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Resonating Valence Bond calculations on small anionic lithium clusters

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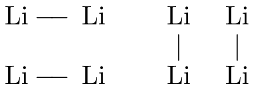
Abstract. We recast the Resonating Valence Bond theory, first introduced by Linus Pauling, in a nonorthogonal *ab initio* Valence Bond formalism and apply the method to study some properties of the anionic clusters Li_n^- $(2 \le n \le 5)$. We show how to choose appropriate structures and orbitals, and also how to use the so-called metallic orbitals. The problem of interpreting the role of a specific Valence Bond structure looking up its weight in the general wave function is elucidated. Information about the excited states of the systems is obtained. The theory can make good qualitative predictions on the electronic behaviour of the clusters by using a wave function that is a linear combination of a small set of structures. Pauling's theory is shown to be quite appropriate for describing anionic systems, specially the small ones, where the loosely bounded electron largely influences the properties of the systems. We verify the preference of some clusters for linear geometries.

PACS. 31.15.Qg Molecular dynamics and other numerical methods – 31.15.Rh Valence bond calculations – 71.24.+q Electronic structure of clusters and nanoparticles

1 Introduction

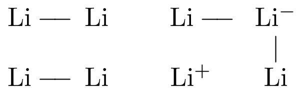
To describe chemical bonds related to interatomic forces in metals only the band theory (by forming Bloch functions of the atomic orbitals) has been successful, not only because of the known computational difficulty of making Valence Bond (VB) calculations, but also because there has been a long-standing belief that localized covalent bonds cannot be present in metals. In spite of this, an alternative VB theory for metals has been known since 1938 due to Linus Pauling [1], based on empirical arguments, though.

Pauling introduced the concept of *metallic orbital*, necessary for describing the main properties of metals: conductivity and mobility. Besides the ordinary covalent (shared electron pair) bond, there are also those bonds connected to the metallic orbital. Let us give an example [2], that is important for the understanding of the role of the metallic orbital. Consider a lithium crystal. There are two ways in which the bonds can be arranged to form Li_2 molecules,



$$\begin{array}{ccc} \mathrm{Li} - \mathrm{Li} & \mathrm{Li} & \mathrm{Li} \\ & | & | \\ \mathrm{Li} - \mathrm{Li} & \mathrm{Li} & \mathrm{Li} \end{array}$$

These structures are resonant and the energy of this synchronized resonance contributes to the stabilization of the crystal. The stabilization becomes greater if there is also unsynchronized resonance such as



$$\begin{array}{ccc} \mathrm{Li} - \mathrm{Li} & \mathrm{Li} - & \mathrm{Li}^- \\ & & | \\ \mathrm{Li} - \mathrm{Li} & \mathrm{Li}^+ & \mathrm{Li} \end{array}$$

in which one bond resonates independently from one position to another.

This new sort of resonance requires that the atom receiving an extra electron (forming Li^-) has an orbital available for its reception, the so-called *metallic orbital*. The structures related to this unusual ressonance we call *Pauling structures*. It is the unsynchronized resonance of covalent bonds through a metal that provides a simple explanation of its characteristic electric conductivity. The valence bonds resonate from one position to another at electronic frequencies, as determined by the resonance energy. In the presence of an applied electric field the electrons tend to move from atom to atom, by shifting single bonds exactly as indicated in the unsynchronized resonance diagram above.

According to Pauling [3], the RVB theory of metals gives energy bands similar to those obtained in the usual band theory. There is no incompatibility between the two descriptions, which may be considered as complementary. Formally, the name *Resonating Valence Bond* is applied to any VB theory based on a linear combination of resonating structures, no matter whether we use Pauling structures or not. We use this terminology so as to make reference to the former Pauling's RVB theory of metals.

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Only nowadays Pauling's Resonating Valence Bond (RVB) theory could be tested at the *ab initio* level, as done by our group. The metallic behavior of some small alkali metals, such as Li, attracted our attention, as they have a single valence electron per atom. Mohallem *et al.* [4] reported a work in which the Pauling structures, in addition to the usual structures, were used to explain the "metallic behavior" of the Li_4 and Li_6 clusters and some other properties. Vianna *et al.* [5] verified the metal-insulator transition present in the approximation of two H_2 molecules at a RVB level. They showed that the metallic orbital furnishes a correct description of this phenomenon.

In the present work we are interested in studying some small anionic lithium clusters. We know little of this sort of clusters, due to the presence of an extra electron. Traditional VB structures based on covalent and ionic bonds are not enough for describing their electronic state. So, *metallic bonds* must be considered and, therefore, metallic orbitals will become essential for describing correctly their properties.

The most extensive study of these systems was made by Boustani *et al.* [6], where they studied some characteristics of Li_n^- clusters ($2 \le n \le 9$), such as geometric structures and stability, using a relatively small basis set and the multireference diexcited configuration interaction method (MRD-CI). They found that the geometries of the Li_n^- ($n \le 5$) species differ appreciably from those of neutral as well as of cationic Li clusters. In the anionic case they reported a preference for linear conformations explained mainly by the decrease in the electrostatic repulsion for such geometries. From the Li_5^- cluster on, more compact structures are preferred, although there is also a stable linear Li_5^- according to Boustani *et al.*

Our aim is to study the lowest energy states of these clusters ($n < 6$) in their most stable geometries, by using *ab initio* Pauling's RVB method. We will compare our results with Molecular Orbital (MO) calculations and with the literature. In Section 2 we treat the specific methodology used in all calculations. The study of the features of the most interesting anionic lithium clusters is given in Section 3. We then summarize our results and their implications in Section 4.

2 Methodology

Our RVB method is described in details elsewhere [7], but the main ideas are given as follows. The RVB wave function is written as a linear combination of structures that will represent all possible chemical bonds. These structures are similar to the known Lewis structures, that give an intuitive description of the chemical bonding of the system. Choosing the appropriate structures is the first step to carry out the calculations.

