Magnetic susceptibility of the periodic Anderson model

Ting-Kuo Lee and Sudip Chakravarty

Institute for Theoretical Physics, University of California, Santa Barbara, California 93106

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We calculate the thermodynamic potential and the susceptibility of the periodic Anderson model in powers of the hybridization matrix element between the localized and conduction electrons. The results are presented up to and including the terms of fourth order in the hybridization matrix element. When the localized level is far below the Fermi level we find that the magnetic susceptibility can exhibit three distinct tendencies: ferromagnetic, antiferromagnetic, and Kondo-type. But when the localized level is situated near the Fermi level it is found that the magnetic susceptibility has terms reflecting a Curie-Weiss law if the shift of the chemical potential is taken appropriately into account. The relevance of this calculation to mixed-valence compounds is pointed out.

I. INTRODUCTION

The thermodynamic potential and the suscepti-bility of the periodic Anderson model[1] are calcu-lated in powers of the hybridization matrix element between the localized and conduction electrons. The periodic Anderson model, a generalization of the Anderson model for dilute impurities[2] in metals, has been the subject of many investiga-tions[3] in recent years. It is believed that this model contains ingredients essential to our under-standing of mixed-valence compounds.[1] It is sur-prising that in spite of a considerable amount of interest in this model, a systematic and complete account of perturbative results for the thermody-namic quantities does not seem to exist.[4] From a high-temperature expansion of the thermodynamic potential in powers of the hybridization matrix element between the conduction and the localized electrons, we try to exhibit the differences and the similarities between the single-impurity and the periodic Anderson models. The understanding gained, we hope, may be useful to the development of a theory of mixed-valence compounds. We would like to emphasize that this exercise is undertaken to get some insights into the nature of the mixed-valence compounds and is in a sense similar to the calculation due to Scalapino,[5] who addressed the question of the existence of localized magnetic states for Anderson's single-impurity model.

We focus our attention on the calculation of the magnetic susceptibility and find that it can exhibit quite rich and varied behavior. In the case where the localized level is far below the Fermi level, the magnetic susceptibility can exhibit three dis-tinct tendencies: ferromagnetic, antiferromagnet-ic, and Kondo-type. Corresponding to the first two tendencies one finds a susceptibility approxi-mately consistent with a Curie-Weiss law, $\chi \sim (T + \theta)^{-1}$, where θ may be positive or negative depending on the parameters. The two signs of θ

are consequences of the oscillatory character of the Ruderman-Kittel-Kasuya-Yosida (RKKY) in-teraction between impurities. For different sys-tem parameters the susceptibility contains a dom-inant temperature-dependent term of the form $\chi \sim (1/T)\ln T$ characteristic of a single Kondo im-purity. When the localized level is situated near the Fermi level it is found that the magnetic sus-ceptibility has terms reflecting only a Curie-Weiss law, i.e., terms having logarithmic tem-perature dependence cancel, if the shift of the chemical potential is taken into account. Although this fact has been verified up to and including the fourth-order terms, it is perhaps not too prema-ture to speculate that large cancellations would occur in the higher-order terms as well. The ef-fect due to the shift of the chemical potential seems to be another novel feature of the periodic Anderson model. We now turn to the details of the calculation.

II. THE PERTURBATION EXPANSION

The periodic Anderson model describes a sys-tem of N_i magnetic ions, with localized nonde-generate "f" orbitals, arranged periodically on a lattice and embedded in a sea of s-like conduction electrons. The Hamiltonian is taken to be

$$H = H_0 + H_{fs} , \qquad (2.1)$$

where

$$H_0 = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}\sigma} C^\dagger_{\vec{k}\sigma} C_{\vec{k}\sigma} + \sum_{i\sigma} E_\sigma f^\dagger_{i\sigma} f_{i\sigma}$$

$$+ \frac{U}{2} \sum_{i,\sigma} f^\dagger_{i\sigma} f_{i\sigma} f^\dagger_{i-\sigma} f_{i-\sigma}, \qquad (2.2)$$

and

$$H_{fs} = \sum_{\vec{k}, i, \sigma} \left(\frac{v_k}{\sqrt{V}} e^{i\vec{k}\cdot\vec{R}_i} C^{\dagger}_{\vec{k}\sigma} f_{i\sigma} \right.$$
$$\left. + \frac{v_k^*}{\sqrt{V}} e^{-i\vec{k}\cdot\vec{R}_i} f^{\dagger}_{i\sigma} C_{\vec{k}\sigma} \right) , \qquad (2.3)$$

