Progress of Theoretical Physics, Vol. 62, No. 2, August 1979

Perturbation Expansion for the Asymmetric Anderson Hamiltonian

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(Received March 5, 1979)

The single orbital Anderson Hamiltonian with d-orbital fixed to the Fermi level ($\varepsilon_d=0$) is discussed by a perturbation method with respect to electron correlation U. In this model the Coulomb repulsion U reduces the occupied d-electron number and, on the other hand, enhances the d-electron effective mass and normalized susceptibility ($\tilde{\chi}_s$). As the result of competition of these effects, the specific heat at low temperature decreases and the magnetic susceptibility increases with U for $U<\Delta$ and then decreases for large U.

§ 1. Introduction

The single orbital Anderson Hamiltonian[1] is written as follows:

$$H=H_0+H', \tag{1}$$

$$H_0=\sum_{k,\sigma}\varepsilon_k n_{k\sigma}+\sum_{k,\sigma}V(c_{k\sigma}^\dagger c_{d\sigma}+c_{d\sigma}^\dagger c_{k\sigma}), \tag{2}$$

$$H'=\sum_{\sigma}\varepsilon_d n_{d\sigma}+Un_{d\uparrow}n_{d\downarrow}, \tag{3}$$

where $c_{k\sigma}^\dagger$ and $c_{k\sigma}$ are creation and annihilation operators for the conduction electron with wave vector k and spin σ, and $c_{d\sigma}^\dagger$ and $c_{d\sigma}$ are those for the localized d-electron at the energy level ε_d. V represents the transfer integral between the s- and d-state and U is the Coulomb energy between two d-electrons.

It is known in this Hamiltonian that the magnetic susceptibility, χ_s, is given by[1)~4)]

$$\chi_s=\frac{1}{2}(g\mu_\mathrm{B})^2\rho_d(0)\tilde{\chi}_s, \tag{4}$$

$$\tilde{\chi}_s=\tilde{\chi}_{\uparrow\uparrow}-\tilde{\chi}_{\uparrow\downarrow}, \tag{5}$$

where $\rho_d(0)$ is the density of states for d-electron at the Fermi energy. $\tilde{\chi}_{\uparrow\uparrow}$ and $\tilde{\chi}_{\uparrow\downarrow}$ are normalized susceptibilities due to parallel and antiparallel spin correlation, respectively.

The T-linear term of the specific heat, γT, is given by $\tilde{\chi}_{\uparrow\uparrow}$ as[3),4)]

$$\gamma=\frac{2\pi^2k_\mathrm{B}^2}{3}\rho_d(0)\tilde{\gamma}\quad\text{and}\quad\tilde{\gamma}=\tilde{\chi}_{\uparrow\uparrow}. \tag{6}$$

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Hereafter, we omit $(g\mu_B)^2/2$ and $2\pi^2 k_B^2/3$ for simplicity.

In Ref. 3), physical quantities for the symmetric case with respect to the electrons and holes, namely $\varepsilon_d = -U/2$, have been obtained by the perturbation calculation.[3] We denote physical quantities in the symmetric case with superscript 's'. In the symmetric Anderson Hamiltonian, $\tilde{\chi}^s_{\uparrow\uparrow}$ is equal to the even part of $\tilde{\chi}^s{}_s$, $\tilde{\chi}_{\text{even}}$, and $-\tilde{\chi}^s_{\uparrow\downarrow}$ to the odd part, $\tilde{\chi}_{\text{odd}}$. These are given by the following expansions:[3]

$$\tilde{\chi}^s_{\uparrow\uparrow} = \tilde{\chi}_{\text{even}} = 1 + \left(3 - \frac{\pi^2}{4}\right) u^2 + 0.0553 u^4 + \cdots , \tag{7}$$

$$-\tilde{\chi}^s_{\uparrow\downarrow} = \tilde{\chi}_{\text{odd}} = u + 3\left(5 - \frac{\pi^2}{2}\right) u^3 + \cdots , \tag{8}$$

$$u = U/\pi\Delta \quad \text{and} \quad \Delta = \pi\rho V^2,$$

where ρ is the density of states at the Fermi level for conduction electrons. Using Eqs. (7) and (8), we obtain the susceptibility:

$$\tilde{\chi}_s{}^s = 1 + u + 0.5326 u^2 + 0.1956 u^3 + 0.0553 u^4 + \cdots , \tag{9}$$

which is similar to exponential u. Therefore, we expect the fifth order term of $\tilde{\chi}_{\text{odd}}$ is of the order 10^{-2}.

