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J.C. Parlebas, R.H. Victora, L.M. Falicov. Exact solution of a four-site crystal model for an intermediate-valence system. *Journal de Physique*, 1986, 47 (6), pp.1029-1034. <10.1051/jphys:019860047060102900>. <jpa-00210279>

HAL Id: jpa-00210279

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Submitted on 4 Feb 2008

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HAL Authorization

Classification
 Physics Abstracts
 71.10

Exact solution of a four-site crystal model for an intermediate-valence system

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(Reçu le 20 décembre 1985, accepté le 6 février 1986)

Résumé. — Nous présentons une résolution exacte d'un cristal tétraédrique à quatre sites qui constitue le plus petit modèle possible d'un cristal cubique à faces centrées, et ceci dans le cas d'un système à valence intermédiaire. Notre modèle comprend : (a) une orbitale étendue et une autre localisée par site ; (b) un terme de transfert interatomique entre les orbitales étendues ; (c) un terme d'hybridation interatomique entre orbitales étendues et localisées ; et (d) une forte répulsion coulombienne intraatomique entre états localisés de spin opposés. En utilisant la symétrie du cristal nous calculons exactement les états propres et les valeurs propres du Hamiltonien à N -corps ; en particulier, nous présentons le cas d'un électron par site, ce qui se présente dans le cérium.

Abstract. — An exact solution of a four-site tetrahedral crystal model, the smallest face-centred cubic crystal, is presented for the case of an intermediate-valence system. The model consists of : (a) one extended and one localized orbitals per atom ; (b) an interatomic transfer term between the extended orbitals ; (c) an interatomic hybridization term between extended and localized orbitals ; and (d) a strong intraatomic Coulomb repulsion between opposite-spin localized states. Many-body eigenstates and eigenvalues of the Hamiltonian are calculated exactly with the aid of the symmetry of the crystal for the case of one electron per atom, which corresponds to metallic cerium.

1. Introduction.

The physics of anomalous rare-earth elements and compounds involves a phenomenon known as intermediate valence, which has received considerable attention in the last few years [1-3]. This phenomenon is essentially caused by the competing effects of three types of forces : (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) hybridization effects which mix f - and conduction-band states.

Several theoretical approaches to the intermediate valence problem have been proposed. The periodic Anderson Hamiltonian [2, 3], which is an extension to a periodic lattice of the well known Anderson magnetic impurity problem [4], seems to be the most appropriate Hamiltonian to describe the important features of most anomalous rare-earth crystals. To our knowledge this Hamiltonian has never been

solved exactly for a three dimensional lattice, although many approximate solutions and schemes have been proposed and published. In addition exact solutions for a homopolar diatomic molecule and for an isolated three-atom cluster have been worked out by Lin and Falicov [5] and by Arnold and Stevens [6] respectively. The ground state of the one-dimensional periodic Anderson Hamiltonian with one site and two electrons per unit cell and arbitrary strength of the repulsive interaction U has been calculated by Jullien and Martin [7].

In this contribution we present exact calculations for the three-dimensional periodic Anderson Hamiltonian in the smallest face-centred cubic crystal, i.e. a four-site tetrahedral cluster with periodic boundary conditions. Many-body eigenstates and eigenvalues are obtained in a similar way to that previously employed to solve the one-orbital per site Hubbard Hamiltonian [8]. To simulate the case of metallic cerium we restrict ourselves in this short paper to the case of one electron per site, i.e. to four electrons in the tetrahedral crystal. In section 2 we introduce the model, write the

Hamiltonian and define the various contributions to it. Exact solutions for a variety of cases are then obtained and presented in section 3. The solution involves a systematic application of group theory and the reorthogonalized Lanczös procedure for generating the Hamiltonian matrix and its eigenvalues. Section 4 contains the conclusions.

