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MANY BODY THEORY FOR SPECTROSCOPIES OF Ce MIXED VALENCE COMPOUNDS

O. GUNNARSSON and K. SCHÖNHAMMER

Max-Planck-Institut für Festkörperforschung,
D-7000 Stuttgart 80, F.R.G.
*Institut für Theoretische Physik, Universität Göttingen,
D-3400 Göttingen, F.R.G.

Abstract: Spectroscopic and thermodynamic properties of Ce mixed valence compounds are studied for the Anderson model. The large orbital and spin degeneracy $N_f$ of the f-level allows us to treat $1/N_f$ as a small parameter. In this way exact results can be obtained for $N_f = \infty$ and $T = 0$, and even for $N_f = 1$ or 2 accurate results are obtained if corrections of order $1/N_f$ are considered. Comparison between theory and experiment for core level X-ray photoemission spectra leads to estimates of the parameters in the model. With these parameters the model can also give a fairly good description of other spectroscopies, such as $M_4$ $\epsilon$XAS, 4f PES and BIS. The values of the parameters place the known Ce intermetallics in or close to the Kondo limit. In this limit the f-spectral function has a narrow Kondo resonance close to the Fermi energy, which has been seen spectroscopically for some of the systems. This resonance is related to a large density of low-lying excitations, which explains the large low temperature susceptibility and specific heat of these systems.

I. Introduction

The 4f-orbital in the lanthanide series has a small spatial extent and is located inside the 5s5p core. As a result the 4f-4f Coulomb interaction $U$ is large and the hybridization $\Delta$ between the 4f-state and the conduction states is small. In some lanthanide compounds two f-configuration $4f^n$ and $4f^{n+1}$ are, however, sufficiently close in energy so that the mixing of these configurations must be taken into account, in spite of the weak coupling $\Delta$. Such compounds have unusual and interesting properties. At low temperatures the spin susceptibility and the linear temperature coefficient in the specific heat are very large, suggesting a large density of low lying excited states [1].

For Ce compounds these and other thermodynamic properties were often interpreted in terms of a very small $\Delta$ (~0.01 eV) and an almost perfect (within ~0.1 eV) degeneracy of the $f^0$ and $f^1$ configurations [2,3]. This could give a narrow resonance at the Fermi energy and a large density of states.

In the last 5 - 10 years there has been much interest in electron spectroscopies, since they suggest very different values of the parameters. Valence photoemission spectroscopy (PES) shows a rather
broad f-related peak at 2 eV binding energy, suggesting that the $f^0 - f^1$ energy separation is of the order 2 eV and that $\Delta$ is of the order 1 eV [4]. Later it was realized that the PES spectrum also has f-weight at the Fermi energy [5], creating a lively debate about the interpretation of the spectra.

Since both the thermodynamic and spectroscopic data provide rather indirect information about the parameters of the system, it is desirable to study a microscopic model to determine what information the different experiments can provide. Theoretical studies of Ce compounds are often based on the Anderson impurity model. A great progress in the treatment of this model was the idea of Anderson [6] and Ramakrishnan [7,8] to treat $1/N_f$ as a small parameter, where $N_f$ is the degeneracy of the f-level. We have developed a method for calculating spectra in a $1/N_f$ expansion [9, 10] which gives exact $T = 0$ spectra for $N_f = \infty$. Later, alternative methods were developed for a finite $T$ but an infinite $U$ [11].

II. Model

We use the Anderson impurity model

$$H = \sum_{\nu=1}^{N_f} \left\{ \int d\varepsilon \varepsilon \psi^\dagger_\nu \psi_\nu + \varepsilon_f \psi^\dagger_f \psi_f + \int d\varepsilon [V(\varepsilon) \psi^\dagger_\nu \psi_\nu + h.c.] \right\}$$

$$+ U \sum_{\nu < \mu} n_{\nu} n_{\mu}$$

where the first term describes the conduction states, the second the 4f-state, the third the hopping between these states and the fourth the 4f-4f Coulomb interaction. The index $\nu$ is a combined spin and orbital index for the $N_f$-fold degenerate f-level. The conduction states have been transformed to the same representation $\nu$ [10]. The hopping matrix element $V(\varepsilon)$ is assumed to be independent of $\nu$. The conduction density of states is absorbed in $V(\varepsilon)$. For the core spectroscopies we also include the terms [12]

$$H_c = \varepsilon_c n_c - U_{fc} (1-n_f) \sum_{\nu} n_{\nu}$$

where $\varepsilon_c$ is the energy of the core level and $U_{fc}$ is the Coulomb interaction between the core hole and an f-electron. The large value ($\sim 10$ eV [13]) of $U_{fc}$ causes an important reordering of the f-configurations when a core hole is created.

