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Toward a magnetic description of metals in terms of interstitial molecular orbitals. II. One-dimensional infinite system: The lithium chain

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Using the unrestricted Hartree-Fock (UHF) version of the *ab initio* CRYSTAL computer program, the ferromagnetic HF solution is obtained for a one-dimensional chain of Li atoms. This solution is much lower in energy than the restricted Hartree-Fock solution for the singlet state and is built of bond-centered singly occupied monoelectronic functions. The lowest UHF solution is even much lower in energy and consists of an antiferromagnetic spin-density wave, i.e., a spin alternation on bond-centered singly occupied monoelectronic functions. These results support the validity of the interstitial picture of simple metals, as recently suggested by McAdon and Goddard. The delocalization between the interstices (here bonds) is weak and may be treated through a distance dependent Heisenberg Hamiltonian, whose parameters are extracted from the previous UHF solutions. The final estimate of the cohesive energy and bond distance are compared to the results of various density-functional methods.

I. INTRODUCTION

An approach to studying the chemical bonding in alkali- and noble-metal systems was proposed some time ago by McAdon and Goddard.[1,2] From a generalized-valence-bond[3] (GVB) study of lithium clusters, they concluded that the electronic structure of metallic systems should be described using singly occupied interstitial molecular orbitals (MO's) localized at the bond midpoint, for one-dimensional (1D) systems, at the center of triangles for two-dimensional (2D) ones, and at the center of tetrahedra for three-dimensional (3D) systems. This description cumulates the advantages of including most of the delocalization (i.e., the kinetic energy is lowered with respect to the atomic one) since the MO's are spread in interstices between atoms, and of minimizing the electronic repulsion, since the electrons are located in different space regions. On the other hand, it diminishes the nuclear attraction (the electrons are located far from the nuclei), but at short enough interatomic distances typically $R < 4.3$ Å (for a lithium chain) this defect is much weaker than the balance of the two preceeding effects. A comparison with extensive *ab initio* MO configuration-interaction (CI) calculations showed the relevance of this approach.[4] The GVB procedure is quite complex and time consuming and therefore limited to systems of a rather small number of electrons (typically to ten electrons). In Ref. 4, some of the authors (M.B.L. and J.P.M.) have proposed and attempted an alternative procedure on clusters. This is a two step model.

(i) Singly occupied interstice-supported MO's are variationally defined using an unrestricted Hartree-Fock (UHF) procedure. The UHF delocalized MO's are then localized using a Boys's unitary transformation[5] in order to obtain the required set of interstice-supported MO's.

(ii) The spin-distribution and spin-fluctuation problem is treated with a magnetic Heisenberg Hamiltonian. The energies of the various UHF solutions (corresponding to the different spin attributions) are used to define the effective diagonal energies of the Heisenberg Hamiltonian as well as the effective exchange parameters. This method tested on ideal lithium clusters brings about 80% of the correlation energy.

In this paper we would like to apply the preceding method to infinite systems and more precisely on an infinite chain of lithium atoms. Section II will give details on the UHF procedure on crystals and the CRYSTAL computer code, as well as an analysis of the restricted Hartree-Fock (RHF) and UHF monoelectronic descriptions. Section III will explicitly give the correlated description through a magnetic treatment, discuss the results, and compare them to density-functional calculations. Section IV will give the conclusions and prospectives.

II. MONOELECTRONIC DESCRIPTIONS

A. The CRYSTAL UHF program

The orbital optimization is done using the CRYSTAL computer code.[6(a)] CRYSTAL is an *ab initio* Hartree-Fock linear combination of atomic orbitals (LCAO) program for the treatment of periodic systems like polymers (1D), slabs (2D), or crystals (3D). CRYSTAL performs the calculation of wave functions, energies, and properties both at the restricted Hartree-Fock (RHF) level and at the unrestricted Hartree-Fock[6(b)] level. The core electrons can be treated exactly (all electrons calculation) or by the means of pseudopotentials.

