The geometry structures and electronic properties of Li_mB_n $(m+n=12)$ clusters*

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The geometric structures, electronic properties, total and binding energies, harmonic frequencies, the highest occupied molecular orbital to the lowest unoccupied molecular orbital energy gaps, and the vertical ionization potential energies of small Li_mB_n $(m+n=12)$ clusters were investigated by the density functional theory B3LYP with a 6-311+G (2d, 2p) basis set. All the calculations were performed using the Gaussian09 program. For the study of the Li_mB_n clusters, the global minimum of the B_{12} cluster was chosen as the starting point and the boron atoms were gradually replaced by Li atoms. The results showed that as the number of Li atoms increased, the stability of the Li_mB_n cluster decreased and the physical and chemical properties became more active. In addition, on average there was a large charge transfer from the Li atoms to the B atoms.

Keywords: Li_mB_n $(m+n=12)$ clusters, density functional theory, geometry structures, electronic properties

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1. Introduction

Nano-clusters have the potential for the development of new nano-structures because they present different physical and chemical properties compared to their bulk counterparts. As a large branch of chemistry and physics, boron clusters and metal borides have attracted much attention due to their unusual chemical and physical properties.[1–12] For example, alkali-metal borides have been considered as a promising material for hydrogen storage.[10–12] However, the simulation of solid-state metal-sandwiched (MS) structures[13] has revealed that there are no stable alkali-metal borides M_xB_y (M = Na, K, Rb, Cs) in the crystalic phase for x larger than 0.15. In other words, there must be a large excess in boron content to provide the thermodynamic stability of the MS phase. In this respect, it would be interesting to determine the geometry structures and the electronic properties of the binary alkali-metal boride series. Li *et al.*[14,15] investigated the ground-state geometries, electronic structures, and vibrational frequencies of alkali metal borides MB_5 (M = Li, Na, K, Rb, Cs), alkaline earth metal MB_5^+ (M = Be, Mg, Ca, Sr) clusters, and alkali metal borides MB_7 (M = Li, Na, K, Rb, Cs) by *ab initio* self-consistent field and density functional theory (DFT) methods. Zhao *et al.* investigated the geometries of the MB_{10} (M = Li, Na, K) clusters at the B3LYP/6-311+G (d) level.[16] Due to their potential application for hydrogen storage, Yildirim *et al.*[12] investigated the Li–B and Li–B–H small clusters with the DFT. We studied the Na_mB_n $(m+n=6)$ clusters and their hydrogen storage capabilities.[17] More recently, we have investigated the structures and stabilities of the alkali-metal atoms Li and Na decorated B_6 clusters and their hydrogen storage properties.[18,19]

To the best of our knowledge, the electronic structures and the chemical bonding in many binary alkali-metal borides are not fully understood, and the alkali metal–B bond has not been completely described. In the present work, the stable structures, the binding energies (E_b), the highest occupied molecular orbital to the lowest unoccupied molecular orbital (HOMO-LUMO) energy gaps (E_{gap}), the vertical ionization potential energies (E_{vip}), and the vibrational frequencies of the ground state Li_mB_n $(m+n=12)$ clusters are studied. In addition, the atomic charges of the ground state Li_mB_n clusters are also investigated. In Section 2, we give the computational procedure, and the results and a detailed discussion are presented in Section 3. Finally, we draw a conclusion in the last section.

2. Computational methods

In this paper, we investigate the physical and chemical properties of Li_mB_n $(m+n=12)$ clusters and compare the results to those of the stable B_{12} clusters. The geometry optimizations and calculations are performed in the DFT framework. The generalized gradient approximation is employed with Becke's three-component hybrid exchange parameter functional[20] and the Lee–Yang–Parr (LYP) nonlocal correlation functional.[21] The 6-311+G (2d, 2p) basis set

