Funnel hopping: Searching the cluster potential energy surface over the funnels

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We designed a cluster surface smoothing method that can fast locate the minimum of the funnels in the potential energy surface (PES). By inserting the cluster surface smoothing approach into the gradient-based local optimization (LO)-phase and the global optimization (GO)-phase as a second LO-phase, the GO-phase can focus on the global information oWalesf the PES over the various funnels. Following the definition of "basin-hopping" method [D. J. and J. P. K. Doye, J. Phys. Chem. A **101**, 5111 (1997)], this method is named as "funnel hopping." Taking a simple version of the genetic algorithm as the GO-phase, the funnel-hopping method can locate all the known putative global minima of the Lennard-Jones clusters and the extremely short-ranged Morse clusters up to cluster size $N=160$ with much lower costs compared to the basin-hopping methods. Moreover the funnel-hopping method can locate the minimum of various funnels in the PES in one calculation. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3152121]

I. INTRODUCTION

Global optimization (GO) is an active field with rapid growth for many chemical and physical problems, such as structural optimization, chemical engineering design, and molecular biology. In general, the GO of an arbitrary function requires a search through the whole conformational space. The problem is generally nondeterministic polynomial-time (NP)-hard due to the fact that the conformational space grows exponentially with the problem size. Cluster geometry optimization is such a NP-hard problem, where the number of local minima in the potential energy surface (PES) increases exponentially with cluster size.[1] The goal of cluster geometry optimization is to determine the structural organization for a set of atoms or molecules that minimizes the total potential energy by searching the whole PES. Determining the lowest-energy structures is an important piece of information, which can help in understanding the properties of real clusters.[2,3]

Due to the size effects, compared to bulk materials, the favorite structures of small clusters are always very novel, e.g., the fullerene clusters,[4] the cage- and cubiclike water clusters,[5–7] the cage- and tubelike and chiral Au clusters,[8] and the magic nanoalloy clusters.[9,10] The ground-state (or global minimum) geometry structures are determined by the electronic structures, but generally, it is too expensive to have a systematic GO directly using a quantum mechanics method. Alternatively, model and empirical potentials are largely used to fit the interactions among particles and the results are generally acceptable in a certain precision. For very large systems, it is usual to adopt a pair-potential model to approximate the interactions, which depends only on the distance between each pair of particles. Due to their simplicity and practical relevance, Lennard-Jones (LJ) (Ref. 11) and Morse[12] functions are the two most widely used pair-potential models. In particular, the Morse function can be used to estimate both long- and short-range interactions.[13–15]

In the past 20 years, a number of efficient GO methods has been proposed for cluster geometry optimization problems, such as genetic algorithms (GAs),[16–23] the other population-based evolutionary methods,[24–28] basin hopping (BH) and its variants,[29–34] simulated annealing and its variants,[35–37] and some other GO methods.[38–45] The most widely used GO methods are GAs and BH. GA is an analog of natural processes in biological evolution. Within the GA approach, a population of clusters is evolved, using evolutionary operators such as crossover, mutation, and natural selection. BH method can be taken as a Monte Carlo (MC) plus local minimization. GAs and BH methods have been successfully applied to cluster geometry optimization problems for a variety of systems and by a variety of groups. However, although the other GO methods may have higher efficiency in optimization, they are generally only applied by the proposers themselves and so the application is very limited. The reason may be that most of the users are more familiar with GA and MC methods and the performance of the basic GA or BH method is acceptable for general simple applications.

Actually, all of the successful GO methods for structural optimization problems are based on at least two phases, i.e., GO-phase plus a local optimization (LO)-phase. The PES of clusters with many local minima can be viewed as a collection of basins of attraction, each associated with a local minimum.[46] The LO-phase is a gradient-based local minimization procedure, which can relax a rough cluster structure to the associated local minimum at the least costs. A two-phase

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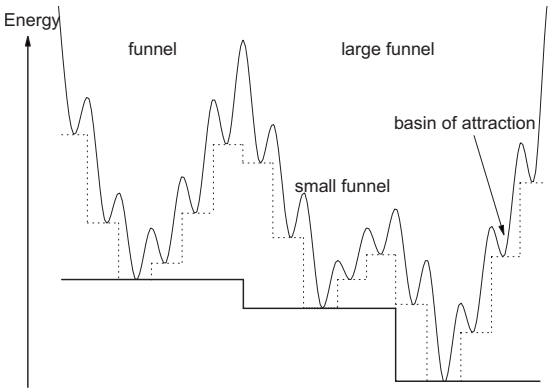

