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# Evolution of the electronic and structural properties of microclusters

B. K. Rao, S. N. Khanna, and P. Jena
*Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284*

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The equilibrium geometries of the ground state of neutral and ionized clusters of Li, Be, Mg, and C atoms have been obtained by minimizing the total energies of these clusters with respect to all independent bond lengths, bond angles, and spin structures. Our method is based on the all-electron self-consistent field–linear combination of atomic orbitals–molecular orbital (SCF-LCAO-MO) method. The exchange interaction is treated at the unrestricted Hartree-Fock level and the correlation contribution is included by using the perturbative Möller-Plesset scheme and configuration interaction. The equilibrium geometries of $\mathrm{Li}_N$ clusters for $1 < N < 6$ are planar. $\mathrm{Be}_3$ and $\mathrm{Mg}_3$ clusters are in the shape of an equilateral triangle whereas $\mathrm{Be}_4$ and $\mathrm{Mg}_4$ are in the shape of a perfect tetrahedron. $\mathrm{C}_N$ clusters for $N < 3$ are linear, but $\mathrm{C}_4$ is a rhombus contrary to earlier predictions. It is demonstrated that the ground-state geometries of both neutral and ionized clusters of simple metals, including their preferred spin-multiplet structures, can be understood in terms of a simple bonding-antibonding picture. The "magic numbers" in the mass spectra are discussed in terms of the electronic structure of clusters. It is shown that the magic numbers associated with the initially "neutral" or initially "ionized" clusters can be different and that the fragmentation of clusters during the ionization process can add to the ambiguity in the interpretation of magic numbers. Finally, we elaborate on the relationship between equilibrium geometries and preferred spin-multiplet structures by confining our discussion to $\mathrm{Li}_4$ and $\mathrm{Na}_4$ clusters.

## I. INTRODUCTION

The nature of the evolution of crystals from agglomeration of atoms has been a topic of interest for many years. Researchers have always wondered how the various structural and electronic properties change as the crystal grows and how many atoms it takes to reproduce a crystal. There has never been a satisfying answer because various properties of the bulk state do not always evolve in the same manner. It is only recently that these questions have taken on a new meaning. This is largely due to the effort of experimentalists who have been able to produce and analyze, in the last decade, clusters of alkali-metal,[1-3] rare-gas,[4] and covalently bonded[5,6] atoms ranging from two to a few hundred atoms per cluster. They have studied a variety of properties such as "magic numbers"[1] in the mass spectra, near-neighbor distances,[7] ionization potentials,[2,8] binding and dissociation energies, polarizabilities,[9] and magnetic properties.[10] These studies reveal a nonmonotonic dependence of these properties on cluster size. Many properties do not even approach the bulk value even when the cluster contains hundreds of atoms. While it is clear that even "large" clusters cannot be considered as fragments of the bulk phase, it does not illustrate how the structural evolution takes place. For this, one must start at the very beginning from a single atom and then add one atom after another to see how the geometries and properties change.

This is where we begin in the present paper. Our approach is a theoretical one where we calculate the equilibrium geometries of clusters consisting of up to seven atoms per cluster of both metallic and covalently bonded elements by finding the minimum energy configuration. Unfortunately, the geometries we have obtained cannot be verified by experiments due to their extremely small size. However, electronic properties calculated for these equilibrium structures can be compared with experiment. A consistent agreement between experimental and theoretical quantities, can, therefore, be viewed as evidence for the accuracy of the calculated geometries.

From the computed geometries, one can see how larger clusters evolve from smaller ones. By identifying the fragmented portion of bulk crystals with appropriate cluster geometry, one can also illustrate the preferred channels for crystal growth. In Sec. II we outline very briefly the numerical procedure adopted in this paper. The equilibrium geometries of clusters studied and their interpretation in terms of a bonding-antibonding picture are described in Sec. III. The origin of the magic numbers in the mass spectra and the difficulties in the experimental interpretation are discussed in Sec. IV. The evolution of extended structure is presented in Sec. V. Section VI is devoted to a discussion of the spin multiplicity of clusters as determined by the dimensionality of the clusters. The results are summarized in Sec. VII.

## II. NUMERICAL PROCEDURE

For details of the numerical procedure employed in this paper, we refer the reader to a recent paper by Rao and Jena,[11] and the work of Hehre *et al.*[12] In the following we only give enough details necessary for the reader to follow smoothly the remaining portion of the paper. Our method is based on the self-consistent field–linear combination of atomic orbitals–molecular orbital (SCF-LCAO-MO) method. The exchange interaction is treated with the unrestricted-Hartree-Fock (UHF) approximation. The correlation contribution to the total energy is calculated using two different levels of approximations. The first one involves a perturbative treatment of pair excitations of valence and core electrons whereas the other uses the configuration interaction (CI) of all single and double excitations. The molecular orbitals are expressed as a linear combination of atomic orbitals which are represented by contracted Gaussian orbitals. For Li we have used the well-known STO-6G basis set[12] for 1*s*, 2*s*, and 2*p* functions. For Be and C we have used the split-valence 6-31G functions, whereas for Mg, STO-6G* has been employed. The reader is referred to the article of Rao and Jena[11] for a detailed comparison of the results of small clusters obtained from various basis sets.