In this paper, we discuss the asymmetric Anderson Hamiltonian in which d-level is fixed to the Fermi level, namely $\varepsilon_d = 0$. Though this case is a special one of the asymmetric cases, it includes the essential property of the asymmetric Anderson Hamiltonian, namely valence change. We deal with this model by the perturbation method with respect to u, choosing Eq. (2) as the unperturbed Hamiltonian and Eq. (3) as perturbation to H_0.

In carrying out the perturbation calculation, it is convenient to divide H' into the following two parts, H_1' and H_2':

$$H' = H_1' + H_2' - U/4 , \tag{10}$$

$$H_1' = U\left(n_{d\uparrow} - \frac{1}{2}\right)\left(n_{d\downarrow} - \frac{1}{2}\right), \tag{11}$$

$$H_2' = \left(\varepsilon_d + \frac{U}{2}\right) \sum_{\sigma} n_{d\sigma} . \tag{12}$$

Though H_2' vanishes in the symmetric case, this term gives the potential, $U/2$, in the present asymmetric case. In the following, we can deal with H_2' as a perturbational potential added to the symmetric Anderson Hamiltonian. The thermal Green function for d-electron in the unperturbed state is written as

$$G_0(\omega) = [i\omega + i\Delta \operatorname{sgn} \omega]^{-1}, \tag{13}$$

which is an odd function of ω.

§ 2. *d*-electron number

The localized *d*-electron number is given by the Friedel sum rule as[5)]

$$n_{d\sigma}=\frac{1}{2}-\frac{1}{\pi}\,\mathrm{Tan}^{-1}\frac{\Sigma(0)}{\Delta}\,, \tag{14}$$

where $\Sigma(0)$ is *d*-electron self-energy at the Fermi level. $\Sigma(0)$ can be calculated as follows.

If we put $H_2'=0$, Eq. (1) reduces to the symmetric Anderson Hamiltonian, in which $\Sigma^s(0)$ is given by integral of odd-number product of the odd-function G_0 and vanishes. The first order term of $\Sigma(0)$ with respect to H_2' is obtained by using the charge susceptibility of the symmetric case, $\tilde{\chi}_c{}^s$, as

$$\frac{U}{2}\tilde{\chi}_c{}^s=\frac{U}{2}(\tilde{\chi}^s_{\uparrow\uparrow}+\tilde{\chi}^s_{\uparrow\downarrow})=\frac{U}{2}(\tilde{\chi}_{\mathrm{even}}-\tilde{\chi}_{\mathrm{odd}})\,, \tag{15}$$

where $\tilde{\chi}_{\mathrm{even}}$ and $\tilde{\chi}_{\mathrm{odd}}$ are given by Eqs. (7) and (8), respectively. The even-order terms with respect to H_2' also vanish by the same reason as the zeroth order term.

The third and fifth order terms with respect to H_2' are easily obtained up to the sixth order term with respect to U, since it is necessary to include only the third and the first order terms with respect to H_1'. Therefore, we comment only on a useful relation in diagrammatic calculation.

As a simple example, we calculate the fifth order terms shown in Fig. 1, where the cross represents the potential term, H_2'. The sum of these three diagrams is given as

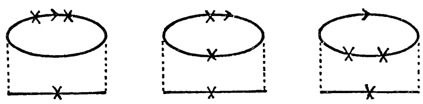

Fig. 1. Three fifth order self-energy diagrams, whose sum can be calculated more easily than the separate contributions. The crosses represent the potential H_2'.

