Abstract

We present a systematic study of the geometry, energetics, electronic structure and bonding in various Al-Li clusters viz. $\text{Al}_n\text{Li}_n$ ($n=1\text{-}11$), $\text{Al}_2^-$, $\text{Al}_2^2-$, $\text{Al}_2\text{Li}$, $\text{Al}_2\text{Li}^-$, and $\text{Al}_6\text{Li}_8$ using Born-Oppenheimer molecular dynamics method within the framework of density functional theory. The growth patterns in these cluster are found to be divided in two broad categories: the first consisting of a quinted roof of $\text{Al}_2\text{Li}_2$ ($n=2\text{-}4$) and the second consisting of a pentagonal ring ($n=7\text{-}9$). A covalent bonding between Al-Li in $\text{Al}_2\text{Li}_2$ is seen, whereas, in larger clusters, it is ionic. A three dimensional growth of the Al cluster in $\text{Al}_4^2-$, $\text{Al}_5\text{Li}_5$, and $\text{Al}_6\text{Li}_8$ leads to a transition from localized to delocalized bonding. In clusters with more than six Al atoms, the eigenvalue spectrum is divided into two groups: a lower group of jellium-like states and a higher group of localized bonds arising out of $p$ complex. Thus, a mixture of localized, delocalized, and ionic bonding is seen in these clusters. Finally, we have discussed the tetravalent behavior of Al atoms arising due to a charge
transfer from the Li atoms to the Al atoms.
The discovery of \( C_{60} \) buckminsterfullerene [1], observation of magicity in metallic clusters [2], unusual thermodynamical properties of clusters like Na [3], Sn [4] etc., has given rise to an explosive growth of research in the field of cluster physics. Extensive theoretical and experimental [5–7] work has been carried out to understand the physical and chemical properties of clusters like size-evolutionary pattern in cluster geometry, thermodynamics, vibrational and rotational properties, optical properties, electronic structure, and bonding, chemical reactivity, as well as the emergence of the bulk properties with the increase in cluster size.

Recently observed aromaticity [8] and antiaromaticity [9–12] in inorganic molecules, and in particular Al-Li clusters, has stimulated further research in these systems. These properties are well-known and important in organic chemistry [13]. However, recently the first experimental and theoretical evidence of aromaticity in all-metal system viz. Al\(^{2-}\) and \( M\text{Al}^{4-} \) (\( M = \text{Li, Na, Cu} \)) was reported by Wang and coworkers [8]. They found the Al\(^{2-}\) dianion to be square-planar possessing \( 2 - \pi \) electrons, thus conforming the structural criterion for aromaticity. The concept of antiaromaticity, introduced by Breslow [14] et al., corresponds to the destabilization seen in the cyclic systems with \( 4n - \pi \) electrons. Although, such molecules do not occur outside of organic chemistry, the first all-metal antiaromatic compound viz., Al\(_4\)Li\(_4\) was theoretically reported by Shetty [9,11] et al. and others [12].

Aluminum-lithium clusters, which we study in this paper, are also interesting due to their unusual structural and bonding properties that are quite different from those of the pure clusters of the constituent elements. Both pure Al and Li clusters have been extensively studied using the spherical jellium model (SJM) [2]. However, it is observed that although the SJM has been quite successful in describing the gross electronic structure and the stability of alkali metal atom clusters [2,15], the Al clusters present an interesting contrast. Rao and Jena [16] have done a comprehensive study of the aluminum cluster using \textit{ab initio} density functional theory. They found that in small Al clusters, the effective valency of
Al is one [16] due to a large energy gap of about 5\text{eV} separating the 3s\textsuperscript{2} and 3p\textsuperscript{1} orbitals. However, Rao [17] et al. as well as Dhavale [18] et al. did not find any signature of such monovalent behavior, contrary to the expectations. Investigation by Cheng [19] et al. shows that a single Al atom in Li clusters introduces a localized bond between the Al impurity and the Li host. They also found a magic cluster AlLi\textsubscript{5}, and suggested that Al\textsubscript{n}Li\textsubscript{5n} can aggregate at least for some values of \( n \geq 2 \) and may exhibit properties characteristic to an assembly of such clusters from the AlLi\textsubscript{5} subunits. Akola [20] et al., however, found that this idea does not apply after \( n = 2 \). Further, their investigation on bonding in a Li-rich Al-Li cluster shows a substantial charge transfer from Li atom and nearby Al atom, strengthening the ionic Al-Li bond, while the Al-Al bond gained a more covalent nature. Such charge transfer has been observed by Kumar [21] in several mixed Al-Li clusters. He found a layered Al\textsubscript{10}Li\textsubscript{8} compound to be magic with electronic and geometric shell closing. This was the first instance where a shell closure in \( s - p \) bonded metal cluster was found to occur at 38 valence electrons. Note that the magic numbers for alkali metal atom clusters [2] are 2, 8, 18, 20, 40,..., whereas, some of the magic Al clusters are Al\textsubscript{7}\textsuperscript{+}, Al\textsubscript{7}\textsuperscript{−}, Al\textsubscript{11}\textsuperscript{−}, Al\textsubscript{13}\textsuperscript{−}, etc [16,22].