Consider a set of f_S^N (Wigner number [8]) spin eigenfunctions $\{\Theta_k\}$ that spans an irreducible representation (irrep) Γ_α of given symmetry of the group of $N!$ permutations, S_N. This set can be obtained from a Rumer diagram, see for instance [8]. Each Θ_k represents one possible pairing of spins. Then, consider an orbital configuration $\Omega = K_1 K_2 \ldots K_N$ that is a product of nonorthogonal atomic orbitals K_i.

Associating a spin eigenfunction Θ_K to the orbital product Ω and antisymmetrizing under the interchange of any pair of electrons, we have a structure

$$\Phi_k = A\Omega\Theta_k$$

where A is the antisymmetrizer operator.

From the f_S^N independent structures $\{\Phi_k\}$, we select only those that match the spatial symmetry of the system. Therefore, different sets of orbitals should be necessary to set a wave function that is invariant under all the spatial symmetry operations of the system. It is necessary to check whether there is any kind of linear dependence among structures of the different sets of orbitals. Sometimes, examining the dissociation tendencies of the system is helpful to choose an appropriate set of structures. The wave function is then a linear combination of these carefully chosen structures,

$$\Psi = \sum\nolimits_i C_i \Phi_i, \qquad \langle \Psi | \Psi \rangle = 1\,.$$

The most important structures are those with considerable weights. This property has to do with the coefficients (C_i) of each structure (Φ_i) in the RVB wave function (Ψ). The structure weight (W_i) is defined as

$$W_i = \sum\nolimits_j C_i S_{ij} C_j\,,$$

where C_i is the coefficient of structure Φ_i and S_{ij} is the overlap between structures Φ_i and Φ_j. According to the multi-structure wave function defined above,

$$\langle \Psi | \Psi \rangle = \sum\nolimits_{ij} C_i C_j \langle \Phi_i | \Phi_j \rangle = \sum\nolimits_{ij} C_i C_j S_{ij} = \sum\nolimits_i W_i = 1$$

For comparison purposes, we renormalize the structure weights so that the weightiest structure has weight 1.

The matrix elements to be evaluated are

$$H_{kl} = \langle \Phi_k | H | \Phi_l \rangle\,, \qquad S_{kl} = \langle \Phi_k | \Phi_l \rangle\,,$$

where H is the electronic Hamiltonian in the Born-Oppenheimer approximation, as usual. The structure coefficients C_k are obtained solving the usual secular equation:

$$\mathbf{HC} = \mathbf{ESC}\,.$$

MO-SCF, MO-SCF with MBPT2 correction and CISD with quadratic convergence (QCISD) methods [9] were also carried out with the same basis set for comparison purposes. The results of literature [6] were recalculated and some discrepancies were detected.

3 RVB study of some anionic lithium clusters

A. Calculation details

RVB calculations were applied to some states of Li_n^- clusters ($2 \le n \le 5$). We are interested in the set of small

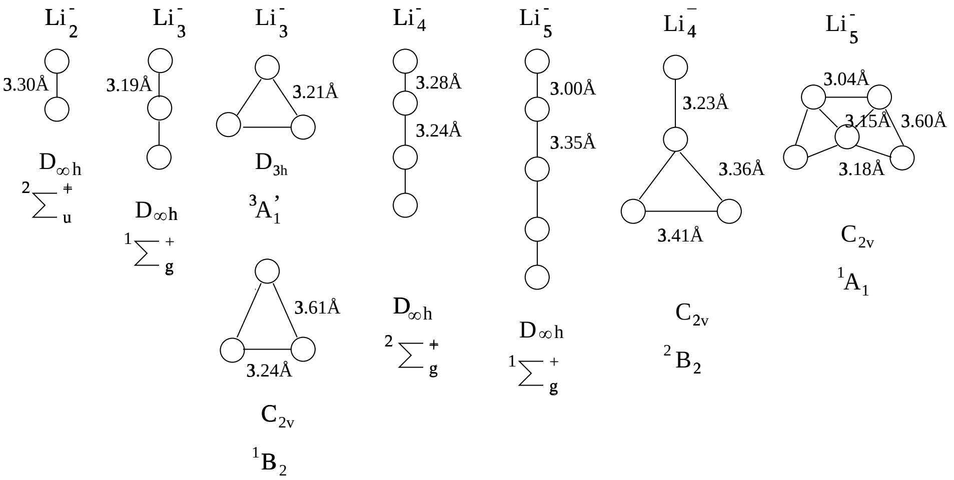

Fig. 1. Geometry, point group and electronic state of the anionic lithium clusters.

anionic lithium clusters shown in Figure 1, where their geometry, point group and electronic state are also given.

We associate to each atom a $(10s2p)$ atomic centred Gaussian basis set contracted to $[4s2p]$ (Tab. 1). Each orbital is expanded in the basis functions of all centres and optimized variationally. We treat only the valence electrons and keep the inner shell electrons (Li$1s$) in a core obtained by Hartree Fock (HF) calculations. To optimize the orbitals, we implemented a version of the Davidon-Fletcher-Powell variable metric method [10], mixed with Pulay's Direct Inversion of Iterative Subspace (DIIS) procedure for accelerating convergence [11]. The required gradient vector is obtained through the generalized Brillouim theorem [12]. The algorithm is similar to that adopted in reference [13]. The orbitals are allowed to delocalize during the optimization, which leads to vanishing coefficients for conventional ionic structures, that is, VB structures with doubly occupied orbitals. The unconventional ionic structures used in this work allow two valence electrons in the same Li atom, but occupying different orbitals. Sometimes, it is necessary to choose different optimized orbitals for covalent and ionic structures in order to improve the accuracy and energy of the calculations.

