

Systematic *ab initio* configuration-interaction study of alkali-metal clusters: Relation between electronic structure and geometry of small Li clusters

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The electronic and geometric structure of small neutral Li_n ($n=2-9$) and cationic Li_n^+ ($n=2-9$) clusters is investigated with the optimal self-consistent-field energy and geometry search and with the multireference diexcited configuration-interaction method. The optimal geometries of neutral and cationic Li clusters are very different. Very small Li_n ($n \leq 6$) clusters prefer planar geometries [deformed sections of the (111) fcc-lattice plane]. The optimal geometries of somewhat larger Li_n ($6 \leq n \leq 9$) clusters are composed from condensed deformed tetrahedra. This switch in the geometrical structure of clusters can be easily understood on the basis of some simple qualitative arguments. Predicted relatively large stabilities of Li_4 and Li_8 as well as of Li_3^+ and Li_9^+ can help to interpret the "magic numbers" observed when alkali-metal clusters are prepared and detected under differing experimental conditions. The theory predicts stability of relatively small doubly charged alkali-metal clusters which seems to be in variance with the customary ideas of "Coulomb explosion." The general trend of the dependence of ionization potentials of alkali-metal clusters on the cluster nuclearity agrees with experiments. The present work confirms some conclusions of the "electron-shell model" but puts them on a more general basis, independent of conceptual and methodological details. Furthermore, it reveals new aspects and leads to predictions.

I. INTRODUCTION

Recently, the theory of the electronic structure of small metallic and covalent clusters has received great interest from theoretical physicists and quantum chemists as well, for obvious reasons. Clusters can exhibit some interesting specific properties. A very popular and intriguing example of such properties is the claimed occurrence of exceptionally large abundances for some cluster sizes detected during cluster preparation (so-called "magic" numbers).¹⁻⁵

Two extreme points of view considering the cluster stability can be found in the literature: In the first, it is assumed that the geometry of the framework of atomic nuclei is the prevalent factor, e.g., two-center potentials can be used to determine cluster stability.^{6,7} In the second extreme viewpoint the electronic shell structures are considered as being of the only decisive importance, and, consequently, the smearing of the nuclear charges over a sphere represents an acceptable assumption.⁵ The properties and mainly the degeneracies of the respective one-electron functions determined mainly by the spherical symmetry of the system ("super-atom" model) should play the main role for the proper understanding of clusters.

Customary quantum-mechanical treatments, in which the influence of the atomic positions on electronic structure is explicitly considered, can elucidate the validity and the limitations of simplified methods used in the field of cluster theory. Evidently, the large number of electrons present in any cluster of practical interest represents a large hindrance in employing more sophisticated quantum chemistry methods and therefore, the appropriate simple theories are very desirable in the cluster theory. Nevertheless, it is worth investigating such simple systems like lithium clusters where more general and quite sophisticated approaches are feasible. One can hope that the achieved knowledge from such investigation of alkali-metal clusters can be useful also in a broader context.

For this reason, many quantum-mechanical studies on the electronic structure of small alkali-metal clusters have been carried out.^{5,8-26} The majority of the results obtained with different methods are quite parallel and show that the underlying principles of the electronic and geometric structure of small metallic and covalent clusters are so simple that they do not depend—at least to some extent—on the methodological details of the employed quantum-mechanical treatments. On the other hand, a systematic investigation of the most simple clusters is still very limited.

Let us summarize the conjectures which can be drawn from the present stage of the cluster theory:²⁷

(1) In general, the compactness of the cluster is favorable for the cluster stability and it tends usually to force a symmetry of a cluster as high as possible.

(2) The Jahn-Teller effect, pseudo-Jahn-Teller effect or related phenomena [when the degeneracy of molecular orbitals (MO's) is not complete] can cause the deformation of the cluster geometry towards a less symmetric geometrical configuration. This effect stabilizes, for example, planar cluster geometries which exhibit smaller degeneracies of the relevant one-electron functions [molecular orbitals (MO's) or natural orbitals (NO's)] than three-dimensional geometries of high symmetry.

(3) Since the chemical bonds in covalent and metallic clusters can be quite delocalized, some topological properties of the bonds in clusters can be important.^{28,29}

(4) The availability of polarization functions in the atomic-orbital (AO) basis set (e.g., *p*-type atomic orbitals) is of principal importance for the proper characterization of electronic and geometric properties of small alkali-metal clusters.^{10,11,27} It can be shown that *ab initio* calculations predict the dimerization of the Li₂ moieties to be an unfavorable process, if the *p*-type polarization functions are not included in the AO basis set (cf. Fig. 1).

Systematic investigation on small sodium clusters Na_{*n*} has been carried out by Martins *et al.*^{20,21} for *n* ≤ 8 and *n* = 13 with self-consistent pseudopotential local-spin-density method considering the Hellmann-Feynman forces. Rao and Jena¹² have studied the shapes and stabilities of lithium clusters with Hellmann-Feynman forces as well, but using the unrestricted Hartree-Fock approximation. McAdon and Goddard²⁵ have applied the generalized valence-bond method to investigate small Li clusters with the aim to formulate some general rules governing the structures of Li clusters. Even the simple Hückel-type treatment of the Li_{*n*} clusters gives quite satisfactory results although it is not able to yield an explanation of the cluster stability as such.²⁹

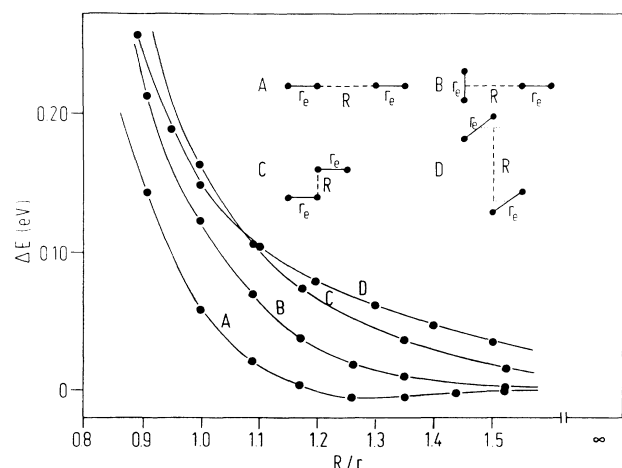


FIG. 1. Energy change (ΔE) due to the approach of two Li₂ (with a constant bond length $r_e = 3.02 \text{ \AA}$) as a function of their mutual distance R . The MRD-CI procedure and uncontracted Gaussians in the AO basis set (see Ref. 55) have been employed.

The earlier investigation of the electronic and geometric properties of Li clusters with multireference diexcited configuration-interaction method yielded very high stability for planar clusters with the number of atoms smaller or equal to six as well as for very compact Li_{*n*} cluster geometries exhibiting fivefold rotation symmetry for *n* = 6, 7, 13.^{30,31}

Although, the majority of results obtained from various treatments are in qualitative agreement, there are some quite serious discrepancies among different quantum-mechanical investigations. Moreover, the theoretical results on the alkali-metal nonamer were very scarce until now but just the comparison of the electronic properties of the octamers and nonamers is of great interest for the discussion of experimentally found behavior of the abundances in this interval.

Present study treats systematically small neutral lithium clusters Li_{*n*} (*n* = 2–9) and gives also some preliminary results on Li₁₀ and Li₁₄ which makes plausible some predictions about the stability of larger Li clusters. The Li_{*n*}⁺ cations (*n* = 2–9) have been systematically investigated as well, since usually the alkali metal cation clusters are recorded by mass spectroscopical methods. Moreover, the discussion about the role of different number of electrons present in the clusters of the same nuclearity is intriguing from a general point of view.

Some experimental works have reported that the doubly charged metal clusters can be detected with the mass spectroscopy methods only if the cluster size exceeds an appropriate limit.^{32,33} The predictions based on the comparison between the electrostatic repulsion of two elementary point charges and the binding energy (Coulomb explosion) lead to relatively very large cluster sizes allowing for the stability of the doubly charged clusters. Recently, some experimental works claim the finding of very small doubly charged clusters.³⁴ Therefore, in the present paper pilot calculations of the doubly charged clusters have been included.

The method applied is the optimal energy and geometry search based on Hartree-Fock approach.³⁵ For the self-consistent-field (SCF) optimal geometries the multi-reference-diexcited configuration-interaction (MRD-CI) (Refs. 36 and 37) has been applied and the limited optimization of the MRD-CI energy is carried out. For some crucial examples the reliability of the MRD-CI method has been checked by comparing the results obtained from the direct CI procedure.^{38,39} The consideration of the electron correlation is important mainly if the electronic states exhibit comparable energies for different geometrical arrangements of clusters with the same nuclearity.