The Al-Li bulk is especially interesting due to the fact that it forms a stable alloy at over the wide range of concentration. However, the most stable intermetallic B32 phase corresponds to the 50:50 concentration [23]. In this B32 phase, a mixture of covalent and ionic bonding is seen due to a remarkable charge transfer from the Li atoms to the Al atoms. Moreover, the close resemblance of the density of states (DOS) (without any band gap) [24] to that of the covalently bonded diamond structure indicates a tetravalent behavior of Al atom. Thus, based on these observations, one can expect that the behavior of Al in Al\textsubscript{n}Li\textsubscript{n} clusters would be similar to that of the tetravalent atom Si [25], Ge [26], Sn, and Pb [27]. Indeed, our present work shows that in certain clusters, structure and bonding of Al\textsubscript{n} is similar to that of the group IV A clusters. Moreover, earlier work on the heterogeneous Al-Li clusters has focussed on specific aspects like systematics in the geometry, stability, shell closure, magic behavior etc. Bonding in such clusters was discussed on the basis of total charge density as well as the difference of the self-consistent charge density, \( \rho_{scf} \), and the superimposed
atomic charge densities $\rho_{\text{superimposed}}$ of the constituent atoms. On the contrary, analysis of the molecular orbitals (MOs) has revealed some unusual properties like aromaticity and antiaromaticity in all-metal Al-Li clusters. In our earlier work, we have examined some of the issues concerning the geometry and the stability of various Al-Li clusters viz. Al$_n$Li$_n$ ($n = 1, 10, 13$) [28], Al$_n$Li$_7$ ($n = 1-7$) [29], AlLi$_n$ ($n = 1, 8$) [29] and Al$_{13}$Li$_n$ ($n = 1-4, 10, 19, 20, 21$) [30]. We have found that the geometry of these clusters was dictated by the geometry of the core Al cluster enclosed in the Li cage. On account of these calculations being performed by the density based molecular dynamics (DBMD) method, with the approximate kinetic energy functional, an analysis of the bonding and electronic structure was not possible. In the present work, we study the systematics of the geometry, energetics, electronic structure and the bonding properties in various Al-Li clusters viz. Al$_n$Li$_n$ ($n = 1-11$), Al$_2^-$, Al$_2$Li, Al$_2$Li$^-$, and Al$_6$Li$_8$ using Kohn-Sham formulation of the density functional theory (DFT) within the pseudopotential and the generalized gradient approximation (GGA). The bonding in these clusters is discussed via the electron localization function (ELF) [31] as well as the behavior of the occupied molecular orbitals. We find that as the clusters grow, although the bond between Al-Al in all these clusters is predominantly covalent, an effective delocalization of the charge density is seen. Moreover, the eigenvalue spectrum of the clusters with more than six Al atoms can be separated into lower jellium-like and higher localized orbitals. In section II we shall describe the computational details, followed by a discussion of the results in section III.

II. COMPUTATIONAL DETAILS

The ground state geometry as well as other low-lying structures was obtained in two stages. In the first stage, Born-Oppenheimer molecular dynamics (BOMD) [32] based on Kohn-Sham (KS) [33] formulation of density functional theory (DFT) was employed. The computer code used for this purpose was developed in our own group. The total energy during each of the molecular dynamics step was minimized using damped equation
of motion [34]. The calculations were performed using norm-conserving pseudopotentials of Bachelet [35] et al., in the Kleinman-Bylander [36] form with s part treated as nonlocal. The exchange-correlation potential was calculated using the local density approximation (LDA) given by Ceperley-Alder [37]. A cubic supercell of 40a.u. with an energy cutoff of 17 Ry was used.

