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Toward a magnetic description of metals in terms of interstitial molecular orbitals: Exploiting the multiplicity of symmetry-broken Hartree-Fock solutions on small alkali-metal clusters

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For one-dimensional (1D), 2D, and 3D finite clusters of Li atoms, numerous symmetry-broken unrestricted Hartree-Fock (UHF) solutions are of lower energy than the symmetry-adapted one. The lowest solution provides, after a localizing unitary transform, a set of interstitial singly occupied molecular orbitals (MO's), each of them being essentially between a few atoms. These MO's are very similar to those obtained by McAdon and Goddard from more elaborate wave functions and support their proposal of a new picture of the electronic assembly in metallic clusters. In the lowest UHF solution the spins are distributed among the interstices in order to achieve the best spin alternation between neighboring interstices. Starting from these interstitial MO's, one may change the spin distribution and obtain other UHF solutions of (slightly) higher energy, the spacing of which is ruled by a Heisenberg Hamiltonian. On two Li_6 clusters the exact MO–configuration-interaction wave function in the basis was projected on the subspace of these various UHF solutions; the norm of the projection is close to 1, and the projected eigenvector is the lowest eigenvector of a Heisenberg Hamiltonian. From the energies of the various interstitial UHF solutions, a Heisenberg Hamiltonian may be obtained at very low cost and its diagonalization provides a good approximation of the exact energy (in the basis set). This procedure will be used for infinite lattices in order to calculate cohesive energies.

I. INTRODUCTION

A quite revolutionary description of the electronic wave function of the bulk of alkali or noble metals has recently been proposed by McAdon and Goddard.[1,2] This tentative picture proposes to use *interstitial singly occupied* molecular orbitals (MO's) which are localized on bonds for one-dimensional (1D) systems, on triangles for 2D triangular lattices and on tetrahedra for 3D compact lattices. The physical support of such a description is easy to understand as a compromise between the electronic delocalization, which diminishes the kinetic energy, but which is constrained inside a local region of space, and the electronic repulsion, which is minimized by avoiding electron pairing and using one domain per electron. This proposal originates from *ab initio* generalized-valence-bond (GVB) calculations on small alkali-metal clusters in ideal geometries.

The GVB wave function is highly constrained. For an n-valence-electron cluster of n atoms of alkali metal, the valence wave function takes the form

$$\psi=\mathcal{A}(a,b,c,\ldots,n)\left[\sum_{I} C_I \mathcal{P}_{SI}\right],$$

where $a,b,c,\ldots,n$ represent a unique set of nonorthogonal one-electron MO's (which means that the space part of the wave function is unique) and where $\mathcal{P}_{SI}$ represents one member of the set of linearly independent n-electron singlet spin functions. Both the content of the MO's, $a,b,\ldots,n$ and the coefficients C_I are determined variationally. This wave function goes besides the Hartree-Fock (HF) approximation, and for molecules it treats quite satisfactorily the part of the correlation effects which is inside the valence shell (internal or nondynamical correlation). It is now well known that in *ab initio* calculations of such clusters (i) correlation effects play a crucial role for predicting correctly both energies and structures,[3] and (ii) the correlation within the s band is of little effect; the main corrections come from double excitations toward MO's built from the p band;[4–6] the crucial role of p atomic orbitals (AO's) in small clusters is not essentially an s-p band mixing (a static hybridization) but an energy lowering of the effective energy of ionic valence-bond structures, as explained in some length in Refs. 7 and 8; the $Li^- \cdots Li^+$ structures are stabilized by local $s^2 \rightarrow p^2$ double excitations which introduce the angular correlation on Li^-, resulting in a strong lowering of the effective interelectronic repulsion (the U parameter of the Hubbard Hamiltonian). This effect was also analyzed by Goodgame and Goddard,[9] who proposed to shift the monocentric repulsion integrals in their so-called modified-GVB scheme for completely different molecules. One may wonder whether the compromise between delocalization and repulsion exhibited by the GVB calculations of Refs. 1 and 2, which disregard these dynamical correlation effects, is not an artifact which would disappear in more flexible wave functions. In the GVB calculations the p AO's actually play a large role, through a large s-p hybridization of the MO's (which may introduce part of the dynamical correlation in an unclear and biased manner); the s-p mixing is apparently surprisingly high ($s/p=1/1$ for cyclic Li_{10}). One of the purposes of the present paper is to check the relevance of the interstitial model by comparison with extensive *ab initio* MO–configuration-interaction (CI) wave functions which do not introduce any prejudice (except for the atomic basis set limitation).

Rather than using a GVB approach, which is very computationally expansive, and limited to small clusters, we shall go through the use of symmetry-broken unrestricted HF (UHF) solutions. Actually McAdon and Goddard have shown the existence of strong symmetry breakings on one-dimensional cyclic chains of alkali- or noble-metal atoms.[10] One instability is a bond-centered charge-density wave of singlet type leading to the Peierls distortion; a second class of solution consists in atom-centered spin-density waves (triplet-type instability, or ASDW[11]), but the lowest solution is a bond-centered spin-density wave. A localization of the UHF MO's of α (or β) spin provides a set of singly occupied interstitial MO's, located between two adjacent atoms. Section II of the present paper is devoted to the study of interstitial UHF solutions. We show that (i) such types of solutions are not restricted to 1D systems, they also occur on 2D or 3D systems, providing bond-centered, triangle-centered, or tetrahedra- (or pyramid)-centered singly occupied MO's, and (ii) for a given cluster one may obtain *several* UHF solutions for any value of S_z (except for the upper S_z value, the highest multiplet where the UHF solution is unique); these solutions are closely related, their localized MO's are located on the same regions of space, they essentially differ by the spin distribution over the set of interstices. This variety of UHF solutions had only been noticed previously for 1D cyclic chains and atom-centered ASDW solutions,[12] for which besides the spin-alternated density wave, one may obtain UHF atom-centered solutions with random spin distributions.

McAdon and Goddard have noticed,[2] for 1D cycles at least, that the UHF single occupied MO's of the upper multiplet are practically identical to the GVB MO's of both the upper multiplet and lowest ($S_z=0$) solution. In order to test the validity of the interstitial singly occupied description we decided to project the best MO-CI wave function onto the subspace generated by all the determinants built from the UHF MO's by changing the spin distribution and keeping a single occupation of these MO's. This comparison is rather difficult to perform and was limited to two Li_6 clusters; the precise procedure and the results are reported in Sec. III. They support the validity of the interstitial representation. Moreover the projection of the exact wave function onto this subspace of "neutral" structures appears to look like the solution of a Heisenberg Hamiltonian, as also noticed in Ref. 2 for cyclic systems. Actually one may see the electronic wave function as obtained in a two-step procedure: first the delocalization-repulsion balance defines the space part of the function, and then the spin distribution is ruled by a Heisenberg-type problem.

Taking advantage of this remark, Sec. IV proposes to use the energies of the various UHF solutions in order to determine the effective interactions of a Heisenberg Hamiltonian. The resulting energies compare very well with the exact energies. The simplicity of such a procedure immediately suggests a possible extension to the study of the metallic bulk by obtaining a few symmetry-broken *ab initio* UHF solutions, and defining from them effective spin interactions, the solution of the infinite Heisenberg Hamiltonians may be approached finally by perturbing the most spin-alternated single determinant by the less spin-ordered ones.

II. MULTIPLICITY OF INTERSTICE-CENTERED UHF SOLUTIONS

A. Method

In this section one shall consider that the energy of a single determinant

$$\Phi_0=\mathcal{A}\left[\prod_{i=1}^{n}\varphi_i S_i\right],$$

(where φ_i is an orbital and S_i is an α or β spin function)

$$E_0=\langle\Phi_0|H|\Phi_0\rangle/\langle\Phi_0|\Phi_0\rangle$$

is a function of both the MO parameters and interatomic distances.

