



Recent progresses of global minimum searches of nanoclusters with a constrained Basin-Hopping algorithm in the TGMin program



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ABSTRACT

Finding the global minima of nanoclusters is of great importance in cluster science and nanoscience. We have developed an efficient global minimum search program, named Tsinghua Global Minimum (TGMin, first released in 2012), based on the Basin-Hopping algorithm to find the global minima of nanoclusters, as well as periodic systems. We have recently made several improvements to the original Basin-Hopping algorithm, including a constrained perturbation function, a covalent-radius-based relaxation algorithm, an improved ultrafast shape recognition algorithm, and a planeness-check mechanism. The TGMin program has been successfully applied to search the global minima of a number of nanoclusters and periodic structures, including B₃₀, B₃₅, B₃₆, B₃₉, B₄₀, CoB₁₈, RhB₁₈, MnB₁₆, and Au₇ on the α -Al₂O₃(0001) surface. An overview of the TGMin code and several of its recent applications are presented here.

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1. Introduction

Nanoclusters have attracted wide attentions because of their novel size-dependent properties and potentials for applications in material science and catalyses. Nanoclusters can display totally different and tunable physical and chemical properties relative to those of the bulk, simply by changing the cluster size. Determination of the global minimum structure is the key step to identify properties of nanoclusters, but this is still a major challenge because exploring the full potential energy surfaces of nanoclusters is extremely computationally expensive. A variety of global minimum search algorithms and methods have been proposed to overcome this challenge, including the statistical mechanical methods [1], the global reaction route mapping (GRRM) strategy [2–4], the genetic algorithm (GA) [5–7], the particle swarm optimization algorithm (PSO) [8,9], the stochastic surface walking (SSW) algorithm [10], the Kick method [11,12], the minima hopping approach [13], and the Basin-Hopping (BH) algorithm [14–16]. It is necessary to choose a suitable algorithm for different systems based on the physical and chemical properties and the com-

putational cost. For large systems with structures close to their bulk materials, the statistical mechanical methods may be a better choice. On the other hand, for small clusters with potential energy surfaces that can be reconstructed with affordable and accurate *ab initio* methods, the GRRM strategy may be preferred, which can also yield information about transition states. For nanoclusters with tens of atoms, however, their potential energy surfaces are too complicated to be investigated in detail. The popular Basin-Hopping algorithm, which does not need to traverse the detailed potential energy surface, may be the method of choice for such systems. Several global optimization programs based on the BH algorithm have been developed, in conjunction with DFT methods [17–19], DFTB methods [20,21] or (semi-)empirical [22,23] potentials for local geometry optimization.

The current work presents an enhanced BH algorithm based on the Python program for searching global minima of nanoclusters, as well as for periodic systems. The article is organized as the following: the enhanced algorithm will be introduced in Section 2 and a few recent applications of the algorithm will be described in Section 3. A brief conclusion is given in Section 4.

2. Algorithm

The Tsinghua Global Minimum (TGMin) package [24] is based on the BH algorithm, in which an initial locally-optimized, ran-

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domly selected seed structure, X_{seed} , is required. A new structure X_k will then be generated from the seed structure: $X_k = X_{seed} + \lambda d_k$, where d_k is a displacement vector and λ is the step size. Let X'_k represent the locally optimized structure and it will only be accepted as a new seed structure when $E(X'_k) < E(X_{seed})$ or the Metropolis acceptance criterion

$$p = \exp\{-[E(X'_k) - E(X_{seed})]/k_b T\} > p_k \quad (1)$$

is satisfied, where p_k is a number randomly selected from the uniform distribution of $[0, 1]$, k_b is the Boltzmann constant and T is the effective temperature used to control the acceptance ratio. Otherwise, X_{seed} remains the seed structure for several more iterations. With higher T , high energy structures will have greater probability to be accepted as the new seed structures.

The BH algorithm is highly efficient and easy to implement for relatively small clusters. However, for large clusters, it has several drawbacks. First, the step size λ has to be properly set. If λ is too small, the new structure X_k optimized from the perturbed structure X_k may be the same as the seed. If the λ is too large, X_k may change drastically, leading to unreasonable high-energy structures, which may require much more computing time in geometry optimization. Second, duplicated structures may occur during the global optimization. If the displacement step is too small, the perturbed structure X_k may go back to its seed structure X_{seed} after geometry optimization. The perturbed structures X_i and X_j may also be the same if no similarity check (Section 2.3) is performed. The third problem is that the perturbed structures X_k should be physically reasonable: the atoms in these clusters should not be too close or too far from each other. The last problem is that the BH algorithm is a relatively local algorithm. For complicated potential energy surfaces with several funnels, if one starts from a structure in one funnel, it may be difficult to hop to another funnel and find the more stable structures therein. To solve these problems, we have added several constraints to the original BH algorithm in our TGMIn code, as described below.