$$-\left(\frac{U}{2}\right)^3U^2\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}G_0{}^2(\omega)\int_{-\infty}^{\infty}\frac{dx}{2\pi}\{G_0{}^3(x)G_0(x+\omega)+G_0{}^2(x)G_0{}^2(x+\omega)$$

$$+G_0(x)G_0{}^3(x+\omega)\}=-\frac{U^5}{8}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}G_0{}^2(\omega)\int_{-\infty}^{\infty}\frac{dx}{2\pi}\{2G_0{}^3(x)G_0(x+\omega)$$

$$+G_0{}^2(x)G_0{}^2(x+\omega)\}\,. \tag{16}$$

Using

$$\int_{-\infty}^{\infty}\frac{dx}{2\pi}\frac{d}{idx}[G_0^2(x)G_0(x+\omega)]=\int_{-\infty}^{\infty}\frac{dx}{2\pi}\Big[-2G_0^3(x)G_0(x+\omega)$$
$$-G_0^2(x)G_0^2(x+\omega)-G_0^2(x)\frac{2}{\Delta}\delta(x+\omega)\Big]=0\,,$$

we obtain

$$\text{Eq. (16)}=\frac{U^5}{8\pi\Delta}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}G_0^4(\omega)=\frac{U}{2}\Big(\frac{\pi^2}{12}u^4\Big). \tag{17}$$

The relations and methods similar to this example are useful to calculate other physical quantities as well as the self-energy.

Thus, $\Sigma(0)$ is expanded up to the sixth order term as

$$\frac{\Sigma(0)}{\Delta}=\frac{\pi}{2}u\Big[1-u+\Big(3-\frac{\pi^2}{4}\Big)u^2+\Big(\frac{19}{12}\pi^2-15\Big)u^3+\Big(\frac{\pi^4}{16}-\frac{29}{36}\pi^2+0.0553\Big)u^4$$
$$+\Big(\frac{824}{108}\pi^2-\frac{61}{80}\pi^4\Big)u^5+\cdots\Big], \tag{18}$$

where in the sixth order term we have neglected the fifth order term of $\tilde{\chi}_{\text{odd}}$ in Eq. (15), as it is expected to be 10^{-2}. Equation (18) is written as

$$\Sigma(0)/\Delta=\pi/2\cdot u[1-u+0.5326u^2+0.6269u^3-1.8071u^4+1.0270u^5].$$

We show $\Sigma(0)$ and $n_{d\sigma}$ as functions of u in Fig. 2, where the full curve represents the result obtained from the series expansion up to the sixth order term and the dotted curve up to the fifth order term. For $u>0.5$, the two curves are separated from each other, which shows our perturbational calculation is meaningful within $U<1.5\Delta$. In Fig. 2 $n_{d\sigma}$ decreases to 0.35 at $u=0.5$ with increasing u and increases rapidly with negative u. Though our calculation gives no conclusion for large u region, it is known that $n_{d\sigma}$ tends to zero in the limit $u\to\infty$[6)~8)] and to unity in the limit $u\to-\infty$.

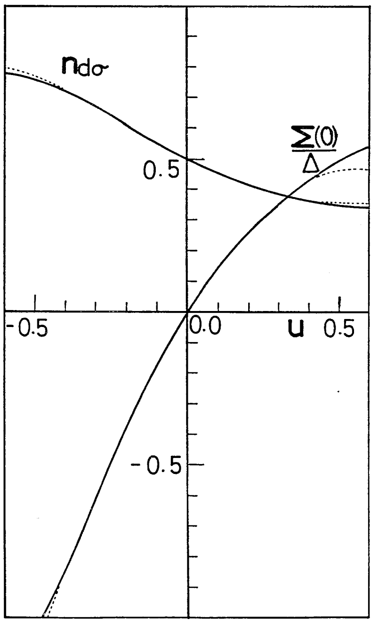

Fig. 2. The d-electron self-energy at the Fermi level, $\Sigma(0)$, and occupied d-electron number, $n_{d\sigma}$, as functions of $u=U/\pi\Delta$. The full curves include the terms up to the sixth order term and the dotted curves up to the fifth order term.

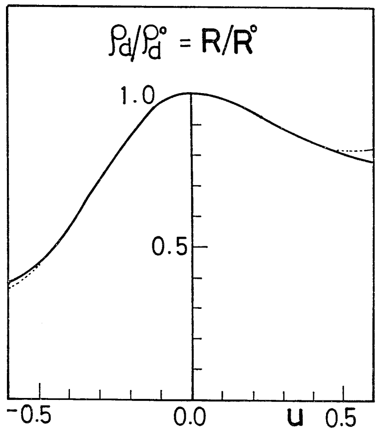

Fig. 3. Density of states of d-electrons at the Fermi energy. This curve also shows the resistivity at $T=0$ as a function of u.

