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# Electronic Spectral Density in Heavy-Fermion Metals

V. Zlatić,[a] S. K. Ghatak,[b] and K. H. Bennemann
*Institute for Theoretical Physics, Freie Universität Berlin, D-1000 Berlin 33, Federal Republic of Germany*

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The electronic spectral density in heavy-fermion metals is determined by use of the periodic Anderson Hamiltonian with interatomic hybridization. The electronic density of states $N(\epsilon)$ exhibits pronounced structure consisting of a narrow peak centered at the Fermi level and two broad side peaks. These results are used to interpret x-ray photoemission spectroscopy and bremsstrahlung isochromat spectroscopy data. The electronic mass enhancement $m^*/m$ is calculated as a function of the intra-atomic Coulomb interaction.

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Recently, heavy-fermion metals like $UBe_{13}$, $UPt_3$, $CeCuSi_2$, etc., which exhibit an anomalously large electronic specific heat have been studied intensively.[1] High-resolution x-ray photoemission (XPS) and bremsstrahlung isochromat spectroscopy (BIS)[2] yield electronic spectra which are typically several electronvolts wide below and above $\epsilon_F$. This is in sharp contrast to the one-electron density-of-states $N(\epsilon)$ calculation[3] which in addition also fails to account for a large $N(\epsilon)$ at $\epsilon_F$. The bremsstrahlung experiments yield a spectral weight typically 6–7 eV wide and fairly asymmetrical in shape.[2]

To study the structure in $N(\epsilon)$ we perform a model calculation using the periodic Anderson model.[4] In heavy-fermion compounds the separation between $f$ ions is typically 5–6 Å and therefore $f$-band formation results from the hybridization of the localized $f$ levels with the conduction-band states (which are a mixture of $s$, $p$, and $d$ states). Previous theoretical studies[5] of heavy-fermion systems attempted to determine the electronic structure by extending the Kondo-impurity results using intra-atomic hybridization between $f$ and band states. This hybridization produces a gap at $\epsilon_F$ in the symmetrical case. In contrast, we assume interatomic $f$-state hybridization as in recent band calculations.[3] The Hamiltonian used is given by

$$H=\sum_{k,\sigma}\epsilon_{k\sigma}n_{k\sigma}+\sum_{l,\sigma}\epsilon_l f^\dagger_{l\sigma}f_{l\sigma}+\sum V_{ij}(f^\dagger_{i\sigma}d_{j\sigma}+\text{H.c.})+U\sum_{l}n_{l\uparrow}n_{l\downarrow}. \tag{1}$$

Here, the first term describes conduction electrons; the second term, $f$ electrons at energy $\epsilon_l$; $V_{ij}$, hybridization between $f$ states and $s,p,d$ band states at sites $i$ and $j$; and $U$, intra-atomic Coulomb interaction between $f$ electrons. For simplicity we use the same hybridization matrix element $V_{ij}$ for $s$, $p$, and $d$ electrons. Since $V_{ij}$ hybridizes $f$ states with non-$f$ states located at neighboring ions, we have in Bloch representation $V_k=v\epsilon_k$ which holds for the case of electron-hole symmetry. Note that for the nonsymmetric case one probably has $V_k\propto\epsilon_k-\bar{\epsilon}$. One may then include $\bar{\epsilon}$ in on-site energy parameters or put $\bar{\epsilon}=0$. For the case of electron-hole symmetry the density of states (DOS) $N(\epsilon)$ obviously has a peak at $\epsilon_F$.

In order to determine $N(\epsilon)$ we solve the Hamiltonian in Hartree-Fock approximation (HF) and treat the remaining correlation

$$H'=\frac{U}{N}\sum_{k,k',q}f^\dagger_{k+q\uparrow}f^\dagger_{k'-q\uparrow}f_{k'\downarrow}f_{k\uparrow} \tag{2}$$

as a perturbation.[5] Here, electron-hole symmetry has been assumed, $\epsilon_l=-U/2$. The HF Green's functions for electrons of either spin is given by

$$G^0(k,\omega_n)=\sum_{s=+,-}\frac{\alpha_k^s}{i\omega_n-\epsilon_k^s},\quad \epsilon_k^\pm=\frac{\epsilon_k+\tilde{\epsilon}_l\pm\Omega_k}{z}, \tag{3}$$

$$\alpha_k^\pm=\frac{1}{2}\left(1\pm\frac{\tilde{\epsilon}_k-\epsilon_k}{\Omega_k}\right),\quad \Omega_k=[(\epsilon_k-\tilde{\epsilon}_l)^2+4v^2\epsilon_k^2],^{1/2}\quad \tilde{\epsilon}_l=\epsilon_l+\tfrac{1}{2}Un_f. \tag{4}$$