For geometry optimization, we start with a cluster of atoms located at arbitrary positions. The total energy of the cluster is calculated self-consistently. The gradient force at every atom site is then evaluated. The atoms are moved along the direction of the forces and the above process is repeated until the force at every atom site vanishes (the threshold for this was set at 0.0003 hartree/a.u. in our calculations). Care is also taken to avoid saddle points on the energy surface. These procedures were repeated for all clusters (neutral or ionized) studied here.

## III. EQUILIBRIUM GEOMETRIES

### A. Based upon self-consistent calculations

The optimized geometries for clusters of neutral Li, Be, Mg, and C atoms are presented in Fig. 1. The results on Li clusters up to $N=5$ have been discussed fully elsewhere and are presented here only for the sake of completeness. Clusters of $\mathrm{Li}_N$ ($N \leq 5$), $\mathrm{Be}_3$, $\mathrm{Mg}_3$, and $\mathrm{C}_N$ ($N \leq 4$) are all planar. Local-density calculations[13] of Na clusters predict planar geometries for $N \leq 5$ while Al clusters[14] for $N > 3$ possess three-dimensional geometries. The spins of these clusters for the ground-state configurations are also given in Fig. 1. Unlike the alkali clusters, $\mathrm{Be}_4$ and $\mathrm{Mg}_4$ have a three-dimensional structure in the form of a perfect tetrahedron. $\mathrm{C}_4$, however, is planar and has a rhombic shape, while $\mathrm{C}_3$ is linear. It is worth noting that while the ground state of $\mathrm{C}_4$ is a spin-singlet rhombus, it is only 0.32 eV below the spin-triplet linear configuration. This is in agreement with the result of Whiteside *et al.*,[15] but is in contradiction with earlier speculation[16] that $\mathrm{C}_N$ ($N < 8$) would be linear. Recent calculations of Raghavachari and Logovinski[15] on carbon clusters for $N > 4$ show that odd-numbered clusters have linear geometry while the structure of even-numbered clusters are cyclic. In the following we provide a simple description based upon the bonding-antibonding picture which illustrates the role of electronic structure on the ground-state geometries of simple metal clusters. This cannot, unfortunately, be carried over to describe $\mathrm{C}_N$ cluster geometries where the bonding is strongly covalent.

### B. Interpretation in terms of electronic structure

Recently, an interpretation[13,17] based on the angular character of the atomiclike orbitals ($s, p_x, p_y, p_z, \ldots$) has been put forth to understand the planar structure of the alkali-atom clusters. This, in essence, is related to the electronic shell model[1] where one treats the valence electrons only and fills the energy levels successively. This can also be reinterpreted by noticing the bonding-antibonding characters[18] of the molecular orbitals (MO's) of the valence electrons. For this purposes, one can construct MO's by linear combination of atomic orbitals. In Table I, such a set of MO's is given. This particular combination is not unique. This is provided only as an example.

In the case of positively charged alkali-atom trimers (e.g., $\mathrm{Li}_3^+$, $\mathrm{Na}_3^+$), there are two valence electrons. Therefore, only $\psi_1$ will be occupied. This is a bonding orbital and is obviously spherically symmetric. This is comparable to the 1*s* state of the shell model.[1] The distribution of the atoms should, therefore, be symmetric, i.e., in

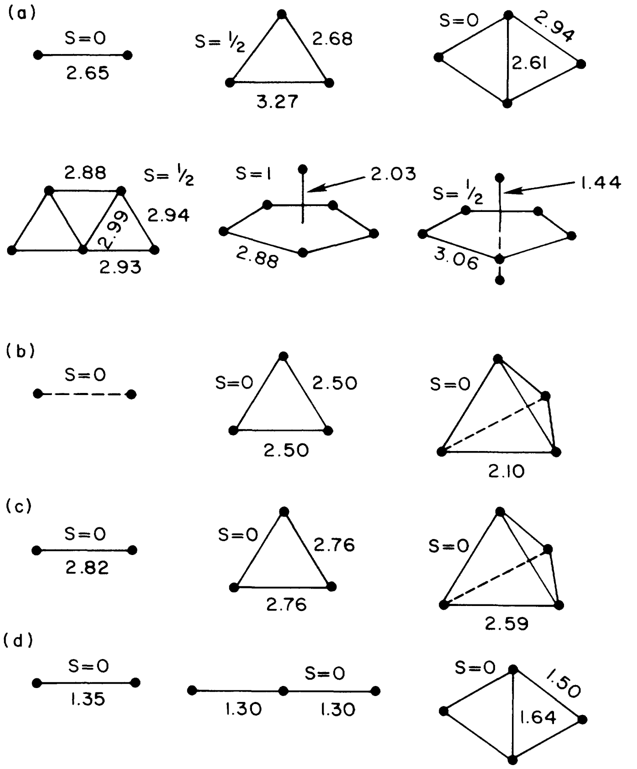


FIG. 1. Optimized geometries and spin multiplicity of neutral (a) Li, (b) Be, (c) Mg, and (d) C clusters. The bond lengths are given in angstroms. $\mathrm{Be}_2$ is shown with dashes as it is not bound.

TABLE I. Mutually orthogonal molecular orbitals for clusters containing three and four valence electrons. $\phi$'s correspond to the valence-electron wave function of the atoms.

| $N=3$ | $N=4$ |
|---|---|
| $\psi_1=\phi_A+\phi_B+\phi_C$ | $\psi_1=\phi_A+\phi_B+\phi_C+\phi_D$ |
| $\psi_2=(\phi_B+\phi_A)-(\phi_C+\phi_A)$ | $\psi_2=\phi_B-\phi_D$ |
| $\psi_3=(\phi_B-\phi_A)+(\phi_C-\phi_A)$ | $\psi_3=\phi_A-\phi_C$ |
| | $\psi_4=(\phi_A+\phi_C)-(\phi_B+\phi_D)$ |

an equilateral triangle. Our SCF calculations of $Li_3{}^+$ and the calculations of Martins *et al.*[13] on $Na_3{}^+$ agree with this completely.

