Structural evolution and bonding characteristics of neutral Cs₂Bₙ clusters

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ABSTRACT
In this study, the unbiased crystal structure analysis by particle swarm optimisation (CALYPSO) combined with the density functional theory (DFT) method were used to perform a structure search for neutral Cs₂Bₙ (n = 1–12) clusters, as well as the corresponding global minimum of the potential energy surface were determined. The ground-state structures of the Cs₂Bₙ (n = 1–12) clusters have four types of geometries: planar, arch bridge, double pyramid, and shield shape. Subsequently, the relative stability of the ground-state structures was systematically analysed based on three effective rules, which indicates that the C7V Cs₂B₈ with a double pyramid structure has unusual stability. The results of the molecular orbitals (MOs) and density of states analysis (DOS) show that the B-2s and 2p atomic orbitals of Cs₂B₈ are the main components of MOs. In addition, from the results of adaptive natural density partitioning (AdNDP) and localised orbital locator (LOL), it can be seen that the excellent stability of Cs₂B₈ originates from the delocalised large π bonds with aromaticity and the s–p bonding of B–B. Our results reveal the structural growth mode of Cs₂Bₙ clusters and enrich the chemical bonding properties of boron-based clusters.

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1. Introduction
Boron and its compounds have attracted the extensive attention of researchers because of their abundant excellent properties and chemical structures in recent years [1]. In the meantime, it is also used as hydrogen storage [2] and drug delivery carrier [3] material. The electron-deficient state in which the valence electrons of the B atom are less than the number of valence orbitals, it is beneficial to form covalent bond molecules with most atoms through delocalised multi-centre bonds, so that the properties and structures of boron compounds are rich and diverse. The electron-deficient boron tends to generate planar or quasi-planar clusters at small as well as medium sizes [4], with aromatic structures similar to...
hydrocarbons [5], this is owing to the π-electron delocalised bonds in the Bₙ clusters fit the Hückel rule of aromaticity and antiaromaticity in cyclic hydrocarbons [6,7,8]. The delocalised π or σ bonds in Bₙ clusters predicted by Zubarev [9] and Boldyrev [10] exhibit aromaticity or antiaromaticity. A typical example is the neutral B₁₄ cluster, whose 3D structure was redefined as a planar structure with aromaticity [11]. Among the neutral pure boron clusters, the clusters with an atomic number less than 16 are almost all planar structures, especially the Bₙ clusters when n = 7–15, which have been proved to be planar structures with aromaticity by experimental and theoretical studies [6,12]. In 2007, Oger’s team [13] reported that the B₁₆⁺ cluster is an intermediate structure of a plane-to-cylindrical when studying cationic boron clusters, namely the minimum value of the first three-dimensional structure appears at n = 17. In the anion system of pure boron clusters [8,14], the planar or quasi-planar structures up to 25 B atoms, even higher anionic boron clusters (B₃₅,₃₆−) continue to exhibit a planar pattern with a hexagonal central hexagonal hole [15,16]. In addition, it was found from Boustani’s study [15] that B₁₉ exhibits different structural skeletons at different charge states: B₁₉− is a two-dimensional structure, but neutral and cation B₁₉ are both 3D pyramidal structures, their results show that electrons can influence the geometry of boron clusters. Therefore, it is of great necessity for us to study the 2D and 3D structures of boron clusters in different electronic states for understanding their structural evolution characteristics.

