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The Spin-Coupled Description of Lithium Clusters. II. Planar Arrangements of Rhombus Units

Elena Tornaghi[1], David L. Cooper[2], Joseph Gerratt[3], and Mario Raimondi[1]

[1]*Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano e*
Centro CNR per lo Studio delle Relazioni tra la Struttura e la Reattività
Chimica, Via Golgi 19, 20133 Milano, Italy
[2]*Department of Chemistry, University of Liverpool, P.O. Box 147,*
Liverpool L69 3BX, UK
[3]*Department of Theoretical Chemistry, University of Bristol, Cantocks Close,*
Bristol BS8 1TS, UK

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Spin-coupled theory is applied to the valence electrons of small planar lithium clusters constructed from rhombus units sharing vertices or edges. The study is motivated by the special importance of the rhombus unit in small lithium clusters and in fragments of the body-centred cubic (bcc) lattice cut according to the 110 plane.

The spin-coupled descriptions which emerge for idealized fragments of the bcc 110 plane are based on orbitals which are localized *between* different nuclei, and which may be termed *interstitial orbitals* or IOs. Many of the IOs are associated with external edges of the clusters and exhibit only minor variations from cluster to cluster or between different spin multiplicities. A key feature in determining the locations of the IOs for a given cluster appears to be the difference between the number of valence electrons and the number of external edges. Even for those systems which have orbitals located in the interior, all of the orbitals retain interstitial rather than atom-centred forms.

Certain characteristic features, which appear to be essentially independent of cluster size, may be important for the development of a spin-coupled theory of the electronic structure of metals.

INTRODUCTION

The overwhelming majority of contemporary studies of bulk metals, as well as much of the language employed to describe such systems, are firmly rooted in the framework of band theory. Valence bond studies are comparatively rare, in spite of the fact that the fundamental early work in this area, namely Pauling's model of metals[1], is very rich in appealing qualitative concepts.

In the original Pauling resonating-valence-bond theory of metals, the wavefunction was represented as an admixture of two kinds of terms: synchronized resonance between non-ionic structures, requiring two or more bonds to shift simultaneously, and ionic structures in which one bond can resonate independently from the others. This intervention of ionic structures was considered crucial for rationalizing the occurrence of metallic properties such as conduction, and also contributed a significant proportion of the total resonance stabilization energy. All of the structures were based on atom-centred orbitals.

We have embarked on a series of studies of metal-atom clusters using spin-coupled theory, which can be considered the proper modern generalization of the ideas of Heitler and London[2] and of Coulson and Fischer[3] to many-electron systems. The model takes into account significant aspects of electron correlation whilst retaining a simple orbital picture. A previous spin-coupled study[4] (Paper I) concentrated both on optimal geometrical arrangements of lithium atoms and on fragments of a lithium body-centred cubic (bcc) lattice cut according to 100 or 110 planes. These calculations highlighted, in particular, the special significance of the rhombus unit.

Finite clusters of lithium atoms have been much studied with a wide variety of computational techniques. It is not appropriate here to present an exhaustive survey of such work: a representative selection of such papers includes Refs. 5-10. Motivated both by the findings of Paper I and by the obvious importance of the rhombus unit in the bcc 110 plane, the present study is concerned with small planar lithium clusters constructed from rhombus units sharing vertices or edges. The spin-coupled description of such systems reveals certain characteristic features which appear to be essentially independent of cluster size.

The dangers of extrapolating the results of calculations on finite clusters, which necessarily give too much prominence to surface effects and too little to long-range interactions, are self-evident. Nonetheless, the compelling regularity of the spin-coupled descriptions for different-sized clusters suggest that at least some of the key features will be preserved on passing to very large systems. In this way, the present study should contribute to our long-term aim of developing a »local« theory of the electronic structure of metals.

THEORY

In general, the spin-coupled wavefunction is based on an orbital approximation with one distinct, singly-occupied orbital for each electron, and with no restrictions on the overlaps between these orbitals or on the modes of pairing up the individual electron spins. Both spin-coupled theory and spin-coupled valence bond theory have now been applied to a very wide range of problems and numerous reviews are available.[11-15] As a consequence, only details of particular relevance to the present work are summarized here.

Spin-coupled theory was utilized in the present work explicitly for the n 'valence' electrons of each Li_n cluster. The corresponding spin-coupled orbitals are denoted ϕ_μ. The $\mathrm{Li}(1s^2)$ 'core' electrons, which are of somewhat less interest, were accommodated in doubly-occupied orbitals, ψ_i, taken from a suitable restricted Hartree-Fock (RHF) calculation. Such a spin-coupled wavefunction Ψ_{SM} can be written in the form

$$\Psi_{\mathrm{SM}} = (n!)^{\frac{1}{2}} \sum_{k=1}^{f_S^n} c_{\mathrm{Sk}}\, \mathcal{A}\, (\psi_1^2 \psi_2^2 \cdot\cdot\, \psi_{\mathrm{n}}^2 \;\; \phi_1 \phi_2 \cdot\cdot\, \phi_{\mathrm{n}} \;\; \Theta_{\mathrm{pp}}^{2\mathrm{n}}\, \Theta_{\mathrm{SM;k}}^{\mathrm{n}}) \tag{1}$$

where $\mathcal{A}$ is the usual antisymmetrizer and the c_{Sk} are termed spin-coupling coefficients. This wavefunction, which is an eigenfunction of the spin operators $\hat{S}^2$ and $\hat{S}_z$, involves two types of spin function: Θ^{2n}_{pp} is the perfect-pairing spin function for the 2n core electrons and $\Theta^n_{SM;k}$ is one of the linearly-independent n-electron spin functions for the valence electrons, each labelled by the index k. The dimension, f^n_S, of the full spin space for a system of n electrons with total spin S is given, for any value of the projection M, by

$$f^n_S = \frac{(2S+1)\,n!}{(\frac{1}{2}n + S + 1)!\,(\frac{1}{2}n - S)!} \tag{2}$$

The fully-optimized orbitals which emerge from spin-coupled calculations on molecular systems are typically found to be highly localized around individual atomic centres but show small deformation towards neighbouring centres. The parentage of these orbitals is usually very obvious, and there are often marked similarities between the spin-coupled orbitals and the functions postulated by classical VB theory. Useful chemically-appealing concepts such as directed covalent bonds, hybridization, charge transfer and resonance arise naturally, without any preconceptions as to the form of the orbitals. The spin-coupling coefficients measure the importance of each of the allowed modes of spin coupling, and provide information on the way in which bonding is realised.

For each Li_n system, we first carried out an appropriate restricted Hartree-Fock (RHF) calculation with a 6-21G basis set[16] consisting of a total of m atom-centred functions. The first n MOs were used to describe the core electrons and then all the remaining MOs, both occupied and virtual, were used as basis functions for the n spin-coupled orbitals:

$$\phi_\mu = \sum_{p=n+1}^{m} c_{\mu p}\,\psi_p \tag{3}$$

The variational parameters, namely the orbital coefficients $c_{\mu p}$ and the spin-coupling coefficients c_{Sk}, were fully optimized simultaneously. As no constraints were imposed on the overlaps between the ϕ_μ, and because the full spin space was employed, the form of the spin-coupled orbitals is a unique outcome of the energy minimization.

At convergence, each occupied orbital ϕ_μ satisfies an orbital equation of the type[17]

$$\hat{F}_\mu^{(\mathrm{eff})}\ \phi_\mu = \varepsilon_\mu \phi_\mu \tag{4}$$

where the operators $\hat{F}_\mu^{(eff)}$ are all distinct, and each gives rise to a set of functions $\phi_\mu{}^{(i)}$ with orbital energies $\varepsilon_\mu{}^{(i)}$. One of these functions corresponds to the occupied orbital already found, while the others are excited or 'virtual' solutions. The operators $\hat{F}_\mu^{(eff)}$, which are constructed with quantities pertinent to n–1 orbitals (with the exclusion of orbital ϕ_μ), express the field acting on one electron in the presence of n–1 others. In this sense, the orbitals $\phi_\mu{}^{(i)}$ may be considered the proper one-particle states for the n correlated electrons.

