PHYSICAL REVIEW VOLUME 154, NUMBER 3 15 FEBRUARY 1967

Ground-State Energy Shift due to the *s-d* Interaction

J. KONDO*
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 11 August 1966)

A calculation of the ground-state energy of a localized spin embedded in a normal metal is described. The unperturbed state is taken as the state of the unperturbed Fermi sphere multiplied by a spin state with $S_z=S$. Configurations with 1, 2, $\cdots$ electron-hole pairs excited are taken into account by a perturbation theory. Then a self-consistency equation to determine the ground-state energy is obtained. This equation has a solution which reduces to the Rayleigh-Schrödinger perturbation theory. In the case of antiferromagnetic exchange interaction, however, there is another solution which is lower than the Rayleigh-Schrödinger theory by a BCS-type expression. Thus the ground-state energy is expressed for small and negative J as

$$E=-4(\ln 2)S(S+1)J^2\rho^2D-kDe^{1/2J\rho}$$

for a band structure described in the text. Here k is a constant of order unity. A consideration of the spin configuration of the perturbed state is given.

1. INTRODUCTION

A PARAMAGNETIC impurity in a metal causes a singular scattering of the conduction electrons.[1] Suhl[2] found unstable complex poles of the t matrix by using a dispersion theory. Nagaoka[3] investigated the electron Green's functions in a self-consistent way and showed that there occurs a quasi-bound state coupled antiparallel to the localized spin in the case of antiferromagnetic exchange interaction.

Our present concern is the energy and the wave function of the ground state of a single paramagnetic impurity embedded in a normal metal. Attempts[4,5] have been made to investigate these points by using variation functions. These calculations show that the ground-state energy involves the BCS-type expression and so this cannot be expanded in terms of the exchange interaction J. On the contrary, Yosida and Miwa[6] showed that the perturbation expansion of the energy shift due to the *s-d* interaction shows no singularity at least up to the fourth order in J. Then there occurs a question[7] of whether the energy can be expanded in terms of J or not. The purpose of this paper is to give an answer to this question and to give a correct expression of the energy shift for sufficiently small J.

2. PRELIMINARY CONSIDERATION

In this section we calculate the ground-state energy shift as a function of the Zeeman splitting Δ of the localized spin by using a perturbation expansion in J but not in Δ. Our Hamiltonian is composed of two parts:

$$\begin{aligned} &H=H_0+V;\\ &H_0=\sum_{ks}\epsilon_k a_{ks}^*a_{ks}-S_z\Delta,\\ &V=-(J/N)\sum_{kk'}\{(a_{k\uparrow}^*a_{k'\uparrow}-a_{k\downarrow}^*a_{k'\downarrow})S_z\\ &\qquad\qquad+a_{k\uparrow}^*a_{k'\downarrow}S_-+a_{k\downarrow}^*a_{k'\uparrow}S_+\}, \end{aligned}\tag{1}$$

where notations have the usual meanings.[1] We consider the Zeeman splitting only for the localized spin. The unperturbed ground state is assumed to be the state in which all the conduction levels below the Fermi energy are occupied by up- and down-spin electrons and the z component of S has a maximum value S. We take the *s-d* interaction V as a perturbation and calculate the ground-state energy shift up to the fourth order in J.

We first consider the second-order term, which is given by

$$\begin{aligned} &\langle\psi_0V(E_{\text{u.p.}}-H_0)^{-1}V\psi_0\rangle\\ &\quad=-2(J/N)^2\{S^2\sum_{kk'}f_k(1-f_{k'})/(\epsilon_{k'}-\epsilon_k)\\ &\qquad\qquad+S\sum_{kk'}f_k(1-f_{k'})/(\epsilon_{k'}-\epsilon_k+\Delta)\}, \end{aligned}\tag{2}$$

where $f_k=1$ for $k\leq k_F$ and $f_k=0$ for $k>k_F$, and $E_{\text{u.p.}}$ means the unperturbed energy, $\langle\psi_0H_0\psi_0\rangle$. We assume a square band, whose density of states $N\rho$ is constant over the width of $2D$. We also assume that the Fermi level is at the center of the band. Then we have

$$\begin{aligned} &\langle\psi_0V(E_{\text{u.p.}}-H_0)^{-1}V\psi_0\rangle\\ &\quad=-4(\ln 2)S(S+1)J^2\rho^2D-2J^2\rho^2S\Delta\ln(2\Delta/D). \end{aligned}\tag{3}$$

The second term involves $\Delta\ln\Delta$, which shows no singularity at $\Delta=0$.