The CRYSTAL program typically uses isolated atom or ion eigenfunctions as trial vectors. The RHF solution, as well as the atom-centered solutions at long interatomic distances, are easily reached that way. The atom-centered solutions at shorter distances are reached starting from a Fock matrix obtained in a previous (long-distance) calculation. The bond-centered solutions are slightly more difficult to obtain since they are in different symmetry than the atom-centered solutions. The ferromagnetic (FM) UHF solution at say 6.0 a.u. is obtained starting from the atomic trial density matrix by locking the β minus α occupation to one electron for a few cycles. The antiferromagnetic (AFM) solution at the same distance is obtained from the ferromagnetic one by locking the β minus α occupation to zero electrons. The FM and the AFM solutions at other distances are then obtained using this previously converged Fock matrix.

B. Basis sets

The calculations have been made with two different basis sets. The first basis set, denoted as A, is a minimal basis set. The core $1s$ orbital has been taken as in the Dunning basis for Li,[7] and the valence and polarization $2s$ and $2p$ orbitals are chosen supported by one Gaussian function of which exponent ζ has been optimized in order of which to minimize the energy of the antiferromagnetic UHF solution. The basis set A is then

	Exp.	Coef.
$1s$	16.120	0.154 33
	2.9362	0.535 33
	0.794 65	0.444 63
$2s$	0.06	
$2p$	0.06	

This basis set may seem incredibly poor but in finite systems a large part of the effect of diffuse functions is the reproduction of the outer tails of the wave functions which are poorly described by Gaussian functions. In infinite systems this defect is partly fixed by the unoccupied functions located on the neighboring atoms. The atom benefits from an effective enlarged basis set in the bulk compared to the isolated one; this may result in an overestimation of the cohesive energy. The basis-set superposition error is distance dependent and may be evaluated as the energy difference between the treatment of an atom in its basis set and the same calculation with basis functions located at the position of the other atoms in the infinite systems. Doing such calculations with the above basis set gives (at 6.0 a.u.) -7.317996 a.u. and -7.321146 a.u., i.e., an energy stabilization of 0.086 eV. All energies are corrected by the basis-set superposition error, which anyway is very small.

The second basis set, denoted as B, is a valence double-ζ plus polarization basis set, the core electrons are treated through a pseudopotential.[8] This basis has been optimized in order to reproduce the exact valence energy and wave function in the infinite basis limit. The basis B is

	Exp.	Coef.
s	2.464 158	-0.0164
	1.991 405	0.0358
	0.581 880	0.1321
	0.070 935	0.6071
s'	0.027 095	1
p	0.140 790	0.600 123
	0.043 806	0.493 980

C. RHF and UHF solutions

In the infinite linear chain of lithium atoms, the RHF solution is not bound compared to the energy of free atoms in both basis sets A and B [Figs. 1(a) and 1(b)]. The equilibrium distance is 5.9 a.u., the corresponding energy being 0.11 eV *above* the atomization asymptote for the B basis set. The equilibrium distance is a little shorter, around 5.84 a.u., in the small basis set, the energy being 0.084 eV above the atomization one.

One can define two classes of UHF solutions: the atom-centered solutions which are of lower energy at large interatomic distances and the bond-centered solutions which are of lower energy at short distances. In each class the ferromagnetic solution is the highest one, the lowest one being the antiferromagnetic solution with full spin alternation between adjacent sites (atoms or bonds).

As for small cyclic clusters (Ref. 4), the atom-based ferromagnetic UHF solution is repulsive (see Fig. 1) while the interstice-based ferromagnetic UHF solution is bound. The equilibrium distances of the latter are quite long, due to the strong electronic repulsion of the ferromagnetic spin alignment; they are, respectively, 6.51 and 6.18 a.u. for basis sets A and B, while binding energies are 0.32 and 0.25 eV. Figure 2(a) shows the population of the different atomic orbitals (in the basis set B) for the ferromagnetic solutions. The interstitial solution has a very important content of p orbitals, even higher than the s one at very short distances; the s and p content are equal at 5.55 a.u. The p content is linearly decreasing with the interatomic distance but still high at 7.8 a.u., around 37%. One can also notice the spatial expansion of the s part, taking more weight on the diffuse s orbital when the interatomic distance increases. On the contrary, the atomic solution is essentially of s content, the p content hardly reaching 10% at the lowest computed distances.

