Electrostatic guidelines and molecular tailoring for density functional investigation of structures and energetics of \((\text{Li})_n\) clusters

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A molecular electrostatic potential (MESP)-guided method for building metal aggregates is proposed and tested on prototype lithium \((\text{Li})_n\) clusters from \(n=4\) to 58. The smaller clusters are subsequently subjected to direct density functional theory based geometry optimization, while the larger ones are optimized via molecular tailoring approach (MTA). The calculations are performed using PW91-PW91 as well as B3LYP functionals, and the trends in the interaction energies are found to be similar. The MESP-guided model for building metal clusters is validated by comparing the resulting cluster geometries with the ones reported in the literature up to \(n=20\). A comparison of the ionization potential and polarizability (up to \(n=22\)) with their experimental counterparts shows a fairly good agreement. A new MTA-based scheme for calculating the ionization potential and polarizability values of large metal clusters is proposed and tested on \(\text{Li}_{40}\) and \(\text{Li}_{58}\) clusters. Further, the existence of “magic numbered clusters” up to \(n=22\) is justified in terms of “maximum hardness principle” as well based on molecular electron density topography and distance descriptors. © 2008 American Institute of Physics. [DOI: 10.1063/1.2993169]

I. INTRODUCTION

In the recent years, understanding the electronic structure of metal and molecular clusters has attracted attention of theoretical as well as experimental physicists and chemists. Metal clusters play a significant role in catalysis, biomedicine, solid batteries, microelectronics, etc. The alkali metal clusters are good model systems for studying the structural features and size-dependent electronic properties. The primary aim of these extensive studies is to bridge the gap between clusters and condensed matter and also assist in understanding the nucleation phenomena and phase transitions. One of the well-known size-dependent characteristics is the existence of stable clusters with specific sizes called “magic numbers.”

From several theoretical models proposed for exploring the structures, energetics, and properties of metallic clusters, the foremost are Hückel-type model and jellium model. The jellium model has been successfully applied to sodium and potassium clusters, but it is found not to work well for lithium clusters. That has necessitated the introduction of newer theoretical approaches for handling lithium clusters \((\text{Li})_n\). Sugino and Kamimura developed localized orbital Hartree–Fock (HF)-derived formalism for exploring small cluster geometries, enabling the attainment of local energy minima for clusters of size \(\leq 14\). Rothlisberger et al. used the first-principles molecular dynamics methods, within the local density approximation (LDA), for studying metal clusters with \(n=20\). Small lithium clusters have also been studied using the configuration interaction (CI) and coupled cluster (CC) methods. Boustani et al. and Blanc et al. studied \((\text{Li})_n\) clusters up to \(n=9\) at multireference CI level. These calculations reported different local minima for clusters up to \(n=14\) providing an explanation for the magic numbered clusters. Rao et al. studied lithium clusters up to \(n=6\) through a CI method and compared the optical absorption with its experimental counterpart. For a recent comprehensive review on metal clusters, see Baletto and Ferrando.

The above theoretical methods are compute-intensive leading to a bottleneck for exploring large metal clusters. To overcome the computational limitations, the density functional theory (DFT) based on the Kohn–Sham formalism is generally employed. Fornier et al. made use of the so-called Tabu algorithm for locating \((\text{Li})_n\) cluster energy minima up to \(n=20\) using generalized gradient approximations (GGA) exchange-correlation functionals. Gardet et al. studied the energetics and structural properties of \((\text{Li})_n\) up to \(n=20\), with GGA functionals. Higher lithium clusters were built by addition of Li or Li2 moieties into the parent cluster so as to engender maximum number of pentagonal bipyramidal (PBP) motifs in them. Clusters generated by this model were seen to possess high stabilization energies enabling location of energetically most favorable clusters for \(n=18\) and 20. However, the validity of this model has, as yet, not been assessed for building larger clusters, prompting a search for a systematic approach for this purpose.

The common experimental methods for exploring metal clusters include electron spin resonance (ESR), matrix isolation infra-red (IR), Raman spectroscopy, etc. Small lithium clusters can be generated through the matrix isolation or supersonic jet expansion and can be explored via the above spectroscopic methods. It is experimentally difficult to generate smaller clusters of specific sizes, and there is no reliable experimental method to map the geometries of these clusters. However, spectral methods combined with \textit{ab initio} calculations do help in this respect.
Employing the jellium model, Ekart and Beck showed that the sodium clusters of sizes of 8, 20, 40, 58, and 92 exhibit special (magic) behavior. Knight et al. experimentally verified this observation via mass spectrometry, wherein the magic numbered clusters show more intense peaks compared to clusters of other sizes. The magic numbers vary for van der Waals–type clusters and for the strongly interacting covalent or metallic crystals. It is also found that the clusters with less Jahn–Teller distortion are energetically more preferred over clusters with more distortion. The investigation of special stability of general metal clusters thus warrants the use of electronic structure methods.