As we calculate higher order terms, we find that the J^n terms involve terms proportional to $\Delta\{\ln(\Delta/D)\}^r$ $(0\leq r\leq n-1)$, which show no divergence at $\Delta=0$. We retain

---

* On leave of absence from Electro-technical Laboratory, Tokyo, Japan.

[1] J. Kondo, Progr. Theoret. Phys. (Kyoto) **32**, 37 (1964).

[2] H. Suhl, Phys. Rev. **138**, A515 (1965); Physics **2**, 39 (1965); Phys. Rev. **141**, 483 (1966); H. Suhl and D. Wong, Physics (to be published).

[3] Y. Nagaoka, Phys. Rev. **138**, A1112 (1965).

[4] J. Kondo, Progr. Theoret. Phys. (Kyoto) **36**, 429 (1966).

[5] K. Yosida, Phys. Rev. **147**, 223 (1966).

[6] K. Yosida and H. Miwa, Phys. Rev. **144**, 375 (1966).

[7] First raised by Y. Nagaoka (private communication).

only the most "divergent" term ($r=n-1$). This procedure is valid when $J\rho$ is small compared with unity. We retain only the lowest order term ($\sim J^2$) of the terms which do not involve the logarithm, which is also valid for small $J\rho$. We then find

$$\begin{aligned}E=E_{\mathrm{FS}}-S\Delta-4(\ln 2)S(S+1)J^2\rho^2D+O(J^3\rho^3)\\ -2J^2\rho^2S\Delta[\ln(\Delta/D)]\{1+2J\rho\ln(\Delta/D)\\ +[2J\rho\ln(\Delta/D)]^2+\cdots\},\end{aligned}\quad(4)$$

where E_{FS} is the energy of the unperturbed Fermi sphere. We have calculated the first three terms of the series involving the logarithm. We may expect that the series is a geometrical one. When we put $\Delta=0$, (4) becomes identical with the result of Yosida and Miwa and shows no divergence. We note that this does not necessarily mean that the result of Yosida and Miwa is valid, because the series diverges for sufficiently small values of Δ unless Δ is exactly equal to zero. If we assume that the series is a geometrical one and write (4) as

$$\begin{aligned}E=E_{\mathrm{FS}}-S\Delta-4(\ln 2)S(S+1)J^2\rho^2D+O(J^3\rho^3)\\ -2J^2\rho^2S\Delta\ln(\Delta/D)\{1-2J\rho\ln(\Delta/D)\}^{-1},\end{aligned}\quad(5)$$

this expression behaves properly for all values of Δ for positive J but diverges at $\Delta=\Delta_c\equiv De^{1/2J\rho}$ for negative J. In the former case we may expect that (5) is correct (in the limit of $J\rho$ small compared with unity). On the contrary, in the case of negative exchange interaction, (5) may be valid only for Δ *well* above Δ_c. When Δ is larger than but close to Δ_c, its behavior is not reasonable, so that it does not seem to represent the correct value of the energy, even though the series in (4) converges absolutely. For Δ smaller than Δ_c, (5) is absolutely incorrect. This can be seen by calculating the average of S_z from (4).

$$\begin{aligned}\langle S_z\rangle=-\frac{dE}{d\Delta}=S+2J^2\rho^2S\ln(\Delta/D)\\ \times\{1+2J\rho\ln(\Delta/D)+[2J\rho\ln(\Delta/D)]^2+\cdots\}\\ =S[1+2J^2\rho^2[\ln(\Delta/D)]\{1-2J\rho\ln(\Delta/D)\}^{-1}],\end{aligned}\quad(6)$$

where we have again kept only the most divergent terms.[8] This gives an unreasonable result, $\langle S_z\rangle>S$, for $\Delta<\Delta_c$. For this reason there is no point in regarding the perturbation result of the energy for $\Delta=0$ as legitimate for negative J, even when there is no singularity in perturbation theory.

We now expect that, in a correct theory, the BCS-type expression which was obtained by variation methods takes the place of the last term of (5) when we let $\Delta\rightarrow 0$. It is the task of the next section to show that this is the case.