For the neutral trimers of alkali atoms, either $\psi_2$ or $\psi_3$ should be singly occupied by the third electrons. These orbitals are antibonding in nature. In the case of $\psi_2$, atoms *AB* and *AC* are bonded, while there is antibonding between *B* and *C*. Therefore, the apex of the triangular configuration should *increase* from 60°. On the other hand, if $\psi_3$ is occupied, atoms *B* and *C* are antibonded and there is bonding between atoms *AB* and *AC*. This will *decrease* the apex angle from 60°. These two situations show up for $Li_3$ in our SCF calculations when we plot (see Fig. 2) the energy of $Li_3$ as a function of the apex angle of the triangle. For $\theta=53°$ and 72° there are distinct minima. Similar behavior has been obtained by Martins *et al.*[13] for $Na_3$ clusters. The valence-electron densities for these two angles are given in Fig. 3 for $Li_3$ clusters. The bonding and antibonding among the atoms are clearly noticeable. One can, of course, hybridize the *s* and *p* states (here $\psi_1$ and $\psi_2$ or $\psi_3$) and get perfect symmetry which would lead to an equilateral triangle. However, the above explanation has implicitly broken the symmetry by removing the degeneracy possible in hybridization and consequently the Jahn-Teller distortion of the triangle occurs.

A similar exercise,[18] when done by using the orbitals presented in Table I for tetramers, shows that spin-triplet $Li_4$ is a tetrahedron while the spin singlet is a planar rhombus. These have been observed in our *ab initio* calculations[11] and also by Koutecky and Fantucci.[13]

## IV. MAGIC NUMBERS

One of the most striking features in the mass spectra of small clusters has been the existence of conspicuous peaks in its intensity distribution as a function of number of atoms in the clusters. For example, in alkali-metal systems, clusters containing 2, 8, 20, 40,. . . atoms are more abundant than those with adjoining sizes. The origin of these "magic numbers" (which are analogous to those found in nuclear shell structure) has been recently associated[1] with the filling of the electronic shells in metal clusters. For a simple physical understanding of the above shell structure based upon the ground-state energetics of the clusters, assume that the effective potential experienced by the valence electrons of a cluster due to the positive ion cores is spherically symmetric. For such a potential, orbital angular momentum is a good quantum number and the energy levels of the electrons in the cluster can be characterized by their *s*,*p*,*d*,. . . characters. In Fig. 4(a) we give the schematic plot of a few valence-electron energy levels. For a cluster containing three valence electrons, for example, the third electron has to go to the *p*

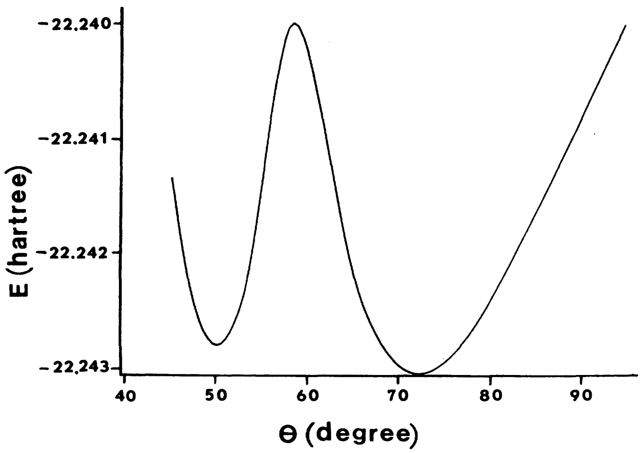
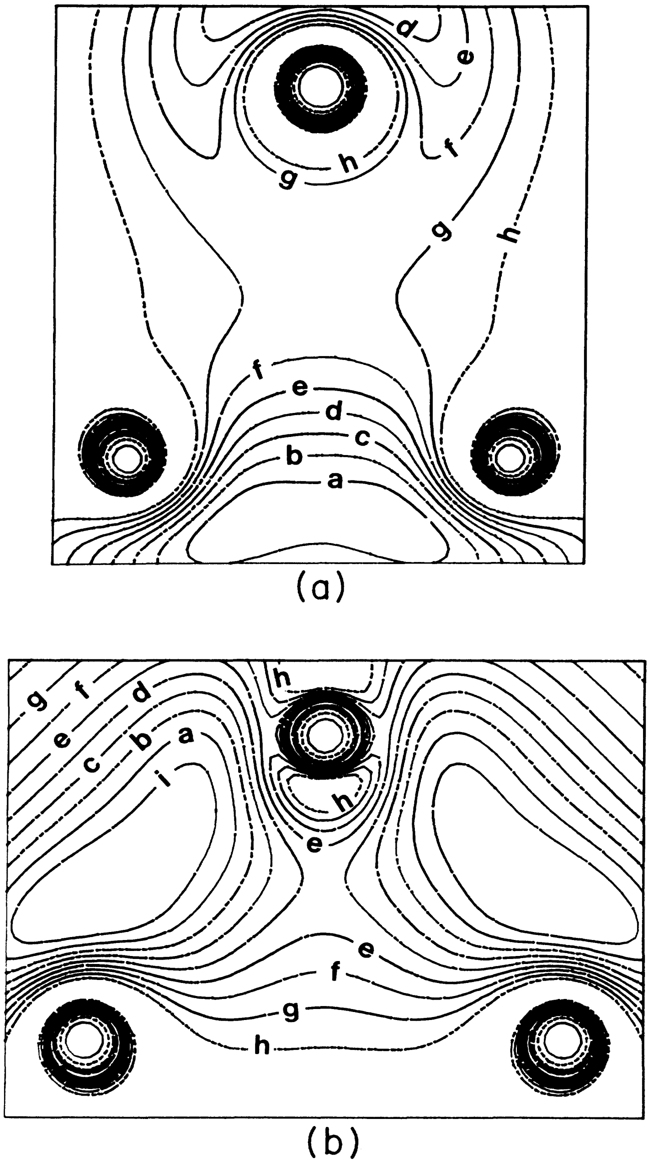