Some of the experimentally explored electronic structure properties of clusters are ionization potential (IP), polarizability, chemical potential, dissociation energy, optical properties, etc. The literature works on property calculations have a limitation in optimizing the geometries at higher level of theory using adequate basis set. Hence, the theoretical parameters are calculated employing the scaled geometry using a common factor to the HF level geometry. Rao et al. employed CI and Møller-Plesset (MP2) level of theory to study neutral, cationic, and hydrogenated lithium clusters. Bonačić-Koutecky et al. have studied clusters up to Li₉, using multireference CI method with a large basis set to obtain the local minimum geometries and highly accurate IPs. Dugourd et al. have reported the IP for (Li₉) clusters up to n=26, obtained through photoionization. Wheeler and Shafer have reported the IPs of (Li₉) and (Li₉)₉ clusters at CCSD/cc-pwCVQZ level theory. Chandramur et al. found a good correlation between the computed IPs and polarizabilities of (Li₉) and (Na₉) clusters of size up to n=10 at MP2 and B3LYP/6-31+G(d) level. Some newer approaches for enabling equally reliable DFT-based treatment of large clusters are hence warranted.

At this juncture, some of the interesting questions we would like to address in the current work are as follows. (i) Is there an electron density–based systematic method for building large metal clusters? (ii) Is there a simpler scheme to obtain electronic parameters such as IP and polarizability of large metal clusters? (iii) Could energy- or electronic property–based descriptors be used for explaining magic numbered clusters?

II. METHODOLOGY

Overcoming the inadequacy of HF theory and computational efforts in dealing with large systems has necessitated theoretical studies being limited to Kohn–Sham DFT. Two favored approximations for exchange-correlation functional are the LDA and GGA. It is reported that LDA functionals are good for exploring relative energies of structures, while GGA functionals work well for property evaluations. The agreement of experimental properties of metal clusters with those calculated with GGA functionals, viz., the PW91-PW91 and VWN with 6-31+G(d), 6-311+G(d), DZP2, and cc-pV5Z Gaussian basis sets, has been reported in the literature. The complexity of determining the local energy minima of metal clusters has been discussed, and it is reported that there is no general systematic approach for handling this problem. One way to embark upon such a systematic study is to explore the electron density or a related derived quantity, viz., molecular electrostatic potential (MESP). MESP-based information has been used in generating initial structures of molecular clusters, while to the best of authors’ knowledge, it has not yet been explored for building metal clusters. The MESP, V(r) at a point r, due to nuclear charges \{Z₉\} placed at \{R₉\} and the electron density \(\rho(r)\) of the molecule under consideration, is given by

\[ V(r) = \sum_{A} \frac{Z_{A}}{|r - R_{A}|} - \int \frac{\rho(r')}{|r - r'|} d^{3}r'. \]

The first and second terms on the right hand side of Eq. (1) represent the bare nuclear and electronic potentials, respectively. The sign of the V(r) in any particular region depends on whether the nuclear or electronic effects are dominant there. Topographical details of a scalar field are brought out in terms of its critical point (CPs), viz., maxima, minima, and saddles, at which all the first order partial derivatives of the function vanish. The latter may be classified as \((R, \sigma)\), where \(R\) denotes the rank (number of nonzero eigenvalues of the Hessian matrix) and \(\sigma\) the signature (algebraic sum of the signs of the eigenvalues).

The most negative region of the parent cluster acts as a harbinger for the attack of the incoming electropositive lithium atom. Initial larger clusters can be generated by placing the lithium atom at the MESP minimum of the parent cluster. Such a MESP-based approach for generating large molecular clusters has recently been reported. In the present work, we extend it to build \((Liₙ)\) clusters. These clusters are optimized further at \(ab initio\) level of theory. For the stationary point geometries, density matrices are calculated using the \(ab initio\) package GAUSSIAN03. The MESP is evaluated using the INDPROP package. Larger cluster optimizations are performed using the molecular tailoring approach (MTA), a linear scaling algorithm, which has been thoroughly benchmarked at different levels of theory for large molecules and clusters.

