PHYSICAL REVIEW B VOLUME 33, NUMBER 3 1 FEBRUARY 1986

Interpolative solution for the periodic Anderson model of mixed-valence compounds

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(Received 12 April 1985)

A general solution for the periodic Anderson model of mixed-valence compounds is presented. The method uses Green-function techniques and is based on the introduction of an appropriate self-energy by interpolating between two extreme limits: Small intrasite Coulomb interaction and small hopping integral between the d and f levels of the same site. The method has been checked for a simple model of an impurity, and the conclusion is that its accuracy for calculating the density of states is better than 10%. We have applied the general method to a one-dimensional chain, with two electrons per site, a degeneracy of spin $\frac{1}{2}$ for the f level and zero temperature, and have calculated its electronic density of states. We give results for the electronic bands near the fundamental gap and the integrated density of states for different parameters, and show that the paramagnetic phase is always insulating in agreement with a kind of Luttinger's sum rule.

I. INTRODUCTION

The problem of a magnetic impurity in a metal has been extensively analyzed in the last ten years. It is worth mentioning in this context the renormalization-group method, that has been successfully applied to analyzing the Kondo problem[1] and related Anderson Hamiltonians,[2,3] and the exact solution given by Tsvelich and Wigmann[4] to the Anderson problem of a spin-$\frac{1}{2}$ impurity.

The mixed-valence regime of impurity Anderson problem has also received a great attention due to rare-earth compounds; dilute mixed-valence alloys are analyzed by means of that Hamiltonian, and even concentrated alloys are treated similarly when the effect of the coherence among rare-earth impurities can be neglected. Scaling analyses[5,6] and renormalization-group results[3] show that the mixed-valence regime does not present a universal behavior, due to marginal operators that play a nonnegligible role. A different solution, based on a perturbation theory with the inverse of the impurity orbital degeneracy as the expansion parameter, has been recently proposed to analyze that regime.[7-9] In spite of these efforts for dilute impurities, there is a lack of full understanding of the periodic model for a mixed-valence crystal.[10-12]

The aim of this paper is to present a new method which allows us to obtain a general solution of the periodic Anderson Hamiltonian (a preliminary report was published in Ref. 13). The method is a straightforward generalization of a solution for the case of an impurity[14] which uses a Green-function method and the construction of an appropriate self-energy. Although this solution was given for a chemisorption problem, we shall show that it is good enough for an impurity in the mixed-valence regime. The solution given to the mixed-valence regime can be extended to the Kondo regime as well, and allows us to analyze the transition from one time to the other. In this paper we present the solution for $T=0$, so no temperature-dependent property is analyzed, and we concentrate on discussing the density of states and the electronic bands for the periodic Hamiltonian.

II. THE SOLUTION FOR A SINGLE IMPURITY

In a previous paper,[14] a solution to the problem of a magnetic impurity in a metal was given by using a Green-function formalism. The solution was prompted by an analysis of the Anderson-Newns problem of chemisorption, but the structure of the model Hamiltonian for this case is the same as the one for a magnetic impurity in a metal. The method was checked in simple models, appropriate for the chemisorption problem of H on transition metals. In this section we discuss the same solution when applied to the problem of a rare-earth impurity in a transition metal. Let us comment that, in regards to the single impurity problem, the method we are going to discuss is not competitive with many other approaches well known in the literature;[1-4] however, the advantage of this method is that it gives results for the rare-earth-impurity problem accurate enough to suggest that a generalization to the periodic Anderson lattice problem may be used with great confidence. (Indeed, the method has been applied successfully to a one-dimensional Hubbard Hamiltonian.[15]) This may represent a significant step forward for the understanding of the periodic Anderson Hamiltonian.

It is well known that the Anderson Hamiltonian of an impurity

$$\hat{H}=\sum_{\sigma} E_f n_{f,\sigma}+\sum_{i,\sigma} E_d n_{d,i\sigma}+t\sum_{\substack{i,j,\sigma\\ i\neq j}} C^{\dagger}_{di\sigma}C_{dj\sigma} + V\sum_{\sigma}(C^{\dagger}_{d0\sigma}C_{f\sigma}+C^{\dagger}_{f\sigma}C_{d0\sigma})+Un_{f\uparrow}n_{f\downarrow}\ , \tag{1}$$

can be solved[16] by using a Green-function method and by introducing the appropriate self-energy $\Sigma_{ff,\sigma}(\omega)$. In Eq. (1), the f state is assumed to have only the degeneracy of a spin $\frac{1}{2}$, t is the hopping integral between first-nearest neighbors of the d band, V measures the coupling between the f state and the d band at the same site 0, and U is the intrasite Coulomb interaction between electrons of opposite spins in the f level.

The approximate solution proposed in Ref. 14 to solve Hamiltonian (1) is based on the calculation of a self-energy, $\Sigma_{ff,\sigma}(\omega)$, valid for all the ranges of U. This self-energy is calculated by an appropriate interpolation between the two limits, (i) $U/V\rightarrow 0$, and (ii) $V/U\rightarrow 0$. This interpolation is based on the realization that the self-energy for these two limits has the same behavior when ω goes to ∞. In fact, consider for the limit $U/V\rightarrow 0$ the second-order perturbation to the self-energy,[14] $\Sigma^{(2)}_{ff,\sigma}$:

$$\Sigma^{(2)}_{ff,\sigma}=U^2\int_{-\infty}^{E_F}dE_2\int_{E_F}^{\infty}dE_3\int_{E_F}^{\infty}dE_4\frac{n_f^{-\sigma}(E_2)n_f^{-\sigma}(E_3)n_f^{\sigma}(E_4)}{\omega+E_2-E_3-E_4+i\eta} +U^2\int_{E_F}^{\infty}dE_2\int_{-\infty}^{E_F}dE_3\int_{-\infty}^{E_F}dE_4\frac{n_f^{-\sigma}(E_2)n_f^{-\sigma}(E_3)n_f^{\sigma}(E_4)}{\omega+E_2-E_3-E_4+i\eta}\ , \tag{2}$$

and take in this equation the limit $\omega\rightarrow\infty$. [In Eq. (2), $n_f^{\sigma}(E)$ is the local density of states for the f level, and η is a positive infinitesimal.] It is easy to see that

$$\lim_{\omega\rightarrow\infty}\Sigma^{(2)}_{ff,\sigma}(\omega)=U^2\frac{n_f^{-\sigma}(1-n_f^{-\sigma})}{\omega}\ , \tag{3}$$

where $n_f^{-\sigma}$ is the total electronic charge per spin in the f level.

