New approach to the theory of intermediate valence.
I. General formulation

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We present a new approach to the theory of intermediate valence, applicable to a specific kind of such solids. It consists of: (i) diagonalization of all intra-atomic terms in the Hamiltonian, including hybridization; (ii) elimination by means of a projection of all states beyond a low-energy manifold; (iii) conversion of the remaining states into equivalent fermion states; (iv) expression of the intra- and interatomic states in terms of the new fermion operators; and (v) treatment of this new Hamiltonian in a mean-field approximation. This approach, although valid in restricted cases, avoids all the problems of the alternative treatments.

I. INTRODUCTION

The phenomenon of intermediate valence has received much attention in the last few years, and has been the subject of recent reviews[1,2] and conferences.[3,4] It occurs in solids with highly correlated f states, in which the occupation of those states is neither fixed, as in atoms or molecules, nor bandlike in character like in more conventional s-, p-, and d-like solids. The proximity in the energy of two configurations, $(4f)^n$ and $(4f)^{n+1}$, the large energy required to excite any of the other configurations and the sizeable hybridization mixing of the f states and the ordinary band states (originating from s, p, and d orbitals), give rise to a multiplicity of effects. The most important ones are[3]: (i) the presence of two well-defined f-electron spectra, as observed, e.g., by electron photoemission, (ii) lattice parameters and other static or quasistatic parameters which do not follow the systematic behavior of well-defined valence states and which fall at intermediate values, (iii) the likelihood of phase transitions induced by pressure, temperature, or alloying effects, and (iv) unusual magnetic susceptibilities and specific heats.

The cause of these uncommon properties lies in the competing effects of three types of energies: (a) the strong electron-electron repulsion in the f shell which makes it unfavorable to have more than two configurations; $(4f)^n$ and $(4f)^{n+1}$, (b) the strong solid-state effects which completely delocalize the conduction-electron states, and (c) the hybridization effects which, to a given degree of strength, mix the f- and conduction-band states.

It is interesting to note that any two of these effects are more or less routinely taken into account when studying ordinary phenomena: (b) and (c) together are the ordinary basis of band theory; (a) and

(c) are routinely used in studying atomic effects in a crystal field; and (a) and (b) together are the basis for studying ordinary rare-earth compounds with well-defined f-state occupations.

When all three of these effects are present, serious difficulties appear. One way of attacking them, in the spirit of the Hubbard Hamiltonian,[5] is to solve the band problem [(b) and (c)] to any degree of accuracy, and then include correlations as an afterthought. This has not been thus far a very fruitful approach. A different way of facing the problem, the independent-manifold approach, consists of separating f and band states completely [(a) and (b)] and then include the hybridization as a perturbation. This has been a successful approach to study phase transitions,[6] but is not very convenient for looking at other properties,[7] except at high temperatures.[8]

In this paper we start from a third approach, the so-called atomic limit. We include all f-state correlations and f-to-band-states hybridization locally, and add the solid-state band-spreading effects *a posteriori*. By means of a projection technique (valid only under some well-defined conditions) we eliminate all states of unacceptable configuration and those with unfavorable energies, and, when intersite band terms are included, we obtain an effective Hamiltonian for new fermion operators. This contains, in addition to the ordinary band contribution, two- and three-particle interaction terms. This new fermion Hamiltonian can be treated by ordinary methods of many-body physics, in particular decoupling schemes related to the Hartree-Fock and analogous mean-field approximations.

It is interesting to discuss at this point the relative strength of the various energies involved in this problem. We denote by: U_{ff} the electron-electron repulsion in the f shell; E the energy difference

between the two relevant configurations $(4f)^{n+1}$ and $[(4f)^n$ conduction electron]; t the conduction-electron hopping energy; V the f-electron—conduction-electron hybridization energy; t_{ff} the single-f-electron hopping energy; u_{fd} the average f-electron—conduction-electron interaction energy; z the number of nearest neighbors (coordination number); and ν the total number of electrons per atom in excess of n.

