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Perturbation Expansion for the Asymmetric Anderson Hamiltonian

II. General Asymmetry[2])

By

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The asymmetric single-orbital Anderson model is studied by the rapidly convergent perturbation method of Yosida and Yamada. Low-temperature specific heat, resistivity, thermoelectric power, and renormalized position of the virtual bound state are evaluated to the second order in Coulomb correlation for arbitrary asymmetry. The effect of asymmetry on the properties of the model is discussed. It is found that the correlation effects are most pronounced in the case of electron–hole symmetry and are strongly reduced with the increase of asymmetry.

Das asymmetrische Ein-Orbital-Andersonmodell wird mittels der schnell konvergierenden Störungsmethode von Yosida und Yamada untersucht. Spezifische Wärme bei tiefen Temperaturen, Widerstand, Thermospannung und renormierte Lage der virtuellen gebundenen Zustände werden bis zur zweiten Ordnung der Coulomb-Korrelation für beliebige Symmetrie berechnet. Der Einfluß von Asymmetrie auf die Modelleigenschaften wird diskutiert. Es wird gefunden, daß die Korrelationseffekte im Falle von Elektron–Loch-Symmetrie am ausgeprägtesten sind und mit wachsender Asymmetrie stark reduziert werden.

1. Introduction

In a previous paper [1] (hereafter cited as I) we studied the low-temperature behaviour of the asymmetric single-orbital Anderson model [2] by the rapidly convergent perturbation method of Yosida and Yamada [3 to 5], extended to the case without electron–hole symmetry. We calculated analytically the second-order (in $u = U/\pi\Delta$) d-electron self-energy for low temperatures, low energies, and small deviations from the symmetric case ($k_B T/\Delta$, ω/Δ, and $E_d/\Delta \ll 1$), which enabled us to evaluate the change in the density of states, specific heat, and transport coefficients due to the intraionic Coulomb correlation and get some insight into the effect of asymmetry on the properties of the model. However, all analytical results were limited to the region of small asymmetry ($E_d/\Delta \ll 1$) and could thus be applied only to dilute alloys with nearly half-filled virtual bound state, such as AlMn. Moreover, the self-energy calculated up to $(E_d/\Delta)^2$ for small E_d/Δ created the wrong impression that the correlation and asymmetry combine to diminish the radius of convergence of the perturbation expansion. On the other hand, it is to be expected from the form of the perturbation expansion that its coefficients for large asymmetry die out the more rapidly as functions of E_d/Δ the higher their order.

In order to understand how the asymmetry affects the properties of the model, one has to know the behaviour of the above-mentioned physical quantities for arbitrary asymmetry up to the $E_d/\Delta \gg 1$ limit. This paper deals, therefore, with the second-order theory of the single-orbital Anderson model for arbitrary asymmetry. We cal-

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[2]) Part I see phys. stat. sol. (b) **99**, 251 (1980).

culate the same physical quantities as in I, but without the restriction to $E_d/\Delta \ll 1$. We find that the effects of the Coulomb correlation are most pronounced in the case of electron–hole symmetry and are strongly reduced with the increase of asymmetry. We also compare some of our results for $T = 0$ with those obtained in a different way by Yamada [6] for the special case of the asymmetric Anderson Hamiltonian with d-orbital fixed to the Fermi level.

2. Calculations

The quantity we calculate is the lowest-order non-vanishing contribution to the proper self-energy part $\Sigma_d^R(\omega)$ of the exact retarded d-electron Green function

$$G_d^R(\omega) = \frac{1}{\omega - E_d - \operatorname{Re} \Sigma_d^R(\omega) + i[\Delta - \operatorname{Im} \Sigma_d^R(\omega)]}. \tag{2.1}$$

$\Sigma_d^R(\omega)$ is here defined as the retarded self-energy without the Hartree-Fock part $\Sigma_d^{HF} = \langle n_d \rangle U$ which is included in the Hartree-Fock parameter $E_d = \varepsilon_d + \langle n_d \rangle U$. The lowest-order term of $\Sigma_d^R(\omega)$ is the one quadratic in $u = U/\pi\Delta$ and it has been calculated in I for low temperatures ($k_B T/\Delta \ll 1$) as given by the expressions (2.11) and (2.12) of I. Although the $T = 0$ part of the integral in the first term of (2.11) in I cannot be calculated analytically even if expanded in powers of ω/Δ, one can transform it in such a way as to reduce its uncalculable part to a simple and slowly varying function of E_d/Δ which can be easily taken into account.