Obviously, if the energy difference between different cluster forms is relatively small the calculated energy in the framework of Born-Oppenheimer approximation is not, exactly speaking, the appropriate measure of the cluster stability. Therefore, the approximate zero-point vibration energy is also calculated. However, at least an estimate of the entropy would be desirable if one would like to be very exact. In principle, the vibrational entropy can be estimated from the computed frequencies but we assume that the purely electronic energy values yield enough information for the present purpose.

II. METHODOLOGICAL PART

In this investigation relatively simple AO basis sets have been employed because this makes it possible to treat larger Li clusters. The basis set *A* (Refs. 40 and 41) which is a minimal basis set augmented by one *p*-polarization function (6,1/2,1) gives generally parallel results as larger AO basis sets and can therefore be considered as reliable. The 6-31 G AO basis set *B* (10,4/3,2), (Ref. 42) is used to check the results obtained with the nearly minimal basis set *A*.

The optimal geometries are determined by the Hartree-Fock procedure with the AO basis set *A*.^{40,41} In earlier works^{11,30,43-45} and in the context of the present study a broad investigation of various probable cluster geometries had been carried out. The interatomic distances in selected parts of the fcc, bcc, and hcp lattice as well as in steps of the pentagonal growth and various tetrahedral geometries have been optimized so that the less probable topologies have been excluded from the choice of the starting points for the best cluster geometry search. The employed procedure does not permit one to obtain an estimate of the number of possible local minima on the energy hypersurface.

The optimal energy search has been carried out very often with some symmetry constraints for obvious reasons. It has been checked without any symmetry constraints if all normal-mode frequencies of the cluster structure found are real. The cases for which this has not been carried out are explicitly mentioned. Starting from the SCF optimal geometries the corrections due to the correlation effects have been partly introduced employing the MRD-CI method.^{36,37} For example, for the fixed SCF topology all distances of the SCF optimal geometry have been scaled with a common factor. The energies of the optimal states have been then recalculated with the AO basis set *B* (10,4/3,2). The transformation of the virtual orbitals carried out according to Ref. 46 and the appropriate elimination of the transformed virtual orbitals makes the CI calculations with the basis set *B* computationally easier.

III. OPTIMAL GEOMETRIES OF SMALL NEUTRAL AND CATIONIC Li CLUSTERS

The geometries, the symmetries, and the electronic ground states of the most stable neutral Li clusters determined by the best SCF energy search with subsequent "CI scaling" procedure (cf. Sec. II) using basis set *A* are drawn in Fig. 2. The forms found as energetically next most favorable are collected in Fig. 3 where only the results of SCF search without the "CI scaling" procedure are given. The SCF and CI energy differences ΔE_{SCF} and ΔE_{CI} between the given structure obtained from the best-energy search and the cluster with the optimal geometry are also given in Fig. 3.

The geometries of important Li cations which result from the (HF) Hartree-Fock best energy search (without the "CI scaling" procedure) employing the basis set *A* are shown in Figs. 4 and 5. The binding energy per atom, E_B/n , is defined for neutral clusters as

$$E_B/n = -E_n/n + E_1 = (-E_n + nE_1)/n \quad (1)$$

and for cationic clusters as

$$E_B^+/n = [-E_n^+ + (n-1)E_1 + E_1^+]/n, \quad (2)$$

where E_n and E_n^+ is the energy of neutral and cationic clusters with n Li atoms, respectively. The E_B/n or E_B^+/n can be considered as a suitable measure of the cluster stability. They are given as functions of the nuclearity in Fig. 6. In Tables I and II and in Ref. 47 stabilities of neutral and cationic clusters, respectively, obtained in the basis *A* are reported.

The second differences of cluster energy as functions of number of atoms are defined as

$$\Delta^2 E_n = E_{n+1} + E_{n-1} - 2E_n \quad (3)$$

and

$$\Delta^2 E_n^+ = E_{n+1}^+ + E_{n-1}^+ - 2E_n^+ \quad (4)$$

The functions $\Delta^2 E_n$ and $\Delta^2 E_n^+$ are other quantities which yield useful information on the development of the cluster stability with the cluster size (see Fig. 7).

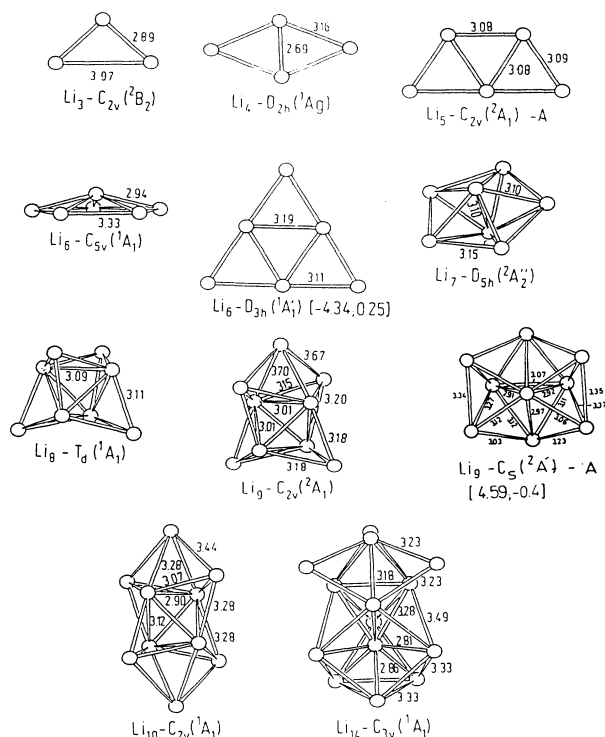


FIG. 2. Geometries of energy optimized neutral Li clusters. The interatomic distances (Å) resulting from the SCF optimal geometry search followed by the partial MRD-CI optimization ("scaling" procedure described in Sec. II) are shown. The symmetry group of the cluster as well as the irreducible representation and the spin multiplicity of the respective state (in the bracket) are given. If the energies of two cluster geometries are nearly degenerated, the SCF and CI energy differences in kcal/mol (first and second number in the square bracket) are also given for one of the isomers.

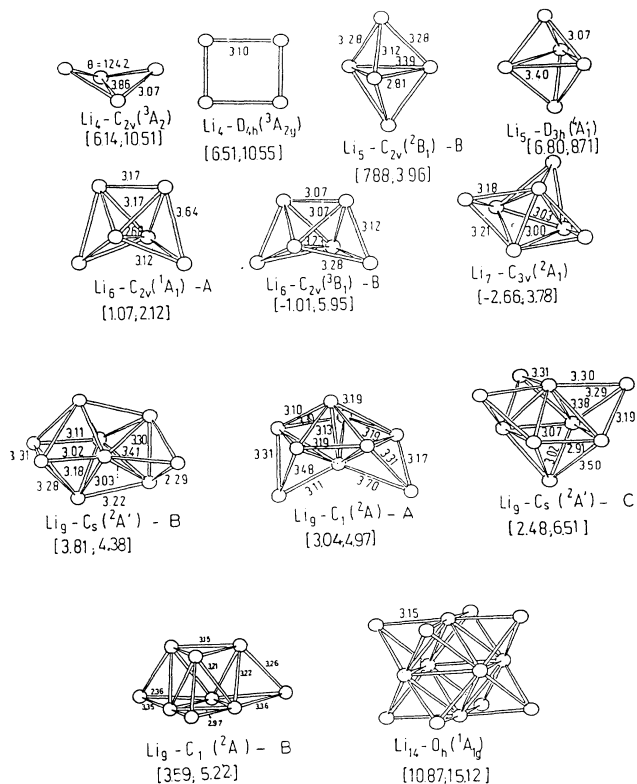


FIG. 3. Geometries of “second best” neutral Li clusters. The interatomic distances (Å) resulting from the SCF optimal geometry search are shown. The symmetry group of the cluster as well as the irreducible representation and the spin multiplicity of the considered state (in the bracket) are given. First and second number in the square bracket are the SCF and CI energy difference (kcal/mol) in respect to the optimal cluster geometry of the isomer (see Fig. 2).

The following features of these results can be pointed out.