On the other hand, for $V\rightarrow 0$, we can analyze the density of states for the f level, by considering its atomic limit. It is well known[14,17] that in this limit, $\Sigma_{ff,\sigma}(\omega)$ takes the form

$$\Sigma^{\text{atomic}}_{ff,\sigma}=U^2\frac{n_f^{-\sigma}(1-n_f^{-\sigma})}{\omega-E_f-(1-n_f^{-\sigma})U}\ . \tag{4}$$

This self-energy behaves as

$$\lim_{\omega\rightarrow\infty}\Sigma^{\text{atomic}}_{ff,\sigma}=U^2\frac{n_f^{-\sigma}(1-n_f^{-\sigma})}{\omega}\ , \tag{5}$$

for $\omega\rightarrow\infty$, this limit coinciding with Eq. (3).

Equations (3) and (5) suggest the introduction of an interpolated self-energy, $\Sigma_{ff,\sigma}(\omega)$, which gives the correct limits for $U\rightarrow 0$ and $V\rightarrow 0$. To this end, we rewrite Eq. (4) as

$$\Sigma^{\text{atomic}}_{ff,\sigma}(\omega)=U^2\frac{n_f^{-\sigma}(1-n_f^{-\sigma})/\omega-E_0}{1-\dfrac{E_f+(1-n_f^{-\sigma})U-E_0}{\omega-E_0}}\ , \tag{6}$$

where E_0 is an effective level for the f state which is used later on to introduce self-consistency. Equation (6) suggests the use of the self-energy

$$\Sigma_{ff,\sigma}(\omega)=\frac{\Sigma^{(2)}_{ff,\sigma}(\omega)}{1-\dfrac{E_f(1-n_f^{-\sigma})U-E_0}{n_f^{-\sigma}(1-n_f^{-\sigma})}\dfrac{\Sigma^{(2)}_{ff,\sigma}(\omega)}{U^2}}\ , \tag{7}$$

where $\Sigma^{(2)}_{ff,\sigma}(\omega)$ is calculated by using the effective Hamiltonian

$$\hat{H}_{\text{eff}}=\sum_{\sigma}E_0 n_{f,\sigma}+\sum_{i}E_d n_{d,i\sigma}+t\sum_{\substack{i,j,\sigma\\ i\neq j}}C^{\dagger}_{di\sigma}C_{dj\sigma} +V\sum_{\sigma}(C^{\dagger}_{d0\sigma}C_{f\sigma}+C^{\dagger}_{f\sigma}C_{d0\sigma})\ . \tag{8}$$

The role played by E_0 in the effective Hamiltonian, $\hat{H}_{\text{eff}}$, is to introduce self-consistency[14] between the charges n_f^{σ} as calculated from the final solution and as obtained from Hamiltonian (8).

Once we have defined $\Sigma_{ff,\sigma}(\omega)$, we can calculate most of the properties of interest for the impurity:[16] quasiparticle spectrum, ground-state energy, etc., We have checked this method by considering a simple model, similar to the one discussed in Ref. 14. We simulate the metal by a single atom. The corresponding Hamiltonian is

$$\hat{H}=\sum_{\sigma}E_d n_{d,\sigma}+\sum_{\sigma}E_f n_{f\sigma} +\sum_{\sigma}V(C^{\dagger}_{d,\sigma}C_{f\sigma}+C^{\dagger}_{f\sigma}C_{d,\sigma})+Un_{f\uparrow}n_{f\downarrow}\ . \tag{9}$$

We have chosen parameters appropriate to a rare-earth impurity in a d-metal matrix, and have calculated the exact solution of (9) and the approximate one as given by our method.

We present results for the following set of parameters in arbitrary units: $E_d=0$, $U=8$, and (i) $E_f=0.1$, $V=5$, 1, 0.5, 0.2, and 0.04; (ii) $E_f=-0.1$, $V=5$, 1, 0.5, 0.2, and 0.04. E_f has been chosen close to zero: For this case the accuracy of our approximation is the lowest one. Table I shows the levels and their weights for the exact and approximate solutions. These tables show that our approximate solution is quite close to the exact one for high V

TABLE I. f levels (in arbitrary units, see text) and weights for different values of the parameters appearing in the Hamiltonian (9). Results for the approximate solution obtained from Eq. (7) and the exact one are given.