The interstitial antiferromagnetic solution is strongly bound (see Fig. 1); the orthogonalization constraint between nearest-neighbor bond-centered orbitals being released, a better delocalization takes place and allows the kinetic energy to decrease. The equilibrium distances are, respectively, 6.17 and 5.94 a.u. in basis sets A and B while corresponding binding energies are 0.44 and 0.46 eV per atom. The atom-centered antiferromagnetic solution, while weakly attractive, remains very high in energy. Figure 2(b) shows the atomic orbitals (AO's) populations of the antiferromagnetic solutions. One can see that the p content of both atom-centered and bond-centered solutions is smaller than in the ferromagnetic case. This is due to the release of the nearest-neighbor orthogonality constraint which is partly fulfilled in the ferromagnetic solution by taking higher p components. The atom-centered antiferromagnetic solution has then almost no p contribution, the latter being non-negligible only at shorter distances and always smaller than 4%. The bond-centered solution has still a high p contribution, slowly decreasing with the interatomic distance but staying in the range of 30% to 40%. Figures 3(a) and 3(b) show the charge- and spin-density maps for the interstitial antiferromagnetic solution, at 6 a.u., computed in basis set B. One can see that the maxima of the charge density are located at the bond midpoints, the density decreasing regularly as one goes from there towards the nuclei; it increases again around the nuclei in order to make the cusp with the core electrons (here simulated by a pseudopotential), giving small secondary minima at the nuclei locations. The spin-density map shows the spin alternation, one bond being occupied by α electrons, the nearest-neighbor ones by β electrons. The spin density is zero on the nuclei, while alternatively maximum and minimum at

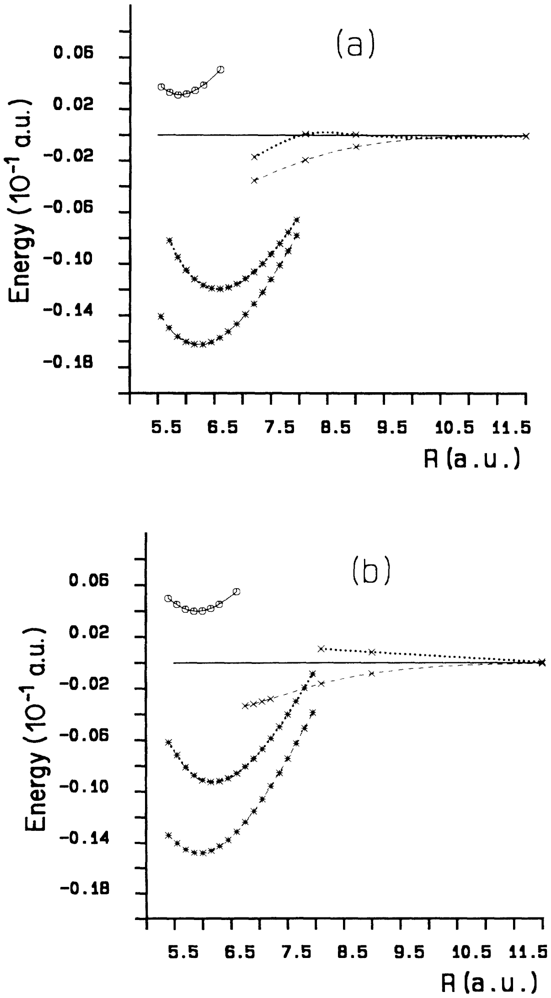

FIG. 1. Potential-energy curves of the linear lithium chain. ——, restricted Hartree-Fock approximation; — — —, unrestricted Hartree-Fock approximation, $s_z=0$, spin-density wave; · · · ·, unrestricted Hartree-Fock approximation, $S_z=\max$, ferromagnetic solution; $*$, interstice centered; ×, atom centered. (a) Basis set A. (b) Basis set B.

