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New model for the mixed-valence phenomenon in rare-earth materials

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A model of a single rare-earth atom in a transition metal is derived, and terms describing screening of charge fluctuations in the resonant $l = 3$ scattering channels by the $l = 2$ channels are included. Using the Tomonaga approximation, in which charge fluctuations are represented by bosons, the screening channels are replaced by a boson field, and the model takes on a particularly simple form, the Anderson model of a magnetic impurity, now coupled to the boson field. The mean-field theory of this model suggests that, unlike in the original Anderson model, the impurity can be in a state of slowly fluctuating valence, which we identify with the mixed-valence phenomenon in certain rare-earth materials. These results suggest that the mixed-valence effect may be purely electronic in origin.

I. INTRODUCTION

Rare-earth atoms in certain solids are found to be in an unusual electronic state called "mixed valence"[1] where the valence of the atom is slowly fluctuating between two different charge states, on a time scale such that x-ray photospectroscopy measurements ($\tau \approx 10^{-18}$ sec) indicate a random "alloy" of the two configurations, and resolve the characteristic spectrum of each, while Mössbauer measurements ($\tau \approx 10^{-10}$ sec) show all the rare-earth atoms in the sample to be identical, with properties intermediate between those of the two pure configurations.

The mixed-valence state is understood to occur when the Fermi level is pinned to the narrow highly correlated band derived from the atomic transition $f^n \rightleftharpoons f^{n-1} + e^-$. The phenomenon has attracted much recent experimental and theoretical interest, but its nature has not yet fully been resolved; the review cited as Ref. 1 contains an extensive survey of the literature.

Two aspects of the problem may be separated: one is that of the nature of the metal-insulator transition from magnetic semiconductor to mixed-valence metal exhibited by chalcogenides such as SmS; the other is the understanding of the electronic state of the mixed-valence metal itself, best exemplified by alloys such as $CeAl_3$,[2] $YbAl_3$,[3] etc. Here we will be concerned with this latter question: the work presented here is part of an attempt to identify simple model systems that behave in ways that reproduce the experimental behavior of mixed-valence materials.

The model we present is an impurity model; we hope to learn about the properties of a rare-earth solid by examining the "dilute limit" of a single rare-earth impurity in a d-band material. If the f level is near the Fermi level, the behavior of the system will be dominated by resonant scattering in the $l = 3$ channels. The important new feature of this model, which will be shown to give rise to mixed-valence effects, is the inclusion of screening effects due to the $l \neq 3$ scattering channels (in particular $l = 2$, as the conduction band of the metal is a d band); this stabilizes $l = 3$ charge fluctuations, greatly enhancing their lifetimes.

To justify studying a model with a single rare-earth "impurity," and thus ignoring interactions between rare-earth atoms on different sites, we cite the experimentally observed behavior of $CeAl_3$.[2] As the material is cooled, the resistivity rises spectacularly to a maximum of 140 Ω cm at 37 K. A crude calculation of the maximum possible resistance of this material due to incoherent scattering at each site by resonance with the f orbital gives 188 Ω cm. Only at lower temperatures, below 10 K, does significant coherence between valence fluctuations on different sites develop, and the resistivity drops, eventually vanishing as T^2 when the material enters a Fermi-liquid regime. Unlike normal rare-earth materials, there is no apparent transition to magnetism at any temperature.

The interpretation we put on these observations is that two competing processes are at work, each with its own characteristic temperature: one involves valence fluctuations of the rare-earth atom, and may be studied in an impurity model; the other involves interactions between rare-earth atoms on different sites. In most materials, this has the higher characteristic temperature, which, as this process usually leads to magnetism, is the Néel temperature. The onset of magnetism stabilizes the configurations of the rare-earth atoms against spin fluctuations.

In mixed-valence materials, the fluctuations processes dominate, and, as the material is cooled, the fluctuation regime intervenes before any transition to a magnetic state is possible; in

this regime, the material can be regarded as a superposition of essentially independent impurities. One goal of a study of a single-impurity model should be the determination of the characteristic fluctuation temperature in terms of the model parameters. This involves difficulties similar to those encountered in the Kondo problem, and is postponed for later study.

The organization of this paper is as follows: In Sec. II, we set up a model of a rare-earth impurity in a d-band metal; in Sec. III, we discuss the symmetry reduction of models of an impurity in a periodic system, and in Sec. IV, apply this to our model. In Sec. V, we discuss the Tomonaga[4] approximation (in which charge fluctuations are represented by bosons) as applied to models of an impurity in a Fermi gas. In Sec. VI, we use this to simplify our model, and obtain it in its final form, which is just the Anderson[5] model of a magnetic impurity, generalized to include a linear coupling to a boson field. We have previously presented[6] a systematic study of this model in mean-field approximation, and we summarize the results in Sec. VII. In Sec. VIII, the discussion and summary, we indicate the relevance to the mixed-valence problem and note that a renormalization-group treatment of the model, in the spirit of the treatment of the Kondo[7] problem, is required.