Approximate		Exact		Approximate		Exact	
Level	f weight	Level	f weight	Level	f weight	Level	f weight
$E_f=0.1$, $V=5$, $U=8$				$E_f=-0.1$, $V=5$, $U=8$			
−13.68	0.02	−13.70	0.02	−13.73	0.02	−13.75	0.02
−3.69	0.34	−3.70	0.35	−3.74	0.35	−3.75	0.35
6.38	0.59	6.36	0.59	6.29	0.58	6.27	0.58
19.19	0.04	19.23	0.04	18.98	0.04	19.01	0.04
$E_f=0.1$, $V=1$, $U=8$				$E_f=-0.1$, $V=1$, $U=8$			
−2.44	0.11	−2.51	0.07	−2.46	0.12	−2.53	0.09
−0.47	0.16	−0.51	0.19	−0.47	0.16	−0.53	0.195
1.51	0.55	1.45	0.56	1.42	0.52	1.35	0.52
9.60	0.18	9.79	0.18	9.31	0.19	9.50	0.19
$E_f=0.1$, $V=0.5$, $U=8$				$E_f=-0.1$, $V=0.5$, $U=8$			
−1.16	0.14	−1.23	0.08	−1.19	0.18	−1.24	0.12
−0.19	0.11	−0.23	0.16	−0.18	0.095	−0.24	0.16
0.81	0.54	0.75	0.56	0.72	0.475	0.66	0.49
8.75	0.21	8.92	0.20	8.45	0.24	8.62	0.23
$E_f=0.1$, $V=0.2$, $U=8$				$E_f=-0.1$, $V=0.2$, $U=8$			
−0.44	0.14	−0.50	0.07	−0.48	0.27	−0.50	0.17
-0.06	0.08	−0.085	0.14	−0.05	0.04	−0.09	0.13
9.36	0.57	0.34	0.60	0.28	0.39	0.24	0.42
8.34	0.21	8.45	0.19	8.05	0.30	8.15	0.28
$E_f=0,1$ $V=0.04$, $U=8$				$E_f=-0,1$ $V=0.04$, $U=8$			
−0.12	0.02	−0.14	0.01	−0.14	0.41	−0.14	0.37
−0.01	0.07	−0.01	0.08	−0.002	0.003	−0.01	0.05
0.13	0.82	0.125	0.83	0.04	0.16	0.03	0.17
8.20	0.09	8.23	0.08	7.91	0.42	7.92	0.41

($V \gg |\epsilon_f|$). When V decreases, we find a maximum discrepancy between the two solutions for $V \simeq 0.1$; indeed for V much less than 0.1, that is $V \ll |\epsilon_f|$, both solutions are closer to each other. It is worth noticing that in any case our approximate solution reproduces all the important features of the levels of the exact case and that the total charge in the occupied levels is quite close to the one given by the exact solution, i.e., for $V=0.2$ and $E_f=0.1$, the f level has an occupancy of 0.22 in the approximate solution, a value to be compared with the occupancy of 0.21 for the exact case (for $V=0.2$ and $E_f=-0.1$, the occupancies are 0.31 and 0.30, respectively). The only significant discrepancy that our results show, when compared with the exact ones, is related to the weights of the two levels, i.e., for $E_f=-0.1$ and $V=0.2$, the weights of the two lowest f levels for the approximate solution are 0.27 and 0.04 instead of 0.17 and 0.13, while on the other hand, the total weight of the two lowest levels (including f and d levels) is not exactly one by a few percent (for $E_f=0.1$ and $V=0.2$, that weight is 1.05). These differences are not too much important because the sum of the weights for the two occupied f levels is very well approximated by our solution. Considering all together these comments and the results shown in Table I, we conclude that our approximate solution has an accuracy, in the worst of the cases, better than 10%.

On the other hand, let us comment that these results are similar to the ones we have calculated with a three-atom chain for the metal; we do not discuss this case for the sake of brevity.

The results shown in Table I correspond to very high values of U. This is the usual case for the rare-earth impurities. For that high-U value, we can slightly modify the procedure given above. To this end, we analyze the behavior of $\Sigma_{ff,\sigma}(\omega)$, as given by Eq. (3), for $U \rightarrow \infty$. Accordingly, we write $\Sigma_{ff,\sigma}(\omega)$ as

$$\Sigma_{ff,\sigma}(\omega)=-\frac{n_f^{-\sigma}(1-n_f^{-\sigma})U^2}{E_f+(1-n_f^{-\sigma})U-E_0}\left[1-\frac{n_f^{-\sigma}(1-n_f^{-\sigma})U^2}{E_f+(1-n_f^{-\sigma})U-E_0}\Sigma_{ff,\sigma}^{(2)-1}\right]^{-1}, \tag{10}$$

and consider that $U \gg E_f-E_0$ (E_f and E_0 remain finite) and that $\Sigma_{ff,\sigma}^{(2)-1}$ goes like $1/U^2$. Equation (10) can be developed as a series in $1/U$ for $U \to \infty$, which yields

$$\lim_{U\to\infty}\Sigma_{ff,\sigma}(\omega)=-n_f^{-\sigma}U+\frac{n_f^{-\sigma}}{1-n_f^{-\sigma}}(E_f-E_0)-\frac{(n_f^{-\sigma})^2U^2}{\Sigma_{ff,\sigma}^{(2)}}+O\left[\frac{1}{U}\right]. \tag{11}$$

Neglecting terms going like $1/U$, we find that, for $U\to\infty$, $\Sigma_{ff,\sigma}$ is equivalent to the one-body potential

$$-n_f^{-\sigma}U+\frac{n_f^{-\sigma}}{1-n_f^{-\sigma}}(E_f-E_0)\,, \tag{12a}$$

plus the self-energy

$$\Sigma_{ff,\sigma}^{\infty}=-\frac{(n_f^{-\sigma})^2U^2}{\Sigma_{ff,\sigma}^{(2)}}\,. \tag{12b}$$

Note that $(-n_f^{-\sigma}U)$ in Eq. (12a) cancels out the Hartree contribution $n_f^{-\sigma}U$, in such a way that we can define the following renormalized energy for the f level as

$$\epsilon_f^{\infty}=E_f+\frac{n_f^{-\sigma}}{1-n_f^{-\sigma}}(E_f-E_0)\,. \tag{13}$$

Equations (13) and (12b) define the energy the self-energy for the rare-earth impurity in the limit $U\to\infty$. It is worth commenting that for $\omega\to\infty$, $\Sigma_{ff,\sigma}^{\infty}(\omega)$ behaves as [see Eqs. (3) and (5)]

$$\lim_{\omega\to\infty}\Sigma_{ff,\sigma}^{\infty}\to\frac{n_f^{-\sigma}}{1-n_f^{-\sigma}}\omega\,. \tag{14}$$

This shows that the total density of states in the f level is given by

$$\left[1+\frac{n_f^{-\sigma}}{1-n_f^{-\sigma}}\right]^{-1}=1-n_f^{-\sigma}\,.$$

This is the expected result, since in the high-U limit we cannot introduce more than one electron in the f level: If we have $n_f^{-\sigma}$ electrons with spin $(-\sigma)$, the maximum density of states available for electrons with spin σ is $(1-n_f^{-\sigma})$.

