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TOPICAL REVIEW — CALYPSO structure prediction methodology and its applications to materials discovery

Cluster structure prediction via CALYPSO method*

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Cluster science as a bridge linking atomic molecular physics and condensed matter inspired the nanomaterials development in the past decades, ranging from the single-atom catalysis to ligand-protected noble metal clusters. The corresponding studies not only have been restricted to the search for the geometrical structures of clusters, but also have promoted the development of cluster-assembled materials as the building blocks. The CALYPSO cluster prediction method combined with other computational techniques have significantly stimulated the development of the cluster-based nanomaterials. In this review, we will summarize some good cases of cluster structure by CALYPSO method, which have also been successfully identified by the photoelectron spectra experiments. Beginning with the alkali-metal clusters, which serve as benchmarks, a series of studies are performed on the size-dependent elemental clusters which possess relatively high stability and interesting chemical physical properties. Special attentions are paid to the boron-based clusters because of their promising applications. The $NbSi_{12}$ and BeB_{16} clusters, for example, are two classic representatives of the silicon- and boron-based clusters, which can be viewed as building blocks of nanotubes and borophene. This review offers a detailed description of the structural evolutions and electronic properties of medium-sized pure and doped clusters, which will advance fundamental knowledge of cluster-based nanomaterials and provide valuable information for further theoretical and experimental studies.

Keywords: CALYPSO method, cluster structure prediction, boron cluster, silicon cluster

PACS: 31.15.A−, 36.40.−c, 36.40.Mr **DOI:** 10.1088/1674-1056/ab4274

1. Introduction

A cluster is defined as an ensemble of chemically bonded atoms or molecules, and is an intermediate between isolated atoms or molecules and bulk solids or polymers. Since the properties of the clusters depend on the cluster size, their studies led to significant amount of work in different research areas such as catalysis, biomedicine, optoelectronics, etc. Earlier experimental studies were focused at alkali metal clusters,[1] ionic clusters,[2] and interactions of small gas species with positively charged clusters.[3] Based on the mass-spectrometry data, Knight *et al.*[1] developed the spherical jellium model, which became classic and significantly contributed[4] to cluster science.

A number of functional clusters are produced experimentally, which can serve as building blocks for nanomaterial applications.[5–9] For example, the novel, efficient, green catalysts based on the single atom cluster, which can be synthesis by different strategies.[10–14] The size-dependent monodisperse samples of Au_{11} cluster[15] have been reported by mass-selected soft-landing method.[10] A class of novel catalysts consists of Pt single atoms and cluster deposit on the surface of graphene nano-sheets have been synthesized by Atomic Layer Deposition (ALD) method, which are manifested much higher reactivity for methanol oxidation and superior CO tolerance compared with traditional Pt/C catalyst.[11] Meanwhile, the single-atom Pt/FeO_x catalysts[12] are synthesized by using co-precipitation method, which have a great potential to riches the noble-metal catalysts in chemical industry based on single atom or cluster. Wu *et al.*[16] have synthesized a novel bimetal nanocluster $Pt@Ag_{24}$ with a different electronic gap, which offer novel insights for rational design of metal nanoclusters and provide a guidance for follow-up works.[17,18]

Up to now, many theoretical models have been proposed for studying the geometric structures and electronic properties of clusters, such as shell model,[19] superatom,[20–24] and superlattice.[25,26] The ground state structures of clusters are the prerequisite to understand the corresponding electronic properties and tune their practical applications in next stage. Despite the enormous progress that has been made, the true lowest-energy structures in medium-sized cluster are, how-

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ever, still a challenging problem. On one hand, the global minima are subtle sensitivity for the selected density functional theory, and the conventional method used for small clusters is not practical for larger clusters. On the other hand, the lowest-energy structures in the whole potential energy surface are exponentially increased with the number of atoms in the cluster increasing.[27,28] Here, we focus on the cluster structure predication through Crystal structure AnaLYsis by Particle Swarm Optimization (CALYPSO)[29–31] method. Its effectiveness and validity have been demonstrated in many cluster systems.[27,32–37]

2. Methods

CALYPSO method has its own performances for predication cluster structures, which includes five main steps.[31] The efficiency of Particle Swarm Optimization (PSO) algorithm used in CALYPSO method for cluster structure predication is relied on the 'self-improving' strategy, which can overcome large barriers in the global potential energy landscapes.[38–40] About 48 point groups are randomly adopted to restrict the generation cluster structures. Meanwhile, the bond characterization matrix (BCM) technique based on the distances of all bond in the cluster structure is utilized to estimate the similar structures. As for each generation, the metropolis criterion[41] has been applied during the local optimizations, and the optimized structures can be accepted when the energy are lower than their parent structures. Generally, in our cluster structure searches, we have generated 30 generation structures. Each generation contains 50 structures, 70% of which are generated from the previous generation structure using PSO, other 30% are produce randomly to ensure continuous diversity. For each cluster size, about 1500 low energy isomers are obtained, and the top 50 low energy structures with energy differences less than 3 eV are collected as candidates for further re-optimization, in which the high-level *ab initio* calculations with a large basis set or precise pseudopotentials are adopted at each cluster size. More detailed process of CALYPSO structure predications can be found in our recent publication.[42]

