\
&= \frac{9}{28\pi} (1 - 8\sin^2 \theta + 6\sin^4 \theta)
\end{aligned} \tag{E.27}$$

2) Contribution from $j = 7/2$. Define

$$\begin{aligned}
f_{\frac{7}{2}\frac{1}{2}}^{\pm}(\theta) &= f_{\frac{7}{2}\frac{1}{2}}^{1\pm} + f_{\frac{7}{2}\frac{1}{2}}^{2\pm} \\
&= \sum_{m_j} \sqrt{\left(\frac{7}{2} \pm m_j\right)\left(\frac{7}{2} \mp m_j + 1\right)} \sqrt{\frac{7 \mp 2(m_j \mp 1)}{14}} \sqrt{\frac{7 \pm 2m_j}{14}} |Y_{3m_j, \mp \frac{1}{2}}(\hat{r})|^2 \\
&\quad + \sum_{m_j} \frac{7 \mp 2(m_j \mp 1)}{14} \frac{7 \pm 2m_j}{14} |Y_{3m_j, \mp \frac{1}{2}}(\hat{r})|^2 \\
&= \sum_{m_j} \frac{(7 \pm 2m_j)(9 \mp 2m_j)}{28} \left(1 + \frac{1}{7}\right) |Y_{3m_j, \mp \frac{1}{2}}(\hat{r})|^2 \\
&= \frac{8}{7} \sum_{m_j} \frac{(7 \pm 2m_j)(9 \mp 2m_j)}{28} |Y_{3m_j, \mp \frac{1}{2}}(\hat{r})|^2 \\
&= \frac{8}{7} \frac{1}{28} (56|Y_{33}|^2 + 96|Y_{32}|^2 + 120|Y_{31}|^2 + 16|Y_{30}|^2)
\end{aligned}$$

$$= \frac{8}{14\pi} [5 + 3 \cos^2 \theta] = g_{j=\frac{1}{2}} f_{\frac{1}{2}}^{1\pm} \quad (\text{E.28})$$

Then

$$\begin{aligned} f_{\frac{1}{2}}^{\pm}(\theta) &= [\cos^2 \theta \frac{8}{14\pi} (1 + 3 \sin^2 \theta) + \frac{\sin^2 \theta}{4} 2 \frac{8}{14\pi} (5 + 3 \cos^2 \theta)] \\ &= \frac{2}{7\pi} [2 \cos^2 \theta + 6 \sin^2 \theta \cos^2 \theta + 5 \sin^2 \theta + 3 \sin^2 \theta \cos^2 \theta] \\ &= \frac{2}{7\pi} [2 + 3 \sin^2 \theta + 9 \sin^2 \theta \cos^2 \theta] \\ &= \frac{2}{7\pi} [2 + 3 \sin^2 \theta + 9 \sin^2 \theta (1 - \sin^2 \theta)] \\ &= \frac{2}{7\pi} [2 + 12 \sin^2 \theta - 9 \sin^4 \theta] \end{aligned} \quad (\text{E.29})$$

3) Contribution from Van-Vleck terms. Define

$$\begin{aligned} f_{\frac{5}{2}}^{\pm}(\theta) &= \sum_{m_j, m_{j'}, \alpha, \beta} \langle j, m_j | S_{\pm} | j', m_{j'} \rangle \langle j', m_{j'} | \hat{r} \rangle \sigma_{\alpha, \beta}^{\mp} \langle \hat{r} | j, m_j \rangle \\ &= \sum_{m_j, m_{j'}, m_3, m'_3, \alpha, \beta} \langle j, m_j | S_{\pm} | j', m_{j'} \rangle \langle j', m_{j'} | 3m'_3; \frac{1}{2}\alpha \rangle \\ &\quad \times \langle 3m'_3; \frac{1}{2}\alpha | \sigma_{\alpha, \beta}^{\mp} | 3m_3; \frac{1}{2}\beta \rangle \langle 3m_3; \frac{1}{2}\beta | j m_j \rangle Y_{3m_3}^*(\hat{r}) Y_{3m'_3}(\hat{r}) \end{aligned} \quad (\text{E.30})$$