In Table II we give the results calculated for the one-atom chain and $U\to\infty$, $E_d=0$, $E_f=0.1$, and $V=0.2$. Comparing these results with Table I we see that, indeed, $U=8$ corresponds to a very high-U value.

III. THE SOLUTION FOR A PERIODIC ANDERSON LATTICE

In this section we discuss how to generalize our method to a periodic Anderson lattice. We start by writing the corresponding Hamiltonian

$$\hat{H}=\sum_{i,\sigma}E_f n_{fi\sigma}+\sum_{i,\sigma}E_d n_{di\sigma}+t\sum_{i\neq j}C_{di\sigma}^{\dagger}C_{dj\sigma}+V\sum_{i,\sigma}(C_{di\sigma}^{\dagger}C_{fi\sigma}+C_{fi\sigma}^{\dagger}C_{di\sigma})+U\sum_{i}n_{fi\uparrow}n_{fi\downarrow}\,, \tag{15}$$

which is analogous to Hamiltonian (1). This Hamiltonian can also be solved by using Green-function techniques and by introducing the self-energies, $\Sigma_{ff,ij,\sigma}(\omega)$. This is an obvious generalization of the impurity case: In the present case we have to introduce off-diagonal self-energies associated with the indirect interaction between f levels. By using the translational symmetry of the lattice, we introduce a k vector and the corresponding self-energy $\Sigma_{ff,\sigma}(\mathbf{k},\omega)$. The periodic Anderson problem can be solved by calculating that self-energy, $\Sigma_{ff,\sigma}(\mathbf{k},\omega)$. Now, we propose to calculate $\Sigma_{ff,\sigma}(\mathbf{k},\omega)$ by a procedure similar to the one followed in Sec. II.

The crucial point is the behavior of $\Sigma_{ff,\sigma}(\mathbf{k},\omega)$ for $\omega\to\infty$. As discussed in Sec. II, we consider two different limits: (i) $U/V\to 0$, and (ii) $V/U\to 0$, and look for an interpolation between the corresponding self-energies. Thus, consider the second-order perturbation to the self-energy for the limit $U\to 0$. A standard calculation[18] yields

$$\Sigma_{ff,\sigma}^{(2)}(\mathbf{k},\omega)=U^2\sum_{\mathbf{q}_1,\mathbf{k}'}\int_{-\infty}^{E_F}dE_2\int_{E_F}^{\infty}dE_3\int_{E_F}^{\infty}dE_4\frac{n_f^{-\sigma}(\mathbf{k}',E_2)n_f^{-\sigma}(\mathbf{k}'+\mathbf{q}+\mathbf{G},E_3)n_f^{\sigma}(\mathbf{k}-\mathbf{q}+\mathbf{G}',E_4)}{\omega+E_2-E_3-E_4+i\eta}$$
$$+U^2\sum_{\mathbf{q},\mathbf{k}'}\int_{E_F}^{\infty}dE_2\int_{-\infty}^{E_F}dE_3\int_{-\infty}^{E_F}dE_4\frac{n_f^{-\sigma}(\mathbf{k}',E_2)n_f^{-\sigma}(\mathbf{k}'+\mathbf{q}+\mathbf{G},E_3)n_f^{\sigma}(\mathbf{k}-\mathbf{q}+\mathbf{G}',E_4)}{\omega+E_2-E_3-E_4+i\eta}\,, \tag{16}$$

where $\mathbf{G}$ and $\mathbf{G}'$ have to be chosen in such a way that $(\mathbf{k}'+\mathbf{q}+\mathbf{G})$ and $(\mathbf{k}-\mathbf{q}+\mathbf{G}')$ belong to the first Brillouin zone (BZ), and the summation on $\mathbf{q}$ and $\mathbf{k}'$ extend to the same first BZ. In Eq. (16), $n_f(\mathbf{k},E)$ is the Fourier transform extended to the first BZ of

$$n_f(\mathbf{R}_{ij},E)=-\frac{1}{\pi}\,\mathrm{Im}G_{ff}(\mathbf{R}_{ij},E)\,,$$

where $\mathbf{R}_{ij}$ is the vector joining two lattice points. Equation (16) can be Fourier transformed and written as

$$\Sigma^{(2)}_{ff,\sigma}(R_{ij},\omega)=U^2\int_{-\infty}^{E_F}dE_2\int_{E_F}^{\infty}dE_3\int_{E_F}^{\infty}dE_4\frac{n_f^{-\sigma}(\mathbf{R}_{ij},E_2)n_f^{-\sigma}(\mathbf{R}_{ij},E_3)n_f^{\sigma}(\mathbf{R}_{ij},E_4)}{\omega+E_2-E_3-E_4+i\eta}$$

$$+U^2\int_{E_F}^{\infty}dE_2\int_{-\infty}^{E_F}dE_3\int_{-\infty}^{E_F}dE_4\frac{n_f^{-\sigma}(\mathbf{R}_{ij},E_2)n_f^{-\sigma}(\mathbf{R}_{ij},E_3)n_f(\mathbf{R}_{ij},E_4)}{\omega+E_2-E_3-E_4+i\eta}\;. \tag{17}$$

Taking the limit $\omega\rightarrow\infty$ and noting that $\int_{-\infty}^{\infty}n_f(\mathbf{R},E)dE=\delta_{\mathbf{R},0}$, Eq. (17) yields

$$\lim_{\omega\rightarrow\infty}\Sigma^{(2)}_{ff,\sigma}(\mathbf{R}_{ij},\omega)=U^2\frac{\delta_{\mathbf{R}_{ij},0}[\delta_{\mathbf{R}_{ij},0}-n_f^{-\sigma}(\mathbf{R}_{ij})]n_f^{-\sigma}(\mathbf{R}_{ij})}{\omega}\;; \tag{18a}$$

this is zero except for $\mathbf{R}=0$; for this case

$$\lim_{\omega\rightarrow\infty}\Sigma^{(2)}_{ff,\sigma}(\mathbf{R}_{ij},=0,\omega)=U^2\frac{(1-n_f^{-\sigma})n_f^{-\sigma}}{\omega}\;. \tag{18b}$$