II. MODEL OF A RARE-EARTH IMPURITY IN A d-BAND METAL

To set up a model complex enough to fully describe a rare-earth atom in a nonmagnetic transition metal would be a laborious task; the large number of intra-atomic exchange terms necessary to reproduce a realistic configurational spectrum for the rare-earth atom would only confuse the simple picture we are trying to convey. Our basic philosophy is to find the simplest model that includes enough features to reproduce mixed-valence behavior.

First, we discard the richness of the rare-earth atomic structure, and use a nondegenerate Anderson-model-type "extra orbital" for the f orbital of the impurity atom. Next, we retain only the d band of the host metal, regarding it as a tight-binding band, whose Wannier functions are the atomic d orbitals. We retain a degenerate band; this will turn out to be an important feature, as will be the different symmetries of the impurity-site Wannier functions (d orbitals) and the extra impurity orbital (a nondegenerate s-like orbital masquerading as an f orbital).

To the Hubbard-type correlation term between electrons in the impurity orbital which is the key feature of the Anderson model, we add a Falicov–Kimball-type[8] term describing correlation between the electrons in the impurity orbital and those in the impurity-site Wannier orbitals. This will give the screening effect mentioned in Sec. I: the coupling constant will not be left as a free parameter, but in Sec. IV, we will show how to fix it using the neutrality condition of the Friedel sum rule to ensure that the impurity charge is at all times (at least approximately) screened.

In the usual second-quantized fermion creation/destruction-operator formalism, the Hamiltonian describing the d band is

$$H^0=\sum_{\vec{k}\alpha\sigma}\epsilon_{\vec{k}\alpha}c^\dagger_{\vec{k}\alpha\sigma}c_{\vec{k}\alpha\sigma}, \tag{2.1}$$

$$c_{\vec{k}\alpha\sigma}=\frac{1}{\sqrt{N}}\sum_{im}e^{i\vec{k}\cdot\vec{R}_i}A_{\alpha m}(\vec{k})c_{im\sigma}, \tag{2.2}$$

where $\vec{k}$ is summed over the reduced Brillouin zone; $\alpha=1,\ldots,d_0$ is a band index, and the fermion operators $c^\dagger_{im\sigma}$ ($m=1,\ldots,d_0$) create particles in the d_0 Wannier orbitals on site i.

The impurity atom is described by

$$H^{\rm imp}=E_a\sum_\sigma n_{a\sigma}+Un_{a\uparrow}n_{a\downarrow}+g\sum_{m\sigma\sigma'}n_{0m\sigma}n_{a\sigma'}, \tag{2.3}$$

where $n_{a\sigma}=a^\dagger_\sigma a_\sigma, n_{0m\sigma}=c^\dagger_{0m\sigma}c_{0m\sigma}$; $a^\dagger_0$ creates a particle in the impurity orbital, and $c^\dagger_{0m\sigma}$ is the impurity-site Wannier-orbital creation operator. The correlation terms U,g describe the extra correlation due to the highly localized nature of the impurity f orbitals, over and above the correlation in the orbitals of the d band, which has notionally been removed from the problem by a Landau Fermi-liquid renormalization.

Finally we must include the small hybridization term between the impurity orbital and the band wave functions, which allows particles to hop in or out of the f level. This will be a very small term, since because of the different symmetries of the d and f orbitals, the f electron can only hop into the Wannier orbital on a neighboring site, not the impurity site itself, and the overlap with such sites is very small indeed. The hybridization term is

$$H^{\rm mix}=\sum_{\vec{k}\alpha\sigma}(V_{\vec{k}\alpha}c^\dagger_{\vec{k}\alpha\sigma}a_0+{\rm H.c.}). \tag{2.4}$$

It would be incorrect to make the usual simplification $V_{\vec{k}\alpha}=$ const; an electron can only hop from $a^\dagger_\sigma$ to a combination of the $c^\dagger_{\vec{k}\alpha\sigma}$ *having the same point symmetry* as the impurity orbital. This must be reflected in the $\vec{k}$ dependence of $V_{\vec{k}\alpha}$, and will be of vital significance to the development of the model; we return to this point in Sec. IV.

Without $H^{\rm mix}$, the Hamiltonian $H^0+H^{\rm imp}$ is in diagonal form, and the charge state of the impurity,

$n_a = 0$, 1, or 2, is a good quantum number. If the multiplicity of the bands, d_0, is large, the value of g necessary to satisfy the Friedel rule is small, and the individual phase shifts much less than π, so we can treat the scattering in linear (Born) approximation. We can then find a single value of g that ensures overall charge neutrality of the impurity, whatever charge state n_a it is in. Before we can find this value, we must first use symmetry to simplify the Hamiltonian.