To study the limit $N_f \rightarrow \infty$, we must specify how $V(\varepsilon)$ varies when $N_f$ is varied. By defining

$$\bar{V}(\varepsilon) = \sqrt{N_f} V(\varepsilon)$$

and requiring that $\bar{V}(\varepsilon)$ is independent of $N_f$, we obtain a well defined limit $N_f \rightarrow \infty$ at $T = 0$. We also define

$$\Delta(\varepsilon) = \pi V(\varepsilon)^2$$

and use the average $\frac{\Delta_{av}}{\varepsilon}$ over the occupied band to represent the strength of the coupling.
In this section we discuss the \( \frac{1}{N_f} \) treatment of the Anderson model. The ground-state properties are calculated in a variational approach. This requires the introduction of a many-electron basis set. We introduce the "Fermi sea" basis state

\[
|0\rangle = \phi^+_{\psi_F} \prod_{i=1}^{N_f} \phi^+_{\psi_V} |\text{vacuum}\rangle
\]

(5)

This couples to the state

\[
|\epsilon\rangle = \frac{1}{\sqrt{N_f}} \sum \psi^+_V \psi_{\epsilon V} |0\rangle
\]

(6)

with one \( f \)-electron and one conduction hole. For a finite \( U \) these states couple to \( f^2 \) states, which are not shown explicitly here. The states (6) couple to states

\[
|E\epsilon\rangle = \frac{1}{\sqrt{N_f}} \sum \psi^+_{E V} \psi_{\epsilon V} |0\rangle
\]

(7)

with one electron-hole pair. In this way an infinite sequence of basis states can be generated. The ground-state \( |E_0(N)\rangle \) of the \( N \)-particle system is expressed as

\[
|E_0(N)\rangle = \sum_i c_i |i\rangle
\]

(8)

where \( \{|i\rangle\} \) is the basis set used, e.g. the states (5-7). For the calculations the matrix elements of \( H \) are needed.

\[
\langle\epsilon | H | 0\rangle = V(\epsilon)
\]

(9)

\[
\langle E\epsilon | H | \epsilon'\rangle = V(E) \delta(\epsilon - \epsilon')/N_f
\]

(10)

These results illustrate the use of the \( \frac{1}{N_f} \) arguments. For \( N_f \to \infty \), the coupling (9) stays constant while the coupling (10) vanishes. For \( U = \infty \) (states with more than one \( f \)-electron suppressed) only the states \( |0\rangle \) and \( |\epsilon\rangle \) are needed for \( N_f \to \infty \). For a finite \( N_f \) the states (7) give a contribution of the order \( 1/N_f \). For a more systematic discussion see Ref. 15.

In the so-called sudden approximation, many of the spectra of interest can be related to a one-particle Green's function. For the core level PES spectrum, for instance, one obtains

\[
\rho_c(\epsilon) = \frac{1}{\pi} \text{Im} \ g_c(\epsilon-i0)
\]

(11)

\[
g_c(z) = \langle E_0(N) | \phi^+_C \frac{1}{z+H-E_0(N)} \phi_c | E_0(N) \rangle
\]

(12)
where $\psi_c$ is the annihilation operator for a core electron. To calculate $g_c(z)$ we introduce a basis set $\{|\mu>\}$ for the (N-1)-electron system. It is formally assumed that $\{|\mu>\}$ is a complete basis set

$$ \sum_\mu |\mu><\mu| = 1 $$

and $g_c(z)$ is written as

$$ g_c(z) = \sum_\mu \sum_\gamma <\psi^+_c|E_0(N)|\psi_c|^2 <\mu|^{1} \frac{1}{z+E_0(N)} |\nu><\nu|\psi_c|E_0(N)> $$