By using $\Sigma(0)$ given by Eq. (18), we obtain the density of states, $\rho_d(0)$, for d-electrons at the Fermi level as

$$\rho_d(0) = -\frac{1}{\pi}\,\mathrm{Im}\,G(0+i\delta) = [\pi\Delta(1+(\Sigma(0)/\Delta)^2)]^{-1}, \tag{19}$$

which is shown in Fig. 3. As the scattering t-matrix is proportional to the d-electron Green function $G(0)$,[3),4)] the resistivity due to the impurity at the zero temperature is given by

$$\frac{R(u)}{R(u=0)} = \frac{\rho_d(u)}{\rho_d(u=0)} = [1+(\Sigma(0)/\Delta)^2]^{-1}. \tag{20}$$

§ 3. Ground state energy

The ground state energy, E_g, is obtained in a way similar to the self-energy. For example, the second order term with respect to H_2' is obtained from $-\sum_\sigma \frac{1}{2}\chi_c^s(U/2)^2$. Finally, E_g is given by the following:

$$E_g = E_g(u=0) + \pi\Delta\Big[\frac{1}{4}u - 0.2869u^2 + \frac{1}{4}u^3 + \Big(-0.7492+\frac{7\pi^2}{96}\Big)u^4 + \Big(\frac{15}{4}-\frac{5\pi^2}{12}\Big)u^5 - \Big(\frac{31\pi^4}{960}-\frac{103\pi^2}{288}+\frac{0.0553}{4}\Big)u^6\Big] \tag{21}$$

$$= E_g(u=0) + \pi\Delta[0.25u - 0.2869u^2 + 0.25u^3 - 0.0295u^4 - 0.3623u^5 + 0.3704u^6], \tag{22}$$

where we have neglected the sixth order term of the ground state energy for the symmetric case, which is expected to be negligibly small. $E_g(u=0)$ is given by

$$E_g(u=0) = -\frac{2\Delta}{\pi}\Big(\log\frac{D}{\Delta}+1\Big), \tag{23}$$

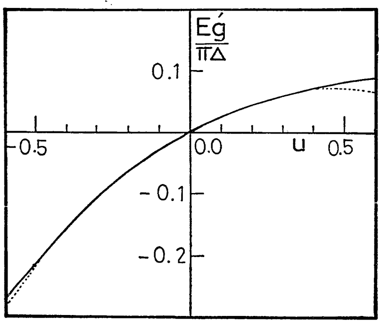

Fig. 4. The ground state energy as a function of u. The full curve shows the result including up to the sixth order term and the dotted one up to the fifth order term.

$2D$ being the conduction band width.

For comparison we give the ground state energy for the symmetric case, which is given by[3]

$$E_g^s = E_g(u=0) + \pi\Delta\left[-\frac{1}{4}u - 0.0369u^2 + 0.0008u^4 + O(u^6)\right]. \tag{24}$$

Comparing Eq. (22) with Eq. (24), we notice that convergence of expansion series in the symmetric case is very smooth in contrast with the asymmetric case. If we put $H_1'=0$, we can obtain the exact result[2] as

$$E_g = E_g(u=0) + \frac{U}{\pi}\cot^{-1}\frac{U}{2\Delta} + \frac{\Delta}{\pi}\log\left[1+\left(\frac{U}{2\Delta}\right)^2\right] - \frac{U}{4}. \tag{25}$$

$E_g' = E_g - E_g(u=0)$ given by Eq. (22) is shown in Fig. 4 as a function of u. The ground state energy E_g' does not exceed the order of Δ for positive u and decreases rapidly with negative u to reach $U(<0)$ in the limit $u \to -\infty$.