The conventional band approach to mixed-valence systems assumes[3,9,10]

$$U_{ff} \gg 2zt \gg E,V,u_{fd} \gg t_{ff} \ .$$

Under all conditions for rare-earth compounds t_{ff} is a very small quantity and can be neglected; we do so in our theory. It should be kept in mind however that it may be a significant contribution to some actinide mixed-valent solids. The role of the interaction u_{fd} is threefold: it drives possible phase transitions,[6,11–14] it contributes to the conduction-band f-electron hybridization,[13] and it produces a screening of the f-electron core.[15,16] It is, however, not crucial in the phenomenon and we neglect it completely in our approach.

If the hybridization V is small compared with the bandwidth $(2zt)$, it is possible to look at the system as an incoherent mixed-valent state,[10] but this requires the configuration energy difference E to be small enough so that

$$E < \Gamma \simeq \pi V^2/2zt \ .$$

The so-called localized model, used by Kaplan et al.[16,17] corresponds essentially to the limit

$$t \ll V < E \ ,$$

which has also been discussed by Stevens.[18]

Our approach is similar to the localized model, but its conditions are not so stringent. It requires that the Fermi level of the condition-electron band in the ground-state mixed-valent configuration falls considerably below the bottom of the band of the other (orthogonal, excited) mixed configuration. This can be put in the form

$$2z\nu t < (E^2 + V^2)^{1/2} \ll U_{ff} \ ,$$

with no particular restrictions on E and V individually.

In Sec. II we introduce the original Hamiltonian and define its properties. In Sec. III we study special limiting values, in particular the atomic limit of zero bandwidth. In Sec. IV we define our projection technique, determine its range of applicability, introduce the new fermion operators and arrive at the new Hamiltonian. Section V discusses the approximate methods of treating the new Hamiltonian. Section VI is the summary and conclusions. In the following pa-

per[19] we apply this method to study the magnetic susceptibility of several model bands with this approach, and determine the instabilities of the systems toward formation of ferromagnetic and antiferromagnetic states.

II. THE ORIGINAL HAMILTONIAN

Our system consists of a lattice of ions that can exist in two different valence states and a band of conduction electrons. The ionic and band states are coupled by a hybridization term. There is also a uniform external magnetic field.

In terms of Wannier state creation $(c_{i\sigma}^\dagger)$ and destruction $(c_{i\sigma})$ operators of site i and spin σ, the nearest-neighbor only band Hamiltonian is given by

$$\mathcal{H}_b = \sum_{\langle ij \rangle \sigma} t\, c_{i\sigma}^\dagger c_{j\sigma} + \sum_i h\,(c_{i\uparrow}^\dagger c_{i\uparrow} - c_{i\downarrow}^\dagger c_{i\downarrow}) \ . \tag{2.1}$$

We have chosen the center of gravity of the band as our zero of energy, $\langle ij \rangle$ indicates nearest-neighbor pairs, t is the band hopping parameter, and h gives the value of the magnetic field multiplied by $\frac{1}{2} g_e \mu_B$.

For the sake of simplicity and definiteness[20] we assume the ground-state ionic configuration $(4f)^n$ to be a singlet $|G\rangle$. The excited configuration $(4f)^{n+1}$ is a doublet, $|+\rangle$ and $|-\rangle$, and we completely neglect all other configurations. With the index M indicating the excited states $|+\rangle$ or $|-\rangle$, the ionic part of the Hamiltonian is

$$\mathcal{H}_i = \sum_{jM} E_M B_{jM}^\dagger B_{jM} \ , \tag{2.2}$$

where the operators B and $B^\dagger$, defined elsewhere,[21] are modified Fermi operators such that $B_{jM}^\dagger B_{jM'}^\dagger \equiv 0$ for any M and M'. In Eq. (2.2) E_M is the energy necessary to create the ionic state $|M\rangle$ from the singlet state $|G\rangle$ by adding to the ion one electron from the center of gravity of the band. The effect of the magnetic field is included in E_M, i.e.,

$$E_\pm = E \pm g_0 h \ , \tag{2.3}$$

where g_0 is the ratio of the ionic to the conduction-electron g factors. The last term in our Hamiltonian is the hybridization

$$\mathcal{H}_h = \sum_{jM\sigma} (V_{M\sigma} B_{jM}^\dagger c_{j\sigma} + V_{M\sigma}^* c_{j\sigma}^\dagger B_{jM}) \ , \tag{2.4}$$

where, invoking conservation of spin and choosing a specific phase, we assume

$$V_{+\uparrow} = V_{-\downarrow} = V = V^*; \quad V_{+\downarrow} = V_{-\uparrow} = 0 \ . \tag{2.5}$$

It should be noted that in using the $B^\dagger, B$ operators we have completely left out of our model any configuration other than $(4f)^n$ and $(4f)^{n+1}$.

