Perturbation Expansion for the Anderson Hamiltonian

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The partition function for the Anderson Hamiltonian is expanded in a power series of U, the Coulomb integral between d-electrons at an impurity site, and for the case in which electron-hole symmetry is maintained it is found that the odd-order terms vanish and the even-order terms can be described by the imaginary-time integrals of the fourth power of the Pfaffian constructed from the one-particle Green function. In the approximation that the Green function is replaced by its asymptotic form, almost all diagrams are cancelled and only bubble diagrams remain, and so one cannot avoid instability by this approximation.

§1. Introduction

Many attempts have been made so far to improve the static Hartree-Fock approximation originally used in treating the Anderson Hamiltonian[1] for dilute alloys. One of them is the Schrieffer-Mattis theory[2] which discussed the ground state of the Anderson Hamiltonian by the low-density approximation. Recent theoretical developments have been made in connection with the Kondo problem. These are the theory of spin fluctuations or the random phase approximation,[3] the method of renormalized RPA[4),5] and the functional integral method.[6] They were partly successful but could not clarify the whole nature of this Hamiltonian. Particularly, the intermediate case between two extremes of magnetic and non-magnetic states in the sense of Hartree-Fock was not treated satisfactorily.

In these situations it might be of some help to investigate the Anderson Hamiltonian by perturbation theory. This paper describes the direct perturbation expansion of the partition function in a power series in the intra-Coulomb integral U by starting from the non-magnetic ground state of the unperturbed Hamiltonian including the s-d mixing term and no correlation. It is shown for a neutral case that each term of the perturbation expansion can be described by the imaginary-time integral of the fourth power of the Pfaffian constructed from d-electron Green functions. This formulation in terms of the Pfaffian is checked by applying to a soluble one-particle Hamiltonian, and then each term of perturbation is calculated by approximating the d-electron Green function by its asymptotic form. This approximation is found to correspond to retaining only bubble diagrams and to have the same instability as RPA. Finally, for large U the perturbation expansion is formulated in

terms of deviations from the Hartree-Fock solution and its first term is evaluated.

§2. Expansion of the partition function

Our object is the following Anderson Hamiltonian:

$$H=\sum_{k\sigma}\varepsilon_k c^\dagger_{k\sigma}c_{k\sigma}+V\sum_{k\sigma}(c^\dagger_{k\sigma}c_{d\sigma}+c^\dagger_{d\sigma}c_{k\sigma}) +\sum_\sigma \varepsilon_d c^\dagger_{d\sigma}c_{d\sigma}+\frac{1}{2}U\sum_\sigma c^\dagger_{d\sigma}c_{d\sigma}c^\dagger_{d-\sigma}c_{d-\sigma}, \tag{1}$$

where $c^\dagger_{k\sigma}$ and $c_{k\sigma}$ are the creation and annihilation operators for the conduction electron with wave vector $\boldsymbol{k}$ and spin σ, and $c^\dagger_{d\sigma}$ and $c_{d\sigma}$ are those for the localized d-electron on an impurity atom whose energy level is denoted by ε_d. V represents the transfer integral between the s- and d-states the $\boldsymbol{k}$-dependence of which is neglected in this paper and U is the Coulomb correlation energy between two d-electrons at the impurity atom. Here, we also assume a single d-orbital.

In the following, we confine our considerations to the symmetric case with respect to the electrons and holes, namely

$$\varepsilon_d=-\frac{1}{2}U. \tag{2}$$

Then, the Hamiltonian is divided into the unperturbed part H_0 and the perturbation H' as follows:

$$H=H_0+H', \tag{3}$$

$$H_0=\sum_{k\sigma}\varepsilon_k c^\dagger_{k\sigma}c_{k\sigma}+V\sum_{k\sigma}(c^\dagger_{k\sigma}c_{d\sigma}+c^\dagger_{d\sigma}c_{k\sigma})-\frac{1}{4}U, \tag{4}$$

$$H'=U\left(c^\dagger_{d\uparrow}c_{d\uparrow}-\frac{1}{2}\right)\left(c^\dagger_{d\downarrow}c_{d\downarrow}-\frac{1}{2}\right). \tag{5}$$

This way of treating the terms including U and ε_d as perturbation corresponds to taking deviations from the non-magnetic Hartree-Fock solution as perturbation.