The damped equation of motion scheme [34] permits use of a fairly moderate time step \( \approx 100 \text{a.u.} \). Starting from a random configuration, the Al\(_n\)Li\(_n\) clusters were heated to 1400-1700K, and allowed to span the phase space for a few thousand iterations. In our previous investigations [28–30] on Al\(_n\)Li\(_n\) clusters, it was found that the Li atoms segregate at the surface with the Al atoms forming an inner core. In order to avoid any such segregation during the molecular dynamics run, we have interchanged the Al and the Li atoms. This has ensured that the cluster visits all its local minima as well as the global minimum. At the end of each ionic displacement, the norm of the eigenstates defined as \( | h\psi_i - \epsilon_i \psi_i |^2 \) (where \( \epsilon_i \) is an eigenvalue corresponding to eigenstate \( \psi_i \) of the Kohn-Sham Hamiltonian \( h \)) was within the range of \( 10^{-4} - 10^{-7} \text{a.u.} \).

In the second stage, various low-lying structures were obtained by conjugate gradient and/or steepest descent [32] method starting from various suitable configurations during the molecular dynamics run. This was done using the ultrasoft pseudopotentials [38] within the generalized gradient approximation (GGA) implemented in the VASP [39] package. The Perdew-Wang [40] exchange-correlation potential for GGA has been used. The size of the simulation cell was varied according to the cluster studied (see Table-I).

Table - I

Size of the supercell (in Å) for various clusters, where \( n \) is the total number of atoms in the clusters.
The geometries were optimized with a kinetic energy cutoff of 11.87 Ry. The structures were considered to have converged when the forces on each ion was less than 0.01 eV/Å with a convergence in the total energy within the range of $10^{-4} - 10^{-6}$ eV. In general, we find that there are many isomeric structures nearly degenerate to the lowest energy state. Few of the structures can be obtained by interchanging the Al and the Li atoms or by rearranging the position of Li atoms. In the present work, we discuss only the lowest few geometries.

The nature of the bonding has been investigated using the electron localization function (ELF) [31] along with the molecular orbitals (MO). Such ELF have been found to be useful for elucidating the bonding characteristics of a variety of systems, especially in conjunction with the charge density. The value of the ELF lies between 0 and 1, where 1 represents a perfect localization of the valence charge density.

### III. RESULTS AND DISCUSSION

#### A. Structure, energetics and stability

The ground state geometries of $\text{Al}_n\text{Li}_n$ clusters can be grouped into two broad categories, for $n = 2 - 4$ and $n = 7 - 9$, depending on the growth pattern. In the first category a quinted roof-like structure of $\text{Al}_2\text{Li}_2$ is seen. The second category shows a pentagonal ring which is a signature of a icosahedral growth. The ground state geometries of $n = 5, 6, \text{ and } 10$
clusters show neither the quinted roof nor a pentagonal ring. In what follows, we discuss the structure and stability of these clusters. The stability is discussed via the binding energy ($E_b$), the dissociation energy ($\Delta E$) and the second difference in the total energy with respect to a single Al-Li pair ($\Delta^2 E$), and the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (figure 2). These quantities are defined as:

$$E_b[\text{Al}_n\text{Li}_n] = -E[\text{Al}_n\text{Li}_n] + n (E[\text{Al}] + E[\text{Li}])$$

$$\Delta E[\text{Al}_n\text{Li}_n] = E[\text{Al Li}] + (E[\text{Al}_n\text{Li}_n] - E[\text{Al}_{n-1}\text{Li}_{n-1}])$$

$$\Delta^2 E[\text{Al}_n\text{Li}_n] = E[\text{Al}_{n+1}\text{Li}_{n+1}] + E[\text{Al}_{n-1}\text{Li}_{n-1}] - 2E[\text{Al}_n\text{Li}_n]$$