As noted above, larger metal clusters are generated using the MESP of smaller motifs and optimized at B3LYP/6-31G(d) level of theory, imposing no constraints, using MTA. In MTA, the whole cluster is divided into a set of main fragments \(\{f_{i}, f_{j}, \ldots, f_{k}\}\) and overlapping fragments, viz., secondary, \(f_{i} \cap f_{j}\), tertiary overlapping fragments, \(f_{i} \cap f_{j} \cap f_{k}\), etc. The total energy and gradients for the whole cluster are calculated from the fragment energies \(E_{i}, E_{j}, \ldots, E_{i} \cap f_{j}, \ldots, E_{i} \cap f_{j} \cap f_{k}\) using the cardinality expression

\[ E = \sum E_{i} - \sum E_{i} \cap f_{j} + \ldots + (-1)^{k-1} \sum E_{i} \cap f_{j} \cap \ldots \cap f_{k}. \]

(2)

Further, the fragment energy gradients can be patched to get the total cluster atomic gradients via the general expression as per Eq. (3),
2.84 Å. See text for details.

164314-3 Structure and energetics of (Li)$_n$ clusters

Algorithm 31 is embedded in GAMESS code 33 and a few final popularized 37 the use of Laplacian of MED, viz.,
and strain in the bonds. Bader and co-workers have
MED, MED Laplacian, and ellipticities at the BCPs are well
bond CP

The next section discusses the geometries and energetics of (Li)$_n$ clusters. Section III A discusses MESP-guided method to build metal clusters and MTA optimization. The following section gives a comparison of resulting geometry with literature one. In Sec. III C a statistical distance analysis is reported. Section IV presents the cluster properties, viz., MED, IP, and polarizability with a comparison with their experimental counterparts.

A. MESP-guided cluster building model and CG-MTA optimization

The MESP of the optimized Li$_2$ molecule at B3LYP/6-31+G(d) level in Fig. 2 [2-4] shows a degenerate MESP ring at $-0.024$ a.u. around the bond connecting two lithium atoms and is expected to act a harbinger for the attack of an incoming electropositive lithium atoms. Table I lists the energies and the interaction energies of the most stable (Li)$_n$ clusters along with the corresponding electronic properties. Energies and the respective interaction energies of all the studied clusters are reported in Table S1 and S2. Interaction energies are computed with respect to Li$_2$ molecular energy as discussed earlier. The resulting optimized Li$_4$ cluster with an interaction energy of $-16.0$ kcal/mol is shown in Fig. 2 [4-1] with four MESP minima at $-0.028$ a.u. On saturating all the MESP minima of Li$_4$ with lithium atoms followed by further optimization yields an Li$_8$ local minimum cluster with an interaction energy of $-52.4$ kcal/mol. Li$_8$ cluster (Fig. 2 [8-III]) has 12 MESP (3, +3) CPs at $-0.034$ a.u. These MESP minima drive the cluster growth in a tubelike fashion (in path A) and result into the second most stable Li$_{20}$ cluster with an interaction energy of $-244.3$ kcal/mol. The Li$_{20}$ cluster (Fig. 2 [20-II]) has two MESP minima yielding on addition of two Li atoms, the Li$_{12}$ cluster, with an interaction energy of $-262.6$ kcal/mol. Six MESP minima are displayed by Li$_{12}$
(in Fig. 2 [22-II]) resulting into Li$_{28}$ on addition of six Li atoms. 12 MESP minima of Li$_{28}$ (in Fig. 2 [28-I]) engender Li$_{40}$ (in Fig. 2 [40-I]) with the interaction energy of $-601.6$ kcal/mol, the most stable 40-mer within the series (cf. Table S2).

A second growth path (denoted by B) can be traced starting from Li$_4$ (Fig. 2 [4-I]) by partly saturating the MESP minima, i.e., by saturating only two CPs of Li$_4$, after optimization this cluster results into Li$_6$ cluster with interaction energy of $-39.0$ kcal/mol, as reported in Table S1. The MESP CPs at $-0.027$ a.u. of the pentagonal pyramidal Li$_6$ cluster (Fig. 2 [6-II]) direct the attack of the next six lithium atoms so as to result in an Li$_{12}$ cluster. Li$_{12}$ cluster (Fig. 2 [12-I]) has ten MESP minima and engenders a Li$_{22}$ cluster with an interaction energy of $-287.6$ kcal/mol. The Li$_{12}$ acts as a prototype cluster for the formation of icosahedral geometries.