2. Formulation and general remarks.

We consider a four-site tetrahedral crystal model with identical atoms; the sites are labelled $i = 1, 2, 3, 4$. We restrict ourselves to one extended and one localized orbitals per atom. Although all orbitals are spherically symmetric we label them c-like (the extended orbital) and f-like (the localized one). The creation (destruction) operators for the extended orbitals are denoted by $c_{i\sigma}^\dagger (c_{i\sigma})$, and those for the localized orbitals by $f_{i\sigma}^\dagger (f_{i\sigma})$. The four-site Anderson Hamiltonian can thus be written

$$H = H_c + H_f + H_{hyb} + H_{ff}, \quad (2.1)$$

where

$$H_c = t \sum_{ij\sigma} c_{i\sigma}^\dagger c_{j\sigma}, \quad (2.2)$$

$$H_f = E_0 \sum_{i\sigma} f_{i\sigma}^\dagger f_{i\sigma}, \quad (2.3)$$

$$H_{hyb} = -V \sum_{ij\sigma} (f_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger f_{i\sigma}), \quad (2.4)$$

$$H_{ff} = U \sum_i f_{i\uparrow}^\dagger f_{i\uparrow} f_{i\downarrow}^\dagger f_{i\downarrow}. \quad (2.5)$$

The prime means $i \neq j$. The terms (2.2) to (2.5) describe :

(a) extended orbitals with mean energy chosen to be zero (the origin of the energy scale) and an interatomic transfer (hopping) integral t which might be either positive or negative; if t is positive the one electron band energies [8] are a singlet at $-3|t|$ (which can be called an s state) and a triplet at $+|t|$ (which can be called p state); if t is negative the lowest one-electron level is the p triplet at $-|t|$ and the excited state is the s singlet at $+3|t|$;

(b) localized f orbitals with energy E_0 ; we let E_0 take any value, positive or negative;

(c) an interatomic (transfer) hybridization contribution which mixes extended and localized orbitals in different sites and whose strength is V ; since the hybridization only contributes terms of the form V^2 [see for instance (3.1), (3.2) and (3.3)] the sign of V is unimportant;

(d) a Coulomb repulsion U (always a positive number) between two electrons in f orbitals located at the same site; we allow U to assume any value, up to the atomic limit $U \rightarrow \infty$.

There are various symmetries to be exploited in this system. The number n of electrons is a good quantum number which can take any integral value between

zero and sixteen (the total number of spin orbitals in the four-site crystal). In this paper we restrict ourselves to $n = 4$, which represents a mixed-valence system with one electron per site, similar to Ce metal. We denote by ψ_{4G} the ground state of (2.1) for $n = 4$; its energy is denoted by E_{4G} . The mean f-occupation number per site in this ground state is defined by

$$n_f = (1/4) \left\langle \psi_{4G} \left| \sum_i f_{i\sigma}^\dagger f_{i\sigma} \right| \psi_{4G} \right\rangle. \quad (2.6)$$

Because of the absence of spin-orbit coupling terms in the Hamiltonian (2.1), the total spin S of the system is also a good quantum number. Therefore the $n = 4$ states can be characterized by the only possible values of the total spin $S = 0, 1$, or 2 . They correspond to singlets, triplets and quintets respectively.

The spatial symmetry of H is defined by its point and space groups. The point group of interest in our case (inversion symmetry provides no useful information when only spherically symmetric orbitals appear) is the full tetrahedral group T_d of 24 elements. The character table is given in reference [8]. Because the crystal contains only four atoms, the space group contains only four translations and the Brillouin zone has only four k -vectors: the zone centre Γ and the three square-face-centre points X . There are altogether 96 space-group operations (192 if inversion is included), which yield ten irreducible representations (twenty if inversion is included), five of which appear in this problem (see Table I).