with

$$\begin{aligned} \langle j = \frac{5}{2}, m_j | S_{\pm} | j' = \frac{7}{2}, m_{j'} \rangle &= \sum_{m_3, m'_3, \alpha, \beta} \langle \frac{5}{2} m' | 3m_3; \frac{1}{2}\alpha \rangle \langle 3m_3; \frac{1}{2}\alpha | S_{\pm} | 3m'_3; \frac{1}{2}\beta \rangle \langle 3m'_3; \frac{1}{2}\beta | \frac{7}{2} m \rangle \\ &= \sum_{m_3} \langle \frac{5}{2} m' | 3m_3 \frac{1}{2} \pm \frac{1}{2} \rangle \langle 3m_3 \frac{1}{2} \mp \frac{1}{2} | \frac{7}{2} m \rangle \\ &= \mp \sqrt{\frac{7 \mp 2m'}{14}} \sqrt{\frac{7 \mp 2m}{14}} \\ &= \mp \frac{1}{14} \sqrt{(5 \mp 2m)(7 \mp 2m)} \end{aligned} \quad (\text{E.31})$$

where $m' = m \pm 1$.

Insert in, the Eq. (E.31) into the Eq. (E.30) gives

$$\begin{aligned}
 f_{\frac{1}{2}\frac{1}{2}}^{\pm}(\theta) &= \sum_m \mp \frac{1}{14} \sqrt{(7+2m)(5+2m)} \left(\frac{7}{2}m \middle| 3m \pm \frac{1}{2}; \frac{1}{2} \mp \frac{1}{2}\right) \\
 &\quad \times \left(3m \pm \frac{1}{2}; \frac{1}{2} \pm \frac{1}{2} \middle| \frac{5}{2}m \pm 1\right) |Y_{3m \pm \frac{1}{2}}(\hat{r})|^2 \\
 &= \sum_m \frac{1}{14^2} (7 \mp 2m)(5 \mp 2m) |Y_{3m \pm \frac{1}{2}}(\hat{r})|^2 \\
 &= \frac{3}{14\pi} [2 + \sin^2 \theta]
 \end{aligned} \tag{E.32}$$

Then

$$\begin{aligned}
 f_{\frac{1}{2}\frac{1}{2}}(\theta) &= \cos^2 \theta \frac{3}{14\pi} (2 - \sin^2 \theta) + \frac{\sin^2 \theta}{4} 2 \frac{3}{14\pi} (2 + \sin^2 \theta) \\
 &= \frac{3}{28\pi} [4 \cos^2 \theta - 2 \sin^2 \theta \cos^2 \theta + 2 \sin^2 \theta + \sin^4 \theta] \\
 &= \frac{3}{28\pi} [4 - 2 \sin^2 \theta (1 - \sin^2 \theta) - 2 \sin^2 \theta + \sin^4 \theta] \\
 &= \frac{3}{28\pi} [4 - 4 \sin^2 \theta + 3 \sin^4 \theta]
 \end{aligned} \tag{E.33}$$

For the cubic crystal, such as CeSn_3 , $\text{Y}_{1-x}\text{U}_x\text{Pd}_3$, we fixed field in the z direction and do the reference frame averaging whether Sn atom is in the xz plane or the xy plane. Note that yz plane is equivalent to xz .

For YbCuAl case which has the hexagonal symmetry, we have to consider three possible field directions, along the x , y and z axis. Then $J_x = \cos \alpha J_z - \sin \alpha J_y$ and $\sigma_x = A\sigma_z - B\sigma_y$, where

$$\begin{aligned}
 A &= \frac{1}{4} (25 \cos^5 \theta - 26 \cos^3 \theta + 5 \cos \theta) \\
 B &= \frac{1}{4} \sin \theta (25 \cos^4 \theta - 14 \cos^2 \theta + 1)
 \end{aligned} \tag{E.34}$$

which is derived below. The explicit form of the rotation matrices is given by

$$d_{m'm}^{(j)}(\theta) = \sum_k (-1)^{k-m+m'} \frac{\sqrt{(j+m)!(j-m)!(j+m')!(j-m')!}}{(j+m-k)!(j-k-m')!(k-m+m')!k!}$$

$$\times (\cos \frac{\theta}{2})^{2j-2k+m-m'} (\sin \frac{\theta}{2})^{2k-m+m'} \quad (\text{E.35})$$

where we take the sum over k whenever none of the arguments of factorials in the denominator are negative. Al has an $I = 5/2$ nuclear spin and the NMR shift was obtained from derivative spectra of the central $(1/2 \leftrightarrow -1/2)$ NMR transition.