III. POINT SYMMETRY AND THE IMPURITY PROBLEM IN A PERIODIC SYSTEM

In this section, we briefly review the generalization of partial wave analysis to *periodic* systems with an impurity center.[9] Consider a Hamiltonian of the form

$$H = H^0 + \sum_{\vec{k}\vec{k}'} v(\vec{k},\vec{k}') c^\dagger_{\vec{k}} c_{\vec{k}'}, \tag{3.1}$$

$$H^0 = \sum_{\vec{k}} \epsilon(\vec{k}) c^\dagger_{\vec{k}} c_{\vec{k}}, \tag{3.2}$$

which is invariant under the symmetry operations of point group $\mathcal{P}$, of order p. H^0 is also invariant under the operations of space group $\mathcal{S}$, of which $\mathcal{P}$ is a subgroup. For completeness, we can understand $\vec{k}$ here in the extended Brillouin zone representation, and it is summed over all $\vec{k}$ space. If P is an element of $\mathcal{P}$, $\epsilon(P\vec{k}) = \epsilon(\vec{k})$, and except at special symmetry points of measure zero in $\vec{k}$ space, each eigenstate $\vec{k}$ of H^0 is a member of a p degenerate set $\vec{k}^*$, the *star* of $\vec{k}$. (If $\mathcal{S}$ contains other point-symmetry operations not in $\mathcal{P}$, H^0 has other degeneracies which in this context are "accidental".) We can analyze $\vec{k}^*$ into irreducible representations of $\mathcal{P}$, labeled by Γ, with dimensionality d_Γ. To satisfy the group representation theory theorem.

$$\sum_\Gamma d_\Gamma^2 = p \tag{3.3}$$

each Γ must appear d_Γ times in $\vec{k}^*$. Each set $\{c^\dagger_{\vec{k}}\}$ belonging to $\vec{k}^*$ can be transformed into the new basis set $\{c^\dagger_{\Gamma\mu\vec{k}^*\lambda}\}$, where Γ labels the representation and $\mu = 1, \ldots, d_\Gamma$ its components; the index $\lambda = 1, \ldots, d_\Gamma$ is necessary as the representation appears with the frequency of its dimensionality.

In this new basis, H^0 takes the form

$$H^0 = \sum_{\Gamma\mu} H^0_{\Gamma\mu}, \quad H^0_{\Gamma\mu} = \sum_{\vec{k}^*\lambda} \epsilon(\vec{k}^*) n_{\Gamma\mu\vec{k}^*\lambda}, \tag{3.4}$$

where $\vec{k}^*$ is summed over the primitive fraction $1/p$ of $\vec{k}$ space, and n is the number operator $c^\dagger c$. The densities of states $\sigma^0_{\Gamma\mu}(\omega)$ satisfy

$$\sigma^0_{\Gamma\mu}(\omega) = \sum_{\vec{k}^*\lambda} \delta(\omega - \epsilon(\vec{k}^*)) = \frac{d_\Gamma}{p} \sigma^0_{\rm tot}(\omega). \tag{3.5}$$

In the context of a basis that reflects point group $\mathcal{P}$, this "accidental" proportionality between the densities of states of different representations is all that is visible of the underlying invariance of H^0 under $\mathcal{S}$.

Since H commutes with the elements of $\mathcal{P}$, symmetry quantum numbers $\Gamma\mu$ are conserved during scattering. Condensing $\vec{k}^*, \lambda$ into a single index i, H takes the form

$$H = \sum_{\Gamma\mu} H_{\Gamma\mu}, \tag{3.6}$$

$$H_{\Gamma\mu} = \sum_i \epsilon_{\Gamma i} n_{\Gamma\mu i} + \sum_{ij} v^\Gamma_{ij} c^\dagger_{\Gamma\mu i} c_{\Gamma\mu j}. \tag{3.7}$$

As only accidental degeneracy remains in $H_{\Gamma\mu}$, the scattering problem in each symmetry subspace has the character of a one-dimensional problem. As in the familiar spherically symmetric case, we can formally define "phase shifts" $\delta_\Gamma(\omega)$, through the change in density of states:

$$\Delta\sigma_{\Gamma\mu}(\omega) = \frac{1}{\pi}\frac{d}{d\omega}\delta_\Gamma(\omega), \quad \delta_\Gamma(-\infty) = 0. \tag{3.8}$$

As the wave functions do not have the simple exponential form of spherical waves, δ_Γ has no literal meaning as a "phase shift."