FIG. 1. A diagram illustrating the effects of the BH and funnel-hopping potential energy transformation for a one dimensional example. The thin solid line is the potential energy of the original surface, the dot line is the transformed energy of BH, and the thick solid line is the transformed energy of funnel hopping.

optimization is to combine a standard gradient-based LO-phase for finding local minima with a GO-phase for searching over the various basins of attraction. This is just the basic idea of the BH method[29] and all of the successful cluster geometry optimization methods are a kind of BH in concept. The gradient-based LO-phase can significantly improve the optimization ability of GO methods. For example, it is difficult to optimize the LJ clusters even for cluster size $N \leq 13$ without the local optimization procedure,[36] while the BH method can located the putative global minima of LJ clusters up to $N=110$.[29,47]

There are a variety of funnels in the PES of clusters. Each funnel represents a kind of cluster motif (such as icosahedral, decahedral, close packed, etc) and contains a huge amount of basins of attraction with the same motif. Moreover, a large funnel can contain a variety of small funnels and structures contained in a small funnel are more similar. Although the number of local minima in the PES increases exponentially with cluster size,[1] the number of possible cluster motifs does not increase so much; so we can roughly think that the number of local minima in each funnels also increases exponentially with cluster size. Generally, unbiased GO methods are driven by random perturbations (or mutations in GAs), so their local search ability is very weak. At a very large cluster size, it is even difficult to locate the minimum of a large funnel due to the weak local search ability of the GO-phase (just like the GO-phase even cannot find the minimum of a single basin of attraction without the gradient-based LO procedure at large cluster size).

The basic idea of this work is to insert a second LO-phase between the first gradient-based LO-phase and the GO-phase. The goal of the second LO-phase is to locate the minimum of the funnel that contains current configuration with the least cost. Then the GO-phase can focus on the global information of the PES over the various funnels. Following the definition of BH, such a method can be named as "funnel hopping" as illustrated in Fig. 1. Actually, the basic idea of multiphase of LO procedure has somewhat been adopted in some GO methods by moving the surface atoms and has achieved better performance in optimization of LJ clusters.[22,40,42]

Cluster GO problems are relevant for GO algorithms, as it provides excellent benchmarks to determine the performance of optimization algorithms. Short-ranged Morse clusters are considered to be more challenging than those described by the LJ potential and are very difficult to be optimized by the BH-type methods even for cluster size $N \leq 80$.[21,28,48] To check the idea of funnel hopping, we design a GO procedure with double-phase LO procedures and apply it to the geometry optimization of the LJ and short-ranged Morse clusters up to $N=160$. The first LO-phase method adopted in this work is the limited-memory BFGS (L-BFGS),[49] the second LO-phase is a funnel optimizer by cluster surface smoothing (CSS), and the GO-phase is a simple version of GA as adopted by Deaven and Ho,[17] Johnston,[23] and Hartke,[22] among others.

II. THE POTENTIAL

The LJ and Morse potentials are the two most famous pair potentials, which often act as the benchmark systems to evaluate the newly developed cluster geometry optimization methods. The LJ potential function is very simple,

$$\mathrm{LJ}(r) = \varepsilon[(r_0/r)^{12} - 2(r_0/r)^6], \tag{1}$$

where r is the interatomic distance, r_0 is the equilibrium pair distance, and ε is the pair well depth. In this work, we set $\varepsilon = r_0 = 1$ for simplification and then the LJ function can be written as $\mathrm{LJ}(r) = r^{-12} - 2r^{-6}$. The Morse function is $\mathrm{M}(r) = e^{2\rho(1-r)} - 2e^{\rho(1-r)}$, where ρ is the parameter of the potential. As shown in Fig. 2, low values of ρ give a long-ranged potential and high values a short-ranged potential. At $\rho=6$, the Morse function is very similar to the LJ function and the two potential functions can be unified by a modified Morse function.[50] The potential range is the most important factor for a pair potential determining the favorite cluster motifs; e.g., with ρ increasing the sequences of global minima of Morse clusters are disordered, core shell, icosahedral, decahedral, and close packed.[13,15,51] At $\rho=14$, Morse clusters are notoriously difficult to be optimized by an unbiased GO method, where the favorite motifs are decahedral, tetrahedral, and close packed.