The ground state geometry of Al$_2$Li$_2$ is a quinted roof (figure 1a(i)). This cluster is one of the most stable clusters of Al$_n$Li$_n$. The planar geometry (figure 1a(ii)) is the low-lying structure of the Al$_2$Li$_2$. Such planar structure, with some bending has been observed by Kumar [21] in the magic cluster Al$_{10}$Li$_8$. He found that in spite of having 8 valence electrons, the planar structure does not show any magical behavior. However, his search was restricted to just one structure, whereas, we have found a different geometry to be the lowest energy structure of Al$_2$Li$_2$. Our investigation shows that the quinted roof of Al$_2$Li$_2$ does exhibit some magical behavior. A substantial rise in the binding energy (figure 2a) is seen when two Al-Li dimers combine to form Al$_2$Li$_2$ cluster. Moreover, a peak in the dissociation energy ($\Delta E$) (figure 2b), a minima in the second difference in energy ($\Delta^2 E$) (figure 2c) and a large HOMO-LUMO gap (figure 2d) also signifies a relatively high stability of this cluster. A similar quinted roof structure is also seen in the ground state structure of the clusters Al$_3$Li$_3$ and Al$_4$Li$_4$. However, the Al$_3$Li$_3$ is not energetically as stable as Al$_2$Li$_2$ (see figure 1b(i)). The lowest energy structure of Al$_4$Li$_4$ shows two units of Al$_2$Li$_2$ (figure 1c(i)). These two units are arranged such that an Al$_4$ rectangle is formed. This rectangular shape gives rise to an antiaromatic nature in this cluster [9,12]. This structure has been extensively studied by us [9,11,41] and others [12]. The two low-lying structures of Al$_4$Li$_4$ (figure 1c(ii) and 1c(iii)) show a square-plane and a quinted roof of four Al atoms, respectively.
In Al₅Li₅ cluster, a square-plane of Al₄ is seen, with the fifth Al atom capping this plane (figure 1d). Such square-planar geometry of Al₄ was also observed in the all-metal aromatic compounds Al₄²⁻ and MAl₄ (M = Li, Na, and Cu) [8]. Al₅Li₅ shows the first three dimensional structure of Alₙ in AlₙLiₙ clusters. Recall that the appearance of such three dimensional geometry in pure Al clusters [16] is seen for Al₆. The Al₅Li₅ cluster is the most stable among the clusters studied. This is clear from the binding energy, ΔE, Δ²E, and the HOMO-LUMO gap plots shown in figure 2a-2c, respectively. An interesting aspect of the Al₅Li₅ cluster is the formation of a plane composed of four Li atoms with one Al atom at the center, akin to the face of a fcc cell. A similar structure for Al₅Na₅ was predicted by Dhavale [18] et al. A complete fcc structure can be formed by fourteen atoms: six Al atoms at the face centered sites and eight Li atoms at the vertices of the cube. Such structure is shown in figure 1e(i). This structure was first studied by Shah [28] et al. using DBMD. They found this structure to be the lowest energy structure of Al₆Li₈. We have also studied this structure by employing KS-BOMD method. We find that this fcc structure, with slight distortion, is 1.11eV higher than that the most stable structure of Al₆Li₈, shown in figure 1e(ii). It can be noted that the fcc structure and the lowest energy structure of Al₆Li₈ are nearly similar, the main difference being the elongation of one of the Al₄ square-planes in the fcc structure into a rectangle. It is interesting to note that the series Al₄²⁻, Li-Al₄⁻, Al₅Li₅, and Al₆Li₈ shows a three dimensional octahedral growth of Al cluster surrounded by Li atoms. This results in an effective delocalization of the electron density (see section III B). The Al₆Li₆ cluster also shows a geometry similar to that of Al₅Li₅, with distortions in the Al₄ square-plane (figure 3a(i)). In the first low energy structure (figure 3a(ii)), a tetrahedra of Al₄ is seen, while the other low lying structure shows an octahedra of Al₆. The octahedral structure is the ground state geometry of the six atom pure Al cluster [16].