The imaginary part of $\Sigma_{(2)}^R(\omega)$ which comprises only the contributions from the last two terms of (2.11) in I can be written in compact form as

$$\operatorname{Im} \Sigma_{(2)}^R(\omega) = -\frac{\Delta}{2} \frac{u^2}{(1 + (E_d/\Delta)^2)^3} \left[\left(\frac{\omega}{\Delta}\right)^2 + \frac{\pi k_B T}{\Delta}\right]^2 \times \left[1 + \frac{2}{3} \frac{(E_d/\Delta)}{1 + (E_d/\Delta)} \frac{\omega}{\Delta}\right] \tag{2.2}$$

for low temperatures and low energies up to the $(\omega/\Delta)^3$ and $(\omega/\Delta)\,(k_B T/\Delta)^2$ terms. The real part of the self-energy can not be written so neatly. We find

$$\begin{aligned}
\operatorname{Re} \Sigma_{(2)}^R(\omega) = {} & -\Delta u^2 \left\{a_0\left(\frac{E_d}{\Delta}\right) + a_1\left(\frac{E_d}{\Delta}\right)\left(\frac{\omega}{\Delta}\right) + a_2\left(\frac{E_d}{\Delta}\right)\left(\frac{\omega}{\Delta}\right)^2 + \right. \\
& \left. + a_3\left(\frac{E_d}{\Delta}\right)\left(\frac{\omega}{\Delta}\right)^3 + \dots - \frac{\pi^2}{3}\left(\frac{k_B T}{\Delta}\right)^2 \left[a_0^T\left(\frac{E_d}{\Delta}\right) + a_1^T\left(\frac{E_d}{\Delta}\right)\left(\frac{\omega}{\Delta}\right) + \dots\right] + \dots\right\}; \\
a_0(x) = {} & \frac{x}{1 + x^2}\left[\frac{\pi^2}{4} - g(x)\right], \\
a_1(x) = {} & \frac{1}{1 + x^2}\left\{\frac{1}{1 + x^2}\left[2 - \frac{\pi^2}{4} + x^2\left(\frac{\pi^2}{4} - 2g(x)\right)\right] + \frac{1}{x} \operatorname{arc\,tan} x + \right. \\
& \left. + \operatorname{arc\,tan}^2 (x)\right\}, \\
a_2(x) = {} & \frac{1}{(1 + x^2)^2}\left\{\frac{1}{4x}\left(\frac{1}{x} \operatorname{arc\,tan} x - \frac{1}{1 + x^2}\right) + \frac{9}{4} \operatorname{arc\,tan} x + \right. \\
& \left. + 2x \operatorname{arc\,tan}^2 (x) + \frac{x}{1 + x^2}\left[\frac{13}{4} - \frac{3\pi^2}{4} + \frac{\pi^2}{4} x^2 + (1 - 3x^2)\, g(x)\right]\right\},
\end{aligned}$$

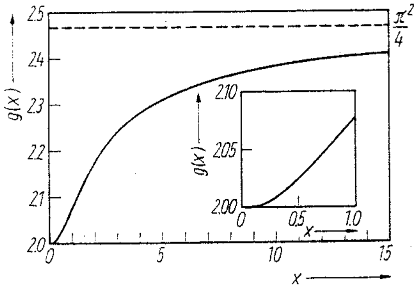


Fig. 1. The function $g(x)$. Inset shows the quadratic behaviour for small x

$$
\left.
\begin{aligned}
a_3(x) &= \frac{1}{(1+x^2)^2}\left\{\frac{1}{12x^2}\left(\frac{1}{x}\operatorname{arc\,tan} x - \frac{1}{1+x^2}\right) + \frac{7}{12x}\operatorname{arc\,tan} x - \right.\\
&\quad - \frac{1-3x^2}{1+x^2}\left[\frac{1}{x}\operatorname{arc\,tan} x + \operatorname{arc\,tan}^2(x)\right] - \frac{5}{4(1+x^2)} - \frac{11}{9(1+x^2)^2} + \\
&\quad \left. + \frac{\pi^2}{4} + \frac{4x^2}{(1+x^2)^2}\left[\frac{3}{2} - \frac{\pi^2}{2} + (1-x^2)\,g(x)\right]\right\},\\
a_0^T(x) &= \frac{1}{2}\frac{x}{(1+x^2)^3} - \frac{1+5x^2}{4x(1+x^2)^2}\left(\frac{1}{x}\operatorname{arc\,tan} x - \frac{1}{1+x^2}\right),\\
a_1^T(x) &= \frac{1}{3}\frac{8-9x^2}{(1+x^2)^4} - \frac{1+3x^2}{4x^2(1+x^2)^2}\left(\frac{1}{x}\operatorname{arc\,tan} x - \frac{1}{1+x^2}\right).
\end{aligned}
\right\}
\tag{2.3}
$$

The function $g(x)$, given by

$$
\left.
\begin{aligned}
g(x) &= \frac{1}{x}\int_0^x \left[\operatorname{arc\,tan}^2(t) + \frac{2}{t}\operatorname{arc\,tan}(t)\right] \mathrm{d}t = \\
&= \begin{cases} 2 + \frac{1}{9}x^2 - \frac{4}{75}x^4 + \dots & |x| < 1 \\[2mm] \frac{\pi^2}{4} - \frac{\pi(1-\ln 2)}{|x|} + \frac{1}{x^2} - \frac{\pi}{6}\frac{1}{|x|^3} + \dots & |x| > 1, \end{cases}
\end{aligned}
\right\}
\tag{2.4}
$$

is represented in Fig. 1. In the case of low asymmetry ($E_\mathrm{d}/\Delta \ll 1$), the expressions (2.2) and (2.3) expanded in powers of E_d/Δ reduce to our earlier result for the self-energy given by (2.13) in I. (There is an error in the second line of (2.13) of I — it should be 409/90 instead of 319/90.) Using $\Sigma^\mathrm{R}_{(2)}(\omega)$ given by (2.2) and (2.3) we can discuss the effects of arbitrary asymmetry on various properties of the model for not too large a correlation.