III. THE FUNNEL-HOPPING METHOD

A. The first LO-phase

In this work, the first LO-phase is performed with the L-BFGS (Ref. 49) method. L-BFGS is a powerful quasi-Newton conjugate gradient method, where both the function to minimize and its gradient must be supplied. L-BFGS can relax a structure to its neighboring local minimum at the least costs.

B. The second LO-phase

The PES of clusters can be thought as a collection of various funnels, where one funnel represents one cluster motif. In a large funnel, there may be a great many local minima with the same motif. Moreover, there may be a number of small funnels in a large funnel. After the gradient-based local minimization procedure (the first LO-phase), the core of the

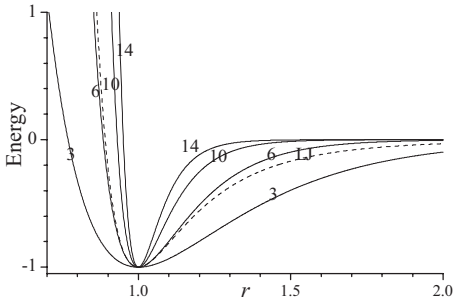

FIG. 2. Plots of the Morse potentials for different values of ρ (as labeled in the figure) and the LJ potential (dashed line).

cluster is generally well optimized due to the pressure of the outer shell and so the basic motif (such as icosahedral, decahedral, close packed, and disordered) of the cluster is determined by the motif of the core.

However, the cluster surface of an arbitrary local minimum is generally not so well organized and so the surface energy is high. For GO methods (such as GA and MC), the cluster surface is optimized by stochastic strategies and the efficiency is very low at large cluster size, which is the bottleneck in the geometry optimization of large clusters.

The goal of the second LO-phase is to solve the bottleneck in the surface optimization. We designed a CSS method to optimize the surface of an arbitrary local minimum. CSS can locate the minimum energy of current motif by reorganizing the cluster surface step by step, i.e., can find the minimum of the funnel in PES that contains current configuration. The CSS method is similar to the dynamic lattice searching[40] method, which can smooth the cluster surface by optimizing the approximate lattice. The flow chart of the CSS is plotted in Fig. 3. CSS starts with a local minimum and iteratively searches lower-energy local minimum in a greedy strategy:

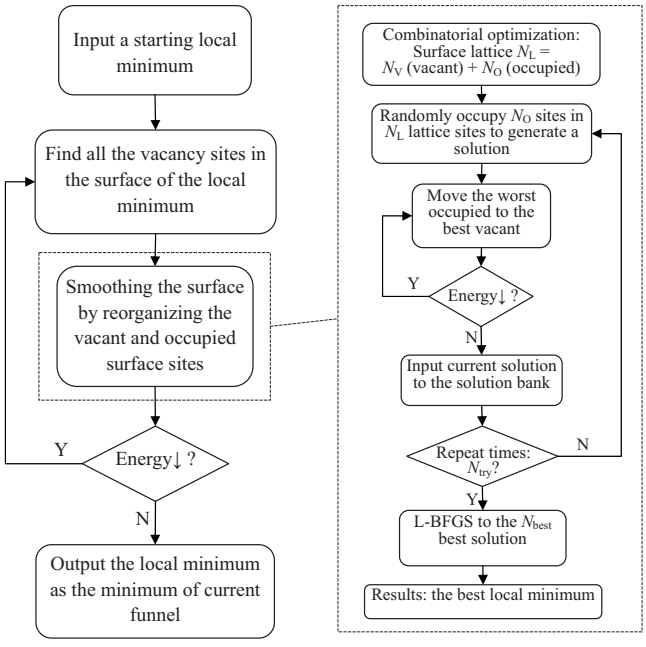

FIG. 3. Flow chart for the CSS program.

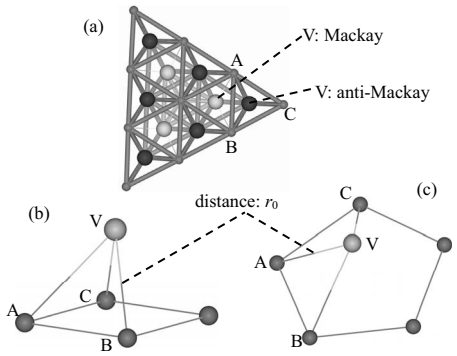

FIG. 4. Illustrations of the surface vacancy: (a) Mackay (white) and anti-Mackay (black) vacancy sites in the (111) surface, (b) vacancy site in the (100) surface, and (c) vacancy of the vertex of a pentagon. The vacancy site (V) is determined by the triangle (ABC) in the cluster surface, where $VA=VB=VC=r_0$ (the nearest neighbor distance).

