

Structural and electronic properties of stable Li_n ($n=2-10$) clusters: A density functional study



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ABSTRACT

Structure and relative stability of Li_n clusters for $n=1-10$ were investigated using density functional methods based DMol³ program. The structures of Li clusters were determined in terms of Li–Li bond length and the results are in very good agreement with experimental values. Stability of the clusters was determined from their relative energy values binding energies and second difference energy. We also determined fragmentation energy of each size of cluster. We arrived at some interesting result like the transition of Li_n from 2-dimension to 3-dimension for a particular value of n and also the variation of HOMO–LUMO gap with cluster size. Many structures are characterized for the first time in this work.

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1. Introduction

Nanometer sized systems have been a topic of great interest for experimental and theoretical investigation [1–2]. While numerous researchers in this field use a different kind of techniques and materials, most of them shared common systems like clusters or quantum dot. Cluster is the group of atoms ranging from 2–10,000 atoms. Here we dealt with the metallic cluster. Metal clusters are nanodimensional materials which are an intermediate state of matter between molecular limit and bulk limit. Materials on nanoscale can suddenly show very different physical and chemical properties compared to what they show on macroscale because cluster property are size dependent. For example, opaque substance become transparent (copper) inert materials become catalysts (platinum). Solids become liquid at room temperature (gold), insulator become semiconductor (silicon). Nanoclusters not only exhibit interesting electronic and optical properties but also represent the critical components in the potential nanoscale electronic and photonic device applications [3,4]. This is due to the quantum size effects which describes the quantization of energy for the electrons in solid with great reductions in particle size. This effect does not come into play in going from macro-dimensions while it becomes dominant in the nanometer size range. In nanosize the co-ordination number become different for the atoms which are on the surface and high activity is due to the more exposure of atoms to the surrounding for example a 13 atom icosahedra cluster has 12 surface atoms and only one interior atom. Besides, the optical and electronic properties of nanosized

clusters, they are also representative of how molecular structure evolves into bulk solid state phenomena [5].

There have been a number of theoretical calculations which have focused on the structure of the alkali clusters. Companion [6] has studied the structure of Li_3 and Li_4 , Pickup [7] has examined the Li_n cluster ($n=3-6$); Gelb et al. [8] have carried out a study on certain forms of Na_n ($n=3-6$); and Richtsmeier et al. [9] have carried out a study of the structure of group-I alkali metal clusters, Mn ($n=4-6$). Koutecky et al. [10] have carried out a systematic study on the relation between electronic structure and geometry of small Li clusters, Li_n ($n=2-9$). For the first time in this study we have optimized 42 isomer for Li_n ($n=2-10$) clusters. Out of these, 10 most stable isomers are found out from the relative energy of the isomers. This is further confirmed by comparing their binding energies. In order to determine the size evolution of the stability of the clusters and their electronic properties, we have determined the cluster energy, binding energy per atom, bond energy, the second difference of binding energy and the fragmentation energy of the most stable isomer for each value of n .

2. Theory and calculation

The cluster energy (E) is given by

$$E = n E(\text{Li}_1) - E(\text{Li}_n)$$

$E(\text{Li}_n)$ is the energy of cluster with n atoms.

The average binding energy per atom is computed from

$$E_b(n) = [n E(\text{Li}_1) - E(\text{Li}_n)]/n$$

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The bond energy is given by

$$\text{Bond energy} = E/m$$

m is the total number of Li–Li bonds in the cluster.

The fragmentation energy for a cluster of size n has been calculated from

$$D(n, n-1) = E(\text{Li}_{n-1}) + E(\text{Li}_1) - E(\text{Li}_n)$$

The second difference in energy Δ^2 indicates an enhanced stability of a cluster relative to its heavier and lighter neighbors. Actually $\Delta^2 E_b$ is a measure of stability of the clusters which is in general is correlated with experimental mass spectral intensities, rather than with the binding energy [11]. For the most stable structure of the cluster size n the second difference in binding energy

$$\Delta^2 E_b(n) = 2E_b(n) - E_b(n-1) - E_b(n+1)$$

$E_b(n)$ is the binding energy of cluster with n atoms.