§ 4. Susceptibility and specific heat

The magnetic susceptibility is given by Eq. (4) and the coefficient of T-linear term of the specific heat is given by Eq. (6). These quantities are determined by $\tilde{\chi}_{\uparrow\uparrow}$ and $\tilde{\chi}_{\uparrow\downarrow}$, which are obtained as

$$\begin{aligned}\tilde{\chi}_{\uparrow\uparrow} = \tilde{\gamma} &= \left[1 + \left(3 - \frac{\pi^2}{4}\right)u^2 + \left(\frac{3\pi^4}{16} - \frac{25}{12}\pi^2 + 0.0553\right)u^4\right.\\ &\quad \left. + \left(\frac{161}{18}\pi^2 - \frac{7}{8}\pi^4\right)u^5 + \cdots\right]\\ &= 1 + 0.5326u^2 - 2.2422u^4 + 3.0452u^5 + \cdots,\end{aligned} \tag{26}$$

$$\begin{aligned}-\tilde{\chi}_{\uparrow\downarrow} &= u - \left(\frac{7\pi^2}{4} - 15\right)u^3 + \frac{\pi^2}{3}u^4 + \left(\frac{23}{16}\pi^4 - \frac{502}{36}\pi^2\right)u^5\\ &= u - 2.2718u^3 + 3.2899u^4 + 2.3994u^5 + \cdots,\end{aligned} \tag{27}$$

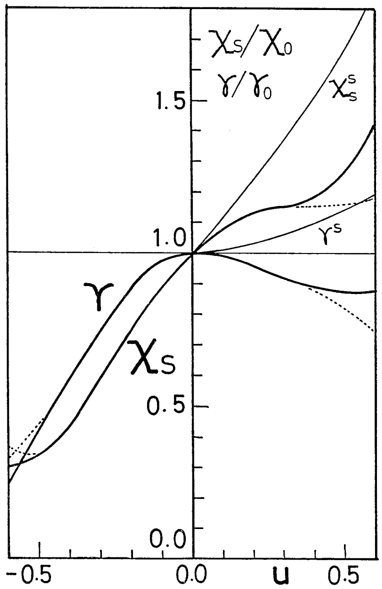

Fig. 5. The susceptibility and the coefficient of the T-linear term of specific heat. The full curves show the result up to the fifth order term and the dotted ones up to the fourth order term. χ_s^s and γ^s are χ_s and γ in the symmetric case, respectively.

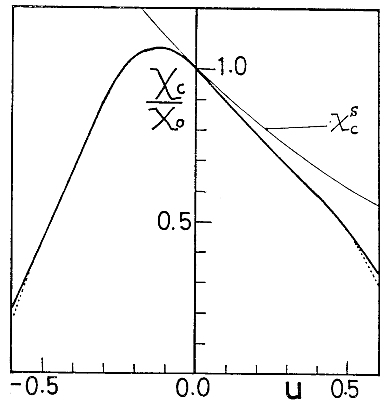

Fig. 6. The charge susceptibility, χ_c, as a function of u. The full curve shows the result up to the fifth order term and the dotted curve up to the fourth order term. χ_c^s is χ_c in the symmetric case.

where the fifth order term of $\tilde{\chi}_{\rm odd}$ for the symmetric Anderson model is neglected.

Using the above result and Eq. (19), we obtain χ_s and γ shown in Fig. 5. χ_s increases for positive u, and γ, on the other hand, decreases with u. The reason is as follows: Though $\tilde{\chi}_{\uparrow\uparrow}$ increases with u due to electron correlation, $\rho_d(0)$ decreases with u. The u^2-term of $\pi\Delta\rho_d(0)$ is $-(\pi^2/4)u^2$ and overcomes the u^2-term of $\tilde{\chi}_{\uparrow\uparrow}$, $(3-(\pi^2/4))u^2$. As the result, γ decreases as $(1-(\pi^2/2-3)u^2+\cdots)/\pi\Delta$. In the case of χ_s, the increase due to electron correlation in $\tilde{\chi}_s$ overcomes the decrease of $\rho_d(0)$.

For negative u, χ_s and γ decrease rapidly with increasing the absolute value of u.

Comparing Eqs. (26) and (27) with Eqs. (7) and (8), we notice that as mentioned in the previous section, the expansion series in the symmetric case converge more rapidly than in the asymmetric case. The difference of convergency between the two cases is due to the valence change. That is, while d-electron number is fixed to 1/2 in the symmetric case, it changes from 1/2 to zero in the asymmetric case.