The partition function for the Hamiltonian (1) can be expanded as follows:

$$Z=Z_0\left[1+\sum_{n=1}^{\infty}(-1)^n\int_0^\beta d\tau_n\int_0^{\tau_n}d\tau_{n-1}\cdots\int_0^{\tau_2}d\tau_1\langle H'(\tau_n)H'(\tau_{n-1}):\cdots H'(\tau_1)\rangle\right], \tag{6}$$

where Z_0 denotes the partition function for the unperturbed Hamiltonian

$$Z_0=\mathrm{Tr}\left[\exp(-\beta H_0)\right], \quad \beta=1/kT, \tag{7}$$

$\langle\ \rangle$ means the following thermal average

$$\langle A\rangle = \mathrm{Tr}\,[\exp(-\beta H_0)A]\,/\mathrm{Tr}\,[\exp(-\beta H_0)] \tag{8}$$

and $H'(\tau) = e^{\tau H_0} H' e^{-\tau H_0}$.

For $\beta\to\infty$ the expression (6) gives $\exp(-\beta E_g)$ where E_g is the ground state energy. From now on we confine ourselves to the limiting case of $\beta\to\infty$ for simplicity.

Inserting (5) into (6), we obtain for the perturbed ground state energy

$$\exp(-\beta E_g') = 1+\sum_{n=1}^{\infty}(-1)^n U^n \int_0^\beta d\tau_n \int_0^{\tau_n} d\tau_{n-1}\cdots\int_0^{\tau_2} d\tau_1 G_n, \tag{9}$$

$$G_n = \left\langle \left(c_{d\uparrow}^\dagger(\tau_n)c_{d\uparrow}(\tau_n)-\frac{1}{2}\right)\left(c_{d\downarrow}^\dagger(\tau_n)c_{d\downarrow}(\tau_n)-\frac{1}{2}\right)\left(c_{d\uparrow}^\dagger(\tau_{n-1})c_{d\uparrow}(\tau_{n-1})-\frac{1}{2}\right)\right.$$
$$\left.\cdots\left(c_{d\uparrow}^\dagger(\tau_1)c_{d\uparrow}(\tau_1)-\frac{1}{2}\right)\left(c_{d\downarrow}^\dagger(\tau_1)c_{d\downarrow}(\tau_1)-\frac{1}{2}\right)\right\rangle, \tag{10}$$

where $\langle\ \rangle$ denotes the expectation value for the unperturbed ground state wave function. This time-dependent type of perturbation expansion has recently been used for the *s-d* exchange Hamiltonian by Anderson and Yuval.[7]

Noting that the unperturbed Hamiltonian is given by the sum of one-particle Hamiltonians for up- and down-spin electrons and for this Hamiltonian the relation

$$\langle c_{d\sigma}^\dagger(\tau)c_{d\sigma}(\tau)\rangle = n_{d\sigma} = \frac{1}{2} \tag{11}$$

holds, we can rewrite (10) as

$$G_n = \Big[\sum_{\mathrm{P}}{}'(-1)^{\mathrm{P}}\langle T_\tau c_{d\uparrow}^\dagger(\tau_n)c_{d\uparrow}(\tau_{\mathrm{P}[n]})\rangle\langle T_\tau c_{d\uparrow}^\dagger(\tau_{n-1})c_{d\uparrow}(\tau_{\mathrm{P}[n-1]})\rangle\cdots$$
$$\cdots\langle T_\tau c_{d\uparrow}^\dagger(\tau_1)c_{d\uparrow}(\tau_{\mathrm{P}[1]})\rangle\Big]^2, \tag{12}$$

where T_τ is the time-ordering operator, $\mathrm{P}[n]$ is the n-th integer in a permutation of the n integers from 1 to n and the summation is taken over all the permutations in which $\mathrm{P}[m]\neq m$ for all m. The permutations which satisfy $\mathrm{P}[m]=m$ for some members give vanishing contributions to (12) because of (11).