Since there are 16 spin orbitals and each can be either empty or occupied by an electron, there are altogether $2^{16} = 65\,536$ possible eigenstates of (2.1); for a given number n of electrons there are only $[16!/n!(16-n)!]$ eigenstates. In table I the 1 820 eigenstates corresponding to $n = 4$ are classified according to their spatial and spin symmetries into fifteen symmetry-factorized problems. Listed there also (in parenthesis) are the reduced 1 462 states of finite energy in the limit $U \rightarrow \infty$. The latter are the important states in the mixed-valence problem: not all available states in ordinary molecular and band theory are available when strong f-electron interaction is present.

3. The ground state for four electrons ($n = 4$).

3.1 THE NON-INTERACTING CASE. — We begin by examining the eigenstates in the case in which $U = 0$, i.e. the Hamiltonian (2.1) consists of only the first three terms. It is possible under these circumstances to express the total energy as the sum of one-electron orbital energies. The one-electron spectrum consists of two non-degenerate Γ_1 orbitals of energies

$$E^\pm(\Gamma_1) = (1/2) \{ E_0 - 3t \pm [(E_0 + 3t)^2 + 36V^2]^{1/2} \} \quad (3.1)$$

Table I. — *Decomposition of the eigenstates into the possible space and spin symmetries. Figures in parenthesis correspond to the $U \rightarrow \infty$ limit.*

Symmetry	Singlets	Triplets	Quintets	Configuration
Γ_1	2 (2)	0 (0)	0 (0)	c^4f^0
	4 (4)	4 (4)	0 (0)	c^3f^1
	11 (7)	6 (5)	2 (2)	c^2f^2
	4 (1)	4 (1)	0 (0)	c^1f^3
	2 (0)	0 (0)	0 (0)	c^0f^4
Γ_2	0 (0)	1 (1)	1 (1)	c^4f^0
	2 (2)	4 (4)	2 (2)	c^3f^1
	3 (3)	6 (5)	2 (2)	c^2f^2
	2 (1)	4 (3)	2 (2)	c^1f^3
	0 (0)	1 (0)	1 (1)	c^0f^4
Γ_3	3 (3)	1 (1)	0 (0)	c^4f^0
	7 (7)	8 (8)	1 (1)	c^3f^1
	13 (10)	12 (10)	4 (4)	c^2f^2
	7 (3)	8 (4)	1 (1)	c^1f^3
	3 (1)	1 (0)	0 (0)	c^0f^4
$\Gamma_4(X_1)$	3 (3)	1 (1)	0 (0)	c^4f^0
	11 (11)	12 (12)	1 (1)	c^3f^1
	20 (13)	20 (17)	4 (4)	c^2f^2
	11 (4)	12 (5)	1 (1)	c^1f^3
	3 (0)	1 (0)	0 (0)	c^0f^4
$\Gamma_5(X_2)$	1 (1)	3 (3)	0 (0)	c^4f^0
	9 (9)	12 (12)	3 (3)	c^3f^1
	12 (9)	20 (17)	4 (4)	c^2f^2
	9 (4)	12 (7)	3 (3)	c^1f^3
	1 (0)	3 (1)	0 (0)	c^0f^4

and two Γ_4 triplets of energies

$$E^\pm(\Gamma_4) = (1/2) \{ E_0 + t \pm [(E_0 - t)^2 + V^2]^{1/2} \}. \quad (3.2)$$

In the singular case of no hybridization, $V = 0$, and depending on the relative values of E_0 and t , the ground state configuration is s^2p^2 , s^2f^2 , p^4 , or f^4 . For non-zero values of V , levels within each symmetry satisfy the non-crossing rule, but the Γ_1 singlets and the Γ_4 triplets can cross each other. These configuration transitions occur along the following discontinuity lines

$$V = 0, \quad (3.3)$$

$$4V^2 + 2E_0t - 3t^2 = 0.$$

As a consequence of the configuration transitions, in the $\{E_0, V\}$ plane of figures 1 and 2 discontinuities appear along the abscissa axis and along the dotted lines which represent the second equation (3.3). In order of increasing one-electron energies, the level orderings are

$\Gamma_1 \Gamma_4 \Gamma_4 \Gamma_1$ or $\Gamma_1 \Gamma_4 \Gamma_1 \Gamma_4$ for $t > 0$ (Fig. 1);

$\Gamma_1 \Gamma_4 \Gamma_4 \Gamma_1$ or $\Gamma_4 \Gamma_1 \Gamma_4 \Gamma_1$ for $t < 0$ (Fig. 2).