where V is the total volume of the system. The energies $\epsilon^{\star}_{\vec{k}\sigma}$ and E_{σ} contain the Zeeman energies (the g factor for conduction and f electrons are taken to be the same) and are given by

$$\epsilon^{\star}_{\vec{k}\sigma} = \epsilon^{\star}_{\vec{k}} + \tfrac{1}{2} g\sigma\mu_B H_{\text{ext}} \qquad (2.4)$$

and

$$E_{\sigma} = E_f + \tfrac{1}{2} g\sigma\mu_B H_{\text{ext}} . \qquad (2.5)$$

The f electrons described by the operators f_i and $f_i^{\dagger}$ interact by a strong on-site Coulomb repulsion U. The hybridization of the localized and the conduction electrons can take place at each lattice site $\vec{R}_i$, exhibited by the term H_{fs}. We now consider H_{fs} as the perturbation to calculate the thermodynamic potential Ω,

$$\Omega = -T \ln Z = -T \ln \text{Tr} \left[e^{-\beta(H_0 - \mu N)} \left(1 + \sum_{n=1}^{\infty} (-1)^n \int_0^{\beta} d\tau_1 \cdots \int_0^{\tau_{n-1}} d\tau_n H_{fs}(\tau_1) \cdots H_{fs}(\tau_n) \right) \right] , \qquad (2.6)$$

where

$$H_{fs}(\tau) = e^{(H_0 - \mu N)\tau} H_{fs} e^{-(H_0 - \mu N)\tau} . \qquad (2.7)$$

μ is the chemical potential and N is the total number of electrons:

$$N = \sum_{\vec{k}\sigma} C^{\dagger}_{\vec{k}\sigma} C_{\vec{k}\sigma} + \sum_{i\sigma} f^{\dagger}_{i\sigma} f_{i\sigma} . \qquad (2.8)$$

We have set $\hbar = k_B = 1$, and hence $\beta = 1/T$ is the inverse temperature. It is easy to see that the nonzero terms in Z are of even order in H_{fs} and can be expressed as

$$Z = Z^{(0)} + Z^{(2)} + Z^{(4)} + \cdots , \qquad (2.9)$$

where $Z^{(0)}$ is the partition function for unhybridized conduction and f electrons. To fourth order in the perturbation we have

$$\Omega \sim -T \ln Z^{(0)} - T \frac{Z^{(2)}}{Z^{(0)}} - T \left[\frac{Z^{(4)}}{Z^{(0)}} - \frac{1}{2} \left(\frac{Z^{(2)}}{Z^{(0)}} \right)^2 \right]$$

$$\equiv \Omega^{(0)} + \Omega^{(2)} + \Omega^{(4)} . \qquad (2.10)$$

The calculation of $\Omega^{(4)}$ is straightforward but tedious; by generalizing the diagrammatic techniques of Keiter and Kimball[6] we can greatly reduce the work. These rather obvious generalizations of the techniques of Keiter and Kimball will not be detailed, but only the final results will be given here. Furthermore, we shall, for the sake of simplicity and clarity, present the results for the case when U is infinite. In reality this is probably all that one needs, since in mixed-valence compounds $U \sim 5$–10 eV. All other parameters in the Hamiltonian are quite small compared to U. We now introduce the following notations:

$$n_{f\sigma} \equiv \exp[-\beta(E_{\sigma} - \mu)] z_f^{-1} , \qquad (2.11)$$

$$z_f \equiv 1 + \exp[-\beta(E_{\uparrow} - \mu)] + \exp[-\beta(E_{\downarrow} - \mu)] , \qquad (2.12)$$

and

$$n_0 \equiv z_f^{-1} . \qquad (2.13)$$

$n_{f\sigma}$ and n_0 are the occupation probabilities of the f level; since the unperturbed Hamiltonian is lattice translationally invariant, we shall drop the site index of these occupation probabilities. This convention should not be misleading, since the averages required in the calculation of the perturbation series of the thermodynamic potential are all calculated with respect to the unperturbed Hamiltonian.