By introducing *d*-electron Green function for $\beta\to\infty$

$$G_{12} = -\langle T_\tau c_{d\sigma}(\tau_1)c_{d\sigma}^\dagger(\tau_2)\rangle$$
$$= -\frac{\Delta}{\pi}\int_0^\infty \frac{d\varepsilon}{\varepsilon^2+\Delta^2}e^{-\varepsilon(\tau_1-\tau_2)} \qquad \tau_1>\tau_2$$
$$= \frac{\Delta}{\pi}\int_{-\infty}^0 \frac{d\varepsilon}{\varepsilon^2+\Delta^2}e^{-\varepsilon(\tau_1-\tau_2)} \qquad \tau_1<\tau_2, \tag{13}$$

where Δ is the resonance width given by $\pi\rho|V|^2$, ρ being the density of states for the conduction electrons, G_n is given by the square of the determinant

$$G_n=|D_n|^2=\begin{vmatrix} 0 & G_{12} & G_{13} & G_{14} & \cdots\cdots & G_{1n} \\ G_{21} & 0 & G_{23} & G_{24} & \cdots\cdots & G_{2n} \\ \vdots & & & & & \vdots \\ G_{n1} & \cdots\cdots & & & \cdots\cdots & G_{nn-1}0 \end{vmatrix}^2. \tag{14}$$

Since the Green function (13) is odd in its argument, the determinant in (14) is antisymmetric. Therefore, the odd-order determinants identically vanish and the even-order determinants are expressed by the square of the Pfaffian

$$\backslash D_n|=|G_{12}\ G_{13}\cdots\cdots G_{1n}\ |=\sum\pm G_{1a}G_{bc}\cdots G_{lm}\,, \tag{15}$$
$$\begin{matrix} G_{23}\cdots\cdots G_{2n} \\ \vdots \\ G_{n-1n}| \end{matrix}$$

where the suffixes $1, a, b, c, \cdots l, m$ of each term under the summation are a permutation of the first n integers, each Green function G_{rs} has $s>r$, all different terms of this type are included and the total number of terms is $(n-1)(n-3)\cdots 5\cdot 3\cdot 1$. The sign attached to each term is positive or negative according as the permutation is even or odd.[8] For example, for $n=4$,

$$\backslash D_4|=|G_{12}\ G_{13}\ G_{14}\ |=(G_{12}G_{34}-G_{13}G_{24}+G_{14}G_{23}). \tag{16}$$
$$\begin{matrix} G_{23}\ G_{24} \\ G_{34}| \end{matrix}$$

Thus, it is shown that (9) becomes

$$\exp(-\beta E_g')=1+\sum_{n=1}^{\infty}U^{2n}\int_0^{\beta}d\tau_{2n}\int_0^{\tau_{2n}}d\tau_{2n-1}\cdots\int_0^{\tau_2}d\tau_1(\backslash D_{2n}|)^4, \tag{17}$$

where $\backslash D_{2n}|$ is the $2n$-th order Pfaffian constructed from d-electron Green functions.

§3. Application to one-body Hamiltonian

In this section, we apply the above result to one-body Hamiltonian

$$H=\sum_k\varepsilon_k c_k^\dagger c_k+V\sum_k(c_k^\dagger c_d+c_d^\dagger c_k)+Uc_d^\dagger c_d. \tag{18}$$

The exact ground state energy is given for this Hamiltonian by

$$E_g=\frac{U}{\pi}\cot^{-1}\frac{U}{\Delta}+\frac{\Delta}{2\pi}\log\left(1+\left(\frac{U}{\Delta}\right)^2\right). \tag{19}$$