The ground-state energies are

$$E_{4G}(U = 0) = 2 E^-(\Gamma_1) + 2 E^-(\Gamma_4)$$

for the $\Gamma_1 \Gamma_4 \Gamma_4 \Gamma_1$ and $\Gamma_1 \Gamma_4 \Gamma_1 \Gamma_4$ orderings;

$$E_{4G}(U = 0) = 4 E^-(\Gamma_4)$$

for the $\Gamma_4 \Gamma_1 \Gamma_4 \Gamma_1$ ordering.

For vanishing hybridization the f-occupation number n_f exhibits step-like discontinuities. For $t > 0$, as shown in figure 3(b), $n_f = 1$ in the f^4 configuration ($E_0 < -3t$); $n_f = 0.5$ in the s^2f^2 configuration ($-3t < E_0 < t$); and $n_f = 0$ in the s^2p^2 configuration ($t < E_0$). For $t < 0$, as shown in figure 4(b), $n_f = 1$ for the f^4 configuration ($E_0 < -|t|$), and $n_f = 0$ for the p^4 configuration ($E_0 > -|t|$). For arbitrary hybridization the n_f curves as function of E_0 are recognizable distortions of the single or double step functions. It should be noted that even in the non-interacting case f-orbital occupancies different from either zero or one are obtained only when the f-level lies in the neighbourhood of the conduction band, the Fermi level in particular.

It should be noted as a curiosity that in the case $t < 0$ the level-crossing discontinuity described by