Unexpectedly this function possesses a very large number of minima, each corresponding to a self-consistent solution of the Hartree-Fock problem. This section illustrates this point through *ab initio* calculations on Li_n clusters of various dimensionalities; in general the interatomic distances will be kept equal to 6 bohrs (which is close to the bulk nearest-neighbor distance). The core electrons are left out of the problem, their effect being treated through a nonempirical l-dependent pseudopotential;[13] the valence basis set involves two s atomic orbitals and one p atomic orbital.

From interstitial trial vectors, it is quite easy to obtain the lowest-energy UHF solution for $S_z=0$ (with most alternant spin distribution) or for $S_z=n/2$. A Boys localizing unitary transformation[14] is applied successively on the sets of α and then β occupied MO's. This process consists in maximizing the distances between the centroids of the orbitals, or in minimizing the second moment of the electronic position operator

$$r_i^0=\langle\varphi_i|r|\varphi_i\rangle\ ,$$

$$\sum_{\substack{i\\ \text{same spin}}}\langle\varphi_i|(r-r_i^0)^2|\varphi_i\rangle=\min\ .$$

One then obtains equivalent localized MO's φ_i' for both the lowest $S_z=0$ and the $S_z=n/2$ solutions, and one verifies that these MO's are similar, i.e., defined on the same region of space. Then one may reach other symmetry-broken UHF solutions by using these localized MO's as space parts of the trial vectors and changing the spin distribution. One hopes to be in the drainage basin of an other variational solution which is reached iteratively. The eigenvectors of the new solution are again localized through the Boys procedure, and compared to the preceding ones in order to check that they only differ by small deviations. The 1D problem is exhaustively described through the simple case of the cyclic Li_6 problem.

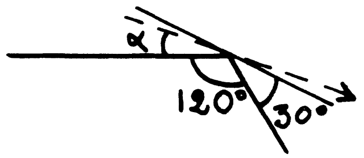
The generality of the phenomenon will be illustrated less intensively on a few typical 2D and 3D systems.

B. 1D cyclic problem

A regular circle of Li_6 will be taken as a basic example. As shown in Refs. 2 and 10, (i) the bond-centered upper multiplet $S_z=3$ UHF solution is bounded with respect to the atoms, while the $S_z=3$ atom-centered solution is strongly repulsive (Fig. 1 gives the evolution of the corresponding energies as functions of the interatomic distance); (ii) the bond-centered alternant spin-density wave $S_z=0$ UHF solution is very stable. It presents a minimum close to 6 bohrs. The corresponding atom-centered solution is much less bounded and disappears as a real minimum for $r<5.8$ bohrs (cf. Fig. 1).

We have obtained the two other $S_z=0$ bond-centered UHF solutions which correspond to less-ordered spin distributions; the solution in which four spin alternations between adjacent bonds are kept, and the one which only preserves two spin alternations. Of course, the larger the number of spin alternations is the lower the UHF energy is.

The Boys criterion gives highly localized equivalent MO's, since the largest coefficient outside of the concerned bond is always smaller than 0.05. The main coefficients (those on the concerned bond) are given in Table 1(a). The p components of these MO's are almost tangent to the circle, pointing *out* of the bond. The ideal angle between a tangent p orbital and the bond would be 30° for a hexagon; the calculated ones are slightly smaller (19°–27°) [cf. Table 1(a)]:



From Table 1(b) one might distinguish two types of hybrid atomics orbitals, according to the neighborhood; if the atom is involved in two bond MO's of parallel spin, the hybrids have a larger p component (0.32–0.350) than when the atom is located between two bonds of different spins ($C_p \sim 0.280-0.290$). The self-consistent hybrids appear to be essentially sensitive to the spin-alternated or spin-frustrated character of the concerned atom.

The connection between the MO's $\varphi_i(3)$ obtained for $S_z=3$ and those $\varphi_i(0)$ of the alternant spin-density wave $S_z=0$ may be studied through the overlap matrix $\langle \varphi_j(3)|\varphi_i(0)\rangle$ of the occupied MO's (Table II). The projection of the $\varphi_i(0)'$ MO's onto the subspace Vect $\{\varphi_i(3)\}_{i=1,6}$ is very large:

$$\sum_j \langle \varphi_i(0)|\varphi_j(3)\rangle^2 = 0.9979 ,$$

which means that the "valence" subspaces of all the determinants built from the six MO's $\varphi_i(0)$ or from the six MO's $\varphi_j(3)$ are almost identical. However, the overlap between the MO's built on the same bond,

$$\langle \varphi_i(0)|\varphi_i(3)\rangle = 0.9667 ,$$

is much smaller. The difference between $\varphi_i(3)$ and $\varphi_i(0)$ may be understood as follows. One may notice that the $\varphi_i(3)$ are orthogonal and may be considered as an orthogonal localized basis for the "valence" space. The $S_z=0$ $\varphi_i(0)$ α-spin MO has important overlaps (0.339) with the adjacent bond MO's of β spin. One may consider the $\varphi_i(3)$ MO's as the result of an $S^{-1/2}$ orthogonalization of the $\varphi_i(0)$ MO's. It is well known that the $S^{-1/2}$ orthogonalization is a localizing transformation.[15] The orthagonal set $\varphi_i(3)$ may be considered as a bond-minimal monoelectronic basis set, from which we may define neutral, singly ionic, and doubly ionic structures in a VB language which uses bond MO's instead of AO's. Now it is clear that the apparently neutral $S_z=0$ determinant

$$\Phi^0_{\mathrm{UHF}} = |\varphi_1(0)\bar{\varphi}_2(0)\varphi_3(0)\bar{\varphi}_4(0)\varphi_5(0)\bar{\varphi}_6(0)|$$

incorporates ionic components and is significantly different from

$$\Phi^{0'} = |\varphi_1(3)\bar{\varphi}_2(3)\varphi_3(3)\bar{\varphi}_4(3)\varphi_5(3)\bar{\varphi}_6(3)|$$

which is really neutral. The importance of the change in the bond MO's, i.e., of the incorporation of ionic com-

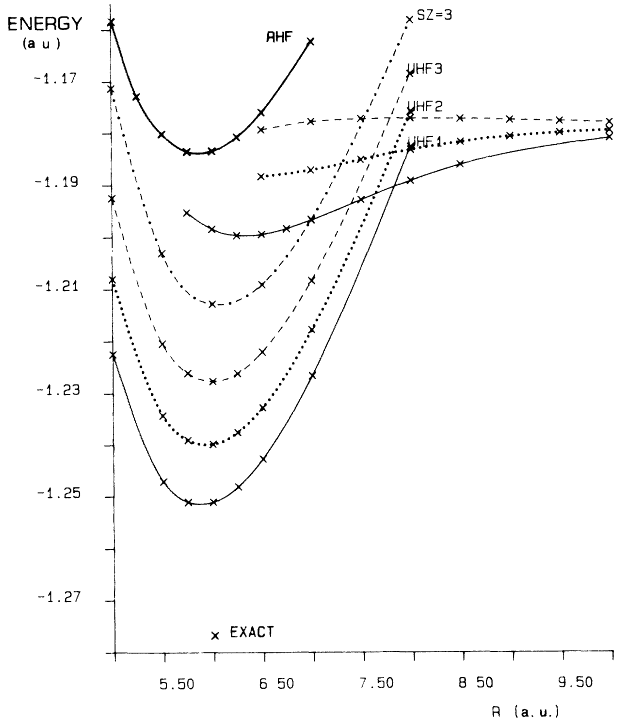
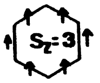
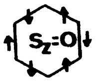
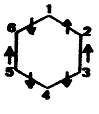
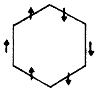


FIG. 1. SCF energies of cyclic Li_6 as a function of interatomic distances (in a.u). Solid line denotes RHF. The three curves dissociating into ground-state atoms concern atom-centered UHF solutions, with three different spin distributions: solution with 6 spin alternations ($a\bar{b}c\bar{d}e\bar{f}$); solution with 4 spin alternations ($ab\overline{cd}e\bar{f}$); and solution with 2 spin alternations ($abc\overline{def}$). The four lowest curves (near 6 a.u.) concern bond-centered UHF solutions. One is the $S_z=3$ ferromagnetic solution and the three others are $S_z=0$ solutions with, respectively, 6 UHF1, 4 UHF2, and 2 UHF3 spin alternations.