By dividing (18) into the unperturbed Hamiltonian H_0

$$H_0=\sum_k \varepsilon_k c_k^\dagger c_k + V\sum_k (c_k^\dagger c_d + c_d^\dagger c_k) + U/2$$

and the perturbation H'

$$H'=U\left(c_d^\dagger c_d - \frac{1}{2}\right),$$

for the perturbed ground state energy the following expression is obtained by the same process as before:

$$\exp(-\beta E_g')=1+\sum_{n=1}^{\infty} U^{2n}\int_0^\beta d\tau_{2n}\int_0^{\tau_{2n}} d\tau_{2n-1}\cdots\int_0^{\tau_2} d\tau_1 |D_{2n}|^2, \tag{20}$$

where squared even-order Pfaffians appear instead of the fourth power in (17).

From (20), the ground state energy E_g' is given by

$$E_g'=-\frac{1}{\beta}\sum_{n=1}^{\infty}\frac{U^{2n}}{(2n)!}\int_0^\beta d\tau_{2n}\int_0^\beta d\tau_{2n-1}\cdots\int_0^\beta d\tau_1 (|D_{2n}|)^2_{\text{connected}}. \tag{21}$$

Since $|D_{2n}|^2$ gives $(2n-1)!$ connected terms which are equivalent to $-G_{12}G_{23}G_{34}\cdots G_{2n-1,2n}G_{2n,1}$, this can be written as

$$E_g'=-\frac{1}{\beta}(-1)\sum_{n=1}^{\infty}\frac{U^{2n}}{2n}\int_0^\beta d\tau_{2n}\int_0^\beta d\tau_{2n-1}\cdots\int_0^\beta d\tau_1 G_{12}G_{23}G_{34}\cdots G_{2n,1}. \tag{22}$$

The $2n$-th order term can be calculated by introducing the Fourier transform of $G(\tau)$

$$G(\tau)=\frac{1}{\beta}\sum_{\omega_n} e^{-i\omega_n\tau}G(\omega_n), \tag{23}$$

$$G(\omega_n)=1/(i\omega_n+i\Delta\,\text{sign}\omega_n), \tag{24}$$

$$\omega_n=\frac{1}{\beta}(2n+1)\pi,$$

as

$$\begin{aligned} E_{g,2n}' &= \frac{1}{\beta}\frac{U^{2n}}{2n}\sum_{\omega_n}[G(\omega_n)]^{2n} \\ &= \frac{1}{\beta}\frac{U^{2n}}{2n}\frac{1}{(i)^{2n}}\frac{\beta}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega}{(\omega+\Delta\,\text{sign}\omega)^{2n}} \\ &= \frac{\Delta}{\pi}\frac{(-1)^n}{2n(2n-1)}\left(\frac{U}{\Delta}\right)^{2n}, \end{aligned} \tag{25}$$

where the summation over discrete ω_n is replaced by integration for $\beta\to\infty$.

The summation over n combined with the term of $\frac{1}{2}U$ included in H_0 reproduces the correct ground state energy given by (19).

§4. Asymptotic approximation

In contrast with the one-particle Hamiltonian (18), the evaluation of $\backslash D_{2n}|^4$ for the Anderson Hamiltonian is difficult. So we consider the approximation in which the d-electron Green function is replaced by its asymptotic form. In the expression for $G(\tau)$ given by (13) the function before the exponential in the integrand may be taken as a slowly varying function compared with the exponential for $\tau \gg 1/\Delta$. Then, $G(\tau)$ may be approximated by its asymptotic form

$$G(\tau) \cong \begin{cases} \dfrac{1}{\pi\Delta}\dfrac{1}{|\tau|} & \text{for} \quad \tau<0, \\ -\dfrac{1}{\pi\Delta}\dfrac{1}{\tau} & \text{for} \quad \tau>0. \end{cases} \tag{26}$$

This asymptotic form of $G(\tau)$ is compared with the true function of $G(\tau)$ in Fig. 1.

