Bull. Mater. Sci. (2021) 44:212
https://doi.org/10.1007/s12034-021-02500-8

Molecular graph theory based study on Li_n cluster: a correlation between physical property and topological descriptors

PAWAN CHETRI[1,*], BIJIT BORA[2] and TAPAN KUMAR BAISHYA[3]

[1]Department of Physics, Debraj Roy College, Golaghat 785621, India
[2]Department of Mathematics, Joya Gogoi College, Khumtai 785619, India
[3]Department of Mathematics, Debraj Roy College, Golaghat 785621, India
*Author for correspondence (chetripawan2009@gmail.com)

MS received 24 April 2021; accepted 24 May 2021

Abstract. Minimized structures obtained for Li_n (lithium) clusters (n = 2–10) using DFT-based DMol^3 program (Chetri *et al* 2013 *Physica B* **430** 7480) were considered for constructing the molecular graph. The constructed molecular graphs are used to calculate the topological descriptors. These topological descriptors provide various real numbers for different structures. The computed results of binding energy per atom, average bond length and total energy for Li_n cluster (n = 2–10) are plotted against all the topological descriptors. $R_{-1/2}$ and M_1 are found to be the best descriptors to estimate binding energy per atom, total energy and average bond length. Further, these two descriptors are linked to the change in number of atoms in Li_n (n = 2–10) clusters such that a mathematical relations are established between them. This study enables us to calculate binding energy per atom, average bond length and total energy for Li_n cluster (where n is any real number) at a very low computational power.

Keywords. Topological descriptors; DFT; lithium; cluster; binding energy; average bond length.

1. Introduction

Systems at nanoregime have been of great interest in the field of material science, owing to its extraordinary properties. Clusters can be an ideal approach to understand how the atoms assemble to form nanomaterials. The groups ranging from 2 to 10000 atoms are known as clusters. Clusters are believed to be an intermediate state between single atom and bulk system [1,2]. Datta and Pati Swapan [3] compared the structure and bonding aspects in lithium and beryllium clusters. Brito *et al* [4] carried out *ab-initio* calculation of small neutral lithium clusters using various theoretical approaches, including Monte Carlo method [4]. Kushwaha *et al* [5] studied free energy and redox potential as well as investigated relative stability of Li_n ($n \leq 8$) clusters and found that Li_3 has the lowest negative redox potential. Zhang *et al* [6] doped Li cluster with Ga and Mn such that forming trimetallic cluster. The trimetallic cluster showed larger relative binding energy compared to pure Li clusters. Kushwaha and Nayak [7] used first-principles density functional theory (DFT) and continuum dielectric model to investigate the origin of oscillatory nature of binding energy per atom of Li_n ($n \leq 8$) cluster. In a recent study, Rodríguez and Sánchez [8] studied the adsorption of lithium cluster on graphene and its ability to capture hydrogen molecules.

Topological descriptors are numerical parameters of a graph, which characterize its topology and are usually graph invariant. The topological descriptors of molecular graphs are very much useful to study various physico-chemical properties of the chemical compounds. They are also used to develop quantitative–structure–activity relationship (QSAR) and quantitative structure–property relationship (QSPR) of chemical compounds. There are more than 140 topological descriptors that have been defined by various researchers. The first topological index was introduced by Wiener [9] in 1947, which is a distance-based topological index known as Wiener index and has many famous mathematical and chemical applications [9,10]. In 1975, Randić [11] introduced the 'branching index' R (R_{-1} and $R_{-\frac{1}{2}}$) which was used to measure carbon atom skeleton of saturated hydrocarbons. Working independently by Bollobás and Erdös [10] and Amić *et al* [12] generalized this index as 'General Randić Index' and defined as

$$R_\alpha(G) = \sum_{uv \in E(G)} (d_u d_v)^\alpha$$

Taking $\alpha = -\frac{1}{2}$ in the above expression, we get the Randić index $R_{-\frac{1}{2}}(G)$ as

$$R_{-\frac{1}{2}}(G) = \sum_{uv \in E(G)} \frac{1}{\sqrt{d_u d_v}}$$

Published online: 18 July 2021

The first and second Zagreb indices $M_1(G)$ and $M_2(G)$ were introduced by Gutman and Trinajstić [13–15]. $M_1(G)$ and $M_2(G)$ are defined as

$$M_1(G) = \sum_{uv \in E(G)} (d_u + d_v)$$

$$M_2(G) = \sum_{uv \in E(G)} (d_u d_v)$$

Now, it is seen that $M_2(G)$ is obtained from 'General Randić index' by taking $\alpha = 1$.