$$\begin{aligned} d_{\frac{1}{2}\frac{1}{2}}^{(\frac{1}{2})}(\theta) &= \sum_k (-1)^{k-\frac{1}{2}+\frac{1}{2}} \frac{\sqrt{(\frac{5}{2}+\frac{1}{2})!(\frac{5}{2}-\frac{1}{2})!(\frac{5}{2}+\frac{1}{2})!(\frac{5}{2}-\frac{1}{2})!}}{(\frac{5}{2}+\frac{1}{2}-k)!(\frac{5}{2}-k-\frac{1}{2})!(k-\frac{1}{2}+\frac{1}{2})!k!} \\ &\quad \times (\cos \frac{\theta}{2})^{2\cdot\frac{1}{2}-2k+\frac{1}{2}-\frac{1}{2}} (\sin \frac{\theta}{2})^{2k-\frac{1}{2}+\frac{1}{2}} \\ &= \sum_k (-1)^k \frac{3!2!}{(3-k)!(2-k)!k!k!} (\cos \frac{\theta}{2})^{5-2k} (\sin \frac{\theta}{2})^{2k} \\ &= 12 \left[\frac{1}{3!2!0!0!} (\cos \frac{\theta}{2})^5 - \frac{1}{2!1!1!1!} (\cos \frac{\theta}{2})^3 (\sin \frac{\theta}{2})^2 + \frac{1}{1!0!2!2!} (\cos \frac{\theta}{2}) (\sin \frac{\theta}{2})^4 \right] \\ &= (\cos \frac{\theta}{2})^5 - 6(\cos \frac{\theta}{2})^3 (\sin \frac{\theta}{2})^2 + 3(\cos \frac{\theta}{2}) (\sin \frac{\theta}{2})^4 \\ &= \frac{1}{2} \cos \frac{\theta}{2} [5 \cos^2 \theta - 2 \cos \theta - 1] = \alpha \end{aligned} \quad (\text{E.36})$$

$$= d_{-\frac{1}{2}-\frac{1}{2}}^{(\frac{1}{2})} \quad (\text{E.37})$$

$$\begin{aligned} d_{\frac{1}{2}-\frac{1}{2}}^{(\frac{1}{2})}(\theta) &= \sum_k (-1)^{k+\frac{1}{2}+\frac{1}{2}} \frac{\sqrt{(\frac{5}{2}-\frac{1}{2})!(\frac{5}{2}+\frac{1}{2})!(\frac{5}{2}+\frac{1}{2})!(\frac{5}{2}-\frac{1}{2})!}}{(\frac{5}{2}-\frac{1}{2}-k)!(\frac{5}{2}-k-\frac{1}{2})!(k+\frac{1}{2}+\frac{1}{2})!k!} \\ &\quad \times (\cos \frac{\theta}{2})^{2\cdot\frac{1}{2}-2k-\frac{1}{2}-\frac{1}{2}} (\sin \frac{\theta}{2})^{2k+\frac{1}{2}+\frac{1}{2}} \\ &= \sum_k (-1)^{k+1} \frac{2!3!}{(2-k)!(2-k)!(k+1)!k!} (\cos \frac{\theta}{2})^{4-2k} (\sin \frac{\theta}{2})^{2k+1} \\ &= 12 \left[-\frac{1}{2!0!2!1!} (\cos \frac{\theta}{2})^4 (\sin \frac{\theta}{2}) + \frac{1}{1!1!1!2!} (\cos \frac{\theta}{2})^2 (\sin \frac{\theta}{2})^3 + \frac{1}{0!2!0!3!} (\sin \frac{\theta}{2})^5 \right] \\ &= -3(\cos \frac{\theta}{2})^4 (\sin \frac{\theta}{2}) + 6(\cos \frac{\theta}{2})^2 (\sin \frac{\theta}{2})^3 - (\sin \frac{\theta}{2})^5 \\ &= -\frac{1}{2} \sin \frac{\theta}{2} [5 \cos^2 \theta + 2 \cos \theta - 1] = -\beta \end{aligned} \quad (\text{E.38})$$

