Photoemission from Ce Compounds: Exact Model Calculation in the Limit of Large Degeneracy

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A method is presented for calculating the core and valence spectra of a Ce compound in the impurity model at zero temperature. In the sudden limit this method becomes exact for large degeneracy of the f level. In this limit the valence spectrum has an f peak close to the Fermi energy, ϵ_F, even if the f level is fairly far below ϵ_F, and usually there is a second f peak at larger binding energy. These results correlate well with recent experiments for many Ce compounds. Both the core and valence spectra provide information about the occupancy of the f level and about its coupling to the conduction band.

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Recently, there has been much interest in photoemission from Ce compounds.[1-5] Core spectra[1,2] of several mixed-valence Ce compounds suggest[1] a substantially larger occupancy, n_f, of the f level than usually assumed. At the same time these experiments demonstrate that calculations are needed to estimate quantitatively parameters such as n_f and Δ,[1] where Δ describes the coupling between the f level and the conduction states. The f level is usually assumed to be very close to the Fermi energy, ϵ_F, in a mixed-valence system, and further below ϵ_F in a three-valent Ce compound. However, valence spectra of several supposedly mixed-valence systems show a strong f peak a few electronvolts below ϵ_F.[3,4] Furthermore, many Ce compounds, even three-valent ones, apparently have an additional, weaker, peak close to the Fermi energy.[4,5] Another peak is observed just above ϵ_F in bremsstrahlung isochromat spectroscopy (BIS)[6] for several systems. As these results cannot be simply explained in a one-particle picture this raises questions about the meaning of the f peaks observed and about the relation between these peaks and the "bare" f level in a microscopic model. In particular, it suggests the usefulness of using the same microscopic model for studying different experiments.

Mixed-valence systems are often described in an Anderson impurity model.[7] An important progress in the study of this model was the observation by Ramakrishnan[8] and by Anderson[9] that $1/N_f$ can be considered as a small parameter, where N_f is the degeneracy of the f level. For Ce, $N_f=6$ if only the lower, $j=\frac{5}{2}$, component of the spin-orbit-split f level is considered, and $N_f=14$ if the spin-orbit splitting is neglected. In this paper, we show that in the sudden limit both the core level and valence photoemission spectra of the impurity model at zero temperature can be calculated exactly for $N_f\to\infty$. This applies both to the mixed-valence and the spin-fluctuation limits. The valence spectrum is qualitatively different for $N_f=1$ and $N_f=\infty$. For $N_f=\infty$, there is a sharp rise in the valence spectrum at ϵ_F, and a peak just above ϵ_F in the BIS spectrum, even if the f level, ϵ_f, is rather far below ϵ_F.

We use a slightly modified version of the Anderson impurity Hamiltonian,

$$H=\sum_{p\sigma}\epsilon_p n_{p\sigma}+[\epsilon_f-U_{fc}(1-n_c)]\sum_{m\sigma}n_{m\sigma}+\epsilon_c n_c+\sum_{pm\sigma}V_{pm}(\psi_{m\sigma}^{\dagger}\psi_{p\sigma}+\text{H.c.})+\tfrac{1}{2}U\sum_{m\sigma\neq m'\sigma'}n_{m\sigma}n_{m'\sigma'}, \quad (1)$$

where ϵ_p describes the conduction states, ϵ_f the f level, and V_{pm} the hopping between these levels. The f-f and core-hole-f Coulomb integrals are given by U and U_{fc}, and ϵ_c determines the core-level position. For V_{pm} we assume[10]

$$\sum_p V_{pm}V_{pm'}{}^{*}\delta(\epsilon-\epsilon_p)$$

$$=\sum_p|V_p|^2\delta(\epsilon-\epsilon_p)\delta_{mm'}\equiv F(\epsilon)\delta_{mm'}. \quad (2)$$

We use a semielliptical $F(\epsilon)$ with the width $2B$, and introduce $\Delta=\pi F(\epsilon_F)$, where $\epsilon_F=0$ is the Fermi energy. To leading order in $1/N_f$, the coupling Δ enters the calculation in the combination $N_f\Delta$ or $(N_f-1)\Delta$. We therefore study $N_f\Delta=\text{const}$, since the photoemission spectra then converge in the limit $N_f\to\infty$.