The appearance of a pentagonal ring, which is a precursor to the icosahedral growth, is seen for n = 7 (Al₁₃ is a distorted icosahedra in its ground state [42]). The ground state geometry of Al₇Li₇ shows a pentagonal bipyramid of Al₇ which is capped by the Li atoms (figure 3b(i)). Appearance of a similar pentagonal ring in pure Al clusters (in neutral as...
well as singly charged form) is seen for Al$_9$ [16] as well as in tetravalent atom clusters viz. Sn, and Pb [27] for seven atom clusters. Incidentally, these clusters are isoelectronic similar to Al$_7$Li$_7$ with 28 valence electrons. The low energy structure of Al$_7$Li$_7$ (figure 3b(ii)) also shows a pentagonal ring. The ground state geometry of $n = 8$, 9, and 11 clusters (figure 3c(i), 4a(i) and 4c(i), respectively) also shows such pentagonal rings. However, the lowest energy structure of Al$_{10}$Li$_{10}$ cluster (figure 4b(i)) is completely different from that of the Al$_7$Li$_7$ to Al$_9$Li$_9$ and Al$_{11}$Li$_{11}$, in that no signature of the pentagonal ring is seen. In fact, the geometry is similar to that of Sn$_{10}$ i.e. a tetracapped trigonal prism (TTP) [43] with some distortions. This TTP structure is enclosed in a Li cage resulting in its distortion. It also shows magical behavior, since, it exhibits a peak in the dissociation energy ($\Delta E$), a minima in the second difference in energy ($\Delta^2E$), and a large HOMO-LUMO gap (figure 2a-2c, respectively).

We have done an analysis of the interatomic bond distances in order to understand the mixing and segregation behavior of the Al and the Li atoms. In figure 2d, we plot the minimum interatomic bond distances for Al-Al, Al-Li and Li-Li. We find that in smaller clusters ($n \leq 4$) the Al-Al bond is dominant. However, from $n = 5$ onwards, the Al-Li distance is comparable to the Al-Al bond distances. Recall that at $n = 5$, the first three dimensional Al$_n$ structure emerges, thereby increasing the surface area. This helps the Li atoms to maximize the Al-Li bonds and thereby move closer to the Al atoms.

It is well known that the density based method is not as accurate as the Kohn-Sham method, nonetheless, it has been extensively used to investigate the geometry, and stability of various Al-Li clusters [28–30]. Here, we make some pertinent comments on the difference in the geometry of the Al$_n$Li$_n$ clusters obtained by these two methods. Our results show that the geometries of some clusters were well predicted by DBMD. For instance, the structure of Al$_2$Li$_2$ was found to be a quinted roof by both the methods (see ref. 28 for DBMD results). Geometries of other clusters like Al$_7$Li$_7$ to Al$_9$Li$_9$ show some substitutional disorder. However, there are certain clusters where the geometries were quite different by the KS method. For example, the structures of Al$_3$Li$_3$, predicted by DBMD, is a capped trigonal bipyramid [28]. When optimized by KS, this structure gets Jahn-Teller distorted into a
structure with a quinted roof of Al$_2$Li$_2$. The evolution in the geometry by DBMD method shows an earlier appearance of three dimensional structure of Al$_n$ at $n = 4$ (Al$_4$ is tetrahedra in Al$_4$Li$_4$), as compared to the capped square of Al$_5$ in Al$_5$Li$_5$ by KS method.

**B. Bonding**

1. Al$_2$Li$_2$

As noted above, Al$_2$Li$_2$ is one of the most stable clusters. This cluster has 8 valence electrons, which corresponds to a closed shell in the jellium sense. However, the behavior of the MOs as well as the eigenvalue spectrum does not resemble that of the SJM. Kumar [21] found that the bonding between Al-Li in the planar Al$_2$Li$_2$ structure (figure 1a(ii)) is ionic. On the contrary, our investigation shows a covalent bond between Al$_2$ and the Li atoms, in addition to the covalent bond between Al-Al. In order to get a better insight of the bonding in Al$_2$Li$_2$, we have studied various clusters viz. Al$_2$, Al$_2^-$, Al$_2^{2-}$, Al$_2$Li, Al$_2$Li$^-$, and Al$_2$Li$^2$. This series represents a growth of Al$_2$Li$_2$ from the Al$_2$ dimer. In figure 5, we show the eigenvalue spectrum, binding energy per atom, and the Al-Al bond distance for the optimized geometries of these clusters. The eigenvalue spectrum of Al$_2$ shows a triply degenerate HOMO state. These states are partially filled two $\pi$ and one $\sigma$ bond (figure not shown). Addition of a Li atom splits the HOMO state (figure 5a) forming a $\sigma$ bond with the $p_y - p_y$ $\pi$ orbital of the Al$_2$ dimer (isodensity surfaces not shown). This also introduces a small HOMO-LUMO gap of about 0.15eV. The second Li atom further splits the HOMO state introducing a substantial gap of 0.68eV. However, in this case, the two Li atoms form a dimer, which is then covalently bonded to the Al$_2$ dimer. These covalent bonds are shown in figure 6. Moreover, a charge transfer from the Li atoms to the bonding region between the Al and Li takes place (figure not shown). This further strengthens the covalent bond between them.