3. Computational method

The isomers of gold clusters Li_n ($n=2-10$) have been fully optimized using the Kohn–Sham Theory [12,13]. We used the generalized gradient approximation (GGA) in our calculations. At the GGA level, we have chosen the BLYP functional [14,15] which incorporates Becke's exchange and Lee–Yang–Parr correlation. The basis set chosen is DNP [16]. The DNP basis functions are the double-numerical atomic orbital augmented by polarization functions, i.e., functions with angular momentum one higher than that of the highest occupied orbital in the free atom. The size is comparable with the Gaussian 6-31G** basis set, but the DNP basis set is supposed to be more accurate than a Gaussian basis set of similar size. This basis set is suitable even for treating completely dissociated atoms. The experiment is done for all electrons. Fine grid mesh points are employed for the matrix integrations. Self-consistent field procedures are done with a convergence criterion of 10^{-5} Ha on the energy and electron density. Maximum allowable force is 0.002 Ha/Å and vibrational steps used are 0.01 Bohr.

All the calculations are carried out using the DMol³ program [17]. The nature of the stationary points has been characterized by running vibrational frequency calculations at the same level of theory. In order to determine the ground electronic state for a given cluster size, test calculations were spin unrestricted for odd atoms while spin restricted for even number of lithium atoms. For a given cluster size, the most stable structure is determined from the relative energy of the isomers. This is further confirmed by comparing their binding energies.

4. Results and discussion

4.1. Structures and energetics

In order to determine the best exchange–correlation functional to be used for the calculations, we made a comparative study of the bond length and vibrational frequency of the Lithium dimer using various functionals. The results are presented in Table 1. The experimental value of the bond length for Lithium dimer is 2.67 Å. PW-91 give good correspondences to binding energy but failed to give the frequency value with accuracy while HCTH give good correspondence to vibrational frequency but failed to give energy value. So we took BLYP as our functional, which shows an average approximation in both energy and vibrational frequency. For all the Li_n clusters ($n=2-10$) a number of low-energy structures are obtained along with the most stable structure (Fig. 1). Total energy of all the clusters and their relative energies along with the symmetry point group are given in Table 2. Each structure is

Table 1

Comparison among all the functionals with the experimental result.

Method	Bond length (Å)	Frequency of vibration (cm^{-1})	Binding energy (eV/atom)
BLYP/DNP	2.710	360.7	0.46
BOP/DNP	2.711	368.7	0.42
HCTH/DNP	2.710	346.6	0.71
PBE/DNP	2.710	378.0	0.46
PW91/DNP	2.711	374.2	0.48
RPBE/DNP	2.711	382.6	0.46
VWN_BP/DNP	2.711	379.7	0.40
EXPERIMENTAL	2.670	351.0	0.53

Experimental values are taken from Ref. [18].

identified by its shape and symmetry. The energy differences are given relative to the most stable structure. In case of gold cluster, it is reported that the isomer having energy difference within 0.2 eV are considered as “isomer coexistence interval” [19] but nothing has been till now reported for lithium. However, in our case we estimate that DFT cannot distinguish the structures whose energy difference falls within the ca. 0.1 eV (as lithium is smaller system than gold.) range. We take this energy as the “isomer-coexistence interval”. The binding energy per atom, the second difference of binding energy, the fragmentation energy, the average bond length, the HOMO–LUMO energy gap, the vibrational energies (for the most stable structure) are given in Table 3. Here, we will first discuss and compare structure and energetics of Li_n clusters and then their electronic properties.

Li₂: We first present our calculated values of Li_2 and compare them with the reported experimental and theoretical values. The calculated bond length, binding energy per atom and vibrational frequency for Li_2 are 2.710 Å, 0.46 eV/atom and 360.7 cm^{-1} respectively. These GGA calculated values are in satisfactory agreement with experimental results ($R_e=2.67 \text{ Å}$, $E_b=0.53 \text{ eV/atom}$ and $\omega_{\text{vib}}=351 \text{ cm}^{-1}$) [18]. The BLYP/DNP level of theory gives 1.5% error in bond length, 1.3% error in binding energy and 2.7% error in vibrational frequency. However, our values are a lot better and seem to give correct result as much as possible. It is also better than some of the theoretical values reported earlier [18]. The GGA results of Guo et al. [18] using the PBE/TNP exchange–correlation functional, found the vibrational frequency for Li_2 to be 407 cm^{-1} . This theoretical calculation shows an error in the calculated vibrational frequencies of $> 15\%$.

Li₃: Three isomers (3a–3c) are obtained with the triangular one being lowest in energy. This is in agreement with DFT results of Hutter et al. [20] who predicted a triangular structure. This also resembles with Yang et al. [30] under the method of MACQM but disagrees with respect to the form of the triangle. The former studies showed that it should be an isosceles triangle while the later one showed that it should be equilateral whereas our study also found that it should be equilateral. We also found that the V shaped and triangular structure has the same energy while the linear one placed 0.1 eV higher than these.