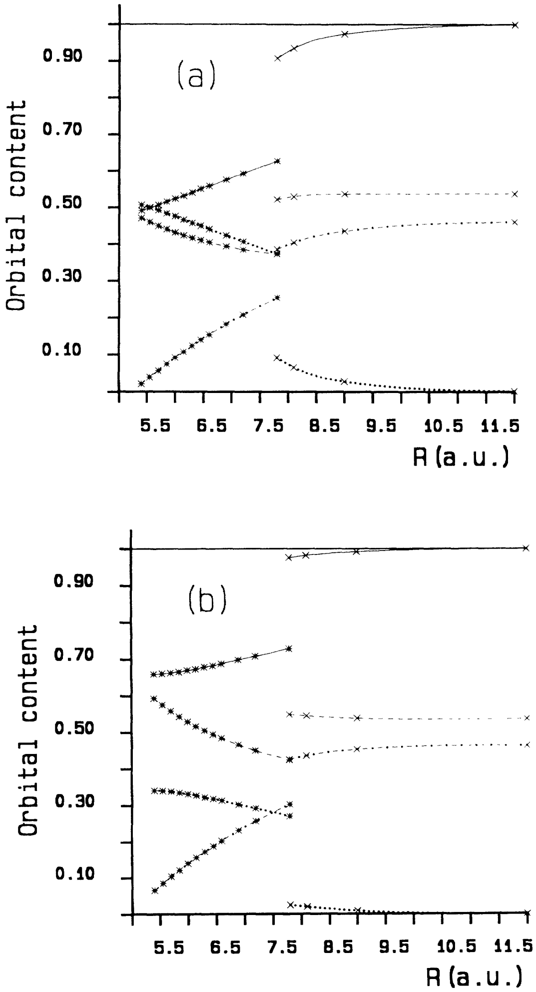

FIG. 2. Atomic orbital composition of the different unrestricted Hartree-Fock solutions in basis set B. ——, total valence s contribution; — — —, s contribution; —·—·—, s' contribution; · · · ·, p_z contribution; $*$, interstice centered; ×, bond centered. (a) Ferromagnetic UHF solution. (b) Antiferromagnetic, spin-density wave, UHF solution.

the bond midpoints. The fact that the charge density exhibits a local maximum at the nuclei locations, while the spin density is null, shows the inclusion of ionic configurations (s_i^2 or p_i^2) in this "pseudoneutral" spin-density wave (see below).