III. SPECIAL LIMITS OF THE HAMILTONIAN

We now consider the limiting cases of the Hamiltonian

$$\mathcal{H} = \mathcal{H}_b + \mathcal{H}_i + \mathcal{H}_h . \tag{3.1}$$

a. $t = V = 0$. This is a perfectly ionic case with no hybridization between the various orbitals. Each ion may be in 12 different states with $n + \nu$ electrons $0 \leq \nu \leq 3$

$$
\begin{array}{ll}
\nu = 0, & |G0\rangle \\
\nu = 1, & |+0\rangle \ |-0\rangle \ |G\uparrow\rangle \ |G\downarrow\rangle \\
\nu = 2, & |+\uparrow\rangle \ |+\downarrow\rangle \ |-\uparrow\rangle \ |-\downarrow\rangle \ |G\uparrow\downarrow\rangle \\
\nu = 3, & |+\uparrow\downarrow\rangle \ |-\uparrow\downarrow\rangle
\end{array} \tag{3.2}
$$

Some of these states are schematically shown in Fig. 1. The ions in the $|G\rangle$ configuration have energy zero and those in the $|M\rangle$ configurations, have energies E_M. For $E_M > 0$ the ground state of the whole system is highly degenerate, except in the cases of exactly n and $n + 2$ electrons per ion.

b. $V = 0$, $t \neq 0$. This situation corresponds to the "standard state" introduced by Stevens.[18] The Wannier states spread into a band and we have a collection of ions, either $(4f)^n$ or $(4f)^{n+1}$, embedded in a metallic state but not coupled to it. If E is at a higher energy than the top of the band, the ground state of the whole system involves only the $(4f)^n$ configuration for any number of electrons per atom between n and $n + 2$. This case is identical to that of
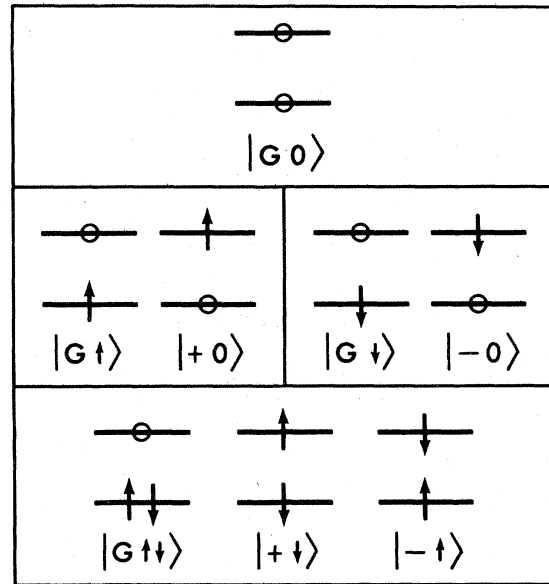

FIG. 1. Eight unperturbed states of the atomic Hamiltonian which, through hybridization, give rise to the four lowest intermediate-valence states.

rare-earth metals with ordinary well-defined valence.

c. $t = 0$, $V \neq 0$. This is the starting point of our calculation. It consists of a collection of ions, each with a well-defined number of electrons $(n + \nu)$, where ν varies between 0 and 3, but with hybrid Wannier and f states. The two nonvanishing energy

TABLE I. Hybridized ionic states for $h = 0$.