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is employed for the geometry optimizations and the vibrational frequency calculations. The electronic structures, total binding energies, E_{gap}, E_{vip}, and the atomic charge distributions are calculated at the same level. All the computations are carried out using the Gaussian 09W[22] program package. The geometric structures of the ground states of the Li_mB_n $(m+n=12)$ clusters are generated directly using the Gaussview program. The binding energy and the E_{vip} of the optimized clusters are calculated by the following equations:

$$E_b = mE_{Li} + nE_B - E_{tot}(Li_mB_n), \quad (1)$$

$$E_{vip} = E_{tot}(Li_mB_n)^+ - E_{tot}(Li_mB_n), \quad (2)$$

where E_b is the total binding energy, E_{Li} (E_B) is the energy of a single neutral lithlium (boron) atom, E_{tot} (Li_mB_n) is the total energy of the Li_mB_n cluster, and $E_{tot}(Li_mB_n)^+$ is the total energy of the Li_mB_n cation cluster with the geometric structure of the neutral ground state Li_mB_n cluster. The average binding energy per atom (E_{ba}) of the optimized cluster is obtained by dividing the total binding energy by 12. The E_{gap} is calculated by taking the difference between the energies corresponding to the HOMO and the LUMO. In addition, in order to obtain the ground state structures of the Li_mB_n $(m+n=12)$ clusters, the possible lower lying states have also been investigated for all clusters. The calculation data and the structures of the possible lower lying states are not presented here. The average charges on the B and the Li atoms of the natural population are plotted in Fig. 5 as a function of the number of Li atoms.

3. Results and discussion

The ground state Li_mB_n clusters are shown in Fig. 1, and the E_{tot}, E_{ba}, E_{gap}, E_{vip}, and harmonic frequencies are presented in Table 1. All the data in Table 1 are obtained either directly from the optimization or from Eqs. (1) and (2). The atomic charge distribution and the average charge per B/Li atom of the Li_mB_n clusters are given in Table 2. The results are discussed in the following subsections.

Table 1. The properties of the ground state Li_mB_n clusters.

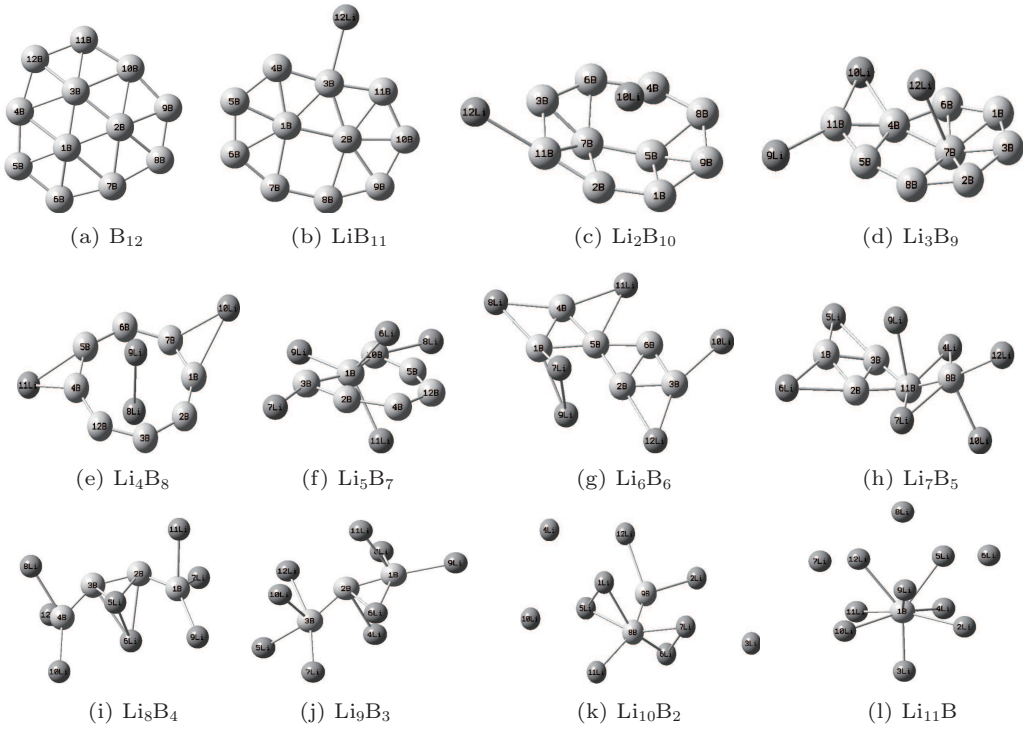
Cluster	E_{tot}/a. u.	E_{ba}/eV	E_{gap}/eV	E_{vip} /eV	Lowest/ highest frequency/cm^{-1}
B_{12}	–298.0362	4.7272	3.6164	8.8113	200.48/1324.84
LiB_{11}	–280.7656	4.5020	2.9688	7.4770	77.43/1496.93
Li_2B_{10}	–263.4645	4.2075	2.6594	6.5515	104.62/1369.01
Li_3B_9	–246.1970	3.9895	3.3778	6.5640	82.80/1410.63
Li_4B_8	–228.8840	3.6681	2.9454	6.0647	45.08/1518.04
Li_5B_7	–211.5774	3.3840	2.6126	5.1134	82.09/1332.47
Li_6B_6	–194.2511	3.0097	2.0605	4.6608	58.41/1182.59
Li_7B_5	–176.9380	2.6884	1.5380	3.8833	45.29/1157.29
Li_8B_4	–159.6106	2.3343	1.1189	3.3776	45.45/1297.30
Li_9B_3	–142.2942	2.0053	1.1421	3.6993	35.58/1145.91
$Li_{10}B_2$	–124.9656	1.6486	1.5535	4.0489	39.38/1205.01
$Li_{11}B$	–107.6214	1.2565	1.0751	3.8399	80.74/536.25