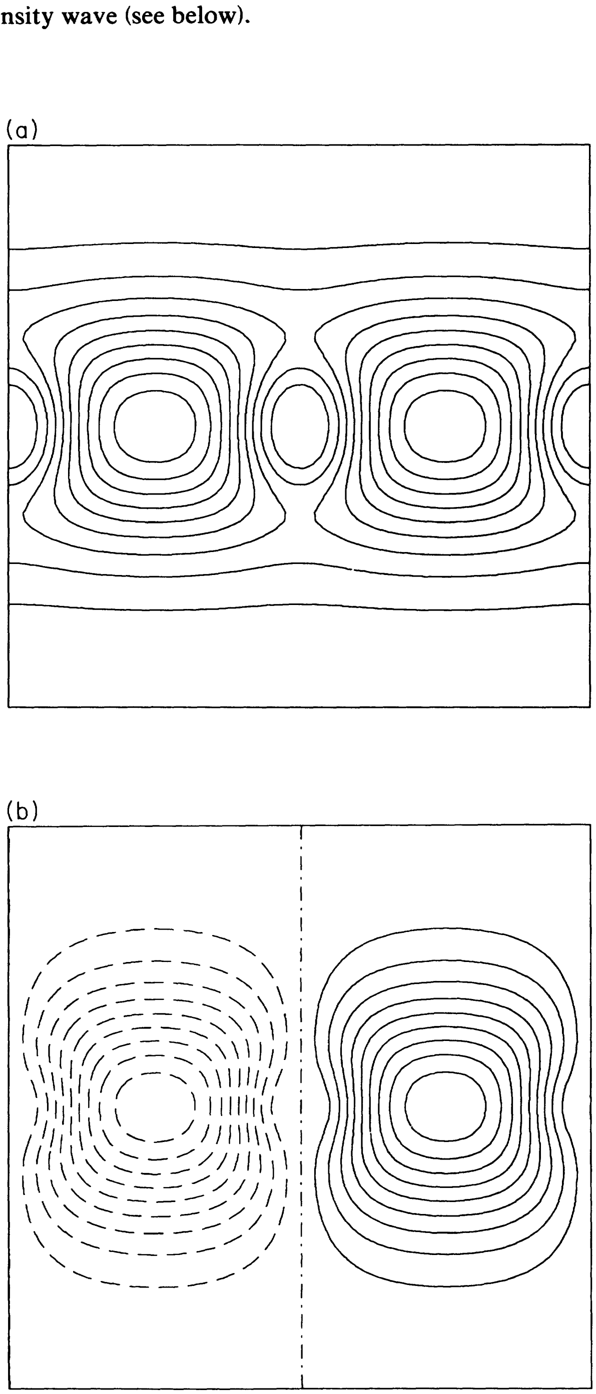

FIG. 3. (a) Valence-electron density map. Lithium atoms are represented by solid circles. The isodensity lines are drawn with interval $0.001e/(\text{bohr})^3$. Highest value is $0.01e/(\text{bohr})^3$. (b) Spin-density map of the antiferromagnetic solution. Lithium atoms are represented by solid circles. The isodensity lines are drawn with interval $0.001e/(\text{bohr})^3$, the highest value is $0.01e/(\text{bohr})^3$. Solid, dashed, and dotted-dashed lines correspond to positive, negative, and zero values.

III. THE CORRELATED DESCRIPTION

A. Preliminary discussion

The correlation is traditionally defined from the symmetry-adapted RHF solution. From this point of view the 1D lithium chain is highly correlated. The antiferromagnetic UHF solution already includes the major part of this correlation. Again, from a traditional point of view the lithium 1D chain would be considered as an s half-filled band problem. *Ab initio* calculations on finite clusters[10] indicate that the solution contains large ionic valence-bond (VB) components with double occupation of s orbitals on the same atom. The overestimation of these situations is only partially repaired by the internal correlation (within the valence s bond) but the dynamical correlation (involving nonvalence virtual orbitals) is crucial and goes essentially through the $s^2 \rightarrow p^2$ intraatomic double excitations.

The UHF interstitial solutions suggest a qualitatively different picture. After a localization unitary transformation of the occupied MO's, the ith singly occupied MO between atoms i and $i+1$ has the form

$$\varphi_i = \lambda s_i + \mu p_i + \lambda s_{i+1} - \mu p_{i+1} + \text{tail} ,$$

where the tails are small and spread over neighboring atoms. This MO incorporates a complete intrabond delocalization. One may notice that in the ferromagnetic UHF solution, the product $\varphi_{i-1}\varphi_i$ gives the following weights: $2\lambda^2(\lambda^2+\mu^2)$ to the neutral situation where the atom i is singly occupied in orbital s_i; $2\mu^2(\lambda^2+\mu^2)$ to the neutral situation where the atom i is singly occupied in orbital p_i; $2\lambda^2\mu^2$ to the unique ionic situation where the atom i is doubly occupied in $s_i p_i$ which is triplet.

In the antiferromagnetic UHF solution the product $\varphi_{i-1}\bar{\varphi}_i$ gives the following weights: $\lambda^2(\lambda^2+\mu^2)$ to the neutral situations where the atom i is singly occupied in orbital s_i or $\bar{s}_i$; $\mu^2(\lambda^2+\mu^2)$ to the neutral situations where the atom i is singly occupied in orbital p_i or $\bar{p}_i$; λ^4 to the ionic situation where the s_i orbital is doubly occupied; μ^4 to the ionic situation where the p_i orbital is doubly occupied; $\lambda^2\mu^2$ to the ionic situation $|s_i\bar{p}_i|-|p_i\bar{s}_i|$ which is triplet.

Therefore, the delocalization essentially takes place within the bond, without introducing too large ionic components, thus achieving part of the work of the internal correlation in the RHF-based approach. This description also introduces significant weights on $s^2 \rightarrow p^2$ atomic situations, responsible for an external or dynamical correlation effect.

B. A novel valence space

The above discussion suggests the definition of a new valence space and a new half-filled band problem. This valence space is spanned by the bond MO's. An orthogonal basis set of it is provided by the ferromagnetic interstitial UHF MO's. As a first step one will consider the internal correlation within this new valence space. This will be approximately performed in the next section using an effective Heisenberg Hamiltonian. Of course, the second step would be the treatment of the external correlation brought by the excitations from the new valence to the new nonvalence MO's. Actually, on each bond, besides the *s*-type nodeless bonding MO's, one can define *p*-type antibonding MO's with a nodal plane at the center of the bond, etc. Note that this new definition of the valence space leads to new definitions of the nondynamical and dynamical correlation energies.

