Electronic structure and geometries of heteroatomic clusters

B. K. Rao and P. Jena

Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284-2000

The equilibrium geometries and the electronic structure of heteroatomic clusters involving alkali-metal-atom hosts and aluminum and magnesium impurity atoms have been studied using the self-consistent-field linear combination of atomic orbitals–molecular orbital method. The total energies of the clusters have been calculated by including exchange interaction within the unrestricted Hartree-Fock approximation and the correlation contribution within using the configuration interaction involving the double excitations of the valence electrons. The heteroatoms are found to have significant effect on the topology of the host clusters. The relative stabilities and ionization potentials of heteroatomic clusters exhibit odd-even alternation in agreement with experimental data. The evolution of the binding energies of the heteroatom with cluster size testifies to the delocalized nature of the electrons of the host cluster. While the energy gained in adding an additional alkali-metal atom to the existing heteroatomic cluster continues to oscillate with cluster size, the heteroatom binding energy varies monotonically.

I. INTRODUCTION

Recent studies[1-3] of small atomic clusters reveal little resemblance between the equilibrium geometries and electronic structures of clusters with their corresponding bulk (solid) phases. The various structural and electronic properties of clusters are not only size-specific, but also they evolve differently. Alkali-metal clusters are the most widely studied systems since their electronic structure in the bulk phase can be described very well by a nearly-free-electron picture. In this context, the success of the jellium model[4] in describing the relative stabilities of these clusters provides confidence in ones belief that electrons, even in very small clusters (which are in some sense "molecules"), may behave like free electrons.

To enhance understanding on this topic experiments have been performed on binary atomic clusters.[5,6] These include clusters[5] of $K_N Na$, $K_N Mg$, and $K_N Zn$. The electronic structure of bulk magnesium can be described like that of alkali metals by a nearly-free-electron picture. Thus, if electrons in clusters behave in a way similar to that in their bulk phase, one should be able to explain the relative stabilities of compound clusters by the jellium model.[4] In this model, nearly-free electrons fill the energy levels in a spherical potential well successively. The relative stability of a cluster is enhanced when its valence electrons fill a quantum level completely. Thus alkali-metal-atom clusters consisting of $2, 8, 20, \ldots$ electrons (which correspond to the filling of $s, sp, spds, \ldots$ levels, respectively) should show pronounced peaks in the mass spectra—a prediction in remarkable agreement with experiment. Pursuing this analogy to compound clusters, for example, $K_7 Na$ and $K_6 Mg$ should exhibit pronounced peaks since in both the cases there are eight "valence" electrons. While Kappes *et al.*[5] saw a pronounced peak for $K_7 Na$, they did not observe this for the $K_6 Mg$ cluster in their mass spectra.

They thus concluded that the jellium model is too simple to account for the properties of compound clusters.

In this paper we discuss the electronic structure of heteroatomic clusters consisting of Na, Mg, and Al in Li_N host clusters with up to seven atoms of lithium. Our calculations do not assume a premeditated geometry (jellium or otherwise) for the clusters. We determine the equilibrium geometries starting from first principles and use the electronic structure of the ground-state system to understand the relative stabilities of heteroatomic clusters. We have chosen Li_N instead of K_N as the host cluster because all homonuclear alkali-metal-atom clusters behave in a similar way. In addition, due to the small number of electrons in Li, it is possible to perform the quantum-mechanical calculations at a more accurate level.

Another aspect of the studies of the compound clusters is that these have interesting analogies with the studies of defects in bulk metals. It is well known that a point defect in a metal perturbs the host electron distribution as well as the arrangement of the host atoms in the vicinity of the defect. Usually these perturbations are small and are confined to a local environment. The first near-neighbor atoms may relax radially by no more than 10% of their unperturbed distance while the changes in the second near-neighbor distances are virtually negligible. In small clusters, however, a single "foreign" atom represents a significant fraction of the host. It is, therefore, of interest to see how the geometries of homonuclear clusters are altered due to the addition of the foreign atoms.

In Sec. II we outline briefly the numerical procedure used in this paper. Our results on the equilibrium geometries and the electronic structure (electron density distribution, molecular energy levels, binding energies, and ionization potentials) are presented in Sec. III. A summary of conclusions is given in the last section.