The geometries of the Li_n^- clusters were determined by analytical gradient minimization procedure at HF level [9]. As usual, such geometries were also used in the RVB calculations. Theoretical vibrational analysis has been performed at the HF level to check whether the stationary point on the BO surface is a local minimum.

B. How to choose the structures

The RVB structures are the principal tool of the method. As we have already stated, they represent the possible chemical bonds present in the systems. For instance, consider the neutral Li_3 cluster that has 3 valence electrons. Its ground state is $^2B_2$ C_{2v}. There is also an excited species of symmetry $D_{\infty h}$, which is considered now.

Table 1. The $[4s, 2p]$ basis set.

Exponents	Contraction coefficients
S type	
921.30	0.001367
138.70	0.010425
31.940	0.049859
9.3530	0.160701
3.1580	0.344604
1.1570	0.425197
0.4446	0.169468
S type	
0.0200	1.000000
S type	
0.0472	1.000000
S type	
1.0514	1.000000
P type	
0.1135	1.000000
P type	
0.0700	1.000000

Its more important RVB structures are

$$\mathrm{o}-\mathrm{o}\quad \mathrm{o}\cdot \quad (E_1)\,,$$

$$\cdot\mathrm{o}\quad \mathrm{o}-\mathrm{o}\quad (E_2)\,,$$

where a line represents a pairing of electrons (a covalent bond) and a lonely point represents an unpaired electron. Even if we use more RVB structures, only one orbital on each atom will be necessary to best represent a structure. Of course, we use a linear combination of each symmetric pair, like $C_1(E_1 + E_2)$, for keeping the global symmetry of the system.

The treatment of the anionic Li_3^- cluster is quite different. There are four valence electrons and its ground state

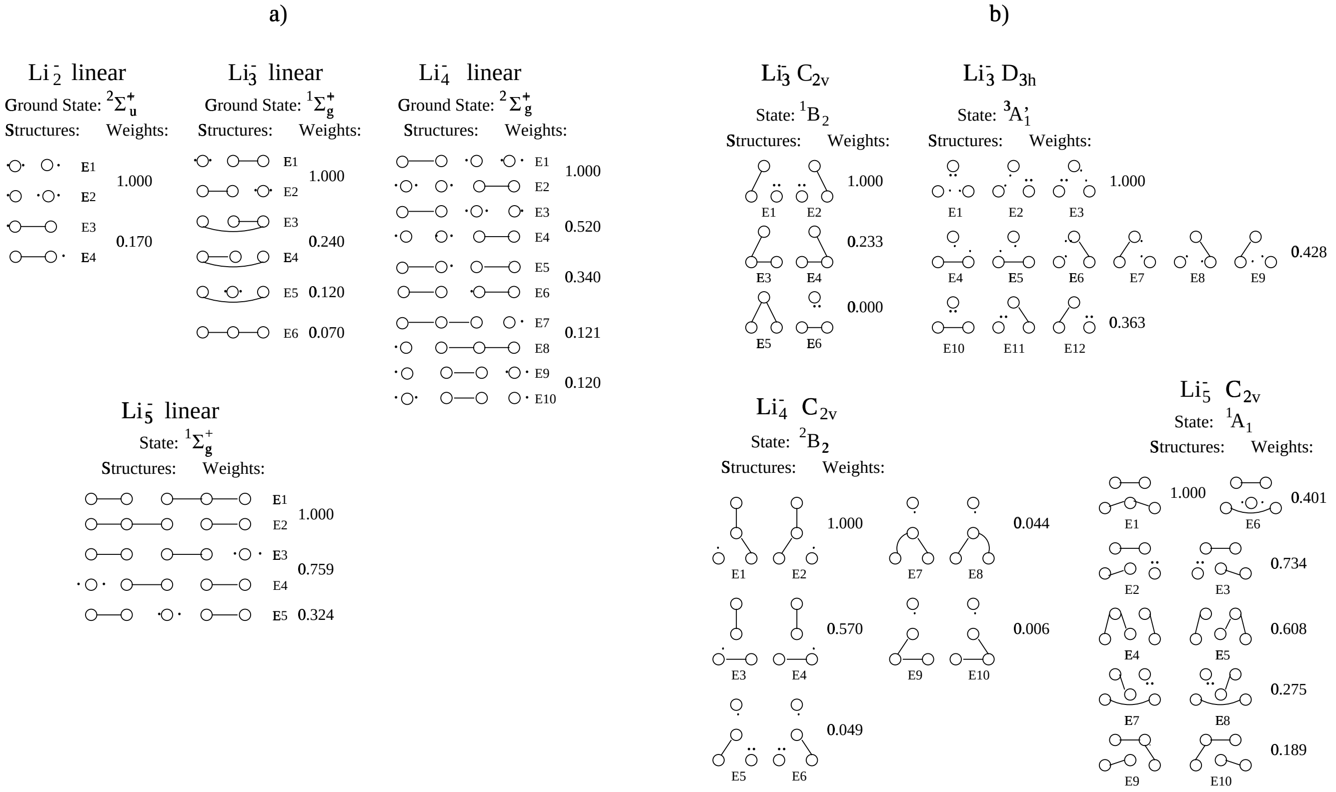

Fig. 2. (a) The RVB structures of linear anionic lithium clusters. (b) The RVB structures of some plane anionic lithium clusters.

is $^1\Sigma_g{}^+ \ D_{\infty h}$. The main RVB structures are

$$\mathrm{o}-\mathrm{o} \quad \cdot\mathrm{o}\cdot \quad (E_1)\,,$$

$$\cdot\mathrm{o}\cdot \quad \mathrm{o}-\mathrm{o} \quad (E_2)\,,$$

$$\mathrm{o}-\mathrm{o}-\mathrm{o} \quad (E_3)\,.$$

The structures corresponding to the symmetric pair E_1 and E_2 (ionic structures) are the most representative ones. Two points around the same centre represent two electrons at the same atom, with paired spins, but occuping different orbitals. In the case of structure E_3, a typical *Pauling structure* [4], it is fundamental to use two orbitals on the same atom (the central atom). Otherwise, representing the Li_3^- cluster without the Pauling structure would be an incomplete representation. There are no structures like that in the neutral case. This situation occurs in all anionic clusters considered here and, as long as their size increases, the role of the Pauling structures becomes stronger, as we will discuss soon. In accordance with Pauling [1], one of the two orbitals is named "metallic orbital", but it does not need to be different from the other one. In the Li_3^- case the two central orbitals are symmetric and points towards the periferic atoms.