3. Results and discussion

3.1. Elemental clusters

The alkali metal Li cluster is a classic benchmark to understand various electronic properties of simple metal clusters since Li atom possesses only one valence electron.[43–46] Geometric structures of medium or large sized Li_n ($n = 20, 40, 58$) magic clusters have been identified by CALYPSO method.[31] The Li_{20} cluster with C_s symmetry is the lowest energy structure and in good agreement with previous work.[47] The perfect 45-atom polyicosahedron along with five missing vertex atoms and mackay icosahedron motif are characterized to be the lowest-energy structures for Li_{40} and Li_{58} clusters, respectively.[23] Na is another free-electron-like metal.[48–51] The geometric and electronic properties of medium sized (range from 10 to 25 atoms) Na clusters have been studied by CALYPSO method and DFT calculations.[32] Our results have confirmed most geometric structures of previous studies,[50] and also identified a novel honeycomb-like structure of Na_{20} cluster. The honeycomb-like Na_{20} cluster is chemically stable with a large energy gap, which is in good agreement with Na mass spectra experiment.[1]

The alkaline earth metals always involve chemical bonding as typical interaction by their *n*s and *n*p valence orbitals.[52,53] A detailed chemical bonding analysis of Mg cluster indicates that Mg_{17} cluster is the first locally π-aromatic homonuclear all-metal cluster, which perfectly meets electronic superatom jellium shell model and Hückel's $4N+2$ rule.[35] Noble metals, such as Au, Ag, and so on, have been extensively studied by experiments and theoretical calculations due to their wide applications in different fields including sensing,[54] catalysis,[55] and biomedicine.[56] Small sized neutral and anionic Au clusters and their interactions with O_2 are explored by the combined CALYPSO method and *ab initio* calculations.[57] The molecular orbitals and chemical bonding results indicated that Au_5 cluster is potential catalyst. The Au_5O_2 cluster possess the locally maximized adsorption energy. A new global minimum of Ag_{13}^- cluster with symmetry of C_{2v} is observed by CALYPSO method.[58] This structure is lower in energy than previous reported bilayer structure.[59] The neutral and charged Pd clusters are investigated[60] and a tetrahedral structure Pd_4^- cluster with T_d symmetry is uncovered, which shows high stability by the lone pair localized bonds. All these unexpected structures of elemental clusters are displayed in Fig. 1. Moreover, a series of elemental clusters including Si,[27] Cu,[61] and S[37] clusters, are also discovered by CALYPSO method and DFT calculations.

3.2. Binary clusters

3.2.1. Boron and doped boron cluster

Boron, with electron configurations of $1s^2 2s^2 2p^1$,[62] shows predominantly bonding capacity. It is neighbor of carbon element that can easily form fullerene-like structures with sp^2 and sp^3 bond.[46] The sized-selected B cluster has attracted much interest due to the intriguing geometrical structures and unique electronic properties. The global minima planar or quasi-planar structures in both neutral and anionic clusters have investigated up to 38 atoms.[63–65] The 38-atom B cluster is uncovered by CALYPSO method. It is highly