Introducing other atoms into boron clusters may be a way to expand our cognition of its structure and electronic properties. In the small-sized MB₆ (M = Be, Mg, Ca, and Sr) clusters, BeB₆ and MgB₆ with Csᵥ symmetry have pyramidal structures, while CaB₆ and SrB₆ have low point group symmetry. At the same time, these four MB₆ molecules have two σ-type delocalised bonds and three π-type delocalised bonds, thus exhibiting multiple aromaticity [17]. In the larger doping system, the theoretical study of CB₇− and CB₈− shows that C atoms are inclined to replace B atoms at the edge position rather than the centre [18]. In 2008, Schleyer and collaborators [19] doped Co and Fe into B₈ and B₉ clusters, and they obtained three perfect hypercoordinated planar boron structures, including CoB₈−, FeB₉²− and FeB₉−. In addition, a series of doped species similar to the above CoB₈−, FeB₉²− and FeB₉− clusters have also been reported to occupy the central position of the wheel-like molecules [20]: RhB₉, IrB₉, TaB₁₀−, NbB₁₀⁺, and VB₁₀−, and they have extremely high symmetry and aromaticity. Therefore, to understand these unusual structures, Wang and colleagues [21] used density functional theory (DFT) and photoelectron spectroscopy (PES) to investigate the formation mechanism of TaB₁₀−. They deemed that the B₈ ring is too small to encapsulate the Ta atoms, the perfect wheel-like molecule can be formed when the ring is enlarged. In the study of large-scale doped species, Li et al. [22] used first-principles combined with PES to analyze TaB₂₀−, a global minimum of the tubular molecule C₃ B₂−Ta@B₁₈− and a perfect nanodrum-like isomer D₁₀D Ta@B₂₀− were found. In summary, the geometrical configurations and properties of boron-based clusters are rich and diverse, as well as we need to further explore them. Furthermore, it can also provide theoretical support for the construction of new functional materials at some level.

Previous studies have discussed the structure, electronic properties, and bonding characteristics of two metal atom-doped boron clusters by using DFT methods, such as Fe₂B₉ [23], Co₂B₉ [24], Sc₂B₉ [25] and V₂B₉ [26]. However, there is no research on the doping of two caesium atoms into small-sized Bₙ clusters. To make up for the deficiency in this field, firstly, we adopted the crystal structure analysis by particle swarm optimisation (CALYPSO) method combined with DFT to search for the global minimum of Cs₂Bₙ (n = 1–12) clusters. In the next place, the ground-state structures and low-energy isomers are determined based on energy and point group symmetry, we will also elucidate the evolution characteristics and electronic states of these geometries. Finally, the molecular orbitals (MOs) and chemical bonding of caesium-boron clusters were analyzed using the Multiwfn programme.

2. Computational detail

To determine the global minimum of the Cs₂Bₙ (n = 1–12) clusters, we used the CALYPSO programme [27] combined with the DFT method to search for their structures. In previous work [28], the CALYPSO programme was used to predict the structure of crystals or clusters, which proved that the method is effective and reliable. In this study, we predicted the structures of Cs₂Bₙ (n = 1–12) clusters based on B3PW91/SDD [29]. To make the potential energy surface converge, a total of 50 generations were calculated for each cluster. Each generation generates 30 isomers, 60% of which are generated by the particle swarm optimisation algorithm, and the rest are yielded randomly. Therefore, our Cs-doped clusters of various sizes have about 1500 candidate structures. Later, we excluded similar structures based on the energy difference of 3eV to obtain low-energy species. In addition, the Gaussian 09 programme [30] package was used to perform the initial optimisation and frequency calculation for the low-energy isomers at the PBE0/LANL2DZ
level [31, 32]. The purpose of the second structural optimisation and energy calculation for Cs₂Bₙ (n = 1–12) clusters at the level of PBE0/def2-TZVP + 6-311G(d) [32, 33] (the def2-TZVP basis set was used for Cs atoms and the all-electron 6-311G(d) basis set for B atoms) is to obtain more stable structures. In the process of the geometric structure optimisation, we considered two cases such as different spin multiplicity as well as imaginary frequency, which respectively ensured the diversity of the structure skeletons and the authenticity of the local minimum. Furthermore, we determined that the PBE0 function is a reliable choice for boron cluster systems through previous reports [34]. Apart from this, the natural bond orbital (NBO) [35] was applied to analyze the charge transfer between Cs and B atoms. Finally, to further understand the bonding mechanism and orbital composition of the Cs₂Bₙ (n = 1–12) clusters, we take the relatively stable structure as an example to explain. At the same time, using the Multiwfn programme [36] to calculate and analyze its MOs, the density of states (DOS), adaptive natural density partitioning (AdNDP) [37], and localised orbital locator (LOL) [38] one by one.