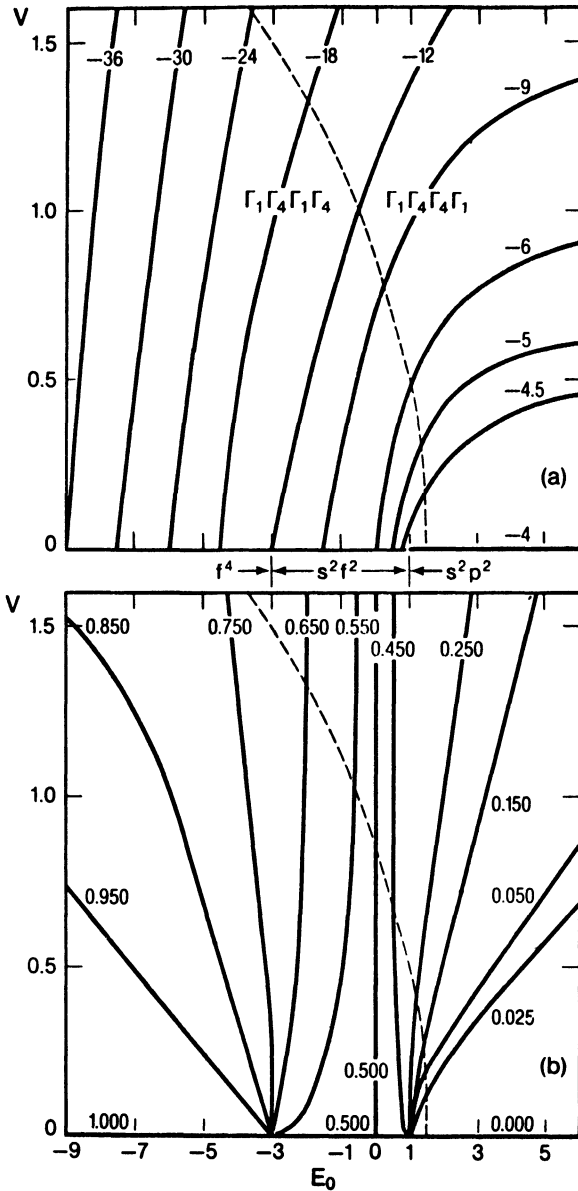


Fig. 1. — The ground state for four electrons, $t = +1$ and $U = 0$ (the non-interacting case). (a) Lines of constant energy E_{4G} in the $\{E_0, V\}$ plane. (b) Lines of constant f-orbital occupation number per site in the $\{E_0, V\}$ plane.

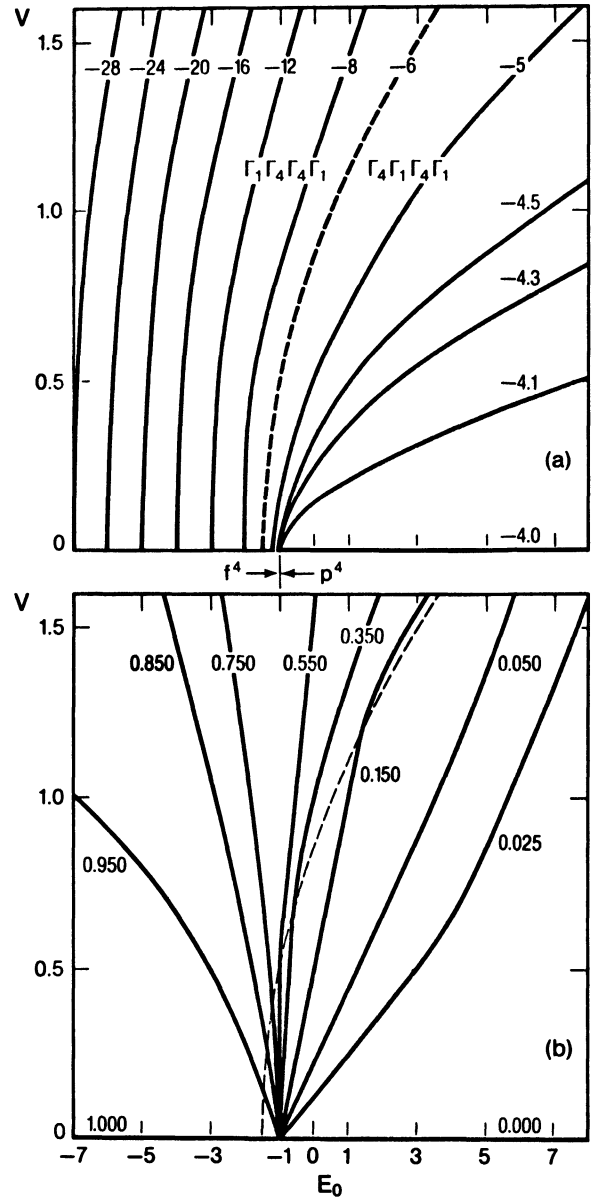


Fig. 2. — The ground state for four electrons, $t = -1$ and $U = 0$ (the non-interacting case). (a) Lines of constant energy E_{4G} in the $\{E_0, V\}$ plane. (b) Lines of constant f-orbital occupation number per site in the $\{E_0, V\}$ plane.

the second equation (3.3) coincides with a line of constant total energy $E_{4G} = -6|t|$.