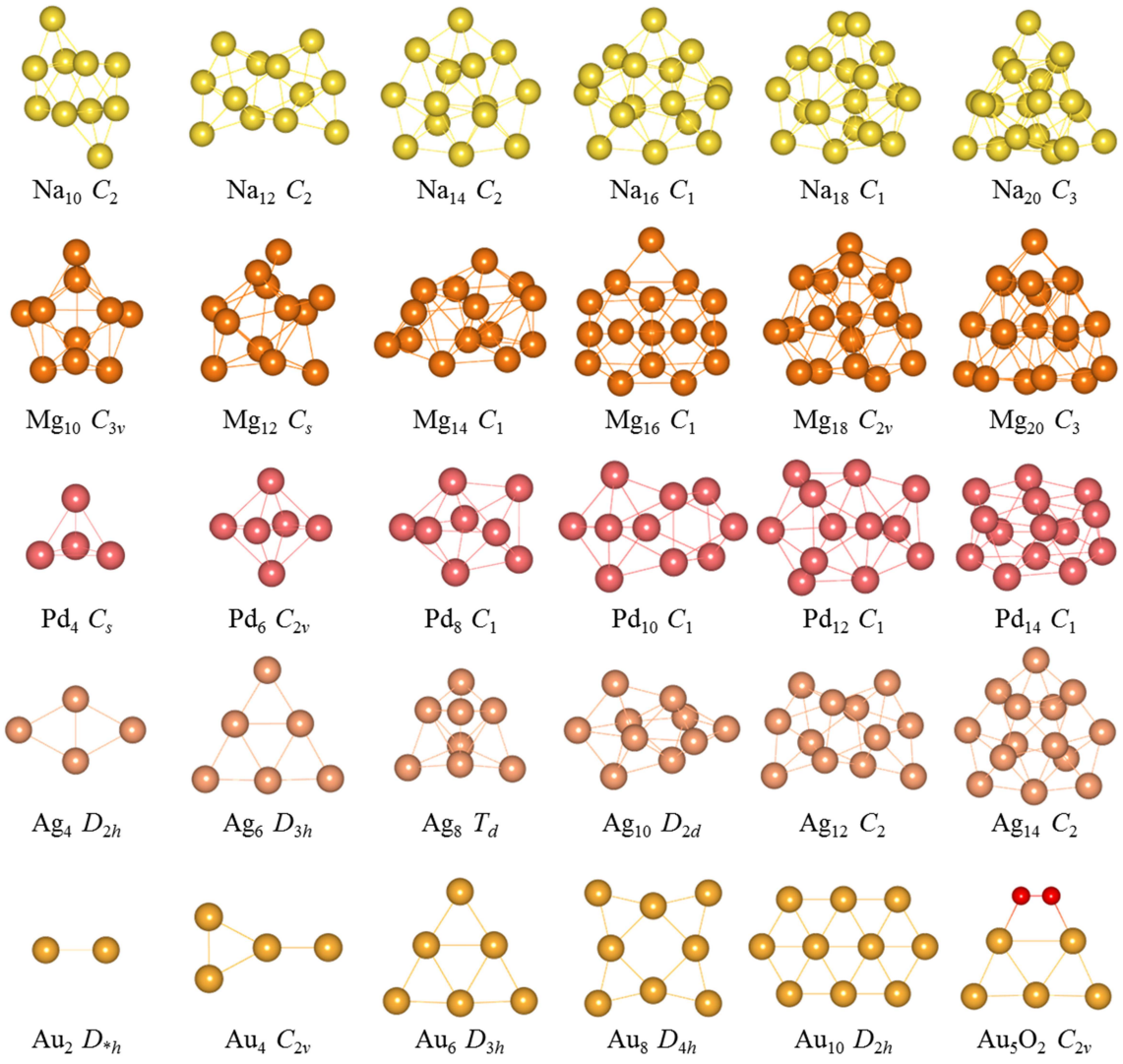


Fig. 1. Geometries of low-energy configurations of Na, Mg, Pd, Ag, and Au clusters.

chemical stability with a large energy gap and a high double aromaticity.[66] We have also accomplished some works in this research field. Unlike previous works, we mainly focused on the guest elements doped into the host B clusters by using CALYPSO method. Our new geometrical structures are shown in Figs. 2 and 3. The tubular structure Li_2B_{24} is uncovered by Li-doped B cluster.[67] It is a triply aromatic cluster, which is the viable embryo for boron tubes. The alkaline earth metal Mg-doped B clusters have presented a highly stable tubular drum-shaped geometry of MgB_{18} cluster.[68] Similarity, Be-doped B clusters have displayed essential similarities to borophene. For example, an fascinating monolayer metallo-borophene BeB_{16}^- cluster (Fig.4) with C_{2v} symmetry monolayer has been found.[69] When an Al atom with equivalent valence electron of B atom has doped into B cluster, what will happen?[70] As shown in Fig. 2, the addition of Al atom has little effect on the geometry of the pure B cluster. A circular planar AlB_{18}^- cluster is observed with large energy gap and π-aromaticity, which leads to the good electronic stability. As an extension of boron based materials, transition-metal (TM) doped boron clusters are also probed in recent years. The more representative elements are the 4rd period element (Sc, V, Cr, Co, etc.) doped B clusters. The perfect fruits are can-like cationic $B_{27}Sc^{2+}$[71] with triple ring tubular shape and D_{8h} symmetry and half-sandwich Cr/CoB_n clusters.[72,73] The ZrB_{12} cluster shows the abnormal case, which indicates that the Zr atom can distort the B_{12} ligand framework.[42] As for 4d and 5d TM (Mo, Ru, Ta, etc.) dope into B_{12} cluster, the B_{12} host is barely affected by the doped atoms, only slightly bent, and the TM-doped clusters almost adopt half-sandwich geometry.[33,74,75] All these TM-doped B cluster works have enriched the geometries of B-based nanostructures.[33,42,74,75] Specially, the recently observed two typical structures, TaB_{12}^-[34] and BeB_{16}^-,[69] deserve attention, because their goodish stabilities and geometries make them the potential candidates for constructing the new nanomaterials.