3. CALCULATION

From the consideration of the previous section we expect that the ground-state energy of our system may be divided into two parts; one can be expanded in terms of J and the other cannot:

$$E=E_0+(E_2+E_3+\cdots),\quad(7)$$

where E_2, E_3 are the second- and third-order terms of J, namely, $E_2=-4(\ln 2)S(S+1)J^2\rho^2D$, etc. As we mentioned, E_0 may not be equal to the unperturbed energy $E_{\mathrm{u.p.}}\equiv E_{\mathrm{FS}}-S\Delta$, but may involve the BCS term. Then from Eq. (7) we see that the perturbation expansion should be applied not to $E-E_{\mathrm{u.p.}}$ but to $E-E_0$. To do this we use a perturbation scheme which is a mixture of the Rayleigh-Schrödinger and Brillouin-Wigner methods.

We expand the ground-state wave function as

$$\psi=\psi_0+\psi_1+\psi_2+\cdots,\quad(8)$$

where ψ_0 is the unperturbed ground state, and ψ_i is the state in which there are i electron-hole pairs present. Putting (8) into the wave equation $(H_0+V)\psi=E\psi$ and arranging terms according to the number of electron-hole pairs, we obtain a set of equations:

$$H_0\psi_0+{}^0(V\psi_1)=E\psi_0,\quad(9a)$$

$$H_0\psi_1+V\psi_0+{}^1(V\psi_1)+{}^1(V\psi_2)=E\psi_1,\quad(9b)$$

$$H_0\psi_2+{}^2(V\psi_1)+{}^2(V\psi_2)+{}^2(V\psi_3)=E\psi_2,\quad(9c)$$

where ${}^2(V\psi_1)$, for example, means that part of $V\psi_1$ which contains two electron-hole pairs. We solve these equations for ψ_1, ψ_2, $\cdots$ by a perturbation expansion. We put

$$\psi_1=\psi_1^{(1)}+\psi_1^{(2)}+\cdots,\quad(10a)$$

$$\psi_2=\psi_2^{(2)}+\psi_2^{(3)}+\cdots,\quad(10b)$$

where $\psi_i^{(j)}$ is the jth-order part of ψ_i. Putting (10) together with (7) into (9b) and (9c) and solving for $\psi_i^{(j)}$, we obtain

$$\psi_1^{(1)}=\frac{1}{E_0-H_0}V\psi_0,\quad(11a)$$

$$\psi_1^{(2)}=\frac{1}{E_0-H_0}{}^1\!\left(V\frac{1}{E_0-H_0}V\psi_0\right)\text{ etc.}\quad(11b)$$

Putting these into (9a), we obtain, up to the fourth

---

[8] This expression becomes identical with that obtained by Yosida and Okiji [K. Yosida and A. Okiji, Progr. Theoret. Phys. (Kyoto) 34, 505 (1965)], for $\Delta=0$ and $T\neq 0$, when Δ is replaced by kT.

order in J,

$$
\begin{aligned}
E &= E_0+E_2+E_3+\cdots \\
&= E_{\text{u.p.}} \\
&\quad +\left\langle \psi_0 V\frac{1}{E_0-H_0}V\psi_0\right\rangle \\
&\quad +\left\langle \psi_0 V\frac{1}{E_0-H_0}V\frac{1}{E_0-H_0}V\psi_0\right\rangle \\
&\quad +\left\langle \psi_0 V\frac{1}{E_0-H_0}V\frac{1}{E_0-H_0}V\frac{1}{E_0-H_0}V\psi_0\right\rangle \\
&\quad -E_2\left\langle \psi_0 V\frac{1}{(E_0-H_0)^2}V\psi_0\right\rangle . \qquad (12)
\end{aligned}
$$

This is a self-consistency equation to determine E_0. We look for a solution $E_0(\Delta=0)$ in the limit $\Delta\rightarrow 0$. Evidently there is a solution, $E_0(\Delta=0)=E_{\text{u.p.}}$. Then Eq. (12) reduces to the usual Rayleigh-Schrödinger perturbation theory. But we shall show that there is another solution which is lower than this when the *s-d* exchange interaction is negative.

To show this, we calculate matrix elements of the right-hand side. This is straightforward but tedious. We find that the nth-order terms involve terms proportional to $a\{\ln(a/D)\}^r$ $(0\leq r\leq n-1)$, where $a\equiv E_{\text{u.p.}}-E_0(\Delta=0)$. Again we retain the most divergent terms $(r=n-1)$. Then we find

$$
\begin{aligned}
E(\Delta=0) &= E_0(\Delta=0)+E_2+E_3+\cdots \\
&= E_{\text{u.p.}}-4(\ln 2)S(S+1)J^2\rho^2 D+O(J^3\rho^3) \\
&\quad -2J^2\rho^2 S(S+1)a\ln(a/D)\{1+2J\rho\ln(a/D) \\
&\quad +[2J\rho\ln(a/D)]^2+\cdots\}. \qquad (13)
\end{aligned}
$$