Li₄: For Li_4 we have obtained five stable structures as shown in Fig. 1(4a–4e). The calculations reveal that the rhombus Fig. 1(4a) has the minimum energy structure. The result is in accordance with Hutter et al. [20] and also with Boustani et al. [10] but clearly disagrees with Gou et al. [21] where they showed that tetrahedral is the minimum energy structure. The bond length is found to be 3.007, 3.007, 3.009, and 3.009 Å and the diagonal is of 2.603 Å. The average bond length is found to be 2.927 Å while the binding energy per atom is 0.66 eV.

Li₅: In case of Li_5 , we optimized five structures out of which three stable structures were obtained within the range of 0.1 eV (which is known as isomer coexisting interval) as shown in Fig. 1(5c–5e). The lowest energy cluster is a “3-dimensional (2)” shaped one (5e). This

structure has a binding energy per atom value of 0.72 eV which is higher than that for the structures 5c and 5d. There is a 3-dimensional (1) shaped structure (5a) lying 0.121 eV higher in energy. A higher energy planar structure is also found in our BLYP/DNP level calculation. This structure is 0.11 eV higher in energy than the “3-dimensional (2)” shaped structure. Our results are in almost good agreement with the results of Hutter et al. [20]. The binding energy per atom for the structures 5a and 5b is 0.69 eV.

Li_6 : In case of Li_6 , we have optimized eight structures out of which three are nearly degenerate lowest lying structure; 6(a), 6(e) and 6(h). Within the DFT error octahedron is found to be the most stable 6(a), which is in accordance with Hutter et al. [20].

The other structures; parallelogram 6(e) lies 0.054 eV higher while chair shaped 6(h) lies 0.046 eV higher than the octahedron. Thus the three structures are found within the isomer coexistence interval. The binding energy per atom is 0.1 eV higher for octahedron than parallelogram and chair shaped structures. The other structures are pentagonal pyramid which is 0.12 eV higher in energy, hexagonal which is 1.12 eV higher which shows that the metal like Li never combine in hexagonal form (ring structure), triangular whose energy is 0.2 eV higher, see-saw structure having energy 0.7 eV higher and tri-capped triangle where three triangles combine have 0.12 eV higher energy than the most stable one.

