PHASE TRANSITIONS IN HIGHLY-CORRELATED f-ELECTRON SYSTEMS WITH
FLUCTUATING VALENCE

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Prepared for

Third International Conference

on

Electronic Properties of Actinide Materials

Grenoble, France

August 30, 1979 - September 1, 1979

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

**Operated under Contract W-31-109-Eng-38 for the
U. S. DEPARTMENT OF ENERGY**

755/79/20

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FLUCTUATING VALENCE*

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Abstract :

A formalism is presented for treating electrons in highly- correlated spin-orbit coupled multiplet levels in f-shells, which are also hybridized with valence or conduction states. This is achieved by introducing operators which cause transitions between the configurations, but project out all other configurations. The Zwanzig-Mori projection operator technique is exploited to derive results for the electron Green's functions, which are then solved self-consistently. The lowest order self-consistent solutions bear a certain resemblance to unrestricted Hartree-Fock theory. Higher order terms exhibit Kondo-like singularities under certain conditions. It is shown that several phases, both configurational and magnetic, are possible depending on the relative values of the conduction electron bandwidth, the hybridization energy and the values of the Coulomb and exchange integrals.

The band theory of metals, in conjunction with the local density functional formation to account for exchange and correlation effects, has on the whole been very successful in explaining most of the properties of metallic systems, including the light actinide metals and compounds (1,2). However, in materials where the f-electrons are more localized and yet are still in the vicinity of the Fermi level, such as the rare earth metals and compounds of the so-called "mixed valence" type or the heavier actinides, correlation effects in the f-shells must be treated more carefully for a proper description of the possible phases (magnetic or non-magnetic) which result, and of their temperature dependence. The basic problem with a completely band like description is that it allows arbitrary numbers of electrons to hop into f-shells from conduction bands, thus allowing f^{n+1} , f^{n+2} , ...etc configurations which actually have drastically reduced probability due to the large correlation energy on the f-shell. Further, it is hard to build in directly the spin-orbit and Hund's Rule interactions on the f-shells which give rise to the familiar multiplet structure in the free ion.

Let us suppose that there are two configurations f^n and f^{n-1} between which it is possible for an f-shell to fluctuate without a large cost in correlation energy. The approach suggested here is to start with the full J-multiplet structure of these configurations as basis and hybridize the level $\{E_a(f^n) - E_a(f^{n-1})\}$ (the "atomic" f-electron excitation energy) with conduction band states, while projecting out all the configurations f^{n-2} , f^{n+1} , ...etc. This leads to a self-consistent "energy-band" like picture but with some important differences. For instance, all electrons do not obey Fermi-Dirac statistics as in the band picture. Localized f-electrons obey statistics which becomes Boltzmann-like as the f-level moves away from the Fermi energy. The kinematic restrictions on the filling of the f-shell can also give rise to phase transitions where the f-shell fills continuously or discontinuously as the f-level is lowered relative to the conduction bands (depending on the Coulomb interaction between the conduction electrons and f-electrons); or where the f-shells can polarize magnetically (even without the indirect exchange mechanism). As we shall see, the magnetic susceptibility also behaves quite differently with temperature from the Pauli susceptibility expected from a simple band model.

Let us assume for simplicity that the ground multiplet state of the atomic f^{n-1} configuration is a singlet. Let us label states of atomic f^n multiplet by α . (These may refer to crystal-field-split states if necessary). We define operators that create and annihilate an f-electron (or hole) in this configuration at site i, by

$$\left. \begin{aligned} c_{i,\alpha}^\dagger |f^{n-1}, i\rangle &= |f^n, \alpha, i\rangle \\ c_{i,\alpha} |f^n, \alpha, i\rangle &= |f^{n-1}, i\rangle \end{aligned} \right\} \quad (1)$$

but with the property that

$$c_{i,\alpha}^\dagger c_{i,\beta}^\dagger = c_{i,\alpha} c_{i,\beta} = 0 \quad (2)$$

thus projecting out all other configurations. The commutation rules for these operators are similar to those of other Fermion operators except that

$$[c_{i,\alpha}, c_{j,\beta}^\dagger]_+ = Q_{\alpha\beta}^i \delta_{ij} \quad (3)$$

where the quantum average of the operator $Q_{\alpha\beta}^i$ is

$$\langle Q_{\alpha\beta}^i \rangle = \delta_{\alpha\beta} [1 - \sum_{\gamma \neq \alpha} \langle n_{i,\gamma} \rangle] \quad (4)$$