IV. SYMMETRY REDUCTION OF THE MODEL AND THE CHARGE NEUTRALITY CONDITION

Suppose that $a^\dagger_0$ belongs to the (singlet) irreducible representation Γ^0 of $\mathcal{P}$. Applying the results of the previous section, the Hamiltonian becomes

$$\begin{aligned} H = &\sum_{\Gamma\mu i\sigma} \epsilon_{\Gamma i} n_{\Gamma\mu i\sigma} + E_a \sum_\sigma n_{a\sigma} + U n_{a\uparrow} n_{a\downarrow} \\ &+ g \sum_\sigma n_{a\sigma} \sum_{\Gamma\mu ij\sigma} v^\Gamma_{ij} c^\dagger_{\Gamma\mu i\sigma} c_{\Gamma\mu j\sigma} \\ &+ \sum_{i\sigma} (v_i c^\dagger_{\Gamma^0 i\sigma} a_\sigma + \text{H.c.}). \end{aligned} \tag{4.1}$$

Using (2.2), (2.3) we find that $v^\Gamma_{ii} > 0$, and

$$\sum_{\Gamma\mu i} v^\Gamma_{ii} \delta(\omega - \epsilon_{\Gamma i}) = \sigma(\omega), \tag{4.2}$$

where $\sigma(\omega)$ is the conduction-band density of states projected onto the impurity site. In the limit $V_i = 0$ (all i), $n_a = 0$, 1 or 2 is a good quantum number. In Born approximation, for a given n_a, the phase shifts in the different scattering channels are given by

$$\delta_\Gamma(\omega) \simeq -\pi g n_a \sum_i v^\Gamma_{ii} \delta(\omega - \epsilon_{\Gamma i}). \tag{4.3}$$

In the charged-electron gas, the impurity must be exactly screened whatever the value of n_a; in our model with uncharged fermions and a short-range potential that mimics screening, we will pick g to satisfy the Friedel sum rule as accurately as possible. We must satisfy

$$n_a + \frac{1}{\pi} \sum_{\Gamma\mu\sigma} \delta_\Gamma(\epsilon_F) = 0. \tag{4.4}$$

From (4.3), we see that this is achieved in Born approximation if $2g\sigma(\epsilon_F) = 1$. When the density of states at the Fermi level is large, as in a d band, g will be small and the Born approximation should be valid. For small V_i this screening potential will act to effectively neutralize the slow fluctuations of n_a.

The set of impurity-site Wannier functions may be analyzed into irreducible representations of $\mathcal{O}$. In the event that Γ^0 is not contained in this set, another important simplification is possible, as then v_{ij}^Γ will be zero when $\Gamma = \Gamma^0$ and there will be no interference between the resonant scattering via the f level and scattering in the other channels by the screening potential g. This will be the case if, for instance, $\mathcal{O}$ contains an inversion center, as then irreducible representations are labeled by parity, and $l = 2$ ($\{c_{0m}^\dagger\}$) and $l = 3$ (Γ^0) wave functions have opposite parity. If Γ^0 is contained in the set of Wannier functions, the properties of the model will not be qualitatively changed, but an unnecessary complication will be introduced. From here on, we will assume that this is not the case, and the model takes the form:

$$H = H^f + H^d, \tag{4.5}$$

$$H^f = \sum_{i\sigma} \epsilon_{\Gamma^0 i} n_{\Gamma^0 i\sigma} + E_a \sum_\sigma n_{a\sigma} + U n_{a\uparrow} n_{a\downarrow} + \sum_{i\sigma} (V_i c_{\Gamma^0 i\sigma}^\dagger a_\sigma + \text{H.c.}), \tag{4.6}$$

$$H^d = \sum_{\Gamma\neq\Gamma^0,\mu\sigma} \left[\sum_i \epsilon_{\Gamma i} n_{\Gamma\mu i\sigma} + \left(g \sum_{\sigma'} n_{a\sigma'} \right) \times \sum_{ij} v_{ij}^\Gamma c_{\Gamma\mu i\sigma}^\dagger c_{\Gamma\mu j\sigma} \right], \tag{4.7}$$

and

$$g \sum_{\Gamma\neq\Gamma^0,\mu i\sigma} v_{ii}^\Gamma \delta(\omega - \epsilon_{\Gamma i}) = \frac{\sigma(\omega)}{\sigma(\epsilon_F)}. \tag{4.8}$$

We recognize (4.6) on its own as just the nondegenerate Anderson model; the new feature is H^d, acting in an *entirely different subspace* to screen charge fluctuations in the impurity orbital. A naive extension of the Anderson model might omit this feature entirely; in its usual form the Anderson model has been implicitly symmetry-reduced, and the necessity for the reintroduction of the discarded channels is not explicitly apparent. A model with a screening term added only in the Γ^0 subspace has entirely different characteristics, and will not show the mixed-valence properties we describe later.

As it stands, H^d is adequate to describe the screening response, provided g is small enough so that a linear approximation can be made. In that case, it is possible to transform H^d into a simpler, if less physically transparent, form which is just as good for representing the effects of screening in a truly charged electron gas. This is the Tomonaga[4] approximation, in which fermion particle-hole pairs in the subspace described by H^d are replaced by bosons. If properly chosen, the boson field used to describe screening will still include all the infrared problems associated with the low-frequency response of systems with a free Fermi surface. (This is discussed in Sec. V.) The part that lattice relaxation plays in screening in real materials can also be simply included in the boson picture.

On these grounds, instead of discussing the model (4.5)–(4.7) directly, we will make the Tomonaga transformation. This choice is partly a matter of taste; no precision is lost by it, as (4.7) is itself only an approximation to screening, and we feel that some useful simplification results.

