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THEORY OF ELEMENTARY EXCITATIONS IN INTERMEDIATE VALENCE MATERIALS*

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THEORY OF ELEMENTARY EXCITATIONS IN INTERMEDIATE VALENCE MATERIALS*

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We review the formalism for calculating the properties of systems represented by an Anderson lattice Hamiltonian. First, a mean-field theory for the one electron Green's function is presented and then extended to include spin and charge fluctuations which lead to a many-body resonance near the Fermi level. The dynamical spin susceptibility and neutron scattering cross section are also evaluated. Finally, we present a calculation which indicates the possibility of a Cooper-pairing mechanism induced by electron correlations.

1. Introduction

In these lectures, we will present various levels of a theoretical framework to understand the thermodynamics and elementary excitations of a model system involving strong intrasite electron correlations, with a view to understanding the properties of the Anderson and Kondo lattices. First, we present the underlying operator formalism and indicate how it may be applied to obtain the simplest mean-field type theory for the Anderson lattice. Then, we show how the formalism may be extended to calculate the dynamical susceptibility, and also to the Kondo regime. Finally, we shall present some results relating to Cooper pairing of the electrons, driven by strong correlation effects, as a possible new mechanism for superconductivity in such materials.

Our starting point is the assumption that strong Coulomb correlations between f-electrons have the result that all f-shell configurations other than f^n and f^{n-1} are projected out. This is equivalent to stating that U_{ff} is large. For simplicity, consider the case where $n=1$, and let $|i,0\rangle$ denote the state at site i where there are no

f-electrons (or a full multiplet) and $|i,m\rangle$ denote the state corresponding to the m^{th} state of the multiplet corresponding to the f-electron (or f-hole). (The states may equally well be crystal-field-split states.) We define operators (analogous to the standard basis operators¹),

$$f_{im}^+ \Delta |i,m\rangle \langle i,0| \quad ; \quad f_{im} = |i,0\rangle \langle i,m| \quad . \quad (1.1)$$

It is obvious from (1.1) that

$$f_{im}^+ f_{im}^+ = 0 \quad (1.2)$$

for all m, m' , and the completeness property requires that

$$|i,0\rangle \langle i,0| + \sum_m |i,m\rangle \langle i,m| = 1 \quad (1.3)$$

for each site i . Such operators, however, do not obey the usual Fermion anticommutation rules, but satisfy

$$[f_{im}^+, f_{jm'}^+]_+ = [f_{im}, f_{jm'}]_+ = 0 \quad ; \quad (1.4a)$$

$$[f_{im}, f_{jm'}^+]_+ = \delta_{ij} Q_{mm'}^i, \quad (1.4b)$$

where

$$Q_{mm'}^i \equiv \delta_{mm'} (1 - \sum_{m''} f_{im''}^+ f_{im''}) + f_{im}^+ f_{im} \quad . \quad (1.4c)$$

Note that the expectation value $\langle Q_{mm}^i \rangle$ is of $O(\frac{1}{N})$ where N is the number of states in the multiplet. We now write down the Hamiltonian for the Anderson lattice in the form

$$\begin{aligned} H = & \sum_{i,m} \epsilon_{fm} f_{im}^+ f_{im} + \sum_{k\sigma} \epsilon_{k\sigma} c_{k\sigma}^+ c_{k\sigma} \\ & + \sum_{k\sigma} (N_L)^{-1/2} v_{k\sigma}^m [f_{im}^+ c_{k\sigma} e^{-ik \cdot r_i} + \text{h.c.}] \\ & + \sum_{i,m} \epsilon_m f_{im}^+ f_{im} \delta V \\ & + \frac{1}{2} B(V) \delta V^2 - g_J \mu_B^H \sum_{i,m} \langle m | J_z | m \rangle f_{im}^+ f_{im} \end{aligned} \quad (1.5)$$

where ϵ_{fm} is the energy of the multiplet state m , $\epsilon_{k\sigma}$ that of an unperturbed conduction state of wavevector k and spin σ , N_L the total number of lattice sites, $c_{k\sigma}$, $c_{k\sigma}^+$ the Fermion operators for conduction states, δV a volume deformation, $B(V)$ the Bulk Modulus

and e_m a deformation potential for state m , H an applied magnetic field and g_J the Lande factor for the multiplet.