Using $\tilde{\chi}_{\uparrow\uparrow}$ and $\tilde{\chi}_{\uparrow\downarrow}$, we can obtain the charge susceptibility, which is shown in Fig. 6. The charge susceptibility χ_c decreases with increasing u as a result of shift of d-level due to positive $\Sigma(0)$. In the limit $u\to\infty$, χ_c tends to zero slowly as $[\log u]^{-2}$ in the asymmetric case,[6),7)] while it tends to zero rapidly as $\exp[-u]$ in the symmetric case.[3)] It should be noted that χ_c increases for negative and small u. This effect and reduction of Δ increase the charge fluctuation additively, if screening effect by conduction electrons or phonons is included in the Anderson Hamiltonian.[9)]

§ 5. Discussion

We have presented a perturbation calculation for the asymmetric Anderson Hamiltonian for $U<1.5\Delta$. For large U region we can make discussion by using the scaling theory[6)] by Haldane. The scaling law for the asymmetric Anderson Hamiltonian in the case $D>U$ is as follows:

$$\varepsilon_d{}^* = \varepsilon_d + \frac{\Delta}{\pi} \log \frac{U}{\Delta} . \tag{28}$$

By this scaling law, $\varepsilon_d{}^*$ shifts upward over the Fermi level with increasing u for the case fixing ε_d to the Fermi level. Therefore, for $U \gg \Delta \simeq |\varepsilon_d|$, $n_{d\sigma}$, χ and γ tend to zero.[7)~10)] Thus, this case leaves the valence mixing region. In order to remain in the valence mixing region, ε_d must be shifted downward from the Fermi level[6)~8)] with increasing U. As this scaling law tells that $\varepsilon_d (= \varepsilon_d{}^* - \Delta/\pi \log U/\Delta)$ with large U is scaled to $\varepsilon_d{}^*$ with small U, it is sufficient for the valence mixing region to discuss the case with $\varepsilon_d \simeq 0$ and small U, where essential properties are included.

Though we have discussed the asymmetric case with $\varepsilon_d = 0$, the symmetric Anderson Hamiltonian ($\varepsilon_d = -U/2$) shows also charge fluctuation, as far as u is small, and it is not essentially different from asymmetric case. For large u region, in contrast with $\varepsilon_d = 0$, the symmetric system changes gradually from charge fluctuating region into the singlet ground state region with increasing u. Therefore, $\chi_s{}^s$ and γ^s increase monotonically with increasing u. χ_s and γ in general asymmetric cases (ε_d is not fixed to the Fermi level) decrease monotonically for fixed u, as d-electron number departs from the symmetric case.

Acknowledgements

The author would like to express his sincere thanks to Professor K. Yosida, Professor A. Sakurai, Dr. S. Inagaki and Professor H. Fukuyama for valuable discussions and comments. He also thanks the members of I.S.S.P. for their hospitalities during his stay.

References

1) P. W. Anderson, Phys. Rev. **124** (1961), 41.
2) K. Yosida and K. Yamada, Prog. Theor. Phys. Suppl. No. 46 (1970), 244.

3) K. Yamada, Prog. Theor. Phys. **53** (1975), 970.
4) K. Yosida and K. Yamada, Prog. Theor. Phys. **53** (1975), 1286.
K. Yamada, Prog. Theor. Phys. **54** (1975), 316.
H. Shiba, Prog. Theor. Phys. **54** (1975), 967.
A. Yoshimori, Prog. Theor. Phys. **55** (1976), 67.
5) D. C. Langreth, Phys. Rev. **150** (1966), 516.
6) F. D. M. Haldane, Phys. Rev. Letters **40** (1978), 416.
7) S. Inagaki, to be published in Prog. Theor. Phys.
8) K. Yosida and A. Sakurai, Prog. Theor. Phys. **61** (1979), 1597.
9) F. D. M. Haldane, Phys. Rev. **B15** (1977), 281; **B15** (1977), 2477.
10) H. Fukuyama and A. Sakurai, Prog. Theor. Phys. **62** (1979), No. 3.