FIG. 2. MESP-guided method for building Li$_n$ clusters. The MESP isosurface is at $-0.022$ a.u. See text for details.

TABLE I. The most stable cluster, energies (a.u.), interaction energies (kcal/mol) [$\Delta E$ is defined as $E$(Li)$_n$ $-nE$(Li)$_1$/2], cation energies, anion energies (in a.u.), theoretical (experimental) AIP, EA, and hardness [Ref. 38] is defined as (AIP-EA)/2 (in eV) at B3LYP/6-31+G(d) level of theory. See text for details.

<table>
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<th>Geometry</th>
<th>Li$_n$</th>
<th>$\Delta E$</th>
<th>(Li$_n^+$)</th>
<th>(Li$_n^-$)</th>
<th>AIP</th>
<th>EA</th>
<th>Hardness</th>
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<td>$-14.821$</td>
<td>$77$</td>
<td>$-15.030$</td>
<td>57</td>
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<td>69</td>
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<td>$-29.888$</td>
<td>40</td>
<td>$-30.077$</td>
<td>52</td>
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<tr>
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<td>13</td>
<td>$-41.4$</td>
<td>$-44.953$</td>
<td>94</td>
<td>$-45.141$</td>
<td>28</td>
</tr>
<tr>
<td>Li$_8$[8-I]</td>
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<td>$-73.3$</td>
<td>$-60.010$</td>
<td>91</td>
<td>$-60.201$</td>
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<td>$-75.209$</td>
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<td>19</td>
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<td>$-150.593$</td>
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<td>$-165.489$</td>
<td>09</td>
<td>$-165.657$</td>
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<td>13</td>
<td>$-601.6$</td>
<td>$-301.126$</td>
<td>90</td>
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<td>84</td>
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<td>Li$_{58}$[58-I]</td>
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<td>02</td>
<td>$-861.0$</td>
<td>$-436.680$</td>
<td>00</td>
<td>$-436.770$</td>
<td>37</td>
</tr>
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</table>
tery. The MESP-guided method could locate nonicosahedral to icosahedral geometrical transformation to happen between \( n = 22 \) and 28, because on saturating the deepest MESP minimum of \( \text{Li}_{22} \) will result in the formation of first icosahedron in the cluster. Earlier literature work has estimated this geometrical transition to occur in the range of 19 < \( n < 26 \). The distribution of MESP minima of \( \text{Li}_{22} \) (Fig. 2 [22-I]) directs the incoming lithium atoms and yields a \( \text{Li}_{23} \) cluster. The MESP distribution of \( \text{Li}_{28} \) (Fig. 2 [28-I]) shows 12 minima. These CPs direct the growth of the cluster into the energetically stable \( \text{Li}_{40} \) cluster (Fig. 2 [40-II]) with interaction energy of \(-552.0 \) kcal/mol.

Similarly, another MESP-based growth path (viz., by C) can be traced starting from the square pyramidal geometry of \( \text{Li}_6 \) [6-I] and MESP CPs finally direct the cluster growth into the other two \( \text{Li}_{40} \) clusters (cf. Fig. 2 [40-IX and 40-IV]), with interaction energies of \(-468.6 \) and \(-516.7 \) kcal/mol, respectively. In the same way, other larger clusters can be probed by starting from \( \text{Li}_8 \) (Figs. 2 [8-III] and \( \text{Li}_8 \) [6-II]), which direct the lithium atoms to get attached in a tubelike way (depicted as paths D and E) shown in Fig. 2 [40-III and 40-V] with interaction energies of \(-522.1 \) and 501.2 kcal/mol with CG-MTA based geometry optimization.

MESP-based growth criterion offers a systematic, stepwise procedure for consecutive addition of even number of lithium atoms into the parent clusters. The MESP-guided method on subsequent optimization seems to direct the cluster growth so as to have maximum compactness and symmetry. The initial guess geometries generated randomly are found to be poor since the magnitude of the gradients turns out to be high compared to the one generated via MESP guidance. A critical comparison of the optimized geometries with the ones reported in the literature up to 20-mers is made in the next subsection.