V. THE TOMONAGA-BOSON APPROXIMATION APPLIED TO IMPURITY MODELS

In the Tomonaga[4] approximation, the collective excitation modes of a Fermi gas are represented by a set of boson modes. The usual formulation[4] deals with an interacting Fermi gas in one dimension, and is mainly used for the investigation of possible superconducting states of such a system. Tomonaga formulations of impurity problems[10] have previously been achieved by using this "one-dimensional" formalism, which relies on a special type of band structure (a "flat" density of states with sharp cutoffs, reflecting a linearized dispersion relation about the Fermi level), and uses momentum variables. We now reformulate the method for impurity systems with an arbitrary density of states, using energy variables.

Consider the general scattering problem

$$H^0 = \sum_i \epsilon_i c_i^\dagger c_i, \quad H = H^0 + \sum_{ij} v_{ij} c_i^\dagger c_j. \tag{5.1}$$

This is not, in general, soluble in closed form unless the scattering potential is *separable*, $v_{ij} = g v_i^* v_j$.

We define the charge fluctuation operator $\rho(E)$

$$\rho(E) = \sum_{ij} v_{ij} \delta(\epsilon_i - \epsilon_j + E)(c_i^\dagger c_j - \langle c_i^\dagger c_j \rangle_{H^0}), \tag{5.2}$$

$$\int_{-\infty}^{\infty} dE\,\rho(E) = \sum_{ij} v_{ij}(c_i^\dagger c_j - \langle c_i^\dagger c_j\rangle_{H^0}), \tag{5.3}$$

where $\langle\ \rangle_{H^0}$ denotes the expectation value in the system described by H^0. This operator has the properties $\rho^\dagger(E) = \rho(-E)$, and

$$[\rho(E), H^0] = E\rho(E). \tag{5.4}$$

The commutation relations seem complicated:

$$[\rho(E), \rho(E')] = \sum_{ijk} v_{ik}v_{kj} \times [\delta(\epsilon_i - \epsilon_k + E)\delta(\epsilon_k - \epsilon_j + E') - \delta(\epsilon_i - \epsilon_k + E')\delta(\epsilon_k - \epsilon_j + E)]c_i^\dagger c_j. \tag{5.5}$$

Nevertheless, they are essentially bosonlike, as we see by taking the expectation value of the commutator in H^0

$$\langle[\rho(E), \rho(E')]\rangle_{H^0} = \delta(E + E')\sum_{ij} |v_{ij}|^2\delta(\epsilon_i - \epsilon_j + E) \times (\langle n_i\rangle_{H^0} - \langle n_j\rangle_{H^0}). \tag{5.6}$$

By normalizing ρ, we can define the bosonlike operator $\phi(E)$, $E > 0$

$$\phi(E) = \rho(E)/\alpha(E). \tag{5.7}$$

$$\langle[\phi(E), \phi^\dagger(E')]\rangle_{H^0} = \delta(E - E'),$$
$$\langle[\phi(E), \phi(E')]\rangle_{H^0} = 0. \tag{5.8}$$

By comparison with (5.6),

$$|\alpha(E)|^2 = \sum_{ij} |v_{ij}|^2\delta(\epsilon_i - \epsilon_j + E)(\langle n_i\rangle_{H^0} - \langle n_j\rangle_{H^0}). \tag{5.9}$$

As $E \to 0$, for low temperatures,

$$\frac{|\alpha(E)|^2}{E} \to \text{const} = \left(\frac{\delta_B(\epsilon_F)}{\pi}\right)^2 + O(T^2), \tag{5.10}$$

where $\delta_B(\omega)$ is the fermion phase shift of (5.1), in Born approximation [Eq. (4.3)]. The spirit of the Tomonaga approximation is to adopt the simpler "mean" commutation relations (5.8), and treat the ϕ as exact boson operators. From (5.4) we see that H^0 must take the form (5.11), and the Hamiltonian becomes

$$H^0 = E^0 + \int_0^\infty dE\,E\phi^\dagger(E)\phi(E), \tag{5.11}$$

$$H = H^0 + \sum_i v_{ii}\langle n_i\rangle_{H^0} + \int_0^\infty dE[\alpha(E)\phi(E) + \text{H.c.}]. \tag{5.12}$$

In less cumbersome notation, changing from a continuous to a discrete energy variable,

$$H = \langle H\rangle_{H^0} + \sum_i \omega_i\phi_i^\dagger\phi_i + \sum_i (\alpha_i\phi_i + \text{H.c.}), \tag{5.13}$$

$$\sum_i |\alpha_i|^2\delta(E - \omega_i) = |\alpha(E)|^2, \tag{5.14}$$

$$[\phi_i, \phi_j^\dagger] = \delta_{ij}, \quad [\phi_i, \phi_j] = 0. \tag{5.15}$$

To test the Tomonaga approximation, we note that the separable-potential problem is exactly soluble in both formulations: We find that the Tomonaga solution is an expansion of the true solution to lowest order, that is, Born approximation. This is best seen by examining the diagrammatic linked-cluster expansion for the free energy (Fig. 1). The Tomonaga approximation evidently exactly reproduces the first- and second-order diagrams, but entirely omits all higher terms. It is thus a small coupling-constant approximation, and will be valid provided perturbation theory is not divergent.