C. Proposal for a magnetic treatment of the internal correlation

We shall assume that, as occurred in finite clusters, the space defined by the orbitals of the ferromagnetic and the antiferromagnetic solutions are the same. The antiferromagnetic UHF MO's are free from orthogonality constraints between adjacent MO's. They take delocalization tails on the adjacent bonds, which are responsible for the energy lowering. If one starts from the ferromagnetic interstitial localized MO's $\{\varphi_i\}$ the UHF antiferromagnetic solution may be written at the first order of perturbation

$$\psi_{\mathrm{AF}} = |\cdots \bar{\varphi}_{i-1}\varphi_i\bar{\varphi}_{i+1}\varphi_{i+2}| + \lambda_i \sum |\cdots \bar{\varphi}_{i-1}\varphi_{i+1}\bar{\varphi}_{i+1}\varphi_{i+2}|$$

(mixing with locally ionic determinants) with

$$\lambda_i = \frac{\langle \varphi_i|F|\varphi_{i+1}\rangle}{\Delta E_{NI}} ,$$

where ΔE_{NI} is the energy difference between neutral and ionic situations. The energy gain per site is (due to the leftward and rightward charge transfers)

$$2\frac{\langle \varphi_i|F|\varphi_{i+1}\rangle^2}{\Delta E_{NI}} = g ,$$

which is the traditional amplitude of the effective exchange integral in Heisenberg Hamiltonians according to Anderson's treatment.

We therefore suggest treating the correlation energy within the new valence shell through the definition of a Heisenberg Hamiltonian implicitly defined on the ferromagnetic orthogonal MO's,

$$H = \sum_{i<j} g_{ij}(r_{ij})(a_{i\uparrow}^{\dagger}a_{j\downarrow}^{\dagger} - a_{i\downarrow}^{\dagger}a_{j\uparrow}^{\dagger})(a_{i\uparrow}a_{j\downarrow} - a_{i\downarrow}a_{j\uparrow}) + R(r_1, \ldots, r_i) ,$$

where $a_{i,\sigma}^{\dagger}$ and $a_{i,\sigma}$ are the usual creation and annihilation operators on site i and spin σ, g_{ij} is the effective exchange between sites i and j, R is the energy of the ferromagnetic determinant. The Heisenberg Hamiltonian is acting on the space spanned by all determinants built from all possible spin attributions on a given space part.

In view of the preceding discussion the amplitude of the effective exchange will be defined as

$$g = E_{\mathrm{coh}}(\text{antiferro}) - E_{\mathrm{coh}}(\text{ferro}) .$$

The use of a magnetic Hamiltonian and the above evaluation of the effective exchange is only valid if the interbond delocalization is small, a hypothesis supported by both our previous studies of clusters and the similarity of the densities for the ferromagnetic and antiferromagnetic UHF solutions. Once the intrabond delocalization, which is large, has been incorporated in the definition of the new valence local MO's, the remaining delocalization between bonds is small.

The solution of the Heisenberg Hamiltonian is hoped to give a good approximation of a full valence configuration interaction in the new acceptance of the valence space.

D. Results of the magnetic treatments

The unit cell, in the CRYSTAL self-consistent-field (SCF) calculations, is taken as two bonded atoms, i.e., double than the smallest unit cell defined by the topology only. All energies are given per unit cell if not explicitly specified. The energy zero is taken as twice the energy of the atom in the considered basis set.

The Heisenberg Hamiltonian is completely defined and Bethe and Hulthen[9] showed analytically in the 1930s that for a linear chain the ground-state energy is $R - 2g\,\mathrm{Ln}2$.

The Heisenberg ground state, whose energy has been calculated according to the procedure exposed in the preceding section, is bound by 0.495 eV in the basis set A and 0.47 eV in the basis set B. The equilibrium distances are, respectively, 6.02 and 5.82 a.u. In basis set B the equilibrium distance of Li_2 is 5.30 a.u. while the exact binding energy in the basis is 0.865 eV. The Heisenberg ground state (as well as the antiferromagnetic interstitial UHF solution) is also bound with respect to the dimer. Since the experimental equilibrium distances of the crystal are, respectively, 5.85 a.u. for the fcc phase, 5.88 a.u. for the hcp phase, and 5.71 a.u. for the bcc phase, one should expect the one-dimensional infinite system equilibrium distance to be shorter. However, lack of flexibility in the present basis sets results in an increase of the equilibrium distances; the experimental equilibrium distance of Li_2 is 5.05 a.u. to be compared to the 5.30 a.u. found in the B basis set.