### B. A comparison of theoretical geometries with literature ones

The geometries of the structures thus generated are compared with the ones reported in the literature. Even though both PW91-PW91/cc-pVTZ and B3LYP/6-31+G(d) density functionals give comparable geometries and relative trends in energies up to \( n = 22 \), only the B3LYP functional is employed for dealing with larger lithium clusters. The present work mainly focuses on a comparison of even numbered lithium clusters with experimental ones because matrix isolation studies confirmed the absence of stable existence of odd numbered paramagnetic clusters.\(^{19}\)

The experimental bond length in \( \text{Li}_2 \) is 2.75 Å, whereas the one in the current work at B3LYP/6-31+G(d) level is 2.73 Å. The energies (in a.u.) and interaction energies (in kcal/mol) with reference to \( \text{Li}_2 \) building blocks of lithium clusters are reported in Table I. Boustani et al.\(^{13} \) have reported the local minima of \( \text{Li}_n \) clusters up to \( n = 14 \) at CI level of theory and Gardet et al.\(^{18} \) up to \( n = 20 \) using Dirac-VWN and B88P86 density functionals. Boustani et al.\(^{13} \) reported three \( \text{Li}_1 \) local minima of \( D_{2h} \), \( C_{2v} \), and \( D_{4h} \) symmetries with the lowest energy cluster belonging to \( D_{2h} \) point group with interaction energy of \(-15.9 \) kcal/mol relative to \( \text{Li}_2 \) molecule. The respective \( \text{Li} \cdot \cdot \cdot \text{Li} \) distances reported at CI level are 2.69 and 3.16 Å are comparable with the one in the current work at 2.61 and 3.04 Å (Fig. 3) and also with the values reported by Gardet et al.\(^{18} \) The present work could not locate the other local minima reported by Boustani et al.\(^{13} \) belonging to the \( C_{2v} \) and \( D_{4h} \) point groups. These geometries converged to the most stable \( D_{2h} \) one on optimization. Other energetically favorable local minima located in the current work are also documented in Fig. 3.

Gardet et al.\(^{18} \) and Boustani et al.\(^{13} \) reported three local minimum geometries of \( \text{Li}_6 \) belonging to \( C_{5v} \), \( C_{2v} \), and \( C_{3v} \) point groups at DFT and CI levels of theory, respectively. The reported lowest energy \( \text{Li}_5 \) cluster belongs to the \( C_{5v} \) point group at both the levels\(^{13} \) and the geometrical parameters (shown in Fig. 3) are 3.10 and 3.15 Å at CI and 2.85 and 3.14 Å at B3LYP levels. The reported geometrical parameters in the present work are shown in Fig. 3, 6-II and the respective values are 2.83 and 3.17 Å, with interaction energy of \(-39.0 \) kcal/mol (cf. Table I). In the present work, the lowest energy cluster belongs to the \( C_{2v} \) point group (Fig. 3, 6-I) with an interaction energy of \(-41.4 \) kcal/mol. The \( C_{3v} \) geometrical parameters (6-III) reported by Boustani et al.\(^{13} \) are 3.11 and 3.19 Å and by Gardet et al.\(^{18} \) are 2.98 and 2.98 Å, respectively. In the current work, these parameters turn out to be 3.01 and 3.00 Å, respectively.

The lowest energy geometry of \( \text{Li}_8 \) (8-I) belongs to the \( T_d \) point group.\(^{18} \) The present calculations at B3LYP and PW91-PW91 could locate this energetically most favorable with interaction energy (Tables I and S1) of \(-73.3 \) kcal/mol. The second cluster belongs to \( D_{2h} \) point group (8-II) and the third one to \( C_{2v} \) point group, in agreement with the results of Gardet et al.\(^{18} \) The calculated bond lengths are in agreement with the ones reported in the literature, with \( \text{Li} \)--\( \text{Li} \) bond distances at 3.04 and 2.92 Å. The energetically favorable \( n = 18 \) belongs to the \( C_{5v} \), \( D_{3h} \), and \( D_{4h} \) point groups, with \( C_{5v} \) geometry being energetically the lowest. All the energetically favorable clusters of \( \text{Li}_{18} \) obtained in the present study (18-I, 18-II, and 18-III) are displayed in Fig. 3 and the respective energies reported in Table S1.