ν Number of electrons	σ Spin	E_0 Energy	Subspace
0	0	0	$|G0\rangle$
1	$+\frac{1}{2}$		$|G\uparrow\rangle, |+0\rangle$
1	$+\frac{1}{2}$	$\frac{1}{2}[E \pm (E^2 + 4V^2)^{1/2}]$	
1	$-\frac{1}{2}$		$|G\downarrow\rangle, |-0\rangle$
1	$-\frac{1}{2}$		
2	$+1$		$|+\uparrow\rangle$
2	-1	E	$|-\downarrow\rangle$
2	0		$2^{-1/2}(|+\downarrow\rangle - |-\uparrow\rangle)$
2	0	$\frac{1}{2}[E \pm (E^2 + 8V^2)^{1/2}]$	$|G\uparrow\downarrow\rangle, 2^{-1/2}(|+\downarrow\rangle + |-\uparrow\rangle)$
2	0		
3	$+\frac{1}{2}$	E	$|+\uparrow\downarrow\rangle$
3	$-\frac{1}{2}$		$|-\uparrow\downarrow\rangle$

parameters are V and E, and therefore we use V/E as a reduced parameter. The 12 states defined by Eq. (3.2) are now part of a coupled general 12-fold subpace. However, since the number of electrons and the z component of the total spin are good quantum numbers, the 12×12 matrix factorizes readily into eight blocks: five 1×1, two 2×2, and one 3×3. In Table I we display the resulting diagonalized states for $h = 0$.

In the case $E > 0$ [singlet $(4f)^n$ more stable than the triplet $(4f)^{n+1}$] there are four of the 12 states of Table I which have energies, for small h, at or below the zero of energy. These states are:

(i) one with $\nu = 0$, $\sigma = 0$, and $E = 0$ which we denote by

$$|0\rangle \equiv |G0\rangle \; ; \tag{3.3}$$

(ii) two states with $\nu = 1, \sigma = \pm\frac{1}{2}$ denoted by

$$|\uparrow\rangle \equiv \alpha_u |G\uparrow\rangle + \beta_u |+0\rangle \; , \tag{3.4}$$

$$|\downarrow\rangle \equiv \alpha_d |G\downarrow\rangle + \beta_d |-0\rangle \; ; \tag{3.5}$$

(iii) one state with $\nu = 2, \sigma = 0$, given by

$$|\uparrow\downarrow\rangle \equiv \alpha_s |G\uparrow\downarrow\rangle + \delta_u |+\downarrow\rangle + \delta_d |-\uparrow\rangle \; , \tag{3.6}$$

where for $h = 0$, $\delta_u = -\delta_d$.

Each one of these states is the lowest-energy state of one of the four manifolds depicted as separate blocks in Fig. 1.

It should be noted that for $E < 0$, there is an eight-fold set of states of lower energy instead of the four-fold one discussed here.

IV. PROJECTION TECHNIQUE AND NEW FERMION OPERATORS

When all energy parameters h, t, and $k_B T$ are considerably smaller than $|E|$, we could simplify our problem by including, for the purpose of the band hopping terms, only the low-energy subset of states. If $E > 0$ these states are those given by Eqs. (3.3)–(3.6).

We project now our Hamiltonian onto this subspace and completely eliminate the other eight high-energy states. It should be noted that:

(i) All coefficients $\alpha_u, \beta_u, \alpha_d$, etc. appearing in Eqs. (3.3)–(3.6) are functions of V/E, h, and g_0. (ii) The $\mathcal{K}_i + \mathcal{K}_h$ part of the Hamiltonian is, by construction, automatically taken into account. (iii) Any four states can be directly interpreted as the four occupation states of a spin-$\frac{1}{2}$ system, and therefore any Hamiltonian referring to those states can be directly written in terms of fermion (spin $\frac{1}{2}$) creation and destruction operators. (iv) Our new Hamiltonian should reduce to the original $\mathcal{K}_b$ (and the new operators should reduce to $c_{i\sigma}^\dagger, c_{i\sigma}$) when $V \to 0$.

We denote the energy of the four states (3.3)–(3.6) by 0, $E_\uparrow$, $E_\downarrow$, and $E_{\uparrow\downarrow}$. These last three are functions of V/E, h, and g_0. We also define the new fermion operators $\gamma_{i\sigma}^\dagger$, $\gamma_{i\sigma}$ such that, for each site,

$$|\uparrow\rangle = \gamma_\uparrow^\dagger |0\rangle, \quad |\downarrow\rangle = \gamma_\downarrow^\dagger |0\rangle \; ,$$
$$|\uparrow\downarrow\rangle = \gamma_\uparrow^\dagger \gamma_\downarrow^\dagger |0\rangle = -\gamma_\downarrow^\dagger \gamma_\uparrow^\dagger |0\rangle \; , \tag{4.1}$$

and such that the ordinary fermion anticommutation rules are satisfied.