$$= -d_{-\frac{1}{2}\frac{1}{2}}^{(\frac{1}{2})} \quad (\text{E.39})$$

Then A and B are defined as

$$\begin{aligned} A &= \alpha^2 - \beta^2 = \frac{1}{4}(25 \cos^5 \theta - 26 \cos^3 \theta + 5 \cos \theta) \\ B &= 2\alpha\beta = \frac{1}{4} \sin \theta (25 \cos^4 \theta - 14 \cos^2 \theta + 1) \end{aligned} \quad (\text{E.40})$$

Then

$$f_{jj'}(\alpha, \theta) = A \cos \alpha f_{jj'}^z(\theta) + \frac{B}{4} \sin \alpha [f_{jj'}^+(\theta) + f_{jj'}^-(\theta)]. \quad (\text{E.41})$$

For $j = 5/2$ we get

$$\begin{aligned} f_{\frac{5}{2}\frac{5}{2}}(\alpha, \theta) &= [A \cos \alpha \frac{9}{28\pi} (1 - 4 \sin^2 \theta) + \frac{B}{4} 2 \sin \alpha (-\frac{9}{14\pi}) (3 - 2 \sin^2 \theta)] \\ &= \frac{9}{28\pi} [A \cos \alpha (1 - 4 \sin^2 \theta) - B \sin \alpha (3 - 2 \sin^2 \theta)] \end{aligned} \quad (\text{E.42})$$

and for $j = 7/2$ we obtain,

$$\begin{aligned} f_{\frac{7}{2}\frac{7}{2}}(\alpha, \theta) &= [A \cos \alpha \frac{4}{7\pi} (1 + 3 \sin^2 \theta) + \frac{B}{4} 2 \sin \alpha \frac{4}{7\pi} (5 + 3 \cos^2 \theta)] \\ &= \frac{2}{7\pi} [2A \cos \alpha (1 + 3 \sin^2 \theta) + B \sin \alpha (5 + 3 \cos^2 \theta)]. \end{aligned} \quad (\text{E.43})$$

For YbCuAl compound we don't consider van Vleck contribution because of the large spin orbit splitting as discussed in section 3.3.

Appendix F

The Full $4f$ Green's Function

The full $4f$ Green's function is defined by

$$G_{4fjm}(\tau) = -\langle T_\tau [|0\rangle \langle jm|](\tau) |jm\rangle \langle 0| \rangle \quad (\text{F.1})$$

with the equal time value

$$G_{4fjm}(0) = [\langle f_{jm}^\dagger f_{jm} \rangle + \langle b^\dagger b \rangle]. \quad (\text{F.2})$$

This full $4f$ Green's function is needed to get conduction electron T matrix which determines the conduction electron self energy for coherence lattice effects. In the language of pseudo boson and fermion operator, the above equation is become

$$G_{4fjm}(\tau) = \lim_{\lambda \rightarrow -\infty} \frac{e^{-\beta\lambda} \langle T_\tau [f_{jm} b^\dagger](\tau) b f_{jm}^\dagger \rangle_\lambda}{e^{-\beta\lambda} \langle Q \rangle_\lambda}. \quad (\text{F.3})$$

The full $4f$ spectral density $\rho_{4fjm}(\omega, T)$ is defined by

$$G_{4fjm}(\tau) = \frac{1}{\beta} \sum_n e^{-i\omega_n \tau} \int \frac{d\zeta}{\pi} \frac{\rho_{4fjm}(\zeta, T)}{i\omega_n - \zeta}. \quad (\text{F.4})$$

A total $4f$ response function is fermionic in character since it is the response function for $f_{jm}^\dagger b$, a composite fermion-boson operator.

If we define the a full 4f self energy $\Sigma_{4fjm}(\omega)$ by

$$G_{4fjm}(\omega) = \frac{1}{\omega - \epsilon_{fj} - \Sigma_{4fjm}(\omega)} \quad (\text{F.5})$$

where $G_{4fjm}(\omega)$ is the Fourier transform of $G_{4fjm}(\tau)$ analytically continued to real frequencies.