FIG. 2. Variation of energy as a function of the apex angle for $Li_3$ clusters.



(a)

(b)

FIG. 3. Valence-electron charge-density distributions for isomeric structures of $Li_3$. (a) $\theta=53°$, (b) $\theta=72°$. The density values are marked in atomic units as *a*, 0.009; *b*, 0.008; *c*, 0.007; *d*, 0.006; *e*, 0.005; *f*, 0.004; *g*, 0.003; *h*, 0.002; and *i*, 0.01, respectively.

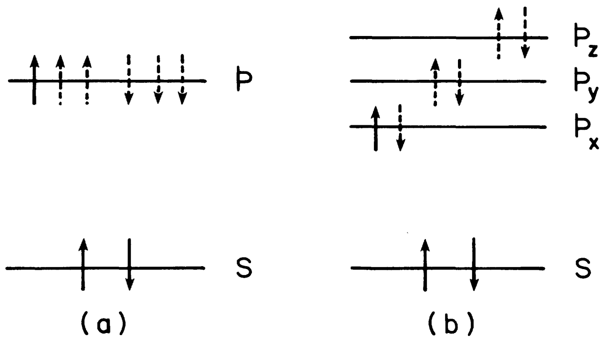


FIG. 4. Schematic plot of energy levels in clusters with (a) spherical effective potential and (b) nonspherical potential. Occupied orbitals are indicated by solid arrows. Other possible occupations are shown as dashed arrows.

shell. Since this promotion needs additional energy as is evident from the gap, a trimer is less likely to form than a dimer—giving rise to $N=2$ as a magic number. Similarly, clusters with $N=8,20,\ldots$ can be understood to exhibit increased abundances.

Experimentally, however, additional features have been seen in the mass spectra that cannot be explained by the above simple analysis. One such observation is the odd-even alternation in the cluster stability: the even-neutral alkali clusters[3] are more stable than odd ones. Similar odd-even alternations have been observed[19] in noble-metal clusters. In charged clusters, the odd ones are more stable than even ones. To understand the origin of this odd-even alternation, we must realize that real clusters, especially when they are small, do not possess spherical symmetry. Consequently, the degeneracies in the $p$ shell, as shown in Fig. 4(a), will be lifted. We show in Fig. 4(b) the energy levels for clusters that do not possess spherical symmetry. When a $p$ shell is split into $p_x$-, $p_y$-, and $p_z$-like levels, excess energies are necessary only when one fills a subshell and has to occupy the next higher subshell. Thus, energetically, clusters containing an odd number of electrons would be less likely to form than even ones. This description applies to clusters independent of their charge state and atomic composition. The experimental observation of cluster stability of neutral and charged clusters agrees with this finding and one can state, that based upon a molecular energy-level picture, clusters containing an even number of valence electrons would show increased stability over odd ones. For the purpose of illustration, we give in Fig. 5 the SCF molecular energy levels of valence electrons of neutral clusters.

The odd-even alternation can be studied in more detail in terms of the energetics of formation. For this, we define the energy needed to add an extra atom to an existing cluster by

$$\Delta E_N = E_N - E_{N-1} - E_1 \ . \tag{1}$$

Thus a minimum in $\Delta E_N$ as a function of $N$ would indicate the likelihood of that cluster formation being preferred over its immediate neighbors. In Fig. 6 we plot $\Delta E_N$ for neutral $\mathrm{Li}_N$ and $\mathrm{Na}_N$ clusters. The energies for $\mathrm{Na}_N$ clusters are taken from the work of Martins *et al.*[13] The minima for even clusters are consistent not only with the increased abundance observed experimentally but also with the analysis based upon the successive filling of the MO's as previously discussed. The apparent discrepancy between the behavior of $\Delta E_N$ for $\mathrm{Li}_6$ and $\mathrm{Na}_6$ is due to