The RVB structures chosen to perform the calculations and their respective weights are shown in Figures 2(a) and 2(b). In almost all cases two orbitals centred on each atom to best represent the bonding of the systems are necessary. Exceptions are the case of the plane Li_4^- which will be clarified soon and the plane Li_5^- that is a difficult one. In this latter case, we must use three orbitals centred on the central atom to represent a RVB structure, because there are at least three different bonds: one pointing towards the top pair of atoms and the other two bonds associated with the atoms of the base of the cluster. This choice of orbitals accelerates convergence and improves the accuracy of the calculated energies. The metallic character of this sort of cluster increases with the number of atoms, which makes necessary the use of an increasing number of VB orbitals centred on the same atom. Therefore the number of resonating VB structures also increases as shown in Figure 2(b) for the plane Li_5^- cluster. Note that all structures have considerable weights in this case.

C. Characterizing the state of the system

Adapting the whole set of structures by symmetry, we will be sure about the electronic state of the system, looking at the structure coefficients. In the Li_2^- case, for instance, combinations of structures (shown in Fig. 2(a)) like $(E_1 - E_2)$ and $(E_3 - E_4)$ furnishes the energy of its ground state $^2\Sigma_u{}^+$. On the other hand, combinations of structures like $(E_1 + E_2)$ and $(E_3 + E_4)$ will lead us to the excited state $^2\Sigma_g{}^+$. In the case of other linear clusters the sum of completely symmetric pairs of structures furnishes information about the ground state. For instance, this is the case of combination of structures like (E_1+E_2), $(E_3 + E_4)$ and so on, of the linear Li_4^-. For the linear Li_5^- cluster, if the structures $(E_1 + E_2)$, $(E_3 + E_4)$ and E_5 are used to set the RVB wave function, the state of the cluster will be the state $^1\Sigma_g{}^+$.

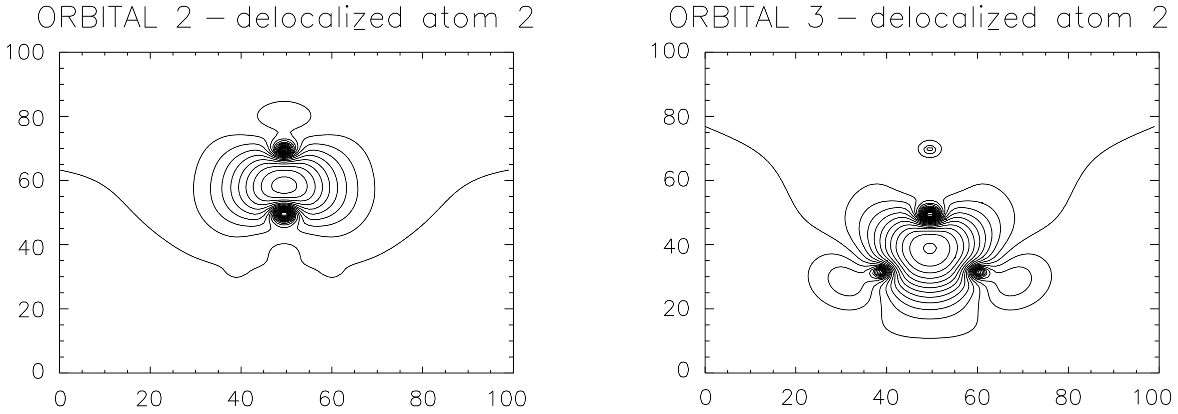

Fig. 3. The orbitals 2 and 3 of the C_{2v} Li_4^- cluster, both centred on the central atom of the cluster.

Table 2. Ground and excited states of SCF optimized anionic lithium clusters.

Cluster	Simmetry	State	$E^{\mathrm{HF(a)}}_{(4s,2p)}$	$E^{\mathrm{VB(b)}}_{(4s,2p)}$	$E^{\mathrm{HF+corr(c)}}_{(3s,1p)}$	$E^{\mathrm{CISD(d)}}_{(4s,2p)}$
Li_2^-	$D_{\infty h}$	$^2\Sigma_u{}^+$	−14.88018	−14.88791	−14.79592	−14.90652
Li_3^-	$D_{\infty h}$	$^1\Sigma_g{}^+$	−22.31938	−22.35205	−22.22021	−22.37836
	D_{3h}	$^3A'_1$	−22.32759	−22.33109		−22.36139
	C_{2v}	$^1B_2$	−22.32034	−22.32664		−22.35508
Li_4^-	$D_{\infty h}$	$^2\Sigma_g{}^+$	−29.78694	−29.80279	−29.63000	−29.83340
	C_{2v}	$^2B_2$	−29.77854	−29.79509	−29.57176$^{\mathrm{(e)}}$	−29.82730
Li_5^-	$D_{\infty h}$	$^1\Sigma_g{}^+$	−37.20089	−37.25616	−37.04217	−37.28067
	C_{2v}	$^1A_1$	−37.20554	−37.25654	−37.04342	−37.29677

(a) Hartree-Fock energy of the SCF optimized cluster using the $[4s, 2p]$ basis set (a.u.).

(b) Valence Bond energy of the SCF optimized cluster using the $[4s, 2p]$ basis set (a.u.). All structures of Figures 2(a) and 2(b) are considered for each cluster.