This is the NCA equation for the full 4f propagator $G_{4fjm}(\omega)$.

$$\begin{aligned} G_{4fjm}(\omega) &= \frac{1}{Z_{4f}} \int \frac{d\xi}{\pi} [B^{(-)}(\xi) G_{jm}(\omega + \xi + i\delta) - A_{jm}^{(-)}(\xi) D(\xi - \omega - i\delta)] \\ \rho_{4fjm}(\omega) &= -\text{Im} G_{4fjm}(\omega) \\ &= \frac{1}{Z_{4f}} \int \frac{d\xi}{\pi} [B^{(-)}(\xi) A_{jm}^{(-)}(\omega + \xi) + A_{jm}^{(-)}(\xi) B(\xi - \omega)] \\ \text{Re} G_{4fjm} &= \frac{1}{Z_{4f}} \int \frac{d\xi}{\pi} [B^{(-)}(\xi) \text{Re} G_{jm}(\omega + \xi) - A_{jm}^{(-)}(\xi) \text{Re} D(\xi - \omega)] \\ &= \text{P} \int \frac{d\xi}{\pi} \frac{\rho_{4fjm}(\xi, T)}{\omega - \xi} = \int \frac{d\xi}{\pi} \frac{\rho_{4fjm}(\xi, T) - \rho_{4fjm}(\omega, T)}{\omega - \xi}. \end{aligned} \quad (\text{F.6})$$

We expect the exact relations

$$-\text{Im} \Sigma_{4fjm}(0, 0) = \Gamma \quad (\text{F.7})$$

$$\left. \frac{\partial \text{Im} \Sigma_{4fjm}(\omega, T)}{\partial \omega} \right|_{\omega=0, T=0} = 0 \quad (\text{F.8})$$

to hold [1], though this is not the case for the NCA.

LIST OF REFERENCES

- [1] D.L. Cox and N. Grewe, Z. Phys. B **71**, 321 (1988).

Appendix G

Inclusion of Coherence

When multiple scattering is accounting for, the conduction electron Green's function in the Eq. (C.1) become dressed by self energy corrections which account for multiple scattering off at $4f$ sites. As a results, $I(c_k, c_{k'})$ in Eq. C.8 is generalized to

$$I_{jj'}(c_k, c_{k'}) = \frac{1}{Z_{4f}} j_3(kr) j_3(k'r) \frac{1}{\beta^2} \sum_{\omega, \nu} \int \frac{d\xi}{\pi} \frac{A_c(c_k, \xi)}{i\omega - \xi} \int \frac{d\xi'}{\pi} \frac{A_c(c_{k'}, \xi')}{i\omega - c_{k'}} \int \frac{d\zeta}{\pi} \frac{B(\zeta)}{i\nu - \zeta} \\ \times \int \frac{d\rho}{\pi} \frac{A_{jm}(\rho)}{i(\omega + \nu) - \rho} \int \frac{d\rho'}{\pi} \frac{A_{j'm'}(\rho')}{i(\omega + \nu) - \rho'}. \quad (G.1)$$

We can define the conduction electron self energy Σ_c by

$$G_c(k, \xi) = \frac{1}{\xi - c_k - \Sigma_c(\xi)}. \quad (G.2)$$

Then

$$A_c(c_k, \xi) = -\text{Im} G_c(k, \xi) \\ = -\text{Im} \frac{1}{\xi - c_k - \Sigma_c(\xi)}. \quad (G.3)$$

The conduction electron self energy is calculated using the average-T matrix (ATA) approximation.

The ν summation is the same as Eq. (C.9). Then the Eq. (G.1) becomes

$$I_{jj'}(c_k, c_{k'}) = \frac{1}{Z_{Af}} j_3(kr) j_3(k'r) \frac{1}{\beta} \sum_{\omega} \int \frac{d\xi}{\pi} \frac{A_c(c_k, \xi)}{i\omega - \xi} \int \frac{d\xi'}{\pi} \frac{A_c(c_{k'}, \xi')}{i\omega - c_{k'}} \int \frac{d\zeta}{\pi} B(\zeta) \\ \times \int \frac{d\rho}{\pi} A_{jm}(\rho) \int \frac{d\rho'}{\pi} A_{j'm'}(\rho') \frac{2f(\rho) - 2N(\zeta)}{(\rho - \rho')(\rho - i\omega - \zeta)}. \quad (G.4)$$