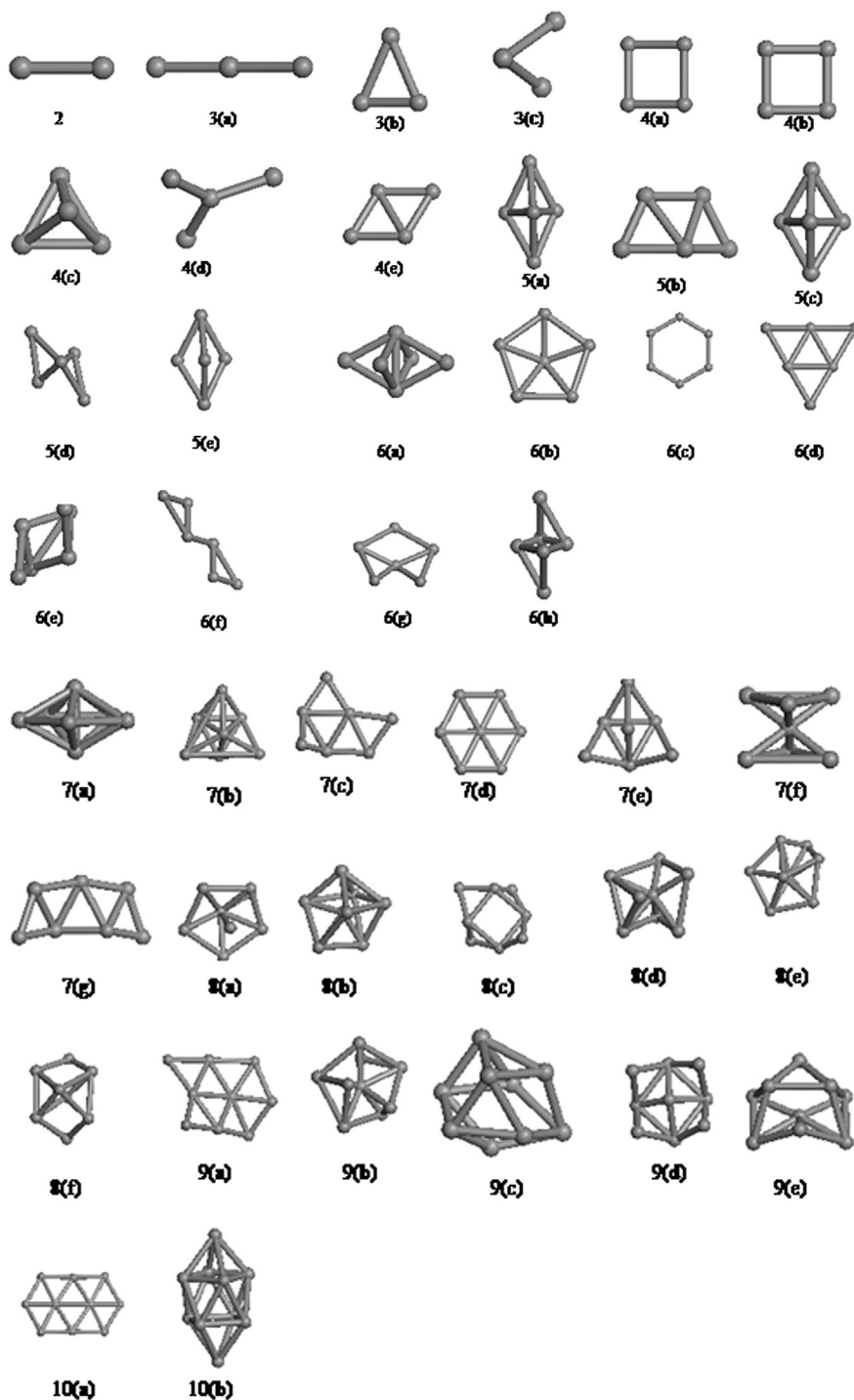


Fig. 1. The calculated structures of lithium clusters (Li_n , $n = 2-10$) at BLYP/DNP level of calculations.

Table 2

Shape, symmetry, total energy and relative energy values for Li_n clusters, $n=2-10$ optimized at the BLYP/DNP level of theory.

n	Structure no.	Shape	Symmetry	Total energy (eV)	Relative energy (eV)
2	2	Linear	$D_{\infty h}$	−407.91409	
3	3(a)	Linear	$D_{\infty h}$	−611.82603	0.10
3	3(b)	Triangle	D_{3h}	−611.92251	0.00
3	3(c)	V shape	C_{2v}	−611.92252	0.00
4	4(a)	Rhombus	D_{2h}	−816.13585	0.49
4	4(b)	Square planar	D_{4h}	−816.13495	0.49
4	4(c)	Pyramid	T_d	−816.20527	0.42
4	4(d)	Tetrahedral	C_1	−815.72322	0.90
4	4(e)	Rhombus 2	D_{2h}	−816.62403	0.00
5	5(a)	3 Dimensional (1)	C_{2v}	−1020.92009	0.12
5	5(b)	Planar	C_1	−1020.93252	0.11
5	5(c)	Rectangular pyramid	D_{3h}	−1021.04142	0.00
5	5(d)	X shape	C_{2v}	−1021.03960	0.00
5	5(e)	3 Dimensional (2)	D_{3h}	−1021.04190	0.00
6	6(a)	Octahedron	D_{4h}	−1225.73325	0.00
6	6(b)	Pentagonal pyramid	C_s	−1225.61414	0.12
6	6(c)	Hexagonal	C_1	−1224.51570	1.22
6	6(d)	Triangular	C_1	−1225.53845	0.19
6	6(e)	Parallelogram	C_{2v}	−1225.67898	0.05
6	6(f)	See-saw	C_{2h}	−1225.03246	0.70
6	6(g)	Tri-capped triangle	C_{5v}	−1225.60844	0.12
6	6(h)	Chair shaped	D_{4h}	−1225.68687	0.05
7	7(a)	Umbrella	C_1	−1430.44691	0.00
7	7(b)	Capped tetragon	C_{3v}	−1430.31210	0.13
7	7(c)	Capped triangle	C_1	−1430.25198	0.19
7	7(d)	Hexagon	C_1	−1429.69357	0.75
7	7(e)	Bi-edge capped trigonal bipyramid	C_{3v}	−1430.31155	0.14
7	7(f)	Eclipsed sandwich	D_{3d}	−1429.86282	0.58
7	7(g)	Extended W	C_1	−1430.44484	0.00
8	8(a)	Pentagonal	C_1	−1635.01045	0.00
8	8(b)	Tetrahedron with capped faces	C_s	−1634.97406	0.04
8	8(c)	Tetra-edge capped rhombus	$D_{\infty h}$	−1635.01087	0.00
8	8(d)	Capped hexagon	C_1	−1634.97425	0.04
8	8(e)	3 Dimensional structure	C_s	−1635.01022	0.00
8	8(f)	Bi-edge capped octahedron	C_s	−1634.94051	0.07
9	9(a)	Bi-edged capped hexagon(1)	C_1	−1838.48788	0.94
9	9(b)	Bi-edged capped hexagon(2)	C_1	−1839.38038	0.05
9	9(c)	Condensed trigonal bipyramid	C_{2v}	−1839.24574	0.18
9	9(d)	Tetra-edged capped square pyramid	C_{2v}	−1839.38734	0.04
9	9(e)	Boat	C_{2v}	−1839.42875	0.00
10	10(a)	Tri-capped hexagon	C_1	−2043.26478	0.72
10	10(b)	Square antiprism	C_1	−2043.98649	0.00