3.2 THE INTERACTING CASE. — For finite values of the interaction U we focus our attention on four symmetries — three singlets $^1\Gamma_1$, $^1\Gamma_3$, and $^1\Gamma_4$, and one triplet $^3\Gamma_5$ — which have degenerate [8] energies at $U = 0$. The total energies are determined independently for each space and spin symmetry by means of the reorthogonalized Lanczös method. This method generates a tridiagonal Hamiltonian matrix, with the Hamiltonian itself acting as generator of successive states of a given symmetry. Eigenvectors are explicitly orthogonalized to previous eigenvectors to avoid

numerical instabilities. As can be seen from table I the orders of the determinants to solve are 23 for $^1\Gamma_1$, 33 for $^1\Gamma_3$, 48 for $^1\Gamma_4$, and 50 for $^3\Gamma_5$. In all cases studied corresponding to $t = \pm 1$ and $V = 0.5$ it is found that the non-magnetic degenerate singlet $^1\Gamma_3$ is the ground state. The energy of the studied states are shown in figure 5 (for $t = +1$) and figure 6 (for $t = -1$). For all values of U there are very low-lying excited states, especially the triplet $^3\Gamma_5$ which lies everywhere very close to the ground state, and becomes degenerate with it in some instances (see Figs. 5 and 6). This almost-degeneracy is the signature of a « nearly magnetic » situation, which should lead to large spin fluctuations in the infinite lattice case.

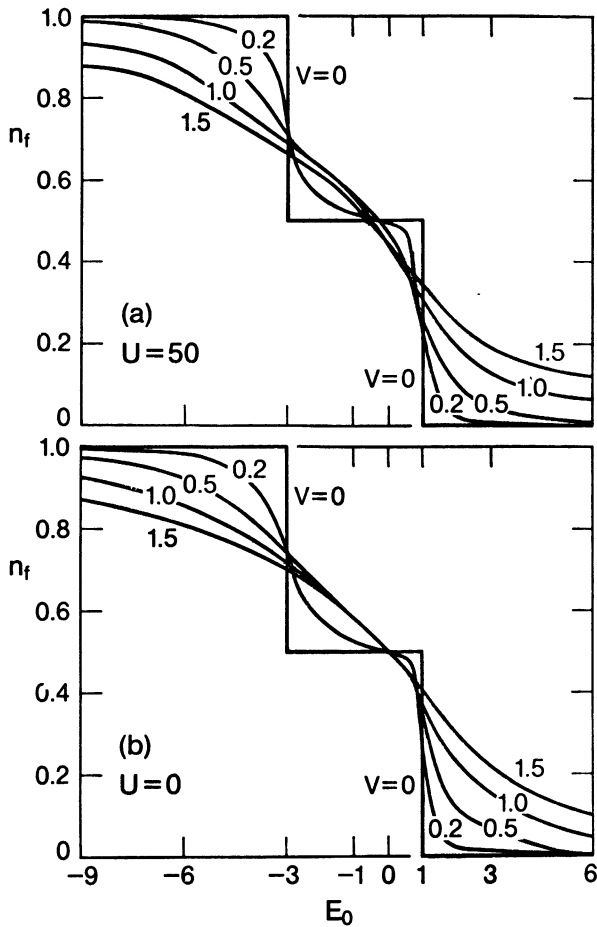


Fig. 3. — The f-occupation in the $n = 4$ ground state ${}^1\Gamma_3$ as a function of E_0 for $t = +1$ and for various hybridization strengths in the (a) strong interacting limit $U = 50$, and (b) the non-interacting case $U = 0$.