Let's do the ω sum,

$$(B) = \frac{1}{\beta} \sum_{\omega} \frac{1}{i\omega - \xi} \frac{1}{i\omega - \xi} \frac{1}{(\rho - i\omega - \zeta)} \\ = \frac{f(\xi)}{(\xi - \xi')(\rho - \xi - \zeta)} + \frac{f(\xi')}{(\xi' - \xi)(\rho - \xi' - \zeta)} + \frac{f(\rho - \zeta)}{(\rho - \zeta - \xi)(\rho - \zeta - \xi')} \\ = \frac{f(\xi)}{(\xi - \xi')(\rho - \xi - \zeta)} + \frac{f(\xi')}{(\xi' - \xi)(\rho - \xi' - \zeta)} - \frac{f(\rho - \zeta)}{(\xi - \xi')} \left(\frac{1}{\xi + \zeta - \rho} - \frac{1}{\xi' + \zeta - \rho} \right) \\ = \frac{2f(\xi) - 2f(\rho - \zeta)}{(\xi - \xi')(\xi + \zeta - \rho)}. \quad (G.5)$$

With Eq.(G.5), the $I_{jj'}(c_k, c_{k'})$ is written

$$I_{jj'}(c_k, c_{k'}) = j_3(kr) j_3(k'r) \int \frac{d\xi}{\pi} A_c(c_k, \xi) \int \frac{d\xi'}{\pi} A_c(c_{k'}, \xi') \int \frac{d\zeta}{\pi} B(\zeta) \int \frac{d\rho}{\pi} A_{jm}(\rho) \\ \times \int \frac{d\rho'}{\pi} A_{j'm'}(\rho') \frac{(2f(\rho) - 2N(\zeta))(2f(\xi) - 2f(\rho - \zeta))}{(\xi - \xi')(\rho - \rho')(\xi + \zeta - \rho)}. \quad (G.6)$$

In the above equation the ξ' integration is given by

$$\int \frac{d\xi'}{\pi} \frac{A_c(c_{k'}, \xi')}{\xi - \xi'} = \text{Re}G_c(k'\sigma', \xi). \quad (G.7)$$

Putting, Eq. (G.7), Eq. (C.13) and Eq. (C.14) together, $I_{jj'}(c_k, c_{k'})$ becomes

$$I_{jj'}(c_k, c_{k'}) = 4j_3(kr) j_3(k'r) \int \frac{d\xi}{\pi} A_c(c_k, \xi) \text{Re}G_c(k'\sigma', \xi) \int \frac{d\zeta}{\pi} B(\zeta) \int \frac{d\rho}{\pi} \\ A_{jm}(\rho) \text{Re}G_{j'm'}(\rho) \frac{(e^{-\beta\zeta} + e^{-\beta\rho})(f(\xi) - f(\rho - \zeta))}{\xi + \zeta - \rho}. \quad (G.8)$$

also with $f(\rho - \zeta)(e^{-\beta\zeta} + e^{-\beta\rho}) = e^{-\beta\rho}$

$$I_{jj'}(c_k, c_{k'}) = j_3(kr) j_3(k'r) \frac{4}{Z_{Af}} \int \frac{d\xi}{\pi} A_c(c_k, \xi) \text{Re}G_c(k'\sigma', \xi) \int \frac{d\zeta}{\pi} \int \frac{d\rho}{\pi}$$

$$\left[\frac{(B^{(-)}(\zeta)A_{jm}(\rho)\text{Re}G_{jm'}(\rho)f(\xi))}{\xi + \zeta - \rho} + \frac{B(\zeta)A_{jm}^{(-)}(\rho)\text{Re}G_{j'm'}(\rho)(f(\xi) - 1)}{\xi + \zeta - \rho} \right]. \quad (\text{G.9})$$

