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Gutzwiller-type approach of the size-dependent valence change in small Pr aggregates

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We give a theoretical approach to the valence change in small Pr_n aggregates [transition: $4f^3(5d6s)^2 \rightarrow 4f^2(5d6s)^3$], our study limited to $n \leq 4$. The quantum-mechanics problem (Anderson Hamiltonian) exhibits various difficulties: f-valence mixing and strong intra-atomic f correlations. For dealing with this problem we use an extension to the mixed-band systems of the Gutzwiller method. The extension is detailed and controlled by an application to the Hubbard s chain, for which the exact solution is known. As the number of f electrons and sites of our Pr_n system is relatively small, we take into account the full f degeneracy. We find the transition for $n=3$, which is close to the experimental result, $n=5$. A physical explanation of the phenomenon is proposed.

I. INTRODUCTION

The Gutzwiller method is a very powerful tool that has been used in the solution of many problems in which the intra-atomic correlation energy is large (but not infinite) and strongly influences the electronic (or more generally fermionic) properties. In its original version, it was first proposed for studying band structures at $T=0$ in s cubic lattices described by the Hubbard Hamiltonian.[1,2] Then, several extensions were proposed. Among them one may mention various studies: Hubbard s lattices at finite temperatures;[3] susceptibility and compressibility of normal-liquid $^3\mathrm{He}$;[4] systems with a limited number of atoms (i.e., aggregates) with s (Ref. 5) or π (Ref. 6) wave functions; modification of the momentum distribution used in the Gutzwiller theory.[7] In these works no important changes in the principles of the Gutzwiller method were made, the basic assumption always being that all the sites were equivalent (or nearly equivalent in the case of aggregates).

Recently, progress appeared with the application of the Gutzwiller technique to mixed-band problems[8,9] or, which is formally equivalent, to s systems with two kinds of sites (for instance, antiferromagnetic systems).[10–12] In this paper, we intend to develop such an extension to the study of small rare-earth aggregates which exhibit a mixing of $4f$ and valence levels and pose an intriguing problem since, for most of the rare-earth elements (except Ce, Gd, Eu, and Yb) the electronic configuration changes with the increase of the size, from $4f^{\nu}6s^2$ (atom) to $4f^{\nu-1}(5d6s)^3$ (bulk).

We shall consider the case of praseodymium aggregates in which the transition from $\nu=3$ to $\nu=2$ has been observed[13] in photoabsorption studies. These experiments have been performed on Pr, Nd, and Sm aggregates embedded in a solid Ar matrix. Their size is deduced from the ratio of the metal to Ar weights deposited during the sample preparation. The measurement of the L_{III} absorption threshold, which is very sensitive to the f population, leads to the knowledge of the electronic configuration and the conclusion of this work is that the valence change occurs for n_c nearly 5.

It is worth noticing that free rare-earth aggregates have begun to be investigated by the liquid-metal ion source (LMIS) technique (for Pr see Ref. 14, for other rare-earth elements see Refs. 15 and 16). These works give interesting information on the aggregates since the emission intensities are related to the stabilities of the corresponding species.

In the next section we give the principles of the method and apply it, in Sec. III, to the study of a ring of s sites described by the Hubbard Hamiltonian. This application will serve as a control since an exact solution of the problem exists. We will see that the Gutzwiller method gives an energy very close to the exact energy of the ground state.

II. PRINCIPLES OF THE METHOD

Let us consider a system where the basis wave functions, indexed by g, can be divided into two kinds, A and B. The Hamiltonian contains a one-electron part and a correlation part with intra-atomic energies U_A and U_B. It is always possible to write the one-electron energy E_H in the form[12]

$$E_H = \sum_{\substack{k,k'\sigma \text{ occupied} \\ g,g'}} \varepsilon_{k\sigma} a_g^{k\sigma} a_{g'}^{k\sigma} a_g^{k'\sigma} a_{g'}^{k'\sigma} , \tag{1}$$

$$E_H = \sum_{g,g',\sigma} p_\sigma(g,g') , \tag{2}$$

where the expression of the propagator $p_\sigma(g,g')$ between sites g and g' can easily be obtained from a combination of formulas (1) and (2). In relation (1) $k\sigma$ is an index for the molecular one-electron wave functions with eigenenergy $\varepsilon_{k\sigma}$ and eigenvector coefficients $a_g^{k\sigma}$.