This behavior of $\Sigma^{(2)}_{ff,\sigma}(\mathbf{R}_{ij},\omega)$ when $\omega\rightarrow\infty$ shows that

$$\lim_{\omega\rightarrow\infty}\Sigma^{(2)}_{ff,\sigma}(\mathbf{k},\omega)=U^2\frac{(1-n_f^{-\sigma})n_f^{-\sigma}}{\omega}\;. \tag{19}$$

On the other hand, for $V\rightarrow 0$, we expect that only the diagonal self-energy, $\Sigma_{ff,ii}(\omega)$, is relevant: This term includes the contributions related to the intrasite interaction for the isolated f shell. According to our discussion in Sec. II, we expect that in this limit $(V\rightarrow 0)\Sigma_{ff,ii,\sigma}(\omega)$ is given by

$$\lim_{V\rightarrow 0}\Sigma_{ff,ii,\sigma}(\omega)=U^2\frac{n_f^{-\sigma}(1-n_f^{-\sigma})}{\omega-E_f-(1-n_f^{-\sigma})U}\;. \tag{20}$$

Since $\Sigma_{ff,ij}(\omega)$ for $i\neq j$ and $V\rightarrow 0$ can be neglected, we can also write the equation for $\Sigma_{ff,\sigma}(\mathbf{k},\omega)$ as

$$\lim_{V\rightarrow 0}\Sigma_{ff,\sigma}(\mathbf{k},\omega)=U^2\frac{n_f^{-\sigma}(1-n_f^{-\sigma})}{\omega-E_f-(1-n_f^{-\sigma})U}\;, \tag{21}$$

where this self-energy behaves as $U^2n_f^{-\sigma}(1-n_f^{-\sigma})/\omega$, for $\omega\rightarrow\infty$. Equations (17), (19), and (21) are the basic equations allowing us to introduce a self-energy $\Sigma_{ff,\sigma}(\mathbf{k},\omega)$ which interpolates between the two limits $U\rightarrow 0$ and $V\rightarrow 0$. As in Sec. II, we introduce the self-energy

$$\Sigma_{ff,\sigma}(\mathbf{k},\omega)=\frac{\Sigma^{(2)}_{ff,\sigma}(\mathbf{k},\omega)}{1-\dfrac{E_f+(1-n_f^{-\sigma})U-E_0}{n_f^{-\sigma}(1-n_f^{-\sigma})}\dfrac{\Sigma^{(2)}_{ff,\sigma}(\mathbf{k},\omega)}{U^2}}\;, \tag{22}$$

where $\Sigma^{(2)}_{ff,\sigma}(\mathbf{k},\omega)$ is given by Eq. (17) but using instead of $n_f^{-\sigma}(\mathbf{k},E)$ the effective density of states, $n_{f,\text{eff}}^{-\sigma}(\mathbf{k},E)$, calculated by means of the one-electron effective Hamiltonian

$$\hat{H}_{\text{eff}}=\sum_{i,\sigma}E_0n_{fi,\sigma}+\sum_{i,\sigma}E_dn_{di,\sigma}+t\sum_{\substack{i,j,\sigma\\ i\neq j}}C^\dagger_{di\sigma}C_{dj\sigma}$$

$$+V\sum_{i,\sigma}(C^\dagger_{di\sigma}C_{fi\sigma}+C^\dagger_{fi\sigma}C_{di\sigma})\;. \tag{23}$$

The effective level E_0 is calculated by imposing self-consistency in n_f for H_{eff} and the final solution calculated with the self-energy $\Sigma_{ff,\sigma}(\mathbf{k},\omega)$. Note that once we know $\Sigma_{ff,\sigma}(\mathbf{k},\omega)$, we can write down the Green function $\tilde{G}^{\sigma}(\mathbf{k},\omega)$ as

$$\tilde{G}^{\sigma}(\mathbf{k},\omega)=\begin{vmatrix}G_{dd}(\mathbf{k},\omega) & G_{df}(\mathbf{k},\omega)\\ G_{fd}(\mathbf{k},\omega) & G_{ff}(\mathbf{k},\omega)\end{vmatrix}=\begin{vmatrix}-\omega+\epsilon_d(\mathbf{k})+E_d & V\\ V & -\omega+E_f+U\langle n_f^{-\sigma}\rangle+\Sigma_{ff,\sigma}(\mathbf{k},\omega)\end{vmatrix}^{-1}\;, \tag{24}$$

where $\epsilon_d(\mathbf{k})=t\sum_{i=\text{NN}}e^{i\mathbf{k}\cdot\mathbf{R}_i}$. From Eq. (24), we calculate the different Green-function components, and their associated charges

$$n_f^{\sigma}(\mathbf{k},\omega)=-\frac{1}{\pi}\,\text{Im}G^{\sigma}_{ff}(\mathbf{k},\omega)\;, \tag{25a}$$

$$n_d^{\sigma}(\mathbf{k},\omega)=-\frac{1}{\pi}\,\text{Im}G^{\sigma}_{dd}(\mathbf{k},\omega)\;. \tag{25b}$$

This ends our discussion for the general method. At this point it is convenient to comment that the case $U\rightarrow\infty$, in

TABLE II. f levels (in arbitrary units, see text) and weights for $U\rightarrow\infty$, $V=0.2$, $E_d=0$, and $e_f=0.1$ in the Hamiltonian (9). Results for the approximate solution obtained from Eq. (11) and the exact one are given.