The relative energy values in bold represent the most stable cluster for correspond value of n .

Li_7 : In case of Li_7 , we have optimized seven structures. The two structures are found within the isomer coexistence interval and those are umbrella 7(a) and extended W 7(g), though according to our calculation umbrella structure has more stability than extended W by 0.002 eV. Both the structures have binding energy of 0.86 eV. This study is against the work done by Hutter et al. [20]. The other structures optimized are capped tetragon which is 0.13 eV higher, capped triangle having energy 0.2 eV higher, hexagon which is 0.7 eV higher in energy, bi-edge capped trigonal bipyramid which is 0.14 eV higher and eclipsed sandwich which is 0.58 eV more than the most stable one.

Li_8 : We have optimized six structures and interestingly all the six structures are within the isomer coexistence interval within

the DFT error, tetra-edge capped rhombus 8(c) is found to be the most stable structure. Except bi-edge capped octahedron 8(f) all have binding energy per atom of 0.88 eV whereas bi-edge capped octahedron have 0.01 eV lesser than that.

Li_9 : In case of Li_9 , we tried five structures. Out of these five structures the most stable one was boat shape 9(e) having binding energy per atom of 0.89 eV. Including boat shape two other structures also have the possibility of existence and those are bi-edge capped hexagon (1) 9(b) and tetra-edge capped square pyramid 9(d). These two structures respectively have 0.048 and 0.041 eV energy higher than that of the most stable one. Other optimized structures are bi-edged capped hexagon 9(a) having energy 0.9 eV higher and condensed trigonal bipyramid 9(c) which is 0.18 eV higher in energy than the boat shape structure.

Li_{10} : when ten Li atoms combine then it can have several structures. In our study we have optimized two structures and found that square antiprism 10(b) is more stable than tri-capped hexagon 10(a). Square antiprism is 0.72 eV lower in energy than tri-capped hexagon. The respective binding energy is 0.91 and 83 eV.

4.2. Variation of Li–Li bond length

The variation of bond length is tackled by calculating the average bond length and the total bond length per atom for the entire Li_n cluster. The calculated values are listed in Table 3. In order to compare the variation of Li–Li bond length of Li_n clusters with the increase of cluster size we choose the most stable structure for each of the clusters. The variation of Li–Li total bond length per atom of all the lowest energy structures as a function of cluster size is shown in Fig. 2. The longer the bond, the weaker is the bond strength. So, the plot of total bond length per atom vs. the number of atoms could indicate the variation of bond strength with coordination number. The total bond length per atom of Li_n clusters increases as we go from $n=2$ (1.35 Å) to $n=3$ (2.92 Å). Then for $n=4$ it almost remains the same. From $n=5$ onwards it increases for odd n values and decreases for even n values. The odd–even oscillation can be understood by the fact of spin stabilization [22]. For Li_2 there are two valence (free) electrons which pair up to give no repulsion while for Li_3 one electrons however remains unpaired due to which greater repulsion takes place and which changes the bond length as that of Li_2 (sharp jump proves this). As we move towards Li_4 , the repulsion is found to be smaller as the lone electron is stabilized by the 4th electron. For Li_5 one unpaired electron's repulsion is stabilized by the other two paired electrons and so on. There is an additional change in bond length of Li_5 and this is due to the change of packing of Li atoms as it transits from 2-dimension to 3-dimension.

4.3. Variation of binding energy

Our calculated binding energy is in very good agreement with the experimental value of 0.46 eV/atom [18]. The variation of calculated binding energy per atom (E_b) of the most stable structure for each cluster as function of cluster size is shown in Fig. 3. As can be seen from the plot, the per atom binding energy increases with cluster size. The increase of $E_b(n)$ with n indicates the greater stability as the cluster grows in size. This may be due to the fact that with increasing cluster size, the average number of nearest neighbors increases, which promotes greater average number of interactions per atom. For the same cluster size, binding energy can be used to determine the relative stability of the isomers [23].