(1) Find all the possible vacancy sites in the surface of the local minimum by calculating and analyzing the cluster surface. First, calculate the cluster surface to locate all the triangles in the cluster surface. Second, for each triangle (ABC), locate the point V, where $VA=VB=VC=r_0$, i.e., V is the nearest neighbor of A, B, and C, which is a possible vacancy site.[52] Figure 4 gives illustrations for some cases: (a) all the possible Mackay and anti-Mackay vacancy sites in the (111) face, (b) vacancy sites in the (100) face, and (c) vacant vertex site of a pentagon. The calculated vacancy sites will change a little after relaxation especially for the long-ranged potential. Such a surface analysis method is biased to the space-filled clusters (such as metal clusters and molecular clusters) and is not available for clusters based on covalent bond (such as C clusters) where the structure may be the planar or cagelike.

(2) Optimize the cluster surface to obtain a new local minimum by reorganizing the occupied and vacant surface sites. The surface reorganization procedure will be described below.

(3) If the new local minimum has lower potential energy, accept it as the current local minimum and go back to step (1). Otherwise, there is no lower-energy local minimum found by optimizing the surface of current local minimum, so we think that the current local minimum has the lowest surface energy and is the minimum of current funnel in the PES.

The flow chart of the surface optimization procedure is also given in Fig. 3. Supposing the numbers of vacant surface sites are N_V and the number of occupied surface sites is N_O, the surface reorganization is a simple combinatorial optimization problem: occupy the proper N_O sites from the total lattice sites ($N_L=N_V+N_O$), where all the vacancy sites and surface sites are considered. The combinatorial problem is solved by a stochastic procedure, where a greedy strategy is adopted to search the surface lattices:

(a) Calculate the energy of each pair sites (occupied and vacancy) in advance (for many-body potential, calculate the pair distances only). Initialize a blank solution bank.

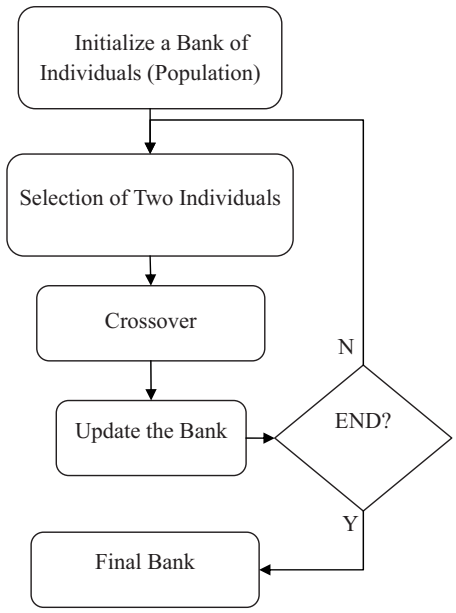

FIG. 5. Flow chart for the GA program.

(b) Randomly occupy N_O sites from N_L lattice sites to generate a solution.
(c) Iteratively move the highest-energy occupied site to the lowest-energy vacancy site until the energy does not decrease. The energy of a lattice site is the sum of the interactions of the site between all the occupied sites.
(d) Input the current best solution to the solution bank.
(e) Repeat steps (b)–(d) for N_{try} times.
(f) Perform the L-BFGS procedure (the first LO-phase) to the N_{best} lowest-energy solution in the solution bank and take the lowest-energy local minimum after L-BFGS as the result of this surface reorganization procedure.

The greedy lattice searching procedure may converge at various solutions, so we repeat is for N_{try} times. The calculated vacant surface sites are approximate and after relaxation the structure will change a little, so the N_{best} lowest-energy solutions in the N_{try} lattice searching procedures are relaxed by the L-BFGS procedure instead of only the best solution. In this work we set $N_{\text{try}}=200$ and $N_{\text{best}}=5$.