(1) One can notice a pronounced general trend of increasing cluster stability with increasing nuclearity for both neutral and positively charged Li clusters. The functions $\Delta^2 E_n$ and $\Delta^2 E_n^+$ with maxima for even and odd n , respectively, show that this increase in stability is not smooth and that the functions E_B/n and E_B^+/n exhibit instead some “bumps” or even minima:

(i) The quantities E_B/n and $\Delta^2 E_n$ exhibit minima for Li_3 and Li_9 . The maxima of $\Delta^2 E_n$ for $n=4$ and 8 can be connected with “magic” numbers, that is, with the cluster sizes that correspond to the largest abundances detected by some mass spectroscopical experiments on alkali-metal clusters in which the stability of neutral clusters is assumed to be dominant.

(ii) The pronounced maxima of $\Delta^2 E_n^+$ and of E_B^+/n for Li_3^+ , Li_7^+ , and Li_9^+ and minima of the same functions for Li_4^+ , Li_8^+ can be interpreted as signs of the high stability of the cationic Li clusters with the odd number of atoms (and consequently with even number of electrons).

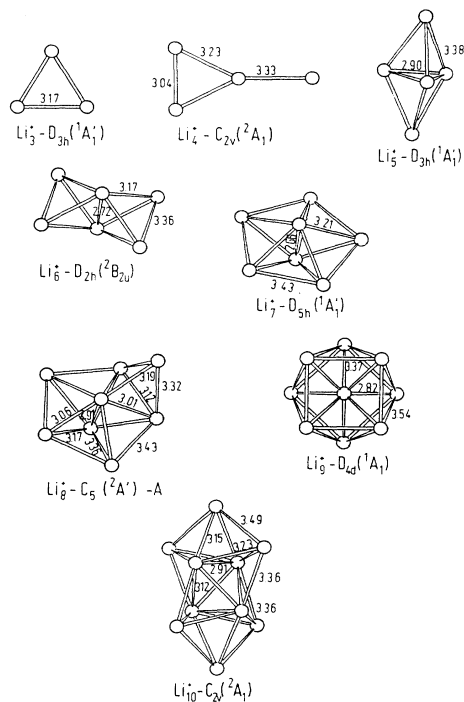


FIG. 4. Geometries of energy optimized cationic clusters. The interatomic distances (Å) resulting from the SCF optimal geometry search are shown. The symmetry group of the cluster as well as the irreducible representation and the spin multiplicity of the respective state (in the bracket) are given.

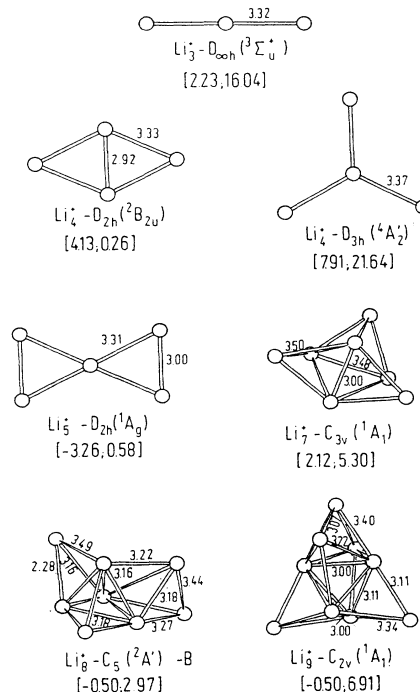


FIG. 5. Geometries of “second best” cationic clusters. The interatomic distances (Å) resulting from the SCF optimal geometry search are shown. The symmetry group of the cluster as well as the irreducible representation and the spin multiplicity of the respective state (in the bracket) are given. The first and second number in the square bracket is the SCF and CI energy differences in respect to the most stable isomer, respectively.

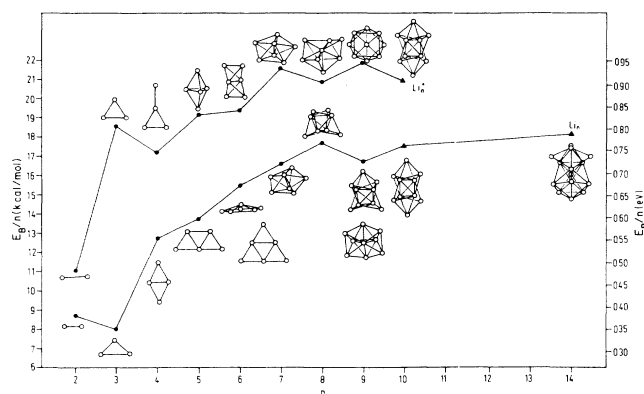


FIG. 6. Binding energy per atom E_B/n and E_B^+/n [cf. Eqs. (1) and (2)] as functions of the number n atoms in Li_n and Li_n^+ clusters, respectively. The graphs of the most stable clusters are schematically shown. The extrapolated MRD-CI energies E_n (AO basis A) with Davidson corrections are used in evaluation of E_B/n and E_B^+/n .

It is possible to assume that the maxima for $n=3,7,9$ are related to the maxima of the abundances found in experiments in which the stability of ionized cluster is of a principal importance.

(2) The difference in the energy

$$\delta E_n = E_n - (E_{n-1} + E_1) \quad (5)$$

characterizing the dissociation channel $\text{Li}_n \rightarrow \text{Li}_{n-1} + \text{Li}$ exhibits maxima for clusters with odd number of atoms showing their smaller stability for this dissociation channel. This maximum is particularly small for $n=7$, which is clearly due to the general change of the character of this cluster geometry which can be viewed as a border case between planar (for $n < 7$) and three-dimensional geometries (for $n \geq 7$). The energy differences

$$\delta E'_n = E_n - (E_{n-2} + E_2) \quad (6)$$

for the dissociation channel $\text{Li}_n \rightarrow \text{Li}_{n-2} + \text{Li}_2$ has quite different behavior from δE_n but the maxima occurring for Li_3 and Li_9 demonstrate that these clusters are unstable to both dissociation channels (Fig. 8).

Analogously, the quantities δE_n^+ and $\delta E'_n^+$ can be defined for the dissociation channels $\text{Li}_n^+ \rightarrow \text{Li}_{n-1}^+ + \text{Li}$ and $\text{Li}_n^+ \rightarrow \text{Li}_{n-2}^+ + \text{Li}_2$. The maxima of δE_n^+ indicating smaller stability exist for Li_4^+ , Li_8^+ , and Li_{10}^+ (Fig. 9).

It is remarkable that $\Delta^2 E_n$ and δE_n as well as $\Delta^2 E_n^+$ and δE_n^+ give very similar answers about stabilities of clusters.

(3) The development of the characteristic geometries with the size for the most stable neutral clusters exhibit some striking regularities: Very small clusters with 3–6 Li atoms can be considered as deformed sections of the (111) plane in fcc crystal lattice. The geometries of most

stable Li heptamer, octamer, and larger clusters can be understood as “condensed” deformed tetrahedrons appropriately sharing their triangular sides. The change of the character of the construction of the best cluster geometries can be seen from Fig. 10 in which the corresponding SCF E_B/n are compared with those calculated for fcc or hcp topologies with optimized interatomic distances (cf. Ref. 43). Starting from Li_7 , the fcc topologies are much less favorable than the clusters built from tetrahedra. The irregularities in the properties, stability, ionization potentials of the pentamer, hexamer, and heptamers can be deduced from the changing of the character of the cluster shape in this interval of the cluster size.

The $\text{Li}_8 T_d$ cluster exhibits two very special characteristics: the tetrahedral subunits do not need to be deformed from steric reasons, and simultaneously, the eight valence electrons can just fill up a nondegenerate s -type MO and a triply degenerate p -type MO (“closed-shell” electronic structure). The nonamer can no longer enjoy such a favorable situation. This fact can be put in connection with the drop in stability for $n=9$. The acceptable geometries of Li_n clusters for $n > 9$ can be thought of as being constructed by adding further Li atoms to the very symmetrical $\text{Li}_8 T_d$ or $\text{Li}_7 D_{5h}$ topologies. These cluster geometries can have either some atoms with small coordination numbers or they must exhibit noticeable deformations in order to achieve compact cluster arrangement.

The ninth Li atom in Li_9 can be added perpendicular to one side of the inner tetrahedron of the $\text{Li}_8 T_d$. The resulting structure is topologically equivalent to the pentagonal bipyramid with two additional atoms capping two neighboring faces of one of its pyramidal subunits. The energy of this isomer of Li_9 is nearly equal to the energy of the Li_9 geometry built by capping two neighboring faces of different pyramidal substructures. Evidently, different geometries of less stable Li_9 (compared with very stable Li_8) can exhibit very similar binding energies.