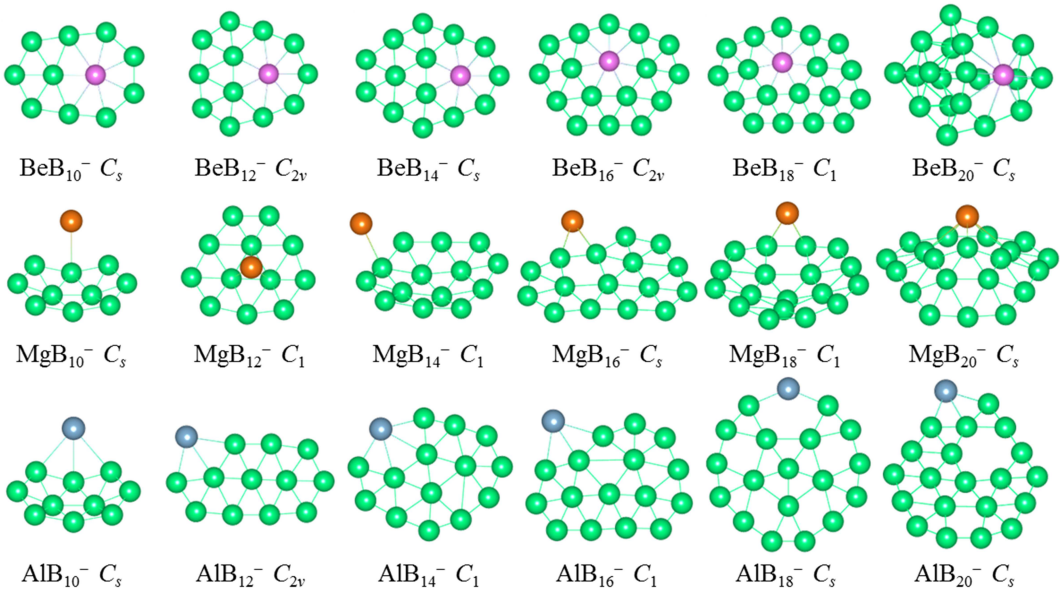


Fig. 2. Geometries of low-energy configurations of Be, Mg, Al doped medium-sized B clusters.

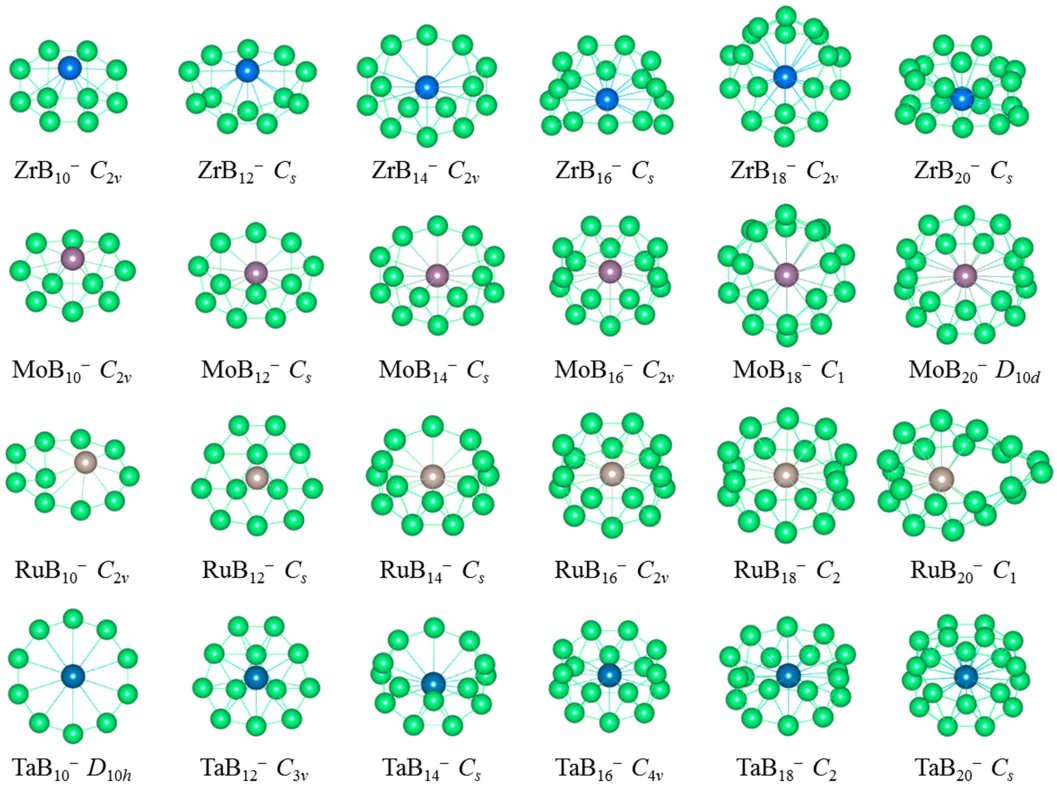


Fig. 3. Geometries of low-energy configurations of transition metal atom (Zr, Mo, Ru, Ta) doped medium-sized B clusters.