We also introduce the number operators

$$\nu_{i\sigma} \equiv \gamma_{i\sigma}^\dagger \gamma_{i\sigma} \; , \tag{4.2}$$

and the projection operators

$$P_{i0} \equiv (1 - \nu_{i\uparrow})(1 - \nu_{i\downarrow}) \; ,$$
$$P_{i\uparrow} \equiv \nu_{i\uparrow}(1 - \nu_{i\downarrow}) \; ,$$
$$P_{i\downarrow} \equiv (1 - \nu_{i\uparrow})\nu_{i\downarrow} \; ,$$
$$P_{i\uparrow\downarrow} \equiv \nu_{i\uparrow}\nu_{i\downarrow} \; . \tag{4.3}$$

With these the projected Hamiltonian H becomes

$$H = H_0 + H_b \; , \tag{4.4}$$

where

$$H_0 = \sum_j (E_\uparrow P_{j\uparrow} + E_\downarrow P_{j\downarrow} + E_{\uparrow\downarrow} P_{j\uparrow\downarrow}) \tag{4.5}$$

and

$$H_b = t \sum_{\langle ij\rangle\sigma} \gamma_{i\sigma}^\dagger \gamma_{j\sigma}[A_\sigma + B_\sigma(\nu_{i\bar\sigma} + \nu_{j\bar\sigma}) + D_\sigma \nu_{i\bar\sigma}\nu_{j\bar\sigma}] \; . \tag{4.6}$$

In Eq. (4.6), $\bar\sigma$ indicates the spin opposite to σ, and the coefficients A_σ, B_σ, and D_σ are functions of the coefficients $\alpha_u, \beta_u, \alpha_d$, etc. appearing in Eqs. (3.3)–(3.6). In the calculation of these expressions care should be taken of including the relative phases of the various creation and destruction operators, as well as the ordering of the various multifermion states. The correct expressions for these coefficients with our choice of phases, are

$$A_\uparrow = (\alpha_u)^2, \quad B_\uparrow = \alpha_u(X_\uparrow - \alpha_u) \; ,$$
$$D_\uparrow = (X_\uparrow - \alpha_u)^2 \; , \tag{4.7}$$

where

$$X_\uparrow \equiv -(\alpha_d \alpha_s + \beta_d \delta_d) \; .$$

Equivalent expressions are obtained for the $\downarrow$ coefficients by exchanging $\uparrow \leftrightarrow \downarrow$ and $u \leftrightarrow d$.

It is interesting to note that the hybridization of the original Hamiltonian is responsible for the appearance in Eqs. (4.5) and (4.6) of two- and three-particle terms (four and six γ or $\gamma^\dagger$ operators). When $V = 0$, only the α coefficients remain finite in Eqs.

(3.3)–(3.6): $|\alpha| = 1$, $\beta = \delta = 0$, and $E_{\uparrow\downarrow} = E_\uparrow + E_\downarrow$. We then obtain

$$H(V=0) = \sum_{j\sigma} E_\sigma \nu_{j\sigma} + t \sum_{\langle ij\rangle\sigma} \gamma^\dagger_{i\sigma}\gamma_{j\sigma} \ , \qquad (4.8)$$

i.e., a simple band Hamiltonian in the presence of a magnetic field.