The matrix elements $<\mu|(zH-E_0(N))|\nu>$ are calculated and the corresponding matrix is inverted. Performing the sums in Eq. (14) gives $g_c(z)$. To be able to perform the calculations, the $1/N_f$ idea is used also in the choice of $\{|\mu>\}$. For the calculation of $g_c(z)$, the basis set $\{|\mu>\}$ is obtained by removing the core electron $c$ from the ground-state basis set $\{|i>\}$. Similarly, one can calculate spectra related to X-ray absorption spectroscopy (XAS), valence photoemission spectroscopy (PES) and Bremsstrahlung isochromat spectroscopy (BIS).

A crucial question is the accuracy of the $1/N_f$ expansion. Properties such as the ground-state energy, the f-occupancy $n_f$, the static, T=0 spin- and charge-susceptibilities are accurately reproduced, even for $N_f=2$ or $N_f=1$, if contributions of the order $1/N_f$ [9, 16] or $(1/N_f)^2$ [15, 17] are included. Fig. 1 shows results for the core level PES spectrum.
We have studied $N_f = 1$, since it is the most unfavourable case for a $1/N_f$ method, and since the exact result can be obtained by solving numerically [18] the Nozières-de Dominicis integral equation [19]. Fig. 1a shows results for a realistic broadening ($2\Gamma = 1.8$ eV). The dotted curve gives the $(1/N_f)^0$ result (states (5-6) included). While the peak positions are rather well reproduced, the peak weights are off by a factor of 2. The broken curve shows the results obtained when one (state (7)) of the two states of order $(1/N_f)^1$ is included. In this case the peak weights are also rather accurate. If the remaining states of order $(1/N_f)^1$ are included, the approximate and exact results essentially agree within the plotting accuracy. In Fig. 1b the $(1/N_f)^1$ results are therefore shown with a greatly reduced broadening. The asymmetry of the exact result due to the infrared singularity is then clearly visible. The $(1/N_f)^1$ results reproduce the asymmetry well, except close to the threshold. This is remarkable, since the infrared singularity is due to the excitation of an infinite number of electron-hole pairs, while the $(1/N_f)^1$ theory only includes one electron-hole pair. For a larger value of $N_f$, we expect the $(1/N_f)^1$ results to be even more accurate. Elsewhere [10] we have demonstrated that the $1/N_f$ approach also gives accurate results for the f-level PES spectrum even for $N_f = 1$, if corrections of order $(1/N_f)^1$ are included.

4. Spectroscopic properties of Ce compounds

In this section we discuss a typical example of how the results of an impurity calculation can be compared with a Ce compound. In Fig. 2 we show results for CeNi$_2$. In these calculations the 4f spin-orbit splitting was taken into account. The shape of $\Delta(eV)$ was estimated from the valence spectrum for the photon energy 112 eV as indicated in the inset. The top panel in Fig. 2a shows the 3d XPS spectrum. The spectrum has a 3d 3/2 and a 3d 5/2 contribution, which in the calculation is included by adding two spectra with the relative weights 4:6 and shifted by 18.4 eV. The figure illustrates that for appropriate values of $n_f$ and $\Delta$ a good description of experiment can be obtained. The calculated peaks are somewhat too narrow which is probably mainly due to the neglect of multiplet effects. In the calculations of the remaining spectra of CeNi$_2$, the values of $n_f$ and $\Delta_{av}$ are kept fixed. The bottom panel of Fig. 2a shows the 3d-4f XAS spectrum. In this case the neglected multiplet effects are clearly visible. The bottom panel in Fig. 2b shows the f-level PES spectrum. The calculation correctly gives a pronounced two-peak spectrum, although the high binding energy peak has too little weight and is somewhat too low in energy. The Fermi energy peak is partly due to a so-called Kondo-peak, i.e. due to many-body effects. Hybridization effects are, however, also important. The f-level is located at -1.6 eV in the middle of the large conduction density of states. The hybridization then pushes f-weight to both sides of the conduction density of states peak. This effect contributes to the peak at the Fermi energy and leads to the peak at -3 eV. The top curves show the BIS spectrum. A background due to inelastic effects and transitions into the conduction states has been added. For simplicity a straight line is used, although the background should vanish below the Fermi energy. We have further more included broadening and multiplet effects as described in Ref. 20. The $f^1$ and $f^2$ peaks in XAS and BIS, the two peaks in the f-level PES and the $f^0$, $f^1$ and $f^2$ peaks in XPS, provide 5 relative intensities. These intensities depend primarily on the two adjustable parameters $n_f$ and $\Delta_{av}$. The rather good description of these intensities is therefore a demanding test of the theory. Particularly striking is the large difference in the $f^1$ weights in the BIS and XAS spectra. This large difference is explained by the theory, as discussed in Ref. 10.
Similar results have been obtained for CeRu₂, CeIr₂, and CeAl, for which the 3d XPS, the f-level PES and the BIS spectra were studied [20]. The f-level PES spectrum has also been studied for the Ce pnictides [21], for Pr, PrRu₂ [15], PrAl₂ and NdAl₂ [20]. There has also been extensive work by several other groups, as reviewed in, for instance, Ref. 10.