Now, we consider the determinant $|D_4|$ or the square of the Pfaffian $\backslash D_4|^2$

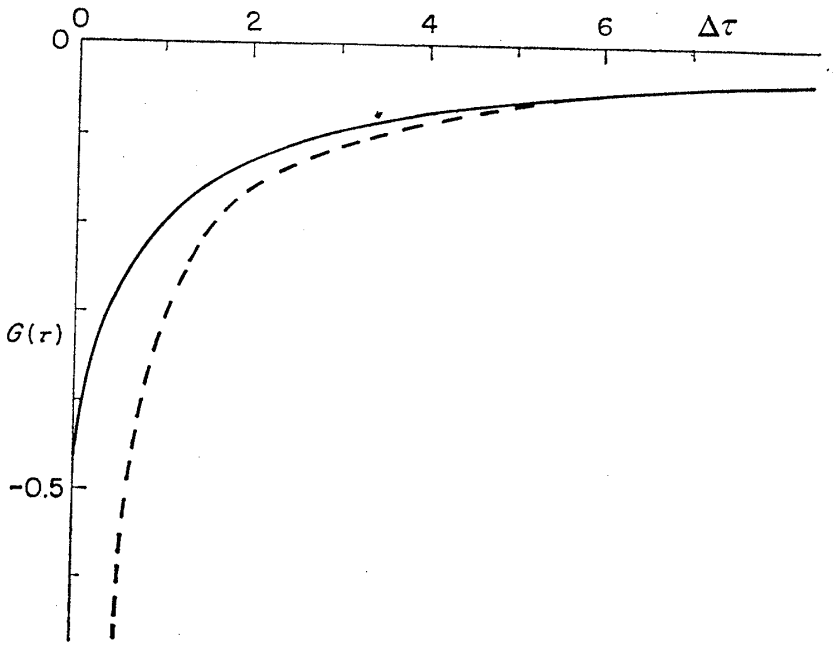

Fig. 1. τ-dependence of $G(\tau)$ as compared with its asymptotic form (dotted line).

for $2n=4$. From (16), we obtain

$$|D_4| = (\backslash D_4|)^2 = G_{12}^2G_{34}^2 + G_{13}^2G_{24}^2 + G_{14}^2G_{23}^2 - 2G_{12}G_{34}G_{13}G_{24} - 2G_{13}G_{24}G_{14}G_{23} + 2G_{14}G_{23}G_{12}G_{34}. \tag{27}$$

It is easy to show that the cross terms in (27) identically vanish in all together, that is,

$$G_{12}G_{34}G_{13}G_{24} + G_{13}G_{24}G_{14}G_{23} - G_{14}G_{23}G_{12}G_{34} \equiv 0 \tag{28}$$

with (26) for $G(\tau)$. This relation holds generally for any order. That is, the cross terms appearing in the square of the Pfaffian with its elements G_{ij} given by $1/(\tau_i-\tau_j)$ identically vanish. This can be proved as follows.

The original antisymmetric determinant of even order $|D_{2n}|$ can be expressed as

$$|D_{2n}| = -\sum_{p=2}^{2n}\sum_{q=2}^{2n} G_{1p}G_{q1}D'_{pq}, \tag{29}$$

where D'_{pq} is the co-factor of G_{qp} in the determinant $|D'|$ of order of $2n-1$ derived from $|D|$ by omitting the first row and column. $-$ sign in (29) results from the definition of D'_{pq} which is given by

$$|D'| = \sum_p G_{qp}D'_{pq}. \tag{30}$$

(29) is divided into diagonal and off-diagonal parts as

$$|D_{2n}| = \sum_{p=2}^{2n} G_{1p}^2D'_{pp} + \sum_{\substack{p,q=2 \\ p\neq q}}^{2n} G_{1p}G_{1q}D'_{pq}. \tag{31}$$

For the asymptotic form, the relation

$$G_{1p}G_{1q} = (G_{1p}-G_{1q})G_{pq} \quad \text{for} \quad p\neq q, \tag{32}$$

holds. Therefore, the second terms can be written with this relation as

$$+2\sum_{p=2}^{2n} G_{1p}\sum_{\substack{q=2 \\ q\neq p}}^{2n} G_{pq}D'_{qp} = 2\sum_{p=2}^{2n} G_{1p}|D'|, \tag{33}$$

where the relation that D'_{qp} is symmetric with respect to q and p and (30) are used. Since D' is an antisymmetric determinant of an odd order, we can see that (33) identically vanishes.