Approximate		Exact	
Level	f weight	Level	f weight
	$E_f=0.1$, $V=0.2$, $U=\infty$		
−0.42	0.18	−0.49	0.08
−0.05	0.05	−0.08	0.13
0.37	0.53	0.34	0.59

the mixed-valence regime, can be explicitly analyzed, similar to the discussion in Sec. II. Without going into details, let us only write down the final results for the f level and its self-energy as

$$\Sigma^{\infty}_{ff,\sigma}(\mathbf{k},\omega) = -\frac{(n_f^{-\sigma})^2 U^2}{\Sigma^{(2)}_{ff,\sigma}(\mathbf{k},\omega)} , \tag{26}$$

$$\epsilon_f^{\infty} = E_f + \frac{n_f^{-\sigma}}{1-n_f^{-\sigma}}(E_f - E_0) ; \tag{27}$$

results which are quite similar to the ones obtained for the single impurity in Eqs. (12b) and (13).

On the other hand, it is worth commenting that the general solution takes a quite simple way in the symmetric case. Here, $E_f = E_d - \frac{1}{2}U$ and $E_0 = E_d$ so that the interpolation formula for $\Sigma_{ff,\sigma}(\mathbf{k},\omega)$ [Eq. (22)] goes over $\Sigma^{(2)}_{ff,\sigma}(\mathbf{k},\omega)$. In this case, our method reduces to the calculation carried out by Yamada and Yoshida,[19] which appears to be a good interpolation between $U \rightarrow 0$ and $U \rightarrow \infty$. In this context, let us comment that for a symmetric diatomic molecule with a Hubbard interaction, the second-order solution for the self-energy coincides with the exact result, therefore, supporting our conclusion about the behavior of $\Sigma_{ff,\sigma}(\mathbf{k},\omega)$ for the symmetric case.

IV. RESULTS AND DISCUSSION

In this section we present the results obtained for a one-dimensional model, zero temperature, and two electrons per site. The general method presented in Sec. III is independent of the dimensionality of the crystal, but the discussion has been given for zero temperature. A generalization of our procedure to finite temperatures is straightforward: it is only necessary to introduce temperature effects by means of Matsubara's technique in the self-energy and the Green function.[20]

First, we consider the case of finite U and analyze the change in the intermediate valence as a function of the f level. In Fig. 1 we show the charge per atom in the f state (q_f) as a function of E_f for several values of U and $V = 0.4t$. Note that for $U = 0$ there is a linear relationship between q_f and E_f in the region of variation of q_f; the slope of this straight line is a function of V, increasing as V decreases. As U increases, there appears a transition region going from the previous linear relationship between q_f and U, to a constant value of q_f. This region is rather narrow and is localized around $E_f - E_d \approx 0$. Once this region is crossed, q_f remains near 1, up to a value of $E_f - E_d \approx -U$. When E_f decreases below this value q_f increases again, with a dependence on E_f given by a straight line parallel to the one appearing for $U = 0$. Eventually, for $U \rightarrow \infty$, q_f is practically 1 for all values of $E_f - E_d$ less than zero. These results can be understood by noting that for $(E_f - E_d) > -U$, the intra-atomic repulsion prevents two electrons from filling the f level. As soon as $(E_f - E_d) < -U$, the second electron fills the level and q_f grows. On the other hand, for $(E_f - E_d)$ positive, q_f decreases becoming less than 1: For this case correlation effects are negligible, since the probability of finding two electrons in the f level is small, and the dependence of q_f on E_f follows the straight line corresponding to $U = 0$. The present results indicate a continuous dependence of q_f on E_f and show that the simplest version of the Anderson lattice (with no f-d correlation) cannot describe the sharp valence transitions found in anomalous rare-earth compounds.[10]

Our results show how correlation effects increase with U. In the mixed-valence problem, U is rather high and in the following we concentrate on discussing this high-U limit by taking $U \rightarrow \infty$, and by applying the method discussed in Sec. III. In our actual calculations, we have slightly modified the method discussed in Sec. III by calculating the second-order-diagonal and off-diagonal self-energies, $\Sigma^{(2)}_{ff,11,\sigma}(\omega)$ and $\Sigma^{(2)}_{ff,12,\sigma}(\omega)$, respectively, instead of $\Sigma^{(2)}_{ff,\sigma}(\mathbf{k},\omega)$. It is much more cumbersome to calculate the $\mathbf{k}$-dependent self-energy, $\Sigma^{(2)}_{ff,\sigma}(\mathbf{k},\omega)$, than a few components of $\Sigma^{(2)}_{ff,ij,\sigma}(\omega)$. Note that these self-energies are related by the equation

$$\Sigma^{(2)}_{ff,\sigma}(\mathbf{k},\omega) = \sum_j \Sigma^{(2)}_{ff,1j,\sigma}(\omega) e^{ikR_{j1}} . \tag{28}$$

In Figs. 2—5 we show the f density of states for the

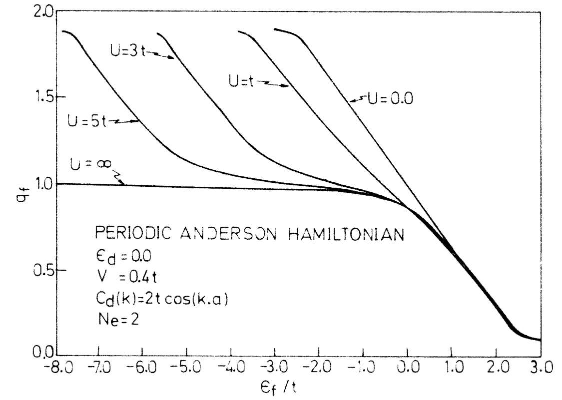

FIG. 1. Charge per atom in the f level as a function of E_f for several values of U.

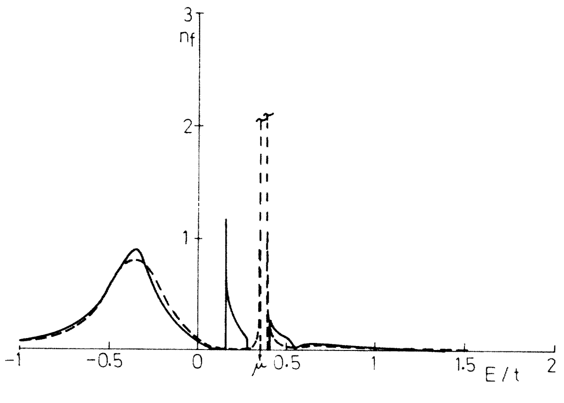

FIG. 2. f density of states for $V = 0.4t$ and $q_f = 0.9$ ($\epsilon_f = -0.31t$). Dashed line: a local self-energy is used in the calculation. Full line: full self-energy. $\mu \equiv$ Fermi level for the solution with the full self-energy.