Then, one may write E_H in the form

$$E_H = \sum_{\sigma} E_{A\sigma} + E_{B\sigma} + E_{AA\sigma} + E_{BB\sigma} + E_{AB\sigma} \tag{3}$$

with

$$E_{A\sigma}=\sum_{g\in A} p_\sigma(g,g') \,, \tag{4}$$

$$E_{\sigma}=\sum_{\substack{g\in A,g'\in A\\ g\neq g'}} p_\sigma(g,g') \,, \tag{5}$$

$$E_{AB\sigma}=\sum_{\substack{g\in A,g'\in A\\ g\in B,g'\in A}} p_\sigma(g,g') \,. \tag{6}$$

$E_{B\sigma}$ and $E_{BB\sigma}$ take the same form as $E_{A\sigma}$ and $E_{AA\sigma}$ with the index B replacing A.

The general Gutzwiller expression of the energy can be written

$$\begin{aligned}E_G=\sum_\sigma\,[&E_{A\sigma}\tilde{q}_\sigma(\eta_A=1)+E_{AA\sigma}\tilde{q}_{AA\sigma}(\eta_A)\\&+E_{B\sigma}\tilde{q}_{BB\sigma}(\eta_B=1)+E_{BB\sigma}\tilde{q}_{BB\sigma}(\eta_B)\\&+E_{AB\sigma}\tilde{q}_{AB\sigma}(\eta_A,\eta_B)]\\&+\tilde{\chi}_A(\eta_A)U_A+\tilde{\chi}_B(\eta_B)U_B \,.\end{aligned} \tag{7}$$

The $\tilde{q}$ and $\tilde{\chi}$ terms, respectively, modify the hopping and the correlation one-electron energies. They are variational functions of two parameters η_A and η_B where $\eta_A=\eta_B=1$ corresponds to $U_A=U_B=0$. They also depend on the parameters of the problem, i.e., L_A and L_B, the numbers of wave functions in the basis; $N_{A\sigma}$ and $N_{B\sigma}$, the number of electrons; $N^H_{A\sigma}$ and $N^H_{B\sigma}$, the corresponding quantities in the one-electron calculation. In the general procedure $N_{A\sigma}$ and $N_{B\sigma}$ can be different from $N^H_{A\sigma}$ and $N^H_{B\sigma}$ and can be considered as variational parameters. It has been shown[10] that $\tilde{q}_{AB\sigma}$ can simply be expressed as

$$\tilde{q}_{AB\sigma}\sim(\tilde{q}_{AB\sigma}\tilde{q}_{BB\sigma})^{1/2} \,. \tag{8}$$

III. CONTROL OF THE METHOD

One may first mention the calculations made on small s aggregates which can be compared with the exact solution of the Hubbard Hamiltonian.[17] The values of the two electronic energies are very close over a wide range of $U/|\beta|$ values (β is the transfer term between neighboring sites). Another situation where the method can be controlled is the study of a non-dimerized s ring since the Hamiltonian, which we write as

$$H=\beta\sum_{\substack{i,j=i\pm1\\ \sigma}} c^\dagger_{i\sigma}c_{j\sigma}+U\sum_{i\sigma} n_{i\sigma}n_{i-\sigma} \,, \tag{9}$$

has received an exact solution.[18–20]

For studying this problem with the Gutzwiller method one may first be tempted to use the original version (with only one kind of site) but when $U/|\beta|$ is large the energy obtained is very far from the exact one.[21] The other possibility is to study a regular spin-density-wave (SDW) configuration though it is known that such a configuration cannot be the exact ground state which is only partly antiferrogmagnetic.[18–20] This point will be discussed later.

Then, we suppose that the ring is made of a regular series of A and B sites ($ABAB\ldots$) where the A (B) sites have an excess of ↑ (↓) electrons. We will call $N_{A\uparrow}>N_\uparrow/2$ and $N_{B\downarrow}>N_\downarrow/2$ the numbers of ↑ (↓) electrons on A (B) sites, where $N\uparrow$ ($N\downarrow$) is the total number of ↑ (↓) electrons. In this paper we only study the half-filled band:

$$N_\uparrow+N_\downarrow=L \,,$$

where $L=L_A+L_B$ is the total number of sites, which is taken of the form $L=4j+2$ where j is an integer.