(c) Hartree-Fock energy plus Davidson correlation energy calculated using the $[3s, 1p]$ basis set of [6] (a.u.). These results are given in the literature [6].

(d) CISD energy calculated with quadratic convergence using the $[4s, 2p]$ basis set (a.u.).

(e) There is an inconsistence in the literature [6]. The UHF energy calculated with the $[3s, 1p]$ basis set in [6] is −29.55251 a.u. Redoing the calculations, using the same basis set, we found −29.57176 a.u. The first result was disconsidered.

The plane Li_3^- will be important in the study of dissociation of the plane Li_4^- [14]. Its properties are in agreement with the other anionic trimers and with the literature [15]. There are two main plane species: a triplet of symmetry A'_1 (symmetry group D_{3h}) and a singlet of symmetry B_2 (symmetry group C_{2v}) and higher energy. The most stable state is $^3A'_1$ and the state $^1B_2$ is a transition state. In Figure 2(b) we can see that the completely symmetric structures E_1 and E_4 are not appropriate to describe this transition state, so they vanished.

The lowest energy state of the plane Li_4^- is $^2B_2$ and the difference between two structures of the same symmetric pair is the combination expected. Because of this, in case of plane Li_4^-, completely symmetric structures like E_3 or E_4, with the extra electron near the central atom, must vanish to represent the $^2B_2$ state. Note that for the structures E_7 and E_8 of plane Li_4^-, we use two different orbitals on the central atom, one of them pointing toward the top atom and the other one spreading inside the lower triangle (see Fig. 3), so that the combination $(E_7 - E_8)$ becomes necessary for setting the lowest energy wave function. Only one orbital on the first atom is enough for describing all set of structures of the plane Li_4^- shown in Figure 2(b). If we want an excited state of the plane Li_4^-, with symmetry A_1 for instance, we must use the completely symmetric structures like those mentioned above and the sum of the symmetric pairs.

In case of plane Li_5^-, the ground-state wave function is formed by the linear combination of the completely symmetric structures and the sum of the symmetric pairs of structures shown in Figure 2(b).

D. The influence of the extra electron on the shape of the small anionic lithium clusters

The existence of linear species as the most stable ones is, as a matter of fact, intriguing. The state $^1B_2$ of the Li_3^- C_{2v} is a transition state, according to Gutowski *et al.* [15]. Among the Li_4^- clusters, the $D_{\infty h}$ species is in fact energetically preferable (see Tab. 2). The ground state $^1A_1$ of the Li_5^- C_{2v} cluster is practically degenerate with the state $^1\Sigma_g{}^+$ of the Li_5^- $D_{\infty h}$ cluster. The latter is found to be, in fact, an unstable state, in disagreement with the

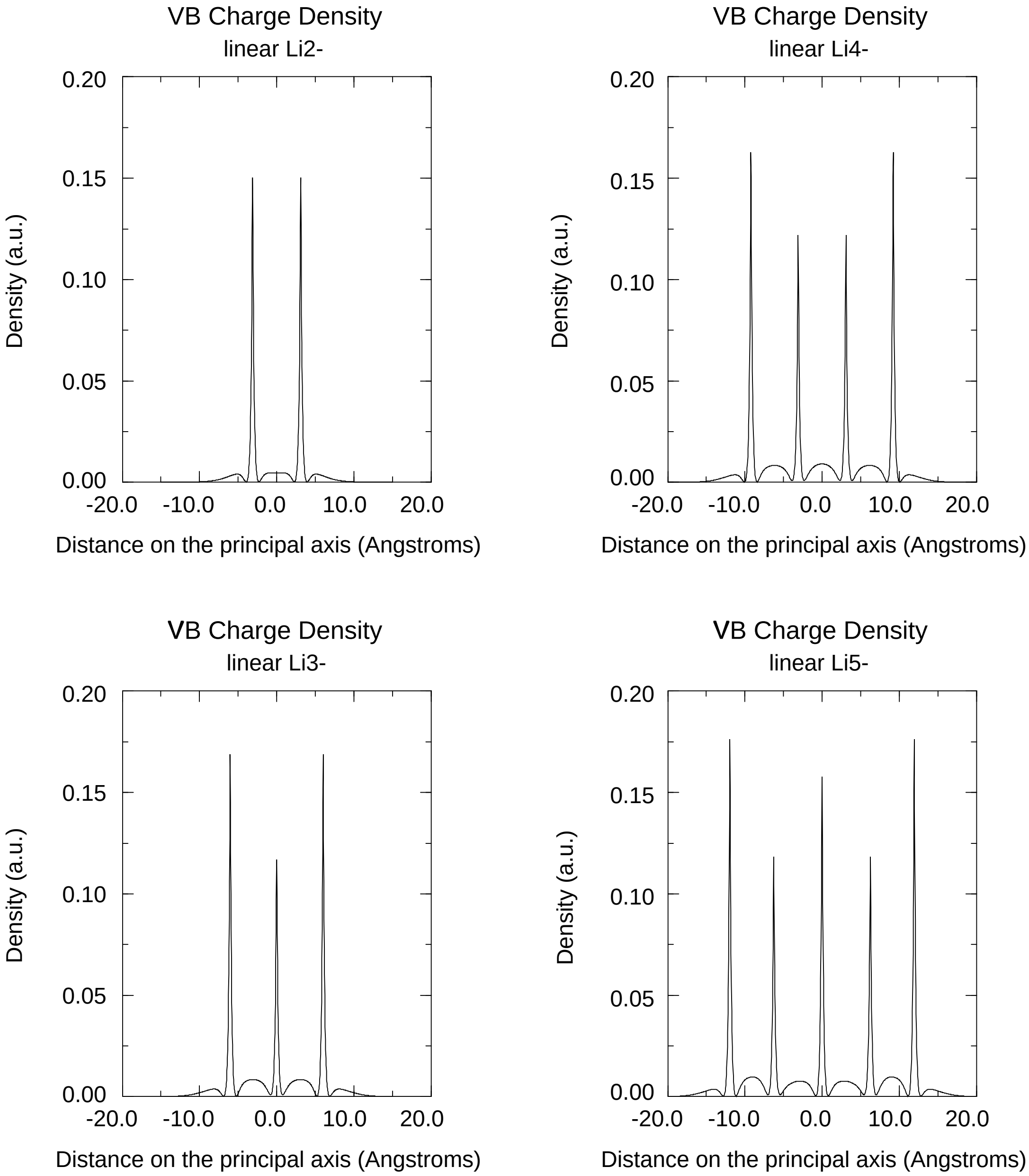

Fig. 4. RVB charge densities along the x-axis of the linear anionic lithium clusters calculated using all RVB structures.