Zhong [16] defined the harmonic index of a graph G as

$$H(G) = \sum_{uv \in E(G)} \frac{2}{d_u + d_v}$$

The inverse sum index [17] of a graph G is defined as

$$I(G) = \sum_{uv \in E(G)} \frac{d_u d_v}{d_u + d_v}$$

The symmetric division index (SDD) [18] of a connected graph G, which is a good predictor of the total surface area of polychlorobiphenyls [19], is defined as

$$\mathrm{SDD}(G) = \sum_{uv \in E(G)} \left(\frac{\min(d_u, d_v)}{\max(d_u, d_v)} + \frac{\max(d_u, d_v)}{\min(d_u, d_v)} \right)$$

Here we shall construct M-polynomials for molecular graphs of Li_n $(n = 2, \ldots, 10)$ and then we shall calculate above defined degree-based topological descriptors for Li_n clusters.

There are also few more studies on Li clusters [20,21], but our study is inspired from Chetri *et al* [1]. We have considered the stable structures obtained using DMol^3 (density functional theory based software) of Li_n clusters (n = 2–10) [1]. Based on these structures, we worked on topological descriptor (index) such that each structure corresponds to a real number. Further, we establish the relation between topological descriptors (indices) with binding energy per atom and average bond length, and developed an equation by which these properties can be explained for any numbers of Li atom.

2. Methodology

2.1 *Topological descriptors via M-polynomial*

Various graph polynomials have been introduced, such as Hosoya polynomial [22], Zhang-Zhang or Clar covering polynomial [23], matching polynomial [24], Schultz polynomial [25], Tutte polynomial [26], Omega polynomial [27] etc., which have numerous significances and applications in the chemical graph theory as well as in the theory of graphs. Some of these polynomials are also used to calculate topological indices of various chemical graphs. In 2015, M-polynomial was introduced by Deutsch and Klavžar [28]. Since then, it has been used by various researchers [29–32] in the field of chemical graph theory to calculate topological indices of various molecular graphs.

Let $G = (V, E)$ be a simple connected graph. $V(G)$ and $E(G)$ denotes the set of vertices and the set of edges of the graph G, respectively, and $d_u(G)$ denotes the degree of the vertex $u \in V(G)$. Then, the M-polynomial for the graph G is defined as [28]:

$$M(G; x, y) = \sum_{\delta(G) \le i \le j \le \Delta(G)} m_{ij}(G) x^i y^j,$$

where $m_{ij}(G)$ denotes the number of edges $uv \in E(G)$, such that $\{d_u(G), d_v(G)\} = \{i, j\}$, $\delta(G) = \min\{d_v(G) | v \in V(G)\}$, and $\Delta(G) = \max\{d_v(G) | v \in V(G)\}$.

Instead of calculating degree-based topological indices of a particular chemical graph independently from the formulae given in the literature, one can calculate these degree-based topological indices from the M-polynomial of the graph directly using table 1 due to Deutsch and Klavžar [28].

Table 1. Topological descriptor and derivation from $M(G; x, y)$ or $f(x, y)$.

Topological descriptor	Notation	Derivation from $f(x,y)$
First Zagreb	$M_1(G)$	$(D_x + D_y)(M(G; x, y))\big\|_{x=y=1}$
Second Zagreb	$M_2(G)$	$(D_x D_y)(M(G; x, y))\big\|_{x=y=1}$
Symmetric division index	$\mathrm{SDD}(G)$	$(D_x S_y + D_y S_x)(M(G; x, y))\big\|_{x=y=1}$
Harmonic index	$H(G)$	$2S_x J(M(G; x, y))\big\|_{x=1}$
Inverse sum index	$I(G)$	$S_x J D_x D_y (M(G; x, y))\big\|_{x=1}$
General Randić index	$R_\alpha(G)$	$(D_x^\alpha D_y^\alpha)(M(G; x, y))\big\|_{x=y=1}$

Where $D_x(f(x,y)) = x\frac{\partial(f(x,y))}{\partial x}$, $D_y(f(x,y)) = y\frac{\partial(f(x,y))}{\partial y}$, $S_x(f(x,y)) = \int_0^x \frac{f(t,y)}{t} dt$, $S_y(f(x,y)) = \int_0^y \frac{f(x,t)}{t} dt$, $J(f(x,y)) = f(x,x)$ and $Q_\alpha(f(x,y)) = x^\alpha f(x,y)$, $\alpha \neq 0$.