![Graph of CeNi₂ spectra](image)

**Fig. 2** The experimental (dots) and theoretical (full line) spectra of CeNi₂. The experimental XAS spectrum is from Ref. 22 and the other results from Ref. 20. The dashed curves in the XAS and BIS calculations show the assumed backgrounds. In the XPS spectrum ε is the kinetic energy and otherwise it is the binding energy.

5. Thermodynamic properties of Ce compounds - The low energy scale

As discussed in the introduction, the thermodynamic properties of Ce compounds have often been interpreted in terms of parameters A and \(|e_f-e_F|\), which are one to two orders of magnitude smaller than the spectroscopic estimates. It is therefore of great interest to calculate a thermodynamic quantity such as the static, T = 0 susceptibility \(\chi(0)\), using the spectroscopic parameters. We have calculated \(\chi(0)\) taking into account the spin-orbit splitting of the 4f level and the finite value of U. Exactly the same \(\Delta (e)\) was used as in the core level XPS calculation. The f-level position \(e_f\) was adjusted so that the experimental susceptibility was obtained. The corresponding value of \(n_f\) was calculated and used as a thermodynamic estimate of \(n_f\). Since the calculations only include the f-level contribution to the susceptibility, the conduction electron contribution has been subtracted from the experimental susceptibilities. This was done by considering reference compounds with La, Y or Lu, which have an empty or a full f-shell. Depending on which reference compound was used, slightly different results are obtained, leading to a spread in the thermodynamic estimate of \(n_f\). Similarly, we
obtain a spread in the spectroscopic estimates of \( n_f \), since we can optimize the agreement with experiment for each spectroscopy by varying \( n_f \) slightly. This way we obtain the spectroscopic (thermo-
dynamic) estimates 0.78-0.83 (0.76-0.83) for CeNi\(_2\), 0.77-0.82
(0.81-0.82) for CeIr\(_2\), 0.79 (0.84-0.89) for CeRu\(_2\) and 1.03 (1.03)
for CeAl\(_2\). This shows that essentially the same parameters can be
used to describe both thermodynamic and spectroscopic properties.
It is interesting that the input parameters in the calculation, \( \varepsilon_f \)
and \( N_f A(\varepsilon) \), are of the order eV (the large energy scale), although
the large susceptibilities of these systems suggest that there is also
a small energy scale in the problem. Actually the calculation
of the ground-state energy and the susceptibility for \( U = \infty \) and to
lowest order in \( (1/N_f) \) produces the so called Kondo energy

\[
\delta = B \exp \left( \frac{\varepsilon_f}{V^2} \right)
\]  

where we have assumed that \( -\varepsilon_f >> V^2 \). This energy enters in the sus-
cceptibility as

\[
\chi = \frac{1}{3} j (j + 1) \delta^{-1}
\]  

where \( j = (N_f - 1)/2 \) is the spin of the localized level. The expen-
tential behaviour of Eq. (16) explains why the "large" parameters
\( \varepsilon_f \) and \( V^2 \) can give the "small" \( \delta \) and the large values of \( \chi \sim 1/6 \).
In the actual calculations the spin-orbit splitting and the finite
value of \( U \) were taken into account.

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