3. Results and discussions

3.1. Geometric structures

Using the computational scheme for structure prediction and geometry optimisation described in Section II, the ground-state and metastable structures of the neutral Cs₂Bₙ (n = 1–12) clusters as well as the corresponding pure clusters were determined and presented in Figure 1. In Figure 1, the isomers of each cluster are represented by labels: na, nb, nc, nd and ne, here n denotes the number of B atoms, a is the most stable structure, while b, c, d and e indicate the low-energy structures of corresponding clusters. Furthermore, the point group symmetries, electronic states, and relative energies are displayed below the corresponding isomers. Meanwhile, the above properties of the ground-state structures for the neutral Cs₂Bₙ (n = 1–12) clusters are summarised in Table 1.

In order to intuitively understand the structural features and evolution laws of the Cs₂Bₙ clusters, we take the pure boron cluster with the same computational level as the Cs₂Bₙ clusters as the comparison object. The results of the study are as follows: (1) Firstly, we found the geometries of B₅–13 are the same as reported by Tai’s team [39], but the electronic states and symmetries of B₈,12 are different from ours. In addition, it deserves mentioning that the B₁₄ cluster with C₂ᵥ symmetry is similar to the result of Tai et al. [39]. (2) In almost all the ground-state structures of Cs₂Bₙ clusters, the two doped Cs atoms are more likely to occupy the edges of the overall skeleton instead of the centre. (3) Interestingly, none of the ground-state structures inherit the skeleton features of the corresponding Bₙ clusters. The main reason for this phenomenon is that the introduced Cs atoms lead to the reconstruction of the overall configuration. (4) We found small clusters can directly form larger ones by attracting boron atoms in different directions. In Bₙ clusters, there are three types of this change: Firstly, there is an obvious structural evolution process among the small-sized B₃,4,5 clusters with planar structures; Next, the four clusters of the pentagon B₆, hexagon B₇, heptagon B₈ and double pyramid B₉ introduce a B atom sequentially, and then form a larger structure; Finally, the difference from the previous structural evolution is that two atoms are introduced into B₁₀,₁₁,₁₂ to form the larger B₁₂,₁₃,₁₄ clusters. In all lowest-energy structures of the Cs₂Bₙ clusters, the number of intermediate B atoms in the basic structure Cs₂B₂,3,4,5 is continuously increased to generate larger Cs₂B₃,4,5,6,7,8,9,12 clusters in turn; The Cs₂B₁₁ cluster is yielded by adding a B atom at the top position of Cs₂B₁₀.

Then, the metastable structures (b, c, d and e) of Cs₂Bₙ clusters were studied to further reveal their structural characteristics and evolution laws. The low-energy isomers of Cs₂B are linear structures. For the Cs₂B₂ cluster, 2b and 2a are all three-dimensional structures, but 2c, 2d and 2e are linear structures. Compared with the above properties of the ground-state structures of the Cs₂Bₜ clusters are similar to those described above, the main reason for this result is that the atoms are arranged in different order when the isomers reach energy minimisation (positive frequency). Interestingly, compared with the corresponding ground-state structures of the Cs₂B₉,9,10,11,₁₂ clusters, except for 9b, 10b, 10e and 11b, the geometries formed by the B atoms in the intermediate positions of the other isomers are different from those of the ground-state structures, which is also one of the important reasons why the ground-state structures are quite different from the isomers. It is worth noting that there is a clear structural evolution process among metastable species, such as 1-7b, 1-3 and 5d, and 5-7e. In addition, most of the lowest-energy structures have higher point group symmetry than metastable structures, and their electronic states are mostly singlet or doublet.