2. Mean-Field Theory for the One-Electron Green's Functions

We are now in a position to use the Equation-of-Motion method² to calculate the single electron Green's Functions in lowest order. While this may appear to be a very crude solution to the problem (analogous to the "Hubbard I"-type approximations used for transition metals³), it has certain interesting features worth noting on the way to a better solution. It gives a natural generalization for the lattice case of the known lowest-order results for the single impurity problem, such as those of Varma and Yafet⁴ or Ramakrishnan.⁵ It exhibits a renormalization of the bare f -level similar to that obtained by Haldane⁶ using rather general scaling arguments. One also obtains, almost trivially, results derived for the spin $1/2$ f -level case using diagrammatic techniques⁷, and is easily generalized to the full multiplet case. The basic idea is to decouple higher order Green's functions arising from the non-trivial anticommutation rules (Eqs. (1.4)) back down to lowest order. Physically, this corresponds to imbedding each f -electron shell in a mean lattice; thus, it is basically a mean-field type of theory. We start by defining operators for propagating excitations on the lattice, analogous to the $C_{k\sigma}$, $C_{k\sigma}^+$:

$$f_{km}^+ = N^{-1/2} \sum_i f_{im}^+ e^{-ik \cdot r_i}, \text{ etc.} \quad (2.1)$$

One may attempt to write down a ground-state Fermi liquid type wavefunction using these operators but it turns out to be very hard to evaluate because of the non-trivial anticommutation rules for the f -operators. The Green's function method, on the other hand, avoids the necessity of having to consider wavefunctions at all. Let us consider the usual (retarded) thermal Green's functions⁸

$$G^{AB}(\omega) \equiv \langle A; B \rangle_\omega \quad (2.2)$$

and let us choose A , B to be f_{km} or $C_{k\sigma}$ and f_{km}^+ or $C_{k\sigma}^+$, respectively. Their equations of motion are given by⁸

$$\begin{aligned} \omega G_{km}^{mm'}(\omega) = & \langle [f_{km}, f_{km'}^+]_+ \rangle \\ & + \langle \langle [f_{km}, H] ; f_{km'}^+ \rangle_\omega \rangle, \end{aligned} \quad (2.3)$$

with similar equations for the other one-particle Green's functions. For simplicity, let us consider first the case where we have a simple spin- $1/2$ f -doublet so m can be replaced by a spin index σ .

By Eqs. (1.4), (1.5) we have

$$[f_{k\sigma}, H] = (\epsilon_f - g\mu_B H - e\langle n^f \rangle / B(V)) f_{k\sigma} + N_L^{-1/2} \sum_{jk'\sigma'} e^{i(k-k') \cdot r_j} V_{k'\sigma'} Q_{\sigma\sigma'}^j c_{k'\sigma'}, \quad (2.4)$$

where ϵ_f is the unperturbed position of the f-level, and $e_\sigma \equiv e$. We have eliminated δV by minimizing the energy with respect to it.

Using the representation (1.4c) for $Q_{\sigma\sigma'}^j$ and decoupling the last product in Eq. (2.4), we obtain

$$[f_{k\sigma}, H] \approx \epsilon_{f\sigma}^* f_{k\sigma} + V_{k\sigma} \langle Q_\sigma \rangle c_{k\sigma}, \quad (2.5)$$

where

$$\epsilon_{f\sigma}^* = \epsilon_f - g\mu_B H\sigma - e\langle n^f \rangle / B(V) + \sum_{k'} \{ -V_{k'\sigma} \langle f_{k',\bar{\sigma}}^+ c_{k',\bar{\sigma}} \rangle \}, \quad (2.6)$$

where $\bar{\sigma}$ denotes the spin opposite to σ and

$$\langle Q_\sigma \rangle = 1 - \langle \frac{n^f}{\sigma} \rangle. \quad (2.7)$$

The equation of motion for the conduction electron operator $c_{k\sigma}$ is rigorously

$$[c_{k\sigma}, H] = \epsilon_{k\sigma} c_{k\sigma} + V_{k\sigma} f_{k\sigma}. \quad (2.8)$$

Let $G_{k\sigma}(\omega)$ stand for the matrix

$$\begin{pmatrix} G_k^{ff}(\omega) & G_k^{cf}(\omega) \\ G_k^{fc}(\omega) & G_k^{cc}(\omega) \end{pmatrix}$$

where f refers to the f-spin index and c to the conduction electron spin index, both being σ in this case. From Eqs. (2.3), (2.5) and (2.6), we obtain

$$G_{k\sigma}^{-1}(\omega) = \begin{pmatrix} \frac{\omega - \epsilon_{f\sigma}^*}{\langle Q_\sigma \rangle} & V_{k\sigma} \\ V_{k\sigma}^* & \omega - \epsilon_{k\sigma} \end{pmatrix}. \quad (2.9)$$