We have carried out a larger number of optimum SCF energy searches for Li_9 with various starting points. One can conclude that with large probability no geometry of the Li_9 cluster exists which has larger E_B/n than the lithium octamer.

The participation of the octahedral subunits in the cluster geometry seems to be energetically unfavorable for very small alkali-metal clusters. The octahedral subunits which are characteristic for fcc and bcc crystal lattices might be incorporated in the cluster frame only for those large cluster sizes for which the filling up of the space with condensed tetrahedral units is already very difficult.

(i) The very characteristic transition interval for $n=5-7$ deserves a detailed discussion. The 2B_1 state of the nonplanar $\text{Li}_5 C_{2v}$ cluster having the shape of two condensed slightly deformed tetrahedra represents a minimum but has SCF and CI energy higher than the 2A_1 state of the planar $\text{Li}_5 C_{2v}$ by 7.88 and 3.96 kcal/mol, respectively.

The $\text{Li}_6 C_{5v}$ and the planar $\text{Li}_6 D_{3h}$ which correspond to two local energy minima on the Li_6 hypersurface have practically the same CI energies. The SCF energy for the ${}^1A'$ state of $\text{Li}_6 D_{3h}$ is slightly lower than the SCF energy of the 1A_1 ground state of $\text{Li}_6 C_{5v}$ ($\Delta E_{\text{SCF}} = -4.3$

TABLE I. Ground and excited states of optimized neutral clusters, basis *A*.

Cluster	Symmetry	State	SCF ^a	E_B/n (kcal/mol)			V_{IP} (eV)		ZPE ^f (kcal/mol)
				CI-ext. ^b	CI-Dav. ^c	Ver. ^d	Ad. ^e		
Li ₂	$D_{\infty h}$	$1\Sigma_g^+$	1.47	8.66 ^g	8.66 ^g	5.12	5.0	0.44 <i>n</i>	
		$3\Sigma_u^+$	-6.23	-5.45	-5.45				
Li ₃	C_{2v}	$2B_2$	0.97	8.01 ^g	8.05 ^g	4.18	3.95	0.94 <i>n</i> <i>n</i>	
		$2A_1$	-6.18	2.64	2.82				
		$4A_2$	-4.04	-2.38	-2.33				
Li ₄	D_{2h}	$1A_g$	3.74	12.44 ^g	12.77 ^g	4.61	4.55	1.88 <i>n</i>	
		$3B_{1g}$	0.47	8.4	8.73				
	C_{2v}	$3A_2$	2.23	9.89	10.14			1.69	
		D_{4h}	$3A_{2g}$	2.14	9.89				10.13
Li ₅	$C_{2v}-A$		$2A_1$	5.18	12.99 ^g	13.78 ^g	4.48	4.15	2.51 <i>n</i> <i>n</i>
		$2B_2$	1.25	8.71	9.81				
		$4B_2$	1.01	7.99	8.65				
	$C_{2v}-B$	$2B_1$	3.61	12.14	12.98	2.38 <i>n</i>			
		$4A_2$	2.49	10.28	10.78				
	D_{3h}	$4A'_1$	3.82	11.52	12.03	SP			
Li ₆		C_{5v}	$1A_1$	5.48	14.53 ^g	15.56 ^g	4.53	4.32	3.45 <i>n</i>
	$3E_1$		2.76	9.87	10.82				
	D_{3h}	$1A'_1$	6.2	14.48 ^g	15.52 ^g	3.32 <i>n</i>			
		$3E'$	3.2	9.54	10.50				
$C_{2v}-A$	$1A_1$	5.3	14.24	15.21	3.45 <i>n</i>				
	$3B_1$	4.33	12.06	13.11					
$C_{2v}-B$	$3B_1$	5.65	13.62	14.57	3.51 <i>n</i>				
	$1A_1$	4.03	13.38	14.45					
Li ₇	D_{5h}	$2A_2''$	6.43	15.52 ^g	16.65 ^g	3.91	3.82	4.20 <i>n</i>	
		$4E_1'$	3.14	11.12	12.95				
	C_{3v}	$2A_1$	6.81	15.03	16.11			4.33 <i>n</i>	
		$4E$	3.69	10.71	11.72				
Li ₈	T_d	$1A_1$	7.91	16.47 ^g	17.77 ^g	4.57	4.23	5.14 <i>n</i>	
		$3T_1$	4.8	12.37	13.68				
Li ₉	C_{2v}	$2A_1$	7.20	15.36 ^g	16.79 ^g	3.70	3.15	5.33 <i>n</i> <i>n</i>	
		$2B_1$	5.35	13.46	15.13				
		$4B_1$	4.45	11.98	13.53				
	C_s-A	$2A'$	6.69	15.36 ^g	16.83 ^g	3.17	<i>n</i> <i>n</i>		
		C_s-B	$2A'$	6.78	14.95			16.30	
	C_1-A	$2A$	6.86	14.81	16.23	<i>n</i>			
	C_s-C	$2A'$	6.92	14.69	16.06	<i>n</i>			
	C_1-B	$2A$	6.80	14.68	16.19	<i>n</i>			
	Li ₁₀	C_{2v}	$1A_1$	7.77	16.12	17.61	3.91	3.87	6.90

TABLE I. (Continued)

Cluster	Symmetry	State	SCF ^a	E_B/n (kcal/mol)		V_{IP} (eV)		ZPE ^f (kcal/mol)
				CI-ext. ^b	CI-Dav. ^c	Ver. ^d	Ad. ^e	
Li ₁₄	C_{3v}	1A_1	8.50	16.60	18.23			SP
	O_h	$^1A_{1g}$	7.73	15.39	17.15			<i>n</i>

^a SCF binding energy per atom where $E_1 = 7.37809$ a.u., $E_1^+ = -7.18354$ a.u.

^b E_B/n calculated with extrapolated MRD-CI energies.

^c E_B/n calculated with MRD-CI energy with Davidson corrections.

^d Vertical ionization potential.

^e Adiabatic ionization potential.

^f ZPE means the zero-point vibration energy. The symbol SP (saddle point) in this column means that the normal-mode analysis yields some imaginary values. The symbol *n* means that the normal-mode analysis has not been carried out.

^g The energy of the "CI scaled" geometry.

kcal/mol). The competition between the planar geometries and cluster forms constructed from condensed tetrahedral subunits leads to almost equal energies for two different geometries of Li hexamers. Both Li hexamers can be obtained by adding one Li atom to the C_{2v} pentamer. Some deformations of angles and a small deviation from planarity is necessary to acquire from the planar Li₅ C_{2v} the pentagonal pyramid Li₆ C_{5v} , which exhibits a very low height (0.80 Å). The SCF energies for the 1A_1

states of the tripyramid Li₆ C_{2v} and of Li₆ C_{5v} are nearly the same. The CI energy of the former is only slightly higher ($\Delta E_{CI} = 2.12$ kcal/mol), as well as with respect to the energy of the $^1A'$ state of Li₆ D_{3h} ($\Delta E_{CI} = 2.07$ kcal/mol). The 3B_1 state of Li₆ C_{2v} has the second lowest SCF energy from all hexamers. Since the electron correlation lowers the energies of triplet states less than energies of singlet states, which is a well-known effect, the CI energy of the 3B_1 state of Li₆ C_{2v} is nearly 6 kcal/mol

TABLE II. Ground and excited state of optimized ionized clusters, basis *A*.

Cluster	Symmetry	State	SCF ^a	E_B/n (kcal/mol)		ZPE ^d (kcal/mol)
				CI-ext. ^b	CI-Dav. ^c	
Li ₂ ⁺	$D_{\infty h}$	$^2\Sigma_g^+$	12.34			0.38
Li ₃ ⁺	D_{3h}	$^1A'_1$	13.83	18.33	18.60	1.13
	$D_{\infty h}$	$^3\Sigma_u^+$	13.09	13.28	13.28	0.82
Li ₄ ⁺	C_{2v}	2A_1	13.22	17.10	17.20	1.50
	D_{2h}	$^2B_{2u}$	12.20	17.02	17.13	SP
	D_{3h}	$^4A'_2$	11.25	11.78	11.79	SP
Li ₅ ⁺	D_{3h}	$^1A'_1$	12.16	18.77	19.16	3.07
	D_{2h}	1A_g	12.78	18.69	19.04	2.38
	D_{2h}	$^3B_{1g}$	4.5	11.73	12.00	<i>n</i>
Li ₆ ⁺	D_{2h}	$^2B_{2u}$	12.24	18.88	19.41	3.64
Li ₇ ⁺	D_{5h}	$^1A'_1$	13.41	20.87	21.58	4.26
	C_{3v}	1A_1	13.30	20.00	20.82	4.20
Li ₈ ⁺	$C_s - A$	$^2A'$	12.77	19.95	20.91	4.77
	$C_s - B$	$^2A'$	12.83	19.57	20.54	4.89
Li ₉ ⁺	C_{2v}	1A_1	13.14	20.49	21.59	5.77
	D_{4d}	1A_1	13.09	21.31	22.36	5.83
Li ₁₀ ⁺	C_{2v}	2A_1	12.29	19.72	20.95	<i>n</i>

^a SCF binding energy per atom where $E_1 = 7.37809$ a.u., $E_1^+ = -7.18254$ a.u.