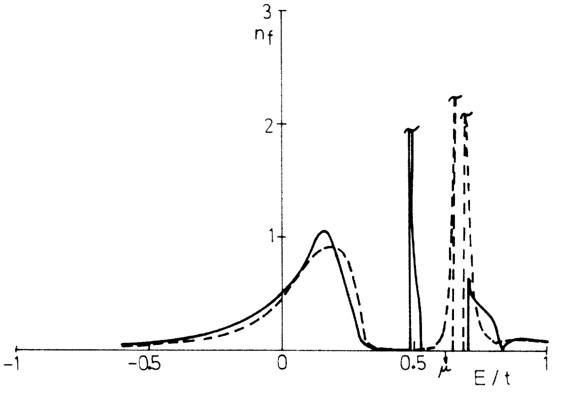

FIG. 3. Same as in Fig. 2, for $q_f=0.8$ ($\epsilon_f=0.22t$).

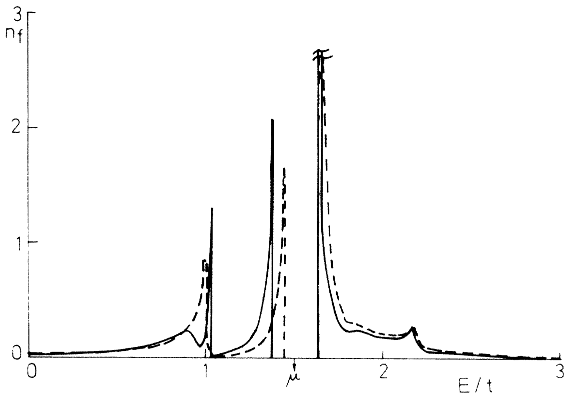

FIG. 5. Same as in Fig. 2, for $q_f=0.46$ ($\epsilon_f=1.40t$).

cases $V=0.4t$, and $q_f=0.9$, 0.8, 0.7, and 0.46, corresponding to $\epsilon_f=-0.31$, 0.22, 0.56, and 1.40. In the same figures is shown the same density of state calculated by neglecting $\Sigma_{ff,12,\sigma}(\omega)$ in Eq. (28); this calculation has been made in order to check the validity of substituting $\Sigma_{ff,\sigma}(\mathbf{k},\omega)$ by a local self-energy, $\Sigma_{ff,11,\sigma}(\omega)$. The most important result coming out of these calculations is that, up to the accuracy of our calculations ($\sim 1\%$), the Fermi level (μ) always lies in the energy gap no matter the value of E_f, in agreement with considerations based on the Luttinger's sum rule.[11] Let us remark that this result is a further check to the procedure given in this paper, since the self-consistency imposed in n_f does not guarantee the Luttinger's sum rule (see in this respect the comments of Sec. II for the approximate solutions of two levels).

Figures 2–5 show the important effect of correlation on the f density of states, this effect increasing with the valence charge q_f. In all the cases, we find two peaks around the fundamental gap and a third peak at lower energies; this latter peak is a typical effect associated with electronic correlation whose importance decreases with q_f. From these figures we can also see how the energy gap increases with decreasing q_f. It is worth commenting that the energy gap is very sensitive to the approximation made to calculate $\Sigma^{\sigma}_{ff}(\mathbf{k},\omega)$. As Figs. 2–5 show, the energy gap is too small if we neglect the off-diagonal self-energies components; a good calculation of the electronic density of states for the Anderson lattice has to include the strong effects of those off-diagonal self-energies. This effect is much more important for q_f close to 1; for q_f small (say, less than 0.5), a calculation of the energy gap and the density of states which only includes the diagonal self-energy gives quite reasonable results.[21]

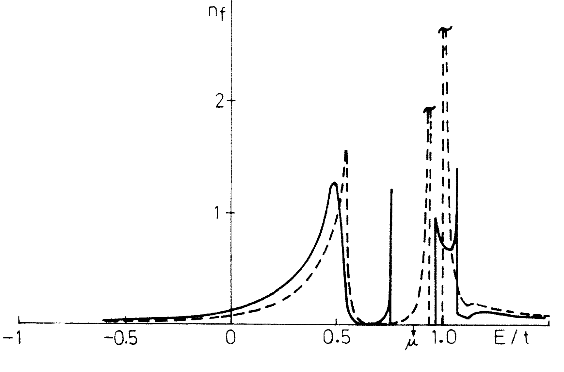

FIG. 4. Same as in Fig. 2, for $q_f=0.7$ ($\epsilon_f=0.56t$).

Finally, in Figs. 6–9 we show the electronic bands near the fundamental gap for the cases analyzed in Figs. 2–5. We only show the energy region for which sharp levels appear; outside this region, the levels are broadened by correlation effects as measured by the imaginary part of $\Sigma_{ff,\sigma}(\mathbf{k},\omega)$. Figures 6–9 also show the important effects introduced by correlation. For q_f close to 1, the energy gap appears between $\mathbf{k}$ points close to $\pi/2$. As q_f decreases, the minimum of the conduction band and the maximum of the valence bands approach the $\mathbf{k}$ points 0

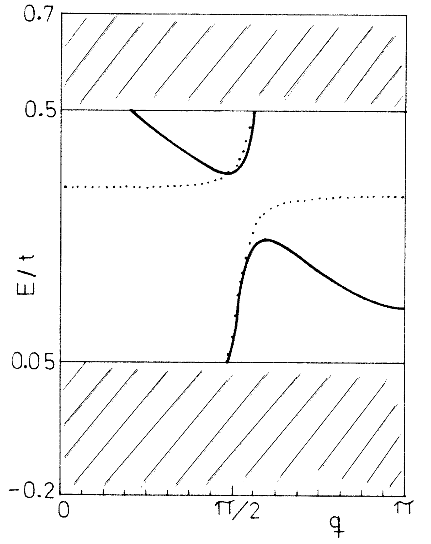

FIG. 6. Electronic bands near the fundamental gap for $V=0.4t$ and $q_f=0.9$ ($\epsilon_f=-0.31t$). Dashed line: a local self-energy is used in the calculation. Full line: full self-energy.