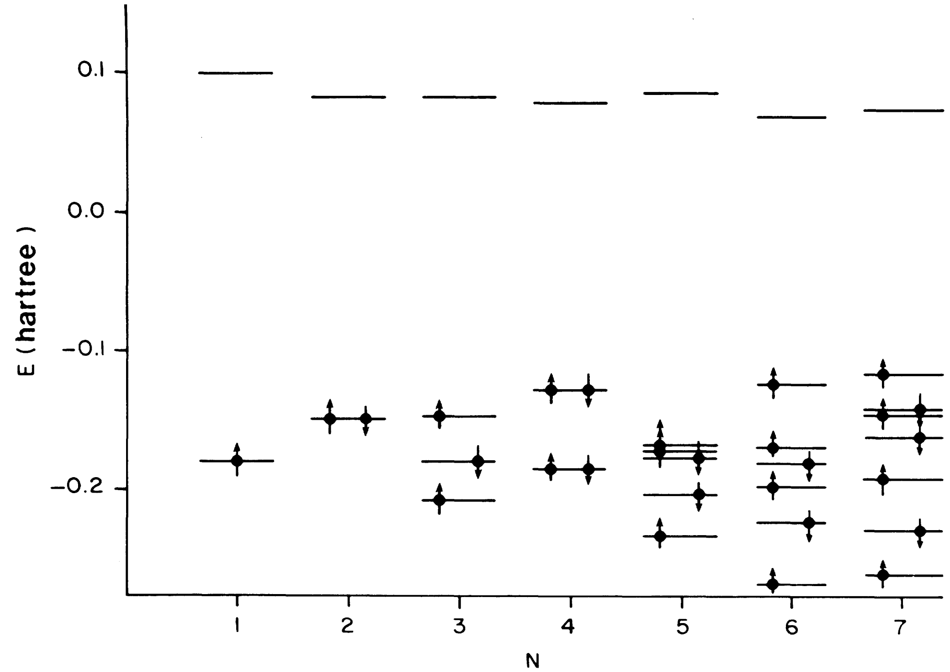


FIG. 5. SCF molecular energy levels of valence electrons and their occupations of neutral $\mathrm{Li}_N$ clusters in the ground state. The nearest unoccupied states are also shown.

the fact that Martins *et al.*[13] had assumed the spin state of $Na_6$ to be singlet. It is, however, found that $Li_6$ in triplet configurations has lower energy. When this is taken into account, $Li_6$ is found to be more stable than its neighbors. This aspect is discussed in more detail in Sec. VI.

In Fig. 7 we plot

$$\Delta E_N^+ = E_N^+ - E_{N-1}^+ - E_1 \tag{2}$$

as a function of $N$. Here, again, clusters containing an even number of valence electrons ($N$ odd) exhibit increased stability. This is consistent with the qualitative description given earlier.

We now consider the photofragmentation process. In a typical experiment, clusters born in a nozzle expansion of the gas are ionized. During this process, the ionized cluster of $N$ atoms can fragment into smaller species consisting of ionized $M$-atom cluster and neutral $(N-M)$-atom cluster. The energy needed for this fragmentation can be written as

$$\Delta E_{NM}^+ = E_N^+ - (E_M^+ + E_{N-M}), \quad N > M \geq 1 \ . \tag{3}$$

An analysis[20] of $\Delta E_{NM}$ for alkali clusters indicates that the predominant channel produces $Li_3{}^+$ and $Na_3{}^+$ clusters. Thus, if significant fractions of ionized clusters photofragment, this could lead to a population of trimers that could compete with the preferred formation of dimers in the fusion process. Consequently, the interpretation of magic numbers can be more complicated.

Finally, we consider the relative stability of clusters once they are formed. For example, a $Li_2$ cluster can accept a Li atom to transform to $Li_3$. In a similar way, three Li atoms can nucleate to form $Li_3$. If the former process is energetically less favorable than the latter one, the process would tend to leave $Li_2$'s alone for growing. The energy gain in forming $Li_3$ and $Na_3$ in either of the above two channels is defined by

$$\Delta E = 3E_1 - E_3 \ , \tag{4a}$$

$$\Delta E = (E_1 + E_2) - E_3 \ . \tag{4b}$$

From our calculated energies, we find the process in Eq. (4a) to be more likely than in Eq. (4b) for both Li and Na clusters—clearly establishing the dimers to be among the magic numbers.

In a recent paper, Ishii *et al.*[21] have made similar observations about alkali-atom clusters using a spherical jellium model. They have used a spin-polarized local-density-functional approach and have included the effect of distortion of the jellium sphere. This removes the energy gain observed for half-filled shells[17] due to exchange and predicts high stability for clusters with a shell-closing number of valence electrons.

To study the abundances of polyvalent clusters, we plot in Fig. 8 $\Delta E_N$ for $Be_N$, $Mg_N$, and $C_N$ clusters. Unlike in the case of alkali clusters, we find $C_3$ to be a magic-number cluster. $Be_4$ and $Mg_4$ both show possibilities of being magic numbers. No experiments are available for $Be_N$ and $Mg_N$ clusters to verify our result. However, our result for $C_N$ clusters are in agreement with experiment.[5]

## V. EVOLUTION OF EXTENDED STRUCTURES

The evolution of crystals from clusters can be studied by observing the variation of the nearest-neighbor distance. Using the geometries, we have calculated the root-

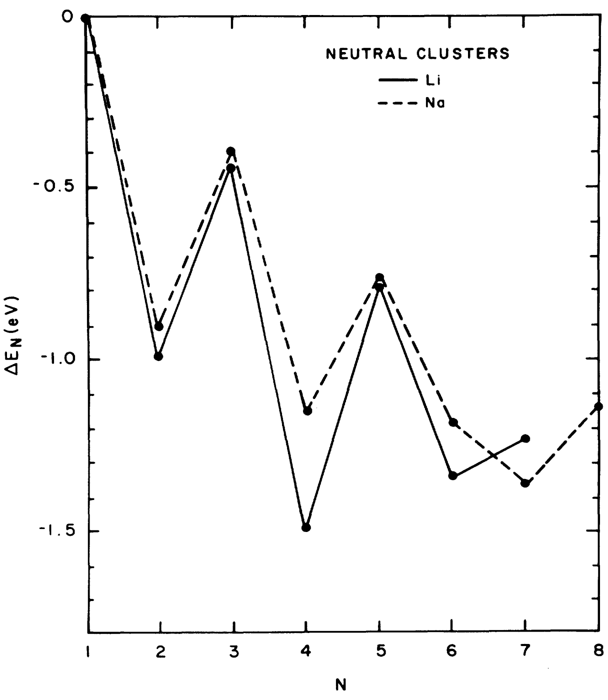


FIG. 6. Plot of $\Delta E_N$ vs $N$ [see Eq. (1)] for $Li_N$ and $Na_N$ clusters.