3. Results and discussions

3.1 *Molecular graphs of Li_n $(n = 2-10)$ clusters*

In this study, we have constructed the molecular graph from the most stable structures of lithium clusters [1] as shown in figure 1. The authors claimed various structures to be of same energy for a given number of lithium atoms. For example, when $n = 3$, i.e., Li_3 both v-shaped and triangle-shaped structures have same binding energy. Therefore both the structures provide ground state configuration. We have considered randomly only one structure out of all the stable structures for a given value of n.

3.2 *M-polynomials for molecular graphs of Li_n $(n = 2-10)$*

In this section we shall construct M-polynomials for the molecular graphs (figure 1a–i) of Li_n $(n = 2-10)$.

(1) M-polynomial of the molecular graph (figure 1a) of Li_2

$$M(G;x,y) = \sum_{\delta(G)\le i\le j\le \Delta(G)} m_{ij}(G)x^i y^j = m_{11}(G)xy = xy.$$

(2) M-polynomial of the molecular graph (figure 1b) of Li_3

$$M(G;x,y) = \sum_{\delta(G)\le i\le j\le \Delta(G)} m_{ij}(G)x^i y^j = m_{22}(G)x^2y^2 = 3x^2y^2.$$

(3) M-polynomial of the molecular graph (figure 1c) of Li_4

$$M(G;x,y) = \sum_{\delta(G)\le i\le j\le \Delta(G)} m_{ij}(G)x^i y^j = m_{23}(G)x^2y^3 + m_{33}(G)x^3y^3 = 4x^2y^3 + x^3y^3.$$