E. Possible role of the dynamical correlation and comparison with density-functional calculations

The analysis of the VB bond probabilities performed in Sec. III A shows that in the interstitial model, the most probable situations of the atom are neutral (therefore only weakly correlated with the electrons on neighbor atoms). Among the ionic instantaneous situations, the local triplets are weakly correlated, therefore the dynamical correlation contribution will essentially go through the ionic singlet situations which have a relatively small weight in the wave function. In other words, in the interstitial picture, the adjacent electrons do not come close to each other. It is then reasonable to expect that the dynamical correlation (in our new valence definition) is small.

We thought it useful to compare our results with density-functional evaluations of the correlation energy. These procedures do not make the distinction between internal and dynamical parts of the correlation energy.

The correlation energy has been evaluated by using correlation-only density-functional formulas, integrating *a posteriori* (that is, after the self-consistent Hartree-Fock cycle has been performed) the Hartree-Fock charge density. Three "nonlocal" functions (that is, functionals containing terms depending not only on the charge density but also on the gradient of the charge density) have been applied[11–13] to the RHF, ferromagnetic, and antiferromagnetic charge densities. The potential-energy curves are reported in Fig. 4 for basis set *B*. Tables I(a) and I(b) give the different equilibrium distances and binding energy for the different density-functional approximations [Table I(a) refers to basis set *A*, and Table I(b) to basis set *B*].

The various density-functional results (after substraction of the atomic correction in Perdew's formulation) are consistent, i.e., they are stable under changes of the functional and/or of the basis set. Finally the results obtained from the AF UHF solution are in good agreement with our Heisenberg values. An important point is the difference between the density-functional (DF) results from the RHF and $\langle S_z \rangle = 0$ UHF densities. The DF cohesive energies obtained from the RHF density seems unreasonable [it is much smaller than $D_e(\mathrm{Li}_2)/2$], which supports the idea that the RHF density is poor and misses a crucial effect. Both the consistence between the AF bond-centered DF results and those of the Heisenberg picture and the likeliness of the resulting cohesive energy plead in favor of the interstitial picture as physically meaningful.

TABLE I. Cohesive energy E_{coh} and interatomic distance (R_e) for a 1*D* chain of Li atoms. (a) All electrons minimal basis set. (b) Valence electrons (2*s*,*lp*) basis set.

Description	R_e (bohr)	E_{coh} (eV)
	(a)	
RHF	5.84	−0.08
+DF *a*	5.72	0.23
b	5.74	0.29
Interstitial ferromagnetic	6.51	0.32
+DF *a*	6.37	0.28
b	6.45	0.37
Antiferromagnetic	6.17	0.44
+DF *a*	5.89	0.50
b	5.97	0.59
Heisenberg solution	6.02	0.495
	(b)	
RHF	5.90	−0.11
+DF *a*	5.82	0.24
b	5.78	0.29
c	5.77	0.24
Interstitial ferromagnetic	6.18	0.25
+DF *a*	6.15	0.28
b	6.18	0.31
c	6.16	0.31
Antiferromagnetic	5.94	0.46
+DF *a*	5.86	0.53
b	5.86	0.58
c	5.85	0.54
Heisenberg solution	5.82	0.47

[a] Using the density functional defined in Ref. 11.

[b] Using the density functional defined in Ref. 12.

[c] Using the density functional defined in Ref. 13.

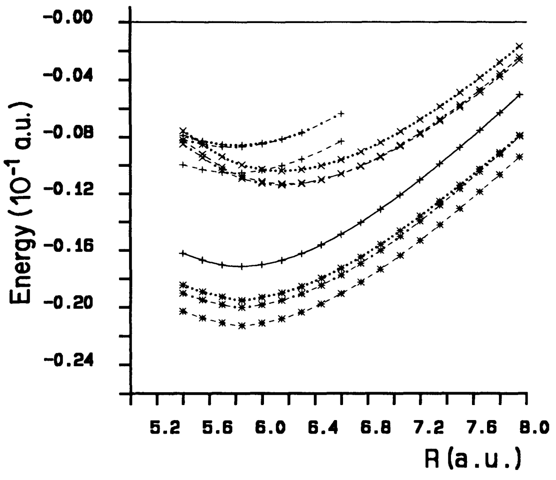

FIG. 4. Potential-energy curves using (basis set *B*). Density-functional corrections: ∗, from UHF spin-density-wave antiferromagnetic zeroth order; ×, from UHF ferromagnetic zeroth order; +, from RHF zeroth order; — — —, Perdew (Ref. 12); · · · ·, Colle and Salvetti (Ref. 11); —·—·—·, Perdew (Ref. 13); ——, Heisenberg Hamiltonian.