Thus the poles of the one-electron Green's function are at

$$E_{k\sigma}^{\pm} \equiv \frac{1}{2} (\epsilon_{f\sigma}^* + \epsilon_{k\sigma} \pm \Lambda_{k\sigma}) ; \quad (2.10a)$$

$$\Lambda_{k\sigma} \equiv [(\epsilon_{f\sigma}^* - \epsilon_{k\sigma})^2 + 4|V_{k\sigma}|^2 \langle Q_{\sigma} \rangle]^{1/2} \quad (2.10b)$$

which would correspond to one-electron hybridized "bands" for the non-interacting case (i.e., for $f_{k\sigma}, f_{k\sigma}^+$ obeying ordinary fermion statistics) if $\epsilon_{f\sigma}^*$ was replaced by ϵ_f and $\langle Q_{\sigma} \rangle$ by 1. There is a "hybridization gap" of order $\pi|V|^2 \langle Q_{\sigma} \rangle / W$ (W is the conduction band width), which is, however, an indirect (zone-boundary) gap (see Fig. 1). From Eq. (2.9) it is obvious that the self-energy matrix $\Sigma_{k\sigma}(\omega)$ (defined as $G_{k\sigma}^{(0)-1}(\omega) - G_{k\sigma}^{-1}(\omega)$, where $G_{k\sigma}^{(0)}(\omega)$ is the Green's function matrix for the non-interacting case) is real for all ω , i.e., Fermi-liquid-like behavior has been "built in" the model from the outset by the very nature of the decoupling approximation. The thermodynamic averages of the f -electron occupation, etc. can be obtained from the general relations of the form⁸

$$\langle A B \rangle_T = \frac{1}{\pi} \int_{-\infty}^{+\infty} d\omega f(\omega - \mu) \lim_{\eta \rightarrow 0^+} \text{Im} \langle B; A \rangle_{\omega + i\eta} \quad (2.11)$$

where A, B are any one-electron operators, $f(\omega - \mu)$ is the Fermi function, and μ the chemical potential. The explicit expressions in the case of our model are given in Ref. (9). The chemical potential μ is determined by the condition

$$\sum_{\sigma} \{ \langle n_{\sigma}^f \rangle + \langle n_{\sigma}^c \rangle \} = n_e ; \quad (2.12)$$

n_e being the given number of electrons per unit cell. Eqs. (2.6), (2.9), (2.11) and (2.12) must be solved self-consistently at any temperature and applied field H for given $\epsilon_f, V_{k\sigma}, \epsilon_{k\sigma}$. The self-consistent determination of the chemical potential μ is, of course, a new feature not present in the impurity case.

From the results of such calculations we may obtain quantities such as the f -occupation, susceptibility, electronic specific heat and unit cell volume as functions of the position of the f -level, temperature, etc. Such numerical calculations were carried out for simple model systems and reported in Ref. 9 (although lattice effects were ignored there). We gain further insight into our model by neglecting the k -dependence of the hybridization matrix elements and assume the unperturbed conduction band is characterized by a constant density of states $\rho (= 1/W$ per spin).

Let us define an effective density of f-states $\tilde{n}_\sigma^f(\omega)$ such that

$$\langle n_\sigma^f \rangle = \int_{-\infty}^{+\infty} \tilde{n}_\sigma^f(\omega) f(\omega - \mu) d\omega ; \quad (2.13)$$

and let $n_\sigma^c(\omega)$ be the conduction electron density of states (DOS).

From Eq. (2.11) it may be shown that

$$\begin{aligned} n_\sigma^c(\omega) &= \rho; \tilde{n}_\sigma^f(\omega) = V^2 \langle Q_\sigma \rangle^2 \rho / (\omega - \epsilon_f^*)^2 \text{ for } \omega \text{ outside the gap } \Delta \\ n_\sigma^c(\omega) &= \tilde{n}_\sigma^f(\omega) = 0 \text{ for } \omega \text{ inside the gap } \Delta. \end{aligned} \quad (2.14)$$

with

$$\Delta = 4V^2 \langle Q_\sigma \rangle \rho, \quad (2.15)$$

and where

$$\langle Q_\sigma \rangle = 1 - \langle n_\sigma^f \rangle = 1 - \frac{1}{2} \langle n^f \rangle \quad (2.16)$$

for the paramagnetic case with zero applied field. The effective density of one-electron-like excitations is shown in Fig. 2. A peculiarity (compared to conventional one-electron DOS) is that the total number of available states is given by

$$\int_{-\infty}^{+\infty} [\tilde{n}_\sigma^f(\omega) + n_\sigma^c(\omega)] d\omega = 2[1 + \langle Q_\sigma \rangle] = 4 - \langle n^f \rangle \quad (2.17)$$