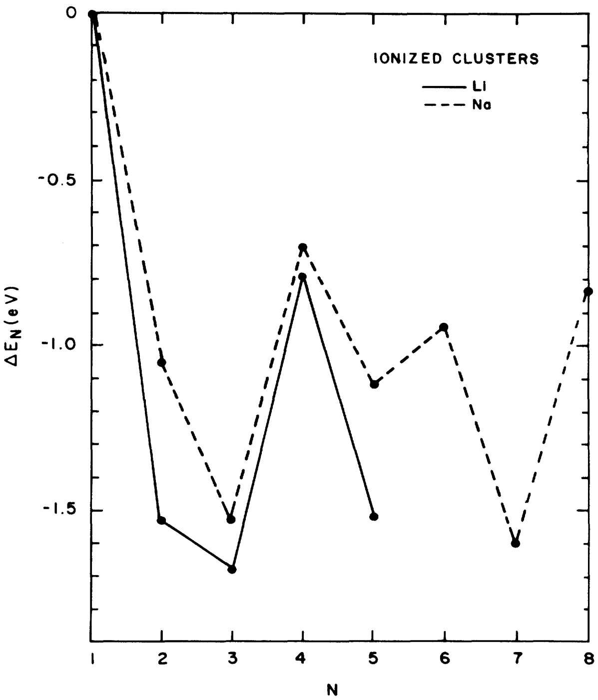


FIG. 7. Plot of $\Delta E_N^+ \sim N$ [see Eq. (2)] for $Li_N{}^+$ and $Na_N{}^+$ clusters.

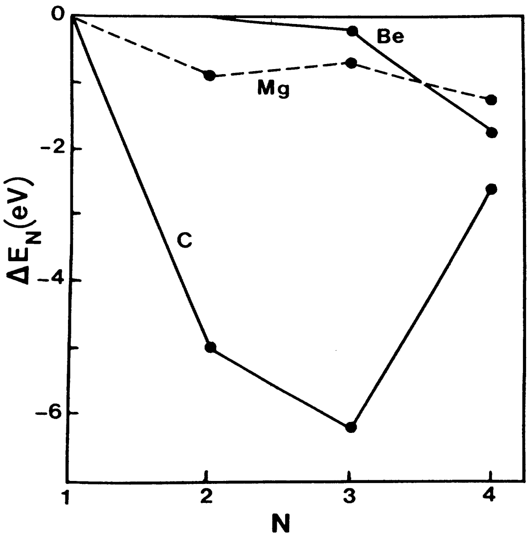


FIG. 8. Plot of $\Delta E_N \sim N$ [see Eq. (1)] for $Be_N$, $Mg_N$, and $C_N$ clusters.

mean-square distance, $\langle R \rangle$,

$$\langle R \rangle = \left[ \sum_{\substack{i,j \\ (i<j)}}^{N} R_{ij}^2 / N \right]^{1/2} , \tag{5}$$

where $R_{ij}$ is the distance between two nearest-neighbor atoms. The results normalized to a bulk value are plotted for Li and Na in Fig. 9. It is interesting to note that the nearest-neighbor distance in clusters containing only seven atoms is within 2% of the bulk value.

The evolution of the electronic structure as clusters grow has been studied by calculating the electron-density distribution, binding energy per atom, and molecular energy levels as a function of size. We are interested in learning at what stage the electronic properties of clusters appear bulklike. In Fig. 5 we had plotted the energy levels for the ground-state structures of $Li_N$ clusters ($N \leq 7$). Note that the "band gap" defined as the gap between the highest occupied MO and the first excited state decreases from a maximum of 7.7 eV in the free atom to 5.18 eV in the seven-atom cluster. Clearly, the metallic band structure has not evolved in these microclusters. The fact that the energetics do not evolve as fast as structural parameters can be further illustrated by plotting the binding energy per atom,

$$E_b = -(E_N - NE_1)/N \tag{6}$$

for $Li_N$ clusters in Fig. 10. Here, $E_N$ is the total energy of $N$-atom clusters and $E_1$ is the energy of a free atom. Note that the variation of this energy with size is not monotonic and has not approached an asymptotic value unlike the equilibrium bond length shown in Fig. 9. Furthermore, the cohesive energy of Li is much higher (1.58 eV) than the binding energy of the largest cluster studied.

We have also plotted in Fig. 10 the interstitial valence-electron density as a function of size. Note again that the valence-electron density approaches the bulk value of $0.007a_0^{-3}$. These large values of interstitial electron densities are indicative of the delocalized nature of electrons and carry rudimentary signature of metallic bonding.