^b E_B/n calculated with extrapolated MRD-CI energies.

^c E_B/n calculated with MRD-CI energy with Davidson corrections.

^d ZPE means the zero-point vibration energy. The symbol SP (saddle point) in this column means that the normal-mode analysis yields some imaginary values. The symbol *n* means that the normal-mode analysis has not been carried out.

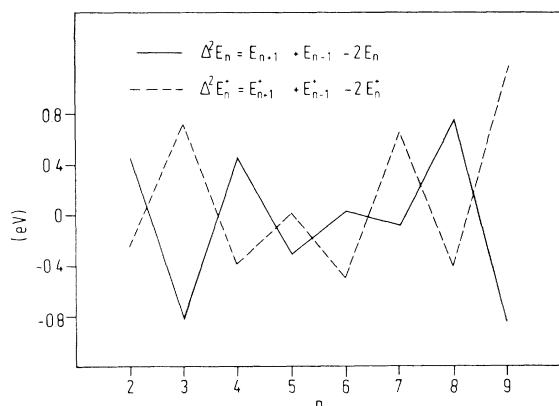


FIG. 7. Second differences of the cluster energies $\Delta^2 E_n$ and $\Delta^2 E_n^+$. The extrapolated MRD-CI energies E_n (AO basis A) with Davidson corrections are used.

higher than the energies of the singlet ground states of Li_6 C_{5v} and Li_6 D_{3h} . At this point our results are not in agreement with the results of Rao and Jena who found that the triplet state of the Li_6 pentagonal pyramid has the lowest energy from all Li hexamers.⁴⁸

The sequence of the SCF energies for the ground state of Li_7 heptamers with different geometries is reversed if the correlation effects are taken into account. The SCF energy of Li_7 D_{5h} is higher than the SCF energy of the C_{3v} isomer, whereas the CI energy of the Li_7 D_{5h} with the shape of the pentagonal bipyramid is 3.78 kcal/mol lower than the CI energy of the Li_7 C_{3v} . It is worth pointing out that Li_7 C_{3v} has a form of a tetrahedron with three pyramids built on its three faces. It can be consequently considered as T_d -type geometry (which is optimal for Li_8) with one pyramid missing. Very symmetrical Li_7 D_{5h} and Li_8 T_d clusters have already structures formed from slightly deformed tetrahedrons.

(ii) The structure of the Li_{14} cluster is specially interesting since the elementary cell of the fcc lattice contains 14 centers. The optimization for this quite large system has been carried out with symmetry constraints. The lowest

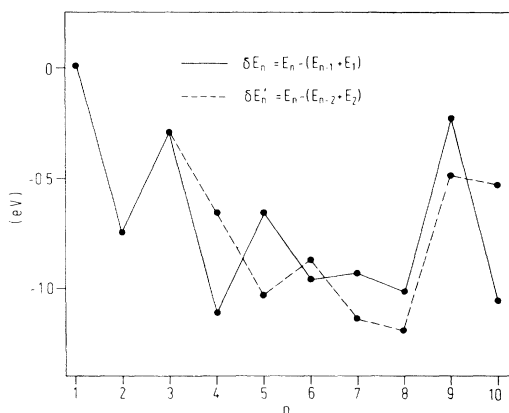


FIG. 8. Dissociation energies ΔE_n and ΔE_n^+ for channels $\text{Li}_n \rightarrow \text{Li}_{n-1} + \text{Li}$ and $\text{Li}_n \rightarrow \text{Li}_{n-2} + \text{Li}_2$. AO basis A .

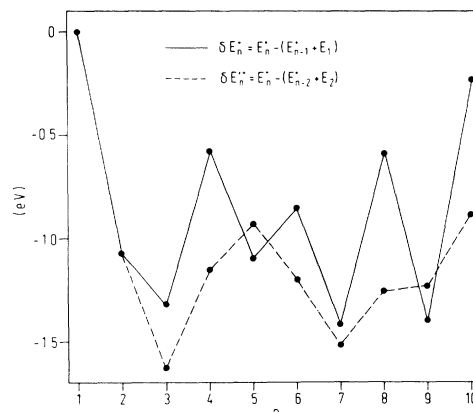


FIG. 9. Dissociation energies δE_n and δE_n^+ for channels $\text{Li}_n^+ \rightarrow \text{Li}_{n-1}^+ + \text{Li}$ and $\text{Li}_n^+ \rightarrow \text{Li}_{n-2}^+ + \text{Li}_2$. AO basis A .

HF and CI energies have been reached with C_{3v} symmetry constraints. The best energy search with the T_d symmetry constraints leads to the more symmetrical Li_{14} O_h geometry of the fcc elementary cell although both SCF and CI energies of the Li_{14} O_h are considerably higher than the corresponding energies of Li_{14} C_{3v} ($\Delta E_{\text{SCF}} = 10.87$, $\Delta E_{\text{CI}} = 15.12$ kcal/mol). The starting T_d geometry is a natural continuation of the construction principle leading to optimal Li_9 and Li_{10} structure: Six centers are added towards the middles of the six sides of

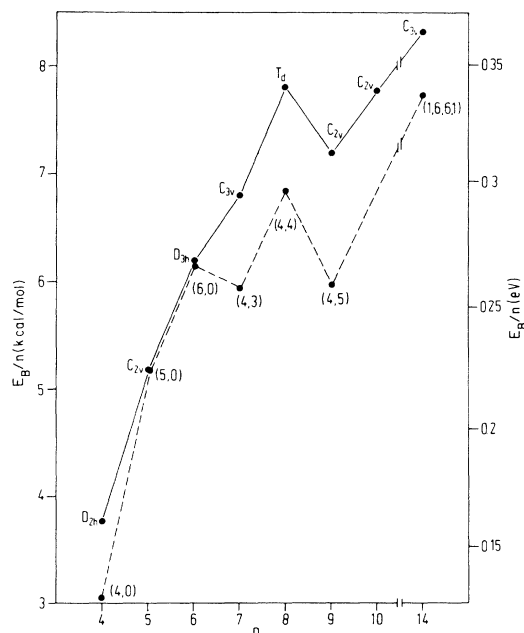


FIG. 10. Comparison of SCF binding energies per atom (AO basis A) for Li clusters with optimal SCF geometries, — (cf. Figs. 2 and 3), and optimal Li clusters which are sections of the fcc crystal lattice, — — —. The "fcc" clusters are labeled by the number in the first, second, etc., (111) plane.

the inner tetrahedron in $\text{Li}_8 T_d$. Interestingly enough, during the energy optimization this goes over to the O_h structure with one central octahedron, typical for the fcc lattice. Nevertheless, both structures are only saddle points on the energy hypersurface of Li_{14} . The more stable $\text{Li}_{14} C_{3v}$ isomer can be constructed by adding one $\text{Li}_7 C_{3v}$ on the top of another $\text{Li}_7 C_{3v}$. Since fairly large differences among interatomic distances are present, we do not assume that the saddle point corresponding to the $\text{Li}_{14} C_{3v}$ is near the optimal geometry. Further investigation is planned.

(4) The optimized geometries of charged clusters differ drastically from the shapes of neutral clusters with the same number of Li atoms. The heptamers Li_7 and Li_7^+ with the shape of pentagonal bipyramids and perhaps Li_{10} and Li_{10}^+ are the exceptions (for the decamers the optimal energy search has not been complete enough). The Li_9^+ which is very stable has a very compact symmetrical structure of a D_{4d} square antiprism.

(5) The calculated interatomic distances for the fairly stable planar as well as for the three-dimensional Li clusters do not substantially differ from the experimentally found interatomic distance in the fcc Li crystal (3.10 Å). Larger deviations in the interatomic distances with respect to the one in lattice are obtained for $\text{Li}_{10} C_{2v}$ and $\text{Li}_{14} C_{3v}$. The normal frequencies analysis shows that the $\text{Li}_{10} C_{2v}$ is a real SCF energy minimum which is not the case of $\text{Li}_{14} C_{3v}$. This circumstance can be brought in connection with the difficulty to continue the growing of the cluster with n larger than 8 simply by condensing the tetrahedra without any appreciable geometry deformation.