When applying Eq. (7) we see that various simplifications occur. We have $E_A=E_B=0$, because the one-electron diagonal term in Eq. (9) is zero, and $E_{AA}=E_{BB}=0$, because we only consider nearest-neighbor hoppings. Then we have

$$E_H=\sum_\sigma E_{AB\sigma} \tag{10}$$

and using Eq. (8) we are led to the minimization of

$$E_G=\sum_\sigma E_{AB\sigma}(\tilde{q}_{AA\sigma}\tilde{q}_{BB\sigma})^{1/2}+U(\tilde{\chi}_A+\tilde{\chi}_B) \,. \tag{11}$$

In systems where the number of electrons is large the $\tilde{q}$ and $\tilde{\chi}$ functions can be expressed in terms of variational parameters ν_A and ν_B (different from η_A and η_B) which, physically, represent the number of doubly occupied sites on A and B sites.[1,2,10] Then $\tilde{\chi}_A$ and $\tilde{\chi}_B$ are simply given by ν_A and ν_B. The various $\tilde{q}(\nu)$ functions are given in Ref. 10.

For a given $U/|\beta|$, besides the ν variational parameters we can vary the numbers $N_{A\uparrow}$ and $N_{B\downarrow}$, i.e., the amplitude of the SDW, which will be considered as other variational parameters. As a consequence, the $\tilde{q}$ values in the noncorrelated limit are different from unity; for example, we have

$$\tilde{q}_{AA\uparrow}(\eta_A=1)=\tilde{q}_{AA\uparrow}\left[\nu_A=\frac{N_{A\uparrow}N_{A\downarrow}}{(L/2)}\right]=\frac{N_{A\uparrow}}{N^H_{A\uparrow}}=\frac{N_{A\uparrow}}{(L/4)} \tag{12}$$

and a similar formula for B site and ↓ spin.

In Fig. 1 we give the electronic energy obtained in our calculations, in the exact solution and in the approximate solution (VMC: variational Monte Carlo) of Ref. 21. It can be seen that our degree of accuracy is comparable to

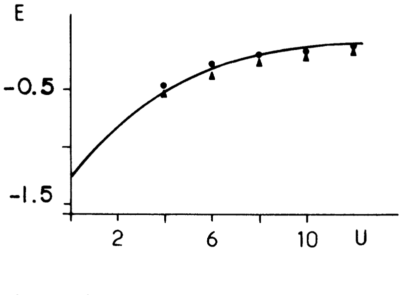

FIG. 1. Electronic energy E per atom for a chain in the half-filled case, vs U [●, the present calculation; ▲, the exact solution (Ref. 18); continuous line, the VMC calculation (Ref. 21)]. E and U are given in $|\beta|$ units.

TABLE I. Alternate magnetization M_s.

$U/\|\beta\|$	M_S (Ref. 26)	M_S (present calculation)
4	0.62	0.51
6	0.70	0.93
8	0.80	0.96

the VMC calculation and that both results are very close to the exact one. The optimum alternate magnetization per atom ($M_s = 2N_{A\uparrow}/L = 2N_{B\downarrow}/L$) is given in Table I. As we already mentioned, this characteristic, which is also obtained in other approximate methods,[21,22] is contrary to the exact solution.[18] The study of the exact spin correlation function $q_l = \langle s_i^z s_{i+l}^z \rangle$ (for large $U/|\beta|$ see, for instance, Refs. 23 and 24) shows that there is only a local antiferromagnetic order ($|q_l| \rightarrow 0$ when l increases). By creating a SDW, we have forced the system into an excited state. However, the fact that we obtain an energy very close to the exact one shows that this state is only slightly excited with respect to the ground state. The similarity of the energies allows us also to think that the Gutzwiller method is a good simple tool to handle such Hubbard problems.