V. SELF-CONSISTENT-FIELD APPROXIMATION

To handle the new Hamiltonian we use the standard Hartree-Fock (self-consistent-field) approximation. We replace the four-particle operators in Eqs. (4.5) and (4.6) by sums of two-particle operators and C numbers, i.e.,

$$\gamma^\dagger_1\gamma^\dagger_2\gamma_3\gamma_4 \rightarrow \langle\gamma^\dagger_1\gamma_4\rangle\gamma^\dagger_2\gamma_3 + \langle\gamma^\dagger_2\gamma_3\rangle\gamma^\dagger_1\gamma_4$$
$$- \langle\gamma^\dagger_1\gamma_3\rangle\gamma^\dagger_2\gamma_4 - \langle\gamma^\dagger_2\gamma_4\rangle\gamma^\dagger_1\gamma_3$$
$$- \langle\gamma^\dagger_1\gamma_4\rangle\langle\gamma^\dagger_2\gamma_3\rangle + \langle\gamma^\dagger_1\gamma_3\rangle\langle\gamma^\dagger_2\gamma_4\rangle \ , \qquad (5.1)$$

where $\langle \cdots \rangle$ indicates expectation values with the state under consideration. This decoupling scheme is directly related to the decoupling of the two-particle Green function into two terms containing two one-particle Green's functions[22] (see Appendix). For the six-operator (three-particle) terms in Eq. (4.6), the equivalent decoupling involves many more terms. These are once again directly related to the decoupling of the three-particle Green function into terms which are products of one- and two-particle Green's functions[22] (see Appendix). If in addition we neglect all states for which there is a spiral arrangement of the spins, i.e., we consider only states in which

$$\langle\gamma^\dagger_{i\downarrow}\gamma_{j\uparrow}\rangle = 0 \ , \qquad (5.2)$$

the simplification is considerable. For example we obtain

$$\gamma^\dagger_{i\uparrow}\gamma_{j\uparrow}\nu_{i\downarrow}\nu_{j\downarrow} \rightarrow \langle\nu_{i\downarrow}\nu_{j\downarrow}\rangle(\gamma^\dagger_{i\uparrow}\gamma_{j\uparrow} - \langle\gamma^\dagger_{i\uparrow}\gamma_{j\uparrow}\rangle) + \langle\gamma^\dagger_{i\uparrow}\gamma_{j\uparrow}\gamma^\dagger_{i\downarrow}\gamma_{j\downarrow}\rangle(\gamma^\dagger_{j\downarrow}\gamma_{i\downarrow} - \langle\gamma^\dagger_{j\downarrow}\gamma_{i\downarrow}\rangle)$$
$$+ \langle\gamma^\dagger_{j\downarrow}\gamma_{j\uparrow}\gamma^\dagger_{i\uparrow}\gamma_{i\downarrow}\rangle(\gamma^\dagger_{i\uparrow}\gamma_{j\downarrow} - \langle\gamma^\dagger_{i\downarrow}\gamma_{j\downarrow}\rangle) + \langle\nu_{j\downarrow}\gamma^\dagger_{i\uparrow}\gamma_{j\uparrow}\rangle(\nu_{i\downarrow} - \langle\nu_{j\downarrow}\rangle)$$
$$+ \langle\gamma^\dagger_{i\uparrow}\gamma_{j\uparrow}\nu_{i\downarrow}\rangle(\nu_{j\downarrow} - \langle\nu_{j\downarrow}\rangle) + \langle\gamma^\dagger_{i\uparrow}\gamma_{j\uparrow}\rangle\langle\nu_{j\downarrow}\rangle\langle\nu_{i\downarrow}\rangle - \langle\gamma^\dagger_{i\uparrow}\gamma_{j\uparrow}\rangle\langle\gamma^\dagger_{i\downarrow}\gamma_{j\downarrow}\rangle\langle\gamma^\dagger_{j\downarrow}\gamma_{i\downarrow}\rangle \ . \qquad (5.3)$$

With this decoupling scheme the Hamiltonian (4.4) becomes a new Hartree-Fock Hamiltonian

$$H_{\rm HF} = \sum_{j\sigma} U_\sigma \gamma^\dagger_{j\sigma}\gamma_{j\sigma} - \sum_{\langle ij\rangle\sigma} W_\sigma \gamma^\dagger_{i\sigma}\gamma_{i\sigma} + K \ , \qquad (5.4)$$

where the constants U_σ, W_σ, and K depend self-consistently on expectation values of the form $\langle\gamma^\dagger\gamma\rangle$ and $\langle\gamma^\dagger\gamma\gamma^\dagger\gamma\rangle$ as well as on the coefficients A_σ, B_σ, D_σ, $E_\uparrow$, $E_\downarrow$, and $E_{\uparrow\downarrow}$ of Eqs. (4.5)–(4.7). It is now evident that Eq. (5.4) is a simple one-particle band Hamiltonian with nearest-neighbor hopping. But it must be remembered that the parameters which determine this Hamiltonian are not constants but self-consistent quantities, functions of the state. As a consequence it describes a system with interactions which is capable of spontaneously breaking its symmetry to produce ground states other than the normal, paramagnetic one.[23]