literature [6]. In order to check this, we have made tests with various basis sets of different sizes, starting from the $[3s, 1p]$ of [6], up to the 6-311G(d). In all cases, we verify the presence of imaginary frequencies at SCF level. From the Li_6^- cluster on, it is known that they have similar shapes to their corresponding neutral systems. In this case there are no linear geometries.

One of the reasons for the preference of less compact structures (Li_n^-, $2 \le n \le 5$) can be seen from the RVB distribution of electronic charge in the linear Li_n^- ions. There are higher peaks of charge at the extreme regions of their principal axis, as seen in Figure 4. An upper view of the RVB charge density is also shown in Figure 5. The electrostatic repulsion is relatively weak for such geometries, making the linear clusters the most stable ones. In the Li_5^- case, a tendency of the charge density to turn out more compact is seen, because the central peak is almost similar to the extreme ones (Fig. 4). We could say that we are in a threshold situation: from the Li_5^- cluster on the lowest energy clusters are no more the linear ones; the Li_5^- $D_{\infty h}$ is in fact an unstable state.

The charge density for plane Li_3^-, Li_4^- and Li_5^- clusters are shown in Figure 6. (For all density maps (Fig. 6) the structures shown in Figure 2(b) were used.) Observe the presence in Figure 6 of three-body bonds [4], as they are named, common in plane clusters. They are characterized by peaks of charge inside their internal triangles. The C_{2v} Li_5^- charge density is more delocalized, which makes it

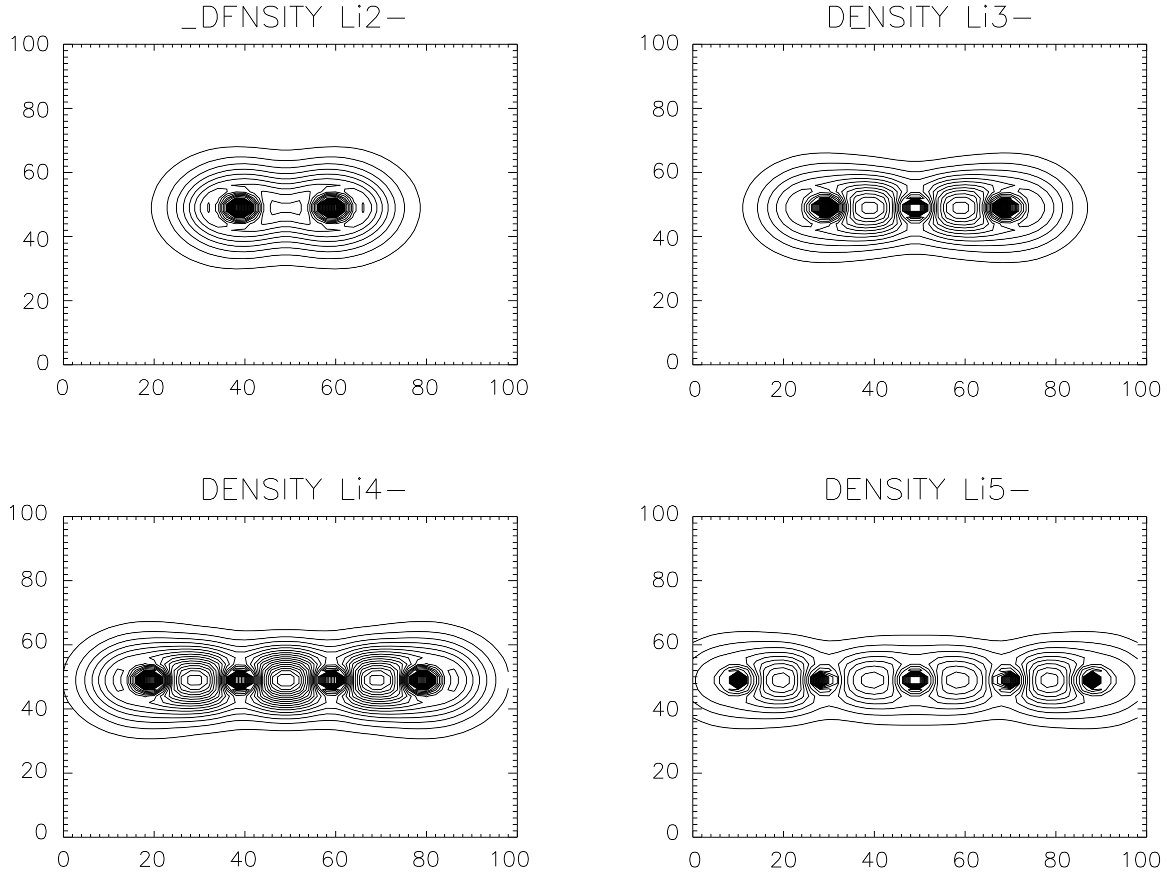

Fig. 5. Maps of density of all linear anionic lithium clusters.

necessary to use a larger number of structures, as it is seen in Figure 2(b), to best represent the considerable metallic character of the system. Observe that all structure weights of the C_{2v} Li_5^- cluster are relevant. There is no principal structure that by itself could represent the VB wave function as a whole, which happens for every cluster up to Li_5^-. This is a consequence of a localized wave function, as the density maps show in Figures 5 and 6. The results of the C_{2v} Li_5^- cluster suggest us how to treat larger plane clusters in a RVB approach.