(6) The $\text{Li}_6^{2+} D_{2h}$ and $\text{Li}_8^{2+} C_s$ (cf. Fig. 11) corresponds to the real minima and are stable to the atomization with values 11.07 and 14.28 kcal/mol of the E_B^{2+}/n defined as

$$E_B^{2+}/n = [-E_n^{2+} + (n-2)E_1 + 2E_1^+]/n \quad (7)$$

$\text{Li}_6^{2+} D_{2h}$ can be considered as three Li_2 moieties with relative large mutual distances. The positive charge is spread over the whole system but the charges on the outer two Li dimers are larger. $\text{Li}_8^{2+} C_s$ has the form of a strongly deformed pentagonal bipyramid with one additional atom capping one of its faces. The maximal positive charge is situated at the capping center and at a most distant vertex of the deformed pentagon. In this way the Coulomb repulsion is minimized and the stability of these doubly charged clusters is achieved. The binding energies per atom (E_B^{2+}/n) for Li_6^{2+} and Li_8^{2+} are smaller than the quantities E_B^+/n for Li_3^+ and Li_4^+ , respectively. Consequently, the dissociation of Li_8^{2+} in two Li_4^+ as well as of Li_6^{2+} in two Li_3^+ is a favorable process but local minima for small doubly charged alkali-metal clusters do exist. It depends on the energy of Li_n^{2+} according to the Franck-Condon principle and experimental conditions if doubly charged cationic clusters are observable. The ideas of the Coulomb explosion^{32,33} must be completed in this way.

(7) The spin densities of clusters with odd number of electrons (cf. Fig. 12) are determined in the one-electron approximation by the form of the singly occupied MO's which is usually very similar to that of the NO's with

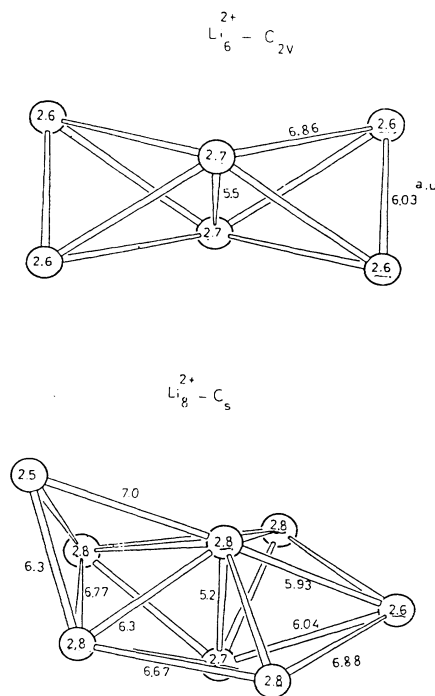


FIG. 11. The geometries and charge distributions in the Li_n^{2+} , the interatomic distances (a.u.), and Mulliken atomic charges (in the circles) are shown.

near to one derived from many-electron state occupation numbers (NOON's) functions.

The distribution of the spin density is useful for the interpretation of electron-spin-resonance experiments (cf. Refs. 49 and 50).

IV. REMARKS ON THE RELIABILITY OF THE METHOD USED

A question can be raised if the quantum-chemical methods employed are capable to predict truthfully, relatively small differences in the electronic energy of various cluster arrangements. First, one can doubt whether the AO basis set is large enough to permit the electron density to respond properly at very different arrangements of atomic nuclei. The comparison of the binding energy as function of the number of atoms obtained with the AO basis sets *A* (6,1/2,1) and *B* (10,4/3,2) shows that the basic results are quite independent of the basis used.⁵¹ Figure 13 documents this property very clearly. Since different AO basis sets can have different capability to describe the electronic structure of individual atoms and of molecules, a slightly modified quantity E_B'/n is introduced in Fig. 13.

$$E_B'/n = -E_n/n + E_2/2 = E_B/n - E_B/2 \quad (8)$$

which is shifted only by a constant quantity with respect to E_B/n .

The second problem is the truncation of the CI expansion. The reliability of the extrapolation procedure of the MRD-CI can be checked against the results provided by

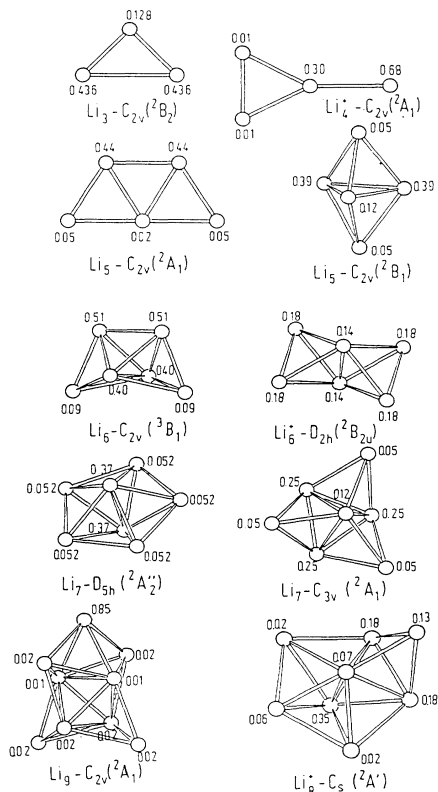


FIG. 12. Spin populations of Li clusters with odd numbers of electrons and the triplet state of Li_6 (C_{2v}).

the “direct CI” method^{38,39} which takes into account all singly and doubly excited configurations generated from the set of reference configurations. For example, the extrapolated MRD-CI values for the ground-state energy differ from the direct CI values by 3.15 kcal/mol and 3.13 kcal/mol for $\text{Li}_6 C_{2v}$ and $\text{Li}_6 C_{5v}$, respectively. The extrapolated MRD-CI and the direct CI yield the energy differences of 0.014 and 0.031 eV between practically degenerated isomers $\text{Li}_6 C_{5v}$ and $\text{Li}_6 C_{2v}$. It is, consequently, possible to assume that the extrapolation technique of the MRD-CI procedure yields reliable results in this context.

The calculated average binding energy for neutral lithium clusters Li_n with the number of Li atoms larger than 9, increases less rapidly than for the Li clusters with smaller nuclearity. Either this fact indicates a real difficulty to build up the clusters from only slightly deformed tetrahedra or it is due to the methodical deficiencies, e.g., to the increase of size consistency error. Evidently the freezing of the core MO’s if the correlation is taken into account for valence electrons artificially decreases the size consistency error for very small clusters but this error cannot be excluded for slightly larger clusters. Also, due to the frozen core the intershell correlation effects which can be important are neglected. For illustration, the E_B/n function derived from the SCF energies is shown in Fig. 10. The shape of the E_B/n function for $n > 9$ seems to be moderately steeper in the Hartree-Fock than in the MRD-CI calculations which can be due to the size con-

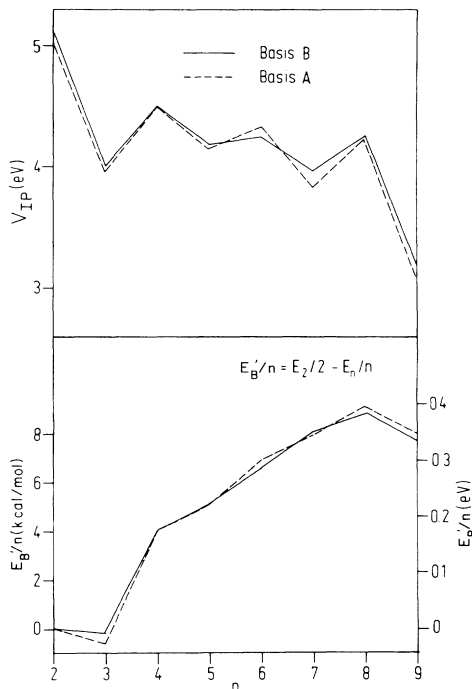


FIG. 13. Influence of the AO basis set on the results of the calculations. (a) Adiabatic ionization potentials calculated with the basis set A (6,1/2,1) and the basis set B (10,4/3,2). (b) Binding energy per atom, E_B'/n [cf. Eq. (8)], determined with the basis sets A and B .

sistency error of the truncated CI method.