3. Results and Discussions

3.1 The asymmetry parameter

In our formalism the measure of the asymmetry of the model is E_d/Δ, E_d being the position and Δ the half-width of the virtual bound state in the Hartree-Fock approximation. The parameter which has usually been used as a measure of the asymmetry of the Hamiltonian is $x = -\varepsilon_\mathrm{d}/U$ (equal to $\frac{1}{2}$ in the case of electron–hole symmetry), although one might prefer $\eta = \frac{1}{2} - x = \frac{1}{2} + \varepsilon_\mathrm{d}/U$ (which is zero in the symmetric

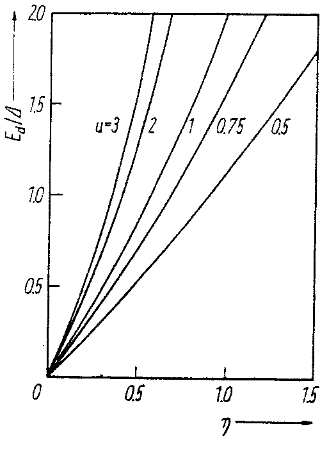


Fig. 2. E_d/Δ as a function of $\eta = \frac{1}{2} + \varepsilon_d/U$ for various values of $u = U/\pi\Delta$ at $T = 0$

case). Both x or η contain only the quantities which appear in the Hamiltonian, namely the position of the impurity level with respect to the Fermi level, ε_d, and the intraionic Coulomb integral U. At arbitrary temperature the Hartree-Fock parameter E_d is the solution of the equation (derived in the Appendix)

$$\pi\eta u = \frac{E_d}{\Delta} + u \operatorname{Im} \psi \left[\frac{1}{2} + \frac{\Delta}{2\pi k_B T}\left(1 + i\,\frac{E_d}{\Delta}\right)\right], \tag{3.1}$$

where $\psi(z)$ is the digamma function. At $T = 0$ this equation reduces to

$$\pi\eta u = \frac{E_d}{\Delta} + u \arctan\left(\frac{E_d}{\Delta}\right). \tag{3.2}$$

For a given u, (3.1) or (3.2) gives a single-valued correspondence between η and E_d/Δ. A numerical solution of (3.2) for various values of u is given in Fig. 2. For relatively low asymmetry ($|E_d/\Delta| < 1$) (3.2) can be solved approximately with the result

$$\frac{E_d}{\Delta} = \frac{\pi\eta u}{1 + u}\left[1 + \frac{\pi^2}{3}\,\frac{u^3}{(1 + u)^3}\,\eta^2 - \frac{\pi^4}{5}\,\frac{u^5\,(1 - \frac{2}{3}\,u)}{(1 + u)^6}\,\eta^4 + \ldots\right]. \tag{3.3}$$

The convergence of this expansion is best for small u, but even for $u \gg 1$ it is still good for small enough η.

As can be seen from (3.1), E_d is also temperature dependent. For the fixed values of u and η, $|E_d/\Delta|$ grows with the increase of temperature and reaches its maximum value $|\pi\eta u|$ in the limit $T \to \infty$, that is,

$$\lim_{T\to\infty} E_d(T) = \eta U = \varepsilon_d + \tfrac{1}{2}\,U\,.$$

$|E_d(\infty) - E_d(0)|/|E_d(0)|$ grows with the increase of u for a given η and decreases with the increase of η for a given u. For $u < 1$ this ratio is always less than unity. We are not going to investigate in detail the dependence of E_d on temperature since we are interested only in qualitative dependence of various quantities on the asymmetry and not in the exact values of E_d at given temperatures. Moreover, since we are going to discuss the low-temperature properties of the model for not large values of u, we will completely ignore the temperature correction to E_d which is quite negligible in that case. Of course, if one wants to investigate the behaviour of the model for finite temperatures, one has to solve (3.1) and find $E_d(T)$ for given values of u and η.

3.2 *Renormalized position of the resonant level*

As noted in I, the quantity $\tilde{E}_d = E_d + \Sigma_d^R(0)|_{T=0}$ can be interpreted as the renormalized position of the virtual bound state (v.b.s.), which is related to the number of localized d-electrons of a given spin orientation via the Friedel sum rule (Shiba [7]).