II. NUMERICAL PROCEDURE

In the following we give a brief review of the numerical method used in the present work. The reader is referred to our earlier paper[2] for more details. The unrestricted Hartree Fock (UHF) method has been augmented by configuration interaction to calculate the total energies of the clusters. The molecular orbitals have been expressed as linear combinations of atomic orbitals which themselves are approximated by linear combinations of Gaussian functions. Correlation correction has been incorporated through configuration interaction (CI) using all double excitations of the valence electrons. The ground-state geometries are obtained for the clusters by minimizing the total energies with respect to all independent bond angles and bond lengths. We start with the constituent atoms at arbitrary positions. After obtaining the total energy of the cluster for this arrangement of the atoms the gradient forces are calculated. The atoms are then moved along the direction of the forces before calculating the total energy again. This procedure is repeated till the forces vanish at every atomic site. To avoid local minima in the energy surface, one repeats the optimization procedure several times by starting from different initial geometries until consistent results are obtained. One must also consider the spin optimization[2,7,8] for the clusters in searching for the ground state. To perform this, one has to go through the above procedure for several possible spin configurations of the cluster and determine which spin state yields the lowest energy.

At this point we would like to mention that for cluster calculations of this type one always faces a dilemma about the choice of the atomic wave functions. The choice of the basis set is often made not in terms of what is desirable, but rather what is practical for the problem at hand. Ideally, the larger the basis set the closer the approximation is to the exact Hartree-Fock results. However, beyond a certain point the increase of the length of the basis set does not do too much for the energies except make the calculations more expensive. Thus one has to use careful judgement[2] in choosing the basis set for such calculations. We have used the well known Slater-type orbital, STO-6G, basis set[9] for all the atoms. This uses six Gaussians to fit each atomic wave function. To present excitations, p states are added after the valence s states in each case. For the atoms used in the present calculations these are considered to be adequate.

III. RESULTS AND DISCUSSIONS

In order to understand if the electronic energy levels of the atoms can be used to elucidate the observed abundances in the mass spectra of compound clusters, we plot in Fig. 1(a) the energy levels of the valence electrons of Li, Na, K, Mg, and Al atoms. Note that the Li $2s$ level and Na $3s$ level are very close in energy. Thus replacing a lithium atom by a sodium atom is not expected to change the nature of the bonding in a cluster. Consequently the properties (geometries and electronic structure) of Li_N and $Li_{N-1}Na$ should be similar. This can be seen to be the case from the calculated structures of
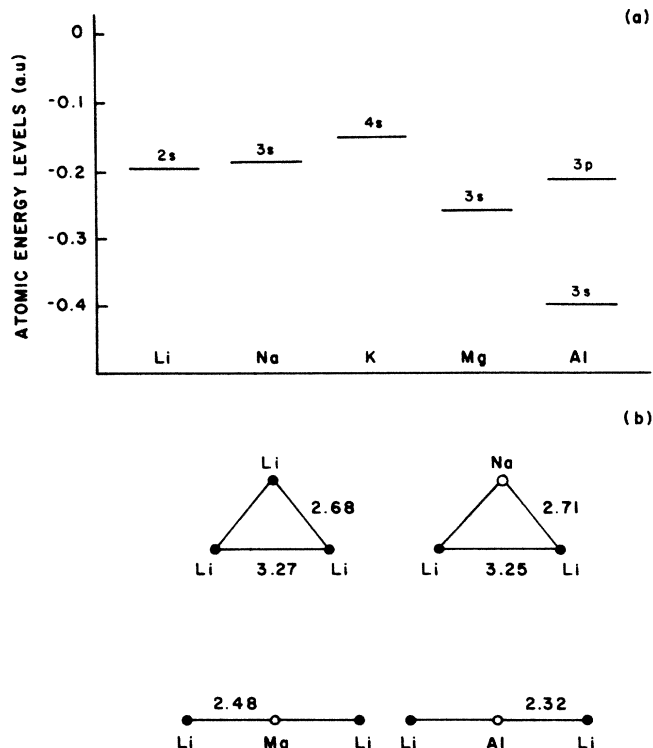

FIG. 1. (a) Valence-electron energy levels (in atomic hartree units) for lithium, sodium, potassium, magnesium, and aluminum atoms. (b) Equilibrium geometries of Li_3, Li_2Na, Li_2Mg, and Li_2Al clusters. The bond lengths are in angstroms.