2.1. Constrained perturbation algorithm

The best perturbation algorithm should generate new structures, which are sufficiently different and also close to the seed structure so that the BH search can jump out of the current basin, but do not hop too far from the seed. In our program, the displacements of the atoms are controlled by the maximum step size λ and displacement angle θ . The definition of θ is given by Fig. 1. The angle is required to be within a given range. If it is too small, atoms will move outwards; if it is too large, atoms will move inwards. Typically θ (in degrees) is randomly drawn from the uniform distribution of $[60.0, 100.0]$. In the case of global minimum search for cage-like clusters (B_{40} for instance), the allowed range of θ is usually between 75 and 105°, so the displacement vectors do not break

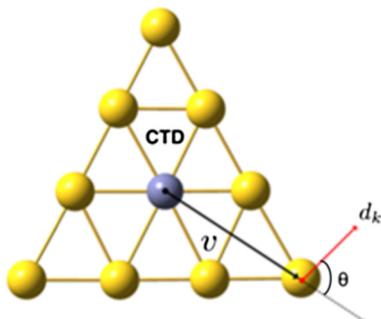


Fig. 1. The definition of displacement angle. CTD is the centroid of the cluster. v is the vector from CTD to an atom and d_k is the displacement vector for this atom.

the cage structure. According to our experience, nanoclusters with more low-coordination atoms tend to have higher energies. Hence, we have applied a new constraint according to this assumption: only atoms with low coordination number are allowed to be perturbed.

2.2. Covalent-radii based relaxation

Not all structures generated from the perturbation algorithm are chemically reasonable. Some atoms may be too close to other atoms, while some may be too far from the others. These unreasonable structures can cause severe SCF convergence problems during geometry optimization using some DFT programs. A reasonable distance between two atoms should be close to the sum of their covalent radii [25–27]. Hence, we have implemented a pre-relaxation algorithm to make sure each atom has a reasonable distance with at least one atom. For two atoms i and j , let r_i and r_j be their covalent radius, d_{ij} be their distance and d_{tol} be a small distance tolerance. If $d_{ij} < r_i + r_j + d_{tol}$, atoms i and j are considered to be adjacent. If $d_{ij} < r_i + r_j - d_{tol}$, atom i and j are considered to be too close and a virtual spring force will be applied to push atoms i and j away from each other. After the pre-relaxation, all atomic distances should be reasonable and the SCF convergence can be greatly improved.

2.3. Similarity check algorithm

To avoid duplicated runs during the global minimum search, we have implemented a modified version of the Ultrafast Shape Recognition algorithm (USR) [28–30] to compare the similarities of the structures. The original USR algorithm uses 12 descriptors as the fingerprints for each structure. The similarity of two structures **1** and **2** are obtained by the equation:

$$S^{1,2} = \frac{1}{1 + \frac{1}{12} \left(\sum_{i=1}^{12} |d_i^1 - d_i^2| \right)} \quad (2)$$

where d^1 and d^2 are the USR descriptors for structures **1** and **2**.

The standard USR algorithm uses only coordinates, which works well for clusters with only one type of atomic species. But for bimetallic or more complicated clusters, the USR algorithm may fail to identify different structures. For example, the two Au_9Zn clusters in Fig. 2 are not distinguishable by the standard USR algorithm.

We have added another 12 descriptors calculated from the coordinates of a selected atomic species. The equation then becomes:

$$S^{1,2} = \frac{1}{1 + \frac{1}{24} \left(\sum_{i=1}^{12} |d_i^1 - d_i^2| + \sum_{i=1}^{12} |d_i^{M,1} - d_i^{M,2}| \right)} \quad (3)$$

where $d^{M,1}$ and $d^{M,2}$ are the extra USR descriptors of structures **1** and **2** using the coordinates of atom M .

With this improvement, we can get a better accuracy for filtering out duplicated isomers.

2.4. Planeness-check algorithm

In the standard BH algorithm, only the energies of the structures are included in the Metropolis acceptance criterion. Other chemical properties, such as the structure morphology, are excluded. Some clusters, such as small gold and boron clusters, tend to have planar isomers rather than non-planar structures. In the case of the B_{20} cluster [31], the most stable isomer is a D_{10d} drum structure while other low-lying isomers are all planar. Thus, global minimum searches of the planar and non-planar structures

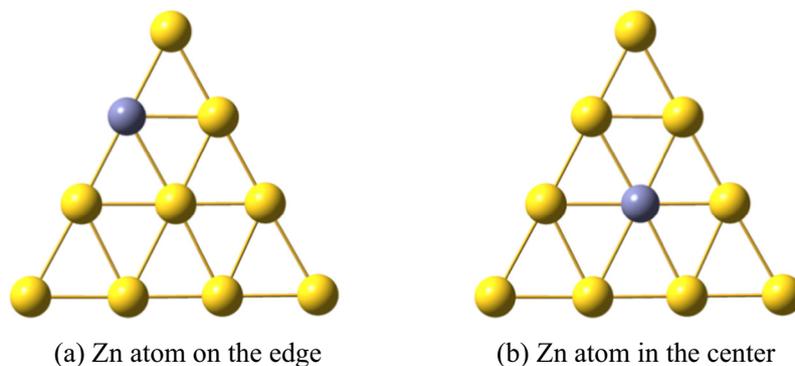


Fig. 2. Two isomers of the Au_9Zn cluster. The golden atoms are Au and the blue atom is Zn. Isomers (a) and (b) are different, but they cannot be distinguished by the standard ultrafast shape recognition algorithm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

should be run separately. For a cluster with its three principle rotation inertia I_a , I_b and I_c ($I_a \leq I_b \leq I_c$), the planeness P can be expressed by:

$$P = \frac{I_c}{I_a + I_b} \quad (4)$$

If the structure is completely planar, $P = 1.0$. Otherwise P is smaller than 1.0. Fig. 3 shows the planeness of different isomers of the B_{20} cluster. With this parameter we can quantitatively distinguish planar and non-planar structures.