Where $J(\xi)$ is defined by

$$J(\xi) = \int dk \frac{k^2 j_3(kr)}{\xi - \epsilon_k - \Sigma_c(\xi)}. \quad (\text{G.10})$$

equation can be written

$$\int k^2 dk \int k'^2 dk' l_{jj'}(\epsilon_k, \epsilon_{k'}) = - \int \frac{d\xi}{\pi} \text{Im} J(\xi) \text{Re} J(\xi) [f(\xi) l_{1jj'}(\xi) + (1 - f(\xi)) l_{2jj'}(\xi)] \quad (\text{G.11})$$

where

$$\begin{aligned} l_{1jj'}(\xi) &= \frac{2}{Z_{Af}} \int \frac{d\zeta}{\pi} \int \frac{d\rho}{\pi} \frac{(B^{(-)}(\zeta)A_{jm}(\rho)\text{Re}G_{jm'}(\rho))}{\xi + \zeta - \rho} \\ &= \frac{1}{Z_{Af}} \int \frac{d\zeta}{\pi} B^{(-)}(\zeta) \text{Re}G_{jm}(\zeta + \xi) \text{Re}G_{j'm'}(\zeta + \xi) \end{aligned} \quad (\text{G.12})$$

$$\begin{aligned} l_{2jj'}(\xi) &= \frac{-2}{Z_{Af}} \int \frac{d\zeta}{\pi} \int \frac{d\rho}{\pi} \frac{B(\zeta)A_{jm}^{(-)}(\rho)\text{Re}G_{j'm'}(\rho))}{\xi + \zeta - \rho} \\ &= \frac{2}{Z_{Af}} \int \frac{d\rho}{\pi} A_{jm}^{(-)}(\rho) \text{Re}G_{j'm'}(\rho) \text{Re}D(\rho - \xi) \end{aligned} \quad (\text{G.13})$$

G.1 Average T-matrix Approximation

In this appendix, a brief derivation of the ATA via a diagrammatic resummation of intersite hybridization processes will be provided. General derivations with intuitive decoupling procedures and diagrammatic technique may be found in the review article of Elliot, Krumhansl and Leath [1]. The appropriate lattice sums respecting the

excluded sites may be found in article by Grewe [2]. In this approximation, the full $4f$ -electron Green's functions are directly dealt with through Feynman diagrams [3]. the NCA is used to estimate The full $4f$ -electron Green's function $G_{4f}(\omega)$ is evaluated within the NCA method (see Appendix F).

The first order expansion term of the conduction electron Green's function is given by

$$G_c^{(1)}(\omega, \vec{k}) = G_{c0}^2[G_f(\omega)V^2] \quad (\text{G.14})$$

In the second order expansion term of the conduction electron Green's function is given by

$$G_c^{(2)}(\omega, \vec{k}) = G_{c0}^2[G_f(\omega)V^2]^2(G_{c0}(\omega, \vec{k}) - D(\omega)) \quad (\text{G.15})$$

where $D(\omega)$ is defined in Eq. (2.75) and arises from the restriction that the conduction electron can not scatter off the same f electron site twice. This is the first order contribution with the site restriction. The second term renormalize the full $4f$ Green's function in the first order correction. This is the general structure of the expansion; the full $4f$ Green's function in the first term will be renormalized by terms from the higher order expansion.

There are three terms at the third order perturbation, given by

$$G_c^{(3)}(\omega, \vec{k}) = G_{c0}^2[G_f(\omega)V^2]^3(G_{c0}^2(\omega, \vec{k}) - 2G_{c0}(\omega, \vec{k})D(\omega) + D(\omega)^2) \quad (\text{G.16})$$

Clearly, the second term is the beginning of the renormalization of the first term in the second order of perturbation theory, and the third term is the second order renormalization of the term in the first order of perturbation theory.

We can easily sum up the above expansion terms which show simple geometric series. Then, conduction electron self energy is given by

$$\begin{aligned}
 \Sigma_c(\omega) &= \frac{[V^2 G_f(\omega)]}{1 + [V^2 G_f(\omega)] D(\omega)} \\
 &= \frac{V^2}{G_f^{(-1)}(\omega) + V^2 D(\omega)} \\
 &= \frac{V^2}{\omega - \epsilon_f - \Sigma_f(\omega)}. \tag{G.17}
 \end{aligned}$$

The second line in above equations show the renormalization of the $G_f(\omega)$ by the $D(\omega)$.

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