The Fermi distribution function $f^{\star}_{\vec{k}\sigma}$ for the conduction band is

$$f^{\star}_{\vec{k}\sigma} = \{1 + \exp[\beta(\epsilon^{\star}_{\vec{k}\sigma} - \mu)]\}^{-1} . \qquad (2.14)$$

The zeroth-order thermodynamic potential is simply

$$\Omega^{(0)} = T \sum_{\vec{k}\sigma} \ln(1 - f^{\star}_{\vec{k}\sigma}) - T \sum_{i\sigma} \ln z_f . \qquad (2.15)$$

The second-order term is

$$\Omega^{(2)} = \sum_{\vec{k}, \sigma, i} \frac{|v_k|^2}{V} \left(\frac{f^{\star}_{\vec{k}\sigma} n_0}{\epsilon^{\star}_{\vec{k}\sigma} - E_{\sigma}} - \frac{(1 - f^{\star}_{\vec{k}\sigma}) n_{f\sigma}}{\epsilon^{\star}_{\vec{k}\sigma} - E_{\sigma}} \right) . \qquad (2.16)$$

The fourth-order term can be written as a sum of two distinct parts. The first, $\Omega_1^{(4)}$, is due to the interaction of the conduction electrons with a single f orbital at site $\vec{R}_i$. This term is what one obtains from treating the system as a collection of noninteracting impurities. More explicitly,

$$\Omega_1^{(4)} = -\sum_{i,\vec{k},\vec{k}'} \frac{|v_k|^2 |v_{k'}|^2}{V^2} \left[\sum_{\sigma,\sigma'} \frac{f_{\vec{k}\sigma} f_{\vec{k}'\sigma'} n_0}{(\epsilon_{\vec{k}\sigma}^+ - E_\sigma)(\epsilon_{\vec{k}'\sigma'}^+ - E_{\sigma'})} \left(\frac{\beta}{2} + \frac{1}{\epsilon_{\vec{k}\sigma}^+ - E_0} \right) \right.$$

$$+ \sum_\sigma \frac{(1 - f_{\vec{k}\sigma}^+)(1 - f_{\vec{k}'\sigma}^+) n_{f\sigma}}{(\epsilon_{\vec{k}\sigma}^+ - E_\sigma)(\epsilon_{\vec{k}'\sigma}^+ - E_\sigma)} \left(\frac{\beta}{2} - \frac{1}{\epsilon_{\vec{k}\sigma}^+ - E_\sigma} \right)$$

$$+ \sum_\sigma \frac{(1 - f_{\vec{k}\sigma}^+) f_{\vec{k}'\sigma}^+ n_0}{(\epsilon_{\vec{k}\sigma}^+ - \epsilon_{\vec{k}'\sigma}^+)(\epsilon_{\vec{k}'\sigma}^+ - E_\sigma)^2} + \sum_{\sigma\sigma'} \frac{(1 - f_{\vec{k}\sigma}^+) f_{\vec{k}'\sigma}^+ n_{f\sigma}}{(\epsilon_{\vec{k}\sigma}^+ - E_\sigma - \epsilon_{\vec{k}'\sigma'}^+ + E_{\sigma'})} \left. \frac{1}{(\epsilon_{\vec{k}\sigma}^+ - E_\sigma)^2} \right]$$

$$+ \frac{\beta}{2} \sum_{i,\vec{k},\vec{k}'} \frac{|v_k|^2 |v_{k'}|^2}{V^2} \sum_{\sigma,\sigma'} \left(\frac{f_{\vec{k}\sigma}^+ n_0 - (1 - f_{\vec{k}\sigma}^+) n_{f\sigma}}{\epsilon_{\vec{k}\sigma}^+ - E_\sigma} \right) \left(\frac{f_{\vec{k}'\sigma'}^+ n_0 - (1 - f_{\vec{k}'\sigma'}^+) n_{f\sigma'}}{\epsilon_{\vec{k}'\sigma'}^+ - E_{\sigma'}} \right) . \tag{2.17}$$

The last term in Eq. (2.17) comes from $\frac{1}{2}(Z^{(2)}/Z^{(0)})^2$ in Eq. (2.10).

The second contribution, $\Omega_2^{(4)'}$, arises from the interaction between two localized f orbitals at two different sites $\vec{R}_i$ and $\vec{R}_j$ mediated by the conduction electron. When localized moments exist, $\Omega_2^{(4)'}$ is the contribution due to the RKKY interaction. For $\Omega_2^{(4)'}$ we have

$$\Omega_2^{(4)'} = -\sum_{i \neq j} \sum_{\vec{k},\vec{k}',\sigma} \frac{|v_k|^2 |v_{k'}|^2}{V^2} e^{i(\vec{k} - \vec{k}') \cdot (\vec{R}_i - \vec{R}_j)} \left[\frac{f_{\vec{k}\sigma}^+ f_{\vec{k}'\sigma}^+}{(\epsilon_{\vec{k}\sigma}^+ - E_\sigma)(\epsilon_{\vec{k}'\sigma}^+ - E_\sigma)} \left(\frac{n_0^2}{\epsilon_{\vec{k}\sigma}^+ - E_\sigma} + \frac{\beta}{2} n_0 n_{f\sigma} + \frac{n_0 n_{f\sigma}}{\epsilon_{\vec{k}\sigma}^+ - E_\sigma} \right) \right.$$