At this juncture, the strength of the MESP-guided method for building metal cluster can be assessed by comparing this method with the one proposed by Gardet et al.\(^{18} \) viz., the method of maximizing the number of PBP motifs to build \( \text{Li}_{20} \) from \( \text{Li}_{18} \) shown in Fig. 4. Even though these two routes increase the number of PBP motifs in the \( \text{Li}_{20} \) clusters, the MESP-based method predicts the existence of the most stable \( \text{Li}_{20} \) \( C_{2v} \) cluster (20-I) with an interaction energy of \(-253.2 \) kcal/mol. This cluster is generated from the \( \text{Li}_{18} \) cluster by placing the \( \text{Li} \) atoms at the MESP minima, while the other \( \text{Li}_{20} \) \( C_{2v} \) cluster (20-II) with interaction energy of \(-244.3 \) kcal/mol is generated by placing lithium atoms arbitrarily at some other point for maximizing the number of PBP motifs. The energetic trends reported in Table S1 also show that the \( C_{2v} \) geometry (20-I) is energetically more stable by 8.9 kcal/mol than the \( C_{v} \) geometry (20-II). The MESP-guided method is seen to work well and enables in locating the energetically favorable clusters reported in the literature up to \( n = 20 \) and is also able to generate many other energetically favorable configurations.
As $n$ increases from 20 to 40, the ones with hexagonal bipyramid (HBP) core are seen to become more stable than the ones with PBPs. The most stable Li$_{40}$ cluster has stabilization energy of $-601.6$ kcal/mol (cf. Table I). In the two most stable Li$_{40}$ clusters (40-I and 40-II), one can notice the formation of body centered cube (bcc)-type arrangement of lithium atoms in the outer layer of the clusters as shown in Fig. 5 [40-I]. The central core of the cluster remains unaltered, on growing the cluster from Li$_{40}$ to Li$_{58}$. A limited search over 11 trial geometries generated with MESP guidelines has been done, and the most stable cluster among them (58-I) is seen to have interaction energy of $-861.0$ kcal/mol. The Li–Li bond length is seen to reduce as the cluster size increases. The central core part still bears maximum number of HBP motifs that act as a harbinger for the formation of bcc-type arrangement at the outer layers. This may be conjectured as the starting point for the phase transition from icosahedral to HBP cluster core.

C. Statistical distance distribution analysis of clusters

A further statistical distance analysis is performed on the most stable cluster with $n=2-58$. For analyzing these geometries, the centers of mass (c.m.) of the cluster are determined for $n=18, 20, 22$, and 24 clusters and the atomic in-
Dexing is given on the basis of distribution of atoms from this point (i.e., the one near to c.m. is atom no. 1, next atom no 2, and so on up to atom no. 18). The number of near neighbors in 2–3.25 Å range for each atom index is counter and depicted in Fig. 6. The range of the distance distribution is taken to be the $d_{Li_2}$, where $d_{Li_2}$ is the Li−Li distance in Li$_2$ molecule. The 0.75 Å is taken because the added lithium atoms get displaced from the MESP minimum typically by this magnitude after the cluster optimization. From Fig. 6, it is noticed that, even though the Li$_{18}$ core shrinks with cluster size, each atom falling within the same radial distribution has same number of near neighbors. This indicates that the clusters are not much perturbed on consecutive addition of Li atoms into the cluster.

A detailed statistical distance analysis on the most stable lithium clusters is presented in Table S3. The total number of Li·Li interaction in this range increases with the cluster size as well as the number of distances less than the Li–Li dimer bond is also increasing with cluster size. The inner Li·Li bonds shrink than the outer ones with cluster size.
The stable existence of magic numbered clusters compared to the neighboring clusters can be seen on the basis of average distance descriptor in Table S3. The average Li····Li bond distance of magic numbered clusters is less than neighboring clusters because of the high comparative compactness compared to neighboring ones.

IV. ELECTRONIC PROPERTIES OF (Li)$_n$ CLUSTERS

A. MED

A summary of the results of MED, MED Laplacian, and ellipticity at the BCP is presented in Tables II and S4 for the most stable lithium clusters with $n=2$–58. The MED value at the BCP is generally found to increase with cluster size until $n=8$ and the function value remained almost steady thereafter. The clusters with $n=2$, 8, and 20 are seen to possess higher MED values. Further, the Laplacian values for clusters with $n=2, 8, 20, 40, 58$ exhibit negative values. This may be an indicator of relative stability of these clusters. Also, these clusters show high percentage of bonds with ellipticities less than one, which indicate an enhanced stabilization energy.

More Li$_{58}$ clusters need to be examined for checking the veracity of this observation.