With these four constrained algorithms added, we have implemented a new BH-based global optimization Python program, called TGMIn (Tsinghua Global Minimum), for efficient global minimum searches for nanoclusters and periodic systems. We have also developed interfaces to ADF [32], Gaussian09 [33], and CP2K [34] for local geometry optimization and Torque/PBS, LFS for job management. The overall workflow of the constrained BH algorithm is illustrated in Fig. 4.

3. Applications

The TGMIn program has been tested with numerous nanoclusters, including the well-known Au_{20} , B_{20} , and C_{60} , and has been successfully applied to find the global minima of many free and substrate-supported nanoclusters and periodic structures. A few selected examples are presented here.

3.1. C_{60}

The famous C_{60} fullerene cluster has a soccer-ball shape with a very high I_h symmetry [35]. We conducted a global minimum search test of C_{60} with TGMIn using the CP2K program and DFTB method with the planeness check disabled. The initial seed was a randomly generated structure with C_1 symmetry. The maximum displacement step size was set to be 0.80 Å and the displacement angle range was between 80 and 100°. We found the I_h symmetry fullerene structure after about 10,000 structures were optimized. The lowest energy of each Monte Carlo step is shown in Fig. 5.

3.2. Au_{20}

The T_d symmetry tetrahedral Au_{20} cluster was first reported by Li et al. in 2003 with limited structural optimization [36], in conjunction with a very characteristic photoelectron spectrum of Au_{20} , which suggested a highly stable and possibly symmetric neutral Au_{20} . We did a test global minimum search for Au_{20} starting from a randomly constructed 3D structure. The geometry optimization was done by the CP2K package at the PBE level [37] with the GTH potential [38] and the MOLOPT DZVP basis set [39]. The energy cutoff used was 280 Ry. The maximum displacement step size for Au_{20} was 2.7 Å. The minimum coordination number for perturbing an atom was set to be 7. The deep-lying tetrahedral global minimum was found in only 36 Monte Carlo steps, as shown in Fig. 6.

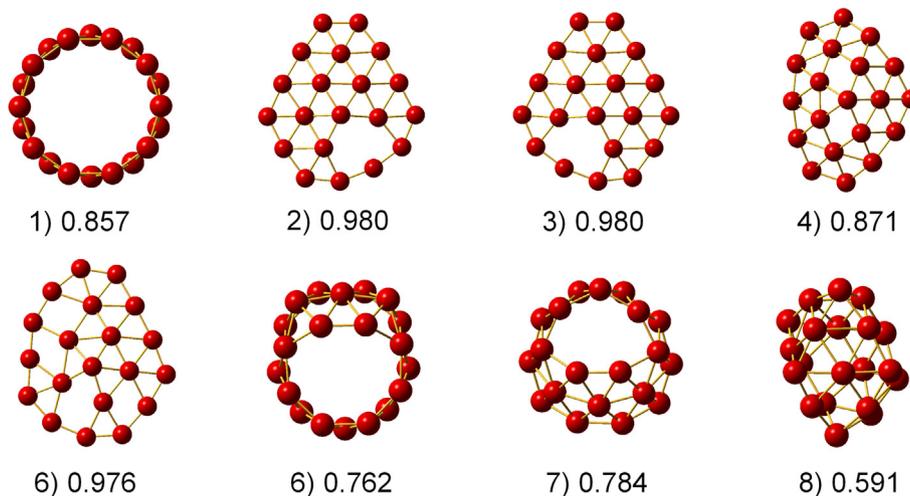


Fig. 3. The planeness of different isomers of B_{20} .