$$+ \frac{(1 - f_{\vec{k}\sigma}^+)(1 - f_{\vec{k}'\sigma}^+)}{(\epsilon_{\vec{k}\sigma}^+ - E_\sigma)(\epsilon_{\vec{k}'\sigma}^+ - E_\sigma)} \left(\frac{\beta}{2} n_0 n_{f\sigma} - \frac{n_{f\sigma}^2}{\epsilon_{\vec{k}\sigma}^+ - E_\sigma} - \frac{n_0 n_{f\sigma}}{\epsilon_{\vec{k}\sigma}^+ - E_\sigma} \right)$$

$$+ \frac{(1 - f_{\vec{k}\sigma}^+) f_{\vec{k}'\sigma}^+}{\epsilon_{\vec{k}\sigma}^+ - \epsilon_{\vec{k}'\sigma}^+} \left(\frac{n_0}{\epsilon_{\vec{k}'\sigma}^+ - E_\sigma} + \frac{n_{f\sigma}}{\epsilon_{\vec{k}\sigma}^+ - E_\sigma} \right)^2$$

$$+ \frac{(1 - f_{\vec{k}\sigma}^+) f_{\vec{k}'\sigma}^+ n_0 n_{f\sigma}}{(\epsilon_{\vec{k}\sigma}^+ - E_\sigma)(\epsilon_{\vec{k}'\sigma}^+ - E_\sigma)} \left. \left(\beta + \frac{1}{\epsilon_{\vec{k}'\sigma}^+ - E_\sigma} - \frac{1}{\epsilon_{\vec{k}\sigma}^+ - E_\sigma} \right) \right] . \tag{2.18}$$

It is convenient to write the right-hand side of Eq. (2.18) as a sum of two terms:

$$\Omega_2^{(4)'} = \Omega_2^{(4)} + \Omega_3^{(4)} , \tag{2.19}$$

where

$$\Omega_2^{(4)} = -\sum_{i \neq j} \sum_{\vec{k},\sigma} \frac{|v_k|^4}{V^2} \left(\frac{\beta}{2} \frac{n_0 + n_{f\sigma}}{(\epsilon_{\vec{k}\sigma}^+ - E_\sigma)^2} [f_{\vec{k}\sigma}^+ n_0 + (1 - f_{\vec{k}\sigma}^+) n_{f\sigma}] + \frac{n_0 + n_{f\sigma}}{(\epsilon_{\vec{k}\sigma}^+ - E_\sigma)^3} [f_{\vec{k}\sigma}^+ n_0 - (1 - f_{\vec{k}\sigma}^+) n_{f\sigma}] \right)$$

$$+ \frac{\beta}{2} \sum_{\vec{k}, i \neq j, \sigma} \frac{|v_k|^4}{V^2} \left(\frac{f_{\vec{k}\sigma}^+ n_0 - (1 - f_{\vec{k}\sigma}^+) n_{f\sigma}}{(\epsilon_{\vec{k}\sigma}^+ - E_\sigma)} \right)^2 , \tag{2.20}$$

and

$$\Omega_3^{(4)} = -\sum_{i \neq j} \sum_{\vec{k} \neq \vec{k}',\sigma} \frac{|v_k|^2 |v_{k'}|^2}{V^2} e^{i(\vec{k} - \vec{k}') \cdot (\vec{R}_i - \vec{R}_j)}$$

$$\times \left[\left(\frac{\beta}{2} - \frac{1}{\epsilon_{\vec{k}\sigma}^+ - E_\sigma} \right) \frac{n_0 n_{f\sigma}}{(\epsilon_{\vec{k}\sigma}^+ - E_\sigma)(\epsilon_{\vec{k}\sigma}^+ - E_\sigma)} + \frac{(1 - f_{\vec{k}\sigma}^+) n_{f\sigma}^2 - f_{\vec{k}\sigma}^+ n_0^2 - 2 f_{\vec{k}\sigma}^+ n_0 n_{f\sigma}}{(\epsilon_{\vec{k}\sigma}^+ - E_\sigma)^2 (\epsilon_{\vec{k}\sigma}^+ - \epsilon_{\vec{k}'\sigma}^+)} \right] . \tag{2.21}$$