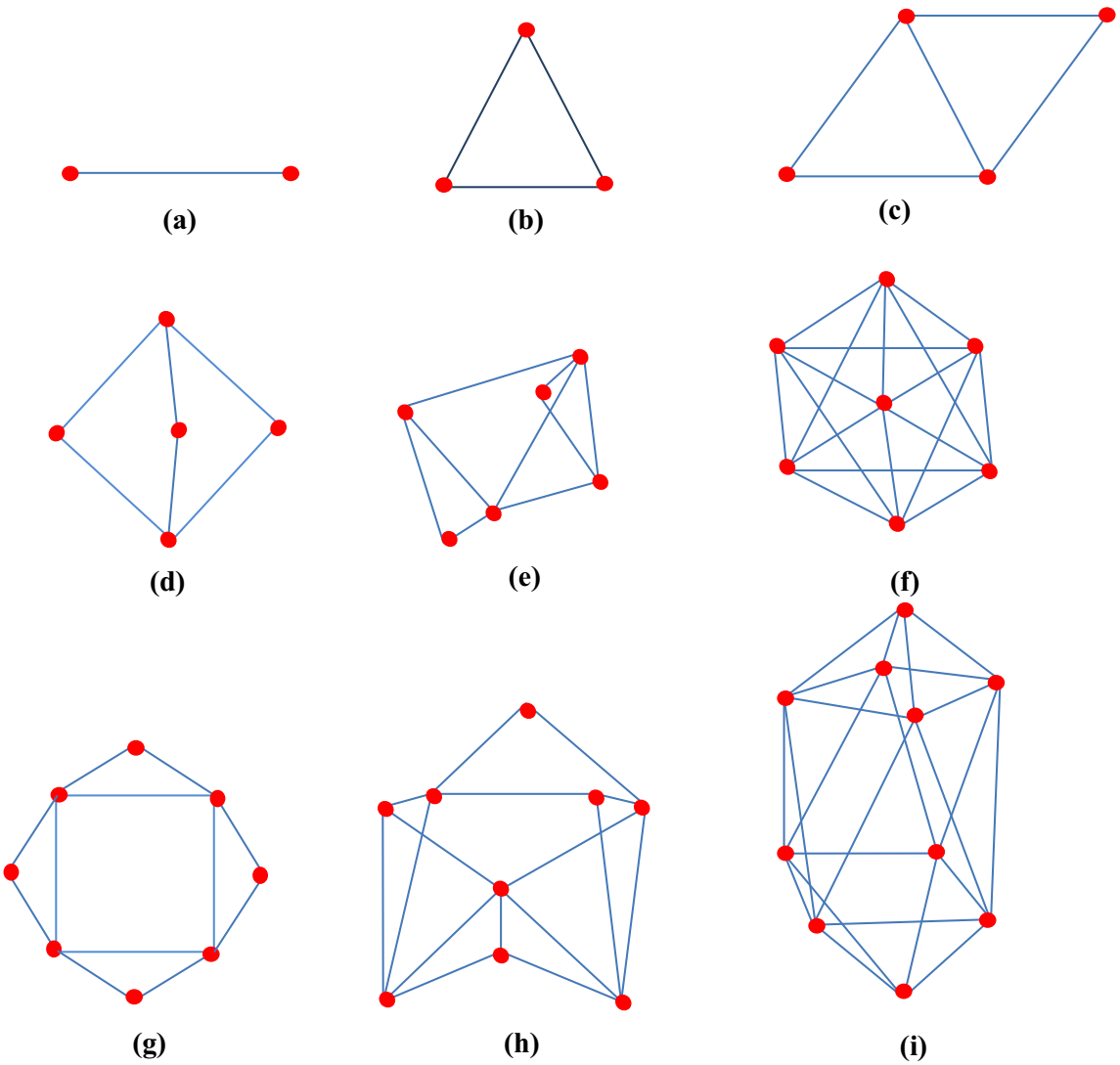

Figure 1. (**a–i**) Molecular graph of Li_n (n = 2–10) cluster. Red dots represent Li atom.

(4) M-polynomial of the molecular graph (figure 1d) of Li_5

$$\begin{aligned} M(G;x,y) &= \sum_{\delta(G)\le i\le j\le \Delta(G)} m_{ij}(G)x^i y^j \\ &= m_{22}(G)x^2y^2 + m_{24}(G)x^2y^4 \\ &= 2x^2y^2 + 4x^2y^4. \end{aligned}$$

(5) M-polynomial of the molecular graph (figure 1e) of Li_6

$$\begin{aligned} M(G;x,y) &= \sum_{\delta(G)\le i\le j\le \Delta(G)} m_{ij}(G)x^i y^j \\ &= m_{25}(G)x^2y^5 + m_{55}(G)x^5y^5 \\ &= 8x^2y^5 + x^5y^5. \end{aligned}$$

(6) M-polynomial of the molecular graph (figure 1f) of Li_7

$$\begin{aligned} M(G;x,y) &= \sum_{\delta(G)\le i\le j\le \Delta(G)} m_{ij}(G)x^i y^j \\ &= m_{23}(G)x^2y^3 + m_{24}(G)x^2y^4 \\ &\quad + m_{34}(G)x^3y^4 + m_{44}(G)x^4y^4 \\ &= 2x^2y^3 + 2x^2y^4 + 4x^3y^4 + 3x^4y^4. \end{aligned}$$

(7) M-polynomial of the molecular graph (figure 1g) of Li_8

$$\begin{aligned} M(G;x,y) &= \sum_{\delta(G)\le i\le j\le \Delta(G)} m_{ij}(G)x^i y^j \\ &= m_{24}(G)x^2y^4 + m_{44}(G)x^4y^4 \\ &= 8x^2y^4 + 4x^4y^4. \end{aligned}$$

(8) M-polynomial of the molecular graph (figure 1h) of Li_9

$$\begin{aligned} M(G;x,y) &= \sum_{\delta(G)\le i\le j\le \Delta(G)} m_{ij}(G)x^i y^j \\ &= m_{24}(G)x^2y^4 + m_{33}(G)x^3y^3 \\ &\quad + m_{34}(G)x^3y^4 + m_{35}(G)x^3y^5 \\ &\quad + m_{44}(G)x^4y^4 + m_{45}(G)x^4y^5 \\ &= 2x^2y^4 + x^3y^3 + 6x^3y^4 + x^3y^5 + 2x^4y^4 \\ &\quad + 4x^4y^5. \end{aligned}$$