The resultant $N(\epsilon)$ for $\tilde{\epsilon}_l=0$ has a narrow peak at $\epsilon_F$ of width

$$B_-=\tfrac{1}{2}B([1+4v^2]^{1/2}-1)\simeq Bv^2$$

and height $\alpha^-/\beta_-$ and in addition a wide band of height proportional to $v^2$. $B$ is the half-width of the rectangular conduction band. Note that contrary to the case of intra-atomic hybridization, this peak arises from states at the middle of the conduction band. The correlations described by $H'$ affect $N(\epsilon)$ strongly. We study this by calculat-

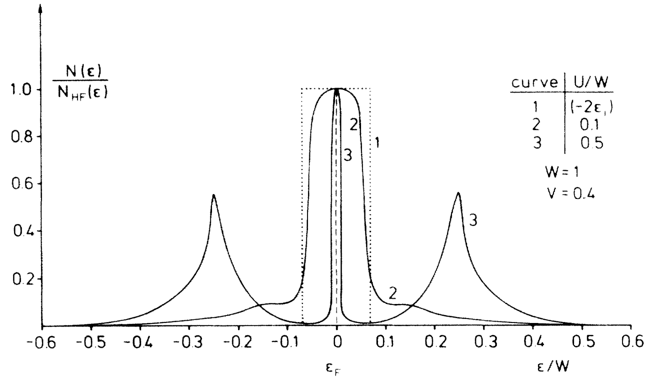

FIG. 1. Density of states $N(\epsilon)$ resulting from the hybridization of the original $f$ state with the conduction band and from correlation. $N_{\rm HF}(\epsilon)$ refers to treatment of the correlations within Hartree-Fock approximation. $W$ ($\simeq 8$ eV), $U$, and $v$ denote the width of the conduction band, the intra-atomic Coulomb interaction, and the interatomic hybridization constant, respectively. The width of central peak is reduced by a factor $\eta = 1 - \partial\Sigma/\partial\epsilon|_{\epsilon=0}$ which enhances the specific-heat coefficient (Ref. 3).

ing the electron self-energy $\Sigma(k,\omega_n)$ up to second order in $U$. Note that the third-order corrections vanish for the case of electron-hole symmetry, which we assume, and that a similar calculation of $\Sigma(k,\omega_n)$ yields good results for the single-impurity problem.[1] Therefore, we determine the self-energy by

$$\Sigma(k,\omega_n) = \frac{U^2T}{N}\sum_{q,m} G(k+q,\omega_n)\chi_q(\omega_n+\omega_m), \tag{5}$$

where the local susceptibility $\chi_q$ is in lowest approximation given by

$$\chi_q^0(\omega_n) = -\frac{T}{N}\sum_k G^0(k,\omega_n)G^0(k+q,\omega_n+\omega_m). \tag{6}$$

Note that $\Sigma(k_{\rm F}\omega)$ is zero at $\omega=0$ for a symmetrical band with $\epsilon_k = \epsilon_{-k}$ and $\epsilon_{k-K/2} = -\epsilon_k$, where $K$ is the reciprocal-lattice vector. The Green's function $G^0(k,\omega)$ is given, after renormalization due to $H'$, by

$$G(k,\epsilon) = [\epsilon - \Sigma(k,\epsilon) - V_k^2/(\epsilon - \epsilon_k)]^{-1}. \tag{7}$$

Clearly, $G(k,\epsilon)$ can be cast into the same form as $G^0(k,\epsilon)$, replacing $\epsilon_i$ by $\epsilon_i + \Sigma$ in $\alpha^{\pm}$ and $\epsilon_k^{\pm}$. $N(\epsilon)$ follows from $G(k,\epsilon)$ with use of $N(\epsilon) = -(1/\pi N)\sum_k {\rm Im}\, G(k,\epsilon)$.