3.2. Relative stability

In this work, the analysis of the average binding energies (Eₘ) can reveal the size-induced inherent stability of the neutral Bₙ₊₂ and Cs₂Bₙ (n = 1–12) clusters. For mentioned clusters, the calculation method of Eₘ values
Figure 1. Most stable structures of $\text{B}_n\text{C}_{n+2}$ clusters and low-lying isomers of $\text{Cs}_2\text{B}_n$ ($n = 1–12$) clusters, along with the point group symmetry, electronic states and relative energy.
is:
\[
E_b(Cs_2B_n) = \left[ nE(B) + 2E(Cs) - E(Cs_2B_n) \right] / (n + 2)
\]
\[
E_b(B_{n+2}) = \left[ (n + 2)E(B) - E(B_{n+2}) \right] / (n + 2)
\]
where \( E \) represents the total energy of the corresponding clusters or atoms, and \( n \) is the number of B atoms. Figure 2(a) shows how the \( E_b \) values of the \( B_{n+2} \) and Cs\(_2B_n\) (\( n = 1–12 \)) clusters change with increasing the number of atoms. In the size range studied here, it can be seen from the curve features that the \( E_b \) of doped clusters is always lower than that of pure clusters, which indicates the stability of the \( B_n \) clusters will decrease after doping with Cs atoms. As the number of B atoms increases, the energy difference between the \( E_b \) of the doped clusters and the pure boron clusters gradually decreases, because the contribution ratio of Cs atoms has fallen in the larger-sized doped clusters. Furthermore, the \( E_b \) curves of these two clusters have the same changing trend, namely they show an upward trend as a whole, and their growth rates are getting smaller.

The second-order difference energy (\( \Delta_2E \)) is also an inherent manifestation of the relative stability of different species, which describes the size-induced changes in cluster stability. The equations of the \( \Delta_2E \) corresponding to the above clusters are as follows:
\[
\Delta_2E(Cs_2B_n) = E(Cs_2B_{n-1}) + E(Cs_2B_{n+1}) - 2E(Cs_2B_n)
\]
\[
\Delta_2E(B_{n+2}) = E(B_{n+1}) + E(B_{n+3}) - 2E(B_{n+2})
\]

As shown in Figure 2(b), the \( \Delta_2E \) values of the \( B_{n+2} \) as well as Cs\(_2B_n\) (\( n = 1–12 \)) clusters exhibit similar odd-even oscillating behaviours in our study. There are several obvious peaks at \( n = 3, 6, 8 \) and 10, they reflect the stronger relative stability of the \( B_{5,8,10,12} \) and \( Cs_2B_{3,6,8,10} \) clusters. Interestingly, the \( C_{7V} \) \( Cs_2B_8 \) cluster has the largest \( \Delta_2E \) value of 2.86 eV.

In cluster science, the ability of electrons to transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) is called the energy gap (\( E_g \)), which is also the main

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**Table 1.** Electronic States, symmetries, average binding energies \( E_b \) (eV), HOMO–LUMO energy gaps \( E_g \) (eV), and charges on the Cs atoms of the neutral Cs\(_2B_8\) and \( B_{n+2} (n = 1–12) \) clusters.