In Fig. 3, we have displayed the low-lying isomers of several TM-doped B clusters and paid special attention to Ta-doped B clusters. A C_{3v} half-sandwiched TaB_{12}^- cluster is identified as magic, in which the B_{12} host is slightly bent to bond with Ta atom, by CALYPSO method and DFT calculations. The simulated photoelectron spectrum (PES) of TaB_{12}^- cluster are shown in Fig. 4. It can be seen from Fig. 4 that the vertical detachment energy (VDE) of TaB_{12}^- is 3.24 eV and the adiabatic detachment energy (ADE) is about 3.18 eV. Meanwhile, we have also conducted an adaptive natural density partitioning (AdNDP) analysis, as shown in Fig. 5. Obviously, the Ta–B chemical bonds can be divided into four categories. Nine 2c–2e σ bonds (ON = 1.90–1.91 e) on the edge B_9 ring, three 3c–2e σ bonds (ON = 1.80–1.95 e) linked the inner B_3

triangle and outer B_9 ring, four delocalized 4c–2e $\sigma+\pi$ bonds (ON = 1.84–1.95 e), and four totally delocalized 13c–2e bonds (ON = 2.00 e). Recently, we have found a fascinating monolayer BeB_{16}^- cluster by joint CALYPSO method and DFT calculations, which is a new family of metal borophene.[76,77] It is different from other TM-doped B_{16} clusters, such as CoB_{16}^-,[78] MnB_{16}^-,[79] and FeB_{16}^-,[80] which adapt perfectly drum-like configuration. The simulated PES of BeB_{16}^- cluster, as shown in Fig. 6, is relatively simple, in which the first VDE and ADE values are 4.08 and 3.79 eV, respectively. The corresponding chemical bonding patterns are presented in the Fig. 7. The first line is twelve 2c-2e σ bonds at the outer B_{12} ring. The second line are five 3c-2e σ bonds that connect the inner and outer boron atoms, and four 4c–2e σ bonds. The last line are five π bonds (four 4c–2e and one 17c–2e) with ten electrons, which satisfy the Hückel rule ($4n+2$, $n=2$), leading to the π-aromaticity of BeB_{16}^- cluster.

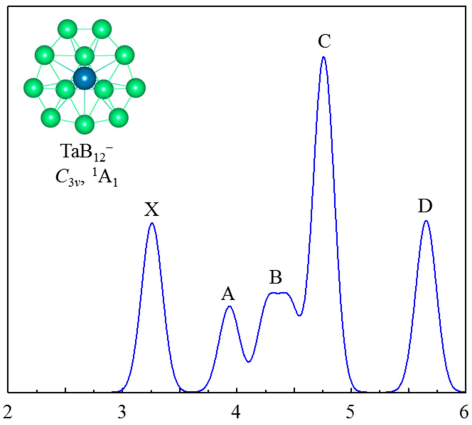


Fig. 4. Simulated photoelectron spectrum of TaB_{12}^- cluster.[33]

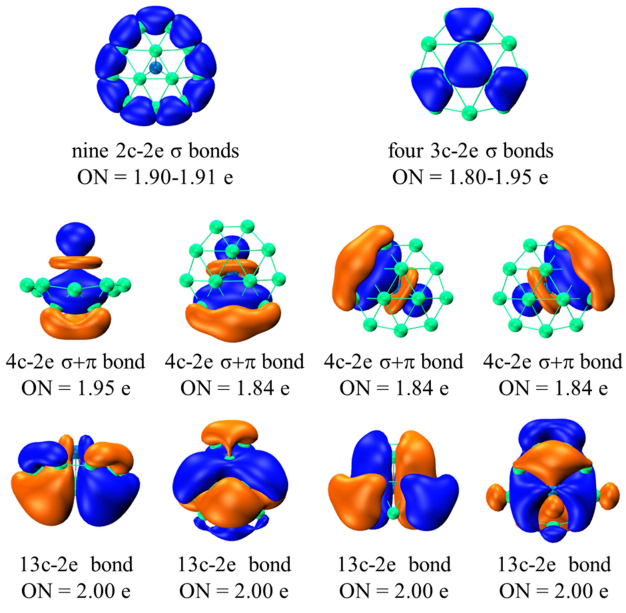


Fig. 5. Chemical bonding pattern of TaB_{12}^- cluster analyzed by AD-NDP method. Adapted with permission from Ref. [33]. Copyright 2018 American Chemical Society.