As it faithfully reproduces the second-order diagrams, the Tomonaga approximation reproduces the "orthogonality" or infrared catastrophe[11] associated with these (and higher order) terms. The Anderson "orthogonality theorem" asserts that there is no overlap between the ground state of an infinite system of fermions with a free Fermi surface, and the new ground state in the presence of any finite scattering potential. This is because, however weak the potential is, it will, if we wait long enough, excite an infinite number of essentially zero-energy particle-hole pairs. In the Tomonaga representation, this appears as a divergence in the *occupation* of the lowest-energy boson modes, in such a way that the total *energy* associated with these modes remains finite and vanishes as the strength of the scattering potential is reduced to zero.

The ground state of (5.13) is related to that of H^0 by

$$|0\rangle_H = \exp\left(-\frac{1}{2}\sum_i \frac{|\alpha_i|^2}{\omega_i^2}\right)\exp\left(-\sum_i \frac{\alpha_i}{\omega_i}\phi_i^\dagger\right)|0\rangle_{H^0}. \tag{5.16}$$

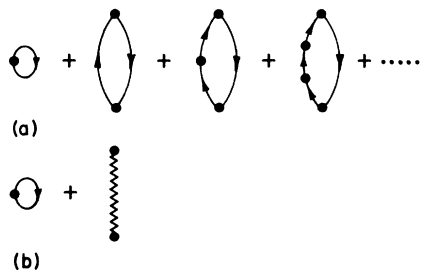

FIG. 1. Linked cluster expansion for (a) the scattering problem (5.1); (b) its Tomonaga representation.

The overlap is given by

$$ {}_H\langle 0|0\rangle_{H^0} = \exp\left(-\frac{1}{2}\sum_i \frac{|\alpha_i|^2}{\omega_i^2}\right) = \exp\left(-\frac{1}{2}\int_0^\infty dE \frac{|\alpha(E)|^2}{E^2}\right). \tag{5.17} $$

Because $|\alpha(E)|^2$ is linear as $E \to 0$, (5.10), the integral has a logarithmic infrared divergence; if the spectrum is discrete on a scale (bandwidth)/N, the overlap vanishes as $N^{-\epsilon}$, where $|\alpha(E)|^2 \sim 2\epsilon E$ as $E \to 0$. The vacuum amplitude $\langle 0|e^{iH^0 t}\, e^{-iHt}|0\rangle_{H^0}$, which is the amplitude for the system still to be in the ground state of H^0 time t after the scattering potential has been switched on, also shows this behavior

$$ \langle 0|e^{iH^0 t}\, e^{-iHt}|0\rangle_{H^0} = \exp\left(-i\sum_i \frac{|\alpha_i|^2 t}{\omega_i}\right) \times \exp\left(-\sum_i \frac{|\alpha_i|^2 \sin^2(\omega_i t/2)}{\omega_i^2}\right). \tag{5.18} $$

This is suppressed as $t^{-\epsilon}$ at large times, as the system relaxes around the scatterer. (This amplitude is related to the x-ray problem, as discussed by Schotte and Schotte,[10] and is the sum of closed-loop diagrams in that problem.)

Finally, a word of caution on the Tomonaga approximation as described here. If the scatterer has an internal degree of freedom that may be changed by scattering, and a degenerate ground state, higher-order terms diverge, perturbation theory does not work, and the Tomonaga approximation is not valid. The above procedure, with small modifications, can be applied to the Kondo model, for example, but the resulting model, a spin coupled to a *vector* boson field, no longer shows the Kondo effect. Other Tomonaga approaches to the Kondo problem, based on splitting the scattering potential into "direct" and "spin-flip" terms, including the "direct" term in H^0 and expressing *single* fermions (as well as pairs) in terms of bosons, are apparently more successful, but somewhat problematical.[12]

VI. TOMONAGA REPRESENTATION OF OUR MODEL

Applying these results to H^d (4.7), we define a boson field for each channel and take the linear combination of these modes describing fluctuations of total charge in all the screening channels. The Tomonaga approximation is valid as scattering in these channels cannot change n_a. Our model becomes just the standard Anderson model with a linear coupling to a boson field.