Table 3
Cluster energy, binding energy/atom, bond energy, second differential of binding energy (Δ^2Eb), fragmentation energy, total bond length per no. of atoms, average bond length, HOMO–LUMO (H–L) gap. (All the energies are in eV.)

Structure no.	Cluster energy	Binding energy per atom	Bond energy	Δ^2Eb	Fragmentation energy	Total bond length per no. of atoms	Average bond length (Å)	H–L gap
2	0.92890	0.46	0.93		0.92890	1.35	2.7	1.49
3(a)	1.34824	0.45	0.67			2.88	4.32	0.01
3(b)	1.44471	0.48	0.48	0.3328	0.51581	2.92	2.92	0.47
3(c)	1.44473	0.48	0.72			3.07	4.61	0.01
4(a)	2.16546	0.54	0.54			2.9	2.9	0.01
4(b)	2.16456	0.54	0.54			2.90	2.9	1.41
4(c)	2.23489	0.56	0.56			2.90	1.93	1.99
4(d)	1.75283	0.44	0.44			2.96	3.94	0.00
4(e)	2.65364	0.66	0.66	0.1310	1.20893	2.93	2.34	0.94
5(a)	3.45710	0.69	0.38			2.93	1.83	0.36
5(b)	3.46954	0.69	0.50			2.97	2.12	0.68
5(c)	3.57844	0.72	0.45			2.93	1.83	0.74
5(d)	3.57661	0.72	0.60			2.90	2.42	0.75
5(e)	3.57892	0.72	0.60	−0.0281	0.92527	2.99	2.49	0.65
6(a)	4.77766	0.80	0.53	−0.7764	1.19874	2.78	1.85	0.74
6(b)	4.65855	0.78	0.52			3.01	1.81	1.34
6(c)	3.56011	0.59	0.59			2.94	2.94	0.89
6(d)	4.58286	0.76	0.51			2.98	1.99	1.26
6(e)	4.72340	0.79	0.52			3.11	2.07	0.73
6(f)	4.07687	0.68	0.58			2.92	2.5	0.32
6(g)	4.65286	0.78	0.58			2.98	2.23	0.58
6(h)	4.73128	0.79	0.59			2.98	2.23	0.78
7(a)	5.99873	0.86	0.37	0.0338	0.93527	2.94	1.58	0.47
7(b)	5.86392	0.84	0.34			3.16	1.47	0.60
7(c)	5.80380	0.83	0.53			3.02	1.92	0.58
7(d)	5.24539	0.75	0.44			3.01	1.75	0.29
7(e)	5.86337	0.84	0.53			2.94	1.87	0.61
7(f)	5.41464	0.77	0.45			3.02	1.76	1.53
7(g)	5.99666	0.86	0.55			2.94	1.87	0.47
8(a)	7.06967	0.88	0.59			2.89	2.1	0.84
8(b)	7.03328	0.88	0.44			3.04	1.74	1.55
8(c)	7.07009	0.88	0.59			2.98	1.83	0.84
8(d)	7.03347	0.88	0.50	0.0221	1.07136	2.91	1.66	1.53
8(e)	7.06944	0.88	0.39			2.96	1.97	0.83
8(f)	6.99973	0.87	0.50			2.93	1.95	1.15
9(a)	7.05450	0.78	0.44			3.00	1.69	0.37
9(b)	7.94700	0.88	0.50			2.96	1.78	0.39
9(c)	7.81236	0.87	0.49			2.98	2.23	1.22
9(d)	7.95396	0.88	0.50			2.93	1.88	0.45
9(e)	7.99537	0.89	0.44	−0.0130	0.92527	3.00	1.69	0.41
10(a)	8.33880	0.83	0.44			3.03	1.60	0.90
10(b)	9.06051	0.91	0.38		1.06514	2.98	1.49	0.81