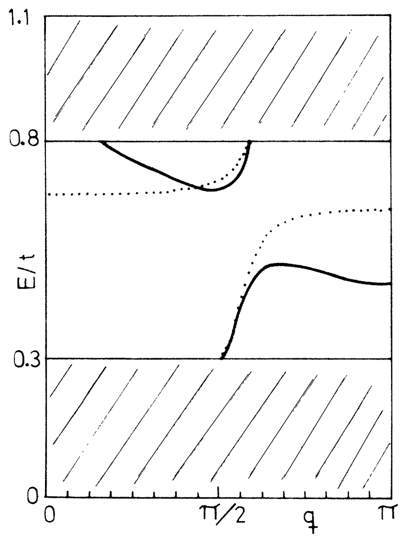

FIG. 7. Same as in Fig. 6, for $q_f=0.8$ ($\epsilon_f=0.22t$).

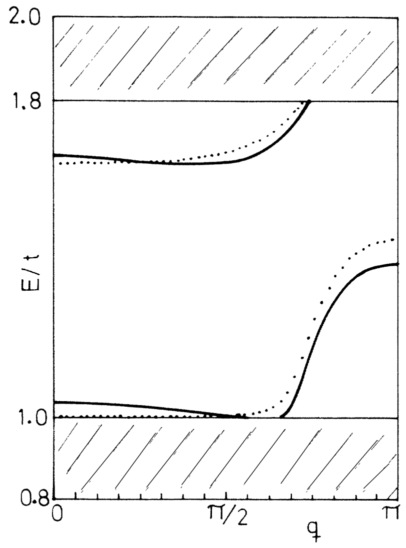

FIG. 9. Same as in Fig. 6, for $q_f=0.46$ ($\epsilon_f=1.40t$).

and π, respectively. Thus, the maximum of the valence band appears at $k=\pi$ for $q_f \lesssim 0.7$, while the minimum of the conduction band appears at $k=0$ for $q_f \lesssim 0.45$. Below this latter value, correlation effects are not very important and the fundamental gap appears between the center and the edge of the Brillouin zone as corresponds to the case $U=0$.

Our results can only be compared with the ones obtained by Jullien and Martin[22] through finite-cell calculations. In order to compare the two calculations we have calculated the different energy gaps associated with the transitions $\pi/2 \rightarrow \pi/2$, $0 \rightarrow \pi/2$ and $0 \rightarrow 0$. Our results are shown in Fig. 10 for $q_f=0.46$ as a function of the intrasite Hubbard interaction (note that for $U>2t$, the different gaps are constant, showing that we have reached the high-U limit). These results are very similar to the ones found by Jullien and Martin (see Fig. 6 of Ref. 22) (we have found, however, some discrepancies with these calculations in the Kondo regime[13]).

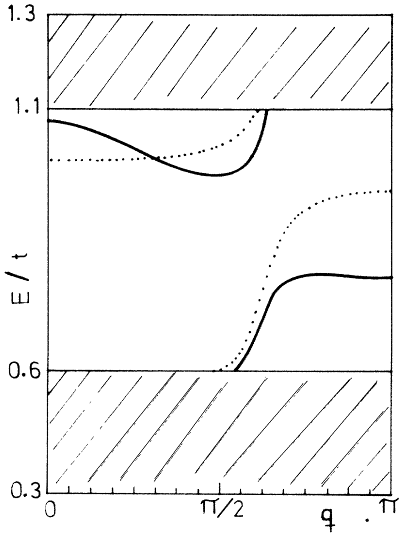

FIG. 8. Same as in Fig. 6, for $q_f=0.7$ ($\epsilon_f=0.56t$).

In conclusion, we have presented a method to analyze the quasiparticle density of states, as well as other related properties, of the Anderson Hamiltonian, where the f state has been assumed to have the degeneracy of a spin $\frac{1}{2}$. Although the method can be used to treat the Anderson lattice for any dimension, for finite temperatures and for any degeneracy of the f state, we have only presented results in one dimension, two electrons per site, and zero temperature. For this case we find the following results: (i) the paramagnetic phase is always insulating no matter the f valence and the magnitude of U; (ii) the transition from a phase of valence 1 to an intermediate valence is continuous and this intermediate region appears for values of E_f quite close to E_d.

Let us finally comment that the discussion of Sec. II as well as the results coming out of our calculation and their

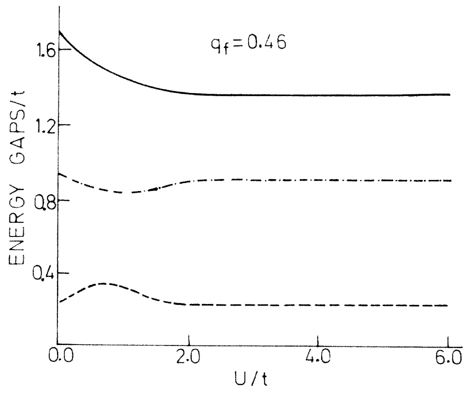

FIG. 10. Different energy gaps (see text) as a function of U/t for $q_f=0.46$ ($\epsilon_f \simeq 1.40t$).

good agreement with other results[22] and the Luttinger's sum rule,[11] suggest that the method given in this paper is accurate enough to take our results with great confidence.

ACKNOWLEDGMENT

It is a pleasure to thank Professor C. Balseiro for any helpful discussions.

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