$$ H = \sum_{i\sigma} \epsilon_i n_{i\sigma} + E\sum_\sigma n_{a\sigma} + U n_{a\uparrow} n_{a\downarrow} + \sum_i \omega_i \phi_i^\dagger \phi_i + g\sum_\sigma n_{a\sigma} \sum_i (\alpha_i \phi_i + \text{H.c.}) + \sum_i (V_i c_{i\sigma}^\dagger a_\sigma + \text{H.c.}), \tag{6.1} $$

where

$$ E = E_a + g\sum_{m\sigma} \langle c_{0m\sigma}^\dagger c_{0m\sigma}\rangle_{H^0} \tag{6.2} $$

and we define the odd function

$$ f(\omega) = g^2 \sum_i |\alpha_i|^2 [\delta(\omega-\omega_i) + \delta(\omega+\omega_i)] = g^2 \sum_{\Gamma\mu ij\sigma} |v_{ij}^\Gamma|^2 \delta(\epsilon_{\Gamma i} - \epsilon_{\Gamma j} + \omega) \times (\langle n_{\Gamma\mu i\sigma}\rangle_{H^0} - \langle n_{\Gamma\mu j\sigma}\rangle_{H^0}). \tag{6.3} $$

For $\omega >$ (d bandwidth), $f(\omega)$ is zero, and as $\omega \to 0$,

$$ f(\omega) \sim 2\epsilon\omega = \omega \sum_{\Gamma\mu\sigma} \left(g\sum_i v_{ii}^\Gamma \delta(\epsilon_F - \epsilon_{\Gamma i})\right)^2 \quad (T=0). \tag{6.4} $$

The charge neutrality condition (4.8) implies

$$ \sum_{\Gamma\mu\sigma} \left(g\sum v_{ii}^\Gamma \delta(\epsilon_F - \epsilon_{\Gamma i})\right) = 1, \tag{6.5} $$

and as $g v_{ii}^\Gamma \geq 0$, we have the inequality $1/4p < \epsilon < \frac{1}{2}$. Each of the $2d_0$ impurity-site Wannier functions is associated with a different scattering channel. If the crystal-field splitting is weak, each of these channels has the same phase shift, and $\epsilon \sim 1/4d_0$. The derivation assumed that scattering was weak in all channels; in that case ϵ must be small: This is satisfied for large d_0.

The model is completely specified by the quantities E, U, $f(\omega)$, and $\Delta(\omega)$, where

$$ \Delta(\omega) = \pi \sum_i |V_i|^2 \delta(\omega - \epsilon_i). \tag{6.6} $$

Two parameters are needed to describe $f(\omega)$: the cutoff or bandwidth, and the linear slope for small ω. $\Delta(\omega)$ can be characterized by one parameter, its value at ϵ_F. No cutoff in $\Delta(\omega)$ is required for the model to be well-behaved (apart from a divergent ground state energy shift, independent of U, g, which can be subtracted).

A simple "canonical" choice for the model might be

$$ f(\omega) = 2\epsilon\omega\theta(D - |\omega|), \tag{6.7} $$

$$ \Delta(\omega) = U_c/\pi. \tag{6.8} $$

This last is standard for the Anderson model; U_c/π is the resonance width of the impurity orbital, and no magnetism appears in mean-field theory for

$U < U_c$. D is the effective d bandwidth, and $\epsilon \approx 1/(4d_0)$, where d_0 is the multiplicity of the band ($\epsilon \approx 0.05$ for a d band).

Finally, we note that $f(\omega)$ is in principle temperature dependent [see (5.10), for example]; when using the Tomonaga model to derive the temperature dependence of the properties of the original model, (4.5), this should be taken into account. However, the Fermi-liquid theory implicit in (4.5) is itself temperature dependent, so we may as well neglect the temperature dependence of $f(\omega)$, and regard (6.1) as our fundamental model.

VII. RESULTS OF A MEAN-FIELD THEORY TREATMENT OF THE MODEL

The properties of (6.1) in mean-field approximation have been systematically explored in Ref. 6. The only role played by the boson field in this approximation involves its static relaxation in response to the mean charge in the impurity orbital. This gives rise to an effective attractive interaction C between particles in the extra orbital:

$$C = 2g^2 \sum_i \frac{|\alpha_i|^2}{\omega_i} = 4\epsilon D. \tag{7.1}$$

Mean-field properties can be characterized by four parameters: E (measured from the Fermi level), U, C, and $U_c(T)$, where $U_c(0) = U_c$ [Eq. (6.8)], and $U_c(T)$ is an increasing function of temperature; for $T \gg U_c(0)$, $U_c(T) \simeq 4T$. As these parameters are varied, various "phase transitions" occur, and in Fig. (2) we present phase diagrams of the mean-field states of the model. Though artifacts of the approximation, these phase transitions mark regions of transition between qualitatively different regimes of the model.

The main features of Fig. 2 are (i) a "magnetic" region (shaded) where the mean-field solution has broken spin-rotation symmetry, characterized by a vector "order parameter" $\langle \vec{S}_a \rangle \neq 0$, where $\langle \vec{S}_a \rangle$ is the mean-spin polarization of the impurity orbital; (ii) first-order phase transitions (full lines), across which the mean impurity charge $\langle n_a \rangle$ is discontinuous. These may either be between two nonmagnetic states, or between "magnetic" and nonmagnetic states, in which case $\langle \vec{S}_a \rangle$ is also discontinuous; (iii) the transition to magnetism, as it involves breaking symmetry, may also be second order (broken lines). For $U_c \ll C$ [Fig. 2(a)], all transitions are first order; for $U_c \gg C$ [Fig. 2(d)], which is the Anderson model limit, all transitions are second order. Figures 2(b) and 2(c) show how these two limiting cases pass into one another. As the effective U_c increases with temperature, Figs. 2(a)–2(d) also indicate how the mean-field solutions change as temperature is raised.