The diagonal co-factor in the first term of (31), D'_{pp}, is again an antisymmetric determinant of order of $2n-2$ and is given by the square of the Pfaffian, $\backslash D_{2n-2}|^2$ and we can apply the same procedure to this new lower-order antisymmetric determinant. Thus, for $\backslash D_6|^2$ we have

$$\begin{aligned}|D_6|^2 = {} & G_{12}^2(G_{34}^2G_{56}^2+G_{35}^2G_{46}^2+G_{36}^2G_{45}^2)\\ & +G_{13}^2(G_{24}^2G_{56}^2+G_{25}^2G_{46}^2+G_{26}^2G_{45}^2)\\ & +G_{14}^2(G_{23}^2G_{56}^2+G_{25}^2G_{36}^2+G_{26}^2G_{35}^2)\\ & +G_{15}^2(G_{23}^2G_{46}^2+G_{24}^2G_{36}^2+G_{26}^2G_{34}^2)\\ & +G_{16}^2(G_{23}^2G_{45}^2+G_{24}^2G_{35}^2+G_{25}^2G_{34}^2). \end{aligned} \tag{34}$$

With the use of these results, the ground state energy E_g for the system with the Anderson Hamiltonian is given as

$$\begin{aligned}E_g = {} & -\frac{U}{4}-\frac{1}{\beta}\Big[\frac{U^2}{2!}\int_0^\beta d\tau_2\int_0^\beta d\tau_1 G_{12}^4+2\frac{U^4}{4!}\int_0^\beta d\tau_4\int_0^\beta d\tau_3\cdots\int_0^\beta d\tau_1(G_{34}^2G_{12}^2G_{24}^2G_{13}^2\\ & +G_{24}^2G_{13}^2G_{14}^2G_{23}^2+G_{14}^2G_{23}^2G_{34}^2G_{12}^2)+2\frac{U^6}{6!}\int_0^\beta d\tau_6\cdots\int_0^\beta d\tau_1\\ & \{G_{12}^2G_{13}^2G_{34}^2G_{56}^2(G_{25}^2G_{46}^2+G_{26}^2G_{45}^2)+\cdots\}+\cdots\Big], \end{aligned} \tag{35}$$

where only the connected terms in $|D_{2n}|^2$ are taken under the integral signs. Although this result is derived by assuming the asymptotic form for $G(\tau)$, if one uses here the exact Green function given by (13), (23) and (24), we obtain the following expression for E_g:

$$\begin{aligned}E_g &= -\frac{U}{4}-\frac{1}{2\beta}\sum_\omega\sum_n\frac{U^{2n}}{n}\Big[\frac{1}{\beta}\sum_{\omega_n}G(\omega_n)G(\omega+\omega_n)\Big]^{2n}\\ &= -\frac{U}{4}+\frac{1}{2\beta}\sum_\omega\log[1-U^2\chi_0^2(\omega)], \end{aligned} \tag{36}$$

$$\begin{aligned}\chi_0(\omega) &= -\frac{1}{\beta}\sum_{\omega_n}G(\omega_n)G(\omega+\omega_n)\\ &= \frac{\Delta}{\pi|\omega|(|\omega|+2\Delta)}\log\Big[1+\frac{|\omega|(|\omega|+2\Delta)}{\Delta^2}\Big]. \end{aligned} \tag{37}$$

This result is the same as that derived recently by Hamann[6] who applied the method of functional integral to the Anderson Hamiltonian and retained only harmonic terms with respect to the time dependent potential acting on d-electrons in the exponent of the partition function before taking functional average. Our result shows that the asymptotic form for $G(\tau)$ only leaves the contributions from bubble diagrams and contributions from other diagrams are cancelled with one another by this approximation.