C. The GO-phase

From an arbitrary cluster structure, the minimum of the funnel in the PES can be located by the double LO-phases, so the GO-phase can focus on the global information of the PES over the variety of funnels. The crossover operator of GA can reasonably realize the transition between funnels, so we select a basic GA as the GO-phase. The flow chart of the GO-phase is plotted in Fig. 5:

(1) Initialization. Randomly generate N_{pop} individual structures to form a bank of populations, where each individual is optimized by the double LO-phases. Set the iteration number iter=0.
(2) Selection. Randomly select two individuals from the bank as the parents of current iteration.
(3) Crossover. Perform the Deaven–Ho[17] cut and splice crossover operation on the two parents to generate a child and then optimize the child with the double LO-phases. Here, the children are bred one by one instead of generation by generation.
(4) Updating. Input the child into the bank. If there is no same individual in the bank (directly checking by the energy) and the child has lower energy than the worst individual in the bank, replace it. Otherwise, discard the child.
(5) Iteration. Increase iter by one. If iter does not reach the maximal iteration number N_{iter}, go back to step (2). Otherwise, terminate the calculation and output the final bank.

The GA method given here is a very simple version. Details of the standard cluster GA method can be found in a review by Johnston.[23] The population diversity is the key issue in the evolutionary methods and so cluster similarity checking is very important. However, it is not a problem at all in this study, because after the double LO-phases, similar structures will converge at the same minimum of the funnel. Moreover, a small mutation generally cannot lead to transitions between funnels and too large a mutation is unreasonable, so the mutation operations are abandoned here. The final bank may contain the minima of various low-lying funnels instead of only the global minimum one.

IV. RESULTS AND DISCUSSION

A. Global optimization results

To check the GO ability of the funnel-hopping method described above, we apply it to the geometry optimization of the LJ clusters and the extremely short-ranged ($\rho=14$) Morse clusters up to cluster size $N=160$. The parameters of the GA are population size $N_{\text{pop}}=20$ and maximal iteration number $N_{\text{iter}}=1000$. For each cluster size, we carry out ten separate runs and for each run the calculation is terminated when the putative global minimum is found or the iteration number reaches the maximal iteration number. We successfully located all the known putative global minima given in the literature[47,53] for both potentials but no new global minimum found.

The successful rates of the LJ clusters are 10/10 in the ten separate runs for each cluster size. In Fig. 6(a), we plot the mean central processing unit (CPU) time of locating the global minima as the function of the cluster sizes. It can be seen that the average time of hitting the global minima is in 2 min even for the most difficult case, which is much faster even compared to the most efficient BH-type methods.[37]

The short-ranged Morse cluster is much more difficult to be optimized than LJ clusters. Figure 6(b) plots the mean CPU time per hit of the global minima and the probabilities of hitting the global minima of the short-ranged Morse clusters as the function of the cluster sizes. At very small cluster size (about $N<40$), the optimization is very simple for our method, the global minima can be located in the initialization

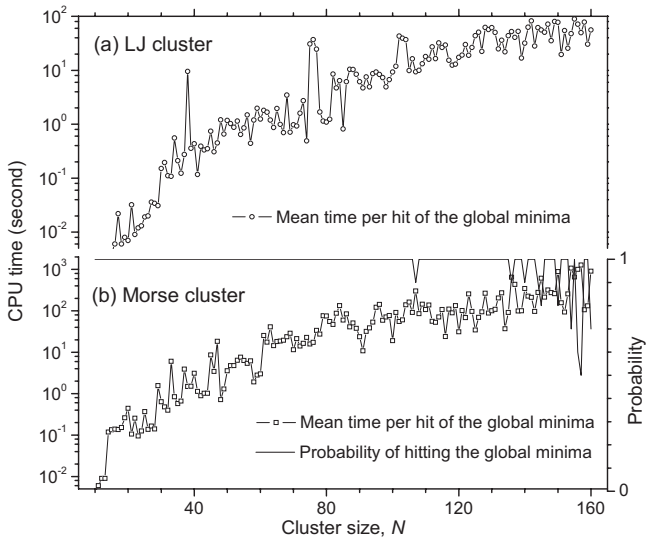

FIG. 6. Mean CPU time of the ten separate runs of hitting the putative global minima of the LJ clusters (a) and the short-ranged Morse clusters (b) for cluster size $N \leq 160$. The probabilities of hitting the putative global minima of the short-ranged Morse clusters are also given. Values of the partially successful runs of Morse clusters ($N=107,140,144,145,150,154,156,157$) include the time of the failure runs. The calculations were carried out on an Intel Itanium2 Madsion processor (1.5 GHz).