(9) M-polynomial of the molecular graph (figure 1i) of Li_{10}

$$\begin{aligned} M(G;x,y) &= \sum_{\delta(G)\le i\le j\le \Delta(G)} m_{ij}(G)x^i y^j \\ &= m_{45}(G)x^4y^5 + m_{55}(G)x^5y^5 \\ &= 8x^4y^5 + 16x^5y^5. \end{aligned}$$

3.3 *Topological descriptors of molecular graphs of Li_n clusters*

In this section we shall calculate the topological descriptors of the molecular graphs given in figure 1a–i using the relations given in table 1.

3.4 *Application of topological descriptors*

In this section we shall establish a relation between topological descriptors with binding energy per atom, average bond length and total energy of the most stable structure for Li_n (n = 2–10) cluster.

The calculated values of topological descriptors for different numbers of Li atoms are shown in table 2. The change in number of Li atoms lead to the change in value of binding energy per atom (B.E. per atom), average bond length and total energy as quoted in ref. [1]. The values shown in table 3 are taken from ref. [1]. We have investigated the variation of all the topological descriptor with B.E. per atom, average bond length and total energy. We tried polynomial fitting for each plot so that we can develop an equation. The adj. R^2 value for each plot is shown in table 4. It can be seen that $R_{-1/2}$ and M_1 have the best value (i.e., adj. R^2 is closest to 1) for B.E. per atom, total energy and average bond length, respectively. The maximum value of adj. R^2 assures the best fit for the data and hence the equation derived from it contains minimum error. As $R_{-1/2}$ found to be the best topological descriptor for B.E. per atom and total energy, so the plot is shown in figure 2. Similarly, M_1 qualifies to be the best topological descriptor for the estimation of average bond length, as shown in figure 3. Again $R_{-1/2}$ was found to be the best topological descriptor for total energy as well and hence the plot is shown in figure 4.

The equation obtained between $R_{-1/2}$ *vs.* B.E. per atom is as follows:

$$\begin{aligned} \frac{\text{B.E.}}{\text{Atom}} &= C + B_1R_{-1/2} + B_2R_{-1/2}^2 + B_3R_{-1/2}^3 + B_4R_{-1/2}^4 \\ &\quad + B_5R_{-1/2}^5 + B_6R_{-1/2}^6 \end{aligned} \tag{A}$$

$$C = 4.488, B_1 = -10.544, B_2 = 10.415,$$
$$B_3 = -5.040, B_4 = 1.303, B_5 = -0.172, B_6 = 0.009.$$

Similarly, the equation obtained between M_1 and average bond length is as follows:

$$\text{Average bond length} = D + B_1M_1 + B_2(M_1)^2 \tag{B}$$

$$D = 2.846,\ B_1 = -0.016,\ B_2 = 4.425 \times 10^{-5}$$

Again, the equation between $R_{-1/2}$ and total energy is as follows:

$$\text{Total energy} = -(F + B_1R_{-1/2} + B_2R_{-1/2}^2) \tag{C}$$

$$F = -104.477, B_1 = 512.466, B_2 = -16.334$$

The equations A, B and C show that we can calculate the binding energy per atom, average bond length and total energy of Li cluster from the values of those two topological descriptors. These three equations provide us the easier way to do so, but the value of topological descriptors is limited to n = 10 as can be seen in table 2. Therefore, we have established a relation between $R_{-1/2}$ and M_1 with number of Li atoms as shown in figure 5a and b, respectively. These relations allow us to calculate

Table 2. Li_n (n = 2–10), shape of molecular graph and real values of different topological descriptors.

		Topological descriptors					
Li_n	Molecular graph (figure 1a–i)	$M_1(G)$	$M_2(G)$	SDD(G)	$H(G)$	$I(G)$	$R_{-\frac{1}{2}}$
Li_2	Linear (a)	2	1	2	1	½	1
Li_3	Triangle (b)	12	24	6	1.5	3	1.5
Li_4	Rhombus (c)	26	33	10.66	1.93	6.3	1.96
Li_5	3 Dimensional (d)	32	40	14	2.33	7.33	2.41
Li_6	Parallelogram (e)	66	105	25.2	2.48	13.93	2.73
Li_7	Capped tetragon (f)	74	124	23.66	3.36	17.92	3.43
Li_8	Tetra-edged capped rhombus (g)	80	128	16	3.66	18.66	3.83
Li_9	Boat (h)	120	224	33.96	4.35	29.21	4.42
Li_{10}	Square antiprism (i)	232	560	48.40	4.98	57.78	4.99

Table 3. Li_n (n = 2–10), binding energy per atom (eV), average bond length (Å) and total energy (eV) [1].