E. The RVB energies

In Table 2, energy values of states of the Li_n^- clusters are given, for some different basis set and various levels of calculation. They explain why a larger $[4s, 2p]$ basis set is used in the present work, compared to the $[3s, 1p]$ basis set used in reference [6]: The differences of our results to those of reference [6] have the same magnitude as our MO correlation energies, $E_{\mathrm{QCISD}}-E_{\mathrm{HF}}$, for the larger basis set. The energy values obtained with the $[4s, 2p]$ basis set seem to be the best energies reported so far for those systems.

The RVB energy values are lower than the HF values, as expected, but they are higher than the QCISD values. Considering that we are using a very small set of RVB structures, this result is expected [13,16]. On the other hand, we believe that the use of a small well-chosen set of structures is appropriate for getting a correct description of the bonding of the system with a compact and intuitive wave function. The Li_5^- $D_{\infty h}$ case is very illustrative. Using 10 orbitals, we can built 1050 RVB structures. However, only 5 structures are enough for describing the properties of the system. Numerical results can be improved by enlarging the initial set of structures without any further orbital optimization (VB-CI). If we used all possible RVB structures, we would have a result equivalent to that obtained making a MO full-CI calculation. The great advantage of working with the RVB method appears when we are interested in qualitative aspects. Looking at the charge densities in Figure 4, for instance, we could say that the Li_5^- $D_{\infty h}$ cluster prefers to dissociate according to the channel $\mathrm{Li}_5^- \rightarrow \mathrm{Li}_2 + \mathrm{Li}_3^-$ because the bonds between the central atom and its first neighbors are weaker than the other ones. This behaviour is in accordance with the linear Li_5^- structures of Figure 2(a) and with the literature [6]. A study of the use of the RVB method for dissociation purposes is done elsewhere [14].

F. Stability of the anionic lithium clusters

Once calculated the RVB energies, it is interesting to investigate what the RVB wave function informs us about the stability of those anionic lithium clusters. A relevant quantity is the dependence of the binding energy per atom

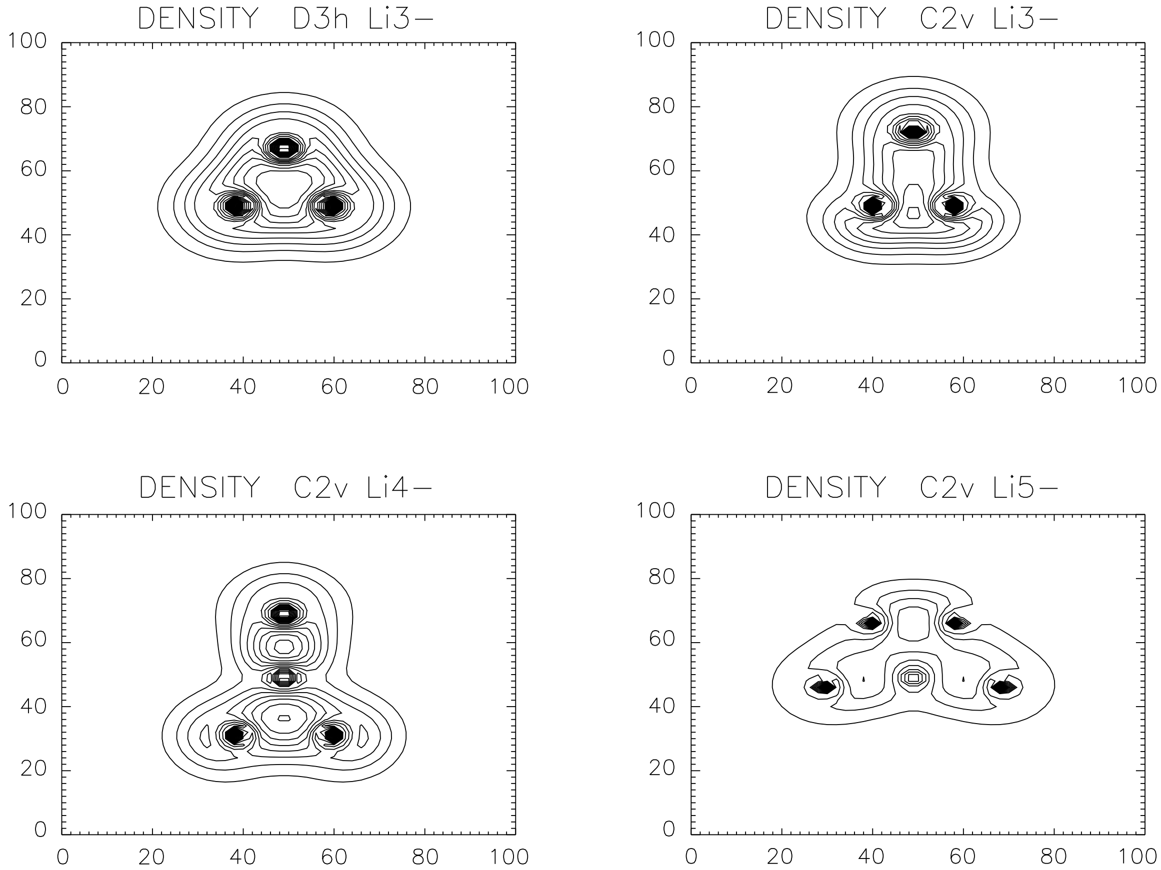

Fig. 6. RVB charge densities of $D_3h\mathrm{Li}_3^-$, C_{2v} Li_3^-, Li_4^- and Li_5^- clusters.