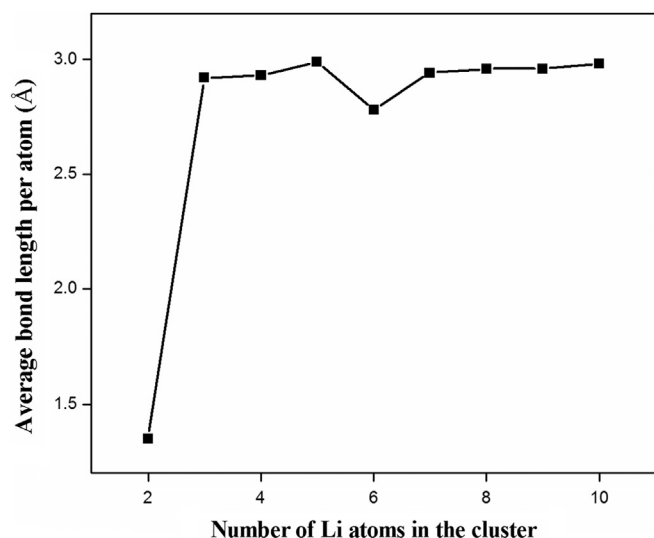


Fig. 2. The calculated structures of lithium clusters (Li_n ; $n=7-10$) at BLYP/DNP level of calculations.

4.4. Variation in fragmentation energy and second differential of binding energy

In order to analyze the stability and size-dependent properties of lithium clusters, we also calculated fragmentation energies, $D(n, n-1)$ and second differences in binding energy. The fragmentation energies are sensitive to the relative stabilities that can be observed in mass abundance spectra. Fig. 4 shows $D(n, n-1)$ of lithium clusters which oscillate as the cluster size increases and indicate that the clusters with even number of atoms are more stable than the clusters with odd number of atoms [22] due to spin stabilization in even number of atoms as discussed earlier in this paper. Li_4 and Li_6 have the highest and almost the same fragmentation energy showing their maximum stability.

Fig. 5 shows the variation of the second differential of binding energy per atom with cluster size n [10]. In cluster physics, the quantity Δ^2Eb is commonly known to represent the relative stability of a cluster of size n with respect to its neighbors [22,24]. The plot shows that Δ^2Eb decreases from $n=3$ to $n=6$ where it achieves its minimum value showing that Li_6 is highly stable than its neighbor. From $n=6$ onward the value increases.

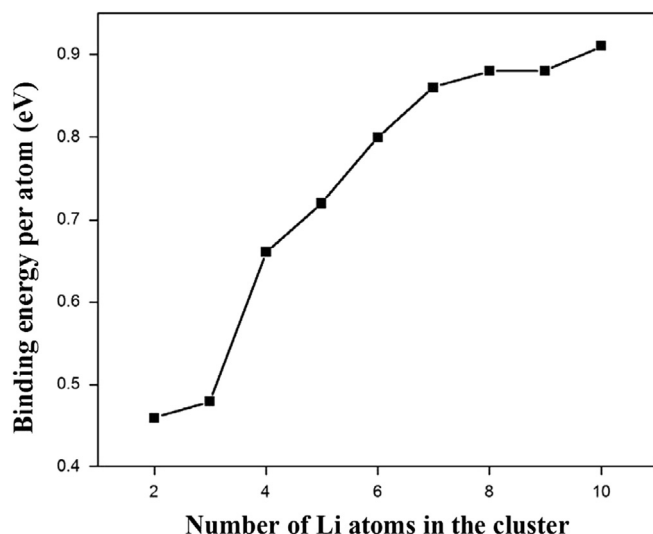


Fig. 3. Plot of binding energy (eV) against number of Li atoms.

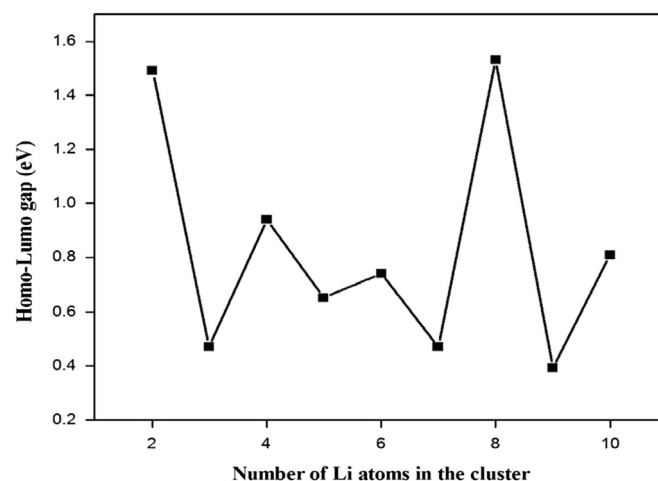


Fig. 6. Plot of HOMO–LUMO gap (eV) against number of Li atoms.