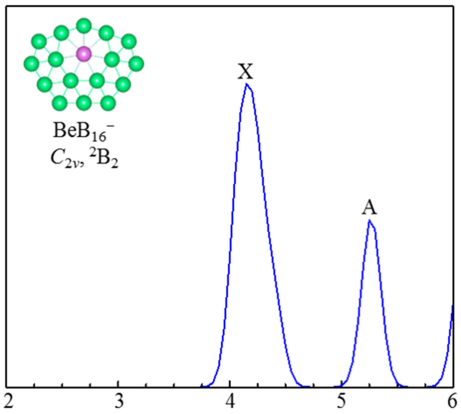


Fig. 6. Simulated photoelectron spectrum of the ground state of BeB_{16}^- cluster.[69]

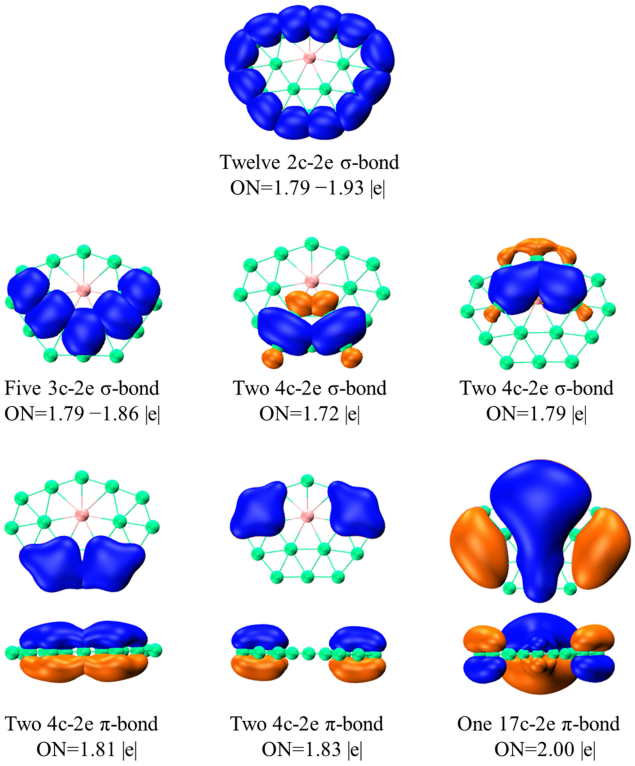


Fig. 7. Chemical bonding pattern of BeB_{16}^- cluster analyzed by ADNDP method.[69]

3.2.2. Silicon and silicon-based cluster

Silicon is the most important semiconducting material in the microelectronics industry. If current miniaturization trends continue, minimum device features will soon approach the size of atomic clusters. Thus, understand the size-depend structure evolution and electronic properties of Si clusters is of certain technological interest.[81,82] We have explored the growth behaviors of medium sized neutral, anionic and cationic Si clusters.[27] The results indicated that the geometrical structures of Si cluster transfer form prolate structure to spherical-like geometries at $n=26$ for neutral cluster, $n=27$ for anions, and $n=25$ for cations. The calculated results accord well with previous experimental data and theoretical findings.[81,82] Nb is a typical positive element, which can dope into Si clusters to

tune their electronic properties. Based on CALPSO method, we have obtained an anionic $NbSi_{12}$ cluster,[34] as shown in Fig. 8. It is a high-symmetry structure (D_{6h}) with Nb atom occupied in the center of the hexagonal prism of Si framework, which can be distinguished as an ideal motif of Nb-Si nanotube. Two Nb atoms doped Si_n^- cluster has been investigated by Lu *et al.* using experimental PES in combination with a CALYPSO structure search.[83] $Nb_2Si_{12}^-$ cluster is different from Nb_2Si_{12} cluster, which is a capped hexagonal antiprism structure with one Nb atom encapsulated inside Si_{12} cage and the Nb atom capped on the top of the hexagonal antiprism.[83] Meanwhile, a large number Si-based clusters have been reported by Zheng *et al.* through anion PES experiment and DFT calculations, such as $CoSi_{10}^-$,[84] $Cr_3Si_{12}^-$,[85,86] $AuSi_n$,[87] and BSi_n[88,89] clusters. These findings offer insights into the outstanding structural and electronic properties of Si-based clusters.