Using the second-order self-energy (2.3) we can write $\tilde{E}_d$ as

$$\tilde{E}_d = E_d\left[1 - b\left(\frac{E_d}{\Delta}\right)u^2 + \dots\right] \tag{3.4}$$

with the function

$$b(x) = \frac{\pi^2/4 - g(x)}{1 + x^2} = \begin{cases} \left(\frac{\pi^2}{4} - 2\right) - \left(\frac{\pi^2}{4} - \frac{17}{9}\right)x^2 + \dots & |x| < 1 \\ \frac{\pi(1 - \ln 2)}{|x|^3} - \frac{1}{x^4} + \dots & |x| > 1 \end{cases} \tag{3.5}$$

given in Fig. 3. One can see from (3.4) and (3.5) that the Coulomb correlation pushes the renormalized position of the v.b.s. closer to the Fermi level (with respect to the Hartree-Fock position). This effect reaches its maximum for the symmetric case and becomes strongly reduced with the increase of asymmetry. As E_d/Δ approaches large values for a given u, $\tilde{E}_d$ returns to the H-F value E_d.

For relatively low asymmetry ($E_d/\Delta \lesssim 0.25$) $\tilde{E}_d$ is given by [1]

$$\tilde{E}_d \approx (1 + u)\,\tilde{\chi}_c^s(u)\,E_d\,,$$

where $\tilde{\chi}_c^s = \tilde{\chi}_{\uparrow\uparrow}^s + \tilde{\chi}_{\uparrow\downarrow}^s = \tilde{\chi}_{even} - \tilde{\chi}_{odd}$ is the charge susceptibility for the system with electron–hole symmetry. Since $\tilde{\chi}_c^s(u) \geqq 0$ for any value of u, the slope of $\tilde{E}_d$ as a function of E_d at $E_d = 0$ is always positive irrespective of u. The spurious critical value of u (see the discussion following Fig. 7 of I), at which the slope of $\tilde{E}_d$ seems to change sign, and which depends on the order to which one has calculated $\tilde{\chi}_c^s(u)$, may thus be understood as the limit of the applicability of the expansion of $\tilde{\chi}_c^s(u)$ to a given finite order in u.

3.3 *Specific heat*

The low-temperature impurity specific heat is given by [8]

$$C_v = \frac{2\pi^2}{3}\,k_B^2\,\varrho_d(0)\,\tilde{\gamma}T\,,$$

where $\varrho_d(\omega)$ is the density of states (per spin) for the localized electrons and $\tilde{\gamma}$ is the enhancement factor given by (3.4) of I. Thus we have

$$C_v = \frac{2\pi k_B}{3}\,\frac{1}{1 + (\tilde{E}_d/\Delta)^2}\left(\frac{\tilde{\gamma}k_B T}{\Delta}\right), \tag{3.6}$$

and noticing that $\tilde{E}_d$ is fixed by the Friedel sum rule (as is E_d in the H-F approximation), we can see that the low-temperature specific heat is enhanced by $\tilde{\gamma}$ over the H-F value due to the intraorbital Coulomb correlation.

The enhancement factor $\tilde{\gamma}$ is given by

$$\tilde{\gamma} = 1 + a_1\left(\frac{E_d}{\Delta}\right)u^2 + \dots \tag{3.7}$$

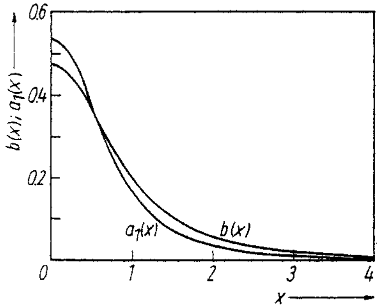


Fig. 3. The functions $b(x) = a_0(x)/x$ and $a_1(x)$

with

$$a_1(x) = \begin{cases} \left(3 - \dfrac{\pi^2}{4}\right) - \left(\dfrac{25}{3} - \dfrac{3\pi^2}{4}\right) x^2 + \dots & |x| < 1 \\ \dfrac{\pi}{|x|^3}\left(\dfrac{3}{2} - 2\ln 2\right) + O(|x|^{-5}) & |x| > 1 \end{cases}$$

represented in Fig. 3. Here we find again that the asymmetry works against the intra-ionic Coulomb correlation, this time reducing the enhancement of the low-temperature specific heat. As with $\tilde{E}_d$, this reduction of the correlation effects is even in E_d, i.e. it is the same for the resonant levels spaced equally above and below the Fermi level.