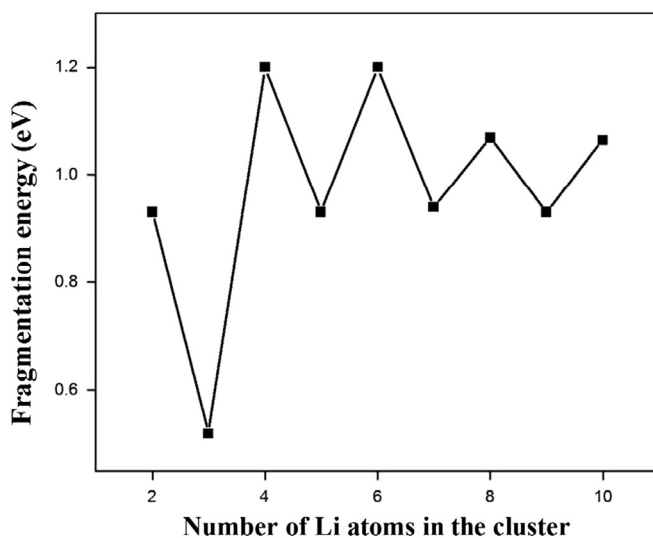


Fig. 4. Plot of fragmentation energy (eV) against number of Li atoms.

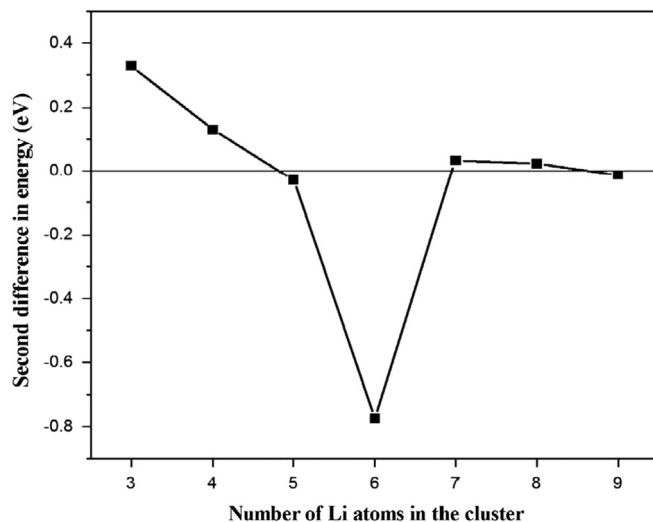


Fig. 5. Plot of second difference in energy (eV) against number of Li atoms.

4.5. HOMO–LUMO gap

The energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for each stable structure has been calculated. A large HOMO–LUMO gap has been considered as an important requisite for the chemical stability of lithium clusters [25]. The HOMO–LUMO gap for all the 42 stable structures are given in Table 3. The variation in the HOMO–LUMO gap for the most stable structures for each cluster size is shown in Fig. 6. As seen from the plot, the HOMO–LUMO energy gap shows an odd–even oscillation [22,26,27]. The even-numbered clusters have larger HOMO–LUMO gap and are relatively more chemically stable than the odd-numbered neighbors. Odd–even alterations in the HOMO–LUMO gap values have often been predicted by earlier calculations for other metal clusters [28,29]. Odd–even oscillation behaviors can be understood by the effect of electron pairing in orbitals. Even sized clusters have an even number of *s* valence electrons and a doubly occupied HOMO, while it is singly occupied for odd-sized clusters. The electron in a doubly occupied HOMO feels a stronger effective core potential due to the fact that the electron screening is weaker for electrons in the same orbital than for inner-shell electrons.

5. Conclusion

We have investigated low-energy geometries, binding energy, relative stability, HOMO–LUMO gap etc. of lithium clusters Li_n , n varying from 2 to 10 using BLYP/DNP level of theory. Different initial guess geometries were considered for all the clusters which lead to a number of structural isomers for each cluster size. Of these isomers, many new structures are reported. The minimum energy structures for all the clusters are found to be planar with coexistence of 3-D structures within the DFT error. It is observed that some of our minimum energy structures are also obtained by using the HF method. Odd–even alterations are evident in the HOMO–LUMO gaps and fragmentation energy. Even-numbered clusters are found to be relatively more stable compared to the odd-numbered ones indicating that electron spin-pairing stabilizes these clusters. We also found that the structure of Li_n cluster show a transition from 2-dimensional to 3-dimensional for $n=5$, there onwards it can exist in both if their energy corresponds to isomer coexistence interval. The systematic investigations of structural and electronic properties of small lithium clusters present in this study will provide an insight into understanding more complicated other metals cluster.

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