Table 3. Binding energy per atom as a function of the number of atoms of the anionic lithium clusters.

Cluster	Simmetry	State	$\frac{E_b^-}{n}$ RVB (a)	$\frac{E_b^-}{n}$ CISD (a)
Li_2^-	$D_{\infty h}$	${}^2\Sigma_u{}^+$	6.91	8.97
Li_3^-	$D_{\infty h}$	${}^1\Sigma_g{}^+$	11.49	14.48
Li_4^-	$D_{\infty h}$	${}^2\Sigma_g{}^+$	11.68	14.60
Li_5^-	C_{2v}	${}^1A_1$	12.17	15.71

(a) Values in kcal/mol.

with the number of atoms $\frac{E_b^-}{n}$. This function is defined as

$$\frac{E_b^-}{n} = \frac{[E_1^- + (n-1)E_1 - E_n^-]}{n},$$

where E_k^- is the energy of the anionic cluster with k atoms (Tab. 2). The E_1 value calculated with the $[4s, 2p]$ basis set (Tab. 1) is -7.43121 a.u. E_1^- is calculated as $E_1^-(\mathrm{RVB}) = -7.43469$ a.u. and $E_1^-(\mathrm{CISD}) = -7.44673$ a.u. The results of the calculations are reported in Table 3.

The RVB energy values of Table 3 show a trend that agrees with the CISD trend and with calculations found in the literature [6]. Large even-odd oscillations are not expected in the interval $(2 \le n \le 5)$. In fact maximum peaks are waited at $n = 3$ and $n = 7$, in agreement with the shell model of Knight [17], when the valence shell of anionic clusters is full occupied.

Another quantity that informs us about the stability of those small anionic clusters is the electron affinity of Li_n clusters. It is important to know wheather these clusters are able to receive an extra electron. The adiabatic electron affinity is given as the difference of energy between the optimal neutral clusters and the energy of Li_n^- in its optimal geometry. Energies of neutral Li_n clusters in their optimal geometries, calculated using the $[4s, 2p]$ basis set, are shown in Table 4, as well as the number of RVB structures used in the calculations.

The adiabatic electron affinities (EA) calculated are also shown in Table 4. We can see that in fact the Li_n clusters are allowed to receive an extra electron and form anionic stable anionic species. The result is also in agreement with Boustani *et al.* [6].

4 Concluding remarks

We can reach the following conclusions from this work:

1) The basis set $[4s, 2p]$ is fundamental for working with small anionic lithium clusters. Compared to the $[3s, 1p]$ from [6], we obtained a relevant decrease in the energy values at all levels.

2) Pauling's RVB theory is appropriate for a VB description of anionic metallic systems. It would be difficult

Table 4. Energy values of neutral lithium clusters calculated with the $[4s, 2p]$ basis set (Tab. 1). The values of their adiabatic electron affinities are also given.

Cluster	Simmetry	State	$E^{\mathrm{RVB}\,(a)}$	$N^{\mathrm{RVB}\,(b)}$	$E^{\mathrm{CISD}\,(c)}$	$EA^{\mathrm{RVB}\,(d)}$	$EA^{\mathrm{CISD}\,(d)}$
Li_2	$D_{\infty h}$	$^1\Sigma_g{}^+$	−14.87383	(3)	−14.89355	8.83	8.14
Li_3	C_{2v}	$^2B_2$	−22.31842	(4)	−22.33895	22.98	24.73
Li_4	D_{2h}	^1A_g	−29.78122	(10)	−29.81043	13.54	14.41
Li_5	C_{2v}	$^2A_1$	−37.23070	(13)	−37.26734	16.21	18.47

(a) Valence Bond energies of the SCF optimized cluster using the $[4s, 2p]$ basis set (a.u.).

(b) Number of structures used in the RVB calculations.

(c) CISD energies of the SCF optimized cluster calculated with quadratic convergence using the $[4s, 2p]$ basis set (a.u.).

(d) Valence Bond and CISD adiabatic electron affinities of Li_n clusters (kcal/mol).

to describe correctly the electronic properties of such anionic clusters using the traditional VB methodologies.

3) A small number of RVB structures is enough for getting qualitative predictions of the behaviour of the systems considered here. The structures must be chosen carefully, though. It is noted that the number of structures necessary for a complete description of the properties of the anionic lithium clusters increases with the size of the cluster.

4) In case of the anionic lithium clusters, linear species are the most stable ones ($n < 5$). The linear Li_5^- is in fact an exception, its state $^1\Sigma_g{}^+$ is an unstable state. This property has not been predicted before. Calculations on a HF level for the linear Li_5^- show imaginary frequencies with different basis sets. Only the planar Li_5^- species is stable. The RVB density along the principal axis of the linear Li_5^- cluster has almost similar peaks of charge on each atom, indicating a preference for more compact shapes. In fact from the Li_5^- species on, all anionic clusters are plane or three-dimensional.

5) The C_{2v} Li_5^- cluster is interesting because its relevant metallic character is shown as we examine its charge density in Figure 6. This is more diffuse than the charge density of other plane clusters treated in this work. We verify that a larger number of resonating structures, like those shown in Figure 2(b), are necessary to describe the C_{2v} species, and that they all have considerable weights. More than two orbitals may be necessary on a centre to represent the resonance among so different structures. On the other hand, in case of the linear clusters and even the C_{2v} Li_4^- one, it is noted that there is always one or two pairs of structures that by itself can represent the RVB wave function, that is more localized than the C_{2v} Li_5^- wave function. This latter cluster is the limit between the simple clusters and the most complex ones, giving us a hint of how to treat larger plane clusters in the RVB approach.

6) In general the RVB energy values are in agreement with those obtained with higher correlation methods in a qualitative sense. Quantitatively they are higher than the QCISD energies but considering that we are working with very small sets of structures, the result is expected.

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