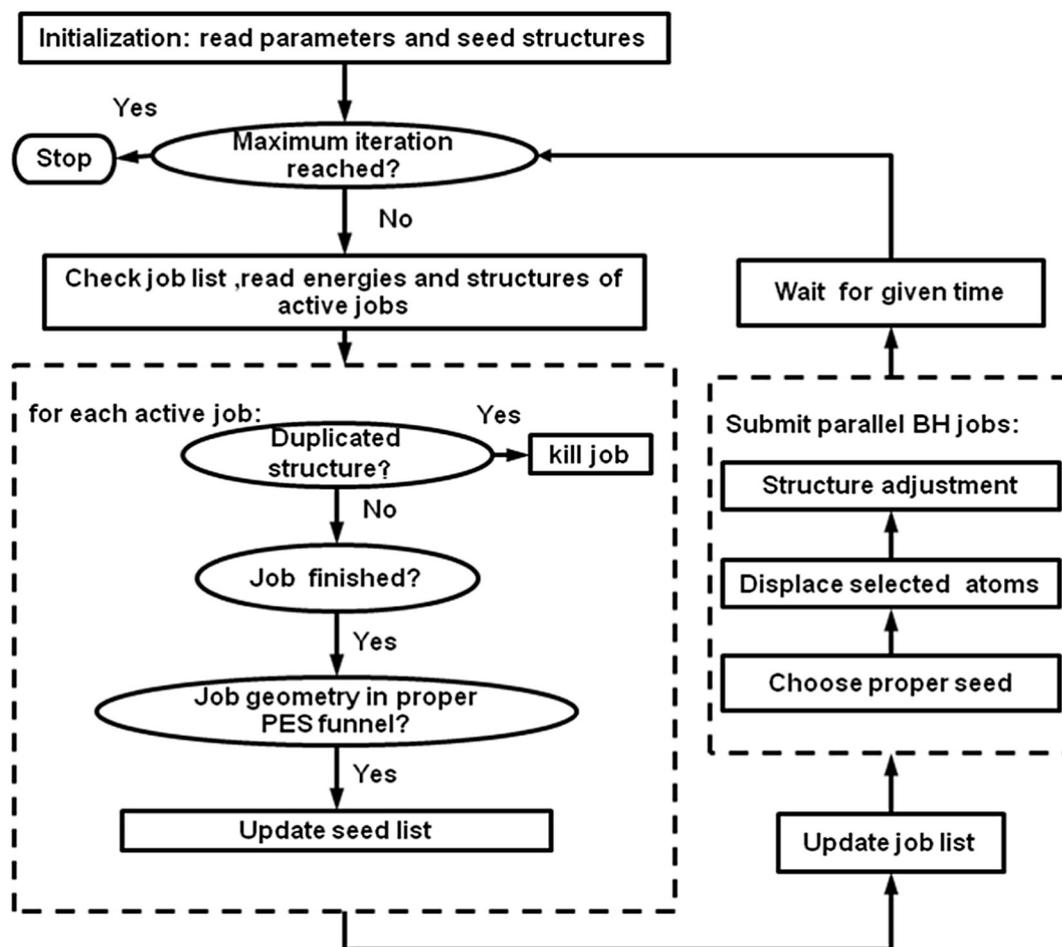
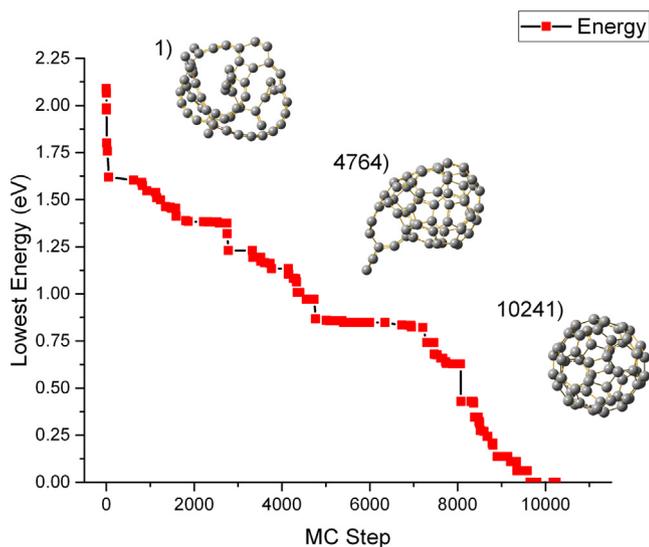
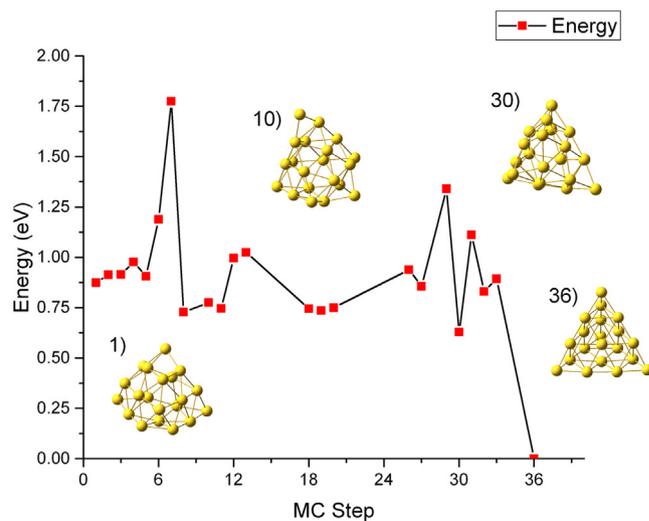


Fig. 4. The overall workflow of TGMIn.

Fig. 5. The lowest energy of each Monte Carlo step during the global minimum search of C_{60} .

3.3. B_{20}

The B_{20} cluster was considered to be the possible transition point between 2D and 3D structures for neutral boron clusters [31,40]. We searched the global minimum of B_{20} with the same

Fig. 6. The energies of the optimized structures of each Monte Carlo step during global minimum search of Au_{20} .