The asymptotic form is a good approximation for $G(\tau)$ as far as τ is large compared with $1/\Delta$. Thus, if the contributions from the region of $(\tau_j-\tau_{j-1})\lesssim 1/\Delta$ to the total integral are comparatively small (36) will give a good approximation for the ground state energy. This condition will be satisfied for lower-order perturbation terms which are important for small U but for higher-order perturbation terms which will become important for large U this will not be satisfied. Unfortunately, (36) shows the same instability

as RPA if $U/\pi\Delta$ exceeds unity. For such large value of U the present approximation is no longer valid. In order to avoid this instability a more accurate treatment will be needed in evaluating each term of perturbation.

§5. Perturbation expansion with respect to deviations from Hartree-Fock for large U

As we have seen above, the asymptotic approximation for $G(\tau)$ is invalid for large U. In the case of very large U, the expansion of the partition function with respect to the mixing parameter V is usually made. This expansion is found to be equivalent to the perturbation approach for the s-d exchange Hamiltonian.[9] As another approach, we attempt to formulate a perturbation expansion with respect to deviations from the Hartree-Fock solution which is taken as an unperturbed state.

For this case the Anderson Hamiltonian is divided into the following two parts:

$$H_0=\sum_{k\sigma}\varepsilon_k c^\dagger_{k\sigma}c_{k\sigma}+V\sum_{k\sigma}(c^\dagger_{k\sigma}c_{d\sigma}+c^\dagger_{d\sigma}c_{k\sigma}) +\sum_\sigma(\varepsilon_d+Un_{d-\sigma})c^\dagger_{d\sigma}c_{d\sigma}-Un_{d\uparrow}n_{d\downarrow}, \tag{38}$$

$$H'=U(c^\dagger_{d\uparrow}c_{d\uparrow}-n_{d\uparrow})(c^\dagger_{d\downarrow}c_{d\downarrow}-n_{d\downarrow}), \tag{39}$$

where $n_{d\sigma}$ represents the average number of d-electrons in the Hartree-Fock solution obtained self-consistently by unperturbed Hamiltonian H_0 and is given by

$$n_{d\uparrow}=G_\uparrow(0^-)=\frac{1}{2}+\frac{1}{\pi}\tan^{-1}\frac{aU}{\Delta}, \tag{40}$$

$$n_{d\downarrow}=\frac{1}{2}-\frac{1}{\pi}\tan^{-1}\frac{aU}{\Delta},$$

$$a=\frac{1}{2}-n_{d\downarrow}=n_{d\uparrow}-\frac{1}{2}. \tag{41}$$

The unperturbed ground state energy is calculated as

$$E_g^0=-\frac{U}{4}(1+4a^2)+\frac{\Delta}{\pi}\log\left[1+\left(\frac{aU}{\Delta}\right)^2\right], \tag{42}$$

and d-electron Green functions for $\beta\to\infty$ are given by

$$G_\sigma(\tau)=-\frac{\Delta}{\pi}\int_0^\infty\frac{d\varepsilon e^{-\varepsilon\tau}}{(\varepsilon-\sigma aU)^2+\Delta^2}, \quad \tau>0,$$

$$=\frac{\Delta}{\pi}\int_{-\infty}^0\frac{d\varepsilon e^{-\varepsilon\tau}}{(\varepsilon-\sigma aU)^2+\Delta^2}, \quad \tau<0. \tag{43}$$