In order to form ionic bond between Al and Li, a charge transfer from Li atom to Al
atom should take place. This would lead to a net negative charge on the Al\textsubscript{2} dimer and enhance its stability. The binding energy (figure 5b) of the negatively charged clusters viz. Al\textsubscript{2}\textsuperscript{-}, Al\textsubscript{2}\textsuperscript{2-}, and Al\textsubscript{2}Li\textsuperscript{-}, does show an increase over that of the corresponding neutral clusters. However, their HOMO state are multiply degenerate and partially filled orbitals (figure 5a). Moreover, a contraction of the Al-Al bond upon addition of an electron or a Li atom is seen, the contraction on addition of a Li atom being more than that due to the addition of an electron. Thus, a charge transfer is not preferred in this system.

2. Al\textsubscript{4}Li\textsubscript{4}

The bonding in Al\textsubscript{4}Li\textsubscript{4} cluster has been extensively studied by us [9,11,41] and others [12]. This cluster has been found to be antiaromatic with 4 − π electrons. For the sake of completeness, we discuss the bonding of this cluster. This cluster, as discussed earlier, is composed of two Al\textsubscript{2}Li\textsubscript{2} units arranged edge-to-edge to form a Al\textsubscript{4} rectangle. This rectangular structure leads to the antiaromaticity in this cluster. In this cluster \textit{sp}\textsuperscript{2} hybridization of Al takes place leaving one empty un-hybridized \textit{p} orbital. The valence electron of each of the four Li atoms is then transferred to this empty \textit{p\textsubscript{z}} orbital, thus providing 4 − π electrons for antiaromaticity. Interestingly, its first low-lying structure (figure 1c(ii)) can also be considered as a candidate for antiaromaticity. It has a planar Al\textsubscript{4} structure. An analysis of the MOs shows that this cluster also has 4 − π electrons similar to the lowest energy structure, thereby conforming the structural and electron count criteria for antiaromaticity. However, a detailed analysis of the magnetic field induced ring currents has to be done in order to understand the antiaromaticity in this structure.

3. Al\textsubscript{5}Li\textsubscript{5} and Al\textsubscript{6}Li\textsubscript{8}

As discussed in section III A, the structures of Al\textsubscript{5}Li\textsubscript{5} and Al\textsubscript{6}Li\textsubscript{8} (in fcc geometry) clusters show a square-plane of Al\textsubscript{4}. Such Al\textsubscript{4} square-plane in Al\textsubscript{4}\textsuperscript{2-} and Li-Al\textsubscript{5} has lead to aromaticity in these clusters [8]. Moreover, these clusters show a three dimensional octahedral growth of
the Al cluster. Hence, it is interesting to discuss the change in bonding, and hence the effect on the aromaticity in the clusters, Al$_4^{2-}$, Li-Al$_4^{-}$, Al$_5$Li$_5$ and Al$_6$Li$_8$. Recall that Al$_4^{2-}$ and Li-Al$_4^{-}$ are aromatic clusters with 2 − π electrons [8]. The HOMO state in these clusters are completely delocalized π orbitals. There are two more delocalized σ bonds: one composed of radial p orbitals, and the other composed of perpendicular p orbitals. Due to the presence of a Al$_4$ square-plane, the bonding in Al$_5$Li$_5$ and Al$_6$Li$_8$ clusters is expected to be similar to that in Al$_4^{2-}$. In that case, these clusters would have 2 − π electrons similar to that of Al$_4^{2-}$ and Li-Al$_4^{-}$, and show some signature of aromaticity. Interestingly, the HOMO state of Al$_5$Li$_5$ does show such a delocalized π bond between the Al$_4$ square (figure 8a). However, a lone electron is seen at the fifth Al atom that caps this square. This reduces the number of π electrons to one. Thus, due to the presence of just 1 − π electron the aromaticity is lost. The HOMO state of Al$_6$Li$_8$, on the other hand, is quite different than that seen in the previous clusters (figure 8b). It shows a localized bond composed of a p orbital of the Al atom. Moreover, its eigenvalue spectrum (figure 7) shows nearly a jellium-like structure. However, an analysis of the behavior of the molecular orbitals (figure not shown) of Al$_6$Li$_8$ shows that the lower ten states are jellium-like, whereas, the higher states are localized bonds composed of p orbitals. The 6$^{th}$ state in Al$_5$Li$_5$ and the 10$^{th}$ state in Al$_6$Li$_8$ are σ-bonded, composed of radial p orbitals (figure 8c, and 8d, respectively), and are analogous to the radial p orbitals of Al$_4^{2-}$. However, these bonds involve all the Al atoms, thus leading to a higher degree of delocalization.