We may again assume that the series is a geometrical one. Then we have, from (13) and $E_2=-4(\ln 2)S(S+1)J^2\rho^2 D$ etc.,

$$
a=\frac{2J^2\rho^2 S(S+1)a\ln(a/D)}{1-2J\rho\ln(a/D)}. \qquad (14)
$$

As we mentioned before, there is a solution $a=0$, which is the only one for positive J. But for negative J, we have another one which satisfies

$$
1-2J\rho\ln(a/D)=2J^2\rho^2 S(S+1)\ln(a/D). \qquad (15)
$$

In order to be consistent with our approximation of keeping the most divergent terms, we should write this as

$$
1-2J\rho\ln(a/D)=O(J\rho). \qquad (16)
$$

Then we have

$$
a=kDe^{1/2J\rho}(J<0), \qquad (17)
$$

where k is a constant of order unity. Then the ground-state energy is expressed by

$$
E=E_{\text{FS}}-4(\ln 2)S(S+1)J^2\rho^2 D+O(J^3\rho^3)-kDe^{1/2J\rho}. \qquad (18)
$$

This is exact in the limit of small $J\rho$. As we expected, the extra term cannot be expanded in terms of J. On the other hand, for positive J the last term of (18) is missing; the usual perturbation theory gives the correct result.

4. DISCUSSION

Our ground state is $(2S+1)$-fold degenerate when $\Delta=0$. This does not necessarily mean that the susceptibility of the localized spin follows Curie's law down to the absolute zero. In order to clarify this point, we calculated the average of S_z in the limit of $\Delta\rightarrow 0$ by using the wave function (8). This is obtained by differentiating both sides of (12) with respect to Δ and setting $\Delta=0$. Then we have

$$
\begin{aligned}
\langle S_z\rangle &= -\left.\frac{dE}{d\Delta}\right|_{\Delta=0} = -\left.\frac{dE_0}{d\Delta}\right|_{\Delta=0} \\
&= S \\
&\quad +\left\langle V\frac{S_z-S}{(E_0-H_0)^2}V\right\rangle \\
&\quad +2\left\langle V\frac{S_z-S}{(E_0-H_0)^2}V\frac{1}{E_0-H_0}V\right\rangle \\
&\quad +2\left\langle V\frac{S_z-S}{(E_0-H_0)^2}V\frac{1}{E_0-H_0}V\frac{1}{E_0-H_0}V\right\rangle \\
&\quad +\left\langle V\frac{1}{(E_0-H_0)^2}V\right\rangle\left\langle V\frac{S-S_z}{(E_0-H_0)^2}V\right\rangle \\
&\quad +2E_2\left\langle V\frac{S-S_z}{(E_0-H_0)^3}V\right\rangle \\
&\quad +\left\langle V\frac{1}{E_0-H_0}V\frac{S_z-S}{(E_0-H_0)^2}V\frac{1}{E_0-H_0}V\right\rangle, \qquad (19)
\end{aligned}
$$

where E_0 and H_0 mean $E_0(\Delta=0)$ and $H_0(\Delta=0)$. When the most divergent terms are retained, this is calculated as

$$
\begin{aligned}
\langle S_z\rangle-S &= 2J^2\rho^2 S[\ln(a/D)]\{1+2J\rho\ln(a/D) \\
&\quad +[2J\rho\ln(a/D)]^2+\cdots\} \\
&= \frac{2J^2\rho^2 S\ln(a/D)}{1-2J\rho\ln(a/D)}. \qquad (20)
\end{aligned}
$$

Unfortunately our approximation of keeping the most divergent terms is not accurate enough to evaluate $\langle S_z\rangle-S$ correctly [see (16)]. To do this we must sum all of the divergent terms, which we have not succeeded in doing. However, from (16) and (20) we see that the change of S_z due to the *s-d* interaction is of the order of unity, i.e., independent of J. Our conjecture on the ground-state wave function then is the following: We take $S=\frac{1}{2}$ as the simplest case. Our ground states are represented by that of the Fermi gas multiplied by the up- or down-spin state of the localized spin. The above result indicates that because of the *s-d* interaction, the state with the opposite spin direction is mixed by an amount of order unity. Since the exchange interaction conserves the total spin, the spin which was initially carried by the localized spin is now taken over by the conduction electrons. We may quite naturally expect that the twofold degeneracy of our ground state comes from the two directions of the spin carried by the conduction electrons and thus is trivial. This argument reconciles the apparent spin degeneracy of our ground state with the singlet spin state which was assumed in the previous variational approach.[4,5]