We may now write the Hamiltonian as

$$\begin{aligned} \mathcal{H} = & \sum_{j\alpha} \epsilon_\alpha c_{j\alpha}^\dagger c_{j\alpha} + \sum_{ij} \sum_{\eta\eta_2\sigma} T_{ij}^{\eta\eta_2\sigma} a_{i\eta\sigma}^\dagger a_{j\eta_2\sigma} + \sum_{ij} \sum_{\eta\sigma\alpha} [V_{ij}^{\eta\alpha} a_{i\eta\sigma}^\dagger c_{j\alpha} + \text{c.c.}] \\ & + \sum_{i\alpha\beta} \sum_{\eta\eta_2\sigma\sigma'} [U_{\alpha,\eta\sigma,\beta,\eta_2\sigma'} - J_{\alpha,\eta\sigma,\eta_2\sigma'/\beta}] c_{i\alpha}^\dagger c_{i\beta}^\dagger a_{i\eta\sigma}^\dagger a_{i\eta_2\sigma'} \end{aligned} \quad (5)$$

where $a_{i\eta\sigma}^\dagger$ is the usual creation operator for a conduction electron in orbital η with spin σ on site i ; $T_{ij}^{\eta\eta_2\sigma}$ is the conduction electron hopping matrix element, $V_{ij}^{\eta\alpha}$ the hybridization matrix element with the f -level, U, J are the (intrasite) Coulomb and exchange integrals, and $E = [E(f^n, \alpha) - E(f^{n-1})]$. We may now calculate the one-electron Green's function, bearing in mind the peculiar commutation rules for the $c, c^\dagger$ operators (Eq. (3)). This is done using the Mori-Zwanzig Projection Operator formalism. We discuss here, for brevity, the lowest order (Mean-Field) result for the simplified case of an orbitally non-degenerate (spin doublet) f -level hybridizing with an orbitally non-degenerate (s -like) band with both spins. Let us label the space-and-time Fourier transforms of the (f - f) Green's function $\langle\langle c_{i,\uparrow}; c_{j,\uparrow}^\dagger(t) \rangle\rangle$ by $\Gamma_k^{\uparrow\uparrow}(\omega)$, and that of the (f - s) Green's function $\langle\langle a_{i,\uparrow}; c_{j,\uparrow}^\dagger(t) \rangle\rangle$ by $A_k^{\uparrow\uparrow}(\omega)$.

The result is the pair of equations

$$\begin{aligned} [\omega - \alpha_{k\uparrow}^{(f)}] \Gamma_k^{\uparrow\uparrow}(\omega) - \alpha_{k\uparrow}^{(s)} A_k^{\uparrow\uparrow}(\omega) &= \langle Q_{\uparrow\uparrow} \rangle = 1 - \langle n_{f\uparrow} \rangle \\ - \frac{\alpha_{k\uparrow}^{(s)}}{1 - \langle n_{f\uparrow} \rangle} \Gamma_k^{\uparrow\uparrow}(\omega) + [\omega - \alpha_{k\uparrow}^{(s)}] A_k^{\uparrow\uparrow}(\omega) &= 0 \end{aligned} \quad (6)$$

with a similar pair of equations for down spins, and for the (s - s) and (s - f) Green's functions.

In Eqs. (6)

$$\left. \begin{aligned} \alpha_{k\uparrow}^{(f)} &= \epsilon_f + U[\langle n_{f\uparrow} \rangle + \langle n_{f\downarrow} \rangle] - J\langle n_{f\uparrow} \rangle + \frac{1}{N} \sum_k V_k \langle m_{k\downarrow} \rangle [1 - \langle n_{f\downarrow} \rangle]^{-1} \\ \alpha_{k\uparrow}^{(s)} &= [1 - \langle n_{f\uparrow} \rangle] V_k + U\langle m_{\uparrow} \rangle - J[\langle m_{\uparrow} \rangle + \langle m_{\downarrow} \rangle] \\ \alpha_{k\uparrow}^{(s)} &= \epsilon_d(k) + U[\langle n_{f\uparrow} \rangle + \langle n_{f\downarrow} \rangle] - J\langle n_{f\uparrow} \rangle \end{aligned} \right\} \quad (7)$$

where $\epsilon_d(k)$ is the unhybridized s -band energy; V_k the Fourier transform of V_{ij}^{4f} , $\langle m_{\uparrow} \rangle = -\langle c_{i\uparrow}^\dagger a_{i\uparrow} \rangle$, $\langle m_{\downarrow} \rangle = -\langle c_{i\downarrow}^\dagger a_{i\downarrow} \rangle$ and $\langle m_{k\downarrow} \rangle$ is the Fourier transform of $-\langle c_{i\downarrow}^\dagger a_{ji} \rangle$. The solutions for the eigenvalues from Eq. (6) are

$$E_{k\uparrow}^{\pm} = \frac{1}{2} (a_{k\uparrow}^{(1)} + a_{k\uparrow}^{(3)}) \pm \frac{1}{2} [(a_{k\uparrow}^{(1)} - a_{k\uparrow}^{(3)})^2 + 4a_{k\uparrow}^{(2)2} / (1 - \langle n_{f\downarrow} \rangle)]^{1/2} \quad (8)$$

and the projected density of f-states

$$N_{f\uparrow}(\omega) = \frac{1}{\pi} \sum_k \left[(E_{k\uparrow}^+ - a_{k\uparrow}^{(3)}) / (E_{k\uparrow}^+ - E_{k\uparrow}^-) \delta(\omega - E_{k\uparrow}^+) + \frac{(E_{k\uparrow}^{(3)} - E_{k\uparrow}^-)}{E_{k\uparrow}^+ - E_{k\uparrow}^-} \delta(\omega - E_{k\uparrow}^-) \right] \quad (9)$$

etc. with similar equations for $N_{d\uparrow}(\omega)$ and for down-spins.