So far we have treated μ as an independent variable. The average number of electrons N, a function of μ and T, is determined by the equation

$$-\frac{\partial \Omega}{\partial \mu} = N . \tag{2.22}$$

In order to calculate the magnetic susceptibility for a fixed number of electrons N, we begin by expanding μ in powers of the hybridization matrix element v,

$$\mu = \mu^{(0)} + \mu^{(2)} + \mu^{(4)} + \ldots ; \tag{2.23}$$

the superscripts in Eq. (2.23) refer to the powers of v. If we now require that

$$N = -\frac{\partial \Omega^{(0)}(\mu^{(0)})}{\partial \mu^{(0)}} \tag{2.24}$$

we obtain

$$\mu^{(2)} = \left(\frac{\partial \Omega^{(2)}(\mu^{(0)})}{\partial \mu^{(0)}}\right)\left(-\frac{\partial^2 \Omega^{(0)}(\mu^{(0)})}{\partial \mu^{(0)2}}\right)^{-1} , \tag{2.25}$$

and

$$\mu^{(4)} = \left(\frac{\partial \Omega^{(4)}(\mu^{(0)})}{\partial \mu^{(0)}} + \mu^{(2)}\frac{\partial^2 \Omega^{(2)}(\mu^{(0)})}{\partial \mu^{(0)2}} + \frac{1}{2}(\mu^{(2)})^2 \frac{\partial^3 \Omega^{(0)}(\mu^{(0)})}{\partial \mu^{(0)3}}\right)\left(-\frac{\partial^2 \Omega^{(0)}(\mu^{(0)})}{\partial \mu^{(0)2}}\right)^{-1} . \tag{2.26}$$

The susceptibility is now given by

$$\chi = \chi^{(0)} + \chi^{(2)} + \chi^{(4)} + \cdots , \tag{2.27}$$

where

$$\chi^{(0)} = -\left(\frac{\partial^2 \Omega^{(0)}}{\partial H_{ext}^2}\right) , \tag{2.28}$$

$$\chi^{(2)} = -\left(\frac{\partial^2 \Omega^{(2)}}{\partial H_{ext}^2}\right) + \left(\frac{\partial \chi^{(0)}}{\partial \mu}\right)\mu^{(2)} , \tag{2.29}$$

and

$$\chi^{(4)} = -\left(\frac{\partial^2 \Omega^{(4)}}{H_{ext}^2}\right) + \left(\frac{\partial \chi^{(0)}}{\partial \mu}\right)\mu^{(4)}$$
$$+ \frac{1}{2}(\mu^{(2)})^2\left(\frac{\partial^2 \chi^{(0)}}{\partial \mu^2}\right) + \mu^{(2)}\left[\frac{\partial}{\partial \mu}\left(-\frac{\partial^2 \Omega^{(2)}}{\partial H_{ext}^2}\right)\right] . \tag{2.30}$$

All the partial derivatives appearing in Eqs. (2.28)–(2.30) are to be evaluated at $H_{ext} = 0$ and $\mu = \mu^{(0)}$.

In what follows we shall choose $\mu^{(0)}$ as the origin of the energy scale unless it is stated otherwise. In order to carry out the integrations explicitly, we use a constant density of states for the conduction electrons. Summations of the form $(1/V)\sum_k |v_k|^2 g(\epsilon_k)$ will be replaced by $\rho_0 v^2 \int_{-D}^{D} d\omega\, g(\omega)$, where ρ_0 is the conduction-electron density of states per unit volume at the Fermi energy $\mu = \mu^{(0)} = 0$. The bandwidth D is assumed to be much larger than $|E_f|$ and also larger than the temperature. Various interesting cases for the magnetic susceptibility are now discussed in the following sections.

III. THE LOCAL-MOMENT REGIME

If the energy of the localized f orbital is far below the Fermi level, i.e., $D \gg -E_f \gg T \gg \rho_0 v^2$, then the f orbital is always occupied at low temperatures. We can then obtain

$$\frac{\chi^{(0)}}{(\frac{1}{2}g\mu_B)^2 V} = 2\rho_0 + \frac{n_i}{T} \tag{3.1}$$

and

$$\frac{\chi^{(2)}}{(\frac{1}{2}g\mu_B)^2 V} = \rho_0 n_i v^2\left(\frac{1}{E_f^2} - \frac{2}{T|E_f|}\right) , \tag{3.2}$$

where n_i is the density N_i/V. The second-order correction due to the chemical potential given by the second term in Eq. (2.29) is negligible, since in the local-moment regime it is easy to show that $\partial \chi^{(0)}/\partial \mu^{(0)} \sim 0$. In order to see this, note that