These virtual orbitals may be used to form excited spin-coupled structures in a subsequent non-orthogonal CI or spin-coupled valence bond (SCVB) calculation. The resulting SCVB wavefunction is dominated by the spin-coupled configuration for all nuclear geometries. Higher roots of the same secular problem provide SCVB descriptions of excited states, which tend to be dominated by a very small number of the excited structures. It is important in the current context to point out that the virtual orbitals satisfy a generalized Brillouin theorem so that a singly-excited configuration constructed by replacing an occupied orbital, ϕ_μ, with one of the corresponding virtual orbitals, $\phi_\mu^{(i)}$, cannot interact directly with the spin-coupled configuration.

RESULTS

The converged spin-coupled wavefunction for an optimal arrangement of four lithium atoms, namely a rhombus[6] of side 5.552 bohr and of internal angle 127°, was described in Paper I. The wavefunction consists of four equivalent, singly-occupied orbitals which can be transformed into one another by operations of the D_{2h} molecular point group: one of these orbitals is depicted in Figure 1 as contours of ϕ_μ in the molecular plane. Instead of being centred on the individual atomic centres, as one might have first expected, the orbitals are localized *between* pairs of nuclei, *i.e.* on the perimeters of the rhombus. It is convenient to refer to such spin-coupled orbitals as *interstitial orbitals* or IOs. The largest overlaps, $\langle\phi_1|\phi_2\rangle=\langle\phi_3|\phi_4\rangle=0.57$, involve orbitals associated with sides forming acute angles and the mode of spin coupling for this cluster is overwhelmingly dominated by the perfect-pairing function

$$\tfrac{1}{2}\,[\alpha(1)\beta(2)-\alpha(2)\beta(1)]\,[\alpha(3)\beta(4)-\alpha(4)\beta(3)] \qquad (5)$$

with singlet-coupled pairs 1-2 and 3-4.

In the present work, idealized geometries for fragments of the bcc 110 plane were generated by repetition of the basic $Li_4(D_{2h})$ rhombus, as shown in Figure 2. No at-

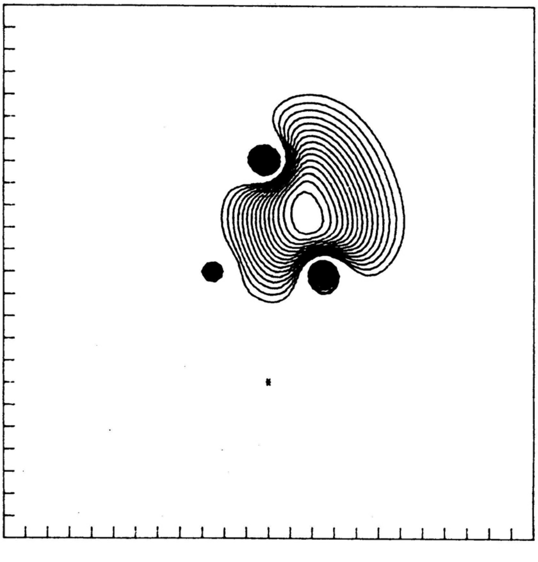

Figure 1. One of four equivalent spin-coupled orbitals for the valence electrons of singlet $Li_4(D_{2h})$. Throughout this paper, orbitals are depicted as contours of ϕ_μ in the molecular plane.

tempt was made to optimize the resulting geometries, since it is most unlikely that this would change the qualitative description of the spin-coupled wavefunctions. Such geometry optimization would, of course, lead to small changes in the computed binding energies.

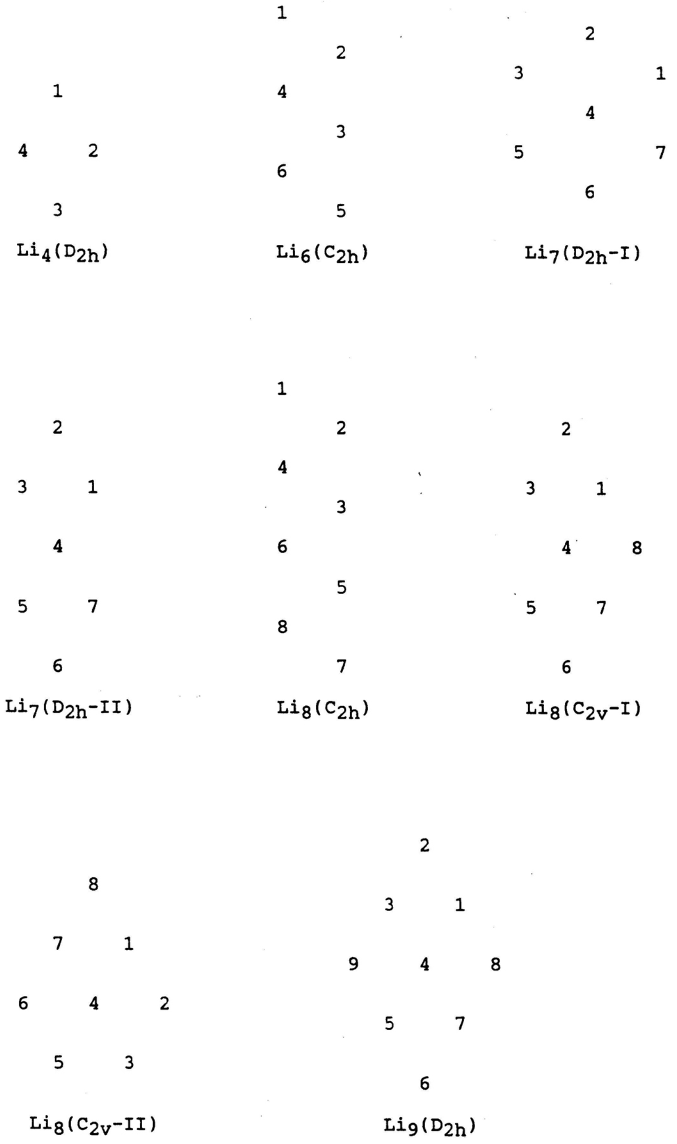

Figure 2. Schematic representations of the lithium clusters listed in Table I.

Each of the different geometrical arrangements with the same atomicity is denoted in the present work by its molecular point group. In the case of Li_7, the two different D_{2h} geometries are distinguished by Roman numerals I and II. A similar notation is necessary for Li_8 clusters with C_{2v} symmetry. When it is necessary to distinguish particular states, the symmetry label is extended with the value of $2S+1$. Thus, the lowest quartet state of $Li_7(D_{2h}\text{-II})$, for example, is denoted $Li_7(D_{2h}\text{-II};4)$, whereas the ground state is $Li_7(D_{2h}\text{-II};2)$. No new calculations were carried out for $Li_6(C_{2h})$ or for $Li_7(D_{2h}\text{-I})$, as these systems were described in detail in Paper I, albeit with slightly different geometries.

For some of the cases considered here, we find that the single-configuration spin-coupled calculation converges onto one of a small number of equivalent symmetry-broken solutions. The correct symmetry-adapted wavefunction is then obtained by carrying out a very small SCVB calculation involving just the different symmetry-broken solutions.

The results reported in Table I highlight the lowering of the total energy that is due to the correlation effects included in the spin-coupled wavefunction. These effects are responsible in some cases for reversing the order of spin multiplicities predicted from the RHF calculations. Experience for analogous systems suggests that the spin-coupled calculations are likely to be much more reliable in this respect than the RHF calculations. Overlap matrices are recorded in Table II for $Li_4(D_{2h};1)$ and for all the clusters not considered in our previous work.