3.1. The structures and energetics of the Li_mB_n $(m+n=12)$ clusters

Before studying the ground state structures and the energetics of the Li_mB_n $(m+n=12)$ clusters, we investigated all kinds of possible structures including linear, planar, and close-packed configurations of B_{12} clusters with the B3LYP/6-311+G (2d, 2p) method. To search for the ground state structure of the B_{12} clusters, many possible initial configurations, which have different bond lengths, point groups, and spin multiplicities, were used for the geometry optimizations. Furthermore, previous studies on the B_n clusters were also employed as a guide.[5,23] From the geometry optimizations, together with the frequency analysis, 13 different configurations of the B_{12} clusters were obtained. The ground state B_{12} cluster was chosen from a comparison of all the possible configurations and is shown in Fig. 1(a) (in order to save space, the other B_{12} cluster configurations are not shown). The E_{tot}, E_{ba}, E_{gap}, and the lowest and highest frequencies of the ground state B_{12} cluster are listed in Table 1. Atis *et al.*[5] studied the B_{12} clusters and obtained the E_{tot}, E_{ba}, E_{gap}, and the lowest and highest frequencies of the ground state B_{12} cluster as 8108.46 eV, 4.599 eV, 3.609 eV, 200 cm^{-1}, and 1326 cm^{-1}, respectively. Liu *et al.*[23] found that the E_{ba}, E_{gap}, and E_{vip} of the ground state B_{12} cluster were 4.695 eV, 3.595 eV, and 8.619 eV, respectively. Our calculation results for the ground state B_{12} cluster agree with the previous theoretical results, which indicates that our method is suitable.

In the study of the Li_mB_n $(m+n=12)$ clusters, many possible initial configurations are used for the geometry optimization, and then a number of possible structures are obtained. Here, only the most stable isomer for each size is selected, as shown in Fig. 1. The initial structure of the Li_mB_n cluster is formed by replacing one B atom with an Li atom in the lowest energy structure of the $Li_{m-1}B_{n+1}$ cluster, e.g., the initial structure of the LiB_{11} cluster is constructed by substi-

tuting one B with Li, which is located at a different site in the ground state B_{12} cluster. Another B atom in the lowest energy structure of LiB_{11} is replaced by one Li atom to construct the initial Li_2B_{10} cluster. In this way, a procedure is followed to form the remaining initial Li_mB_n clusters. We choose the lowest energy configurations of the Li_mB_n $(m+n=12)$ clusters that have no imaginary frequency as the ground state structures.