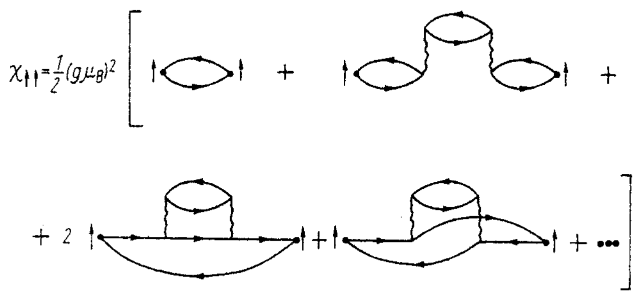
There is an exact relation

$$\tilde{\gamma} = \tilde{\chi}_{\uparrow\uparrow} \tag{3.8}$$

which holds between $\tilde{\gamma}$ and the contribution to the static impurity susceptibility

$$\chi_{\uparrow\uparrow} = \tfrac{1}{2} (g\mu_B)^2 \varrho_d(0)\, \tilde{\chi}_{\uparrow\uparrow} \tag{3.9}$$

which originates from the correlation between electrons with parallel spin. This relation was first proved by Yamada [4] for the symmetric case and later by Yoshimori [8] for the general case. In order to check the consistency of our second-order results, we calculate $\chi_{\uparrow\uparrow}$ given by [4]



(3.10)

for the asymmetric case. The first two diagrams in (3.10) represent the zeroth- and second-order RPA contribution and the last two give the lowest-order correction due to Coulomb correlation. Evaluating these diagrams we find

$$\chi_{\uparrow\uparrow}^{(2)} = \frac{1}{2} (g\mu_B)^2 \frac{1}{\pi\Delta} \tilde{\chi}_0(0) \left[\tilde{\gamma}^{(2)} - 2\left(\frac{E_d}{\Delta}\right) \tilde{\chi}_0(0) \frac{1}{\Delta} \Sigma^R_{(2)}(0)\right], \tag{3.11}$$

where $\tilde{\gamma}^{(2)}$ is given by the expression (3.7) and $\tilde{\chi}_0(0) = \pi\Delta\varrho_d^{HF}(0) = [1 + (E_d/\Delta)^2]^{-1}$. Expanding $\varrho_d(0)$ in (3.9) up to u^2 and comparing the resulting expression with (3.11) we find $\tilde{\gamma}^{(2)} = \tilde{\chi}_{\uparrow\uparrow}^{(2)}$ as expected.

3.4 Transport coefficients

The transport coefficients for dilute alloys are evaluated from the Boltzmann equation and are thus determined by the transport integrals [9]

$$K_n = \frac{2}{3}\varrho_c(0)\, v_F^2 \int_{-\infty}^{\infty} \varepsilon^n \tau(\varepsilon) \left(-\frac{\partial f}{\partial \varepsilon}\right) d\varepsilon\,, \tag{3.12}$$

where v_F and $\varrho_c(0)$ are the conduction electron velocity and density of states (per spin) at the Fermi level, f is the Fermi-Dirac distribution function, and $\tau(\varepsilon)$ is the energy- and temperature-dependent transport relaxation time. We neglect here the contributions due to the energy dependence of the density of states and velocity of the conduction electrons, since they are small compared to the contribution arising from the energy dependence of $\tau(\varepsilon)$. (In (3.12) we have also assumed a spherically-symmetric Fermi surface and cubic lattice of the host.) In the multiple scattering approximation we can write for $\tau(\varepsilon)$

$$\frac{1}{\tau(\varepsilon)} = -2c\,\mathrm{Im}\, t_{kk}(\varepsilon)\,,$$

where $t_{kk}(\varepsilon)$ is the diagonal element of the scattering matrix for the single impurity,

$$t_{kk'} = V_{kd}\, G_d^R(\omega)\, V_{dk'}\,,$$

and $c = N_{imp}/N$ is the impurity concentration. Using (3.2) of I and $\Delta = \pi\,|V_{kd}|^2\,\varrho_c(0)$ we have

$$\frac{1}{\tau(\varepsilon)} = c\,\frac{2\Delta}{\varrho_c(0)}\,\varrho_d(\varepsilon)\,. \tag{3.13}$$

One obtains therewith the contribution of impurities to the resistivity

$$R(T) = (e^2K_0)^{-1} \tag{3.14}$$

and the diffusion part of the thermoelectric power (TEP)

$$S_d(T) = -\frac{1}{|e|\,T}\frac{K_1}{K_0}. \tag{3.15}$$

For low temperatures ($k_BT \ll \Delta$) we apply the Sommerfeld expansion to K_n to obtain the lowest-order temperature corrections to $R(T)$ and $S_d(T)$. Thus we find

$$R(T) = \frac{R_0}{1 + (\tilde{E}_d/\Delta)^2}\left[1 - \frac{\varkappa}{1 + (\tilde{E}_d/\Delta)^2}\,\frac{\pi^2}{3}\left(\frac{k_BT}{\Delta}\right)^2 + \dots\right], \tag{3.16}$$

where $R_0 = 3c/\pi e^2\,\varrho_c^2(0)\,v_F^2$ is the resistivity in the unitarity limit (maximum possible scattering, reached for $E_d = T = 0$) and

$$\varkappa = \tilde{\gamma}^2 + 2I_0''\left[1 - \left(\frac{\tilde{E}_d}{\Delta}\right)^2\right] + \frac{\tilde{E}_d}{\Delta}(R_0'' + 2R_T)\,. \tag{3.17}$$