so that the maximum filling of these 4 hybridized bands (2 per spin) is with 3 electrons, not 4, as required by the correlation restriction of only one f-electron per site. It may also be shown that the total number of states in the lower band K^- satisfies $1 < K^- < 2$. Thus, at $T=0$, for one electron per unit cell, μ must always lie in the lower band; whereas for two electrons per unit cell, μ must lie in the upper band. This result was also obtained by Roberts and Stevens⁷. For the case of 2 electrons/cell, in the non-interacting case, μ would always lie in the gap. Thus the present result implies a violation of Luttinger's Theorem¹⁰ which states that the Fermi surface volume in the interacting case at $T=0$ should be identical to that in the non-interacting case, as has been emphasized by Martin¹¹. In the present model it may be shown for the paramagnetic case that

$$V_{FS} = V_{FS}^{(0)} + \frac{2\pi^3}{\Omega_a} \frac{\langle n^f \rangle^2}{[1 - 1/2 \langle n^f \rangle]}, \quad (2.18)$$

where V_{FS} is the volume inside the Fermi surface, $V_{FS}^{(0)}$ that in the non-interacting case, Ω_a the unit cell volume and $\langle n^f \rangle$ the average number of f-electrons per site. In the case where $\langle n^f \rangle = 1$, this would yield a difference corresponding to one electron exactly between V_{FS} and $V_{FS}^{(0)}$. In the full multiplet case the discrepancy between V_{FS} and $V_{FS}^{(0)}$ vanishes as $1/N$, however. Evaluation of $\epsilon_{f\sigma}^*$ defined in Eq. (2.6), gives using Eq. (2.11)

$$\epsilon_{f\sigma}^* = \epsilon_f - g\mu_B H\sigma - \frac{e\langle n^f \rangle}{B(V)} + V^2 \langle Q \rangle \ln \left| \frac{W}{\epsilon_{f\sigma}^* - \mu} \right|. \quad (2.19)$$

The second and third terms are merely the Zeeman and deformation potential terms respectively, while the last term yields a logarithmic upward renormalization of the f-level which has been found for the single-impurity problem previously^{4,5} and is similar to the general scaling result of Haldane⁶ for the single impurity.

The generalization of the above theory to the full N-fold multiplet case is quite straight forward, but will not be given here for reasons of space. The main point is that, as stated above, $\langle Q_{mm} \rangle$ becomes $O(\frac{1}{N})$. The hybridization of the multiplet with a single conduction band produces $(N+2)$ hybridized "bands", and the hybridization splitting of these bands is reduced by a factor of $O(\frac{1}{N})$. The f-levels thus can renormalize up towards the Fermi level or even above it.

While calculations for quantities such as the f-occupation, susceptibility, resistivity, etc. from the above model are qualitatively in agreement with experiment (at least in the strongly mixed-valence regime where $\epsilon_f^* \rightarrow \mu$), a rigorous justification for the above simple mean-field decoupling theory (e.g., from scaling ideas or other methods) is lacking. It is interesting to note, however, that for large N the above results become almost identical to those derived by Read and Newns¹² by completely different methods. Our present feeling is that there is some merit to carrying out detailed numerical calculations for a real (as opposed to a model) system with the full multiplet structure included, in the case of large N and in the strongly mixed valence limit. This has not as yet been done. In the Kondo regime, however, the above type of theory is clearly not good enough, and we shall discuss improvements to it in Section 4.

Fig. 1. Schematic of k -dependence of positions of poles of the one-electron Green's function from the mean-field theory.

Fig. 2. Effective densities of "f-like" and conduction-like states for our simple model obtained from the mean-field theory.

3. The Two-Particle Green's Function and the Dynamical Susceptibility

As is well-known¹³, the magnetic scattering of neutrons from a crystal is given by the scattering function

$$S(\vec{Q}, \omega) = f^2(\vec{Q}) [1 - e^{-\beta\hbar\omega}]^{-1} \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{Q}_\alpha \hat{Q}_\beta) \text{Im } \chi^{\alpha\beta}(\vec{q}, \omega) \quad (3.1)$$

where $\vec{Q}$ is the wavevector transfer of the neutron, $\hbar\omega$ its energy loss, $\hat{Q}$ is a unit vector along $\vec{Q}$, β is $1/kT$, $f(\vec{Q})$ is the magnetic form factor for the magnetic ions, and $\chi^{\alpha\beta}(\vec{q}, \omega)$ is the dynamical susceptibility at the reduced wavevector $\vec{q}$ and frequency ω . Let us consider only scattering by the f-electrons for our simple model system of spin $-1/2$ f-doublets. In the paramagnetic case, we need only consider $\chi^{+-}(\vec{q}, \omega)$, which may be related to the 2-particle Green's function by

$$\chi^{+-}(\vec{q}, \omega) = (g\mu_B)^2 \frac{1}{N} \sum_{\ell} \sum_{k_1 k_2 \sigma} \langle f_{k_1 + q \sigma}^+ f_{k_1 \sigma} ; f_{k_2 \sigma}^+ f_{k_2 + q \sigma} \rangle_\omega \quad (3.2)$$