Li_n (n = 2–10)	Binding energy per atom (eV)	Average bond length (Å)	Total energy (eV)
Li_2	0.46	2.7	–407.91409
Li_3	0.48	2.92	–611.92252
Li_4	0.66	2.34	–816.62403
Li_5	0.72	2.42	–1021.04142
Li_6	0.80	1.85	–1225.73325
Li_7	0.86	1.87	–1430.44691
Li_8	0.88	1.83	–1635.01045
Li_9	0.89	1.69	–1839.42875
Li_{10}	0.91	1.49	–2043.98649

Table 4. Topological descriptor, adj. R^2 value for the fitted curve of topological descriptors against the data for B.E. per atom, average bond length and total energy.

	Adj. R^2		
Topological descriptor	B.E. per atom	Average bond length	Total energy
M_1	0.96	0.91	0.97
M_2	0.97	0.86	0.94
SDD	0.91	0.82	0.82
H(G)	0.97	0.81	0.98
$R_{-1/2}$	0.98	0.85	0.997
I(G)	0.96	0.90	0.97

the values of these descriptors for any number of Li atoms. Hence, for any number of Li atoms in a Li cluster, we can calculate the values of $R_{-1/2}$ and M_1, which ultimately gives the value of binding energy, average bond length and total energy from equations A, B and C. The equation between $R_{-1/2}$ and M_1 with number of Li atoms (n) are

$$R_{-1/2} = A + B_1 n + B_2 n^2 \quad \text{(D)}$$

$$A = 0.263, B_1 = 0.371, B_2 = 0.009$$

$$M_1 = B + B_1 n + B_2 n^2 + B_3 n^3 + B_4 n^4 + B_5 n^5 \quad \text{(E)}$$

$$B = -207, B_1 = 255.627, B_2 = -118.145,$$
$$B_3 = 26.282, B_4 = -2.703, B_5 = 0.104$$

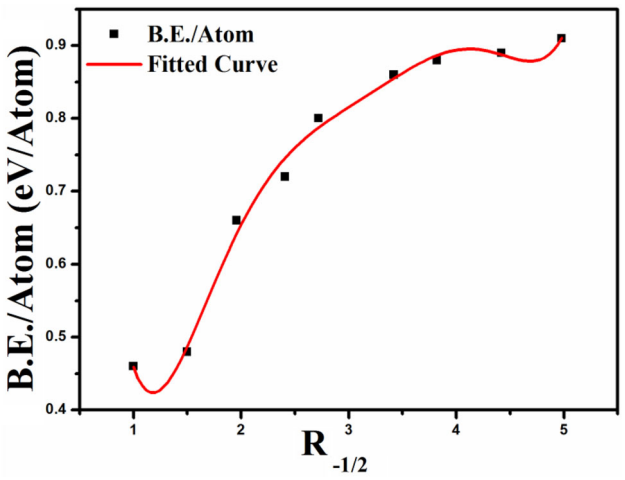

Figure 2. Curve fitting of B.E. per atom against $R_{-1/2}$.

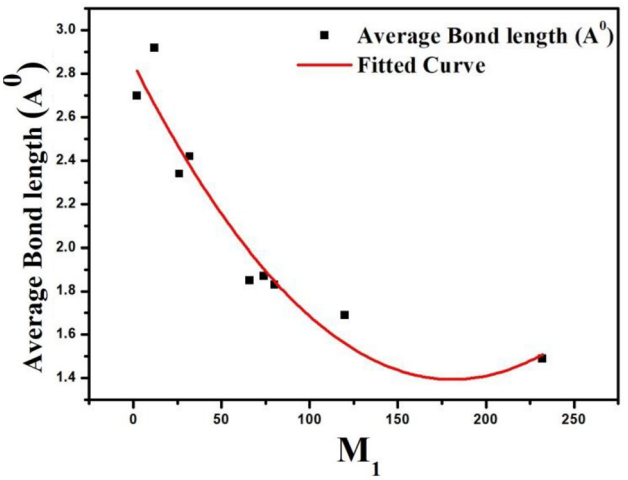

Figure 3. Curve fitting of average bond length against M_1.