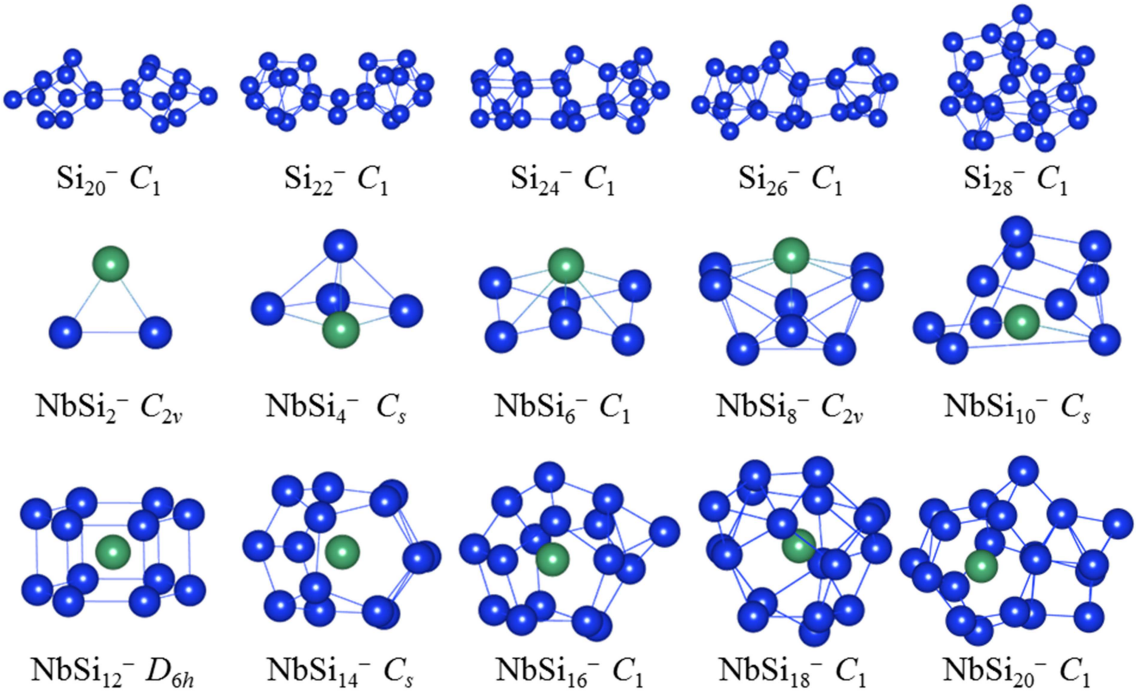


Fig. 8. Geometries of low-energy configurations of pure Si and Nb-doped Si clusters.

3.2.3. Other functional clusters

Binary alloy clusters have been subjected to intensive studies due to their unexpected stabilities and unique electronic properties. We have adopted CALYPSO method to investigate the Mg–Al binary alloy clusters,[90] as shown in Fig. 9. Our results indicated that the ground state structures of $MgAl_n$ cluster and the corresponding Al_{n+1} clusters prefer to be similar geometries for $n = 5$–16, and the lowest-energy configurations of $MgAl_n$ begins to a different structural evolutionary trend compared to the Al_n cluster in the cluster size range of $n = 17$–20. An ionic bonded $MgAl_6$ cluster, with 20 valence electrons and large energy gap, is identified to be magic cluster.[90] Moreover, another similar work,[91] focused on $Mg_{28-n}Al_n$ cluster, has reported five different stoichiometries of Mg–Al clusters, which present outstanding thermodynamic stabilities. As for $RuGe_n$ cluster, we have reported a systematic study of the relative stability and electronic properties of Ru-doped Ge clusters in the size range of $3 \leq n \leq 12$.[92] The global minimum anionic $RuGe_n^-$ clusters with $n = 3$–6 as well as their neutral counterparts have Ru-capped structures (except for $RuGe_5^-$); half-encapsulated structures are found for $RuGe_7^{-/0}$ and $RuGe_8^{-/0}$; and the larger clusters $RuGe_n^{-/0}$ ($n = 9$–12) feature endohedral geometries. Subsequently, the multicharged Ru-doped Ge_n clusters with the formula $RuGe_n^q$ ($n = 2$–12, $q = -2, -3$) are discussed by CALYPSO method coupled with DFT calculations. Leading candidates for the lowest-energy forms are identified.[36] In addition, a large number of novel binary or ternary clusters with Ag or Au noble metal have been explored by CALYPSO method,[93,94] which will provide guidance to future synthesis and design of functional nanomaterials.

Size-selected clusters with dozens of or hundreds atoms possess catalytic and adsorption properties. For example, nano-sized Au particles, which exhibit abnormal strong catalytic capabilities in a great deal of chemical reactions, have been the subject of intense research. Among these studies, the CO oxidation catalyzed by nanometer Au particles has been

extensively investigated not only for the mitigation of toxic pollutant CO but also for some other practical applications, such as developing CO sensors and improving the efficiency of CO_2 lasers. Previous studies have suggested that CO reacts with molecularly adsorbed oxygen on catalytic Au particles to form carbonate species, which are then converted to CO_2. It is therefore important to deeply understand the interaction mechanizations of Au clusters with CO. However, in contrast to the enormous progress that has been made in studies of anionic Au clusters, the physical pictures of neutral clusters are much less clear, due to the shortage of direct experimental probes for the uncharged species. Therefore, more detailed studies are needed to further understanding whether and how these neutral clusters interact with CO, CO_2, O_2, and other molecules.