DFT method used for Au_{20} . Starting from a random three-dimensional structure with the planeness check disabled, we found the D_{10d} drum-like (tubular) structure of B_{20} (Fig. 7) after about 870 Monte Carlo steps. As a comparison, with the maximum planeness set to be 0.870, we were able to find the D_{10d} structure within 424 steps from the same initial seed. The low-lying isomers of B_{20} are

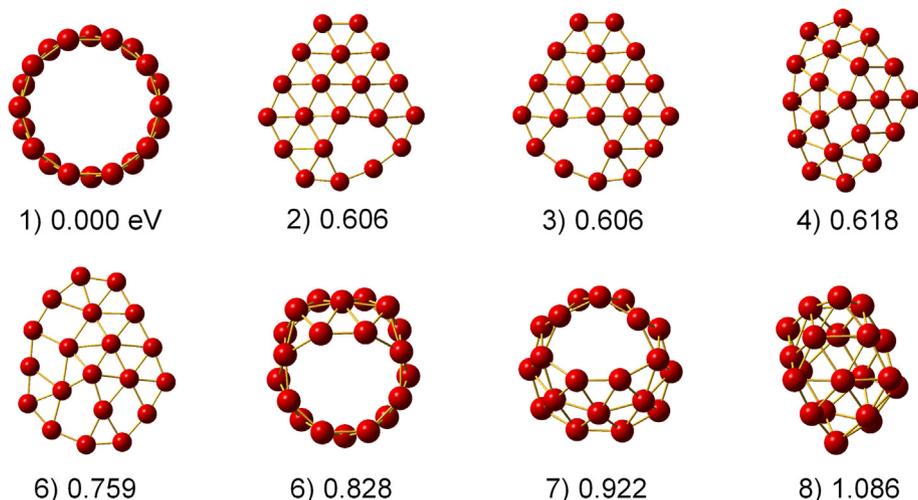


Fig. 7. The low-lying isomers of B_{20} within 1.0 eV of its global minimum.

given in Fig. 7. It should be pointed out that the tubular B_{20}^- anion was also found to be the global minimum, but the experimentally observed B_{20} was a planar isomer [31]. This conundrum has not been resolved and has been discussed in more detail in Ref. [40].

The correlations of the relative energies of the low-lying isomers and their planeness are presented in Fig. 8. It seems that structures with higher planeness tend to have lower energies, but the global minimum D_{10d} structure is not a planar structure. The global minimum search can be accelerated significantly if the planeness range can be set properly.

3.4. B_{35} and B_{36}

The B_{36} cluster was the first boron cluster whose global minimum structure was found by TGMIn [41], following initial searches using the Cartesian Walking method that was primarily focusing on planar structures [42]. Preliminary structure searches using the Cartesian Walking method found a planar B_{36}^- structure with a hexagonal vacancy. Subsequently, TGMIn was used for unbiased

searches to locate the global minimum structure of B_{36}^- and confirmed the hexagonal structure of B_{36}^- . Geometry optimization was done by the CP2K package at the PBE level with the GTH potential and the MOLOPT DZVP basis set. The global minimum structures of B_{36} and B_{36}^- were found to be both quasi-planar: the neutral B_{36} has C_{6v} symmetry and the anion is slightly distorted to C_{2v} symmetry. The neutral B_{36} has a perfect hexagonal symmetry and can be viewed as a motif for extended monolayer boron, a new 2D material named as “borophene” by Piazza et al. (Fig. 9) [41]. The global minimum of B_{35} is very similar to B_{36} , but has one more hexagonal vacancy [43] (Fig. 10), which was also found by the TGMIn code. The planar B_{35} cluster was shown to be an even more flexible motif to build borophenes with different hexagonal hole patterns and densities [43].

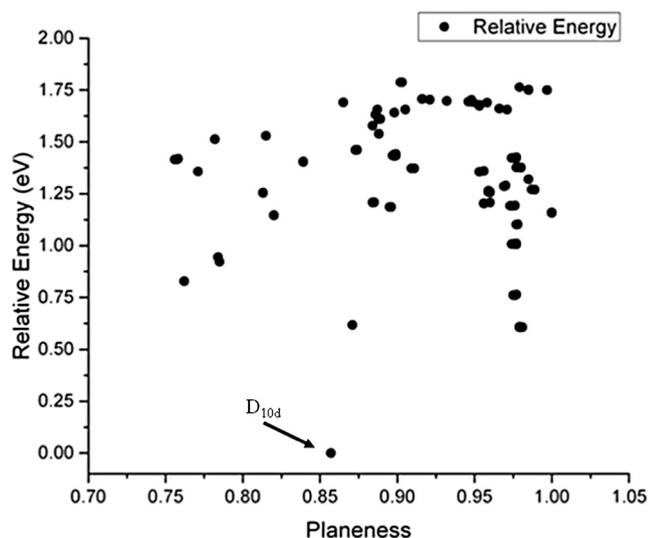


Fig. 8. Correlations of the energies within 2.0 eV of the global minimum and the planeness of the B_{20} isomers. Structures with higher planeness tend to have lower energies, but the deep-lying global minimum D_{10d} structure is not a planar structure.