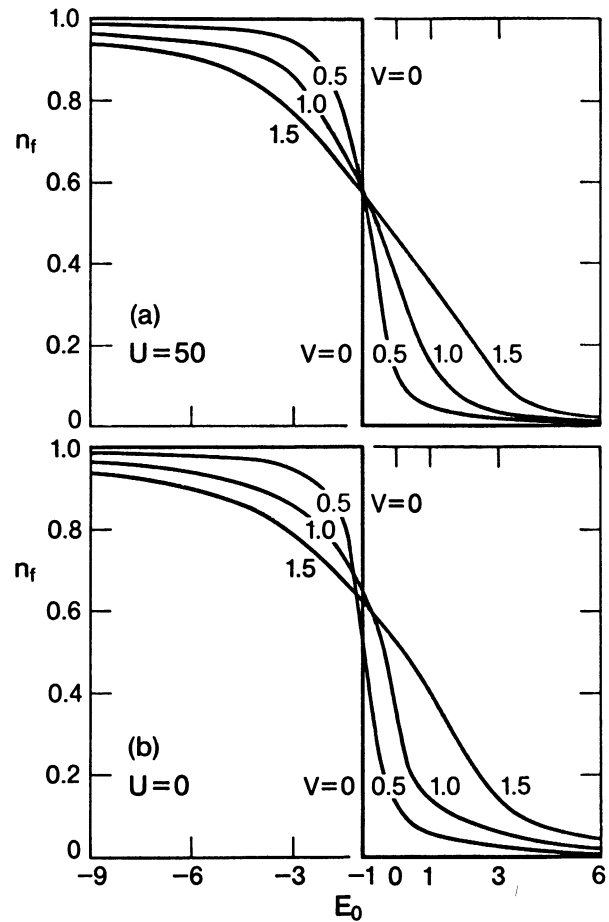


Fig. 4. — The f-occupation in the $n = 4$ ground state ${}^1\Gamma_3$ as a function of E_0 for $t = -1$ and for various hybridization strengths in the (a) strong interacting limit $U = 50$, and (b) the non-interacting case $U = 0$.

Figures 3(a) and 4(a) show n_f , the f-orbital average occupancy for a large interaction, $U = 50 |t|$, in the cases of positive and negative t respectively. The rather surprising result to be obtained from those figures is that the very strong interaction limit differs only slightly from the non-interacting case as far as n_f is concerned. In fact all integrated electronic properties in the case of one electron per site are *dominated not by the electron-electron interaction but by the one-electron effects*, even when the interaction strength tends to infinity. Figures 3 and 4 clearly show that the ground state properties of the one-electron-per-site case (which is relevant in the $\alpha - \gamma$ transition in metallic cerium) is a sensitive function of the one-electron parameters t , E_0 and V , but insensitive to the value of U . Similar results have been found for other finite geometries [5, 6].

4. Conclusions.

The simple four-centre Anderson Hamiltonian with two extended and two localized spin states and one electron per site gives a satisfactory description of

intermediate-valence systems, such as cerium. The non-perturbative (exact) solution of such many-body system yields the following results :

- (a) the ground state is always a non-magnetic singlet;
- (b) a spin triplet lies always very close to the ground state and, for some values of the parameters, may become degenerate with it;
- (c) the strong electron-electron intraatomic interaction between localized orbitals restricts the number of accessible many-body states, but has a very small influence in the integrated properties of the ground state.

Several extensions of the present work suggest themselves. The calculation for other occupation numbers n is straightforward. In particular the ground states for $(n \pm 1)$, when referred to the ground state for n , would yield crucial information on the charge fluctuations for the infinite lattice : these fluctuations, as opposed to the ground-state integrated properties, should depend strongly on the electron-electron interaction U . It also may be of interest to include in the