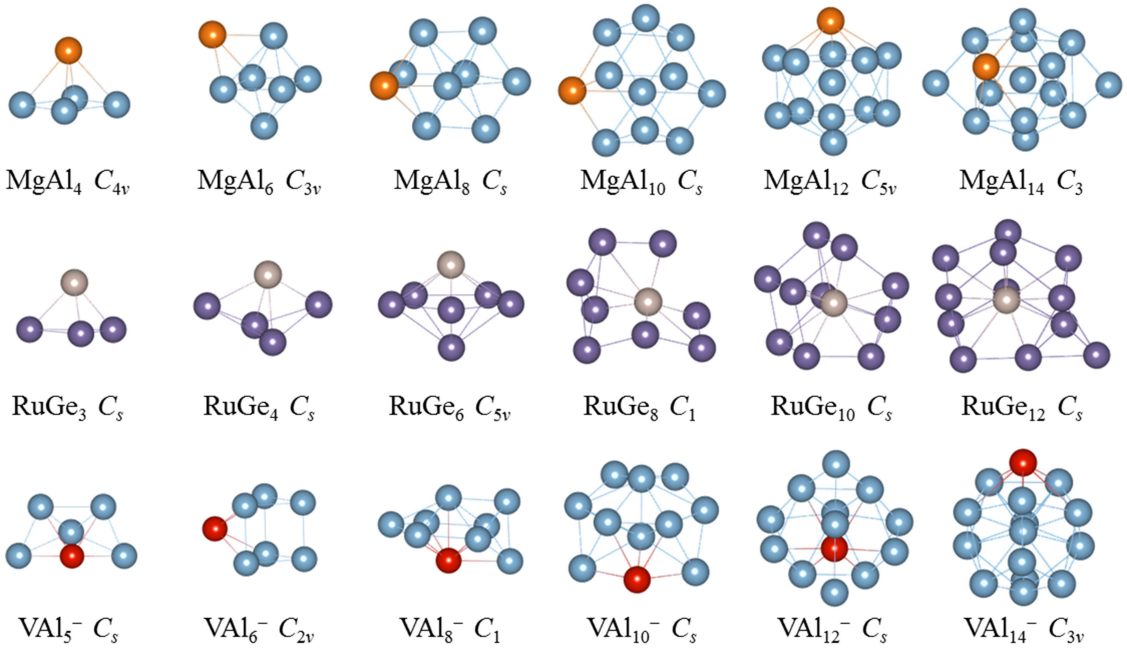


Fig. 9. Geometries of low-energy configurations of Mg–Al, Ru–Ge, and V–Al clusters.

4. Conclusion and perspectives

CALYPSO, an efficient structure prediction method, has made significant contribution to uncover numerous intriguing clusters.[95–107] A large number of high symmetry geometric structures with goodish stability and novel bonding patterns are discovered, which are the perfect embryos for nanotubular, borophene and other building blocks. For example, 1D metalloboronanotube α-Ta_3@B_{48}(3,0) with infinite -Ta-Ta- wire coordinated inside can be built by Ta-doped boron clusters.[108] Similar to the boron cluster, silicon-based ferromagnetic wheel structure $V_3Si_{12}^-$ (or V_3Si_{12})[109] is another candidate for nanotube materials. Other doped silicon cluster, such as NbSi[34,110] and WSi,[111] are also the perfect motif for nano-materials. Moreover, using the metal and non-metal cluster as superatom building blocks for different hierarchically assembled nano-materials allows cluster to be incorporated into target materials with tailored properties.[79] In our recent work, the 2D robust Dirac structures CoB_6 and ferromagnet NiB_6 monolayer have been obtained based on the unit CoB_6 and NiB_6 cluster,[99,112] which confirms the above mentioned point of view and stimulate our next step research. We firmly believe that more potential building blocks for future nanomaterials will be identified by CALYPSO method. It is worth noting that we are mainly focused on the medium-sized clusters with size range mostly up to about 20 atoms in our recent works.[27,32–37] With cluster size increasing, the determination of the true global minimum structure of large and complex cluster systems is still a challenging issue, due to the much increased complexity of the potential surface as well as the exponential increase of the low-lying structures with the number of atoms in the cluster. Fortunately, with the rapidly development of modern supercomputers combined with CALYPSO method, we see the dawn of victory to solve this scientific problem.

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