4. Al$_n$Li$_n$ (n = 7 − 11)

The bonding in these clusters (Al$_n$Li$_n$, n = 7 − 11), is quite different from that of the smaller clusters. A mixture of localized and delocalized bonds is seen. Analysis of the behavior of the MOs shows that the eigenvalue spectrum of Al$_n$Li$_n$ can be classified into two groups: the lower n states are jellium-like, whereas, the higher states forms a complex band of localized bonds. The lower states can be identified as 1$s$, 1$p$, 1$d$, 2$s$, ..., in
conformation to the SJM. A typical representative isodensity plot of these orbitals is shown in figure 9. Further, the eigenvalue spectrum 7 shows a clear energy separation of these orbitals from the higher orbitals. In order to study this more extensively, we have performed the spherical harmonics analysis of the KS orbitals [44]. We find that the lower $n$ orbitals have a clear $s$ character (75-85%), whereas, the higher orbitals show a clear $p$ character. The lower orbitals corresponds to the 3$s$ orbital of the Al atom, which hybridize to form a jellium. However, this description cannot be extended to the higher states. The higher states, composed of Al-$3p$ orbital, forms a complex band of localized bonds. This localized bonding is also reflected in the ELF discussed below.

The localized bonding in the Al-Li clusters can be analyzed via the electron localization function plots. Previous investigations show that even in large Al-Li clusters, the Al-Al bond is covalent. However, our analysis on the structural properties shows a clustering of Al atoms enclosed in Li cage. This clustering could lead to a delocalization of the electron density. In order to study this more extensively, we have done an analysis of the electron localization function in the Al$_n$Li$_m$ clusters. In figure 10, we show the isovalued surface of the ELF for the clusters Al$_2$Li$_2$, Al$_5$Li$_5$, and Al$_{10}$Li$_{10}$, respectively. The Al-Al bond in these systems is seen at the ELF values of 0.85, 0.8, and 0.72, respectively. It is known that an ELF value greater than 0.7 corresponds to a localized bond [31]. Thus, the Al-Al bonds in these clusters are covalent in accordance with the previous observation. However, as the cluster grows, the localization of the electron density in these clusters is reduced. Further, the localization in Al$_5$Li$_5$ is only in the plane forming the square (for out of plane, the ELF value is 0.7). A similar behavior of the ELF for Al$_7$Li$_7$ (not shown in figure) is seen, in that, a localized bond along the pentagon (ELF value = 0.78) and delocalized bond in the perpendicular direction (ELF value = 0.6).
IV. TETRAVALENT BEHAVIOR OF Al IN Al\textsubscript{n}Li\textsubscript{n} CLUSTERS