![Graph of interactions](image)

**FIG. 6.** The number of interactions with Li···Li distances between 2 and 3.25 Å vs atom index for (Li)$_n$ clusters with $n=18, 20, 22, 24$. See text for details.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>$\alpha$</th>
<th>$\rho(r)$</th>
<th>$\nabla^2\rho(r)$</th>
<th>ellipticity $\varepsilon$</th>
<th>$N_{\nu&lt;1}/N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$[2-I]</td>
<td>197.3 (221.4)</td>
<td>0.0125, 0.0125</td>
<td>$-0.0008$, $-0.0008$</td>
<td>0.000, 0.000</td>
<td>2/2</td>
</tr>
<tr>
<td>Li$_4$[4-I]</td>
<td>357.6 (326.6)</td>
<td>0.0113, 0.0113</td>
<td>$-0.0015$, $-0.0015$</td>
<td>0.772, 0.772</td>
<td>7/7</td>
</tr>
<tr>
<td>Li$_6$[6-I]</td>
<td>461.5 (360.4)</td>
<td>0.0128, 0.0128</td>
<td>0.0014, 0.0014</td>
<td>0.042, 0.145</td>
<td>8/8</td>
</tr>
<tr>
<td>Li$_8$[8-I]</td>
<td>609.3 (561.5)</td>
<td>0.0129, 0.0129</td>
<td>$-0.0007$, $-0.0007$</td>
<td>0.000, 0.000</td>
<td>23/23</td>
</tr>
<tr>
<td>Li$_{12}$[12-I]</td>
<td>801.6 (956.5)</td>
<td>0.0116, 0.0116</td>
<td>0.0011, 0.0011</td>
<td>0.054, 0.057</td>
<td>12/23</td>
</tr>
<tr>
<td>Li$_{18}$[18-I]</td>
<td>1074.4 (1167.3)</td>
<td>0.0111, 0.0111</td>
<td>0.0008, $-0.0003$</td>
<td>1.110, 8.774</td>
<td>10/65</td>
</tr>
<tr>
<td>Li$_{20}$[20-I]</td>
<td>1239.4 (1202.4)</td>
<td>0.0123, 0.0123</td>
<td>$-0.0006$, 0.0008</td>
<td>0.522, 1.873</td>
<td>20/60</td>
</tr>
<tr>
<td>Li$_{22}$[22-I]</td>
<td>1327.1 (1337.5)</td>
<td>0.0117, 0.0117</td>
<td>0.0001, 0.0009</td>
<td>2.662, 4.959</td>
<td>14/49</td>
</tr>
<tr>
<td>Li$_{40}$[40-I]</td>
<td>1391.0</td>
<td>0.0114, 0.0114</td>
<td>$-0.0009$, $-0.0013$</td>
<td>1.390, 1.260</td>
<td>45/139</td>
</tr>
<tr>
<td>Li$_{58}$[58-I]</td>
<td>…</td>
<td>0.0150, 0.0125</td>
<td>$-0.0006$, $-0.0009$</td>
<td>0.850, 1.290</td>
<td>67/159</td>
</tr>
</tbody>
</table>

TABLE II. Electronic properties of Li$_n$ clusters in a.u. wherever applicable: Theoretical (experimental) polarizability (in a.u.$^3$), MED [$\rho(r)$], MED Laplacian [$\nabla^2\rho(r)$] at BCP, ellipticity ($\varepsilon$), and ratio of number of bonds less than 1 ($N_{\nu<1}$) to total number of bond CPs (N). See text for details.
A comparison of the B3LYP/6-31+G(d) level AIP of theory with its experimental counterparts is given in Table I. Wheeler et al. reported the AIP (Li), for n = 4 at CCSD and Chandrakumar et al. for n = 2–10, at MP2 levels of theory. The calculated AIPs of Li2 molecule at B3LYP level of theory and through photoionization experiments, respectively, are (all values in eV) 5.25 [5.14]. The Li2 AIPs at MP2 and CCSD, respectively, are 4.89 and 5.14. The Li4 AIP is 4.53 [4.31], and at MP2 and CCSD, respectively, are 4.40 and 4.74. For Li6 and Li8 AIPs are 4.25 [4.20] and 4.16 [4.49] at MP2 and are 4.63 and 4.60, respectively. The calculated AIP values for n = 18, 20, and 22 indicate a fair agreement with their experimental counterparts but does not show small fluctuations displayed by the experimental values. The AIPs reported by Chandrakumar et al. at B3LYP level of theory are comparable with the values in the current work. Although the AIPs at MP2 and B3LYP levels of theory are slightly overestimated, the ones at CCSD level are comparable with the corresponding experimental ones.