$$\frac{1}{(\frac{1}{2}g\mu_B)^2 V}\frac{\partial \chi^{(0)}}{\partial \mu^{(0)}} = \frac{1}{V}\sum_{\vec{k}\sigma}\frac{\partial^2 f_{\vec{k}\sigma}}{\partial \epsilon_{\vec{k}\sigma}^2} + \frac{n_i}{T}\sum_\sigma n_0 n_{f\sigma}$$

$$= -\int_{-D}^{D}\frac{\partial \rho(\epsilon)}{\partial \epsilon}\left(\frac{\partial f}{\partial \epsilon}\right)d\epsilon + \rho(\epsilon)\left(\frac{\partial f}{\partial \epsilon}\right)\Big|_{-D}^{D}$$

$$+ \frac{n_i}{T^2}n_0(1-n_0)$$

$$\simeq \left(\frac{\partial \rho(\epsilon)}{\partial \epsilon}\right)_{\epsilon = \mu^{(0)}} . \tag{3.3}$$

For a flat density of states $[\partial\rho(\epsilon)/\partial\epsilon]$ vanishes, and for a general density of states this term is independent of temperature and of no further concern. In deriving Eq. (3.3) we have also dropped all exponentially small temperature-dependent

terms. Thus $(\partial^2\chi^{(0)}/\partial\mu^{(0)2}) \sim 0$, and hence the fourth-order susceptibility is

$$\chi^{(4)} = -\frac{\partial^2}{\partial H_{ext}^2}\left(\Omega_1^{(4)} + \Omega_2^{(4)} + \Omega_3^{(4)}\right) + \frac{\partial}{\partial\mu}\left(-\frac{\partial^2\Omega^{(2)}}{\partial H_{ext}^2}\right)\mu^{(2)},$$

(3.4)

where it is understood that H_{ext} should be set to zero and μ should be set to $\mu^{(0)}$ after the derivatives are calculated.

The single-site contribution to the fourth-order susceptibility is given by

$$-\left(\frac{\partial^2\Omega_1^{(4)}}{\partial^2 H_{ext}^2}\right)_{H_{ext}=0}\frac{1}{(\frac{1}{4}g^2\mu_B^2 V)}$$

$$= (\rho_0 v^2)^2 n_i\left(\frac{2}{TE_f^2}\ln\frac{T^2}{D|E_f|} + \frac{3}{TE_f^2}\right.$$

$$\left. + \frac{1}{E_f^3} + \frac{2}{E_f^3}\ln\left|\frac{E_f}{D}\right|\right). \quad (3.5)$$

At low temperatures the Kondo term $\ln(T^2/D|E_f|)$ dominates. This is in agreement with the results obtained previously.[7] The contribution due to $\Omega_2^{(4)}$ can be expressed as

$$-\left(\frac{\partial^2\Omega_2^{(4)}}{\partial H_{ext}^2}\right)_{H_{ext}=0}\frac{1}{(\frac{1}{4}g^2\mu_B^2 V)} = \rho_0 v^4\left(\frac{n_i^2}{2D^2T^2}\right).$$

(3.6)

In Eq. (3.5) we have kept only the leading-order term consistent with the inequality $D \gg |E_f| \gg T$.

We have mentioned earlier that, in the local-moment regime, the part of the susceptibility arising from $\Omega_3^{(4)}$ is intimately related to the RKKY interaction. We can now rewrite $\Omega_3^{(4)}$ as

$$\Omega_3^{(4)} = -\sum_{i\neq j,\sigma}n_{f\sigma}^2\left(\frac{1}{V^2}\sum_{\vec{k}\neq\vec{k}'}e^{i(\vec{k}-\vec{k}')\cdot(\vec{R}_i-\vec{R}_j)}\right.$$

$$\left. \times\frac{|v_k|^2|v_{k'}|^2}{(\epsilon_{\vec{k}\sigma}-E_\sigma)^2}\frac{(1-f_{\vec{k}\sigma})}{(\epsilon_{\vec{k}\sigma}-\epsilon_{\vec{k}'\sigma})}\right)$$

$$\equiv -\sum_{i\neq j,\sigma}n_{f\sigma}^2 J(\vec{R}_i-\vec{R}_j). \quad (3.7)$$