TABLE I

Results of spin-coupled calculations for small clusters of lithium atoms. The shapes of those clusters are shown in Figure 2. B.E. is the binding energy per atom

System	2S+1	f_S^n	otal energy (in hartree)		*B.E.* (in kcal/mol)
			spin-coupled	RHF	
Optimized bcc 110 geometries[a]					
Li_4 D_{2h}	1	2	−29.78040	−29.74865	9.08
	3	3	−29.75917	−29.73439	5.74
Li_6 C_{2h}	3	9	−44.67112	−44.63555	9.14
	1	5	−44.66914	−44.60320	8.93
Li_7 D_{2h}-I	2	14	−52.11382	−52.06334	8.91
	4	14	−52.10018		7.69
Idealized bcc 110 geometries					
Li_7 D_{2h}-II	2	14	−52.10026	−52.04590	7.70
	4	14	−52.09917	−52.03441	7.60
Li_8 C_{2h}	1	14	−59.55860	−59.48226	8.91
	3	28	−59.55398	−59.47159	8.55
Li_8 C_{2v}-I	1	14	−59.55798	−59.46427	8.86
	3	28	−59.55743	−59.46111	8.82
Li_8 C_{2v}-II	1	14	−59.56094	−59.40923	9.09
	3	28	−59.53978	−59.48084	7.43
Li_9 D_{2h}	2	42	−67.00270	−66.84682	8.86
	4	48	−66.98292	−66.87400	7.48

[a] Results for these systems are reproduced from Paper I, in which $Li_6(C_{2h})$ is denoted $Li_6(6,0,0\text{-}110)$ and $Li_7(D_{2h})$ is denoted $Li_7(7,0,0\text{-}110)$.

TABLE II

Overlap integrals between spin-coupled orbitals.

	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	ϕ_7	ϕ_8
$\mathrm{Li_4(D_{2h};1)}$								
ϕ_1	1							
ϕ_2	0.57	1						
ϕ_3	0.18	0.23	1					
ϕ_4	0.23	0.18	0.57	1				
$\mathrm{Li_7(D_{2h}\text{-}II;2)}$								
ϕ_1	1							
ϕ_2	0.56	1						
ϕ_3	−0.01	−0.01	1					
ϕ_4	−0.01	−0.01	0.56	1				
ϕ_5	0.10	0.08	0.24	0.18	1			
ϕ_6	0.08	0.10	0.18	0.24	0.55	1		
ϕ_7	0.38	0.38	−0.07	−0.07	0.29	0.29	1	
$\mathrm{Li_7(D_{2h}\text{-}II;4)}$								
ϕ_1	1							
ϕ_2	0.58	1						
ϕ_3	0.01	0.00	1					
ϕ_4	0.01	0.01	0.58	1				
ϕ_5	0.10	0.07	0.33	0.30	1			
ϕ_6	0.30	0.33	0.07	0.10	0.53	1		
ϕ_7	0.27	0.25	−0.25	−0.27	−0.42	0.42	1	
$\mathrm{Li_8(C_{2h};1)}$								
ϕ_1	1							
ϕ_2	0.59	1						
ϕ_3	0.12	0.15	1					
ϕ_4	0.18	0.12	0.57	1				
ϕ_5	0.15	0.12	0.01	0.00	1			
ϕ_6	0.12	0.18	0.00	0.00	0.57	1		
ϕ_7	0.37	0.20	−0.04	−0.06	0.30	0.22	1	
ϕ_8	0.20	0.38	0.30	0.22	−0.04	−0.06	−0.26	1
$\mathrm{Li_8(C_{2h};3)}$								
ϕ_1	1							
ϕ_2	0.35	1						
ϕ_3	0.12	0.04	1					
ϕ_4	0.30	0.04	0.61	1				
ϕ_5	−0.01	0.11	0.00	−0.01	1			
ϕ_6	−0.04	0.15	−0.01	−0.01	0.57	1		
ϕ_7	0.26	0.49	0.02	0.03	0.30	0.23	1	
ϕ_8	0.43	0.30	0.34	0.32	−0.03	−0.03	0.06	1
$\mathrm{Li_8(C_{2v}\text{-}I;1)}$								
ϕ_1	1							
ϕ_2	0.31	1						
ϕ_3	−0.01	0.29	1					
ϕ_4	0.00	0.34	0.59	1				
ϕ_5	0.29	−0.01	−0.02	−0.03	1			
ϕ_6	0.34	0.00	−0.03	−0.04	0.59	1		
ϕ_7	0.36	0.08	−0.01	−0.03	0.21	0.09	1	
ϕ_8	0.08	0.36	0.21	0.09	−0.01	−0.03	0.40	1

TABLE II – continued

	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	ϕ_7	ϕ_8	ϕ_9
Li$_8$(C$_{2v}$-I;3)									
ϕ_1	1								
ϕ_2	0.16	1							
ϕ_3	–0.04	0.29	1						
ϕ_4	0.00	0.35	0.58	1					
ϕ_5	0.29	–0.04	–0.01	–0.01	1				
ϕ_6	0.35	0.00	–0.01	–0.01	0.58	1			
ϕ_7	0.39	0.06	0.03	0.02	0.21	0.10	1		
ϕ_8	0.06	0.39	0.21	0.10	0.03	0.02	0.50	1	
Li$_8$(C$_{2v}$-II;1)									
ϕ_1	1								
ϕ_2	0.09	1							
ϕ_3	0.08	0.56	1						
ϕ_4	0.63	0.00	0.00	1					
ϕ_5	0.32	0.01	–0.07	0.64	1				
ϕ_6	0.78	0.08	0.09	0.63	0.55	1			
ϕ_7	0.55	–0.07	0.01	0.64	0.13	0.32	1		
ϕ_8	0.92	0.13	0.13	0.63	0.38	0.92	0.38	1	
Li$_8$(C$_{2v}$-II;3)									
ϕ_1	1								
ϕ_2	0.03	1							
ϕ_3	–0.01	0.61	1						
ϕ_4	0.43	–0.03	–0.03	1					
ϕ_5	0.07	0.17	0.28	0.16	1				
ϕ_6	0.13	–0.01	0.03	0.43	0.44	1			
ϕ_7	0.44	0.28	0.17	0.16	0.29	0.07	1		
ϕ_8	0	0	0	0	0	0	0	1	
Li$_9$(D$_{2h}$;2)									
ϕ_1	1								
ϕ_2	0.61	1							
ϕ_3	0.22	0.33	1						
ϕ_4	0.01	0.08	0.44	1					
ϕ_5	–0.02	–0.02	–0.10	0.08	1				
ϕ_6	–0.02	–0.02	–0.07	0.02	0.57	1			
ϕ_7	0.06	0.00	–0.01	–0.06	0.02	0.15	1		
ϕ_8	0.29	0.18	0.36	0.03	–0.04	–0.03	0.46	1	
ϕ_9	0.06	0.12	0.50	0.59	0.17	0.20	0.36	0.25	1
Li$_9$(D$_{2h}$;4)									
ϕ_1	1								
ϕ_2	0.10	1							
ϕ_3	0.10	0.63	1						
ϕ_4	0.13	–0.03	–0.03	1					
ϕ_5	0.37	0.34	0.24	–0.09	1				
ϕ_6	0.36	0.09	0.08	–0.06	0.49	1			
ϕ_7	0.16	–0.03	–0.03	0.58	–0.09	0.10	1		
ϕ_8	0.36	0.23	0.34	–0.11	0.43	0.05	–0.08	1	
ϕ_9	0.68	0.13	0.14	0.04	0.36	0.11	0.00	0.54	1

We turn now to the qualitative interpretation of the wavefunctions for the various systems. In $Li_6(C_{2h})$, as for $Li_4(D_{2h})$, the number of valence electrons is equal to the number of external edges. It is thus not surprising that we find[4] that each of the six spin-coupled orbitals takes the form of an IO associated with an external edge of the cluster. Moving on to $Li_7(D_{2h}$-I), we face a situation in which the number of valence electrons exceeds the number of external edges. As described in Paper I, six of the orbitals take the form of IOs associated with the external edges, while the seventh is an IO centred on the »internal side« between atoms 4 and 5. Such a solution is, of course, symmetry broken.