Li_3 and Li_2Na in Fig. 1(b) where the bond lengths are virtually identical. Such a simple picture, however, does not apply for Li_2Mg and Li_2Al even though the $3p$ electronic energy level of Al lies very close to that of Li $2s$. The geometries as seen from Fig. 1(b) are qualitatively different indicating that the number of electrons in a cluster is an important factor in determining its properties.

The equilibrium geometries for Li_NMg ($N \leq 7$) and Li_NAl ($N \leq 4$) clusters are given in Fig. 2(a) and Fig. 2(b), respectively. The geometries of Li_NMg clusters are in general agreement with those observed by Koutecky and Fantucci[10] in Li_NBe. When one compares these with the geometries for pure lithium atom clusters[2,11] one immediately notices that the geometries have been modified due to the presence of the "foreign" atom. One further notices that the geometries of the compound clusters are symmetric around the heteroatom even though the geometries of Li_N clusters are less symmetric. The latter is governed by the Jahn-Teller effect where the reduction of symmetry lifts the degeneracy of the electronic energy levels and thereby lowers the total energy of the system.[8] This energy gain is typical of the order of a few tenths of an eV. In compound clusters, this is offset by the electronic interaction between the impurity atom and the host atoms. For example, Li_2 has a binding energy of 0.995 eV while that for LiMg is 3.204 eV. Therefore, the host cluster can benefit by in-
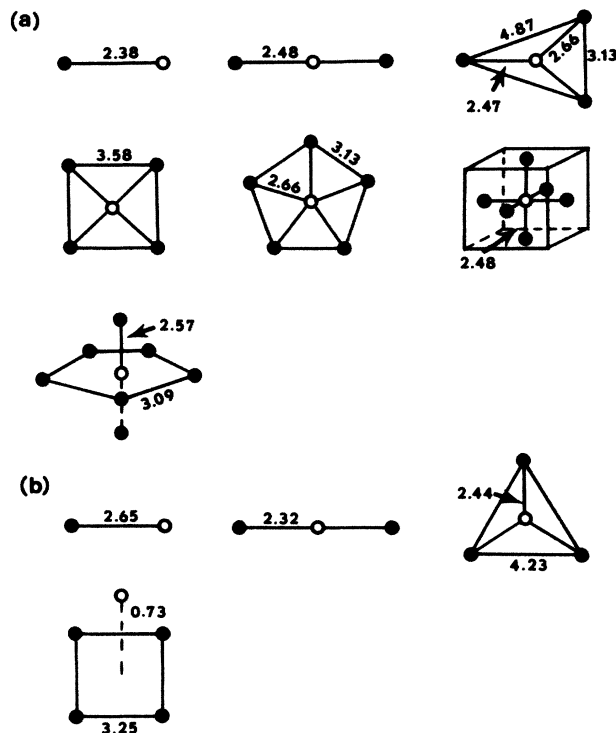
FIG. 2. Equilibrium geometries of (a) Li_NMg and (b) Li_NAl clusters. The bond lengths are given in angstroms. Solid circles represent Li atoms and open circles represent the foreign atoms.
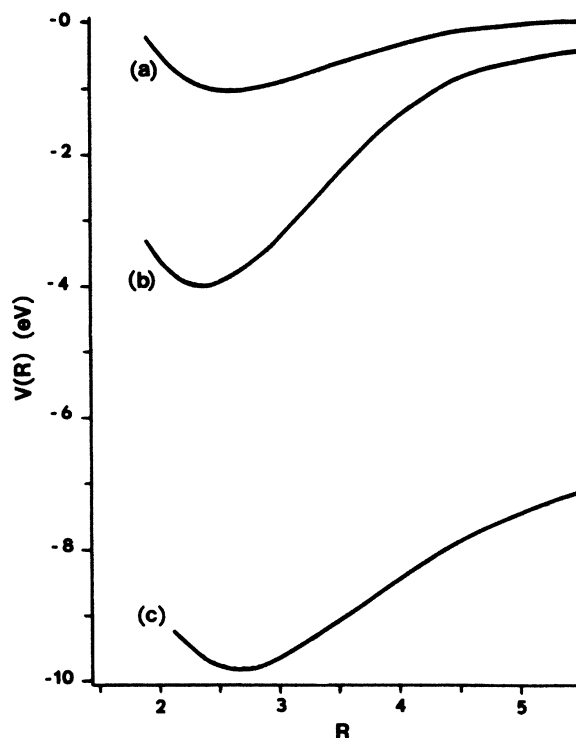
FIG. 3. Plot of pair potentials $V(R)$ against R (internuclear distance) for (a) Li_2, (b) LiMg, and (c) LiAl. The energy is given in electron volts. R is in angstroms.