We evaluate the Green's functions by the Equation-of-Motion Method. Let us consider the operators

$$\begin{aligned} N_1^+(k\sigma, q) &\equiv f_{k+q\sigma}^+ \cdot f_{k\sigma} ; & N_2^+(k\sigma, q) &\equiv c_{k+q\sigma}^+ \cdot f_{k\sigma} \\ N_3^+(k\sigma, q) &\equiv f_{k+q\sigma}^+ \cdot c_{k\sigma} ; & N_4^+(k\sigma, q) &\equiv c_{k+q\sigma}^+ \cdot c_{k\sigma} \end{aligned} \quad (3.3)$$

Define the general Green's function

$$G_{kk'\sigma\sigma'q}^{ij}(\omega) \equiv \langle N_i^+(k\sigma, q) ; N_j^+(k'\sigma', q) \rangle_\omega \quad (3.4)$$

In evaluating $[N_i^+(k\sigma, q), H]$ we may use the definitions (1.1) to treat products of many f operators on a single site exactly, but on different sites, we decouple four-operator products back down to two in all possible ways. We use the commutation relations given by Eqs. (1.4), and obtain

$$\begin{aligned} [N_1^+(k\sigma, q), H] &= (\epsilon_{f\sigma} - \epsilon_{f\bar{\sigma}}) N_1^+(k\sigma, q) + v_{k+q} \langle Q_\sigma \rangle N_2^+(k\sigma, q) \\ &\quad - v_k \langle Q_\sigma \rangle N_3^+(k\sigma, q) + \langle f_{k\sigma}^+ f_{k\sigma} \rangle \frac{1}{N} \sum_K v_{K+q} N_2^+(K\sigma, q) \\ &\quad - \langle f_{k+q\sigma}^+ f_{k+q\bar{\sigma}} \rangle \frac{1}{N} \sum_K v_K N_3^+(K\sigma, q) \\ &\quad - \{v_k \langle f_{k\sigma}^+ c_{k\sigma} \rangle - v_{k+q} \langle f_{k+q\sigma}^+ c_{k\bar{\sigma}} \rangle\} \frac{1}{N} \sum_K N_1^+(K\sigma, q) \end{aligned} \quad (3.5)$$

with similar equations for the commutators of H with N_2^+ , N_3^+ , N_4^+ . The last three terms in Eq. (3.5) arise from the kinematic restrictions to single occupation of the f-sites built into the f-operators, which we may term a "blocking effect". Substitution of Eq. (3.5) into the equations of motion leads to a set of four coupled integral equations for the $G_{kk',\sigma\sigma'}^{ij}(\omega)$, which can however be solved, since by Eq. (3.2) we need only $\sum_{kk',\sigma} G_{kk',\sigma\sigma}^{11}(\omega)$. The solutions for $\chi^{+-}(\vec{q},\omega)$ has the following structure

$$\chi^{+-}(\vec{q},\omega) = [\{1 + \pi(\vec{q},\omega)\}^{-1} \cdot \underline{Z}(\vec{q},\omega)]_1 \quad (3.6)$$

where $\pi(\vec{q},\omega)$ is a 4x4 matrix and $\underline{Z}(\vec{q},\omega)$ is a four-vector. These are functions of $\langle n_{k\sigma}^f \rangle$, $\langle n_{k+q\sigma}^f \rangle$, $\langle n_{k\sigma}^c \rangle$, $[\omega + E_{k\sigma}^+ - E_{k+q\sigma}^+]^{-1}$, etc.