In the sudden approximation, the core-level

spectrum is given by

$$\rho_c(\epsilon) = \sum_n |\langle E_n^{N-1}|\psi_c|E_0^N\rangle|^2 \delta(\epsilon - E_0^N + E_n^{N-1}), \quad (3)$$

where $|E_0^N\rangle$ is the ground state, $|E_n^{N-1}\rangle$ are the final eigenstates of (1) containing a core hole, and ψ_c is the annihilation operator for the core level. There are many[11] calculations of the core spectrum for the nondegenerate version of (1) and a few[12] for the spin-degenerate ($N_f = 2$) case. To obtain (3) in the limit $N_f \to \infty$, we calculate the exact ground state and the relevant exact final eigenstates, which exhaust the sum rule

$$\sum_n |\langle E_n^{N-1}|\psi_c|E_0^N\rangle|^2 = 1. \quad (4)$$

We first assume that $U = \infty$, so that hopping into states with more than one f electron can be neglected. It is straightforward to generalize the proof to finite U. To describe the relevant final states, we introduce the basis state[13] $|0\rangle$, with all the conduction states below ϵ_F occupied, and the states $|km\sigma\rangle = \psi_{m\sigma}^\dagger \psi_{k\sigma}|0\rangle$, where k refers to a conduction state below ϵ_F. The Hamiltonian (1) is diagonalized in this subspace, which gives

$$|n\rangle = a_0^n|0\rangle + \sum_{km\sigma} a_{km\sigma}^n |km\sigma\rangle. \quad (5)$$

We let H act on $|n\rangle$ and find

$$H|n\rangle = E_n|n\rangle + \sum_{\kappa km\sigma} V_{\kappa m} a_{km\sigma}^n \psi_{\kappa\sigma}^\dagger \psi_{k\sigma}|0\rangle, \quad (6)$$

where κ is a state above ϵ_F. The norm of the second term is

$$\sum_{\kappa k\sigma mm'} V_{\kappa m} V_{\kappa m'}^* a_{km\sigma}^n a_{km'\sigma}^{n*} = \sum_\kappa |V_\kappa|^2 \sum_{km\sigma} |a_{km\sigma}^n|^2 \le \sum_\kappa |V_\kappa|^2, \quad (7)$$

where we have used (2) and the fact that (5) is normalized. Thus, in the limit $N_f\Delta = \text{const}$ and $N_f \to \infty$, the norm of the second term in (6) goes to zero, and $|n\rangle$ becomes an eigenstate of H. The exact initial ground state $|E_0^N\rangle$ is obtained in the same way, using basis states with a core electron.[14] The final eigenstates (5) span the subspace used and therefore exhaust the sum rule (4). This procedure leads to the exact spectrum.

In practice, we rewrite Eq. (3) in terms of a resolvent operator $(z+H)^{-1}$ and insert $\sum|i\rangle\langle i|$ on both sides of this operator, where the states $|i\rangle$ include $|0\rangle$, $|km\sigma\rangle$, and, for finite U, states with double occupancy. This is referred to as a first-order calculation. For finite N_f, it leads to an approximate spectrum, which can be improved by using the additional states $\psi_{\kappa\sigma}^\dagger\psi_{k\sigma}|0\rangle$. This we call a second-order calculation. In general these calculations require a matrix inversion, but the first-order calculation can be performed analytically in the limit $U \to \infty$.[14] In Fig. 1, we show a core-level spectrum with values for n_f and $N_f\Delta$ typical for mixed-valence Ce compounds. The similarity of the first- and the second-order calculations suggests that the first-order calculation is almost converged for $N_f = 6$. The peaks at -1.5, 9, and 13 eV correspond to the final f^0, f^1, and f^2 states, respectively. From the weights of the f^0 and f^2 peaks we can deduce n_f and Δ, respectively.[14]