(a) B_{12} (b) LiB_{11} (c) Li_2B_{10} (d) Li_3B_9

(e) Li_4B_8 (f) Li_5B_7 (g) Li_6B_6 (h) Li_7B_5

(i) Li_8B_4 (j) Li_9B_3 (k) $Li_{10}B_2$ (l) $Li_{11}B$

Fig. 1. The structures of the ground state Li_mB_n clusters.

For the LiB_{11} clusters, we obtain 14 different structures, and the ground state LiB_{11} cluster is shown in Fig. 1(b). As can be seen, all the boron atoms tend to form a boron cluster and coordinate the Li atom to form a fan-like structure. The boron cluster has a similar form to that of the optimized bare B_{11} [5,7] with an average B–B bond length of 1.6619 Å, which is slightly smaller than that in the bare B_{11} (1.670 Å),[5] and the Li–B distance is 2.0029 Å. This shows that the presence of one Li atom does not change the overall cluster size of B_{11}.

In the Li_2B_{10} clusters, two B atoms in the B_{12} clusters are replaced by Li atoms. We obtain 11 different configurations. The lowest energy structure of the Li_2B_{10} clusters is shown in Fig. 1(c). It is based on the optimized B_{10}^+ cluster,[7,16] which has a convex shape with two hexagonal pyramids. One Li atom is positioned at the border of the convex shape by binding to a boron atom, which looks like a scoop. The other Li atom sits above the concave. The average bond length of the B_{10} increases from 1.6105 Å[5] to 1.6285 Å. In other words, these two Li atoms stretch the bare B_{10} cluster, and increase the overall cluster size. The average distance between Li and B atoms is about 2.1232 Å, which is slightly longer than that in the ground state LiB_{11} cluster.

Eleven different Li_3B_9 clusters were obtained, and the most stable structure of the Li_3B_9 clusters is presented in Fig. 1(d). It is based on the optimized B_9^+, which has a planar wheel shape.[7] Two Li atoms are positioned at the plane of the B_9 by binding to the same boron atom, and the third Li lies above the planar B_9 cluster. The average B–B bond length of the ground state Li_3B_9 cluster is 1.6519 Å, which is shorter than that of the bare B_9 (1.709 Å).[5] And the average Li–B distance of the ground state Li_3B_9 cluster is 2.1052 Å.

There are nine different structures for the Li_4B_8 clusters, and the ground state is shown in Fig. 1(e). It is based on the fifth isomer of the B_8 clusters,[5] which is a ring. The average B–B bond length is shorter (1.5362 Å) than that of the optimized simple B_8 ring (1.5400 Å).[5] Two Li atoms binding together locate at the center of the ring, and the Li–Li bond is perpendicular to the B_8 planar ring. The other two Li atoms are positioned at the rim of the ring, with an average Li–B bond length of 2.2121 Å.

In the same way, we have constructed 15, 16, 14, 14, 11, 7, and 9 different configurations for the Li_5B_7, Li_6B_6, Li_7B_5, Li_8B_4, Li_9B_3, $Li_{10}B_2$, and $Li_{11}B$ clusters, respectively. The ground state Li_mB_n $(m+n=12)$ clusters for $m=5$–11 are

shown in Figs. 1(f)–1(l). From Fig. 1, one can see that the structures of the ground state Li_mB_n $(m+n=12)$ clusters for $m=5$–11 become complicated as the number of Li atoms increases. The B atoms still tend to combine together, and the Li atoms are present around the combined B atoms.