Let us note that the experimental bcc crystal cohesive energy is 1.63 eV. One can then expect the cohesive energy of the infinite chain to be significantly lower. The cohesive energies calculated from the interstitial solutions, either through the Heisenberg picture or density-functional corrections, are close to 0.5 eV which seems a reasonable order of magnitude, as discussed below.

IV. CONCLUSION

This paper confirms the relevance and applicability of the interstitial correlated picture for the valence electrons of alkali metals. That picture came from a particular *ab initio* description of small alkali-metal clusters which incorporates the nondynamical part of the electronic correlation. The method, however, could not be used for infinite systems and the picture could not be confirmed by *ab initio* calculations. The existence of dramatic Hartree-Fock instabilities for such materials has made possible the design of a strategy for an *ab initio* correlated picture of the bulk of simple metals. That strategy does not introduce any questionable (exchange) correlation potential and remains strictly *ab initio*. It exploits the multiplicity of symmetry-broken HF solutions corresponding to various spin distributions to define a Heisenberg Hamiltonian, which treats the residual electronic delocalization *between* the interstices, the main part being already incorporated in the interstitial orbitals. The present work confirms on a simple example the feasability of that strategy, through the existence of strong symmetry breakings of the HF solutions, demonstrated by the use on the new unrestricted version of the *ab initio* HF program CRYSTAL.

The importance of electronic correlation in such materials is confirmed by the weakness (or negative value) of the RHF cohesive energy. A very surprising result is the cohesive energy for the ferromagnetic solution. Notice that this solution is symmetry adapted and it confirms the preference for an interstitial definition of the singly occupied MO's. The singly occupied MO's of the antiferromagnetic solution are nearly identical to the preceding ones. Although of symmetry-broken character, that solution (or its spin-exchanged counterpart) gives a lower bound to the cohesive energy.

The use of a Heisenberg Hamiltonian for the next step seems relevant and the resulting cohesive energy seems reasonable. The only missing contribution is the part of the dynamical correlation effect of the electrons of two adjacent interstices. When they occupy two distinct atoms, this should be a dispersion-type contribution, which may be estimated from the triplet state potential curves of Li_2 to be about 0.1 eV. When the two electrons meet on the same atom either in an $s\bar{s}$ situation [probability$\simeq(0.62)^2$] or in a $p\bar{p}$ situation [probability$\simeq(0.42)^2$] the effect of the Coulomb cusp should be rather important [it should be much smaller in the triplet ($s\bar{p}-p\bar{s}$) situations which are governed by the Fermi hole]. Remember that the correlation in the $s\bar{s}$ ground state of Li^- is 0.43 eV. One may thus reasonably estimate the missing part of the cohesive energy brought by the dynamical correlation to about 0.15 to 0.20 eV. This would bring the final cohesive energy near 0.60 to 0.65 eV. This value is slightly larger than that of Li_2 (0.52 eV) and significantly smaller than that of the bulk. For the ferromagnetic state the contribution of correlation energy should be smaller than 0.1 eV. These evaluations fall very close to the results of the density-functional results starting from the intersticial UHF densities.

Let us notice that the here-reported DF calculations are *a posteriori* first-order corrections, and therefore upper bounds to the variational calculations with these potentials. It would be interesting to know whether the inclusions of the (exchange) correlation potential in the Fock operator would cancel the symmetry breakings. This problem has never received the attention that it deserves, even in molecular physics where it would be easily studied.

Finally this work shows the occurrence of some kind of "phase transition" under the explosion of the cluster or metal, i.e., under a homothetic increase of the interatomic distances, since the wave function moves suddenly from an interstice-supported localization of the electrons to an atom-supported density. The extension to 2D lattices is underway.

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