The cluster $Li_7(D_{2h}$-II) presents a very different situation from $Li_7(D_{2h}$-I) in that the number of external edges now exceeds the number of valence electrons. The separation between atoms 1 and 7 (or 3 and 5) in $Li_7(D_{2h}$-II) is 6.65 bohr, whereas the corresponding separation in $Li_7(D_{2h}$-I) is 9.95 bohr. Thus 3-5 and 1-7 may be classified as external edges in $Li_7(D_{2h}$-II) but not in $Li_7(D_{2h}$-I). The converged spin-coupled orbitals for the doublet ground state of $Li_7(D_{2h}$-II) are shown in Figure 3. We find that six of the orbitals, ϕ_1-ϕ_6, take the form of IOs associated with external edges. Two orbitals, ϕ_1 and ϕ_2, are localized in one rhombus whereas four orbitals, ϕ_3-ϕ_6, are localized in the other. However, IOs ϕ_5 and ϕ_6, which are associated with the edges which meet at the central atom (atom 4), show significant deformation towards the unoccupied sides of the neighbouring rhombus. The seventh orbital, ϕ_7, has the same basic form as the others, but it is associated with *three* atoms instead of two, and is located in a triangular site.

In general terms, spin-coupled orbitals ϕ_1-ϕ_6 for $Li_7(D_{2h}$-II;4) are very similar to those for $Li_7(D_{2h}$-II;2), except for increased distortion of ϕ_5 and ϕ_6. However, orbital ϕ_6 is now located in the other rhombus from ϕ_5. Orbital ϕ_7 differs significantly from that just described for the doublet state: instead of an orbital localized between three atoms in one of the rhombuses, ϕ_7 takes the form of an out-of-phase combination of two such functions, one associated with each rhombus. For both spin multiplicities, the overlap integrals between IOs associated with adjacent external edges meeting at an acute angle are very similar to those in $Li_4(D_{2h};1)$.

The solutions for the $Li_7(D_{2h}$-I) and $Li_7(D_{2h}$-II) clusters correspond to asymmetric distributions of the electron density. The correctly symmetry-adapted wavefunctions, generated by means of small SCVB calculations, may be interpreted in terms of charge-density waves. This provides an obvious link to such questions as conductivity and electron mobility.

Three idealized bcc 110 arrangements have been considered for Li_8, labelled C_{2v}-I, C_{2h} and C_{2v}-II in Figure 2. For the first two cases, the numbers of valence electrons and of external edges coincide, so that it is reasonable to anticipate IOs analogous to those for the $Li_4(D_{2h})$ rhombus and to expect the perfect-pairing spin function to dominate. This is indeed the case, as shown in Figures 4 and 5. In the case of $Li_8(C_{2h};1)$, however, we observe delocalization of IOs ϕ_1 and ϕ_2 into neighbouring external sites, even though these are already occupied.

The spin-coupled orbitals for the triplet excited states of $Li_8(C_{2h})$ and $Li_8(C_{2v}$-I) are very similar to those for the singlet ground states. However, the marked deformation in $Li_8(C_{2h};1)$ of orbitals ϕ_1 and ϕ_2 towards adjacent external edges is not present in the corresponding triplet state. For both spin multiplicities of both geometrical arrangements, the general form of the overlap matrices (see Table II) is similar to that for $Li_4(D_{2h};1)$.

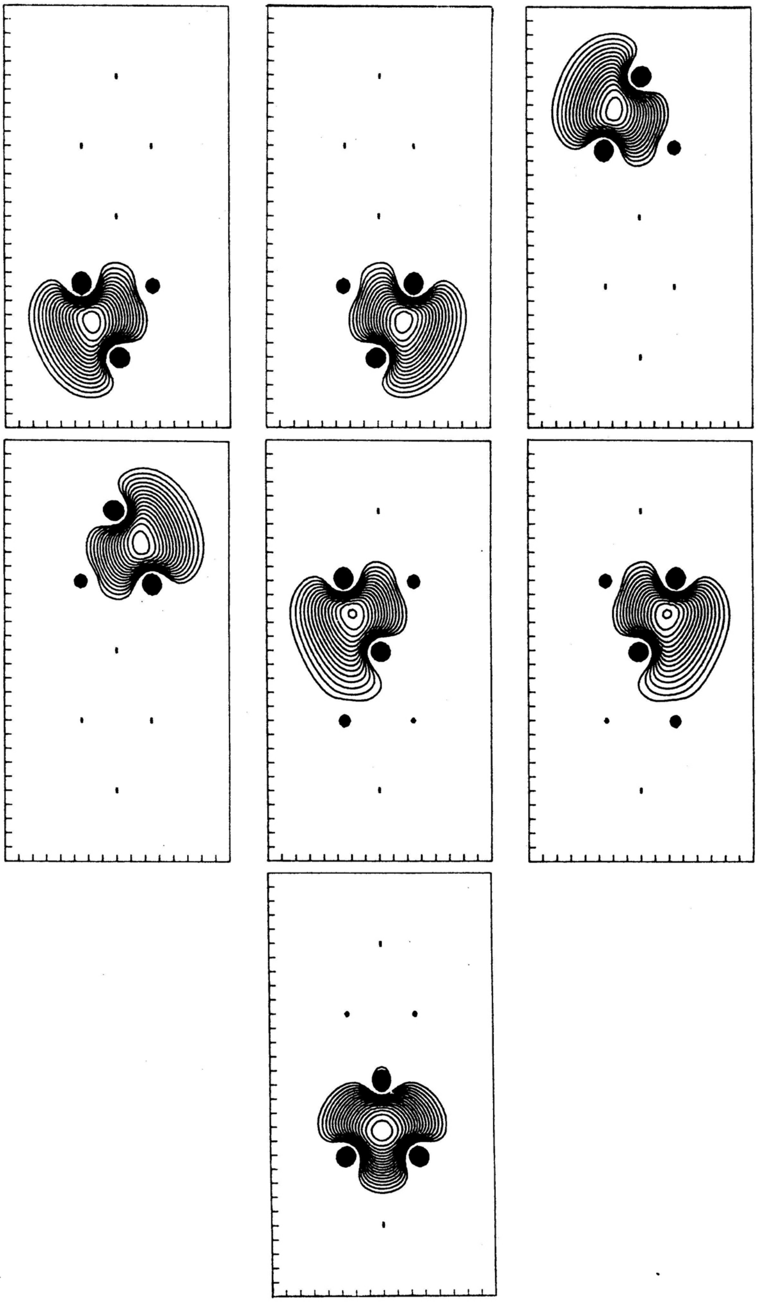

Figure 3. Spin-coupled orbitals for the doublet ground state of $Li_7(D_{2h}$-II).
Row 1: ϕ_1, ϕ_2, ϕ_3; row 2: ϕ_4, ϕ_5, ϕ_6; row 3: ϕ_7.