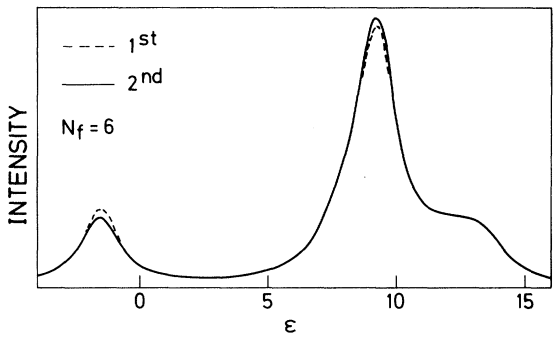

FIG. 1. The core-level spectrum for $N_f\Delta = 1.4$, $U_{fc} = 10$, $\epsilon_f = -1.1$, $U = 7$, and $2B = 6$, with all energies in electronvolts. These parameters lead to $n_f = 0.8$. We have used a Lorentzian broadening with full width at half maximum of 1.8 eV.

We can proceed in a similar way for the valence spectrum. We use the sudden approximation and introduce a transition operator, which describes emission from the f level.[15] We use the final states $\psi_{k\sigma}|\tilde{0}\rangle$ and $\psi_{m\sigma'}^\dagger\psi_{k\sigma}\psi_{k'\sigma}|\tilde{0}\rangle$, where $|\tilde{0}\rangle = \psi_c^\dagger|0\rangle$. In the limit $U = \infty$ and $N_f \to \infty$, diagonalization of H in this subspace leads to exact eigenfunctions, which fulfill the sum rule equivalent to (4) and therefore yield the exact spectrum. Expressing the spectrum in terms of resolvent matrix elements requires the inversion of a matrix. The nondiagonal terms give a vanishing contribution for $N_f \to \infty$. Neglecting these terms also for finite N_f ("diagonal approximation"), we obtain

$$\rho_v(\epsilon) = (1-n_f)N_f \sum_k |V_k|^2 \operatorname{Im} g(z - \Delta E + \epsilon_f - \epsilon_k)/(\Delta E - \epsilon_f + \epsilon_k)^2 \quad (8)$$

where

$$g(z) = \left(z - \epsilon_f - N_f \sum_k \frac{|V_k|^2}{z - \epsilon_k}\right)^{-1} \quad (9)$$

and $\Delta E = E_0^N - \langle\tilde{0}|H|\tilde{0}\rangle$, which is given by the ground-state calculation. The sum over k is limited to states below ϵ_F, since conduction states above ϵ_F do not enter in the limit $N_f \to \infty$, because of arguments similar to Eq. (7). This cutoff at ϵ_F leads to a pole in (9). Integrating this pole contribution yields, for $\Delta E - \epsilon_f < \epsilon < \epsilon_F$,

$$\rho_v(\epsilon) = \frac{(1-n_f)^2 N_f \Delta/\pi}{(\epsilon - \epsilon_f + \Delta E)^2}. \quad (10)$$

In the spin-fluctuation limit, when ϵ_f is far below ϵ_F, this "Kondo" peak[16] is very narrow and has a small weight. Using Friedel's sum rule[17] for arbitrary degeneracy, one obtains the exact relation

$$\rho_v(\epsilon_F) = (N_f/\pi\Delta)\sin^2(\pi n_f/N_f), \quad (11)$$

assuming a broad valence band with a constant density of states. For $N_f \to \infty$ our result for $\rho_v(\epsilon_F)$ [Eq. (10)] obeys this exact relation between $\rho_v(\epsilon_F)$ and n_f [Eq. (11)], as it should, and for $N_f = 6$ the deviation is less than 10%.