The E_{ba} versus the number of Li atoms is plotted in Fig. 2. We can visually find that the E_{ba} of the ground state Li_mB_n $(m+n=12)$ clusters decreases linearly as the number of Li atoms increases. The slope is about 0. 3177 eV, i.e., the replacement of the B atoms by Li atoms causes a decrease in the stability of the cluster, which in turn may cause an increase in the reactivity of the cluster. Figure 3 shows the E_{gap} as a function of the number of Li atoms. The E_{gap} decreases in a stepwise manner with the Li atoms increasing, which indicates a decrease in the stability of the clusters. The E_{gap} can be used as a measure of the chemical hardness.[24] In general, a "hard" molecule has a larger energy gap, and is more stable than that with a smaller gap. Compared with the neighboring clusters, the Li_3B_9 and $Li_{10}B_2$ clusters have large energy gaps, which indicates their relative stabilities compared with their neighboring counterparts.

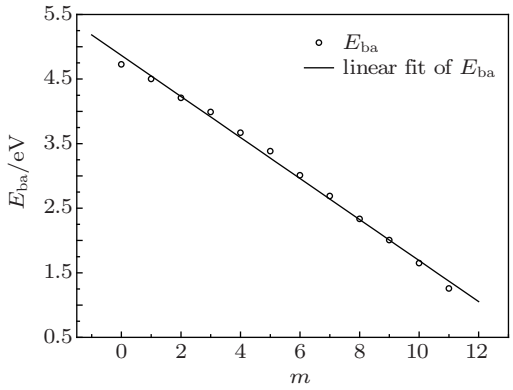


Fig. 2. The average binding energies of the ground states of the Li_mB_n clusters.

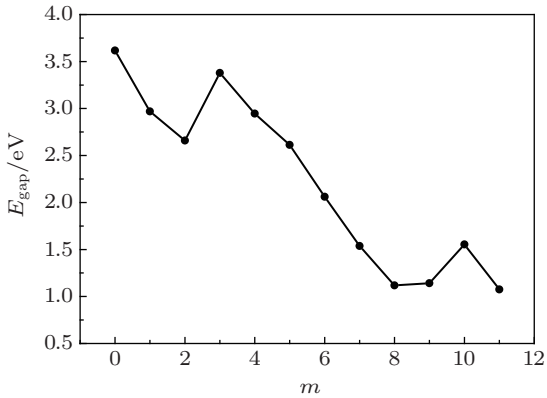


Fig. 3. The HOMO-LUMO energy gaps of the ground states of the Li_mB_n clusters.

To further investigate the stability of the Li_mB_n clusters, the E_{vip} of the ground state Li_mB_n clusters are calculated and presented in Fig. 4. The E_{vip} of the cluster refers to the bonding energy of a neutral cluster losing an electron. The higher the E_{vip}, the higher the cluster stability. As seen in Fig. 4, E_{vip} also decreases in a stepwise manner with the Li atom increasing, which indicates an increase in the capability of losing electrons for the Li_mB_n $(m+n=12)$ clusters. This implies that the capability of the involving reaction increases as the number of Li atoms increases. And there are two slight peaks in Fig. 4 for $m=3$, 10.

Considering the results of both E_{gap} and E_{vip}, we find that the Li_3B_9 and $Li_{10}B_2$ clusters have higher stabilities compared with their neighboring clusters, which indicates the possibility of a stable existence. So $m=3$ and 10 are the magic numbers. On the other hand, the $m=2$ and 8 clusters tend to be unstable.

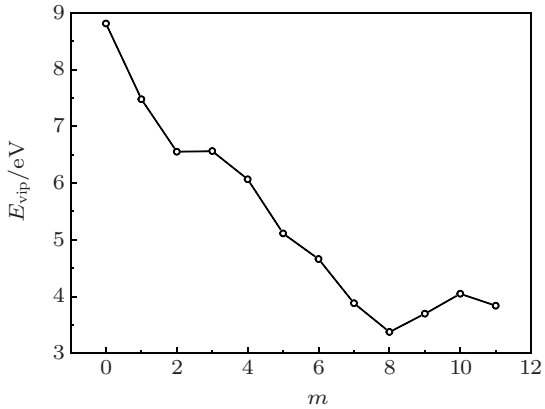


Fig. 4. The vertical ionization potential energies of the ground states of the Li_mB_n clusters.