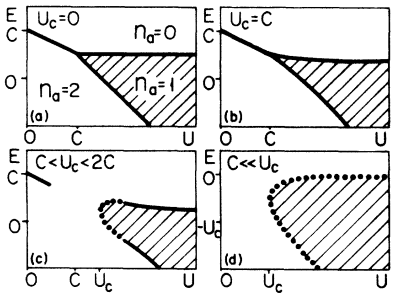

FIG. 2. Mean-field theory phase diagrams in the (E, U) plane for the Anderson model coupled to a boson field, (6.1). Note "magnetic" region (shaded), first-order phase transitions (full lines), and second-order transitions (broken lines). C is the effective attraction between electrons mediated by the bosons; U_c is a measure of the resonance width of the impurity orbital.

Apart from the singular case $U_c = 0, T = 0$ (where mean-field theory is exact), all these phase transitions are spurious. Fluctuating regimes intervene between different "phases," restoring continuity. The system remains nonmagnetic, and full spin rotation symmetry is maintained in the "magnetic" regime by the slow precession of the mean-spin-vector $\langle \vec{S}_a \rangle$; we identify this as the Kondo effect. Slow charge fluctuations restore continuity in the neighborhood of "first-order transitions"; this we identify with the mixed-valence effect.

This fluctuating behavior is not reproducible by simple perturbation theory in U_c, which, since the frequency has smooth but nonanalytic dependence on U_c, is divergent in the limit $V_i \to 0, T \to 0$ (that is, $U_c \to 0$). In this limit, in the neighborhood of the phase transitions, the behavior as $U_c \to 0$ depends qualitatively on whether C is finite or equal to zero (Anderson model), since in the former limiting case $C \gg U_c$, while in the latter $U_c \gg C$.

Away from the magnetic region and the phase boundaries, the mean-field solutions are essentially correct; to obtain the true low-temperature behavior in the anomalous regions, sophisticated renormalization treatments are needed to expose the non-analytic dependence on U_c as it goes to zero.

VIII. DISCUSSION

Physically, as the f orbitals are highly localized, their correlation term will be large, and their hybridization with the d band small, so we expect $U_c \ll C \ll U$. In this regime mean-field theory predicts magnetism for $0 > E - \frac{1}{2}C > -(U - C)$, with first order transitions separating magnetism and nonmagnetic states as E is varied. A discontinuity in impurity charge is associated with these transitions, and in Ref. 6, we showed that in a compo-

site system regarded as an ensemble of isolated impurities — the "dilute" limit of a rare-earth solid — the Fermi level may be pinned so as to place the equivalent impurity system exactly on a first-order phase boundary.

The long-time low-energy behavior associated with the resulting mixed-valence state involves a complex interplay of charge and spin fluctuations; both the fermion and boson systems have potentially singular low-energy properties (for example, the factor $t^{-\epsilon}$ characterizes the long-timescale boson response to charge fluctuations in the impurity orbital). The evaluation of the quantities equivalent to the Kondo timescale[7] T_K awaits a suitable renormalization-group treatment of the model: work on this is in progress.

The actual problem of the rare-earth solid with an "impurity orbital" at *each* lattice site is much more complex. We may expect slow valence fluctuations between different charge states similar to those we find in the single-impurity case; however coherence between fluctuations on different sites may be expected to develop at low temperatures.

It is often conjectured that phonons play a vital role in the mixed-valence phenomenon. Nevertheless, the fact that the model considered here apparently mimics the effect when the screening by other electron scattering channels is treated suggests that the phenomenon may be essentially an electronic effect, though no doubt greatly modified by the strong phonon coupling to valence fluctuations.

To summarize our results: we generalized the Anderson model of a magnetic impurity to include a term allowing screening of the charge in the impurity orbital so as to satisfy the Friedel sum rule. The model then described coupling between the $l = 3$ (resonant impurity scattering) channels and the $l = 2$ (screening) channels. Using the Tomonaga approximation, we showed that the screening terms was equivalent to a linear coupling to a certain boson field. We have previously treated the resulting model (Anderson model coupled to bosons) in mean-field approximation, and we discussed these results, indicating how they implied mixed-valence behavior (not present in the Anderson model without screening) for certain values of the model parameters. These long-timescale valence fluctuations were associated with an infrared divergence of perturbation theory, and further elucidation of their properties was postponed until a suitable renormalization-group treatment had been carried out. Work on this is now in progress. These results suggest that the mixed valence effect in certain rare-earth compounds may be essentially purely electronic in origin.

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