TABLE I(a) Main components of the localized MO's of Li_6 ($r=6$ bohrs) on the s, s', and p AO. α is the angle of the p components with respect to the axis of the bond. (b) s and p component on atoms involved in two bond MO's. The numbers are the minimum and maximum coefficients, respectively.

(a)

	OM ij	s_i	s_i'	p_i	α_i	s_j	s_j'	p_j	α_j
	all	0.325	0.098	0.351	21°		idem		
	all	0.358	0.112	0.273	24°		idem		
	1 2	0.374	0.125	0.286	24°	0.315	0.090	0.322	22°
	2 3	0.309	0.079	0.321	24°	0.379	0.136	0.291	27°
	5 6	0.354	0.105	0.268	21°	0.362	0.119	0.273	23°
	1 2	0.379	0.134	0.287	23°	0.305	0.078	0.322	19°
	2 3	0.331	0.104	0.340	26°		idem		

(b)

	s	s'	p
	0.350–0.380	0.105–0.136	0.268–0.291
	0.305–0.331	0.078–0.104	0.321–0.351

ponents in the $S_z=0$ solutions may be seen by comparing $\langle\Phi^{0'}|H|\Phi^{0'}\rangle=-1.192\,331$ a.u. and $\langle\Phi^0_{\mathrm{UHF}}|H|\Phi^0_{\mathrm{UHF}}\rangle=-1.251\,122$ a.u. at $r=6$ bohrs. This is a very large energy difference. One may notice that $\langle\Phi^{0'}|H|\Phi^{0'}\rangle$ is even higher than $\langle\Phi^3_{\mathrm{UHF}}|H|\Phi^3_{\mathrm{UHF}}\rangle$ ($\Phi^3_{\mathrm{UHF}}=|\varphi_1(3)\varphi_2(3)\varphi(3)\varphi_4(3)\varphi_5(3)\varphi_6(3)|$), the corresponding energy being $-1.212\,899$ a.u. Since both determinants ($\Phi^{0'}$ and Φ^3_{UHF}) are written with the same set of orthogonal MO's, their energy difference reduces to the exchange integrals $\sum_{ll'}K_{ll'}$ where l and l' are adjacent MO's. One may deduce that $K_{ll'}$ is about 0.0034 a.u. The same procedure may be repeated for the other spin distributions; the corresponding mean energies appear in Table III, showing an almost constant energy spacing. Of course, the delocalization introduced by the variational adjustment of the MO's reverses the energy ordering, producing energy splittings of opposite sign, but as regular as the previous ones, which may be translated by the use of

TABLE II. Overlap matrix of the $S_z=0$ and $S_z=3$ UHF MO's.

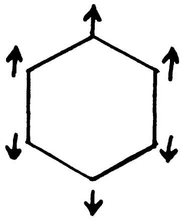
$S_z=3$ $S_z=0$						
α-MO's	−0.9667	0.0156	0.0156	−0.1773	−0.0046	−0.1773
	−0.0156	0.9667	−0.0156	0.1773	−0.1773	−0.0046
	0.0156	0.0156	−0.9667	0.0046	0.1773	−0.1773
β-MO's	−0.1773	−0.1773	0.0046	−0.9667	−0.0156	0.0156
	−0.0046	0.1773	0.1773	−0.0156	−0.9667	−0.0156
	0.1773	0.0046	0.1773	−0.0156	0.0156	0.9667

TABLE III. Energies of bond-centered UHF solutions $R=6$ bohrs, in a.u.

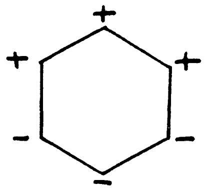
S_z	Spin alternations	UHF MO's	Upper multiplet MO's
0	6	$-1.251\,122$	$-1.192\,331$
0	4	$-1.239\,838$	$-1.198\,745$
0	2	$-1.227\,722$	$-1.205\,449$
3	0	$-1.212\,899$	

an effective negative exchange integral K^{eff} between adjacent bonds.

The *bond-length dependence* of those various UHF solutions appears in Fig. 1. They all present a minimum close to 6 bohrs, $r_{\min}$ being slightly smaller when the number of spin alternations increases. One might wonder whether and when the various $S_z=0$ UHF solutions lose their symmetry breaking to join the symmetry-adapted restricted Hartree-Fock (RHF) solution. One may observe that when r tends to infinity the UHF $S_z=0$ and RHF wave functions keep a different character; if one uses a minimal s basis set the energy asymptote will be the same ($3U/2$, where in the Hubbard Hamiltonian terminology U is the monocentric bielectronic repulsion), but the RHF wave function introduces some VB components such as



or



with nonvanishing coefficients,[16] which are necessarily absent from the spin-alternant bond-centered UHF solution; the identity of the asymptote does not imply a matching of the wave functions. For nonminimal basis sets the identity of the asymptotes is questionable; it depends on the relative energy of the $\mathrm{Li}^+\mathrm{Li}^-$ ionic pairs with respect to that of the $\mathrm{Li}^*(2p)+\mathrm{Li}(2s)$ neutral pairs.

When r tends to zero the system tends toward a united atom limit $Z=18$ (Ar atom), which certainly has a closed-shell ground state without HF instability. In practice, when r becomes too small the overlap of the atomic orbitals leads to numerical troubles and the core potentials begin to overlap and to become meaningless. We have simply verified that for $r=2.5$ bohrs the UHF solution remains below the RHF one.

An extensive study of the HF instabilities in such a small highly symmetrical problem would be welcome; it would require the use of enlarged basis sets, and a careful study of the appearance of other symmetry-broken solutions. We have found, for instance, UHF solutions which involve alternant-bond-centered MO's in a region of the molecule and almost closed-shell MO's in the other parts of the molecule.

C. 2D problem

Li_4 is known from accurate *ab initio* MO-CI (Ref. 17) and from local-spin-density (LSD) (Ref. 18) calculations to have a rhombic planar structure; the restricted Hartree-Fock determinant is built from two doubly occupied MO's of a_1 and b_2 symmetries, respectively. We found (cf. Table IV) two distinct UHF solutions; one involves two types of singly occupied MO's located on either triangles or atoms; this symmetry breaking only stabilizes the energy by less than 0.1 eV. The other solution, which doubles the cohesion energy with respect to the RHF one, implies a peripheric spin-density wave supported by bond MO's. This solution is directly related to the GVB description obtained in Ref. 2.

Both MO-CI (Ref. 17) and LSD (Ref. 18) calculations predict that Li_5 will adopt a planar conformation built from three fused nearly equilateral triangles. We obtained easily three UHF solutions below the RHF one (cf. Table V), which may all be seen as built from bond MO's supported by the five external bonds (some delocalization takes place in the internal triangle). The most stable

TABLE IV. HF instabilities on rhombic Li_4.

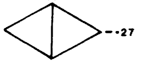
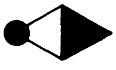
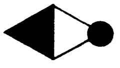
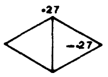
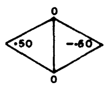
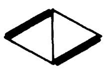
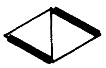
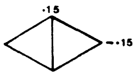
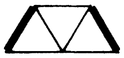
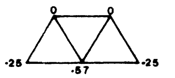
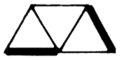
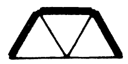
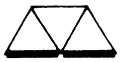
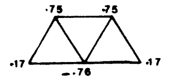
	MO content					
	α-spin	β-spin	Net charges	Atomic spin densities	Energy (a.u.)	Binding energy per/atom (eV)
RHF	a_1b_2	a_1b_2		0	-0.8028	0.115
UHF1					-0.8059	0.136
UHF2				0	-0.8186	0.222

TABLE V. HF instabilities of Li_5.