PHYSICAL REVIEW VOLUME 154, NUMBER 3 15 FEBRUARY 1967

Form Factors and Ultraviolet Spectra of Semiconductors at High Pressure*

DAVID BRUST AND L. LIU
Department of Physics, Northwestern University, Evanston, Illinois

(Received 15 August 1966)

Using the observed pressure dependence of a small set of band edges in Ge and Si, the pressure dependence of the pseudopotential form factors is deduced. Using these pressure-dependent form factors, the energy band structure and ultraviolet spectra are computed as a function of applied pressure. The results appear to give very reasonable agreement when compared with the observed pressure dependence of the reflectivity.

I. INTRODUCTION

BAND-structure calculations in semiconductors at atmospheric pressure have progressed enormously in the last few years. In the case of the group-IV elements (particularly Ge and Si) we can calculate not only the details of the band edges, but also properties depending on the band structure far from the energy gap such as the principal features of ultraviolet reflectivity spectra[1,2] and photoelectric emission yield and distribution curves.[3–5] Pseudopotential band structures are now also available for a number of partially ionic compounds,[6] and will presumably also lead to a similar interpretation of ultraviolet data.[7]

Application of large hydrostatic pressures with a consequent decrease in the crystal-lattice dimension results in observable band-structure changes in semiconductors. The experimental situation is described at length in a review article by Paul and Warschauer.[8] In germanium, Paul and Brooks[9] found by analyzing their high-pressure resistivity and electron-mobility data that the fundamental gap increases with a coefficient of 5×10^{-6} eV kg^{-1} cm^2.[10] This is the pressure coefficient, then, of the L_1 conduction-band minimum relative to the top of the valance band ($\Gamma_{25'}$). In silicon, on the other hand, the resistivity data showed that the conduction-band minima (Δ_1) move down under pressure. The coefficient was deduced to be[11] -1.5×10^{-6} eV kg^{-1} cm^2, and was reasonably well confirmed by high-pressure studies of the indirect absorption edge.[12,13] The direct optical gap in Ge ($\Gamma_{25'}\rightarrow\Gamma_{2'}$) which is nearly degenerate with the indirect gap was observed to shift under pressure at the rate of 12 eV kg^{-1} cm^2.[13–15] The Δ_1 conduction-band edge in Ge lies $\sim$0.2 eV above the absolute minima. When pressure is applied to Ge, Δ_1 approaches L_1 and eventually becomes the absolute

---

* This research was supported by the Advanced Research Projects Agency of the Department of Defense through the Northwestern University Materials Research Center.

[1] D. Brust, J. C. Phillips, and F. Bassani, Phys. Rev. Letters **9**, 94 (1962).

[2] D. Brust, Phys. Rev. **134**, A1337 (1964).

[3] D. Brust, M. L. Cohen, and J. C. Phillips, Phys. Rev. Letters **9**, 389 (1962).

[4] D. Brust, Phys. Rev. **139**, A489 (1965).

[5] E. O. Kane, Phys. Rev. **146**, 558 (1966); in Proceedings of the International Conference on the Physics of Semiconductors, Kyoto, Japan, 1966 (unpublished).

[6] M. L. Cohen and T. K. Bergstresser, Phys. Rev. **141**, 789 (1966).

[7] T. K. Bergstresser, M. L. Cohen, and D. Brust (to be published).

[8] W. Paul and D. M. Warschauer, *Solids Under Pressure*, (McGraw-Hill Book Company, Inc., New York, 1963), p. 179.

[9] W. Paul and H. Brooks, Phys. Rev. **94**, 1128 (1954).

[10] We shall use kg/cm^2 as the unit of pressure throughout this paper. To within about 4% this is equal to the other standard pressure units, i.e., the bar and the atmosphere.

[11] W. Paul and G. L. Pearson, Phys. Rev. **98**, 1755 (1955).

[12] W. Paul and D. M. Warschauer, J. Phys. Chem. Solids **5**, 102 (1958).

[13] L. J. Neuringer, Phys. Rev. **113**, 1495 (1959).

[14] H. Y. Fan, M. L. Shepherd, and W. G. Spitzer, *Photoconductivity Conference* (John Wiley & Sons, Inc., New York, 1956), p.184.

[15] M. Cardona and W. Paul, J. Phys. Chem. Solids **17**, 138 (1960).