creasing its bonding as much as possible with the Mg atom. This can be achieved by placing the magnesium atom in a relatively symmetric position with respect to all the lithium atoms. In the case of LiAl, the binding energy is 9.578 eV, which is even larger than that of LiMg. As expected, Li_NAl clusters are also symmetric around the aluminum atom [see Fig. 2(b)]. Thus, in strongly bonded compound clusters, the importance of Jahn-Teller distortion is expected to be significantly reduced. The nature of bonding can be further illustrated by comparing the pair potentials of Li_2, LiMg, and LiAl. These are plotted in Fig. 3. Note that the potential wells for LiMg and LiAl are much deeper than that of Li_2. Thus the topologies of larger Li clusters involving Mg and Al atoms are directed by their rudementary pairwise interaction.

The relative stabilities of these clusters can be studied by determining the energy gained in adding a lithium atom to an existing cluster of Li_{N-1}, $Li_{N-1}Mg$, or $Li_{N-1}Al$. For this we use the equation

$$\Delta E_N = E(Li_NX) - E(Li_{N-1}X) - E(Li) , \qquad (1)$$

where X represents Mg or Al for compound clusters. For pure Li_N clusters X represents a dummy. The values of ΔE_N are given in Table I. For Li_N clusters there are dips in the values of ΔE_N for even values of N. This compares very nicely with the odd-even alternation observed in the peaks of the mass spectra[4] for alkali-

metal atoms. The even values correspond to even numbers of electrons in the clusters (as each atom provides one valence electron). These clusters are more stable relative to those in the adjacent sizes. Interestingly enough, exactly the same behavior is seen in Table I for the Li_NMg clusters—in agreement with experiments.[5] Because magnesium has even number of valence electrons, the dips for even values of N are not affected. On the other hand, Li_NAl clusters show dips at odd values of N. Again, the odd number of valence electrons of aluminum is responsible for shifting the dips to odd values of N. No experimental data are yet available on alkali-metal clusters containing Al atoms to verify this prediction. Thus, when the total number of valence electrons is even, the cluster is relatively more stable. The origin of this lies in the filling of the electronic energy levels. For an even number of valence electrons, the last two electrons occupy the same molecular orbital with opposite spins. However, when an odd number of valence electrons is present in a cluster, the odd electron has to go to a higher molecular orbital. This additional cost in energy makes the odd valence electron clusters relatively less stable.

This point can be further examined by looking at the ionization potentials of the clusters. The vertical ionization potentials (IP) of all these clusters are given in the last column of Table I. For stable clusters, more energy would be required to remove an electron. Therefore, for each dip in the value of ΔE, one should get a peak in the

TABLE I. Total energy and atomization and binding energies, vertical ionization potentials (IP) and ΔE of Li_N, $Li_N Mg$, and $Li_N Al$ clusters.

Cluster	Total Energy (a.u.)	Atomization energy (eV)	Adatom binding (eV)	ΔE_N (eV)	IP (eV)
LiAl	−248.410 222	9.578	−9.578	−9.586	4.998
Li_2Al	−255.865 859	11.085	−10.110	−1.515	2.021
Li_3Al	−263.345 435	13.243	−11.845	−2.166	3.597
Li_4Al	−270.802 470	14.788	−11.911	−1.553	3.016
LiMg	−206.215 915	3.204	−3.204	−3.204	1.704
Li_2Mg	−213.744 803	6.704	−5.729	−3.499	3.673
Li_3Mg	−221.165 067	7.248	−5.851	−0.545	3.139
Li_4Mg	−228.628 321	8.963	−6.085	−1.714	3.603
Li_5Mg	−236.055 887	9.706	−6.190	−0.743	1.993
Li_6Mg	−243.529 690	11.707	−6.660	−2.001	3.718
Li_7Mg	−250.949 096	12.228	−6.060	−0.521	2.046
Li	−7.400 238			0.0	4.860
Li_2	−14.837 075	0.995		−0.995	4.439
Li_3	−22.253 448	1.434		−0.439	3.194
Li_4	−29.708 516	2.926		−1.491	3.840
Li_5	−37.137 382	3.704		−0.779	3.594
Li_6	−44.586 966	5.047		−1.342	4.231
Li_7	−52.032 436	6.277		−1.230	2.952

value of the ionization potential. This is exactly what happens. These peaks occur at even values of N for Li_N and $Li_N Mg$ clusters and at odd values of N for $Li_N Al$ clusters. These results are consistent with the behavior exhibited by K_N and $K_N Mg$ clusters.[5]