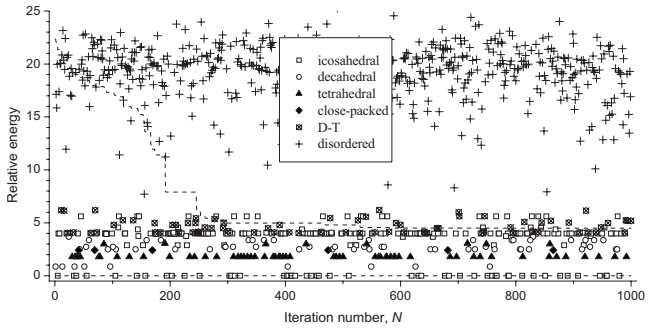

FIG. 7. Optimization procedure of the LJ_{100} clusters. The y-axis gives the potential energy of the present structure as a function of the iteration number in GA. The energy is relative to the global minimum energy. The structures in different motifs are given in different symbols (as labeled), where D-T means the motif is between decahedral and tetrahedral. The dashed lines give the minimal and maximal energy of the bank of population (population size $N_{pop}=30$).

of populations and the time is in one second. For $N \leq 80$, the average time of hitting the global minima is in one minute and the probabilities of hitting the global minima are 10/10, where the optimization efficiency is significantly higher than that of the BH-type methods.[21,48] Moreover, at larger cluster size, the average time of hitting the global minima is also in 20 min even for the most difficult case. Global minima of the short-ranged Morse clusters are decahedral or close packed.[15] We found that close-packed motifs are easier optimized than the decahedral motifs. For example, the probabilities of hitting the close-packed global minima are 10/10 for most of cases except for $N=136$, where the motif of the global minimum is face-centered cubic (fcc), while for many decahedral cases, e.g., $N=107$, 140, 144, 145, 150, 154, 156, 157, and 160, the probabilities are less than 1. This indicates that the second LO-phase based on the CSS operator may be a little biased to the close-packed motif.

B. Hopping over the funnels in the PES

By the CSS operator and crossover operator in GA, the funnel hopping method can realize hopping between funnels in the PES and can locate the minimum of various funnels. To illustrate the performance of funnel hopping, taking LJ_{100} as the test case, Fig. 7 plots the potential energy of the located structure as a function of the iteration number in GA, and some typical located motifs are plotted in Fig. 8; the first isocahedral motif is the global minimum, the second and third icosahedral motifs are icosahedral plus antilayers, and the fourth icosahedral motif is polyicosahedral. The three decahedral motifs are Marks decahedral, decahedral plus antilayers on one side, and decahedral plus antilayers on both sides, respectively. The close-packed motif is a fcc tetrahedron plus four regular antilayers on the four (111) faces, which is the global minima of the short-ranged Morse clusters. The first tetrahedral motif is the magic number 98-atom Leary tetrahedral[54] plus two atoms and the second tetrahedral is packed by a five-atom edged tetrahedron. The disordered structure is somewhat a liquidlike structure and has much higher energy. Figure 7 shows that structures in various motifs can be located subsequently and the number of located structures of each ordered motifs (e.g., icosahedral, tetrahedral, decahedral, and close packed) is very limited, which means that the second LO-phase can sufficiently locate the minimum of each funnels in the PES. Moreover, many high-energy liquidlike disordered motifs are located during the optimization (about 50%), which indicates that there may be a large area of the liquidlike disordered configurations in the PES and there is no obvious low-energy funnel in this area, so the CSS operation may converge at various high-energy disordered structures when the configuration jumps into this area.

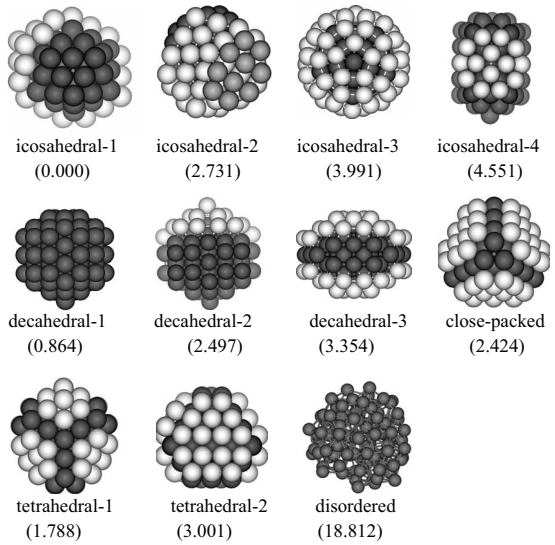

FIG. 8. Some typical motifs of LJ_{100} clusters labeled in Fig. 7. Enclosed is the relative energy of the motif. The disordered motif is randomly chosen from the optimization results.