	MO content α	MO content β	Atomic spin densities	Energies (a.u.)	Binding energy per atom (eV)
RHF	$a_1b_2a'_1$	$a_1b_2a'_1$		−1.0189	0.199
UHF1				−1.0323	0.272
UHF2				−1.0300	0.259
UHF3				−1.0214	0.212

UHF solutions present four spin alternations between adjacent bonds. The upper one has only two such spin alternations. Three other UHF solutions corresponding to other spin distributions on the external bonds might be searched.

One of the two nearly degenerate stable conformations of Li_6 is a planar equilateral triangle built from four fused nearly equilateral triangles.[17,18] This problem has been studied in more details than the preceding ones, in order to compare with the cyclic Li_6 case. The RHF MO's may be transformed into three equivalent MO's, each one being located in one of the external triangles, with negligible tails (largest coefficient inferior to 0.04 on the other atoms) and a larger amplitude on the external atoms, resulting in non-negligible net charges ($0.19e^-$ on those atoms). This structure is strongly ionic in the VB sense,[19] and it is much more stable than the cyclic conformations; this is certainly why we only found two UHF solutions below the RHF one. One is a product of two bond-supported singly occupied MO's on the two sides of a summit atom, two triangle-supported MO's on the two other external triangles, and two atom-supported MO's on the external atoms. It lies 0.21 eV below the RHF solution; the other one (UHF1 of Table VI) is still lower (0.29 eV below the RHF solution), it is a purely bond-centered spin-density wave on the external bonds, and it keeps more or less the same content as for cyclic Li_6 as noticed in Ref. 2. The amazing fact is that starting from the localized MO's of this last solution (which are equivalent) as trial vectors of the UHF self-consistent process and changing the spin distribution one may reach a whole family of stationary points of the energy. Keeping $S_z=0$ we have obtained two other UHF solutions (UHF2 and 3) which destroy a certain number of spin alternations between adjacent bonds and which are *higher* in energy than the RHF one. We also have changed the number of α electrons and have obtained UHF solutions for $S_z=1$, 2, or 3, always composed of localized singly occupied bond MO's (cf. Table VI). The comparison between the MO's of the lowest $S_z=0$ UHF solution (UHF1 in Table VI) and those of the $S_z=3$ UHF multiplet (UHF8 in the same table) may be judged from the overlap matrix of Table VII. The norm of the projection of the MO's of the spin-density wave solution onto the MO's of the upper multiplet is very large, 0.9893, but the overlap of the bond MO's, $\langle\varphi_1(1)|\varphi_1(8)\rangle$, is much smaller (0.8923). This multiplicity of solutions will be exploited in Sec. III.

A planar Li_{10} cluster built of fused equilateral triangles has been studied in Ref. 2 in a GVB approach and has been investigated here through UHF solutions. The clus-

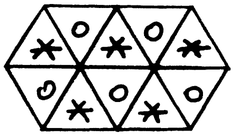
TABLE VI. UHF instabilities of triangular Li_6.

	MO content	Energy	S_z	Number of g_1	Number of g_2
RHF	$(a_1)^2(e)^4$	−1.2304	0		
UHF1		−1.2410	0	3	3
UHF2		−1.1987	0	3	1
UHF3		−1.1988	0	1	1
UHF4		−1.2188	1	2	2
UHF5		−1.2170	1	2	2
UHF6		−1.1513	1	2	0
UHF7		−1.1864	2	1	1
UHF8		−1.1420	3	0	0

TABLE VII. Overlap matrix between the spin density wave ($S_z=0$) UHF solution and the $S_z=3$ solution.

$S_z=0$	$S_z=3$					
α-MO's	0.8923	−0.0173	−0.0333	−0.1275	0.4060	−0.0055
	0.0333	−0.8923	0.0173	−0.0055	−0.1275	−0.4060
	−0.0173	−0.0333	0.8923	−0.4060	−0.0055	0.1275
β-MO's	0.1275	−0.0055	0.4060	−0.8923	−0.0333	−0.0173
	−0.4060	−0.1275	0.0055	−0.0173	−0.8923	0.0333
	0.0055	−0.4060	−0.1275	−0.0333	0.0173	−0.8923

ter involves ten triangles and one might imagine that one will reach a triangle-supported spin-density wave:

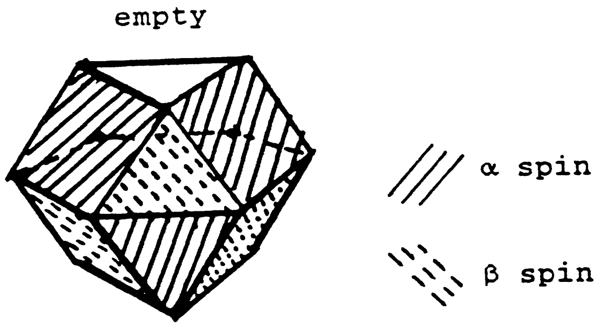


Starting the self-consistent procedure from such localized MO's one obtains an UHF solution 1.42 eV below the RHF one; four of the α-spin Boys-localized MO's are actually localized on external bonds, while the last keeps a triangular character on the internal triangle (cf. Fig. 2). The β-spin MO's occupy the complementary interstices. Starting from those MO's and changing the spin distribution, one may reach 42 other $S_z=0$ UHF solutions. We did not perform an extensive study of those solutions but found some of them (see Table VIII) as examples. All of them except one (UHF9 in Table VIII), which exhibits the maximum number of spin frustrations, are stable with respect to the RHF solution. Even with its very unfavorable spin distribution, UHF9 is only 0.0027 eV above the RHF determinant. The upper multiplet $S_z=5$ can also be reached, starting from the lowest $S_z=0$ MO's. Its Boys-localized MO's remain located on the eight external bonds and the two internal triangles. With an energy of −1.9999 a.u. it is higher in energy than the RHF solution but remains weakly bound with respect to the atoms (by 0.0958 eV per atom). The s-p mixing is bigger than for the $S_z=0$ solution, the coefficients being of 1/1 for $S_z=5$ instead of 3/2 for $S_z=0$.

One may notice (cf. Table VIII) that *all* solutions lead to positive net charges on the internal atoms ($\sim 0.4e^-$ to $0.2e^-$). The most negative charged external atoms in an UHF solution are those which bear a spin alternation ($\sim 0.1e^-$ to $0.2e^-$). Regarding spin densities, they are important on the external atoms which bear a spin frustration ($\rho \sim \pm 1.0e^-$).

D. 3D problem

We studied a Li$_{13}^{+}$ three-dimensional cluster, a fragment of an hcp lattice. We hoped to see the appearance of tetrahedra-supported singly occupied MO's. The trial vectors involved six tetrahedra-supported (three α and three β spins) MO's and six square-pyramid-supported MO's (again with three α and three β spins). Two tetrahedra are left empty. The spin distribution is chosen in order to insure the maximum number of spin alternations, minimizing the contact surfaces between equal spins. The following scheme,



gives a clear picture of the spin distribution, the external surfaces defining unequivocably the corresponding volumes, the last summit being the central atom. The result of the self-consistent procedure is the corresponding surface spin-density wave; the coefficients of the MO's on the internal atom are oscillating and introduced by the