In Table I we have also given the atomization energy of the clusters and the binding energy for the impurity atom in various clusters. We define the atomization energy as the (positive) energy needed to split the cluster to its constituent atoms. The binding energy of the foreign atom is defined as

$$E_B = E(Li_N X) - E(Li_N) - E(X) , \qquad (2)$$

where X represents the foreign atom. A negative value for E_B means that the compound cluster is stable against dissociation. Both the atomization and the binding energies tend to saturate with increasing cluster size (see Table I). Obviously, as the number of host atoms approaches infinity, the binding energy should be identical to the energy gained by placing the foreign atom in bulk lithium. What is interesting here is that with as few as seven lithium atoms, the binding energy appears to almost saturate. This results due to an efficient screening of the foreign atom by the "delocalized" electrons in the Li clusters further providing evidence that the electronic structure of small alkali-metal clusters can be characterized by metallic bonding. Thus the interaction of the foreign atom with the host cluster atoms can be governed by the local environment as is often the case with point defects in metals. The sudden jump of the atomization energy for Li_2Mg indicates the possibility of a "magic number" for that particular cluster. We would also like to point out that since the impurity atom does

not influence the relative stabilities of the host clusters, its real effect on the properties of the host clusters could be probed by structure-sensitive experiments such as ESR.

We have observed that the impurity atom changes the geometries of the host clusters while apparently not influencing the relative stabilities. This is not an anomalous behavior. One can understand this by examining the details of the bonding among the atoms in the clusters. To start with, we present cluster charge densities for LiMg and Li_2Mg in Figs. 4 and 5, respectively. In each case we first present (a) the total charge density contours and then (b) difference density contours. The latter is obtained by subtracting the superimposed free-atom densities from the self-consistent densities of the cluster. The difference densities show areas of positive contours which are located between the magnesium atom and the lithium atoms. This is indicative of the fact that there is a charge buildup along the line between the atoms. The difference contours also show that a part

TABLE II. Mulliken populations at the magnesium site for $Li_N Mg$ clusters.