The AIPs for the Li20 and Li30 clusters are calculated through the MTA fragmentation scheme discussed in Methodology section. These Li20 clusters are divided into two main Li30 fragments and one overlapping fragment of Li16 with R-goodness value of 3.7 A. The optimization procedure is followed separately for the neutral and charged Li40 clusters as mentioned in Methodology section. The AIP, viz., the difference in energy of the most stable Li40 and (Li30)+ clusters is 3.43 eV. This value is lower than the corresponding experimental value for Li22 and higher than the work function of lithium at 2.89 eV. The same procedure is followed for Li30 with 34 atoms constituting the main fragments with one overlapping fragment containing 10 lithium atoms. The AIP in this case turns out to be 3.24 eV (cf. Table I). The agreement of the calculated AIPs with experimental ones clearly indicates that the MTA-fragmentation scheme for AIP evaluation is a fair approximation to deal with larger metal clusters.

A probable justification for the existence of “magic numbered clusters” can also be offered on the basis of density functional descriptors. The parameter “hardness” of a species is defined as the difference of the AIP and the electron affinity (EA). A species with high AIP and low EA is endowed with high hardness value. The “maximum hardness principle” states that the molecules arrange themselves so as to have maximum hardness as possible. It is seen from the hardness value in Table I that the clusters with n = 2, 8, 18, and 22 are endowed with special stability as compared to their immediate neighbors. Again, this high hardness can be heuristically explained in terms of high compactness of the clusters and less strained bonds in magic clusters. Harbola observed a similar trend in hardness value with lithium clusters of varying sizes employing jellium model.

The polarizability values of (Li)n clusters are also reported in Table II. It is seen that the polarizability of the cluster increases with the cluster size, indicating an increased valence electron delocalization with cluster size. The consistency the polarizability values with these different fragmentation schemes is checked for Li20 clusters. The calculations show that with increasing fragment R-goodness the polarizability is calculated with more accurately as compared to that obtained by actual calculations. The MTA-based polarizability of Li20 with three different fragmentation schemes is calculated and the values are 1238, 1244, and 1249 a.u. with increasing R-goodness values (2.6, 2.8, and 3.1 Å) and the actual calculated value is 1263 a.u.. The best MTA-based value is thus seen to be in error by about 1.2% as compared to its actual counterpart. The consistency of the calculated value with a different fragmentation scheme shows that the dependence of polarizability on high R-goodness fragmentation scheme is rather small. The Li40 cluster polarizability is also calculated with a high R-goodness value and also report values obtained by two different schemes are 1391 and 1382 a.u.. Following Ghosh and Chandrakumar, we have also made a plot IP−1/n and α1/3/n for (Li)n clusters. Figure 8 displays this plot and reveals an excellent correlation coefficient of 0.99 between the plotted entities for clusters between n = 2 and 40 at B3LYP/6-31+G(d) level of theory.

In brief, a MTA-based fragmentation scheme for evaluation of the properties, viz., IP and polarizability has been applied to large (Li)n clusters. Further, the existence of magic numbered clusters is justified on the basis of MED and MED Laplacian and ellipticity at the BCPs.

FIG. 7. The MED contours and topography of (a) Li30 (20-I) and (b) Li32 (22-I) pentagon at the center. The blue dots [BCP1, BCP2, and BCP3] are the high MED valued BCP and green dots [BCP] are the highly strained BCPs. The outermost MED contour is at 0.0005 a.u. and the MED contours are separated by 0.0005 a.u. See text for details.

FIG. 8. A relationship between IP−1/n and α1/3/n of (Li)n with n=2–40 at B3LYP/6-31+G(d) level of theory.
V. CONCLUDING REMARKS

The main highlights of the present work can be summarized as follows. Molecular electrostatics-based method of building metal clusters is proposed and tested on prototype lithium metal clusters. Many trial geometries were generated by placing lithium atom near the MESP minima of the previously generated (Li), clusters. The large clusters generated thus generated have been subsequently optimized using the MTA method. It is observed that generally there is no drastic change within the core of the cluster on consecutive addition of lithium atoms to the parent cluster. Use of MTA fragmentation scheme for the evaluation of properties such as IP and polarizability is proposed, and the agreement of the results employing fragmentation approach with the actual value is also verified for large lithium clusters. The special stability employing fragmentation approach with the actual value is proposed, and the agreement of the results of lithium atoms to the parent cluster. Use of MTA fragmentation approach with the actual value is proposed, and the agreement of the results of lithium atoms to the parent cluster.

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