$Z_1(\vec{q},\omega)$ is analogous to a single non-interacting band susceptibility for this two-band model, so that π gives an effective enhancement. The numerical calculations for $S(\vec{Q},\omega)$ are shown in Fig. 3, for a model fcc lattice of ions containing both f and conduction orbitals (with only nearest neighbor hopping integrals). The occupation numbers and bands were calculated from the self-consistent one-electron theory described in the last section. Two points should be noted. First, the enhancement effect due to the f-electron correlations is appreciable only in the dynamic regime $\omega \lesssim \Delta$, the hybridization gap ($\Delta \sim \pi V^2 \rho$). Secondly, in the strongly mixed-valence regime, $S(\vec{Q},\omega)$ exhibits a central peak and a peak at $\omega \sim \Delta$. The latter peak is a maximum when $\vec{q}$ is at the zone-boundary and decreases to zero intensity as $\vec{q} \rightarrow 0$, although it is essentially dispersionless. This is consistent with the gap being an indirect one, as may be seen from Fig. 1. This peak also broadens and decreases in intensity as (kT/Δ) increases. It is interesting to note that such qualitative behavior was found for the peak observed at 10 meV energy transfer in the inelastic neutron scattering from single-crystal paramagnetic ThSe by Grier and Shapiro¹⁴, although the simple two band model presented here is certainly a very crude representation of the more complex "band structure" in a real multiplet system. Finally, the central peak around $\omega = 0$ has a width which is fairly temperature insensitive, in agreement with neutron scattering experiments on mixed-valent systems¹⁵.

4. Incorporation of Fluctuations Effects in the One-Electron Green's Function

We may extend the theory given in Section 2 by using a higher-order decoupling procedure. Using Eq. (1.4c), we may write Eq. (2.4) as

$$[f_{k\sigma}, H] = \epsilon_{f\sigma}^* f_{k\sigma} + v_{k\sigma} c_{k\sigma} - \frac{1}{N} \sum_{j,k_1} v_{k_1} e^{-i(\vec{k}-\vec{k}_1) \cdot \vec{r}_j} [Z_{jk_1}^\sigma - S_{jk_1}^\sigma], \quad (4.1)$$

Fig. 3. $S(Q, \omega)$ for Q at the point $2\pi/a(1,0,0)$ for the model fcc Anderson lattice discussed in the text. The full curve denotes the calculation with the enhancement factor and the dashed curve the unenhanced $S(Q, \omega)$ for $kT/\Delta = 0.18$. The dot-dash curve shows the enhanced $S(Q, \omega)$ for $kT/\Delta = 1.76$.

Fig. 4. Effective densities of "f-like" and conduction-like states for an Anderson lattice with ϵ_f well below the Fermi-level from the one-electron Green's function including spin and charge fluctuation effects.

where we have assumed that $V_{k\sigma}$ is independent of σ . The operators Z and S are defined as

$$Z_{jk_1}^{\sigma} \equiv f_{j\bar{\sigma}}^+ f_{j\bar{\sigma}} c_{k_1\sigma} ; \quad S_{jk_1}^{\sigma} \equiv f_{j\bar{\sigma}}^+ f_{j\sigma} c_{k_1\bar{\sigma}} \quad (4.2)$$

The equations of motion which result from Eqs. (2.8) and (4.1) yield Green's functions involving Z and S . The procedure is to take next the equations of motion of these Green's functions and decouple operators which involve f -operators or c -operators on different sites, except those that occur in the combinations given in Eq. (4.2). In this way, we keep the effects of spin and charge fluctuations on an individual f -shell explicitly in the problem. The method is similar to that used by Nagaoka¹⁶ in his treatment of the single Kondo impurity, although in that case, charge fluctuations (given by the Z -operators cannot occur). The next result of this procedure is that Eq. (2.9) in the mean-field theory is replaced by

$$G_{kc}^{-1}(\omega) = \begin{pmatrix} \frac{\omega - \epsilon_{f\sigma}^*(\omega)}{\langle Q_{\sigma}(\omega) \rangle} & V_k \\ V_k^* & \omega - \epsilon_{k\sigma} \end{pmatrix} \quad (4.3)$$

i.e., the quantities $\epsilon_{f\sigma}^*$ and $\langle Q_{\sigma} \rangle$ in the mean-field theory now become complex and frequency-dependent. The explicit expressions for $\epsilon_{f\sigma}^*(\omega)$ and $\langle Q(\omega) \rangle$ are¹⁷

$$\epsilon_{f\sigma}^*(\omega) = \epsilon_{f\sigma} + \frac{1}{N} \lim_{\eta \rightarrow 0} \sum_k |V_k|^2 [\langle n_{k\bar{\sigma}}^c \rangle - \langle n_{k\bar{\sigma}}^f \rangle + \langle n_{\bar{\sigma}}^f \rangle] / [\omega + i\eta - \epsilon_k]; \quad (4.4a)$$

$$\langle Q_{\sigma}(\omega) \rangle = 1 - \langle n_{\bar{\sigma}}^f \rangle - \frac{1}{N} \lim_{\eta \rightarrow 0} \sum_k V_k^* \langle f_{k\bar{\sigma}}^+ c_{k\bar{\sigma}} \rangle / [\omega + i\eta - \epsilon_k]. \quad (4.4b)$$

The expectation values $\langle n_{k\sigma}^f \rangle$, etc. are still given by Eqs. (2.11), e.g.,

$$\langle n_{k\sigma}^f \rangle = \frac{1}{\pi} \int_{-\infty}^{+\infty} d\omega f(\omega - \mu) \text{Im} G_{k\sigma}^{ff}(\omega) \quad (4.5)$$

etc., and the self-consistent solutions of Eqs. (4.3) to (4.5), together with the condition (2.12) for the chemical potential leads to a set of coupled integral equations for $\epsilon_{f\sigma}^*(\omega)$ and $\langle Q_{\sigma}(\omega) \rangle$.