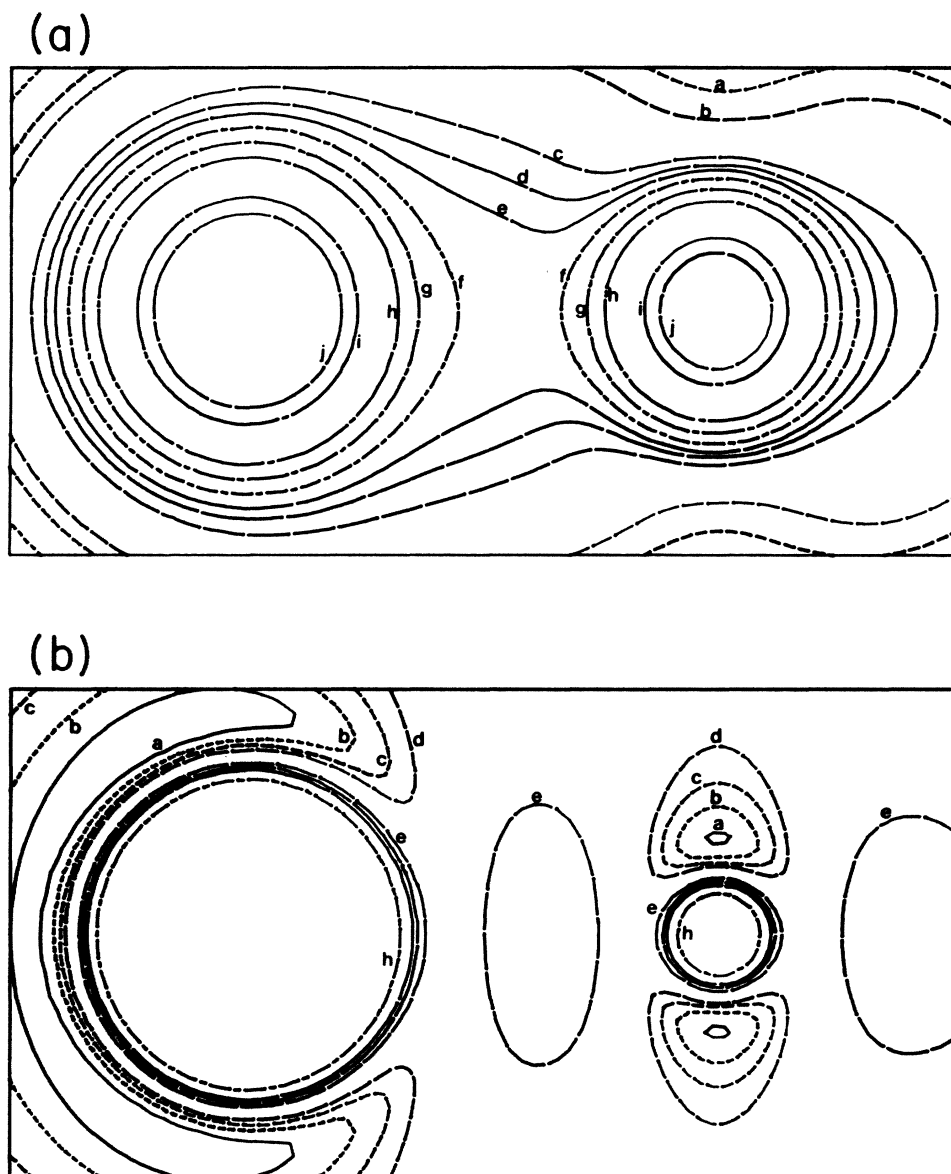|	Mulliken population					
N	$1s$	$2s$	$2p$	$3s$	$3p$	Total
1	2.000	1.981	5.651	0.839	0.404	10.875
2	1.999	1.973	5.667	0.555	0.523	10.717
3	1.999	1.972	5.667	0.506	0.552	10.697
4	1.999	1.969	5.669	0.385	0.643	10.665
5	1.999	1.970	5.668	0.435	0.600	10.672
6	1.999	1.967	5.666	0.293	0.734	10.659

(a)

(b)

FIG. 4. (a) Charge density contour for LiMg cluster. The densities (in atomic units) are given in values of 0.008, 0.01, 0.02, 0.025, 0.03, 0.04, 0.06, 0.1, 0.5, and 1.0 denoted by letters a through j, respectively. (b) Difference charge density (self-consistent cluster–superimposed atomic) for LiMg. The densities (in atomic units) are given at values of -0.006, -0.004, -0.002, 0.0, 0.01, 0.015, 0.02, and 0.04 denoted by letters a through h, respectively.

of this change has been transferred from the core region of the atoms. Similar plots with aluminum as the impurity show even more amount of charge buildup along the bonds. Plots with larger clusters with magnesium and aluminum reinforce this observation.

In Table II we have presented the Mulliken population analysis for the different orbitals of the magnesium atom in different $Li_N Mg$ clusters. One can observe, in general, that magnesium has lost approximately 1.3 electrons in most of the cases. The total charge residing at the magnesium is close to 10.7 instead of 12. These charges are shared by the lithium atoms surrounding the magnesium atom. This is surprising because one nor-

mally expects the lithium atom to expel its $2s$ electron to behave like a Li^+ ion. Here, exactly the opposite happens. The lithium atoms are actually sharing 1.3 extra electrons among themselves. Obviously this sharing becomes easier when the cluster size increases. Therefore, the binding improves with the increase of size. Similar behavior is also noticed for the case of $Li_N Al$ clusters. For example, in the case of $Li_2 Al$ clusters, the total number of electrons at the site of aluminum is 11.88 instead of 13.