C. Discussion

The real PES of clusters is unknown. Here we think that a structure with minimal surface energy is the most stable configuration in current funnel and is the minimum of current funnel. Based on the definition of the funnel-hopping potential energy transformation, the goal of the second LO-phase (CSS procedure) is to locate the minimum of current funnel by minimize the surface energy. The CSS procedure can fast locate the minimum of the current funnel without attempting to jump to other funnels even when the energy of current funnel is relatively high. For example, the cost of one CSS procedure is about 10–30 gradient-based LOs in the optimization of LJ_{100}. Moreover, the CSS procedure has about 50% chance to converge at the high energy liquidlike disordered motifs (Fig. 7) due to the disorder of the core atoms, where we also think that the CSS procedure located the minimum of a very small funnel in disordered packing without any attempts for escaping from the funnel in the second LO-phase. Transition between funnels is the task of the GO-phase.

There also have been some attempts of "funnel search" in the literature.[30,55] For example, Leary[30] proposed a monotonic sequence BH (MSBH) algorithm to locate the minimum of the funnel of LJ clusters, which is based on the random perturbations in the GO-phase. Based on the definition of funnel-hopping potential energy transformation, MSBH is not a funnel-hopping method. First, random perturbations can lead to transitions between funnels after relaxation. Second, there have no obvious criterion for MSBH to judge when the minimum of a funnel is found and the costs of locate the minimum of a funnel are very high. However, the goal of the CSS procedure is to minimize the surface energy of a structure at the least cost and we think that the configuration reaches the funnel minimum in the PES when the structure has the minimal surface energy.

It should be pointed out that the strategy of "moving surface atoms" has been around in the literature for quite some time, such as the "direct mutation" given by Hartke,[22] the lattice searching in the dynamic lattice searching method,[40] and the surface operation given by Takeuchi.[42] The CSS procedure is based on the methods in the literature and is a more systematic study on moving surface atoms. For example, for some cases, 10–20 surface atoms are moved together in the CSS lattice-searching procedure for lower surface energy. Moreover, the goal of the CSS is to locate the minimum of current funnel instead of GO. In this study, the GO-phase is designed as simple as possible to enhance the concept of funnel hopping. There are also some useful strategies that can be adopted in the GO-phase, such as the interior operation given by Takeuchi.[42] For large LJ clusters (about $N>500$), there may be core vacancies[56] for the Mackay icosahedral global minima, so creating and destroying core vacancies should be of concern.

The lattice of the vacancy sites is unknown, which is based on the structure of the local minimum, so the CSS procedure is unbiased, which can located various motifs (as shown in Fig. 8). The testing cases in this study are pair potentials. For many-body potentials the CSS procedure is also applicable, but the calculation in lattice searching will be more extensive. Alternatively, the lattice can also be optimized by counting the number of nearest neighbors instead of potential energy.

The proposed funnel-hopping method can only search the static information at 0 K of the PES of clusters without thermal effects. For some real systems, such as protein folding, the free energy surface may be more important than PES.[57]

V. CONCLUSIONS

In conclusion, we designed a CSS method that can fast locate the minimum of the funnel in PES containing current configuration. By inserting the CSS method into the gradient-based LO-phase and the GO-phase as a second LO-phase, the GO-phase can focus on the global information of the PES over the various funnels. Following the definition of BH, such a method is named as funnel hopping. The second LO-phase can significantly improve the local search ability of the GO methods. Adopting a simple version of GA as the GO-phase, the funnel-hopping method successfully located all the known putative global minima of the LJ clusters and the extremely short-ranged Morse clusters up to $N=160$ and the efficiency is significantly higher than those of the BH-type methods. Moreover, the funnel-hopping method can locate the minimum of various low-lying funnels instead of only the global minimum in one calculation and the other low-energy local minima near to the minimum of funnels cannot be located.

The second LO-phase described in this work is biased to the cluster geometry optimization problems. However for other structural optimization problems, the basic idea of funnel hopping is also considered. Universal GO and gradient-based LO methods have been sufficiently developed by computer and mathematics scientists, but for the complex chemical, physical, and biological problems, there still need to develop more powerful methods that are "biased" to the problems for higher efficiency.

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