Finally the populations $\langle n_{f\uparrow} \rangle$, $\langle n_{f\downarrow} \rangle$, $\langle n_{d\uparrow} \rangle$, $\langle n_{d\downarrow} \rangle$ are obtained self-consistently from

$$\left. \begin{aligned} \langle n_{f\uparrow} \rangle &= [1 - \langle n_{f\downarrow} \rangle] \int d\omega N_{f\uparrow}(\omega) f(\omega) \\ \langle n_{f\downarrow} \rangle &= [1 - \langle n_{f\uparrow} \rangle] \int d\omega N_{f\downarrow}(\omega) f(\omega) \\ \langle n_{d\uparrow} \rangle &= \int d\omega N_{d\uparrow}(\omega) f(\omega) \\ \langle n_{d\downarrow} \rangle &= \int d\omega N_{d\downarrow}(\omega) f(\omega) \end{aligned} \right\} \quad (10)$$

where $f(\omega)$ is the Fermi function. The $\langle n_{f\uparrow} \rangle$, $\langle n_{f\downarrow} \rangle$ are calculated from

$$\langle n_{f\uparrow} \rangle = \frac{1}{N} \sum_k a_{k\uparrow}^{(2)} [f(E_{k\uparrow}^-) - f(E_{k\uparrow}^+)] / (E_{k\uparrow}^+ - E_{k\uparrow}^-) \quad (11)$$

etc. The main physical implications of the above equations are as follows :

(1) $[\langle n_{f\uparrow} \rangle + \langle n_{f\downarrow} \rangle]$ is restricted to be ≤ 1 . (2) The hybridization depends self-consistently on the occupation of the f-states. Thus if $\langle n_{f\uparrow} \rangle \rightarrow 1$, $\langle n_{f\downarrow} \rangle \rightarrow 0$ so that ($\downarrow$) electrons cannot hop into ($\downarrow$) states. Thus as $\langle n_{f\uparrow} \rangle$ increases, hybridization with ($\downarrow$) states will decrease, the ($\uparrow$) states will be lowered relative to the ($\downarrow$) states, providing a mechanism for cooperative spin polarization of the f-shells if f-level is near the Fermi energy (even in the absence of exchange).

Calculations have been performed for an fcc lattice with nearest neighbor (s-s) and (s-f) hopping, for various values of the s-band width (W), hybridization strength (V). Fig. 1 shows the self-consistent solutions for $\langle n_{f\uparrow} \rangle$, $\langle n_{f\downarrow} \rangle$ as ϵ_f is lowered relative to the s-band. One sees that the f-shell starts to fill and then polarizes magnetically, becoming non-magnetic again as ϵ_f goes well below the s-band. (The exchange interaction J was set = 0 for this calculation). Fig. 2 shows the behavior as V is increased. Finally, Figs. 3 and 4 show the behavior of the susceptibility as a function of T (calculated by adding a small magnetic field term to ϵ_f and ϵ_d and computing the induced polarization) for two different values of ϵ_f . At $\epsilon_f = 0.8$ (see Fig. 1) the f-shell is only slightly occupied but paramagnetic. At $\epsilon_f = 0.6$ it is more occupied and thus closer to a polarization instability. The $1/T$ behavior of χ at higher T in Figs. 3 and 4 is due to thermal sampling of increasingly f-like hybridized states above the Fermi level. At lower temperatures, the main contribution is from the conduction band states.

REFERENCES

1. D.D. KOELLING, this conference.
2. M.S.S. BROOKS, this conference.

FIGURE CAPTIONS

- Fig. 1 Populations of upspin (full line) and downspin f-states (dashed line) as unhybridized f-level is shifted relative to the s-band.
- Fig. 2 Same as Fig. 1 but with the hybridization ten times larger (and set equal to the conduction electron hopping matrix elements).
- Fig. 3 χ versus T for $\mathcal{E}_f = 0.6$ and conduction band width and hybridization corresponding to Fig. 1.
- Fig. 4 Same as Fig. 3 but with $\mathcal{E}_f = 0.8$.

Fig 1

Fig 2

$W=2.4$ $V=2$ U

$W=2.4$ $V=0.20$ $FF=0.6$