In order to study the effect of $\Sigma(k,\epsilon)$ on $N(\epsilon)$ we determine first, for simplicity, the local part of the self-energy at $T=0$. The nonlocal part of the self-energy arising from correlation involving different atoms has been shown to be smaller than the local part.[6] We have also calculated the momentum dependence of $\Sigma$ for $\epsilon_k \sim k$. From this we learn that the momentum dependence of $\Sigma$ is important mainly for $N(\epsilon)$ at $\epsilon_{\rm F}$, whereas for energies away from $\epsilon_{\rm F}$, $N(\epsilon)$ is not very much affected by the $k$ dependence of $\Sigma$. The most important contribution (neglecting terms of order of $V^2$) to $\Sigma$ is then given by (see also Ref. 6)

$$\Sigma(0,\epsilon) = U^2(\alpha^-)^3\left\{\int_{-B}^{\epsilon_{\rm F}} d\epsilon_1 \int_{\epsilon_{\rm F}}^{B} d\epsilon_2 \int_{-B}^{\epsilon_{\rm F}} d\epsilon_3 \frac{N_0(\epsilon_1)N_0(\epsilon_2)N_0(\epsilon_3)}{\epsilon - \epsilon_3^+ - \epsilon_1^+ - \epsilon_2^- + i\delta} + \int d\epsilon_1 \int d\epsilon_2 \int d\epsilon_3 \frac{N_0(\epsilon_1)N_0(\epsilon_2)N_0(\epsilon_3)}{\epsilon - \epsilon_3^- - \epsilon_1^- + \epsilon_2^+ + i\delta}\right\}, \tag{8}$$

where $\epsilon_1^{\pm} = \epsilon^{\pm}(\epsilon_1)$, etc. Assuming for simplicity $N_0(\epsilon) = (1/2B)$ one obtains

$$\Sigma(\epsilon) = [U^2(\alpha^-)^3/2B_-^3][\{3(\epsilon + B_-)^2 \ln(\epsilon + B_1) - 3(\epsilon + 2B_-)^2 \ln(\epsilon + 2B_-) + (\epsilon + 3B_-)^2 \ln(\epsilon + 3B_-) - \epsilon^2 \ln\epsilon\} - \{\ \ldots\ \}_{\epsilon \to -\epsilon}].$$

The resulting $N(\epsilon)$ is shown in Fig. 1. For comparison we also show the HF DOS obtained by use of $G^0(k,\epsilon)$. It is interesting to note that for $\epsilon \to 0$ one obtains, with $\Sigma(\epsilon) \cong (\partial\Sigma/\partial\epsilon)\epsilon$, for $G(k,\epsilon)$ the expression

$$G(k,\epsilon) = \eta^{-1}(\epsilon - \epsilon_K)/[\epsilon(\epsilon - \epsilon_k) - V_k^2/\eta]$$

with $n = 1 - \partial\Sigma/\partial\epsilon$. $G$ is similar in form to the HF Green's function $G^0(k,\epsilon)$, but with the important difference that the original hybridization $V_k$ is reduced to $V_{\rm eff} = V_k/\sqrt{\eta}$. As a result the width of the HF central peak is drastically reduced to one which is of the order of the Kondo temperature.[7] Note that such a reduction was also obtained by Rice and Ueda.[8] Note that the correlations described by $H'$ narrow the peak in $N(\epsilon)$ at $\epsilon_{\rm F}$, but $N(\epsilon_{\rm F})$ remains the same as its HF value. This is due to neglect of the $k$ dependence of $\Sigma$. The number of states within this narrow $f$-like band around $\epsilon_{\rm F}$ is reduced, since the peak width decreased. The states removed from this central peak appear as side peaks below and above $\epsilon_{\rm F}$. These side peaks grow and move away from $\epsilon_{\rm F}$ as $U$ increases. A drastic reduction of the central-peak width occurs for $U > \beta_-$. As $U$ increases the spectral width of the $f$ states at $\epsilon_{\rm F}$ becomes broader.[7] The effect of the hybridization on $N(\epsilon)$ can be best seen in $N_{\rm HF}(\epsilon)$. Because of $v$ the shifted level $\epsilon_i$ broadens to a central band of width $B_-$ and $N_{\mathrm{HF}}(\epsilon)=\alpha^-/2\beta_-$.