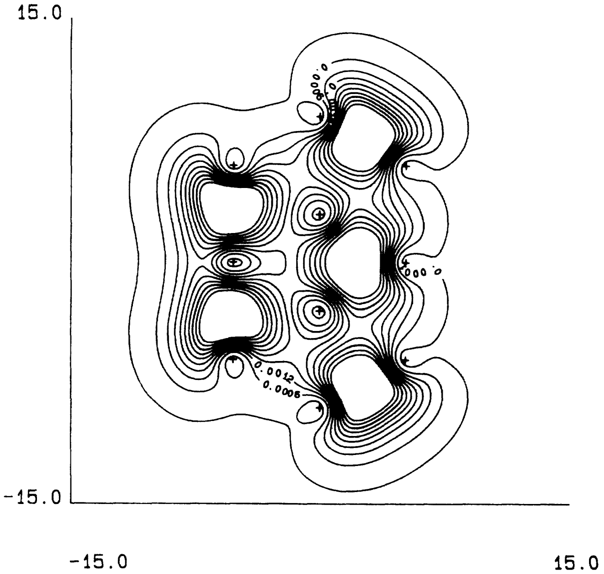
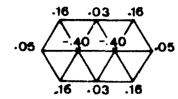
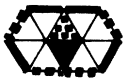
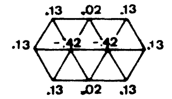
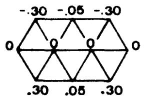
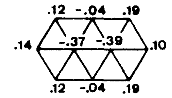
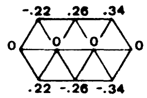
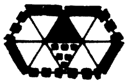
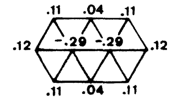
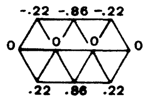
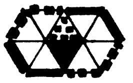
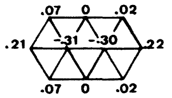
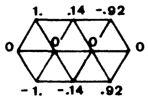
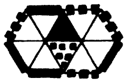
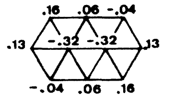
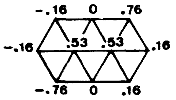
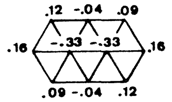
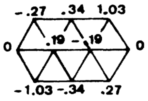
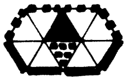
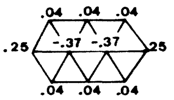
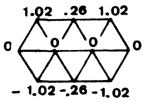
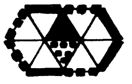
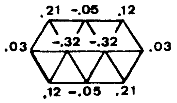
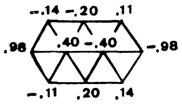
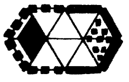
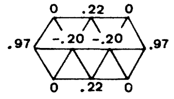
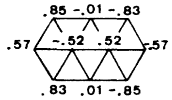
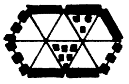
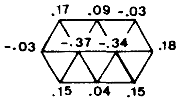
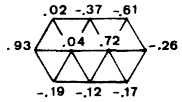
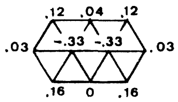
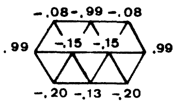
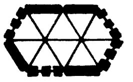
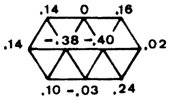
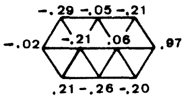
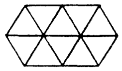
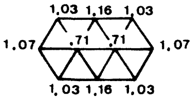


FIG. 2. Density map of α-spin electrons in the lowest UHF solution (UHF1) of planar Li$_{10}$ ($r=6$ bohrs).

TABLE VIII. Some of the UHF solutions for Li_{10}, α-MO, and β-MO.

MO	Content	− (Net charges)	Atomic spin densities	Energies (a.u.)	Binding energy per atom (eV)
RHF				−2.0462	0.222
UHF1				−2.0985	0.364
UHF2				−2.0856	0.329
UHF3				−2.0813	0.317
UHF4				−2.0548	0.245
UHF5				−2.0764	0.304
UHF6				−2.0672	0.279
UHF7				−2.0628	0.267
UFH8				−2.0710	0.289
UHF9				−2.0461	0.222
UHF10				−2.0757	0.302
UHF11				−2.0735	0.296
UHF12				−2.0837	0.324
$S_z=5$				−1.9999	0.096

orthogonality constraint; this atom does not bear any valence electron, either in the RHF or in the UHF solutions. The binding energies per atom are, respectively, 0.37 eV for the RHF and 0.45 eV for the UHF solution.

The surface character of the Boys localized MO's may be appreciated from the distance of the centroids of these MO's $\langle \varphi_i | \mathbf{r} | \varphi_i \rangle$ to the corresponding surface planes, which are 0.38 bohrs inward for the square-supported MO's and 0.02 bohrs for the triangle-supported MO's.

This UHF picture differs significantly from the approximate GVB description proposed by McAdon and Goddard, which suggests[2] a double occupation of the axial tetrahedra (empty in our model), and uses singly occupied tetrahedra and bond MO's, with a lower symmetry than ours. We failed to obtain the corresponding UHF solution, but we do not claim that better solutions could not be obtained. In such a small cluster, the ratio between the number of electrons and the number of interstices remains large, much larger than in the bulk, and this results in some ambiguities, which will not necessarily occur in infinite systems.

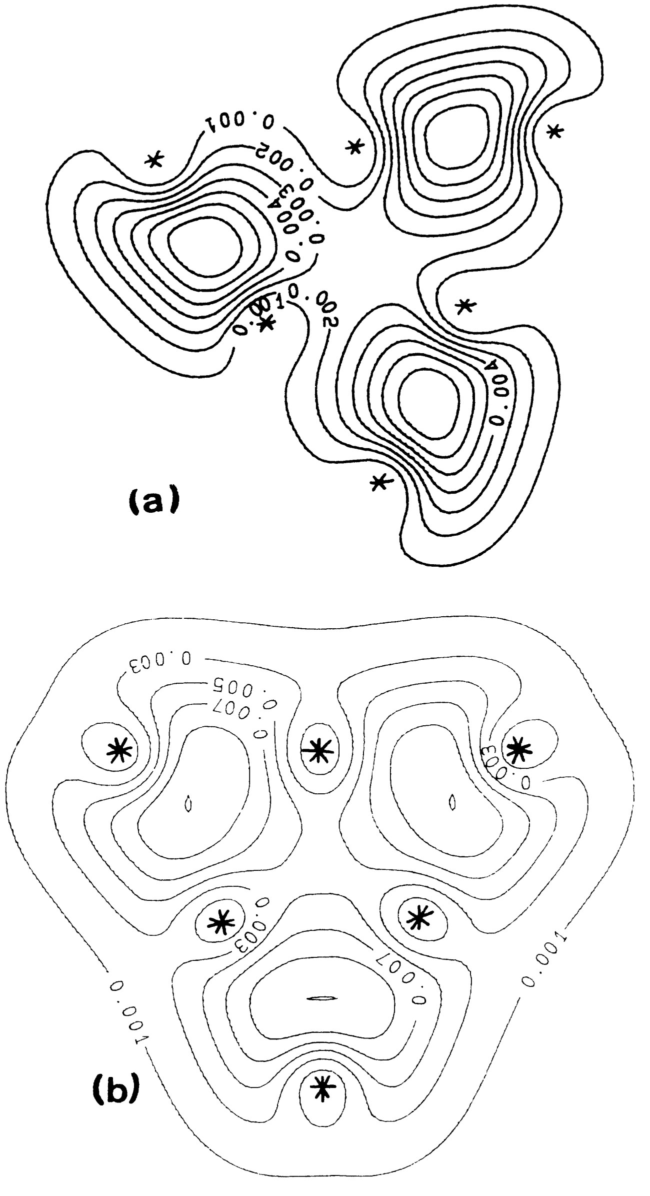


FIG. 3(a) Density map of α-spin electrons in the lowest UHF solution (UHF1) of triangular Li_6 ($r=6$ bohrs); (b) Electronic density map for the same wave function.