For the free-electron density of states, in the limit $|k_F R_{ij}| \gg 1$,

$$J(R_{ij}) = -\pi(\rho_0 v^2)^2\left(\frac{\mu_F}{E_F^2}\right)\frac{\cos(2k_F R_{ij})}{(k_F R_{ij})^3}, \quad (3.8)$$

where the notation has the obvious connotations. Therefore, in the limit $k_F a \to \infty$ (a is lattice spacing), we have

$$-\left(\frac{\partial^2\Omega_3^{(4)}}{\partial H_{ext}^2}\right)_{H_{ext}=0}\frac{1}{(\frac{1}{4}g^2\mu_B^2 V)}$$

$$= -n_i(\rho_0 v^2)^2\left(\frac{\mu_F}{2T^2E_f^2}\right)\sum_{\vec{R}}'\frac{\cos(2k_F R)}{(k_F R)^3}, \quad (3.9)$$

where the prime on the summation implies that $\vec{R}=0$ has to be excluded. On the other hand, if $k_F a < \pi$, only the electronic states with wave vectors less than $2\pi/a$ will contribute; thus

$$\sum_i e^{i(\vec{k}-\vec{k}')\cdot R_i} = N_i\delta_{\vec{k},\vec{k}'}, \quad (3.10)$$

and in this case for constant density of states

$$-\left(\frac{\partial^2\Omega_3^{(4)}}{\partial H_{ext}^2}\right)_{H_{ext}=0}\frac{1}{(\frac{1}{4}g^2\mu_B^2 V)}$$

$$= -n_i(\rho_0 v^2)^2\frac{2}{DT^2}\ln\left|\frac{D}{E_f}\right|. \quad (3.11)$$

The contribution due to the chemical potential is given by

$$\frac{\partial}{\partial\mu^{(0)}}\left(-\frac{\partial^2\Omega^{(2)}(\mu^{(0)})}{\partial H_{ext}^2}\right)_{H_{ext}=0}\left(\frac{\mu^{(2)}}{\frac{1}{4}g^2\mu_B^2 V}\right)$$

$$= -n_i^2\left(\frac{\rho_0 v^4}{E_f^4}\right) + n_i^2\left(\frac{\rho_0 v^4}{T|E_f|^3}\right), \quad (3.12)$$

where we have used the fact that $\mu^{(2)} = (n_i/2)(v^2/|E_f|)$. This contribution due to the chemical potential can be combined with the second-order term, Eq. (3.2), if we replace $|E_f|$ in (3.12) by $\mu^{(2)}+|E_f|$. Finally,

$$\frac{\chi}{\frac{1}{4}g^2\mu_B^2 V} = 2\rho_0 + \frac{n_i}{T} - \frac{2n_i\rho_0 v^2}{T|E_f|}\left(1 - \frac{n_i}{2}\frac{v^2}{|E_f|^2}\right)$$

$$+ \frac{2n_i(\rho_0 v^2)^2}{E_f^2 T}\left(\ln\left|\frac{T^2}{DE_F}\right| + \frac{3}{2}\right)$$

$$+ \frac{n_i(\rho_0 v^2)^2}{DT^2}\left(\frac{n_i}{2\rho_0 D} - 2\ln\left|\frac{D}{E_f}\right|\right). \quad (3.13)$$

This result for the susceptibility can be *related* to the phase diagram of the ground state of a lattice of magnetic impurities exchange coupled to the conduction electrons (Kondo lattice) obtained by Lacroix and Cyrot.[8] At a low enough temperature, and for large $|E_f|$ or small $\rho_0 v^2/|E_f|$, the last term in Eq. (3.13) is much larger than the Kondo term, and the perturbation series has the form $n_i[(1/T)+(\theta/T^2)]$. The sign of θ is positive, corresponding to a ferromagnetic Curie temperature, if $n_e/n_i = 2\rho_0 D/n_i \ll 1$. But for large values of n_e/n_i, the term $2\ln|D/2E_f|$ becomes dominant
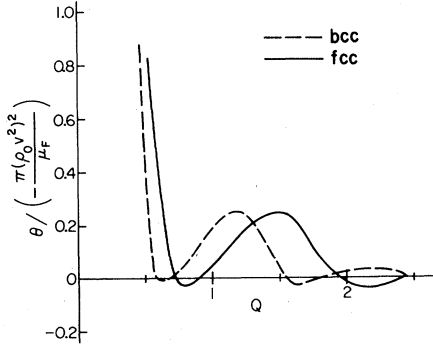
FIG. 1. Curie constant θ as a function of $Q = k_F a / \pi$.

and θ is negative; this corresponds to a antiferro-magnetic Néel temperature.