## VI. SPIN-CONFIGURATION OF THE GROUND STATE OF CLUSTERS

As mentioned earlier, the equilibrium geometry of the ground state of a cluster requires not only the optimization of the topological parameters but also of its spin multiplicity. Given a set of spins, an analogue of Hund's rule for atoms would suggest that maximizing the spins would minimize the energy. If we consider a cluster with high symmetry, the energy levels would have increased degeneracy. In that situation, Hund's-like coupling would

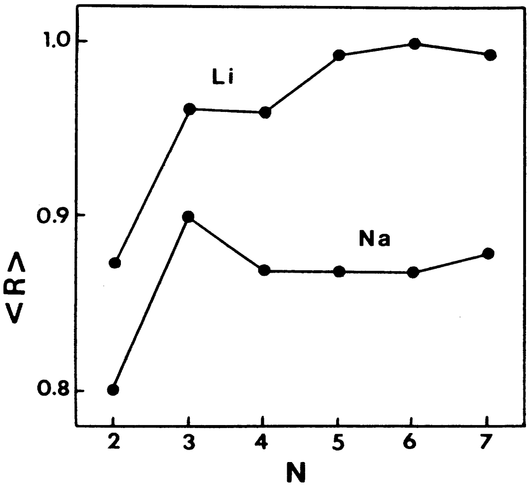


FIG. 9. Root-mean-square nearest-neighbor distance for $Li_N$ and $Na_N$ clusters. The distances are normalized with respect to their bulk values.

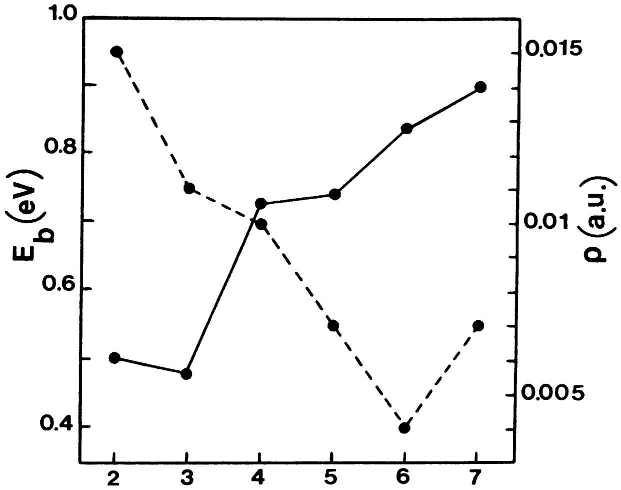


FIG. 10. The variation of binding energy $E_b$ (solid curve) and interstitial valence-electron density $\rho$ (dashed curve) in lithium clusters.

prefer that the electron spins be parallel to gain exchange energy and the cluster would assume a high-spin multiplicity. It is also possible to gain energy by structural distortion where the degeneracies are lifted. This effect, conventionally known as the Jahn-Teller distortion, would usually compete with Hund's rule. Thus, the geometrical and spin structures of clusters are intimately related.

To illustrate the role of the competing mechanism, we discuss the $Li_4$ cluster in detail. There are four valence electrons in this cluster. Two of these having opposite spins can occupy the bonding *s*-like state. The remaining two electrons will occupy the outermost valence states. If we consider a square structure for the $Li_4$ cluster (which is *not* the ground state), the last two electrons can populate two of the degenerate *p*-like states with parallel spins [see Fig. 4(a)]. This triplet state will have a lower energy than the spin singlet state where the two electrons with opposite spins can occupy one of the *p*-like states. In the former case, energy is gained due to exchange coupling between parallel spins. One can, of course, distort the square structure into a rhombus which will then remove the degeneracy between the *p*-like states [Fig. 4(b)]. Energy can then be gained due to the Jahn-Teller effect by populating the lowest of the *p*-like states with two electrons of opposite spins. Here, one would lose the advantage of Hund's rule but gain energy due to structural distortion. Which of these clusters would have lower energy depends on the magnitude of the effects associated with the Jahn-Teller and Hund's rule. Our calculations show that in this situation, Jahn-Teller gain dominates and the equilibrium state is a rhombus with zero spin. One could, of course, consider a triplet-state rhombus structure for $Li_4$. Here, the last two electrons have to occupy the $p_x$- and $p_y$-like states with parallel spins. The additional energy gain due to Hund's rule has to be compared with the energy necessary to lift the fourth electron from the $p_x$-like to the $p_y$-like states. We find that this process is energetically less favorable.

We now supplement the above qualitative discussion with quantitative results. We have calculated the energy of the $Li_4$ cluster confined to a plane as a function of bond angle $\theta$ (shown in the inset of Fig. 11). For each angle $\theta$, we have calculated the total energy for singlet- and triplet-spin configurations by optimizing the bond length $a$ in every situation. As discussed, the singlet rhombus with a bond angle of 53° is *the* ground-state configuration. For a triplet state confined to a *plane*, the equilibrium bond angle is 72°. Note that these two angles are also very close to the equilibrium trimer bond angles shown in Fig. 2. The square triplet is lower in energy than the square singlet. The energy difference between the triplet and singlet states of square $Li_4$, as seen from Fig. 11, is rather small (0.17 eV). To ensure that such a small difference does not result from an inadequate treatment of correlations and basis sets, we have carried out a similar calculation using a much larger basis set (6-311G*) and going up to fourth order in Möller-Plesset perturbation theory[12](MP4) for the correlation. The triplet is still lower than the singlet and the singlet-triplet energy difference increases to 1.07 eV. The similarity between the quantitative results in Fig. 11 and qualitative description in terms of degeneracies reconfirms our argument that the spin structure plays an integral part in the determination of the equilibrium geometry.