In order to diminish these uncertainties the CI energies with Davidson corrections are used for constructing E_B/n and E_B^+/n as well as for evaluation of Δ^2/E_n and $\Delta^2 E_n^+$ (Figs. 6 and 7).

V. SOME OTHER IMPORTANT PROPERTIES OF THE ELECTRONIC STRUCTURES OF SMALL LI CLUSTERS WITH OPTIMAL GEOMETRY

The other electronic states of cluster arrangements corresponding to the minima of the ground-state energy hypersurface have very often distinctly higher energies than their ground states. This property of the optimal cluster geometries is particularly remarkable, since for the other (unstable) cluster shapes very small energy differences between the ground and excited states frequently exist. For instance, the Li clusters which are three-dimensional parts of the fcc or bcc crystal lattice exhibit very often biradicaloid properties (two unpaired electrons localized in different parts of the systems) for which it is typical that the lowest singlet and triplet states are nearly degenerated.

The Mulliken population analysis for the optimal Li_n clusters has been carried out using the natural orbitals obtained from the CI procedure (Fig. 14). The centers with larger coordination number exhibit larger electron density than the centers with smaller number of nearest neighbors. The differences between the Mulliken atomic

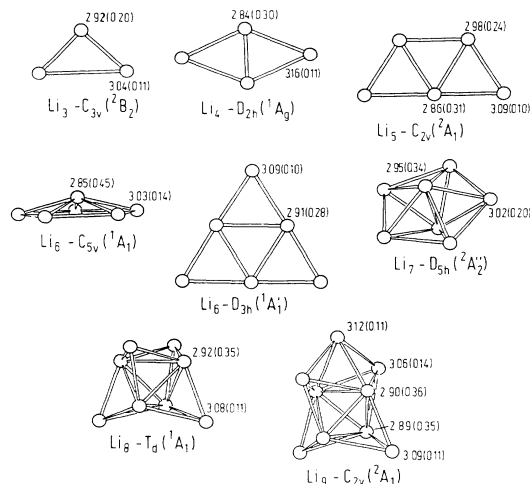


FIG. 14. The Mulliken atomic charges and populations of the p -type AO basis set functions (in the bracket) for some neutral Li clusters.

charges are quite small mainly for very stable Li_6 , Li_7 , and Li_8 . For example, the centers at the inner tetrahedron of $\text{Li}_8 T_d$ with six nearest neighbors have positive charge $+0.08$ a.u., whereas the centers at the apices of the outer pyramids with three nearest neighbors have negative charge -0.08 a.u.; the two apical atoms of the pentagonal bipyramid $\text{Li}_7 D_{5h}$ with five nearest neighbors carry a positive charge of 0.05 a.u. and the five centers on the pentagon periphery with four nearest neighbors has a negative charge of only -0.02 a.u.

The Mulliken atomic populations of electrons occupying p -type basis functions increase generally with the coordination number and reach the values around 0.3 a.u. This tendency shows strikingly the importance of participation of the p -type atomic orbitals. Using the concept of mixing of s and p bands in the theory of sp metals in the

solid-states physics one can interpret this systematical participation of p -AO's as a sign of metallic character.

Since the Mulliken population analysis contains some arbitrary features the one-electron density plots as well as the difference one-electron densities (DOD's) have been determined for most interesting neutral Li clusters. The difference one-electron density, defined as the difference between one-electron density of the cluster and the superposition of the one-electron density of the noninteracting atoms, can give sometimes spurious results if rehybridization due to the interaction is important. Such a rehybridization does not take place in the Li clusters and, therefore, it is possible to interpret the regions with positive and negative values of the DOD as bonding and antibonding regions, respectively. Figure 15 shows some characteristic cuts of the DOD's maps for Li_5 - Li_9 .

In general, the one-electron densities are clearly delocalized but the regions with higher and smaller electron densities are very distinguishable. Consequently, the actual electron distribution is quite far from being homogeneous as it is assumed in the jellium model. On the other hand, both the one-electron density maps (Fig. 16) and the DOD maps (Fig. 15) do not generally show the regions of charge accumulation and enhanced regions of DOD, respectively, between two centers. It is possible to assume that there is no tendency to build either localized or delocalized two-center bonds.

Two-dimensional Li_5 and Li_6 clusters exhibit the enhanced DOD values in the triangular regions similarly as the rhombic Li_4 cluster does. These triangular regions with enhanced DOD values can be interpreted as due to the three center "bonds" and they are typical for the DOD maps of the planar Li_6 and the planar Li_5 . In the case of Li_5 there are two triangular regions and one finds only one region with enhanced DOD values between two centers on the shorter side of the trapezoid. In the three-dimensional Li_7 cluster a region of positive DOD values has a form of a ring with the five Li centers at the penta-

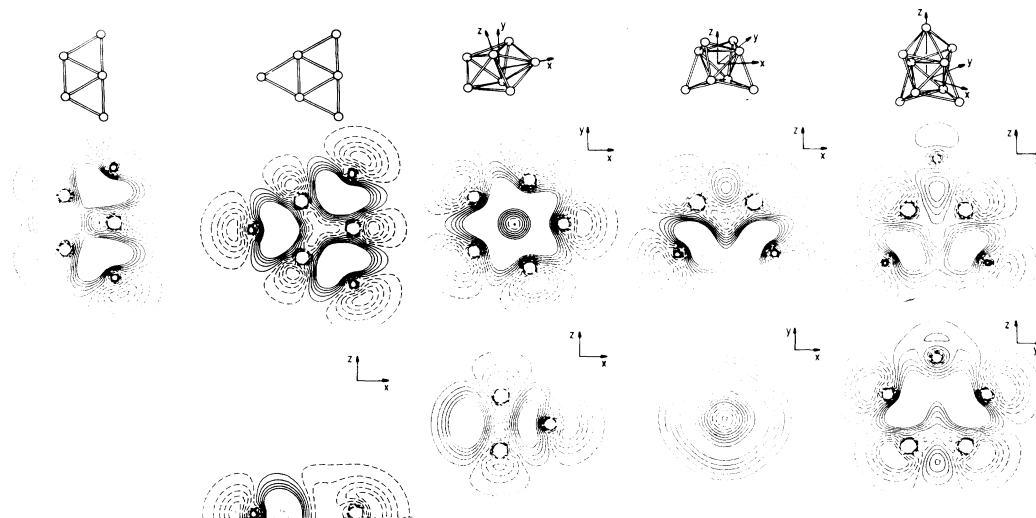


FIG. 15. Difference one-electron density (DOD) maps for Li_n , $n=5-9$. The appropriate coordinate axes define the planes of the cuts. The lines of constant positive, —, and negative, - - -, values of DOD are shown.

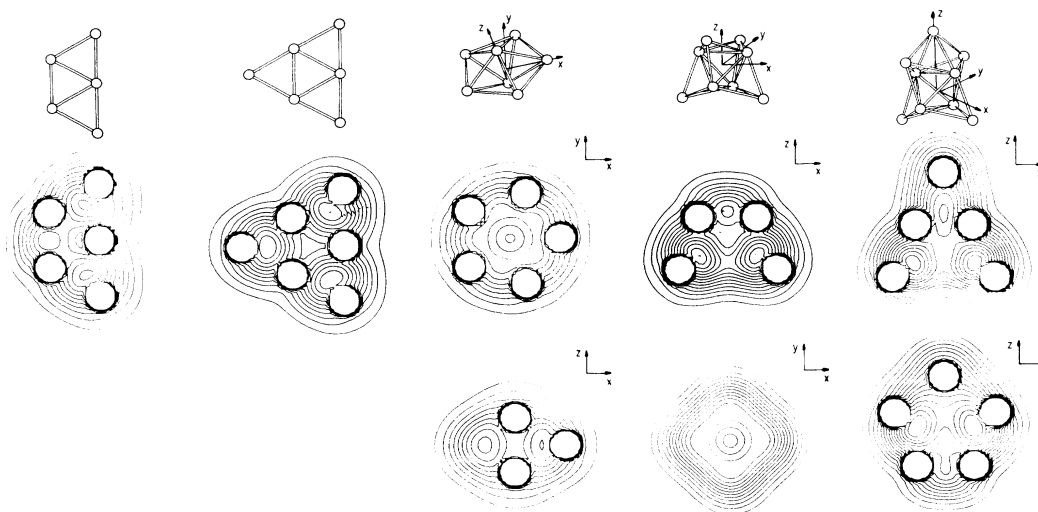


FIG. 16. Total one-electron densities maps derived from the correlated MRD-CI wave functions (AO basis set *A*) for Li_n , $n = 5-9$. The appropriate coordinate axes define the planes of the cuts.

gon lying outside the ring. In the very symmetrical Li_8 T_d the region of the positive DOD values has a form of a nearly spheric shell with the atoms of the inner tetrahedron inside the shell and the apical atoms of the outer pyramids outside the shell. The spheric shell of the large DOD has four “windows” opposite to the Li atoms of the inner tetrahedron.