IV. STUDY OF Pr$_n$ AGGREGATES

A. The method

Let us first give the Anderson Hamiltonian H_A which is commonly used for the study of rare-earth elements,[8,9,25]

$$H_A = \sum_{\substack{i \neq j \\ \lambda,\mu,\sigma}} \beta_{\lambda\mu}^{ij} c_{\lambda i\sigma}^{\dagger} c_{\mu j\sigma} + \sum_{\substack{i \neq j \\ \lambda,l,\sigma}} V_{\lambda l}^{ij} (c_{\lambda i\sigma}^{\dagger} f_{lj\sigma} + f_{lj\sigma}^{\dagger} c_{\lambda i\sigma}) + E_f \sum_{i,l,\sigma} n_{il\sigma} + \tfrac{1}{2} U \sum_{(l,\sigma) \neq (l',\sigma')} n_{il\sigma} n_{il'\sigma'} , \tag{13}$$

where $n_{il\sigma} = f_{il\sigma}^{\dagger} f_{il\sigma}$ is the number of f electrons with spin σ and orbital number l at site i; $c_{\lambda i\sigma}^{\dagger}$ is the creation operator of a valence electron on site i with spin σ and λ denoting one of the five $5d$ components ($2 \leq \lambda \leq 6$) or the orbital $6s$ ($\lambda = 1$).

This Hamiltonian describes the coupling between the valence and the f levels. As in Sec. II we will index them by A and B, respectively.

Let us first examine the one-electron part of the calculation. A first simplification, introduced in Refs. 8 and 9, is to limit the first and second hopping terms in H_A to first neighbors and to neglect the orbital dependence. Then, the i,j,μ,λ indexes can be removed and we can use the simplified notations β and V. Moreover, if we consider (as is done in Refs. 8 and 9) that the V term is much smaller than β and E_f, the expressions E_B, E_{AA}, and E_{AB}, defined by Eqs. (4), (5), and (6), are simply proportional to, respectively, E_f, β, and V. One may also note that $E_A = 0$ [origin of the energies in (13)] and $E_{BB} = 0$ (no direct intersite $f_i \rightarrow f_j$ hopping). Then, relation (3) becomes

$$E_H = a\beta + bE_f + cV , \tag{14}$$

where a, b, and c are coefficients given by the one-electron calculation.

Another simplification comes from the fact that there is no intra-atomic correlation in the valence levels ($U_A = 0$). We have only to take into account intra-atomic correlations in the f band. Consequently η_B is the only variational parameter to be considered and therefore

$$\tilde{q}_{AA}(\eta_A) \equiv \tilde{q}_{AA}(1) . \tag{15}$$

The numbers of electrons N_A and N_B on A and B levels are also important physical parameters (we define them by $N_A = \sum_\sigma N_{A\sigma}$ and $N_B = \sum_\sigma N_{B\sigma}$) since we want to examine the transition from $\nu = 3$ to $\nu = 2$ (change of N_B from $3n$ to $2n$) as the number of atoms n increases. Here, the relative variation of N_B (or N_A) is large and it is not possible to take this quantity as a continuous variational parameter as it was done for $N_{A\uparrow}$ (or $N_{B\downarrow}$) in Sec. III. We will rather undertake separate studies for two discrete and fixed values: $N_B = N_B^H \sim 3n$ and $N_B = N_B^H \sim 2n$. In each study we simply have

$$\tilde{q}_{AA}(\eta_A = 1) = \tilde{q}_{BB}(\eta_B = 1) = 1 . \tag{16}$$

According to this discussion and by using Eqs. (14), (15), and (16) we obtain, for the variational function to be minimized,

$$E_G = a\beta + bE_f + cV[\tilde{q}(\eta)]^{1/2} + \tilde{\chi}(\eta)U , \tag{17}$$

where we have simply written $\tilde{q}_{BB}(\eta_B) = \tilde{q}(\eta)$, $\tilde{\chi}_B(\eta_B) = \tilde{\chi}(\eta)$, and $U_B = U$.

In Ref. 8 the previous method was applied to bulk cerium where the f band contains a number of electrons per atom close to one. Then the authors assimilate the f band to an s band and use the $\tilde{q}$ and $\tilde{\chi}$ functions of the original Gutzwiller paper.

Our treatment is different on two points. Firstly, we establish new $\tilde{q}(\eta)$ and $\tilde{\chi}(\eta)$ functions where we take into account the full degeneracy of the f level. Secondly, in the one-electron calculation we treat separately the various f components.