These integral equations are very hard to solve analytically, since they are highly singular as $\omega \rightarrow 0$ and $T \rightarrow 0$. We may, however, solve for $\epsilon_{f\sigma}^*(\omega)$ in the limit where $|W_1|$, $|W_2| \gg kT \gg V$, where W_1

and W_2 are respectively the lower and upper edges of the conduction band obtaining

$$\epsilon_f^*(\omega) = \epsilon_f + V^2 \rho [\phi_1(\omega) - \gamma] + i\pi f(\omega) + V^2 \pi \psi(\omega, W_1, kT), \quad (4.6)$$

where γ is a frequency-independent constant, which must be determined self-consistently from Eqs. (4.4), and

$$\psi(\omega, W_1, kT) \equiv \int_{W_1}^{\infty} dx \frac{f(x)}{x - \omega}. \quad (4.7)$$

Here $f(x)$ is the Fermi function $[e^{x/kT} + 1]^{-1}$.

In the limit $\omega \rightarrow 0$, the behavior of this solution is

$$\epsilon_f^*(0) \sim \epsilon_f + |\epsilon_f| \ln(T/T_k), \quad (4.8)$$

where

$$T_k = T_0 e^{-|\epsilon_f|/(V^2 \rho)}, \quad (4.9)$$

with $T_0 \sim W$.

This shows that even if the bare ϵ_f is well below the Fermi level, its renormalization at $\omega = 0$ (i.e., at the Fermi level) can bring the effective ϵ_f^* back up to the Fermi level, producing a sharp temperature-dependent resonance at the Fermi level. It can then be shown that the f DOS, $\tilde{n}_f(\omega)$, will have peaks both at $\omega \sim \epsilon_f$ and in the vicinity of the Fermi level (see Fig. 4). This is the lattice analogue of the so-called "many-body resonance" or Abrikosov-Suhl resonance in the case of the single impurity¹⁸. Similar results for the single impurity case have been derived by Lacroix and Cyrot¹⁹ and for the lattice case by Lacroix²⁰ and by Baumgartel and Muller-Hartmann.²¹ In order to see what happens in the more interesting low temperature region, the integral equations will have to be solved (probably numerically). This has not yet been done. Equations (4.4) also have to be generalized to the full multiplet case, where in analogy with the single impurity case, we expect the amplitude of the resonance at the Fermi level to be increased by a factor of N . The existence of this resonance for $T < T_k$ would be consistent with several experimental results for "dense^k Kondo" systems (see for example, the lectures by Wilkins⁽²²⁾ at this School) which is the limit of our Anderson lattice as ϵ_f sinks well below the Fermi level.

5. Correlation-Induced Pairing Instability

We may also use the Equation of Motion Method for the two-

particle Green's functions to investigate whether the Anderson Lattice Hamiltonian (1.5) has a Cooper-pairing type instability, which is not driven by the usual phonon-mediated attraction. In order to show this, we study the dynamical response functions for pair creation. These are related to the two-particle Green's functions of the form $\ll \tilde{N}_i^+(k, q) ; \tilde{N}_j(k', q) \gg$, where

$$\begin{aligned} \tilde{N}_1^+(k, q) &\equiv f_{k+q\uparrow}^+ f_{-k\downarrow}^+ ; & \tilde{N}_2^+(k, q) &\equiv c_{k+q\uparrow}^+ f_{-k\downarrow}^+ \\ \tilde{N}_3^+(k, q) &\equiv f_{k+q\uparrow}^+ c_{-k\downarrow}^+ ; & \tilde{N}_4^+(k, q) &\equiv c_{k+q\uparrow}^+ c_{-k\downarrow}^+ . \end{aligned} \quad (5.1)$$