The electronic population of a metallic cluster exhibits local maxima of the total electronic density between atoms, either on bonds or triangles, according to a recent study[20] of Li_n clusters calculated in an *ab initio* MO-CI approach. The existence of such interstitial maxima is a unique feature, in contrast with normal covalent systems, where the maxima are on atoms. It is interesting to notice that the number of interstitial maxima is lower than the number of GVB or UHF interstitial MO's. For instance, in the triangular Li_6 Ref. 20 exhibits three maxima located inside the outer triangles, while the interstitial MO's are located on the external bonds [cf. Fig. 3(a)]. This is not in contradiction, since the superposition of the α and β e^- densities will restore the density maxima (three in that precise problem) inside the triangles as shown in Fig. 3(b), which only differs from Fig. 6 of Ref. 20 by the neglect of core electrons. A confrontation to the MO-CI wave function cannot rest on such a qualitative similarity and requires a precise study, performed in the next section.

III. COMPARISON BETWEEN THE INTERSTITIAL PICTURE AND ACCURATE MO-CI WAVE FUNCTIONS

As mentioned in the Introduction, we thought it necessary to compare the relevance of RHF and symmetry-broken solutions. The former keeps symmetry and its coefficient in the exact (or nearly exact) MO-CI correlated wave function is given by the CI expansion itself:

$$\psi = C_0 \Phi_0 + \sum_{I \text{ excited}} C_I \Phi_I \,,$$

$$\langle \psi | \Phi_0 \rangle = C_0 \,.$$

One may wonder whether the energy stabilization obtained by leaving the symmetry constraint in the UHF procedure is not gained to the detriment of the wave function, by taking components on excited eigenstates of low energy (but of other symmetry than the ground state). For the two Li_6 isomers (cyclic and triangular) we have calculated (besides C_0) (i) the overlap between the lowest UHF solution Φ^0_{UHF} and ψ, and (ii) the overlap between ψ and the normalized symmetric combination of the two equivalent UHF solutions, i.e., the resonance of the two spin-density waves Φ^0_{UHF} and $\Phi^{0'}_{\mathrm{UHF}}$:

$$(\Phi^0_{\mathrm{UHF}} + \Phi^{0'}_{\mathrm{UHF}})[2(1 + \langle \Phi^0_{\mathrm{UHF}} | \Phi^{0'}_{\mathrm{UHF}} \rangle)]^{-1/2} \,.$$

These numbers appear in Table IX from which it is clear that the overlap with the exact wave function is better for Φ^0_{RHF} than for the UHF solution or the resonant combination of the two UHF solutions. In that sense one may say that the UHF energy gain is obtained through a bias of the wave function. The relevance of the interstitial MO's could be judged more properly by considering subspaces of determinants built from those interstitial MO's only. One might choose one of the following strategies.

TABLE IX. Overlap between the exact MO-CI wave function and RHF or UHF single determinants of Li_6 clusters.

	$\langle \Phi^0_{\mathrm{RHF}} \vert \psi \rangle$	$\langle \Phi^0_{\mathrm{UHF}} \vert \psi \rangle$	$\dfrac{\langle \Phi^0_{\mathrm{UHF}} + \Phi^{0'}_{\mathrm{UHF}} \vert \psi \rangle}{\sqrt{2(1+S)}}$ [a]	$\langle P_{s_2}\psi \vert \psi \rangle^{1/2}$ [b]
cyclic	0.8024	0.5185	0.7307	0.9208
triangular	0.9211	0.6586	0.8550	0.9414

[a] Symmetric combination of the two lowest equivalent UHF solutions.

[b] Norm of the projection of the exact wave function onto the subspace of "neutral" determinants defined from Φ^0_{UHF} MO's.

(i) One might consider the subspace S_1 of all the $S_z=0$ UHF solutions, consisting of different spin distributions on the bond MO's; these configurations may be seen as variational neutral-like VB determinants, each bond bearing one and only one electron.

(ii) One might consider the subspace S'_2 of all the determinants built from the MO's of Φ^0_{UHF}; among these $(C^3_6)^2$ determinants, only C^3_6 are neutral-like in the VB sense.

(iii) One may finally restrict the subspace S'_2 to the subspace S_2 of the last C^3_6 neutral-like determinants generated from the MO's of Φ^0_{UHF}; we adopted this criteria for the sake of simplicity and because it is rather severe. Calling P_{S_1}, P_{S_2}, and $P_{S'_2}$ the projectors on the subspaces S_1, S_2, and S'_2 one may be sure that

$$\langle \psi | P_{S_2}\psi \rangle \langle \langle \psi | P_{S'_2}\psi \rangle$$

and one may expect that

$$\langle \psi | P_{S_1}\psi \rangle \rangle \langle \psi | P_{S_2}\psi \rangle$$

since in S_1 the spin-frustrated determinants are variationally determined while they are not in S_2. The results appear in the last column of Table IX and one may see that combining the neutral-like VB structures obtained from Φ^0_{UHF} gives a better overlap with the exact wave function than the Φ^0_{RHF} solution. This result is a support in favor of the physical meaning of the interstitial MO's, even when they are determined from a symmetry-broken solution.

In order to see the importance of the delocalization tails introduced in the localized MO's of Φ^0_{UHF}, we have repeated the preceding calculation using the MO's of the upper multiplet, which are orthogonal. Let us call P_{S_3} the projector onto the neutral VB determinants built from the MO's of this upper multiplet. Now it turns out that the projection of ψ onto that subspace is very weak:

$$\langle \psi | P_{S_3}\psi \rangle^{1/2} = 0.5996 \text{ for cyclic } Li_6 .$$

This result demonstrates the key role of the delocalization tails of the Φ^0_{UHF} MO's, i.e., of their nonorthogonality. If one remembers (cf. Sec. II) that the MO's of Φ^0_{UHF} are linear combinations of those of $S_z=3$ UHF determinants, one may sat that they define the same "valence" space S'_3 (neutral plus ionic)$=S'_2$. The failure of $P_{S_3}\psi$ is due to the lack of ionic components in S_3, which are correctly incorporated in $P_{S_2}\psi$ through the MO tails. The difference between the MO's of Φ^0_{UHF} and Φ^3_{UHF}, which is not apparent from their spatial shapes [Figs. 4(a) and 4(b)] plays a crucial role and one cannot follow McAdon and Goddard when they say that their GVB MO's are almost the same as those of the UHF upper multiplet. It is more likely to suppose that the GVB MO's are closely related to those of the lowest $S_z=0$ UHF solution.

Actually the GVB wave function and $P_{S_2}\psi$ are a singlet linear combination of neutral-like VB structures incorporating correctly the components on the ionic structures.

It is interesting to analyze the projection of the exact wave function onto the subspace of the neutral-like VB structures, i.e., for instance, $P_{S_2}\psi$. The determinants spanning S_2 have been symmetrically orthogonalized, the $S^{-1/2}$ transformation keeping the spin localization on the various bonds. The coefficients of $P_{S_2}\psi$ on that basis

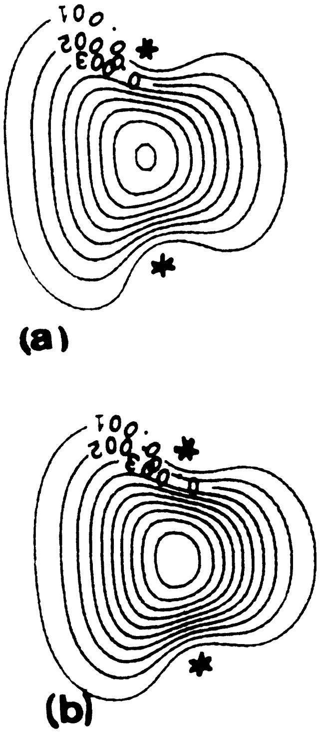


FIG. 4. Density map of a self-consistent localized bond MO of cyclic Li_6 ($r=6$ bohrs). (a) Associated with the lowest $S_z=0$ solution; (b) associated with the $S_z=3$ solution.

show the leading role of the spin alternation since for cyclic Li_6 the determinants with six spin alternations appear with a coefficient 0.451, those with four spin alternations have 0.181, and those with two spin alternations with 0.090. These numbers have to be compared with the coefficients of the lowest eigenvector of the Heisenberg Hamiltonian for a cyclic system, which are 0.479, 0.208, and 0.063, respectively. Therefore the components of the exact wave function onto the neutral-like VB subspace are ruled by a spin Hamiltonian. Calling ψ_H^0 the lowest eigenvector of the Heisenberg Hamiltonian one may calculate $\langle \psi_H^0 | P_{S_2} \psi \rangle / \| P_{S_2} \psi \| = 0.996$, which measures quantitatively the similarity between the two vectors.