Here R_0'' and $-I_0''$ denote the real and the imaginary part of $\Delta[\partial^2\Sigma_d^R(\omega)/\partial\omega^2]_{\omega=T=0}$ and $(\Delta/3)\,(\pi k_BT/\Delta)^2\,R_T$ is the T^2 part of $\mathrm{Re}\,\Sigma_d^R(0)$. The enhancement factor $\varkappa$ calculated with $\Sigma_{(2)}^R(\omega)$ given by (2.2) and (2.3) is represented in Fig. 4 as a function

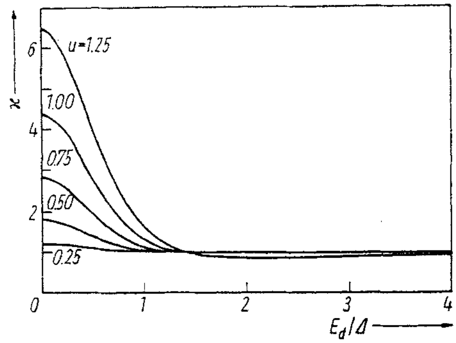


Fig. 4. The enhancement factor $\varkappa$ of the low-temperature resistivity, plotted as a function of E_d/Δ for various values of u

of E_d/Δ for various values of u. One can see that the enhancement is strongest in the symmetric case and drops down quickly with the increase of asymmetry, reaching its H-F value $\varkappa_{HF} = 1$ for $E_d/\Delta \gtrsim 1$.

In the symmetric case the ratio $\sqrt{\varkappa}/\tilde{\gamma}$, given by

$$\frac{\sqrt{\varkappa}}{\tilde{\gamma}} = \left[1 + 2\left(\frac{\tilde{\chi}_{odd}}{\tilde{\chi}_{even}}\right)^2\right]^{1/2}$$

starts with 1 for $u = 0$ and increases rapidly up to $\sqrt{3}$ for $u \gtrsim 1$ [4]. Thus in the s–d limit one finds the low-temperature resistivity scaled by the same parameter $\Delta_{eff} = \Delta/\tilde{\gamma}$ as the T-linear term of the specific heat or TEP (see below). Although we are unable to reach the s–d limit with our second-order results for the asymmetric case, we observe for $u \lesssim 1$ qualitatively the same behaviour of $\sqrt{\varkappa}/\gamma$ as that given by the above expression for $E_d = 0$, that is, $\sqrt{\varkappa}/\gamma$ as a function of u for any given E_d begins to flatten out as u increases, signalling the onset of the universal behaviour. We also notice that the s–d limit is the more quickly approached, the lower the asymmetry is.

For the diffusion part of TEP the Sommerfeld expansion of the transport integrals in (3.15) gives

$$S_d(T) = \frac{2\pi^2 k_B}{3\,|e|}\,\frac{\tilde{E}_d/\Delta}{1 + (\tilde{E}_d/\Delta)^2}\left[\tilde{\gamma}\left(\frac{k_B T}{\Delta}\right) - \frac{\varphi}{1 + (\tilde{E}_d/\Delta)^2}\,\frac{\pi^2}{3}\left(\frac{k_B T}{\Delta}\right)^3 + \dots\right]. \quad (3.18)$$

As we have noted earlier [10], the effects of the Coulomb correlation on the T-linear term of S_d can be simply understood as the separate renormalization of the position of the resonant level ($E_d \to \tilde{E}_d$) and its width ($\Delta \to \Delta/\tilde{\gamma}$). Since $\tilde{E}_d$ is fixed by the charge neutrality condition in the same way as E_d in the H-F approximation, the T-linear term of S_d is enhanced over the H-F value by $\tilde{\gamma}$ just like the T-linear term of the specific heat. The coefficient φ in the cubic term cannot be given such a simple interpretation as it contains many terms of the self-energy, originating from the first-, second-, and third-order derivative of the relaxation time. However, the ratio $\sqrt[3]{\varphi}/\tilde{\gamma}$ shows qualitatively the same behaviour as $\sqrt{\varkappa}/\tilde{\gamma}$, indicating that in the limit of large u the T^3-term of $S_d(T)$ is scaled by the same Δ_{eff} as its T-linear term.

The cubic term which has the opposite sign from the linear term leads to the attenuation of the low-temperature TEP and the appearance of a maximum of $|S_d(T)|$ at some temperature T_M. In the temperature range where $S_d(T)$ can be fairly approximated by (3.18), ($k_B T/\Delta \lesssim 0.5$) the temperature T_M is given by

$$\frac{k_B T_M}{\Delta} = \frac{1}{\pi}\left[\left(1 + \left(\frac{\tilde{E}_d}{\Delta}\right)^2\right)\frac{\tilde{\gamma}}{\varphi}\right]^{1/2}. \quad (3.19)$$