For values of $k_F a \geq 1$ we must use Eq. (3.9) or, more accurately, Eq. (3.7). We have numerically evaluated Eq. (3.7) for free-electron density of states and for several values of $Q = k_F a / \pi$ to determine θ; the results for $|E_f| / \mu_F = 0.91$ are shown in Fig. 1, where we plot θ as a function Q. This exercise serves to emphasize the important role of the band and the lattice structures in determining the sign of θ. We would like to emphasize that the ferro- and antiferromagnetic regions alternate as a function of the band filling n_e / n_i in marked contrast to the diagram obtained by Lacroix and Cyrot.[8]

IV. THE "MIXED-VALENCE" REGIME

When the f level is very close to the Fermi energy, i.e., $|E_f| \ll T$, the occupation probability of the f level is less than unity. We now obtain

$$\frac{\chi^{(0)}}{\frac{1}{4}g^2 \mu_B^2 V} = 2\rho_0 + \frac{2}{3}\frac{n_i}{T} . \tag{4.1}$$

Without the chemical potential correction, the first term on the right-hand side of Eq. (2.29) is given by

$$-\frac{1}{\frac{1}{4}g^2\mu_B^2 V}\left(\frac{\partial^2\Omega^{(2)}}{\partial H_{ext}^2}\right)_{H_{ext}=0}$$

$$= -\frac{2n_i\rho_0 v^2}{3T^2}\left[\frac{1}{3}\ln\left(\frac{D}{T}\right) - \frac{\Psi^{(2)}(\frac{1}{2})}{2\pi^2}\right] , \tag{4.2}$$

where $\Psi^{(1)}$ is a polygamma function.[9] In deriving Eq. (4.2) we have made use of the inequality $D \gg T \gg |E_f|$, which will be used all throughout this section. The first term in Eq. (4.2) was obtained previously by Hewson,[4] but the second term is different from his. Equation (2.23) can easily be shown to be

$$\mu^{(2)} \sim \rho_0 v^2 \ln(D/T) \tag{4.3}$$

in the limit $n_i / T \gg \rho_0$. Thus,

$$\frac{\chi^{(2)}}{\frac{1}{4}g^2\mu_B^2 V} = \frac{2n_i\rho_0 v^2}{3T^2}\left(\frac{\Psi^{(2)}(\frac{1}{2})}{2\pi^2}\right),$$

and hence there are no logarithmic terms in $\chi^{(2)}$. The cancellation occurs in the fourth-order term as well, and for $\chi^{(4)}$ we have

$$\frac{\chi^{(4)}}{\frac{1}{4}g^2\mu_B^2 V} = \frac{n_i(\rho_0 v^2)^2}{T^3}\left(\frac{\Psi^{(2)}(\frac{1}{2})}{2\pi^2}\right)[\frac{4}{3}\Psi^{(0)}(\frac{1}{2})] . \tag{4.4}$$

In obtaining Eq. (4.4) we have noticed that in the limit $T \gg |E_f|$ the terms $\Omega_2^{(4)}$ and $\Omega_3^{(4)}$ contribute practically nothing to the susceptibility; the entire contribution comes from $\Omega_1^{(4)}$. Finally,

$$\frac{\chi}{\frac{1}{4}g^2\mu_B^2 V} = 2\rho_0 + \frac{2n_i}{3T} + \frac{2n_i}{3T^2}(\rho_0 v^2)\left(\frac{\Psi^{(2)}(\frac{1}{2})}{2\pi^2}\right)$$

$$+ \frac{4n_i}{3T^3}(\rho_0 v^2)^2\left(\frac{\Psi^{(2)}(\frac{1}{2})}{2\pi^2}\right)[\Psi^{(0)}(\frac{1}{2})] . \tag{4.5}$$

This is the same as what one would obtain in the single-impurity Anderson model in which n_i is the density of uncorrelated impurities. We should however be cautious of the fact that this holds only if $T \gg \mu^{(2)} = \rho_0 v^2 \ln(D/T)$. Thus, the perturbative method used in this paper must not be used to explain the low-temperature behavior of the mixed-valence compounds.

V. CONCLUSION

In this paper we have presented the results of a perturbation expansion of the periodic Anderson model. Although our main concern has been the susceptibility of this model, it would be straightforward to calculate the specific heat from the expressions for the thermodynamic potential given in the paper.

This work was undertaken to get some insight into the nature of the mixed-valence compounds. If the periodic Anderson model is appropriate to the description of the mixed-valence compounds, then the susceptibility of such compounds should exhibit a rather rich and varied behavior. We must emphasize that the results of the perturbation theory should not be used to explain the low-temperature behavior of the mixed-valence compounds. We do however believe that a systematic perturbation theory as contained in this paper is a relevant step to our understanding of the periodic Anderson model.

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