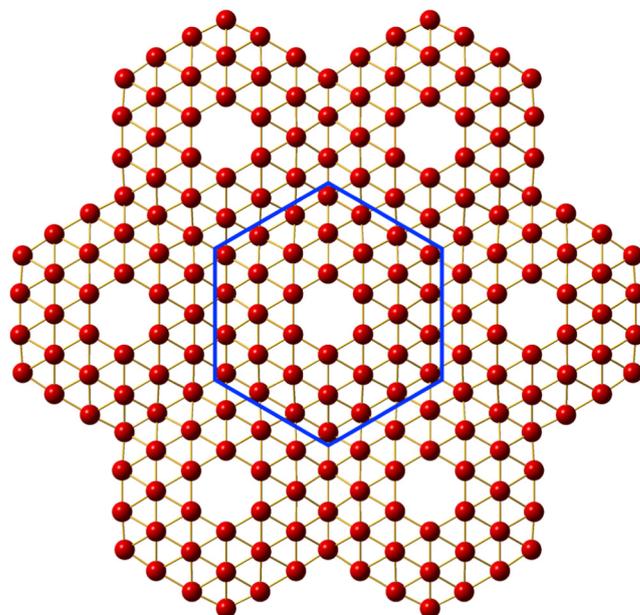


Fig. 9. The relationship between borophene and the planar hexagonal B_{36} cluster. The hexagon in the blue line is a basic neutral B_{36} nanocluster unit.

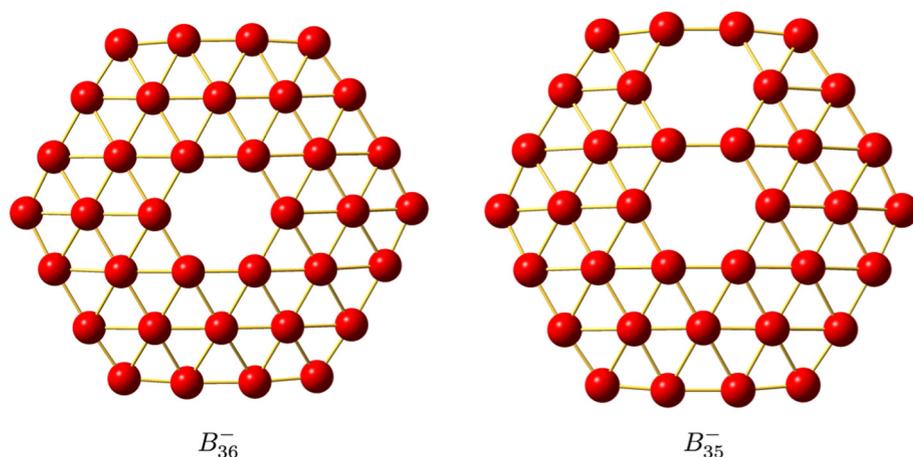


Fig. 10. Comparison of the global minima of B_{36}^- (left) and B_{35}^- (right). For both clusters, the neutral structures are similar to the anions.

3.5. B_{40}

The B_{40} cluster was the first all-boron fullerene-like cluster (named by us as borospherene) discovered using the global minimum search by TGMIn [44], following the investigation on B_{36} and B_{36}^- [41]. Photoelectron spectra of the B_{40} cluster revealed two co-existing isomers. TGMIn searches found two close-lying structures competing for the global minimum: a quasi-planar structure with C_s symmetry and a fullerene-like cage with D_{2d} symmetry (Fig. 11). The calculated vertical detachment energies (VDEs) and adiabatic detachment energies (ADEs) for the low-lying structures agree with the experimental data from photoelectron spectroscopy (PES). The B_{40} borospherene has 16 tetracoordinated and 24 pentacoordinated boron atoms, and consists of two hexagonal and four heptagonal holes on its surface [44]. More than 5000 unique structures, including the fullerene-like cage and the quasi-planar structure, were obtained during the global minimum searches (planar search and 3D search) by TGMIn using CP2K at the PBE level with GTH potential and MOLOPT DZVP basis set. The TGMIn results were also independently confirmed by global searches using the SSW method [44].

3.6. B_{30}^- and B_{39}^-

TGMIn has been used to locate the global minima of several boron clusters following its successes in finding the borophene-type B_{36} and B_{35} clusters and the first borospherene. Here, we highlight two more interesting examples. Using TGMIn, we found the first chiral boron clusters: the quasi-planar B_{30}^- [45] and the B_{39}^- borospherene [46]. The most stable structure of B_{30}^- was found to be quasi-planar with a hexagonal hole and a pair of enantiomers arising from different positions of the hexagonal hole. The global minimum of B_{39}^- was a chiral C_3 borospherene consisting of three hexagons and three heptagons around the C_3 axis (Fig. 12). A close-lying chiral C_2 cage isomer was also found for B_{39}^- [46].