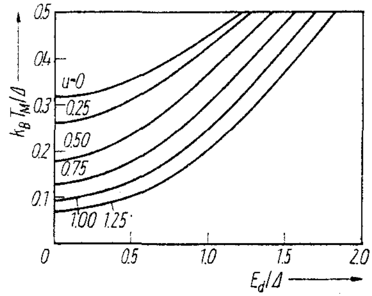


Fig. 5. The position of maximum of the thermoelectric power, determined from the cubic approximation, plotted as a function of E_d/Δ for various values of u

In Fig. 5 we give T_M plotted as a function of E_d/Δ for various values of u, calculated from (3.19) with the second-order expressions for $\tilde{E}_d$, $\tilde{\gamma}$, and φ. Although the numerical values of T_M should not be taken too seriously due to the second-order approximation, especially for $u \gtrsim 0.5$, the qualitative behaviour of T_M is in agreement with that of the previously studied quantities. T_M decreases with the increasing u, while the asymmetry reduces the effect of Coulomb correlation.

3.5 Comparison with Yamada's results at T = 0

In a recent paper Yamada [6] has presented a perturbation calculation for the asymmetric Anderson Hamiltonian with d-orbital fixed to the Fermi level ($\varepsilon_d = 0$ or $\eta = \frac{1}{2}$ in our notation) and at $T = 0$. Although it is an expansion with respect to small u in this particular case of relatively high asymmetry, it can generally be viewed as an expansion in powers of both u and η, whose convergence depends on both of these parameters. One can do this calculation along the same lines as in [6] for arbitrary asymmetry and obtain expressions which reduce to those of Yamada for the special value $\eta = \frac{1}{2}$. Thus, for instance, for $\tilde{E}_d$ (equal to $\Sigma(0)$ in Yamada's notation) one obtains [11]

$$\frac{\tilde{E}_d}{\Delta} = \pi\eta u \left\{\chi_c^s(u) + (\pi\eta u)^2 \left[\frac{1}{3}\,u - \left(\frac{29}{9} - \frac{\pi^2}{4}\right)u^2 + \left(\frac{824}{27} - 3\pi^2\right)u^3 + \dots\right] - \right.$$
$$\left. - (\pi\eta u)^4 \left(\frac{1}{5}\,u + \dots\right) + \dots\right\}. \tag{3.20}$$

For $\eta = \frac{1}{2}$ this expansion reduces to Yamada's relation (18) of [6].

We have shown in I that $\tilde{E}_d$ is given by

$$\frac{\tilde{E}_d}{\Delta} = (1 + u)\,\tilde{\chi}_c^s(u)\left(\frac{E_d}{\Delta}\right) + \beta(u)\left(\frac{E_d}{\Delta}\right)^3 + \dots \tag{3.21}$$

for small E_d/Δ. Expanding $\beta(u)$ in powers of u we find

$$\beta(u) = \left(\frac{\pi^2}{4} - \frac{17}{9}\right)u^2 - Au^3 + \dots, \tag{3.22}$$

where the u^2-term has been obtained from (2.3) and (2.4). In order to compare our expression (3.21) with (3.20) we insert the expression (3.3) for E_d/Δ into (3.21) to obtain

$$\frac{\tilde{E}_{\rm d}}{\Delta} = \pi\eta u \left\{\tilde{\chi}^{\rm s}_{\rm c}(u) + \frac{(\pi\eta u)^2}{(1+u)^3}\left[\frac{1}{3}\,u\tilde{\chi}^{\rm s}_{\rm c}(u) + \beta(u)\right] - \right.$$

$$\left. - \frac{(\pi\eta u)^4}{(1+u)^6}\,u\left[\frac{1}{5}\left(1-\frac{2}{3}\,u\right)\tilde{\chi}^{\rm s}_{\rm c}(u) - \beta(u)\right] + \ldots\right\}. \qquad (3.23)$$

Inserting $\beta(u)$ given by (3.22) and $\tilde{\chi}^{\rm s}_{\rm c}(u)$ given in [6] into (3.23) and expanding the denominators in (3.23) for $u < 1$, we obtain an expression for $\tilde{E}_{\rm d}/\Delta$ which agrees with (3.20) (and Yamada's equation (18) for $\eta = \frac{1}{2}$) up to u^5, while the comparison of u^6 terms yields

$$A = \frac{13\pi^2}{6} - \frac{563}{27} = 0.5323\,.$$

Thus our result for $\tilde{E}_{\rm d}$ and consequently for $\Sigma^{\rm R}_{\rm d}(0) = \tilde{E}_{\rm d} - E_{\rm d}$ agrees with the result obtained in a different way by Yamada up to the fifth order in u (and not up to the third order in u, as we have erroneously concluded in I, due to the incorrect expression (3.22) of I for $E_{\rm d}$ in the case $\eta = \frac{1}{2}$).