| Clusters | sym | \( E_b \) (eV) | \( E_g \) (eV) | \( \Delta_2E \) (eV) | Cs-1 | Cs-2 | Charge |
|----------|-----|---------------|---------------|------------------|------|------|--------|
| \( n = 1 \) | \( 4A_2 \) | Cs\(_2V\) | 0.676 | 1.442 | −1.199 | 0.745 | 0.745 | \( 1A' \) D\(_{3h}\) |
| \( n = 2 \) | \( 3B_2 \) | Cs\(_2V\) | 1.729 | 1.745 | 0.084 | 0.854 | 0.854 | \( 1A' \) D\(_{3h}\) |
| \( n = 3 \) | \( 2A \) | C\(_1\) | 2.600 | 1.985 | 1.000 | 0.847 | 0.868 | \( 1A_1 \) C\(_{2v}\) |
| \( n = 4 \) | \( 3A_1 \) | Cs\(_2V\) | 3.015 | 2.265 | −0.474 | 0.884 | 0.884 | \( 2B_2 \) C\(_{2v}\) |
| \( n = 5 \) | \( 2A_2 \) | C\(_1\) | 3.378 | 2.087 | −0.459 | 0.935 | 0.909 | \( 1A_1 \) C\(_{3v}\) |
| \( n = 6 \) | \( 1A_2 \) | D\(_{2h}\) | 3.708 | 3.055 | −0.383 | 0.955 | 0.955 | \( 1A_1 \) D\(_{3h}\) |
| \( n = 7 \) | \( 2B_1 \) | Cs\(_2V\) | 4.008 | 1.848 | −0.885 | 0.957 | 0.976 | \( 2A_1 \) C\(_{2v}\) |
| \( n = 8 \) | \( 1A_2 \) | Cs\(_2V\) | 4.335 | 3.493 | 2.861 | 0.970 | 0.970 | \( 1A_2 \) C\(_{2v}\) |
| \( n = 9 \) | \( 2A_1 \) | Cs\(_2V\) | 4.344 | 3.349 | −1.134 | 0.978 | 0.978 | \( 2B_2 \) C\(_{2v}\) |
| \( n = 10 \) | \( 1A' \) | Cs\(_3\) | 4.462 | 2.573 | 0.678 | 0.979 | 0.948 | \( 1A' \) C\(_5\) |
| \( n = 11 \) | \( 2A' \) | Cs\(_3\) | 4.511 | 1.642 | −0.593 | 0.984 | 0.955 | \( 1A_1 \) C\(_{2v}\) |
| \( n = 12 \) | \( 1A' \) | Cs\(_3\) | 4.594 | 2.102 | | 0.952 | 0.983 | |
3.3. Charge transfer

Besides the stability analysis, we also feel like obtaining charge transfer information about the lowest-energy structures of the Cs$_2$B$_n$ ($n = 1–12$) clusters, the Natural Population Analysis (NPA) method was used to analyze the charge on the Cs atoms; the specific calculation results are displayed in Table 1. From the results, the two Cs atoms in the doped clusters are positively charged due to the B atoms act as electron acceptors. In addition, since the Pauling electronegativity of the Cs atoms (0.7) is much smaller than that of the B atoms (2.0), the part of the charges is transferred from the Cs to the B atoms (2.0), the part of this curve: as the number of atoms increases, this curve at first increases, reaches a peak at $n = 9$, and then oscillates. In order to obtain more information about charge transfer, we have shown the relevant information of the natural electronic configuration (NEC) of Cs$_2$B$_n$ clusters in Table S1 (see Supplementary Information). From the table, the B-2s orbital has a large electron donation. At the same time, the unfilled B-2$p$ orbital accepts 1.91–2.90 electrons in the corresponding clusters, which illustrates the charge transfer occurred between the $s$ as well as $p$ orbitals of the clusters. With the increase of the clusters size, in general, the occupations of Cs-2$s$, Cs-2$p$, and B-2$p$ orbitals decreases, and the B-2$p$ orbital occupations increases. It is interesting that the occupations of the B-2$s$ and B-2$p$ orbitals of each cluster are the majority of the

total electrons. Therefore, this may be the main reason for the B-B bonding in the doped clusters.