B. Variational functions for f levels

As we already mentioned the $\tilde{q}(\eta)$ and $\tilde{\chi}(\eta)$ functions are known for an s band.[1,2] They can be written

$$\tilde{q}(\eta) = q(\eta)/N(\eta) , \tag{18}$$

$$\tilde{\chi}(\eta) = q(\eta)/N(\eta) , \tag{19}$$

where $N(\eta)$, $q(\eta)$, and $\chi(\eta)$ have the following physical meanings: $N(\eta)$: normalization of the variational wave function Ψ; $q(\eta)$: modification of the hopping term; and $\chi(\eta)$: modification of the correlation terms.

When η varies from 1 to 0, $q(\eta)/N(\eta)$ and $\chi(\eta)/N(\eta)$ decrease, respectively, from 1 to 0 and from $N_\uparrow N_\downarrow / L$ to 0 if $(N\uparrow + N\downarrow) < L$ or to $N_\uparrow + N_\downarrow - L$ if $(N_\uparrow + N_\downarrow) > L$ [where $N\uparrow$ ($N\downarrow$) is the number of $\uparrow$ ($\downarrow$) electrons and L the number of sites].

In an f band, the difference from the s band problem is that the number of configurations is larger because each f level can accommodate 14 electrons. S denotes the set of electronic configurations obtained by distributing νn electrons ($\nu=2$ or 3 and $n=2,3,4$) on n sevenfold degenerate f functions. For each configuration, we count the number α of electron pairs on the same atom, then we write

$$N(\eta)=\sum_{S}\eta^{2\alpha}$$

which can be recast into

$$N(\eta)=\sum_{\alpha\in G}N_1(\alpha)\eta^{2\alpha}\ ,$$

where G is the set of α values. The $q(\eta)$ term is obtained by

$$q(\eta)=\sum_{S,S'}\eta^{\alpha+\alpha'}\ ,$$

where the summation is made on all the couples of configurations which differ from one another by the hopping of one electron with spin conservation.

Moreover, we have, as in Ref. 1,

$$\chi(\eta)=\sum_{S}\alpha\eta^{2\alpha}=\sum_{\alpha\in G}\alpha N_1(\alpha)\eta^{2\alpha}\ .$$

Our functions are given in Table II for $n\leq 3$. We observe that, as expected, in the noncorrelated limit ($\eta=1$) we have $q(1)/N(1)=1$ and in the opposite limit ($\eta=0$) we have $q(0)/N(0)=0$ ($\nu=2$ and 3) and $\chi(0)/N(0)=n$ ($\nu=2$) or $\chi(0)/N(0)=3n$ ($\nu=3$). Our functions have been obtained for $n\leq 4$ by an analytical calculation but we are elaborating a computer program which will give them for larger n values.

C. One-electron calculation and minimization procedure

Let us return to the one-electron calculation. For $n=3$ and 4 we have chosen compact shapes, i.e., the triangle and the tetrahedron. We diagonalize the Hamiltonian (13) (without the U term) in which we suppose that all the valence components are equivalent. This approximation leads to a removal of indexed λ and μ in $\beta_{\lambda\mu}^{ij}$ and $V_{\lambda l}^{ij}$ which become β_{ij} and V_{lij}. We calculate V_{lij} by

$$V_{lij}=\langle 4f_l|4f_{0,i-j}\rangle V\ ,$$

where $f_{0,i-j}$ is the $l=0$ component when the Oz axis is directed along the i—j bond.

Considering a valence band width of 10 eV for the bulk we have derived $\beta\sim 0.8$ eV. We have fixed V by using the relation between the observed half-width Δ, of the order of 0.05 eV and V,[26]

$$\Delta=\pi n(E_F)V^2\ ,$$

where we take for $n(E_F)$ an average density of six electronic states for a width of 10 eV, therefore $V\sim 0.15$ eV. The value of E_f is deduced from the $4f^35d6s\rightarrow 4f^25d6s^2$ atomic transition which is about 3 eV (Ref. 27) and which is equal to E_f-2U, where U is the intra-atomic correlation energy. For $U=3$ eV, which is a typical value for rare earth elements,[26] we obtain $E_f=9$ eV.