The mechanism for this charge transfer can be elucidated by studying the details of the one-electron energy levels. We have presented the values of these for Li_N
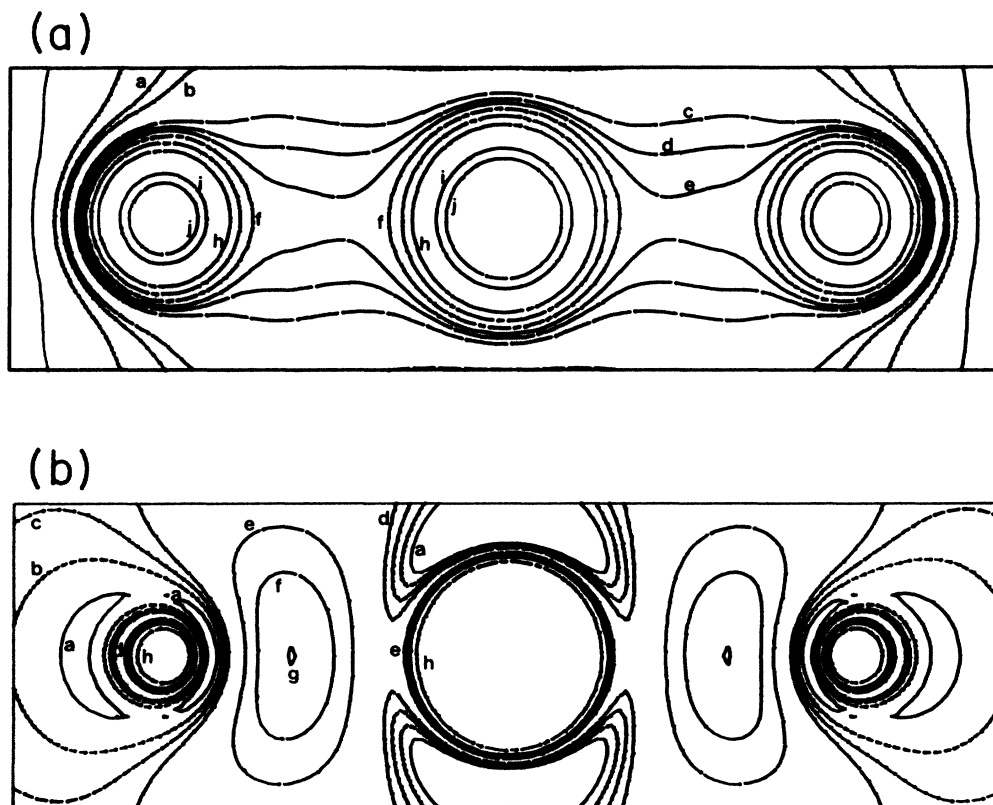
FIG. 5. (a) Charge density contour for Li_2Mg cluster. The scale is the same as in Fig. 4(a). (b) Difference charge density (cluster-atomic) for Li_2Mg. Scale is the same as in Fig. 4(b).

and Li_NMg clusters in Fig. 6. The addition of Mg can be seen to lower the energy levels of the homonuclear clusters in general. This observation is consistent with a recent jellium calculation of Zhang et al.[12] These authors placed a magnesium atom at the center of a spherical charge distribution assumed to mimic the host alkali-metal cluster. Through a self-consistent calculation they observed a lowering of the s states due to the presence of the Mg potential. We further note that for even values of N, all the molecular orbitals are lower for the compound clusters than the pure clusters. This is due to the fact that in each of these there are two more electrons occupying the same orbital with opposite spins. On the other hand, for the odd N clusters the odd valence electron has to go to a higher orbital necessarily, which increases the energy. This effect manifests in the odd-even alternation mentioned before. This also causes another interesting phenomenon. The energy gap between the highest occupied level (HOMO) and the lowest unoccupied level (LUMO) always becomes smaller in the case of odd N when a magnesium atom is added. Examination of the valence levels shows that in each case there is a significant amount of promotion of the valence s levels of the atoms ($2s$ for Li and $3s$ for Mg) into the closest p states. After this promotion, the hybridized orbitals interact strongly among themselves to produce the strong bonds between the magnesium atom and the lithium atoms. Such a situation results in significant charge
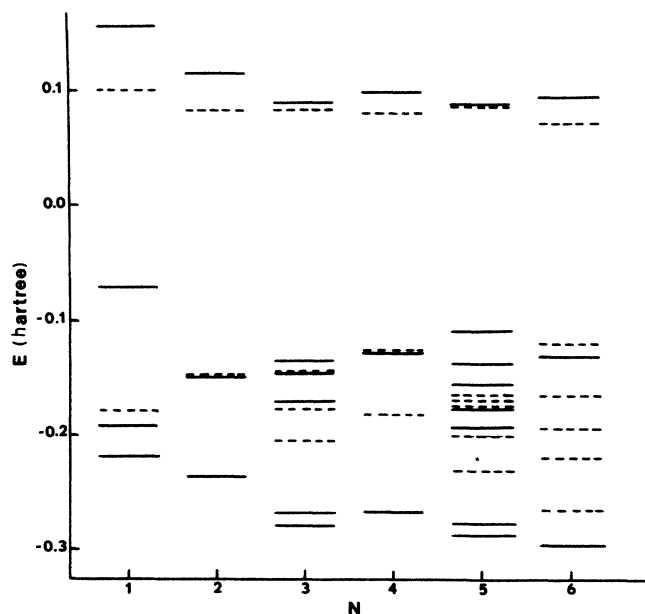