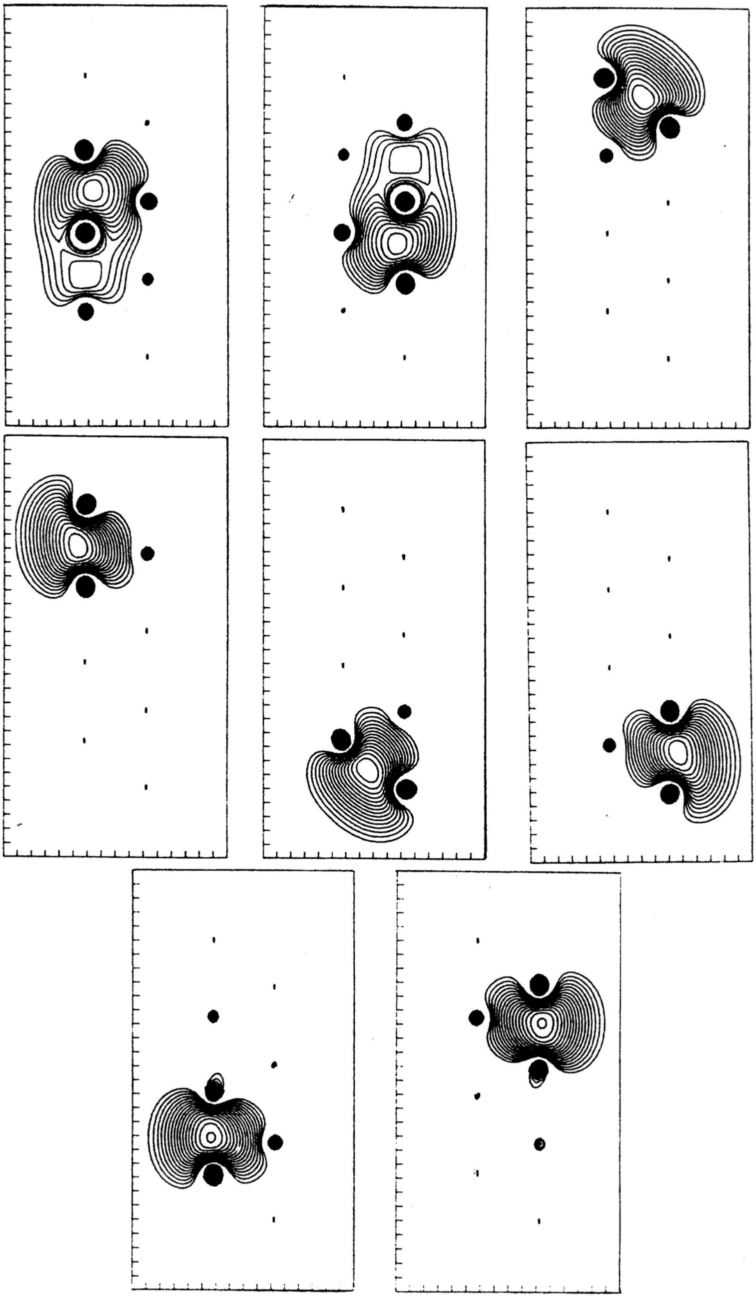

Figure 4. Spin-coupled orbitals for Li$_8$(C$_{2h}$;1).
Row 1: ϕ_1, ϕ_2, ϕ_3; row 2: ϕ_4, ϕ_5, ϕ_6; row 3: ϕ_7, ϕ_8.

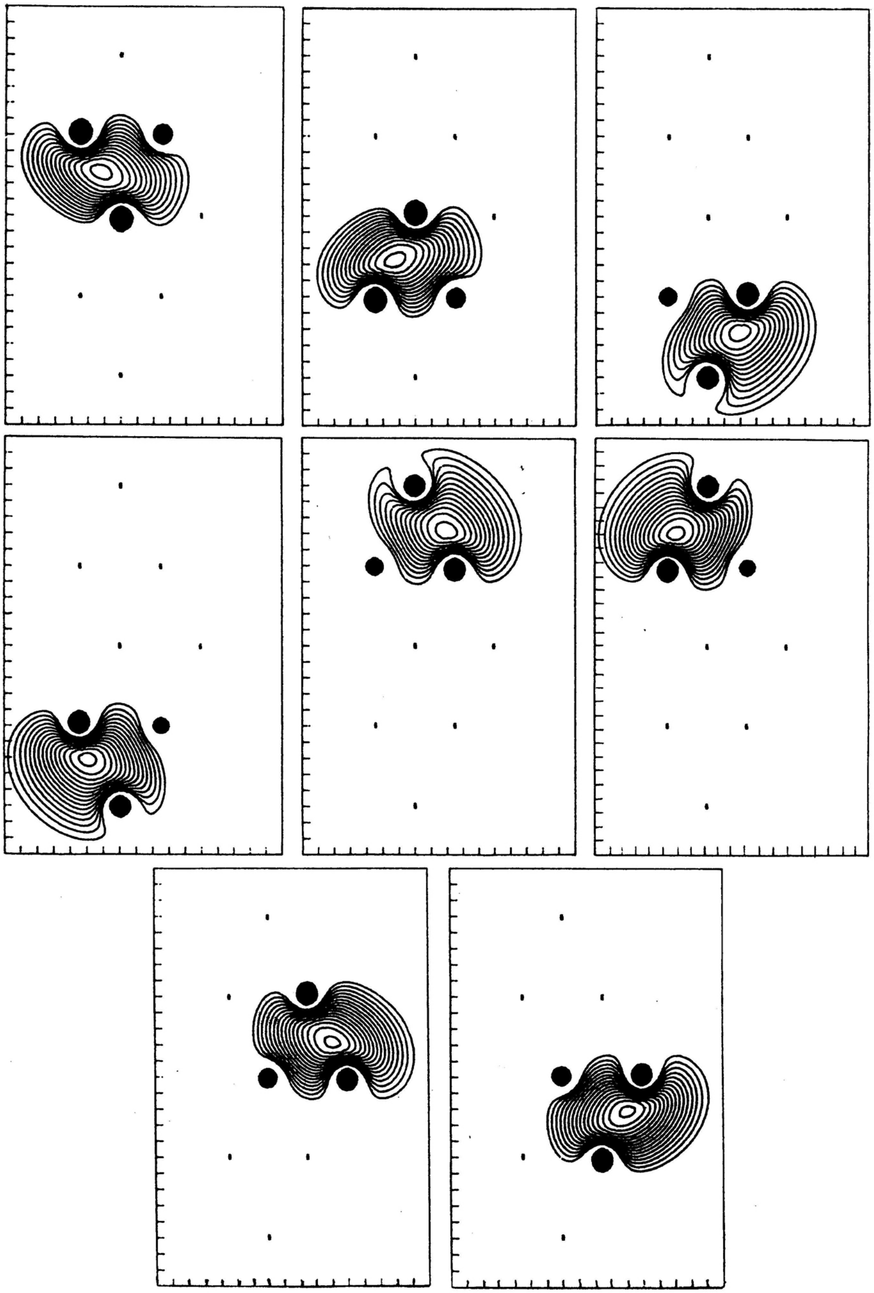

Figure 5. Spin-coupled orbitals for $Li_8(C_{2v}\text{-I};1)$.
Row 1: ϕ_1, ϕ_2, ϕ_3; row 2: ϕ_4, ϕ_5, ϕ_6; row 3: ϕ_7, ϕ_8.