Previous investigations on mixed Al-Li clusters [21,45,46], have shown a substantial charge transfer from the Li atom to the Al atom. Due to such charge transfer, Al behaves as a tetravalent atom in mixed Al-Li clusters with nearly 50:50 percent concentration. In this section, we discuss such behavior of Al\textsubscript{n} cluster in Al\textsubscript{n}Li\textsubscript{n} enclosed in Li cage. Analysis of the geometries of Al\textsubscript{n}Li\textsubscript{n} clusters show some remarkable similarities of the clusters of the Al\textsubscript{n} in Al\textsubscript{n}Li\textsubscript{n} to those of the tetravalent atoms viz., Si, Ge, Sn and Pb. For instance, the behavior of Al\textsubscript{2} in Al\textsubscript{2}Li\textsubscript{2}, observed by Kumar [21], was similar to that of Si\textsubscript{2}, in the sense that the Al-Al bond length of 4.48\text{a.u.} is comparable to that of 4.39\text{a.u.} in Si\textsubscript{2}. Moreover, the transition from the planar to three dimensional geometry at \(n = 5\), the appearance of a pentagonal ring at \(n = 7\), and the formation of the distorted TTP structure of Al\textsubscript{10} in Al\textsubscript{10}Li\textsubscript{10} indicate a tetravalent behavior of the Al atom. The eigenvalue spectrum, in figure 7, of the Al\textsubscript{10}Li\textsubscript{10} show remarkable similarity to that of the Sn\textsubscript{10} cluster. The bonding between Al-Al in these clusters is covalent, which is similar to that in the clusters of tetravalent atoms. Finally, the resemblance of the DOS of the Al-Li in its most stable bulk phase i.e. B32, to that of diamond [24] also indicates a tetravalent behavior of the Al atom in Al-Li systems with 50:50 concentration.

V. CONCLUSION

In the present work, we have reported the systematic investigations of the geometry, energetics, electronic structure and the bonding in various Al-Li clusters viz. Al\textsubscript{n}Li\textsubscript{n} (\(n=1-11\)), \(\text{Al}^2^-\), Al\textsubscript{2}Li, Al\textsubscript{2}Li\textsuperscript{-}, and Al\textsubscript{6}Li\textsubscript{8} using BOMD method within the framework of density functional theory. The bonding in these clusters was discussed via the electron localization function as well as the behavior of the occupied molecular orbitals. The growth pattern is divided into two broad categories: first consisting of a quinted roof of Al\textsubscript{2}Li\textsubscript{2} (\(n=2-4\)) and second consisting of a pentagonal ring (\(n=7-9\)). We find that the 8, 20, and 40 valence
electron systems are magic, exhibiting a peak in the dissociation energy, a minima in the second difference in energy, and a large HOMO-LUMO gap. The structural transition of Al\textsubscript{n} in Al\textsubscript{n}Li\textsubscript{n}, from two dimensional to three dimensional increases the surface area, thereby helping the Li atoms to maximize the Al-Li bonds as a result of which the Li atoms move closer to the Al atoms. The bonding between Al and Li atoms in Al\textsubscript{2}Li\textsubscript{2} is covalent, whereas, in larger clusters it is ionic. A charge transfer from Li atoms to Al atoms makes Al behave as a tetravalent atom like Si, Ge, Sn, and Pb in Al\textsubscript{n}Li\textsubscript{n} clusters. These negatively charged Al\textsubscript{n} structures are stabilized by the positive Li environment. The formation of the three dimensional Al\textsubscript{n} structure destroys the aromatic and antiaromatic nature in these clusters.

In clusters with more than six Al atoms, the behavior of the occupied MOs can be grouped into lower jellium-like and higher localized bonds. Moreover, the bonding between Al and Li atoms is ionic. Thus, a mixture of localized, delocalized, and ionic bonds is seen in these clusters. As the clusters grow, an effective delocalization is of the valence charge density is seen via the electron localization function.

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The antiaromatic properties in Al$_4$Li$_4$ was presented in the *Abstract in the Symposium on Trends in Theoretical Chemistry-2002 (TTC-2002)*, January 17-19, 2003 Indian Association for the cultivation of science Kolkata.


Molecules that are cyclic, planar, conjugated, possessing \((4n+2) \pi\) electrons and having chemical and structural stability are called as aromatic molecules. For details read the special issue on Aromaticity, *Chem. Rev.* **101** (no. 5) (2001).


[44] The character in an orbitals is calculated by projecting the orbitals onto spherical harmonics centered at each ionic sites within a sphere of a specified radius around each ion. The radius of the sphere is taken to be half of the distance of the ion from the nearest ion.


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atoms.
FIGURES

FIG. 1.

FIG. 2.

FIG. 3.

FIG. 4.

FIG. 5.

FIG. 6.

FIG. 7.

FIG. 8.

FIG. 9.

FIG. 10.