The comparison is straightforward for the cyclic problem since the eigenvectors of the Heisenberg Hamiltonian (with effective exchange between adjacent cells only) are independent of the amplitude of the effective exchange. For a less regular system such as the triangular Li_6, two different exchange integrals have to be considered, depending on the relative orientation of the adjacent external bonds (colinear or adjacent on a summit atom) and the lowest eigenvector depends on the ratio between the two spin couplings. The determination of these two parameters from our UHF energies will be explained in the next section. Using these values we obtained $\langle \psi_H^0 | P_{S_2} \psi \rangle / \| P_{S_2} \psi \| = 0.9989$, which shows that the prevailing role of the spin ordering among the neutral-like determinants is not limited to the highly peculiar case of 1D cyclic systems. The connection between the GVB solutions and a Heisenberg problem had been noticed for the 1D cyclic problem in Ref. 2. We believe that the existence of a Heisenberg Hamiltonian written in terms of interstitial units is a general feature and that one may exploit the variety of UHF solutions to determine the amplitude of its matrix elements and to approach the final energy, as will be explained in the next section.

IV. DETERMINATION OF A HEISENBERG HAMILTONIAN FROM THE VARIOUS UHF SOLUTIONS

One more argument in favor of the research of our underlying spin Hamiltonian is brought by Fig. 1, concerning cyclic Li_6; the spacing between the energies of the UHF solutions with 6, 4, 2, and 0 spin alternations (corresponding to $S_2 = 0$, 0, 0, and 3, respectively) is very regular ($E = -1.2511$, -1.2398, -1.2277, and -1.2129 a.u., respectively, at 6 bohrs) as would occur in a Heisenberg Hamiltonian which introduces 6, 4, 2, and 0 effective exchange integrals on the diagonal energies of the determinants.

One may therefore propose to introduce a Heinsenberg Hamiltonian in terms of interstitial MO's. In principle, Heisenberg Hamiltonians are effective Hamiltonians (in the sense of the quasidegenerate perturbation theory) relative to a half-filled band and spanned by an orthogonal basis set of a model space, composed of all neutral-VB determinants in which each cell (each AO in general, here each bond MO) bears one electron and only one.

The upper UHF multiplet solution provides an orthogonal basis of interstitial MO's, and one may, in principle, use them to generate the model space for any value of S_z by considering all possible spin distributions and the same space part with one electron per interstice. The first-order Hamiltonian for $S_z \neq n/2$ would suppress some first-order (positive) exchange K integrals between bonds of alternant spins and would couple determinants which differ by one spin exchange between adjacent interstices through the same exchange. At this level the spectrum would be unrealistic with high-energy singlet states. The perturbative inclusion of the effect of the ionic VB structures changes both the diagonal and off-diagonal matrix elements of the effective Hamiltonian, as shown by Anderson.[21] Considering a determinant in which the bond i bears an α spin and is adjacent to a bond j bearing a β spin,

$$\Phi_I = | \cdots \varphi_i \bar{\varphi}_j \cdots | ,$$

where the φ_k's are the self-consistent MO's of the upper multiplet. These MO's are eigenfunctions of a Fock operator relative to this upper multiplet:

$$F^M \varphi_k = C_k \varphi_k$$

with

$$F^M = h + \sum_k (J_k - K_k) ,$$

where h is the monoelectronic part of the Hamiltonian and J and K are the usual Coulomb and exchange operators. Considering an adjacent ionic VB structure such as

$$a_j^\dagger a_i \Phi_I = | \cdots \varphi_j \bar{\varphi}_j \cdots |$$

then $\langle \Phi_I | H | a_j^\dagger a_i \Phi_I \rangle = \langle \varphi_i | F^I | \varphi \rangle$, where F^I is the Fock operator for the Φ_I determinant,

$$\langle \Phi_I | H | a_j^\dagger a_i \Phi_I \rangle = \langle \varphi_i | F^I - F^M | \varphi_j \rangle \simeq \langle \varphi_i | -K_i | \varphi_j \rangle$$

if one neglects the effect of other exchange integrals located on remote bonds. At first order on the wave function the variational treatment on the determinant Φ_I consists in changing φ_i into φ_i':

$$\varphi_i' = \varphi_i + \sum_{\substack{j \text{ adj.} \\ \text{to } i}} \frac{\langle \varphi_i | F^I | \varphi_j \rangle}{\Delta E_{n-i}} \varphi_j ,$$

where adj. denotes "adjacent" and ΔE_{n-i} is the energy difference between neutral and adjacent ionic determinants. The energy gain brought by the SCF process on Φ_I is at second order,

$$\langle \Phi_{\text{UHF}}^I | H | \Phi_{\text{UHF}}^I \rangle - \langle \Phi_I | H | \Phi_i \rangle \simeq \sum_i \sum_{\substack{j \\ \text{adj.} \\ \text{spin altern.}}} \frac{\langle \varphi_i | F^I | \varphi_j \rangle^2}{\Delta E_{n-i}} .$$

Similarly in the second-order QDPT treatment, the effective energy of Φ_I becomes

$$\langle \Phi_I | H^{\text{eff}} | \Phi_I \rangle = \langle \Phi_I | H | \Phi_i \rangle + \sum_i \sum_{\substack{j \\ \text{adj.} \\ \text{spin altern.}}} \frac{\langle \varphi_i | F^I | \varphi_j \rangle^2}{\Delta E_{n-1}}$$

so that at second order at least the diagonal matrix element of the Heisenberg Hamiltonian may be taken as the self-consistent energy of Φ_I^{UHF},

$$\langle \Phi_I | H^{\mathrm{eff}} | \Phi_I \rangle \simeq \langle \Phi^I_{\mathrm{UHF}} | H | \Phi^I_{\mathrm{UHF}} \rangle \ .$$

This represents a procedure to reach the amplitude g_{ij} of the effective Hamiltonian, which may be written as

$$H^H = \langle \Phi^M | H | \Phi^M \rangle + \sum_{\substack{i,j \\ \mathrm{adj.}}} g_{ij} (a_i^\dagger a_{\bar j}^\dagger - a_{\bar i}^\dagger a_j^\dagger)(a_i a_{\bar j} - a_{\bar i} a_j) \ .$$

Actually $g_{ij} = K_{ij} + \langle \varphi_i | K_i + K_j | \varphi_j \rangle^2 / \Delta E_{n-1}$ and it is well known that one finds the same extradiagonal interaction g_{ij} between determinants which exchange two spins on the ij pair, i.e., between Φ_I and $a_i^\dagger a_{\bar j}^\dagger a_j a_{\bar i} \Phi_I$.

The knowledge of a large enough number of localized UHF solutions is sufficient to build the Heisenberg Hamiltonian. This has been attempted on three different problems.

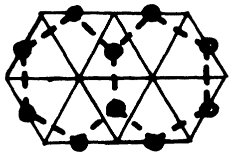
For cyclic Li_6 we had three different $S_z = 0$ solutions to determine g, and we obtained

$$\langle \Phi^M | H | \Phi^M \rangle - \langle \Phi^0_{\mathrm{UHF}} | H | \Phi^0_{\mathrm{UHF}} \rangle = 6g \ ,$$

which leads to $g = -0.006\,37$ a.u. Knowing that the lowest singlet eigenvector is -8.605 g below the upper multiplet, one gets an evaluation of the exact energy of -1.2677 a.u. If one defines g from the energy difference between $\langle \Phi^0_{\mathrm{UHF}} | H | \Phi^0_{\mathrm{UHF}} \rangle$ and the $S_z = 0$ UHF solutions with four or two spin alternations one gets somewhat different values of g ($-0.005\,64$ and $-0.005\,85$ a.u., respectively) but adding -2.605 g to the Φ^0_{UHF} energy leads to a final energy of -1.2615 and -1.2633 a.u., respectively, which is a rather stable estimate. The exact energy is -1.2919 a.u.; if one remembers that the RHF energy was -1.1835 a.u., this means that the use of a Heisenberg Hamiltonian built from the localized UHF solutions brings 80% of the correlation energy (within the considered basis set).