If these response functions diverge for $q, \omega \rightarrow 0$ at some $T = T_c$, it means that there is a spontaneous formation of Cooper pairs, i.e., a pairing instability. Using a decoupling procedure similar to that described in Section 3 for the calculation of the spin response function (where products of several f -operators on the same site were treated exactly but different sites decoupled) we obtain equations of motion of the following form:

$$\begin{aligned} [\tilde{N}_1^+(k, q), H] &= (\epsilon_{f\sigma} + \epsilon_{f\bar{\sigma}}) \tilde{N}_1^+(k, q) + v_{k-q} \langle Q_{\bar{\sigma}} \rangle \tilde{N}_2^+(k, q) \\ &+ v_k \langle Q_{\sigma} \rangle \tilde{N}_3^+(k, q) - \sum_{\sigma} (\epsilon_{f\sigma}^* - \epsilon_{f\sigma}) \frac{1}{N} \sum_{k_1} \tilde{N}_1^+(k_1, q) \\ &+ [\langle n_{k+q\sigma}^f \rangle + \langle n_{f\bar{\sigma}}^f \rangle - 1 - \langle f_{j\sigma}^+ f_{j\sigma} \rangle] \frac{1}{N} \sum_{k_1} v_{k_1+q} \tilde{N}_2^+(k_1, q) \\ &+ [\langle n_{k+q\sigma}^f \rangle + \langle n_{k\bar{\sigma}}^f \rangle - 1 - \langle f_{j\bar{\sigma}}^+ f_{j\bar{\sigma}} \rangle] \frac{1}{N} \sum_{k_1} v_{k_1} \tilde{N}_3^+(k_1, q) . \end{aligned} \quad (5.2)$$

By summing this equation over k , we may show that $\langle \frac{1}{N} \sum_{k_1} \tilde{N}_1^+(k_1, q) \rangle$ is always identically zero as it must be since it corresponds to $\langle f_{i\uparrow}^+ f_{i\downarrow}^+ \rangle$. Thus, the decoupling scheme does not violate the restriction that two f -electrons cannot be on the same site. Hence the fourth term on the right of Eq. (5.2) vanishes. Similar equations may be written down for the other operators in Eq. (5.1), and the solution of the resulting equations for the Green's function yields a vanishing denominator if the following equation is satisfied for $T = T_c$

$$\begin{aligned} \frac{\langle Q \rangle}{N} \sum_k \frac{2v_k^2 \epsilon_k}{A_k A_k} \left[\frac{1}{2E_k^+} \tanh\left(\frac{\beta E_k^+}{2}\right) - \frac{1}{2E_k^-} \tanh\left(\frac{\beta E_k^-}{2}\right) \right] \\ + [\langle Q \rangle - 1] \frac{1}{N} \sum_k \frac{8v_k^2 \epsilon_k}{A_k(A_k^2 - A_k^2)} = 1 \end{aligned} \quad (5.3)$$

where we have dropped the spin index, $\beta_c \equiv 1/k_B T_c$,

$$A_k = \epsilon_f^* + \epsilon_k, \quad (5.4)$$

and $E_k^\pm$, A_k are defined in Eqs. (2.10).

An examination of the solutions of this equation reveal the following features: (1) No solution for T_c exists if the Fermi Level μ lies in the lower band E_k^- (i.e., if ϵ_f^* lies above μ). This would be the case for a system with one electron per unit cell. (2) T_c decreases rapidly as ϵ_f^* moves down below μ . Thus it is only in the strongly mixed-valent regime that T_c is largest. Insertion of typical values of V , conduction bandwidth W and $(\epsilon_f^* - \mu)$ yield T_c of the order of 1 K or less.

The primary instability is in the response of $(C_{k\uparrow}^+ f_{-k\downarrow}^+ - f_{k\uparrow}^+ C_{-k\downarrow}^+)$, i.e., singlet pairing between f-electrons and conduction electrons.

We ascribe this to an attractive interaction between these electrons of a form similar to the Schrieffer-Wolff²³ - $J \vec{\sigma} \cdot \vec{S}$ interaction in the Kondo regime and arising from the same physical origin. In the mixed-valence regime, however, there are f-electrons at the Fermi surface, and thus the attractive interaction leads to a pairing instability. The tendency towards instability with regard to singlet f-d pairing in mixed valence systems has also been discussed by DeMenezies,²⁴ who, however, considers the usual phonon mechanism as the source of the attractive interaction. Our theory has not considered possible pair-breaking mechanisms such as the real scattering of f-electrons by spin or charge fluctuations. One can only appeal to the experimental observation that Fermi-liquid behavior is estimated in these systems at low temperatures. The fluctuation theory of Section 4 can in principle be incorporated into our formalism but this has as yet not been carried out. One might expect that, even in the Kondo regime, a sharp resonance of f-like states at the Fermi level might lead once again to significant T_c 's due to the above mechanism. Further investigation of this pairing mechanism is necessary before one can attempt to identify it with what is observed in the recently discovered "heavy-fermion" superconductors.^{25,26}

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