In the same way we can compare our second-order result for $\tilde{\gamma}$ with Yamada's expression (26) of [6]. Using $\tilde{\gamma}$ for the symmetric case [4],

$$\tilde{\gamma}^{\rm s} = 1 + \left(3 - \frac{\pi^2}{4}\right)u^2 + 0.0553u^4 + \ldots\,,$$

as well as our second-order result (3.7) expanded in powers of $E_{\rm d}/\Delta$, we write $\tilde{\gamma}$ in the form

$$\tilde{\gamma} = \tilde{\gamma}^{\rm s} - \left[\left(\frac{25}{3} - \frac{3\pi^2}{4}\right)u^2 + Bu^3 + \ldots\right]\left(\frac{E_{\rm d}}{\Delta}\right)^2 + \ldots$$

Inserting here the expression (3.3) for $E_{\rm d}/\Delta$, we obtain the agreement with Yamada's (26) of [6] up to the fourth order in u. Moreover, comparing the u^5-terms we find

$$B = 2\pi^2 - \frac{172}{9} = 0.6281\,.$$

We must notice, however, that while Yamada's expansion [6] is the one with respect to asymmetry and thus breaks down for large η, our expansion is the one with respect to deviations from the H-F solution and is thus expected to retain or rather improve its convergence for large asymmetry.

3.6 Conclusion

Various properties which we have calculated here using the second-order perturbation theory for the asymmetric Anderson Hamiltonian with arbitrary asymmetry give a rather consistent picture of an isolated impurity embedded in the sea of conduction electrons. We can conclude that the effects of the intraionic Coulomb correlation reach their maximum in the case of electron–hole symmetry and become less important with growing asymmetry. This reduction of the correlation effects is even in $E_{\rm d}/\Delta$, i.e. the almost filled virtual bound state behaves in the same way as the almost empty one.

Appendix

The number of localized electrons of a given spin direction in the H-F approximation is given by

$$\langle n_{\mathrm{d}\sigma}\rangle = G^0_{\mathrm{d}\sigma}(0^-) = -\frac{1}{\pi}\int\limits_{-\infty}^{\infty} \mathrm{d}\omega\, f(\beta\omega)\,\mathrm{Im}\, G^{0\mathrm{R}}_{\mathrm{d}\sigma}(\omega) = \frac{\Delta}{\pi}\int\limits_{-\infty}^{\infty}\frac{f(\beta\omega)\,\mathrm{d}\omega}{(\omega - E_{\mathrm{d}\sigma})^2 + \Delta^2}\,, \tag{A.1}$$

where $f(x) = (\mathrm{e}^x + 1)^{-1}$ and $\beta = 1/k_{\mathrm{B}}T$. One can write $f(x)$ in terms of the digamma functions as

$$f(x) = \frac{1}{2} - \frac{1}{2\pi i}\left[\psi\left(\frac{1}{2} + i\,\frac{x}{2\pi}\right) - \psi\left(\frac{1}{2} - i\,\frac{x}{2\pi}\right)\right]$$

and since the first (second) digamma function is analytic in lower (upper) complex half-plane, one can transform the real-axis integral in (A.1) to a contour integral in the complex plane, closing the contour with arcs of infinite radii in the lower (upper) half-plane. The theorem of residues then yields

$$\langle n_{\mathrm{d}\sigma}\rangle = \frac{1}{2} - \frac{1}{\pi}\,\mathrm{Im}\,\psi\left[\frac{1}{2} + \frac{\beta\Delta}{2\pi}\left(1 + i\,\frac{E_{\mathrm{d}\sigma}}{\Delta}\right)\right]. \tag{A.2}$$

Combining (A.2) with the relation

$$E_{\mathrm{d}\sigma} = \varepsilon_{\mathrm{d}} + \langle n_{\mathrm{d},-\sigma}\rangle\, U$$

one can obtain the self-consistency equations either for $\langle n_{\mathrm{d}\uparrow}\rangle$ and $\langle n_{\mathrm{d}\downarrow}\rangle$ or $E_{\mathrm{d}\uparrow}$ and $E_{\mathrm{d}\downarrow}$. Choosing the latter we obtain

$$\frac{E_{\mathrm{d}\sigma}}{\Delta} = u\left\{\pi\eta - \mathrm{Im}\,\psi\left[\frac{1}{2} + \frac{\beta\Delta}{2\pi}\left(1 + i\,\frac{E_{\mathrm{d},-\sigma}}{\Delta}\right)\right]\right\}, \tag{A.3}$$

where $\eta = \frac{1}{2} + \varepsilon_{\mathrm{d}}/U$ and $u = U/\pi\Delta$. For our perturbation expansion we take the "non-magnetic" solution $E_{\mathrm{d}\uparrow} = E_{\mathrm{d}\downarrow} = E_{\mathrm{d}}$ of (A.3), which exists at all temperatures and for arbitrary values of u and η, in contrast with the "magnetic" solutions $E_{\mathrm{d}\uparrow} \neq E_{\mathrm{d}\downarrow}$, which exist only for $u > u_{\mathrm{c}}(\eta, T)$. (The critical u is an artifact of the Hartree-Fock theory, and it increases with both the asymmetry and temperature, which thus diminish the region of existence of the "magnetic" solutions.)

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