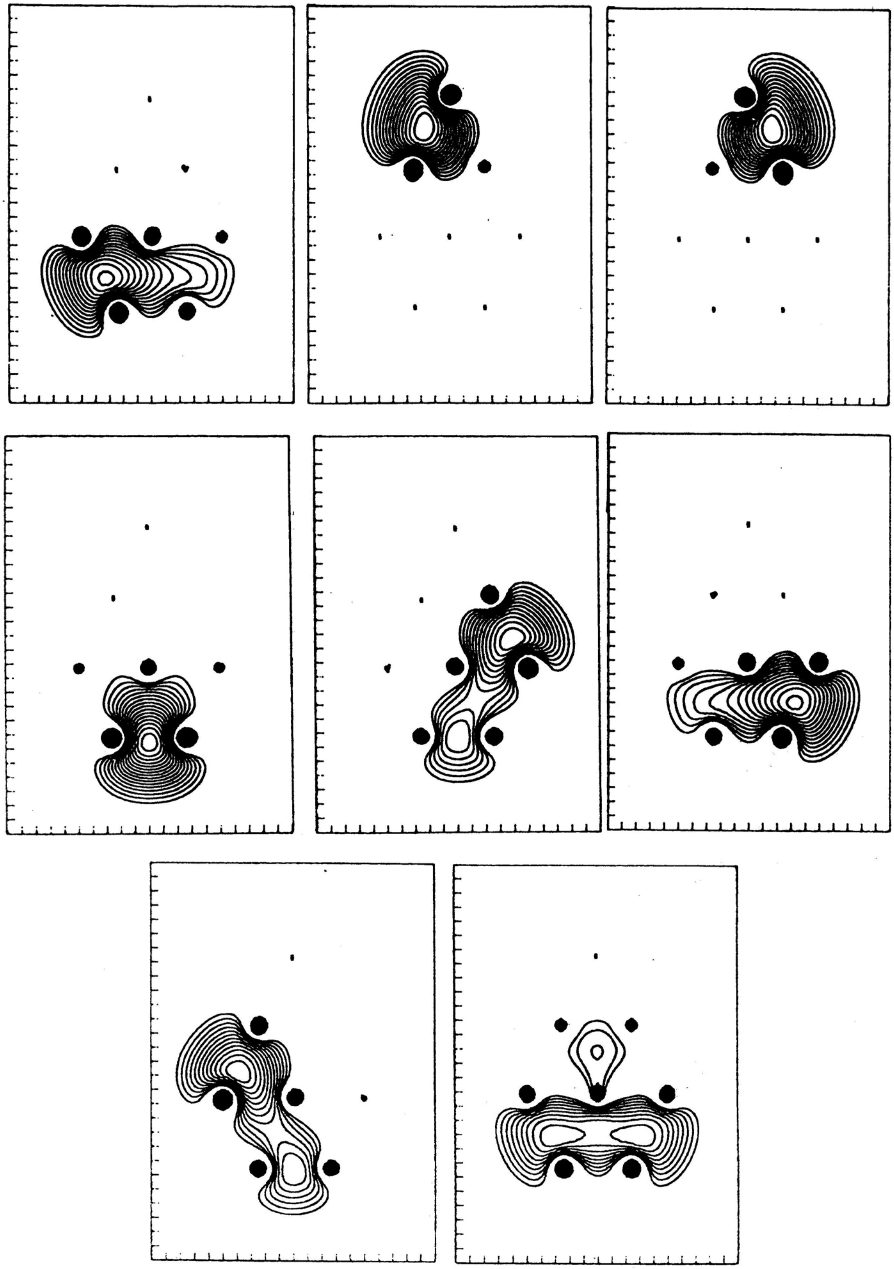

Figure 6. Spin-coupled orbitals for $Li_8(C_{2v}$-II;1).
Row 1: ϕ_1, ϕ_2, ϕ_3; row 2: ϕ_4, ϕ_5, ϕ_6; row 3: ϕ_7, ϕ_8.

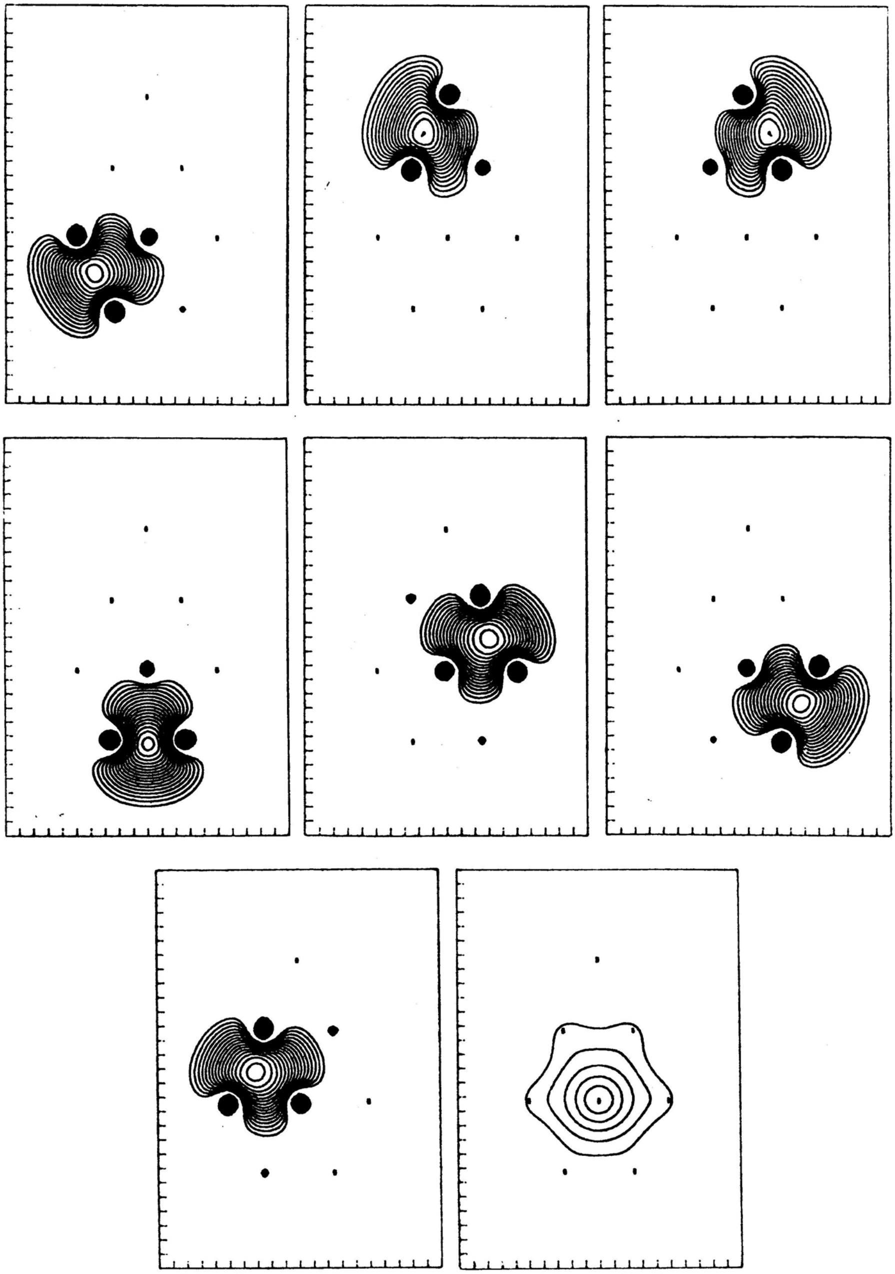

Figure 7. Spin-coupled orbitals for $Li_8(C_{2v}\text{-II};3)$. Orbital ϕ_8, which has 'π' character, is shown in the plane 2 bohr above the molecular plane. Row 1: ϕ_1, ϕ_2, ϕ_3; row 2: ϕ_4, ϕ_5, ϕ_6; row 3: ϕ_7, ϕ_8.