For ground states in which the translational symmetry is conserved, i.e., the paramagnetic (normal) and the ferromagnetic states, a transformation to Bloch states automatically reduces the Hamiltonian to the necessary diagonal form. The new destruction operators $\Gamma_{k\sigma}$ are given by

$$\Gamma_{k\sigma} \equiv (N)^{-1/2} \sum_j \exp(i\vec{k}\cdot\vec{R}_j)\gamma_{j\sigma} \ , \qquad (5.5)$$

in terms of which

$$H_{\rm HF} = \sum_{k\sigma} E_{k\sigma}\Gamma^\dagger_{k\sigma}\Gamma_{k\sigma} \ , \qquad (5.6)$$

where

$$E_{k\sigma} \equiv U_\sigma + |W_\sigma| S(\vec{k}) \qquad (5.7)$$

and

$$S(\vec{k}) \equiv -(\mathrm{sgn}\,W_\sigma) \sum_\delta^{\rm nn} \exp(i\vec{k}\cdot\vec{R}_\delta) \ . \qquad (5.8)$$

The dimensionless quantity $S(\vec{k})$ is a reduced band energy.

VI. SUMMARY AND CONCLUSIONS

For a well-defined case of mixed-valence solids in which the "atomic" spectrum splits into two well separated regions, we have been able to reduce the problem to a more familiar one of many-fermion physics. The approach consists of: (i) inclusion of all intra-atomic contributions and neglect, as a starting point, of the band "hopping" terms, (ii) diagonalization of the intra-atomic terms including the various accessible configurations and the hybridization terms,

(iii) analysis of the spectrum and, if the case so warrants, projecting out of all states except the lowest-energy manifold, (iv) reduction of that manifold to an equivalent set of fermion states and incorporation of the band hopping terms in this new formalism, and (v) treatment of the resulting many-fermion Hamiltonian, which includes two- and three-particle terms, by the standard methods of many-fermion physics.[22] In particular the Hartree-Fock and related schemes should be in many cases very satisfactory, although care should be taken to avoid the normal pitfalls inherent in them.[24]

In the following paper we apply the method here described to calculate the magnetic susceptibility of the paramagnetic state, and its instabilities toward the formation of other (broken symmetry) states.

APPENDIX

The ordinary Hartree-Fock decoupling of the two-fermion Green function

$$G_2(1\,2;1'2') \rightarrow G_1(1;1')G_1(2;2') - G_1(1;2')G_1(1';2) \tag{A1}$$

can be extended to the three-fermion function by standard methods.[22]

$$
\begin{aligned}
G_3(1\,2\,3;1'2'3') \rightarrow\ & G_1(1;1')G_2(2\,3;2'3') + G_1(2;1')G_2(3\,1;2'3') + G_1(3;1')G_2(1\,2;2'3') \\
& + G_1(1;2')G_2(2\,3;3'1') + G_1(2;2')G_2(3\,1;3'1') + G_1(3;2')G_2(1\,2;3'1') \\
& + G_1(1,3')G_2(2\,3;1'2') + G_1(2;3')G_2(3\,1;1'2') + G_1(3;3')G_2(1\,2;1'2') \\
& - 2G_1(1,1')G_1(2;2')G_1(3;3') - 2G_1(2;1')G_1(3;2')G_1(1;3') \\
& - 2G_1(3;1')G_1(1;2')G_1(2;3') + 2G_1(3;1')G_1(2;2')G_1(1;3') \\
& + 2G_1(2;1')G_1(1;2')G_1(3;3') + 2G_1(1;1')G_1(3;2')G_1(2;3')\ .
\end{aligned}
\tag{A2}
$$

This last expression can be further simplified by replacing G_2 by its expression in Eq. (A1).

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