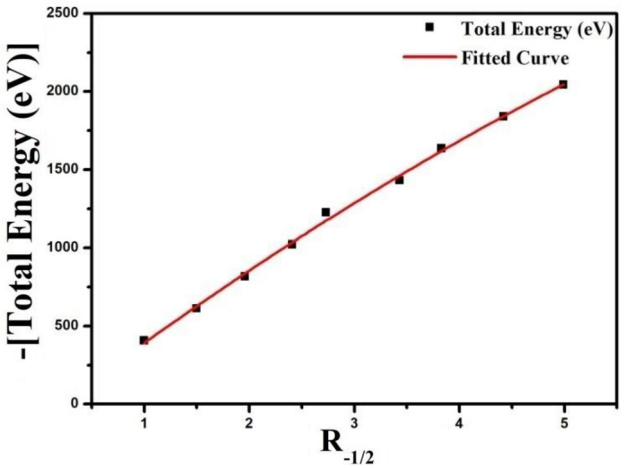

Figure 4. Curve fitting of total energy against $R_{-1/2}$.

Now the equations (D and E) will provide values of $R_{-1/2}$ and M_1 for any number of Li atoms and using these values, the binding energy, average bond length and total energy of Li cluster can be calculated.

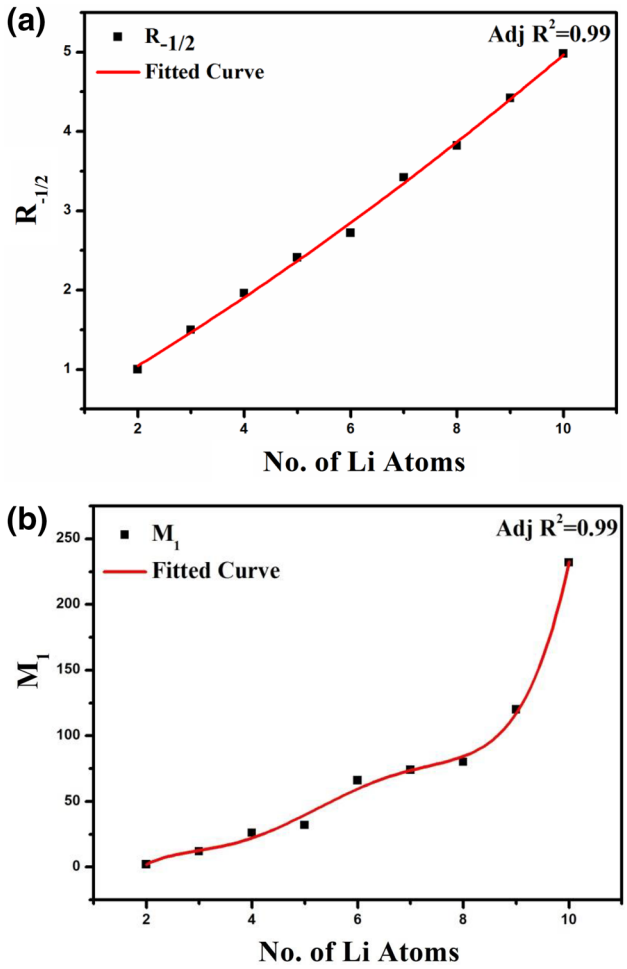

Figure 5. (**a**) Curve fitting of $R_{-1/2}$ *vs.* number of Li atoms. (**b**) Curve fitting of M_1 *vs.* number of Li atoms.