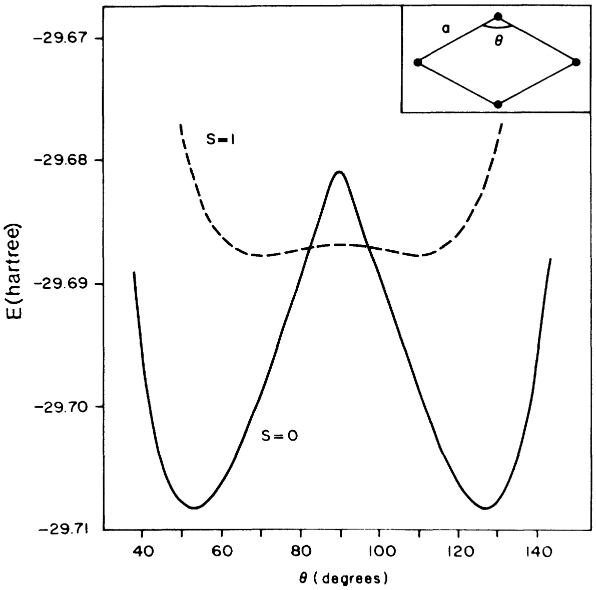


FIG. 11. Variation of energy as a function of apex angle of the $Li_4$ rhombus geometry (see inset). Results are shown for $S=0$ (solid curve) and for $S=1$ (dashed curve) spin states.

For a verification of this observation, and also to observe the effect of another theoretical approach, we have studied[22] a $Na_4$ cluster under identical conditions using the density-functional approach. In this case the core electrons were treated through a nonlocal pseudopotential and the exchange correlation was incorporated in the local-spin-density approximation. Again, as expected, the $Na_4$ cluster showed a behavior similar to $Li_4$ cluster as given in Fig. 11. In both cases the Jahn-Teller distortion is predominant and the triplet state is preferred only if the distortion of the square geometry is not permitted.

It should be emphasized that the *ground state* of the triplet $Li_4$ cluster is *not* a planar rhombus with a bond angle of 72°. When all the structural parameters are allowed to vary, the triplet state assumes a three-dimensional distorted tetrahedral structure. This configuration is lower in energy than the planar triplet by 0.06 eV. In this case, obviously, the effect of Hund's rule has been included by forcing the spin to be a triplet. Still, some Jahn-Teller effect has removed the symmetry and the structure is not completely tetrahedral. It is worthwhile to point out that the preferred spin of an even-electron cluster confined to a plane is *singlet*, and in three dimensions it is *triplet*. This is noticed again in our studies of the $Li_6$ cluster.

The equilibrium geometry of the $Li_6$ cluster is a pentagonal pyramid which is also the structure for the $Na_6$ cluster. We have found that the spin-triplet state of $Li_6$ is 0.13 eV below the spin-singlet state. The energy levels and the geometry of these two states are compared in Fig. 12. In keeping with the earlier discussion for $Li_4$, we find that in the three-dimensional $Li_6$ structure, the electrons can populate all of the $p_x$-, $p_y$-, and $p_z$-like states which are very close to each other in energy. Consequently, the gain due to Hund's-rule coupling plays a dominant role. It is then fair to make a general statement that for planar structures spins are minimized and for three-dimensional structures, they are maximized.

## VII. CONCLUSION

Using SCF-LCAO-MO technique, we have studied the equilibrium geometries and electronic structures of small clusters of Li, Be, Mg, and C atoms. Our results can be summarized as follows. (i) The equilibrium geometries of clusters depend on the number of valence electrons and their bonding character. (ii) A complete understanding of magic numbers requires a knowledge of the binding energy per atom and dissociation of both neutral and ionized clusters. The jellium model which illustrates that the magic numbers arise due to electronic shell structure is not applicable to all clusters. (iii) For clusters containing $s$-valence electrons, we have shown that the equilibrium geometries of neutral as well as ionized species including their spin multiplet structures can be understood in terms of a simple bonding-antibonding picture. (iv) The relationship between spin multiplicity and the dimensionality of the clusters has been illustrated by concentrating on tetramers. It is argued that the geometries of the clusters are ultimately connected with their spin-multiplet structure, and the consideration of the latter is necessary in order to obtain the equilibrium topology.

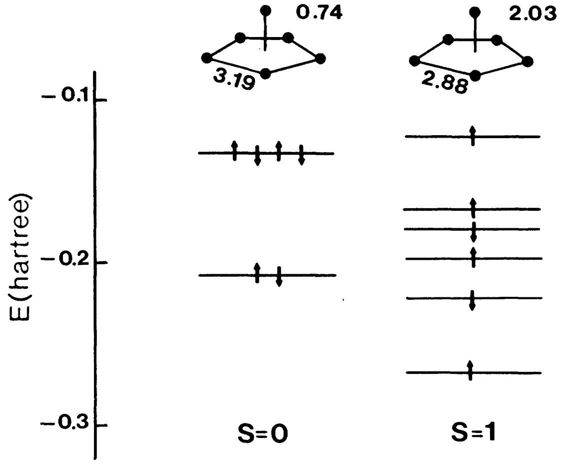


FIG. 12. MO valence energy levels and geometries for $Li_6$ in singlet- and triplet-spin states.

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