3.2. Atomic charge distribution

Table 2 shows the atomic charge of the natural bond orbital (NBO) analysis as well as the average charge of the ground state for the Li_mB_n $(m+n=12)$ clusters. For the ground state LiB_{11} cluster, the charge is mainly on the 3B $(-0.58|e|)$, 4B $(-0.13|e|)$, 5B $(0.12|e|)$, 10B $(0.12|e|)$, 11B $(-0.13|e|)$, and 12Li $(0.68|e|)$ atoms. This indicates a significant charge transfer among them. The Li and 3B atoms in this cluster have a large charge, which indicates the presence of a very large charge transfer from the Li atom to the 3B atom.

The charge distribution of the ground state Li_2B_{10} cluster shows that there are significant charge concentrations on the 3B $(-0.33|e|)$, 11B $(-0.50|e|)$, 8B $(-0.18|e|)$, 7B $(-0.17|e|)$, 10Li $(0.76|e|)$, and 12Li $(0.88|e|)$ atoms. Most of the charge transfers are from 10Li and 12Li to 3B and 5B. For this isomer, the 10Li and 12Li atoms have a slightly smaller positive charge compared with LiB_{11}.

As for the lowest energy isomer of Li_3B_9, there are some negative charge concentrations on the 2B $(-0.22|e|)$, 4B $(-0.54|e|)$, 5B $(-0.32|e|)$, 6B $(-0.29|e|)$, 8B $(-0.21|e|)$, and 11B $(-0.81|e|)$ atoms. Similar to the LiB_{11} and Li_2B_{10} clusters, the Li atoms have a positive charge $(0.88|e|, 0.83|e|,$

0.77|e| on 9Li, 10Li, and 12Li, respectively). The charge transfer from the Li atoms to the B atoms is smaller than that in LiB_{11}, but slightly larger than that in Li_2B_{10}.

For the ground state of the Li_4B_8 cluster, the negative charge is concentrated at 1B, 3B, 4B, 5B, and 7B ($-0.60|e|$, $-0.24|e|$, $-0.60|e|$, $-0.62|e|$, and $-0.62|e|$, respectively), and the Li atoms have some positive charge ($0.67|e|$, $0.67|e|$, $0.91|e|$, $0.91|e|$ on 8Li, 9Li, 10Li, 11Li, respectively). Therefore, there is a large charge transfer from the Li atoms to the B atoms.

For the ground states of other Li_mB_n clusters (i.e. $m = 5$–11), from Table 2, one can see that all the B atoms obtain a very negative charge (exceeding $-0.5|e|$). In particular, for the ground state of $Li_{11}B$, due to its proximity to the center of the structure, the B atom has the most negative charge ($-4.22|e|$). NBO analysis shows that all the Li atoms in the ground states of the Li_mB_n $(m+n=12)$ clusters have a positive charge, while almost all the B atoms have a negative charge, which indicates charge transfers from the metal atoms to all the B atoms. This result supports the metal atoms interacting with the whole B_n cluster and not with a particular B atom.

Table 2. The atomic charge distributions of the Li_mB_n clusters.