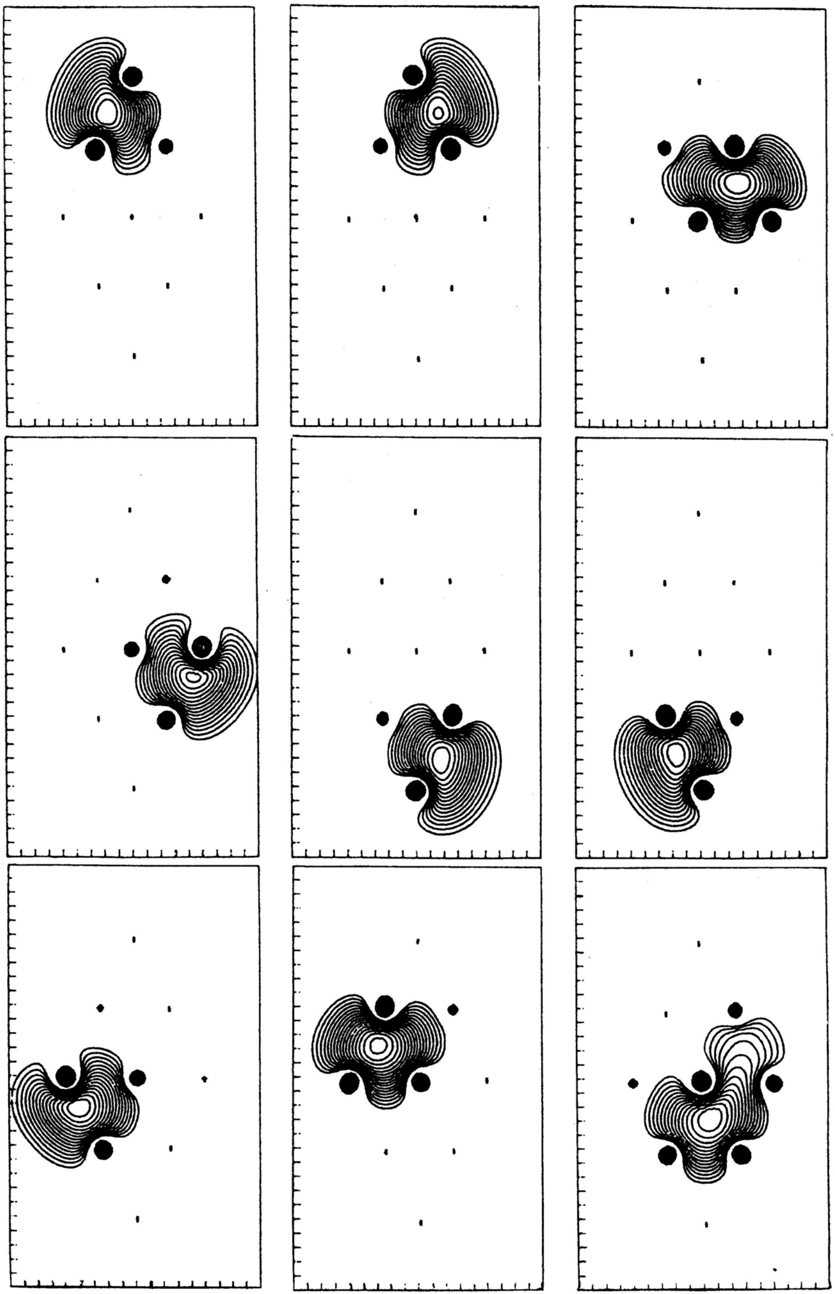

Figure 8. Spin-coupled orbitals for the lowest doublet state of $Li_9(D_{2h})$.
Row 1: ϕ_1, ϕ_2, ϕ_3; row 2: ϕ_4, ϕ_5, ϕ_6; row 3: ϕ_7, ϕ_8, ϕ_9.

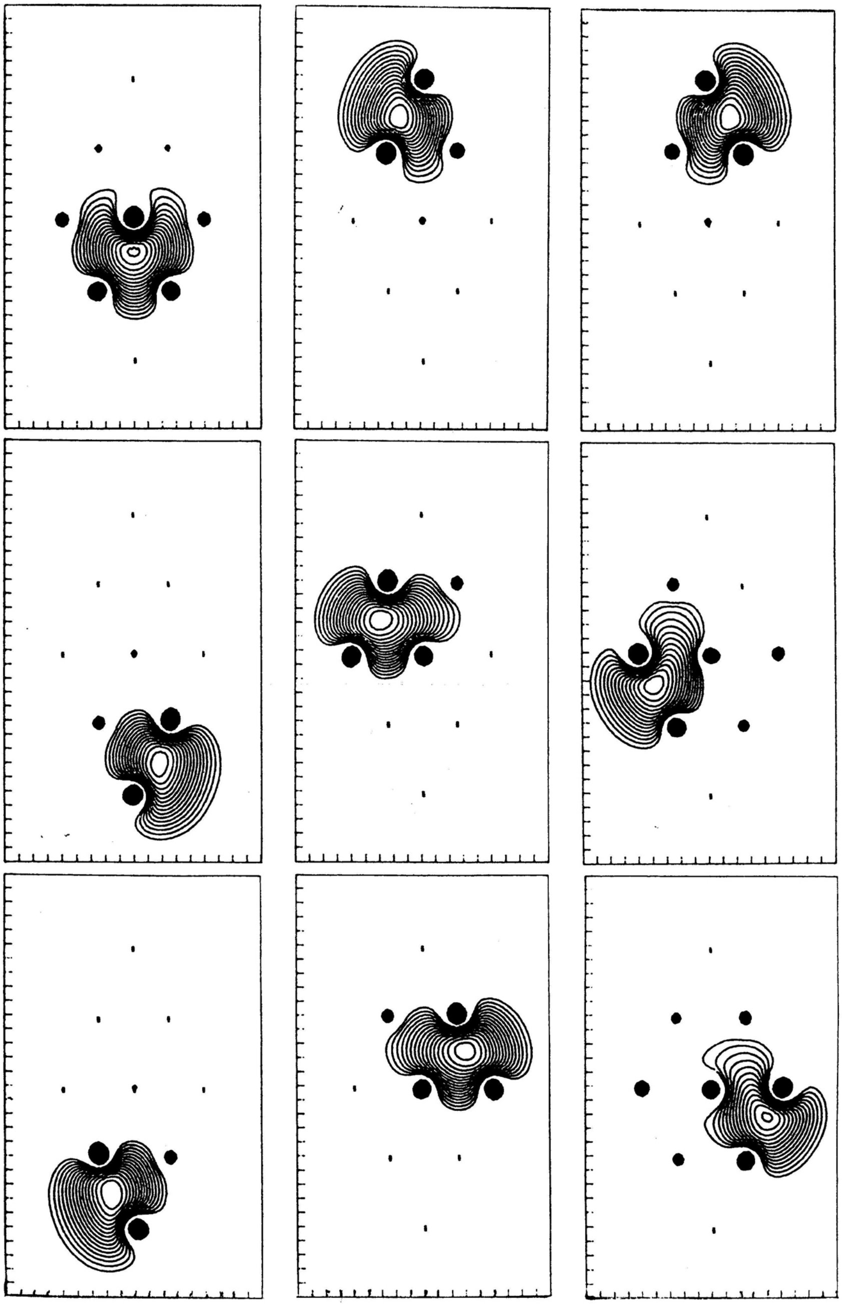

Figure 9. Spin-coupled orbitals for the lowest quartet state of Li$_9$(D$_{2h}$). Row 1: ϕ_1, ϕ_2, ϕ_3; row 2: ϕ_4, ϕ_5, ϕ_6; row 3: ϕ_7, ϕ_8, ϕ_9.

The most important spin coupling for $Li_8(C_{2v}$-I;3) (75% of the wavefunction) corresponds to singlet-coupled pairs 3-4, 5-6 and 7-8, with 'unpaired' electrons occupying orbitals ϕ_1 and ϕ_2. The most significant differences between the overlap matrices for $Li_8(C_{2v}$-I;1) and $Li_8(C_{2v}$-I;3) is a factor of two in the value of $\langle\phi_1|\phi_2\rangle$.

The $Li_8(C_{2v}$-II) cluster presents a situation which is analogous to that of $Li_7(D_{2h}$-I), namely one more valence electron than external edges. The distance between atoms 3 and 5 is less than 5 bohr, so that the $Li_8(C_{2v}$-II) cluster must be considered to possess seven external edges. As shown in Figure 6, seven of the orbitals for the singlet ground state of $Li_8(C_{2v}$-II) take the form of IOs associated with the external edges. However, there is significant delocalization onto other external-edge sites which are already occupied. The remaining orbital, ϕ_8, takes the form of an in-phase combination of IOs associated with the edges between atoms 2 and 3 and between atoms 5 and 6. The most important mode of spin pairing corresponds to singlet-coupled pairs 2-3, 1-4, 5-6 and 7-8.

The spin-coupled orbitals for the triplet excited state of $Li_8(C_{2v}$-II) are shown in Figure 7. There is no symmetry breaking in the spin-coupled solutions for either spin multiplicity. Orbitals ϕ_1-ϕ_7 again take the form of IOs associated with the external edges, but these orbitals exhibit significantly less delocalization than in the case of the singlet state (*c.f.* $Li_8(C_{2h})$). The last orbital, ϕ_8, possesses 'π' character, in that it is symmetric with respect to reflection in the molecular plane. The presence of a 'π' orbital rather than an IO leads to a significantly reduced binding energy per atom. One mode of spin coupling is overwhelmingly dominant in this case (93% of the wavefunction) and corresponds to singlet-coupled pairs 2-3, 1-4 and 5-6, with the 'unpaired' electrons occupying orbitals ϕ_7 and ϕ_8.