These Green functions are no longer odd functions of τ and instead satisfy the relation:

$$G_\sigma(-\tau)=-G_{-\sigma}(\tau). \tag{44}$$

Thus the perturbation expansion for $\exp(-\beta E'_g)$ is obtained as

$$\exp(-\beta E'_g)=1+\sum_{n=2}^{\infty}U^n\int_0^\beta d\tau_n\int_0^{\tau_n}d\tau_{n-1}\cdots\int_0^{\tau_2}d\tau_1|D_{\uparrow n}|^2, \tag{45}$$

$$|D_{\uparrow n}|=\begin{vmatrix} 0 & G_{\uparrow 12} & G_{\uparrow 13}\cdots & G_{\uparrow 1n}\\ G_{\uparrow 21} & 0 & & \vdots\\ \vdots & & & \vdots\\ G_{\uparrow n1} & \cdots\cdots\cdots\cdots & & 0\end{vmatrix}, \tag{46}$$

where the relation

$$|D_{\downarrow n}|=(-1)^n|D_{\uparrow n}| \tag{47}$$

is used which is easily derived by (44). The determinant D_n has no diagonal elements but not antisymmetric. Therefore, odd-order terms do not vanish.

The second order term of the expansion (45) is then written as

$$\begin{aligned}E'_{g2}&=-\frac{1}{\beta}\frac{U^2}{2}\int_0^\beta d\tau_1\int_0^\beta d\tau_2 G_{12}^2G_{21}^2\\&=-\frac{1}{\beta}\frac{U^2}{2}\sum_\omega\left(\frac{1}{\beta}\sum_{\omega_1}G(\omega_1)G(\omega+\omega_1)\right)^2.\end{aligned} \tag{48}$$

Now, $\chi_0(\omega)$ is calculated as

$$\begin{aligned}\chi_0(\omega)&=-\frac{1}{\beta}\sum_{\omega_1}G(\omega_1)G(\omega+\omega_1)\\&=\frac{\Delta}{\pi}\frac{1}{|\omega|(|\omega|+2\Delta)}\log\left(1+\frac{|\omega|(|\omega|+2\Delta)}{\Delta^2+a^2U^2}\right).\end{aligned} \tag{49}$$

With the use of (49) in (48), E'_{g2} is calculated as

$$E'_{g2}=-\frac{1}{4\pi^3}\frac{U^2\Delta^2}{(\Delta^2+a^2U^2)^{3/2}}\int_0^\infty\frac{\log^2(1+x)}{x^2\sqrt{x+\alpha}}dx, \tag{50}$$

$$\alpha=\frac{\Delta^2}{\Delta^2+a^2U^2}\sim\left(\frac{2\Delta}{U}\right)^2. \tag{51}$$

Using $a=1/2$ and the integral for $\alpha=0$ which is evaluated as $(8\pi/3)(1-\log 2)$, we obtain

$$E'_{g2}=-\frac{16}{3\pi^2}(1-\log 2)U\left(\frac{\Delta}{U}\right)^2, \tag{52}$$

and actually see that the perturbed energy vanishes with Δ/U. However, each term of perturbation would have terms with different power of Δ/U.

The perturbation H' disturbs locally the Hartree-Fock solution by increasing localized d-electrons with down spin at the expense of those with up spin.

However, it would be difficult to obtain the singlet bound state by the present scheme of perturbation approach. In order to do this such a special technique as Anderson has used[10] for combining the two degenerate solutions of Hartree-Fock will be needed.

§6. Conclusions

In this paper a simple perturbation theory has been developed for the Anderson Hamiltonian for the system consisting of the conduction electrons and one localized d-electron by starting from the non-magnetic state. For the case in which electron-hole symmetry is maintained, it has been shown that the odd-order terms vanish and the even-order terms can be described by the imaginary time integral of the square of the antisymmetric determinant or the fourth power of the Pfaffian constructed from d-electron Green functions. This result was checked for one-body Hamiltonian which is exactly soluble.

A next step was to investigate the structure of each term in the perturbation expansion on the basis of this description in terms of Pfaffians. This step was, however, not satisfactorily made. What is found here is that if one approximates the d-electron Green function by its asymptotic form all other diagrams cancel one another than bubble diagrams and therefore that instability inherent to RPA or the Hartree-Fock approximation cannot be avoided by this approximation. In order to obtain the energy expression without instability a more accurate treatment should be made. This will be left to a future study.

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