3.4. Molecular orbitals and DOS

Within the scope of our research, the Cs$_2$B$_8$ cluster with a double pyramid structure exhibits excellent stability. Because of its remarkable properties, we further studied its molecular orbital contribution and chemical bonding. In Figure 4, its MOs and corresponding energy levels are analyzed. Moreover, we know that the Cs$_2$B$_8$ cluster is a closed shell structure, so the HOMO is double-occupied and the energy level of LUMO is 3.49 eV higher than it. By using the Multiwf programme, the components of the selected molecular orbitals can be obtained. For the Cs$_2$B$_8$ cluster, the composition of HOMO is only the 97.04% of 2p AO from the B atoms, and the LUMO is generated by 87.66% of the 6s AO of the two doped Cs atoms. For other MOs, only the 2p orbital of the B atoms has 97.01% contribution to the HOMO-1. Regarding the HOMO-m ($m = 2–5$), the contribution of the MOs derives from the B-2s and B-2p AOs. The contribution of the 2s-orbital of B atoms to HOMO-2 is 21.28%, while the HOMO-3, -4, and -5 are 20.69%, 6.85% and 7.46%, respectively. For the 2p orbital of B atoms, the HOMO-2 is 75.90%, 75.56%, 91.09% and 90.96%. There are 1.11% of Cs-5$s$, 5.52% of Cs-5$p$ and 92.73% B-2$p$ AO in HOMO-6. With regard to LUMO + 1, 2, their molecular orbitals are mainly formed by the Cs-6$s$ and B-2$p$ atomic orbitals. The molecular orbital composition of the LUMO + 3, 4 is similar to that of HOMO, and only the B-2$p$ orbital contributes to them. In addition, the specific contributions of various AOs of neutral Cs$_2$B$_8$ clusters are listed in Table S2. Finally, the analysis of molecular orbital composition once again confirmed that the interaction
between the B-\(s\) and B-\(p\) orbitals is the main reason for the stability of the Cs\(2B\)\(_n\) clusters, which agrees with the NEC analysis.

For another, we want to learn more about the contribution of Cs and B atoms to other orbitals adjacent to HOMO in the doped clusters. Thus, the total density of states (TDOS) and partial density of states (PDOS) for the Cs\(2B\)\(_8\) cluster were studied and presented in Figure 5. The corresponding equations are as follows:

\[
\text{TDOS}(E) = \sum_i \delta(E - \epsilon_i) \tag{5}
\]

\[
\text{PDOS}_A(E) = \sum_i \Theta_{A,i}F(E - \epsilon_i) \tag{6}
\]

Where \(\epsilon_i\) is the energy of the corresponding MOs. The \(\Theta_{A,i}\) denotes the contribution of part A to MO\(i\), because we want to know the contribution of Cs and B atoms to the MOs of the Cs\(2B\)\(_n\) clusters, so the part A represents them here. In Figure 5, the green dashed line represents the contribution of the Cs-\(s\) AO, the dark blue dashed line is the contribution from the Cs-\(p\) AO, and the light blue and red solid lines on behalf of the contribution of the B-\(s\) and B-\(p\) AOs, respectively. In the left part of HOMO, it can be easily found that only the Cs-\(p\) atomic orbital in the range of approximately \(-16 \sim -13\) eV contributes to the molecular orbital. Apart from this, the main contribution sources of molecular orbitals are composed of Cs-\(s\) and Cs-\(p\) AOs, and the curves of these two atomic orbitals have the same changing trend. Interestingly, the above-mentioned curve characteristics also exist in the density of states analysis of other doped clusters (in Supplementary Information).

Firstly, the calculated results of the DOS are broadly in line with the above MOs analysis. In addition, the peak positions of the PDOS curves of the B-\(s\) and B-\(p\) orbitals are coincident, which indicates that there is a significant \(s-p\) hybridisation between the two orbitals. In other words, the \(s-p\) hybridisation can promote the formation of the B-B covalent bond in the Cs\(2B\)\(_8\) cluster, and also make the cluster more stable.
3.5. AdNDP and LOL

In order to further explore the bonding features of the $\text{Cs}_2\text{B}_8$ cluster, we conducted a systematic search for the $n$-centre double-electron bonds ($nc$-2e) based on the AdNDP method. When $n$ greater than 2, they are delocalised bonds; otherwise they are defined as localised bonds. Subsequently, the multi-centre bonds of the $\text{Cs}_2\text{B}_8$ cluster and the corresponding occupancy numbers (ONs) are presented in Figure 6. As you can see from the search results, it has both localised and delocalised bonds: including seven $\sigma$ bonds as well as seven $\pi$ bonds. In the $\sigma$-type bonds, there are seven degenerate structures of 2c-2e are yielded by the B$_2$ structure unit in the middle position, their ONs are all 1.931 |e|.