To examine the effect of the $k$ dependence of $\Sigma$ on $N(\epsilon)$ we use the approximation $\epsilon_k=\beta k$. Then the self-energy becomes

$$\Sigma(k,\epsilon)=U^2(\alpha^-)^3\left\{\frac{3k}{B_-}+\frac{1}{2}\left[\frac{(\pi/2-k)^2}{\epsilon-B_-(\pi+k)}+\frac{(\pi/2+k)^2-3k^2}{\epsilon+B_-(\pi-k)}+\frac{k^2}{\epsilon+B_-k}\right]\right.$$
$$\left.+\frac{1}{4B_-^2}\left[(6\epsilon-9\pi B_-)\ln\left|\frac{\epsilon-B_-(\pi+k)}{\epsilon-B_-(\pi-k)}\right|+3(\epsilon+B_-k)\ln\left|\frac{\epsilon^2-(B_-k)^2}{\epsilon^2-B_-^2(\pi-k)^2}\right|\right]\right\},$$

where $k$ is measured with respect to the Fermi momentum $k_{\mathrm{F}}=\pi/2$. It should be noted that the self-energy diverges at certain $k$ values. Around the Fermi energy it follows that

$$\Sigma(k,\epsilon\to 0)=ak+bk^n\ln k$$

with positive constants $a$ and $b$. For $\epsilon_k\sim k$ one has $n=1$. Note that around $k_{\mathrm{F}}$ $\Sigma$ is large and negative. This produces a dip in the DOS at $\epsilon_{\mathrm{F}}$. If $n>1$, as expected from Fermi-liquid theory ($n=3$), then the nonlogarithmic contribution to $\Sigma$ dominates. One expects that this enhances the DOS at $\epsilon_{\mathrm{F}}$. For large $\epsilon$ the $k$ dependence of $\Sigma(k,\epsilon)$ can be neglected and $\Sigma(k,\epsilon)=\frac{1}{4}U^2/(\epsilon+i\delta)$. This produces peaks in $N(\epsilon)$ at energies $\epsilon=\pm U/2$,[5] which correspond to single-particle excitations in the atomic limit ($V_{ij}\to 0$). However, note that in addition to this atomiclike structure which accomodates most of the $f$ states we also obtain a narrow peak at $\epsilon_{\mathrm{F}}$ resulting from many-body states. Although the weight of the "many body" peak at $\epsilon_{\mathrm{F}}$ might be very small, this peak affects the properties of the system profoundly.

In summary, it follows that the local part of self-energy, $\Sigma(k=0,\epsilon)$, determines the overall structure of $N(\epsilon)$. Only at $\epsilon_{\mathrm{F}}$ does $N(\epsilon)$ depend sensitively on the $k$ dependence of $\Sigma$, which determines in particular the weight of the central peak, e.g., $N(\epsilon_{\mathrm{F}})$. Regarding the spectral weight of the $N(\epsilon)$ peak around $\epsilon_{\mathrm{F}}$, we note the following. Using $\Sigma(0,\epsilon)$ we find that for $U/B<1$ the area under the central peak amounts to 0.5 electron and for $U/B>1.5$, to approximately 0.2 electron. These values are expected not to change much if one calculates the central peak with the help of $\Sigma(k,\epsilon)$ which should yield a Lorentzian-type central peak of width of the order of $T_{\mathrm{K}}$.[7] This is suggested by the fact that the satellite peaks are not much affected by the $k$ dependence of $\Sigma$.

To estimate $N(\epsilon)$ around $\epsilon_{\mathrm{F}}$ from specific-heat measurements, one should note that the Sommerfeld specific-heat coefficient is given by[9] $\gamma=\gamma_0[1-(\partial\Sigma/\partial\epsilon)_{\epsilon=0}]$, with $\gamma_0\sim N(\epsilon_{\mathrm{F}})$, $(\partial\Sigma/\partial\epsilon)_{\epsilon=0}<0$. We obtain approximately

$$\left.\frac{\partial\Sigma}{\partial\epsilon}\right|_{\epsilon=0}=\left(\frac{u}{2B}\right)^2(\alpha^-)^3\left(\frac{B}{B_-}\right)^2 3\ln\tfrac{3}{4}.$$

Results for the enhancement factor $\gamma/\gamma_0=m^*/m$ are shown in Fig. 2. Note that even for relatively small values of $U$ the renormalization of $N(\epsilon)$ by $m^*/m-1$ is significant. This should be taken into account when analyzing $N(\epsilon_{\mathrm{F}})$ from experiment.[1,2] Although we considered here the particular choice of parameters corresponding to electron-hole symmetry and vanishingly small on-site hybridization, our results remain qualitatively the same if we add a small constant term to $V_k$ and shift simultaneously the $f$ level so as to remain in the metalic Hartree-Fock ground state.