4. Conclusion

We have extended the work done by Chetri *et al* [1] and provided an easier method to calculate the binding energy, average bond length and total energy for any number of Li atoms in a Li cluster. The work was initiated with the computed values of binding energy, average bond length and total energy for Li cluster obtained by Chetri *et al* [1]. Further, a molecular graph was constructed for the most stable structures [1]. These molecular graphs are important to exactly determine the degree of different number of Li atoms. Further, using these degree and number of Li atoms (vertices), a total of six topological descriptors were calculated. $R_{-1/2}$ and M_1 were determined to be the best fit for explaining binding energy, total energy and average bond length, respectively. Further, a relation established between $R_{-1/2}$ and M_1 with the number of Li atoms. Now, with the help of these fitted equations, binding energy, average bond length and total energy for any number of atoms in Li cluster can be easily calculated. This gives an easier option in comparison to high computational requirement for

different molecular modelling software. Though this method is not sufficient to obtain the minimized structures but can easily provide three of the most important parameters for any Li cluster system.

References

[1] Chetri P, Deka R C and Choudhury A 2013 *Physica B* **430** 7480
[2] Chen S, Ingram R S, Hostetler M J, Pietron J J, Murray R W, Schaaff T *et al* 1998 *Science* **280** 2098
[3] Datta A and Pati Swapan K 2005 *Comput. Lett.* **1** 1574
[4] Brito B G A, Candido L, Rabelo J N T and Hai G Q 2014 *Chem. Phys. Lett.* **616–617** 212
[5] Kushwaha A K, Sahoo M R, Nanda J and Nayak S K 2017 *J. Clust. Sci.* https://doi.org/10.1007/s10876-017-1260-7
[6] Zhang J, Zhao L, Feng X, Zhang H, Zhang M and Luo Y 2017 *J. Clust. Sci.* https://doi.org/10.1007/s10876-017-1226-9
[7] Kushwaha A K and Nayak S K 2018 *Physica E: Low Dimensional Syst. Nanostruct.* **97** 368
[8] Rodríguez M and Sánchez M 2021 *Int. J. Hydrogen Energy* https://doi.org/10.1016/j.ijhydene.2021.04.028
[9] Wiener H 1947 *J. Am. Chem. Soc.* **69** 17
[10] Bollobás B and Erdös P 1998 *Ars Combinatoria* **50** 225
[11] Randić M 1975 *J. Am. Chem. Soc.* **97** 6609
[12] Amić D, Bešlo D, Lućić B, Nikolić S and Trinajstić N 1998 *J. Chem. Inform. Comput. Sci.* **38** 819
[13] Gutman I and Das K C 2004 *Match-Commun. Math. Comput. Chem.* **50** 83
[14] Gutman I and Trinajstić N 1972 *Chem. Phys. Lett.* **17** 535
[15] Trinajstić N, Nikolic S, Milicevic A and Gutman I 2010 *Kemija u Industriji.* **59** 577
[16] Zhong L 2012 *Appl. Math. Lett.* **25** 561
[17] Pattabiraman K 2018 *AKCE Int. J. Graphs Comb.* **15** 155
[18] Gupta C K, Lokesha V, Shetty B S and Ranjini P S 2016 *Southeast Asian Bull. Math.* **41** 1
[19] Lokesha V and Deepika T 2016 *Int. J. Sci. Eng. Res.* **7** 53
[20] Companion A L 1969 *J. Chem. Phys.* **50** 1165
[21] Pickup B T 1973 *Proc. R Soc. London Ser. A* **333** 69
[22] Hosoya H 1998 *Discrete Appl. Math.* **19** 239
[23] Zhang H and Zhang F 1996 *Discrete Appl. Math.* **69** 147
[24] Farrell E J 1979 *J. Combin. Theory Ser. B* **27** 75
[25] Hassani F, Iranmanesh A and Mirzaie S 2013 *Match-Commun. Math. Comput. Chem.* **69** 87
[26] Došlić T 2013 *J. Math. Chem.* **51** 1599
[27] Diudea M V 2006 *Carpath. J. Math.* **22** 43
[28] Deutsch E and Klavžar S 2016 *Iran. J. Math. Chem.* **6** 93
[29] Munir M, Nazeer W, Nizami A R, Rafique S and Kang S K 2016 *Symmetry* **8** 1
[30] Yang H, Baig A Q, Khalid W, Farahani M R and Zhang X 2019 *J. Chem.* https://doi.org/10.1155/2019/7297253. Article ID 7297253
[31] Kwun Y C, Munir M, Nazeer W, Rafique S and Kang S M 2017 *Sci. Rep.* **7** 1
[32] Munir M, Nazeer W, Nizami A R and Kang S M 2016 *Symmetry* **8** 97