One may repeat the procedure on less symmetrical clusters, for instance on the triangular Li_6 structure, which involves two types of adjacent bonds. We used either Φ^M or Φ^0_{UHF}, and UHF2 (cf. Table VI) and we get $g_1 = -0.0118$, $g_2 = -0.0212$ and $E^H = -1.2921$. Using two other combinations of $S_z = 0$ and $S_z = 1$ solutions gave us $E^H = -1.3064$ and -1.3030 a.u. The exact energy in the basis is -1.3027 a.u., while the RHF was -1.2304 a.u.; again our procedure gives more than 80% of the correlation energy.

Finally we repeat the procedure for the Li_{10} cluster. In the Heisenberg procedure one neglects the interaction between nonadjacent regions, in the two Li_6 systems the definition of the adjacent bonds was obvious but in the present system one may consider different possibilities. We make two types of Heisenberg calculations, one involving four different g parameters and one involving six. The first calculation is associated with the following dual structure:



where the open circles represent the centroids of the bond MO's and the dotted lines the considered interactions. The five parameters are determined with some of the UHF solutions, namely UHF1, UHF2, UHF4, UHF10, UHF12 (referred to in Table VII). The four g parameters are

$$g_1 = -0.008\,346 \text{ a.u.},$$

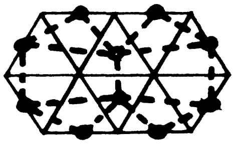
$$g_2 = -0.004\,580 \text{ a.u.},$$

$$g_3 = -0.006\,444 \text{ a.u.},$$

$$g_4 = -0.009\,865 \text{ a.u.},$$

leading to the final energy -2.1243 a.u. One may notice that the most stabilizing interaction is the spin alternation between the two MO's supported by the central triangles which are the most overlapping ones. An evaluation of the exact energy in the basis is -2.1966 a.u., the RHF energy is -2.0462 a.u. set, the Heisenberg solution gives only 52% of the correlation energy.

Taking into account two more interactions, the dual structure being



,

one obtains the g parameters

$$g_1 = -0.008\,346$$

$$g_2 = -0.007\,705$$

$$g_3 = -0.005\,655$$

$$g_4 = -0.008\,230$$

$$g_5 = +0.002\,279$$

$$g_6 = -0.001\,489$$

using the UHF1, UHF2, UHF4, UHF6, UHF10, UHF11, and UHF12 solutions.

One may notice that (i) the g_5 and g_6 parameters neglected in the previous procedure are much smaller than the other ones, and (ii) g_5 is positive—opposite the sign of all the other ones—the spin frustration between the two collinear MO's being more stable than the spin alternation; this phenomenon can also be seen in the fact that the UHF1 solution is of lower energy than the UHF2. The Heisenberg final energy associated with those g parameters is -2.1286 a.u. corresponding to 55% of the correlation energy.

V. CONCLUSION

The present model rests on a two-step mechanism.

(i) The variational definition of singly occupied interstice-supported MO's from an UHF procedure; this step introduces a short-range delocalization of the electrons, each one inside its interstice. This delocalization is already present in the upper UHF solution (ferromagnetic).

(ii) After this preliminary short-range delocalization, the spin-distribution and fluctuation problem is addressed through a magnetic treatment. The lowest UHF solution corresponds to an antiferromagnetic spin-density wave, i.e., a distribution where each interstice bearing an α electron is surrounded by β-electron interstices (as far as possible) and vice versa. The variational UHF treatment brings a further electronic delocalization by including the effect of one-electron transfers between adjacent interstices. The energies of the various UHF solutions may be used to define the effective diagonal energies of a Heisenberg Hamiltonian, and the effective exchange interactions. Diagonalizing the Heisenberg Hamiltonian introduces the spin fluctuations around the most-alternant spin distributions (i.e., the Néel states).

The first step (the short-range delocalization) is absolutely crucial, it brings the energy (even of the uppermultiplet) below the energy of the separated atoms. This is in strong contrast with the normal Heisenberg Hamiltonians, which for weakly delocalized problems are usually supported by atomic orbitals, i.e., do not incorporate delocalization at the zeroth order. The change of elementary cells to build the magnetic model is crucial, going from the atoms to the interstices. The VB language, which is at the basis of magnetic Hamiltonians, must be translated, replacing atoms and atomic orbitals by bonds, triangles, tetrahedra, or larger cells and the corresponding MO of lowest energy (i.e., the most symmetrical one) defined in the interstice. This change of building blocks from the atom to the interstice may explain some apparent contradictions, for instance the fact that some clusters such as the triangular Li_6 may be considered as strongly ionic in an atomic-orbital VB approach[19] and may nevertheless be treated in a Heisenberg Hamiltonian, i.e., an essentially neutral picture, when one moves to bond MO's (which may be polarized).

These remarks suggest a practical strategy for the study of the bulk, consisting of the calculation of several UHF solutions and the extraction of effective spin interactions in order to define a Heisenberg Hamiltonian, ultimately solved in an approximate manner. This procedure might, in principle, be applied to finite clusters, but edge effects induce several difficulties: (i) the interstices are of various dimensionalities (lower dimensionality on the surface than inside the cluster); (ii) the spin couplings are therefore numerous and their extraction is difficult; (iii) the architecture of the cluster is not easy to guess and the independent-geometrical parameters are numerous. A geometry optimization seems difficult in that approach.

These difficulties disappear in the study of infinite regular lattices, since edge effects vanish and the interatomic distance is the unique parameter. The method can be developed in three steps. The first step consists of the research of the optimal interstices. In our opinion, they will be given by the largest most compact nonoverlapping cells, each one bearing one unique electron in the most bonding MO. For instance, on a two-dimensional regular triangular lattice, we believe that the most relevant interstice would consist in a rhombus since each atom will belong to four rhombi, which results in a one-electron population per atom (this is different from the suggestion by McAdon and Goddard[2] of triangle-supported interstices, one triangle over two being empty, which would result in a charge-density wave). In the second step these interstitial MO's will be taken as trial vectors for the self-consistent HF process on the bulk. Different choices of spin distributions may be considered leading to different self-consistent energies. The ferromagnetic solution (all spins parallel) will give us a reference energy. The lowest $S_z=0$ UHF solution may be expected to be obtained by considering a spin-alternation between the interstices; it is likely that the privileged spin alternation occurs between interstices presenting the largest contact surface. For instance in the two-dimensional regular triangular lattice the largest effective spin coupling takes place between rhombi having one bond (two adjacent atoms) in common rather than a single atom. By considering less-ordered spin distributions and the corresponding UHF energies it will become possible to evaluate the effective spin interactions of the Heisenberg Hamiltonian. In the ultimate step the lowest eigenvalue (or more precisely an estimate of the cohesive energy) will be sought by considering the lowest UHF solution (i.e., a Néel state) as a zeroth-order description and by perturbing its energy to second or fourth order (see, for instance, Refs. 22 and 23) under the interaction with the locally disordered structures.

This strategy will be exploited in collaboration with Pisani and co-workers of the Torino University, who conceived an UHF version of their crystal Hartree-Fock program. It will be interesting to see which part of the cohesive energy is brought by the symmetry breaking through the lowest UHF solution, which part is brought by the spin fluctuation (treated by the magnetic Hamiltonian), and which part is not attainable by this model which essentially remains inside the valence shell.

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