Note that the calculated shapes of the side peaks of $N(\epsilon)$ are symmetric in contrast to XPS and BIS results. This is to be expected since "shake up" effects generally cause asymmetric XPS and BIS spectra. These "shake up" effects result from electron-hole pair excitations.[10] The resulting shape asymmetry is characterized by the parameter $\delta\sim N(\epsilon_{\mathrm{F}})$. Consequently, if the spectral weight of the central peak in $N(\epsilon)$ around $\epsilon_{\mathrm{F}}$ is relatively significant, we expect large asymmetric peak shapes in BIS and XPS experiments. For example, we may identify the BIS peak with our calculated side peak at energy $U/2\sim 2$ eV above $\epsilon_{\mathrm{F}}$ and of width of the order of 1 eV. By comparison with results obtained for core-level shape

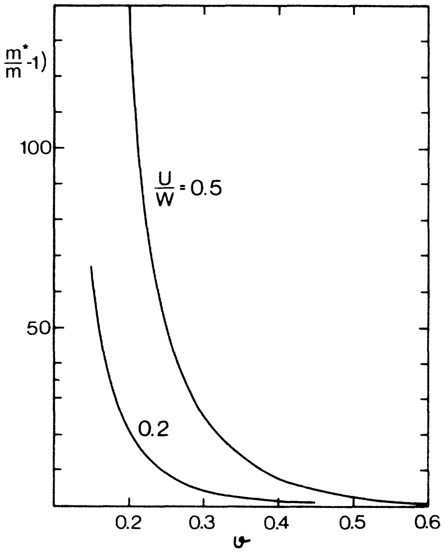

FIG. 2. Relative mass enhancement ($m^*/m-1$) as a function of the hybridization constant.

asymmetries in transition metals we estimate an additional asymmetric broadening of the satellite peaks by 1 to 2 eV. This agrees roughly with BIS results exhibiting a peak at 1–2 eV above $\epsilon_F$ and of width of 3–4 eV with asymmetry of the order of 1–2 eV.[2]

The situation for the XPS peak is similar. The total spectral weight spreads over 4–6 eV,[2,3] while we calculate a spectral width of about 4 eV.

The results presented here for $N(\epsilon)$ are partly similar to those obtained for a single Kondo impurity. Consequently we expect the width $T_K$ of the central peak to increase with temperature,[11] in agreement with neutron-diffraction results.[12] Our calculations neglect effects causing a covalent splitting of the central peak at $\epsilon_F$.

Viewing the large peak in $N(\epsilon)$ at $\epsilon_F$ as resulting from an effective hybridization, one expects for the electron-phonon coupling $g$ in heavy-fermion metals,[13] in analogy to transition metals, $g = g_1 + g_2$, where $g_1 = \partial\tilde{\epsilon}_l/\partial r_{ij}$ and $g_2 = \partial^{V}_{\mathrm{eff}}/\partial r_{ij}$; and $g_1 < g_2 \alpha V_{\mathrm{eff}} << V$. Assuming that the interatomic-distance dependence of $g_2$ follows mainly from $V_{ij}$, then one expects for the pressure dependence of superconductivity similar behavior as for transition metals.

In summary, we have derived results for heavy-fermion systems by using a well-defined theoretical method. The structure in $N(\epsilon)$ arises from the interplay of correlation and interatomic hybridization. Of course, as a result of the perturbative treatment of $U$, we do not obtain a nonanalytic dependence of $\eta$ on $V$. However, the large reduction of $V$ for relatively small hybridization may be interpreted already as an indication for a nonanalytic dependence of $\eta$ on $V$. Unfortunately, a better treatment of $U$ seems presently not feasible, but would probably not change essentially the obtained structure in $N(\epsilon)$. Finally, coherence effects at $\epsilon_F$ in $N(\epsilon)$ require a correct determination of the $k$ dependence of $\Sigma$.

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[a] Permanent address: Institute of Physics of the University, P.O.B. 304, 41001 Zagreb, Yugoslavia.

[b] Permanent address: Department of Physics, Indian Institute of Technology, Kharagpur, India.

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