FIG. 6. One-electron energy levels for the valence electrons of Li_N (dashed lines) and Li_NMg (solid lines) clusters. The lowest unoccupied orbitals are also shown. Energy is given in atomic hartree units.

transfer between the atoms along a bond. Another point to note from Table II is that the core $2s$ and $2p$ levels of magnesium do take sizeable part in the interaction. Therefore, one must be careful while using "frozen core" approaches to study the electronic structure of clusters.

IV. CONCLUSIONS

We have performed total-energy calculations of compound clusters based upon the self-consistent field LCAO-MO method within the unrestricted Hartree-Fock formalism. The correlation contribution was calculated using a configuration interaction procedure involving all double excitations of valence electrons. The equilibrium geometries of clusters were obtained by minimizing the total energy. The study of single-particle energy levels, electron charge density distribution, binding energies, and ionization potentials, reveal the following features. (a) The energetics and the relative stabilities of compound clusters cannot be predicted *a priori* by comparing the energies of the valence orbitals of the constituent atoms. (b) Even a closed-shell atom like magnesium can interact strongly with the other atoms in the cluster. (c) The equilibrium geometries of homonuclear clusters can be modified significantly when an impurity atom is added. (d) While the Jahn-Teller effect plays a significant role in determining the geometry of pure clusters, its effect in compound clusters may be overwhelmed by the electronic bonding considerations. (e) The bonding of Mg and Al atoms with the alkali-metal atoms of the cluster results from a charge transfer from Mg and Al to the alkali-metal atoms. (f) The binding energy of the impurity atom approaches a steady value when the clusters are relatively small, signifying that the interaction between the impurity and the host atoms is governed primarily by the local environment. (g) The odd-even alternation in the relative stabilities and ionization potentials in $Li_N Mg$ clusters is consistent with the experimental observation in the $K_N Mg$ system.

[1]T. D. Mark and A. W. Castleman, Jr., Adv. At. Mol. Phys. **20**, 65 (1985).

[2]B. K. Rao and P. Jena, Phys. Rev. B **32**, 2058 (1985).

[3]J. L. Martins, J. Buttet, and R. Car, Phys. Rev. B **31**, 1804 (1985).

[4]W. D. Knight, K. Clemenger, W. A. deHeer, W. A. Saunders, M. Y. Chou, and M. L. Cohen, Phys. Rev. Lett. **52**, 2141 (1984).

[5]M. M. Kappes, P. Radi, M. Schar, and E. Schumacher, Chem. Phys. Lett. **119**, 11 (1985).

[6]T. P. Martin, J. Chem. Phys. **81**, 4426 (1984).

[7]B. K. Rao, S. N. Khanna, and P. Jena, Chem. Phys. Lett. **121**, 202 (1985).

[8]S. N. Khanna, B. K. Rao, P. Jena, and J. L. Martins, in *Physics and Chemistry of Small Clusters*, edited by P. Jena, B. K. Rao, and S. N. Khanna (Plenum, New York, 1987).

[9]W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys. **51**, 2657 (1969).

[10]J. Koutecky and P. Fantucci, Z. Phys. D **3**, 147 (1986).

[11]B. K. Rao, S. N. Khanna, and P. Jena, Phys. Rev. B **36**, 953 (1987).

[12]S. B. Zhang, M. L. Cohen, and M. Y. Chou (unpublished).