The diagonalization gives us the electronic levels. We consider two situations. In the first case we put $2n$ electrons on the lowest levels, which are predominantly f, and the other $3n$ electrons are put on the first levels, predominantly of valence type. We then arrive at an f valence population which is almost two per atom; the exact populations are given in Table III. Then we calculate the Hückel energy and deduce coefficients a, b, and c of formula (14) that we will use for the case of $4f^2(5d6s)^3$ configuration. The same procedure is used for the $4f^3(5d6s)^2$ configuration which gives us another set of a, b, and c values.

For each configuration we minimize the total energy (17) by using the convenient variational functions obtained before and we compare their stabilities.

D. Results—conclusion

In Table IV we give the η values and the energy difference E_2-E_3 between stabilities of the $2f$ electron case and the $3f$ electron case. We observe that the η values are small which means that we are very close to the localization of the f electrons on the sites. We also note that the configuration with $2f$ electrons per atom begins to become the stablest for $n\geq 3$, a result which is close to the $n_c=5$ experimental one.

Physically, one may try to understand this result. As the f electrons are almost localized on the sites the correlation part of E_2-E_3 is close to n times the $2U$ correlation energy difference of atoms. One must then take into

TABLE II. Polynomial expression for $N(\eta)$ and $q(\eta)$ versus the number of atoms (n) in the cluster and the number of valence electrons (ν).

n	ν	
2	2	$q(\eta)=8\eta^9+16\eta^5$ $N(\eta)=4\eta^{12}+12\eta^6+8\eta^4$
2	3	$q(\eta)=8\eta^{25}+16\eta^{17}+24\eta^{13}$ $N(\eta)=4\eta^{30}+12\eta^{20}+20\eta^{14}+12\eta^{12}$
3	2	$q(\eta)=16\eta^{25}+\eta^{21}+14\eta^{20}+40\eta^{17}+40\eta^{16}+14\eta^{14}+96\eta^{13}+14\eta^{12}$ $+74\eta^{11}+144\eta^{10}+9\eta^9+119\eta^8+105\eta^7+4\eta^6$ $N(\eta)=9\eta^{30}+66\eta^{20}+108\eta^{14}+165\eta^{12}+282\eta^8+60\eta^6$
3	3	$q(\eta)=24\eta^{64}+12\eta^{56}+48\eta^{50}+48\eta^{49}+48\eta^{43}+72\eta^{40}$ $+72\eta^{38}+96\eta^{37}+168\eta^{34}+102\eta^{32}+96\eta^{31}+240\eta^{29}+252\eta^{28}$ $+324\eta^{25}+180\eta^{23}+384\eta^{22}+216\eta^{20}+228\eta^{19}$ $N(\eta)=4\eta^{72}+72\eta^{56}+120\eta^{44}+96\eta^{42}+168\eta^{36}+516\eta^{32}$ $+420\eta^{26}+480\eta^{24}+612\eta^{20}+14\eta^{18}$

TABLE III. Exact f population in our calculations versus the number of atoms (n) and the number of valence electrons (ν).

	$\nu=2$	$\nu=3$
$n=2$	1.998	2.999
$n=3$	1.989	2.986
$n=4$	1.997	2.999

TABLE IV. η and E_3-E_2 versus the number of atoms (n) and the number of valence electrons (ν).

	$\nu=2$	$\nu=3$	E_3-E_2 (eV)
$n=1$			-3
$n=2$	$\eta=0.0249$	$\eta=0.0232$	-1.06
$n=3$	$\eta=0.00520$	$\eta=0.0101$	1.10
$n=4$	$\eta=0.00407$	$\eta=0.00377$	2.54

account the fact that the number of valence electrons is larger ($3n$ instead of $2n$) in the $4f^2$ case. If the n excess valence electrons of this configuration were at the original atomic energy we would obtain

$$E_3-E_2=n(2U-E_f)$$

which is negative. But as valence bonding levels begin to appear for $n=2,3,\ldots$ the loss of energy is less than nE_f and E_3-E_2 becomes positive. This type of calculation can be improved at least along two directions. A better description of the valence band can be carried out, for example by considering separately the $5d$ and $6s$ levels. Exchange energy can be included in the f band. These improvements could lead to a better agreement with experiments; however, we think that this simple treatment gives the main features of the valence-change phenomenon in praseodymium.

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