In Fig. 2 we show the valence spectrum as a function of B, keeping Δ fixed. While the structure at ϵ_F stays almost unchanged, the low-energy part of the spectrum depends strongly on B. For $B = 2$ there is a peak just below $-B$, similar to the split-off peak that can appear also for $N_f = 1$. For $B = 3$ there is still a structure at $-B$, while for $B = 5$ the spectrum is entirely structureless apart from a sharp rise at ϵ_F. The curve for $B = 2$ may be appropriate for Ce, since a band calculation[18] shows that the density of states is small below -2 eV but increases rapidly at -2 eV. Figure 2 illustrates that the assumption of a broad and structureless conduction band can lead to fairly large errors, and it is necessary to include the major features of the band structure in a calculation of this type.

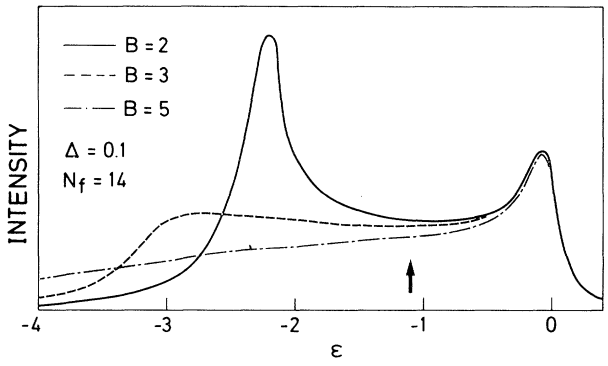

FIG. 2. The valence spectrum as a function of B, where $-B$ gives the bottom of the band. We have used the parameters $N_f\Delta = 1.4$ and $\epsilon_f = -1.1$ eV, and a Lorentzian broadening with full width at half maximum of 0.2 eV. The relevant energy scale for the peak described by Eq. (10) is $|\Delta E - \epsilon_f| = 0.14$ eV.

We have developed a similar theory for BIS, which predicts a peak at $\epsilon_f - \Delta E$. This peak corresponds to an f^1 final state. For $N_f \to \infty$, Eq. (10) also describes the BIS spectrum for energies $\epsilon_F < \epsilon < \epsilon_f - \Delta E$. If double occupancy is allowed there is also an f^2 peak which, if the coupling to the f^1 peak is neglected, is located at $2\epsilon_f + U - \Delta E$.[14] The weight of the f^1 peak diverges for $N_f = \infty$, since there are N_f possibilities to put an electron into one of the f levels. It is therefore more difficult to obtain a systematic $1/N_f$ expansion for the BIS intensities than for the photoemission spectrum, where we can start from a converging $N_f \to \infty$ limit. For temperatures large compared with $\epsilon_f - \Delta E$, one expects a smearing of the peak described by Eq. (10). Our $T = 0$ results are therefore only reliable for $T < \epsilon_f - \Delta E$, which for a mixed-valence system is typically ~ 0.1 eV. This energy scale and the normal measurement temperatures are large compared with the transition temperature of many magnetic Ce compounds. Since the impurity model gives a nonmagnetic ground state, magnetic Ce compounds cannot be described by the model treated here, but will be discussed in a later publication.[14]

We have presented a method for calculating the core level and valence spectrum of a Ce compound. Using the impurity model and the sudden approximation, we obtain the exact photoemission spectrum in the limit of large degeneracy of the f level. This method can also be applied to other rare-earth compounds, to more complicated models including, e.g., multiplet splitting and f-d Coulomb interaction, and to other spectroscopies, e.g., x-ray absorption spectroscopy. For appropriate parameters we obtain core-level spectra similar to the experimental ones.[1,2] Comparison with experimental spectra allows us to estimate the valency and the coupling, Δ, between the f level and the conduction states. For the valence spectrum we find an f structure at the Fermi energy, ϵ_F. A similar structure is believed to have been observed for a large number of Ce compounds.[4,5] Similarly, the BIS spectrum shows an f^1 peak just above ϵ_F, even when ϵ_f is far below ϵ_F. The valence and BIS spectra illustrate that there need not be any simple relation between the energy of the "bare" f level and the position(s) of the observed f peak(s). In a forth-

coming publication we use these methods to estimate the f occupancy and Δ for some Ce compounds.

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