Finally, the $Li_9(D_{2h})$ cluster resembles both $Li_7(D_{2h}$-I) and $Li_8(C_{2v}$-II) in the sense that the number of valence electrons exceeds the number of external edges. The converged spin-coupled wavefunction for $Li_9(D_{2h};2)$ is symmetry broken – the orbitals are shown in Figure 8. To a first approximation, orbitals ϕ_1-ϕ_8 take the form of IOs associated with external edges. However, some of the orbitals are involved to some extent with *three* centres. This is especially true of ϕ_3, which is located between atoms 4, 7 and 8. The last orbital, ϕ_9, is mostly located in the region between atoms 4, 5 and 7, but also shows significant delocalization into the region occupied by ϕ_3. The perfect-pairing spin function, with the 'unpaired' electron occupying ϕ_9, has a weight of 80% in the total wavefunction.

The orbital description of the quartet state of $Li_9(D_{2h})$ (see Figure 9) is reminiscent of that of the $Li_7(D_{2h}$-II;2) system. One of the 48 spin functions is overwhelmingly dominant and corresponds to the singlet-coupled pairs 2-3, 4-7 and 1-9.

DISCUSSION AND CONCLUSIONS

The rhombus unit occurs very widely in lithium clusters and is of course an important feature in fragments of the bcc lattice cut according to the 110 plane. The spin-coupled description of the four valence electrons of $Li_7(D_{2h};1)$ is based on four distinct, non-orthogonal interstitial orbitals or IOs associated with the external edges. In the present work, we have constructed idealized geometries for planar lithium clusters by repetition of this basic rhombus unit. The spin-coupled wavefunctions that emerge in each case show obvious similarities to the description of $Li_4(D_{2h})$. Furthermore, the appearance of the IOs associated with external edges forming acute angles does not change appreciably with increasing cluster size, and the corresponding overlap integrals remain essentially unchanged.

We find that a key feature in determining the characteristics of the orbitals for a given cluster is the difference between the number of valence electrons (n) and the number of external edges (N_E). Beyond determining the values of n and N_E, the numbers of rhombuses sharing vertices or edges appears to play no significant role.

Systems for which $n = N_E$ include $Li_4(D_{2h})$, $Li_6(C_{2h})$, $Li_8(C_{2h})$ and $Li_8(C_{2v}$-I). For these clusters we observe IOs associated with each of the external edges. The clusters $Li_7(D_{2h}$-I), $Li_8(C_{2v}$-II) and $Li_9(D_{2h})$ belong to a second category, for which $n = N_E + 1$. The solutions for these systems consist, to a first approximation, of IOs associated with each of the external edges plus one additional orbital located in the interior of the cluster. Although it might have been tempting to assume that this last orbital would be localized on the 'central' atom, such a supposition would have been entirely incorrect: *all* of the orbitals are associated with interstitial sites. The cluster $Li_7(D_{2h}$-II) belongs to a third category, with $n = N_E$-1. Six of the seven orbitals for this system take the form of IOs associated with external edges and the remaining orbital is associated with triangular sites close to the centre of the cluster.

In most cases, the spin-coupled solutions for the clusters with $n = N_E$ are symmetry broken. When this occurs, the full symmetry-adapted wavefunction can be generated *via* a small SCVB calculation involving just the equivalent symmetry-broken configurations. It seems likely that this occurrence of symmetry-broken spin-coupled solutions, implying asymmetric distributions of the electronic charge and resonating charge-density waves, is an important indicator of the transition from 'molecular' to 'metallic' character.

Particularly for the larger clusters, the energy separations between the different spin multiplicities are fairly small. Furthermore, the value of S tends to have a relatively minor effect on the general form of the orbitals. One clear exception is the $Li_4(D_{2h};3)$ system, described in Paper I, for which the orbitals resemble in-phase and out-of-phase combinations of IOs. Another exception is $Li_8(C_{2v}$-II), for which one of the orbitals for the triplet state possesses 'π' character.

It is useful to compare the general form of our results with those described by Goddard and co-workers[8], who employed the GVB approach within the constraints of strong orthogonality and perfect pairing. The »GVB-SOPP« wavefunction consists of an orbital product, with one orbital for each electron, but these orbitals are optimized in pairs subject to the restriction that orbitals belonging to different pairs are not allowed to overlap with one another. Furthermore, only one mode of spin coupling is retained in the GVB-SOPP wavefunction.

The spin-coupled calculations described in the present work were carried out using the full spin space and without any restrictions on the overlaps between the valence orbitals. It is clear from Table II that each IO typically overlaps significant with at least two other orbitals. Furthermore, although the perfect-pairing function dominates the spin-coupled wavefunction for most of the clusters described here, the total contribution from all the other allowed modes of spin coupling can be as large as 25%. Nonetheless, in spite of the limitations imposed on the GVB-SOPP model, the *general form* of the GVB-SOPP and spin-coupled orbitals are very similar. The key qualitative feature which emerges from both sets of calculations is the occurrence of orbitals localized at interstitial sites. In neither model do the orbitals assume atom-centred forms, as in the Pauling theory of metals.[1] The interstitial nature of the spin-coupled orbitals represents an optimal balance, at this level of theory, between classical-VB covalent and ionic contributions to the bonding in lithium clusters, and highlights also the important role played by 2p character.

In order to make further progress in the development of a spin-coupled theory of metals it will be necessary to investigate larger clusters for which the number of valence electrons greatly exceeds the number of external edges. It will be especially important to characterize the interactions between different orbitals located in the interior of clusters – in the present work, n never exceeds N_E by more than one. However, it seems likely that the orbitals in the larger clusters will retain the same basic interstitial form as described here.

In the limit of an extended system, the localized nature of the spin-coupled orbitals suggests some similarity with Wannier functions, but with the crucial differences that the spin-coupled orbitals are non-orthogonal and are located at interstitial rather than atomic sites. For all of the systems considered in the present work, the low-lying spin-coupled virtual orbitals adopt forms similar to those of the occupied orbitals, but these virtuals may be localized in different interstitial regions of the cluster. The form of the virtual orbitals means that even singly-excited configurations can imply »electron jumps«. The intervention of a perturbation, as in the form of an external electric field, enables these charge-transfer configurations to mix with the ground state configuration. Such a perturbation could also modify the relative weights of different symmetry-broken structures in a full symmetry-adapted wavefunction. These two effects are likely to play a central role in the spin-coupled description of fundamental metallic properties such as conduction.

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SAŽETAK

Teorijski opis litijevih grozdova primjenom metode vezanja spinova eletrona. II. Planarni raspored rompskih jedinica

Elena Tornaghi, David L. Cooper, Joseph Gerratt i Mario Raimondi

Teorija spinskog sprezanja primijenjena je na valentne elektrone malih plošnatih grozdova litija izgrađenih iz romboidnih jedinica koji dijele vrhove ili bridove. Romboidna jedinica u malim grozdovima litija i u dijelovima rešetke bcc (body-centred-cubic), podijeljena plohom 110, izabrana je za proučavanje zbog izuzetne važnosti.

Slika koju daje metoda spinskog sprezanja za idealizirani fragment ravnine bcc 110 temelji se na orbitalama koje su lokalizirane između raznih jezgara, a koje se mogu nazvati »intersticijske orbitale« ili IO. Mnoge IO povezane su s vanjskim krajevima grozdova i pokazuju samo male promjene od grozda do grozda ili između raznih spinskih multipliciteta. Izgleda da je osnovni uvjet za određivanje položaja IO za dani grozd razlika između broja valentnih elektrona i broja vanjskih bridova. Čak i za one sisteme koji imaju orbitale smještene u unutrašnjosti grozda, sve orbitale zadržavaju intersticijske oblike prije nego oblike orbitala smještenih na atomima.

Neke karakteristične osobine koje su u osnovi neovisne o veličini grozda mogu biti važne za razvoj teorije spinskog sprezanja u eletronskoj strukturi metala.