In Figure 6(b), a large delocalised $\pi$-type bond consists of 7 degenerate small $\pi$-bonds whose geometry is a wheel-like structure created by eight boron atoms. The wheel-like B$_8$ cluster has 24 valence electrons, of which 14 are responsible for the interaction between $\sigma$-bonds, the rest of 10 electrons ($4n + 2 = 10$, $n = 2$, Hückel rule) act on the heptagonal ring and the central B atom. Therefore, the lowest-energy structure of the neutral $\text{Cs}_2\text{B}_8$ has a cyclic conjugated system ($\pi$-aromaticity) very similar to benzene, the system energy is low, and the structure is relatively stable. Furthermore, we also found the residual valence electrons of the two Cs atoms are close to 0 in the Multiwfn programme, which is also an important reason why the Cs atoms do not participate in chemical bonding in the AdNDP analysis. So, the electronic stability of the neutral $\text{Cs}_2\text{B}_8$ cluster is attributed to the large second-order differential energy and $\pi$-aromaticity, while doping Cs has little effect on the stability of pure boron clusters.

To further obtain more information about the bond characteristics of the $\text{Cs}_2\text{B}_8$ cluster, we used the LOL approach to study it. As shown in Figure 7, the LOL value was set to 0–0.75, which can show the degree of electron localisation. In particular, the covalent regions are deemed to exist when the LOL value more than 0.5. From different planes of the LOL projection, the covalent bond regions between the B atoms are clear. Notably, the B–B covalent bonds on the heptagonal ring are the most pronounced. However, the yellow or even orange regions of Cs–B and Cs–Cs are almost non-existent, indicating that their LOL values are less than 0.5 and there is no bonding. Therefore, there is no support for the stability of $\text{Cs}_2\text{B}_8$ clusters by Cs atoms. This conclusion is consistent with the calculation result of AdNDP.

4. Conclusions

In summary, we used the CALYPSO structure search combined with DFT to study the geometries, electronic properties, and bonding characteristics of small-scale $\text{Cs}_2\text{B}_n$ ($n = 1–12$) clusters. The ground-state structures of neutral $\text{Cs}_2\text{B}_n$ clusters have four types of geometries: planar structures when $n = 1, 4$ and 5, arch bridge structures for $2 \leq n \leq 3$, double pyramid structures for $6 \leq n \leq 8$, and they are shield-shaped when $n = 9–12$. 

![Figure 6. Analysis of AdNDP chemical bonding and partial structure of the $\text{Cs}_2\text{B}_8$ cluster. ON denotes the occupation number.](image-url)
Figure 7. Analysis of the structural diagram with all atomic labels and 2D colour distribution of the LOL projection in different planes of the Cs$_2$B$_8$ cluster.

Based on our calculations of the $E_b$, $\Delta_2E$, and $E_r$, which determined that the $C_{7v}$ Cs$_2$B$_8$ cluster with the largest second-order differential energy has high relative stability in our study. The molecular orbital composition and density of states calculation results shown that its MOs are mainly composed of B-2$s$ and B-2$p$ AOs and there is a strong s–p hybridisation. At the same time, the chemical bonding analysis of the Cs$_2$B$_8$ cluster indicated that it possesses a large delocalised $\pi$-type molecular orbital with aromaticity, which is one of the important reasons for its high stability. Moreover, we can see the stable covalent bonds between B atoms from the LOL diagram, which can enhance its stability.

In comparison with the other two metal atom-doped boron clusters, the analysis results of the target system are similar to them in terms of structural growth patterns and magic number structures. In addition, the s–p bonding of B–B and the $\pi$-aromaticity for the most stable cluster Cs$_2$B$_8$ are unique. Lastly, we hope the results in this paper will inspire new experiments and theoretical studies on the structural and electronic properties of active metal-doped boron clusters.

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