A tendency towards larger electron delocalization with increasing nuclearity can be observed but regions with low electron density still exist also for larger clusters. It is possible, therefore, to conjecture that in very large clusters delocalization is characteristic of their metallic character but the electron distribution is far from being homogeneous (see Fig. 16).

The calculated vertical and adiabatic ionization potentials of Li_n clusters are shown in Fig. 17. The ionization potential, a generally decreasing function of the increasing cluster size with some superimposed oscillations in values,

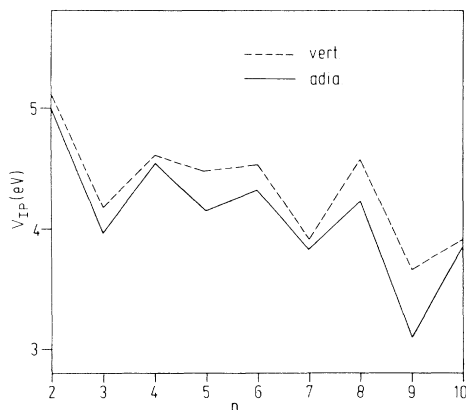


FIG. 17. Vertical and adiabatic ionization potential of Li clusters. MRD-CI calculations with the AO basis set *A* and Davidson corrections.

exhibits maxima for clusters with even number of atoms. The quantitative behavior of the vertical and adiabatic ionization potentials is very similar. The oscillations in values are relatively moderate in the interval between four and eight Li atoms. A comparison of the adiabatic ionization potentials calculated with the AO basis sets (*A* and *B*) (Fig. 13) shows that the oscillations in values are slightly smaller for the larger AO basis set.

VI. DISCUSSION

The apparent similarity in the properties of clusters built from different alkali-metal atoms makes a broader discussion possible and advisable. The optimal geometry and energy search study for clusters carried out with all-electron as well as with effective core potential (pseudopotential) procedure²⁰ yields analogous properties as the study on Li clusters. Consequently, the comparison of the theoretical results for different alkali-metal clusters is meaningful as well as the qualitative comparison of the present theoretical results with the experiments for Na and K clusters.

The optimized geometries of lithium clusters conform with the four rules mentioned in the Introduction (influences of the compactness, of the nodal properties of MO's or NO's, of the topology, and of the polarization functions). The geometrical structures with highest symmetries are unfavorable for clusters with insufficient number of electrons to fill up the degenerated one-electron levels. The occupation numbers of the natural orbitals with one nodal plane for the planar Li_6 D_{3h} are doubly degenerated, whereas the occupation numbers of the similar “*p*-type”-natural orbitals for Li_8 T_d are triply degenerated. This behavior is fully determined by the irreducible representation of the respective symmetry groups, of course. The “highest” natural orbital (it means the NO with the occupation number near to one) for the Li_9 C_{2v} exhibits two nodal planes and can be characterized as having the *d* character. In this way it is possible to under-

stand the occurrence of the planar structures for the very small clusters and the preference of the shapes which are constructed from tetrahedral units for clusters with a nuclearity larger than five. It is worthwhile to mention the connection of the pentagonal-type structures with the structures built from appropriate tetrahedra. Figure 18 shows schematically the connection between both kinds of geometries which can sometimes go over from one type to another by a relatively small deformation of the pyramids from which the arrangement is built.

However, the above-mentioned cluster stability rules very often are not capable of deciding which, among few candidates fulfilling some basic requirements, is the most stable one. For example, the optimal forms of Li_8 and Li_8^+ obtained with our procedure differ from the most stable shapes predicted by Martins *et al.* for Na_8 and Na_8^+ .²⁰ If the geometry given in Fig. 4 of Ref. 20 has been used as the starting point in the best geometry search, the local minimum with the T_d equilibrium geometry has been reached in the present study. The planar Li_4 and Li_6 structures obtained by McAdon and Goddard III (Refs. 24 and 25) agree in principle with optimal planar structures of Li_4 and Li_6 of the present work. However, our optimal energy search for other planar geometries proposed in Ref. 25 yields higher energies than for three-dimensional geometries which do not have the optimum tetrahedral structures.²⁵ The optimal Li_6 triplet has the C_{2v} form but its SCF energy is higher than the SCF energy of the singlet 1A_1 state of the $\text{Li}_6 D_{3h}$. Its CI energy is higher than CI energies of the 1A_1 state of $\text{Li}_6 C_{5v}$ and 1A_1 state of $\text{Li}_6 D_{3h}$ which contradicts the results of Rao and Jena obtained with unrestricted Hartree-Fock (UHF) procedure.⁴⁸ The topological arguments take into account only the influence of the overlapping AO networks and they do not consider other important factors which can destabilize the alkali-metal cluster with a given topology. The simple Hückel calculations give for very small alkali-metal clusters right topologies but they cannot explain the nature of the bonds in the Li clusters.²⁹ Proof of this circumstance is the instability of arbitrary Li_4 clusters towards the dissociation in two Li_2 moieties if only *s* AO's are considered on each Li atom (cf. Fig. 1).

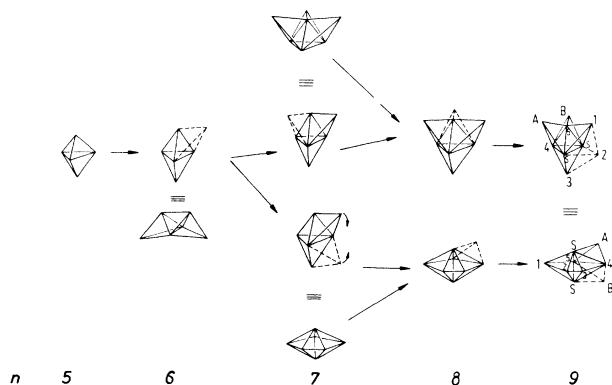


FIG. 18. Schematic depiction of the relation between tetrahedral cluster geometries and cluster forms including pentagonal bipyramids as subunits.

It is, therefore, not at all surprising that the predictions of the present paper do not agree with the results of the Hückel theory for Li_8 and Li_9 as well as for Li_n^+ with $n > 3$. Generally speaking, already the results on Li_n with $n > 8$ differ when different theoretical approaches are employed.

The experiments on clusters allow at the time being only very indirect information on the cluster stability. The procedure for identifying the clusters in the recording devices leads to processes which can be very complicated and can include, according to the circumstances, not only ionization but also dissociation or far-reaching destruction of the originally created clusters. According to Brechignac^{52,53} the energy amount of ionizing photons can be either only sufficient for ionization or it can allow the destruction of clusters of given size. Consequently, it is possible to estimate roughly if the abundances of clusters are mainly determined by original abundance of neutral or—on the contrary—of ionized clusters obtained during the cluster detection. In view of the complex origin of the measured data it can be taken as a very satisfactory fact that the abundances obtained by Schumacher on Na clusters⁵⁴ and by Brechignac on K clusters⁵³ can be interpreted in full agreement with our plots of the quantities Δ^2E and Δ^2E^+ for neutral and ionized clusters, respectively. Indeed, in experiments where the energy of photons is not sufficient for dissociation, the maxima for nuclearities 4 and 8 have been found. On the contrary, in experiments where the ionized clusters should be the determining factor, the dominant maxima for $n=3$ and $n=9$ and less dominant maxima for $n=5$ and 7 are found. If the above-mentioned interpretation of experiments can be considered as valid, the agreement between the experiments and the theory is good.

It is necessary to emphasize that in addition to the high stabilities of the alkali-metal clusters with “closed electron shell” arrangements our predictions and experimental predictions of the additional quite stable cluster sizes follow from the formulated general rules on the cluster stability. The neutral rhombic tetramer is the most striking example of the stability which also seems to be supported by some experiments.

The present theory predicts satisfactorily the general trend of the dependence of the ionization potential upon the cluster size as well as the spin-density distribution in the open-shell alkali-metal clusters.

VII. CONCLUSIONS

The quantum-chemical methods which take the electron-correlation effects into consideration yield an explanation of many characteristic properties of small alkali-metal clusters from a unified point of view. This approach includes in a natural way the features of the simple electron shell model but give additional aspects and results which can be very helpful for the full understanding of the cluster science.

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