3.7. Bimetallic boron clusters

TGMIn has also been shown to be efficient in the global minimum searches of bimetallic boron clusters, such as MnB_{16}^- [47], RhB_{18}^- [48], and CoB_{18}^- [49]. The global minimum changes from 3D drums for CoB_{16}^- [50] and MnB_{16}^- to a quasi-planar species for CoB_{18}^- . The most stable structure of MnB_{16}^- is a C_{4v} drum with two B_8 rings, similar to CoB_{16}^- , while RhB_{18}^- has two co-existing stable isomers: one D_{9d} drum with two B_9 rings and another quasi-planar structure with C_s symmetry. For CoB_{18}^- , the most stable isomer becomes a quasi-plane (metallo-borophene) with C_{2v} symme-

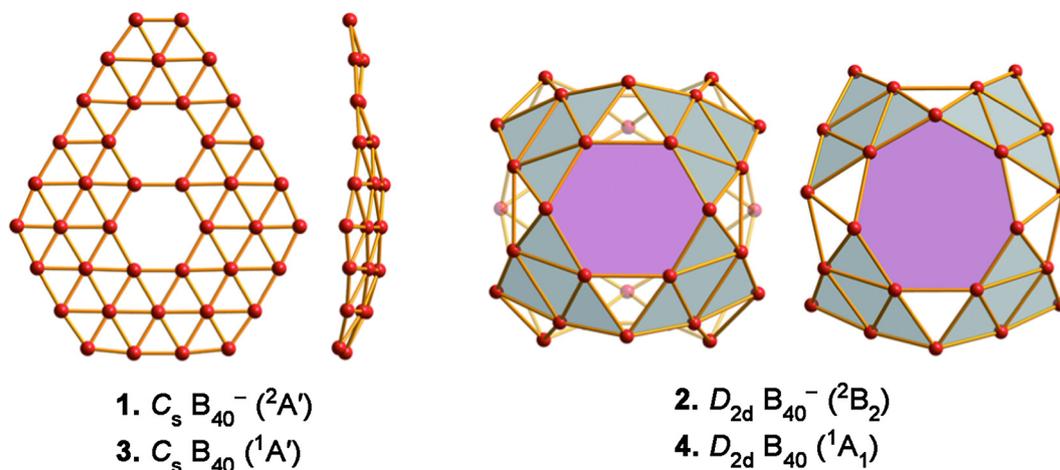


Fig. 11. The top and side views of the two co-existing global minimum isomers of B_{40}^- . The anionic and neutral structures for both isomers are very similar with the same symmetries. The $D_{2d} B_{40}$ cage is overwhelmingly the global minimum for the neutral and is named “borospherene”.

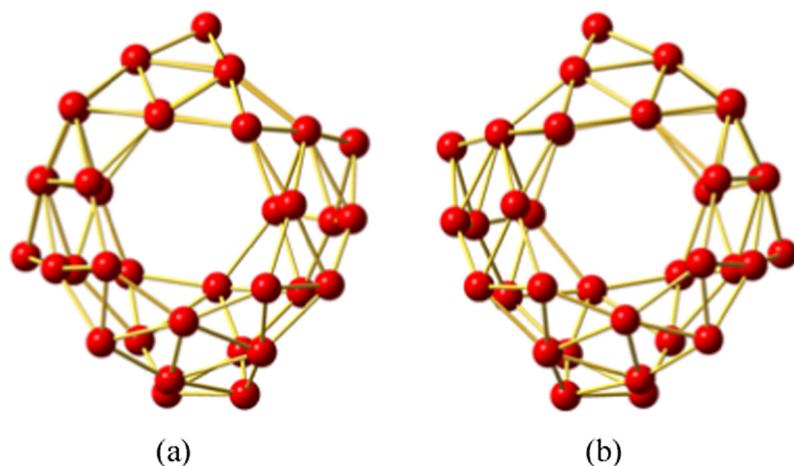


Fig. 12. The optimized global minimum structures of the C_3 chiral isomers of B_{39} . Structures (a) and (b) are the two degenerate enantiomers.

try. The photoelectron spectrum of RhB_{18}^- is compared with simulated spectra of the drum and 2D isomers in Fig. 13. Such good agreement between experiment and theory reaffirms the global minima and low-lying isomers from the TGMin global searches. The geometry optimization for the bimetallic boron clusters were

carried out by ADF at the PBE/DZ level. Obtained low-lying isomers within 1.5 eV were usually optimized again at higher accuracy by ADF at the PBE0/TZP level and their relative energies were calculated at CCSD(T) level by Molpro [51] program. The higher level calculations are necessary to confirm the global minimum, in particular for the comparison with experiment.