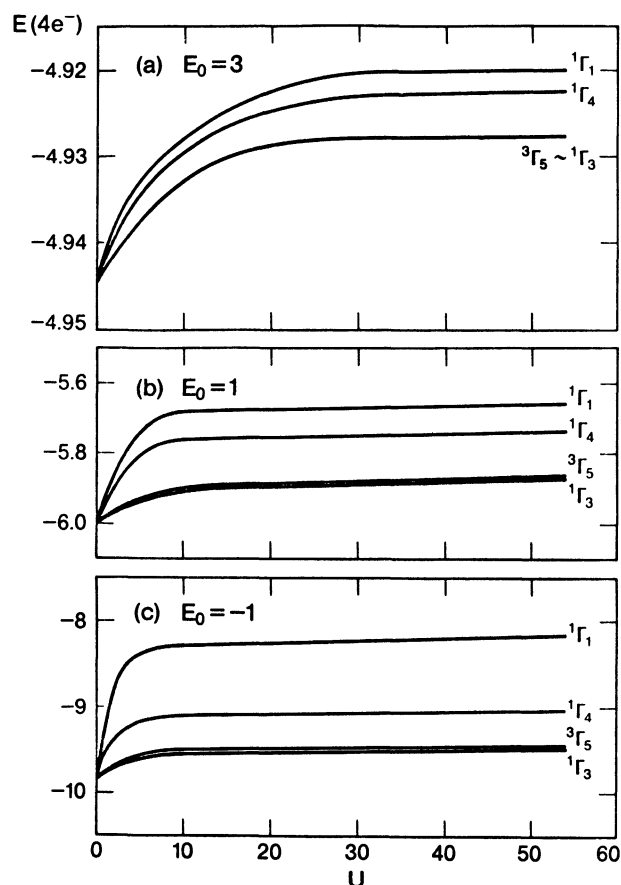


Fig. 5. — Lowest four-electron energies corresponding to the symmetries $1\Gamma_3$, $3\Gamma_5$, $1\Gamma_4$ and $1\Gamma_1$ as functions of the Coulomb repulsion U for $t = +1$, $V = 0.5$, and (a) $E_0 = 3$, (b) $E_0 = 1$, and (c) $E_0 = -1$.

Hamiltonian an interaction between localized and extended states, believed to be responsible for the valence transition [1-3] in metallic cerium.

Acknowledgments.

This work was started when all authors were at the Physics Department of the University of California,

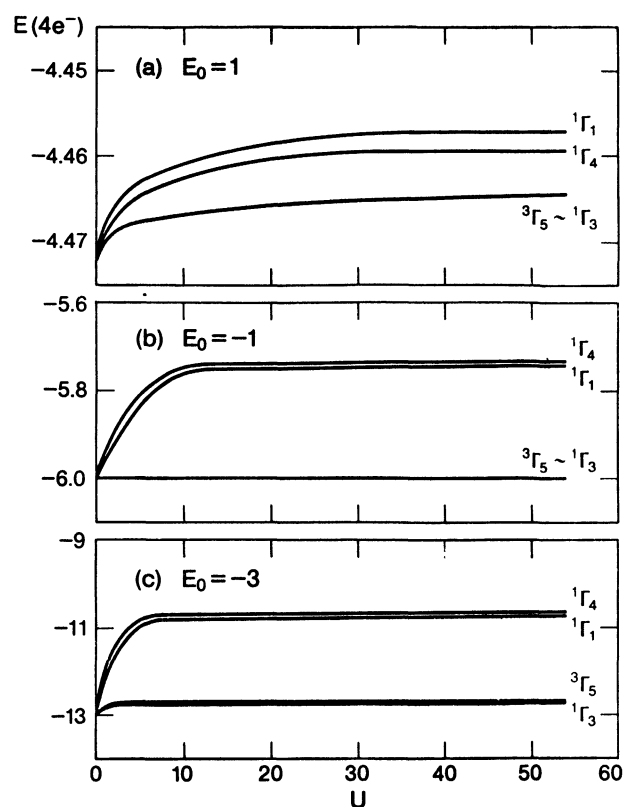


Fig. 6. — Lowest four-electron energies corresponding to the symmetries $1\Gamma_3$, $3\Gamma_5$, $1\Gamma_4$ and $1\Gamma_1$ as functions of the Coulomb repulsion U for $t = -1$, $V = 0.5$ and (a) $E_0 = 1$, (b) $E_0 = -1$, and (c) $E_0 = -3$.

Berkeley. It was supported by the US National Science Foundation through Grant DMR 81-06494. J. C. Parlebas would like to acknowledge a joint fellowship from NATO and the Conservatoire des Arts et Métiers (Paris) which enabled him to spend five months in Berkeley. While at Berkeley R. H. Victora was the holder of an A. T. and T. Bell Laboratories Fellowship.

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