Cluster	Atomic charge												Av. B/Li charge
	1	2	3	4	5	6	7	8	9	10	11	12	
B_{12}	–0.24	–0.21	–0.32	–0.16	0.05	0.06	0.10	0.06	0.06	0.08	–0.22	0.68	0
LiB_{11}	–0.07	–0.07	–0.58	–0.13	0.12	–0.09	0.02	0.02	–0.09	0.12	–0.13	0.89	–0.08/0.89
Li_2B_{10}	–0.10	–0.08	–0.33	–0.08	–0.12	–0.07	–0.17	–0.18	–0.02	0.76	-0.50	0.88	–0.16/0.82
Li_3B_9	–0.06	–0.22	0.01	–0.54	–0.32	–0.29	–0.03	–0.21	0.88	0.83	–0.81	0.77	-0.28/0.83
Li_4B_8	–0.60	–0.18	–0.24	–0.60	–0.62	–0.10	–0.62	0.67	0.67	0.91	0.91	–0.18	–0.40/0.79
Li_5B_7	–0.53	–0.59	–0.82	–0.30	–0.59	0.76	0.84	0.84	0.74	–0.82	0.76	–0.30	–0.56/0.79
Li_6B_6	–1.11	–0.91	–1.02	–0.88	–0.67	–0.58	0.84	0.84	0.84	0.88	0.88	0.88	–0.86/0.86
Li_7B_5	–0.97	–0.58	–0.58	0.58	0.75	0.75	0.60	–1.81	0.66	0.67	–0.75	0.68	–0.94/0.68
Li_8B_4	–1.61	–0.75	–0.75	–1.61	0.22	0.22	0.77	0.77	–0.61	0.61	0.77	0.77	–1.18/0.59
Li_9B_3	–2.31	–1.19	–2.68	0.72	0.83	0.55	0.62	0.74	0.90	0.60	0.71	0.52	–2.06/0.68
$Li_{10}B_2$	0.59	0.59	–0.21	–0.17	0.59	0.67	0.67	–1.86	–1.85	–0.21	0.67	0.51	–1.86/0.37
$Li_{11}B$	–4.22	0.42	0.80	0.65	0.49	0.06	0.06	–0.17	0.34	0.42	0.65	0.49	–4.22/0.39

Figure 5 shows the averaged charge per B/Li atom as a function of the number of Li atoms. As seen in Fig. 5, with the number of Li atoms increasing, the average charge of the B atoms becomes more negative. This starts from $-0.08|e|$ for one Li atom to $-4.22|e|$ for 11 Li atoms, and indicates a raised charge transfer from the Li atoms to the whole B_n cluster as the number of Li atoms increases. Moreover, the interaction between the Li atoms and the whole B_n cluster has a large ionic contribution. From Fig. 5, one can see that the average positive charge of the Li atoms not only decreases, but also has a slight fluctuation as the number of Li atoms increases.

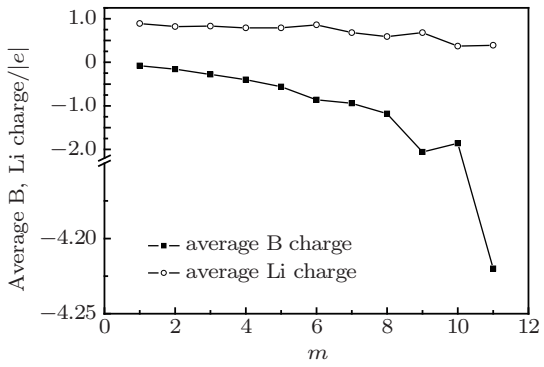


Fig. 5. The average B/Li charges of the ground state Li_mB_n clusters.

4. Conclusion

The geometry structures and the electronic properties of Li_mB_n $(m+n=12)$ clusters were studied by means of the B3LYP/6-311+G (2d, 2p) method. For the Li_mB_n $(m+n=12)$ clusters, the boron atoms tend to form clusters among themselves, and generally take forms similar to their corresponding bare boron clusters, with the Li atoms present around the boron clusters. Furthermore, the number of Li atoms affects the stability of the cluster, i.e., as the number of Li atoms increases, the total energy and the average binding energy of the cluster increase, while the HOMO-LUMO energy gap and the vertical ionization potential energy decrease. The results suggest that the stability of the cluster decreases and the activation of the reactivity for the cluster increases with the number of Li atoms increasing. If E_{ba}, E_{gap}, and E_{vip} are considered together, $m = 3$ and 10 are the magic numbers for the ground states of the Li_mB_n $(m+n=12)$ clusters. In all the ground states of the Li_mB_n $(m+n=12)$ clusters, the Li atoms have a positive charge, which indicates the charge transfer from the Li atoms to the whole B_n cluster. Moreover, the interaction between the Li atoms and the whole B_n cluster has a large ionic contribution part.

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