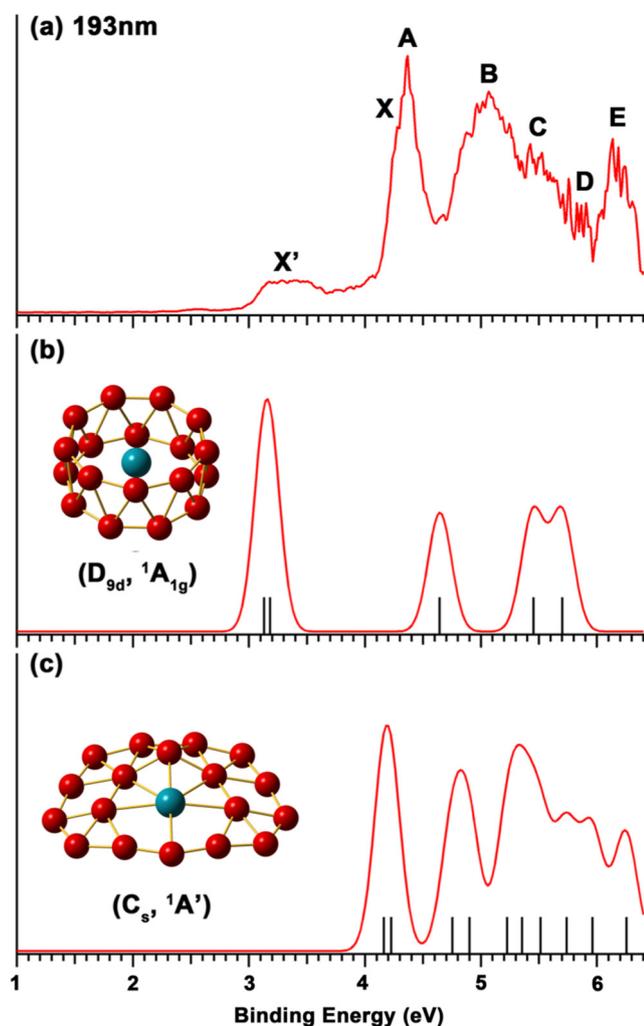


Fig. 13. The photoelectron spectrum of RhB_{18}^- compared with the simulated spectra of two close-lying 2D and 3D isomers.

3.8. Au_7 on $\alpha-Al_2O_3$ (0001) surface

TGMin was designed not only for global minimum searches for nanoclusters, but also for periodic structures, especially nanoclusters supported on surfaces. Liu and co-workers used TGMin with several chemical constraints and successfully found the global minimum structures of the Au_7 cluster on different alumina surfaces [52], as shown in Fig. 14. The optimization was carried out by CP2K at the PBE level with the GTH pseudopotential and the MOLOPT DZVP basis set.

4. Conclusions

We have developed an efficient global minimum search program, TGMin, based on the Basin-Hopping algorithm with several judiciously chosen constraints: a coordination number related perturbation algorithm, a covalent radii based relaxation algorithm, an improved ultrafast shape recognition algorithm for removing structure duplications, and a parameter for planar and nonplanar searching. By adding these chemically-motivated constraints, the TGMin program has been shown to be quite efficient in predicting global minima of not only nanoclusters, but also for periodic surface structures on the surfaces of various support. A number of recent examples have been used to illustrate the power of TGMin, including the recent findings of the structures of B_{26}^- (the smallest planar boron cluster with a hexagonal vacancy) and TaB_{20} clusters (a B_2 - $Ta@B_{18}$ tubular molecular rotor and a 20-membered boron drum) [53,54]. It is expected that TGMin will significantly accelerate the global minimum searches of larger and more complicated nanoclusters and nanostructures.

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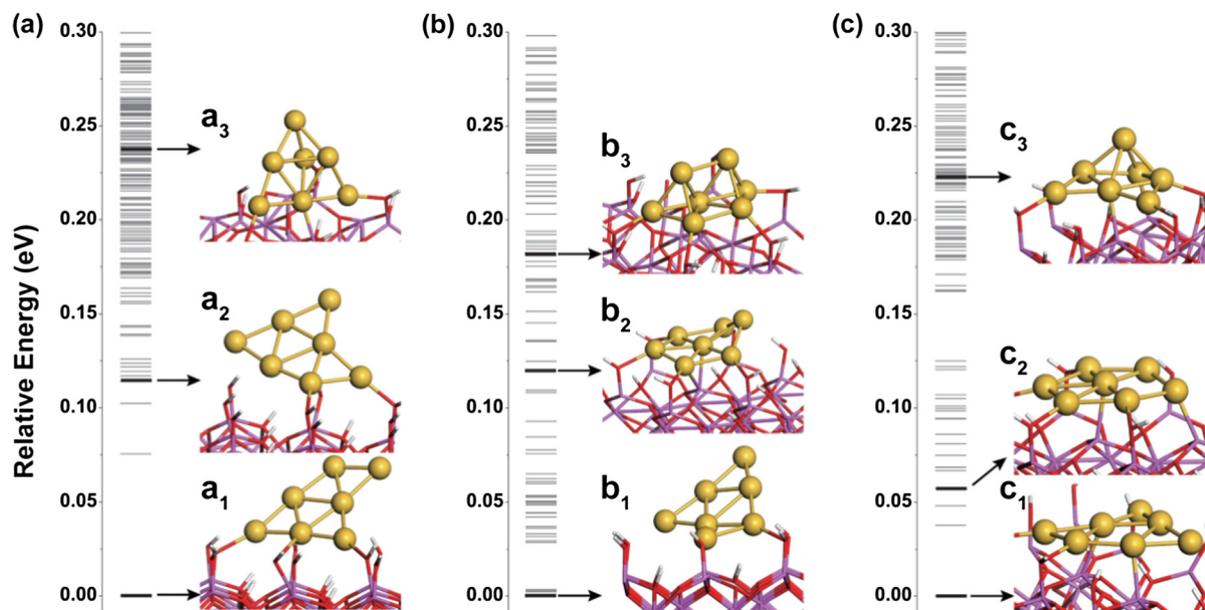


Fig. 14. Geometries and potential energies of the Au₇ cluster on (a) fully hydroxylated α -Al₂O₃(0001) surface, (b) hydroxylated α -Al₂O₃(0001) surface missing one water molecule, and (c) hydroxylated α -Al₂O₃(0001) surface missing two water molecules.

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